Lancaster Environment Centre

Lancaster University

Development and applications of the diffusive gradients in thin-films (DGT) technique for the measurement of polycyclic aromatic hydrocarbons (PAHs) in waters and soils

Qiuyu Rong

Submitted for the degree of Doctor of Philosophy

October 2024

Declaration

I declare that this thesis is my work and has not been submitted for the award of a higher degree or qualification at this university or elsewhere.

Abstract

Polyaromatic hydrocarbons (PAHs) are a group of organic compounds, widely present in the environment, which are carcinogenic, teratogenic, mutagenic and bioaccumulative. They can exist in the environment for a long time and pose potential risks to humans and ecosystems, so they have attracted the attention of research scientists and regulators. It is therefore important to have sampling and analytical techniques to accurately and effectively detect PAHs, to understand their environmental sources, behaviour and fate, to provide a scientific basis for controlling their releases to the environment and to protect ecosystem and human health.

The diffusive gradients in thin films (DGT) technique is an in-situ passive sampling technology, which has been used to measure heavy metals, nutrients and – more recently – some classes of organic pollutants in environmental media. In this thesis, a DGT sampler for PAHs was developed, tested, and used for studies of PAHs in waters and soils. A new sampler casing was designed using aluminum, to reduce adsorption during field deployment. The performance of three binding materials (MIP, HLB and XAD18) was compared in laboratory tests. The absorption capacity and uptake kinetics of the three materials were determined, and their performance under different pH, ionic strength and dissolved organic matter tested. The MIP-DGT sampler performed best and was not affected by environmental conditions across the range pH (3.9-8.1), ionic strength (0.01-0.5 M) and dissolved organic matter concentration (<20 mg L^{-1}). Field tests showed DGT can be used for time-integrated *in situ* measurement of PAHs in waters under a range of environmental conditions.

DGT PAH samplers were deployed in the Nanjing section of the Yangtze River and urban rivers in summer and winter 2021. The concentrations of labile PAHs had marked seasonal differences under the influence of source inputs, river flow differences, and degradation/loss processes. The accumulation of PAHs in the Yangtze River upstream of Nanjing together with seasonal combustion sources, discharges from petrochemical enterprises and ship transportation are discussed as the main sources of PAHs in the studied area. Inputs from Nanjing urban rivers had little impact on the PAH mass loadings in the mainstream of the Yangtze River. The results of two different risk assessment methods showed that PAH concentrations are sufficient to be a potential risk to ecological systems during the winter and in some of the more contaminated industrial areas. This study highlighted how *in situ* DGT water sampling can be used to investigate the sources, fates and behavior of PAHs in aquatic environments.

DGT can also be used to study trace organic contaminants in soil. DGT samplers were deployed in laboratory experiments investigating soil-compound interaction during aging. Six soils with different physicochemical properties were spiked with 4 PAH compounds (phenanthrene, anthracene, fluoranthene and pyrene) with final concentration of 10 mg kg^{-1} and allowed to age for 45 days. DGT sampling was conducted at time intervals, to investigate PAH adsorption/desorption behaviour and to derive kinetic information on their release from the soil solid phase. Soil physical and chemical properties such as pH, TOC, soil particle size and the properties of PAHs themselves all influenced compound behaviour during the aging process. The ability of most of the soils to resupply PAHs from the solid phase to the soil solution decreased with aging time. The DGT-induced fluxes in soils (DIFS) model was used to obtain information on PAH desorption kinetics from the soil solid phase to the soil solution phase. Desorption kinetics and the labile pool size both affected the ability of soils to re-supply PAHs. The labile pool size was affected by pH and TOC.

DGT has been used to explore the relationship between soil and crop plant uptake of PAHs substances. An experiment was conducted, growing lettuce, radish and maize in six different soils, spiked initially with 10 mg kg^{-1} of 4 PAHs. DGT sampling was performed before planting and after harvesting, together with sampling of soil solution and a sequential extraction procedure. DGT measurements showed changes of the resupply of PAHs from the soil solid phase before and after crops planting. The presence of PAHs in the air affected the PAH content of above-ground plant parts. PAHs sampled by DGT, and in soil solution and in the sequential extraction procedure were compared to crop concentrations. None of the soil tests gave clear correlations to the plant concentrations. Possible reasons for this were discussed and recommendations were made for further studies.

The thesis provides the foundation for future work on using DGT to further investigate PAHs (and other compounds) in the environment. Recommendations are made for applications of DGT to provide novel insights on the sources, fates and behaviour of PAHs in the environment.

Acknowledgements

I am grateful to my two supervisors, Prof. Kevin C. Jones and Prof. Hao Zhang. They are always willing to give me guidance and encouragement whenever I need. Not only for academic work, but also gave me a lot of valuable suggestions on my life. Their dedication and seriousness at work have a good influence on me and encourage me to enjoy life. I respect them and am very grateful for their guidance and companionship over the past few years. These experiences will be valuable to my life.

Many thanks to Lancaster Environment Centre (LEC) and School of the Environment, Nanjing University (NJU).

I would like to thank to all my colleagues in the DGT Group for offering me suggestions and supporting during my PhD study. Thanks to Prof. Jun Luo (NJU) and Nanjing group for the support and help for my research. Thanks to Dr. Yanying Li for her great help on research and guides on my life. Thanks to Dr. Hanbing Li, Dr. Zhou Fang and Dr. Hao Cheng for their help on my research. Thanks to Liying Yan for the help on investigation and experiments. Thanks to Danxing Yang for her help and patience to me.

I would like to thank to all my families and friends in Lancaster, Nanjing and Chongqing for their accompany, especially for Miss Tianxiao Li, Miss Hanshuo Zhang, Miss Haiyi Chen, Miss Shiping Liao, Mr Kefei Huang, Miss Zhao Liu, Mr Mingming Shi for their support and help. The happy time that we spent together will stay in my memory for ever.

I would also like to thank to outstanding Chinese table tennis players Sun Yingsha and Wang Chuqin, their pursuit and efforts of dreams always inspire me.

Finally yet importantly, I would like to give my deep and special thanks to my father Xiugao Rong, my mother Huagui Wan, and my lovely sister Xiaohan Rong, for their love, trust and support forever. Also, thanks to myself for all.

Contents

Abbreviations

A	Exposure window area of the DGT device
ABS	Acrylonitrile butadiene styrene
AC	Activated carbon
Ace	Acenaphthene
ACN	Acetonitrile
Acy	Acenaphthylene
AG	Agarose gels
Ant	Anthracene
AREs	Artificial root exudates
ASE	Accelerated solvent extraction
BaA	benzo (a) anthracene
BaP	Benzo(a)pyrene
BC	Black carbon
BPA	Bisphenols
CA	Cellulose acetate membrane
C_b	Concentration in the bulk solution
C_{DGT}	Concentrations measured by DGT
Cse	Analyte concentration extraction measured by solvent extraction
Css	Analyte concentration in soil solution
D_{25}	Diffusion coefficient of analyte at 25 °C
DAD	Diode array (variable UV wavelength) detectors
DBL	Diffusion boundary layer
De	diffusion coefficient
DET	Diffusive equilibrium in thin films
DGT	Diffusive gradients in thin films
DIFS	DGT-induced fluxes in soils

DOM	Dissolved organic matter
EDCs	Endocrine disrupting chemicals
FLD	Fluorescence detectors
Flu	Fluorene
Flua	Fluoranthene
GC-MS	Gas chromatography-mass spectrometry
GCs	Glucocorticoids
h	Hour
HC_5	Hazardous concentration for 5% of species
HCl	Hydrochloric acid
HDPE	High-density polyethylene
HI	Hazard index
HLB	Hydrophile-lipophile balance
HOCs	Hydrophobic organic chemicals
HPCD	Hydroxypropyl-β-cyclodextrin
HPCPs	Household and personal care products
HPLC	High-performance liquid chromatography
IDLs	Instrumental detection limits
IS	Ionic strength
k_1	Adsorption rate constant
k_{-1}	Desorption rate constant
K_d	Soil-water distribution coefficient
Kow	Octanol-water partition coefficient
LLE	Liquid-liquid extraction
LPMD	Low-density polyethylene
MAE	Microwave-assisted extraction
MCE	Mixed cellulose ester membrane
MDLs	Method detection limits
MEC	Measured environmental concentration

MeOH	Methanol
MESCO	Membrane-enclosed sorptive coating
MFO	Multifunctional
min	Minute
MIP	Molecularly imprinted polymer
MPCs	Maximum permissible concentrations
MQ water	Milli-Q water
MWCNTs	Multi-walled carbon nanotubes
MWHC	Maximum water holding capacity
NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
Nap	Naphthalene
NCBs	Nitrochloro-benzenes
NCs	Negligible concentrations
NL	Nylon membrane
OPFRs	Organophosphate flame retardants
PA	Polyacrylamide gels
PAHs	Polycyclic aromatic hydrocarbons
PC	Nucleopore track-etch membrane
PDBS	Passive dispersion sampling bags
PEP	Polar enhanced phase
PES	Polyethersulfone membrane
PFASs	Perfluoroalkyl substances
PFCs	Perfluorinated compounds
Phe	Phenanthrene
PNEC	Predicted no-effect concentration
POCIS	Polar organic chemical integrative sampler
PP	Polypropylene

PSD	Passive sampling devices
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
Pyr	Pyrene
QSAR	Quantitative Structure–Activity Relationships
R	Ratio of DGT estimated to actual pore-water concentration
rpm	Revolution per minute
RQ	Risk Quotient
Rs	Sampling rate
RSD	Relative standard deviation
SFE	Supercritical fluid extraction
SOM	Soil organic matter
SPE	Solid-phase extraction
SPMDs	Semi-permeable membrane devices
SPME	Solid-phase microextraction
SR	Silicone rubber
SSD	Species sensitivity distribution
t	Time
Tc	Response time
TCS	Triclosan
TEFs	Toxicity equivalent factors
TOC	Total organic carbon
TWA	Time weighted average
USEPA	US Environmental Protection Agency
UVD	Ultraviolet detectors
WAX	Weak anion exchanger
WWTP	Wastewater treatment plant
XAD18	Amberlite TM XAD18
δ	Thickness of the diffusion boundary layer

Δg	Thickness of the diffusion layer

List of Figures

List of Tables

Chapter 1 Introduction

1.1 Incentive for the study

PAHs are a group of organic pollutants containing two or more benzene rings in different arrangements that are widely present in the environment (Wild and Jones 1993, Nowakowski, Rykowska et al. 2021). In addition to natural sources, PAH pollution is usually related to human industrial, transport, heating and agricultural production activities, such as emissions from fossil fuels (coal, petroleum) and biomass combustion (Dai, Han et al. 2022, Rokhbar, Keshavarzi et al. 2023). In the past, with rapid economic development, human activities intensified the use of fossil fuels, and PAH emissions increased. It has been reported that air, water, soil/sediment, and biota have all become contaminated by PAHs during the periods of industrialisation, in varying degrees all over the world (Dat and Chang 2017, Balmer, Hung et al. 2019, Eldos, Zouari et al. 2022, Dib, Veerasingam et al. 2024). PAHs are potentially carcinogenic, teratogenic, mutagenic or chronically toxic, and are bioaccumulative, posing a serious threat to human health and ecological safety; they have therefore have attracted great attention from the international community (Stading, Gastelum et al. 2021, Ben Othman, Pick et al. 2023). Therefore, it is very important to accurately and effectively monitor PAHs and understand their fate and behaviour in the environment.

Traditional ‘active sampling’ methods (i.e. taking grab samples) for detecting PAHs in water required a large volume of samples. The collection, storage, transportation, and complex pretreatment of the methods were needed, and it is difficult to identify sudden pollution events by simply taking grab or spot samples (Ahrens, Daneshvar et al. 2015, Cristovao, Bento-Silva et al. 2021). By increasing the sampling frequency or using automatic monitoring or online and offline technologies for monitoring, the monitoring and maintenance costs will be greatly increased, and there are few equipment suitable for trace PAHs monitoring (O'Hara 2009, Piniewski, Marcinkowski et al. 2019). The detection of PAHs in soil also traditionally requires complex extraction, purification, and concentration processes, and methods to reduce the interference of the matrix on sample detection (De Nicola, Concha-Graña et al. 2019, Silalahi, Anita et al. 2021). Passive sampling techniques (for PAH detection) have been well developed over recent decades. However, most passive samplers are rather imprecise and often affected by factors such as temperature, flow rate, biofouling and so on. Most of them have required determination of the sampler-water partition coefficient or calibration for the sampling rate (Moeckel, Harner et al. 2009, Salim and Gorecki 2019). Some calibration methods have been used which can also introduce further uncertainty into the estimation of pollutant concentrations (Monteyne, Roose et al. 2013, Charriau, Lissalde et al. 2016).

As a type of passive sampler, the diffusive gradients in thin films (DGT) method has been widely used for monitoring inorganic substances, speciation analysis and prediction of bioavailability (Zhang 2004, Williams, Zhang et al. 2012, Menegario, Yabuki et al. 2017). More recently, since 2012, DGT has been used to measure organic pollutants in water and soil (Chen, Zhang et al. 2012, Chen, Jones et al. 2014). DGT is an effective monitoring tool that is easy to operate, can pre-enrich pollutants, and is relatively unaffected by fluid dynamics when used in water (Wang, Zou et al. 2019). The use of DGT combined with the DGT-induced fluxes in soils (DIFs) model can provide kinetic information about contaminant behaviour in soils and has been successfully applied to heavy metals, nutrients, and – more recently – to organic pollutants (Ernstberger, Zhang et al. 2005, Luo, Yin et al. 2018, Ren, Wang et al. 2020). DGT has been shown to measure the labile concentration of compounds and can be used to evaluate bioavailability. It has been widely used in the evaluation of inorganic bioavailability (Zhang, Zhao et al. 2001, Soriano-Disla, Speir et al. 2010), and has also been successfully used for organic pollutants such as pesticides, antibiotics and glyphosate (Li, Rothwell et al. 2019, Weng, Rose et al. 2019, Song, Su et al. 2023). DGT has been used for more than 150 organic compounds including antibiotics, pesticides, endocrine disrupting chemicals (EDCs), perfluorinated compounds, etc. (Challis, Hanson et al. 2016, Chen, Pan et al. 2018, Fang, Li et al. 2021, Bonnaud, Miege et al. 2022). This has demonstrated the prospect of DGT in the analysis of trace organic pollutants and has the potential to be used for the detection of PAHs in water and soil.

1.2 Research aims

The aim of this project is to develop a suitable method of DGT for the in-situ measurements of PAHs, which could advance our understanding of the chemical behaviors and kinetic processes of PAHs in waters and soils. Specific objectives were:

(1) to develop the DGT technique for *in situ* measurement of PAHs and verify its suitability and performance under different environmental conditions;

(2) to apply DGT for *in situ* sampling of PAHs in rivers, to explore the distribution, sources and risk assessment of PAHs;

(3) to investigate the labile pool size and the resupply ability of PAHs in soils with different properties during soil aging, by the combination of DGT and the DIFS model;

(4) to investigate the use of DGT to measure the bioavailability of PAHs in soil-plant systems and make comparisons with traditional soil solution and chemical extraction methods.

1.3 Outline for the thesis

The following literature review in **Chapter 2** comprises an introduction to PAHs and a description of passive sampling techniques. The review starts with the necessity of studying PAHs and their behavior and fate in water, sediment, and soil environments as well as considering their possible impact in the environment and on human health. Traditional measurement methods of PAHs are compared and discussed. Then passive sampling techniques are introduced, and the principles and categories of passive samplers are described. Five passive samplers which have been used for PAH detection are introduced, namely SPMDs, Chemcatcher, silicone rubber, ceramic dosimeters, and membrane-enclosed sorptive coating. Finally, the DGT technique is introduced, and its principles are explained. The application of DGT for inorganic and organic chemicals in water and soil environments and its potential advantages are introduced. This lays the foundation for the studies of this thesis.

Chapter 3 describes the development of DGT for the measurement of 8 PAHs in various laboratory studies. Through comparative experiment, a new metal DGT casing was designed to reduce the impact of PAH adsorption on laboratory deployment results. The diffusion coefficients of 8 PAHs were measured. The capacity and uptake kinetics of 3 binding materials (MIP, HLB and XAD18) were tested, and their compliance with the principle of DGT was verified through time dependence and diffusion layer thickness dependence experiments. The effects of pH, ionic strength and dissolved organic matter on the application of DGT were studied. The application of DGT to study PAHs in the environment was verified through field experiments.

Chapter 4 introduces the field application of DGT in the Nanjing section of the Yangtze River and urban rivers in China. Combining DGT with grab sampling, PAHs were detected in the study area in winter and summer. The DGT results were used to explore the relationship between PAH pollution in the Yangtze River mainstream and urban rivers, analyze the possible pollution sources of PAHs and evaluate their ecological risks of this river basin.

In **Chapter 5**, a study is described where DGT samplers were placed in 6 PAH-spiked soils with different physicochemical properties. Combined with the DIFS model, the labile pool size and desorption rate constants of PAHs during the compound-soil aging process were evaluated by determining the ratio R, distribution coefficients (Kd) and response time (Tc). The effects of different soil physical and chemical properties on the results are discussed.

In **Chapter 6**, pot experiments were conducted to grow three crop plant species, namely lettuce, radish, and maize, in 6 soils with different pH and soil organic matter content. These soils had been spiked with known amounts of 4 PAH compounds. The available concentrations of the test compounds in the soil were determined by DGT, and compared to traditional soil solution sampling and a sequential extraction method. The measured values were compared with the concentrations in the plants to investigate the potential of these methods to determine the bioavailability of soil-borne PAHs to the plants.

Chapter 7 provides a summary, conclusions and recommendations for future work.

Chapter 2 Literature review

2.1 Polycyclic aromatic hydrocarbons

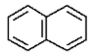
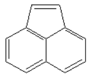
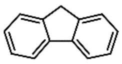
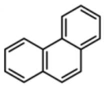
2.1.1 Introduction to PAHs

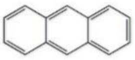
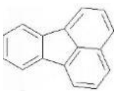
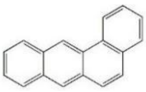
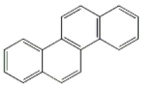
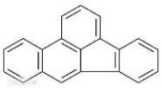
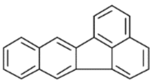
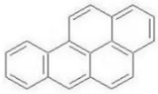
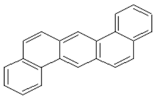
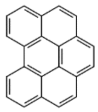
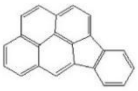
2.1.1.1 Definition and types of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a group of hydrocarbons that are composed of two or more benzene rings arranged in a linear, angular or tandem arrangement (Wilson and Jones 1993, Nowakowski, Rykowska et al. 2021). According to the number of benzene rings, PAHs can be divided into low molecular weight PAHs (2-3 rings) and high molecular weight PAHs (4-7 rings). According to the connection between the benzene rings, PAHs can be divided into aromatic fused ring type and aromatic non-fused ring type. The aromatic fused ring type refers to hydrocarbons with at least two common carbon atoms in adjacent benzene rings in the molecule, such as naphthalene, anthracene and phenanthrene. The aromatic non-fused ring type refers to the compounds that have adjacent benzene rings in the molecule with only one carbon atom connected, such as biphenyl and terphenyl. In most research, PAHs refer to the fused-ring type.

PAHs in pure concentrated form are usually colourless, light yellow or white solids. The difference in the number of benzene rings and the type of connection causes changes in molecular weight and molecular structure, which in turn leads to different physical and chemical properties. The greater the number of benzene rings, the greater the molecular weight and the lower the vapour pressure of PAHs (Southworth 1979). In nature/the environment, PAHs do not occur in the pure concentrated form. In the air they can occur as gases or on particles, as a function of their vapour pressure and the ambient conditions. In waters, PAHs can occur on/in particles, in/on colloids and in the dissolved form – again dependent on their properties and the ambient conditions. PAHs are persistent and difficult to decompose physically, chemically and biologically, and will exist for a long time after entering the environment. The octanol-water partition coefficient (Kow) shows that these chemicals are lipophilic and hydrophobic, and so they can partition to solids and can accumulate in organisms. PAHs can undergo long-range atmospheric transport and can reach areas far away from their pollution sources (Halsall, Sweetman et al. 2001, Lian, Zhang et al. 2022). PAHs have potentially adverse effects on human health. The International Agency for Research on Cancer identified 30 types of carcinogenic PAHs as long ago as 1983. The US Environmental Protection Agency listed 16 PAHs as priority pollutants (USEPA 1993, Karaca 2016). The physical and chemical properties of these 16 PAHs are shown in Table 2.1. As the number of the rings of PAHs increases, the toxicity, persistence, and resistance to degradation of PAHs increase, while their volatility decreases. Among them, Benzo[a]pyrene (BaP), Benzo[a]anthracene (BaA), Benzo[b]fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Indeno[1,2,3-cd]pyrene (IcdP), Dibenz[a,h]anthracene (DahA), Benzo[g,h,i]perylene (BghiP) are considered to have strong carcinogenicity. Research indicated that PAHs do not directly cause cancer, but the metabolism of PAHs leads to carcinogenic metabolites, forming DNA adducts and causing mutations in tumor suppressor genes or oncogenes (Chaturvedi and Lakshman 1996, Geacintov, Cosman et al. 1997, Moorthy, Chu et al. 2015). The metabolism of PAH can form reactive oxygen species (ROS), disrupt the redox balance in cells, then lead to DNA damage and affect cell proliferation, finally causing cell inflammation and death, and increasing the risk of tumor development (Kwack and Mu Lee 2000, Tsay, Tchou-Wong et al. 2013, Stading, Gastelum et al. 2021).

Table 2.1 The physicochemical properties of the 16 ‘priority’ PAHs

Compounds	Molecular weight (Da)	Formula	Structure	Henry constant	lgKow	Water solubility (μg L^{-1})
Naphthalene	128.18	$C_{10}H_8$		43.0	3.37	30200
Acenaphthylene	152.20	$C_{12}H_8$		11.55	4.00	3930
Acenaphthene	154.21	$C_{12}H_{10}$		24.0	3.92	3400
Fluorene	166.22	$C_{13}H_{10}$		8.50	4.18	1900
Phenanthrene	178.23	$C_{14}H_{10}$		4.0	4.57	1180

Anthracene	178.23	$C_{14}H_{10}$		6.0	4.54	86
Fluoranthene	202.26	$C_{16}H_{10}$		0.659	5.22	260
Pyrene	202.26	$C_{16}H_{10}$		1.1	5.30	135
Benzo (a) anthracene	228.29	$C_{18}H_{12}$		0.102	5.86	11
Chrysene	228.29	$C_{18}H_{12}$		0.106	5.91	1.9
Benzo (b) fluoranthene	252.32	$C_{20}H_{12}$		0.504	6.00	8
Benzo (k) fluoranthene	252.32	$C_{20}H_{12}$		0.111	5.80	3.8
Benzo (a) pyrene	252.32	$C_{20}H_{12}$		0.009	6.04	14
Dibenzo (a, h) anthracene	278	$C_{22}H_{14}$		0.007	6.75	0.5
Benzo (g, h, i) perylene	276.33	$C_{22}H_{12}$		0.001	6.58	0.3
Indeno (1, 2, 3-cd) pyrene	276.33	$C_{22}H_{12}$		N/A	7.00	0.5

2.1.1.2 Sources of PAHs

PAHs are formed by incomplete combustion. They are widely present in the atmosphere, water, soil, sediment environment, and their sources can be divided into natural sources and anthropogenic (man-made) sources (Dai, Han et al. 2022, Rokhbar, Keshavarzi et al. 2023). Natural sources are mainly due to volcanic activity, forest and grassland fires (Howsam and Jones 1998, Abdel-Shafy and Mansour 2016). At the same time, terrestrial and aquatic organisms such as algae, bacteria, and diagenesis in sedimentary environments can also lead to the production of (at least some of) these compounds (Wakeham, Schaffner et al. 1980, Lima, Farrington et al. 2005). Anthropogenic sources are the main sources of PAHs to the environment nowadays; these include combustion during power generation (oil, coal, gas, wood burning), releases from chemical industries, emissions from vehicle exhausts, domestic cooking and heating, smoking etc. (Soumeya, Cheraitia et al. 2021, Kicinska and Dmytrowski 2023). For example, during the operation of power plants, coke plants, and smelters, PAHs are discharged into the environment with exhaust gas and wastewater. The natural volatilization and leakage of fossil fuels also increase the content of PAHs in the environment. Transport sources are mainly the exhaust emissions and fuel leakage of cars, ships and other vehicles. The large amounts of PAHs produced by coal and wood burning are usually the main domestic sources, together with cooking, cigarette burning (Zhu and Wang 2003, St Helen, Dempsey et al. 2013, Zhang, Zhang et al. 2022). Other flue gases such as solid waste and waste incineration are also important sources of PAHs (Johansson and van Bavel 2003, Tsai, Chen et al. 2009).

The distribution of PAH sources in different countries and regions varies greatly. In the United States, wood stoves are popular in many rural homes, and communities often use wood-burning stoves and fireplaces to heat houses and businesses (USEPA 1998, Kramer, Campbell et al. 2020). In Brazil, Democratic Republic of Congo and Angola, deforestation and wildfires have caused large amounts of PAHs emissions (Shen, Huang et al. 2013, Souza, Santos et al. 2018). PAHs in China are mainly derived from the burning of biomass such as straw and firewood, followed by household coal burning and coke industries. Eastern and southern provinces have higher emission densities, while western and northern provinces have greater emission intensity (Xu, Liu et al. 2006, Wang, Zhu et al. 2013). The PAHs in the Arctic are mainly derived from long-range transport of emissions from fossil fuels and biomass combustion. The increase in oil exploration and transportation activities will also increase the local pollution input (Balmer, Hung et al. 2019). It can be seen from this that vegetation coverage, different energy structure and development status lead to differences in the sources of PAHs in different regions.

PAH concentrations are generally high in urban areas because of human activity. In Nanjing, from urban to suburban to rural areas, soil PAHs pollution has a gradient from high to low. The reason is that the distribution of pollutants in urban soils is mainly affected by atmospheric deposition, discharges and spillages from industrial activities, transportation, population density and urbanization (Wang, Wu et al. 2015). PAHs were detected in cities, industrial locations and rural areas in southern Spain, for example. The concentrations in urban and suburban industrial areas were significantly higher. As the distance from the emission source increases, the pollution level of PAHs in rural areas decreases (Varea, Galindo et al. 2011).

2.1.2 Fate and behavior of PAHs

2.1.2.1 PAHs in water

PAHs can enter the environment with wastewater, or they can be adsorbed on atmospheric particulates and enter water bodies through wet and dry deposition (Gaurav, Mehmood et al. 2021, Han, Yu et al. 2023). PAHs in the soil can also enter water bodies with surface runoff, groundwater, and soil irrigation (Baek, Field et al. 1991, Wania and Mackay 1996, Chen, Song et al. 2023). Water-gas exchange is important in the environmental behaviour of PAHs and other semi-volatile organic compounds. In addition to the physical and chemical properties of PAHs, the ambient conditions such as wind speed and temperature are also important (Gustafson and Dickhut 1997, Qin, He et al. 2013). PAHs in waters may be in dissolved form and/or adsorbed on suspended particles. Water soluble PAHs can enter the atmosphere through volatilization. Some enter the biological phase through absorption and uptake into the food chain; they also reach sediments following sedimentation. PAHs adsorbed on the sediment particles may re-enter the overlying water following re-suspension and become mobile in the environment again.

PAHs can be degraded in natural waters by direct or sensitized photochemical reactions (Zhang, Sun et al. 2024). Some can absorb solar radiation on the water surface, making direct photodegradation possible. When irradiated with light in pure or natural water, some PAHs may be broken down (Fasnacht and Blough 2002). The ionic strength and oxygen have little effect on the photolysis process, but when the concentration of humic acid is high, the degradation rate of individual PAHs such as phenanthrene is enhanced (Miller and Olejnik 2001, Bertilsson and Widenfalk 2002, Xie, Gu et al. 2017). The combination of PAHs and dissolved organic matter (DOM) in natural waters may inhibit or enhance photodegradation, depending on whether fluorescence quenching produces PAH reaction intermediates (Schlautman and Morgan 1993, Cai, Zhang et al. 2023).

2.1.2.2 PAHs in sediments

PAHs can enter water environments through dry and wet deposition, surface runoff, wastewater discharge. Due to their low solubility and high octanol-water partition coefficient (Kow) value, they readily combine with suspended particles in the water environment and settle into the sediments (Christensen and Bzdusek 2005, Duran and Cravo-Laureau 2016). The organic carbon content, particle size of the sediments and the properties of PAHs themselves are the main factors affecting their distribution in the sediments (Skic, Boguta et al. 2023). Studies have shown that sediments with smaller particles have stronger adsorption of PAHs (Wang, Wang et al. 2015). At the interface between water and sediments, low molecular weight PAHs were more easily dissolved in the overlying water, while high molecular weight PAHs had a low detection rate in pore water and were more prone to be retained in sediments (Wu, Lin et al. 2022). PAHs can be transferred from contaminated sediments to plant roots, benthic organisms and water. Affected by environmental factors or biological disturbance, PAHs can re-enter the water body through sediment resuspension, becoming a secondary pollution source and posing a threat to aquatic organisms (Maletic, Beljin et al. 2019). After entering aquatic organisms, PAHs are enriched through the food chain and could then affect humans (Kumar, Bolan et al. 2021).

2.1.2.3 PAHs in soil

PAHs are often classified as semi-volatile substances; the lower molecular weight compounds can volatilize into the atmosphere under ambient temperatures, while the higher molecular weight compounds tend to partition to particles/aerosols and become deposited to soils and vegetation closer to source areas. The sources of PAHs in soil and their behaviors are shown in the Fig. 2.1. PAHs in soils can originate from atmospheric deposition, sewage irrigation, industrial sources and sewage sludge/farmyard manure reuse in agriculture (Wild and Jones 1994, Wu, Guo et al. 2018). PAHs in soils can undergo different physical, chemical and biological processes. These include biodegradation, leaching, volatilization, partitioning to colloids and soil organic and inorganic fractions. In general, PAHs have long half-lives (months-years-decades) in soils.

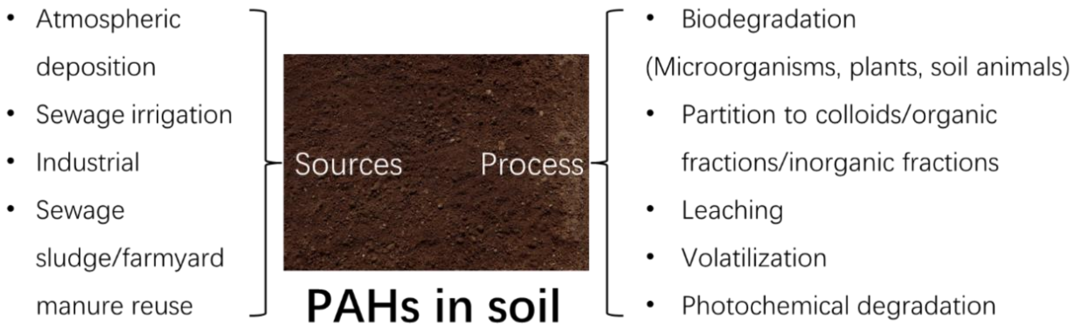


Fig. 2.1 Schematic diagram of some possible sources and fates of PAHs in soil

Cumulative atmospheric deposition can have a major impact on the loading of PAHs in soils. The main factors affecting the exchange of PAHs across the soil-air interface are soil characteristics (including soil organic carbon content, humidity, texture and pore structure), as well as the concentration and type of substances and air temperature (Nam, Thomas et al. 2008, Wang, Wang et al. 2014). Research has shown that more PAHs volatilise from the soil into the atmosphere in summer, while more PAHs settle in the soil in winter – when conditions are colder and more combustion tends to occur (Wang, Cao et al. 2011). The increase in household heating demand, the reduction in atmospheric reactions and photodegradation, and the decrease of air mixing in winter can lead to higher concentrations of PAHs in the atmosphere in winter, resulting in greater atmospheric deposition to soils (Menichini 1992, Li, Tao et al. 2010, Wang, Zhao et al. 2024).

PAHs are readily adsorbed on soil particles and soil organic matter. Hydrophobic organic pollutants like PAHs can partition into soil organic matter and/or undergo surface adsorption to soil minerals, mainly due to the action of chemical bonds such as hydrogen bonds, coordination bonds and dipole bonds (Weber Jr, LeBoeuf et al. 2001). Studies have found a strong correlation between the concentration of PAHs in soil and soil organic matter (Maisto, De Nicola et al. 2006, Yang, Zhang et al. 2010, Kim, Tarafdar et al. 2023). There are obvious differences in the adsorption of PAHs by different components of soil organic matter. The presence of fulvic acid and humic acid can enhance the water solubility of PAHs (Johnson and Amy 1995). Black carbon (BC) is a carbonaceous residue from incomplete combustion of biomass or fossil fuels and is commonly found in soil and sediment. Although the content of BC is usually less than 10% of the TOC, due to its high surface area and microporosity, black carbon has significant adsorption effects on PAHs (Oen, Cornelissen et al. 2006, Yang, Lampert et al. 2012, Gao, Li et al. 2023). In Swiss soil, BC was significantly positively correlated with lighter PAHs, while in Delhi soils, heavier PAHs were more associated with it (Agarwal and Bucheli 2011).

Soil minerals are the main inorganic components of the soil. Because of their layered structure, high specific surface and ion exchange characteristics, soil minerals have strong adsorption capacity and catalytic properties for organic pollutants. Using quartz, goethite-coated quartz, quartz-montmorillonite mixture to adsorb phenanthrene, pyrene and benzo(a)pyrene, it was shown that different minerals can rapidly sorb PAHs and with higher capacities for the higher molecular weight species. Sorption approached equilibrium over a few hours (Müller, Totsche et al. 2007). Researchers also used the Langmuir model to describe the desorption hysteresis of PAHs from clay minerals (Yang, Jin et al. 2013).

Microbial degradation occupies an important position in the transformation of pollutants and it is one of the main ways to remove PAHs from soils and sedimentary environments. Zeng isolated two strains of Mycobacterium from PAHs-contaminated farmland soil, which could degrade pyrene, phenanthrene, fluoranthene, anthracene, and benzo [a] pyrene (Zeng, Lin et al. 2010). Most microorganisms degrade low-ring PAHs, but only a few strains can degrade the high-ring PAHs. Basidiomycetes and white rot fungi have been identified as being capable of degrading the more recalcitrant PAHs (Field, De Jong et al. 1992, Steffen, Schubert et al. 2007, Zhang, Zhang et al. 2016). Research has shown that *Pseudomonas aeruginosa* and *Sphingomonas* could generate surfactants that increase the solubility of PAHs, thereby enhancing their substrate bioavailability (Déziel, Paquette et al. 1996, Johnsen and Karlson 2004). The formation of a mycelial network by zoospores produced by rhizosphere oomycetes can enhance the bioavailability of PAHs, which is beneficial for improving bioremediation (Sungthong, van West et al. 2015).

Plants can also promote the degradation of PAHs, and plant co-cultivation can enhance the process. PAHs can be directly absorbed by plant roots and degraded and transformed in their tissues. Research has confirmed that benzene, naphthalene and benzo(a)pyrene are oxidized and converted into hydroxyl compounds by microsomal mono-oxidase in plants (Blum and Fridovich 1985). PAHs can also be lost in gaseous form after being taken up by plants. The volatilisation of naphthalene could account for 32-45% of the total removal of PAHs from soils by tall fescue

(*Festuca arundinacea*) and alfalfa (*Medicago sativa*) (Schwab, Al-Assi et al. 1998). Plant root exudates can also enhance degradation of PAHs; for example exudates of white mulberry (*Morus alba*) removed 15-20% of benzo(a)pyrene in 24 hours in one study (Rentz, Alvarez et al. 2005). The soil is rich in soil animal populations, which are intimately linked to soil health and the ability to degrade complex molecules. The movement of soil animals in the soil can improve its porosity/permeability, mix nutrients through the surface layers, and facilitate the degradation of PAHs by aerobic bacteria. Earthworm activities can help spread fungal propagules, significantly increase fungal infection rates, increase the number of bacteria that degrade PAHs in the soil, and enhance the activity of related enzymes (Martinkosky, Barkley et al. 2017, Yang, Hadibarata et al. 2020). The activities of ciliates and nematodes can also increase the contact surface area of pollutants and degrading bacteria and promote the degradation of pollutants (Rogerson and Berger 1983).

Microbial degradation and volatilization are the main removal processes for low molecular weight PAHs from waters and soils. However, PAHs with four or more rings have low water solubility, making them difficult to be biodegraded (Wilson and Jones 1993, Meulenberg, Rijnaarts et al. 1997). Therefore, abiotic degradation/loss processes can also be important degradation pathways for some PAHs.

PAHs are mainly accumulated in the soil surface, associated with the SOM. Studies have shown that photochemical conversion in the soil ‘surface skin’ can play a significant role in the disappearance of organic pollutants from soil (Balmer, 2000). The photochemical degradation of PAHs in soil generally occurs at the soil / air interface, that is, within 1 cm of the soil surface, and the direct photolysis process generally occurs in the soil surface <0.4 mm. Some substances present in the soil can be used as photosensitizers, such as organic matter in the soil. Under sunlight, these substances can undergo photosensitization reactions with organic pollutants in the soil to degrade the organic matter. The photocatalytic reaction process can also be carried out in deeper soil surface layers (Hebert and Miller 1990). Low- and medium-molecular-weight PAHs are more easily adsorbed and photodegraded in fine-textured soils and have higher volatility in coarse-textured soils. In contrast, high molecular weight PAHs are more photodegraded in coarse-structured soils. The products produced by photolysis have higher toxicity than the parent PAHs, including oxy-, nitro- and hydro-PAHs (Marques, Mari et al. 2017).

2.1.3 Impact on the environment and humans

2.1.3.1 Impact on Water Environment

The toxicity of PAHs to aquatic plants and microorganisms varies greatly, depending on the species, compounds and environmental conditions. Exposure of algae to naphthalene leads to rapid reduction of chlorophyll, changes in cellular and inorganic composition, such as reduction of Mn and K. It results in a decrease in protein levels and an increase in carbohydrates and lipids (Soto, Hellebust et al. 1977, Hutchinson, Hellebust et al. 1981). These changes often result in increased mortality, but if the plants are placed in uncontaminated water, many cultures can recover after the exposure concentration decreases, due to the high volatility of many PAHs. Other studies found that PAHs affected microalgal activity, the change of cell morphology, redox reactions and photosynthesis, but bacterial activity, physiological condition and abundance were not affected by the same concentrations (Carman, Fleeger et al. 1995, Ben Othman, Pick et al. 2023).

The sedimentation of petroleum-based pollutants in water bodies often leads to their rapid and short-term accumulation in fish. The cutthroat trout (*Salmo clarki*) was exposed to crude oil for 90 days, and the main PAHs in its tissue were the same as that in the crude oil. Alkylated mono- and dicyclic aromatic hydrocarbons were accumulated most readily and naphthalene was the dominant aromatic component in the fish (Woodward, Mehrle Jr et al. 1981).

Long-term and sublethal exposure of PAHs can reduce the growth rate and survival rate of biological species. PAHs can have teratogenic and mutagenic properties, so there have been reports of abnormalities in fish (trout, zebrafish), including cardiac dysfunction, oedema, kidney disease, spine curvature, and reduced size of the jaw and other craniofacial structures (Woodward, Mehrle Jr et al. 1981, Incardona, Collier et al. 2004). Benzo(a)pyrene can cause chromosomal abnormalities and induce natural mutations in fish cells, resulting in a decrease in the success rate of hatching of sand sole (*Pegusa lascaris*) eggs and an increase in developmental abnormalities (Hose, Hannah et al. 1982). It may also result in decreased gonad maturity and reproductive success rate of fish, and transfer of pollutants from mother to offspring. This may lead to teratogenic effects such as internal haemorrhaging, oedema, and eye and yolk deformities (Hall and Oris 1991). The bioconcentration of PAHs through the food chain may also result in enhanced transfers to humans.

2.1.3.2 Impact on soil environment

In soil systems, some organic contaminants will be degraded or converted into harmless substances by plants, microorganisms and soil animals; some will also be taken up by plants via their root system and/or foliar uptake. There can be transfer of soil-borne PAHs into organisms via skin contact and respiration.

PAHs entering the soil can disturb microorganisms and soil animals. Research found that the composition, abundance and decomposition of invertebrates (nematodes, collembolans and mites) and microorganisms were affected in soil contaminated with PAHs (Blakely, Neher et al. 2002). Some organisms are sensitive to changes in contact with soil particles, and their types and numbers are reduced. Among them, nematodes are more suitable to be used as effective indicator organisms for PAHs-contaminated soil monitoring than other microarthropods. PAH concentration has a certain degree of stimulation on soil invertebrates of different ecological levels. The number of nematodes and micro-arthropods, collembola, earthworm weight, and nematode taxonomic diversity were positively correlated with PAH concentrations in one study (Erstfeld and Snow-Ashbrook 1999). This may be because soil microorganisms use PAHs as food. When PAH concentrations increase, a large number of soil microorganisms multiply, use PAHs or decompose PAHs into harmless derivatives, thereby stimulating the food chain of soil organisms, resulting in the mass reproduction of higher-level organisms in the food chain.

Plants can accumulate PAHs from the air and/or the soil. Uptake by plant roots depends mainly on the Henry's law, the octanol-water partition coefficient and water solubility of PAHs, as well as the soil organic carbon content and the type of plant (Simonich and Hites 1995, Tarigholizadeh, Sushkova et al. 2024). PAHs that pass through the endodermis and enter the interior of rice roots account for 60% of the total PAHs accumulated in root tissue, and lateral roots absorb more than nodal roots. Root mass, root lipid content and specific surface area will lead to differences in absorption (Jiao, Xu et al. 2007). Soybeans can absorb PAHs and transfer them to their stems and leaves. The stems and leaves can also absorb PAHs from the air and transfer them to their roots

(Edwards, Ross-Todd et al. 1982, Kumar, Verma et al. 2023). Due to enrichment in the food chain, long-term consumption of suburban crops and leafy vegetables may increase residents' exposure. Due to the close relationship between crops and human activities, the research of PAHs on crop toxicity has attracted attention. A total of 6 crops - both monocotyledonous and dicotyledonous plants - were cultivated with fluorene, anthracene, pyrene and chrysene at 1, 10, 50 and 100 mg kg^{-1} in soil. In the early stage of plant growth, when the soil concentration was less than 10 mg kg^{-1}, it had a stimulating effect on crop growth, while the lowest phytotoxicity threshold was 100 mg L^{-1} (Maliszewska-Kordybach and Smreczak 2000, McCann and Solomon 2000). This may be because PAHs have a ring structure similar to plant growth hormones such as auxin and gibberellin. Although PAHs can promote the growth of crops to a certain extent, the stress of PAHs can cause changes in plant morphology and tissue structure, reducing adverse effects such as crop yield (McCann and Solomon 2000). Different plants have different responses to stress. PAHs decreased *Arabidopsis thaliana* shoot and root growth, deformed trichomes and diminished root hairs, induced chlorosis, late flowering, and the appearance of white spots, which can eventually lead to necrosis (Alkio, Tabuchi et al. 2005). Observed by electron microscopy, when *A. thaliana* was exposed to phenanthrene, its organelles became deformed and the cell structure was disordered (Liu, Weisman et al. 2009). While bean germination was not affected by PAHs, its later growth was restricted (Smith, Flowers et al. 2006).

2.1.3.3 Impact on human health

People who work in industries related to soot cleaning, coal tar, and asphalt have a higher incidence of skin cancer (Boström, Gerde et al. 2002). Animal experiments first proved that PAHs have mutagenic, carcinogenic and other toxicological effects. Mouse experiments have shown that different PAHs cause lung adenomas, and there is a certain interaction between different components. Benzo[a,b]anthracene and BaP cause tumours and are carcinogenic to rodents (Dipple 1985, Nesnow, Mass et al. 1998). PAHs can enter animals through the skin, respiratory tract, and digestive tract, and have potential teratogenic, carcinogenic and mutagenic properties, and neurotoxicity (Grova, Salquebre et al. 2011, Sun, Song et al. 2021, Xu, Liu et al. 2024).

Chemical carcinogenesis refers to the process by which chemical substances cause normal cells to transform and develop into tumours. Exposure to PAHs may increase the risk of lung cancer, oral cancer, larynx cancer, pharyngeal cancer, esophageal cancer and bladder cancer (Becher, Ramroth et al. 2005, Kamangar, Strickland et al. 2005, Bosetti, Boffetta et al. 2007, Paget-Bailly, Cyr et al. 2012, Mosallaei, Hashemi et al. 2023). Most research has related to lung cancer, with the association between lung cancer and cigarette smoking, and PAH emissions across different regions, countries and at the global scale (Zhang, Tao et al. 2009, Olsson, Fevotte et al. 2010, Motorykin, Matzke et al. 2013, Cuadras, Rovira et al. 2016). Studies at coke oven plants, gas production plants, and aluminium smelters found that occupational exposure to PAHs by inhalation is associated with increased lung cancer risk (Armstrong, Hutchinson et al. 2004).

PAHs can also cause reproductive toxicity and genotoxicity. A research study of men attending an infertility clinic for diagnostic purposes found that urine 1-hydroxypyrene (a biomarker of PAHs) was positively correlated with the sperm morphology abnormality rate and percentage, and the environmental level of PAHs exposure would affect the quality of men's semen (Jurewicz, Radwan et al. 2013). Exposure to PAHs from coke-oven emissions could have an impact on semen quality and sperm DNA integrity and would contribute to increased levels of bulky DNA adducts in sperm (Jeng, Pan et al. 2013). Exposure to PAHs during pregnancy not only adversely affects the health of the pregnant woman, but also adversely affects the fetus transfers via the blood and umbilical cord. Benzo(a)pyrene can enter the bloodstream and may cause intra-uterine growth restriction or other developmental abnormalities by affecting placental cells (Fadiel, Epperson et al. 2013). Research on non-smoking, healthy and non-occupationally exposed women and their newborns showed that prenatal PAH exposure was related to infant birth weight, birth length and birth head circumference changes, and the sensitivity of different races to PAHs was different (Choi, Jedrychowski et al. 2006).

The current research on the human impact of PAHs has mainly focused on their carcinogenicity. When PAHs are exposed to sunlight, this can produce phototoxic effects when irradiated by ultraviolet light. They are converted into other derivatives through metabolism and radiation. For example, nitro-PAHs are phototoxic and can cause erythrocyte hemolysis in human blood. Its phototoxicity mainly depends on oxygen (Kagan, Wang et al. 1990). In this regard, researchers used Quantitative Structure–Activity Relationships (QSAR) and other methods to develop different models to determine the phototoxicity of PAHs (Betowski, Enlow et al. 2002, de Lima

Ribeiro and Ferreira 2005).

2.1.4 Conventional measurement methods for PAHs

For the determination of PAHs, environmental samples have the characteristics of low analyte concentrations with complex components and many interfering substances, which are susceptible to changes due to environmental influences. The concentration of PAHs in drinking water, natural water and wastewater is generally in ng L^{-1} to μg L^{-1} range (Busetti, Heitz et al. 2006, Chen 2007, Zhang, Dong et al. 2012). The concentration of PAHs in farmland soil and urban soil ranges from μg kg^{-1} to mg kg^{-1} (Kayali-Sayadi, Rubio-Barroso et al. 2000, Morillo, Romero et al. 2007, Tao, Zhang et al. 2008), while the concentration in polluted sites can reach several to hundreds mg kg^{-1} (Haleyur, Shahsavari et al. 2018, Guarino, Zuzolo et al. 2019). Therefore, samples must undergo complex pre-treatment before analysis to exceed the instrument detection limit and reduce the influence of sample matrix on detection. Fig. 2.2 shows the process of traditional methods for detecting PAHs.

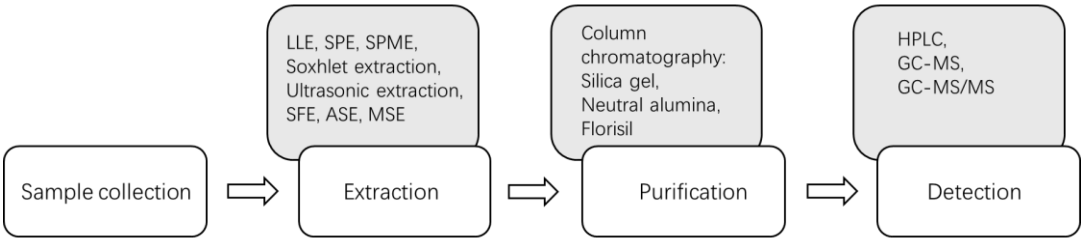


Fig. 2.2 The process of conventional methods for detecting PAHs

2.1.4.1 Extraction method of PAHs

The pre-treatment techniques for PAHs in water samples mainly include liquid-liquid extraction (LLE), solid-phase extraction (SPE) and solid-phase microextraction (SPME). The methods for solid samples such as soil and sediment mainly use Soxhlet extraction, ultrasonic extraction, microwave-assisted extraction (MAE), accelerated solvent extraction (ASE), and supercritical fluid extraction (SFE). Table 2.2 is a comparison of common measurement methods of PAHs.

Liquid-liquid extraction (LLE) is a classic and commonly used extraction method. It has good recovery and does not require special equipment, so it has a wide range of applications. The principle of LLE is to use the different distribution coefficients of the components in the two incompatible phases, so as to achieve the separation and enrichment. In LLE, it is very important to choose a suitable extraction solvent, not only to ensure sufficient extraction but also good selectivity. However, LLE also has several disadvantages; it is a complicated and time-consuming process, a low degree of automation, large consumption of organic solvents, and easy to cause secondary pollution. In addition, the results of LLE can be poorly reproducible, with high detection limits.

Solid phase extraction (SPE) technology is a fast, effective and convenient method for monitoring environmental pollutants. It is based on the principle of liquid-solid separation and extraction. The main process of this technology is to activate the adsorbent, add samples to make the analyte adsorb on the adsorbent as much as possible, then wash to remove a small amount of impurities, and finally elute the analyte with a small amount of suitable solvent for subsequent instrument detection. SPE is often used for pre-treatment of water samples, but also for purification of solid samples. For the extraction of PAHs in water, C_{18} is the most commonly used adsorbent (Marcé and Borrull 2000, Brown and Peake 2003). In addition, porous organoclay composite, polyvinylidenefluoride (fluorocarbon polymer sorbent) and other materials are also used (Ake, Wiles et al. 2003, Oliferova, Statkus et al. 2005). In order to increase the extraction efficiency of high-ring PAHs, nanomaterials such as multi-walled carbon nanotubes (MWCNTs), gold nanoparticles (Au NPs), and TiO_2 nanotubes are used in SPE technology (Ma, Xiao et al. 2010, Kefi, El Atrache et al. 2011, Wilson, Hewitt et al. 2014). The disadvantage of SPE is that the recovery rate may not be high, and the adsorbent may become blocked due to the pore size.

Solid-phase microextraction (SPME) is a solvent-free technique. This technology was first developed by scholars at Waterloo University in Canada on the basis of SPE. The use of chemically modified fused silica fibers with thermal desorption could shorten the extraction time without using solvent (Arthur and Pawliszyn 1990). The core part of the technology is the coating, which is a stationary phase that can adsorb analytes from various samples (Xu, Feng et al. 2012). The fused stone optical fiber coated with different materials is immersed in the sample or placed in the headspace, and the substance to be tested is transferred to the stationary phase by stirring or heating. After the adsorption reaches equilibrium, it is separated by thermal desorption of the stationary phase. It can be directly used in conjunction with chromatography for analysis. Therefore, this method integrates sampling, extraction, concentration and sample injection. The existing research on SPME found that it can be used for the pre-treatment of PAHs in different substrates such as water, soil, sediment, and food (King, Readman et al. 2003, Kumari, Patel et al. 2013, Rasolzadeh and Hashemi 2019). However, the extraction head of the solid phase microextraction device is expensive and easy to wear. When the amount of use increases, the adsorbent coating may be lost or there is a residual effect, so it is not suitable for batch sample preparation (Zhang, Yang et al. 1994).

Soxhlet extraction is a classic method for extracting PAHs from the solid phase. Because of its high recovery rate, wide application range and good reproducibility, it is used as the standard method for PAHs determination. The basic principle is that after the solvent is heated and boiled, the vapor rises through an air pipe, and the solvent reflux and siphon effect are used to enrich the soluble matter in the solid (Banjoo and Nelson 2005). However, the Soxhlet extraction method takes a long time and the operation is relatively cumbersome. Generally, it requires continuous extraction for 6-24 hours or even 72 hours, and the amount of organic solvent used is large.

Ultrasonic extraction can effectively extract a variety of inorganic and organic substances and is one of the PAH extraction methods recommended by the US Environmental Protection Agency (USEPA 1986). This method uses the effects of strong vibration, high acceleration, cavitation generated by ultrasonic waves to accelerate removal of the target analytes into the extraction solvent. Although the ultrasonic extraction method is not as reproducible as the Soxhlet extraction method, the extraction time of PAHs in soil is shorter. It is simple with a high extraction efficiency (Luque-García and Luque de Castro 2003, Olivella 2006, Peng and Lim 2022). The ultrasonic extraction method is used more in the extraction of structurally stable organic substances, and it is a commonly used extraction method for modern PAH pre-treatment.

Supercritical fluid extraction (SFE) is a sample extraction technology that has developed rapidly in recent years. Not only can it meet the requirements of ideal extraction methods, but it can also be used online with a variety of modern analytical instruments, such as GC, GC/ MS, HPLC and supercritical fluid chromatography (Hawthorne and Miller 1987). Extraction by the SFE method can be completed in 10 to 60 minutes. The disadvantage is that the equipment is expensive, and for the operator it has higher requirements. Also, the soil moisture content affects the recovery rate. Both CO_2 and N_2O have been studied as supercritical fluid for the extraction of PAHs, but

N_2O is not recommended. Because N_2O is an oxidant, it may cause an explosion when extracting solid samples with high organic content (Hawthorne, Langenfeld et al. 1992, Bøwadt and Hawthorne 1995, Benner 1998). The extraction efficiency of pure CO_2 is generally less than 50%, so it can be modified with organic reagents. Using 10% dichloromethane modified CO_2 as the fluid can get a good recovery rate (Bøwadt and Hawthorne 1995, Benner 1998).

Microwave associated extraction (MAE) uses microwave energy (a type of non-ionizing radiation) to improve the extraction efficiency, that is, to accelerate the extraction process of the target extract in the sample by microwave heating. This microwave energy causes molecular movement through ion migration and dipole rotation, but does not cause molecular structure changes (Wang, Meng et al. 2007). This technology greatly reduces the use and extraction time of organic solvents and increases the number of samples which can be processed by using a multi-container system or automated system that allows multiple samples to be extracted simultaneously (Oukebdane, Portet-Koltalo et al. 2010). However, the extraction time of this method is not easy to control. If the time is too long, the analyte could be lost, and if the time is too short, the extraction will not be complete. Moreover, when the local temperature is too high in microwave extraction, the components may be decomposed, which will obviously affect the extraction results.

Accelerated solvent extraction (ASE) is a method using conventional solvent (same as the solvent used in Soxhlet extraction) that increases the elution rate at a higher temperature (50-200 °C) and pressure (5-200 atm). The ASE method sends the sample to be loaded into a stainless-steel extraction tank in the heating furnace cavity, and the extractant is input into the extraction tank by a pump, so that the sample is statically extracted at the set temperature and pressure, and the extraction liquid automatically enters the collection bottle through a filter membrane. The extraction tank and pipeline is flushed with N_2 so that all the extraction liquid enters the collection bottle to be tested. The entire extraction process takes about 5-15 minutes (Heemken, Theobald et al. 1997). ASE is convenient, fast with low solvent consumption and can give a high recovery rate. The entire extraction operation is in a closed system that can reduce the pollution caused by solvent evaporation. ASE is mainly used to extract PAHs in soil, sediment and biological samples (Heemken, Theobald et al. 1997, Tao, Cui et al. 2002, Martinez, Gros et al. 2004), while Olivella 's research shows that this technology can also be used to extract PAHs from large-volume water samples (Olivella 2006).

Table 2.2 Comparison of common pre-treatment methods

Methods	principle	time	advantages	disadvantages
LLE	Different partition coefficients of substances in two liquids	long	Classic method, low cost, high recovery rate	Time and reagent consuming, easy to cause cross-contamination, complicated operation steps, wasting a lot of manpower and material resources
SPE	Solid-liquid separation extraction	20-45 min	High extraction efficiency, less use of solvents, and large enrichment multiples	Interference from complex matrix impurities, insufficient selectivity of solid phase
SPME	equilibrium partition in the sample and extraction coating	10-30 min	Simple operation, less use of organic solvents and easy automation	High cost
Soxhlet extraction	Different solubility in different solvents	24-48 h	Classic and mature method, good reproducibility	Large workload, long operation time and large environmental pollution
Ultrasonic extraction	Cavitation and secondary effects of ultrasound	30-60 min	Fast extraction speed and easy operation without special equipment	Relatively poor reproducibility, not suitable for easily degradable components under ultrasonic

				conditions
SFE	Strong solubility and high permeability of supercritical fluids	30-60 min	Fast extraction speed and easy automation	Complex device, high cost, and it is dangerous to operate under high pressure
ASE	Strong solubility of solvents at high temperatures	10-15 min	Easy to operate, safe and reliable	High cost
MSE	Selective extraction of analytes by microwave heating	4-20 min	Save resources, high extraction efficiency and environmentally friendly	high cost for equipment, not suitable for easily degradable components under microwave conditions

2.1.4.2 Purification method of PAHs

In general, the solvent used for the extraction of soil PAHs is non-selective. Not only are the PAHs in the extraction solution, but also other non-target organic substances that can have qualitative and quantitative effects on the target compounds. Therefore, it is necessary to purify the extract to make the components of PAHs better separated and in a cleaner matrix, to improve the accuracy of analysis. Column chromatography is the most common purification method. There are three commonly used column chromatography adsorbents: silica gel, neutral alumina, and Florisil. Among them, silica gel is the most widely used in the analysis and purification of PAHs. Neutral alumina is generally mixed with silica gel in a certain ratio to form a mixed silica gel column, due to its unsatisfactory removal effect on alkanes. The purification by using Florisil is simple to operate, has good reproducibility, and has good separation and purification effects on high molecular weight PAHs (Navarro, Cortazar et al. 2006, Ratola, Lacorte et al. 2006, Sorensen, Silva et al. 2016).

2.1.4.3 Detection method of PAHs

After extraction and purification, PAHs need to be detected. The most commonly used techniques are high performance liquid chromatography (HPLC), and gas chromatography-mass spectrometry (GC-MS). High performance liquid chromatography (HPLC) is used for the separation and quantitative determination of PAHs, especially for the detection of high molecular weight PAHs. HPLC has the characteristics of good selectivity and high sensitivity. Detectors include ultraviolet detectors (UVD), fluorescence detectors (FLD), and diode array (variable UV wavelength) detectors (DAD). The fluorescence detector in series with one of the other two can complement each other. The detection limit of PAHs in water could typically be 0.3-1.6 ng L^{-1} for water sample in 1 L (MEPC 2009).

Gas chromatography-mass spectrometry (GC-MS) uses a mass spectrometric detector, which can better reduce the influence of soil matrix and instrument noise and is suitable for the determination of multi-component PAHs. The detection limit of PAHs in water could be 2.2-22 ng L^{-1} using GC-MS (MEPC), and the detection limit of PAHs in soil could reach 0.08-0.17 mg kg^{-1} for ~20 g soil samples (MEPC 2016).

2.2 Passive samplers

At present, the most commonly used technique for sampling PAHs in waters is ‘active’ sampling. ‘Grab’ samples are obtained, which then need to be extracted, purified and enriched after transporting back to the laboratory. However, due to the low concentration of PAHs in the environment, it is necessary to get large volumes of water samples to reduce the detection limit of target compounds in the samples. The sample pretreatment process for both water and soil samples are complicated and time-consuming. Meanwhile, during the storage and transportation of samples, the physical and chemical properties of the chemicals may change, and there may also be cross contamination, resulting in inaccurate measurement results (Zi, Xiao et al. 2022). In addition, active sampling methods only provide the concentration of target compounds in the water sample at the moment of sampling. The impact of sudden events such as illegal discharge, rainfall, or leakage can result in the instantaneous concentration not accurately reflecting the concentration of the target compound within a period of time (Cristovao, Bento-Silva et al. 2021). An alternative but very expensive ‘active sampling’ uses a programmable autosampler, which collects and stores prescribed volumes of water at set times. These can be bulked to give average water samples, across a day or a week, for example.

In contrast, passive sampling technology can perform in-situ sampling, collecting the time-weighted average concentration of target chemicals over a period of time, making the results more representative. Passive samplers are relatively cheap, so they can be used to collect many samples in space and time. Therefore, passive sampling methods have attracted increasing attention and developed rapidly in recent years.

2.2.1 The principle of passive sampling technology

Passive sampling means that target substances could freely transfer from the sampling medium to the passive sampler without external forces. It relies on chemical potential differences (Kot-Wasik, Zabiegala et al. 2007). It is generally believed that this process is the passive diffusion of the target substance from the water phase to the receiving phase of the sampler, until the system reaches equilibrium or sampling is completed. Huckins proposed a first-order kinetic model to describe this process (Huckins, Manuweera et al. 1993). The exchange kinetics between the aqueous phase and the sampler can be described by the formula

$$C_s(t) = C_W \frac{k_1}{k_2}(1 - e^{-k_2 t}) \qquad \textit{(Eq. 2.1)}$$

Where t is the passive sampling time, C_S is the concentration of the target substance in passive sampling devices (PSD) at time t, C_W is the concentration in water, k_1 and k_2 are the uptake and offload rate constants (Vrana, Allan et al. 2005), respectively. When PSD are exposed to the environment, the accumulation of target substances can be divided into three stages: linear accumulation, curve enrichment, and ultimately reaching equilibrium state (shown in Fig. 2.3).

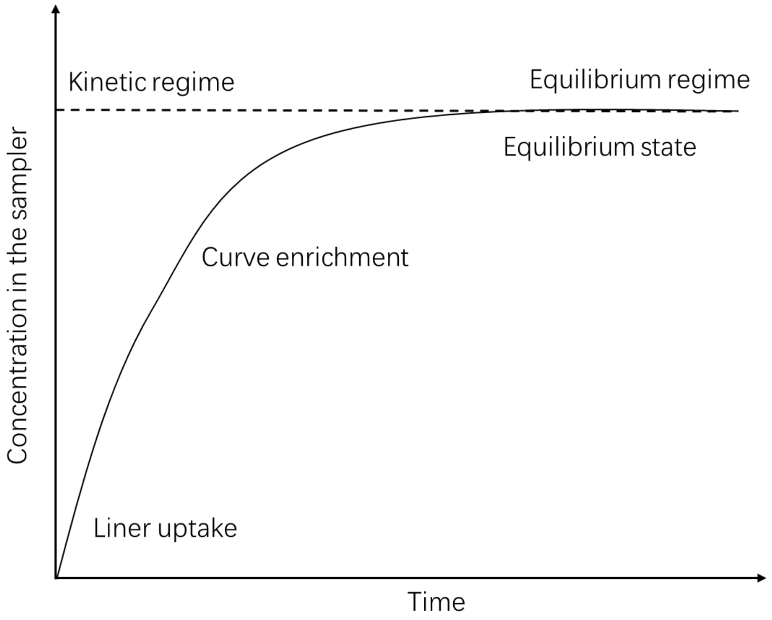


Fig. 2.3 Principle of the passive sampler

2.2.2 Types of passive samplers

According to the exposure time of the sampler, the sampler could operate as an equilibrium sampler or a kinetic sampler. An equilibrium sampler must be exposed for sufficient time for equilibrium to be approached/attained. After the equilibrium is established, the concentration of dissolved pollutants in the water can be calculated using the distribution coefficient K between the receiving phase and the water body.

$$C_s = C_W \frac{k_1}{k_2} = C_w K \qquad \textit{(Eq. 2.2)}$$

The equilibrium passive sampler can relatively quickly achieve equilibrium, and its response time should be shorter than the time over which the target substance fluctuates in the water environment (Zabiegala, Kot-Wasik et al. 2010). After the system reaches equilibrium, if the concentration of pollutants in the water changes, the balance will be re-established (St George, Vlahos et al. 2011). Common equilibrium passive samplers include solid-phase microextraction (SPME) (Vrana, Allan et al. 2005), passive dispersion sampling bags (PDBS) (Vroblesky and Petkewich 2000), and the multi-layer diffusion sampler (Tang, Cape et al. 2001). Equilibrium will also depend on temperature, so the influence of temperature needs to be known. Equilibrium samplers do not rely on sampling time. As long as the equilibrium is reached, the concentration of pollutants in the environment can be directly inferred through the known distribution coefficient. However, since it takes a long time to ensure equilibrium, this type of sampler is not suitable for short-term pollution events or rapidly changing environmental monitoring. At the same time, the accuracy of the distribution coefficient has a great impact on the monitoring results, and it needs to be very accurately measured (Smedes 2009, Ghosh, Kane Driscoll et al. 2014).

For a kinetic sampler, the accumulation of pollutants in the sampler increases linearly with time during the sampling time – assuming the external concentration is stable. The offload rate k_2 should be negligible compared to the uptake rate k_1. The formula can be transformed into

$$C_s = C_w k_1 t \qquad \textit{(Eq. 2.3)}$$

Or

$$M_s = C_W R_s t \qquad \textit{(Eq. 2.4)}$$

Where M_S is the mass of the analyte captured in the passive sampler, R_S is the sampling rate of the analyte in water, and t is the exposure time. The weighted time averaged concentration C_W of the analyte in water can be calculated using formula Eq. 2.4 (Mazzella, Debenest et al. 2008). The kinetic sampler has a larger capacity for pollutants than the equilibrium sampler, reflecting the average level of pollutants during the sampling period, and can be used in water environments with low pollutant concentrations or high capacity of target substances (Vrana, Allan et al. 2005). Commonly used kinetic samplers include semi-permeable membrane devices (SPMD) (Wang, Bi et al. 2009), Polar organic chemical integrative sampler (POCIS) (Bayen, Segovia et al. 2014), Chemcatcher (Vrana, Mills et al. 2007), ceramic dosimeters (Martin, Patterson et al. 2003), and the Diffusive Gradients in Thin-films (DGT) technique (Zhang, Davison et al. 1998). The kinetic sampler does not need to wait for equilibrium and can obtain pollutant information in a relatively short period of time to reflect the fluctuation of the target compounds. It reflects the average concentration during the sampling period, which is conducive to long-term monitoring of the environment. By setting the sampling time, concentrations at different times can be obtained. However, this type of sampler is sensitive to environmental conditions such as temperature, flow rate and needs to be calibrated. These types of samplers are not suitable to measure the instantaneous concentration of pollutants (Caban, Lis et al. 2022).

2.2.3 Passive samplers for PAHs

At present, passive samplers have been developed to collect various pollutants in the water environment. With the demand for monitoring new pollutants, the types of passive samplers are gradually increasing. The passive sampling devices used for monitoring PAHs so far have mainly been SPMDs, Chemcatcher, silicone rubber, ceramic dosimeters and membrane-enclosed sorptive coating.

Semi-permeable membrane devices (SPMDs)

SPMDs have traditionally been one of the most widely used passive sampling devices for hydrophobic organic pollutants in water. SPMDs are generally made with semi permeable membranes and filled with high molecular weight neutral lipids inside (Fig. 2.4). The most commonly used material is low-density polyethylene (LPMD), with a filler of triglycerides. Nonpolar/weakly polar molecules (molecular weight <1000 Da) ($\log_{kow}>2$) in free state in water could enter the device through the micropores of the polymer membrane by passive diffusion and then be retained with the neutral lipids. However, large molecular pollutants attached to colloids or humic acids in water cannot enter the SPMD due to their volume limitations, thus achieving separation. The SPMD is deployed for a specified sampling time, then the device is collected, rinsed and dialysis is performed to recover the target substances using organic solvents. The measurement of PAHs by SPMDs is relatively mature and widely used for monitoring in environments such as freshwater (Parrott, Backus et al. 1999), seawater (Marrucci, Marras et al. 2013), and wastewater (Augulyte and Bergqvist 2007). SPMD was used to monitor the concentrations of multifunctional oxidase (MFO) and PAHs in the McKinzie River water (Parrott, Backus et al. 1999), and to monitor 16 types of PAHs in water wells, and the results showed good consistency compared to traditional methods. At the same time, PAHs that could not be detected by traditional methods could also be detected in wells with low concentration (Gustavson and Harkin 2000). The feasibility of using high-density polyethylene (HDPE) materials to monitor PAHs in water was confirmed (Muller, Manomanii et al. 2001). However, a large amount of solvent is required to extract the target analytes after sampling and then concentrate, which results in many analytical steps (Salim and Gorecki 2019). At the same time, the leakage of triolein during the field or laboratory process poses a risk of contamination, which may lead to repeated sampling (Tureyen, Yakan et al. 2022).

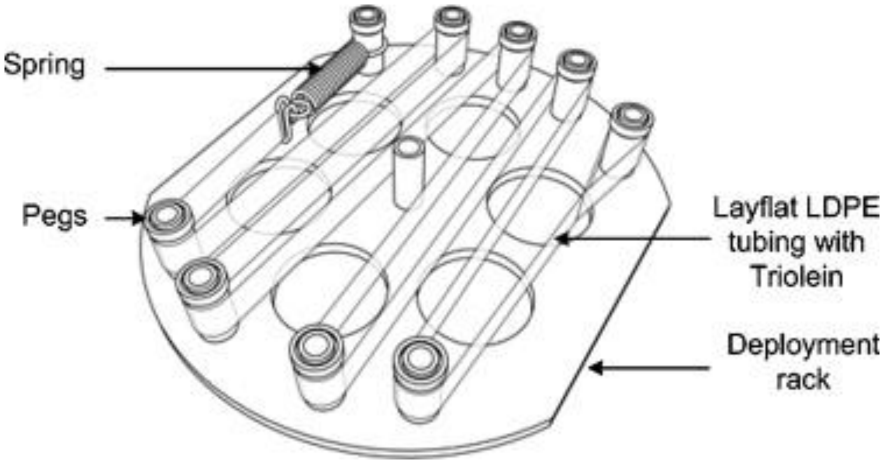


Fig. 2.4 Schematic diagram of the SPMD and its standard deployment system

Chemcatcher

Chemcatcher is a passive sampling technique developed by Kingston et al. in 2000 (Kingston, Greenwood et al. 2000). It is composed of a diffusion membrane and a solid adsorbent, as shown in Fig. 2.5. Different receiving phases or diffusion membranes are used for different target substances, making them applicable to both polar and non-polar substances. A C18 Empore disk is generally used as the receiving phase, and Low density polyethylene (LDPE) is used as the diffusion membrane to collect non-polar organic pollutants with log K_{ow} >4. Polyether sulfone can be used as a diffusion membrane to collect highly polar pollutants (Kingston, Greenwood et al. 2000). The application performance of Chemcatcher was tested in three European rivers in different seasons to monitor PAHs and other hydrophobic organic compounds (Vrana, Mills et al. 2010). It was also successfully used to monitor PAHs in Portsmouth Harbour in the UK, and reduced "cavity" in the sampler body to a minimum to give higher sampling rates (Lobpreis, Lopuchin et al. 2010). Chemcatcher requires a calibration procedure to confirm the sampling rate of the target compounds, and the different calibration methods increase the uncertainty of TWA concentration determination (Charriau, Lissalde et al. 2016). At the same time, due to low environmental concentrations of hydrophobic compounds, some studies have increased the sampling rate by adding n-octanol to the interstitial space, but this led to limitations in GC-MS analysis (Vrana, Mills et al. 2005).

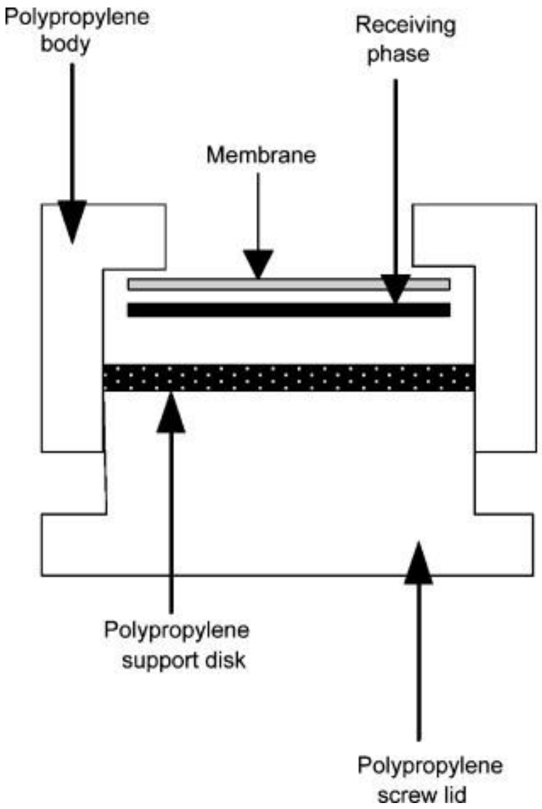


Fig. 2.5 Schematic diagram of Chemcatcher (Seethapathy, Gorecki et al. 2008)

Silicone rubber (SR)

The silicone rubber passive sampler is used for sampling by installing silicone rubber strips on stainless steel cages and brackets, as shown in the Fig. 2.6 (Monteyne, Roose et al. 2013). The silicone rubber was verified as a suitable alternative to SPMDs by comparing the characteristics of passive sampler materials, transmission resistance and distribution coefficient (Rusina, Smedes et al. 2007). A 4-year monitoring of PAHs in Belgian coastal ports using PDMS sheets as materials (Monteyne, Roose et al. 2013). By deploying silicone rubber passive samplers with deuterated performance reference compounds, the concentrations of 16 PAHs in 9 streams in Australia were estimated after wildfires (Schafer, Hearn et al. 2010). The effects of temperature and salinity on the measurement of PAHs and PCBs by silica rubber passive samplers was determined at 4 different temperatures (4, 12, 20, and 30°C) and 3 different salinity levels (0, 18, and 36 g/L) (Jonker, van der Heijden et al. 2015). During the process of linear accumulation, SR also requires calibration of the sampling rate. However, different methods for estimating the sampling rate (Rs) lead to significant differences in the free dissolved concentration of compounds, even up to 30% (Motorykin, Matzke et al. 2013).

Fig. 2.6 Mounting silicone rubber strips on the sampler cage (Monteyne, Roose et al. 2013)

Ceramic dosimeters

The ceramic dosimeter consists of a ceramic tube filled with a water saturated adsorbent and sealed at both ends with a lid made of polytetrafluoroethylene, as shown in Fig. 2.7. Ceramic membranes can serve as both diffusion barriers and containers for adsorbent materials (Weiß 2007). Adsorbent material Dowex Optipore L-493 was used to detect the concentration of naphthalene in water (Martin, Patterson et al. 2003). Another study used a ceramic dosimeter passive sampling device filled with Amberlite IRA-743 to detect PAHs in groundwater, and the sampler performed well in long-term tests (Bopp, Weiss et al. 2005). However, even though the ceramic dosimeter had a clear correlation with the extracted sample, the concentration measured by the adsorption dosimeter was quite different sometimes, probably due to evaporation and adsorption of solutes in the pipeline in field applications (Martin, Piepenbrink et al. 2001).

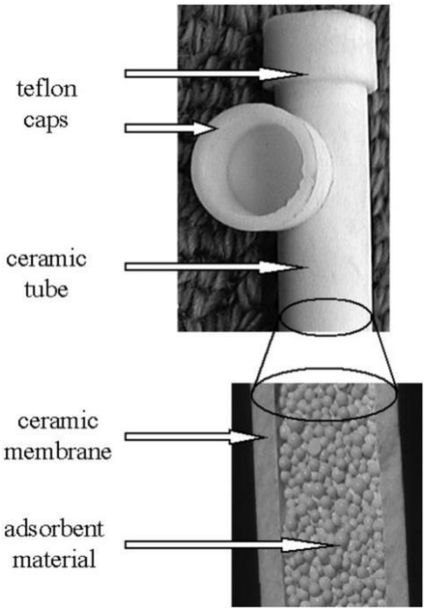


Fig. 2.7 Dosimeter design and cross section filled with adsorbent material (Martin, Patterson et al. 2003)

Membrane-Enclosed Sorptive Coating (MESCO)

Membrane-Enclosed Sorptive Coating consists of a bar coated with poly(dimethylsiloxane) (PDMS) enclosed in a dialysis membrane bag, as shown in Fig. 2.8. A week-long monitoring of hydrophobic organic pollutants, including PAHs and PCBs was conducted by using membrane-enclosed sorptive coating samplers in the laboratory (Vrana, Popp et al. 2001). It was used to test the effect of different flow rates on the performance of the samplers; on-site testing was then conducted to monitor the concentrations of PAHs, OCPs, and PCBs (Vrana, Paschke et al. 2006). The main disadvantages of MESCO are the low recoveries caused by bi-distilled water between two dialysis membranes and limited exposure times for sampling, caused by the low stability of the dialysis membrane (Valenzuela, Menezes et al. 2020).

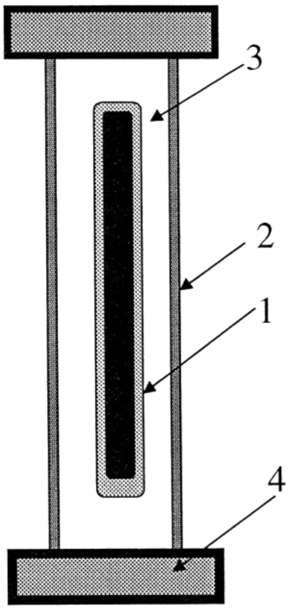


Fig. 2.8 Schematic diagram of the MESCO passive sampling device (Vrana, Popp et al. 2001). A Gerstel-Twister bar used for stir bar sorptive extraction (component 1) is enclosed in a dialysis membrane bag made from regenerated cellulose (component 2). The dialysis membrane bag is filled with 3 mL of bi-distilled water (component 3) and sealed at each end with Spectra Por enclosures (component 4).

Diffusive gradients in thin films (DGT)

Diffusive gradients in thin films (DGT) was first proposed by Davison and Zhang in 1994 as a passive sampling technique, which was developed from the diffusive equilibrium in thin film (DET) technique (Davison and Zhang 1994). Fig. 2.9 shows a schematic diagram of the DGT device. It requires measurement of diffusion coefficients in the laboratory before using, but then has advantages over other samplers, in that it is not affected by water flow conditions. Based on the principle of DGT, the absorption of target chemicals by DGT devices is only affected by temperature, in a way that can be measured and 'corrected', without being affected by other factors (Zhang and Davison 1995). DGT was first applied to the monitoring of metals in the environment and began to be applied to the monitoring of organic pollutants in 2012 (Zhang and Davison 1995, Chen, Zhang et al. 2012). There is now a wide international community of scientists who use DGT – it has been used in over 400 laboratories in more than 60 countries. There are over 1600 peer-reviewed publications on DGT, describing the development and testing of different samplers for inorganic (metals, nutrients, radioisotopes) and organic compounds and then using DGT for monitoring programmes, and to study biogeochemical processes in the laboratory and the field. This all provides a solid platform to build on, in developing a novel passive sampler for PAHs and then using it to improve understanding of PAHs in the environment.

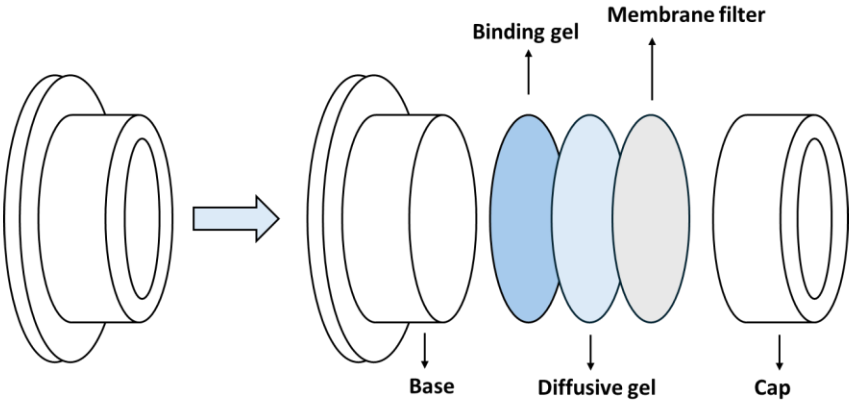


Fig. 2.9 Schematic diagram of a DGT device

2.2.4 DGT

2.2.4.1 Principle of DGT

The DGT technique is based on Fick's first law of diffusion. The transport of the target chemical from the bulk solution to the binding phase is only affected by diffusion. The diffusion flux (F) of a chemical diffusing through a unit cross-sectional area perpendicular to the diffusion direction per unit time is proportional to the concentration gradient at that cross-section. This is represented by

$$F = D\frac{(C_b - C')}{\Delta g + \delta} \qquad (Eq.\ 2.5)$$

Where D is the diffusion coefficient, C_b is the water concentration, and C' is the concentration at the interface between the adsorption and the diffusion gel. It is generally believed that the adsorption gel can quickly adsorb the target substance, so the interface concentration is effectively 0. Δg is the thickness of the diffusion layer (diffusive gel +filter membrane), and δ is the thickness of the diffusion boundary layer (DBL). Generally, when using DGT to sample in flowing water bodies, the DBL thickness can be ignored, so the formula can be simplified to

$$C_b = \frac{M\Delta g}{DAt} \qquad \textit{(Eq. 2.6)}$$

By defining the diffusion flux F, the formula can be obtained based on the total amount per unit area per unit time

$$F = \frac{M}{At} \qquad \textit{(Eq. 2.7)}$$

Where M represents the total amount diffused through the diffusion layer, A is the window area of the DGT device, and t is the exposure time. Therefore, the concentration of substances in water can be calculated through formula conversion.

$$C_b = \frac{M\triangle g}{DAt} \qquad \textit{(Eq. 2.8)}$$

To calculate the concentration of the target substance in the water, it is necessary to measure M. The adsorption gel is placed into a certain volume of elution solution, the concentration of the elution solution is measured and M is calculated using the formula

$$M = \frac{C_e(V_g+V_e)}{f_e} \qquad \textit{(Eq. 2.9)}$$

Where C_e is the concentration of the target substance in the elution solution, V_g is the volume of the adsorption gel, which is generally ignored in actual measurements, V_e is the volume of the elution solution, and f_e is the elution efficiency of the eluent for the test substance (measured experimentally).

2.2.4.2 Advantages and applications of DGT

As mentioned before, one of the advantages of DGT compared with other passive samplers that are easily affected by water flow and need to be calibrated on site is that it is only affected by temperature and can be calibrated by calculation. Since its development, DGT has been widely used by scientists and laboratories in more than 60 countries to conduct research and its use has a strong community. DGT also has the function of pre-concentrating target compounds on site. In addition to protecting the gel, the use of the filter membrane can also minimize particle adhesion, making the sample matrix cleaner and thus reducing background interference (Pichette, Zhang et al. 2007, Hutchins, Panther et al. 2012). For the development of new analytes, a set of standard laboratory testing and development procedures have been established. As the sections below show, a wide understanding of the possible applications of DGT help to improve understanding of water/soil biogeochemistry of pollutants.

DGT has been applied to obtain the average concentration of the analyte during the sampling time, measure the different speciation of the same element, measure the bioavailability of the target substance, and perform high-resolution measurements (sub millimeter level) (Zhang 2004, Williams, Zhang et al. 2012, Han, Williams et al. 2018).

Examples of applications in water environment

The DGT device has been validated for monitoring pollutants in environments such as rivers, lakes, wastewaters, seawater, and groundwater. Ion exchange resin was used as an adsorbent material for the detection of Zn, Cd, Cu, Ni, Mn, and Fe in seawater (Zhang and Davison 1995). DGT with iron oxide as binding gel can be used for the detection of dissolved phosphorus in natural water (Zhang, Davison et al. 1998). DGT was used for the detection of Cd, Cu, and Mn in river and estuarine waters (Denney 1999). Buzier et al. applied DGT to wastewater environments to obtain information on the speciation of Cu and Cd (Buzier, Tusseau-Vuillemin et al. 2006). Uranium can be obtained by DGT to measure its concentration in river water (Turner, Mills et al. 2014). DGT was first applied to the collection of organic pollutants in 2012, for in-situ measurement of antibiotics (Chen, Zhang et al. 2012). Subsequently, DGT was used to measure the concentrations of 40 antibiotics in wastewater (Chen, Zhang et al. 2013). HLB-DGT is used for monitoring polar drugs and insecticides in water (Challis, Stroski et al. 2018). XAD-DGT was used for monitoring perfluoroalkyl substances (PFASs) (Guan, Li et al. 2018). The monitoring of organic compounds by DGT mainly focused on hydrophilic compounds so far. With the gradual development of DGT sampling technology for organic pollutants, various new materials have been used for monitoring over 150 different organic pollutants of many different classes (Fang, Li et al. 2021, Bonnaud, Miege et al. 2022, Bonnaud, Mazzella et al. 2023). Among these organic compounds, pharmaceuticals (>60), pesticides (>30) and hormones (>20) were the main categories of substances. Pharmaceuticals are mainly hydrophilic (log $K_{ow} < 2$) to moderately hydrophilic (log $K_{ow} < 3$). More than 75% of pesticides are hydrophilic to moderate hydrophilic, while hormones are moderately hydrophobic (log $K_{ow} > 3$) and hydrophobic (log $K_{ow} > 4$). Table 2.3 gives information about DGT developed for detecting a wide range of different organic analytes. Fig. 2.10 presents photographs of DGT being used in water environments. As Table 2.3 shows, DGT has so far mainly been developed to measure hydrophilic compounds rather than hydrophobic compounds. DGT sampling of highly hydrophobic chemicals is hampered by their low water solubility.

Table 2.3 Configuration of DGT for some of the organic analytes developed so far in the literature.

Analyte class	Binding material	References
Antibiotics	XAD18	(Chen, Zhang et al. 2013, Challis, Hanson et al. 2016, Xie, Chen et al. 2018)
Bisphenols (BPA)	AC	(Zheng, Guan et al. 2014)
Endocrine disrupting chemicals (EDCs)	HLB	(Chen, Pan et al. 2018)
Glucocorticoids（GCs）	PEP-2	(Yan, Rong et al. 2022)
Household and personal care products (HPCPs)	HLB	(Chen, Li et al. 2017)
Illicit drugs	XAD18	(Guo, Zhang et al. 2017)
Nitrochloro-benzenes (NCBs)	HLB	(Zhang, Zhu et al. 2019)
Organophosphate flame retardants (OPFRs)	HLB	(Zou, Fang et al. 2018)
Pesticides and herbicides	HLB	(Challis, Hanson et al. 2016, Li, Chen et al. 2019)
Perfluorinated compounds (PFCs)	WAX, XAD18	(Guan, Li et al. 2018, Fang, Li et al. 2021)
Psychiatric pharmaceuticals	HLB	(Fang, Li et al. 2019)
Pharmaceuticals	HLB	(Challis, Hanson et al. 2016)

XAD18-Amberlite TM XAD18; HLB-hydrophile-lipophile balance; AC-activated carbon; WAX-weak anion exchanger; PEP-2-polar enhanced phase

Fig. 2.10 Photos of DGT being used in field campaigns and applications of DGT sampler auxiliary devices in different aquatic environments. B and C (Gabet, Sanz et al. 2021), D (dgtresearch.com)

Examples of applications in soil

DGT can be used to measure the concentration of metals in soil solution and reflect the dynamic exchange process of analytes between soil solid phase and soil solution (Harper, Davison et al. 1998, Zhang, Davison et al. 1998). The dynamic and unstable pool size information can be obtained through the DIFS model. Ernstberger et al. measured the distribution and exchange rates of Zn, Cd, and Ni in solid and solution phases in five different soils using DGT combined with DIFS model (Ernstberger, Zhang et al. 2005). Heidari et al. used DGT to study the kinetics of phosphorus release in soil (Heidari, Reyhanitabar et al. 2017). DGT has also been used to study the desorption and behaviour of antibiotics and atrazine in soils (Chen, Jones et al. 2014, Zheng, Sheng et al. 2023). After DGT is placed in the soil, the soil is disturbed in a controlled manner to reduce the concentration of analytes in the soil solution at the DGT-soil interface and stimulate the resupply of soil solid phase to the soil solution. Similarly, plants absorb elements or target substances from the soil, leading to a decrease in that substance in the soil water and replenishment from the solid phase. As a result, a portion of the non-stable substances adsorbed by the soil will be released and serve as a supplement. Studies have also shown that there is a relationship between the DGT-labile portion in soils and the bioavailability of substances in soil. Pérez found through field experiments that the correlation between Cd measured by DGT and the concentration measured in wheat and potatoes was not high, but it was better correlated with their edible parts (Pérez and Anderson 2009). Black et al. studied the bioavailability of metals in soil by comparing $Ca(NO_3)_2$ extraction, EDTA extraction, DGT and other methods, and conducted correlation studies with the accumulation of wheat and ryegrass. The results showed that DGT could predict the bioavailability of Cd to these plants well (Black, McLaren et al. 2011). Dai et al. found through comparison between DGT and traditional chemical methods that DGT can be used to evaluate the bioavailability of As in soil, and DGT measurement of the bioavailable fraction is not affected by soil properties (Dai, Nasir et al. 2018). In recent years, DGT has also been trialed to evaluate the bioavailability of organic pollutants in soil. Li et al. found that DGT and soil solution extracts can predict the bioavailability of atrazine absorbed by maize (Li, Rothwell et al. 2019). Song et al. also found a stable linear relationship between the concentration of DGT and the concentration of antibiotics in plant roots and shoots. The absorption of antibiotics by plants is related to plant species, antibiotic species, and soil properties (Song, Su et al. 2023). Fig. 2.11 shows some of the different applications of DGT for organic chemicals in soil and sediments. Fig. 2.12 are actual photos of DGT applications for organic compounds.

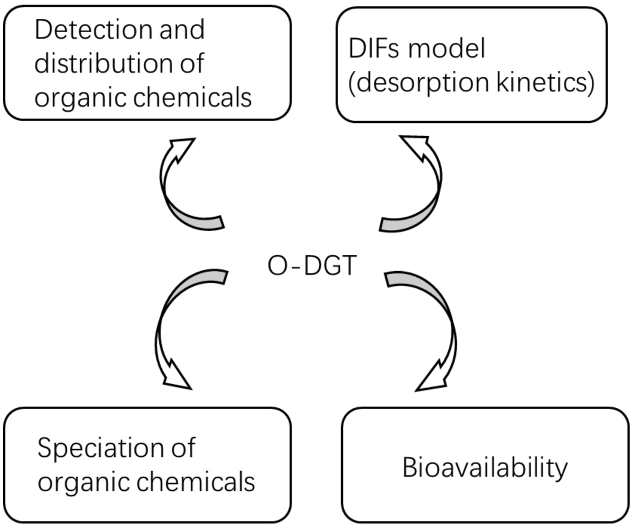


Fig. 2.11 Potential applications of DGT for organic chemicals in soils and sediments

Fig.2.12 Application of DGT to monitor organic chemicals in soils. To evaluate random errors during the experimental process, reduce the impact of soil heterogeneity on the experimental results, and enhance the credibility of the results, three parallel samples are commonly used in soil applications. The DGT probe photo was from a study of per- and polyfluoroalkyl substances (Yang, Liu et al. 2022).

2.2.5 Selection of target chemicals and materials

Based on the principle of DGT, the analyte diffuses through the diffusion gel, so the polarity of the chemical has a great impact on its uptake by DGT. As from previous studies mentioned in this chapter, DGT has mainly been applied in the research of inorganic and hydrophilic organic compounds since its development. However, through the study of model compounds, it was found that DGT has the ability to be applied to a wider range of octanol/water partition coefficients (log kow 0.8-9.5) in the future (Wang, Zou et al. 2019). The 16 priority controlled PAHs proposed by the USEPA are usually analysed and studied together, with a log kow range of 3.37-7.00, which is in the range of the model compounds just mentioned. Method development carried out in this thesis tested the range of PAHs which could be sampled by DGT.

Molecularly imprinted polymers (MIPs) are synthetic polymer materials with characteristics such as recognition specificity and structural predictability. It can create steric cavities through the complexation and removal of template molecules, creating binding sites in polymers and selectively binding to target molecules (Ncube, Kunene et al. 2017). At present, MIPs have been developed and applied in the separation and extraction of PAHs (Li and Wang 2013, Kibechu, Sampath et al. 2017), providing a good foundation for the development of DGT for PAHs in this experiment.

2.3 Summary

As highlighted by the review, PAHs are widely present in various environments and can pose risks to ecosystems and human health. Reliable and stable measurement and monitoring techniques are crucial for understanding their behavior and fate in the environment, and are essential for accurate environmental assessments and risk management. The review provided a comprehensive discussion and comparison of traditional methods for PAHs and summarized various passive sampling techniques applicable to their measurement. Passive sampling technology has the advantage of in-situ monitoring and can pre-concentrate trace organic compounds in the environment. Compared with passive technologies such as SPMD and Chemcatcher, DGT has the advantage of not requiring on-site calibration and is only affected by temperature – which can be corrected. Furthermore, the application of DGT in soil provides kinetic information on the dynamics of adsorption and desorption of compounds, helping the understanding of these processes. It also has the potential to evaluate the bioavailability of organic pollutants.

Although the development and application of DGT for trace organic pollutants is a relatively new field, it has been successfully developed and applied in different water environments and soils, covering over 150 types of organic pollutants. This lays the foundation for the research in this thesis.

Therefore, the overall objective of this research was to develop DGT technology for monitoring PAHs and explore its applications in water and soil environments. Due to the hydrophobicity and semi volatility of PAHs, the adsorption of them by filter membranes and sampler casings, the volatilization during the development and use of DGT may pose certain challenges for research. Addressing these issues is challenging, but a required first step.

Chapter 3 Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems

Qiuyu Rong[1], Yanying Li[2], Jun Luo[3], Liying Yan[3], Kevin C. Jones[1*] and Hao Zhang[1*]

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning 116023, P. R. China

[3]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023 P. R. China

*Corresponding authors

* Email: k.c.jones@lancaster.ac.uk

* Email: h.zhang@lancaster.ac.uk

Rong, Q., Li, Y., Luo, J., Yan, L., Jones, K. C., & Zhang, H. (2024). Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems. *Journal of Hazardous Materials*, 470, 134199.

Abstract

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants and need to be measured reliably in waters and other media, to understand their sources, fate, behaviour and to meet regulatory monitoring requirements. Conventional water sampling requires large water volumes, time-consuming pre-concentration and clean-up and is prone to analyte loss or contamination. Here, for the first time, we developed and validated a novel diffusive gradients in thin-films (DGT) passive sampler for PAHs. Based on the well-known DGT principles, the sampler pre-concentrates PAHs with typical deployment times of days/weeks, with minimal sample handling. For the first time, DGT holding devices made of metal and suitable for sampling hydrophobic organic compounds were designed and tested. They minimize sorption and sampling lag times.

Following tests on different binding layer resins, a MIP-DGT was preferred – the first time applying molecularly imprinted polymers (MIPs) for PAHs. It samples PAHs independent of pH (3.9−8.1), ionic strength (0.01−0.5 M) and dissolved organic matter <20 mg L^{-1}, making it suitable for applications across a wide range of environments. Field trials in river water and wastewater demonstrated that DGT is a convenient and reliable tool for monitoring labile PAHs, readily achieving quantitative detection of environmental levels (sub-ng and ng L^{-1} range) when coupled with conventional GC-MS or HPLC.

Keywords: Diffusive gradients in thin-films (DGT), passive sampler, polycyclic aromatic hydrocarbons, molecularly imprinted polymers (MIPs), aquatic environment

3.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are recognized as hazardous priority organic compounds. They are formed by incomplete combustion, and although they can be produced by volcanic activity and forest fires, human activities are the main sources of PAHs to the environment in recent decades. Important anthropogenic sources include: combustion of coal, oil and gas during power generation, domestic heating, vehicle emissions etc; the discharge of waste gas and wastewater by industry; cooking; the burning of solid waste and garbage (Tsai, Chen et al. 2009, Souza, Santos et al. 2018, Balmer, Hung et al. 2019, Kramer, Campbell et al. 2020). The persistence and long-distance transport potential of PAHs has led to their widespread presence in air, water, soil and other environmental media (Li, Tao et al. 2010, Wu, Guo et al. 2018, Sushkova, Minkina et al. 2019, Sun, Song et al. 2021). PAHs can enter humans and animals through the skin, respiratory tract and digestive tract, and have potential teratogenic, carcinogenic and mutagenic properties, and neurotoxicity (Grova, Salquebre et al. 2011, Li, Ni et al. 2017). Previous research has found that exposure to PAHs may increase the risk of lung cancer and a range of other cancers (i.e. oral, larynx, pharyngeal, esophageal and bladder) (Golozar, Fagundes et al. 2012, Rota, Bosetti et al. 2014, Manoli, Kouras et al. 2016); they have therefore been classified as carcinogens by the International Agency for Research on Cancer (IARC). Therefore, countries and international organizations such as the European Union, the United States, and China have policies and regulations for the management of PAHs. The United States Environmental

Protection Agency (USEPA) identifies 16 priority PAHs for monitoring and control. Accurate and effective monitoring of PAHs is a prerequisite for understanding their source, distribution, migration, risk assessment and management.

Monitoring of PAHs in water is usually by simple grab sampling, giving an ‘instantaneous’ concentration. However, it is known that concentrations will vary with flow conditions and discharges from sources, so multiple samples with high frequencies are required for the results to be representative. This can be costly and presents practical difficulties, particularly in remote/inaccessible areas (Novic, O'Brien et al. 2017, Mutzner, Vermeirssen et al. 2019). Current methodologies for determining PAH concentrations in water samples involve high-performance liquid chromatography (HPLC), gas chromatography coupled with mass spectrometry (GC-MS) and GC-MS/MS. However, the typically low concentrations of PAHs in aquatic environments (often in the ng L^{-1} range), pose significant challenges in terms of sample preconcentration and preparation. So, the transportation, storage, and complex sample pre-treatment processes can affect the analysis and accurate measurement of PAHs. Therefore *in situ* passive sampling of trace constituents in waters has attracted increasing attention in recent decades, because it can address many of these issues. Passive sampling integrates concentrations over the deployment time (typically days, weeks, months) by accumulating trace chemicals from the sampling environment, to give a time weighted average concentration. In previous research, semi-permeable membrane devices (SPMDs), POCIS, Chemcatcher, silicone rubber and ceramic dosimeter passive sampling devices have all been used to monitor PAHs in rivers, seawater, groundwater and other aquatic environments (Bopp, Weiss et al. 2005, Vrana, Mills et al. 2006, Harman, Brooks et al. 2011, Jonker, van der Heijden et al. 2015). However, changes in environmental factors such as flow rate and temperature can affect the performance of all these types of samplers, so they are generally regarded as semi-quantitative tools. With these designs of passive sampler, it is necessary to calibrate the results from laboratory uptake experiments and kinetic models, or from the loss rates of performance reference compounds (PRCs) which are added to the samplers before deployment (Booij, van Bommel et al. 2014, Chang, Lee et al. 2015). Although there has been much research on calibration methods, deviations in results may still be caused by changes in environmental conditions in practical applications (Allan, Christensen et al. 2016). In contrast, the Diffuse

Gradients in Thin films (DGT) passive sampler was invented to give quantitative *in situ* measurements without any field calibration. Based on Fick’s first principle of diffusion, the diffusion flux to a DGT sampler is only related to the environmental concentration of the tested substance and temperature (Davison and Zhang 1994, Chen, Zhang et al. 2012). Therefore, DGT has inherent advantages over other passive samplers for environmental monitoring and process-based studies.

The DGT technique has been widely used in the determination of inorganic substances (i.e. heavy metals and nutrients) in water, soil, and sediment since its development in 1994 (Davison and Zhang 1994, Zhang, Ding et al. 2014, Menegario, Yabuki et al. 2017, Galceran, Gao et al. 2021). It has been used for selected organic chemicals since 2012 and has also been extensively developed and applied (Chen, Zhang et al. 2012, Guibal, Buzier et al. 2019, Wang, Jones et al. 2020). Macroporous adsorbent resin (XAD18) and hydrophilic lipophilic balanced resin (HLB) are the most widely used adsorption materials. XAD18 resin based DGT was used for monitoring antibiotics (Chen, Zhang et al. 2013), illicit drugs (Guo, Zhang et al. 2017, Zhang, Zhang et al. 2018), PFOA and PFOS (Guan, Li et al. 2018). HLB resin-based DGT can sample pesticides, insecticides, pharmaceuticals (Challis, Hanson et al. 2016), organophophorus flame retardants (Zou, Fang et al. 2018), antibiotics, household and personal care products (Chen, Li et al. 2017, Wang, Jones et al. 2020). In addition, XAD1 resin, MAX, XDA1 resin, active carbon, WAX, C8, and C18 materials have been used in DGT devices for the measuring of antibiotics (Xie, Chen et al. 2018), anionic pesticides (Guibal, Buzier et al. 2017), endocrine disruptors (Xie, Chen et al. 2018), bisphenols (Zheng, Guan et al. 2014), per and polyfluoro alkyl salts (PFASs) (Fang, Li et al. 2021), and organotin (Cole, Mills et al. 2018), respectively.

As will be apparent from the list of compound groups just given, the existing organic DGT sampling devices have been restricted to measuring hydrophilic compounds so far, rather than hydrophobic compounds of low aqueous solubility. Hydrophobic compounds are mostly non-polar and can also have high affinity for filter membranes used in DGT samplers and the sampler casing material which is usually made from acrylonitrile butadiene styrene (ABS). These factors can affect their diffusion in the sampler and pose a challenge when applying DGT to hydrophobic compounds. However, in Wang et al’s recent research, limitations of using existing DGT sampler for monitoring compounds of high K_{OW} or with several aromatic rings were explored by using model compounds, with a log K_{OW} range of 0.8−9.5 (Wang, Zou et al. 2019).

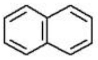
Therefore, the purpose of this study was to develop and test a novel DGT passive sampler that can be used for the in-situ accurate measurement of PAHs (log K_{OW} range from 3.45 for the 2-ringed naphthalene to 6.75 for the 6-ringed Dibenz(a,h)anthracene) in waters. Nine of the 16 priority PAHs were selected as test chemicals. Five metal materials were tested as sampler casing materials, because metals normally have a lower sorption of PAHs and other hydrophobics, and a new DGT device was designed. Three binding materials were tested, and the uptake kinetics and capacity of binding gels were determined. The diffusion coefficients of PAHs through the diffusive gel were measured for the first time, and the effects of diffusion layer thickness, deployment time, pH, ionic strength and organic matter concentration on the performance of the DGT samplers were studied. The newly developed DGT samplers were then applied *in situ* in the field - a river and a wastewater treatment plant.

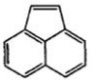
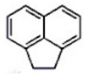
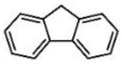
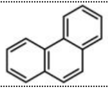
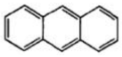
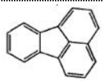
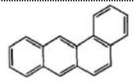
3.2 Materials and methods

3.2.1 Chemicals and Reagents

High purity standards were used. They covered 9 of the 16 priority PAHs specified by the U.S. EPA, as follows: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua), Pyrene (Pyr) and Benzo (a) anthracene (BaA). Table 3.1 gives their physical and chemical properties. Three different materials, MIP (CNW, Germany), Amberlite XAD 18 (Sigma-Aldrich, China) and Oasis HLB (Waters, U.K.) were used as binding materials. Details are given in the supporting information (SI).

Table 3.1 Physicochemical properties of selected PAHs

Compounds	Abbreviation	MW (Da)	Formula	Log K_{OW}	S_w25°C (mg L^{-1})	Structure
Naphthalene	Nap	128.18	$C_{10}H_8$	3.45	30.2	

Acenaphthylene	Acy	152.20	$C_{12}H_8$	4.08	3.93	
Acenaphthene	Ace	154．21	$C_{12}H_{10}$	4.22	3.40	
Fluorene	Flu	166.22	$C_{13}H_{10}$	4.38	1.90	
Phenanthrene	Phe	178.23	$C_{14}H_{10}$	4.46	1.18	
Anthracene	Ant	178.23	$C_{14}H_{10}$	4.54	0.086	
Fluoranthene	Flua	202.26	$C_{16}H_{10}$	5.20	0.260	
Pyrene	Pyr	202.26	$C_{16}H_{10}$	5.30	0.135	
Benzo (a) anthracene	BaA	228.29	$C_{18}H_{12}$	5.91	0.011	

Sw25°C – the solubility of chemicals in water at 25℃.

3.2.2 Analytical methods

The separation of target compounds was performed with a PAH C18 column (4.6 × 250 mm, 5 μm, Waters). For the determination of the 9 PAHs, high performance liquid chromatography combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) was used. Details of analysis are provided in the SI and the parameters of detectors are shown in Table 3.2 (a, b). The instrumental detection limits (IDLs) for HPLC were calculated according to the standard deviation from a measured concentration of standard (7 times) and method detection limits (MDLs) were calculated on the basis of IDLs, the recoveries for water samples and DGT samples (shown in Table 3.3)

Table 3.2 Detector parameter for PAHs detection

a UV detector event setting

Time (min)	Event	Parameter (nm)
0	wavelength	254
6	wavelength	220
7.8	wavelength	225

10.3	wavelength	210
11	wavelength	254
14	wavelength	235
16	wavelength	254

b Excitation and emission wavelengths of fluorescence detectors

Time (min)	Excitation wavelength (nm)	Emission wavelength (nm)
0	280	340
9	270	324
11	275	350
12.2	250	390
13.5	270	440
14.5	300	400
17	277	376

Table 3.3 Recoveries and instrument detection limits (IDLs) of selected PAHs detected by HPLC and method detection limits (MDLs) for water and DGT samples of 7-day field application

Compound	IDLs (μg L^{-1})	Recoveries (%)		MDLs	
		SPE	DGT	water sample (μg L^{-1})	7 days DGT deployment (ng L^{-1})
Nap	0.03	63.2±5.8	98.9±1.8	0.10	0.19
Acy	0.24	66.9±3.8	103.5±5.7	0.71	1.48
Ace	0.04	73.6±7.0	90.8±7.9	0.10	0.26
Flu	0.08	81.1±10.3	89.0±3.6	0.19	0.56
Phe	0.12	73.9±10.9	97.7±4.8	0.32	0.84
Ant	0.03	71.9±3.94	101.8±11.2	0.08	0.19
Flua	0.12	92.6±7.6	92.8±4.8	0.27	1.12
Pyr	0.05	91.4±6.7	95.3±2.9	0.12	0.46
BaA	0.07				

IDLs calculated using equation: $IDL = t_{(n-1,0.99)} \times S$, where S is the standard deviation from a measured concentration of standard, for testing 7 times, t(n-1,0.99) =3.143;

MDLs calculated using equation: $MDL = \frac{IDL}{R \times CF}$, where R is the absolute recovery for water sample, CF is the concentration factor, and CF is 0.5 for laboratory water samples;

MDLs For DGT calculated using equation: $MDL = \frac{M \triangle g}{DAt}$, where $M = \frac{IDL \times V}{R}$, where R is the absolute recovery for DGT sample, V is 1 mL, results calculated for 7-day deployment under 25℃ condition;

The D values were selected from Table 3.6.

3.2.3 Gel preparation

All materials for DGT samplers were supplied from DGT Research Ltd (Lancaster, UK, www.dgtresearch.com). Diffusive gels and binding gels were prepared according to well documented procedures (Zhang and Davison 1999, Chen, Zhang et al. 2012). To make gels of defined thickness, a 0.8 mm or a 0.5 mm PTFE spacer was placed between two glass plates, when making gels, to control the thickness of the diffusion gel and binding gel, respectively. MIP, XAD 18 and HLB resin were tested as the binding materials. Binding gels were made by mixing 2 g (wet weight) of binding materials and 10 mL MQ water with 0.2 g agarose. All the gels were cut into discs with a diameter of 2.51 cm and stored in 0.01 M NaCl solution at 4℃.

3.2.4 Adsorption by DGT casing materials and design for new metal device

In order to ensure low blanks and consistent results all the glass containers used were soaked in 5% nonionic surfactant solution for 4 h, rinsed with tap water and then rinsed with deionized water. After drying in an oven, they were heated in a muffle furnace at 500°C for 4 h. All containers were rinsed with methanol before use. Blank tests were carried out throughout the process.

The various materials used to make the DGT sampler were subjected to adsorption experiments on target PAHs. Traditional ABS plastic DGT casing and five common metal materials (aluminum, aluminum alloy, stainless steel, brass and copper) were exposed to 100 mL solution contained 50 μg L^{-1} of the mixture of 9 compounds (Benzo (a) anthracene was 10 μg L^{-1} because of its low water solubility). They were shaken for 24 h on an orbital shaker (25°C) at 100 rpm. All materials were immersed in MQ water as blanks, and the PAHs solutions alone served as controls. The ratio of PAHs adsorbed by various materials in 24 h were obtained by the detection of the concentration of the solution before and after deployment. Based on the existing design, a new metal device was first designed and developed for DGT measurement of PAHs.

3.2.5 Adsorption by filter membranes and diffusive gels

It was necessary to test different gels and filter membranes, to select the most appropriate for use in sampling PAHs. Polyacrylamide gels (PA), agarose gels (AG), eight different filter membranes (cellulose acetate membrane, CA; mixed cellulose ester membrane, MCE; nylon membrane, NL; nucleopore track-etch membrane, PC; polyethersulfone membrane, PES; polypropylene, PP; polytetrafluoroethylene, PTFE; polyvinylidene fluoride, PVDF) were placed in 10 mL brown glass bottles. The operation of the adsorption test was the same as the adsorption test on DGT holders.

3.2.6 Elution efficiency

Stable and reliable elution efficiency is crucial for the accurate determination of pollutants using DGT technology. Based on previous studies, the extraction efficiency of organic pollutants using acetonitrile ultrasound extraction meets the experimental requirements (Chen, Li et al. 2017). Binding gels were added into 10 mL of target PAHs solution. After shaking for 24 h, gels were taken out and ultrasonic extracted for 30 minutes with 5 mL and 10 mL acetonitrile. The extraction experiments were performed with three binding gels at two concentrations (10 μg L^{-1} and 100 μg L^{-1}), to confirm that a stable recovery rate could be achieved.

3.2.7 Binding capacity and uptake kinetics of binding gel

To measure the adsorption capacity of the binding gel for the target PAHs, the gel disc was immersed in 500 mL solutions containing 0.01 M NaCl and mixed PAHs. All the solutions were shaken for 48 h at 24±1°C. The concentrations of Nap, Acy, Ace, Flu and Phe were 20, 40, 100, 200 μg L^{-1}. Because of their lower water solubility, the concentrations of Ant, Flua, and Pyr were 20, 40, 60, 80 μg L^{-1}. According to the concentration difference before and after the experiment, the adsorption amount of the test chemicals on the binding gel was calculated.

To measure the uptake kinetics of the target compounds, binding gel discs were immersed in 40 mL of 0.01 M NaCl solution containing 50 μg L^{-1} mixed PAHs and placed on a horizontal shaker at 100 rpm. The sampling time was set from 5 min to 36 h, and three parallels were set for each time point. A 0.5 mL aqueous solution sample was taken each time, 0.5 mL acetonitrile added, and then filtered with a 0.22 μm PTFE filter for HPLC detection.

3.2.8 Diffusion coefficient measurements

The method to determine diffusion coefficients using a diffusion cell has been reported in previous studies (Zhang and Davison 1999, Chen, Li et al. 2017). The diffusion cell used was made from stainless steel to reduce adsorption, and a cover was added to reduce the volatilization of PAHs during the experiment. The two compartments were connected through a window with a diameter of 1.5 cm. A 0.8 mm diffusive gel with an appropriate spacer was placed between the two compartments and then clamped tightly. A 50 mL of 0.01 M NaCl solution containing PAHs (concentration shown in the Table 3.4) was added to the source compartment, and another 50 mL of 0.01 M NaCl solution without PAHs was added to the other (receptor) compartment at the same time. A stirrer was used to evenly stir the solution in both compartments. The pH was 5.92±0.32 and the temperature was 19.0±0.2°C during the experiment. An aliquot of 0.5 mL was taken from each of the two compartments every 30 min and analyzed by HPLC.

A linear fitting curve was obtained by plotting the mass of the measured compound in the receptor compartment of the diffusion cell versus time, with the slope being the mass of the compound diffused per unit time (M/t) (See SI Text 3 for details). The diffusion coefficients (De) of each PAH were calculated:

$$D_e = Slope \frac{\triangle g}{C_s A} \qquad \text{(Eq. 3.1)}$$

Where *Cs* is the concentration of the test compounds in the source compartment; *A* is the area of the window on the diffusion cell; Δg is the thickness of the diffusive gel. This was performed at known temperature.

The diffusion coefficient at different temperatures was then calculated using the method published by Zhang and Davison (Zhang and Davison 1995):

$$logD_t = \frac{1.37023(t-25)+8.36\times10^{-4}(t-25)^2}{109+t} + log\frac{D_{25}(273+t)}{298} \qquad \textit{(Eq. 3.2)}$$

Where D_t is the diffusive coefficient of the compound at temperature t; D_{25} is the diffusion coefficient of the compound at temperature 25 °C.

Table 3.4 Concentration of PAHs in source compartment for diffusion coefficient test

Compound	Cs (μg L^{-1})
Nap	500
Acy	500
Ace	500
Flu	500
Phe	500
Ant	50
Flua	50
Pyr	50

3.2.9 Diffusive layer thickness and time dependence

To investigate the relationship between the DGT measurements and the thickness of diffusive gel, DGT samplers were assembled with diffusive gels of different thicknesses (0.5 to 2.0 mm) and placed in 150 mL of mixed 10 μg L^{-1} PAHs solution (pH=6, 0.01 M NaCl). The samples were shaken on an orbital shaker (25°C) at 100 rpm.

To investigate the relationship between DGT measured mass and the deployment time, assembled DGT samplers were placed in 150 mL of mixed 10 μg L^{-1} PAHs solution (pH=6, 0.01 M NaCl) and shaken on an orbital shaker (25°C) at 100 rpm. To ensure stable solution concentrations, the PAH solution was replaced every 24 h. DGT samplers were taken out at different time points from

24 to 168 h.

3.2.10 Effects of pH, ionic strength and DOM

To investigate the effects of different environmental conditions on DGT performance, two types of DGT samplers, MIP-DGT and HLB-DGT, were deployed in solutions of different ionic strength (IS), pH and dissolved organic matter (DOM) concentrations. For the effect of pH, DGT samplers were deployed in 150 mL of 10 μg L^{-1} PAHs solutions (0.01 M NaCl) across a pH range from 4 to 8. For the effect of ionic strength, DGT samplers were exposed to 150 mL 10 μg L^{-1} PAHs solutions (pH 5.8±0.3) with NaCl ranging from 0.01 to 0.5 M. DGT samplers were deployed in 150 mL of 10 μg L^{-1} mixed PAHs solutions with DOM concentrations ranging from 0 to 20 mg L^{-1} (0.01 M NaCl, pH 5.9±0.2,), to test the effects of DOM on DGT performance. After being deployed for 24 h, all the samplers were taken out and rinsed with MQ water. Each binding gel was placed in an amber vial, ultrasonically extracted for 30 min with 5 mL acetonitrile and analysed by HPLC.

3.2.11 Field application in a river and a WWTP

To test the applicability of newly developed DGT for field measurements, DGT samplers were deployed *in situ* in the Qinhuai River in Nanjing and a wastewater treatment plant in Chongqing, China. The DGT samplers were deployed in triplicate and arranged 30 cm below the water surface. DGT samples were retrieved at day 7 and 14, respectively. The samplers were rinsed with MQ water and sealed in clean plastic bags for transport. Traditional grab samples were taken on day 1, 7 and 14, pre-concentrated and purified by a solid-phase extraction method. For each grab sample, 200 ng of decafluorobiphenyl was added to 1 L and the sample filtered through a 0.7 μm filter, then passed through a SPE column. 10 mL of dichloromethane was then used to elute the PAHs adsorbed on the column. The eluent was concentrated under nitrogen and the solvent was replaced with acetonitrile. The sample was finally diluted to 0.2 mL for HPLC analysis (see SI for details).

3.2.12 Quality assurance/Quality control

The linear correlation (R^2) of the standard curve for all PAHs were greater than 0.99. The RSD range of the mixed standard sample of 0.5 μg L^{-1} PAHs (Acy was 2 μg L^{-1}) was between 1.7-7.0%, indicating good precision of the method. Quality control standards (10 μg L^{-1}) were run every 12 samples and good results obtained. Field blank samples and laboratory blank samples were used to check for possible contamination during sample transportation, field deployment and laboratory processing. The examined compounds in these blank samples were not found at detectable levels. The results of the spiked recovery experiment showed that recoveries of the volatile Nap and Acy were slightly < 70%, while recoveries of the other PAHs ranged from 72% to 93% (Table 3.3). In environmental samples, the recoveries of surrogate chemical decafluorobiphenyl were 67-120%, which meets the requirements for detecting PAHs in water.

3.3 Results and discussion

3.3.1 Adsorption by DGT casing material and selection of new casing material

Since the development of the DGT technique, the casing of commercial DGT samplers has only been made of ABS plastic. The results of adsorption experiments (Fig. 3.1) demonstrate that there was significant adsorption (from 20-50%) by the plastic casing for all the test PAHs. Therefore, it was necessary to test and select new materials for the DGT casing, to reduce interference with the accuracy of DGT measurement of the target chemicals. With the development of manufacturing technology, metal products are increasingly being used in various fields. Five common metals (aluminum, aluminum alloy, stainless steel, brass and copper) were selected for PAHs adsorption tests here, to find the most suitable material to manufacture the DGT device (Fig. 1). Aluminum and aluminum alloy performed best. For aluminum, adsorption was < 5% for five compounds, < 10% for two compounds and ~15% for another compound. In addition to volatile naphthalene and acenaphthylene, with the increase of log K_{OW}, PAHs are more easily adsorbed by the material. Stainless steel exhibited higher adsorption (~15-30%) of 4-ring PAHs (fluoranthene, pyrene, benzo (a) anthracene). Adsorption to copper and brass was even higher than that of these three materials. The price of the raw materials followed the sequence stainless steel<aluminum<aluminum alloy<brass<copper. However, for actual product fabrication, the price of aluminum DGT was about two-thirds that of stainless steel. Furthermore, due to the in-situ applications of DGT, the portability of the sampler also needs to be considered. The density of metal materials is in the order of aluminum<aluminum alloy<stainless steel<brass<copper. The weight of stainless steel, copper and brass products of the same size are about three times that of aluminum and aluminum alloy. Therefore, based on the adsorption test results, production cost and weight, aluminum was selected as the new material to manufacture DGT devices for PAHs/hydrophobic organic compounds.

Two metal DGT casings were designed based on the existing DGT devices (Fig. 3.2). Because of different ductility of metal and plastic, the design on the left can be locked with two screws, while the design on the right is locked using screw threads. A groove was added on the DGT base to prevent the binding gel and diffusive gel from being crushed and damaged. The depth of the groove can be set according to actual needs. In field applications, the left design was selected for easy and convenient operation.

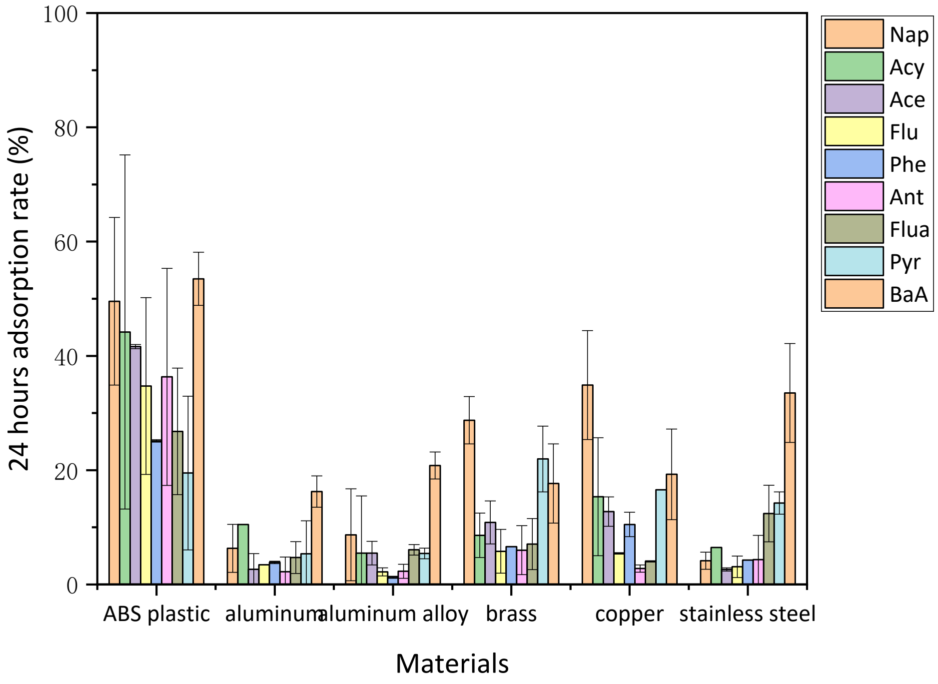


Fig. 3.1 Adsorption of 9 target compounds onto DGT holders and 5 metal materials. Error bars were obtained from the standard deviations of three replicates.

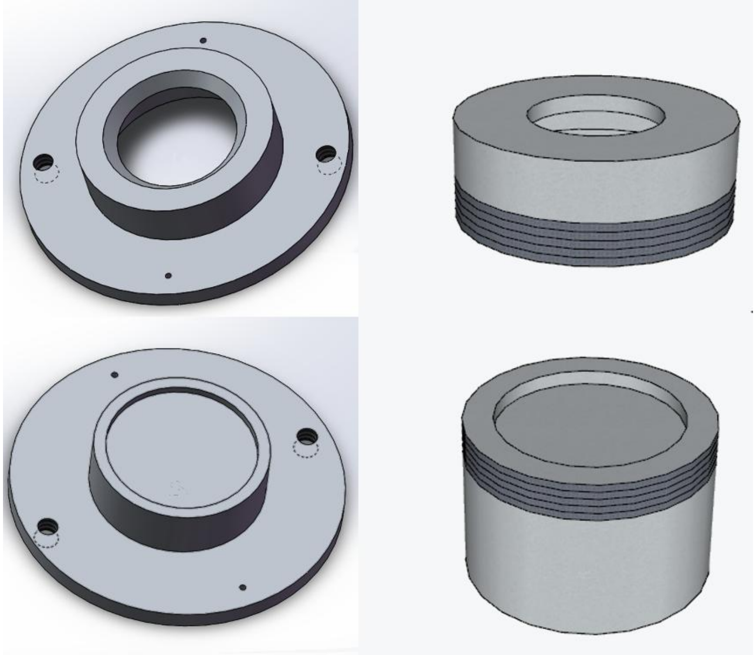


Fig. 3.2 Two different designs of new DGT sampler casings fabricated from metals (The left one was finally selected for use)

3.3.2 Adsorption by filter membranes and diffusive gels

The agarose gel had lower adsorption of the target compounds (except BaA) than the polyacrylamide gel (see Fig. 3.3a). Therefore, agarose gel was selected as the diffusive gel for the subsequent experiments. All the test compounds were significantly adsorbed (nearly 100%) by CA, MCE, NL, PES, PP and PVDF filters (Fig. 3.3b). PC and PTFE had less sorption of the compounds than the other filters, especially for the low ring PAHs. However, the PC membrane performed the best, with < 15% for four compounds and < 20% for two. It was therefore selected for the subsequent experiments. Due to the high adsorption of BaA on all materials, it was excluded from subsequent experiments, which were conducted on the remaining 8 PAHs. Suitable materials or standard experimental methods could be sought for experiments of higher ring PAHs in future, and not only for BaA.

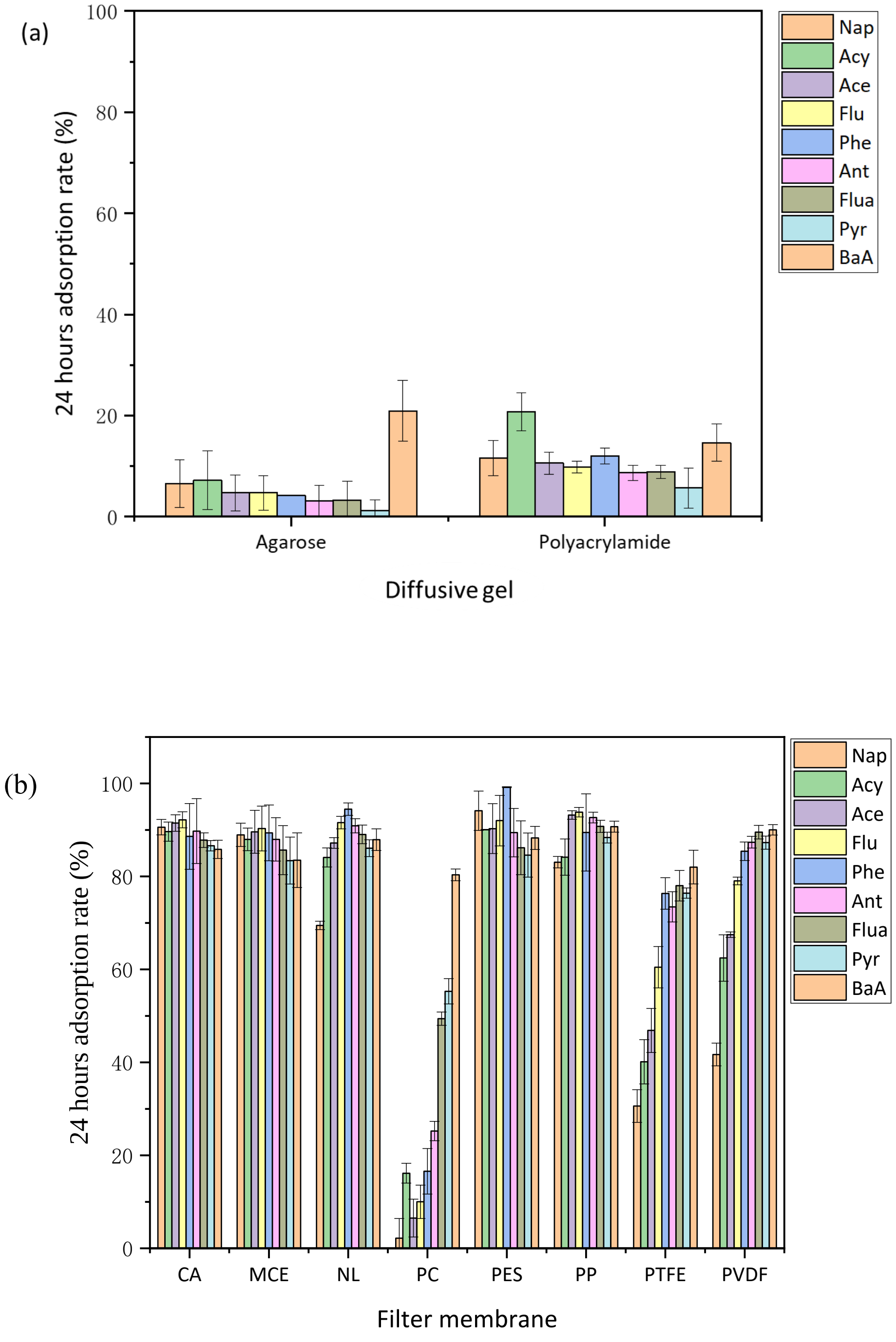
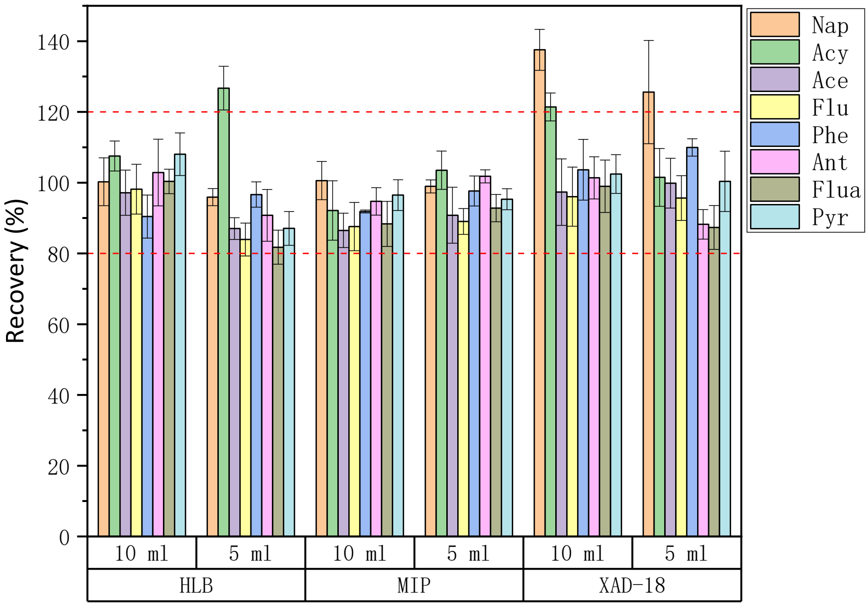


Fig. 3.3 Adsorption of 9 target compounds onto (a) polyacrylamide and agarose diffusive gels, (b) 8 different filter membranes (CA, MCE, NL, PC, PES, PP, PTFE and PVDF). Error bars were obtained from the standard deviations of three replicates.

3.3.3 Elution efficiency

The results (Fig. 3.4) showed that the elution efficiencies of the three binding gels in a 10 μg L^{-1} PAH solution were stable for most compounds, in the range 84% to 108%. The elution efficiency decreased slightly in the 100 μg L^{-1} solution, in the range 72-106%. For the three types of gels, elution efficiency from the MIP gel was most stable (from 83-103%) and the influence of solution concentration and elution solution volume was less than for the other two gels. The above results indicate that the use of 5 mL acetonitrile and ultrasonic extraction for 30 min can provide stable and reliable elution efficiency.

(a)



(b)

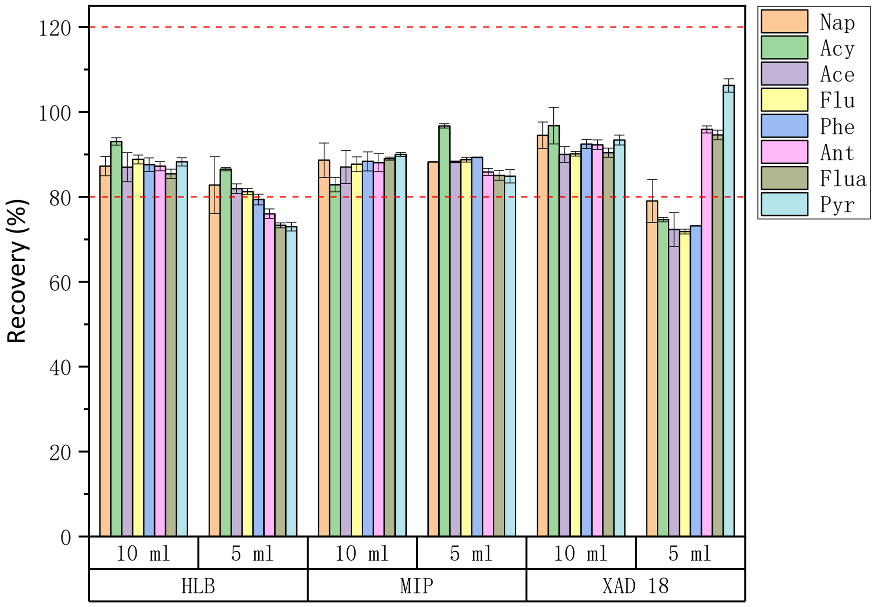


Fig. 3.4 Elution efficiencies of 3 binding gels (a) 10 μg L^{-1} for polycyclic aromatic hydrocarbons solution, (b) 100 μg L^{-1} for polycyclic aromatic hydrocarbons solution. Error bars were obtained from the standard deviations of three replicates.

3.3.4 Binding capacity of binding gels

The DGT samplers need a sufficient binding capacity to ensure long-term deployment in water, even if the concentration of pollutant is high. Therefore, it is necessary to determine the binding capacity of the gels. For the HLB and MIP binding gels, the uptake mass of all 8 PAHs increased linearly with increasing concentration in the bulk solutions, indicating the capacities were not reached. XAD18 gel increased for most of the compounds, except for anthracene (Fig. 3.5). The adsorbable mass of binding gels can be calculated based on Eq. 3.3:

$$M = \frac{C_{DGT}DAt}{\triangle g} \qquad \textit{(Eq. 3.3)}$$

According to the test concentration, the results (Table 3.5) showed the minimal capacity of the three gels for these PAHs. The HLB gel had a higher capacity than MIP and XAD18 gel. The capacity on the HLB gel disc was within the range of 9-42 μg per disc (the lowest for Ant and the highest for Flu). If the samplers were deployed for 2 weeks, the concentrations of Ant and Flu that can be accurately measured within the binding capacity would be at least 32 and 162 µg L^{-1}, respectively. These are much higher than reported environmental concentrations (Zakaria, Takada et al. 2002, Wang, Bi et al. 2009, Zhang, Wei et al. 2012, McDonough, Khairy et al. 2014), indicating it is suitable for long-term deployment in natural and polluted environments.

Table 3.5 Estimated capacities of three binding gels (µg per gel) and maximum water concentration (µg L^{-1}) for typical deployment time

Chemical	HLB	MIP	XAD-18	C_{HLB}	C_{MIP}	C_{XAD18}
Nap	43.4	36.0	28.0	131	108	84.7
Acy	41.0	27.9	10.1	162	110	39.8
Ace	41.0	31.3	29.5	134	102	96.5
Flu	48.6	39.0	27.5	162	130	91.8
Phe	40.2	32.1	34.9	139	111	121
Ant	9.10	10.5	29.2	31.6	36.4	101
Flua	16.2	7.00	5.00	68.2	29.5	21.0
Pyr	11.4	9.80	11.5	46.1	39.6	46.6

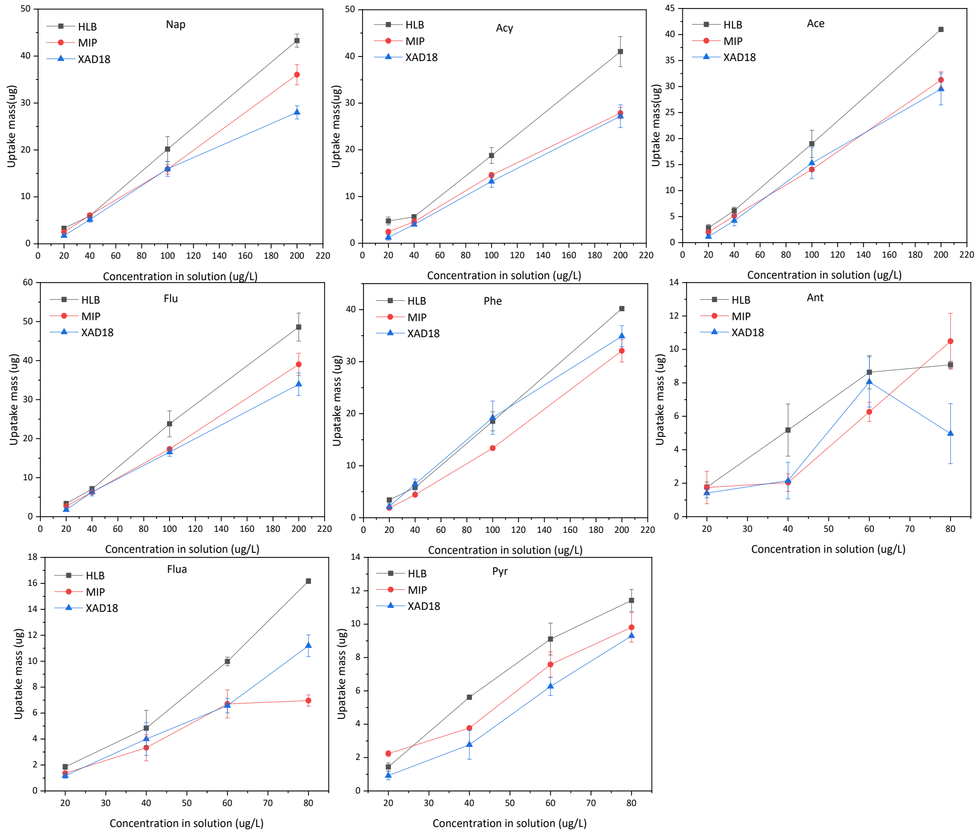


Fig. 3.5 Masses (μg) of PAHs taken by HLB, MIP and XAD-18 gels in 500 mL PAHs solutions of various concentration (pH=6, IS=0.01 M, T=23±0.8°C; n=3). Error bars were calculated from the standard deviation (SD) for three replicates.

3.3.5 Uptake kinetics of resin gels

The uptake of PAHs by the three gels increased linearly with time in the first 30 min, and then the uptake rate slowed down slightly (Fig. 3.6). After two hours of interaction, the uptake masses of various compounds were 20-30% of the total amount added. After 30 h, the amount taken up was about 70% of the total amount. For most target compounds, the uptake rates of the three gels were XAD 18 > MIP > HLB.

The rapid initial uptake is the key aspect to enable fully quantitative performance of DGT, which requires zero concentration at the binding gel/diffusive gel interface (Li, Chen et al. 2019). According to the DGT Eq. 3.3, the minimum uptake amount by the binding gel for the first 5 min was about 2 ng. The results presented in Fig. 3.6 show 13-84 ng for the three types of gels. The results showed that the uptake rates of all three gels for the target PAHs were much higher than theoretical uptake rates of DGT samplers in a 50 μg L^{-1} PAHs solution, which indicated these binding gels enable good performance of DGT measurements.

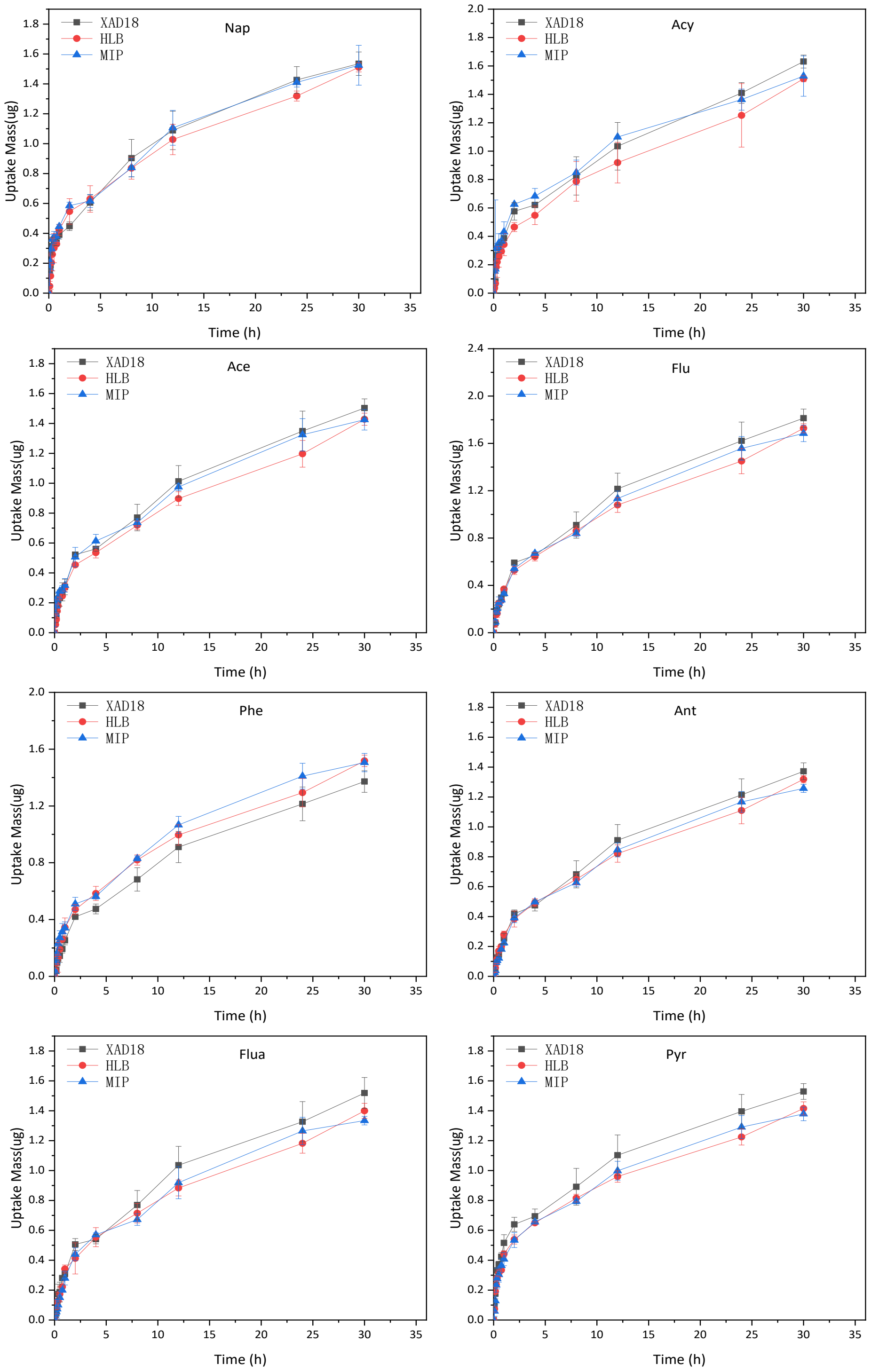


Fig. 3.6 Uptake kinetics of PAHs by HLB, MIP and XAD-18 binding gels in 40 mL solution of ca. 50 μg L^{-1} test chemicals (pH=6, IS=0.01M, T=24±0.4°C; n=3). Error bars were calculated from the standard deviation (SD) for three replicates.

3.3.6 Diffusion coefficient measurements

The results of the diffusion cell experiment (mass versus time) are shown in Fig. 3.7. The amounts of PAHs that diffused from the source compartment to the receptor compartment through diffusive gel were highly linearly correlated with time ($R^2>0.96$). The diffusion coefficients of PAHs at 19 °C were calculated by using Eq. 3.1, knowing the slopes of linear plots in Fig. 3.7. For further calculation of D values at different temperature, the diffusion coefficients at 25 °C (D_{25}) were calculated with equation 3.2 and ranged from 5.00-6.96 × 10^{-6} cm^2s^{-1}. D values were then calculated for 8 PAHs from 1 to 35 °C and these are listed in Table 3.6.

According to previous research, log K_{OW} had a linear relationship with the diffusion coefficient of chemicals (Zou, Fang et al. 2018, Fang, Li et al. 2021). As shown in Fig. 3.8, the diffusion coefficients versus log K_{OW} values of all 8 PAHs were plotted, $R^2 > 0.94$ which indicated a significant correlation between these two parameters. This provides a route for estimating the diffusion coefficients of other PAHs with lower water solubility that were not measured in this study.

Table 3.6 Diffusion coefficients (De) for 8 PAHs at temperatures from 1 to 35 °C (10^{-6} cm^2s^{-1})

T (°C)	Nap	Acy	Ace	Flu	Phe	Ant	Flua	Pyr
1	3.25	3.04	3.00	2.94	2.83	2.83	2.33	2.43
2	3.37	3.16	3.11	3.06	2.94	2.94	2.42	2.52
3	3.50	3.28	3.23	3.17	3.05	3.05	2.51	2.62
4	3.63	3.40	3.35	3.29	3.16	3.16	2.61	2.71
5	3.76	3.52	3.47	3.41	3.28	3.27	2.70	2.81
6	3.89	3.65	3.60	3.53	3.39	3.39	2.80	2.91
7	4.03	3.77	3.72	3.65	3.51	3.51	2.89	3.02
8	4.17	3.91	3.85	3.78	3.64	3.63	3.00	3.12

9	4.31	4.04	3.98	3.91	3.76	3.75	3.10	3.23
10	4.46	4.18	4.12	4.04	3.89	3.88	3.20	3.34
11	4.60	4.31	4.25	4.17	4.02	4.01	3.31	3.45
12	4.76	4.45	4.39	4.31	4.15	4.14	3.42	3.56
13	4.91	4.60	4.53	4.45	4.28	4.27	3.53	3.67
14	5.06	4.74	4.68	4.59	4.42	4.41	3.64	3.79
15	5.22	4.89	4.83	4.74	4.56	4.55	3.75	3.91
16	5.38	5.04	4.97	4.88	4.70	4.69	3.87	4.03
17	5.55	5.20	5.13	5.03	4.84	4.83	3.99	4.15
18	5.72	5.35	5.28	5.18	4.98	4.98	4.11	4.28
19	5.89	5.51	5.44	5.34	5.13	5.12	4.23	4.41
20	6.06	5.67	5.60	5.49	5.28	5.27	4.35	4.53
21	6.23	5.84	5.76	5.65	5.44	5.43	4.48	4.67
22	6.41	6.01	5.92	5.81	5.59	5.58	4.61	4.80
23	6.59	6.17	6.09	5.98	5.75	5.74	4.73	4.93
24	6.77	6.35	6.26	6.14	5.91	5.90	4.87	5.07
25	6.96	6.52	6.43	6.31	6.07	6.06	5.00	5.21
26	7.15	6.70	6.60	6.48	6.23	6.22	5.14	5.35
27	7.34	6.88	6.78	6.65	6.40	6.39	5.27	5.49
28	7.53	7.06	6.96	6.83	6.57	6.56	5.41	5.64
29	7.73	7.24	7.14	7.01	6.74	6.73	5.55	5.79
30	7.93	7.43	7.33	7.19	6.92	6.90	5.70	5.94
31	8.13	7.62	7.51	7.37	7.09	7.08	5.84	6.09
32	8.34	7.81	7.70	7.56	7.27	7.26	5.99	6.24
33	8.54	8.00	7.89	7.75	7.45	7.44	6.14	6.40
34	8.75	8.20	8.09	7.94	7.64	7.62	6.29	6.55
35	8.97	8.40	8.28	8.13	7.82	7.81	6.44	6.71

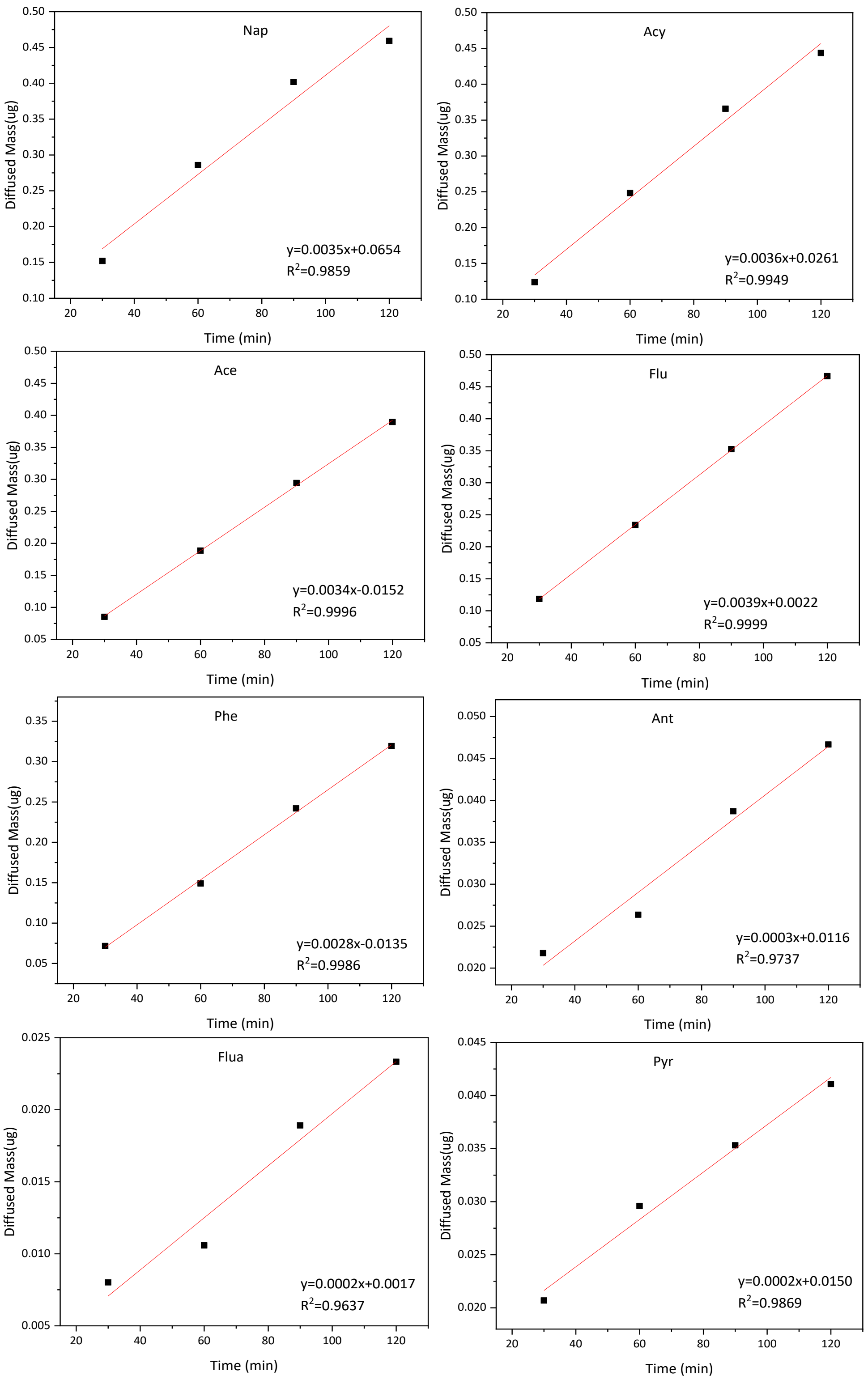


Fig. 3.7 Masses of PAHs diffused through agarose gel at different times in the diffusion cell (IS=0.01 M, pH=5.9±0.3 and T=19±0.2°C).

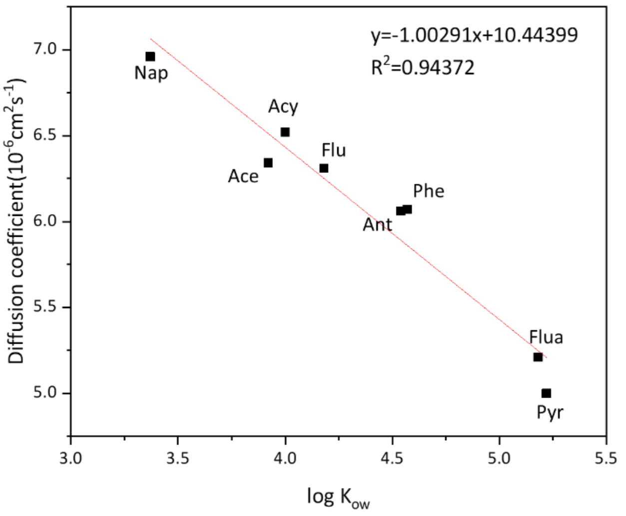


Fig. 3.8 Dependence of diffusion coefficients of PAHs on log K_{OW}

3.3.7 Diffusion layer thickness and time dependence

To test if the newly developed passive sampler obeys DGT theory, experiments with different diffusion layer thickness and deployment time were carried out systematically. PAHs are semi volatile compounds. To reduce the losses of PAHs during experiments, DGT samplers were placed in a closed brown bottle for short-term deployments. As shown in Fig. 3.9, the measured mass of the target PAHs diffused through the diffusive gel was not inversely proportional to the thickness of the diffusive gel and all the data points were below the theoretical lines of DGT. This is likely due to insufficient stirring of the solution during the experiment, and the diffusive boundary layer (DBL) generated at the interface between the DGT and the solution. The DBL thickness, δ, can be measured by deploying DGT samplers with different diffusive gel thicknesses at the same time. According to the Eq. 3.4 the value of δ can be estimated using the slopes and intercepts obtained from the plots of 1/M versus Δg.

$$\frac{1}{M_{DGT}} = \frac{\Delta g}{DC_{DGT}At} + \frac{\delta}{DC_{DGT}At} \qquad \textit{(Eq. 3.4)}$$

The results of deployment with an orbital shaker at 80 rpm are shown in Fig. 3.10. The estimated DBL is given on the graphs and in Table 3.7. The derived values for the different compounds were in the range 0.06-0.08 cm (see Fig. 3.10). The changes in stirring speeds were considered to be different solution flow rates, and DBL increased with the decrease of speed. When the stirring rate ≥ 100 rpm, the DBL were approximately 0.02 cm, with DBL thickness of 0.04 cm at 60 rpm and 0.15 cm in the unstirred solution (Warnken, Zhang et al. 2006). Similarly, the range of DBL under flowing and static conditions were 0.01-0.05 cm and 0.04-0.13 cm, respectively (Challis, Hanson et al. 2016). In this study, due to insufficient stirring from the oriental shaker, the DBL was relatively high, which is consistent with these research results. The measured mass of the target PAHs by the device was inversely proportional to the total diffusion layer thickness (the diffusive gel and boundary layer). The measured mass of PAHs was consistent with the theoretical line, except for anthracene (Fig. 3.11). The DBL values were considered in all subsequent laboratory deployment experiments when calculating DGT measured concentrations in the laboratory.

The concentration of PAHs in the environment are generally at the ng L^{-1} level, so the in-situ deployment time of DGT needs to be long enough to accumulate sufficient mass for detection. It is therefore necessary to study the impact of deployment time on the performance of DGT. The results (Fig. 3.12) showed that with the increase of deployment time, the mass of PAHs accumulated on DGT with MIP and HLB gels increased linearly (R^2=0.9777-0.9993) over 7 days of the experiment. The accumulation of most chemicals was consistent with the theoretical line and the ratio of the PAHs concentrations measured by DGT (C_{DGT}) to their concentrations in the bulk solutions (C_b) were between 0.8-1.2 (Table 3.8). On XAD18 DGT, naphthalene was not accumulated linearly, and actual accumulation of most chemicals was lower than the theoretical line (Fig. 3.13). The accumulation of anthracene was much lower than the theoretical value; this is because the water solubility of anthracene is extremely low and DGT only measures water-soluble anthracene. For the treatment of solution samples, the matrix contains acetonitrile, which led to higher measured solution concentrations, so the predicted accumulated mass was higher than the actual value.

The accumulation of all the compounds by DGT was lower than the theoretical value on the first day (Fig. 3.12). This is because of the affinity of filter membranes and DGT samplers for the compounds, so that there is a lag time before compounds reach the binding gel. It is therefore recommended that the time for deployment should exceed one week; deployments of several weeks or a couple of months are typical and ideal for monitoring purposes (Wang, Zou et al. 2019). Fig. 3.12 shows the masses accumulated in binding gels for 7 days deployment time; intercepts on the time-axis show the lag times required for different chemicals (Table 3.9). This was <15 h for all 8 PAHs, indicating that the DGT samplers made from aluminum material effectively reduces the impact of lag time. The lag times of MIP-DGT were shorter than those for HLB-DGT, which may be due to the high specificity of MIP for adsorbing PAHs. This is consistent with the results of the previous uptake kinetic experiment. The above results of different diffusion layer thickness and deployment time indicate that the DGT samplers for PAHs can be used for measuring the concentrations of the target compounds quantitatively with high precision and accuracy.

Table 3.7 Diffusive boundary layer thickness (δ) of 8 PAHs in closed bottle on optical shaker at 100 rpm at 25°C

Chemical	δ (cm)
Nap	0.07
Acy	0.08
Ace	0.06
Flu	0.06
Phe	0.07
Ant	0.08
Flua	0.08
Pyr	0.08

Table 3.8 The ratio of the target compound concentrations measured by DGT (C_{DGT}) to their concentrations in the bulk solutions (C_b)

Gel	Day	Nap	Acy	Ace	Flu	Phe	Ant	Flua	Pyr
HLB	1	0.56	0.77	0.91	0.70	0.70	0.31	0.81	0.78
	2	0.61	1.09	1.10	0.83	0.60	0.40	0.98	0.90
	3	0.58	1.13	1.07	0.82	0.69	0.44	1.06	1.08
	4	0.67	1.26	1.14	0.95	0.83	0.52	1.18	1.15

	5	0.80	1.09	1.09	0.89	0.75	0.50	1.18	1.21
	6	0.71	1.15	1.03	0.83	0.71	0.51	1.17	1.20
	7	0.67	1.10	0.94	0.86	0.65	0.53	1.15	1.14
MIP	1	0.55	0.90	0.92	0.67	0.72	0.32	0.75	0.77
	2	0.55	1.03	0.95	0.70	0.67	0.39	0.86	0.81
	3	0.65	1.05	1.05	0.83	0.74	0.49	1.00	0.96
	4	0.55	0.85	0.93	0.75	0.61	0.42	0.84	0.83
	5	0.68	1.13	1.15	0.89	0.71	0.56	1.06	1.09
	6	0.75	0.91	0.97	0.94	0.75	0.59	1.04	1.03
	7	0.79	1.11	1.20	0.99	0.75	0.62	1.06	1.09

Table 3.9 Lag times (h) for 8 PAHs in the DGT with HLB and MIP gel

Chemicals	DGT with HLB gel	DGT with MIP gel
Nap	14.5	4.3
Acy	5.9	2.1
Ace	6.8	4.2
Flu	7.7	7.6
Phe	5.0	1.2
Ant	12.7	11.0
Flua	10.1	8.4
Pyr	11.6	7.8

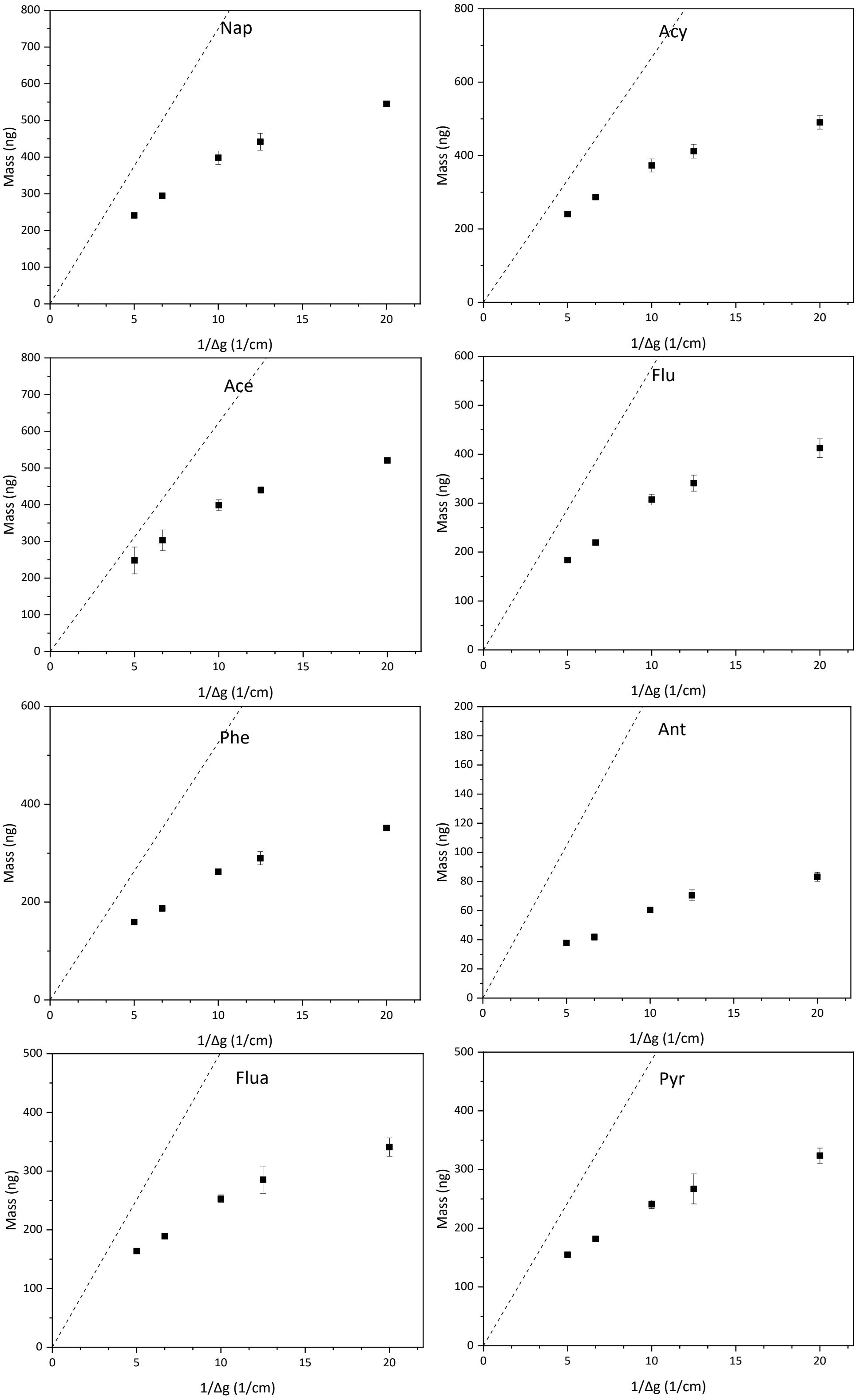

Nap
Acy
Ace
Flu
Phe
Ant
Flua
Pyr
Mass (ng)
1/Δg (1/cm)
0
5
10
15
20
0
100
200
300
400
500
600
700
800

Fig. 3.9 Measured mass of 8 PAHs for DGT with different diffusive gel thickness. The dotted line represents the theoretical adsorption in gel at different diffusion thicknesses. Error bars were calculated from the standard deviation (SD) for three replicates.

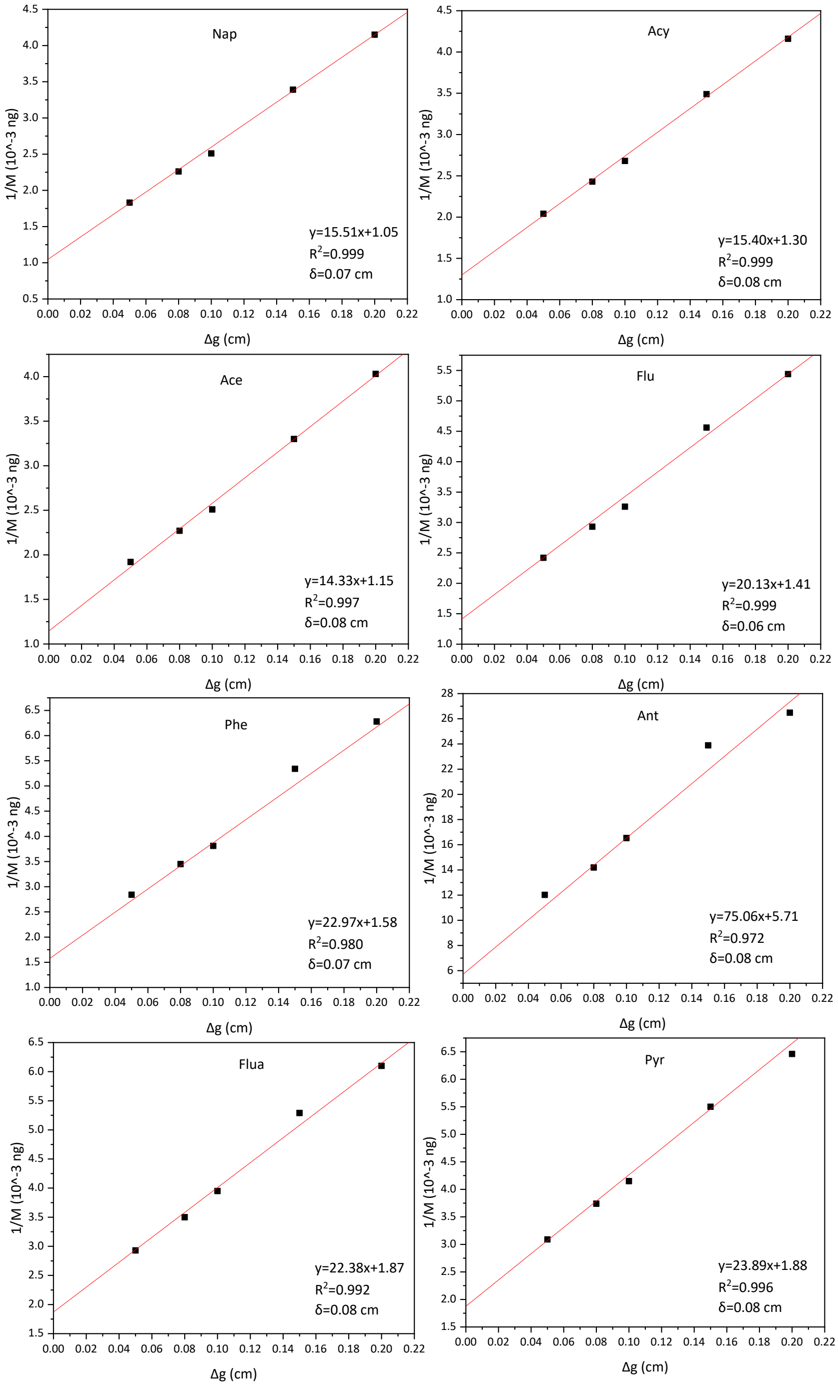


Fig. 3.10 Relationship of 1/M (M is accumulated mass by DGT samplers) and Δg (diffusion layer thickness). Diffusive boundary layer thickness (δ) was determined using Eq. 3.4.

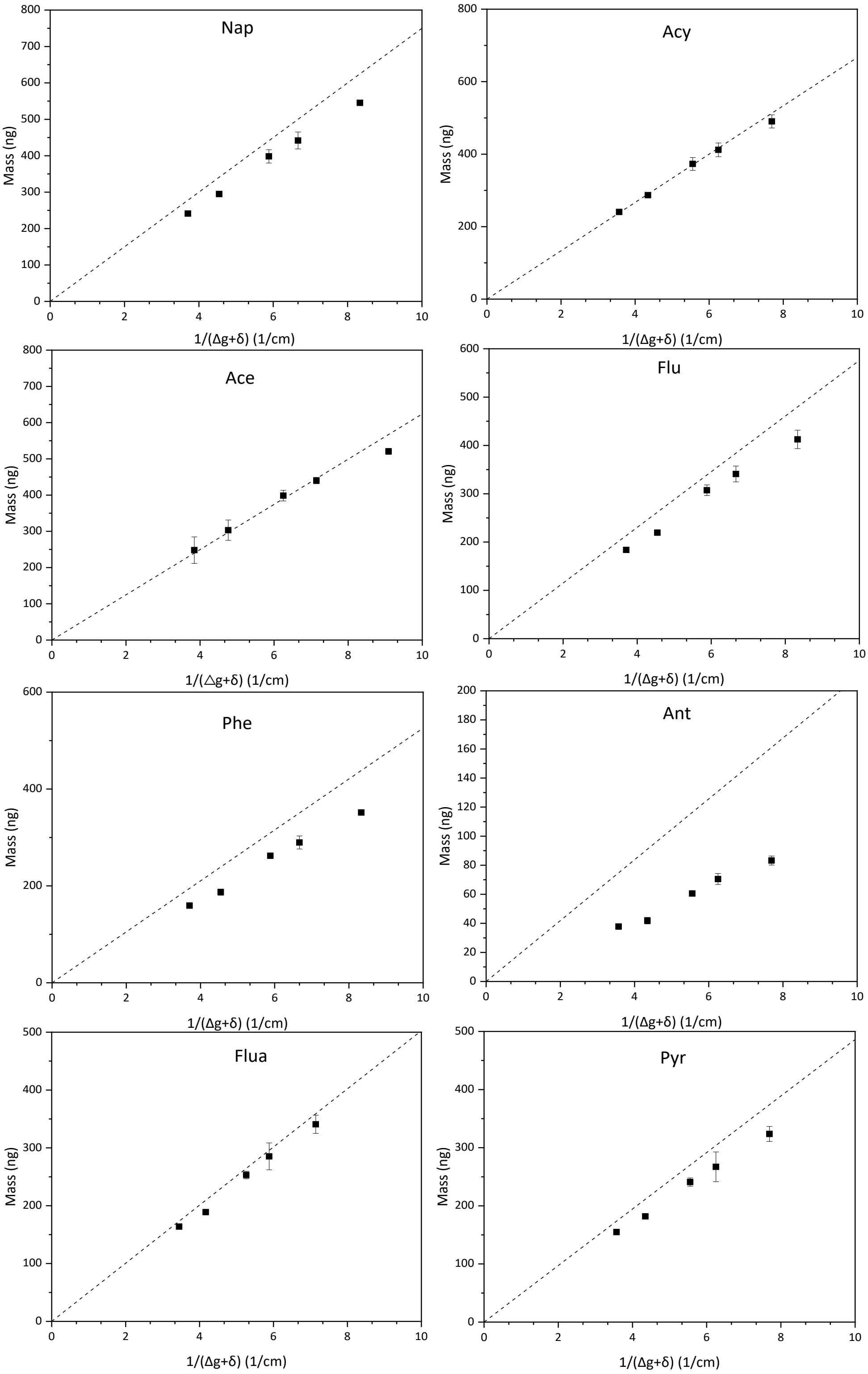


Fig. 3.11 Measured mass of 8 PAHs for DGT with different diffusive gel thickness and corrected for the DBL. The dotted line represents the theoretical adsorption in gel at different diffusion thicknesses. Values are means ± SD of three replicate analyses.

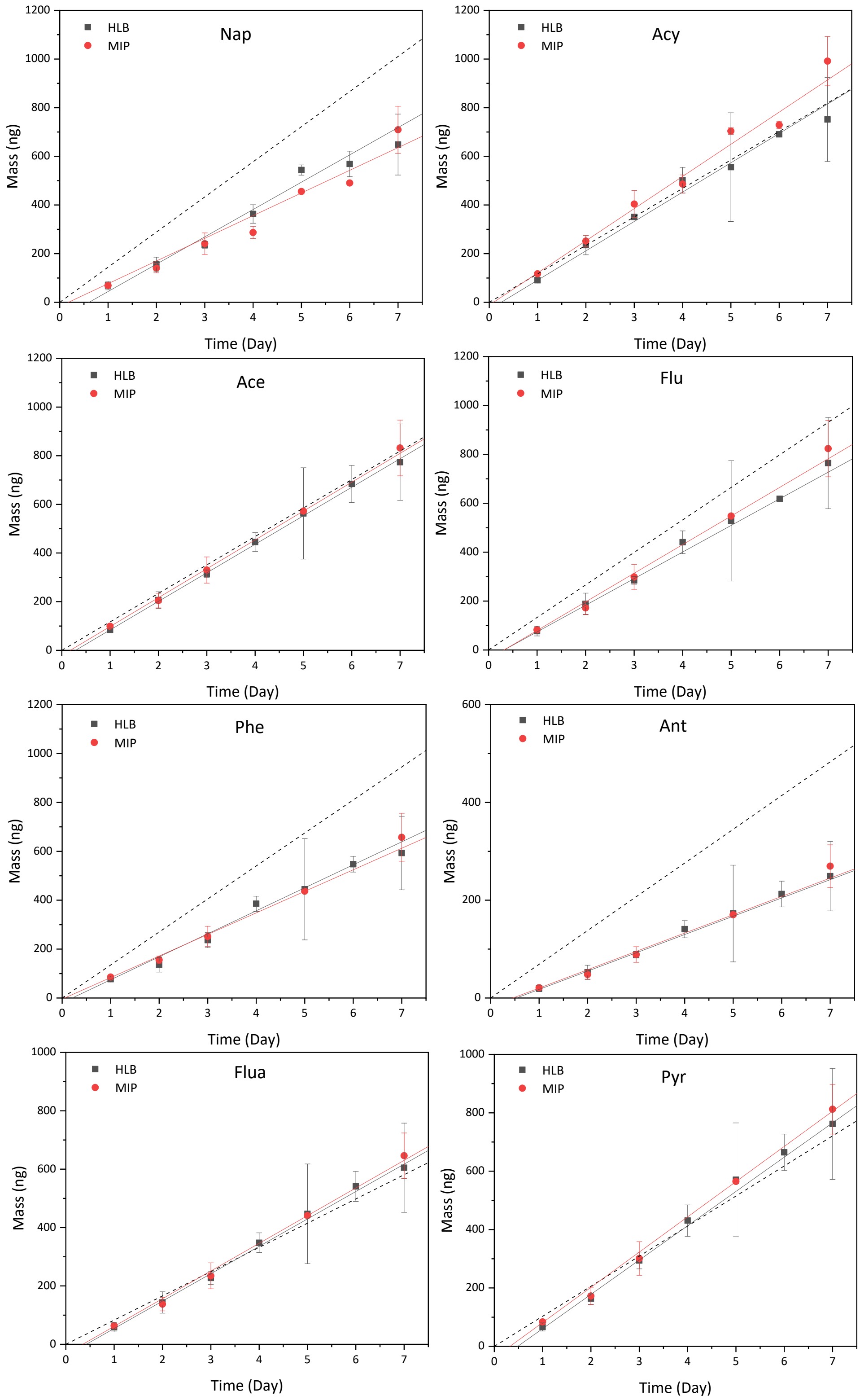


Fig. 3.12 Measured mass of 8 PAHs in the binding layer of DGT samplers with HLB and MIP gel for different times. The dotted line represents the theoretical adsorption in gel at different diffusion thicknesses. Values are means ± SD of three replicate analyses.

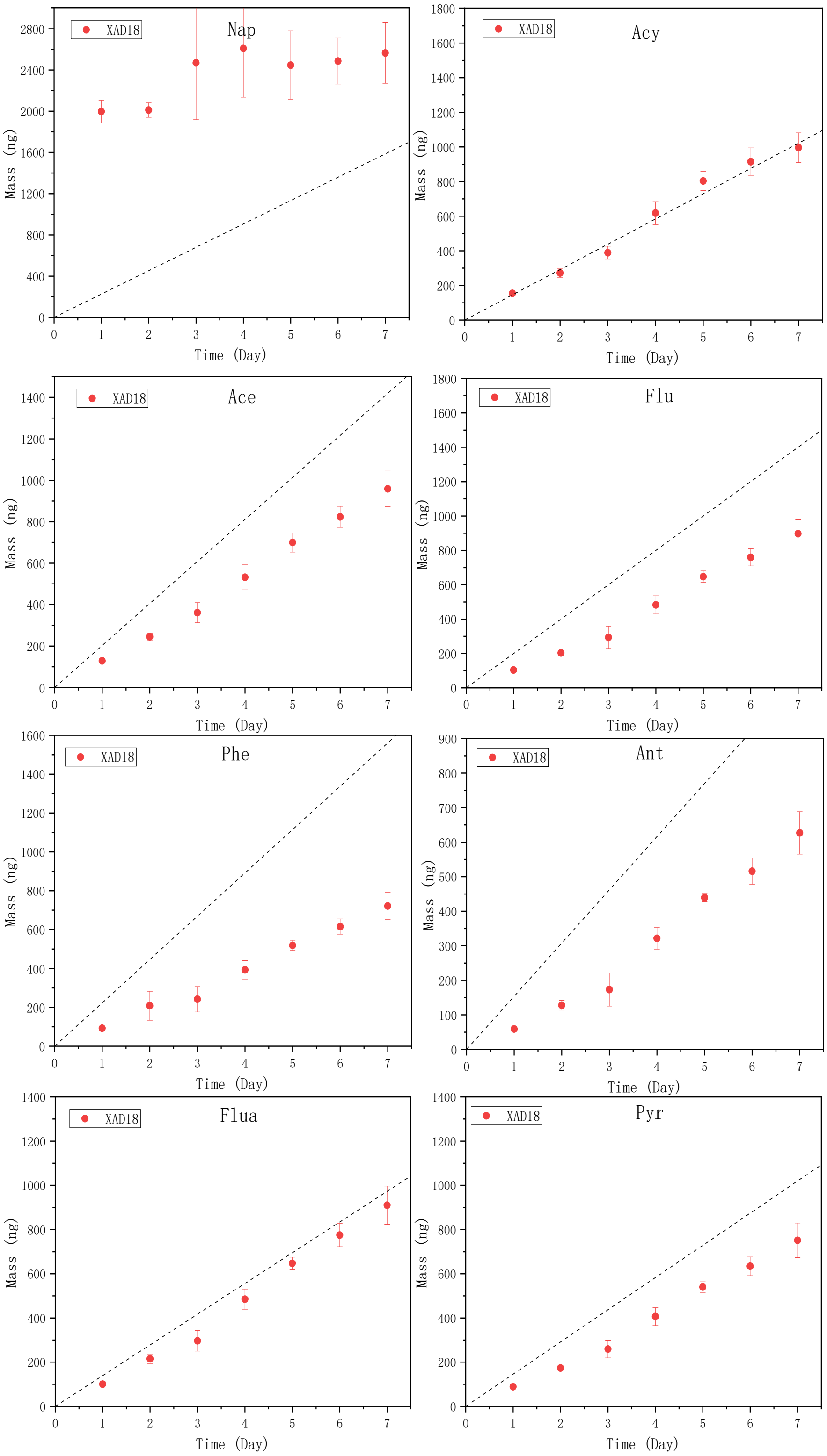

XAD18
Nap
Mass (ng)
0
400
800
1200
1600
2000
2400
2800
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Acy
Mass (ng)
0
200
400
600
800
1000
1200
1400
1600
1800
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Ace
Mass (ng)
0
200
400
600
800
1000
1200
1400
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Flu
Mass (ng)
0
200
400
600
800
1000
1200
1400
1600
1800
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Phe
Mass (ng)
0
200
400
600
800
1000
1200
1400
1600
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Ant
Mass (ng)
0
100
200
300
400
500
600
700
800
900
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Flua
Mass (ng)
0
200
400
600
800
1000
1200
1400
Time (Day)
0
1
2
3
4
5
6
7
XAD18
Pyr
Mass (ng)
0
200
400
600
800
1000
1200
1400
Time (Day)
0
1
2
3
4
5
6
7

Fig. 3.13 Measured mass of 8 PAHs in the XAD18 gel of DGT samplers for different times. The dotted line represents the theoretical adsorption in gel at different diffusion thicknesses. Values are means ± SD of three replicate analyses.

3.3.8 Effects of pH, ionic strength and DOM

The environmental conditions of natural water vary greatly, which may affect the performance of DGT. For reliable and widespread use of DGT, it is important that such effects are small and/or well characterized. The effects of different pH, ionic strength and DOM on DGT performance were therefore tested. Due to the chemical reactivity of aluminium under acidic conditions, which led the to the pH of the test solutions being unstable, DGT casing made from stainless-steel were used in the pH study. Most of the compounds had a ratio (C_{DGT}/C_b) between 0.8 - 1.2; some had low ratio values due to the different lag times of each PAH (Fig. 3.14). The stability of the ratio under different conditions indicates whether the performance of DGT was affected by pH. The ratio of MIP-DGT was stable across the pH range of 4-8, while the ratio for the HLB sampler decreased at pH=4.

The effect of IS on DGT measurements was investigated in solutions with IS ranging from 0.01 to 0.5 M. There was no significant effect of IS on MIP-DGT performance. In the DGT with HLB gel, the ratio (C_{DGT}/C_b) had a slight decrease with increasing IS for phenanthrene, anthracene, fluoranthene and pyrene (Fig. 3.15). IS can affect the diffusion process by changing the surface charge density of the target chemicals (Lucas, Rate et al. 2012). Increasing numbers of benzene rings in the molecular structure of PAHs, can make them more vulnerable to the change of charge density. Meanwhile, the increase of IS may lead to a salting-out effect, which could decrease the solubility of PAHs. An effect of high IS concentration (0.5 M) was reported in a study of bisphenol A (BPA) with activated carbon DGT binding gel (Zheng, Guan et al. 2014).

The results of experiments with DOM have shown that there were no obvious effects on the performance of MIP-DGT within the DOM range 0 - 20 mg L^{-1}. This range is applicable to most environmental conditions (Tipping, Corbishley et al. 2009, Vogt, Porcal et al. 2023), but further experiments may be needed at higher DOM concentrations to measure the operational range in soil and sediment deployment. The ratio (C_{DGT}/C_b) remained stable, with most values ranging from 0.8 to 1.2 (Fig. 3.16). For HLB-DGT, most PAHs were not affected by DOM, but the ratio of C_{DGT}/C_b values for anthracene, fluoranthene, and pyrene decreased at higher DOM concentrations. HLB materials have a wide range of adsorption properties. DOM may be adsorbed by binding gel and have a competition with target chemicals on the binding sites. Similar phenomena have also occurred during DGT measurement of Cu (Davison, Lin et al. 2014). MIP has specific adsorption for PAHs and is not easily affected by the changes of DOM during application. In addition, DOM is prone to binding with hydrophobic substances, thereby affecting the diffusion of the target chemicals in the solution (Liu, Zheng et al. 2010). Anthracene, fluoranthene and pyrene have higher hydrophobicity than other PAHs in this study and are more susceptible to interference. When using HLB-DGT to measure triclosan (TCS), the ratio of C_{DGT}/C_b decreased with increasing DOM which is similar to this study (Chen, Li et al. 2017). In general, the MIP-DGT has a better performance than HLB-DGT in waters of different environmental conditions.

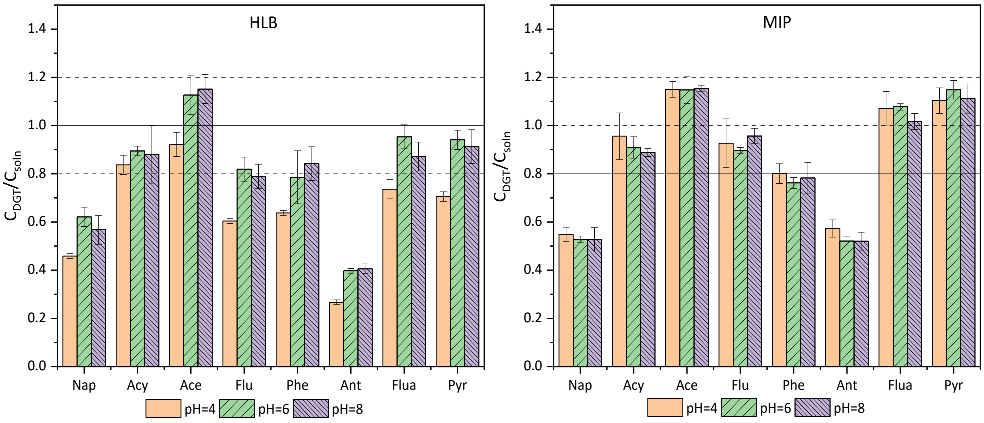


Fig. 3.14 Effect of pH on the ratio of DGT-measured concentrations (C_{DGT}) to their concentrations in the bulk solutions (C_b). The solid horizontal lines represent the target value of 1, and the dotted horizontal lines represent target values at 0.8 and 1.2. Values are means ± SD of three replicate analyses.

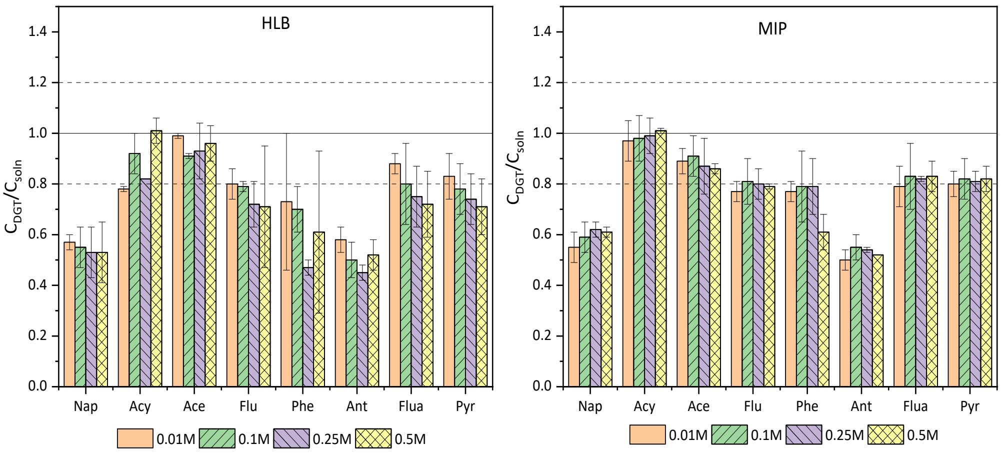


Fig. 3.15 Effect of IS on the ratio of DGT-measured concentrations (C_{DGT}) to their concentrations in the bulk solutions (C_b). The solid horizontal lines represent the target value of 1, and the dotted horizontal lines represent target values at 0.8 and 1.2. Values are means ± SD of three replicate analyses.

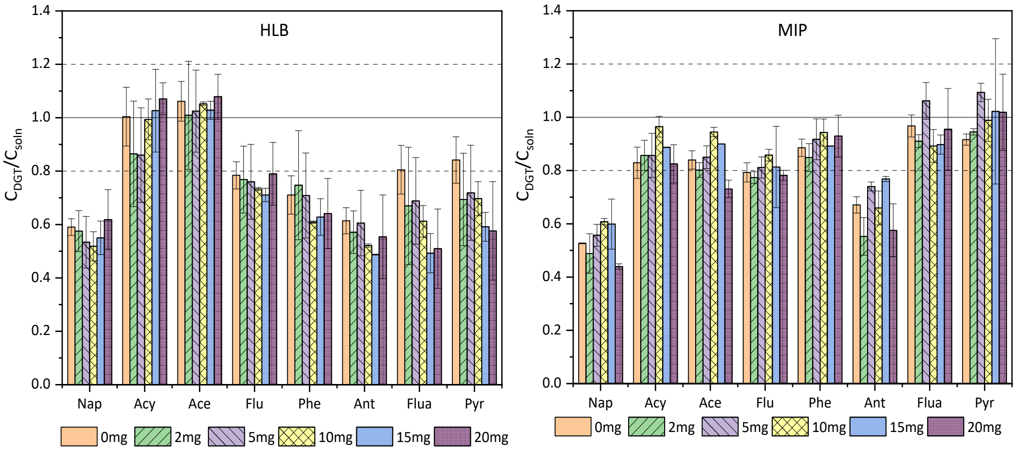


Fig. 3.16 Effect of DOM on the ratio of DGT-measured concentrations (C_{DGT}) to their concentrations in the bulk solutions (C_b). The solid horizontal lines represent the target value of 1, and the dotted horizontal lines represent an acceptable target range of 0.8 and 1.2. Values are means ± SD of three replicate analyses.

3.3.9 Field application in river water and a WWTP

The recoveries, IDLs and the MDLs of the studied chemicals are presented in Table 3.3 for both water and DGT samples. For the 7 days field deployment at 25°C, the MDLs of DGT for PAHs were in the range of 0.19-1.48 ng L^{-1} which are low enough for environmental monitoring. If necessary, the MDLs for DGT can be reduced by prolonging deployed time and reducing solvent volume when test samples. While DGT pre concentrated the compound *in-situ*, the filter membrane and diffusive gel prevent larger molecular substances such as humic acid from entering the binding gel. Even without purification, the matrix of DGT samples were cleaner than that of grab samples and had fewer interference peaks during sample detection. Grab samples need to be concentrated and purified after collection. During these processes, the samples were more prone to loss, especially for low ring PAHs which are more volatile led to lower accuracy than DGT samples.

The concentrations of PAHs measured by DGT in two field applications during 7- and 14- days deployments are compared with the results of grab sampling in Fig. 3.17. For most PAHs, the concentration measured by DGT was similar to that obtained by grab sampling, with ratio values (C_{DGT}/C_b) mostly ranging from 0.8-1.2 for both cases. When DGT was deployed in the river, the concentration of Nap and Acy measured by DGT was higher than the average concentration of grab samples. Higher volatility of low ring PAHs could be the reason, because these compounds are prone to loss during sample pre-treatment during conventional sample handling. For PAHs with higher hydrophobicity, the DGT measured concentrations were mostly lower than those of PAHs in grab samples. This is possibly because that DGT measures the water-soluble fraction, while PAHs adsorbed on suspended solids and in the colloidal state may not be measured by DGT. Similar results were found when DGT and grab samples were compared for determinations of atrazine and household and personal care products (Chen, Li et al. 2017, Li, Chen et al. 2019). It is important to point out that it should not be assumed that grab sample results are ‘right’; differences between the grab results and DGT are to be expected, because we are comparing instantaneous ‘1-off’ samples with time-integrated ones and there are differences in the aqueous fraction sampled, and the sample workup procedures. Knowledge of the importance of these factors is important in interpreting the results. Based on the data, we calculated the relative standard deviation (RSD) of DGT samples and grab samples, with ranges of 3.3-39% and 9.2-150%, respectively. The range of grab sampling results was much higher than that of DGT samples, which reflects that grab sampling is susceptible to different factors. Rainfall and short-term emissions may cause significant fluctuations in sample concentration (Xing, Chow et al. 2013, Baz-Lomba, Harman et al. 2017). Therefore, it is necessary to increase the sampling frequency of grab sampling to make the results more reliable. In contrast, the DGT gives a more representative time integrated sample. For the application in the wastewater treatment plant, the 7 days concentration measured by DGT was close to that obtained by grab sampling and 14 days deployment gave lower concentrations. In such biologically active waters, longer-term deployment of DGT could lead to some degradation of the target chemicals, which may affect the accuracy of the DGT measurement (Wang, Jones et al. 2020). Meanwhile, research has pointed out that the growth of biofilms could lead to a decrease in the diffusion coefficient (Pichette, Zhang et al. 2007, Feng, Zhu et al. 2016). Biofilms that are prone to growth in sewage environments may also lead to this result. Overall, DGT has provided reliable *in situ* measurements in both natural water and wastewater environments.

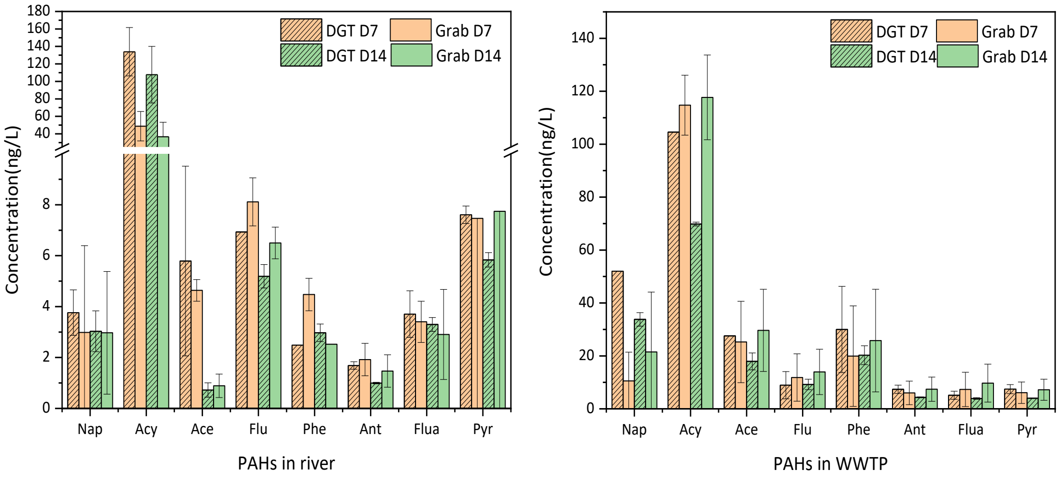


Fig. 3.17 Average concentration of PAHs measured by grab sampling and DGT *in situ* during 7 and 14 days in a river and in a WWTP. Values are means ± SD of three replicates for DGT samples and two replicate for grab samples.

3.4 Conclusions

A novel DGT passive sampler has been successfully developed for measurement of PAHs, based on systematic tests under different conditions and comparative evaluation of three different binding resins. DGT with MIP binding gel is recommended for its stable performance under different environmental conditions. The diffusion coefficients of PAHs through DGT diffusive gels were accurately measured for the first time, using the diffusion cell technique. The good linear relationship with the K_{OW} values of the chemicals could provide a basis for estimating the diffusion coefficients of other PAHs with similar structures for wider applications of the DGT technique. The use of metal material for the DGT casing reduced the sorption of target compounds on the material, effectively reducing the lag time of the deployment and providing more accurate DGT measurements.

Deployment times of less than two weeks are recommended for wastewater application to avoid the potential impact of biofilm and compound degradation. The in-situ field applications of the MIP-DGT samplers demonstrate that DGT is a reliable technique for the measurement of PAHs in natural aquatic systems and in wastewater treatment plant environments. It also shows the feasibility of using the newly developed passive sampler for other hydrophobic compounds of low aqueous solubility, which will expand the application range of the DGT technique greatly. Based on the robustness of the DGT samplers, it can be widely used in different aquatic environments in the future to explore the dynamic changes of PAHs in different environments, including surface water (fresh water and seawater), groundwater, and sediment-water interfaces. This will advance our understanding of the fate and behavior of PAHs in different environments. In general terms, DGT reduces errors in sampling, by providing a time-weighted average concentration, rather than an instantaneous one and samples the labile fraction from waters. There are sample preparation and analysis advantageous too, since DGT pre-concentrates *in situ*, reducing the risks of analyte losses or contamination during sample handling and work-up. DGT requires less lab time and solvents, reducing laboratory and labour costs, compared to conventional grab sampling.

Supporting information

The supplementary detailed information, tables and figures are listed in Supporting Information.

Supporting information for:

Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems

Qiuyu Rong[1], Yanying Li[2], Jun Luo[3], Liying Yan[3], Kevin Jones[1*] and Hao Zhang[1*]

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning 116023, P. R. China

[3]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023 P. R. China

*Corresponding authors

* Email: k.c.jones@lancaster.ac.uk

* Email: h.zhang@lancaster.ac.uk

Contents of Supporting Information

Text 1 Chemicals and Reagents

Nine PAHs were selected in this study, and the detailed information are listed in Table S3.1. Naphthalene (Nap) was purchased from Macklin (Shanghai, China). Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Pyrene (Pyr) and Benzo (a) anthracene (BaA) were purchased from Aladdin (China). Fluoranthene (Flua) was obtained from Accustandard (USA). Stock solutions were prepared at 1000 mg L^{-1} in acetonitrile and stored at -20 °C in amber glass bottles.

Reagents are at least analytical reagent and with high purity, organic solvents are HPLC grade.

Sodium chloride (NaCl) and hydrochloric acid (HCl) were purchased from Sinopharm Chemical Reagent (China). Humic acid, sodium bicarbonate ($NaHCO_3$) and sodium hydroxide (NaOH) were obtained from Aladdin (China). Acetonitrile (ACN) were obtained from Merck (Germany). Water used in the experiments was supplied from a Milli-Q water (MQ water) purification system (>18.2 MΩ/cm, Millipore). Agarose was obtained from Bio-Rad Laboratories (UK).

Resins for binding gel: hydrophilic-lipophilic-balanced (HLB) resins were extracted from Oasis-HLB solid-phase extraction (SPE) cartridges purchased from Waters Corporation (UK), XAD 18 resins were purchased from Sigma-Aldrich (China) and MIP were extracted from MIP-PAH SPE tubes purchased from CNW (Germany). All three types of resins are polymer-based.

Text 2 Analytical Method

A high performance liquid chromatography combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) were used for samples. The mobile phase consists of acetonitrile (solvent A) and MQ water (solvent B). The elution gradient began with 50% A and 50% B from 0 min, kept for 5 min, then started to increase, increased to 100% A at 20 min and maintained for 4 minutes. Finally, it returned to the initial conditions within 4 min and kept the column rebalancing. The flow rate was 1.5 mL min^{-1}, and the temperature for the column was set to 30°C. The injection volume was 20 μL per sample. The samples were analyzed by ultraviolet detector and fluorescence detector.

Text 3 The calculation of diffusion coefficient (De)

The method for measuring diffusion coefficients using a diffusion cell is based on Fick's first law of diffusion (Ref 1, 2) (Eq. S3.1)

$$F = De\ (\triangle C/\triangle g) \qquad \text{(Eq. S3.1)}$$

F is the flux through the gel, De is the diffusion coefficient and ($\triangle C/\triangle g$) is the concentration gradient within the gel where $\triangle g$ is gel thickness and $\triangle C$ is the concentration difference between the source compartment and receiving compartment of the diffusion cell.

The PAHs diffuses from the source compartment through the gel into the receiving compartment. A linear concentration gradient is established through the gel for each chemical quickly. As the diffusion cell experiment is only 2 hours, the mass of analyte diffused from the source compartment to the receiving compartment is negligible compared to the total mass of analyte in the source compartment. Therefore, $\triangle C$ equals to the concentration in the source compartment, *Cs*.

The flux can also be expressed as the mass (M) per unit area (A) per unit time (t) (Eq. S3.2).

$$F = M/(At) \qquad (Eq.\ S3.2)$$

Where *A* is the area of the window on the diffusion cell and t is the sampling time.

Combining Eq. S3.1 and S3.2 and assuming $\triangle C$ is constant and equals to *Cs*, give Eq. S3.3.

$$D_e = \frac{M\triangle g}{C_s At} \qquad (Eq.\ S3.3)$$

Experimentally concentrations are measured in the receiving compartment at various times, t. Knowing the volume of the solution in the compartment, the mass, *M*, at various times, *t*, can be calculated. After the first few minutes needed to reach a pseudo steady state, a straight-line of *M* versus *t* can be plotted with a slope of DeACs/△g. The concentration of analyte in the source compartment, *Cs*, is also measured during the experiment. Knowing the values of *A*, *Cs*, $\triangle g$ and the slope of the linear line, the diffusion coefficient *De* of each PAH at the current temperature can be calculated using Eq. S3.4:

$$D_e = Slope\frac{\triangle g}{C_s A} \qquad (Eq.\ S3.4)$$

Reference

1. Atkins P.W., Physical Chemistry, 2nd ed., Oxford University Press, Oxford, UK, 1982.
2. Zhang H and Davison W, 1999, Diffusional characteristics of hydrogels used in DGT and DET techniques, Analytica Chimica Acta 398, 329–340.

Text 4 Field water samples extraction – solid phase extraction (SPE)

The water samples were transported to the lab and stored in the dark at 4ºC. Take 1 L water sample, add 200 ng of decafluorobiphenyl and filtered with Whatman GF/F filter (0.7 µm). SPE cartridges with HLB (60 mg/3 mL, Waters, UK) were preconditioned with 10 mL dichloromethane and 10 mL methanol. Water samples were introduced into the cartridge at a flow rate of 5 mL min^{-1}. After the loading of water samples, the cartridges were rinsed with 10 mL of MQ water and vacuum dried for 10 min. The PAHs were eluted with 10 mL dichloromethane and the eluates were evaporated to near dryness under a gentle stream of nitrogen and add 3 mL of acetonitrile. Concentrate again and filter through a 0.22 μm PTFE filter membrane, and finally accurately dilute to 0.2 mL for testing.

Chapter 4 Occurrence and distribution of PAHs in the Yangtze River and urban river waters of Nanjing, China: insights from *in situ* DGT measurements

Qiuyu Rong[1], Hao Zhang[1], Yanying Li[2], Liying Yan[3], Jun Luo[3*] and Kevin C. Jones[1*]

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning 116023, P. R. China

[3]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023 P. R. China

*Corresponding authors

* Email: k.c.jones@lancaster.ac.uk

* Email: esluojun@nju.edu.cn

Rong, Q., Zhang, H., Li, Y., Yan, L., Luo, J., & Jones, K. C. (2025). Occurrence and distribution of PAHs in the Yangtze River and urban river waters of Nanjing, China: insights from in situ DGT measurements. *Environmental Pollution*, 125921.

Abstract

The diffusive gradients in thin films (DGT) technique has been used for monitoring various organic pollutants in surface water in recent years. This article applies a novel DGT passive sampler to the Nanjing section of the Yangtze River and urban rivers to measure the in-situ concentrations of polycyclic aromatic hydrocarbons (PAHs), analyze their seasonal changes and determine their fate. PAH concentrations had marked seasonality. The concentration of individual PAH was 1.3-18 ng L^{-1} in summer and 4.2-161 ng L^{-1} in winter. Source inputs, flow differences and degradation/losses caused the seasonal differences. Inputs from Nanjing and tributary rivers were minor compared to the cumulative loads of PAHs in the main Yangtze river upstream of the city. Petrochemical enterprises along the Yangtze River, ship transportation, and upstream pollution were the main sources of pollution in this area. Source analysis indicated a mixed source with coal and biomass combustion inputs increasing significantly in winter. Risk assessment indicated that although the Yangtze River protection policy has reduced pollution in recent years, water quality still exceeded PAH ecological thresholds in the river and the chemical industry cluster areas during winter. Further measures are needed to reduce pollution and its associated risks from a catchment perspective.

Keywords: PAHs, DGT, Yangtze River, urban river, ecological risk assessment

4.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widely distributed and abundant groups of organic pollutants in the environment (Uddin and Xu 2024). PAHs are priority pollutants, with mutagenic and carcinogenic properties (Vijayanand, Ramakrishnan et al. 2023). They are formed from incomplete combustion processes, with both natural and anthropogenic sources. Since industrialisation, emissions from human activities such as power generation, petrochemicals, steel smelting, vehicle emissions, space heating and incomplete combustion of biomass have become the main sources of PAHs (Venkatraman, Giribabu et al. 2024, Ziyaei, Mokhtari et al. 2024). Natural emissions include volcanoes and forest fires. PAHs are emitted into the atmosphere and then enter terrestrial and aquatic environments through dry and wet deposition (Gao, Zhu et al. 2024). Runoff from soils and vegetation provides an input to aquatic environments, together with sources such as wastewater discharge, oil leakage, road runoff and sediment re-mobilisation which also lead to the transfer of PAHs to water bodies (Zhao, Gong et al. 2021). Due to their hydrophobicity/lipophilicity, PAHs can transfer to aquatic organisms and potentially cause risks to ecosystems and to human health through ingestion, inhalation, skin contact and other pathways (Moon, Kim et al. 2010, Kim, Jahan et al. 2013). Higher ring PAHs are generally more harmful than lower ring PAHs (Wang, Liu et al. 2024). However, the risks of low ring PAHs cannot be ignored (Manzetti 2013). As the number of rings increases, the lipid solubility of PAHs increases, resulting in stronger toxicity to organisms, mainly manifested as genotoxicity, mutagenicity and carcinogenicity (Sun, Song et al. 2021). Therefore, it is important to understand the distribution, migration, transformation, and risk assessment of PAHs in aquatic environments.

Traditional monitoring of organic chemicals in waters mainly relies on active sampling methods. For example, Cao et al. investigated the spatiotemporal distribution of PAHs in the southern Bohai Sea by taking grab samples (Cao, Wang et al. 2024). Net studied the levels of PAHs, polychlorinated biphenyls, and insecticides in the Somme River in northern France by concentrating 1 L water samples (Net 2014). The collection of 40 grab samples indicated the widespread presence of PAHs in the Amazon basin (Rizzi, Villa et al. 2023). However, grab sampling not only requires the collection, transportation, and preservation of a large number of high volume samples, but also requires complex pre-treatment processes, which are prone to cross contamination and losses of PAHs (Kot 2000). Active sampling is also limited to giving one-off 'instantaneous' concentrations, which may be unrepresentative. Short-term emissions, rainfall and other factors influence such one-off measurements (Baz-Lomba, Harman et al. 2017). Therefore, passive sampling techniques based on time weighted average (TWA) concentrations have developed rapidly in recent years and are being increasingly adopted by monitoring agencies and researchers. Compared with technologies such as SPMD, POCIS, and Chemcatcher, the diffusive gradients in thin-films (DGT) technology has the advantage of not needing on-site calibration (Davison and Zhang 1994, Chen, Zhang et al. 2012). At present, DGT samplers have been developed for over 150 organic pollutants and successfully used in water environments under different environmental conditions (Xie, Chen et al. 2018, Wang, Biles et al. 2020, Liang, Li et al. 2023). DGT measures the labile fraction of pollutants in water, rather than pollutants adsorbed in suspended and colloidal substances. This better reflects the ecological risk of pollutants (Chen, Li et al. 2017, Li, Chen et al. 2019). Recently a DGT passive sampler has been developed for PAHs, ready to be applied for monitoring and risk assessment of PAHs in aquatic environments (Rong, Li et al. 2024).

The Yangtze River is about 6300 km long, flowing from the Qinghai Tibet Plateau in the west to the East China Sea. It passes through 19 provinces in China, with a drainage area of over 1.8 million km^2. It is the most important source of industrial and drinking water in China, and its natural resources serve nearly one-third of the country's population (over 460 million people). Therefore, the water quality of the Yangtze River has a direct impact on the lives of residents and

China’s industrial production (Yang, Chen et al. 2021). In recent decades, human activities such as the construction of chemical enterprises along the river and the discharge of municipal sewage have led to over 25 billion tons of wastewater and pollutants being discharged into the Yangtze River every year, accounting for more than 40% of total wastewater discharge in China (Wong 2007, Wang, Shi et al. 2010). This has caused serious pollution to the Yangtze River and severe damage to its ecological environment. China has therefore introduced a series of policies and regulations, including the Yangtze River Protection Law (China 2020) and the Yangtze River Economic Belt Ecological Environment Protection Plan (China 2017) to carry out activities for the protection and pollution control of the Yangtze River. Nanjing is a major industrial city, with chemical production, electronic production, and automobile manufacturing, amongst the highest in China. Nanjing has a permanent population of about 9.5 million, with over 7 million urban residents. As one of the most economically developed core cities of the Yangtze River Delta metropolitan region of China, industrial production, high population and transportation activities have brought serious pollution problems to this city. The production and domestic water of Nanjing mainly comes from the Yangtze River, and a large amount of wastewater is discharged back into the Yangtze. Previous research related to PAHs has focused on key sections of the mainstream of the Yangtze River. Monitoring of surface waters in Nanjing was conducted before the instigation of the “Yangtze River protection” policies (He, Hu et al. 2011, Wang, Zhou et al. 2017, Yan, Yang et al. 2018). Research has mainly focused on the distribution and source of PAHs in the river basin, but did not address the relationship between the main Yangtze River and other urban rivers and drainage channels supplying the Yangtze.

Therefore, the objectives of this study were to: (i) apply the new DGT passive sampler technology to determine the in-situ concentrations, distribution characteristics and seasonal changes of PAHs in the Nanjing section of the Yangtze River and urban rivers; (ii) identify the sources of PAHs in surface waters and investigate the correlation between the fate and behavior of PAHs in the Yangtze River itself and Nanjing tributaries; (iii) use the DGT in-situ labile concentrations to conduct an ecological risk assessment of PAHs in this region, to provide information on the current situation of PAH pollution in its watershed, and provide a scientific basis for source control of pollutants and water management.

4.2 Materials and methods

4.2.1 Chemicals and reagents

Eight of the 16 priority PAHs specified by the U.S. EPA were selected in this study, namely Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua) and Pyrene (Pyr). The new DGT sampler has been tested and validated for these compounds (Rong, Li et al. 2024). HPLC-grade methanol, acetonitrile and dichloromethane were used in this study. Agarose (Bio-Rad Laboratories, UK) and MIP-PAHs (CNW, Germany) were used to make gels for DGT.

4.2.2 DGT preparation

The method for DGT preparation was the same as used in previous studies (Rong, Li et al. 2024). DGT samplers were assembled in the sequence: polycarbonate (PC) membrane filter (in contact with the water), an agarose diffusive gel and a MIP binding gel in a metal casing before deployment (See details in SI).

4.2.3 Study area

The river system in the main urban area of Nanjing consists of the main stream of the Yangtze River and the Qinhuai River system. The northern and western parts of the urban area belong to the Nanjing section of the Yangtze River, with a drainage area of 117 km^2. The Qinhuai River system is in the southeast of the urban area, with an area of 163 km^2.

Due to human activities, such as urban construction, discharge from wastewater treatment plants, and accessibility for sample retrieval, seven locations in the river system were selected as sampling sites (Fig. 4.1 and Table 4.1). Two sampling sites were located in the Yangtze River and 5 sites were located in parts of urban rivers in the city of Nanjing. More details about the experimental area and sites are provided in the Supporting Information.

Sampling was conducted in January and July 2021. Sampling corresponded to the dry season in winter and the wet season in summer. Sample deployment and collection was the same as previous study (Rong, Li et al. 2024). The exposure time of DGT was 7 days. Grab water samples were taken on day 1 and day 7 of the DGT sampling periods. Both DGT samples and water samples were treated within 24 hours.

Table 4.1 Information of sampling sites in this study

Sites	Longitude	Latitude	Position	Surrounding environment
S1	118°39′10″	31°57′57″	Yangtze River (upper reaches)	Downstream of the steel enterprise, wharfs
S2	118°48′05″	31°57′43″	New Qinhuai River	Enterprises of automobile and key components
S3	118°51′41″	32°00′34″	Qinhuai River	Residential area, WWTPs
S4	118°44′38″	32°04′43″	Qinhuai River (lower reaches)	Residential area
S5	118°46′22″	32°05′16″	Qinhuai River	Residential area, hospital, urban drainage monitoring station
S6	118°57′11″	32°07′25″	Jiuxiang River	Higher education mega center
S7	118°58′47″	32°10′23″	Yangtze River (lower reaches)	Downstream of petrochemical enterprises and industrial zone, wharfs

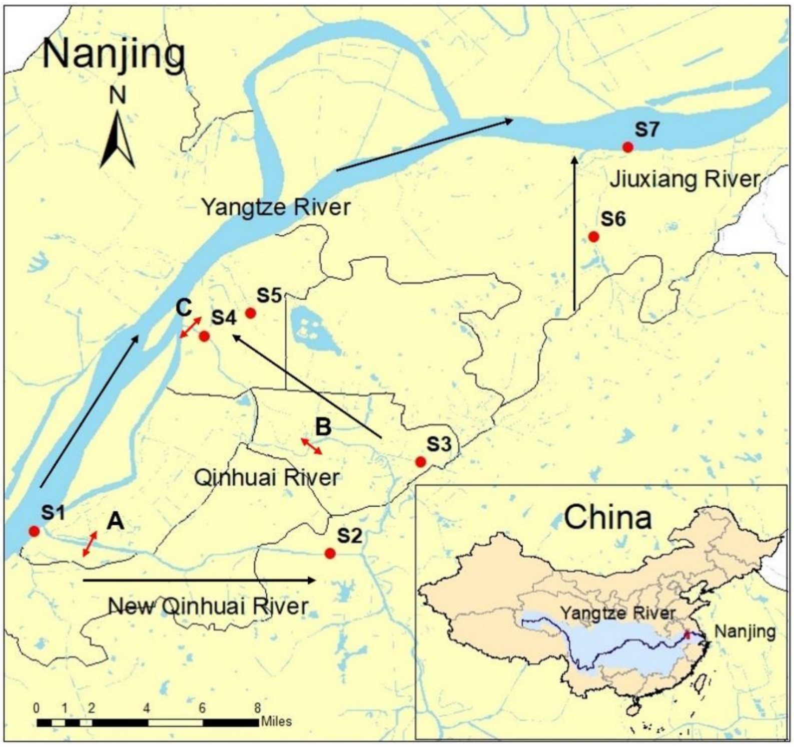


Fig. 4.1 The study area of the Yangtze River and urban river in Nanjing. Inset map of China, showing the position of Nanjing. Arrows show the direction of river flows.

4.2.4 Sample treatment

Sample treatment was conducted as in previous studies (Rong, Li et al. 2024). For DGT samples, each binding gel was placed in an amber vial with 200 ng decafluorobiphenyl, then ultrasonically extracted with acetonitrile. The elution solution was then evaporated to near dryness and made up with 0.2 mL of acetonitrile/MQ water solution (1:1, v: v).

For the water samples, 1 L was filtered through Whatman GF/F filter (0.7 μm) and spiked with 200 ng decafluorobiphenyl. HLB (60 mg/3 mL, Waters, UK) SPE columns were used to concentrate the water samples. After solid phase extraction, PAHs were eluted with dichloromethane and concentrated， then solvent was replaced as acetonitrile/MQ water solution (1:1, v: v). All the samples were finally filtered through 0.22 μm PTFE filter membranes before analysis (See details in SI).

4.2.5 Instrumental analysis

The separation of target compounds was performed with a PAH C18 column (4.6 × 250 mm, 5 µm, Waters). High performance liquid chromatography (HPLC) combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) was used to analyze the 8 PAHs (see details in SI and section 3.2.2).

4.2.6 Calculation of DGT measured concentrations

Based on Fick's law, the concentration of PAHs in water determined by DGT was calculated using Eq. 4.1 (Zhang and Davison 1995):

$$C_{DGT} = \frac{M(\Delta g+\delta)}{DAt} \qquad \textit{(Eq. 4.1)}$$

Where M (ng) is the total amount adsorbed by the binding gel through the diffusion layer, Δg (cm) is the thickness of the diffusion layer, δ (cm) is the thickness of the diffusion boundary layer, D (cm^2 s^{-1}) is the diffusion coefficient of the individual chemicals in the diffuse layer, A (cm^2) is the window area of the device, and t (sec) is the diffusion time during deployment.

4.2.7 Risk assessment

According to technical guidance from the European Union (EU), ecological risk can be assessed using the Risk Quotient (RQ) method. RQ is the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC).

$$RQ = \frac{MEC}{PNEC} \qquad \textit{(Eq. 4.2)}$$

This research used the methods from Kalf and Cao to evaluate the ecological risks of PAHs in the rivers in Nanjing (Kalf, Trudie Crommentuijn et al. 1997, Cao, Liu et al. 2010). Maximum permissible concentrations (MPCs) are concentrations above which the risk of adverse effects is considered unacceptable. Negligible concentrations (NCs) are defined as the MPC/100 and takes possible effects of combination toxicity due to the presence of other substances into account (Kalf, Trudie Crommentuijn et al. 1997). Considering both the ecosystem risk of ∑PAHs with the individual PAHs, RQs (NCs) <1.0 indicates that the ecological risk of an individual PAH may be negligible, while RQ (MPCs) >1.0 indicates that the pollution of a single PAH is deemed 'serious' and could have an effect. When RQs (NCs) >1.0 and RQs (MPCs) <1.0, it indicates that the ecological risk of an individual PAH may be classified as moderate.

Species Sensitivity Distribution (SSD) is also a commonly used method for assessing ecological risks at the system level. It fits the toxicity data of different species to specific chemicals, constructs SSD curves and extrapolates a safe concentration that could protect most organisms in the ecosystem. Here acute toxicity data were used to construct SSD curves. The toxicity data were obtained from the US Environmental Protection Agency ECOTOX database (http://www.epa.gov/ecotox/). The species categories include algae, amphibians, fish, crustaceans, insects and spiders, molluscs and worms (Table 4.2). SSD curves were fit based on the Chinese national ecological environment benchmark calculation software EEC-SSD (https://www.mee.gov.cn/ywgz/fgbz/hjjzgl/mxrj/202203/t20220304_970658.shtml). The specific calculation of the hazard index (HI) is given in the SI.

Table 4.2 Database information available for polycyclic aromatic hydrocarbons (PAHs) and applied in this study

PAHs	Sample size	Aquatic biota included							
		1	2	3	4	5	6	7	8
Nap	26	√	√	√	√	√	√	√	√
Ace	12	√	-	√	√	√	√	-	√
Flu	13	√	-	√	√	√	√	√	√
Phe	10	√	-	√	√	√	√	√	√
Ant	17	√	√	√	√	√	√	√	-
Flua	28	√	√	√	√	√	√	√	√
Pyr	12								

Note: 1- Algae, 2-Amphibians, 3- Crustaceans, 4- Fish, 5- Insect, 6- Invertebrate, 7- Mollusca, 8- Worms;

label "√" indicates that this category of biota is included.

4.2.8 Quality assurance/Quality control

DGT on-site blanks and procedure blanks were used to check for possible contamination, while parallel samples (DGT samples in triplicate, grab samples in duplicate) were used to study repeatability. The target compounds were not found at detectable levels in the blank samples. Quality control standards (10 μg L^{-1}) were prepared and run every 10 samples. Detailed information about the instrument detection limits (IDLs) and method detection limits (MDLs) of the SPE method (grab samples) and the DGT method is given in Table 4.3.

Table 4.3 Instrument detection limits (IDLs) of selected PAHs detected by HPLC and method detection limits (MDLs) for water samples and DGT samples (for 7-day field deployments)

Compound	IDLs (μg L^{-1})	Recoveries (%)		MDLs	
		SPE	DGT	water sample (μg L^{-1})	7 days DGT deployment (ng L^{-1})
Nap	0.03	63.2±5.8	98.9±1.8	0.10	0.04
Acy	0.24	66.9±3.8	103.5±5.7	0.71	0.30
Ace	0.04	73.6±7.0	90.8±7.9	0.10	0.05
Flu	0.08	81.1±10.3	89.0±3.6	0.19	0.11
Phe	0.12	73.9±10.9	97.7±4.8	0.32	0.17
Ant	0.03	71.9±3.94	101.8±11.2	0.08	0.04
Flua	0.12	92.6±7.6	92.8±4.8	0.27	0.22
Pyr	0.05	91.4±6.7	95.3±2.9	0.12	0.09

IDLs calculated using equation: $IDL = t_{(n-1,0.99)} \times S$, where S is the standard deviation from a measured concentration of standard, for testing 7 times, t(n-1,0.99) = 3.1;

MDLs calculated using equation: $MDL = \frac{IDL}{R \times CF}$, where R is the absolute recovery for water samples, CF is the concentration factor; CF is 0.5 for laboratory water samples;

MDLs for DGT calculated using equation: $MDL = \frac{M \triangle g}{DAt}$, where $M = \frac{IDL \times V}{R}$, and where R is the absolute recovery for DGT samples, V is 0.2 mL, results calculated for 7-day deployment at 25°C.

4.3 Results and discussion

4.3.1 Observations on the sampling and analytical procedures

Grab sampling is the usual approach for detection of organic pollutants in waters. However, the value of DGT in organic pollutant monitoring has also been demonstrated in the past decade. In addition to having *in situ* monitoring, biomimetic functions, improved detection limits, and increased sensitivity, DGT also has significant advantages in sample collection and processing analysis (Yin, Guo et al. 2019, Martins de Barros, Lissalde et al. 2023). In this study, a total of eight 2 L glass bottles were used for grab sampling, which required a large amount of space for sampling, transportation, and laboratory storage. The DGT device is small, lightweight, and easy to carry. For studies with multiple and scattered sampling sites, DGT is more convenient to use. The laboratory processing of DGT samples is also simpler. Grab samples require more steps such as solid-phase extraction, elution, concentration, solvent displacement and filtration. The processing time for a single sample exceeded 12 h. The DGT sample only required ultrasonic elution, concentration, solvent displacement, filtration, and a single sample processing time of about 3 h. In addition, ~35 mL of organic reagents were used per grab sample, while DGT samples required <20% of this. Moreover, DGT samples were processed simultaneously, while the processing of bulk water samples was limited by solid-phase extraction devices and required batch processing. So in terms of both time and cost, DGT has obvious advantages. DGT samples have the benefit of pre-concentration, resulting in a cleaner sample matrix and a smoother chromatogram during instrument analysis, making data analysis easier. Previous work has discussed that DGT may be hampered by biofilms or cross-contamination during DGT disassembly (Rougerie, Martins de Barros et al. 2021), but this has little impact on organic pollutants, and biofilm formation has been shown to have almost no effect within an exposure time of less than two weeks (Chen, Li et al. 2017, Wang, Jones et al. 2020). One practical problem can be the loss of DGT samples during field deployment (e.g. loss or vandalism). In this study, <5% of the samples were lost. For large-scale projects, a loss rate of 1-3% is considered acceptable (Rougerie, Martins de Barros et al. 2021). The grab samples were processed with 0.7 μm glass filter membranes, while the DGT was processed through 0.2 μm filter membranes. Therefore, PAHs adsorbed in suspended solids and colloidal states may not be adsorbed by DGT. Similar situations have also been found in the monitoring of pesticides and personal care products (Chen, Li et al. 2017, Li, Chen et al. 2019). This is also one of the advantages of DGT measurement, as its concentration has been shown to be correlated with the form of pollutants and their bioavailability (Han, Naito et al. 2013, Cusnir, Steinmann et al. 2014, Eismann, Menegário et al. 2018). This is beneficial for the risk assessment of pollutants.

4.3.2 Comparison of PAH determinations by DGT and grab samples

The concentrations of 8 individual PAHs obtained through grab sampling ranged from 0.2 to 25.9 ng L^{-1} at all sampling points. The concentration range measured by DGT was similar - between 0.45 and 18.1 ng L^{-1}. Naphthalene had the highest concentrations and Ant was the lowest of the target compounds.

Figure 4.2a provides a comparison of the concentrations/profile of 7 PAHs obtained by grab sampling and DGT sampling. Many samples were obtained in the study, so this figure was prepared as the averages at the Yangtze River and an urban Nanjing river station. In summary, the data show that concentrations determined by grab and DGT samples are similar – note the error bar ranges. However, in general, for the samples at the Yangtze River site, the concentrations of Nap, Ace, Flu, and Phe measured by DGT tended to be slightly higher than those obtained by grab samples. This reflects the differences caused by the sample work-up procedures; these semi-volatile organic compounds are prone to losses by volatilisation from the grab samples during the complex sample workup steps, whereas this is not a problem for the DGT samples because PAHs are directly sampled *in situ*.

In the Nanjing urban river samples, the DGT concentrations of Nap were lower than the Yangtze but the concentration of Pyr were higher. This may be because the urban river sites are more turbid, as they receive more effluent or drainage from the city. Previous research found that PAHs were most concentrated in suspended particulate matter, and their concentrations were lower when water had lower suspended solids (Wang, Yuan et al. 2016, Zheng, Wang et al. 2016). DGT measures water-soluble PAHs, rather than pollutants adsorbed on suspended substances or colloids.

Comparing the concentrations of individual PAHs at various sampling sites, the results obtained from DGT and grab sampling were similar. As shown in Fig. 4.2b, the Ace concentrations measured by the two methods are similar. However, the concentration of Pyr measured by DGT was higher than that obtained by grab sampling at all sampling sites (Fig. 4.2c). This may be due to the higher hydrophobicity of this chemical compared to others and its tendency to accumulate in sediment.

July is the rainy season in Nanjing, and the July sample collection period was accompanied by rainfall. Fig 4.1 and Fig 4.3 give the information about the instantaneous concentrations of grab samples; Nap, Ace, Flu, Ant concentrations on the seventh day were lower than on the first day, which may be due to rainfall dilution during the sampling period. Meanwhile, high rainfall can cause re-mobilisation of sediments and higher total suspended particle (TSP) load in river waters than during dry periods. Pollutants held in sediments may re-partition into the overlying river water. The concentrations of Phe, Flua and Pyr increased in some places from day 1 to day 7. This has also been observed previously for other organic chemicals e.g. pharmaceuticals and glucocorticoids. During heavy rainfall, the concentration of target compounds was higher than other periods (Fang, Li et al. 2019, Yan, Rong et al. 2022). Because active sampling measures the instantaneous concentration it can be affected by rainfall, river water flow, short-term emissions, etc., whereas DGT smooths and integrates such differences over time (Chen, Zhang et al. 2013, Yang, Lu et al. 2019). Grab samples could give us specific information about the changes during the research period. However, to obtain representative results by active sampling requires high-frequency sampling. This is not conducive to on-site operations and increases research and monitoring costs. DGT can effectively reflect the environmental behavior of PAHs by measuring the time weighted average concentration over a period of time.

The subsequent analysis and discussion are based on DGT measured concentrations.

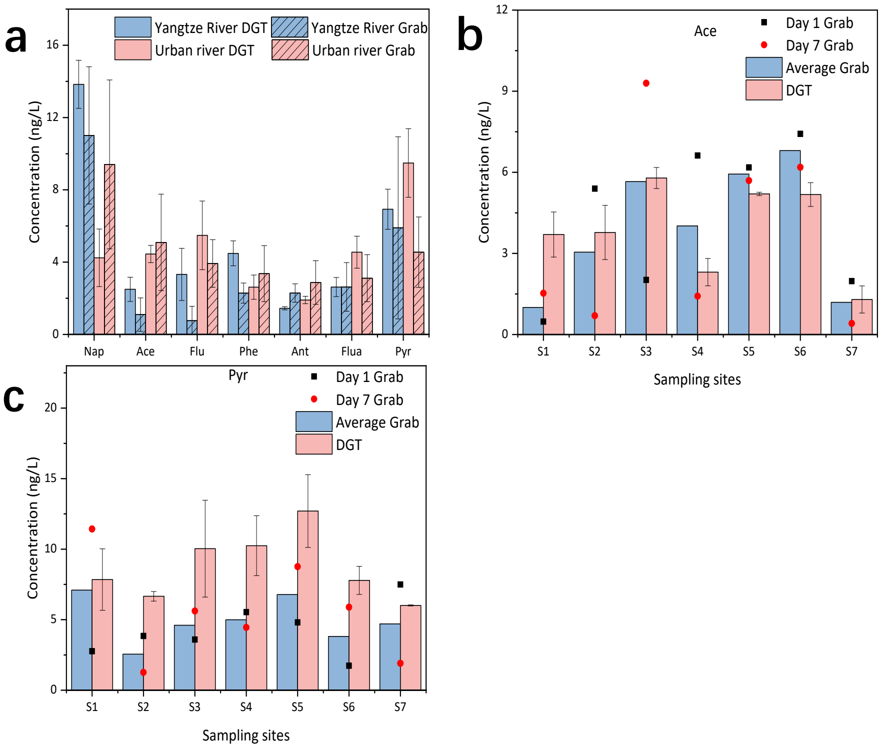


Fig. 4.2 Comparison of DGT and grab samples, a: mean concentrations in Yangtze River (S1, S7) and Nanjing urban river (S2 to S6) samples for each compound; b: the concentration of Ace at all 7 sampling sites; c: the concentration of Pyr at all 7 sampling sites. Values are means ± SD of replicate analyses. The red and black scatter plots represent the instantaneous concentrations of grab sampling on the first and seventh days of DGT deployment, respectively.

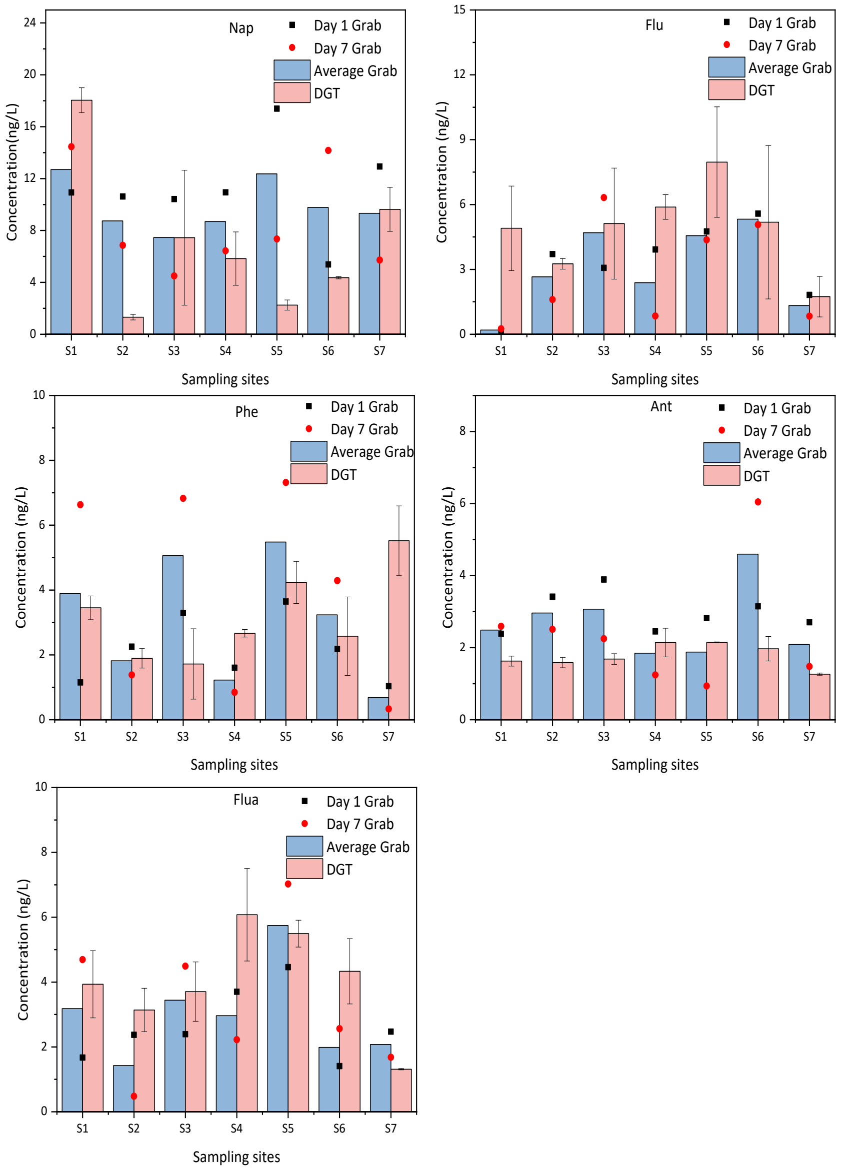


Fig. 4.3 The concentrations of individual PAHs by grab and DGT sampling at all 7 sites. The bar chart represents the average concentration of PAHs during the sampling period, and the red and black scatter plots represent the instantaneous concentrations of grab sampling on the first and seventh days, respectively.

4.3.3 Occurrence of PAHs in different seasons

The concentrations of PAHs in winter and summer samples are shown in Table 4.4. There are obvious seasonal differences. The concentration range of individual PAHs in winter was 4.2-161 ng L^{-1}, with the highest average concentrations being Nap (91.5 ng L^{-1}) and Acy (83.3 ng L^{-1}), and the lowest being Ant (5.9 ng L^{-1}). The concentration range of individual PAHs in summer was 1.3 to 18.0 ng L^{-1} (Nap). The highest average concentration was Pyr (8.8 ng L^{-1}), followed by Nap (7.0 ng L^{-1}), and the lowest was Ant (1.8 ng L^{-1}). The winter concentrations of individual PAH were between 2-15 times higher than the summer. The mean of winter: summer ratios for individual PAHs averaged over all the sites were as follows: Nap, 13; Ace, 15; Flu, 3.1; Phe, 15; Ant 3.3; Flua, 5.0; Pyr, 2.1. So, there were marked differences between compounds in their water-soluble/DGT-labile concentrations and abundance between winter and summer. Generally, the differences between winter and summer are more pronounced for the compounds with fewer benzene rings, which are more volatile and degradable.

The following are factors that vary between winter and summer, which could potentially influence the seasonal differences: seasonally dependent sources to the environment/catchments (He, Fan et al. 2014); rainfall, discharges and river flow – influencing dilution and sediment re-suspension (as noted above, summer flows were ca 3 times higher in the main Yangtze channel than the winter) (Zhang, Liang et al. 2012); degradation/removal of compounds from the water column, via volatilization, photolysis and biodegradation, partitioning to sediments and subsequent deposition. These processes are all affected by temperature.

Due to the demand for heating in winter, the concentration of PAHs in the atmosphere is higher than that in summer, from combustion sources (Daisey 1980, Tang, Hattori et al. 2005). The increase in PAH concentration in the eastern region of China after the autumn harvest period is from straw burning (He, Fan et al. 2014). PAHs exist in the atmosphere in the gas and particle phase, with the lower molecular weight compounds almost exclusively in the gas phase (Xu, Liu et al. 2006). Atmospheric dry deposition is a source of PAHs in water (Guo, He et al. 2009). Air-surface exchange of these compounds occurs, with the net direction influenced by temperature. During warmer weather, the net flux will be from the dissolved/labile phase in river waters to the atmosphere (Barrado, García et al. 2012). The increase in sources has contributed to differences in the concentration of PAHs in the water of Nanjing area between winter and summer.

The rainfall in July was about 6 times that of winter in Nanjing, resulting in a significant dilution effect on pollution concentrations. Similar results have also been found in previous studies on the

Yellow River and Bohai Sea, where PAHs concentrations were diluted by rainfall during the rainy season (Sun, Wang et al. 2009, Chen, Lin et al. 2023).

Based on river water flow, typical mass flows (kg day^{-1}) of PAHs were calculated for summer and winter (Table 4.5). In the urban rivers, the mass flows of pollutants in summer were lower than in winter. Compared to the data of the mainstream of Yangtze River, the amount of pollutants at downstream locations in summer was actually lower than that at the upstream location (see Table 4.5). The higher temperature in summer may lead to the degradation of PAHs. Microbial degradation of PAHs can occur in the water column, particularly for the LMW compounds (Li, Wang et al. 2022, Chen, Lin et al. 2023). Higher ultraviolet radiation in summer can also promote the photodegradation of PAHs (Zhang and Chen 2017). Volatilisation, photolysis and biodegradation rates are all compound specific, removing 2-/3-ring compounds more quickly than 4-ring compounds. The proportion of 2-/3- ring PAHs in summer were lower than in winter in the water samples (Fig. 4.4).

In summary, these seasonal differences in DGT measured labile concentrations are a function of seasonal differences in sources/emissions/discharges, riverine flows and degradation/losses to/from the water column.

Table 4.4 Time weighted average (TWA) concentrations of PAHs measured by DGT in all samples in January and July

	winter				summer				winter/summer ratio
	min	max	mean	SD	min	max	mean	SD	
Nap	51.6	161	91.5	38.4	1.3	18.0	7.0	5.7	13.1
Acy	59.6	146	83.3	29.3	-	-	-	-	
Ace	20.5	88.7	60.1	25.1	1.3	5.8	3.9	1.7	15,4
Flu	9.8	20.2	15.0	3.7	1.7	8.0	4.9	2.0	3.1
Phe	31.6	70.7	47.5	13.1	1.7	5.5	3.2	1.4	15.1
Ant	4.2	8.6	5.9	1.4	1.3	2.1	1.8	0.3	3.3
Flua	13.8	29.5	20.1	5.0	1.3	6.1	4.0	1.6	5.0
Pyr	12.8	24.6	18.0	4.7	6.0	12.7	8.8	2.4	2.1

Table 4.5 The estimated mass of PAHs flowing per day in winter and summer at selected Yangtze River and Nanjing urban river sites.

Season	Site	flow (m^3 s^{-1})	Mass compound/day (kg day^{-1})						
			Nap	Ace	Flu	Phe	Ant	Flua	Pyr
Winter	S1	16850	76.7	102.3	21.2	45.9	8.0	20.1	19.9
	S4	50	0.3	0.3	0.1	0.3	0.0	0.1	0.1
	S6	20	0.2	0.1	0.0	0.1	0.0	0.0	0.0
	S7	16850	234.6	46.1	24.7	83.2	9.2	29.0	34.1
	Input to urban rivers*		0.50	0.47	0.12	0.39	0.05	0.17	0.10
	Input to Yangtze main stream**		157.9	56.3^a	3.4	37.3	1.2	8.9	14.2
Summer	S1	45000	26.3	5.4	7.1	5.0	2.4	5.7	11.4
	S4	200	0.1	0.0	0.1	0.0	0.0	0.1	0.1
	S6	50	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	S7	45000	14.0	1.9	2.5	8.0	1.8	1.9	8.8
	Input to urban rivers*		0.07	0.04	0.08	0.04	0.03	0.08	0.13
	Input to Yangtze main stream**		12.2^a	3.5^a	4.6^a	3.0	0.5^a	3.8^a	2.7^a

S1 is the Yangtze River upstream site, S4 is the Qinhuai River, S6 is the Jiuxiang River, and S7 is the downstream Yangtze River site. Subscript “a” represent negative numbers. * Calculated by total mass flow of S4 and S6, ** calculated by mass flow at S7 minus S1.

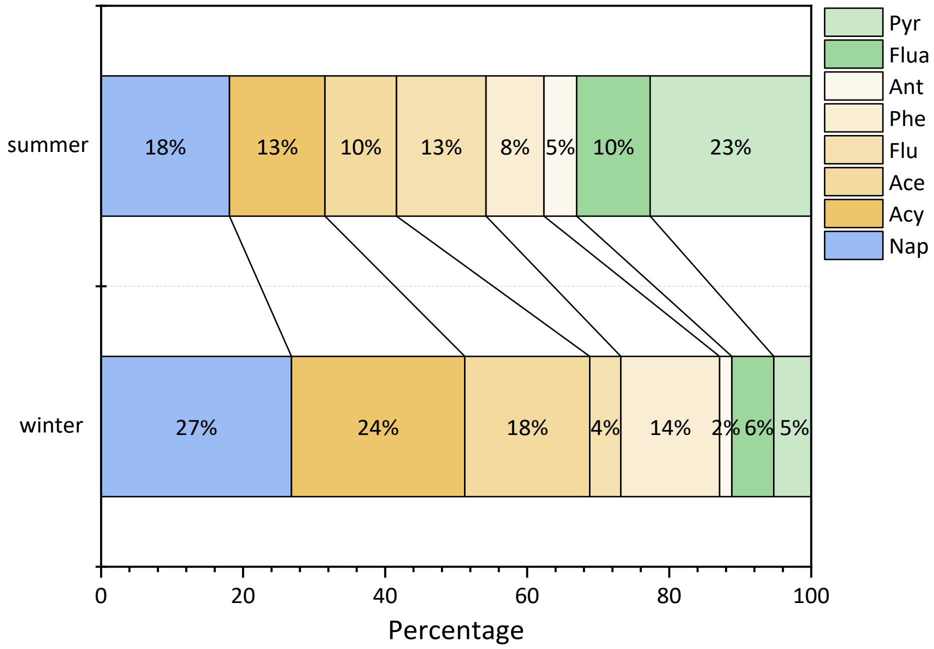


Fig. 4.4 Composition of PAHs in winter and summer in rivers, Nanjing. Chemicals in blue are 2-ring PAHs, in yellow - 3-ring PAHs, green - 4-ring PAH.

4.3.4 PAH composition and features at the sample sites

The concentrations of target PAHs in the samples collected at different sites in July 2021 are shown in Fig. 4.5; the detection frequency of all the analytes was 100%. The mixture of PAHs varied between sites. Compound distributions are shown in Fig 4.6. Naphthalene had higher concentrations at points S1 and S7, on the mainstream of the Yangtze River which serves as the main shipping channel and terminals. The port of Nanjing has a cargo throughput of over 100 million tons a year. Although efforts have been made to improve and protect the ecological environment of the Yangtze, there are still over a hundred chemical enterprises in Nanjing alone along the Yangtze River. Site S1 had the highest concentration of Nap of the sampling sites; it is 8 km downstream of the city's steel industry complex. Point source emissions and ship fuel combustion could be sources of Nap in this area. For 3-ring Phe, the highest concentrations occurred at sites S4, S5 and S7. Site S5 is in residential areas with high population density. Pollutant emissions from the urban area of Nanjing flow into the Yangtze River through the

Qinhuai River (site S5) system. The concentration of Pyr in the mainstream of the Yangtze River was lower than that in urban rivers, with the highest concentration at S5. This may be due to sampling during the rainy season, when high rainfall and river flows cause runoff and remobilize sediments, which can release particle-bound pollutants into the water (Fialová, Grabic et al. 2023). What this comparison of compounds and sites shows is that the mixture of PAHs in the study system can vary in space and time. It would be very difficult to unravel all the factors influencing the mixture of PAHs in this study catchment. It will be a complex function of myriad sources of different types and compound-specific differences in behaviour and degradation in the study environment.

It is instructive to compare the mass flows of PAHs in the main Yangtze River upstream and downstream of the major city of Nanjing, and to compare the mass flows of the Nanjing river with the mass flows of the Yangtze itself (see Table 4.5). It is clear that: i. the PAH load in the main Yangtze far exceeds that being supplied to it by the Nanjing river system, and ii. Nanjing makes a minor contribution compared to the load already in the Yangtze arriving upstream of the city. This is because the Yangtze has flowed many thousands of km before reaching Nanjing, through many major urban areas and has collected PAH inputs from a multitude of point and diffuse sources before reaching Nanjing. As such, source reduction measures in Nanjing and nearby will have a small impact on the PAH burden of the Yangtze itself. Major regional/national reductions in sources would be needed to have a measurable impact on the quality of the Yangtze River flowing through Nanjing.

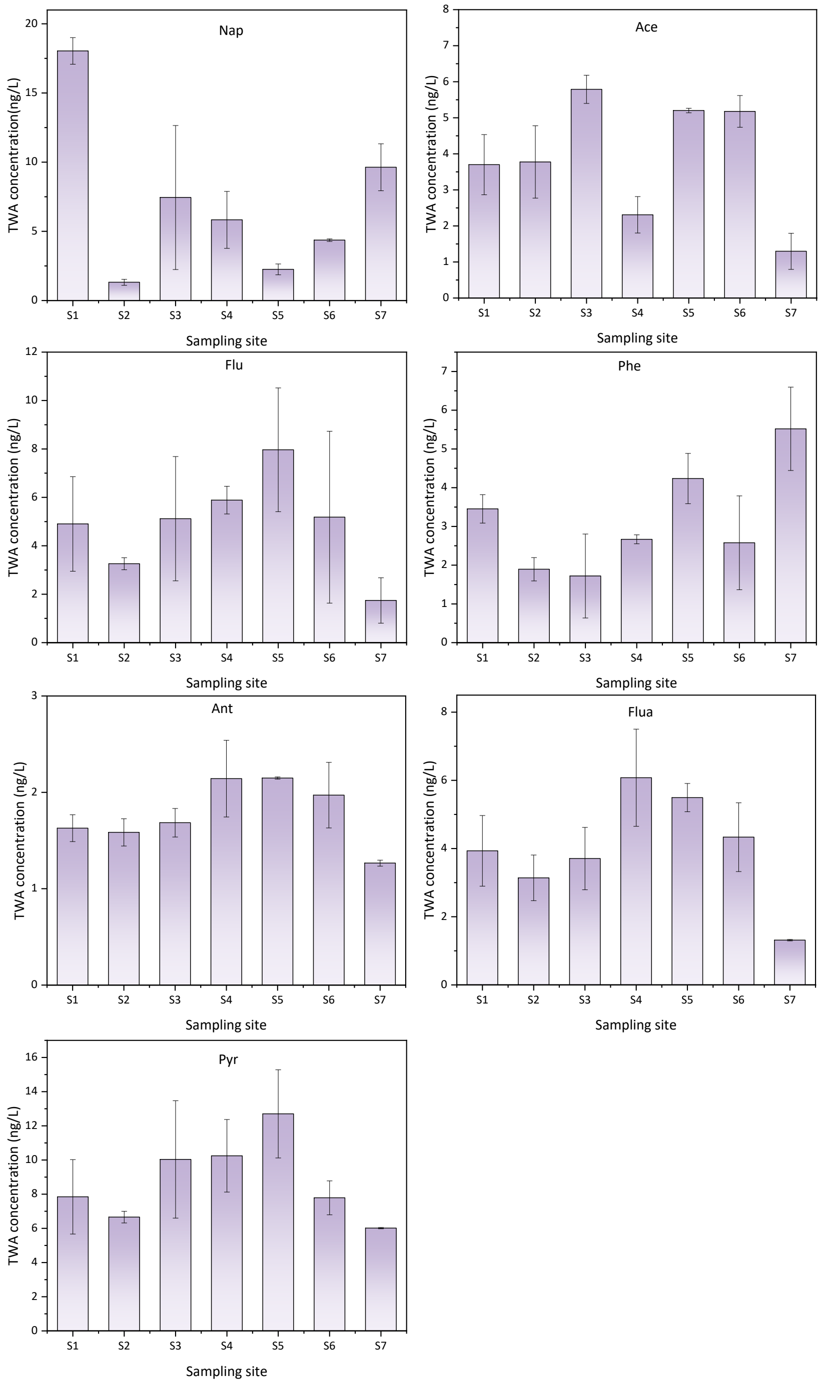


Fig. 4.5 Occurrence of PAHs in sampling sites in July (time weighted average DGT concentrations - ng L^{-1}). Error bars were calculated from the standard deviation (SD) for three replicates.

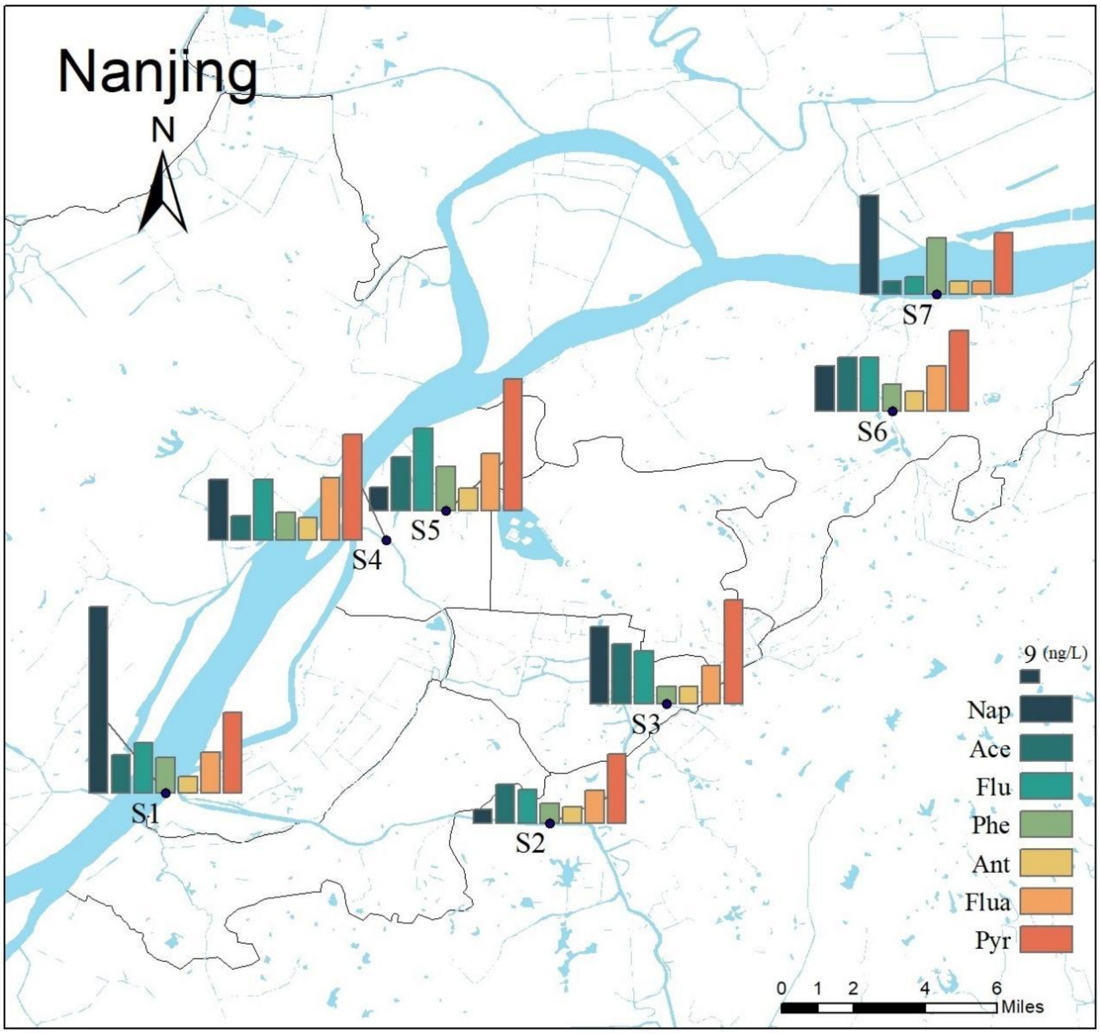


Fig. 4.6 DGT Measured *in-situ* concentrations (ng L^{-1}) of PAHs at the 7 sample sites in July 2021 in the Yangtze River and the Nanjing river system

4.3.5 Comparison with previous studies

The PAH data obtained in this study were compared with other studies, and the results presented in Table 4.6. There have been previous measurements made of PAHs in the Yangtze River and Nanjing rivers by other researchers. These have been reported for the years 2004-2005, 2015, 2018, 2019 and 2020 (He, Hu et al. 2011, Wang, Zhou et al. 2017, Jia, Guo et al. 2021, Zhao, Gong et al. 2021, Yang, Xu et al. 2022). As this study has shown, there are very big differences in PAH concentrations between the wet and dry seasons, so comparisons with other datasets need to take this into account. The concentrations in the Yangtze River and Qinhuai River in 2021 measured in this study were lower than reported in the same region in 2004-2005 and summer for 2015 (He, Hu et al. 2011, Wang, Zhou et al. 2017). The concentration in 2015 was significantly higher than other studies, shortly after pollution control measures were introduced. From 1995 to 2013, the discharge of industrial wastewater in Chinese cities sharply decreased, with some areas experiencing a decrease of >60%. The discharge of heavy metals in the middle and lower reaches of the Yangtze River also decreased. However, compared with the 2000s, the concentration of heavy metals in some parts of the Yangtze River still showed an upward trend in the 2010s, but the upward trend slowed down (Li, Tang et al. 2020). The summer concentrations measured in this study were lower than the concentrations in 2018 (Zhao, Gong et al. 2021). Summer concentrations measured here were comparable to the concentration in 2019, 2020 and the average concentration in the Yangtze River Delta region during the same period in 2019. The winter concentrations measured were higher than those reported for 2019.12 and 2020.10 (Jia, Guo et al. 2021, Yang, Xu et al. 2022). Taking account of the large effect of season, these comparisons indicate that PAHs have probably declined over the last few years; the strongest evidence for this is the comparison between this study and He and Wang’s study (He, Hu et al. 2011, Wang, Zhou et al. 2017).

The major rivers of China have generally improved in quality over the last 20 years, following major government and regional initiatives to reduce aquatic discharges from industry (Zhang, Zhang et al. 2019, Yu, Liu et al. 2021) and the installation of major waste water treatment facilities in all major cities and – step-by-step – rural areas (Wang, Wang et al. 2015). In recent years, Nanjing has cracked down on illegal discharges along the Yangtze River, optimized the layout of industrial zones, and dismantled older docks to reduce pollution to the Yangtze River. Greater pollution control management has also been introduced on ship transportation, and strengthened the construction of city water networks to control the water quality of tributaries entering the main river (Annual report on the ecological environment status of Nanjing and Jiangsu Province, Yangtze River Yearbook). It appears that with the promotion of "the Yangtze River Protection" in China, pollution control and ecological protection along the river have achieved significant results. The PAH concentrations in this Nanjing study are generally lower than in the other major rivers of China – the Yellow River and Haihe River (Sun, Wang et al. 2009, Liu, Zhang et al. 2014), equivalent to that in the upper reaches of the Huaihe River (Liu, Feng et al. 2016), but are higher than in the Pearl River (Li, Wang et al. 2022). Generally, the distribution of PAHs in China's major rivers shows higher levels in the north than the south. Generally northern China has higher PAH emissions from combustion sources and greater industrialization of river catchments than the south (Guo, Wu et al. 2012, Zhang, Zhang et al. 2019). The distribution of PAHs is mainly related to urban economic infrastructure, chemical industry configuration, and climate conditions. The northern region of China is a traditional heavy industrial area, where the combustion of fossil fuels such as coal are the main sources of PAHs (Sun, Pan et al. 2018, Yu, Liu et al. 2021). The demand for winter heating in the northern parts of China (generally north of the Yangzte), with the extensive combustion of coal and other biomass is a major source of PAHs in China (Zhang and Tao 2009). In contrast, southern China has higher temperatures, higher humidity, and stronger ultraviolet radiation, which can promote the photodegradation and microbial degradation of PAHs (Zhang and Chen 2017). These factors collectively lead to higher concentrations of PAHs in the air, waters and soils of north China compared to the south (Han, Liang et al. 2019, Zhang, Zhang et al. 2019).

Levels in this study are generally comparable to the River Nile (Haiba 2017), although the concentrations of 4-ring PAHs appear to be higher in the Nile than in this Nanjing/Yangzte study. Our study also gives levels comparable to those in the Mississippi River (Zhang, Zhang et al. 2007).

Table 4.6 PAHs concentrations in water of some rivers around world (ng L^{-1})

	Location	Year	Chemicals									References
			Nap	Acy	Ace	Flu	Phe	Ant	Flua	Pyr	16 PAHs	
1	Rivers in Nanjing	2021.7	7.0	-	3.9	4.9	3.2	1.8	4.0	8.8		This study
	Rivers in Nanjing	2021.1	91.5	83.3	60.1	15.0	47.5	5.9	20.1	18.0		
2	Yangtze River	2004-2005	6-89	<4	<4	<4-27	4-3345	4-21	3-27	<4-147	12-3576	(He, Hu et al. 2011)
3	Yangtze river	2015.7	5011	346	637	1345	3236	453	600	519		(Wang, Zhou et al. 2017)
	the Qinhuai River		9533	825	2480	3719	5260	409	293	222		
4	Yangtze river	2018.8									180-770	(Zhao, Gong et al. 2021)
5	The Yangtze River Delta region	2019.6	14.5	1.4	3.4	4.5	12.3	1.5	5.5	6.6		(Jia, Guo et al. 2021)
6	Yangtze River (average)	2019-2020	50.0	3.1	6.0	19.3	16.8	2.8	3.6	2.5		(Yang, Xu et al. 2022)
		2019.12									55.1	
	Nanjing section	2020.6									33.7	
		2020.10									94.6	
7	The Yellow River	2005-2006	436.5	6.9	6.8	23.2	104.5	16.5	21.1	11.4		(Sun, Wang et al. 2009)
8	the Pearl river	2020	1.1	0.5	0.3	0.8	8.0	0.8	1.2	1.3		(Li, Wang et al. 2022)
9	the upper stream of Huaihe River	2013-2014	10.4	88.2	-	17.1	13.5	0.9	4.3	3.3		(Liu, Feng et al. 2016)
10	Haihe river	2011	92.4	39.9	2.3	69.2	409.0	91.5	431.0	366.0		(Liu, Zhang et al. 2014)
11	Nile River	2016	7.4	1.9	7.4	9.8	16.6	11.3	193.7	237.0		(Haiba 2017)
12	Mississippi River	2004	1.5-2.5	0-4.1	1.4-18.1	1.3-3.8	7.1-38.6	8.5-23.2	6.9-22.8	5.7-50.2		(Zhang, Zhang et al. 2007)

4.3.6 Source analysis

Based on the earlier calculation of mass flows of PAHs in the Yangtze River upstream and downstream of the Nanjing conurbation, flows from the city itself via the Qinhuai and Jiuxiang Rivers make a minor contribution to the total load in the Yangtze (see Table 4.5). Some of the sources to the Yangtze upstream of Nanjing were briefly mentioned earlier, namely industrial and wastewater discharges upstream, diffusive inputs and runoff from the many large cities and conurbations further upstream, atmospheric deposition to the vast catchment of the Yangtze and its tributaries, soil erosion and sediment re-working.

A method that has been widely used in the literature to gain clues about the sources of PAHs in environmental samples is to consider compound isomer mixtures and ratios (Soclo 2000, Yunker 2002, Tobiszewski and Namiesnik 2012). Of course, compounds/isomer ratios will change over time, if compounds are selectively degraded. LMW PAHs are generally more unstable and degrade faster than heavier ones. This will undermine the use of ratios as source apportionment tools. As discussed earlier in the section on seasonality, there is evidence in this dataset that some of the DGT measured labile LMW compounds are prone to degradation/losses from the river surface waters. So, discussion and interpretation of isomer ratios needs to be done cautiously.

Figure 4.7 shows the ratios of Ant/Ant+Phe and Fla/Fla+Pyr used previously as a tool for identifying and assessing pollution emission sources (Tobiszewski and Namiesnik 2012). This highlights clear differences in the isomer ratios of the DGT samples taken in winter and summer. Overall, the ratios suggest that sources to the rivers in Nanjing in winter and summer are mixed, caused by petroleum and combustion. However, in winter, there is a significant increase in coal and biomass combustion sources. Different from northern China, Nanjing is not a mandatory centralized heating area in China and has less indoor heating demands of residents in winter. But some factory heating exists in winter and small-scale residential heating has been attempted since 2019. Research has found that there was a phenomenon in the suburbs where coal and biomass combustion emit a large amount of gaseous PAHs (Li, Wu et al. 2018). Unfavorable climate conditions for pollutant dispersion occur in winter, resulting in differences in the distribution of pollutants between winter and summer.

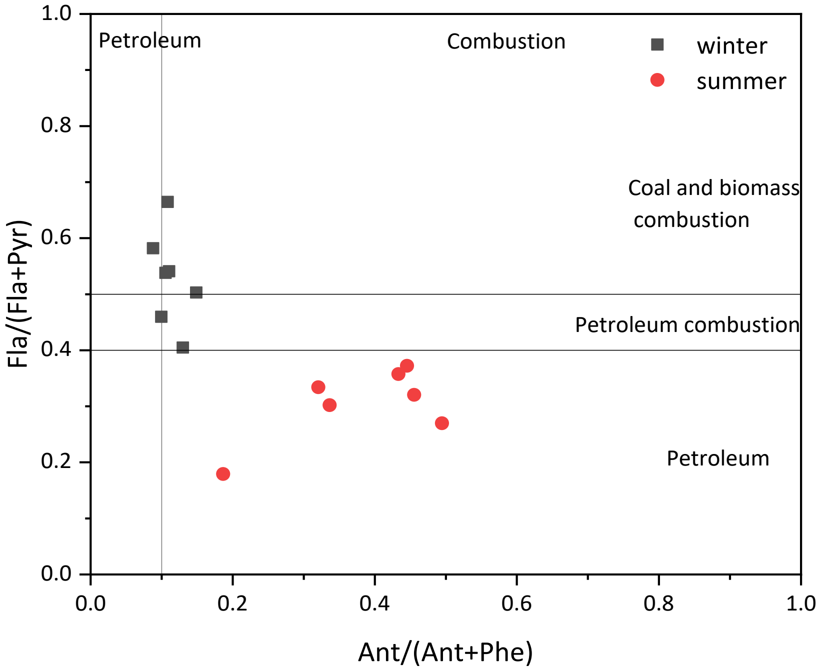


Fig. 4.7 Distributions of anthracene (Ant)/(phenanthrene (Phe) + anthracene (Ant)) ratios and fluoranthene (Fla)/(fluoranthene (Fla) + pyrene (Pyr)) ratios in winter and summer in rivers, Nanijng. Each dot represents a sample location in winter or summer. The lines delineate the ratio values which have been used as markers of coal and biomass combustion, petroleum combustion and petroleum emissions in previous studies (Tobiszewski and Namiesnik 2012). Of course, the ratios also change as compounds degrade/move through the environment.

4.3.7 Risk assessment

PAHs can pose ecological risks to aquatic organisms in rivers. In order to evaluate the potential ecological hazards of PAHs in the rivers of Nanjing, ecological risk assessments were conducted using the data for the different sampling points in winter and summer. As explained earlier, two different approaches were used to assess the ecological risks. The first is the Risk Quotient (RQ) method. With this approach, Table 4.7 indicates that the levels of individual PAHs in summer are low and insufficient to warrant concern. Phe and Nap have almost no ecological risk at all the sites. For the other PAHs, their levels are classified as ‘moderate’. However, with the winter levels, the ecological risk in this region significantly increased. Acy and Ace have ‘high risks’ at sites S1, S4, S5, and S6. These areas include ports, densely populated areas and chemical industries. The other PAHs may pose ‘moderate ecological risks’. This analysis, addressing possible ecological risks for individual PAHs, indicates that although the Yangtze River Protection scheme has effectively reduced the concentration of PAHs in the Nanjing area, further measures are still needed to reduce the ecological risks caused by these pollutants.

The second method to assess ecological risks used the Species Sensitivity Distribution approach. The SSD fitting results obtained through EEC-SSD software are shown in Table 4.8 and Figure 4.8. The smaller the HC_5 value, the greater the toxic effect of the compound. For all species, the order of toxicity effects of the 7 PAHs is Pyr>Ant>Flua>Phe>Flu>Ace>Nap. As the number of benzene rings increases, the toxic effect increases. The calculated risk quotient and the mixture risk of multiple pollutants based on the obtained PNEC values are shown in Table 4.9. As with the first method of risk assessment, the concentration of individual PAHs was generally at the ‘low risk’ level in summer. Nap and Flua were at ‘moderate risk’ in winter. Pyr was at ‘moderate risk’ in both winter and summer. For the assessment of PAH mixtures, the overall risk is ‘moderate’, for sites S4, S5, S6, and S7, although it was deemed as ‘high risk’ in winter.

The ecological risk of the Nanjing River was evaluated with both the risk entropy method and SSD method. Although the individual levels of PAH risk were slightly different, the results indicates that the overall ecological risk was higher in winter, and the risk in the downstream and the industry area of the river was significantly increased. These results indicate that although PAH concentrations seem to have generally declined in the rivers in the Nanjing area, further measures are still needed to reduce the ecological risks caused by PAHs.

Table 4.7 Risk Quotients (RQs) of individual PAHs in different sampling sites in winter and summer, Nanjing, (determined by RQ method)

	S1		S2		S3		S4		S5		S6		S7	
	RQ NCs	RQ MPCs	RQ NCs	RQ MPCs	RQ NCs	RQ MPCs	RQ NCs	RQ MPCs	RQ NCs	RQ MPCs	RQ NCs	RQ MPCs	RQ NCs	RQ MPCs
Summer														
Nap	1.5	0.02	0.1[a]	0.00	0.6[a]	0.01	0.5[a]	0.00	0.2[a]	0.00	0.4[a]	0.00	0.8[a]	0.01
Ace	5.3	0.05	5.4	0.05	8.3	0.08	3.3	0.03	7.4	0.07	7.4	0.07	1.9	0.02
Flu	7.0	0.07	4.7	0.05	7.3	0.07	8.4	0.08	11.4	0.1	7.4	0.07	2.5	0.02
Phe	1.2	0.01	0.6[a]	0.01	0.6[a]	0.01	0.9[a]	0.01	1.4	0.01	0.9[a]	0.01	1.8	0.02
Ant	2.3	0.02	2.3	0.02	2.4	0.02	3.1	0.03	3.1	0.03	2.8	0.03	1.8	0.02
Flua	1.3	0.01	1.1	0.01	1.2	0.01	2.0	0.02	1.8	0.02	1.4	0.01	0.4	0.00
Pyr	11.2	0.1	9.5	0.1	14.3	0.1	14.6	0.2	18.1	0.2	11.1	0.1	8.6	0.09
Winter														
Nap	4.4	0.04	9.5	0.1	4.3	0.04	6.4	0.06	6.9	0.07	8.4	0.08	13.4	0.1
Acy	104.6	1.1[b]	92.5	0.9	85.2	0.9	101.8	1.0[b]	112.5	1.1[b]	208.5	2.1[b]	62.9	0.6
Ace	100.4	1.0[b]	29.2	0.3	85.8	0.9	114.7	1.2[b]	126.8	1.3[b]	98.7	1.0[b]	45.2	0.5
Flu	20.8	0.2	21.4	0.2	14.1	0.1	28.9	0.3	15.5	0.2	24.7	0.3	24.2	0.2
Phe	10.5	0.1	14.7	0.2	14.0	0.1	23.6	0.2	12.6	0.1	16.3	0.2	19.1	0.2
Ant	7.9	0.08	6.1	0.06	7.1	0.07	12.3	0.1	8.1	0.08	8.7	0.09	9.0	0.09
Flua	4.6	0.05	6.0	0.06	6.7	0.07	9.8	0.10	5.6	0.06	7.6	0.08	6.6	0.07
Pyr	19.5	0.2	18.3	0.2	24.7	0.3	21.3	0.2	35.2	0.4	27.5	0.3	33.4	0.3

a (in green)-Negligible environmental risks; b (in red)-High environmental risks; Black color-Moderate environmental risks

S1-S7 related to 7 sampling sites

Note: the calculation of RQ(NCs) and RQ(MPCs) was described in section 2.7; RQs (NCs) <1.0- negligible risk, RQ (MPCs) >1.0- serious risk, RQs (NCs) >1.0 and RQs (MPCs) <1.0- moderate risk

Table 4.8 HC_5 and PNEC of 7 PAHs calculated from SSD curve (ug L^{-1})

Compounds	$HC_{5\ Acu}$	$HC_{5\ Chr}$	PNEC
Nap	690	69	14
Ace	215	21	4.3
Flu	210	21	4.2
Phe	50.5	5.0	1.0
Ant	4.1	0.4	0.1
Flua	5.6	0.6	0.1
Pyr	1.3	0.1	0.0

Table 4.9 Individual and mixture RQs of 7 PAHs calculated from PNECs in different sampling sites in winter and summer, Nanjing, (determined by SSD method)

	S1	S2	S3	S4	S5	S6	S7
summer							
Nap	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ace	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Flu	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Phe	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ant	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Flua	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Pyr	0.3	0.3	0.4	0.4	0.5	0.3	0.2
∑RQ	0.4	0.3	0.4	0.5	0.6	0.4	0.3
winter							
Nap	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ace	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Flu	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Phe	0.0	0.0	0.0	0.1	0.0	0.0	0.1
Ant	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Flua	0.1	0.2	0.2	0.3	0.1	0.2	0.2
Pyr	0.5	0.5	0.7	0.6	0.9	0.7	0.9
∑RQ	0.8	0.8	1.0	1.0	1.2	1.1	1.2

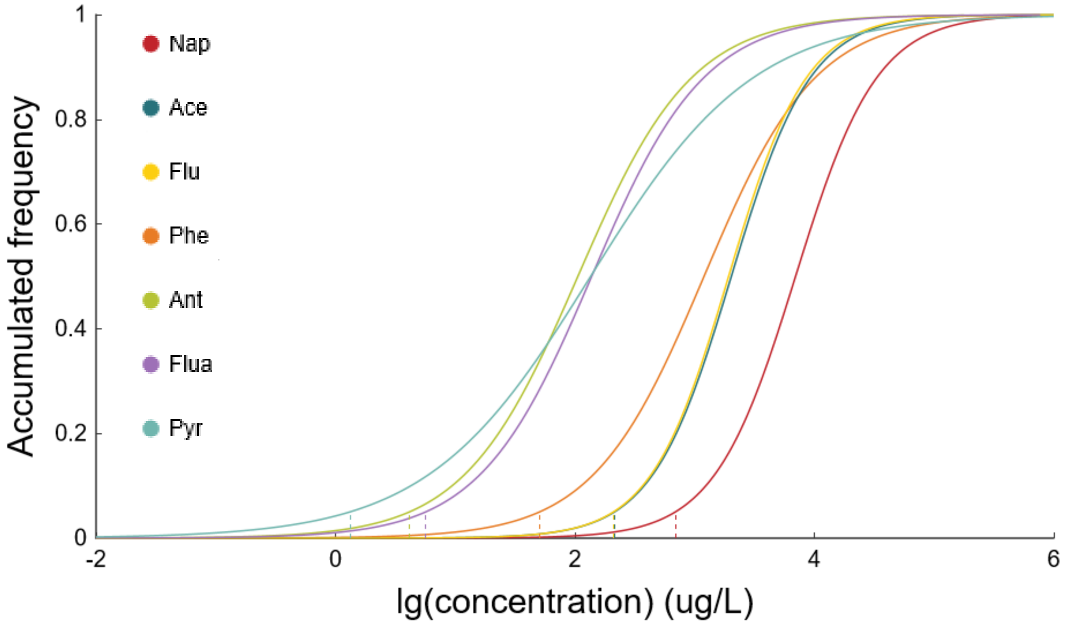


Fig 4.8 SSD fitted curves for all the species for the 7 PAHs. Aquatic biota species included algae, amphibians, crustaceans, fish, insect, invertebrate, mollusca and worms.

4.4 Conclusion

A novel DGT sampler has been successfully used *in situ* for the measurement of hydrophobic compounds PAHs in rivers in Nanjing. The measured labile concentration of PAHs in the Yangtze River and urban rivers had a marked seasonal difference. Compared with previous studies, the concentrations of PAHs in the Yangtze River Nanjing section and other Nanjing rivers have decreased in recent years. Compared with other regions, the concentrations are generally lower than that in major rivers in northern China, and slightly higher than that in southern rivers. This study provides a new approach for effective in-situ monitoring of PAHs in aquatic environments, expanding the application of DGT technique in measuring hydrophobic organic pollutants in aquatic ecosystems.

Analysis of the sources of PAH pollution in the Nanjing region showed that PAHs in the Yangtze River mainly come from upstream accumulated loads, petrochemical enterprises along the Yangtze River, and ship transportation. The input of urban tributaries in Nanjing was small relative to the load in the main Yangtze. The risk assessment of both risk quotient and species sensitivity distribution methods showed that although PAH pollution in the Nanjing area has reduced in recent years, there are still risks in winter and in industrial areas. The government should continue to pay attention to the situation of PAH pollution in the area and maintain continuous monitoring, as well as focus on catchment governance and management.

Supporting information

The supplementary detailed information, tables and figures are listed in Supporting Information.

Supporting information for:

Occurrence and distribution of PAHs in the Yangtze River and urban river waters of Nanjing, China: insights from *in situ* DGT measurements

Qiuyu Rong[1], Hao Zhang[1], Yanying Li[2], Liying Yan[3], Jun Luo[3*] and Kevin C. Jones[1*]

[1]Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom

[2]College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning 116023, P. R. China

[3]State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023 P. R. China

*Corresponding authors

Email: k.c.jones@lancaster.ac.uk and esluojun@nju.edu.cn

Contents of Supporting Information

4.1 Material and methods

4.1 Material and methods

4.1.1 DGT preparation

DGT samplers were assembled in the sequence: polycarbonate (PC) membrane filter (in contact with the water), an agarose diffusive gel and a MIP binding gel in a metal casing before deployment. The new DGT casings designed and tested for PAHs (Rong, Li et al. 2024) were obtained from DGT Research Ltd (Lancaster, UK); PC membrane filters were purchased from

Whatman (UK), agarose diffusive gel (0.8 mm thickness) was supplied from Vision Environ. Tech. Co. Ltd. (Nanjing, China) and MIP binding gel (0.5 mm) was prepared in the laboratory.

4.1.2 Study area

Seven locations in the river system were selected as sampling sites. Two sampling sites were located in the Yangtze River (upstream and downstream of the main Nanjing conurbation) and 5 sites were located in parts of urban rivers in the city of Nanjing. Sample sites S1 and S7 were located in the upper and lower reaches of the Nanjing section of the Yangtze River, S2 was located in the New Qinhuai River, S3-S5 were located in the Qinhuai River, and S6 was located in the Jiuxiang River. Locations A B and C were at the New Qinhuai River Sluice, Wudingmen Sluice, and Sancha River Education Sluice, respectively. Water transfer and control can be carried out by the sluices, according to the needs of flood prevention, river water quantity and quality. The average rainfall in summer (July) in Nanjing is about 6 times that of winter (January), and the river flow in summer is 3 times that of winter. The flow of the main stream of the Yangtze River is more than 200 times higher than that of urban rivers in Nanjing.

4.1.3 Sample treatment

For DGT samples, each binding gel was placed in an amber vial with 200 ng decafluorobiphenyl, then ultrasonically extracted for 30 minutes with 5 mL acetonitrile. The elution solution was then evaporated to near dryness under a gentle stream of nitrogen and made up with 0.2 mL of acetonitrile/MQ water solution (1:1, v: v), then filtered through a 0.22 μm PTFE filter membrane, ready for analysis by HPLC.

For the water samples, 1 L was filtered through Whatman GF/F filter (0.7 μm) and spiked with 200 ng decafluorobiphenyl. HLB (60 mg/3 mL, Waters, UK) SPE columns were used to concentrate the water samples. After solid phase extraction, PAHs were eluted twice with 10 mL dichloromethane and then evaporated to near dryness under a gentle stream of nitrogen and 3 mL of acetonitrile was added. This solution was concentrated again and accurately volumed to 0.2 mL acetonitrile/MQ water solution (1:1, v: v). This was finally filtered through a 0.22 μm PTFE filter membrane before analysis.

4.1.4 Instrumental analysis

A high performance liquid chromatography combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) was used for samples. The mobile phase consists of acetonitrile (solvent A) and MQ water (solvent B). The elution gradient began with 50% A and 50% B from 0 min, kept for 5 min, then started to increase, increased to 100% A at 20 min and maintained for 4 minutes. Finally, it returned to the initial conditions within 4 min and kept the column rebalancing. The flow rate was 1.5 mL min^{-1}, and the temperature for column was set to 30 °C. The injection volume was 20 µL per sample. The samples were analyzed by ultraviolet detector and fluorescence detector.

4.1.5 Risk assessment

According to technical guidance from the European Union (EU), ecological risk can be assessed using the Risk Quotient (RQ) method. RQ is the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC).

$$RQ = \frac{MEC}{PNEC} \qquad \text{(Eq. S4.1)}$$

The PNEC values of Nap, Phe, Ant, and Flua were reported by Kalf (Kalf, Trudie Crommentuijn et al. 1997); Acy, Ace, Flu, and Pyr were calculated from the toxicity equivalent factors (TEFs) for individual PAHs (Cao, Liu et al. 2010). Maximum permissible concentrations (MPCs) are concentrations above which the risk of adverse effects is considered unacceptable. Negligible concentrations (NCs) are defined as the MPC/100 and takes possible effects of combination toxicity due to the presence of other substances into account (Kalf, Trudie Crommentuijn et al. 1997). Considering both the ecosystem risk of ∑PAHs with the individual PAHs, RQs (NCs) <1.0 indicates that the ecological risk of an individual PAH may be negligible, while RQ (MPCs) >1.0 indicates that the pollution of a single PAH is deemed ‘serious’ and could have an effect. When RQs (NCs) >1.0 and RQs (MPCs) <1.0, it indicates that the ecological risk of an individual PAH may be classified as moderate.

Species Sensitivity Distribution (SSD) is also a commonly used method for assessing ecological risks at the system level. It fits the toxicity data of different species to specific chemicals, constructs SSD curves and extrapolates a safe concentration that could protect most organisms in the ecosystem. Here acute toxicity data were used to construct SSD curves. The US Environmental Protection Agency ECOTOX database (http://www.epa.gov/ecotox/) was used to obtain acute effects data for seven PAHs on aquatic organisms. The species categories include algae, amphibians, fish, crustaceans, insects and spiders, molluscs and worms (as shown in Table S4.3). The toxicity data was screened for all organisms in freshwater, with an exposure endpoint of LC_{50}/EC_{50} and an exposure time of ≤10 days. When the same species had multiple toxicological data, the mean of the selected concentration was used (Hose and Van den Brink 2004). After obtaining and sorting data, the Chinese national ecological environment benchmark calculation software EEC-SSD (https://www.mee.gov.cn/ywgz/fgbz/hjjzgl/mxrj/202203/t20220304_970658.shtml) was used to fit the SSD curve and obtain the $HC_{5\,Acu}$ value. In previous studies, acute data was easier to obtain than chronic data, but it significantly underestimated the potential risk of pollutants, and they could be converted through acute:chronic ratio (ACR) (Xu, Li et al. 2015, Del Signore, Hendriks et al. 2016).

$$HC_{5\,Chr} = \frac{HC_{5\,Acu}}{ACR} \qquad (Eq.\ S4.2)$$

$HC_{5\,Acu}$ is defined as a hazardous concentration for 5% of species based on acute toxic data and $HC_{5\,Chr}$ is that based on chronic toxic data. For ease of calculation, a recommended value of 10 was chosen to extrapolate chronic toxicity data (Stephan, Mount et al. 1985, Wang, Scott et al. 2018, Li, Mu et al. 2023). The predicted no-effect concentration (PNEC) was calculated using HC5, which indicates that below this concentration, >95% of organisms can be protected from the adverse effects of pollutants.

$$PNEC = \frac{HC_5}{AF} \qquad (Eq.\ S4.3)$$

AFs depend on the number and quality of available toxicity data: 5 was applied based on the EU risk assessment technical guidance (Commission 2003). The concentration addition model was used to calculate the combining ecological risks of multiple pollutants and characterize their risk using the hazard index (HI), defined as:

$$HI = \sum_{i=1}^{n} \frac{El_i}{Al_i} \qquad (Eq.\ S4.4)$$

The exposure level is represented by the measured environmental concentration (MEC), the acceptable level in the environment is characterized by PNEC, El_i/Al_i is the risk quotient (RQ) of a single component i, and the mixture risk quotient is the sum of the RQ of each component. RQ <0.1 indicates a low risk level, 0.1 ≤ RQ <1.0 represents a moderate level of risk, while RQ ≥ 1 represents a high level of risk.

Species Sensitivity Distribution (SSD) method fits the toxicity data of different species to specific chemicals, constructs SSD curves and extrapolates a safe concentration that could protect most organisms in the ecosystem. Here acute toxicity data were used to construct SSD curves. The US Environmental Protection Agency ECOTOX database (http://www.epa.gov/ecotox/) was used to obtain acute effects data for seven PAHs on aquatic organisms. The species categories include algae, amphibians, fish, crustaceans, insects and spiders, molluscs and worms.

4.1.6 Quality assurance/Quality control

Three parallel DGT samples were deployed at each sampling point. Three DGT samplers were set up as on-site blanks. Milli-Q water was used as the procedural blank sample. DGT on-site blanks and procedure blanks were used to check for possible contamination. The target compounds were not found at detectable levels in the blank samples.

Chapter 5 Assessment of aging effects and kinetic resupply of PAHs in different types of soils

Abstract

The newly developed diffusive gradients in thin films (DGT) technology for detecting polycyclic aromatic hydrocarbons (PAHs) has been successfully used in aquatic environments. This study applied DGT in soils with different properties and combined with the DGT-induced fluxes in soils (DIFS) model to explore the effects of different factors on the resupply of PAHs in soil and to understand the kinetic processes of PAHs in soil. PAHs in soil enter a relatively stable stage after three weeks of aging. The resupply ability of most soils from soil solid to liquid phases decreased with increased aging time. The DGT induced soil flux (DIFS) model results indicated that the size of the labile pool was influenced by both pH and TOC. During soil aging, the resupply of PAHs by soil was more susceptible to the influence of soil pH in the rapidly aging stage, while the desorption of PAHs was more affected by organic matter in the relatively stable stage.

Key words: DGT, PAHs, DIFS, labile pool size, soil kinetic process

5.1 Introduction

Polycyclic aromatic hydrocarbons (PAHs) are common organic pollutants in the environment, which have received attention and attracted research due to their persistence, carcinogenicity, teratogenicity, and mutagenicity (Tarigholizadeh, Sushkova et al. 2024, Wang, Liu et al. 2024). PAHs can be transported and transformed between environmental media such as atmosphere, water, and soil. The soil is a key medium for PAH storage, supply to other compartments and degradation (Wild and Jones 1995, Sweetman, Valle et al. 2005, Aichner, Bussian et al. 2015).

The behaviors and fates of PAHs in the soil environment mainly include adsorption/desorption, volatilization, precipitation-dissolution, redox, complexation, bioaccumulation, transformation/ degradation. Among them, adsorption/desorption plays an important role in the retention, migration and transformation of organic pollutants in soil and their bioavailability (Reid, Jones et al. 2000, Ni, Luo et al. 2008). After PAHs enter soils, a series of adsorption and desorption processes can occur which could cause them to form different speciation and then affect their availability to plants and microorganisms. The bioavailability of organic pollutants is closely related to their environmental risks and soil remediation, so it is particularly important to understand the adsorption and desorption behaviors of organic compounds.

The adsorption of organic pollutants in soil mainly involves surface adsorption theory and distribution theory (Chiou, Peters et al. 1979, Müller, Totsche et al. 2007, Tang, Gudda et al. 2022). Based on the theory, linear, Freundlich and Langmuir isotherms models (Kang and Xing 2005, Yang, Jin et al. 2013, Almouallem, Michel et al. 2023), the multivariate reaction model (Weber Jr, McGinley et al. 1992), and the dual-mode model (Xing and Pignatello 1997) were proposed to explain adsorption mechanisms. Research has shown that soil organic matter is the main adsorption medium for PAHs, but there is no consensus on the correlation between TOC and PAH content in soil. Most studies have indicated a positive correlation between soil PAHs content and black carbon content (Wild and Jones 1995, Yang, Tao et al. 2010, Gao, Li et al. 2023). The organic matter composition also affects the adsorption of PAHs. Xing et al. found that humin has a higher adsorption capacity for hydrophobic organic pollutants (Wang and Xing 2005). Changes in soil pH can affect the structure of soil humus, thereby affecting its adsorption performance (De Paolis and Kukkonen 1997, Chianese, Fenti et al. 2020). The properties of compounds themselves also affect their adsorption behavior in soil. It is generally believed that the stronger the hydrophobicity of compounds, the greater the K_{ow} and K_{oc}, and the stronger their adsorption in soil, making desorption more difficult. The desorption process is not a simple reverse process of adsorption; often only a portion of the adsorbed pollutants can be desorbed, and the remaining portion may not be available for desorption. The term ‘aging’ is used to describe the increased contact time between the compound and the soil. Northcott et al. found that as the degree of aging increases, there is a reduction in the amount of PAH available for extraction and the amount of non-extractable residue increase. These changes were positively correlated with the molecular weight, Kow, and Koc values of the compound (Northcott and Jones 2001). Humic acid and fulvic acid can enhance the water solubility of PAHs, promote their desorption, and the effect of humic acid was more significant (Johnson and Amy 1995).

The adsorption/desorption process of organic pollutants was often studied by batch adsorption and desorption experiments (Fu, Kan et al. 1994, Zhang, Lu et al. 2019). However, batch experiments are often time consuming and the results may lack precision and accuracy due to soil heterogeneity. Although batch experiments can provide information on the adsorption/desorption characteristics of organic pollutants, they often do not address kinetic processes, which are very important in the soil. Therefore, methods are needed to explore the kinetic processes of organic pollutants in soil. Diffusive gradients in thin films (DGT) is a dynamic technique that can measure the labile concentration and flux of pollutants. Compared with traditional chemical extraction methods and soil solution extraction methods, DGT not only measures the labile concentration of metals in soil, but also provides information on kinetic parameters and the kinetic resupply of metals from the soil solid phase to the soil solution (Ernstberger, Davison et al. 2002). Combined with the DGT-induced fluxes in soils (DIFS) model, DGT technology was used to explore the adsorption/desorption process of heavy metals and nutrients, proving that it can probe the kinetic processes occurring in the solid phase-solution phase-DGT system (Ernstberger, Zhang et al. 2005, Luo, Yin et al. 2018, Gao, Gao et al. 2022). More recently, DGT has also been used to evaluate the fluxes and adsorption/desorption of selected organic pollutants. The exchange kinetics of organic pollutants in soil are investigated by obtaining parameters such as labile pool size (K_{dl}), response time (Tc), and adsorption/desorption rate (k_1 and k_{-1}). Ren et al. used DGT to explore the desorption kinetics of tetracycline in soil and found that soil texture had the most significant effect on its desorption (Ren, Wang et al. 2020). Li et al. used the DIFS model to obtain kinetic parameters for further understanding the effects of organic matter, pH and other properties on the availability of atrazine in soil (Li, Han et al. 2021). Huang et al. used DGT to understand the distribution and exchange kinetics of typical perfluoroalkyl sulfonates (PFAS) in soil (Huang, Liu et al. 2023). These studies laid the foundation for the use of DGT and DIFS in this study to evaluate the exchange kinetics and labile pool size of PAHs in soil.

The overall aim of this study is to investigate the changes in PAHs during the aging process and explore the effects of soil pH, TOC and other possible factors on the resupply of PAHs in soil. The DIFS model was used to evaluate response times, desorption rate constants and the labile pool size of PAHs, to quantify and understand the kinetic processes of PAHs in soil.

5.2 Methods and materials

5.2.1 Chemicals and reagents

Four PAHs were selected for this study, and their detailed information is listed in Table 5.1. Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua) and Pyrene (Pyr) were purchased from Aladdin (China). Stock solutions were prepared at 1000 mg L^{-1} in acetonitrile and stored at -20 °C in the amber glass bottles.

Reagents are at least analytical reagents and with high purity, organic solvents are HPLC grade. Acetonitrile (ACN) were obtained from Merck (Germany). Acetone, dichloromethane, n-hexane were purchased from Nanjing reagent (China). Water used in the experiments was supplied from a Milli-Q water (MQ water) purification system (>18.2 MΩ/cm, Millipore). Agarose was obtained from Bio-Rad Laboratories (UK).

Molecularly imprinted polymer (MIP) was extracted from MIP-PAH SPE tubes purchased from CNW (Germany) as resins for binding gel. Flory silica cartridges were purchased for Nanjing Ronghua (China).

Table 5.1 Physicochemical properties of selected PAHs

Compounds	Abbreviation	MW (Da)	Formula	Log K_{ow}	S_w25°C (mg L^{-1})	benzene rings
Phenanthrene	Phe	178.23	$C_{14}H_{10}$	4.46	1.18	3
Anthracene	Ant	178.23	$C_{14}H_{10}$	4.54	0.086	3
Fluoranthene	Flua	202.26	$C_{16}H_{10}$	5.20	0.260	4
Pyrene	Pyr	202.26	$C_{16}H_{10}$	5.30	0.135	4

Sw25°C – the solubility of chemicals in water at 25℃.

5.2.2 Soil samples collection and treatments

5.2.2.1. Soil collection and the determination of soil properties

Six soils of different properties were collected from four cities in China and used for the experiments. Soils were collected with a surface depth of 10-20 cm, then air-dried and passed through a 2 mm sieve to remove roots, stones and other large particles.

The determination of soil properties

pH: A certain volume of soil was taken, 0.01 M CaCl2 solution according to soil: solution (V: V, 1:5) was added. Soil samples were shaken for 1 h and pH measured by pH meter (ORION STAR A214, Thermo Fisher) after standing for 2 h.

Total organic carbon (TOC): A certain amount of soil was weighed, and 1 M HCl was added until no bubbles were generated. Soil samples were placed in an oven for low temperature drying. After drying, TOC was measured by TOC analyzer (Vario TOC, Elementar).

Maximum water holding capacity (MWHC): A certain amount of dry soil ($W1$) was weighed and placed into a funnel filled with soaked filter paper (not exceeding the highest point of the filter paper). The total mass of the filter paper, funnel and soil was measured ($W2$). The funnel filled with soil was fixed into a beaker filled with water (soil and water were on the same plane). After leaving for 4 hours, the funnel was placed in a beaker without water for 2 hours and weighed ($W3$). The maximum water holding capacity of the soil is calculated as:

$$MWHC = (W_3 - W_2)/W_1 \quad (Eq.\ 5.1)$$

Soil texture: A soil sample (0.2 g) was weighed into a 50 mL centrifuge tube, 20 mL of 30% H_2O_2 was added. Samples were kept at room temperature for 3 days and stirred multiple times during the process, then centrifuged at 4000rpm for 10 minutes to remove H_2O_2 solution, washed three times with MQ water, and finally retained 10 mL of suspension. 10 mL of 10% (mass ratio) sodium hexametaphosphate was added into suspension and samples were tested by a laser particle size analyzer to determine the content (%) of components with particle size < 2 µm. Soil texture was classified according to the percentage of sand (2-0.05 mm), silt (0.05-0.002 mm), and clay (<0.002 mm) content using the United States Texture Classification System (USDA) standard.

The six soils were selected to present a range of agricultural and urban greening soils, with different pH (5.3-9.3) and organic matter content (0.45-5.08%). Detailed information on sites and their properties are given in Table 5.2.

Table 5.2 Physicochemical properties of 6 soils in China

Soils	City name	Soil type	pH (H_2O)	TOC (%)	MWHC (%)	Clay (%)	Silt (%)	Sand (%)
CQF	Chongqing	Loam	5.4	1.38	47.7	13.1	73.6	13.3
CQP	Chongqing	Loam (Paddy soil)	5.3	1.34	40.0	12.1	72.0	15.9
DL	Dalian	Loamy sand	9.3	5.08	27.0	4.9	47.6	47.5
GD	Guangdong	Silty clay loam	8.8	1.25	36.3	9.4	65.4	25.2
NJJ	Nanjing	Silty loam	7.5	0.45	52.0	10.3	85.1	4.5
NJQ	Nanjing	Silty loam	7.0	2.35	61.7	11.0	81.8	7.2

TOC-total organic carbon, MWHC- maximum water holding capacity

5.2.2.2 Soil spiking with chemicals

Soils (500 g) were then spiked with PAHs containing a mixture of 50 mg phenanthrene (Phe), 50 mg anthracene (Ant), 50 mg fluoranthene (Flua), and 50 mg pyrene (Pyr) dissolved in acetone through drop-wise addition to the soils and thorough shaking for even distribution. An additional 4500 g of clean soils was added and mixed in each soil to obtain a 10 mg kg^{-1} concentration. An appropriate amount of MQ water was added and mixed well to ensure PAHs was distributed homogenously. The soils were then wetted to 30% MWHC (maximum water holding capacity). These soils were stored in the stainless-steel box with partly opened tin foil sealing and kept in the dark at room temperature and aged for 45 days.

5.2.3 Extraction of polycyclic aromatic hydrocarbons in soils

1 g (0.01g) of soil was weighed into a 35ml glass centrifuge tube with 1.0 g anhydrous sodium sulfate and 0.50 g Cu, and ground into quicksand. After ultrasonic extraction and purification with flory silica cartridges (200 mg/3 mL), the samples were eluted with 10 mL of acetonitrile solvent. The elution was concentrated with nitrogen to near dryness, then samples were diluted to 1 ml and filtered through a 0.2 μm PTFE filter before analysis.

5.2.4 DGT deployment and soil solution sampling

The metal disc DGT devices consisting of PC filter membrane, 0.8 mm agarose diffusive gel, and 0.5 mm MIP agarose binding gel were used. DGT experiments were performed on soil aged for 1, 4, 7, 10, 14, 21, 28, and 45 days after spiking with PAHs. At each time interval about 50 g soil was taken into a culture dish (diameter 90 mm), wetted to 50% MWHC first and left for 24 hours, then water was added to about 100% MWHC and left for another 24 hours before deploying DGT devices. Before placing the DGT device, a layer of soil was smeared evenly on the filter surface of the sampling window to ensure full contact between the DGT and the soil, and then the device was gently pressed onto the soil and kept at room temperature for 24 hours. DGT devices were placed into the 6 soils at each aging time interval, according to the above method, and all experiments were made in triplicate.

After 24 hours deployment, the DGT device was removed from the soil and the surface of the device was rinsed thoroughly with MQ water to remove all the soil particles. The binding MIP gel was removed from the DGT device and placed into a 10 mL amber glass vial. It was eluted in 5 mL acetonitrile ultrasonically for 30 minutes. The eluent was filtered through a 0.22 μm PTFE filter before analysis.

After removing the DGT device, the soil was transferred from the culture dish into a 50 mL centrifuge tube and centrifuged at 3000 rpm for 30 minutes. The soil solution was obtained and filtered with a 0.22 μm PTFE filter into a 2ml injection vial for further analysis.

Then solvent extraction of PAHs in soil was carried out by the method described in section 5.3.2. 1g of centrifuged soil was taken and extracted with acetonitrile by ultrasonic method.

5.2.5 Chemical analysis

A high-performance liquid chromatography combined with an ultraviolet detector (UVD) was used for all samples. The mobile phase consists of acetonitrile (solvent A) and MQ water (solvent B). The elution gradient began with 50% A and 50% B from 0 min, kept for 5 min, then started to increase, increased to 100% A at 20 min and maintained for 4 minutes. Finally, it returned to the initial conditions within 4 min and kept the column rebalancing. The flow rate was 1.5 mL min^{-1}, and the temperature for column was set to 30 °C. The injection volume was 20 μL per sample. The samples were analyzed by ultraviolet detection, and the parameters are shown in Table 5.3.

Table 5.3 UV detector parameters for PAHs detection

Time (min)	Event	Parameter (nm)
0	wavelength	254
6	wavelength	220
7.8	wavelength	225
10.3	wavelength	210
11	wavelength	254
14	wavelength	235
16	wavelength	254

5.2.5 DGT in soils and DIFS model

After DGT is placed in the soil, the PAHs in the soil will pass through the diffusion layer and be quickly taken up by the binding gel in the device. As the deployment time increases and the DGT device continues to adsorb, the concentration of PAHs in the soil solution at the interface of the DGT device may continuously decrease. At this point, due to the concentration difference, the DGT device could induce the re-supply of PAHs from the soil solid phase to the soil solution phase, which could be available to plants. Uptake is related to the concentration of pollutants in the soil solution and solid phase, the diffusion of pollutants in the soil, and the adsorption/desorption kinetics of pollutants in the soil solution and solid phase system (Chen, Jones et al. 2014). Figure 5.1 shows the schematic representation of DGT device, soil solution and solid phase system and relevant processes. After DGT deployment in soil, the soil solution concentration, C_{ss}, will be gradually depleted, inducing desorption (rate constant k_{-1}) from the soil solid phase (C_{se}, concentration of labile analyte on the solid phase). The time averaged concentration at the DGT/soil interface can be calculated using the formula mentioned earlier in Chapter 2,

$$C_{DGT} = \frac{M \triangle g}{DAt} \qquad \textit{(Eq. 5.2)}$$

The ratio of the obtained C_{DGT} to initial soil solution concentration (or bulk soil solution concentration) C_{ss} is calculated as R, which reflects the depletion of soil solution concentration at the interface between DGT and soil. The value of R is affected by the soil solution concentration, labile solid phase pool size of the analyte and the response time of the process (Tc) (Harper, Davison et al. 1998). By comparing the values of R, we can classify the ability to re-supply target chemicals into three types. They are the 'fully sustained case', 'partially sustained case', and 'diffusion only case' (Zhang and Davison 1995) (Figure 5.2).

Fully sustained case. When DGT adsorbs labile chemicals in the soil solution, soil solid phase can quickly re-supply the adsorbed chemicals to the soil solution, and the re-supply rate is fast enough without depletion. In this case, C_{DGT} is close to the initial concentration of the soil solution, that is, the R >0.95.

Diffusion only case. In this case, the soil cannot re-supply the adsorbed chemicals to the soil solution. When DGT adsorbs the targeted chemicals in the soil solution, there is no resupply from the solid phase to the soil solution. The only supply is from the diffusion process in soil. In this case, the concentration at the DGT/soil interface continuously decrease till its minimum. R <0.1.

Partially sustained case. Soil solid phase can re-supply the targeted chemicals to DGT uptake partially, but this re-supply cannot maintain the DGT concentration close to the initial concentration of the soil solution. Due to the continuous uptake of DGT, the concentration at the DGT/soil interface will gradually decrease. The R value can reflect the re-supply ability of soil from soil solid phase into the soil solution. The larger the R value, the stronger its ability to re-supply. In this partially sustained case, $0.1 < R < 0.95$.

A dynamic numerical model of DGT-induced fluxes in soils (DIFS) was developed by Harper et al. to describe the diffusion transport and dynamic exchange of solutes between DGT, soil solution and soil solid phase when the soil is disturbed by DGT uptake (Harper, Davison et al. 1998, Ernstberger, Davison et al. 2002). This model can be used to obtain soil dynamic parameters and labile pool size parameters from DGT measurements (Ernstberger, Davison et al. 2002, Chen, Jones et al. 2014). The model uses K_{dl} (Eq.5.2) and the Tc (Eq. 5.3) to describe the labile pool size and the kinetics of adsorption (rate constant k_1) and desorption (rate constant k_{-1}).

$$K_{dl} = \frac{C_{se}}{C_{ss}} = \frac{k_1}{P_c k_{-1}} \qquad \textit{(Eq. 5.3)}$$

$$T_c = \frac{1}{k_1 + k_{-1}} = \frac{1}{k_{-1}(1 + k_{dl}P_c)} \qquad (Eq.5.4)$$

Cse is the labile concentration of pollutants in the soil solids; Css is the dissolved concentration of pollutants in soil solution. Pc is the particle concentration of the tested soil. Here, K_{dl} is the labile distribution coefficient based on the solid phase components of the labile PAHs that can be resupplied to the soil solution and DGT device due to depletion by DGT deployment. K_d is the conventional distribution coefficient based on extractable concentration of PAHs from the solid phase. Compared with organic reagents such as acetone and dichloromethane which could fully extract PAHs from soil, acetonitrile produces weaker extractions. Therefore, the extractable PAHs concentration measured by acetonitrile was used to represent labile concentration of PAHs as Cse in this study. So, the value of K_{dl} was represented with K_d, estimated by measuring the concentrations of PAH in soil solution and extracted from soil. T_c was obtained from the DIFS model (1999, Lancaster, UK) and k_{-1} was calculated using Eq. 5.3.

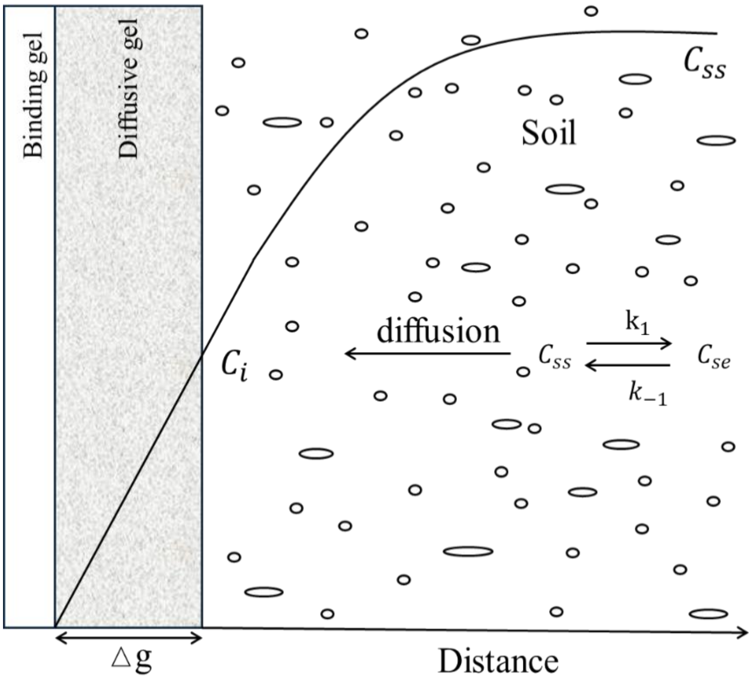


Fig. 5.1 The schematic representation of DGT device, soil solution and solid phase system and relevant processes. C_{ss} is the concentration of analytes in soil solution. C_{se} is the concentration of labile analyte on the solid phase.

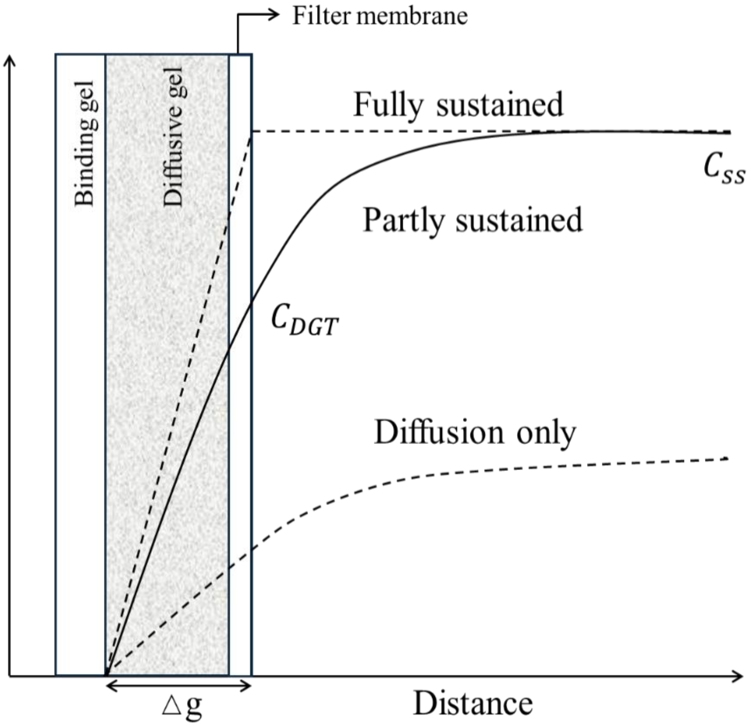


Fig. 5.2 Schematic diagram of ability of resupply by soils. (1) Fully sustained case. (2) Diffusion only case. (3) Partially sustained case.

5.2.6 Quality assurance/Quality control

The laboratory blanks and procedural blanks were used to check for possible contamination, while parallel samples (in triplicate) were used to study repeatability. Quality control standards (10 μg L^{-1}) were prepared and run every 20 samples. The recovery rate of PAHs for the extraction of soil by ACN were 64.0%-74.7%. The instrument detection limits and method detection limits of various PAHs are shown in Table 5.4.

Table 5.4 Instrument detection limits (IDLs) of selected PAHs detected by HPLC and method detection limits (MDLs) for plant samples, and DGT samples (for 1-day deployments)

Compound	IDLs (μg L^{-1})	Recoveries (%)		MDLs	
		Soil extraction	DGT	Soil extraction (ng g^{-1})	1-day DGT deployment (μg L^{-1})
Phe	0.12	64.0	97.7	18.4	0.03

Ant	0.03	67.3	101.8	4.2	0.01
Flua	0.12	68.0	92.8	18.1	0.04
Pyr	0.05	74.7	95.3	7.2	0.02

IDLs calculated using equation: $IDL = t_{(n-1,0.99)} \times S$, where S is the standard deviation from a measured concentration of standard, for testing 7 times, t(n-1,0.99) = 3.1;

MDLs calculated using equation: $MDL = \frac{IDL}{R \times CF}$ (Kasprzyk-Hordern, Dinsdale et al. 2008), where R is the absolute recovery for soil extraction samples, CF is the concentration factor; CF is 10 for soil extraction samples;

MDLs for DGT calculated using equation: $MDL = \frac{M \triangle g}{DAt}$ (Chen, Pan et al. 2018), where $M = \frac{IDL \times V}{R}$, and where R is the absolute recovery for DGT samples, V is 5 mL, results calculated for 1-day deployment at 25℃. (The calculated MDLs of the DGT method was in μg L^{-1} level. The method was sensitive enough for the requirements of the experiment. Samples did not need to be concentrated further. For the earlier studies in Chapter 2, the MDLs of DGT for measuring PAHs could reach ng L^{-1} level).

5.3 Results and Discussion

The pH (5.3-9.3) and organic matter content (0.5% -5.1%) of the six soils were different (see Table 5.2). The soils CQP and CQF exhibited weak acidity. Soil NJQ and NJJ were neutral, but NJJ had the lowest organic matter content of all the soils, while NJQ had a relatively high organic matter content. Soils GD and DL were alkaline, and DL had the highest organic matter content of all the soils. The background concentrations of the target PAHs in the soils are presented in Table 5.5. Their concentrations were negligible compared to the experimental spike concentrations.

Table 5.5 Background concentration of PAHs in 6 soils

mg kg^{-1}	Phe	Ant	Flua	Pyr
CQF	0.06	< DL	0.02	0.01
CQP	0.05	< DL	0.02	0.02
DL	0.04	0.01	0.04	0.04

GD	0.06	0.03	0.04	0.07
NJJ	0.04	0.01	0.02	0.01
NJQ	0.05	0.02	0.03	0.02

5.3.1 Changes of PAH concentrations in soil solution during the aging process

As shown in Figure 5.3, with the increase of aging time, the soil solution concentration (Css) of PAHs in the six soils showed an overall downward trend. The concentration of most PAHs in soil solution remained relatively stable after 3-4 weeks, indicating that the added PAHs almost reached equilibrium within a month. All soils showed a fluctuation in the first three weeks. But, in the alkaline soils DL and GD, the concentration of PAHs in soil solution showed a faster decrease in the first week, while in neutral soils NJJ, NJQ and acidic soils CQP, CQF, the concentration of PAHs fluctuated in the first 10 days and showed a significant downward trend after two weeks of aging. This may be due to the close relationship between pH and soil microbial activity. Research has shown that soil fungi populations are generally greater in acidic and alkaline soils than in neutral soils. Soil enzyme activity is also greater when the soil is alkaline (Pawar 2012). Abundant microbial activity may lead to faster degradation of PAHs in alkaline soils.

In soils CQF, CQP, NJJ and NJQ, the soil solution concentrations of Phe (3 rings) were higher than that of Ant (3 rings) for the first part of the aging, and the concentrations of Flua (4 rings) were higher than that of Pyr (4 rings) (Fig. 5.3). This may be related to the physical and chemical properties of the compounds, with the former having a higher solubility than the latter, making it easier to dissolve into soil solutions. Previous research found that the concentration of organic chemicals is related to soil organic matter (Means, Wood et al. 1980, Calvet 1989, Bogan and Sullivan 2003). An increase in soil organic matter leads to an increase in adsorption sites on the soil surface, which can promote the adsorption of organic chemicals and thus reduce the concentration in soil solution (Calvet 1989, Weissenfels, Klewer et al. 1992). As shown in Figure 5.4, the concentration order of Phe in soil solution is (CQF) CQP >NJQ>GD, the concentrations in soils NJJ and DL fluctuated, and were generally lower than those in soils CQP and CQF, and higher than those in GD and NJQ in the early stage of aging. The concentration order of Flua and

Pyr in soil solution is CQF>CQP>NJJ>GD>NJQ. The concentration in soil DL fluctuated in the first 10 days of aging, possibly due to problems in sample treatment. Organic matter can affect the degradation rate of organic chemicals in soils. Studies have shown that soils with high organic matter content generally limit the degradation of PAHs (Weissenfels, Klewer et al. 1992). Similarly, the concentration of Flua and Pyr in soils NJJ, GD and NJQ showed an opposite trend to the organic matter content, except for the acid soils in this study. The concentration of Phe in different soils showed the fastest decrease in NJJ, followed by GD, while the concentration changes were relatively slow in NJQ and DL soils. The trend in PAHs concentration in soil solution is not always opposite to that of soil organic matter content, as there are other factors - including the composition of organic matter (Ni, Luo et al. 2008), soil texture (Lyszczarz, Lasota et al. 2021), soil microorganisms (Cheng, Lai et al. 2008), soil pH (Emoyan, Akporido et al. 2018), and soil particle size (García-Alonso, Pérez-Pastor et al. 2008) that could also affect the concentration of PAHs in soil solutions.

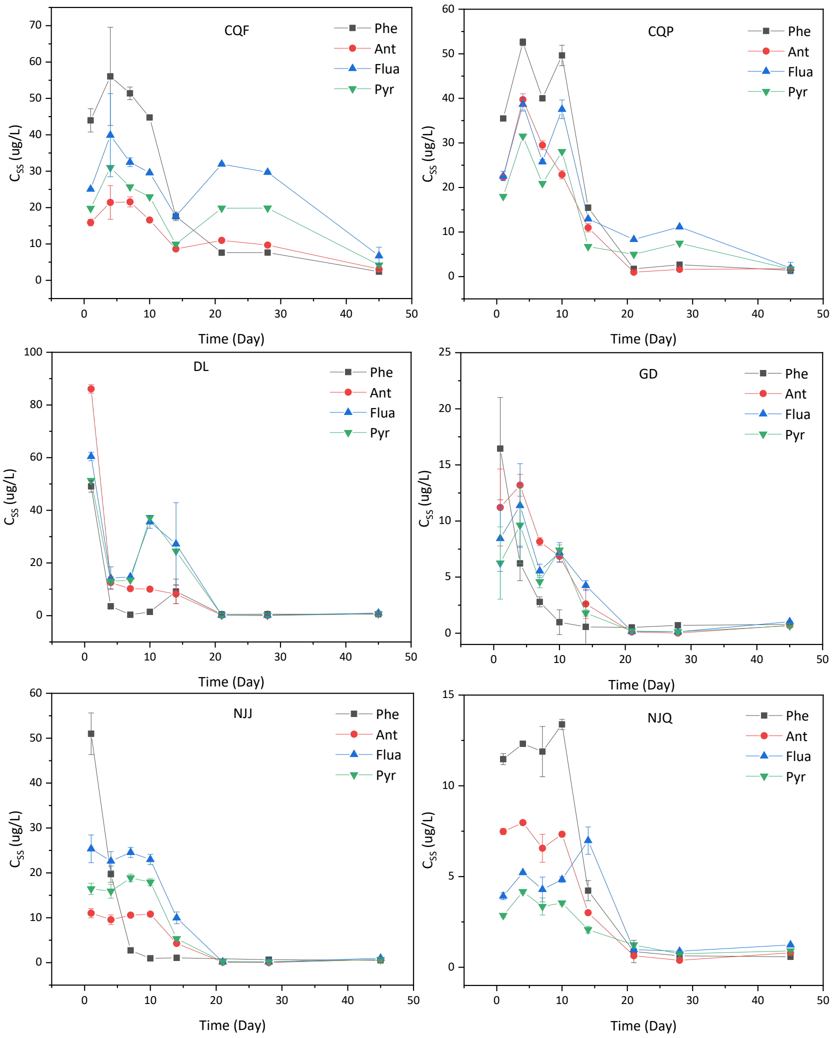


Fig. 5.3 Concentration of 4 PAHs in soil solution in the six soils (acid soils CQP and CQF, neutral soils NJQ and NJJ, alkaline soils GD and DL; the order of TOC content of soils are NJJ<GD<CQP<CQF<NJQ<DL). Values are means ± SD of replicate analyses.

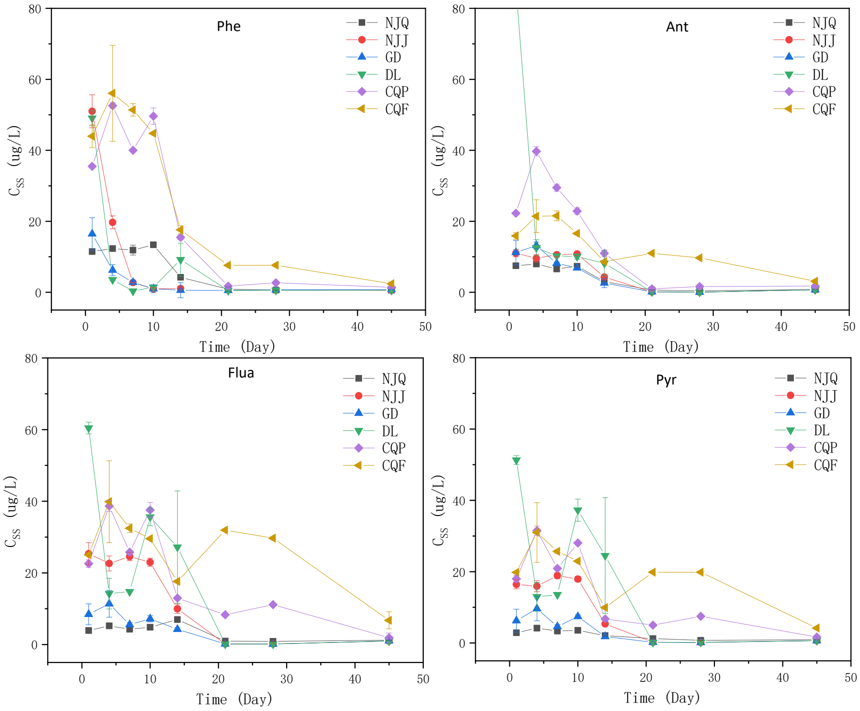


Fig. 5.4 Concentration of individual PAH in soil solution in the six soils (The data of Ant in soil DL was an outlier and not plotted here. Acid soils CQP and CQF, neutral soils NJQ and NJJ, alkaline soils GD and DL; the order of TOC content of soils are NJJ<GD<CQP<CQF<NJQ<DL). Values are means ± SD of replicate analyses.

5.3.2 Changes of extractable PAHs in soils through the experiment

The PAH concentrations in the soil extraction with acetonitrile generally showed a downward trend in the early weeks, then tended to stabilize after about 3 to 4 weeks (Fig. 5.5). However, the influence of aging varied between the different soils. For soil CQF and soil CQP, the concentration of PAHs in soil decreased significantly and rapidly in the first week. For soil DL, the concentrations of 3 -ring Phe and Ant decreased significantly in the first week, while the concentrations of 4-ring Flua and Pyr remained relatively stable in the first two weeks and decreased significantly after two weeks. For soil GD and soil NJJ, Phe rapidly decreased and reached a stable stage in the first 10 days. Ant, Flua, and Pyr showed a slight decrease, but significantly decreased after 2 weeks, and their concentrations reached a relatively stable level after 3 weeks of aging. For soil NJQ, the trends of the four PAHs were similar, with a sustained decrease in the first three weeks and relatively stable after four weeks. It is generally believed that during the aging process, PAHs are prone to be quickly adsorbed on the soil surface before slowly entering the interior of organic matter (Xing 2001, Yang, Zhang et al. 2010). The experimental results are consistent with this conclusion, as most PAHs were rapidly adsorbed in the early stages of aging, with a significant decrease in concentration, while the trend of concentration decrease slowed down in the later stages of aging.

After 45 days of aging, the percentage of the final extraction concentration relative to the first day of extraction concentration is shown in Table 5.6 below. Phe and Ant have decreased more than Flua and Pyr, indicating that the 3-ring PAHs were more affected by aging than the 4 ring substances. NJJ has the lowest TOC content compared to other soils. After 45 days of aging, PAHs that can be extracted were significantly lower in NJJ soil than the soils of NJQ, CQP, CQF. Although the TOC content of DL soil was the highest, the extracted PAHs was similar to the results in NJJ soil, which may be due to the pH and texture of the soil. The increase of soil pH could increase the negative surface charge of soil organic matter (OM) and soil particles, and the repulsive interaction between the soil surface and organic matter caused organic matter to desorb from the solid surface (Zhang, Yang et al. 2013). At the same time, the alkaline environment will increase the dispersion of soil particles, resulting in more soluble OM and subsequently possible higher microbial activity. As the soil used in this study had no sterilization treatment, microorganisms could influence the results. These desorbed PAHs may be degraded more in alkaline soils than in other soils during aging due to greater microbial activity. Soil texture also has an effect on the availability of PAHs in soil. Studies have shown that phenanthrene-related degrading bacteria have higher densities in sand and clay than in silt (Amellal, Portal et al. 2001). The clay contents of the soils used in this study were not much different, but soil DL is a sandy soil with a sand content of 47.5%. Therefore, it may lead to higher degradation of PAHs in this soil than in others, and result in less extractable PAHs compared to other soils in the later stage of aging. Compared with other research, the concentration of PAHs in this experiment declined in a shorter aging time. Luo et al. found that recovery of the PAHs from the aged soils for 200 days by Soxhlet extraction ranged from 75.3 to 84.1% for Phe, Pyr and B[a]P (Luo, Lin et al.

2012). In Ma et al.'s research, the desorbed Phe decreased from 82% to 65% in 150 days aging (Ma, Zhang et al. 2012). Volatilisation, microbial activity, soil extraction methods, soil properties etc. may have a combined effect on the results.

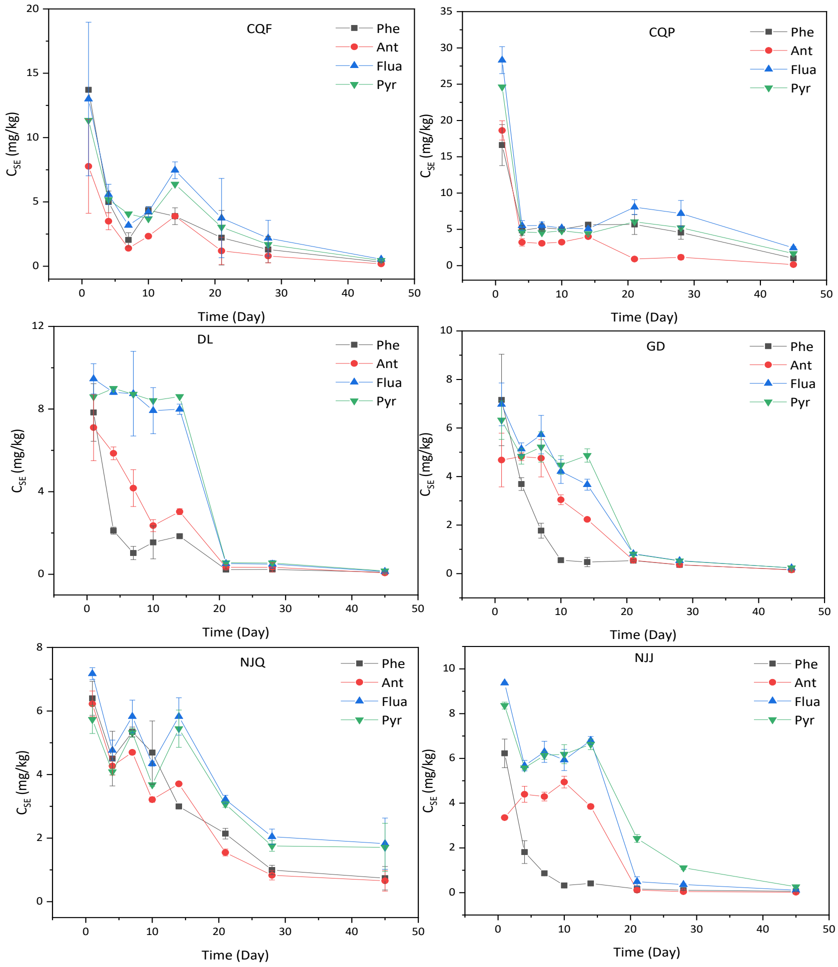


Fig. 5.5 Extractable PAHs concentration (mg kg^{-1}) measured at different times in the six soils. Values are means ± SD of replicate analyses.

Table 5.6 The percentage of the final extractable concentration of PAHs relative to the concentration measured on the first day of the spiking

	Phe	Ant	Flua	Pyr
NJQ	11.50%	10.60%	25.40%	29.80%
NJJ	0.96%	0.60%	1.18%	3.13%
GD	2.26%	3.21%	3.38%	3.76%
DL	1.27%	0.94%	1.46%	1.88%

CQP	6.04%	0.80%	8.65%	6.75%
CQF	2.31%	2.34%	4.19%	3.89%

5.3.3 DGT measured labile concentrations during the aging process

DGT has been used to predict heavy metal uptake by plants, with measured concentrations reflecting fluxes from solid-phase supplies into the soil solution (Luo, Cheng et al. 2014). Previous studies have also used DGT to assess the fate and behavior of antibiotics and atrazine in soil (Chen, Chen et al. 2015, Li, Han et al. 2021). In this study we attempted to use DGT to measure the labile concentration of PAHs in soils during the aging process. A decrease in DGT measured concentrations was observed in all soils for all 4 chemicals, indicating a decrease in the labile portion of PAHs with increasing aging time (Fig. 5.6). Within 14 days, PAHs remained relatively stable in most of the soils, except for soil GD. The DGT concentrations of all chemicals in NJQ were generally lower, which may be due to the clay content with relatively higher soil organic carbon and neutral pH. Research has shown that an increase in soil organic carbon may lead to an increase in surface adsorption sites, thereby enhancing soil adsorption capacity and reducing the concentration of organic chemicals in soil solution and the resupply from soil solid phase to soil solution. The increase of clay fraction also promoted the adsorption of phenanthrene onto the solid matrix (Staninska, Szczepaniak et al. 2015). Because of the difference in available surface area between soil aggregates of different sizes, PAHs concentrations were higher in fine soils (Amellal, Portal et al. 2001). In soil DL and NJJ, Phe and Ant showed a continuous downward trend in the first two weeks, while Flua and Pyr showed a slight decrease in the first two weeks and a significant decrease after two weeks. In soil GD, all target chemicals showed a continuous decrease in DGT concentration during the aging process until they reached a relative equilibrium state. This may be due to the higher microbial activities and the higher soil enzyme activity in alkaline soils, resulting in fastest degradation than in the more acidic soils. pH is an environmental parameter that affects the adsorption of organic matter. Studies have shown that at lower soil pH values, soil organic matter has a higher adsorption of hydrophobic organic chemicals (HOCs) (Kim, Tarafdar et al. 2023). Comparing acidic soils (CQF and CQP) with neutral and alkaline soils, the concentrations of phenanthrene measured by DGT in acidic soils were higher. This may be because the organic matter in acidic soil has a weaker adsorption of PAH, the desorbed PAHs change more slowly during the aging process, and the ability of resupply from the soil solid phase to solution was more stable, while the PAHs in alkaline soils migrated and transformed faster. For all six soils, the DGT measured labile fraction remained low and stable after 21 days, indicating that PAHs rapidly aged after entering the soil and reached equilibrium in about three weeks.

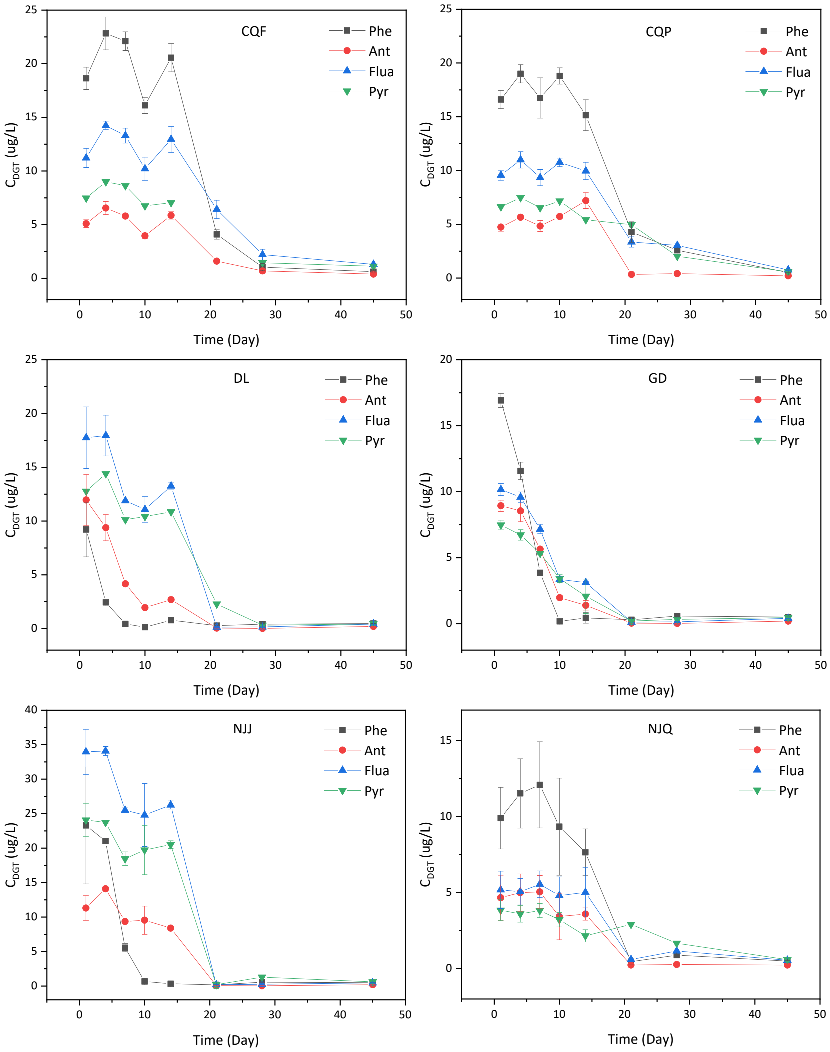


Fig. 5.6 Labile PAHs concentration (μg L^{-1}) measured by DGT at different times over aging process. Values are means ± SD of replicate analyses.

5.3.4 The resupply of PAHs from the solid phase in soils

The R value reflects the supply ability of labile PAHs associated with the solid phase to be supplied to soil solution, induced by depletion in concentration. In previous studies, R values have been used to assess the re-supply of organic chemicals from soil solid to soil solution. These results have been for the ‘partially sustained case’ defined earlier (Li, Han et al. 2021, Song, Su et al. 2023). The R values of four PAHs in six different soils during the experiment are shown in the following tables (Table 5.7-5.10). The R value is the ratio of DGT concentration to soil solution concentration. Based on DGT theory, values with R>1 are not possible and therefore excluded. Underestimating the soil solution concentration could lead to R>1. Measurement of soil solution concentration involves centrifugation and filtration. Filtration may be a major factor leading to the loss of PAHs in soil solution. Research has shown that filtration has a significant impact on the removal efficiency of hydrophobic organic compounds in sewage treatment plants (Deo and Halden 2010). Evaluating the impact of filtration on 156 pollutants by several models, 40% of the substances lost more than 20% due to filtration (Kumar, Adhikari et al. 2022). Secondly, PAHs are semi-volatile substances, and their volatilization during the experimental process may also lead to a decrease in the concentration of PAHs in soil solutions, resulting in R >1. Therefore, in the subsequent discussion, we will exclude all the data of R>1.

According to the DGT measurements, all soils reached a relatively stable stage after 21 days of aging. Therefore, due to the large amount of data, we divided the entire data set into two groups, the rapidly aging stage and the relatively stable stage, to help understand the resupply of PAHs in different soils. The average R values in these two stages are shown in Table 5.11. Any R value greater than 1 has been removed from data assessment. For most soils, the R values of the 4 PAHs in the relatively stable stage were smaller than those in the rapidly aging stage. This indicates that the resupply from the soil solid phase to the soil solution decreased during aging. This is consistent with the aging trend that as the contact time of PAHs with the soil increases, their re-supply/availability decreases.

Table 5.7 R values of Phe in 6 soils

Day	NJQ	NJJ	GD	DL	CQP	CQF

1	0.91±0.03	0.33±0.14		0.22±	0.47±0.02	0.42±0.02
4	0.93±0.03			0.73±0.26	0.36±0.05	0.41±0.03
7					0.42±0.02	0.43±0.02
10	0.83±0.18	0.71±0.06	0.18±0.01	0.09±0.01	0.38±0.02	0.36±0.02
14		0.24±0.07		0.07±0.01	0.83±0.09	1.00±0.07
21	0.52±0.21		0.57±0.05	0.59±0.05		0.54±0.06
28		0.84±0.07	0.82±0.20	0.73±0.18	0.97±0.06	0.14±0.04
45	0.85±0.03	0.76±0.01	0.64±0.01	0.84±0.03	0.36±0.01	0.26±0.01

Table 5.8 R values of Ant in 6 soils

Day	NJQ	NJJ	GD	DL	CQP	CQF
1	0.66±0.10	0.99±0.04	0.81±0.03	0.14±0.03	0.21±0.02	0.32±0.02
4	0.62±0.11		0.62±0.07	0.78±0.08	0.14±0.10	0.31±0.03
7	0.77±0.12	0.88±0.06	0.69±0.03	0.41±0.06	0.16±0.02	0.27±0.01
10	0.58±0.05	0.98±0.11	0.30±0.03	0.19±0.06	0.25±0.02	0.24±0.01
14			0.43±0.11	0.28±0.02	0.56±0.07	0.58±0.04
21	0.37±0.07	0.47±0.02	0.40±0.00	0.44±0.03	0.35±0.03	0.15±0.01
28	0.69±0.09				0.25±0.02	0.07±0.01
45	0.57±0.00	0.29±0.09	0.29±0.01	0.28±0.03	0.12±0.00	0.13±0.00

Table 5.9 R values of Flua in 6 soils

Day	NJQ	NJJ	GD	DL	CQP	CQF
1				0.29±0.04	0.42±0.02	0.45±0.05
4	0.97±0.12		0.81±0.06		0.28±0.02	0.36±0.01
7				0.81±0.08	0.36±0.03	0.41±0.02
10			0.48±0.04	0.30±0.03	0.29±0.01	0.35±0.04
14	0.66±0.20		0.63±0.03	0.42±0.01	0.65±0.06	0.62±0.07
21	0.61±0.00		0.72±0.02		0.40±0.01	0.20±0.03
28					0.27±0.01	0.07±0.02
45	0.58±0.02	0.47±0.01	0.40±0.11	0.43±0.09	0.40±0.00	0.19±0.00

Table 5.10 R values of Pyr in 6 soils

Pyr	NJQ	NJJ	GD	DL	CQP	CQF
1				0.25±0.04	0.37±0.01	0.38±0.01
4	0.87±0.04		0.68±0.06		0.24±0.04	0.29±0.02
7		0.98±0.07		0.75±0.03	0.31±0.02	0.34±0.03
10	0.96±0.10		0.48±0.04	0.28±0.03	0.26±0.02	0.29±0.02
14	0.86±0.2		0.68±0.03	0.44±0.03	0.68±0.08	0.60±0.06
21		0.88±0.06			0.99±0.03	0.25±0.03
28					0.27±0.02	0.07±0.00
45	0.69±0.08	0.91±0.02	0.70±0.10	0.66±0.11	0.35±0.01	0.06±0.00

Table 5.11 Average R values in the rapidly aging stage and relatively stable stage in 6 soils

	Stage	CQF	CQP	DL	GD	NJJ	NJQ
Phe	1	0.41+0.03	0.49+0.20	0.13+0.08	0.18	0.43+0.25	0.89+0.05
	2	0.31+0.21	0.67+0.43	0.72+0.12	0.68+0.13	0.80+0.06	0.68+0.24
Ant	1	0.34+0.14	0.27+0.17	0.36+0.26	0.57+0.20	0.95+0.06	0.66+0.08
	2	0.11+0.04	0.24+0.11	0.36+0.11	0.34+0.08	0.38*	0.54+0.16
Flua	1	0.39+0.05	0.40+0.15	0.45+0.24	0.64+0.17		0.82+0.22
	2	0.16+0.07	0.36+0.07	0.43*	0.56+0.23	0.47+0.06	0.59+0.02
Pyr	1	0.38+0.13	0.37+0.18	0.43+0.23	0.61+0.12	0.98*	0.90+0.06
	2	0.13+0.11	0.31+0.05	0.66*	0.70*	0.90*	0.69+0.00

Stage 1: rapidly aging statge; stage 2: relatively stable stage.

* For those data had no standard deviation (only have 1 data point where R<1).

5.3.5 Labile pool size (K_d) of PAHs in soils

The labile pool size (K_d) of PAHs was calculated at each aging time point by Eq. 5.2 and retaining the data with R < 1 based on the screening of R values. Similar to the treatment for the R data set, K_d results are also divided into two groups. The results are shown in Table 5.12. In soils CQP, GD, NJJ and NJQ, K_d increased significantly in the relatively stable stage of the aging process for almost all the chemicals. According to the fact that both Cse (Fig. 5.5) and Css (Fig. 5.4) decreased with aging time, this indicates that the change in Cse is smaller, which means that the transition from sorbed PAHs to unavailable PAHs is slower than the transition from mobile PAHs to sorbed PAHs. This manifested as an increase in the labile pool size of these soils, indicating the potential ability of PAHs to desorb from the solid phase to the liquid phase is enhanced. The Kd results in soil CQF and DL showed the opposite trend. The overall decrease in the relatively stable stage of the aging (typically during days 21-45) indicated that the labile pool size and consequently the ability to resupply PAHs has decreased during aging.

K_d in soil CQF was amongst the lowest, indicating the smallest labile pool size, possibly due to lower pH of the soil. The amount of TOC in soil NJQ was higher than other soils, except for soil DL. The K_d value of NJQ was one of the highest, indicating its strong adsorption capacity in solid particles. Guan et al. and Li et al. also observed similar results in their research on bisphenol A and atrazine, where Kd was higher in soils with high DOM (Guan, Zheng et al. 2017, Li, Han et al. 2021). As mentioned earlier, there are also other factors which can affect the adsorption and desorption of PAHs in soil. Research has shown that as pH increases, the SOM adsorption capacity for hydrophobic organic contaminants (HOCs) decreases (Pil-Gon, K. I. M. et al. 2023). Although the TOC of soil DL is higher than soil NJQ, its K_d value was lower as the pH of DL soil is much higher than the pH of NJQ soil.

Table 5.12 Estimated labile pool size (K_d, cm^3 g^{-1}) of PAHs in the six soils

	Stage	CQF	CQP	DL	GD	NJJ	NJQ
Phe	Rapidly aging stage	135	232	513	561	280	425
	Relatively stable stage	198	1214	360	584	140	1867
Ant	Rapidly aging stage	262	306	312	533	389	630
	Relatively stable stage	83	578	1572	2537	532	1800
Flua	Rapidly aging stage	264	428	316	633	-	874
	Relatively stable stage	90	964	141	2522	112	2394
Pyr	Rapidly aging stage	340	512	347	1268	325	1548
	Relatively stable stage	115	966	246	358	5717	1885

5.3.6 Re-supply kinetic characteristics of PAHs

The response time T_C is the time it takes for chemicals to recover to the 63% distribution equilibrium position in the soil solid-solution phase after being depleted by a sink, such as DGT. The smaller the T_C, the shorter the time required to reach equilibrium, and the faster the resupply rate from the solid phase to the solution phase. The T_C values of the four studied PAHs ranged from 0.04 to 179000 s (Table 5.13-5.16, the missing value is due to R>1 which is not acceptable for DIFS model, and the red colored values are unreliable data indicated by the DIFS model). Most data ranged from tens to thousands, which is similar to the range of other organic compounds in previous research (Li, Han et al. 2021, Huang, Liu et al. 2023, Zheng, Sheng et al. 2023). The kinetic information is presented in Fig. 5.7 and Fig. 5.8, to show how pH and TOC influence the results. Compared with the rapidly aging stage, the Tc of the relatively stable stage is generally higher (except for Phe in soils CQP and GD, Pyr in soils DL and GD), which indicates that in the rapidly aging stage, PAHs were more unstable and easier to desorb from the solid phase to the liquid phase. In the relatively stable stage, the resupply rate of PAHs by soil decreased. During the rapidly aging stage, when the soil is close to neutral pH, the Tc were relatively small (except for Phe). For Phe, it seems there is an increase with higher pH and there's no correlation with the change of TOC. In the relatively stable stage, Tc increased first and then decreased with the increase of TOC content, and it showed a downward trend when the content of TOC was greater than 2%. Based on the values of K_d and T_C, the adsorption rate constant k_1 and the desorption rate constant k_{-1} can be calculated using eq. 5.3. Compared with the rapid aging stage, k_{-1} decreased in the relatively stable stage. This indicated that the desorption rate of PAHs from the solid phase to solution phase decreases. During the relatively rapidly aging stage, when the soil is close to neutral pH, the T_C were relatively small. In the relatively stable stage, the content of TOC had a more obvious effect on the desorption rate (k_{-1}). As TOC increases, k_{-1} first decreased and then increased (except for Ant). At the same time, k_{-1} was 2-3 orders of magnitude lower than k_1, indicating that the desorption of PAHs from the solid phase in soil is a relatively slow process and the desorption is not sufficient to replenish the amount depleted in the solution phase by DGT.

In general, the effect of pH was more obvious in the relatively rapidly aging stage. This may be due to the more dynamic microbial activities in this stage, that cause changes to soil properties and PAHs in the soil. During the relatively stable stage, the degradation and migration of PAHs were relatively slow. Then, the organic matter content had a greater impact on the ability of the soils to resupply PAHs.

Table 5.13 Estimated Tc and k_{-1} values for Phe obtained from DIFS (for Tc) and Eq. 5.3 (for k_{-1}) at the two aging stages in the six tested soils

	Stage	CQF	CQP	DL	GD	NJJ	NJQ
Tc	Rapidly aging stage	291	180	12000	2320	380	2.5E-04
(s)	Relatively stable stage	815	69.6	4.2	31.2	3.2E-02	86.3
k_1	Rapidly aging stage	3.4E-03	5.6E-03	8.3E-05	4.3E-04	2.7E-03	4.1E+03
(s^{-1})	Relatively stable stage	1.2E-03	1.4E-02	2.4E-01	3.2E-02	3.1E+01	1.2E-02
k_{-1}	Rapidly aging stage	1.0E-05	1.0E-05	5.9E-08	2.1E-07	4.9E-06	5.9E+00
(s^{-1})	Relatively stable stage	2.4E-06	4.9E-06	2.4E-04	1.5E-05	1.2E-01	3.8E-06

Table 5.14 Estimated Tc and k_{-1} values for Ant obtained from DIFS (for Tc) and Eq. 5.3 (for k_{-1}) at the two aging stages in the six tested soils.

	Stage	CQF	CQP	DL	GD	NJJ	NJQ
Tc	Rapidly aging stage	639	1280	514	90.5	1.4E-02	69.6
(s)	Relatively stable stage	13300	1760	555	500	609	232
k_1	Rapidly aging stage	1.6E-03	7.8E-04	1.9E-03	1.1E-02	6.9E+01	1.4E-02
(s^{-1})	Relatively stable stage	7.5E-05	5.7E-04	1.8E-03	2.0E-03	1.6E-03	4.3E-03
k_{-1}	Rapidly aging stage	2.3E-06	1.1E-06	2.3E-06	5.7E-06	9.3E-02	1.4E-05
(s^{-1})	Relatively stable stage	3.5E-07	4.1E-07	4.2E-07	2.2E-07	1.6E-06	1.5E-06

Table 5.15 Estimated Tc and k_{-1} values for Flua obtained from DIFS (for Tc) and Eq. 5.3 (for k_{-1}) at the two aging stages in the six tested soils

	Stage	CQF	CQP	DL	GD	NJJ	NJQ
Tc	Rapidly aging stage	529	538	318	71.4	r>1	9.7
(s^{-1})	Relatively stable stage	1.8E+05	7805	3280	847	3300	1390

k_1	Rapidly aging stage	1.9E-03	1.9E-03	3.1E-03	1.4E-02		1.0E-01
(s^{-1})	Relatively stable stage	5.6E-06	1.3E-04	3.0E-04	1.2E-03	3.0E-04	7.2E-04
k_{-1}	Rapidly aging stage	2.8E-06	1.8E-06	3.6E-06	6.1E-05		7.3E-05
(s^{-1})	Relatively stable stage	2.4E-08	5.5E-08	7.8E-07	1.3E-07	1.4E-06	1.9E-07

Table 5.16 Estimated Tc and k_{-1} values for Pyr obtained from DIFS (for Tc) and Eq. 5.3 (for k_{-1}) at the two aging stages in the six tested soils

	Stage	CQF	CQP	DL	GD	NJJ	NJQ
Tc	Rapidly aging stage	562	657	359	94.6	5.7E-03	0.04
(s)	Relatively stable stage	9320	1090	20.9	23.6	12.7	95.3
k_1	Rapidly aging stage	1.8E-03	1.5E-03	2.8E-03	1.7E-02	1.8E+02	2.6E+01
(s^{-1})	Relatively stable stage	1.1E-04	9.2E-04	4.8E-02	4.2E-02	7.9E-02	1.1E-02
k_{-1}	Rapidly aging stage	2.1E-06	1.2E-06	2.9E-06	2.3E-06	2.8E-01	1.0E-02
(s^{-1})	Relatively stable stage	3.7E-07	4.0E-07	7.1E-05	3.2E-05	7.2E-06	3.4E-06

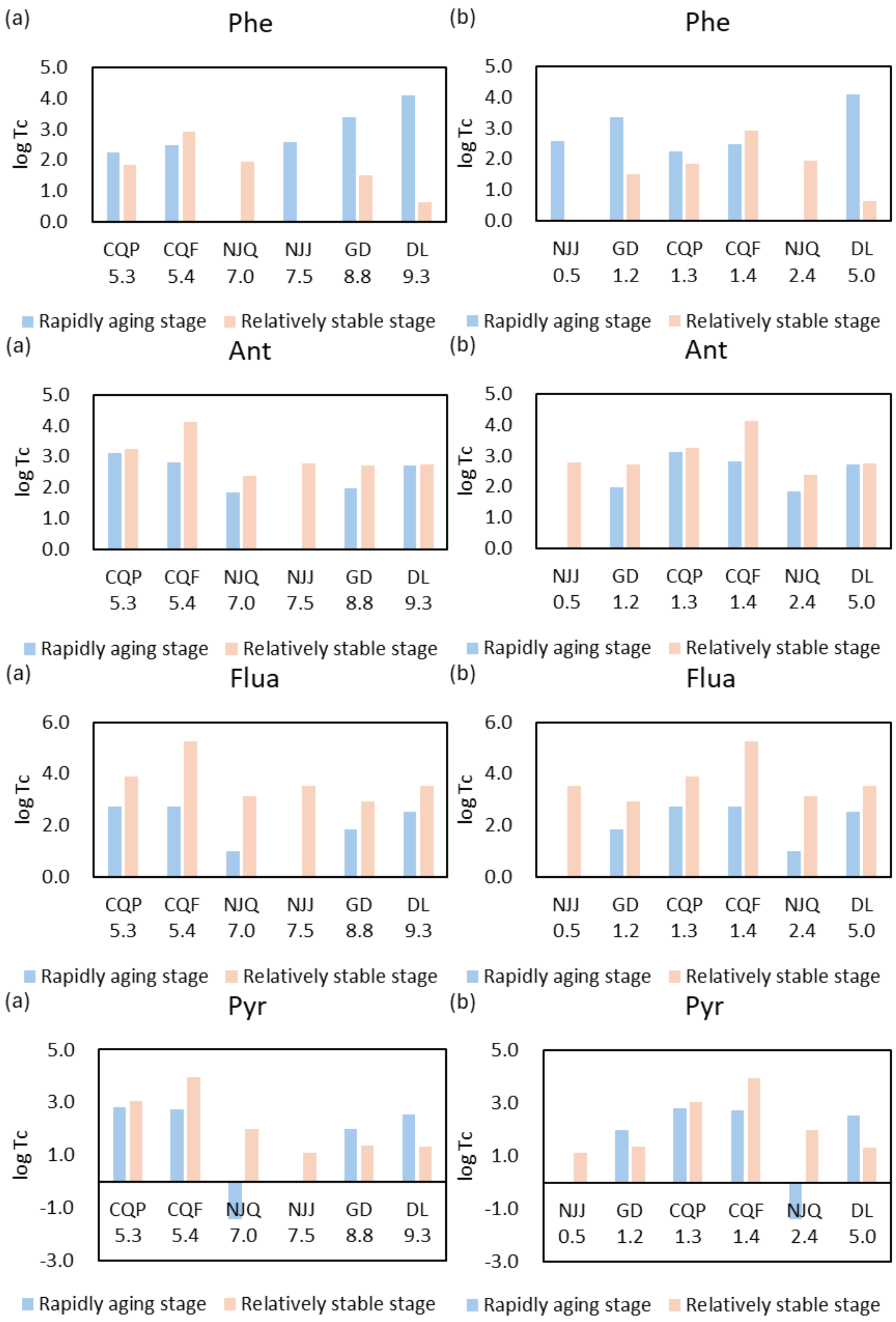


Fig.5.7 Log Tc of PAHs at different soil pH and the content of TOC for 2 aging stage. (a) soil plot with the increase of pH; (b) soil plot with the increase of the TOC content

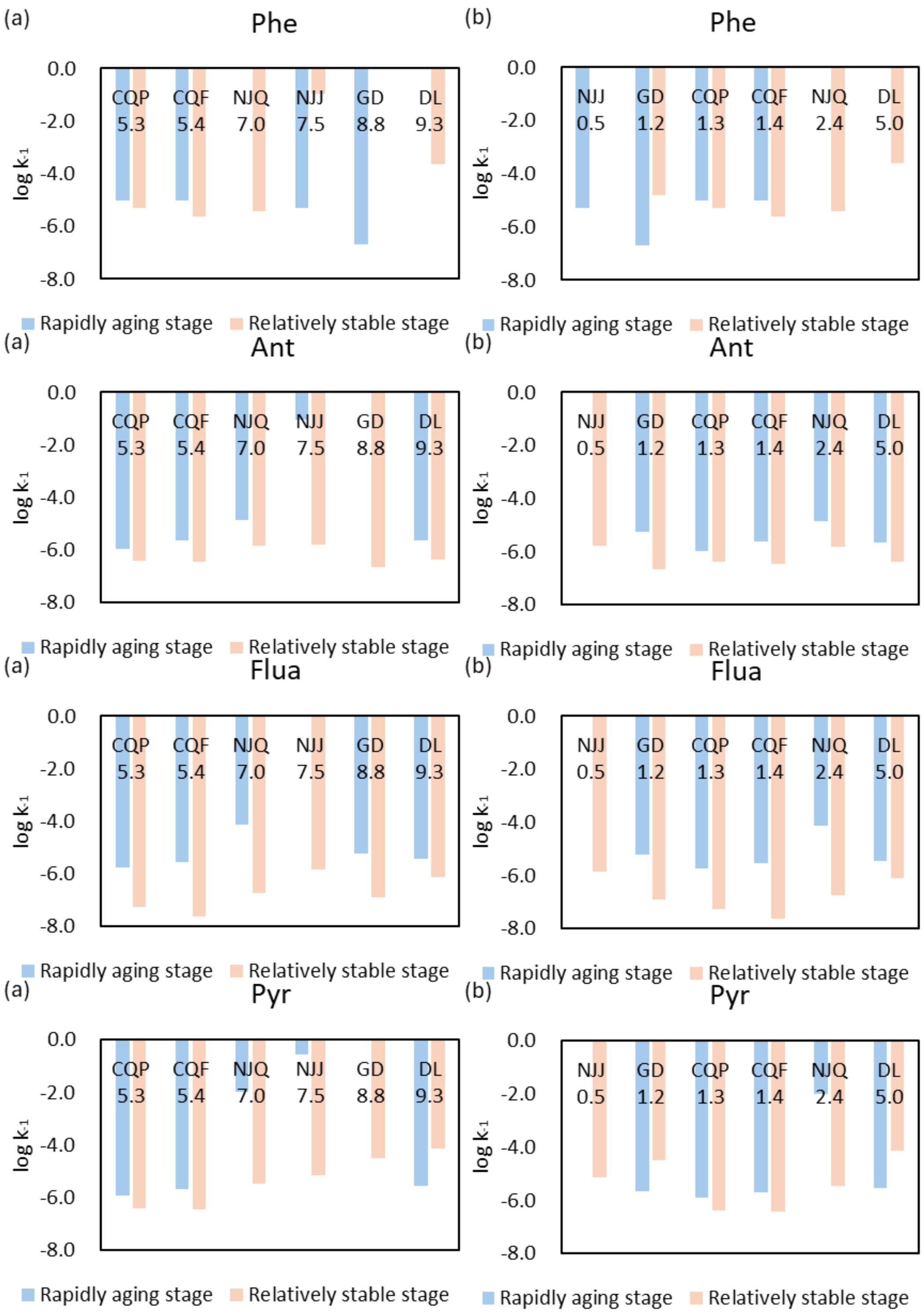


Fig. 5.8 Log k-1 of PAHs at different soil pH and the content of TOC content for 2 aging stages. (a) soil plot with the increase of pH; (b) soil plot with the increase of the TOC content

5.4 Conclusion

The results of this study showed that with the increase of aging time, the adsorption of PAHs by soil was enhanced, and both PAHs in soil solution and the labile PAHs that can be extracted decreased. PAHs in soils entered a relatively stable stage after three weeks aging. Soil physical and chemical properties such as pH, TOC, soil particle size and the properties of PAHs themselves have a comprehensive impact on the results.

When DGT was used to investigate the resupply of PAHs due to depletion, it was found that the resupply ability of most soils from soil solid phase to soil liquid phase decreased with the increase of aging time. Combined with the DGT-induced soil flux (DIFS) model, the information of the desorption kinetics of PAH from soil solid phase to soil solution phase at different stages of aging was obtained. The results showed that the desorption kinetics and labile pool size affect the resupply ability of PAH in soil. The labile pool size was affected by both pH and TOC. During the aging process in soil, the changes in kinetics information (response time and desorption rate constant) were affected by different factors. In the rapidly aging stage, the resupply was more susceptible to the influence of soil pH. When aging entered a relatively stable stage, the desorption of PAHs was more affected by the content of organic matter.

Through the application of DGT, kinetic information about PAHs in soil can be obtained, to help understand their behavior in soil.

Chapter 6 Assessment of speciation and bioavailability of PAHs in soils

Abstract

The diffusive gradients in thin films (DGT) technology can reflect the dynamic information of pollutants re-supplied from soil solid phase to soil solution and has been shown to reliably predict the bioavailability of a series of pollutants (such as heavy metals, radionuclides, nutrients) in the soil system. This study explored the potential of using DGT to evaluate the bioavailability of PAHs in soil and compared it with chemical extraction methods. Pot experiments were conducted by planting three crops (lettuce, radish, and maize) in six soils with different physical and chemical properties. The results showed that the resupply of solid phase PAHs in most soils decreased after planting. Maize roots absorbed more PAHs than stems and leaves. DGT and continuous extraction methods have the potential to evaluate PAHs in lettuce. This study demonstrated that DGT technology could reflect the dynamics of PAHs in soil and provide information on the resupply of PAHs in soil. For the evaluation of the bioavailability of DGT, further optimization is needed, because air-plant transfers can act as a confounding factor for soil-plant transfers.

Key words: DGT, bioavailability, sequential ultrasonic extraction, crop planting

6.1 Introduction

Soil is an essential environmental medium for human survival and an important source and sink of pollutants. With the rapid development of industry and agriculture, contamination of soils with organic chemicals can often occur. Polycyclic aromatic hydrocarbons (PAHs) have attracted attention due to their persistence in the environment and mutagenic/carcinogenic properties. PAHs have been detected in soils worldwide. Wilcke reported the concentrations of the 16 priority PAHs in surface soils around the world from 1996 to 2006, ranging from 3.6 to 170,000 μg kg^{-1}. Concentrations in central Europe were higher than in other areas (Wilcke 2007). This may be due to Europe's earlier industrialization development compared to other regions. The average background concentrations of 15 PAHs in different soils worldwide ranged from <1 to 7840 μg kg^{-1} (mean 328 μg kg^{-1}), following the order of Europe> North America> Asia> Oceania> Africa> South America (Nam, Sweetman et al. 2009). Early estimates suggested that there are over 50000 tons of PAHs in the soil environment of the UK, with over 90% present in the surface soil (Wild and Jones 1995). Background concentrations of PAHs ranged between 42 and 11200 μg kg^{-1} (mean 640 μg kg^{-1}) in the UK (Nam, Thomas et al. 2008). The average concentration of 16 PAHs in surface soil in China was 730 μg kg^{-1}, and the degree of PAH pollution varies greatly among different cities, reaching 2-3 orders of magnitude higher than background. In heavily polluted areas such as Dalian and Jinan, the average soil PAHs pollution concentration can exceed 6000 μg kg^{-1} and 20000 μg kg^{-1} (Zhang and Chen 2017). The concentration of 16 PAHs in different types of soil in central South Africa ranged from 44-39000 μg kg^{-1} (Nieuwoudt, Pieters et al. 2011). The PAHs concentrations in Argentine soil were 50-2100 μg kg^{-1} (Orazi, Arias et al. 2020).

The total concentrations of PAHs in soil do not consider their speciation, form or bioavailability, which can overestimate the environmental risks (Alexander 2000). The concept of bioavailability, which considers that portion in soils which can be taken up/absorbed by organisms is important. Bioavailability can also consider what is bioaccessible and it is important for assessing the potential toxicity of chemicals (Alexander 2000). Semple et al. considered that bioavailability is the amount of chemicals that freely pass through biological membranes from the environmental medium and enter the organism within a given time period (Semple, Doick et al. 2004). Here, it is believed that the bioavailability of PAHs in soil is related to soil properties and the chemical form or association of PAHs. It refers to the amount of PAHs that can interact and respond to organisms during a certain period of time, reflecting the relationship between the migration and transformation behavior of PAHs and biological absorption.

Often methods for evaluating the bioavailability of PAHs in soil use ‘model organisms’ or chemical extraction methods. The model organism method is the direct way to evaluate the bioavailability of pollutants through changes in the concentration of pollutants in the test organisms (e.g. plants or earthworms) or changes in the concentration of pollutants in soil before and after exposure (Zhu, Wang et al. 2018). The bioavailability of pollutants can also be represented by measuring certain physiological or genetic indicators of soil organisms (Baran, Bielińska et al. 2004, Mao, Zhang et al. 2021). Matscheko et al. used earthworms as model organisms and explored different patterns of biological accumulation of PAHs through their survival, fresh weight changes, and other factors (Matscheko, Lundstedt et al. 2009). Johnson et al. used earthworms as model organisms to evaluate the impact of compound aging (i.e. increased contact time with the soil) on the bioavailability of PAHs in soil, and found that the degree of chemical extraction with different solvents was different from the bioavailability measured with earthworms. Different experimental species showed different toxic responses and accumulation potential in different soils (Johnson, Jones et al. 2002). Microorganisms have the ability to degrade and transform organic pollutants. The amount of PAHs degraded by microorganisms or the changes in various physiological indicators caused by PAHs was used to determine the microbial bioavailability of PAHs in soil. Baran et al. found that soil enzyme activity had different responses to different doses of PAH pollution, and was related to soil total organic carbon, pH, and different compounds (Baran, Bielińska et al. 2004). The experimental period for evaluating the bioavailability of pollutants by soil model organisms is relatively long, and due to individual differences between organisms, the repeatability is often poor.

Chemical extraction is also commonly used to simulate the bioavailability of pollutants. Different extractants of different strengths can be used, often sequentially. ‘Mild’ extractants can sometimes reflect/correlate with bioavailability determined using test organisms. Tang and Alexander used n-butanol to gently extract anthracene from soil and found a good correlation with the absorption of anthracene by earthworms, wheat, and barley (Tang and Alexander 2009). Hydroxypropyl-β-cyclodextrin (HPCD) is also a commonly used organic reagent for trying to mimic the bioavailability of PAHs in soils (Hua, Broderick et al. 2007, Khan, Cheema et al. 2011). There is also research evaluating the bioavailability of PAHs using sequential extraction methods. Wu et al. found a correlation between the weight corrected uptake amount by plants (rice, maize, wheat and ryegrass) and PAHs in water-soluble and acid-soluble fractions of soil, using a sequential ultrasonic extraction procedure (Wu and Zhu 2016). The chemical extraction method for simulating the bioavailability of pollutants is a conventional method based on experimental data correlation. Due to the changes in soil properties, environment conditions, and the properties of pollutants themselves, it is difficult to evaluate the bioavailability of multiple pollutants in different environments using a single chemical extraction technique.

Passive sampling technology has made some progress in the evaluation of bioavailability in recent years. It gives minimal disturbances to the soil system and causes very little changes in soil chemistry properties. Diffusive gradients in thin films (DGT) technology was first proposed for the bioavailability assessment of heavy metals (Zhang, Davison et al. 1998). Zhang et al. conducted pot experiments in 30 different soils and found that the concentration of Cu extracted from plants was highly correlated with the effective concentration measured by DGT (Zhang, Zhao et al. 2001). Bade et al. used DGT to evaluate the bioavailability of Pb, Zn and Cu in soil for earthworms, and the results showed that DGT can be used as a biomimetic substitute for earthworms (Bade, Oh et al. 2012). Disla et al. compared different extraction methods to evaluate the bioavailability of heavy metals in soil, and DGT had the widest applicability, successfully predicting the concentrations of Cu, Ni, Pb, and Zn in wheat roots (Soriano-Disla, Speir et al. 2010). Testing and development using DGT to assess the bioavailability of organic pollutants in soils is relatively recent. Early studies have shown DGT to be useful for predicting the bioavailability of pesticides and antibiotics in soil (Li, Chen et al. 2019, Song, Su et al. 2023), for evaluating the availability of root and non-root zone atrazine (Lin, Zhen et al. 2018), and for assessing plant-available glyphosate in soil (Weng, Rose et al. 2019). These studies have demonstrated the potential of DGT in predicting the bioavailability of organic chemicals and lay the foundation for subsequent related research.

The purpose of this study was to explore the potential use of DGT to evaluate the bioavailability of PAHs in soil and to investigate some of the effects of soil properties. Lettuce, radish, and maize were used as three different test plant species in six different soils which had been treated with PAHs. PAH concentrations in the plants were compared to PAHs measured in the soil with DGT, in addition to soil solution concentrations, and sequential ultrasonic extraction methods, to evaluate their ability to predict the bioavailability of PAHs.

6.2 Methods and materials

6.2.1 Chemicals and reagents

Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua) and Pyrene (Pyr) were selected as representative PAHs for these experiments. PAHs were purchased from Nanjing Ronghua with a purity of over 98%. Stock solutions were prepared at 1000 mg L^{-1} in acetonitrile and stored at -20°C in the amber glass bottles. The ingredients of artificial root exudates (AREs) in the experiment are listed in Table 6.1 (Wang, Zhu et al. 2015). All required substances are analytical grade and purchased from Aladdin (China). Anhydrous sodium sulfate and sodium chloride were purchased from Aladdin (China).

Organic solvents were HPLC grade. Acetonitrile (ACN) and methanol (MeOH) were obtained from Merck (Germany). Acetone, dichloromethane, n-hexane were purchased from Nanjing reagent (China). Water used in the experiments was supplied from a Milli-Q water (MQ water) purification system (>18.2 MΩ/cm, Millipore).

Agarose was obtained from Bio-Rad Laboratories (UK). MIP were extracted from MIP-PAH SPE tubes purchased from CNW (Germany) as resins for binding gel. Flory silica cartridges were purchased for Nanjing Ronghua (China).

Table 6.1 Ingredients of artificial root exudates

Amino acids 12.5 mmol L^{-1}	Organic acids 25 mmol L^{-1}	Carbohydrates 50 mmol L^{-1}
L-arginine	L-malic acid	D-fructose
L-cysteine	Succinic acid	D-glucose
Serine		Sucrose

6.2.2 Soil sample collection and treatments

Six soils of different properties were collected from China and used for the experiments. They were selected to represent a range of soils, with varying pH (5.3-9.3) and organic matter content (0.45%-5.08%). The details of soil sites and properties are listed in Table 6.2. All soils were spiked with 4 PAHs at a concentration of 10 mg kg^{-1} following a contamination procedure. The soils were wetted to 30% maximum water holding capacity (MWHC) and stored in a stainless-steel box with partly opened tin foil sealing and kept in the dark at room temperature (25 ± 1 °C). These soils were used for plant experiments after 80 days aging. The information about the soil spiking procedure was given in section 5.2.2.2.

Table 6.2 Physical and chemical properties of 6 soils

Soils	Soil type	pH (H_2O)	TOC (%)	MWHC (%)	Clay (%)	Silt (%)	Sand (%)
CQF	Loam	5.4	1.38	47.7	13.1	73.6	13.3
CQP	Loam (Paddy soil)	5.3	1.34	40.0	12.1	72.0	15.9
DL	Loamy sand	9.3	5.08	27.0	4.9	47.6	47.5
GD	Silty clay loam	8.8	1.25	36.3	9.4	65.4	25.2
NJJ	Silty loam	7.5	0.45	52.0	10.3	85.1	4.5
NJQ	Silty loam	7.0	2.35	61.7	11.0	81.8	7.2

6.2.3 Pot experiments

Crops are indispensable food in human life. At present, most crops are grown in soil, and their edible parts are directly or indirectly exposed to environments containing PAHs. Due to differences in the absorption and migration of PAHs in various plant tissues, three crops were selected for pot experiments based on their edible parts. They are a grain crop (maize), a leafy vegetable (lettuce) and a root crop (radish). Maize seeds (*Zea mays*) were purchased from Hanyu seeds (China). Lettuce seeds (*Lactuca sativa L.*) were purchased from Tianyuanqu seeds (China). Radish seeds (*Raphanus sativus L.*) were purchased from Qingfeng seeds (China). Seeds were soaked in MQ water to pre-germinate on damp filter paper in a greenhouse before sowing. Each plastic flowerpot (diameter 10.5 cm, height 9.0 cm) contained approximately 300 g of PAHs contaminated soil. Plants were planted in six different soils in triplicate. The soil moisture was maintained at 100% MWHC during plant growth by watering once a day. The surface of each plant-pot was covered with aluminum foil to minimize any photodegradation and volatilisation of PAHs and water loss. During the experiment, the temperature was maintained at 25 ± 2°C in a controlled environment greenhouse with 14 hours of light per day. Maize was grown for 3 weeks and was harvested at three leaf period. Lettuce and radish were grown for 5 weeks. The day before harvesting, the plant-pot was not watered. The shoots and roots of maize were harvested separately, while lettuce and radish were collected as the whole plant. Plants were rinsed carefully with MQ water to remove any soil particles, wiped with tissue, and the fresh weight was recorded. Then the samples were freeze dried for 48 hours, and the dry weight recorded immediately before storing samples at -20°C.

Freeze-dried plant samples (weight range between 0.0239 to 0.9169 g) were cut into small pieces and homogenized with a mortar under liquid nitrogen. The accurate amount of the sample was recorded for extraction. The plant sample was put into a 35 ml glass centrifuge tube with 10 ml acetone and dichloromethane solvent (1:1, v: v). The extraction was repeated three times sequentially. Samples were extracted for 20 minutes each time in an ultrasonic water bath, and then centrifuged at 3000 rpm for 10 minutes. After collecting all the extraction solution, it was concentrated to near dryness under nitrogen and dissolved in 2 mL of n-hexane. The concentrated solution was purified with a Flori silica gel column and rinsed with a mixture of dichloromethane and n-hexane (1:1, v: v). The eluent was then concentrated with nitrogen to about 0.5 mL, then concentrated with nitrogen to near dryness after adding 2 mL acetonitrile. It was finally redissolved with 1 mL of acetonitrile and water solution (1:1, v: v). Samples were filtered through 0.22 μm PTFE before HPLC analysis.

6.2.4 Sequential ultrasonic extraction of soils

PAHs in soil were classified into four speciation fractions, namely: water-soluble fraction, organic acid-soluble fraction, organically bound fraction, and residual fraction. The water-soluble fraction was extracted with deionized water, the organic acid-soluble fraction was extracted with AREs solution, the organically bound fraction was extracted with methanol and 1 M NaOH (14:1 v/v), and the residual fraction was calculated by a mass balance approach. A previous study has referred to the bioavailable fractions of organic pollutants as the total amount of the water-soluble and acid-soluble fractions ((Wu and Zhu 2016).

Water-soluble fraction

A total of 1 (±0.0003) g soil was transferred into a 35 mL centrifuge glass tube, then 10 mL of 0.01 M NaCl in de-ionised water was added. The glass tube was wrapped in aluminum foil to reduce potential photodegradation during the experiment. The soil sample was extracted ultrasonically at 25°C for 20 minutes, followed by centrifugation at 3000 rpm for 10 minutes. The step was repeated three times, using 10 mL of fresh extractant each time. Liquid-liquid extraction was then used to extract PAHs from the combined supernatant, with 5 mL of dichloromethane each time, twice in total. The sample was then dehydrated with anhydrous Na_2SO_4, concentrated under a gentle stream of nitrogen, and then finally diluted with 5 mL acetonitrile. The solution was filtered through a 0.22 μm PTFE membrane and then analyzed by HPLC.

Organic acid-soluble fraction

The steps of the extraction of the organic acid-soluble fraction were the same as for the water-soluble fraction, except that a mixed solution of artificial root exudates (AREs) (detailed in Table 6.1) was used as the extraction solvent.

Organically bound fraction

After extracting the water-soluble and organic acid-soluble fractions, 10 mL of methanol and 1 M NaOH solvent (14:1 v/v) was added to the soil sample. The sample was extracted ultrasonically at 25 °C for 20 minutes and centrifuged at 3000 rpm for 10 minutes. The extraction was repeated twice more. The three extracts were then combined and neutralized with 6 M HCl to pH=7.

Residual fraction

Since this part cannot be released in solution, it is calculated by mass balance. This amount was obtained by subtracting the amount extracted in the first three steps from the initial total amount of PAHs added to the soils. Of course this cannot distinguish from the possible losses via biodegradation, photodegradation, and volatilization.

6.2.5 DGT deployment

The standard disc type DGT devices consisting of a PC filter membrane, 0.8 mm agarose diffusive gel, and 0.5 mm MIP agarose binding gel were used. Before the pot experiments for plants, about 50 g soil was taken into a culture dish (diameter 90 mm) and wetted to 100% MWHC for 24 hours before deploying DGT devices. A layer of soil was smeared evenly on the filter surface of the sampling window area first to ensure full contact between the DGT and the soil, and then the device was gently pressed onto the soil and kept at room temperature for 24 hours. DGT devices were also deployed in the soils after plant growth (soils were collected from the plant pots after plants were harvested. All DGT deployments were triplicated. The elution of DGT binding gels was the same as in section 5.2.4 of the study.

After removing the DGT device, the soil was transferred from the culture dish into a 50 mL centrifuge tube and centrifuged at 3000 rpm for 15 minutes. The soil solution was obtained and filtered with a 0.22 μm PTFE filter into a 2mL injection vial for further analysis.

The extraction of PAHs in soil was carried out by the method described in section 6.2.4. 1g of centrifuged soil was taken and sequentially ultrasonically extracted as described above.

6.2.6 Human health risk assessment

Hazard quotient (HQ) model, hazard index (HI) models and incremental lifetime cancer risk (ILCR) model have been used to assess the carcinogenic risk of PAHs based on toxicity equivalent risk and ingestion (Zhu, Huang et al. 2021, Chukwuma, Nweze et al. 2024). This study used ILCR for evaluation.

$$ILCR = \frac{TEQ_{BaP} \times IR_i \times EF \times ED \times SF \times CF}{AT \times BW} \qquad (Eq.\ 6.1)$$

Where TEQ_{Bap} is the total BaP equivalent, IR_i is the amount of vegetables ingested per day (170 g day^{-1}), EF is the exposure frequency (365 d year^{-1}), ED is the exposure duration (70 years), SF is the oral cancer slope factor of benz[a]pyrene (7.3 mg kg^{-1} day^{-1}), CF is a conversion factor (10^{-6} mg ng^{-1}), AT is averaging time (days) for cancer genic development (25,550 days), BW is the body weight for an adult (70 kg) (Al-Nasir, Hijazin et al. 2022).

$$TEQ_{BaP} = \sum_{i=1}^{n} C_i \times TEF_i \qquad (Eq.\ 6.2)$$

where Ci is the concentration of the individual PAH in crops, and TEFi is the corresponding toxic equivalency factor for PAHs. The TEF of 4 PAH congeners are as follows: Phe= 0.001, Ant= 0.01, Flua= 0.001, Pyr= 0.001 (Zhu, Huang et al. 2021, Al-Nasir, Hijazin et al. 2022).

6.2.7 Analytical methods and calculation for the results

High-performance liquid chromatography combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) was used for samples. The specific conditions were given in section 2.2. PAHs measured using DGT were calculated using the formula mentioned earlier in section 3.4, as follows:

$$C_{DGT} = \frac{M \triangle g}{DAt} \qquad \textit{(Eq. 6.3)}$$

The concentration of PAHs in plants (dry weight) were calculated by formula:

$$C_{plant} = \frac{C_m \times V}{m} \qquad \textit{(Eq. 6.4)}$$

Where C_m is the concentration of PAHs measured and calculated by the standard calibration curve, V is the volume of samples, m is the amount of plant samples used for extraction (dry weight).

The soil PAH concentrations in different extractions were calculated as follows:

$$C_w = \frac{C_{mw} \times V_w}{m_s} \qquad \textit{(Eq. 6.5)}$$

$$C_a = \frac{C_{ma} \times V_a}{m_s} \qquad \textit{(Eq. 6.6)}$$

$$C_o = \frac{C_{mo} \times V_o}{m_s} \qquad \textit{(Eq. 6.7)}$$

Where C_w, C_a, C_o is the water-soluble PAH fraction, acid-soluble PAH fraction and organically-soluble PAH fraction in soil, C_{mw}, C_{ma}, C_{mo} is the concentration of PAHs measured and calculated by the standard curve for each fraction, V_w, V_w, V_w is the constant volume for each speciation fraction, m_s is the amount of soil sample used for extraction.

6.2.8 Quality assurance/Quality control

The laboratory blanks and procedure blanks were used to check for possible contamination, while triplicate samples were used to study repeatability. Quality control standards (10 μg L^{-1}) were prepared and run every 20 samples. For plant samples, ultrasonic extraction and silica gel column purification methods were used. The recovery rate range of PAHs in plant samples was 53.5%-87.5% and the relative standard deviation range was 2.2%-9.4%, which indicated that the method is fit for purpose. The instrument detection limits and method detection limits of various PAHs are shown in Table 6.3.

Table 6.3 Instrument detection limits (IDLs) of selected PAHs detected by HPLC and method detection limits (MDLs) for plant samples, and DGT samples (for 1-day deployments)

Compound	IDLs (μg L^{-1})	Recoveries (%)		MDLs	
		Plant extraction	DGT	plant sample (ng g^{-1})	1-day DGT deployment (μg L^{-1})
Phe	0.12	87.5	97.7	4.5	0.03
Ant	0.03	53.5	101.8	1.7	0.01
Flua	0.12	68.0	92.8	6.0	0.04
Pyr	0.05	75.8	95.3	2.4	0.02

IDLs calculated using equation: $IDL = t_{(n-1,0.99)} \times S$, where S is the standard deviation from a measured concentration of standard, for testing 7 times, t(n-1,0.99) = 3.1;

MDLs calculated using equation: $MDL = \frac{IDL}{R \times CF}$(Kasprzyk-Hordern, Dinsdale et al. 2008), where R is the absolute recovery for plant extraction samples, CF is the concentration factor; CF is 30 for plant extraction samples;

MDLs for DGT calculated using equation: $MDL = \frac{M \triangle g}{DAt}$, where $M = \frac{IDL \times V}{R}$(Chen, Pan et al. 2018), and where R is the absolute recovery for DGT samples, V is 5 mL, results calculated for 1-day deployment at 25°C. (The calculated MDLs of the DGT method was in µg L^{-1} level. The method was sensitive enough for the requirements of the experiment. Samples did not need to be concentrated further. For the earlier studies in Chapter 2, the MDLs of DGT for measuring PAHs could reach ng L^{-1} level).

6.3 Results and discussion

6.3.1 Distribution of PAHs in the sequential soil extraction

The distribution of the individual PAHs in the sequential extraction series applied to the 6 soils is shown in Fig. 6.1 and Table 6.4. In the six types of soil, the proportion of organic acid-soluble fraction PAHs was the lowest, while the fractions of volatilization, degradation and residual (V&R) had the highest proportion (except for soil NJQ and CQF). Among the soils, the proportion of water-soluble fraction was 0.02-1.28%, the proportion of organic acid-soluble fraction was 0.01-0.80%, the proportion of organically bound fraction was 0.6-64.2% and the proportion of V&R fraction was 38.0-99.2%.

The proportion of acid-soluble fraction was slightly lower than that of water-soluble fraction. Research has shown that root exudates can lead to the dissolution of soluble organic matter, thereby promoting the desorption of PAHs from soil around the rhizosphere area (Gao, Ren et al. 2010). Meanwhile, organic acids in root exudates can disrupt the microporous structure of soil. Therefore, root exudates are beneficial for improving the bioavailability of pollutants.

The proportions of four-ring PAHs Flua and Pyr in organically extractable form were higher than those of three-ring PAHs Phe and Ant in all soils. This may be because higher-ring PAHs are more adsorbed by soil particles or soil organic matter during soil aging. The three-ring PAHs are more volatile and soluble, and therefore less adsorbed in the soils than the 4-ringed compounds.

The proportions of water-soluble + acid-soluble fractions in soil were related to the soil pH. The content of these forms of PAHs in soil was ranked from low to high as GD < DL < NJJ < CQP < CQF. The overall trend was that with the increase of soil pH, the content of effective PAHs in soil decreases. The extractable PAHs (water-soluble + acid-soluble + organically bound fractions) in soil were positively correlated with soil TOC (except DL), NJJ < GD < CQP < NJQ < CQF. Among them, the organic extractable PAHs in soil NJQ and CQF soils increased significantly, which may be due to their higher organic matter content than other soils, and the PAHs adsorbed on the organic matter during the aging process were extracted. The soil DL has the highest organic matter content, but its extractable PAHs were low. Soil texture could also be a reason that PAHs were more easily lost during the aging process in sandy soil. Therefore, the results of this experiment indicate that the distribution of PAHs in soil was affected by multiple factors, such as compound properties, soil pH, TOC, and soil texture.

Table 6.4 Percentage of different fractions of PAHs in the six soils (%)

Soil	Fractions	Phe	Ant	Flua	Pyr
CQF	W	0.9	1.3	1.1	1.1
	A	0.5	0.2	0.8	0.7
	O	40.6	59.1	60.1	64.2
	V & R	57.9	39.4	38.0	34.0
CQP	W	0.1	0.1	0.1	0.1
	A	0.1	0.1	0.1	0.1
	O	6.3	3.3	23.7	14.8
	V & R	93.6	96.5	76.1	85.1
DL	W	0.1	0.1	0.1	0.1
	A	0.1	0.1	0.0	0.0
	O	3.1	3.4	4.5	4.7
	V & R	96.7	96.4	95.3	95.2
GD	W	0.0	0.1	0.0	0.0
	A	0.1	0.1	0.0	0.0
	O	2.6	3.7	3.5	3.6
	V & R	97.3	96.1	96.4	96.4
NJJ	W	0.1	0.1	0.1	0.1
	A	0.1	0.1	0.0	0.1
	O	1.1	0.6	2.3	4.5
	V & R	98.8	99.2	97.5	95.3
NJQ	W	0.1	0.2	0.5	0.5
	A	0.2	0.1	0.4	0.4
	O	20.5	43.6	60.6	57.3
	V & R	79.3	56.1	38.5	41.9

W - water-soluble fraction, A - acid-soluble fraction, O - organically bound fraction and V & R - volatilization, degradation and residual fraction.

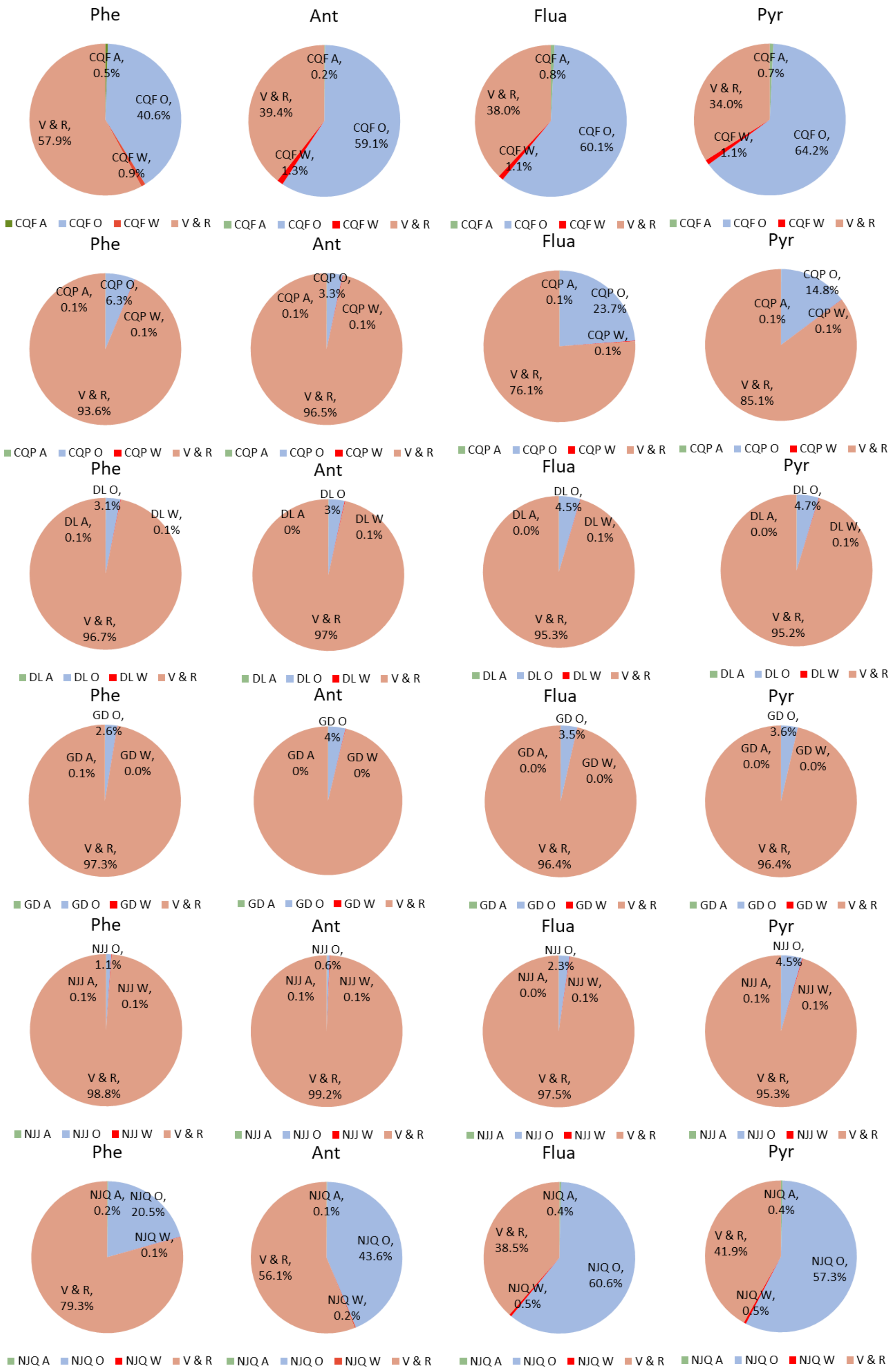


Fig. 6.1 Fraction distribution of 4 different PAHs in 6 soils. Each row presents the 4 PAHs in one soil. The former part of the label is the key representing each soil and the latter part is the key for the sequential extraction fraction, as follows: A = acid-soluble fraction, O = organically bound

fraction, W = water-soluble fraction and V&R = volatilization, degradation and residual fraction (see Table 6.4 for details).

6.3.2 DGT measured concentrations, soil solution concentrations and R values

Before planting, the concentrations of PAHs measured by DGT (C_{DGT}) were similar for most of the soils (see Fig. 6.2). For example, the C_{DGT} only varied between 0.48-0.63 μg L^{-1} for Phe, 0.20-0.25 μg L^{-1} for Ant, 0.24-0.50 μg L^{-1} for Flua and 0.19-0.23 μg L^{-1} for Pyr, respectively.

There were some differences between the C_{DGT} concentrations before and after crop growth in different crops (see Fig. 6.2 and Table 6.5). Results in Table 6.5 showed the average percentage of the reduction in DGT measurements before and after crop planting to the DGT measurements before planting. In each case, concentrations after crop growth were much lower than at the beginning of the experiment. For the reduction measured by DGT before and after planting, soils with lettuce and radish showed similar proportions. This is probably because they had the same growing and cultivation times for both crops. Maize showed a different behavior, with less reduction in measured Phe and Pyr than the other two plants, and little difference for Flua. Ant, which measured by DGT, was significantly lower after maize cultivation than the other two plants, even though the growing time for maize was less than the other two crops. Several factors can influence the difference in C_{DGT} concentrations before and after crop growth, for example, losses by degradation, volatilization, leaching and photo-degradation, uptake by the plants and changes in the form/distribution of the PAH compounds during the experiments.

The R value is the ratio of labile PAHs concentration measured by DGT to PAHs concentration in soil solution. It reflects the depletion of soil solution concentration at the interface between DGT and soil, and is usually used to classify the ability of organic pollutants to resupply from the solid phase to the soil solution. The R values of 4 PAHs in 6 soils before and after planting are shown in Table 6.6. R values varied from 0.11 to 0.41 in all soils before planting, which was in the partially sustained case, indicating that PAHs in the soil are partially resupplied from solid phase to the soil solution. After planting, the R values ranged from 0.03 to 0.71. This mainly showed a decrease in the change of R for PAHs in most soils before and after crops planting, except Phe, which had an increase in R values.

The results showed that the effect of crops planting on the resupply of soil PAHs was obvious. For example, after maize planting, R was <0.1 for Pyr in most soils, indicating that there was no resupply from the solid phase to the soil solution, and the supply of PAHs was mainly from diffusion. After radish planting, the R values of Phe in soils DL, GD, NJJ and NJQ were 0.59-0.75, which was significantly increased, indicating that the solid phase resupply of Phe increased after planting. This effect may come from the production of rhizosphere exudates and biosurfactants produced by microbial activities during crops growth (Guo, Gong et al. 2017, Li, Możdżeń et al. 2021).

In general, the R value of Phe in soil was larger than that of the other three PAHs. This may be because Phe is less hydrophobic than the other three compounds and is more water soluble, so it is more readily distributed in the soil solution. More hydrophobic PAHs, such as Flua and Pyr, are more easily adsorbed on/in soil organic matter and are less readily re-supplied from the soil solid phase to the soil solution.

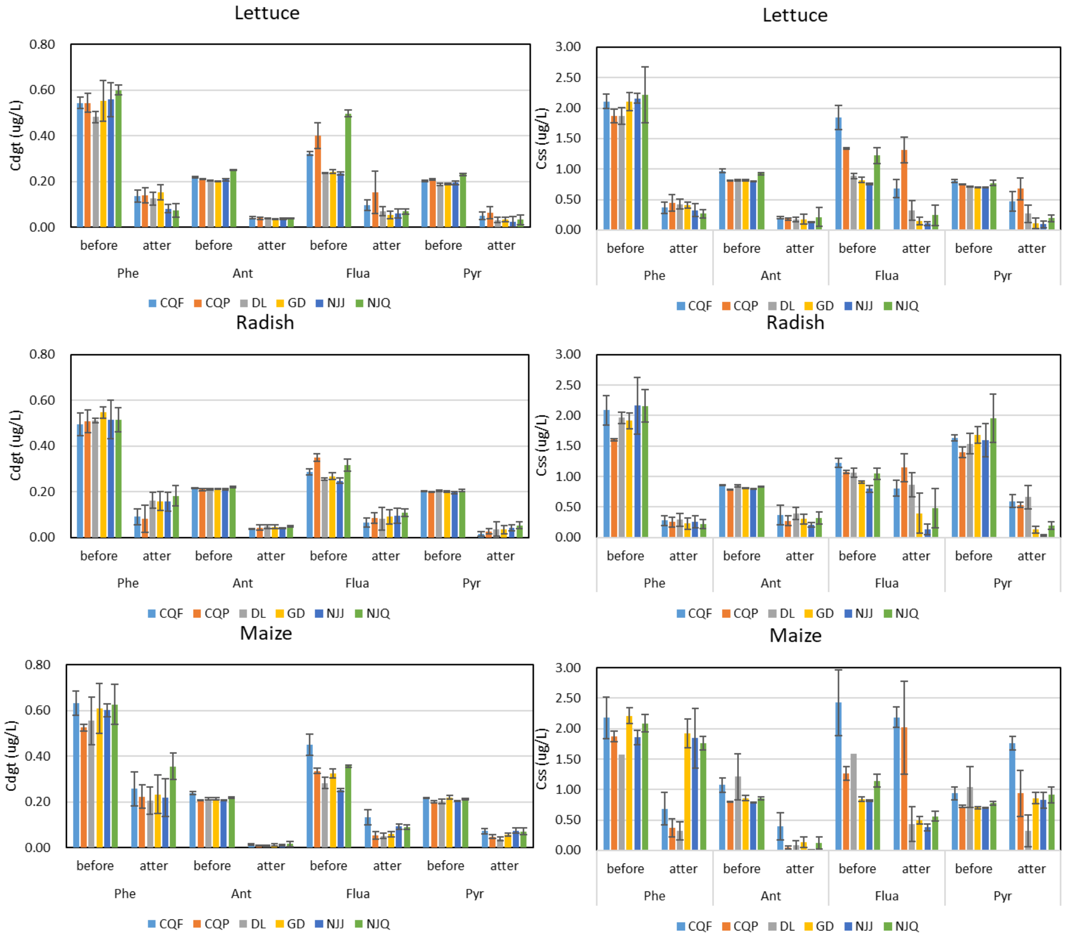


Fig. 6.2 DGT measured concentration and soil solution concentration of PAHs in 6 soils before and after planting. Error bars were calculated from the standard deviation (SD) for three replicates.

Table 6.5 The average percentage of the reduction in DGT measurements made before and after crop planting

Crop	Phe	Ant	Flua	Pyr
Lettuce	78.1%	82.1%	73.5%	80.4%
Radish	73.1%	79.4%	69.2%	82.6%
Maize	58.1%	94.8%	76.1%	71.3%

Table 6.6 R values calculated for the 4 PAHs in the 6 soils before and after planting 3 different crops.

Plant	Soil	Phe		Ant		Flua		Pyr	
		before	after	before	after	before	after	before	after
Lettuce	CQF	0.26	0.38	0.23	0.21	0.18	0.14	0.25	0.12
	CQP	0.30	0.28	0.17	0.24	0.30	0.11	0.19	0.08
	DL	0.26	0.30	0.25	0.22	0.27	0.25	0.26	0.14
	GD	0.26	0.38	0.25	0.22	0.30	0.43	0.27	0.35
	NJJ	0.26	0.25	0.26	0.30	0.31	0.44	0.28	0.37
	NJQ	0.28	0.36	0.27	0.21	0.41	0.33	0.30	0.17
Radish	CQF	0.24	0.24	0.26	0.11	0.24	0.08	0.12	0.03
	CQP	0.32	0.19	0.26	0.22	0.32	0.08	0.14	0.06
	DL	0.26	0.59	0.25	0.13	0.24	0.10	0.13	0.05
	GD	0.29	0.73	0.26	0.16	0.30	0.18	0.12	0.32
	NJJ	0.24	0.62	0.26	0.20	0.31	0.37	0.12	0.71
	NJQ	0.24	0.75	0.26	0.16	0.30	0.29	0.11	0.28
Maize	CQF	0.29	0.37	0.22	0.05	0.20	0.05	0.23	0.03
	CQP	0.28	0.64	0.26	0.24	0.27	0.03	0.28	0.06
	DL	0.22	0.61	0.19	0.06	0.12	0.08	0.21	0.07
	GD	0.28	0.11	0.25	0.09	0.39	0.12	0.31	0.07

NJJ	0.33	0.12	0.26	0.64	0.31	0.24	0.29	0.09
NJQ	0.27	0.19	0.26	0.13	0.31	0.70	0.28	0.37

Data in red are soils where the R increased after crop planting.

6.3.3 Uptake of PAHs by plants

6.3.3.1 Introductory remarks

There have been a number of studies previously on PAHs in plants. These have investigated the potential for uptake from the soil, via the root system and via soil-volatilisation to overlying air, then-shoot uptake (Simonich and Hites 1995, Smith and Jones 2000). There are also a number of studies which have shown that gas phase and particle-phase PAHs transfer to leaves via atmospheric deposition (Simonich and Hites 1995, Smith, Thomas et al. 2001). Other studies have investigated the potential within-plant movement of PAHs and their degradation by metabolism within the plant, or via photo-degradation on leaf surfaces/within leaf structures (Wild, Dent et al. 2005, Wild, Dent et al. 2006). In summary, these studies have shown: 1. Soil-root uptake is generally inefficient and slow; 2. translocation from root-shoot is inefficient and slow (Gao and Collins 2009); 3. Aerial deposition is the main pathway to the above-ground portion of plants, such that plant leaves have been used as biomonitors/indicators of airborne PAH levels (Simonich and Hites 1994, Smith, Green et al. 2001). 4. PAHs can be stored in the waxy cuticles/lipid portions of plants (Wild, Dent et al. 2004, Wild, Dent et al. 2006). All these observations are relevant to the experiments performed here. Even though the experiments were performed in a glasshouse, PAHs are ubiquitous in air and so air-shoot transfers will have occurred. The 3-ringed PAHs (Phe and Ant) used in this experiment exist in air primarily in the gas phase, while the 4-ringed PAHs (Fluo and Pyr) have gas-phase and particle-phase components (Smith, Green et al. 2001). The experiments used spiked soils, treated with 10 mg kg^{-1} of each compound, so the soil concentrations were elevated above the soil background level, to make it easier to detect any soil-plant transfers. However, these concentrations are still realistic of concentrations in contaminated field soils.

These points are made to give context to the experimental results and discussions presented below.

6.3.3.2 Uptake of PAHs by 3 different crop plants

The PAH concentrations in the three plants are shown in Fig. 6.3. Concentrations are presented on a dry weight basis to reduce the impact of plant biomass differences on results. The concentration ranges of Phe in the three plants in the six soils were as follows: lettuce (326-1206 μg kg^{-1}), radish (513-1933 μg kg^{-1}), maize (232-294 μg kg^{-1}). The concentrations for Ant were lettuce (11-36 μg kg^{-1}), radish (10-38 μg kg^{-1}), maize (27-52 μg kg^{-1}). The concentrations for Flua were lettuce (67-165 μg kg^{-1}), radish (151-465 μg kg^{-1}), maize (34-65 μg kg^{-1}). The concentrations for Pyr were lettuce (80-251 μg kg^{-1}), radish (94-307 μg kg^{-1}), maize (47-67 μg kg^{-1}). This is similar to the results of some field simulation experiments. In a sludge-contaminated field experiment, the mean (range) concentrations of 16 PAHs were 205 (130–359) μg kg^{-1} in experimental soils (Jia, Guo et al. 2021). The concentration of PAHs in various tissues of rice ranged from 50 to 705 μg kg^{-1} (Tao, Jiao et al. 2006).

In summary, Phe concentrations were generally much higher in the plants than the other 3 compounds. Phe is the most abundant PAH in air (Smith, Green et al. 2001). In addition to the potential differences in aerial uptake, this may also be because Phe is the most water soluble and its concentrations are higher in the soil water (see Fig.6.2).

There were differences in the uptake by the 3 crops. Radish absorbed more Phe, Flua and Pyr than lettuce and maize. Maize had more Ant than lettuce and radish. Lettuce absorbed Phe, Ant and Flua less than the other two crops, but uptake of Pyr was similar. Previous research has also shown big differences between plant species. This may be related to several factors, such as: leaf surface area and surface properties, for trapping airborne PAHs; the water content, lipid content, the specific surface area of the root system of the plant; the plant's age and growth rates (Gao and Zhu 2004, Arvanaghi, Aminfar et al. 2017). Ant is the most rapidly photodegraded PAH, especially on the surface of leafy plants (Wild, Dent et al. 2005). The larger leaf area and longer growth time (longer light exposure) of lettuce may result in lower Ant content compared to maize. Gao et al. found that the concentrations of Phe and Pyr in roots were not correlated with the water content in the roots, but had a significant positive correlation with the lipid content in the roots (Gao and Zhu 2004). Chiou et al. showed that roots with high water content were associated with highly water-soluble organic matter, and roots with high lipid content were the main storage reservoirs of organic chemicals with a low water solubility (Chiou, Sheng et al. 2001). Sometimes plant data are normalized to their lipid content, but that was not possible to do in this study, because of the low yields.

In a study on rice, it was found that lateral roots absorbed more PAHs than nodal roots (Jiao, Xu et al. 2007). In this experiment, although radish did not grow to the tuberous root stage and its biomass was lower than that of maize, it had many lateral roots, which may be a factor in its higher uptake of PAHs. Maize roots were mainly nodal roots, while the lettuce root system was not well developed.

Table 6.7 shows the lifetime carcinogenic risk of PAHs produced by human consumption of different crops. When the ILCR < 10^{-6}, there is no carcinogenic risk or the carcinogenic risk can be ignored. When the ILCR is in the range 10^{-6} - 10^{-4}, there is a low carcinogenic risk, while when the ILCR > 10-4, there is a higher carcinogenic risk. The results showed most PAHs in plants had low carcinogenic risk. However, consuming lettuce and radish had a higher low risk of carcinogenesis due to the presence of phenanthrene. Maize grown in soil CQF, CQP and DL contained more low carcinogenic risk due to the presence of Ant.

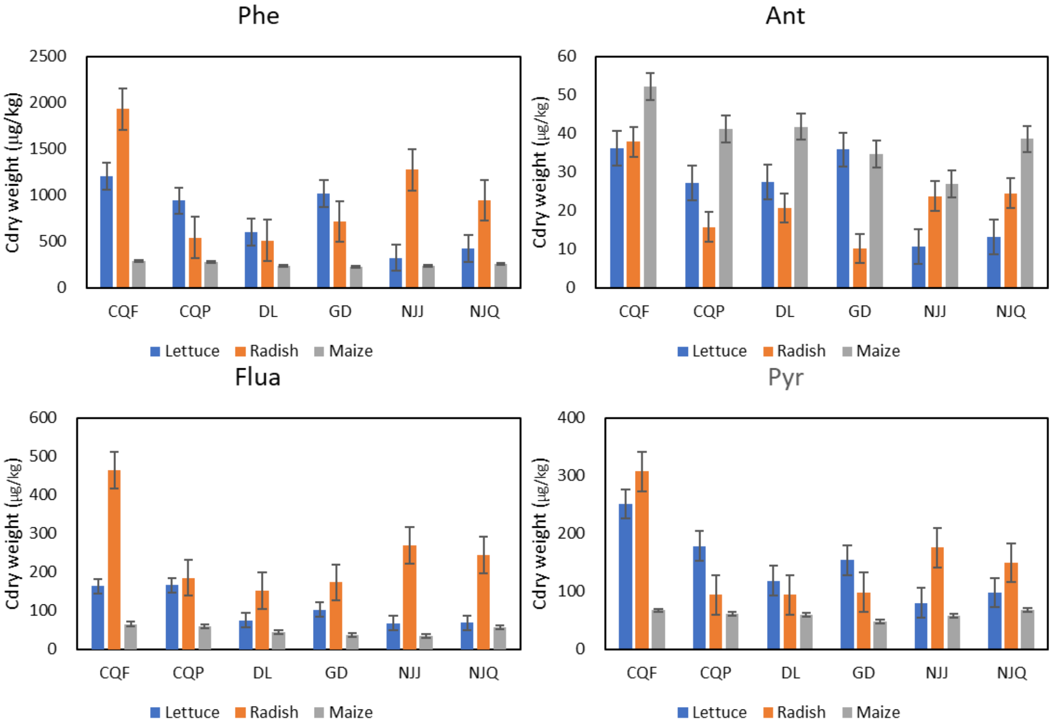


Fig. 6.3 PAHs in the 3 crops in 6 soils. Results are as dry weight. Error bars were calculated from the standard deviation (SD) for three replicates (all the concentrations presented here are for the whole plant of each crop).

Table 6.7 The incremental lifetime cancer risk (ILCR) of PAHs produced by people consuming different crops

Crop	Site	Chemical			
		Phe	Ant	Flua	Pyr
Lettuce	CQF	2.14E-05	6.43E-06	2.90E-06	4.46E-06
	CQP	1.67E-05	4.84E-06	2.94E-06	3.17E-06
	DL	1.07E-05	4.88E-06	1.34E-06	2.09E-06
	GD	1.80E-05	6.36E-06	1.81E-06	2.73E-06
	NJJ	5.77E-06	1.91E-06	1.19E-06	1.42E-06
	NJQ	7.56E-06	2.36E-06	1.21E-06	1.74E-06
Radish	CQF	3.43E-05	6.73E-06	8.25E-06	5.45E-06
	CQP	9.62E-06	2.80E-06	3.29E-06	1.67E-06
	DL	9.10E-06	3.68E-06	2.68E-06	1.67E-06
	GD	1.27E-05	1.82E-06	3.07E-06	1.74E-06
	NJJ	2.26E-05	4.23E-06	4.78E-06	3.11E-06
	NJQ	1.68E-05	4.36E-06	4.34E-06	2.65E-06
Maize	CQF	5.21E-06	9.28E-06	1.16E-06	1.19E-06
	CQP	4.88E-06	7.32E-06	1.06E-06	1.09E-06
	DL	4.28E-06	7.42E-06	7.81E-07	1.06E-06
	GD	4.11E-06	6.16E-06	6.39E-07	8.38E-07
	NJJ	4.23E-06	4.78E-06	6.00E-07	1.03E-06
	NJQ	4.56E-06	6.86E-06	1.01E-06	1.20E-06

6.3.3.3 Uptake of PAHs by different parts of maize

As noted above, different parts of plants take up PAHs differently. Only one of the crop plants – maize – yielded enough sample to be able to separate the roots and the shoots. As shown in Fig. 6.4, the accumulation of PAHs in maize roots was significantly higher than that in stems and leaves. Although effects of air absorption on plants in the previous section was mentioned, the PAHs accumulated in the roots were significantly higher than those in the above-ground parts of the plants. The light during plant growth may also affect the results by causing photodegradation of PAHs absorbed on the surface of maize.

Among the PAHs in the roots of maize, Phe has the highest concentration, about 4-10 times that of the other three compounds. Phe is more water-soluble than these three substances, so the higher concentration in the soil solution affects this result (see Fig. 6.2). However, the concentration of Phe in the soil solution was only about 2-3 times that of the other substances. Therefore, there are other factors that affect the absorption of different PAHs by roots. The resupply ability from soil solids to soil solution was different. This is similar to the results in the R value calculation in section 6.3.2. The R value of Phe increased after planting crops. In addition, the change of rhizosphere secretions during plant growth and the biosurfactants produced by microbial activities will also affect the concentration of PAHs in the soil or their bioavailability (Gao, Yang et al. 2011, Guo, Gong et al. 2017, Li, Możdżeń et al. 2021).

Although the concentrations in the aerial parts of maize were lower than those in the roots, the uptake of different PAHs showed similar results to those in the roots. The concentration of Phe was higher than that of other PAHs. This may be because Phe was most abundant in the air among these chemicals and leaves may absorb more Phe through the air-plant absorption.

This is consistent with the earlier discussion about the relatively efficient supply and trapping of PAHs from the air by the above-ground portion of the plant and is similar to previous research (Mattina, Lannucci-Berger et al. 2003). For wheat, the PAHs concentration in the root system was the highest at any growth stage (Tao, Jiao et al. 2006, Wang, Zhang et al. 2020). PAHs accumulate more in the roots of amaranth than in other parts (Wang, Zhang et al. 2017). At the same time, the absorption of plant had a significant correlation with soil concentration (Gao and Zhu 2004, Li and Ma 2016).

In addition, some research used the transport factors (TF, the ratio of PAHs above-ground concentration to root concentration) to evaluate their ability to transport from roots to aboveground parts in plants (Li and Ma 2016, Sushkova, Minkina et al. 2020). However, this is inappropriate for PAHs because PAHs are semi-volatile substances. The shoots are efficiently contaminated by trapping and retaining airborne compounds, not just by the translocation of compounds which have been taken up by root systems from the soil (Simonich and Hites 1994, Smith, Green et al. 2001). This method may be more suitable for the transfer of non-volatile organic chemicals or heavy metals.

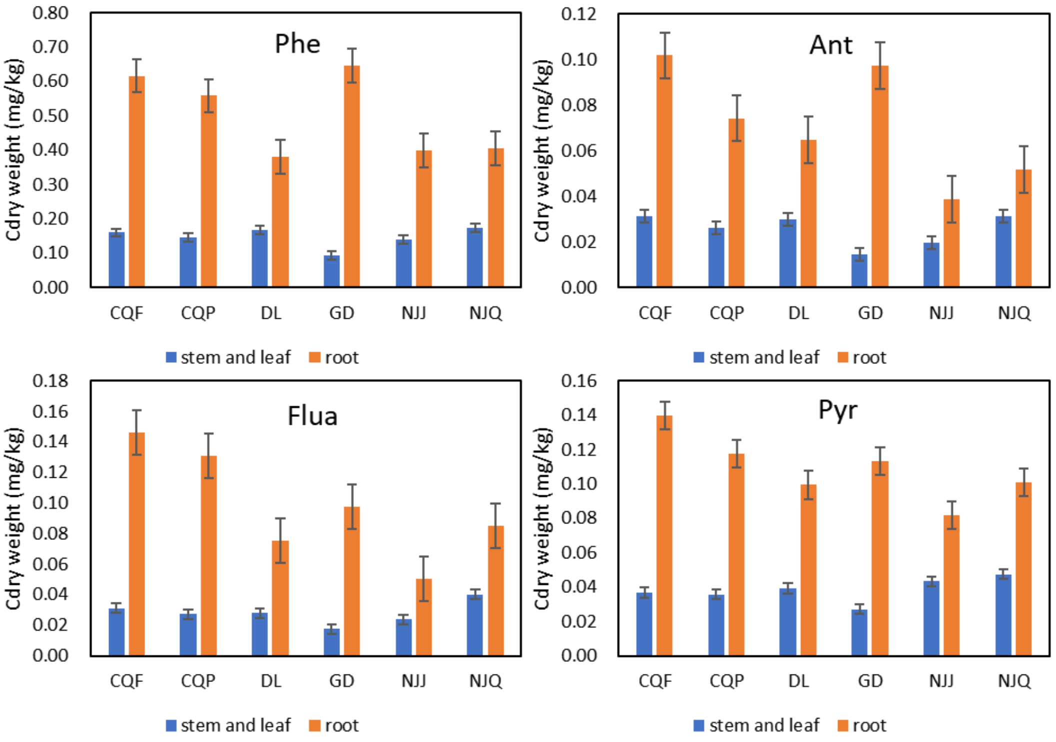


Fig. 6.4 PAHs in the above ground parts - stem and leaf combined, and the roots of maize. Error bars were calculated from the standard deviation (SD) for three replicates.

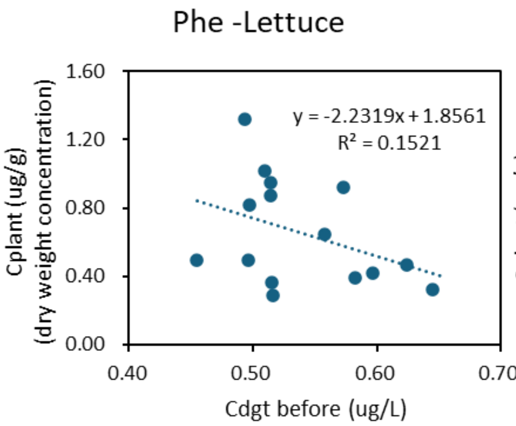
6.3.4 Comparison of soil-borne PAHs to the PAHs in crop plants

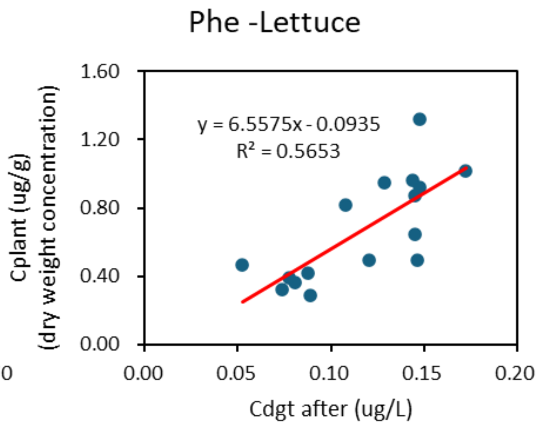
As has been made clear from the previous sections, examining the relationship between PAHs in the soil and the crop plants is complicated by several factors, with air-plant transfers a very important confounding factor. Nonetheless, in the study, a lot of information was obtained about the 4 PAHs in different soils, determined in different forms with different extractants. So it is appropriate to explore further the question of bioavailability and supply of PAHs from the soils to the crop plants.

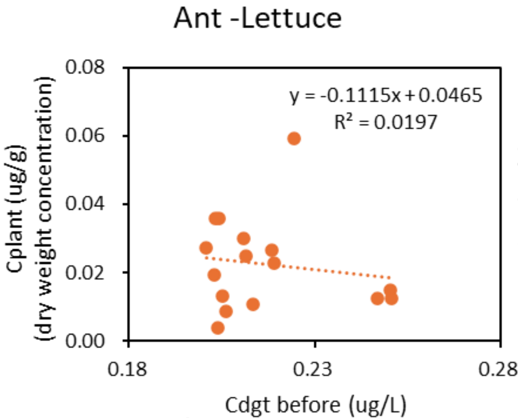
6.3.4.1 Comparison of PAHs speciation in soils and uptake in lettuce

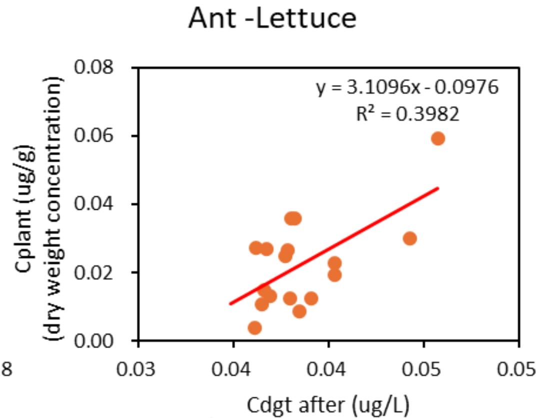
This study attempted to determine the bioavailable PAHs in soil by using DGT, soil solution extraction, and chemical extraction methods. The concentration range of PAHs in soil solution before and after lettuce planting were: Phe (0.22-2.74 μg L^{-1}), Ant (0.12-0.99 μg L^{-1}), Flua (0.08-1.98 μg L^{-1}), Pyr (0.05-0.83 μg L^{-1}). Wu et al. indicated that water-soluble fraction and acid-soluble fraction PAHs obtained from sequential extraction methods could be used for the prediction of bioavailability of PAHs (Wu and Zhu 2016). These two fractions were therefore combined as bioavailable PAHs. The range of PAHs concentration extracted sequentially before and after lettuce planting were: Phe (4.19-128.21 μg L^{-1}), Ant (4.46-46.13 μg L^{-1}), Flua (2.22-100.33 μg L^{-1}), Pyr (1.94-110.12μg L^{-1}). The DGT measured PAHs ranged as follows: Phe (0.05-0.66 μg L^{-1}), Ant (0.03-0.25 μg L^{-1}), Flua (0.04-0.51 μg L^{-1}), Pyr (0.01-0.23 μg L^{-1}). The content of PAHs extracted by chemical extraction method was significantly higher than that extracted as soil solution and by the DGT method, which is similar to the results of other studies (Chen, Jones et al. 2014). This indicates that the ability of chemical extraction method to extract PAHs is stronger, and there may be an overestimation of its bioavailability. The PAHs in soil solution were slightly higher than those measured by DGT, indicating the resupply ability of soil solid to soil solution.

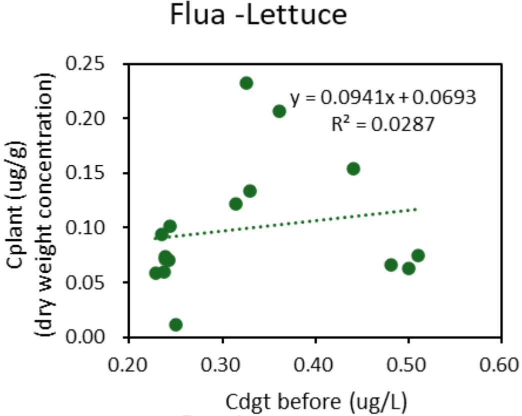
To compare methods for extracting bioavailable PAHs, linear regression analysis was conducted on the PAH concentration in lettuce plants and the different soils methods. Correlation analysis was conducted on the relationship between plant dry weight concentration and concentration extracted by different methods, with $p<0.05$ considered a significant correlation between the two methods. The results are shown in Fig. 6.5-6.8. The results showed that the extraction data obtained after planting generally had a better correlation with PAHs in lettuce than the data obtained for the soils before planting. The DGT r^2 values ranged between 0.26 - 0.57 and the sequential extraction r^2 ranged between 0.48 - 0.66 for the four PAHs. There was no correlation between Ant in soil solution and in plants ($r^2=0.01$), but there was a correlation with the other three PAHs (r^2 ranged 0.31 to 0.61). Chemical extraction was slightly better than DGT in correlating with lettuce concentrations, and both were more effective than soil solutions.

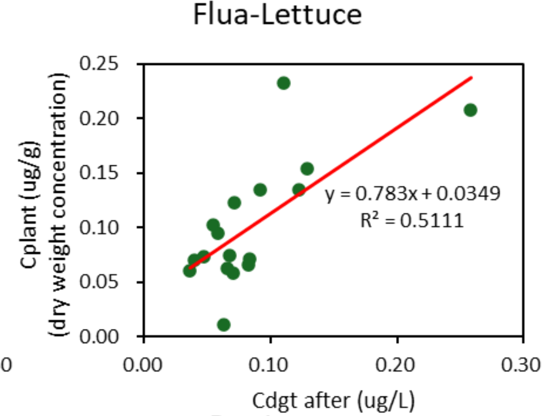

Phe -Lettuce
y = -2.2319x + 1.8561
R² = 0.1521
Cplant (ug/g)
(dry weight concentration)
0.00
0.40
0.80
1.20
1.60
0.40
0.50
0.60
0.70
Cdgt before (ug/L)

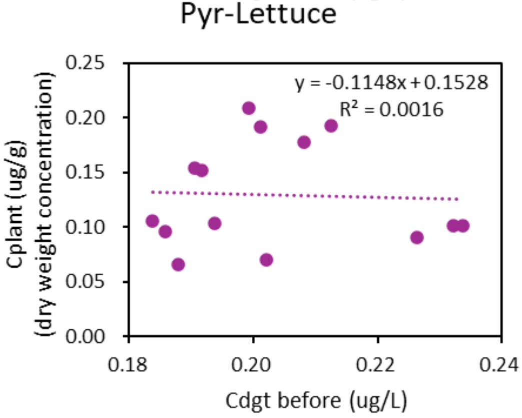

Phe -Lettuce
y = 6.5575x - 0.0935
R² = 0.5653
Cplant (ug/g)
(dry weight concentration)
0.00
0.40
0.80
1.20
1.60
0.00
0.05
0.10
0.15
0.20
Cdgt after (ug/L)


Ant -Lettuce
y = -0.1115x + 0.0465
R² = 0.0197
Cplant (ug/g)
(dry weight concentration)
0.00
0.02
0.04
0.06
0.08
0.18
0.23
0.28
Cdgt before (ug/L)


Ant -Lettuce
y = 3.1096x - 0.0976
R² = 0.3982
Cplant (ug/g)
(dry weight concentration)
0.00
0.02
0.04
0.06
0.08
0.03
0.04
0.04
0.05
0.05
Cdgt after (ug/L)


Flua -Lettuce
y = 0.0941x + 0.0693
R² = 0.0287
Cplant (ug/g)
(dry weight concentration)
0.00
0.05
0.10
0.15
0.20
0.25
0.20
0.30
0.40
0.50
0.60
Cdgt before (ug/L)


Flua-Lettuce
y = 0.783x + 0.0349
R² = 0.5111
Cplant (ug/g)
(dry weight concentration)
0.00
0.05
0.10
0.15
0.20
0.25
0.00
0.10
0.20
0.30
Cdgt after (ug/L)


Pyr-Lettuce
y = -0.1148x + 0.1528
R² = 0.0016
Cplant (ug/g)
(dry weight concentration)
0.00
0.05
0.10
0.15
0.20
0.25
0.18
0.20
0.22
0.24
Cdgt before (ug/L)

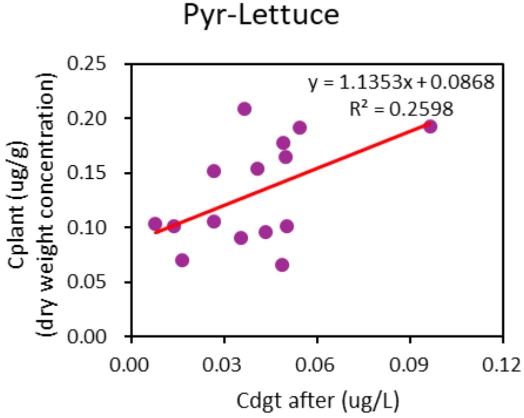
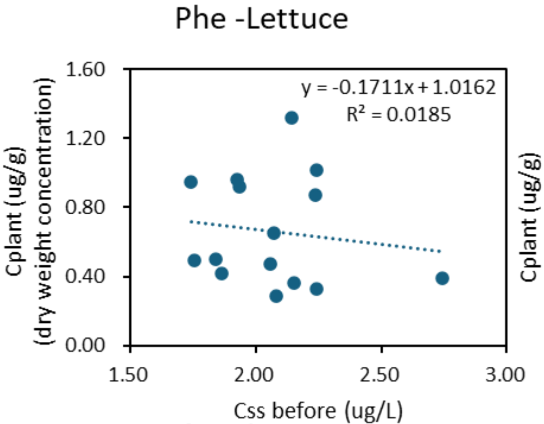
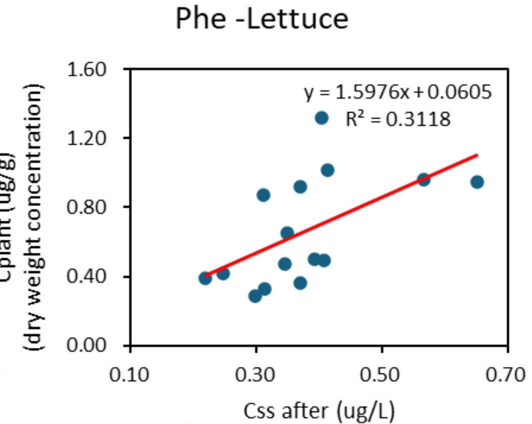
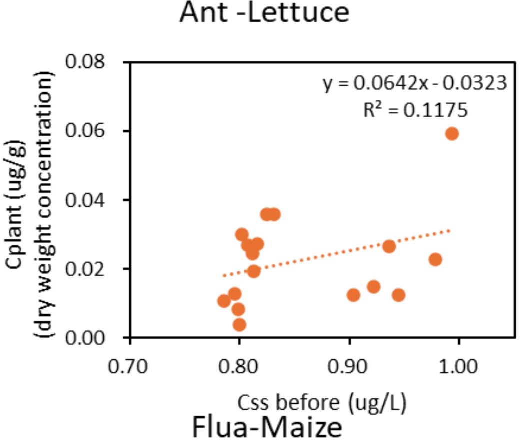
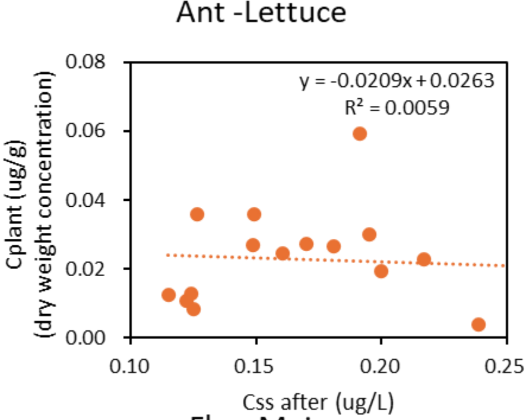

Pyr-Lettuce
y = 1.1353x + 0.0868
R² = 0.2598
Cplant (ug/g)
(dry weight concentration)
0.00
0.05
0.10
0.15
0.20
0.25
0.00
0.03
0.06
0.09
0.12
Cdgt after (ug/L)

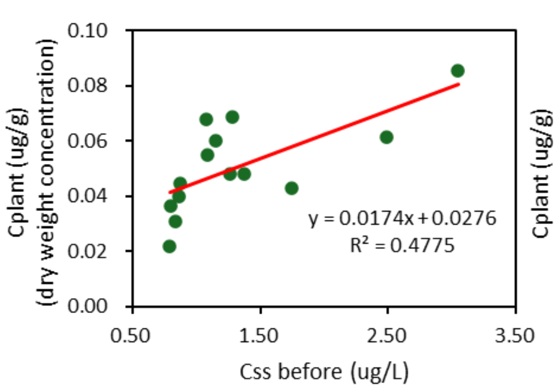
Fig. 6.5 The relationship between plant concentrations and DGT measured soil PAHs before and after lettuce planting (the red solid line indicates a significant correlation between the two sets of data at 0.05 level, $p < 0.05$).

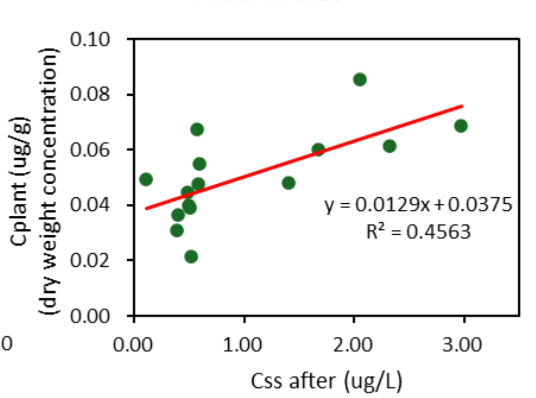

Phe -Lettuce
y = -0.1711x + 1.0162
R² = 0.0185
Cplant (ug/g)
(dry weight concentration)
1.60
1.20
0.80
0.40
0.00
1.50
2.00
2.50
3.00
Css before (ug/L)

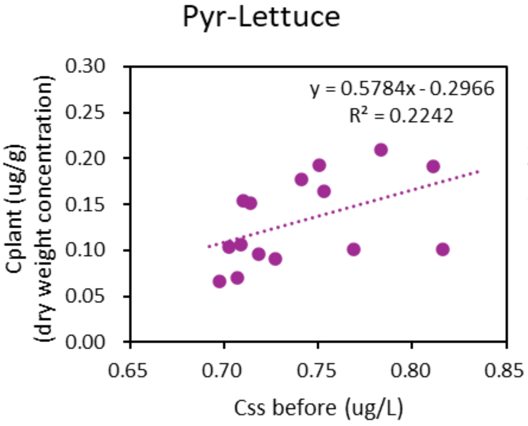

Phe -Lettuce
y = 1.5976x + 0.0605
R² = 0.3118
Cplant (ug/g)
(dry weight concentration)
1.60
1.20
0.80
0.40
0.00
0.10
0.30
0.50
0.70
Css after (ug/L)


Ant -Lettuce
y = 0.0642x - 0.0323
R² = 0.1175
Cplant (ug/g)
(dry weight concentration)
0.08
0.06
0.04
0.02
0.00
0.70
0.80
0.90
1.00
Css before (ug/L)


Ant -Lettuce
y = -0.0209x + 0.0263
R² = 0.0059
Cplant (ug/g)
(dry weight concentration)
0.08
0.06
0.04
0.02
0.00
0.10
0.15
0.20
0.25
Css after (ug/L)


Flua-Maize
y = 0.0174x + 0.0276
R² = 0.4775
Cplant (ug/g)
(dry weight concentration)
0.10
0.08
0.06
0.04
0.02
0.00
0.50
1.50
2.50
3.50
Css before (ug/L)


Flua-Maize
y = 0.0129x + 0.0375
R² = 0.4563
Cplant (ug/g)
(dry weight concentration)
0.10
0.08
0.06
0.04
0.02
0.00
0.00
1.00
2.00
3.00
Css after (ug/L)


Pyr-Lettuce
y = 0.5784x - 0.2966
R² = 0.2242
Cplant (ug/g)
(dry weight concentration)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.65
0.70
0.75
0.80
0.85
Css before (ug/L)

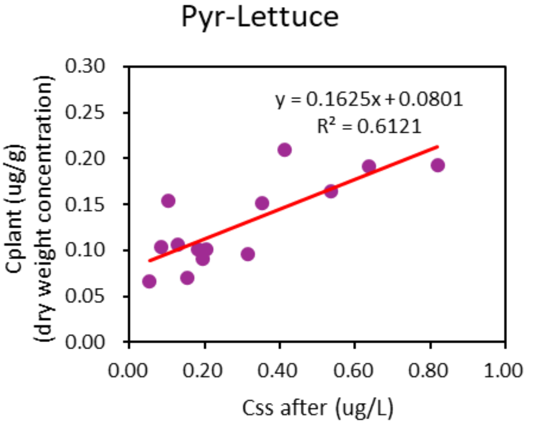

Pyr-Lettuce
y = 0.1625x + 0.0801
R² = 0.6121
Cplant (ug/g)
(dry weight concentration)
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0.00
0.20
0.40
0.60
0.80
1.00
Css after (ug/L)

Fig. 6.6 The relationship between plant PAHs concentrations and soil solution PAH concentrations before and after lettuce planting (the red solid line indicates a significant correlation between the two sets of data at the 0.05 level, p <0.05).

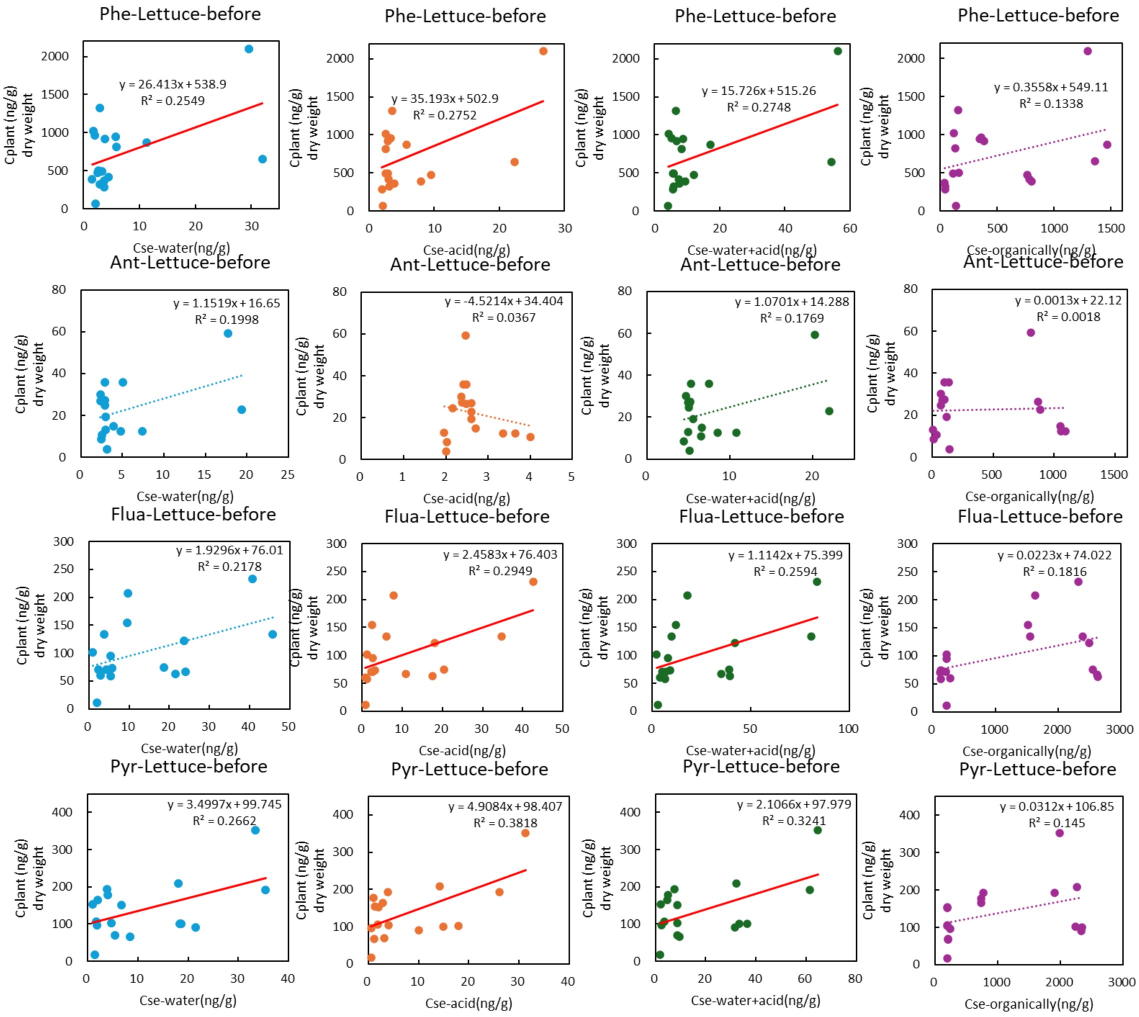


Fig. 6.7 The relationship between plant PAH concentrations and soil extraction concentrations before planting lettuce (blue is water-soluble fraction PAHs, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction PAHs, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at the 0.05 level, p <0.05).

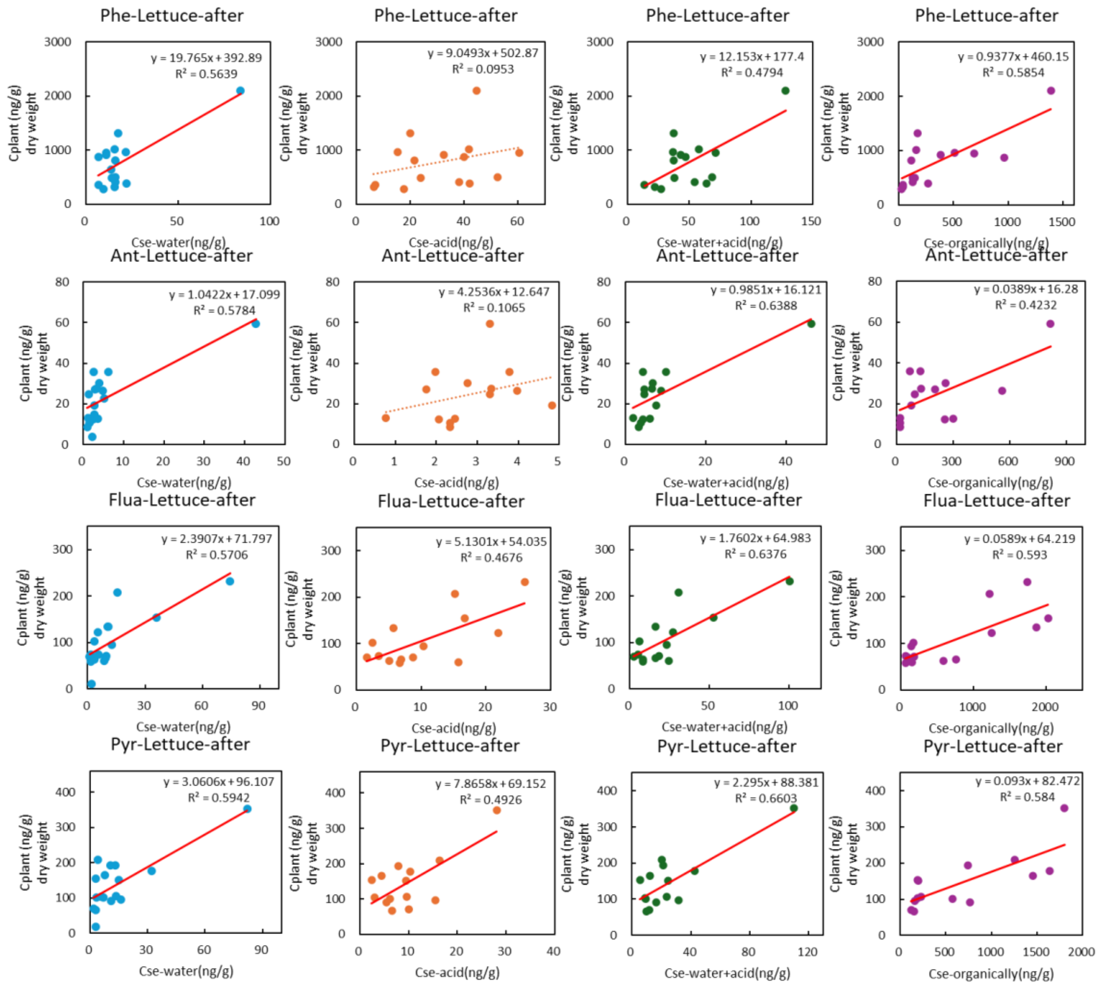


Fig. 6.8 The relationship between plant PAH concentrations and soil extraction concentrations after planting lettuce (blue is water-soluble fraction PAHs, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction PAHs, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at the 0.05 level, $p < 0.05$).

6.3.4.2 Comparison of PAHs speciation in soils and uptake in radish

The concentration range of PAHs in soil solution before and after radish planting were: Phe (0.17-2.70 µg L^{-1}), Ant (0.16-0.87 µg L^{-1}), Flua (0.07-1.28µg L^{-1}), Pyr (0.02-2.31 µg L^{-1}). The range of PAH concentrations extracted sequentially before and after lettuce planting were: Phe (4.19-47.3 µg L^{-1}), Ant (4.46-15.63 µg L^{-1}), Flua (2.22-103.78 µg L^{-1}), Pyr (1.94-119.0 µg L^{-1}). The DGT measured PAHs ranged as follows: Phe (0.06-0.61 µg L^{-1}), Ant (0.04-0.22 µg L^{-1}), Flua (0.05-0.36

μg L^{-1}), Pyr (0.01-0.21 μg L^{-1}).

Using the same data processing as lettuce and exploring the linear relationship between PAHs in plants and the three soil methods, the results are shown in Fig. 6.9-6.12. The chemical extraction method data before radish planting had a better performance than the other two methods (r^2 ranged 0.49 to 0.62). The concentration of soil solution had no relation to PAHs in radishes ($r^2<0.1$, except $r^2=0.15$ for Pyr). DGT measurements of PAHs after planting had a slight negative relationship with PAHs in radish, but this was not statistically significant (r^2 ranged 0.17 to 0.57, except Ant for 0.10).

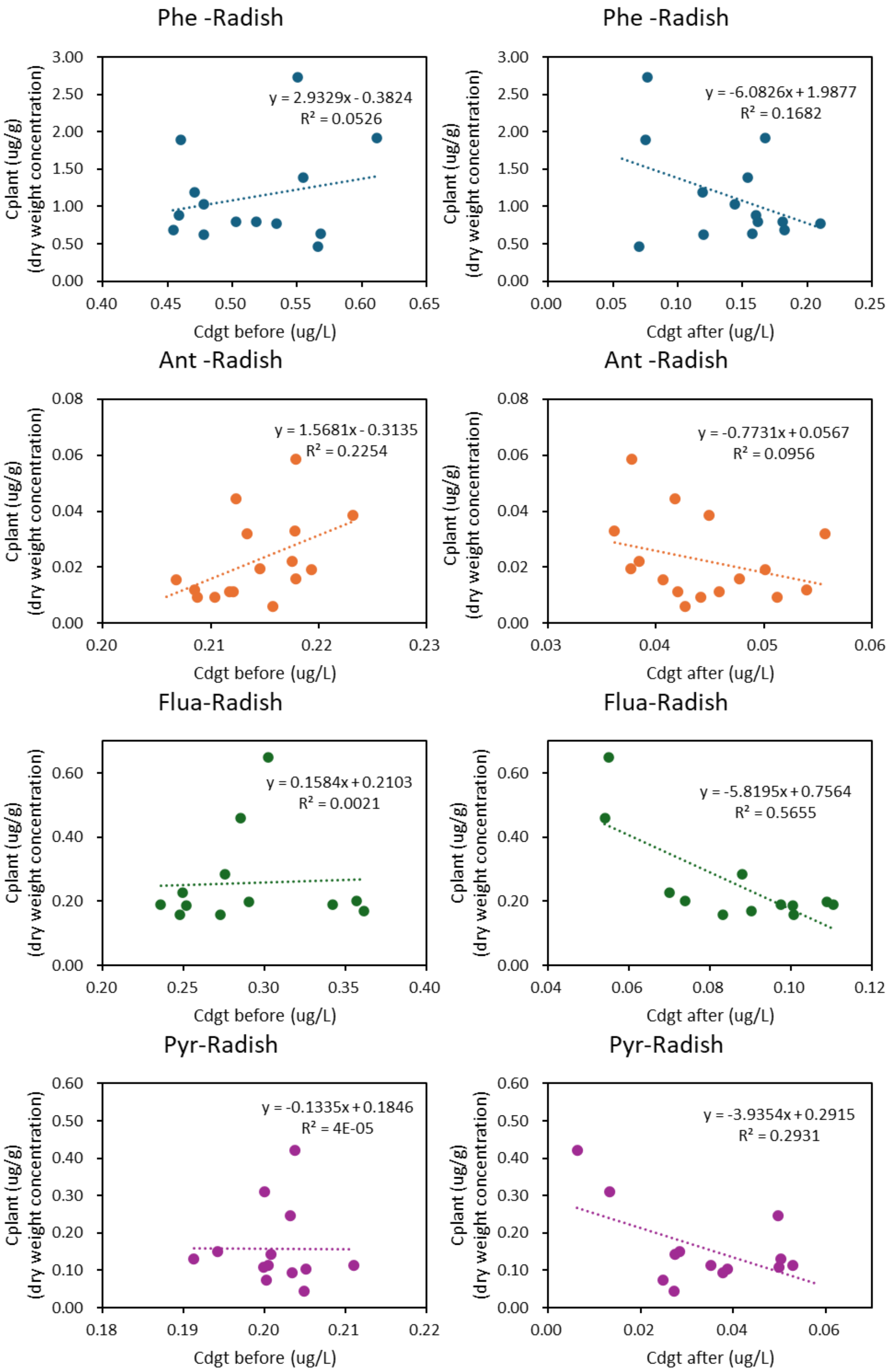


Fig. 6.9 The relationship between plant concentrations and DGT measured PAHs before and after radish planting

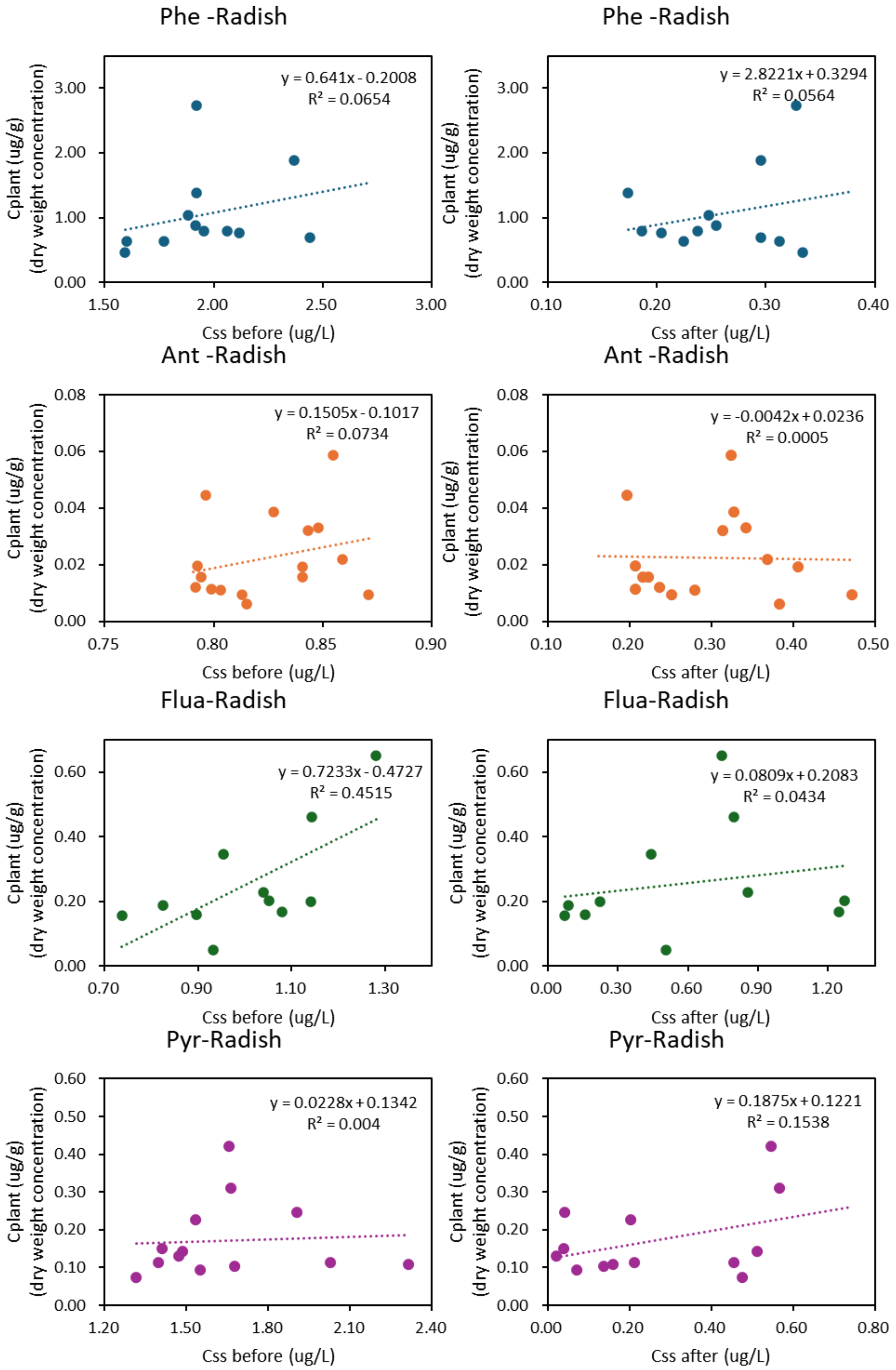


Fig. 6.10 The relationship between plant PAH concentrations and soil solution PAH concentrations before and after radish planting

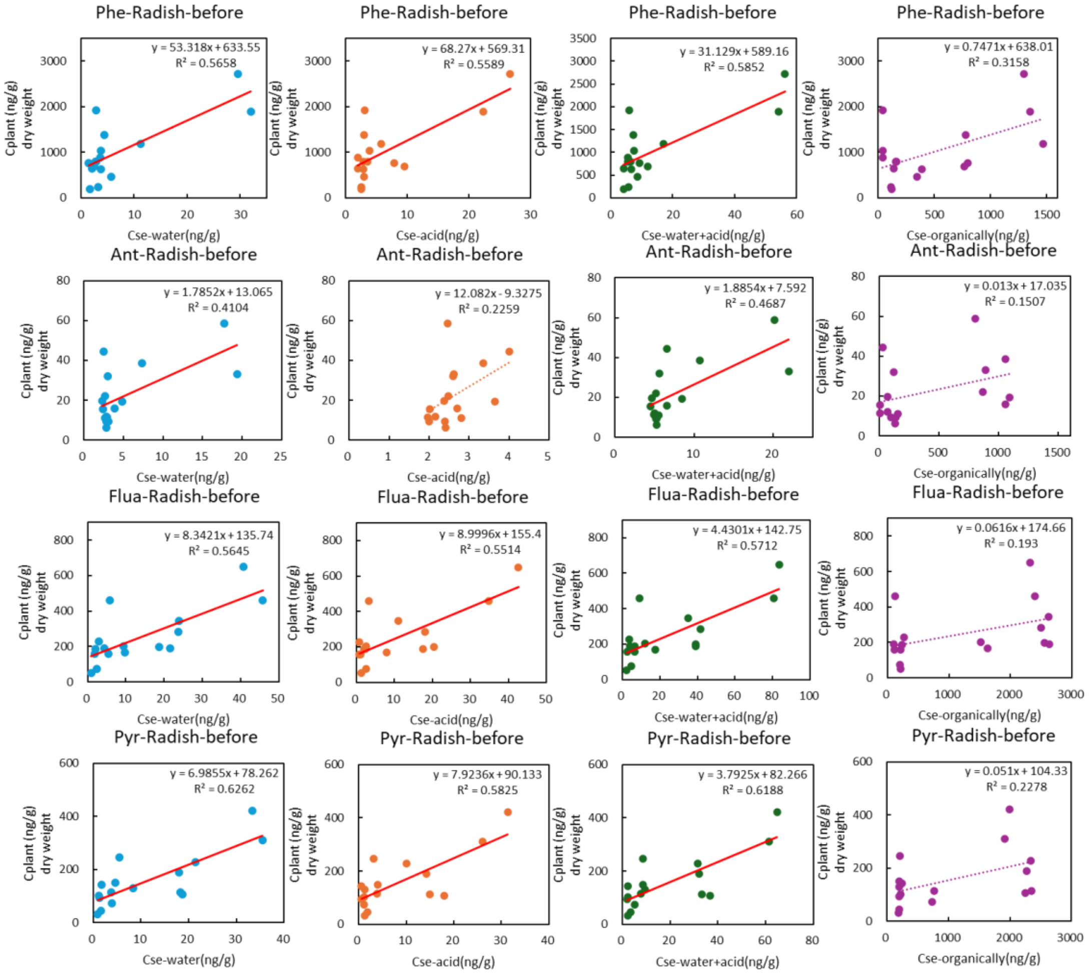


Fig. 6.11 The relationship between plant PAH concentrations and soil extraction PAH concentrations before radish planting (blue is water-soluble fraction, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0. 05 level, p <0.05).

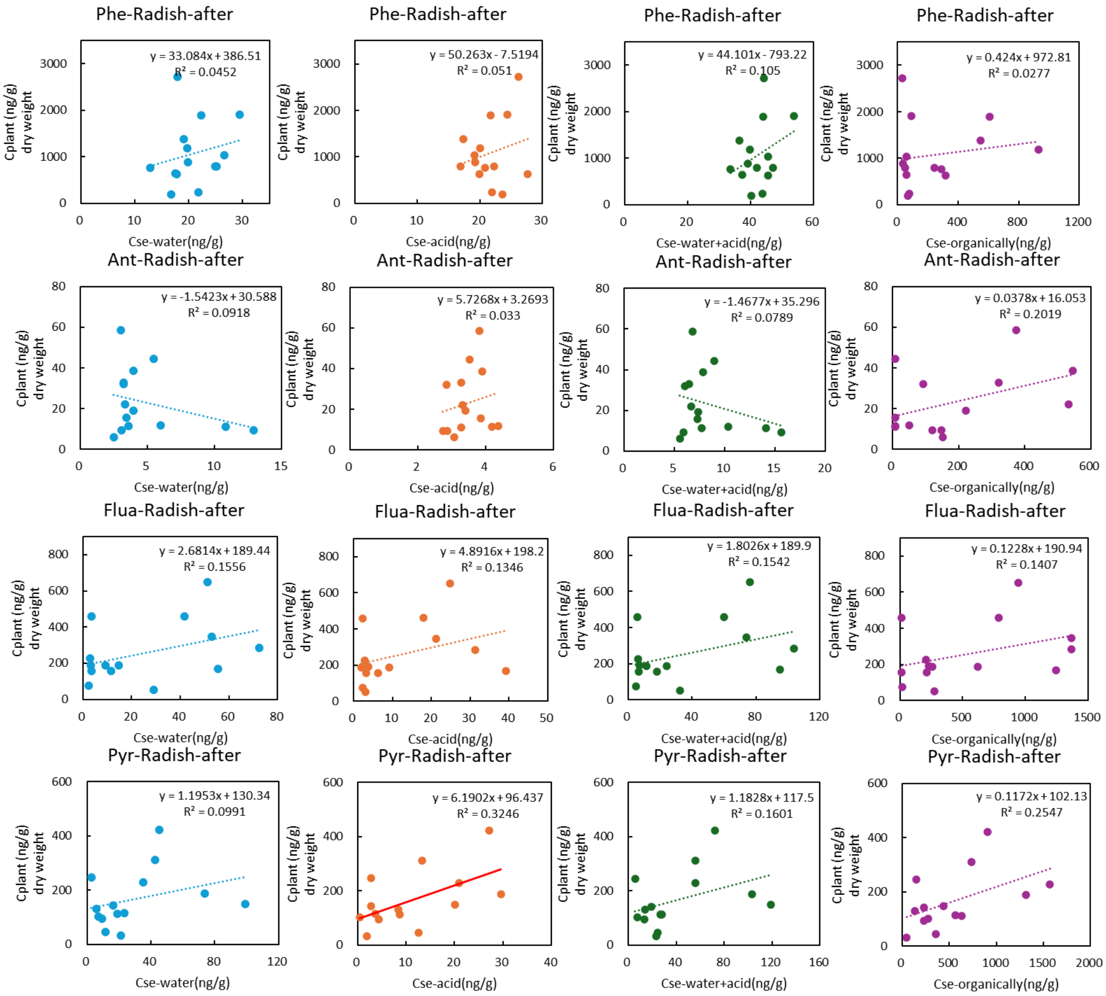


Fig. 6.12 The relationship between plant PAH concentrations and soil extraction PAH concentrations after radish planting (blue is water-soluble fraction, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0. 05 level, $p < 0.05$).

6.3.4.3 Comparison of PAHs speciation in soils and uptake in maize

The concentration range of PAHs in soil solution before and after radish planting were: Phe (0.23-3.45 μg L^{-1}), Ant (0.01-1.48 μg L^{-1}), Flua (0.11-3.04 μg L^{-1}) and Pyr (0.40-1.82 μg L^{-1}). The range of PAH concentrations extracted sequentially before and after lettuce planting were: Phe (4.17-44 μg L^{-1}), Ant (4.75-12.3 μg L^{-1}), Flua (2.77-113 μg L^{-1}) and Pyr (2.31-104 μg L^{-1}). The DGT measured PAHs ranged as follows: Phe (0.14-0.72 μg L^{-1}), Ant (0.01-0.21 μg L^{-1}), Flua (0.04-0.50

μg L^{-1}), Pyr (0.02-0.40 μg L^{-1}).

For maize, the results were shown in Fig 6.13-6.20. There was no obvious correlation between the three methods and PAHs in the plant. Only for maize uptake of Flua and Pyr were there correlations, with the chemical extraction methods with r^2 values from 0.46 to 0.61. These were not statistically significant.

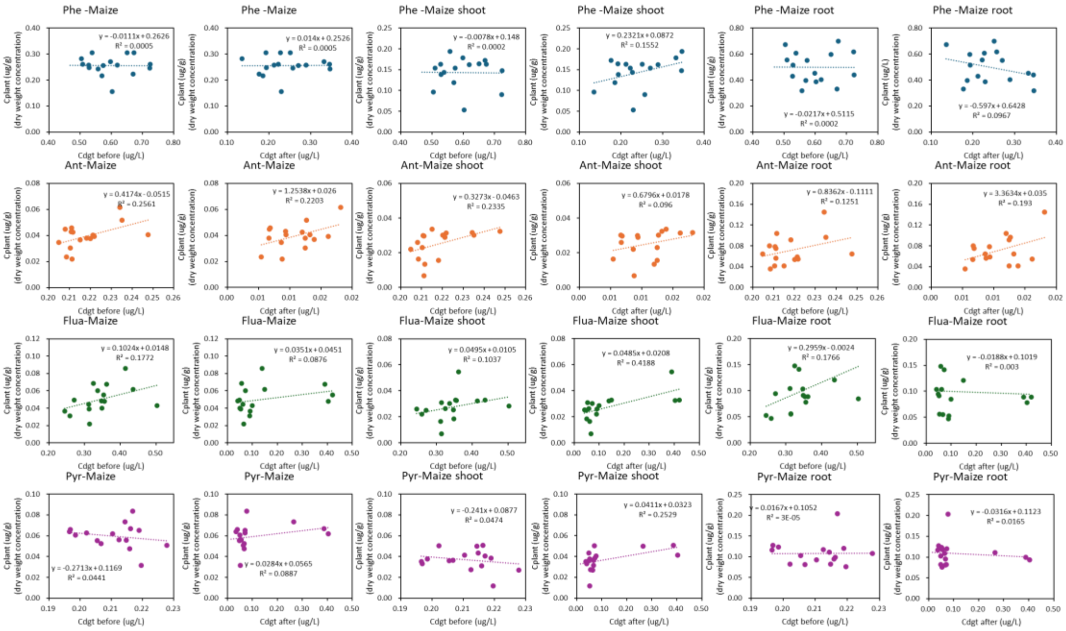


Fig. 6.13 The relationship between plant concentrations and DGT measured PAHs before and after planting maize (plant concentrations for 'Maize' are for the total plant, maize shoot and root are also plotted separately). None of the correlations were statistically significant.

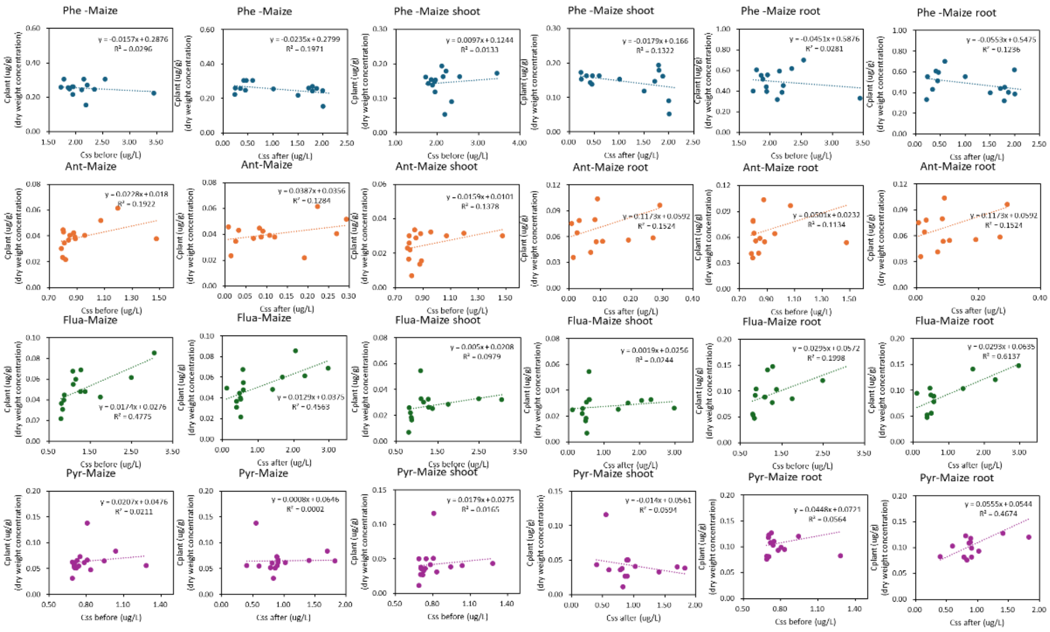


Fig. 6.14 The relationship between plant PAH concentrations and soil solution PAH concentrations before and after maize planting (plant extraction concentration was also divided into shoot and root fractions).

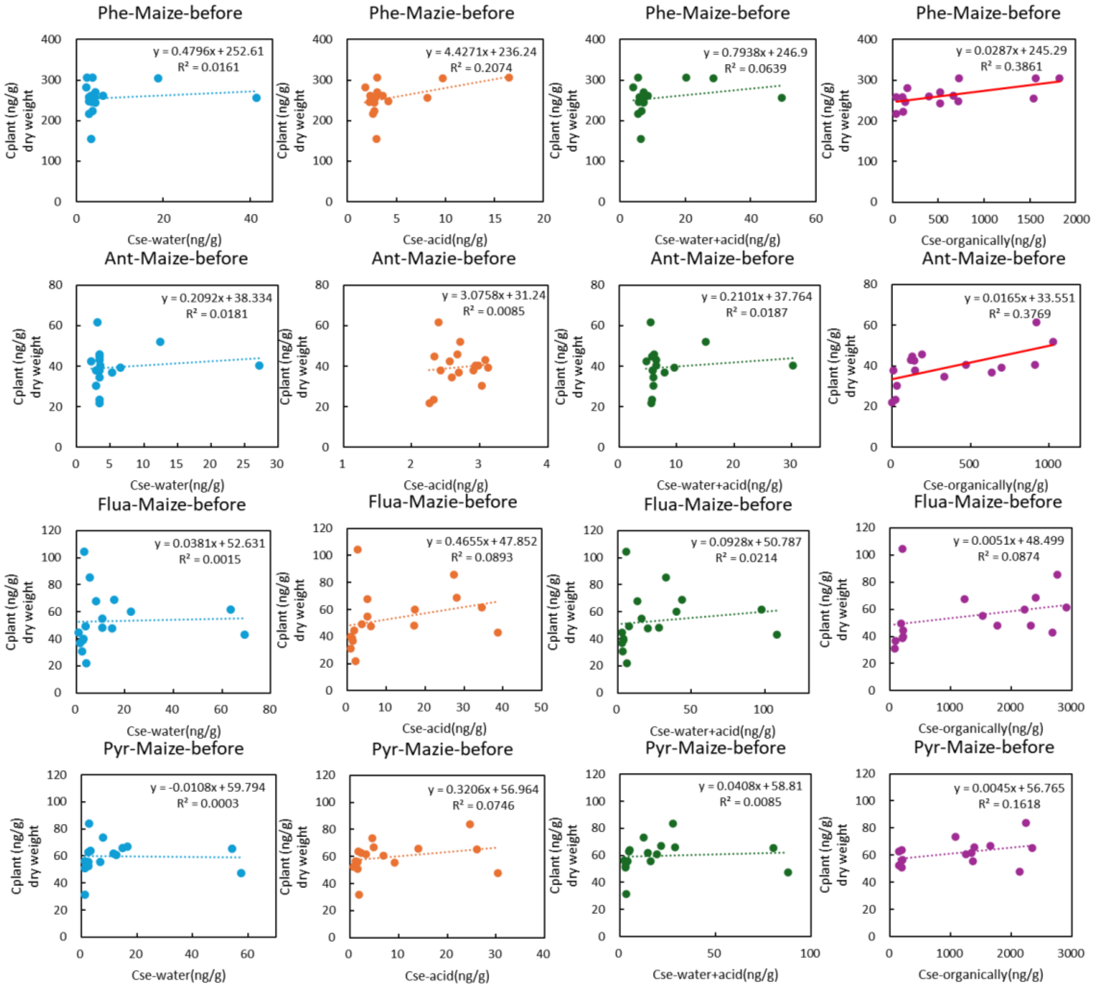


Fig. 6.15 The relationship between plant extraction PAHs concentrations (whole plant) and soil extraction concentration for different speciation of PAHs before planting maize (blue is water-soluble fraction, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0.05 level, $p < 0.05$).

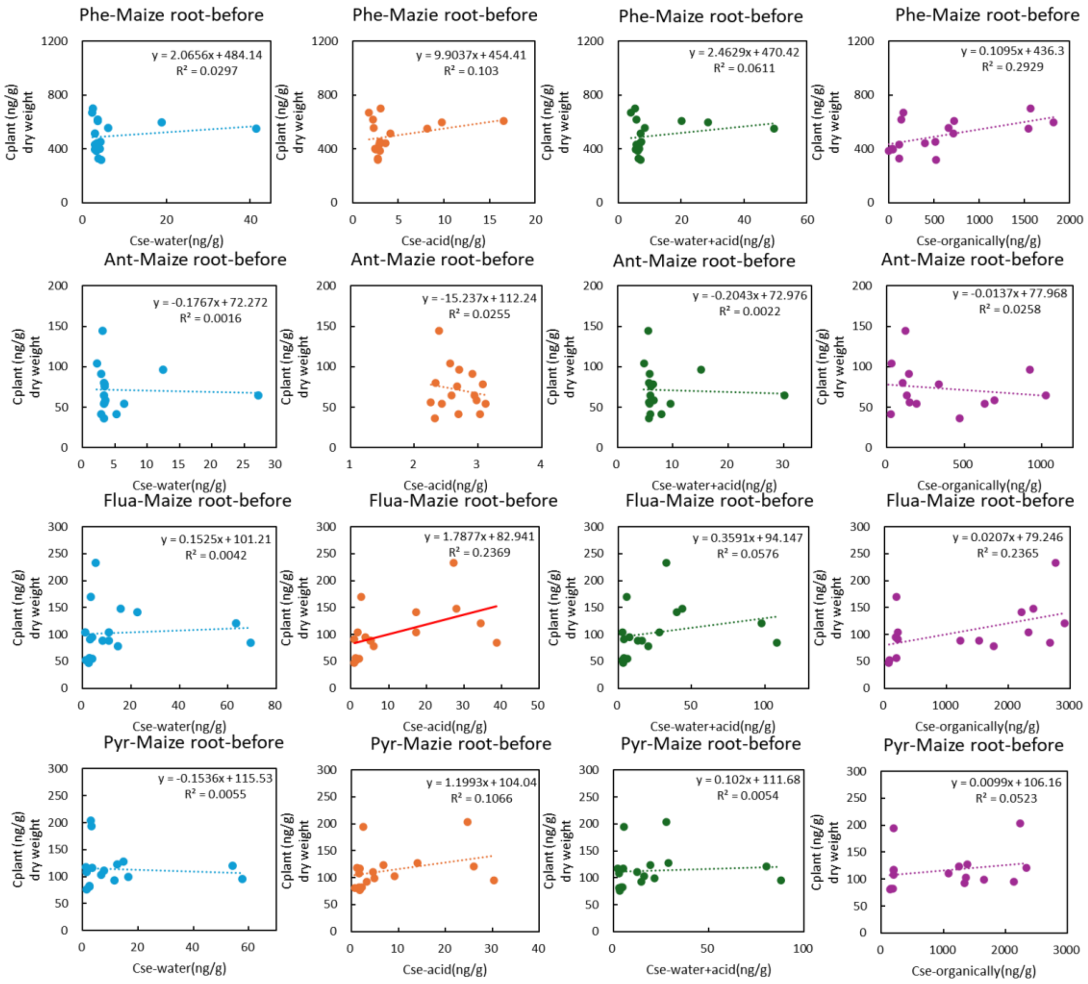


Fig. 6.16 The relationship between plant extraction PAHs concentrations (maize shoot) and soil extraction concentration for different speciation of PAHs before planting maize (blue is water-soluble fraction, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0.05 level, $p < 0.05$).

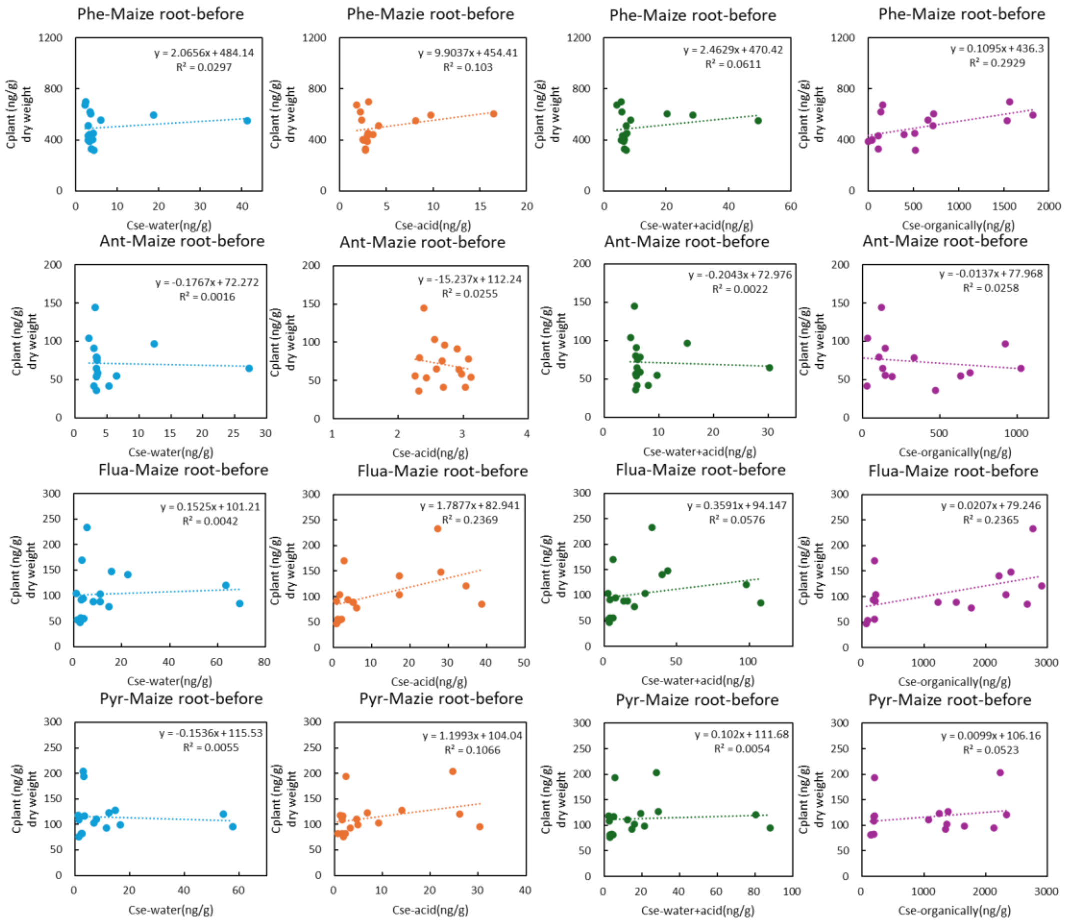


Fig. 6.17 The relationship between plant PAH concentrations (maize root) and soil extraction PAH concentrations before planting maize (blue is water-soluble fraction PAHs, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction PAHs, purple is the residue-fraction).

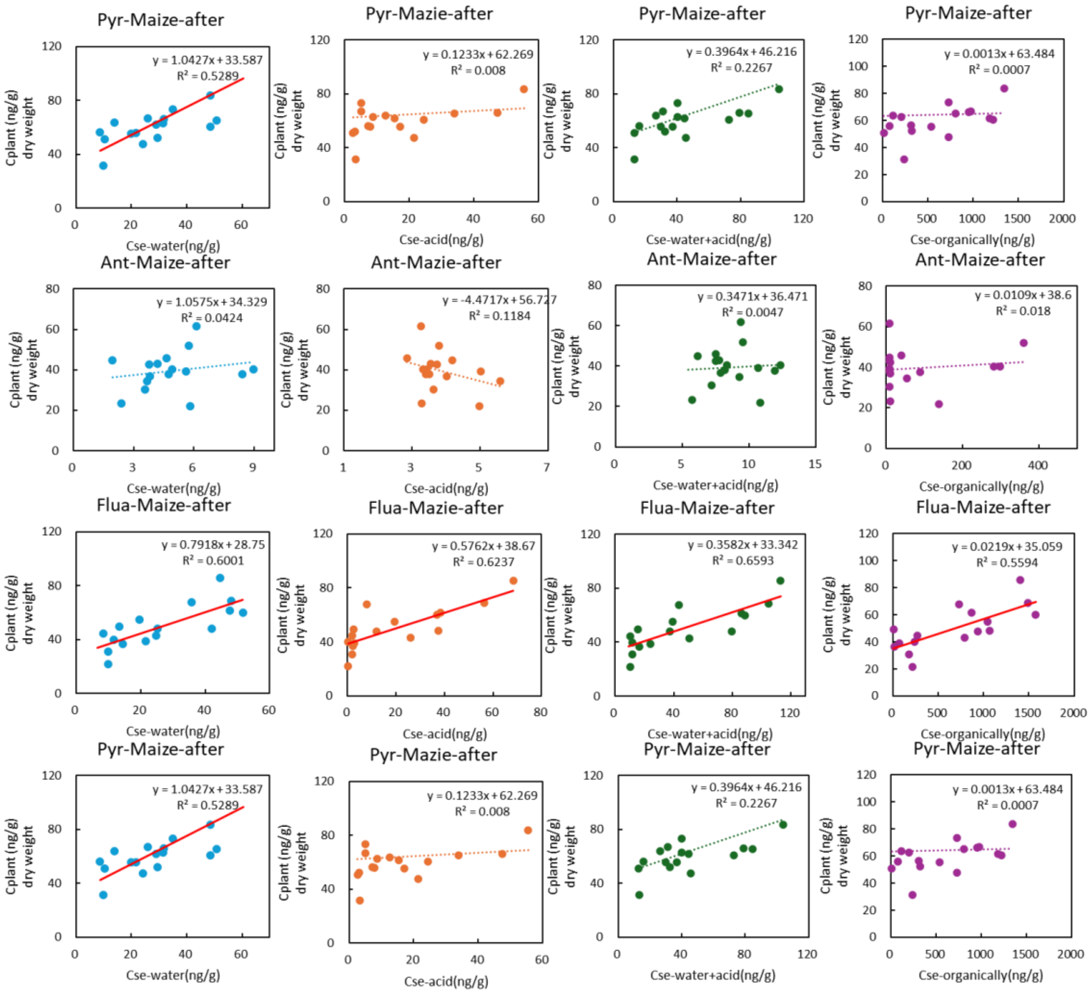


Fig. 6.18 The relationship between plant PAH concentrations (whole plant) and soil extraction concentration after planting maize (blue is water-soluble fraction PAHs in plant, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction PAHs, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0.05 level, $p < 0.05$).

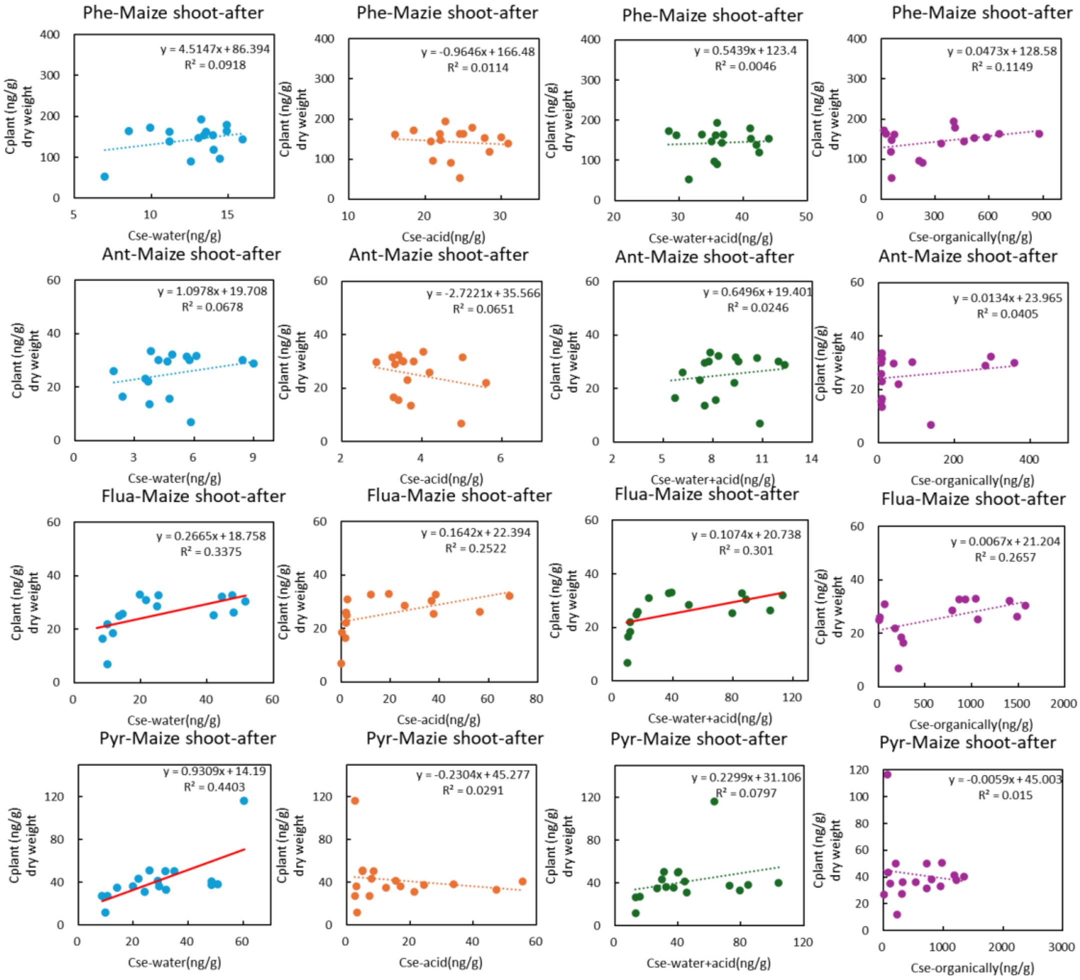


Fig. 6.19 The relationship between plant PAH concentrations (maize shoot) and soil extraction PAH concentrations after planting maize (blue is water-soluble fraction, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction PAHs, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0.05 level, p <0.05).

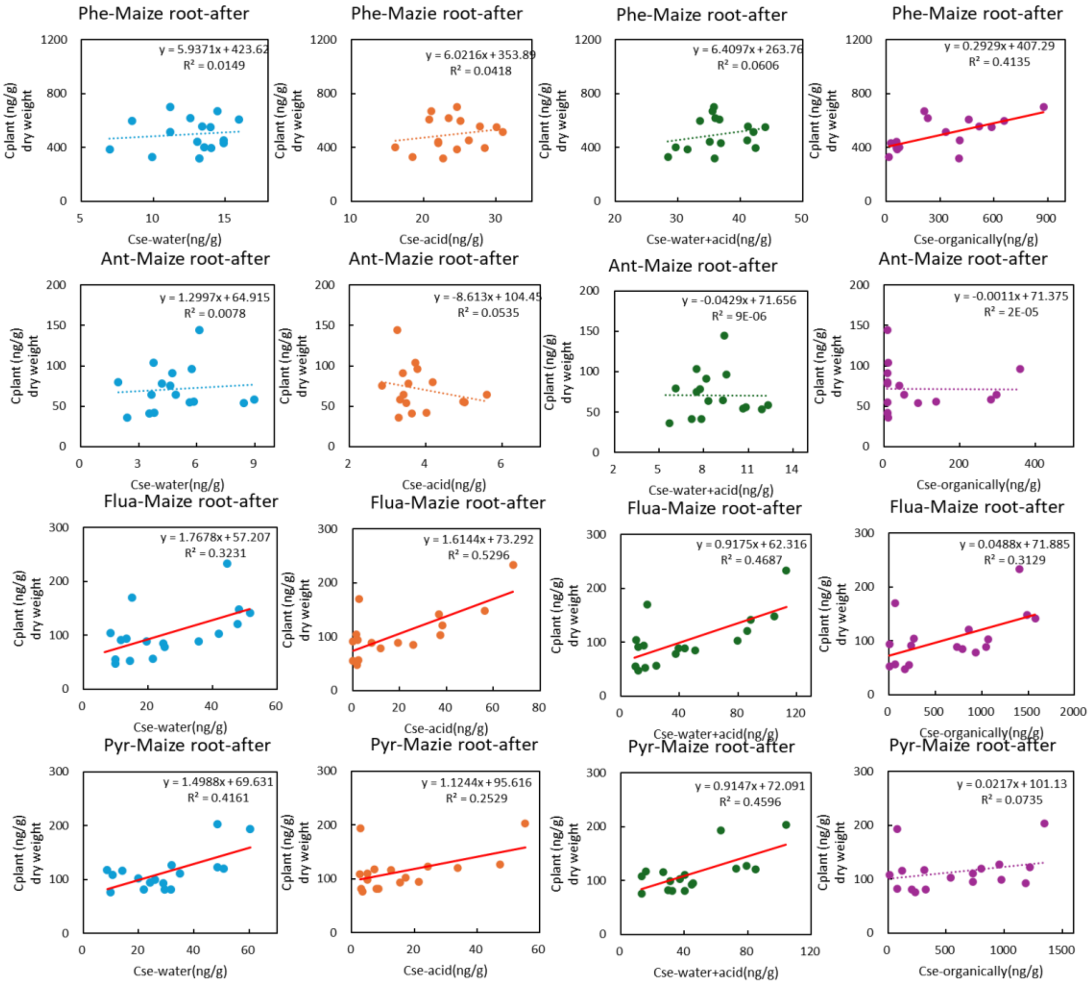


Fig. 6.20 The relationship between plant PAH concentrations (maize root) and soil extraction concentration after planting maize (blue is water-soluble fraction PAHs in plant, orange is acid-soluble fraction, green is the sum of water-soluble fraction and acid-soluble fraction PAHs, purple is the residue-fraction; the red solid line indicates a significant correlation between the two sets of data at 0.05 level, p <0.05).

6.3.4.4 Comparison and discussion of different chemical methods for PAHs

Through pot experiments and corresponding soil measurements, this study evaluated the relationship between PAHs measured by DGT, soil solution and sequential extraction (chemical extraction) methods with the concentration of PAHs in 3 different plant species, in the hope of establishing a chemical method for predicting bioavailability of PAHs in soils. The study had some limitations, which should be considered as context. These include: 1. The experimental design could not control for inputs to the plant from the atmosphere; 2. The range of PAH concentrations in the soils was quite limited, which made it more difficult to look for differences between the soils and the extractability of PAHs; 3. Time was limited, so the crops could not be grown to full maturity, to yield more biomass. This would have made analysis easier and determination of additional information (e.g. plant lipid content; full separation of root and shoot etc) easier. Nonetheless, the study yielded useful information, as follows:

For lettuce, the soil sequential extraction method and the DGT method after the plant was planted broadly correlated with PAH uptake, although this was not statistically significant. The soil solution method did not give a positive relationship. For radish, there was only a certain correlation with the aqueous solution before the plant was planted, and none of the three methods gave a positive relationship with plant uptake. For maize, none of the three evaluation methods gave a strong positive relationship with plant uptake. Only the sequential extraction method had a certain correlation with the bioavailable Flua and Pyr measured in the roots of maize.

DGT has been tested previously with a variety of soils, crops and trace substances in soils and been found to be a good predictor of bioavailability/plant uptake (Zhang, Zhao et al. 2001, Soriano-Disla, Speir et al. 2010). However, the situation for PAHs is more difficult to establish, for the reasons mentioned earlier. Compared with the use of DGT to assess the bioavailability of other organic pollutants, the use of DGT to assess PAHs is less effective. The correlation between the total concentration of atrazine and its metabolites in maize and DGT reached $r^2 > 0.92$ (Li, Rothwell et al. 2019). However, for atrazine, this relationship is not confounded by any aerial transport and shoot uptake. A study on DGT prediction of antibiotics uptake by plants also gave a clear positive correlation (Song, Su et al. 2023). Atrazine and antibiotics are much more water-soluble than PAHs.

6.4 Conclusions, limitations and recommendations

6.4.1 Conclusions

The sequential extraction results showed that the proportion of water-soluble and organic acid-soluble fraction PAHs in the soil was low, that the amount of bioavailable PAHs in the soil was small, and their distribution was related to soil pH. The organic extractable PAHs were higher than the bioavailable fractions, and the four-ring PAHs were more adsorbed to the soil than the three-rings. Soil organic matter and soil texture had an influence.

PAHs measured by DGT and in soil solution showed a significant downward trend from before to after crops planting. Different crops have different effects on PAHs measured by DGT after planting. The R value is used to reflect the resupply ability of PAHs from soil solid phase to soil liquid phase. The results showed that the R values of most soils decreased after planting (except Phe), reflecting the reduced replenishment of PAHs by soil.

The uptake of four PAHs by plants showed that the concentration (dry weight) of lettuce was 11-1206 ug kg^{-1}, radish was 10-1933 ug kg^{-1}, and maize was 27-294 ug kg^{-1}. Phe had the highest concentrations in all the crops; it was the most abundant PAH in the air and was highest in soil solution, because of the higher water solubility. The uptake was different by these three crops. Besides the influence of air-plant absorption, the growing time, leaf area, the type of roots of the crops, etc. affected the results. Different parts of the crop also absorb PAHs differently. In this study, the PAHs absorbed by the roots of maize were higher than those absorbed by the stems and leaves. In addition to air absorption, the concentration of PAHs in the soil solution, the resupply from the soil solid phase to the liquid phase, and the rhizosphere activity during plant growth all have impacts on the results.

Due to the influence of air-plant absorption of PAHs, there are limitations in directly using DGT, sequential extraction, and soil solution methods to estimate the uptake of PAHs in plants in this experiment. However, the results showed that DGT and sequential extraction methods have potential for evaluating PAHs in lettuce. The methods could be optimized based on the results of this study.

6.4.2 Limitations and recommendations

The analytical methods were sufficiently sensitive and robust for the study. However, several factors about PAHs themselves make studies on their behaviour and plant uptake in different soils difficult to control and perform. Some of these have been mentioned before, but it useful to summarise and make recommendations for future work.

- One limitation of this experiment is the narrow range of soil concentrations used. Future experiments could use a wider range of concentrations (e.g. over orders of magnitude) on the same soil first to establish the methods/protocols and then with a wider range of soil properties (e.g. SOM).

Because PAHs are semi-volatile organic pollutants, and absorbed by leaves from the air. Simonich and Hites found that plant leaves mainly absorb PAHs from the ambient air (i.e. the bulk background air) (Simonich and Hites 1994). In addition to contamination from the bulk air, most pot experiments cannot prevent volatile and semi-volatile organic compounds from evaporating from the soil into the air and then entering the plants (Samsøe-Petersen, Larsen et al. 2002). In this study, the volatilization of PAHs and the absorption of PAHs from the air by plants also had a significant impact on the results. Previous studies have found that plants generally absorb more pyrene than phenanthrene (Gao and Zhu 2004). In our experiment, the plants absorbed significantly more Phe than Pyr. This may be because Phe is usually the most abundant PAH in ambient air and is also more easily volatilized into the air than pyrene, thus affecting the experimental results through leaf absorption. Among the three plants, maize grew the largest and had much more stem and leaf biomass than lettuce and radish, so it may have been most affected by air-leaf transfers.

- Another complicating factor with PAHs is their degradation. In this study, in order to simulate field conditions, the soils were not sterilized. During the plant growth, the plants were subject to constant temperature and strong light regularly in the greenhouse every day. Degradation caused by microbial activities and photodegradation may therefore have been enhanced compared to field conditions.

In order to reduce the degradation of PAHs in soil by light during plant growth, the opening parts of the pots were covered with aluminum foil initially. However, the aluminum foil was easily damaged by plant growth. For future experiments, stronger material such as black tape could be used to cover the soil part of the pot after the plant grows to a certain length. This could not only reduce the impact of light on degradation, but also reduce the volatilization of PAHs into the air so that the PAHs absorption by plant from the air could be reduced.

- To better understand the effect of air absorption by plant leaves on bioavailability, the measurement of PAHs in the air is necessary. The combination of the air and soil absorption modelling of PAHs together with DGT measurement and other soil tests could be considered to improve the future experimental design.

Chapter 7 Conclusion and future perspective

7.1 Conclusion

This thesis explored the use of DGT technique for the sampling and detection of trace organic pollutants PAHs and related applications in natural waters and soil. The main conclusions can be summarized as follows:

1) DGT has been successfully developed for the detection of PAHs with MIP as the binding material, agarose gel as the diffusion layer, and nucleopore track-etch membrane as the filter membrane. The development of the metal casing reduced the effects of adsorption and lag time, and also laid the foundation for the future application of DGT in the detection of other hydrophobic organic chemicals. The performance of the DGT was relatively independent of pH (in the range 3.89−8.07), ionic strength (0.01−0.5 M) and dissolved organic matter <20 mg L^{-1}, making it suitable for applications in a wide range of natural environments. Coupled with HPLC with fluorescence or UV detection, or GC-MS, DGT has been used to sample and detect PAHs at the trace levels typical of background waters.
2) The developed new DGT sampler was used in-situ in the Nanjing section of the Yangtze River and urban rivers in China to measure the concentrations of PAHs. The DGT measurement results showed the different seasonal distribution characteristics of PAHs in winter and summer. Based on the spatial and temporal trends and the compound mixtures, evidence is presented that, the main sources of PAHs in the area were petrochemical enterprises along the Yangtze River, ship transportation, and upstream pollution. The inputs from Nanjing and urban tributaries had little impact on the mainstream of the Yangtze River. Risk assessment results showed that the risk increased in the winter and in chemical industry cluster areas. This study is a useful case study, illustrating how DGT can be used to conduct local or regional scale time-integrated studies of water bodies, to identify key sources and processes in the catchment which control the levels of trace organic pollutants.
3) DGT samplers were deployed in 6 soils with different properties to explore the fate and behavior of PAHs in soil during the soil-compound contact time ‘aging’ process. Combined

with DIFS model, the kinetic information of their resupply from soil solid phase to soil solution phase can be obtained. The results showed that soil physical and chemical properties such as pH, TOC, soil particle size and the properties of PAHs themselves have significant impact on the fate of PAHs in soil. With the increase of aging time, the resupply ability from the soil solid phase to the soil solution phase decreased in most soils. This study also indicated that the desorption kinetics and labile pool size affect the resupply ability of PAH in soil; they were affected by both soil pH and TOC. This study suggests that DGT can be used more widely in future, to investigate the dynamics of PAHs and other trace organics in soils, to address practical questions about soil remediation and treatment options, and contaminated land site risk assessment.

4) Through pot experiments, the ability of DGT to predict plant uptake of PAHs was studied. This is the first time that DGT has been used to study the bioavailability of PAHs. DGT, soil solution and soil chemical extraction methods were compared for 4 PAHs in 6 soils with 3 different crop plants. For lettuce, the PAHs concentrations obtained by the soil sequential extraction method and the DGT method after the plants harvested were broadly correlated with PAH uptake by plant. For radish and maize, the correlation between concentration in soils obtained by various methods and concentration in plants was not obvious. This is mainly due to the influence of plant absorption of PAHs from the air. The narrow range of soil PAH concentrations probably also hampered the study. However, DGT technology is shown to sensitively reflect the dynamic forms of PAHs in soils and give information about the resupply of PAHs in soils. The use of DGT as a tool to assess bioavailability of PAHs needs further development. Further carefully controlled studies are warranted.

7.2 Future perspectives

This is the first time that DGT has been used to measure PAHs in waters and soils. Based on this research, improvements can be made in the further development and application of DGT in the environment, and its application possibilities can be expanded.

The study focused on eight PAHs, but the use of DGT has the potential to be extended to a wider range of chemicals. For PAHs with lower water solubility and difficult to obtain diffusion coefficients through diffusion cell experiments, it is possible to consider using models to estimate diffusion coefficients and verify the required parameters through deployment experiments, and then apply DGT to test more PAH compounds – those on the USEPA priority pollutant list and the wider array of PAHs emitted to the environment from various sources. In addition to PAHs, the focus is currently on PAH related metabolites such as nitro, oxidized, and alkylated derivatives. Exploring DGT for these pollutants with higher biological toxicity, bioaccumulation, and environmental persistence is of great significance for pollutant identification and risk assessment. The metal DGT casing developed in this research effectively reduced the impact of adsorption on the experiments of using hydrophobic organic chemicals. While existing DGT samplers are mostly used for the detection of polar organic compounds, in the future it is possible to consider expanding the application of DGT to detect more hydrophobic compounds. The potential development of metal or ceramic materials with required pore sizes may be used as diffusion layers to replace the diffusive gels. Solid diffusion layers are less susceptible to damage than gels and can eliminate the use of filter membranes. This can also be one of the future development directions.

In this study DGT was used for investigating PAHs in surface water and soil, but it has the potential to be applied in a wider range of environments. For example, DGT could be used for the detection and risk assessment of PAHs in groundwater and seawater, for comprehensive measurement of the migration and transformation of PAHs in sediments, or for the migration of PAHs between different environmental matrices (i.e. water-sediment). In the future, DGT will be used in river basins in China. A low-cost DGT deployment method by planning sampling points reasonably will be presented. Using DGT deployment and monitoring to help identify priority controlled pollutants in the watershed and understand their sources. Appropriate intervention measures can be designed using DGT monitoring results and related information. By using DGT data and relevant hydrological information, the pollutant flux of rivers can be calculated, providing relevant information for watershed water quality safety and water resource regulation. DGT will be deployed in the water, sediment, and soil environments of river basins, combined with atmospheric sampling and hydrological data to explore the circulation of pollutants in different media, water and gas exchange, and pollutant migration and transformation in the basin.

Although the study on the bioavailability prediction of PAHs by DGT was affected by air-plant absorption, further work is warranted. DGT can be used as a tool to provide kinetics information of PAHs in soils, for example, and it could be used in more detailed studies of fate e.g. in experiments on biodegradation, or on the forms of PAHs in soils and sediments.

High-resolution and visualization research could be explored in the future for trace organics, following some of the pioneering work already conducted on trace metals and nutrients. DGT has been used for one-dimensional and two-dimensional high-resolution measurements, and it has been applied to soils and sediments in the millimeter and submillimeter range. It is particularly well developed for two-dimensional measurements of heavy metals (chemical imaging). These technologies have not yet been used for trace organic chemicals, and it is possible to consider combining DGT technique with imaging technologies such as two-photon excitation microscopy (TPEM), matrix-assisted laser desorption ionization (MALDI) and desorption electrospray ionization (DESI) technologies to develop more effective functions of DGT. This can explore the fine-scale distributions and associations of trace organic chemicals in future.

References

Abdel-Shafy, H. I. and M. S. M. Mansour (2016). "A review on polycyclic aromatic hydrocarbons: Source, environmental impact, effect on human health and remediation." Egyptian Journal of Petroleum **25**(1): 107-123.

Agarwal, T. and T. D. Bucheli (2011). "Is black carbon a better predictor of polycyclic aromatic hydrocarbon distribution in soils than total organic carbon?" Environ Pollut **159**(1): 64-70.

Ahrens, L., A. Daneshvar, A. E. Lau and J. Kreuger (2015). "Characterization of five passive sampling devices for monitoring of pesticides in water." J Chromatogr A **1405**: 1-11.

Aichner, B., B. M. Bussian, P. Lehnik-Habrink and S. Hein (2015). "Regionalized concentrations and fingerprints of polycyclic aromatic hydrocarbons (PAHs) in German forest soils." Environ Pollut **203**: 31-39.

Ake, C. L., M. C. Wiles, H. J. Huebner, T. J. McDonald, D. Cosgriff, M. B. Richardson, K. C. Donnelly and T. D. Phillips (2003). "Porous organoclay composite for the sorption of polycyclic aromatic hydrocarbons and pentachlorophenol from groundwater." Chemosphere **51**(9): 835-844.

Al-Nasir, F., T. J. Hijazin, M. M. Al-Alawi, A. Jiries, A. Mayyas, A. A.-D. S, R. Al-Dmour, A. Alahmad, O. Y. Al-Madanat and M. I. Batarseh (2022). "Accumulation, Source Identification, and Cancer Risk Assessment of Polycyclic Aromatic Hydrocarbons (PAHs) in Different Jordanian Vegetables." Toxics **10**(11).

Alexander, M. (2000). "Aging, bioavailability, and overestimation of risk from environmental pollutants." Environmental Science & Technology **34**(20): 4259-4265.

Alkio, M., T. M. Tabuchi, X. Wang and A. Colon-Carmona (2005). "Stress responses to polycyclic aromatic hydrocarbons in Arabidopsis include growth inhibition and hypersensitive response-like symptoms." J Exp Bot **56**(421): 2983-2994.

Allan, I. J., G. Christensen, K. Baek and A. Evenset (2016). "Photodegradation of PAHs in passive water samplers." Mar Pollut Bull **105**(1): 249-254.

Almouallem, W., J. Michel, S. Dorge, C. Joyeux, G. Trouve and D. Le Nouen (2023). "A comparative study of the sorption of O-PAHs and PAHs onto soils to understand their transport in soils and groundwater." J Environ Sci (China) **124**: 61-75.

Amellal, N., J. M. Portal and J. Berthelin (2001). "Effect of soil structure on the bioavailability of polycyclic aromatic hydrocarbons within aggregates of a contaminated soil." Applied Geochemistry **16**(14): 1611-1619.

Armstrong, B., E. Hutchinson, J. Unwin and T. Fletcher (2004). "Lung cancer risk after exposure to polycyclic aromatic hydrocarbons: a review and meta-analysis." Environ Health Perspect **112**(9): 970-978.

Arthur, C. L. and J. Pawliszyn (1990). "Solid phase microextraction with thermal desorption using fused silica optical fibers." Analytical chemistry **62**(19): 2145-2148.

Arvanaghi, H. R., Y. Aminfar, A. A. Sadeghan and N. Dolatabadi (2017). "Phytoremediation of polycyclic aromatic hydrocarbons (PAHs): air-plant-soil interactions." Journal of Biological and Environmental Sciences **10**: 178-184.

Augulyte, L. and P. A. Bergqvist (2007). "Estimation of water sampling rates and concentrations of PAHs in a municipal sewage treatment plant using SPMDs with performance reference compounds." Environmental Science & Technology **41**(14): 5044-5049.

Bade, R., S. Oh and W. S. Shin (2012). "Diffusive gradients in thin films (DGT) for the prediction of bioavailability of heavy metals in contaminated soils to earthworm (Eisenia foetida) and oral bioavailable concentrations." Sci Total Environ **416**: 127-136.

Baek, S. O., R. A. Field, M. E. Goldstone, P. W. Kirk, J. N. Lester and R. Perry (1991). "A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior." Water, air, and soil pollution **60**: 279-300.

Balmer, J. E., H. Hung, Y. Yu, R. J. Letcher and D. C. G. Muir (2019). "Sources and environmental fate of pyrogenic polycyclic aromatic hydrocarbons (PAHs) in the Arctic." Emerging Contaminants **5**: 128-142.

Banjoo, D. R. and P. K. Nelson (2005). "Improved ultrasonic extraction procedure for the determination of polycyclic aromatic hydrocarbons in sediments." J Chromatogr A **1066**(1-2): 9-18.

Baran, S., J. E. Bielińska and P. Oleszczuk (2004). "Enzymatic activity in an airfield soil polluted with polycyclic aromatic hydrocarbons." Geoderma **118**(3-4): 221-232.

Barrado, A. I., S. García, E. Barrado and R. M. Pérez (2012). "PM2.5-bound PAHs and hydroxy-PAHs in atmospheric aerosol samples: Correlations with season and with physical and chemical factors." Atmospheric Environment **49**: 224-232.

Bayen, S., E. Segovia, L. L. Loh, D. F. Burger, H. S. Eikaas and B. C. Kelly (2014). "Application of Polar Organic Chemical Integrative Sampler (POCIS) to monitor emerging contaminants in tropical waters." Sci Total Environ **482-483**: 15-22.

Baz-Lomba, J. A., C. Harman, M. Reid and K. V. Thomas (2017). "Passive sampling of wastewater as a tool for the long-term monitoring of community exposure: Illicit and prescription drug trends as a proof of concept." Water Res **121**: 221-230.

Becher, H., H. Ramroth, W. Ahrens, A. Risch, P. Schmezer and A. Dietz (2005). "Occupation, exposure to polycyclic aromatic hydrocarbons and laryngeal cancer risk." Int J Cancer **116**(3): 451-457.

Ben Othman, H., F. R. Pick, A. Sakka Hlaili and C. Leboulanger (2023). "Effects of polycyclic aromatic hydrocarbons on marine and freshwater microalgae - A review." J Hazard Mater **441**: 129869.

Benner, B. A. (1998). "Summarizing the effectiveness of supercritical fluid extraction of polycyclic aromatic hydrocarbons from natural matrix environmental samples." Analytical chemistry **70**(21): 4594-4601.

Bertilsson, S. and A. Widenfalk (2002). "Photochemical degradation of PAHs in freshwaters and their impact on bacterial growth–influence of water chemistry." Hydrobiologia **469**: 23-32.

Betowski, L. D., M. Enlow and L. Riddick (2002). "The phototoxicity of polycyclic aromatic hydrocarbons: a theoretical study of excited states and correlation to experiment." Computers & chemistry **26**(4): 371-377.

Black, A., R. G. McLaren, S. M. Reichman, T. W. Speir and L. M. Condron (2011). "Evaluation of soil metal bioavailability estimates using two plant species (L. perenne and T. aestivum) grown in a range of agricultural soils treated with biosolids and metal salts." Environmental pollution **159**(6): 1523-1535.

Blakely, J. K., D. A. Neher and A. L. Spongberg (2002). "Soil invertebrate and microbial communities, and decomposition as indicators of polycyclic aromatic hydrocarbon contamination." Applied Soil Ecology **21**(1): 71-88.

Blum, J. and I. Fridovich (1985). "Inactivation of glutathione peroxidase by superoxide radical." Archives of Biochemistry and Biophysics **240**(2): 500-508.

Bogan, B. W. and W. R. Sullivan (2003). "Physicochemical soil parameters affecting sequestration and mycobacterial biodegradation of polycyclic aromatic hydrocarbons in soil." Chemosphere **52**(10): 1717-1726.

Bonnaud, B., N. Mazzella, P. Boutet, A. Daval and C. Miège (2023). "Calibration comparison between two passive samplers-o-DGT and POCIS-for 109 hydrophilic emerging and priority organic compounds. ." Science of the total environment **869**: 161720.

Bonnaud, B., C. Miege, A. Daval, V. Fauvelle and N. Mazzella (2022). "Determination of diffusion coefficients in agarose and polyacrylamide gels for 112 organic chemicals for passive sampling by organic Diffusive Gradients in Thin films (o-DGT)." Environ Sci Pollut Res Int **29**(17): 25799-25809.

Booij, K., R. van Bommel, H. M. van Aken, H. van Haren, G. J. Brummer and H. Ridderinkhof (2014). "Passive sampling of nonpolar contaminants at three deep-ocean sites." Environ Pollut **195**: 101-108.

Bopp, S., H. Weiss and K. Schirmer (2005). "Time-integrated monitoring of polycyclic aromatic hydrocarbons (Pahs) in groundwater using the ceramic dosimeter passive sampling device." J Chromatogr A **1072**(1): 137-147.

Bosetti, C., P. Boffetta and C. La Vecchia (2007). "Occupational exposures to polycyclic aromatic hydrocarbons, and respiratory and urinary tract cancers: a quantitative review to 2005." Ann Oncol **18**(3): 431-446.

Boström, C. E., P. Gerde, H, A. anberg, B. Jernström, C. Johansson, T. Kyrklund, ... and R. B. Westerholm (2002). "Cancer risk assessment, indicators, and guidelines for polycyclic aromatic hydrocarbons in the ambient air." Environmental Health Perspectives **110**(suppl 3): 451-488.

Bøwadt, S. and S. B. Hawthorne (1995). "Supercritical fluid extraction in environmental analysis." Journal of Chromatography A **703**(1-2): 549-571.

Brown, J. N. and B. M. Peake (2003). "Determination of colloidally-associated polycyclic aromatic hydrocarbons (PAHs) in fresh water using C18 solid phase extraction disks." Analytica Chimica Acta **486**(2): 159-169.

Busetti, F., A. Heitz, M. Cuomo, S. Badoer and P. Traverso (2006). "Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant." Journal of Chromatography A **1102**(1-2): 104-115.

Buzier, R., M. H. Tusseau-Vuillemin and J. M. Mouchel (2006). "Evaluation of DGT as a metal speciation tool in wastewater." Science of the total environment **358**(1-3): 277-285.

Caban, M., H. Lis and P. Stepnowski (2022). "Limitations of Integrative Passive Samplers as a Tool for the Quantification of Pharmaceuticals in the Environment - A Critical Review with the Latest Innovations." Crit Rev Anal Chem **52**(6): 1386-1407.

Cai, T., X. Zhang, S. Zhang, Y. Ming and Q. Zhang (2023). "Photochemical behaviors of dissolved organic matter in aquatic environment: Generation, characterization, influencing factors and practical application." Environ Res **231**(Pt 2): 116174.

Calvet, R. (1989). "Adsorption of organic chemicals in soils." Environmental health perspectives **83**: 145-177.

Cao, Y., J. Wang, M. Xin, B. Wang and C. Lin (2024). "Spatial distribution and partition of polycyclic aromatic hydrocarbons (PAHs) in the water and sediment of the southern Bohai Sea: Yellow River and PAH property influences." Water Res **248**: 120873.

Cao, Z., J. Liu, Y. Luan, Y. Li, M. Ma, J. Xu and S. Han (2010). "Distribution and ecosystem risk assessment of polycyclic aromatic hydrocarbons in the Luan River, China." Ecotoxicology **19**(5): 827-837.

Carman, K. R., J. W. Fleeger, J. C. Means, S. M. Pomarico and D. J. McMillin (1995). "Experimental investigation of the effects of polynuclear aromatic hydrocarbons on an estuarine sediment food web." Marine Environmental Research **40**(3): 289-318.

Challis, J. K., M. L. Hanson and C. S. Wong (2016). "Development and Calibration of an Organic-Diffusive Gradients in Thin Films Aquatic Passive Sampler for a Diverse Suite of Polar Organic Contaminants." Anal Chem **88**(21): 10583-10591.

Challis, J. K., K. M. Stroski, K. H. Luong, M. L. Hanson and C. S. Wong (2018). "Field evaluation and *in situ* stress testing of the organic-diffusive gradients in thin-films passive sampler." Environmental Science & Technology **52**(21): 12573-12582.

Chang, W. T., C. L. Lee, P. Brimblecombe, M. D. Fang, K. T. Chang and J. T. Liu (2015). "The effects of flow rate and temperature on SPMD measurements of bioavailable PAHs in seawater." Mar Pollut Bull **97**(1-2): 217-223.

Charriau, A., S. Lissalde, G. Poulier, N. Mazzella, R. Buzier and G. Guibaud (2016). "Overview of the Chemcatcher(R) for the passive sampling of various pollutants in aquatic environments Part A: Principles, calibration, preparation and analysis of the sampler." Talanta **148**: 556-571.

Chaturvedi, S. and M. K. Lakshman (1996). "Site-specific modification of the human N-ras proto-oncogene with each diol epoxide metabolite of benzo [a] pyrene and thermal denaturation studies of the adducted duplexes." Carcinogenesis **17**(12): 2747-2752.

Chen, C., T. Lin, X. Sun, Z. Wu and J. Tang (2023). "Spatiotemporal distribution and particle-water partitioning of polycyclic aromatic hydrocarbons in Bohai Sea, China." Water Res **244**: 120440.

Chen, C. E., W. Chen, G. G. Ying, K. C. Jones and H. Zhang (2015). "*In situ* measurement of solution concentrations and fluxes of sulfonamides and trimethoprim antibiotics in soils using o-DGT." Talanta **132**: 902-908.

Chen, C. E., K. C. Jones, G. G. Ying and H. Zhang (2014). "Desorption kinetics of sulfonamide and trimethoprim antibiotics in soils assessed with diffusive gradients in thin-films." Environ Sci Technol **48**(10): 5530-5536.

Chen, C. E., K. C. Jones, G. G. Ying and H. Zhang (2014). "Desorption kinetics of sulfonamide and trimethoprim antibiotics in soils assessed with diffusive gradients in thin-films." Environmental Science & Technology **48**(10): 5530-5536.

Chen, C. E., H. Zhang and K. C. Jones (2012). "A novel passive water sampler for *in situ* sampling of antibiotics." J Environ Monit **14**(6): 1523-1530.

Chen, C. E., H. Zhang, G. G. Ying and K. C. Jones (2013). "Evidence and recommendations to support the use of a novel passive water sampler to quantify antibiotics in wastewaters." Environ Sci Technol **47**(23): 13587-13593.

Chen, H. W. (2007). "Distribution and risk assessment of polycyclic aromatic hydrocarbons in household drinking water." Bull Environ Contam Toxicol **78**(3-4): 201-205.

Chen, W., Y. Li, C. E. Chen, A. J. Sweetman, H. Zhang and K. C. Jones (2017). "DGT Passive Sampling for Quantitative *in situ* Measurements of Compounds from Household and Personal Care Products in Waters." Environ Sci Technol **51**(22): 13274-13281.

Chen, W., S. Pan, H. Cheng, A. J. Sweetman, H. Zhang and K. C. Jones (2018). "Diffusive gradients in thin-films (DGT) for *in situ* sampling of selected endocrine disrupting chemicals (EDCs) in waters." Water Res **137**: 211-219.

Chen, Y., R. Song, P. Li, Y. Wang, Y. Tan, Y. Ma, L. Yang, L. Wu, Z. Du, X. Qi and Z. Zhang (2023). "Spatiotemporal distribution, sources apportionment and ecological risks of PAHs: a study in the Wuhan section of the Yangtze River." Environ Geochem Health **45**(10): 7405-7424.

Cheng, K. Y., K. M. Lai and J. W. Wong (2008). "Effects of pig manure compost and nonionic-surfactant Tween 80 on phenanthrene and pyrene removal from soil vegetated with Agropyron elongatum." Chemosphere **73**(5): 791-797.

Chianese, S., A. Fenti, P. Iovino, D. Musmarra and S. Salvestrini (2020). "Sorption of Organic Pollutants by Humic Acids: A Review." Molecules **25**(4).

China, M. o. E. a. E. o. t. P. s. R. o. (2017). Yangtze River Economic Belt Ecological Environment Protection Plan.

China, M. o. E. a. E. o. t. P. s. R. o. (2020). Yangtze River Protection Law.

Chiou, C. T., L. J. Peters and V. H. Freed (1979). "A physical concept of soil-water equilibria for nonionic organic compounds." Science **206**(4420): 831-832.

Chiou, C. T., G. Sheng and M. Manes (2001). "A partition-limited model for the plant uptake of organic contaminants from soil and water." Environmental Science & Technology **35**(7): 1437-1444.

Choi, H., W. Jedrychowski, J. Spengler, D. E. Camann, R. M. Whyatt, V. Rauh, W. Y. Tsai and F. P. Perera (2006). "International studies of prenatal exposure to polycyclic aromatic hydrocarbons and fetal growth." Environ Health Perspect **114**(11): 1744-1750.

Christensen, E. R. and P. A. Bzdusek (2005). "PAHs in sediments of the Black River and the Ashtabula River, Ohio: source apportionment by factor analysis." Water Res **39**(4): 511-524.

Chukwuma, I. F., E. J. Nweze, F. N. Nworah, V. O. Apeh and T. P. C. Ezeorba (2024). "Concentration and Risk Assessment Analysis of Polycyclic Aromatic Hydrocarbons Associated with Consuming Procambarus Clarkii (Cray fish) in Nigeria. ." Research and Innovation in Food Science and Technology **13**(2): 101-108.

Cole, R. F., G. A. Mills, M. S. Hale, R. Parker, T. Bolam, P. R. Teasdale, W. W. Bennett and G. R. Fones (2018). "Development and evaluation of a new diffusive gradients in thin-films technique for measuring organotin compounds in coastal sediment pore water." Talanta **178**: 670-678.

Commission, E. (2003). "Technical Guidance Document on Risk Assessment in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for existing substances, and Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market." Directive 98/8/EC of the European Parliament and of the Council Concerning the Placing of Biocidal Products on the Market.

Cristovao, M. B., A. Bento-Silva, M. R. Bronze, J. G. Crespo and V. J. Pereira (2021). "Detection of anticancer drugs in wastewater effluents: Grab versus passive sampling." Sci Total Environ **786**: 147477.

Cuadras, A., E. Rovira, R. M. Marce and F. Borrull (2016). "Lung cancer risk by polycyclic aromatic hydrocarbons in a Mediterranean industrialized area." Environ Sci Pollut Res Int **23**(22): 23215-23227.

Cusnir, R., P. Steinmann, F. Bochud and P. Froidevaux (2014). "A DGT technique for plutonium bioavailability measurements." Environ Sci Technol **48**(18): 10829-10834.

Dai, C., Y. Han, Y. Duan, X. Lai, R. Fu, S. Liu, K. H. Leong, Y. Tu and L. Zhou (2022). "Review on the contamination and remediation of polycyclic aromatic hydrocarbons (PAHs) in coastal soil and sediments." Environ Res **205**: 112423.

Dai, Y., M. Nasir, Y. Zhang, J. Gao, Y. Lv and J. Lv (2018). "Comparison of DGT with traditional extraction methods for assessing arsenic bioavailability to Brassica chinensis in different soils " Chemosphere **191**: 183-189.

Daisey, J. M., Kneip, T. J., Hawryluk, I., & Mukai, F. (1980). "Seasonal variations in the bacterial mutagenicity of airborne particulate organic matter in New York City." Environmental Science &

Technology **14**(12): 1487-1490.

Dat, N. D. and M. B. Chang (2017). "Review on characteristics of PAHs in atmosphere, anthropogenic sources and control technologies." Sci Total Environ **609**: 682-693.

Davison, W., C. Lin, Y. Gao and H. Zhang (2014). "Effect of Gel Interactions with Dissolved Organic Matter on DGT Measurements of Trace Metals." Aquatic Geochemistry **21**(2-4): 281-293.

Davison, W. and H. Zhang (1994). "*In situ* speciation measurements of trace components in natural waters using thin-film gels." nature **367**(6463): 546-548.

de Lima Ribeiro, F. A. and M. M. C. Ferreira (2005). "QSAR model of the phototoxicity of polycyclic aromatic hydrocarbons." Journal of Molecular Structure: THEOCHEM **719**(1-3): 191-200.

De Nicola, F., E. Concha-Graña, E. Picariello, V. Memoli, G. Maisto, P. López-Mahía and S. Muniategui-Lorenzo (2019). "An environmentally friendly method for the determination of polycyclic aromatic hydrocarbons in different soil typologies." Environmental Chemistry **16**(7).

De Paolis, F. and J. Kukkonen (1997). "Binding of organic pollutants to humic and fulvic acids: influence of pH and the structure of humic material." Chemosphere **34**(8): 1693-1704.

Del Signore, A., A. J. Hendriks, H. R. Lenders, R. S. Leuven and A. Breure (2016). "Development and application of the SSD approach in scientific case studies for ecological risk assessment." Environmental Toxicology and Chemistry **35**(9): 2149-2161.

Denney, S., Sherwood, J., & Leyden, J. (1999). "*In situ* measurements of labile Cu, Cd and Mn in river waters using DGT." Science of the total environment **239**(1-3): 71-80.

Deo, R. P. and R. U. Halden (2010). "Effect of sample filtration on the quality of monitoring data reported for organic compounds during wastewater treatment." J Environ Monit **12**(2): 478-483.

Déziel, É., G. Paquette, R. Villemur, F. Lepine and J. Bisaillon (1996). "Biosurfactant production by a soil Pseudomonas strain growing on polycyclic aromatic hydrocarbons. Applied and environmental microbiology." Applied and environmental microbiology **62**(6): 1908-1912.

dgtresearch.com. from https://www.dgtresearch.com/product/automatic-sampler-for-dgt-devices/.

Dib, S., S. Veerasingam, T. Alyafei, M. A. Assali, J. Al-Khayat and P. Vethamony (2024). "PAHs and hopanes in the surface sediments of Qatar coast and their ecological risks: Comparison with regional and global coastal regions." Mar Pollut Bull **203**: 116494.

Dipple, A. (1985). Polycyclic aromatic hydrocarbon carcinogenesis: an introduction.

Duran, R. and C. Cravo-Laureau (2016). "Role of environmental factors and microorganisms in determining the fate of polycyclic aromatic hydrocarbons in the marine environment." FEMS Microbiol Rev **40**(6): 814-830.

Edwards, N. T., B. M. Ross-Todd and E. G. Garver (1982). "Uptake and metabolism of 14C anthracene by soybean (Glycine max)." Environmental and experimental botany **22**(3): 349-357.

Eismann, C. E., A. A. Menegário, H. Gemeiner and P. N. Williams (2018). "Predicting Trace Metal Exposure in Aquatic Ecosystems: Evaluating DGT as a Biomonitoring Tool." Exposure and Health **12**(1): 19-31.

Eldos, H. I., N. Zouari, S. Saeed and M. A. Al-Ghouti (2022). "Recent advances in the treatment of PAHs in the environment: Application of nanomaterial-based technologies." Arabian Journal of Chemistry **15**(7).

Emoyan, O. O., S. O. Akporido and P. O. & Agbaire (2018). "Effects of soil pH, total organic carbon and texture on fate of polycyclic aromatic hydrocarbons (PAHs) in soils." Global NEST Journal **20**(2): 181-187.

Ernstberger, H., W. Davison, H. Zhang, A. Tye and S. & Young (2002). " Measurement and dynamic modeling of trace metal mobilization in soils using DGT and DIFS." Environmental Science & Technology **36**(3): 349-354.

Ernstberger, H., H. Zhang, A. Tye, S. Young and W. Davison (2005). "Desorption kinetics of Cd, Zn, and Ni measured in soils by DGT." Environmental Science & Technology **39**(6): 1591-1597.

Ernstberger, H., H. Zhang, A. Tye, S. Young and W. Davison (2005). "Desorption kinetics of Cd, Zn, and Ni measured in soils by DGT. ." Environmental Science & Technology **39**(6): 1591-1597.

Erstfeld, K. M. and J. Snow-Ashbrook (1999). "Effects of chronic low-level PAH contamination on soil invertebrate communities." Chemosphere **39**(12): 2117-2139.

Fadiel, A., B. Epperson, M. I. Shaw, A. Hamza, J. Petito and F. Naftolin (2013). "Bioinformatic analysis of benzo-alpha-pyrene-induced damage to the human placental insulin-like growth factor-1 gene." Reprod Sci **20**(8): 917-928.

Fang, Z., K. Li, Y. Li, H. Zhang, K. C. Jones, X. Liu, S. Liu, L. Q. Ma and J. Luo (2019). "Development and Application of the Diffusive Gradients in Thin-Films Technique for Measuring Psychiatric Pharmaceuticals in Natural Waters." Environ Sci Technol **53**(19): 11223-11231.

Fang, Z., Y. Li, Y. Li, D. Yang, H. Zhang, K. C. Jones, C. Gu and J. Luo (2021). "Development and Applications of Novel DGT Passive Samplers for Measuring 12 Per- and Polyfluoroalkyl Substances in Natural Waters and Wastewaters." Environ Sci Technol **55**(14): 9548-9556.

Fasnacht, M. P. and N. V. Blough (2002). "Aqueous photodegradation of polycyclic aromatic hydrocarbons." Environmental Science & Technology **36**(20): 4364-4369.

Feng, Z., P. Zhu, H. Fan, S. Piao, L. Xu and T. Sun (2016). "Effect of Biofilm on Passive Sampling of Dissolved Orthophosphate Using the Diffusive Gradients in Thin Films Technique." Anal Chem **88**(13): 6836-6843.

Fialová, P., R. Grabic, K. Grabicová, P. Nováková, H. Švecová, S. Kaserzon, K. Thompson and B. Vrana (2023). "Performance evaluation of a diffusive hydrogel-based passive sampler for monitoring of polar organic compounds in wastewater." Science of The Total Environment **864**.

Field, J. A., E. De Jong, G. Feijoo Costa and J. A. De Bont (1992). "Biodegradation of polycyclic aromatic hydrocarbons by new isolates of white rot fungi." Applied and environmental microbiology **58**(7): 2219-2226.

Fu, G., A. T. Kan and M. Tomson (1994). "Adsorption and desorption hysteresis of PAHs in surface sediment." Environmental Toxicology and Chemistry: An International Journal **13**(10): 1559-1567.

Gabet, V. M., M. R. Sanz, I. Amouroux, M. J. Belzunce, P. Bersuder, T. Bolam, ... and H. Zhang (2021). "A Good Practice Guide for the Use of DGTs. Sampling of metals in transitional and coastal waters by Diffusive Gradient in Thin films (DGT) technique." ARPHA Preprints **2**: e70983.

Galceran, J., Y. Gao, J. Puy, M. Leermakers, C. Rey-Castro, C. Zhou and W. Baeyens (2021). "Speciation of Inorganic Compounds in Aquatic Systems Using Diffusive Gradients in Thin-Films: A Review." Front Chem **9**: 624511.

Gao, B., L. Gao and D. Xu (2022). "New insight for the diffusion–resupply kinetics of Cr(VI) in contaminated soil using DGT/DIFS." Ecotoxicology and environmental safety **242**.

Gao, H., H. Li, J. Shi, J. Huang, J. Wei, X. Qu and T. Long (2023). "Black carbon, soil organic matter molecular signatures under different land uses in Shenyang, China and relationship with PAHs." Chemosphere **342**: 140089.

Gao, Y. and C. D. Collins (2009). "Uptake pathways of polycyclic aromatic hydrocarbons in white clover." Environmental Science & Technology **43**(16): 6190-6195.

Gao, Y., Y. Yang, W. Ling, H. Kong and X. Zhu (2011). "Gradient Distribution of Root Exudates and Polycyclic Aromatic Hydrocarbons in Rhizosphere Soil." Soil Science Society of America Journal **75**(5): 1694-1703.

Gao, Y. and L. Zhu (2004). "Plant uptake, accumulation and translocation of phenanthrene and pyrene in soils." Chemosphere **55**(9): 1169-1178.

Gao, Y., N. Zhu, X.-Z. Meng, W.-L. Ma, R.-S. Ma, J.-J. Jin, F.-T. Ai, L.-M. Jin, M.-H. Cai, J.-S. Liu, J.-F. Zhao and S. Lindner (2024). "Sources and ecological risk of polycyclic aromatic hydrocarbons in water and air of the Yangtze River." Environmental Science: Water Research & Technology **10**(2): 389-398.

García-Alonso, S., R. M. Pérez-Pastor, M. L. Sevillano-Castaño, O. Escolano and F. J. García-Frutos (2008). "Influence of Particle Size on the Quality of Pah Concentration Measurements in a Contaminated Soil." Polycyclic Aromatic Compounds **28**(1): 67-83.

Gaurav, G. K., T. Mehmood, M. Kumar, L. Cheng, K. Sathishkumar, A. Kumar and D. Yadav (2021). "Review on polycyclic aromatic hydrocarbons (PAHs) migration from wastewater." J Contam Hydrol **236**: 103715.

Geacintov, N. E., M. Cosman, B. E. Hingerty, S. Amin, S. Broyde and D. J. Patel (1997). "NMR solution structures of stereoisomeric covalent polycyclic aromatic carcinogen− DNA adducts: principles, patterns, and diversity." Chemical research in toxicology **10**(2): 111-146.

Ghosh, U., S. Kane Driscoll, R. M. Burgess, M. T. Jonker, D. Reible, F. Gobas, Y. Choi, S. E. Apitz, K. A. Maruya, W. R. Gala, M. Mortimer and C. Beegan (2014). "Passive sampling methods for contaminated sediments: practical guidance for selection, calibration, and implementation." Integr Environ Assess Manag **10**(2): 210-223.

Golozar, A., R. B. Fagundes, A. Etemadi, M. M. Schantz, F. Kamangar, C. C. Abnet and S. M. Dawsey (2012). "Significant variation in the concentration of carcinogenic polycyclic aromatic hydrocarbons in yerba mate samples by brand, batch, and processing method." Environ Sci Technol **46**(24): 13488-13493.

Grova, N., G. Salquebre, H. Schroeder and B. M. Appenzeller (2011). "Determination of PAHs and OH-PAHs in rat brain by gas chromatography tandem (triple quadrupole) mass spectrometry." Chem Res Toxicol **24**(10): 1653-1667.

Guan, D. X., Y. Q. Li, N. Y. Yu, G. H. Yu, S. Wei, H. Zhang, W. Davison, X. Y. Cui, L. Q. Ma and J. Luo (2018). "*In situ* measurement of perfluoroalkyl substances in aquatic systems using diffusive gradients in thin-films technique." Water Res **144**: 162-171.

Guan, D. X., J. L. Zheng, J. Luo, H. Zhang, W. Davison and L. Q. Ma (2017). "A diffusive gradients in thin-films technique for the assessment of bisphenols desorption from soils." Journal of hazardous materials **331**: 321-328.

Guarino, C., D. Zuzolo, M. Marziano, B. Conte, G. Baiamonte, L. Morra, D. Benotti, D. Gresia, E. R. Stacul, D. Cicchella and R. Sciarrillo (2019). "Investigation and Assessment for an effective approach to the reclamation of Polycyclic Aromatic Hydrocarbon (PAHs) contaminated site: SIN Bagnoli, Italy." Sci Rep **9**(1): 11522.

Guibal, R., R. Buzier, A. Charriau, S. Lissalde and G. Guibaud (2017). "Passive sampling of anionic pesticides using the Diffusive Gradients in Thin films technique (DGT)." Anal Chim Acta **966**: 1-10.

Guibal, R., R. Buzier, S. Lissalde and G. Guibaud (2019). "Adaptation of diffusive gradients in thin films technique to sample organic pollutants in the environment: An overview of o-DGT passive samplers." Sci Total Environ **693**: 133537.

Guo, C., T. Zhang, S. Hou, J. Lv, Y. Zhang, F. Wu, Z. Hua, W. Meng, H. Zhang and J. Xu (2017). "Investigation and Application of a New Passive Sampling Technique for *in situ* Monitoring of Illicit Drugs in Waste Waters and Rivers." Environ Sci Technol **51**(16): 9101-9108.

Guo, G., F. Wu, H. He, R. Zhang, H. Li and C. Feng (2012). "Distribution characteristics and ecological risk assessment of PAHs in surface waters of China." Science China Earth Sciences **55**(6): 914-925.

Guo, M., Z. Gong, R. Miao, D. Su, X. Li, C. Jia and J. Zhuang (2017). "The influence of root exudates of maize and soybean on polycyclic aromatic hydrocarbons degradation and soil bacterial community structure." Ecological Engineering **99**: 22-30.

Guo, W., M. He, Z. Yang, C. Lin, X. Quan and B. Men (2009). "Distribution, partitioning and sources of polycyclic aromatic hydrocarbons in Daliao River water system in dry season, China." J Hazard Mater **164**(2-3): 1379-1385.

Gustafson, K. E. and R. M. Dickhut (1997). "Gaseous exchange of polycyclic aromatic hydrocarbons across the air− water interface of Southern Chesapeake Bay." Environmental Science & Technology **31**(6): 1623-1629.

Gustavson, K. E. and J. M. Harkin (2000). "Comparison of sampling techniques and evaluation of semipermeable membrane devices (SPMDs) for monitoring polynuclear aromatic hydrocarbons (PAHs) in groundwater." Environmental Science & Technology **34**(20): 4445-4451.

Haiba, N. S. A. (2017). "Polycyclic Aromatic Hydrocarbons (PAHs) in the River Nile, Egypt: Occurrence and Distribution." Polycyclic Aromatic Compounds **39**(5): 425-433.

Haleyur, N., E. Shahsavari, M. Taha, L. S. Khudur, E. Koshlaf, A. M. Osborn and A. S. Ball (2018). "Assessing the degradation efficacy of native PAH-degrading bacteria from aged, weathered soils in an Australian former gasworks site." Geoderma **321**: 110-117.

Hall, A. T. and J. T. Oris (1991). "Anthracene reduces reproductive potential is maternally transferred during long-term exposure in fathead minnows." Aquatic Toxicology **19**(3): 249-264.

Halsall, C. J., A. J. Sweetman, L. A. Barrie and K. C. Jones (2001). "Modelling the behaviour of PAHs during atmospheric transport from the UK to the Arctic." Atmospheric environment **35**(2): 255-267.

Han, C., P. N. Williams, J. Ren, Z. Wang, X. Fang, D. Xu, X. Xie, J. Geng, L. Q. Ma and J. Luo (2018). "*In situ* sampling and speciation method for measuring dissolved phosphite at ultratrace concentrations in the natural environment." Water Res **137**: 281-289.

Han, J., Y. Liang, B. Zhao, Y. Wang, F. Xing and L. Qin (2019). "Polycyclic aromatic hydrocarbon (PAHs) geographical distribution in China and their source, risk assessment analysis." Environ Pollut **251**: 312-327.

Han, M., K. Yu, R. Zhang, B. Chen, H. Li, Z. E. Zhang, J. Li and G. Zhang (2023). "Sources of the Elevating Polycyclic Aromatic Hydrocarbon Pollution in the Western South China Sea and Its Environmental Implications." Environ Sci Technol **57**(49): 20750-20760.

Han, S., W. Naito, Y. Hanai and S. Masunaga (2013). "Evaluation of trace metals bioavailability in Japanese river waters using DGT and a chemical equilibrium model." Water Res **47**(14): 4880-4892.

Harman, C., S. Brooks, R. C. Sundt, S. Meier and M. Grung (2011). "Field comparison of passive sampling and biological approaches for measuring exposure to PAH and alkylphenols from offshore produced water discharges." Mar Pollut Bull **63**(5-12): 141-148.

Harper, M. P., W. Davison, H. Zhang and W. & Tych (1998). "Kinetics of metal exchange between solids and solutions in sediments and soils interpreted from DGT measured fluxes." Geochimica et Cosmochimica Acta **62**(16): 2757-2770.

Harper, M. P., W. Davison, H. Zhang and W. Tych (1998). "Kinetics of metal exchange between solids and solutions in sediments and soils interpreted from DGT measured fluxes." Geochimica et cosmochimica acta **62**(16): 2757-2770.

Hawthorne, S. B., J. J. Langenfeld, D. J. Miller and M. D. Burford (1992). "Comparison of supercritical CHClF2, N2O, and CO2 for the extraction of polychlorinated biphenyls and polycyclic aromatic hydrocarbons." Analytical chemistry (Washington, DC) **64**: 1614-1622.

Hawthorne, S. B. and D. J. Miller (1987). "Directly coupled supercritical fluid extraction—gas chromatographic analysis of polycyclic aromatic hydro-carbons and polychlorinated biphenyls from environmental solids." Journal of Chromatography A **403**: 63-76.

He, H., G. J. Hu, C. Sun, S. L. Chen, M. N. Yang, J. Li, Y. Zhao and H. Wang (2011). "Trace analysis of persistent toxic substances in the main stream of Jiangsu section of the Yangtze River, China." Environ Sci Pollut Res Int **18**(4): 638-648.

He, J., S. Fan, Q. Meng, Y. Sun, J. Zhang and F. Zu (2014). "Polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matters in Nanjing, China: Distributions, sources and meteorological influences." Atmospheric Environment **89**: 207-215.

Hebert, V. R. and G. C. Miller (1990). "Depth dependence of direct and indirect photolysis on soil surfaces." Journal of agricultural and food chemistry **38**(3): 913-918.

Heemken, O. P., N. Theobald and B. W. Wenclawiak (1997). "Comparison of ASE and SFE with Soxhlet, sonication, and methanolic saponification extractions for the determination of organic micropollutants in marine particulate matter." Analytical chemistry **69**(11): 2171-2180.

Heidari, S., A. Reyhanitabar and S. Oustan (2017). "Kinetics of phosphorus desorption from calcareous soils using DGT technique." Geoderma **305**: 275-280.

Hose, G. and P. Van den Brink (2004). "Confirming the species-sensitivity distribution concept for endosulfan using laboratory, mesocosm, and field data." Archives of environmental contamination and toxicology **47**: 511-520.

Hose, J. E., J. B. Hannah, D. DiJulio, M. L. Landolt, B. S. Miller, W. T. Iwaoka and S. P. Felton (1982). "Effects of benzo (a) pyrene on early development of flatfish." Archives of Environmental Contamination and Toxicology **11**: 167-171.

Howsam, M. and K. C. Jones (1998). "Sources of PAHs in the environment." PAHs and Related Compounds: Chemistry: 137-174.

Hua, G., J. Broderick, K. T. Semple, K. Killham and I. Singleton (2007). "Rapid quantification of polycyclic aromatic hydrocarbons in hydroxypropyl-beta-cyclodextrin (HPCD) soil extracts by synchronous fluorescence spectroscopy (SFS)." Environ Pollut **148**(1): 176-181.

Huang, Y. R., S. S. Liu, J. X. Zi, S. M. Cheng, J. Li, Ying, , G. G. and C. E. Chen (2023). "*In situ* insight into the availability and desorption kinetics of per-and polyfluoroalkyl substances in soils with diffusive gradients in thin films." Environmental Science & Technology **57**(20): 7809-7817.

Huckins, J. N., G. K. Manuweera, J. D. Petty, D. Mackay and J. A. & Lebo (1993). "Lipid-containing semipermeable membrane devices for monitoring organic contaminants in water." Environmental Science & Technology **27**(12): 2489-2496.

Hutchins, C. M., J. G. Panther, P. R. Teasdale, F. Wang, R. R. Stewart, W. W. Bennett and H. Zhao (2012). "Evaluation of a titanium dioxide-based DGT technique for measuring inorganic uranium species in fresh and marine waters." Talanta **97**: 550-556.

Hutchinson, T. C., J. A. Hellebust and C. Soto (1981). "Effect of naphthalene and aqueous crude oil extracts on the green flagellate Chlamydomonas angulosa. IV. Decreases in cellular manganese and potassium." Canadian Journal of Botany **59**(5): 742-749.

Incardona, J. P., T. K. Collier and N. L. Scholz (2004). "Defects in cardiac function precede morphological abnormalities in fish embryos exposed to polycyclic aromatic hydrocarbons." Toxicol Appl Pharmacol **196**(2): 191-205.

Jeng, H. A., C. H. Pan, W. Y. Lin, M. T. Wu, S. Taylor, G. P. Chang-Chien, G. Zhou and N. Diawara (2013). "Biomonitoring of polycyclic aromatic hydrocarbons from coke oven emissions and reproductive toxicity in nonsmoking workers." J Hazard Mater **244-245**: 436-443.

Jia, T., W. Guo, W. Liu, Y. Xing, R. Lei, X. Wu and S. Sun (2021). "Spatial distribution of polycyclic aromatic hydrocarbons in the water-sediment system near chemical industry parks in the Yangtze River Delta, China." Sci Total Environ **754**: 142176.

Jiao, X. C., F. L. Xu, R. Dawson, S. H. Chen and S. Tao (2007). "Adsorption and absorption of polycyclic aromatic hydrocarbons to rice roots." Environ Pollut **148**(1): 230-235.

Johansson, I. and B. van Bavel (2003). "Levels and patterns of polycyclic aromatic hydrocarbons in incineration ashes." Sci Total Environ **311**(1-3): 221-231.

Johnsen, A. R. and U. Karlson (2004). "Evaluation of bacterial strategies to promote the bioavailability of polycyclic aromatic hydrocarbons." Appl Microbiol Biotechnol **63**(4): 452-459.

Johnson, D. L., K. C. Jones, C. J. Langdon, T. G. Piearce and K. T. Semple (2002). "Temporal changes in earthworm availability and extractability of polycyclic aromatic hydrocarbons in soil." Soil Biology and Biochemistry **34**(9): 1363-1370.

Johnson, W. P. and G. L. Amy (1995). "Facilitated transport and enhanced desorption of polycyclic aromatic hydrocarbons by natural organic matter in aquifer sediments." Environ Sci Technol **29**(3): 807-817.

Jonker, M. T., S. A. van der Heijden, M. Kotte and F. Smedes (2015). "Quantifying the effects of temperature and salinity on partitioning of hydrophobic organic chemicals to silicone rubber passive samplers." Environ Sci Technol **49**(11): 6791-6799.

Jurewicz, J., M. Radwan, W. Sobala, S. Brzeznicki, D. Ligocka, P. Radwan, M. Bochenek and W. Hanke (2013). "Association between a biomarker of exposure to polycyclic aromatic hydrocarbons and semen quality." Int J Occup Med Environ Health **26**(5): 790-801.

Kagan, J., T. P. Wang, A. S. Benight, R. W. Tuveson, G. R. Wang and P. P. Fu (1990). "The phototoxicity of nitro polycyclic aromatic hydrocarbons of environmental importance." Chemosphere **20**(5): 453-466.

Kalf, D. F., Trudie Crommentuijn and E. J. v. d. Plassche. (1997). "Environmental Quality Objectives for 10 Polycyclic Aromatic Hydrocarbons (PAHs)." Ecotoxicology and environmental safety **36**(1): 89-97.

Kamangar, F., P. T. Strickland, A. Pourshams, R. Malekzadeh, Boffetta, P., Roth, M. J., ... and S. M. Dawsey (2005). "High exposure to polycyclic aromatic hydrocarbons may contribute to high risk of esophageal cancer in northeastern Iran." Anticancer research **25**(1B): 425-428.

Kang, S. and B. Xing (2005). "Phenanthrene sorption to sequentially extracted soil humic acids and humins." Environmental Science & Technology **39**(1): 134-140.

Karaca, G. (2016). "Spatial Distribution of Polycyclic Aromatic Hydrocarbon (PAH) Concentrations in Soils from Bursa, Turkey." Arch Environ Contam Toxicol **70**(2): 406-417.

Kasprzyk-Hordern, B., R. M. Dinsdale and A. J. Guwy (2008). "The effect of signal suppression and mobile phase composition on the simultaneous analysis of multiple classes of acidic/neutral pharmaceuticals and personal care products in surface water by solid-phase extraction and ultra performance liquid chromatography-negative electrospray tandem mass spectrometry." Talanta **74**(5): 1299-1312.

Kayali-Sayadi, M. N., S. Rubio-Barroso, C. A. Díaz-Díaz and L. M. Polo-Díez (2000). "Rapid determination of PAHs in soil samples by HPLC with fluorimetric detection following sonication extraction." Fresenius' journal of analytical chemistry **368**: 697-701.

Kefi, B. B., L. L. El Atrache, H. Kochkar and A. Ghorbel (2011). "TiO2 nanotubes as solid-phase extraction adsorbent for the determination of polycyclic aromatic hydrocarbons in environmental water samples." J Environ Sci (China) **23**(5): 860-867.

Khan, M. I., S. A. Cheema, C. Shen, C. Zhang, X. Tang, Z. Malik, X. Chen and Y. Chen (2011). "Assessment of pyrene bioavailability in soil by mild hydroxypropyl-beta-cyclodextrin extraction." Arch Environ Contam Toxicol **60**(1): 107-115.

Kibechu, R. W., S. Sampath, B. B. Mamba and T. A. M. Msagati (2017). "Graphene-based molecularly imprinted polymer for separation and pre-concentration of trace polycyclic aromatic hydrocarbons in environmental water samples." Journal of Applied Polymer Science **134**(37).

Kicinska, A. and P. Dmytrowski (2023). "Anthropogenic impact on soils of protected areas-example of PAHs." Sci Rep **13**(1): 1524.

Kim, K. H., S. A. Jahan, E. Kabir and R. J. Brown (2013). "A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects." Environ Int **60**: 71-80.

Kim, P.-G., A. Tarafdar and J.-H. Kwon (2023). "Effect of soil pH on the sorption capacity of soil organic matter for polycyclic aromatic hydrocarbons in unsaturated soils." Pedosphere **33**(2): 365-371.

King, A. J., J. W. Readman and J. L. Zhou (2003). "The application of solid-phase micro-extraction

(SPME) to the analysis of polycyclic aromatic hydrocarbons (PAHs)." Environmental geochemistry and health **25**(69-75).

Kingston, J. K., R. Greenwood, G. A. Mills, G. M. Morrison and L. B. Persson (2000). "Development of a novel passive sampling system for the time-averaged measurement of a range of organic pollutants in aquatic environments." J Environ Monit **2**(5): 487-495.

Kot-Wasik, A., B. Zabiegala, M. Urbanowicz, E. Dominiak, A. Wasik and J. Namiesnik (2007). "Advances in passive sampling in environmental studies." Anal Chim Acta **602**(2): 141-163.

Kot, A., Zabiegała, B., & Namieśnik, J. (2000). "Passive sampling for long-term monitoring of organic pollutants in water." TrAC Trends in Analytical Chemistry **19**(7): 446-459.

Kramer, A. L., L. Campbell, J. Donatuto, M. Heidt, M. Kile and S. L. Massey Simonich (2020). "Impact of local and regional sources of PAHs on tribal reservation air quality in the U.S. Pacific Northwest." Sci Total Environ **710**: 136412.

Kumar, M., N. S. Bolan, S. A. Hoang, A. D. Sawarkar, T. Jasemizad, B. Gao, S. Keerthanan, L. P. Padhye, L. Singh, S. Kumar, M. Vithanage, Y. Li, M. Zhang, M. B. Kirkham, A. Vinu and J. Rinklebe (2021). "Remediation of soils and sediments polluted with polycyclic aromatic hydrocarbons: To immobilize, mobilize, or degrade?" J Hazard Mater **420**: 126534.

Kumar, R., S. Adhikari and R. U. Halden (2022). "Comparison of sorption models to predict analyte loss during sample filtration and evaluation of the impact of filtration on data quality." Sci Total Environ **817**: 152624.

Kumar, R., V. Verma, M. Thakur, G. Singh and B. Bhargava (2023). "A systematic review on mitigation of common indoor air pollutants using plant-based methods: a phytoremediation approach." Air Qual Atmos Health: 1-27.

Kumari, R., D. K. Patel, P. Chaturvedi, N. G. Ansari and R. Chandra Murthy (2013). "Solid phase micro extraction combined with gas chromatography-mass spectrometry for the trace analysis of polycyclic aromatic hydrocarbons in chocolate." Analytical Methods **5**(8).

Kwack, S. J. and B. Mu Lee (2000). "Correlation between DNA or protein adducts and benzo [a] pyrene diol epoxide I–triglyceride adduct detected in vitro and in vivo. ." Carcinogenesis **21**(4): 629-632.

Li, B., S. Wu, S. Zhou, T. Wang and C. Wang (2018). "Spatiotemporal distribution and dynamic modeling of atmospheric gaseous polycyclic aromatic hydrocarbons in a rapidly urbanizing city: Nanjing, China." Environ Geochem Health **40**(6): 2603-2616.

Li, H. and Y. Ma (2016). "Field study on the uptake, accumulation, translocation and risk assessment of PAHs in a soil-wheat system with amendments of sewage sludge." Sci Total Environ **560-561**: 55-61.

Li, H. and L. Wang (2013). "Highly selective detection of polycyclic aromatic hydrocarbons using multifunctional magnetic-luminescent molecularly imprinted polymers." ACS Appl Mater Interfaces **5**(21): 10502-10509.

Li, H., X. Wang, S. Peng, Z. Lai and Y. Mai (2022). "Seasonal variation of temperature affects HMW-PAH accumulation in fishery species by bacterially mediated LMW-PAH degradation." Sci Total Environ **853**: 158617.

Li, N., K. Możdżeń, Z. Zhang, C. Liu, P. Zandi, M. F. Sardar and C. Zhu (2021). "Rhizosphere effect on removal and bioavailability of PAHs in contaminated agricultural soil." Biologia **76**(3): 841-851.

Li, R., X. Tang, W. Guo, L. Lin, L. Zhao, Y. Hu and M. Liu (2020). "Spatiotemporal distribution dynamics of heavy metals in water, sediment, and zoobenthos in mainstream sections of the middle and lower Changjiang River." Sci Total Environ **714**: 136779.

Li, S. Q., H. G. Ni and H. Zeng (2017). "PAHs in polystyrene food contact materials: An unintended consequence." Sci Total Environ **609**: 1126-1131.

Li, X., S. Tao, W. Liu, X. Li, H. Chen and S. Wu (2010). "Dry deposition of polycyclic aromatic hydrocarbons and its influence on surface soil contamination in Tianjin, China." J Environ Monit **12**(4): 952-957.

Li, Y., C. L. Chen, W. Chen, J. Chen, X. Cai, K. C. Jones and H. Zhang (2019). "Development of a Passive Sampling Technique for Measuring Pesticides in Waters and Soils." J Agric Food Chem **67**(22): 6397-6406.

Li, Y., C. Han, J. Luo, K. C. Jones and H. Zhang (2021). "Use of the Dynamic Technique DGT to Determine the Labile Pool Size and Kinetic Resupply of Pesticides in Soils and Sediments." Environ Sci Technol **55**(14): 9591-9600.

Li, Y., D. Mu, H.-Q. Wu, H.-J. Liu, Y.-H. Wang, G.-C. Ma, X.-M. Duan, J.-J. Zhou, C.-M. Zhang and X.-H. Lu (2023). "Derivation of copper water quality criteria in Bohai Bay for the protection of local aquatic life and the ecological risk assessment." Marine Pollution Bulletin **190**: 114863.

Li, Y., S. Rothwell, H. Cheng, K. C. Jones and H. Zhang (2019). "Bioavailability and metabolism in a soil-crop system compared using DGT and conventional extraction techniques." Environment international **130**: 104924.

Li, Y., S. Rothwell, H. Cheng, K. C. Jones and H. Zhang (2019). "Bioavailability and metabolism in a soil-crop system compared using DGT and conventional extraction techniques." Environ Int **130**:

104924.

Lian, X., G. Zhang, Y. Yang, M. Chen, W. Yang, C. Cheng, B. Huang, Z. Fu, X. Bi, Z. Zhou and M. Li (2022). "Measurement of the mixing state of PAHs in individual particles and its effect on PAH transport in urban and remote areas and from major sources." Environ Res **214**(Pt 4): 114075.

Liang, Y., H. Li, S. Li and S. Chen (2023). "Organic diffusive gradients in thin films (o-DGT) for determining environmental behaviors of antibiotics: A review." J Hazard Mater **459**: 132279.

Lima, A. L. C., J. W. Farrington and C. M. Reddy (2005). "Combustion-Derived Polycyclic Aromatic Hydrocarbons in the Environment—A Review." Environmental Forensics **6**(2): 109-131.

Lin, Z., Z. Zhen, C. Chen, Y. Li, C. Luo, L. Zhong, H. Hu, J. Li, Y. Zhang, Y. Liang, J. Yang and D. Zhang (2018). "Rhizospheric effects on atrazine speciation and degradation in laterite soils of Pennisetum alopecuroides (L.) Spreng." Environ Sci Pollut Res Int **25**(13): 12407-12418.

Liu, H., D. Weisman, Y.-b. Ye, B. Cui, Y.-h. Huang, A. Colón-Carmona and Z.-h. Wang (2009). "An oxidative stress response to polycyclic aromatic hydrocarbon exposure is rapid and complex in Arabidopsis thaliana." Plant Science **176**(3): 375-382.

Liu, J. L., J. Zhang, F. Liu and L. L. Zhang (2014). "Polycyclic aromatic hydrocarbons in surface sediment of typical estuaries and the spatial distribution in Haihe river basin." Ecotoxicology **23**(4): 486-494.

Liu, M., J. Feng, P. Hu, L. Tan, X. Zhang and J. Sun (2016). "Spatial-temporal distributions, sources of polycyclic aromatic hydrocarbons (PAHs) in surface water and suspended particular matter from the upper reach of Huaihe River, China." Ecological Engineering **95**: 143-151.

Liu, Q.-S., T. Zheng, P. Wang, J.-P. Jiang and N. Li (2010). "Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers." Chemical Engineering Journal **157**(2-3): 348-356.

Lobpreis, T., E. Lopuchin, B. Vrana, K. Dercová, G. Mills and R. Greenwood (2010). "Monitoring of polycyclic aromatic hydrocarbons in the Portsmouth Harbour, United Kingdom, using the Chemcatcher® passive sampling devices
" Acta Chimica Slovaca **3**(1): 81-94.

Lucas, A., A. Rate, H. Zhang, S. U. Salmon and N. Radford (2012). "Development of the diffusive gradients in thin films technique for the measurement of labile gold in natural waters." Anal Chem **84**(16): 6994-7000.

Luo, J., H. Cheng, J. Ren, W. Davison and H. Zhang (2014). "Mechanistic insights from DGT and soil solution measurements on the uptake of Ni and Cd by radish." Environ Sci Technol **48**(13): 7305-7313.

Luo, J., D. Yin, H. Cheng, W. Davison and H. Zhang (2018). "Plant Induced Changes to Rhizosphere Characteristics Affecting Supply of Cd to Noccaea caerulescens and Ni to Thlaspi goesingense." Environmental Science & Technology **52**(9): 5085-5093.

Luo, L., S. Lin, H. Huang and S. Zhang (2012). "Relationships between aging of PAHs and soil properties." Environ Pollut **170**: 177-182.

Luque-García, J. L. and M. D. Luque de Castro (2003). "Ultrasound: a powerful tool for leaching." TrAC Trends in Analytical Chemistry **22**(1): 41-47.

Lyszczarz, S., J. Lasota, M. M. Szuszkiewicz and E. Blonska (2021). "Soil texture as a key driver of polycyclic aromatic hydrocarbons (PAHs) distribution in forest topsoils." Sci Rep **11**(1): 14708.

Ma, J., R. Xiao, J. Li, J. Yu, Y. Zhang and L. Chen (2010). "Determination of 16 polycyclic aromatic hydrocarbons in environmental water samples by solid-phase extraction using multi-walled carbon nanotubes as adsorbent coupled with gas chromatography-mass spectrometry." J Chromatogr A **1217**(34): 5462-5469.

Ma, L., J. Zhang, L. Han, W. Li, L. Xu, F. Hu and H. Li (2012). "The effects of aging time on the fraction distribution and bioavailability of PAH." Chemosphere **86**(10): 1072-1078.

Maisto, G., F. De Nicola, P. Iovieno, M. V. Prati and A. Alfani (2006). "PAHs and trace elements in volcanic urban and natural soils." Geoderma **136**(1-2): 20-27.

Maletic, S. P., J. M. Beljin, S. D. Roncevic, M. G. Grgic and B. D. Dalmacija (2019). "State of the art and future challenges for polycyclic aromatic hydrocarbons is sediments: sources, fate, bioavailability and remediation techniques." J Hazard Mater **365**: 467-482.

Maliszewska-Kordybach, B. and B. Smreczak (2000). "Ecotoxicological Activity of Soils Polluted with Polycyclic Aromatic Hydrocarbons (PAHs) - Effect on Plants." Environmental Technology **21**(10): 1099-1110.

Manoli, E., A. Kouras, O. Karagkiozidou, G. Argyropoulos, D. Voutsa and C. Samara (2016). "Polycyclic aromatic hydrocarbons (PAHs) at traffic and urban background sites of northern Greece: source apportionment of ambient PAH levels and PAH-induced lung cancer risk." Environ Sci Pollut Res Int **23**(4): 3556-3568.

Manzetti, S. (2013). "Polycyclic Aromatic Hydrocarbons in the Environment: Environmental Fate and Transformation." Polycyclic Aromatic Compounds **33**(4): 311-330.

Mao, Y., L. Zhang, Y. Wang, L. Yang, Y. Yin, X. Su, Y. Liu, H. Pang, J. Xu, Y. Hu and X. Shen (2021). "Effects of polycyclic aromatic hydrocarbons (PAHs) from different sources on soil enzymes and microorganisms of Malus prunifolia var. Ringo." Archives of Agronomy and Soil Science **67**(14): 2048-2062.

Marcé, R. M. and F. Borrull (2000). "Solid-phase extraction of polycyclic aromatic compounds " Journal of Chromatography A **885**: 273-290.

Marques, M., M. Mari, J. Sierra, M. Nadal and J. L. Domingo (2017). "Solar radiation as a swift pathway for PAH photodegradation: A field study." Sci Total Environ **581-582**: 530-540.

Marrucci, A., B. Marras, S. S. Campisi and M. Schintu (2013). "Using SPMDs to monitor the seawater concentrations of PAHs and PCBs in marine protected areas (Western Mediterranean)." Mar Pollut Bull **75**(1-2): 69-75.

Martin, H., B. M. Patterson, G. B. Davis and P. Grathwohl (2003). "Field trial of contaminant groundwater monitoring: comparing time-integrating ceramic dosimeters and conventional water sampling." Environmental Science & Technology **37**(7): 1360-1364.

Martin, H., M. Piepenbrink and P. Grathwohl (2001). "Ceramic dosimeters for time-integrated contaminant monitoring." Journal of Process Analytical Chemistry **6**(2): 68-73.

Martinez, E., M. Gros, S. Lacorte and D. Barceló (2004). "Simplified procedures for the analysis of polycyclic aromatic hydrocarbons in water, sediments and mussels." Journal of Chromatography A **1047**(2): 181-188.

Martinkosky, L., J. Barkley, G. Sabadell, H. Gough and S. Davidson (2017). "Earthworms (Eisenia fetida) demonstrate potential for use in soil bioremediation by increasing the degradation rates of heavy crude oil hydrocarbons." Sci Total Environ **580**: 734-743.

Martins de Barros, R., S. Lissalde, R. Guibal and G. Guibaud (2023). "Adaptation of the o-DGT for the sampling of 12 hormones: calibration, performance evaluation, and recommendation." Environ Sci Pollut Res Int **30**(26): 68177-68190.

Matscheko, N., S. Lundstedt, L. Svensson, J. Harju and M. Tysklind (2009). "Accumulation and elimination of 16 polycyclic aromatic compounds in the earthworm (Eisenia fetida)." Environmental Toxicology and Chemistry **21**(8): 1724-1729.

Mattina, M. I., W. Lannucci-Berger, C. Musante and J. C. White (2003). "Concurrent plant uptake of heavy metals and persistent organic pollutants from soil." Environmental Pollution **124**(3): 375-378.

Mazzella, N., T. Debenest and F. Delmas (2008). "Comparison between the polar organic chemical integrative sampler and the solid-phase extraction for estimating herbicide time-weighted average concentrations during a microcosm experiment." Chemosphere **73**(4): 545-550.

McCann, J. H. and K. R. Solomon (2000). "The effect of creosote on membrane ion leakage in Myriophyllum spicatum L." Aquatic Toxicology **50**(3): 275-284.

McDonough, C. A., M. A. Khairy, D. C. Muir and R. Lohmann (2014). "Significance of population centers as sources of gaseous and dissolved PAHs in the lower Great Lakes." Environ Sci Technol **48**(14): 7789-7797.

Means, J. C., S. G. Wood, J. J. Hassett and W. L. & Banwart (1980). "Sorption of polynuclear aromatic hydrocarbons by sediments and soils." Environmental Science & Technology **14**(12): 1524-1528.

Menegario, A. A., L. N. M. Yabuki, K. S. Luko, P. N. Williams and D. M. Blackburn (2017). "Use of diffusive gradient in thin films for *in situ* measurements: A review on the progress in chemical fractionation, speciation and bioavailability of metals in waters." Anal Chim Acta **983**: 54-66.

Menichini, E. (1992). "Urban air pollution by polycyclic aromatic hydrocarbons: levels and sources of variability." Science of the total environment **116**(1-2): 109-135.

MEPC Water quality—Determination of polycyclic aromatic hydrocarbons by Gas chromatography-Mass Spectrometry.

MEPC (2009). Water quality—Determination of polycyclic aromatic hydrocarbons —Liquid-liquid extraction and solid-phase extraction followed by high performance liquid chromatographic method (HJ 478-2009).

MEPC (2016). Soil and Sediment—Determination of polycyclic aromatic hydrocarbons by Gas chromatography- Mass Spectrometry Method (HJ 805-2016).

Meulenberg, R., H. H. Rijnaarts, H. J. Doddema and J. A. Field (1997). "Partially oxidized polycyclic aromatic hydrocarbons show an increased bioavailability and biodegradability." FEMS Microbiology Letters **152**(1): 45-49.

Miller, J. S. and D. Olejnik (2001). "Photolysis of polycyclic aromatic hydrocarbons in water." Water research **35**(1): 233-243.

Moeckel, C., T. Harner, L. Nizzetto, B. Strandberg, A. Lindroth and K. C. Jones (2009). "Use of depuration compounds in passive air samplers: results from active sampling-supported field deployment, potential uses, and recommendations. ." Environmental Science & Technology **43**(9): 3227-3232.

Monteyne, E., P. Roose and C. R. Janssen (2013). "Application of a silicone rubber passive sampling technique for monitoring PAHs and PCBs at three Belgian coastal harbours." Chemosphere **91**(3): 390-398.

Moon, H. B., H. S. Kim, M. Choi and H. G. Choi (2010). "Intake and potential health risk of polycyclic aromatic hydrocarbons associated with seafood consumption in Korea from 2005 to 2007." Arch Environ Contam Toxicol **58**(1): 214-221.

Moorthy, B., C. Chu and D. J. Carlin (2015). "Polycyclic Aromatic Hydrocarbons: From Metabolism to Lung Cancer." Toxicological Sciences **145**(1): 5-15.

Morillo, E., A. S. Romero, C. Maqueda, L. Madrid, F. Ajmone-Marsan, H. Grcman, ... and J. Villaverde (2007). "Soil pollution by PAHs in urban soils: a comparison of three European cities." Journal of Environmental Monitoring **9**(9): 1001-1008.

Mosallaei, S., H. Hashemi, M. Hoseini, M. Dehghani and A. Naz (2023). "Polycyclic Aromatic Hydrocarbons (PAHs) in household dust: The association between PAHs, Cancer Risk and Sick Building Syndrome." Building and Environment **229**.

Motorykin, O., M. M. Matzke, K. M. Waters and S. L. Massey Simonich (2013). "Association of carcinogenic polycyclic aromatic hydrocarbon emissions and smoking with lung cancer mortality rates on a global scale." Environ Sci Technol **47**(7): 3410-3416.

Muller, J. F., K. Manomanii, M. R. Mortimer and M. S. McLachlan (2001). "Partitioning of polycyclic aromatic hydrocarbons in the polyethylene/water system." Fresenius J Anal Chem **371**(6): 816-822.

Müller, S., K. U. Totsche and I. Kögel-Knabner (2007). "Sorption of polycyclic aromatic hydrocarbons to mineral surfaces." European Journal of Soil Science **58**(4): 918-931.

Mutzner, L., E. L. M. Vermeirssen and C. Ort (2019). "Passive samplers in sewers and rivers with highly fluctuating micropollutant concentrations - Better than we thought." J Hazard Mater **361**: 312-320.

Nam, J. J., A. J. Sweetman and K. C. Jones (2009). "Polynuclear aromatic hydrocarbons (PAHs) in global background soils." J Environ Monit **11**(1): 45-48.

Nam, J. J., G. O. Thomas, F. M. Jaward, E. Steinnes, O. Gustafsson and K. C. Jones (2008). "PAHs in background soils from Western Europe: influence of atmospheric deposition and soil organic matter." Chemosphere **70**(9): 1596-1602.

Navarro, P., E. Cortazar, L. Bartolome, M. Deusto, J. C. Raposo, O. Zuloaga, G. Arana and N. Etxebarria (2006). "Comparison of solid phase extraction, saponification and gel permeation chromatography for the clean-up of microwave-assisted biological extracts in the analysis of polycyclic aromatic hydrocarbons." J Chromatogr A **1128**(1-2): 10-16.

Ncube, S., P. Kunene, N. T. Tavengwa, H. Tutu, H. Richards, E. Cukrowska and L. Chimuka (2017). "Synthesis and characterization of a molecularly imprinted polymer for the isolation of the 16 US-EPA priority polycyclic aromatic hydrocarbons (PAHs) in solution." J Environ Manage **199**: 192-200.

Nesnow, S., M. J. Mass, J. A. Ross, A. J. Galati, G. Lambert, C. Gennings, ... and G. D. & Stoner (1998). "Lung tumorigenic interactions in strain A/J mice of five environmental polycyclic aromatic hydrocarbons." Environmental Health Perspectives **106**(suppl 6): 1337-1346.

Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., & Ouddane, B. (2014). "Case study of PAHs, Me-PAHs, PCBs, phthalates and pesticides contamination in the Somme River water, France." International Journal of Environmental Research **8**(4): 1159–1170.

Ni, J., Y. Luo, R. Wei and X. Li (2008). "Distribution patterns of polycyclic aromatic hydrocarbons among different organic carbon fractions of polluted agricultural soils." Geoderma **146**(1-2): 277-282.

Nieuwoudt, C., R. Pieters, L. P. Quinn, H. Kylin, A. R. Borgen and H. Bouwman (2011). "Polycyclic Aromatic Hydrocarbons (PAHs) in Soil and Sediment from Industrial, Residential, and Agricultural Areas in Central South Africa: An Initial Assessment." Soil and Sediment Contamination: An International Journal **20**(2): 188-204.

Northcott, G. L. and K. C. Jones (2001). "Partitioning, extractability, and formation of nonextractable PAH residues in soil. 2. Effects on compound dissolution behavior." Environmental Science & Technology **35**(6): 1111-1117.

Novic, A. J., D. S. O'Brien, S. L. Kaserzon, D. W. Hawker, S. E. Lewis and J. F. Mueller (2017). "Monitoring Herbicide Concentrations and Loads during a Flood Event: A Comparison of Grab Sampling with Passive Sampling." Environ Sci Technol **51**(7): 3880-3891.

Nowakowski, M., I. Rykowska, R. Wolski and P. Andrzejewski (2021). "Polycyclic Aromatic Hydrocarbons (PAHs) and their Derivatives (O-PAHs, N-PAHs, OH-PAHs): Determination in Suspended Particulate Matter (SPM) – a Review." Environmental Processes **9**(1).

O'Hara, S. (2009). Silicone rubber passive samplers for water quality monitoring of persistent organic pollutants in the marine environment.

Oen, A. M., G. Cornelissen and G. D. Breedveld (2006). "Relation between PAH and black carbon contents in size fractions of Norwegian harbor sediments." Environ Pollut **141**(2): 370-380.

Oliferova, L., M. Statkus, G. Tsysin, O. Shpigun and Y. Zolotov (2005). "On-line solid-phase extraction and HPLC determination of polycyclic aromatic hydrocarbons in water using fluorocarbon polymer sorbents." Analytica Chimica Acta **538**(1-2): 35-40.

Olivella, M. A. (2006). "Isolation and analysis of polycyclic aromatic hydrocarbons from natural water using accelerated solvent extraction followed by gas chromatography-mass spectrometry." Talanta **69**(1): 267-275.

Olsson, A. C., J. Fevotte, T. Fletcher, A. Cassidy, A. t Mannetje, D. Zaridze, N. Szeszenia-Dabrowska, P. Rudnai, J. Lissowska, E. Fabianova, D. Mates, V. Bencko, L. Foretova, V. Janout, P. Brennan and P. Boffetta (2010). "Occupational exposure to polycyclic aromatic hydrocarbons and lung cancer risk: a multicenter study in Europe." Occup Environ Med **67**(2): 98-103.

Orazi, M. M., A. H. Arias, A. L. Oliva, A. C. Ronda and J. E. Marcovecchio (2020). "Characterization of atmospheric and soil polycyclic aromatic hydrocarbons and evaluation of air-soil relationship in the Southwest of Buenos Aires province (Argentina)." Chemosphere **240**: 124847.

Oukebdane, K., F. Portet-Koltalo, N. Machour, F. Dionnet and P. L. Desbene (2010). "Comparison of hot Soxhlet and accelerated solvent extractions with microwave and supercritical fluid extractions for the determination of polycyclic aromatic hydrocarbons and nitrated derivatives strongly adsorbed on soot collected inside a diesel particulate filter." Talanta **82**(1): 227-236.

Paget-Bailly, S., D. Cyr and D. Luce (2012). "Occupational exposures to asbestos, polycyclic aromatic hydrocarbons and solvents, and cancers of the oral cavity and pharynx: a quantitative literature review." Int Arch Occup Environ Health **85**(4): 341-351.

Parrott, J. L., S. M. Backus, A. I. Borgmann and M. Swyripa (1999). "The use of semipermeable membrane devices to concentrate chemicals in oil refinery effluent on the Mackenzie River." Arctic: 125-138.

Pawar, R. M. (2012). The effect of soil pH on degradation of polycyclic aromatic hydrocarbons (Doctoral dissertation).

Peng, P. L. and L. H. Lim (2022). "Polycyclic Aromatic Hydrocarbons (PAHs) Sample Preparation and Analysis in Beverages: A Review." Food Analytical Methods **15**(4): 1042-1061.

Pérez, A. L. and K. A. Anderson (2009). "DGT estimates cadmium accumulation in wheat and potato from phosphate fertilizer applications." Science of the total environment **407**(18): 5096-5103.

Pichette, C., H. Zhang, W. Davison and S. Sauve (2007). "Preventing biofilm development on DGT devices using metals and antibiotics." Talanta **72**(2): 716-722.

Pil-Gon, K. I. M., A. Tarafdar and K. W. O. N. Jung-Hwan (2023). "Effect of soil pH on the sorption capacity of soil organic matter for polycyclic aromatic hydrocarbons in unsaturated soils." Pedosphere **33**(2): 365-371.

Piniewski, M., P. Marcinkowski, J. Koskiaho and S. Tattari (2019). "The effect of sampling frequency and strategy on water quality modelling driven by high-frequency monitoring data in a boreal catchment." Journal of Hydrology **579**.

Qin, N., W. He, X. Z. Kong, W. X. Liu, Q. S. He, B. Yang, H. L. Ouyang, Q. M. Wang and F. L. Xu (2013). "Atmospheric partitioning and the air-water exchange of polycyclic aromatic hydrocarbons in a large shallow Chinese lake (Lake Chaohu)." Chemosphere **93**(9): 1685-1693.

Rasolzadeh, F. and P. Hashemi (2019). "Magnetic fiber headspace solid-phase microextraction coupled to GC-MS for the extraction and quantitation of polycyclic aromatic hydrocarbons." Mikrochim Acta **186**(7): 432.

Ratola, N., S. Lacorte, A. Alves and D. Barcelo (2006). "Analysis of polycyclic aromatic hydrocarbons in pine needles by gas chromatography-mass spectrometry: comparison of different extraction and clean-up procedures." J Chromatogr A **1114**(2): 198-204.

Reid, B. J., K. C. Jones and K. T. Semple (2000). "Bioavailability of persistent organic pollutants in soils and sediments—a perspective on mechanisms, consequences and assessment." Environmental Pollution **108**(1): 103-112.

Ren, S., Y. Wang, Y. Cui, Y. Wang, X. Wang, J. Chen and F. Tan (2020). "Desorption kinetics of tetracyclines in soils assessed by diffusive gradients in thin films." Environ Pollut **256**: 113394.

Rentz, J. A., P. J. Alvarez and J. L. Schnoor (2005). "Benzo[a]pyrene co-metabolism in the presence of plant root extracts and exudates: Implications for phytoremediation." Environ Pollut **136**(3): 477-484.

Rizzi, C., S. Villa, A. V. Waichman, G. S. de Souza Nunes, R. de Oliveira, M. Vighi and A. Rico (2023). "Occurrence, sources, and ecological risks of polycyclic aromatic hydrocarbons (PAHs) in the Amazon river." Chemosphere **336**: 139285.

Rogerson, A. and J. Berger (1983). "Enhancement of the microbial degradation of crude oil by the ciliate Colpidium colpoda." The Journal of General and Applied Microbiology **29**(1): 41-50.

Rokhbar, M., B. Keshavarzi, F. Moore, M. Zarei, P. S. Hooda and M. J. Risk (2023). "Occurrence and source of PAHs in Miankaleh International Wetland in Iran." Chemosphere **321**: 138140.

Rong, Q., Y. Li, J. Luo, L. Yan, K. C. Jones and H. Zhang (2024). "Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems." J Hazard Mater **470**: 134199.

Rota, M., C. Bosetti, S. Boccia, P. Boffetta and C. La Vecchia (2014). "Occupational exposures to polycyclic aromatic hydrocarbons and respiratory and urinary tract cancers: an updated systematic review and a meta-analysis to 2014." Arch Toxicol **88**(8): 1479-1490.

Rougerie, J., R. Martins de Barros, R. Buzier, D. Devillers, P. Fondaneche, S. Lissalde, J. Leblanc, M. Saut, J. P. Rebillard, N. Mazzella and G. Guibaud (2021). "Diffusive gradients in thin films (DGT): A suitable tool for metals/metalloids monitoring in continental waterbodies at the large network scale." Sci Total Environ **754**: 142147.

Rusina, T. P., F. Smedes, J. Klanova, K. Booij and I. Holoubek (2007). "Polymer selection for passive sampling: a comparison of critical properties." Chemosphere **68**(7): 1344-1351.

Salim, F. and T. Gorecki (2019). "Theory and modelling approaches to passive sampling." Environ Sci Process Impacts **21**(10): 1618-1641.

Samsøe-Petersen, L., E. H. Larsen, P. B. Larsen and P. Bruun (2002). "Uptake of trace elements and PAHs by fruit and vegetables from contaminated soils." Environmental science & technology **36**(14): 3057-3063.

Schafer, R. B., L. Hearn, B. J. Kefford, J. F. Mueller and D. Nugegoda (2010). "Using silicone passive samplers to detect polycyclic aromatic hydrocarbons from wildfires in streams and potential acute effects for invertebrate communities." Water Res **44**(15): 4590-4600.

Schlautman, M. A. and J. J. Morgan (1993). "Effects of aqueous chemistry on the binding of polycyclic aromatic hydrocarbons by dissolved humic materials." Environmental Science & Technology **27**(5): 961-969.

Schwab, A. P., A. A. Al-Assi and M. K. Banks (1998). "Adsorption of Naphthalene onto Plant Roots." Journal of Environmental Quality **27**(1): 220-224.

Seethapathy, S., T. Gorecki and X. Li (2008). "Passive sampling in environmental analysis." J Chromatogr A **1184**(1-2): 234-253.

Semple, K. T., K. J. Doick, K. C. Jones, P. Burauel, A. Craven and H. Harms (2004). "Defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. ." Environmental Science & Technology **38**(12): 228A-231A.

Shen, H., Y. Huang, R. Wang, D. Zhu, W. Li, G. Shen, B. Wang, Y. Zhang, Y. Chen, Y. Lu, H. Chen, T. Li, K. Sun, B. Li, W. Liu, J. Liu and S. Tao (2013). "Global atmospheric emissions of polycyclic aromatic hydrocarbons from 1960 to 2008 and future predictions." Environ Sci Technol **47**(12): 6415-6424.

Silalahi, E. T. M. E., S. Anita and H. Y. Teruna (2021). Comparison of extraction techniques for the determination of polycyclic aromatic hydrocarbons (PAHs) in soil. Journal of Physics: Conference Series, IOP Publishing.

Simonich, S. L. and R. A. Hites (1994). "Vegetation-atmosphere partitioning of polycyclic aromatic hydrocarbons." Environmental Science & Technology **28**(5): 939-943.

Simonich, S. L. and R. A. Hites (1995). "Organic pollutant accumulation in vegetation." Environ Sci

Technol **29**(12): 2905-2914.

Skic, K., P. Boguta, A. Klimkowicz-Pawlas, A. Ukalska-Jaruga and A. Baran (2023). "Effect of sorption properties on the content, ecotoxicity, and bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) in bottom sediments." J Hazard Mater **442**: 130073.

Smedes, F., Geertsma, R. W., Zande, T. V. D., & Booij, K. (2009). "Polymer— water partition coefficients of hydrophobic compounds for passive sampling: Application of cosolvent models for validation." Environmental Science & Technology **43**(18): 7047-7054.

Smith, K. E., M. Green, G. O. Thomas and K. C. Jones (2001). "Behavior of sewage sludge-derived PAHs on pasture." Environmental Science & Technology **35**(11): 2141-2150.

Smith, K. E. and K. C. Jones (2000). "Particles and vegetation: implications for the transfer of particle-bound organic contaminants to vegetation." Science of The Total Environment **246**(2-3): 207-236.

Smith, K. E., G. O. Thomas and K. C. Jones (2001). "Seasonal and Species Differences in the Air—Pasture Transfer of PAHs." Environmental Science & Technology **35**(11): 2156-2165.

Smith, M. J., T. H. Flowers, H. J. Duncan and J. Alder (2006). "Effects of polycyclic aromatic hydrocarbons on germination and subsequent growth of grasses and legumes in freshly contaminated soil and soil with aged PAHs residues." Environ Pollut **141**(3): 519-525.

Soclo, H. H., Garrigues, P. H., & Ewald, M. (2000). "Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas." Marine Pollution Bulletin **40**(5): 387-396.

Song, M., Y. Su, L. Jiang, K. Peng, J. Li, S. Liu and C. ... Luo (2023). "Assessing the bioavailability of antibiotics in soil with the diffusive gradients in thin films (DGT)." Journal of Hazardous Materials **448**: 130935.

Song, M., Y. Su, L. Jiang, K. Peng, J. Li, S. Liu, Y. Sun, C. E. Chen and C. Luo (2023). "Assessing the bioavailability of antibiotics in soil with the diffusive gradients in thin films (DGT)." J Hazard Mater **448**: 130935.

Sorensen, L., M. S. Silva, A. M. Booth and S. Meier (2016). "Optimization and comparison of miniaturized extraction techniques for PAHs from crude oil exposed Atlantic cod and haddock eggs." Anal Bioanal Chem **408**(4): 1023-1032.

Soriano-Disla, J. M., T. W. Speir, I. Gómez, L. M. Clucas, R. G. McLaren and J. Navarro-Pedreño (2010). "Evaluation of Different Extraction Methods for the Assessment of Heavy Metal Bioavailability in Various Soils." Water, Air, & Soil Pollution **213**(1-4): 471-483.

Soto, C., J. A. Hellebust and T. C. Hutchinson (1977). "Effect of naphthalene and aqueous crude oil extracts on the green flagellate Chlamydomonas angulosa. III. Changes in cellular composition." Canadian Journal of Botany **55**(22): 2765-2777.

Soumeya, K.-K., H. Cheraitia, G. Durand and S. Cherif (2021). "Contamination and Sources Identification of Polycyclic Aromatic Hydrocarbons in Water and Sediments of Annaba Bay Basin, Algeria." Water Resources **48**(1): 111-123.

Southworth, G. R. (1979). "Role of volatilization in removing polycyclic aromatic hydrocarbons from aquatic environments." Bull. Environ. Contam. Toxicol.;(United States) **21**: 4/5.

Souza, M. R. R., E. Santos, J. S. Suzarte, L. O. Carmo, M. Frena, F. C. Damasceno and M. R. Alexandre (2018). "Concentration, distribution and source apportionment of polycyclic aromatic hydrocarbons (PAH) in Poxim River sediments, Brazil." Mar Pollut Bull **127**: 478-483.

St George, T., P. Vlahos, T. Harner, P. Helm and B. Wilford (2011). "A rapidly equilibrating, thin film, passive water sampler for organic contaminants; characterization and field testing." Environ Pollut **159**(2): 481-486.

St Helen, G., D. Dempsey, M. Wilson, P. Jacob, 3rd and N. L. Benowitz (2013). "Racial differences in the relationship between tobacco dependence and nicotine and carcinogen exposure." Addiction **108**(3): 607-617.

Stading, R., G. Gastelum, C. Chu, W. Jiang and B. Moorthy (2021). "Molecular mechanisms of pulmonary carcinogenesis by polycyclic aromatic hydrocarbons (PAHs): Implications for human lung cancer." Semin Cancer Biol **76**: 3-16.

Staninska, J., Z. Szczepaniak, P. Cyplik and A. Piotrowska-Cyplik (2015). "The effect of organic and clay fraction on polycyclic aromatic hydrocarbons mobility in soil model systems." Journal of Research and Applications in Agricultural Engineering, **60**(1): 98-101.

Steffen, K. T., S. Schubert, M. Tuomela, A. Hatakka and M. Hofrichter (2007). "Enhancement of bioconversion of high-molecular mass polycyclic aromatic hydrocarbons in contaminated non-sterile soil by litter-decomposing fungi." Biodegradation **18**(3): 359-369.

Stephan, C. E., D. I. Mount, D. J. Hansen, J. Gentile, G. A. Chapman and W. A. Brungs (1985). Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses, US Environmental Protection Agency Washington, DC.

Sun, J., L. Pan, D. C. W. Tsang, Y. Zhan, L. Zhu and X. Li (2018). "Organic contamination and remediation in the agricultural soils of China: A critical review." Sci Total Environ **615**: 724-740.

Sun, J. H., G. L. Wang, Y. Chai, G. Zhang, J. Li and J. Feng (2009). "Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan Reach of the Yellow River, Middle China." Ecotoxicol Environ Saf **72**(5): 1614-1624.

Sun, K., Y. Song, F. He, M. Jing, J. Tang and R. Liu (2021). "A review of human and animals exposure to polycyclic aromatic hydrocarbons: Health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics." Sci Total Environ **773**: 145403.

Sungthong, R., P. van West, M. Cantos and J. J. Ortega-Calvo (2015). "Development of eukaryotic zoospores within polycyclic aromatic hydrocarbon (PAH)-polluted environments: a set of behaviors that are relevant for bioremediation." Sci Total Environ **511**: 767-776.

Sushkova, S., T. Minkina, I. Deryabkina, V. Rajput, E. Antonenko, O. Nazarenko, B. K. Yadav, E. Hakki and D. Mohan (2019). "Environmental pollution of soil with PAHs in energy producing plants zone." Sci Total Environ **655**: 232-241.

Sushkova, S., T. Minkina, S. Tarigholizadeh, E. Antonenko, E. Konstantinova, C. Gülser, ... and R. Kızılkaya (2020). "PAHs accumulation in soil-plant system of Phragmites australis Cav. in soil under long-term chemical contamination." Eurasian Journal of Soil Science **9**(3): 242-253.

Sweetman, A. J., M. D. Valle, K. Prevedouros and K. C. Jones (2005). "The role of soil organic carbon in the global cycling of persistent organic pollutants (POPs): interpreting and modelling field data." Chemosphere **60**(7): 959-972.

Tang, J. and M. Alexander (2009). "Mild extractability and bioavailability of polycyclic aromatic hydrocarbons in soil." Environmental Toxicology and Chemistry **18**(12): 2711-2714.

Tang, L., F. O. Gudda, C. Wu, W. Ling, H. El-Ramady, A. Mosa and J. Wang (2022). "Contributions of partition and adsorption to polycyclic aromatic hydrocarbons sorption by fractionated soil at different particle sizes." Chemosphere **301**: 134715.

Tang, N., T. Hattori, R. Taga, K. Igarashi, X. Yang, K. Tamura, H. Kakimoto, V. F. Mishukov, A. Toriba, R. Kizu and K. Hayakawa (2005). "Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan–Japan Sea countries." Atmospheric Environment **39**(32): 5817-5826.

Tang, Y. S., J. N. Cape and M. A. Sutton (2001). "Development and Types of Passive Samplers for Monitoring Atmospheric NO2 and NH3 Concentrations." The Scientific World JOURNAL **1**: 513-529.

Tao, S., Y. H. Cui, J. Cao, F. L. Xu, R. Dawson and B. G. Li (2002). "Determination of PAHs in wastewater irrigated agricultural soil using accelerated solvent extraction." J Environ Sci Health B **37**(2): 141-150.

Tao, S., X. C. Jiao, S. H. Chen, W. X. Liu, R. M. Coveney, L. Z. Zhu and Y. M. Luo (2006). "Accumulation and distribution of polycyclic aromatic hydrocarbons in rice (Oryza sativa)." Environmental Pollution

140(3): 406-415.

Tao, Y., S. Zhang, Z. Wang and P. Christie (2008). "Predicting bioavailability of PAHs in soils to wheat roots with triolein-embedded cellulose acetate membranes and comparison with chemical extraction." Journal of agricultural and food chemistry **56**(22): 10817-10823.

Tarigholizadeh, S., S. Sushkova, V. D. Rajput, A. Ranjan, J. Arora, T. Dudnikova, A. Barbashev, S. Mandzhieva, T. Minkina and M. H. Wong (2024). "Transfer and Degradation of PAHs in the Soil-Plant System: A Review." J Agric Food Chem **72**(1): 46-64.

Tipping, E., H. T. Corbishley, J.-F. Koprivnjak, D. J. Lapworth, M. P. Miller, C. D. Vincent and J. Hamilton-Taylor (2009). "Quantification of natural DOM from UV absorption at two wavelengths." Environmental Chemistry **6**(6).

Tobiszewski, M. and J. Namiesnik (2012). "PAH diagnostic ratios for the identification of pollution emission sources." Environ Pollut **162**: 110-119.

Tsai, C. J., M. L. Chen, K. F. Chang, F. K. Chang and I. F. Mao (2009). "The pollution characteristics of odor, volatile organochlorinated compounds and polycyclic aromatic hydrocarbons emitted from plastic waste recycling plants." Chemosphere **74**(8): 1104-1110.

Tsay, J. J., K. M. Tchou-Wong, A. K. Greenberg, H. Pass and W. N. Rom (2013). "Aryl hydrocarbon receptor and lung cancer." Anticancer research **33**(4): 1247-1256.

Tureyen, O. E., S. D. Yakan, A. Yilmaz, B. Yetiskin, O. Okay and O. S. Okay (2022). "Polycyclic Aromatic Hydrocarbon Accumulation Performances of Monophasic Butyl Rubber Passive Samplers." Environmental Processes **9**(2).

Turner, G. S., G. A. Mills, M. J. Bowes, J. L. Burnett, S. Amos and G. R. Fones (2014). "Evaluation of DGT as a long-term water quality monitoring tool in natural waters; uranium as a case study." Environmental Science: Processes & Impacts **16**(3): 393-403.

Uddin, M. M. and F. Xu (2024). "Sources, Occurrences, and Risks of Polycyclic Aromatic Hydro-Carbons (PAHs) in Bangladesh: A Review of Current Status." Atmosphere **15**(2).

USEPA (1993). Provisional guidance for quantitative risk assessment of polycyclic aromatic hydrocarbons (Vol. 600). A. O. C. Environmental Criteria, Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, US Environmental Protection Agency.t.

USEPA (1998). Locating and Estimating Air Emissions from Sources of Polycyclic Organic Matter. EPA. Washington, DC.

USEPA, S. (1986). Test methods for evaluating solid waste: physical/chemical methods. http://www.

epa. gov/epaoswer/hazwaste/test/7_series. htm.

Valenzuela, E. F., H. C. Menezes and Z. L. Cardeal (2020). "Passive and grab sampling methods to assess pesticide residues in water. A review." Environmental Chemistry Letters **18**(4): 1019-1048.

Varea, M., N. Galindo, J. Gil-Molto, C. Pastor and J. Crespo (2011). "Particle-bound polycyclic aromatic hydrocarbons in an urban, industrial and rural area in the western Mediterranean." J Environ Monit **13**(9): 2471-2476.

Venkatraman, G., N. Giribabu, P. S. Mohan, B. Muttiah, V. K. Govindarajan, M. Alagiri, P. S. Abdul Rahman and S. A. Karsani (2024). "Environmental impact and human health effects of polycyclic aromatic hydrocarbons and remedial strategies: A detailed review." Chemosphere **351**: 141227.

Vijayanand, M., A. Ramakrishnan, R. Subramanian, P. K. Issac, M. Nasr, K. S. Khoo, R. Rajagopal, B. Greff, N. I. Wan Azelee, B. H. Jeon, S. W. Chang and B. Ravindran (2023). "Polyaromatic hydrocarbons (PAHs) in the water environment: A review on toxicity, microbial biodegradation, systematic biological advancements, and environmental fate." Environ Res **227**: 115716.

Vogt, R. D., P. Porcal, J. Hejzlar, M. C. Paule-Mercado, S. Haaland, C. B. Gundersen, G. I. Orderud and B. Eikebrokk (2023). "Distinguishing between Sources of Natural Dissolved Organic Matter (DOM) Based on Its Characteristics." Water **15**(16).

Vrana, B., I. J. Allan, R. Greenwood, G. A. Mills, E. Dominiak, K. Svensson, J. Knutsson and G. Morrison (2005). "Passive sampling techniques for monitoring pollutants in water." TrAC Trends in Analytical Chemistry **24**(10): 845-868.

Vrana, B., G. Mills, R. Greenwood, J. Knutsson, K. Svensson and G. Morrison (2005). "Performance optimisation of a passive sampler for monitoring hydrophobic organic pollutants in water." J Environ Monit **7**(6): 612-620.

Vrana, B., G. A. Mills, E. Dominiak and R. Greenwood (2006). "Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water." Environ Pollut **142**(2): 333-343.

Vrana, B., G. A. Mills, M. Kotterman, P. Leonards, K. Booij and R. Greenwood (2007). "Modelling and field application of the Chemcatcher passive sampler calibration data for the monitoring of hydrophobic organic pollutants in water." Environ Pollut **145**(3): 895-904.

Vrana, B., G. A. Mills, P. E. Leonards, M. Kotterman, M. Weideborg, J. Hajslova, V. Kocourek, M. Tomaniova, J. Pulkrabova, M. Suchanova, K. Hajkova, S. Herve, H. Ahkola and R. Greenwood (2010). "Field performance of the Chemcatcher passive sampler for monitoring hydrophobic organic pollutants in surface water." J Environ Monit **12**(4): 863-872.

Vrana, B., A. Paschke and P. Popp (2006). "Calibration and field performance of membrane-enclosed sorptive coating for integrative passive sampling of persistent organic pollutants in water." Environ Pollut **144**(1): 296-307.

Vrana, B., P. Popp, A. Paschke and G. Schüürmann (2001). "Membrane-enclosed sorptive coating. An integrative passive sampler for monitoring organic contaminants in water." Analytical chemistry **73**(21): 5191-5200.

Vroblesky, D. A. and M. D. Petkewich (2000). "Field testing of passive diffusion bag samplers for volatile organic compound concentrations in ground water, Naval Industrial Reserve ordnance plant, Fridley, Minnesota, November 1999 and May 2000, (No. 2000-4246).". from https://pubs.usgs.gov/publication/wri004246.

Wakeham, S. G., C. Schaffner and W. Giger (1980). "Polycyclic aromatic hydrocarbons in recent lake sediments—I. Compounds having anthropogenic origins." Geochimica et cosmochimica acta **44**(3): 403-413.

Wang, C., X. Wang, P. Gong and T. Yao (2014). "Polycyclic aromatic hydrocarbons in surface soil across the Tibetan Plateau: spatial distribution, source and air-soil exchange." Environ Pollut **184**: 138-144.

Wang, C., S. Wu, S. L. Zhou, H. Wang, B. Li, H. Chen, Y. Yu and Y. Shi (2015). "Polycyclic aromatic hydrocarbons in soils from urban to rural areas in Nanjing: Concentration, source, spatial distribution, and potential human health risk." Sci Total Environ **527-528**: 375-383.

Wang, C., S. Zhou, S. Wu, J. Song, Y. Shi, B. Li and H. Chen (2017). "Surface water polycyclic aromatic hydrocarbons (PAH) in urban areas of Nanjing, China." Water Sci Technol **76**(7-8): 2150-2157.

Wang, C., L. Zhu and C. Zhang (2015). "A new speciation scheme of soil polycyclic aromatic hydrocarbons for risk assessment." Journal of Soils and Sediments **15**(5): 1139-1149.

Wang, F., D. Zhao, P. Lu, D. Zhang, Z. Guo, N. L. Rose and G. Zhang (2024). "Air-plant interaction and air-soil exchange of polycyclic aromatic hydrocarbons in a large human-influenced reservoir in southwest China." Environ Pollut **355**: 124216.

Wang, J., Y. Bi, G. Pfister, B. Henkelmann, K. Zhu and K. W. Schramm (2009). "Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD)." Chemosphere **75**(8): 1119-1127.

Wang, J., C. Wang, Q. Huang, F. Ding and X. He (2015). "Adsorption of PAHs on the Sediments from the Yellow River Delta as a Function of Particle Size and Salinity." Soil and Sediment Contamination: An International Journal **24**(2): 103-115.

Wang, J., H. Zhang, H. Bao, J. Li, J. Li, W. Xing, H. Hong and F. Wu (2020). "Dynamic distribution and accumulation of PAHs in winter wheat during whole plant growth: Field investigation." Ecotoxicol Environ Saf **202**: 110886.

Wang, J., X. Zhang, W. Ling, R. Liu, J. Liu, F. Kang and Y. Gao (2017). "Contamination and health risk assessment of PAHs in soils and crops in industrial areas of the Yangtze River Delta region, China." Chemosphere **168**: 976-987.

Wang, J. Z., C. Z. Zhu and T. H. Chen (2013). "PAHs in the Chinese environment: levels, inventory mass, source and toxic potency assessment." Environ Sci Process Impacts **15**(6): 1104-1112.

Wang, K. and B. Xing (2005). "Structural and sorption characteristics of adsorbed humic acid on clay minerals. ." Journal of Environmental Quality **34**(1): 342-349.

Wang, R., E. Biles, Y. Li, M. D. Juergens, M. J. Bowes, K. C. Jones and H. Zhang (2020). "*In situ* Catchment Scale Sampling of Emerging Contaminants Using Diffusive Gradients in Thin Films (DGT) and Traditional Grab Sampling: A Case Study of the River Thames, UK." Environ Sci Technol **54**(18): 11155-11164.

Wang, R., H. Cao, W. Li, W. Wang, W. Wang, L. Zhang, J. Liu, H. Ouyang and S. Tao (2011). "Spatial and seasonal variations of polycyclic aromatic hydrocarbons in Haihe Plain, China." Environ Pollut **159**(5): 1413-1418.

Wang, R., K. C. Jones and H. Zhang (2020). "Monitoring Organic Pollutants in Waters Using the Diffusive Gradients in the Thin Films Technique: Investigations on the Effects of Biofouling and Degradation." Environ Sci Technol **54**(13): 7961-7969.

Wang, R., Y. Zou, J. Luo, K. C. Jones and H. Zhang (2019). "Investigating Potential Limitations of Current Diffusive Gradients in Thin Films (DGT) Samplers for Measuring Organic Chemicals." Anal Chem **91**(20): 12835-12843.

Wang, W., B. Meng, X. Lu, Y. Liu and S. Tao (2007). "Extraction of polycyclic aromatic hydrocarbons and organochlorine pesticides from soils: a comparison between Soxhlet extraction, microwave-assisted extraction and accelerated solvent extraction techniques." Anal Chim Acta **602**(2): 211-222.

Wang, X.-H., X. Wang, G. Huppes, R. Heijungs and N.-Q. Ren (2015). "Environmental implications of increasingly stringent sewage discharge standards in municipal wastewater treatment plants: case study of a cool area of China." Journal of Cleaner Production **94**: 278-283.

Wang, X., W. Shi, J. Wu, Y. Hao, G. Hu, H. Liu, X. Han and H. Yu (2010). "Reproductive toxicity of organic extracts from petrochemical plant effluents discharged to the Yangtze River, China." J Environ Sci (China) **22**(2): 297-303.

Wang, X., K. Yuan, B. Chen, L. Lin, B. Huang and T. Luan (2016). "Monthly variation and vertical distribution of parent and alkyl polycyclic aromatic hydrocarbons in estuarine water column: Role of suspended particulate matter." Environ Pollut **216**: 599-607.

Wang, Z., Y. Liu, A. Zhang, L. Yang, C. Wei, Y. Chen, Z. Liu and Z. Li (2024). "Occurrence characteristics, environmental trend, and source analysis of polycyclic aromatic hydrocarbons in the water environment of industrial zones." Environ Res **245**: 118053.

Wang, Z., W. C. Scott, E. S. Williams, M. Ciarlo, P. C. DeLeo and B. W. Brooks (2018). "Identification of novel uncertainty factors and thresholds of toxicological concern for health hazard and risk assessment: Application to cleaning product ingredients." Environment international **113**: 357-376.

Wania, F. and D. Mackay (1996). "Peer reviewed: tracking the distribution of persistent organic pollutants." Environmental Science & Technology **30**(9): 390A-396A.

Warnken, K. W., H. Zhang and W. Davison (2006). "Accuracy of the diffusive gradients in thin-films technique: diffusive boundary layer and effective sampling area considerations." Analytical chemistry **78**(11): 3780-3787.

Weber Jr, W. J., E. J. LeBoeuf, T. M. Young and W. Huang (2001). "Contaminant interactions with geosorbent organic matter: insights drawn from polymer sciences." Water research **35**(4): 853-868.

Weber Jr, W. J., P. M. McGinley and L. E. Katz (1992). "A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments." Environmental Science & Technology **26**(10): 1955-1962.

Weiß, H., Schirmer, K., Bopp, S., & Grathwohl, P. (2007). "Use of ceramic dosimeters in water monitoring." Comprehensive Analytical Chemistry **48**: 279-293.

Weissenfels, W. D., H. J. Klewer and J. & Langhoff (1992). "Adsorption of polycyclic aromatic hydrocarbons (PAHs) by soil particles: influence on biodegradability and biotoxicity." Applied Microbiology and Biotechnology **36**: 689-696.

Weng, Z., M. T. Rose, E. Tavakkoli, L. Van Zwieten, G. Styles, W. Bennett and E. Lombi (2019). "Assessing plant-available glyphosate in contrasting soils by diffusive gradient in thin-films technique (DGT)." Sci Total Environ **646**: 735-744.

Wilcke, W. (2007). "Global patterns of polycyclic aromatic hydrocarbons (PAHs) in soil." Geoderma **141**(3-4): 157-166.

Wild, E., J. Dent, J. L. Barber, G. O. Thomas and K. C. Jones (2004). "A novel analytical approach for visualizing and tracking organic chemicals in plants " Environmental Science & Technology **38**(15): 4195-4199.

Wild, E., J. Dent, G. O. Thomas and K. C. Jones (2005). "Real-time visualization and quantification of PAH photodegradation on and within plant leaves. ." Environmental Science & Technology **39**(1): 268-273.

Wild, E., J. Dent, G. O. Thomas and K. C. Jones (2006). "Visualizing the air-to-leaf transfer and within-leaf movement and distribution of phenanthrene: further studies utilizing two-photon excitation microscopy." Environmental Science & Technology **40**(3): 907-916.

Wild, S. R. and K. C. Jones (1993). "Biological and abiotic losses of polynuclear aromatic hydrocarbons (PAHs) from soils freshly amended with sewage sludge. ." Environmental Toxicology and Chemistry: An International Journal **12**(1): 5-12.

Wild, S. R. and K. C. Jones (1994). "The significance of polynuclear aromatic hydrocarbons applied to agricultural soils in sewage sludges in the UK." Waste management & research **12**(1): 49-59.

Wild, S. R. and K. C. Jones (1995). "Polynuclear aromatic hydrocarbons in the United Kingdom environment: a preliminary source inventory and budget." Environmental Pollution **88**(1): 91-108.

Williams, P. N., H. Zhang, W. Davison, S. Zhao, Y. Lu, F. Dong, L. Zhang and Q. Pan (2012). "Evaluation of *in situ* DGT measurements for predicting the concentration of Cd in chinese field-cultivated rice: impact of soil Cd:Zn ratios." Environ Sci Technol **46**(15): 8009-8016.

Wilson, S. C. and K. C. Jones (1993). "Bioremediation of soil contaminated with polynuclear aromatic hydrocarbons (PAHs): a review." Environmental pollution **81**(3): 229-249.

Wilson, W. B., U. Hewitt, M. Miller and A. D. Campiglia (2014). "Water analysis of the sixteen environmental protection agency-polycyclic aromatic hydrocarbons via solid-phase nanoextraction-gas chromatography/mass spectrometry." J Chromatogr A **1345**: 1-8.

Wong, C. M., Williams, C. E., Collier, U., Schelle, P., & Pittock, J. (2007). "World's top 10 rivers at risk. ." esocialsciences. com Working Papers.

Woodward, D. F., P. M. Mehrle Jr and W. L. Mauck (1981). "Accumulation and sublethal effects of a Wyoming crude oil in cutthroat trout." Transactions of the American Fisheries Society **110**(3): 437-445.

Wu, B., S. Guo, X. Li and J. Wang (2018). "Temporal and spatial variations of polycyclic aromatic hydrocarbons (PAHs) in soils from a typical organic sewage irrigation area." Sci Total Environ **613-614**: 513-520.

Wu, X. and L. Zhu (2016). "Evaluating bioavailability of organic pollutants in soils by sequential ultrasonic extraction procedure." Chemosphere **156**: 21-29.

Wu, Z., T. Lin, L. Hu, T. Guo and Z. Guo (2022). "Polycyclic aromatic hydrocarbons in sediment-porewater system from the East China Sea: Occurrence, partitioning, and diffusion." Environ Res **209**: 112755.

Xie, H., J. Chen, Q. Chen, C. L. Chen, J. Du, F. Tan and C. Zhou (2018). "Development and evaluation of diffusive gradients in thin films technique for measuring antibiotics in seawater." Sci Total Environ **618**: 1605-1612.

Xie, H., Q. Chen, J. Chen, C. L. Chen and J. Du (2018). "Investigation and application of diffusive gradients in thin-films technique for measuring endocrine disrupting chemicals in seawaters." Chemosphere **200**: 351-357.

Xie, Y., Z. Gu, H. M. S. K. Herath, M. Gu, C. He, F. Wang, X. Jiang, J. Zhang and Y. Zhang (2017). "Evaluation of bacterial biodegradation and accumulation of phenanthrene in the presence of humic acid." Chemosphere **184**: 482-488.

Xing, B. (2001). "Sorption of naphthalene and phenanthrene by soil humic acids." Environmental Pollution **111**(2): 303-309.

Xing, B. and J. J. Pignatello (1997). "Dual-mode sorption of low-polarity compounds in glassy poly (vinyl chloride) and soil organic matter. ." Environmental Science & Technology **31**(3): 792-799.

Xing, Z., L. Chow, H. Rees, F. Meng, S. Li, B. Ernst, G. Benoy, T. Zha and L. M. Hewitt (2013). "Influences of sampling methodologies on pesticide-residue detection in stream water." Arch Environ Contam Toxicol **64**(2): 208-218.

Xu, F.-L., Y.-L. Li, Y. Wang, W. He, X.-Z. Kong, N. Qin, W.-X. Liu, W.-J. Wu and S. E. Jorgensen (2015). "Key issues for the development and application of the species sensitivity distribution (SSD) model for ecological risk assessment." Ecological Indicators **54**: 227-237.

Xu, L., J. Feng, J. Li, X. Liu and S. Jiang (2012). "Graphene oxide bonded fused-silica fiber for solid-phase microextraction-gas chromatography of polycyclic aromatic hydrocarbons in water." J Sep Sci **35**(1): 93-100.

Xu, P., B. Liu, H. Chen, H. Wang, X. Guo and J. Yuan (2024). "PAHs as environmental pollutants and their neurotoxic effects." Comp Biochem Physiol C Toxicol Pharmacol **283**: 109975.

Xu, S., W. Liu and S. Tao (2006). "Emission of Polycyclic Aromatic Hydrocarbons in China." Environmental Science & Technology **40**(3): 702–708.

Xu, S., W. Liu and S. Tao (2006). "Emission of polycyclic aromatic hydrocarbons in China." Environmental Science & Technology **40**(3): 702-708.

Yan, L., Q. Rong, H. Zhang, K. C. Jones, Y. Li and J. Luo (2022). "Evaluation and Application of a Novel Diffusive Gradients in Thin-Films Technique for *In situ* Monitoring of Glucocorticoids in Natural Waters." Environ Sci Technol **56**(22): 15499-15507.

Yan, Z., H. Yang, H. Dong, B. Ma, H. Sun, T. Pan, R. Jiang, R. Zhou, J. Shen, J. Liu and G. Lu (2018). "Occurrence and ecological risk assessment of organic micropollutants in the lower reaches of the Yangtze River, China: A case study of water diversion." Environ Pollut **239**: 223-232.

Yang, H., G. Lu, Z. Yan, J. Liu, H. Dong, R. Jiang, R. Zhou, P. Zhang, Y. Sun and M. Nkoom (2019). "Occurrence, spatial-temporal distribution and ecological risks of pharmaceuticals and personal care products response to water diversion across the rivers in Nanjing, China." Environ Pollut **255**(Pt 1): 113132.

Yang, L., M. Jin, C. Tong and S. Xie (2013). "Study of dynamic sorption and desorption of polycyclic aromatic hydrocarbons in silty-clay soil." J Hazard Mater **244-245**: 77-85.

Yang, M., X. Xu, D. Wang, Q. Liu, J. Lyu, L. Lin, D. Wang, Y. Chen and W. Liang (2022). "Distribution characteristics, source and ecological risks assessment of Polycyclic Aromatic Hydrocarbons in water bodies of
typical sections of the Yangtze River " China Environmental Science **42**(11): 5308-5317.

Yang, W., T. Hadibarata, A. H. Mahmoud and A. Yuniarto (2020). "Biotransformation of pyrene in soil in the presence of earthworm Eisenia fetida." Environmental Technology & Innovation **18**.

Yang, W., D. Lampert, N. Zhao, D. Reible and W. Chen (2012). "Link between black carbon and resistant desorption of PAHs on soil and sediment." Journal of Soils and Sediments **12**(5): 713-723.

Yang, Y., Z. Chen, J. Zhang, S. Wu, L. Yang, L. Chen and Y. Shao (2021). "The challenge of micropollutants in surface water of the Yangtze River." Sci Total Environ **780**: 146537.

Yang, Y., S. Liu, R. Wang, C. Li, J. Tang, T. Chen, G. G. Ying and C. E. Chen (2022). "Diffusive gradients in thin films (DGT) probe for effectively sampling of per- and polyfluoroalkyl substances in waters and sediments." J Environ Sci (China) **121**: 90-97.

Yang, Y., S. Tao, N. Zhang, D. Y. Zhang and X. Q. Li (2010). "The effect of soil organic matter on fate of polycyclic aromatic hydrocarbons in soil: A microcosm study." Environ Pollut **158**(5): 1768-1774.

Yang, Y., N. Zhang, M. Xue and S. Tao (2010). "Impact of soil organic matter on the distribution of polycyclic aromatic hydrocarbons (PAHs) in soils." Environ Pollut **158**(6): 2170-2174.

Yin, X., C. Guo, J. Lv, S. Hou, Y. Zhang, X. Jin, Y. Teng and J. Xu (2019). "Biomimetic Accumulation of Methamphetamine and Its Metabolite Amphetamine by Diffusive Gradients in Thin Films to Estimate Their Bioavailability in Zebrafish." Environmental Science & Technology Letters **6**(12): 708-713.

Yu, H., Y. Liu, C. Han, H. Fang, J. Weng, X. Shu, Y. Pan and L. Ma (2021). "Polycyclic aromatic hydrocarbons in surface waters from the seven main river basins of China: Spatial distribution, source apportionment, and potential risk assessment." Sci Total Environ **752**: 141764.

Yunker, M. B., Macdonald, R. W., Vingarzan, R., Mitchell, R. H., Goyette, D., & Sylvestre, S. (2002). "PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition." Organic geochemistry **33**(4): 489-515.

Zabiegala, B., A. Kot-Wasik, M. Urbanowicz and J. Namiesnik (2010). "Passive sampling as a tool for obtaining reliable analytical information in environmental quality monitoring." Anal Bioanal Chem **396**(1): 273-296.

Zakaria, M. P., H. Takada, S. Tsutsumi, K. Ohno, J. Yamada, E. Kouno and H. Kumata (2002). "Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs." Environmental science & technology **36**(9): 1907-1918.

Zeng, J., X. Lin, J. Zhang and X. Li (2010). "Isolation of polycyclic aromatic hydrocarbons (PAHs)-degrading Mycobacterium spp. and the degradation in soil." J Hazard Mater **183**(1-3): 718-723.

Zhang, C., S. Ding, D. Xu, Y. Tang and M. H. Wong (2014). "Bioavailability assessment of phosphorus and metals in soils and sediments: a review of diffusive gradients in thin films (DGT)." Environ Monit Assess **186**(11): 7367-7378.

Zhang, D., Y. Zhu, X. Xie, C. Han, H. Zhang, L. Zhou, M. Li, G. Xu, L. Jiang and A. Li (2019). "Application of diffusive gradients in thin-films for in-situ monitoring of nitrochlorobenzene compounds in aquatic environments." Water Res **157**: 292-300.

Zhang, H. (2004). "In-situ speciation of Ni and Zn in freshwaters: comparison between DGT measurements and speciation models. ." Environmental Science & Technology **38**(5): 1421-1427.

Zhang, H. and W. Davison (1995). "Performance Characteristics of Diffusion Gradients in Thin Films for the *in situ* Measurement of Trace Metals in Aqueous Solution." Analytical Chemistry (Washington) 67(no. 19): 3391-3400.

Zhang, H. and W. Davison (1995). "Performance characteristics of diffusion gradients in thin films for the *in situ* measurement of trace metals in aqueous solution." Analytical chemistry **67**(19): 3391-3400.

Zhang, H. and W. Davison (1999). "Diffusional Characteristics of Hydrogels Used in DGT and DET Techniques." Analytica Chimica Acta **398**: 329-340.

Zhang, H., W. Davison, R. Gadi and T. Kobayashi (1998). "*In situ* measurement of dissolved phosphorus in natural waters using DGT." Analytica Chimica Acta **370**(1): 29-38.

Zhang, H., W. Davison, B. Knight and S. McGrath (1998). "*In situ* measurements of solution concentrations and fluxes of trace metals in soils using DGT." Environmental Science & Technology **32**(5): 704-710.

Zhang, H., S. Zhang, F. He, X. Qin, X. Zhang and Y. Yang (2016). "Characterization of a manganese peroxidase from white-rot fungus Trametes sp.48424 with strong ability of degrading different types of dyes and polycyclic aromatic hydrocarbons." J Hazard Mater **320**: 265-277.

Zhang, H., X. Zhang, Y. Wang, P. Bai, K. Hayakawa, L. Zhang and N. Tang (2022). "Characteristics and Influencing Factors of Polycyclic Aromatic Hydrocarbons Emitted from Open Burning and Stove Burning of Biomass: A Brief Review." Int J Environ Res Public Health **19**(7).

Zhang, H., F. J. Zhao, B. Sun, W. Davison and S. P. Mcgrath (2001). "A new method to measure effective soil solution concentration predicts copper availability to plants." Environmental Science & Technology **35**(12): 2602-2607.

Zhang, J., J. C. Yang, R. Q. Wang, H. Hou, X. M. Du, S. K. Fan, J. S. Liu and J. L. Dai (2013). "Effects of pollution sources and soil properties on distribution of polycyclic aromatic hydrocarbons and risk assessment." Sci Total Environ **463-464**: 1-10.

Zhang, K., B. Liang, J. Z. Wang, Y. F. Guan and E. Y. Zeng (2012). "Polycyclic aromatic hydrocarbons in upstream riverine runoff of the Pearl River Delta, China: an assessment of regional input sources." Environ Pollut **167**: 78-84.

Zhang, L., L. Dong, L. Ren, S. Shi, L. Zhou, T. Zhang and Y. Huang (2012). "Concentration and source identification of polycyclic aromatic hydrocarbons and phthalic acid esters in the surface water of the Yangtze River Delta, China." Journal of Environmental Sciences **24**(2): 335-342.

Zhang, P. and Y. Chen (2017). "Polycyclic aromatic hydrocarbons contamination in surface soil of China: A review." Sci Total Environ **605-606**: 1011-1020.

Zhang, S., Q. Zhang, S. Darisaw, O. Ehie and G. Wang (2007). "Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA." Chemosphere **66**(6): 1057-1069.

Zhang, W., Y. Lu, H. Sun, Y. Zhang, M. Zhou, Q. Song and Y. Gao (2019). "Effects of multi-walled carbon nanotubes on pyrene adsorption and desorption in soils: The role of soil constituents." Chemosphere **221**: 203-211.

Zhang, W., C. Wei, X. Chai, J. He, Y. Cai, M. Ren, B. Yan, P. Peng and J. Fu (2012). "The behaviors and fate of polycyclic aromatic hydrocarbons (PAHs) in a coking wastewater treatment plant." Chemosphere **88**(2): 174-182.

Zhang, X., T. Sun, F. Li, C. Ji and H. Wu (2024). "Risk assessment of trace metals and polycyclic aromatic hydrocarbons in seawater of typical bays in the Bohai Sea." Mar Pollut Bull **200**: 116030.

Zhang, Y. and S. Tao (2009). "Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004." Atmospheric Environment **43**(4): 812-819.

Zhang, Y., S. Tao, H. Shen and J. & Ma (2009). "Inhalation exposure to ambient polycyclic aromatic hydrocarbons and lung cancer risk of Chinese population." Proceedings of the National Academy of Sciences **106**(59): 21063-21067.

Zhang, Y., L. Zhang, Z. Huang, Y. Li, J. Li, N. Wu, J. He, Z. Zhang, Y. Liu and Z. Niu (2019). "Pollution of polycyclic aromatic hydrocarbons (PAHs) in drinking water of China: Composition, distribution and influencing factors." Ecotoxicol Environ Saf **177**: 108-116.

Zhang, Y., T. Zhang, C. Guo, S. Hou, Z. Hua, J. Lv, Y. Zhang and J. Xu (2018). "Development and application of the diffusive gradients in thin films technique for simultaneous measurement of methcathinone and ephedrine in surface river water." Sci Total Environ **618**: 284-290.

Zhang, Z. Y., M. J. Yang and J. Pawliszyn (1994). "Solid-phase microextraction integrates sampling, extraction, concentration and sample introduction into a single step." Anal. Chem **66**: 844-853.

Zhao, Z., X. Gong, L. Zhang, M. Jin, Y. Cai and X. Wang (2021). "Riverine transport and water-sediment exchange of polycyclic aromatic hydrocarbons (PAHs) along the middle-lower Yangtze River, China." J Hazard Mater **403**: 123973.

Zheng, B., L. Wang, K. Lei and B. Nan (2016). "Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area, China." Chemosphere **149**: 91-100.

Zheng, J. L., D. X. Guan, J. Luo, H. Zhang, W. Davison, X. Y. Cui, L. H. Wang and L. Q. Ma (2014). "Activated charcoal based diffusive gradients in thin films for *in situ* monitoring of bisphenols in waters." Anal Chem **87**(1): 801-807.

Zheng, S., F. Sheng, C. Gu, Y. Li, Z. Fang and J. Luo (2023). "DGT method for the *in situ* measurement of triazines and the desorption kinetics of atrazine in soil." Environmental Science and Pollution Research **30**(17): 51061-51074.

Zhu, L. and J. Wang (2003). "Sources and patterns of polycyclic aromatic hydrocarbons pollution in kitchen air, China." Chemosphere **50**(5): 611-618.

Zhu, X., Y. Wang, Y. Zhang and B. Chen (2018). "Reduced bioavailability and plant uptake of polycyclic aromatic hydrocarbons from soil slurry amended with biochars pyrolyzed under various temperatures." Environ Sci Pollut Res Int **25**(17): 16991-17001.

Zhu, Y., H. Huang, Y. Zhang, G. Xiong, Q. Zhang, Y. Li, S. Tao and W. Liu (2021). "Evaluation of PAHs in edible parts of vegetables and their human health risks in Jinzhong City, Shanxi Province, China: A multimedia modeling approach." Sci Total Environ **773**: 145076.

Zi, J., S. Xiao, S. Liu and C. E. Chen (2022). "Passive Sampling: A Greener Technique for the 'Dual Carbon' Goal While Implementing the Action Plan for Controlling Emerging Pollutants." Bull Environ Contam Toxicol **110**(1): 6.

Ziyaei, K., M. Mokhtari, M. Hashemi, K. Rezaei and F. Abdi (2024). "Association between exposure to water sources contaminated with polycyclic aromatic hydrocarbons and cancer risk: A systematic review." Sci Total Environ **924**: 171261.

Zou, Y. T., Z. Fang, Y. Li, R. Wang, H. Zhang, K. C. Jones, X. Y. Cui, X. Y. Shi, D. Yin, C. Li, Z. D. Liu, L. Q. Ma and J. Luo (2018). "Novel Method for *in situ* Monitoring of Organophosphorus Flame Retardants in Waters." Anal Chem **90**(16): 10016-10023.

Paper I

Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems

Journal of Hazardous Materials 470 (2024) 134199

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems

Qiuyu Rong[a], Yanying Li[b], Jun Luo[c], Liying Yan[c], Kevin C. Jones[a,*], Hao Zhang[a,*]

[a] *Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, United Kingdom*
[b] *College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning 116023, PR China*
[c] *State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu 210023 PR China*

HIGHLIGHTS

- A novel DGT sampler for in situ monitoring of PAHs is developed using new metal casing and new binding phase.
- Novel molecular imprinted polymer gel (MIP)-DGT binds PAHs under real environmental conditions.
- The new sampler gave quantitative in situ PAH data in waters at the ng/L range with high precision and accuracy.

GRAPHICAL ABSTRACT

ARTICLE INFO

Keywords:
Diffusive gradients in thin-films (DGT)
Passive sampler
Polycyclic aromatic hydrocarbons
Molecularly imprinted polymer (MIP)
Aquatic environment

ABSTRACT

Polycyclic aromatic hydrocarbons (PAHs) are priority pollutants and need to be measured reliably in waters and other media, to understand their sources, fate, behaviour and to meet regulatory monitoring requirements. Conventional water sampling requires large water volumes, time-consuming pre-concentration and clean-up and is prone to analyte loss or contamination. Here, for the first time, we developed and validated a novel diffusive gradients in thin-films (DGT) passive sampler for PAHs. Based on the well-known DGT principles, the sampler pre-concentrates PAHs with typical deployment times of days/weeks, with minimal sample handling. For the first time, DGT holding devices made of metal and suitable for sampling hydrophobic organic compounds were designed and tested. They minimize sorption and sampling lag times. Following tests on different binding layer resins, a MIP-DGT was preferred – the first time applying MIP for PAHs. It samples PAHs independent of pH (3.9 –8.1), ionic strength (0.01 –0.5 M) and dissolved organic matter < 20 mg L^{-1}, making it suitable for applications across a wide range of environments. Field trials in river water and wastewater demonstrated that DGT is a convenient and reliable tool for monitoring labile PAHs, readily achieving quantitative detection of environmental levels (sub-ng and ng/L range) when coupled with conventional GC-MS or HPLC.

---

* Corresponding authors.
E-mail addresses: k.c.jones@lancaster.ac.uk (K.C. Jones), h.zhang@lancaster.ac.uk (H. Zhang).

https://doi.org/10.1016/j.jhazmat.2024.134199
Received 21 January 2024; Received in revised form 22 March 2024; Accepted 31 March 2024
Available online 2 April 2024

Environmental implications: PAHs are carcinogenic and genotoxic compounds. They are environmentally ubiquitous and must be monitored in waters and other media. This study successfully developed a new DGT passive sampler for reliable in situ time-integrated measurements of PAHs in waters at the ng/L level. This is the first time to use passive samplers for accurate measurements of hydrophobic organic contaminants in aquatic systems without calibration, a big step forward in monitoring PAHs. The application of this new sampler will enhance our understanding of the sources, fate, behavior and ecotoxicology of PAHs, enabling improved environmental risk assessment and management of these compounds.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are recognized as hazardous priority organic compounds. They are formed by incomplete combustion, and although they can be produced by volcanic activity and forest fires, human activities are the main sources of PAHs to the environment in recent decades. Important anthropogenic sources include: combustion of coal, oil and gas during power generation, domestic heating, vehicle emissions etc; the discharge of waste gas and wastewater by industry; cooking; the burning of solid waste and garbage [1–4]. The persistence and long-distance transport potential of PAHs has led to their widespread presence in air, water, soil and other environmental media [5–8]. PAHs can enter humans and animals through the skin, respiratory tract and digestive tract, and have potential teratogenic, carcinogenic and mutagenic properties, and neurotoxicity [9,10]. Previous research has found that exposure to PAHs may increase the risk of lung cancer and a range of other cancers (i.e. oral, larynx, pharyngeal, esophageal and bladder) [11–13]; they have therefore been classified as carcinogens by the International Agency for Research on Cancer (IARC). Therefore, countries and international organizations such as the European Union, the United States, and China have policies and regulations for the management of PAHs. The United States Environmental Protection Agency (USEPA) identifies 16 priority PAHs for monitoring and control. Accurate and effective monitoring of PAHs is a prerequisite for understanding their source, distribution, migration, risk assessment and management.

Monitoring of PAHs in water is usually by simple grab sampling, giving an 'instantaneous' concentration. However, it is known that concentrations will vary with flow conditions and discharges from sources, so multiple samples with high frequencies are required for the results to be representative. This can be costly and presents practical difficulties, particularly in remote/inaccessible areas [14,15]. Current methodologies for determining PAH concentrations in water samples involve high-performance liquid chromatography (HPLC), gas chromatography couple with mass spectrometry (GC-MS) and GC-MS/MS. However, the typically low concentrations of PAHs in aquatic environments (often in the ng/L range), pose significant challenges in terms of sample preconcentration and preparation. So, the transportation, storage, and complex sample pre-treatment processes can affect the analysis and accurate measurement of PAHs. Therefore in situ passive sampling of trace constituents in waters has attracted increasing attention in recent decades, because it can address many of these issues. Passive sampling integrates concentrations over the deployment time (typically days, weeks, months) by accumulating trace chemicals from the sampling environment, to give a time weighted average concentration. In previous research, semi-permeable membrane devices (SPMDs), POCIS, Chemcatcher, silicone rubber and ceramic dosimeter passive sampling devices have all been used to monitor PAHs in rivers, seawater, groundwater and other aquatic environments [16–19]. However, changes in environmental factors such as flow rate and temperature can affect the performance of all these types of samplers, so they are generally regarded as semi-quantitative tools. With these designs of passive sampler, it is necessary to calibrate the results from laboratory uptake experiments and kinetic models, or from the loss rates of performance reference compounds (PRCs) which are added to the samplers before deployment [20,21]. Although there has been much research on calibration methods, deviations in results may still be caused by changes in environmental conditions in practical applications [22]. In contrast, the Diffuse Gradients in Thin films (DGT) passive sampler was invented to give quantitative in situ measurements without any field calibration. Based on Fick's first principle of diffusion, the diffusion flux to a DGT sampler is only related to the environmental concentration of the tested substance and temperature [23,24]. Therefore, DGT has inherent advantages over other passive samplers for environmental monitoring and process-based studies.

The DGT technique has been widely used in the determination of inorganic substances (i.e. heavy metals and nutrients) in water, soil, and sediment since its development in 1994 [23,25–27]. It has been used for selected organic chemicals since 2012 and has also been extensively developed and applied [24,28,29]. Macroporous adsorbent resin (XAD18) and hydrophilic lipophilic balanced resin (HLB) are the most widely used adsorption materials. XAD18 resin based DGT was used for monitoring antibiotics [30], illicit drugs [31,32], PFOA and PFOS [33]. HLB resin-based DGT can sample pesticides, insecticides, pharmaceuticals [34], organophophorus flame retardants [35], antibiotics, HPCPs [29], household and personal care products [36]. In addition, XAD1 resin, MAX, XDA1 resin, active carbon, WAX, C8, and C18 materials have been used in DGT devices for the measuring of antibiotics [37], anionic pesticides [38], endocrine disruptors [37], bisphenols [39], per and polyfluoro alkyl salts (PFASs)[40], and organotin [41], respectively.

As will be apparent from the list of compound groups just given, the existing organic DGT sampling devices have been restricted to measuring hydrophilic compounds so far, rather than hydrophobic compounds of low aqueous solubility. Hydrophobic compounds are mostly non-polar and can also have high affinity for filter membranes used in DGT samplers and the sampler casing material which is usually made from acrylonitrile butadiene styrene (ABS). These factors can affect their diffusion in the sampler and pose a challenge when applying DGT to hydrophobic compounds. However, in Wang et al.'s recent research, limitations of using existing DGT sampler for monitoring compounds of high Kow or with several aromatic rings were explored by using model compounds, with a log Kow range of 0.8 − 9.5 [42].

Therefore, the purpose of this study was to develop and test a novel DGT passive sampler that can be used for the in-situ accurate measurement of PAHs (log Kow range from 3.45 for the 2-ringed naphthalene to 6.75 for the 6-ringed Dibenz(a,h)anthracene) in waters. Nine of the16 priority PAHs were selected as test chemicals. Five metal materials were tested as sampler casing materials, because metals normally have a lower sorption of PAHs and other hydrophobics, and a new DGT device was designed. Three binding materials were tested, and the uptake kinetics and capacity of binding gels were determined. The diffusion coefficients of PAHs through the diffusive gel were measured for the first time, and the effects of diffusion layer thickness, deployment time, pH, ionic strength and organic matter concentration on the performance of the DGT samplers were studied. The newly developed DGT samplers were then applied in situ in the field - a river and a wastewater treatment plant.

2. Materials and methods

2.1. Chemicals and reagents

High purity standards were used. They covered 9 of the 16 priority PAHs specified by the U.S. EPA, as follows: Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua), Pyrene (Pyr) and Benzo (a) anthracene (BaA). Table S1 gives their physical and chemical properties. Three different materials, MIP (CNW, Germany), Amberlite XAD 18 (Sigma-Aldrich, China) and Oasis HLB (Waters, U.K.) were used as binding materials. Details are given in the supporting information (SI).

2.2. Analytical methods

The separation of target compounds was performed with a PAH C18 column (4.6 × 250 mm, 5 μ m, Waters). For the determination of the 9 PAHs, high performance liquid chromatography combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) was used. Details of analysis are provided in the SI. The instrumental detection limits (IDLs) for HPLC were calculated according to the standard deviation from a measured concentration of standard (7 times) and method detection limits (MDLs) were calculated on the basis of IDLs, the recoveries for water samples and DGT samples.

2.3. Gel preparation

All materials for DGT samplers were supplied from DGT Research Ltd (Lancaster, UK, www.dgtresearch.com). Diffusive gels and binding gels were prepared according to well documented procedures [24,43]. To make gels of defined thickness, a 0.8 mm or a 0.5 mm PTFE spacer was placed between two glass plates, when making gels, to control the thickness of the diffusion gel and binding gel, respectively. MIP, XAD 18 and HLB resin were tested as the binding materials. Binding gels were made by mixing 2 g (wet weight) of binding materials and 10 mL MQ water with 0.2 g agarose. All the gels were cut into discs with a diameter of 2.51 cm and stored in 0.01 M NaCl solution at 4 °C.

2.4. Adsorption by DGT casing materials and design for new metal device

In order to ensure low blanks and consistent results all the glass containers used were soaked in 5% nonionic surfactant solution for 4 h, rinsed with tap water and then rinsed with deionized water. After drying in an oven, they were heated in a muffle furnace at 500 °C for 4 h. All containers were rinsed with methanol before use. Blank tests were carried out throughout the process.

The various materials used to make the DGT sampler were subjected to adsorption experiments on target PAHs. Traditional ABS plastic DGT casing and five common metal materials (aluminum, aluminum alloy, stainless steel, brass and copper) were exposed to 100 mL solution contained 50 μg L^{-1} of the mixture of 9 compounds (Benzo (a) anthracene was 10 μg L^{-1} because of its low water solubility). They were shaken for 24 h on an orbital shaker (25 °C) at 100 rpm. All materials were immersed in MQ water as blanks, and the PAHs solutions alone served as controls. The ratio of PAHs adsorbed by various materials in 24 h were obtained by the detection of the concentration of the solution before and after deployment. Based on the existing design, a new metal device was first designed and developed for DGT measurement of PAHs.

2.5. Adsorption by filter membranes and diffusive gels

It was necessary to test different gels and filter membranes, to select the most appropriate for use in sampling PAHs. Polyacrylamide gels (PA), agarose gels (AG), eight different filter membranes (cellulose acetate membrane, CA; mixed cellulose ester membrane, MCE; nylon membrane, NL; nucleopore track-etch membrane, PC; polyethersulfone membrane, PES; Polypropylene, PP; Polytetrafluoroethylene, PTFE; Polyvinylidene fluoride, PVDF) were placed in 10 mL brown glass bottles. The operation of the adsorption test was the same as the adsorption test on DGT holders.

2.6. Elution efficiency

Stable and reliable elution efficiency is crucial for the accurate determination of pollutants using DGT technology. Based on previous studies, the extraction efficiency of organic pollutants using acetonitrile ultrasound extraction meets the experimental requirements [36]. Binding gels were added into 10 mL of target PAHs solution. After shaking for 24 h, gels were taken out and ultrasonic extracted for 30 min with 5 mL and 10 mL acetonitrile. The extraction experiments were performed with three binding gels at two concentrations (10 μg L^{-1} and 100 μg L^{-1}), to confirm that a stable recovery rate could be achieved.

2.7. Binding capacity and uptake kinetics of binding gel

To measure the adsorption capacity of the binding gel for the target PAHs, the gel disc was immersed in 500 mL solutions containing 0.01 M NaCl and mixed PAHs. All the solutions were shaken for 48 h at 24 ± 1 °C. The concentrations of Nap, Acy, Ace, Flu and Phe were 20, 40, 100, 200 μg L^{-1}. Because of their lower water solubility, the concentrations of Ant, Flua, and Pyr were 20, 40, 60, 80 μg L^{-1}. According to the concentration difference before and after the experiment, the adsorption amount of the test chemicals on the binding gel was calculated.

To measure the uptake kinetics of the target compounds, binding gel discs were immersed in 40 mL of 0.01 M NaCl solution containing 50 μg L^{-1} mixed PAHs and placed on a horizontal shaker at 100 rpm. The sampling time was set from 5 min to 36 h, and three parallels were set for each time point. A 0.5 mL aqueous solution sample was taken each time, 0.5 mL acetonitrile added, and then filtered with a 0.22 μm PTFE filter for HPLC detection.

2.8. Diffusion coefficient measurements

The method to determine diffusion coefficients using a diffusion cell has been reported in previous studies [36,43]. The diffusion cell used was made from stainless steel to reduce adsorption, and a cover was added to reduce the volatilization of PAHs during the experiment. The two compartments were connected through a window with a diameter of 1.5 cm. A 0.8 mm diffusive gel with an appropriate spacer was placed between the two compartments and then clamped tightly. A 50 mL of 0.01 M NaCl solution containing PAHs (concentration shown in the Table S4) was added to the source compartment, and another 50 mL of 0.01 M NaCl solution without PAHs was added to the other (receptor) compartment at the same time. A stirrer was used to evenly stir the solution in both compartments. The pH was 5.92 ± 0.32 and the temperature was 19.0 ± 0.2 °C during the experiment. An aliquot of 0.5 mL was taken from each of the two compartments every 30 min and analyzed by HPLC.

A linear fitting curve was obtained by plotting the mass of the measured compound in the receptor compartment of the diffusion cell versus time, with the slope being the mass of the compound diffused per unit time (M/t) (See SI Text 3 for details). The diffusion coefficients (De) of each PAH were calculated:

$$D_e = Slope\frac{\triangle g}{C_s A} \quad (1)$$

Where Cs is the concentration of the test compounds in the source compartment; A is the area of the window on the diffusion cell; Δg is the thickness of the diffusive gel. This was performed at known temperature.

The diffusion coefficient at different temperatures was then calculated using the method published by Zhang and Davison [44]:

$$\log D_t = \frac{1.37023(t-25) + 8.36 \times 10^{-4}(t-25)^2}{109+t} + \log\frac{D_{25}(273+t)}{298} \quad (2)$$

Where D_t is the diffusive coefficient of the compound at temperature t; D_{25} is the diffusion coefficient of the compound at temperature 25 °C.

2.9. Diffusive layer thickness and time dependence

To investigate the relationship between the DGT measurements and the thickness of diffusive gel, DGT samplers were assembled with diffusive gels of different thicknesses (0.5 to 2.0 mm) and placed in 150 mL of mixed 10 μg L^{-1} PAHs solution (pH=6, 0.01 M NaCl). The samples were shaken on an orbital shaker (25 ℃) at 100 rpm.

To investigate the relationship between DGT measured mass and the deployment time, assembled DGT samplers were placed in 150 mL of mixed 10 μg L^{-1} PAHs solution (pH=6, 0.01 M NaCl) and shaken on an orbital shaker (25 ℃) at 100 rpm. To ensure stable solution concentrations, the PAH solution were replaced every 24 h. DGT samplers were taken out at different time points from 24 to 168 h.

2.10. Effects of pH, ionic strength and DOM

To investigate the effects of different environmental conditions on DGT performance, two types of DGT samplers, MIP-DGT and HLB-DGT, were deployed in solutions of different ionic strength (IS), pH and dissolved organic matter (DOM) concentrations. For the effect of pH, DGT samplers were deployed in 150 mL of 10 μg L^{-1} PAHs solutions (0.01 M NaCl) across a pH range from 4 to 8. For the effect of ionic strength, DGT samplers were exposed to 150 mL 10 μg L^{-1} PAHs solutions (pH 5.8 ± 0.3) with NaCl ranging from 0.01 to 0.5 M. DGT samplers were deployed in 150 mL of 10 μg L^{-1} mixed PAHs solutions with DOM concentrations ranging from 0 to 20 mg L^{-1} (0.01 M NaCl, pH 5.9 ± 0.2,), to test the effects of DOM on DGT performance. After being deployed for 24 h, all the samplers were taken out and rinsed with MQ water. Each binding gel was placed in an amber vial, ultrasonically extracted for 30 min with 5 mL acetonitrile and analysed by HPLC.

2.11. Field application in a river and a WWTP

To test the applicability of newly developed DGT for field measurements, DGT samplers were deployed in situ in the Qinhuai River in Nanjing and a wastewater treatment plant in Chongqing, China. The DGT samplers were deployed in triplicate and arranged 30 cm below the water surface. DGT samples were retrieved at day 7 and 14, respectively. The samplers were rinsed with MQ water and sealed in clean plastic bags for transport. Traditional grab samples were taken on day 1, 7 and 14, pre-concentrated and purified by a solid-phase extraction method. For each grab sample, 200 ng of decafluorobiphenyl was added to 1 L and the sample filtered through a 0.7 μm filter, then passed through a SPE column. 10 mL of dichloromethane was then used to elute the PAHs adsorbed on the column. The eluent was concentrated under nitrogen and the solvent was replaced with acetonitrile. The sample was finally diluted to 0.2 mL for HPLC analysis. (see SI for details).

2.12. QA/QC

The linear correlation coefficient (R^2) of the standard calibration curve for all PAHs were greater than 0.99. The RSD range of the mixed standard sample of 0.5 μg L^{-1} PAHs (Acy was 2 μg L^{-1}) was between 1.7–7.0%, indicating good precision of the method. Quality control standards (10 ug/L) were run every 12 samples and good results obtained. Field blank samples and laboratory blank samples were used to check for possible contamination during sample transportation, field deployment and laboratory processing. The examined compounds in these blank samples were not found at detectable levels. The results of the spiked recovery experiment showed that recoveries of the volatile Nap and Acy were slightly < 70%, while recoveries of the other PAHs ranged from 72% to 93% (Table S3). In environmental samples, the recoveries of surrogate chemical decafluorobiphenyl were 67–120%, which meets the requirements for detecting PAHs in water.

3. Results and discussion

3.1. Adsorption by DGT casing material and selection of new casing material

Since the development of the DGT technique, the casing of commercial DGT samplers has only been made of ABS plastic. The results of adsorption experiments (Fig. S1) demonstrate that there was significant adsorption (from 20–50%) by the plastic casing for all the test PAHs. Therefore, it was necessary to test and select new materials for the DGT casing, to reduce interference with the accuracy of DGT measurement of the target chemicals. With the development of manufacturing technology, metal products are increasingly being used in various fields. Five common metals (aluminum, aluminum alloy, stainless steel, brass and copper) were selected for PAHs adsorption tests here, to find the most suitable material to manufacture the DGT device (Fig. S1). Aluminum and aluminum alloy performed best. For aluminum, adsorption was < 5% for five compounds, < 10% for two compounds and ~15% for another compound. In addition to volatile naphthalene and acenaphthylene, with the increase of log K_{OW}, PAHs are more easily adsorbed by the material. Stainless steel exhibited higher adsorption (~15–30%) of 4-ring PAHs (fluoranthene, pyrene, benzo (a) anthracene). Adsorption to copper and brass was even higher than that of these three materials. The price of the raw materials followed the sequence stainless steel<aluminum<aluminum alloy<brass<copper. However, for actual product fabrication, the price of aluminum DGT was about two-thirds that of stainless steel. Furthermore, due to the in-situ applications of DGT, the portability of the sampler also needs to be considered. The density of metal materials is in the order of aluminum<aluminum alloy<stainless steel<brass<copper. The weight of stainless steel, copper and brass products of the same size are about three times that of aluminum and aluminum alloy. Therefore, based on the adsorption test results, production cost and weight, aluminum was selected as the new material to manufacture DGT devices for PAHs/hydrophobic organic compounds.

Two metal DGT casings were designed based on the existing DGT devices (Fig. S2). Because of different ductility of metal and plastic, the design on the left can be locked with two screws, while the design on the right is locked using screw threads. A groove was added on the DGT base to prevent the binding gel and diffusive gel from being crushed and damaged. The depth of the groove can be set according to actual needs. In field applications, the left design was selected for easy and convenient operation.

3.2. Adsorption by filter membranes and diffusive gels

The agarose gel had lower adsorption of the target compounds (except BaA) than the polyacrylamide gel (see Fig. S3a). Therefore, agarose gel was selected as the diffusive gel for the subsequent experiments. All the test compounds were significantly adsorbed (nearly 100%) by CA, MCE, NL, PES, PP and PVDF filters (Fig. S3b). PC and PTFE had less sorption of the compounds than the other filters, especially for the low ring PAHs. However, the PC membrane performed the best, with < 15% for four compounds and < 20% for two. It was therefore selected for the subsequent experiments. Due to the high adsorption of BaA on all materials, it was excluded from subsequent experiments, which were conducted on the remaining 8 PAHs. Suitable materials or standard experimental methods can be sought for higher ring PAHs in future, and not only for BaA.

3.3. *Elution efficiency*

The results (Fig. S4) showed that the elution efficiencies of the three binding gels in a 10 μg L^{-1} PAH solution were stable for most compounds, in the range 84% to 108%. The elution efficiency decreased slightly in the 100 μg L^{-1} solution, in the range 72–106%. For the three types of gels, elution efficiency from the MIP gel was the most stable (from 83–103%) and the influence of solution concentration and elution solution volume was less than for the other two gels. The above results indicate that the use of 5 mL acetonitrile and ultrasonic extraction for 30 min can provide stable and reliable elution efficiency.

3.4. *Binding capacity of binding gels*

The DGT samplers need a sufficient binding capacity to ensure long-term deployment in water, even if the concentration of pollutant is high. Therefore, it is necessary to determine the binding capacity of the gels. For the HLB and MIP binding gels, the uptake mass of all 8 PAHs increased linearly with increasing concentration in the bulk solutions, indicating the capacities were not reached. XAD18 gel increased for most of the compounds, except for anthracene (Fig. S5). The adsorbable mass of binding gels can be calculated based on Eq. (3):

$$M = \frac{C_{DGT}DAt}{\triangle g} \tag{3}$$

According to the test concentration, the results (Table S5) showed the minimal capacity of the three gels for these PAHs. The HLB gel had a higher capacity than MIP and XAD18 gel. The capacity on the HLB gel disc was within the range of 9–42 μg per disc (the lowest for Ant and the highest for Flu). If the samplers were deployed for 2 weeks, the concentrations of Ant and Flu that can be accurately measured within the binding capacity would be at least 32 and 162 μg L^{-1}, respectively. These are much higher than reported environmental concentrations [45–48], indicating it is suitable for long-term deployment in natural and polluted environments.

3.5. *Uptake kinetics of resin gels*

The uptake of PAHs by the three gels increased linearly with time in the first 30 min, and then the uptake rate slowed down slightly (Fig. S6). After two hours of interaction, the uptake masses of various compounds were 20–30% of the total amount added. After 30 h, the amount taken up was about 70% of the total amount. For most target compounds, the uptake rates of the three gels were XAD18 > MIP > HLB.

The rapid initial uptake is the key aspect to enable fully quantitative performance of DGT, which requires zero concentration at the binding gel/diffusive gel interface [49]. According to the DGT Eq. (3), the minimum uptake amount by the binding gel for the first 5 min was about 2 ng. The results presented in Fig. S6 show 13–84 ng for the three types of gels. The results showed that the uptake rates of all three gels for the target PAHs were much higher than theoretical uptake rates of DGT samplers in a 50 ppb PAHs solution, which indicated these binding gels enable good performance of DGT measurements.

3.6. *Diffusion coefficient measurements*

The results of the diffusion cell experiment (mass versus time) are shown in Fig. S7. The amounts of PAHs that diffused from the source compartment to the receptor compartment through diffusive gel were highly linearly correlated with time (R^2 >0.96). The diffusion coefficients of PAHs at 19 °C were calculated by using Eq. (1), knowing the slopes of linear plots in Fig. S7. For further calculation of D values at different temperature, the diffusion coefficients at 25 °C (D_{25}) were calculated with Eq. (2) and ranged from 5.00–6.96 × 10^{-6} cm^{2}s^{-1}. D values were then calculated for 8 PAHs from 1 to 35 °C and these are listed in Table S6.

According to previous research, log K_{OW} had a linear relationship with the diffusion coefficient of chemicals [35,40]. As shown in Fig. 1, the diffusion coefficients versus log K_{OW} values of all 8 PAHs were plotted, $R^2 > 0.94$ which indicated a significant correlation between these two parameters. This provides a route for estimating the diffusion coefficients of other PAHs with lower water solubility that were not measured in this study.

3.7. *Diffusion layer thickness and time dependence*

To test if the newly developed passive sampler obeys DGT theory, experiments with different diffusion layer thickness and deployment time were carried out systematically. PAHs are semi volatile compounds. To reduce the losses of PAHs during experiments, DGT samplers were placed in a closed brown bottle for short-term deployments. As shown in Fig. S8, the measured mass of the target PAHs diffused through the diffusive gel was not inversely proportional to the thickness of the diffusive gel and all the data points were below the theoretical lines of DGT. This is likely due to insufficient stirring of the solution during the experiment, and the diffusive boundary layer (DBL) generated at the interface between the DGT and the solution. The DBL thickness, δ, can be measured by deploying DGT samplers with different diffusive gel thicknesses at the same time. According to the Eq. (4) the value of δ can be estimated using the slopes and intercepts obtained from the plots of 1/M versus Δg.

$$\frac{1}{M_{DGT}} = \frac{\triangle g}{DC_{DGT}At} + \frac{\delta}{DC_{DGT}At} \tag{4}$$

The results of deployment with an orbital shaker at 100 rpm are shown in Fig. 2. The estimated DBL is given on the graphs and in Table S7. The derived values for the different compounds were in the range 0.06–0.08 cm (see Fig. 2). In Warnken's research, the changes in stirring speeds were considered to be different solution flow rates, and DBL increased with the decrease of speed. When the stirring rate ≥ 100 rpm, the DBL were approximately 0.02 cm, with DBL thickness of 0.04 cm at 60 rpm and 0.15 cm in the unstirred solution [50]. Similarly, the range of DBL under flowing and static conditions were 0.01–0.05 cm and 0.04–0.13 cm, respectively [34]. In this study, due to insufficient stirring from the oriental shaker, the DBL was relatively high, which is consistent with these research results. The measured mass of the target PAHs by the device was inversely proportional to the total diffusion layer thickness (the diffusive gel and boundary layer). The measured mass of PAHs was consistent with the theoretical line, except for anthracene (Fig. S9). The DBL values were considered in all subsequent laboratory deployment experiments when calculating DGT measured

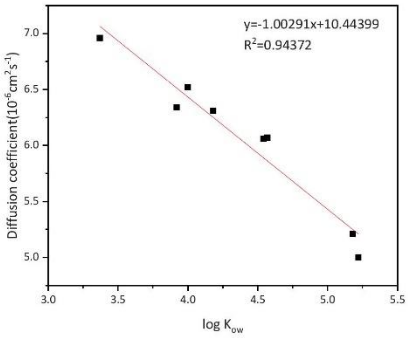


Fig. 1. Dependence of diffusion coefficients of PAHs on log K_{OW}.

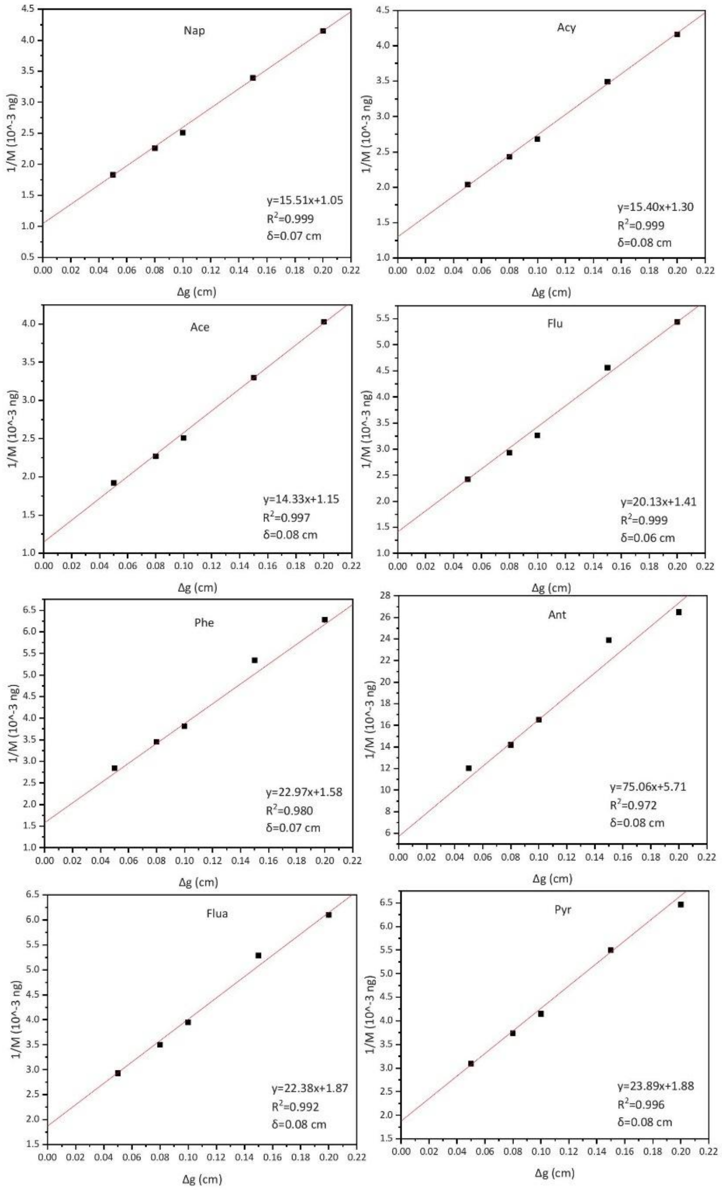


Fig. 2. Relationship of 1/M (M is accumulated mass by DGT samplers) and Δg (diffusion layer thickness). Diffusive boundary layer thickness (δ) was determined using Eq. (4).

concentrations in the laboratory.

The concentration of PAHs in the environment are generally at the ng L^{-1} level, so the in-situ deployment time of DGT needs to be long enough to accumulate sufficient mass for detection. It is therefore necessary to study the impact of deployment time on the performance of DGT. The results (Fig. S10) showed that with the increase of deployment time, the mass of PAHs accumulated on DGT with MIP and HLB gels increased linearly (R^2 =0.9777–0.9993) over 7 days of the experiment. The accumulation of most chemicals was consistent with the theoretical line and the ratio of the PAHs concentrations measured by DGT (C_{DGT}) to their concentrations in the bulk solutions (C_b) were between 0.8–1.2 (Table S8). On XAD18 DGT, naphthalene was not accumulated linearly, and actual accumulation of most chemicals was lower than the theoretical line (Fig. S11). The accumulation of anthracene was much lower than the theoretical value; this is because the water solubility of anthracene is extremely low and DGT only measures water-soluble anthracene. For the treatment of solution samples, the matrix contains acetonitrile, which led to higher measured solution concentrations, so the predicted accumulated mass was higher than the actual value.

The accumulation of all the compounds by DGT was lower than the theoretical value on the first day (Fig. S10). This is because of the affinity of filter membranes and DGT samplers for the compounds, so that there is a lag time before compounds reach the binding gel. It is therefore recommended that the time for deployment should exceed one week; deployments of several weeks or a couple of months are typical and ideal for monitoring purposes [42]. Fig. S10 shows the masses accumulated in binding gels for 7 days deployment time; intercepts on the time-axis show the lag times required for different chemicals (Table S9). This was < 15 h for all 8 PAHs, indicating that the DGT samplers made from aluminum material effectively reduces the impact of lag time. The lag times of MIP-DGT were shorter than those for HLB-DGT, which may be due to the high specificity of MIP for adsorbing PAHs. This is consistent with the results of the previous uptake kinetic experiment. The above results of different diffusion layer thickness and deployment time indicate that the DGT samplers for PAHs can be used for measuring the concentrations of the target compounds quantitatively with high precision and accuracy.

3.8. *Effects of pH, ionic strength and DOM*

The environmental conditions of natural water vary greatly, which may affect the performance of DGT. For reliable and widespread use of DGT, it is important that such effects are small and/or well characterized. The effects of different pH, ionic strength and DOM on DGT performance were therefore tested. Due to the chemical reactivity of aluminium under acidic conditions, which led the to the pH of the test solutions being unstable, DGT casing made from stainless-steel were used in the pH study. Most of the compounds had a ratio (C_{DGT}/C_b) between 0.8 - 1.2; some had low ratio values due to the different lag times of each PAH (Fig. S12). The stability of the ratio under different conditions indicates whether the performance of DGT was affected by pH. The ratio of MIP-DGT was stable across the pH range of 4–8, while the ratio for the HLB sampler decreased at the pH 4. The effect of IS on DGT measurements was investigated in solutions with IS ranging from 0.01 to 0.5 M. There was no significant effect of IS on MIP-DGT performance. In the DGT with HLB gel, the ratio (C_{DGT}/C_b) had a slight decrease with increasing IS for phenanthrene, anthracene, fluoranthene and pyrene (Fig. S13). IS can affect the diffusion process by changing the surface charge density of the target chemicals [51]. Increasing numbers of benzene rings in the molecular structure of PAHs, can make them more vulnerable to the change of charge density. Meanwhile, the increase of IS may lead to a salting-out effect, which could decrease the solubility of PAHs. An effect of high IS concentration (0.5 M) was reported in a study of bisphenol A (BPA) with activated carbon DGT binding gel [39].

The results of experiments with DOM have shown that there were no obvious effects on the performance of MIP-DGT within the DOM range 0 - 20 mg L^{-1}. The ratio (C_{DGT}/C_b) remained stable, with most values ranging from 0.8 to 1.2 (Fig. 3). For HLB-DGT, most PAHs were not affected by DOM, but the ratio of C_{DGT}/C_b values for anthracene, fluoranthene, and pyrene decreased at higher DOM concentrations. HLB materials have a wide range of adsorption properties. DOM may be adsorbed by binding gel and have a competition with target chemicals on the binding sites. Similar phenomena have also occurred during DGT measurement of Cu [52]. MIP has specific adsorption for PAHs and is not easily affected by the changes of DOM during application. In addition, DOM is prone to binding with hydrophobic substances, thereby affecting the diffusion of the target chemicals in the solution [53]. Anthracene, fluoranthene and pyrene have higher hydrophobicity than other PAHs in this study and are more susceptible to interference. When using HLB-DGT to measure triclosan (TCS), the ratio of C_{DGT}/C_b decreased with increasing DOM which is similar to this study [36]. In general, the MIP-DGT has a better performance than HLB-DGT in waters of different environmental conditions.

3.9. *Field application in river water and a WWTP*

The recoveries, IDLs and the MDLs of the studied chemicals are presented in SI Table S3 for both water and DGT samples. For the 7 days field deployment at 25 °C, the MDLs of DGT for PAHs were in the range of 0.19–1.48 ng L^{-1} which are low enough for environmental monitoring. If necessary, the MDLs for DGT can be reduced by prolonging deployed time and reducing solvent volume when test samples. While DGT pre concentrated the compound in-situ, the filter membrane and diffusive gel prevent larger molecular substances such as humic acid from entering the binding gel. Even without purification, the matrix of DGT samples were cleaner than that of grab samples and had fewer interference peaks during sample detection. Grab samples need to be concentrated and purified after collection. During these processes, the samples were more prone to loss, especially for low ring PAHs which are more volatile led to lower accuracy than DGT samples.

The concentrations of PAHs measured by DGT in two field applications during 7- and 14- days deployments are compared with the results of grab sampling in Fig. 4. For most PAHs, the concentration measured by DGT was similar to that obtained by grab sampling, with ratio values (C_{DGT}/C_b) mostly ranging from 0.8–1.2 for both cases. When DGT was deployed in the river, the concentration of Nap and Acy measured by DGT was higher than the average concentration of grab samples. Higher volatility of low ring PAHs could be the reason, because these compounds are prone to loss during sample pre-treatment during conventional sample handling. For PAHs with higher hydrophobicity, the DGT measured concentrations were mostly lower than those of PAHs in grab samples. This is possibly because that DGT measures the water-soluble fraction, while PAHs adsorbed on suspended solids and in the colloidal state may not be measured by DGT. Similar results were found when DGT and grab samples were compared for determinations of atrazine and household and personal care products [36,49]. It is important to point out that it should not be assumed that grab sample results are 'right'; differences between the grab results and DGT are to be expected, because we are comparing instantaneous '1-off' samples with time-integrated ones and there are differences in the aqueous fraction sampled, and the sample workup procedures. Knowledge of the importance of these factors is important in interpreting the results. Based on the data, we calculated the relative standard deviation (RSD) of DGT samples and grab samples, with ranges of 3.3–39% and 9.2–150%, respectively. The range of grab sampling results was much higher than that of DGT samples, which reflects that grab sampling is susceptible to different factors. Rainfall and short-term emissions may cause significant fluctuations in sample concentration [54,55]. Therefore, it is necessary to increase the sampling frequency of grab sampling to make the results more reliable. In contrast, the DGT gives a more representative time integrated sample. For the application in the wastewater

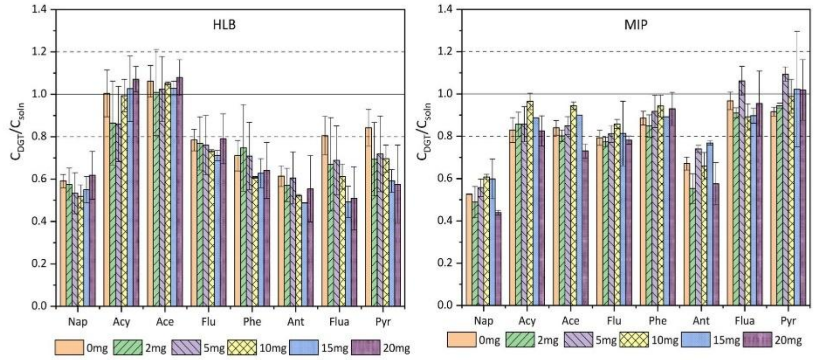


Fig. 3. Effect of DOM on the ratio of DGT-measured concentrations (C_{DGT}) to their concentrations in the bulk solutions (C_b). The solid horizontal lines represent the target value of 1, and the dotted horizontal lines represent an acceptable target range of 0.8 and 1.2. Values are means ± SD of three replicate analyses.

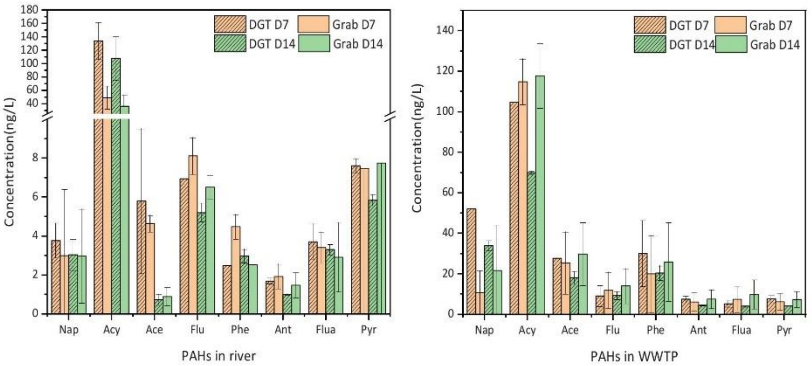


Fig. 4. Average concentration of PAHs measured by grab sampling and DGT in situ during 7 and 14 days in a river and in a WWTP.

treatment plant, the 7 days concentration measured by DGT was close to that obtained by grab sampling and 14 days deployment gave lower concentrations. In such biologically active waters, longer-term deployment of DGT could lead to some degradation of the target chemicals, which may affect the accuracy of the DGT measurement [29]. Meanwhile, research has pointed out that the growth of biofilms could lead to a decrease in the diffusion coefficient[56,57]. Biofilms that are prone to growth in sewage environments may also lead to this result. Overall, DGT has provided reliable in situ measurements in both natural water and wastewater environments.

4. Conclusions

A novel DGT passive sampler has been successfully developed for measurement of PAHs, based on systematic tests under different conditions and comparative evaluation of three different binding resins. DGT with MIP binding gel is recommended for its stable performance under different environmental conditions. The diffusion coefficients of PAHs through DGT diffusive gels were accurately measured for the first time, using the diffusion cell technique. The good linear relationship with the K_{OW} values of the chemicals could provide a basis for estimating the diffusion coefficients of other PAHs with similar structures for wider applications of the DGT technique. The use of metal material for the DGT casing reduced the sorption of target compounds on the material, effectively reducing the lag time of the deployment and provided more accurate DGT measurements.

Deployment times of less than two weeks are recommended for wastewater application to avoid the potential impact of biofilm and compound degradation. The in-situ field applications of the MIP-DGT samplers demonstrate that DGT is a reliable technique for the measurement of PAHs in natural aquatic systems and in wastewater treatment plant environments. It also shows the feasibility of using the newly developed passive sampler for other hydrophobic compounds of low aqueous solubility, which will expand the application range of DGT technique greatly. Based on the robustness of the DGT samplers, it can be widely used in different aquatic environments in the future to explore the dynamic changes of PAHs in different environments, including surface water (fresh water and seawater), groundwater, and sediment-water interfaces. This will advance our understanding of the fate and behavior of PAHs in different environments. In general terms, DGT reduces errors in sampling, by providing a time-weighted average concentration, rather than an instantaneous one and samples the labile fraction from waters. There are sample preparation and analysis advantageous too, since DGT pre-concentrates in situ, reducing the risks of analyte losses or contamination during sample handling and work-up. DGT requires less lab time and solvents, reducing laboratory and labour costs, compared to conventional grab sampling.

CRediT authorship contribution statement

Kevin Jones: Supervision. **Jun Luo:** Supervision. **Liying Yan:** Investigation. **Qiuyu Rong:** Investigation. **Yanying Li:** Investigation. **Hao Zhang:** Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2024.134199.

References

[1] Tsai, C.J., Chen, M.L., Chang, K.F., Chang, F.K., Mao, I.F., 2009. The pollution characteristics of odor, volatile organochlorinated compounds and polycyclic aromatic hydrocarbons emitted from plastic waste recycling plants. Chemosphere 74 (8), 1104–1110. https://doi.org/10.1016/j.chemosphere.2008.10.041.

[2] Kramer, A.L., Campbell, L., Donatuto, J., Heidt, M., Kile, M., Massey Simonich, S.L., 2020. Impact of local and regional sources of PAHs on tribal reservation air quality in the U.S. Pacific Northwest. Sci Total Environ 710, 136412. https://doi.org/10.1016/j.scitotenv.2019.136412.

[3] Souza, M.R.R., Santos, E., Suzarte, J.S., Carmo, L.O., Frena, M., Damasceno, F.C., Alexandre, M.R., 2018. Concentration, distribution and source apportionment of polycyclic aromatic hydrocarbons (PAH) in Poxim River sediments, Brazil. Mar Pollut Bull 127, 478–483. https://doi.org/10.1016/j.marpolbul.2017.12.045.

[4] Balmer, J.E., Hung, H., Yu, Y., Letcher, R.J., Muir, D.C.G., 2019. Sources and environmental fate of pyrogenic polycyclic aromatic hydrocarbons (PAHs) in the Arctic. Emerg Contam 5, 128–142. https://doi.org/10.1016/j.emcon.2019.04.002.

[5] Li, X., Tao, S., Liu, W., Li, X., Chen, H., Wu, S., 2010. Dry deposition of polycyclic aromatic hydrocarbons and its influence on surface soil contamination in Tianjin, China. J Environ Monit 12 (4), 952–957. https://doi.org/10.1039/b919054f.

[6] Wu, B., Guo, S., Li, X., Wang, J., 2018. Temporal and spatial variations of polycyclic aromatic hydrocarbons (PAHs) in soils from a typical organic sewage irrigation area. Sci Total Environ 613-614, 513–520. https://doi.org/10.1016/j.scitotenv.2017.08.316.

[7] Sun, K., Song, Y., He, F., Jing, M., Tang, J., Liu, R., 2021. A review of human and animals exposure to polycyclic aromatic hydrocarbons: Health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics. Sci Total Environ 773, 145403. https://doi.org/10.1016/j.scitotenv.2021.145403.

[8] Sushkova, S., Minkina, T., Deryabkina, I., Rajput, V., Antonenko, E., Nazarenko, O., Yadav, B.K., Hakki, E., Mohan, D., 2019. Environmental pollution of soil with PAHs in energy producing plants zone. Sci Total Environ 655, 232–241. https://doi.org/10.1016/j.scitotenv.2018.11.080.

[9] Grova, N., Salquebre, G., Schroeder, H., Appenzeller, B.M., 2011. Determination of PAHs and OH-PAHs in rat brain by gas chromatography tandem (triple quadrupole) mass spectrometry. Chem Res Toxicol 24 (10), 1653–1667. https://doi.org/10.1021/tx2003596.

[10] Li, S.Q., Ni, H.G., Zeng, H., 2017. PAHs in polystyrene food contact materials: an unintended consequence. Sci Total Environ 609, 1126–1131. https://doi.org/10.1016/j.scitotenv.2017.07.262.

[11] Golozar, A., Fagundes, R.B., Etemadi, A., Schantz, M.M., Kamangar, F., Abnet, C.C., Dawsey, S.M., 2012. Significant variation in the concentration of carcinogenic polycyclic aromatic hydrocarbons in yerba mate samples by brand, batch, and processing method. Environ Sci Technol 46 (24), 13488–13493. https://doi.org/10.1021/es303494s.

[12] Rota, M., Bosetti, C., Boccia, S., Boffetta, P., La Vecchia, C., 2014. Occupational exposures to polycyclic aromatic hydrocarbons and respiratory and urinary tract cancers: an updated systematic review and a meta-analysis to 2014. Arch Toxicol 88 (8), 1479–1490. https://doi.org/10.1007/s00204-014-1296-5.

[13] Manoli, E., Kouras, A., Karagkiozidou, O., Argyropoulos, G., Voutsa, D., Samara, C., 2016. Polycyclic aromatic hydrocarbons (PAHs) at traffic and urban background sites of northern Greece: source apportionment of ambient PAH levels and PAH-induced lung cancer risk. Environ Sci Pollut Res Int 23 (4), 3556–3568. https://doi.org/10.1007/s11356-015-5573-5.

[14] Novic, A.J., O'Brien, D.S., Kaserzon, S.L., Hawker, D.W., Lewis, S.E., Mueller, J.F., 2017. Monitoring herbicide concentrations and loads during a flood event: a comparison of grab sampling with passive sampling. Environ Sci Technol 51 (7), 3880–3891. https://doi.org/10.1021/acs.est.6b02858.

[15] Mutzner, L., Vermeirssen, E.L.M., Ort, C., 2019. Passive samplers in sewers and rivers with highly fluctuating micropollutant concentrations - Better than we thought. J Hazard Mater 361, 312–320. https://doi.org/10.1016/j.jhazmat.2018.07.040.

[16] Bopp, S., Weiss, H., Schirmer, K., 2005. Time-integrated monitoring of polycyclic aromatic hydrocarbons (Pahs) in groundwater using the ceramic dosimeter passive sampling device. J Chromatogr A 1072 (1), 137–147. https://doi.org/10.1016/j.chroma.2004.12.049.

[17] Vrana, B., Mills, G.A., Dominiak, E., Greenwood, R., 2006. Calibration of the Chemcatcher passive sampler for the monitoring of priority organic pollutants in water. Environ Pollut 142 (2), 333–343. https://doi.org/10.1016/j.envpol.2005.10.033.

[18] Harman, C., Brooks, S., Sundt, R.C., Meier, S., Grung, M., 2011. Field comparison of passive sampling and biological approaches for measuring exposure to PAH and alkylphenols from offshore produced water discharges. Mar Pollut Bull 63 (5-12), 141–148. https://doi.org/10.1016/j.marpolbul.2010.12.023.

[19] Jonker, M.T., van der Heijden, S.A., Kotte, M., Smedes, F., 2015. Quantifying the effects of temperature and salinity on partitioning of hydrophobic organic chemicals to silicone rubber passive samplers. Environ Sci Technol 49 (11), 6791–6799. https://doi.org/10.1021/acs.est.5b00286.

[20] Booij, K., van Bommel, R., van Aken, H.M., van Haren, H., Brummer, G.J., Ridderinkhof, H., 2014. Passive sampling of nonpolar contaminants at three deep-ocean sites. Environ Pollut 195, 101–108. https://doi.org/10.1016/j.envpol.2014.08.013.

[21] Chang, W.T., Lee, C.L., Brimblecombe, P., Fang, M.D., Chang, K.T., Liu, J.T., 2015. The effects of flow rate and temperature on SPMD measurements of bioavailable PAHs in seawater. Mar Pollut Bull 97 (1-2), 217–223. https://doi.org/10.1016/j.marpolbul.2015.06.013.

[22] Allan, I.J., Christensen, G., Baek, K., Evenset, A., 2016. Photodegradation of PAHs in passive water samplers. Mar Pollut Bull 105 (1), 249–254. https://doi.org/10.1016/j.marpolbul.2016.02.018.

[23] Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature 367 (6463)), 546–548.

[24] Chen, C.E., Zhang, H., Jones, K.C., 2012. A novel passive water sampler for in situ sampling of antibiotics. J Environ Monit 14 (6), 1523–1530. https://doi.org/10.1039/c2em30091e.

[25] Menegario, A.A., Yabuki, L.N.M., Luko, K.S., Williams, P.N., Blackburn, D.M., 2017. Use of diffusive gradient in thin films for in situ measurements: a review on the progress in chemical fractionation, speciation and bioavailability of metals in waters. Anal Chim Acta 983, 54–66. https://doi.org/10.1016/j.aca.2017.06.041.

[26] Zhang, C., Ding, S., Xu, D., Tang, Y., Wong, M.H., 2014. Bioavailability assessment of phosphorus and metals in soils and sediments: a review of diffusive gradients in thin films (DGT). Environ Monit Assess 186 (11), 7367–7378. https://doi.org/10.1007/s10661-014-3933-0.

[27] Galceran, J., Gao, Y., Puy, J., Leermakers, M., Rey-Castro, C., Zhou, C., Baeyens, W., 2021. Speciation of inorganic compounds in aquatic systems using diffusive gradients in thin-films: a review. Front Chem 9, 624511. https://doi.org/10.3389/fchem.2021.624511.

[28] Guibal, R., Buzier, R., Lissalde, S., Guibaud, G., 2019. Adaptation of diffusive gradients in thin films technique to sample organic pollutants in the environment: An overview of o-DGT passive samplers. Sci Total Environ 693, 133537. https://doi.org/10.1016/j.scitotenv.2019.07.343.

[29] Wang, R., Jones, K.C., Zhang, H., 2020. Monitoring organic pollutants in waters using the diffusive gradients in the thin films technique: investigations on the effects of biofouling and degradation. Environ Sci Technol 54 (13), 7961–7969. https://doi.org/10.1021/acs.est.0c00224.

[30] Chen, C.E., Zhang, H., Ying, G.G., Jones, K.C., 2013. Evidence and recommendations to support the use of a novel passive water sampler to quantify antibiotics in wastewaters. Environ Sci Technol 47 (23), 13587–13593. https://doi.org/10.1021/es402662g.

[31] Zhang, Y., Zhang, T., Guo, C., Hou, S., Hua, Z., Lv, J., Zhang, Y., Xu, J., 2018. Development and application of the diffusive gradients in thin films technique for simultaneous measurement of methcathinone and ephedrine in surface river water. Sci Total Environ 618, 284–290. https://doi.org/10.1016/j.scitotenv.2017.11.068.

[32] Guo, C., Zhang, T., Hou, S., Lv, J., Zhang, Y., Wu, F., Hua, Z., Meng, W., Zhang, H., Xu, J., 2017. Investigation and application of a new passive sampling technique for in situ monitoring of illicit drugs in waste waters and rivers. Environ Sci Technol 51 (16), 9101–9108. https://doi.org/10.1021/acs.est.7b00731.

[33] Guan, D.X., Li, Y.Q., Yu, N.Y., Yu, G.H., Wei, S., Zhang, H., Davison, W., Cui, X.Y., Ma, L.Q., Luo, J., 2018. In situ measurement of perfluoroalkyl substances in aquatic systems using diffusive gradients in thin-films technique. Water Res 144, 162–171. https://doi.org/10.1016/j.watres.2018.07.031.

[34] Challis, J.K., Hanson, M.L., Wong, C.S., 2016. Development and calibration of an organic-diffusive gradients in thin films aquatic passive sampler for a diverse suite of polar organic contaminants. Anal Chem 88 (21), 10583–10591. https://doi.org/10.1021/acs.analchem.6b02749.

[35] Zou, Y.T., Fang, Z., Li, Y., Wang, R., Zhang, H., Jones, K.C., Cui, X.Y., Shi, X.Y., Yin, D., Li, C., Liu, Z.D., Ma, L.Q., Luo, J., 2018. Novel method for in situ

monitoring of organophosphorus flame retardants in waters. Anal Chem 90 (16), 10016–10023. https://doi.org/10.1021/acs.analchem.8b02480.

[36] Chen, W., Li, Y., Chen, C.E., Sweetman, A.J., Zhang, H., Jones, K.C., 2017. DGT passive sampling for quantitative in situ measurements of compounds from household and personal care products in waters. Environ Sci Technol 51 (22), 13274–13281. https://doi.org/10.1021/acs.est.7b03940.

[37] Xie, H., Chen, Q., Chen, J., Chen, C.L., Du, J., 2018. Investigation and application of diffusive gradients in thin-films technique for measuring endocrine disrupting chemicals in seawaters. Chemosphere 200, 351–357. https://doi.org/10.1016/j.chemosphere.2018.02.096.

[38] Guibal, R., Buzier, R., Charriau, A., Lissalde, S., Guibaud, G., 2017. Passive sampling of anionic pesticides using the Diffusive Gradients in Thin films technique (DGT). Anal Chim Acta 966, 1–10. https://doi.org/10.1016/j.aca.2017.02.007.

[39] Zheng, J.L., Guan, D.X., Luo, J., Zhang, H., Davison, W., Cui, X.Y., Wang, L.H., Ma, L.Q., 2015. Activated charcoal based diffusive gradients in thin films for in situ monitoring of bisphenols in waters. Anal Chem 87 (1), 801–807. https://doi.org/10.1021/ac503814j.

[40] Fang, Z., Li, Y., Li, Y., Yang, D., Zhang, H., Jones, K.C., Gu, C., Luo, J., 2021. Development and applications of novel DGT passive samplers for measuring 12 per- and polyfluoroalkyl substances in natural waters and wastewaters. Environ Sci Technol 55 (14), 9548–9556. https://doi.org/10.1021/acs.est.0c08092.

[41] Cole, R.F., Mills, G.A., Hale, M.S., Parker, R., Bolam, T., Teasdale, P.R., Bennett, W. W., Fones, G.R., 2018. Development and evaluation of a new diffusive gradients in thin-films technique for measuring organotin compounds in coastal sediment pore water. Talanta 178, 670–678. https://doi.org/10.1016/j.talanta.2017.09.081.

[42] Wang, R., Zou, Y., Luo, J., Jones, K.C., Zhang, H., 2019. Investigating potential limitations of current diffusive gradients in thin films (DGT) samplers for measuring organic chemicals. Anal Chem 91 (20), 12835–12843. https://doi.org/10.1021/acs.analchem.9b02571.

[43] Zhang, H., Davison, W., 1999. Diffusional characteristics of hydrogels used in DGT and DET techniques. Anal Chim Acta 398, 329–340.

[44] Zhang, H., Davison, W., 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. Anal Chem (Wash) 67 (19), 3391–3400. https://doi.org/10.1021/ac00115a005,.

[45] Zakaria, M.P., Takada, H., Tsutsumi, S., Ohno, K., Yamada, J., Kouno, E., Kumata, H., 2002. Distribution of polycyclic aromatic hydrocarbons (PAHs) in rivers and estuaries in Malaysia: a widespread input of petrogenic PAHs. Environ Sci Technol 36 (9), 1907–1918.

[46] McDonough, C.A., Khairy, M.A., Muir, D.C., Lohmann, R., 2014. Significance of population centers as sources of gaseous and dissolved PAHs in the lower Great Lakes. Environ Sci Technol 48 (14), 7789–7797. https://doi.org/10.1021/es501074r.

[47] Wang, J., Bi, Y., Pfister, G., Henkelmann, B., Zhu, K., Schramm, K.W., 2009. Determination of PAH, PCB, and OCP in water from the Three Gorges Reservoir accumulated by semipermeable membrane devices (SPMD). Chemosphere 75 (8), 1119–1127. https://doi.org/10.1016/j.chemosphere.2009.01.016.

[48] Zhang, W., Wei, C., Chai, X., He, J., Cai, Y., Ren, M., Yan, B., Peng, P., Fu, J., 2012. The behaviors and fate of polycyclic aromatic hydrocarbons (PAHs) in a coking wastewater treatment plant. Chemosphere 88 (2), 174–182. https://doi.org/10.1016/j.chemosphere.2012.02.076.

[49] Li, Y., Chen, C.L., Chen, W., Chen, J., Cai, X., Jones, K.C., Zhang, H., 2019. Development of a Passive Sampling Technique for Measuring Pesticides in Waters and Soils. J Agric Food Chem 67 (22), 6397–6406. https://doi.org/10.1021/acs.jafc.9b00040.

[50] Warnken, K.W., Zhang, H., Davison, W., 2006. Accuracy of the diffusive gradients in thin-films technique: diffusive boundary layer and effective sampling area considerations. Anal Chem 78 (11), 3780–3787.

[51] Lucas, A., Rate, A., Zhang, H., Salmon, S.U., Radford, N., 2012. Development of the diffusive gradients in thin films technique for the measurement of labile gold in natural waters. Anal Chem 84 (16), 6994–7000. https://doi.org/10.1021/ac301003g.

[52] Davison, W., Lin, C., Gao, Y., Zhang, H., 2014. Effect of gel interactions with dissolved organic matter on DGT measurements of trace metals. Aquat Geochem 21 (2-4), 281–293. https://doi.org/10.1007/s10498-014-9244-9.

[53] Liu, Q.-S., Zheng, T., Wang, P., Jiang, J.-P., Li, N., 2010. Adsorption isotherm, kinetic and mechanism studies of some substituted phenols on activated carbon fibers. Chem Eng J 157 (2-3), 348–356. https://doi.org/10.1016/j.cej.2009.11.013.

[54] Xing, Z., Chow, L., Rees, H., Meng, F., Li, S., Ernst, B., Benoy, G., Zha, T., Hewitt, L. M., 2013. Influences of sampling methodologies on pesticide-residue detection in stream water. Arch Environ Contam Toxicol 64 (2), 208–218. https://doi.org/10.1007/s00244-012-9833-9.

[55] Baz-Lomba, J.A., Harman, C., Reid, M., Thomas, K.V., 2017. Passive sampling of wastewater as a tool for the long-term monitoring of community exposure: Illicit and prescription drug trends as a proof of concept. Water Res 121, 221–230. https://doi.org/10.1016/j.watres.2017.05.041.

[56] Pichette, C., Zhang, H., Davison, W., Sauve, S., 2007. Preventing biofilm development on DGT devices using metals and antibiotics. Talanta 72 (2), 716–722. https://doi.org/10.1016/j.talanta.2006.12.014.

[57] Feng, Z., Zhu, P., Fan, H., Piao, S., Xu, L., Sun, T., 2016. Effect of biofilm on passive sampling of dissolved orthophosphate using the diffusive gradients in thin films technique. Anal Chem 88 (13), 6836–6843. https://doi.org/10.1021/acs.analchem.6b01392.

Paper II

Occurrence and distribution of PAHs in the Yangtze River and urban river waters of Nanjing, China: insights from in situ DGT measurements

Environmental Pollution 371 (2025) 125921

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Occurrence and distribution of PAHs in the Yangtze River and urban river waters of Nanjing, China: Insights from in situ DGT measurements☆

Qiuyu Rong[a], Hao Zhang[a], Yanying Li[b], Liying Yan[c], Jun Luo[c,*], Kevin C. Jones[a,**]

[a] Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom
[b] College of Environmental Science and Engineering, Dalian Maritime University, Dalian, Liaoning, 116023, PR China
[c] State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing, Jiangsu, 210023, PR China

ARTICLE INFO

Keywords:
PAHs
DGT
Yangtze River
Urban river
Ecological risk assessment

ABSTRACT

The diffusive gradients in thin films (DGT) technique has been used for monitoring various organic pollutants in surface water in recent years. This article applies a novel DGT passive sampler to the Nanjing section of the Yangtze River and urban rivers to measure the in-situ concentrations of polycyclic aromatic hydrocarbons (PAHs), analyze their seasonal changes and determine their fate. PAH concentrations had marked seasonality. The concentration of individual PAH was 1.3–18 ng/L in summer and 4.2–161 ng/L in winter. Source inputs, flow differences and degradation/losses caused the seasonal differences. Inputs from Nanjing and tributary rivers were minor compared to the cumulative loads of PAHs in the main Yangtze river upstream of the city. Petrochemical enterprises along the Yangtze River, ship transportation, and upstream pollution were the main sources of pollution in this area. Source analysis indicated a mixed source with coal and biomass combustion inputs increasing significantly in winter. Risk assessment indicated that although the Yangtze River protection policy has reduced pollution in recent years, water quality still exceeded PAH ecological thresholds in the river and the chemical industry cluster areas during winter. Further measures are needed to reduce pollution and its associated risks from a catchment perspective.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are one of the most widely distributed and abundant groups of organic pollutants in the environment (Uddin and Xu, 2024). PAHs are priority pollutants, with mutagenic and carcinogenic properties (Vijayanand et al., 2023). They are formed from incomplete combustion processes, with both natural and anthropogenic sources. Since industrialization, emissions from human activities such as power generation, petrochemicals, steel smelting, vehicle emissions, space heating and incomplete combustion of biomass have become the main sources of PAHs (Venkatraman et al., 2024; Ziyaei et al., 2024). Natural emissions include volcanoes and forest fires. PAHs are emitted into the atmosphere and then enter terrestrial and aquatic environments through dry and wet deposition (Gao et al., 2024). Runoff from soils and vegetation provides an input to aquatic environments, together with sources such as wastewater discharge, oil leakage, road runoff and sediment re-mobilisation which also lead to the transfer of PAHs to water bodies (Zhao et al., 2021). Due to their hydrophobicity/lipophilicity, PAHs can transfer to aquatic organisms and potentially cause risks to ecosystems and to human health through ingestion, inhalation, skin contact and other pathways (Moon et al., 2010; Kim et al., 2013). Higher ring PAHs are generally more harmful than lower ring PAHs (Wang et al., 2024). However, the risks of low ring PAHs cannot be ignored (Manzetti, 2013). As the number of rings increases, the lipid solubility of PAHs increases, resulting in stronger toxicity to organisms, mainly manifested as genotoxicity, mutagenicity and carcinogenicity (Sun et al., 2021). Therefore, it is important to understand the distribution, migration, transformation, and risk assessment of PAHs in aquatic environments.

Traditional monitoring of organic chemicals in waters mainly relies on active sampling methods. For example, Cao et al. investigated the spatiotemporal distribution of PAHs in the southern Bohai Sea by taking grab samples (Cao et al., 2024). Net et al. (2014) studied the levels of PAHs, polychlorinated biphenyls, and insecticides in the Somme River in

---

☆ This paper has been recommended for acceptance by Eddy Y. Zeng.
[*] Corresponding author.
[**] Corresponding author.
E-mail addresses: esluojun@nju.edu.cn (J. Luo), k.c.jones@lancaster.ac.uk (K.C. Jones).

https://doi.org/10.1016/j.envpol.2025.125921
Received 25 October 2024; Received in revised form 21 February 2025; Accepted 23 February 2025

northern France by concentrating 1L water samples. The collection of 40 grab samples indicated the widespread presence of PAHs in the Amazon basin (Rizzi et al., 2023). However, grab sampling not only requires the collection, transportation, and preservation of a large number of high volume samples, but also requires complex pre-treatment processes, which are prone to cross contamination and losses of PAHs (Kot et al., 2000). Active sampling is also limited to giving one-off 'instantaneous' concentrations, which may be unrepresentative. Short-term emissions, rainfall and other factors influence such one-off measurements (Baz-Lomba et al., 2017). Therefore, passive sampling techniques based on time weighted average (TWA) concentrations have developed rapidly in recent years and are being increasingly adopted by monitoring agencies and researchers. Compared with technologies such as SPMD, POCIS, and Chemcatcher, the diffusive gradients in thin-films (DGT) technology has the advantage of not needing on-site calibration (Davison and Zhang, 1994; Chen et al., 2012). At present, DGT samplers have been developed for over 150 organic pollutants and successfully used in water environments under different environmental conditions (Xie et al., 2018; Wang et al., 2020a,b; Liang et al., 2023). DGT measures the labile fraction of pollutants in water, rather than pollutants adsorbed in suspended and colloidal substances. This better reflects the ecological risk of pollutants (Chen et al., 2017; Li et al., 2019). Recently a DGT passive sampler has been developed for PAHs, ready to be applied for monitoring and risk assessment of PAHs in aquatic environments (Rong et al., 2024).

The Yangtze River is about 6300 km long, flowing from the Qinghai Tibet Plateau in the west to the East China Sea. It passes through 19 provinces in China, with a drainage area of over 1.8 million km^2. It is the most important source of industrial and drinking water in China, and its natural resources serve nearly one-third of the country's population (over 460 million people). Therefore, the water quality of the Yangtze River has a direct impact on the lives of residents and China's industrial production (Yang et al., 2021). In recent decades, human activities such as the construction of chemical enterprises along the river and the discharge of municipal sewage have led to over 25 billion tons of wastewater and pollutants being discharged into the Yangtze River every year, accounting for more than 40% of total wastewater discharge in China (Wong et al., 2007; Wang et al., 2010). This has caused serious pollution to the Yangtze River and severe damage to its ecological environment. China has therefore introduced a series of policies and regulations, including the Yangtze River Protection Law (China, 2020) and the Yangtze River Economic Belt Ecological Environment Protection Plan (China, 2017) to carry out activities for the protection and pollution control of the Yangtze River. Nanjing is a major industrial city, with chemical production, electronic production, and automobile manufacturing, amongst the highest in China. Nanjing has a permanent population is about 9.5 million, with over 7 million urban residents. As one of the most economically developed core cities of the Yangtze River Delta metropolitan region of China, industrial production, high population and transportation activities have brought serious pollution problems to this city. The production and domestic water of Nanjing mainly comes from the Yangtze River, and a large amount of wastewater is discharged back into the Yangtze. Previous research related to PAHs has focused on key sections of the mainstream of the Yangtze River. Monitoring of surface waters in Nanjing was conducted before the instigation of the "Yangtze River protection" policies (He et al., 2011; Wang et al., 2017; Yan et al., 2018). Research has mainly focused on the distribution and source of PAHs in the river basin, but did not address the relationship between the main Yangtze River and other urban rivers and drainage channels supplying the Yangtze.

Therefore, the objectives of this study were to: (i) apply the new DGT passive sampler technology to determine the in-situ concentrations, distribution characteristics and seasonal changes of PAHs in the Nanjing section of the Yangtze River and urban rivers; (ii) identify the sources of PAHs in surface waters and investigate the correlation between the fate and behavior of PAHs in the Yangtze River itself and Nanjing tributaries; (iii) use the DGT in-situ labile concentrations to conduct an ecological risk assessment of PAHs in this region, to provide information on the current situation of PAH pollution in its watershed, and provide a scientific basis for source control of pollutants and water management.

2. Materials and methods

2.1. Chemicals and reagents

Eight of the 16 priority PAHs specified by the U.S. EPA were selected in this study, namely Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flu), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (Flua) and Pyrene (Pyr). The new DGT sampler has been tested and validated for these compounds (Rong et al., 2024). HPLC-grade methanol, acetonitrile and dichloromethane were used in this study. Agarose (Bio-Rad Laboratories, UK) and MIP-PAHs (CNW, Germany) were used to make gels for DGT.

2.2. DGT preparation

The method for DGT preparation was the same as used in previous studies (Rong et al., 2024). DGT samplers were assembled in the sequence: polycarbonate (PC) membrane filter (in contact with the water), an agarose diffusive gel and a MIP binding gel in a metal casing before deployment (See details in SI).

2.3. Study area

The river system in the main urban area of Nanjing consists of the main stream of the Yangtze River and the Qinhuai River system. The northern and western parts of the urban area belong to the Nanjing section of the Yangtze River, with a drainage area of 117 km^2. The Qinhuai River system is in the southeast of the urban area, with an area of 163 km^2.

Due to human activities, such as urban construction, discharge from wastewater treatment plants, and accessibility for sample retrieval, seven locations in the river system were selected as sampling sites (Fig. S1 and Table S1). Two sampling sites were located in the Yangtze River and 5 sites were located in parts of urban rivers in the city of Nanjing. More details about the experimental area and sites are provided in the Supporting Information.

Sampling was conducted in January and July 2021. Sampling corresponded to the dry season in winter and the wet season in summer. Sample deployment and collection was the same as previous study (Rong et al., 2024). The exposure time of DGT was 7 days. Grab water samples were taken on day 1 and day 7 of the DGT sampling periods. Both DGT samples and water samples were treated within 24 h.

2.4. Sample treatment

Sample treatment was conducted as in previous studies (Rong et al., 2024). For DGT samples, each binding gel was placed in an amber vial with 200 ng decafluorobiphenyl, then ultrasonically extracted with acetonitrile. The elution solution was then evaporated to near dryness and made up with 0.2 mL of acetonitrile/MQ water solution (1:1, v: v).

For the water samples, 1 L was filtered through Whatman GF/F filter (0.7 μm) and spiked with 200 ng decafluorobiphenyl. HLB (60 mg/3 mL, Waters, UK) SPE columns were used to concentrate the water samples. After solid phase extraction, PAHs were eluted with dichloromethane and concentrated, then solvent was replaced as acetonitrile/MQ water solution (1:1, v: v). All the samples were finally filtered through 0.22 μm PTFE filter membranes before analysis (See details in SI).

2.5. Instrumental analysis

The separation of target compounds was performed with a PAH C18 column (4.6 × 250 mm, 5 μm, Waters). High performance liquid chromatography (HPLC) combined with an ultraviolet detector (UVD) and a fluorescence detector (FLD) was used to analyze the 8 PAHs (see details in SI).

2.6. *Calculation of DGT measured concentrations*

Based on Fick's law, the concentration of PAHs in water determined by DGT was calculated using eq. (1) (Zhang and Davison, 1995)

$$C_{DGT} = \frac{M(\Delta g + \delta)}{DAt} \tag{1}$$

Where M (ng) is the total amount adsorbed by the binding gel through the diffusion layer, Δg (cm) is the thickness of the diffusion layer, δ (cm) is the thickness of the diffusion boundary layer, D (cm^2 s^{-1}) is the diffusion coefficient of the individual chemicals in the diffuse layer, A (cm^2) is the window area of the device, and t (sec) is the diffusion time during deployment.

2.7. *Risk assessment*

According to technical guidance from the European Union (EU), ecological risk can be assessed using the Risk Quotient (RQ) method. RQ is the ratio of the measured environmental concentration (MEC) to the predicted no-effect concentration (PNEC).

$$RQ = \frac{MEC}{PNEC} \tag{2}$$

This research used the methods from Kalf and Cao to evaluate the ecological risks of PAHs in the rivers in Nanjing (Kalf et al., 1997; Cao et al., 2010). Maximum permissible concentrations (MPCs) are concentrations above which the risk of adverse effects is considered unacceptable. Negligible concentrations (NCs) are defined as the MPC/100 and takes possible effects of combination toxicity due to the presence of other substances into account (Kalf et al., 1997). Considering both the ecosystem risk of ∑PAHs with the individual PAHs, RQs (NCs) < 1.0 indicates that the ecological risk of an individual PAH may be negligible, while RQ (MPCs) > 1.0 indicates that the pollution of a single PAH is deemed 'serious' and could have an effect. When RQs (NCs) > 1.0 and RQs (MPCs) < 1.0, it indicates that the ecological risk of an individual PAH may be classified as moderate.

Species Sensitivity Distribution (SSD) is also a commonly used method for assessing ecological risks at the system level. It fits the toxicity data of different species to specific chemicals, constructs SSD curves and extrapolates a safe concentration that could protect most organisms in the ecosystem. Here acute toxicity data were used to construct SSD curves. The toxicity data were obtain from the US Environmental Protection Agency ECOTOX database (http://www.epa.gov/ecotox/) and SSD curves were fit based on the Chinese national ecological environment benchmark calculation software EEC-SSD (https://www.mee.gov.cn/ywgz/fgbz/hjjzgl/mxrj/202203/t20220304_970658.shtml). The specific calculation of the hazard index (HI) is given in the SI.

2.8. *QA/QC*

DGT on-site blanks and procedure blanks were used to check for possible contamination, while parallel samples (DGT samples in triplicate, grab samples in duplicate) were used to study repeatability. The target compounds were not found at detectable levels in the blank samples. Quality control standards (10 μg/L) were prepared and run every 10 samples. Detailed information about the instrument detection limits (IDLs) and method detection limits (MDLs) of the SPE method (grab samples) and the DGT method is given in Table S4.

3. Results and discussion

3.1. *Observations on the sampling and analytical procedures*

Grab sampling is the usual approach for detection of organic pollutants and waters. However, the value of DGT in organic pollutant monitoring has also been demonstrated in the past decade. In addition to having in situ monitoring, biomimetic functions, improved detection limits, and increased sensitivity, DGT also has significant advantages in sample collection and processing analysis (Yin et al., 2019; Martins de Barros et al., 2023). In this study, a total of eight 2L glass bottles were used for grab sampling, which required a large amount of space for sampling, transportation, and laboratory storage. The DGT device is small, lightweight, and easy to carry. For studies with multiple and scattered sampling sites, DGT is more convenient to use. The laboratory processing of DGT samples is also simpler. Grab samples require more steps such as solid-phase extraction, elution, concentration, solvent displacement and filtration. The processing time for a single sample exceeded 12 h. The DGT sample only required ultrasonic elution, concentration, solvent displacement, filtration, and a single sample processing time of about 3 h. In addition, ~35 ml of organic reagents were used per grab sample, while DGT samples required <20% of this. Moreover, DGT samples were processed simultaneously, while the processing of bulk water samples was limited by solid-phase extraction devices and required batch processing. So in terms of both time and cost, DGT has obvious advantages. DGT samples have the benefit of pre-concentration, resulting in a cleaner sample matrix and a smoother chromatogram during instrument analysis, making data analysis easier. Previous work has discussed that DGT may be hampered by biofilms or cross-contamination during DGT disassembly (Rougerie et al., 2021), but this has little impact on organic pollutants, and biofilm formation has been shown to have almost no effect within an exposure time of less than two weeks (Chen et al., 2017; Wang et al., 2020a,b). One practical problem can be the loss of DGT samples during field deployment (e.g. loss or vandalism). In this study, <5% of the samples were lost. For large-scale projects, a loss rate of 1–3% is considered acceptable (Rougerie et al., 2021).

3.2. *Comparison of PAH determinations by DGT and grab samples*

The concentrations of 8 individual PAHs obtained through grab sampling ranged from 0.2 to 25.9 ng/L at all sampling points. The concentration range measured by DGT was similar - between 0.45 and 18.1 ng/L. Naphthalene had the highest concentrations and Ant was the lowest of the target compounds.

Fig. 1a provides a comparison of the concentrations/profile of 7 PAHs obtained by grab sampling and DGT sampling. Many samples were obtained in the study, so this figure was prepared as the averages at the Yangtze River and an urban Nanjing river station. In summary, the data show that concentrations determined by grab and DGT samples are similar – note the error bar ranges. However, in general, for the samples at the Yangtze River site, the concentrations of Nap, Ace, Flu, and Phe measured by DGT tended to be slightly higher than those obtained by grab samples. This reflects the differences caused by the sample work-up procedures; these semi-volatile organic compounds are prone to losses by volatilisation from the grab samples during the complex sample workup steps, whereas this is not a problem for the DGT samples because PAHs are directly sampled in situ.

In the Nanjing urban river samples, the DGT concentrations of Nap were lower than the Yangtze but the concentration of Pyr were higher. This may be because the urban river sites are more turbid, as they receive more effluent or drainage from the city. Previous research found that PAHs were most concentrated in suspended particulate matter, and their concentrations were lower when water had lower suspended solids (Wang et al., 2016; Zheng et al., 2016). DGT measures water-soluble PAHs, rather than pollutants adsorbed on suspended substances or

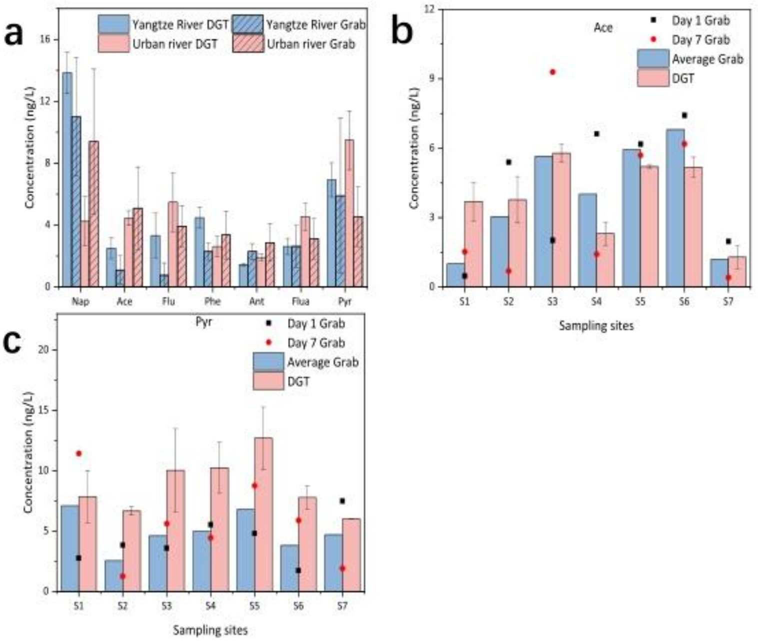


Fig. 1. Comparison of DGT and grab samples, a: mean concentrations in Yangtze River (S1, S7) and Nanjing urban river (S2 to S6) samples for each compound; b: the concentration of Ace at all 7 sampling sites; c: the concentration of Pyr at all 7 sampling sites.

colloids.

Comparing the concentrations of individual PAHs at various sampling sites, the results obtained from DGT and grab sampling were similar. As shown in Fig. 1b, the Ace concentrations measured by the two methods are similar. However, the concentration of Pyr measured by DGT was higher than that obtained by grab sampling at all sampling sites (Fig. 1c). This may be due to the higher hydrophobicity of this chemical compared to others and its tendency to accumulate in sediment.

July is the rainy season in Nanjing, and the July sample collection period was accompanied by rainfall. Fig. 1 and Fig. S2 gives the information about the instantaneous concentrations of grab samples; Nap, Ace, Flu, Ant concentrations on the seventh day were lower than on the first day, which may be due to rainfall dilution during the sampling period. Meanwhile, high rainfall can cause re-mobilisation of sediments and higher total suspended particle (TSP) load in river waters than during dry periods. Pollutants held in sediments may re-partition into the overlying river water. The concentrations of Phe, Flua and Pyr increased in some places from day 1 to day 7. This has also been observed previously for other organic chemicals e.g. pharmaceuticals and glucocorticoids. During heavy rainfall, the concentration of target compounds was higher than other periods (Fang et al., 2019; Yan et al., 2022). Because active sampling measures the instantaneous concentration which can be affected by rainfall, river water flow, short-term emissions, etc., whereas DGT smooths and integrates such differences over time (Chen et al., 2013; Yang et al., 2019). Grab samples could give us specific information about the changes during the research period. However, to obtain representative results by active sampling requires high-frequency sampling. This is not conducive to on-site operations and increases research and monitoring costs. DGT can effectively reflect the environmental behavior of PAHs by measuring the time weighted average concentration over a period of time.

The subsequent analysis and discussion are based on DGT measured concentrations.

3.3. Occurrence of PAHs in different seasons

The concentrations of PAHs in winter and summer samples are shown in Table S5. There are obvious seasonal differences. The concentration range of individual PAHs in winter was 4.2–161 ng/L, with the highest average concentrations being Nap (91.5 ng/L) and Acy (83.3 ng/L), and the lowest being Ant (5.9 ng/L). The concentration range of individual PAHs in summer was 1.3–18.0 ng/L (Nap). The highest average concentration was Pyr (8.8 ng/L), followed by Nap (7.0 ng/L), and the lowest was Ant (1.8 ng/L). The winter concentrations of individual PAH were between 2 and 15 times higher than the summer. The mean of winter: summer ratios for individual PAHs averaged over all the sites were as follows: Nap, 13; Ace, 15; Flu, 3.1; Phe, 15; Ant 3.3; Flua, 5.0; Pyr, 2.1. So, there were marked differences between compounds in their water-soluble/DGT-labile concentrations and abundance between winter and summer. Generally, the differences between winter and summer are more pronounced for the compounds with fewer benzene rings, which are more volatile and degradable.

The following are factors that vary between winter and summer, which could potentially influence the seasonal differences: seasonally dependent sources to the environment/catchments (He et al., 2014); rainfall, discharges and river flow – influencing dilution and sediment re-suspension (as noted above, summer flows were ca 3 times higher in the main Yangtze channel than the winter) (Zhang et al., 2012); degradation/removal of compounds from the water column, via volatilisation, photolysis and biodegradation, partitioning to sediments and subsequent deposition. These processes are all affected by temperature.

Due to the demand for heating in winter, the concentration of PAHs in the atmosphere is higher than that in summer, from combustion sources (Daisey et al., 1980; Tang et al., 2005). The increase in PAH concentration in the eastern region of China after the autumn harvest period is from straw burning (He et al., 2014). PAHs exist in the atmosphere in the gas and particle phase, with the lower molecular weight compounds almost exclusively in the gas phase (Xu et al., 2006). Atmospheric dry deposition is a source of PAHs in water (Guo et al., 2009). Air-surface exchange of these compounds occurs, with the net direction influenced by temperature. During warmer weather, the net flux will be from the dissolved/labile phase in river waters to the atmosphere (Barrado et al., 2012). The increase in sources has contributed to differences in the concentration of PAHs in the water of Nanjing area between winter and summer.

The rainfall in July was about 6 times that of winter in Nanjing, resulting in a significant dilution effect on pollution concentrations. Similar results have also been found in previous studies on the Yellow River and Bohai Sea, where PAHs concentrations were diluted by rainfall during the rainy season (Sun et al., 2009; Chen et al., 2023).

Based on river water flow, typical mass flows (kg/day) of PAHs were calculated for summer and winter (Table 1). In the urban rivers, the mass flows of pollutants in summer were lower than in winter. Compared to the data of the mainstream of Yangtze River, the amount of pollutants at downstream locations in summer was actually lower than that at the upstream location (see Table 1). The higher temperature in summer may lead to the degradation of PAHs. Microbial degradation of PAHs can occur in the water column, particularly for the LMW compounds (Li et al., 2022; Chen et al., 2023). Higher ultraviolet radiation in summer can also promote the photodegradation of PAHs (Zhang and Chen, 2017). Volatilisation, photolysis and biodegradation rates are all compound specific, removing 2-/3-ring compounds more quickly than 4-ring compounds. The proportion of 2-/3- ring PAHs in summer were lower than in winter in the water samples (Fig. S3).

In summary, these seasonal differences in DGT measured labile concentrations are a function of seasonal differences in sources/emissions/discharges, riverine flows and degradation/losses to/from the water column.

3.4. PAH composition and features at the sample sites

The concentrations of target PAHs in the samples collected at different sites in July 2021 are shown in Fig. S4; the detection frequency of all the analytes was 100%. The mixture of PAHs varied between sites. Compound distributions are shown in Fig. 2. Naphthalene had higher concentrations at points S1 and S7, on the mainstream of the Yangtze River which serves as the main shipping channel and terminals. The port of Nanjing has a cargo throughput of over 100 million tons a year. Although efforts have been made to improve and protect the ecological environment of the Yangtze, there are still over a hundred chemical enterprises in Nanjing alone along the Yangtze River. Site S1 had the highest concentration of Nap of the sampling sites; it is 8 km downstream of the city's steel industry complex. Point source emissions and ship fuel combustion could be sources of Nap in this area. For 3-ring Phe, the highest concentrations occurred at sites S4, S5 and S7. Site S5 is in residential areas with high population density. Pollutant emissions from the urban area of Nanjing flow into the Yangtze River through the Qinhuai River (site S5) system. The concentration of Pyr in the mainstream of the Yangtze River was lower than that in urban rivers, with the highest concentration at S5. This may be due to sampling during the rainy season, when high rainfall and river flows cause runoff and remobilize sediments, which can release particle-bound pollutants into the water (Fialová et al., 2023). What this comparison of compounds and sites shows is that the mixture of PAHs in the study system can vary in space and time. It would be very difficult to unravel all the factors influencing the mixture of PAHs in this study catchment. It will be a complex function of myriad sources of different types and compound-specific differences in behaviour and degradation in the study environment.

It is instructive to compare the mass flows of PAHs in the main Yangtze River upstream and downstream of the major city of Nanjing, and to compare the mass flows of the Nanjing river with the mass flows of the Yangtze itself (see Table 1). It is clear that: i. the PAH load in the main Yangtze far exceeds that being supplied to it by the Nanjing river system, and ii. Nanjing makes a minor contribution compared to the load already in the Yangtze arriving upstream of the city. This is because the Yangtze has flowed many thousands of km before reaching Nanjing, through many major urban areas and has collected PAH inputs from a multitude of point and diffuse sources before reaching Nanjing. As such, source reduction measures in Nanjing and nearby will have a small impact on the PAH burden of the Yangtze itself. Major regional/national reductions in sources would be needed to have a measurable impact on the quality of the Yangtze River flowing through Nanjing.

Table 1
The estimated mass of PAHs flowing per day in winter and summer at selected Yangtze River and Nanjing urban river sites.

Season	Site	flow (m^3/s)	Mass compound/day (kg/day)						
			Nap	Ace	Flu	Phe	Ant	Flua	Pyr
Winter	S1	16850	76.7	102.3	21.2	45.9	8.0	20.1	19.9
	S4	50	0.3	0.3	0.1	0.3	0.0	0.1	0.1
	S6	20	0.2	0.1	0.0	0.1	0.0	0.0	0.0
	S7	16850	234.6	46.1	24.7	83.2	9.2	29.0	34.1
	Input to urban rivers*		0.50	0.47	0.12	0.39	0.05	0.17	0.10
	Input to Yangtze main stream**		157.9	56.3^a	3.4	37.3	1.2	8.9	14.2
Summer	S1	45000	26.3	5.4	7.1	5.0	2.4	5.7	11.4
	S4	200	0.1	0.0	0.1	0.0	0.0	0.1	0.1
	S6	50	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	S7	45000	14.0	1.9	2.5	8.0	1.8	1.9	8.8
	Input to urban rivers*		0.07	0.04	0.08	0.04	0.03	0.08	0.13
	Input to Yangtze main stream**		12.2^a	3.5^a	4.6^a	3.0	0.5^a	3.8^a	2.7^a

S1 is the Yangtze River upstream site, S4 is the Qinhuai River, S6 is the Jiuxiang River, and S7 is the downstream Yangtze River site. Subscript "a" represent negative numbers.* Calculated by total mass flow of S4 and S6, ** calculated by mass flow at S7 minus S1.

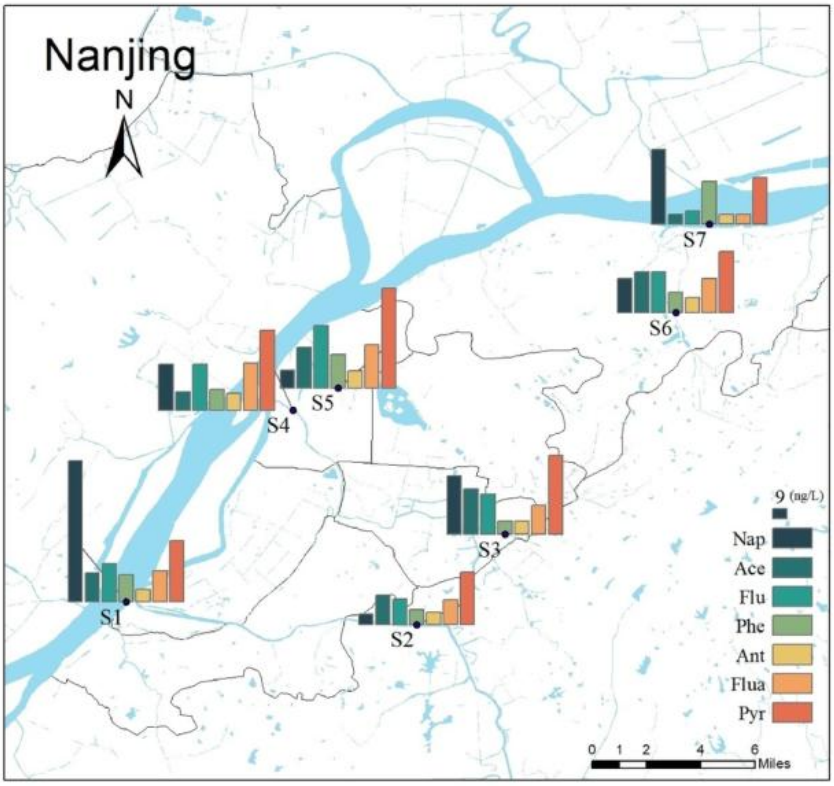


Fig. 2. DGT Measured in-situ concentrations (ng/L) of PAHs at the 7 sample sites in July 2021 in the Yangtze River and the Nanjing river system.

3.5. *Comparison with previous studies*

The PAH data obtained in this study were compared with other studies, and the results presented in Table S6. There have been previous measurements made of PAHs in the Yangtze River and Nanjing rivers by other researchers. These have been reported for the years 2004–2005, 2015, 2018, 2019 and 2020 (He et al., 2011; Wang et al., 2017; Jia et al., 2021; Zhao et al., 2021; Yang et al., 2022). As this study has shown, there are very big differences in PAH concentrations between the wet and dry seasons, so comparisons with other datasets need to take this into account. The concentrations in the Yangtze River and Qinhuai River in 2021 measured in this study were lower than reported in the same region in 2004–2005 and summer for 2015 (He et al., 2011; Wang et al., 2017). The concentration in 2015 was significantly higher than other studies, shortly after pollution control measures were introduced. From 1995 to 2013, the discharge of industrial wastewater in Chinese cities sharply decreased, with some areas experiencing a decrease of >60%. The discharge of heavy metals in the middle and lower reaches of the Yangtze River also decreased. However, compared with the 2000s, the concentration of heavy metals in some parts of the Yangtze River still showed an upward trend in the 2010s, but the upward trend slowed down (Li et al., 2020). The summer concentrations measured in this study were lower than the concentrations in 2018 (Zhao et al., 2021). Summer concentrations measured here were comparable to the concentration in 2019, 2020 and the average concentration in the Yangtze River Delta region during the same period in 2019. The winter concentrations measured were higher than those reported for 2019.12 and 2020.10 (Jia et al., 2021; Yang et al., 2022). Taking account of the large effect of season, these comparisons indicate that PAHs have probably declined over the last few years; the strongest evidence for this is the comparison between this study and He and Wang's study (He et al., 2011; Wang et al., 2017).

The major rivers of China have generally improved in quality over the last 20 years, following major government and regional initiatives to reduce aquatic discharges from industry (Zhang et al., 2019; Yu et al., 2021) and the installation of major waste water treatment facilities in all major cities and – step-by-step – rural areas (Wang et al., 2015). In recent years, Nanjing has cracked down on illegal discharges along the Yangtze River, optimized the layout of industrial zones, and dismantled older docks to reduce pollution to the Yangtze River. Greater pollution control management has also been introduced on ship transportation, and strengthened the construction of city water networks to control the water quality of tributaries entering the main river (Annual report on the ecological environment status of Nanjing and Jiangsu Province, Yangtze River Yearbook). It appears that with the promotion of "the Yangtze River Protection" in China, pollution control and ecological protection along the river have achieved significant results.

The PAH concentrations in this Nanjing study are generally lower than in the other major rivers of China – the Yellow River and Haihe River (Sun et al., 2009; Liu et al., 2014), equivalent to that in the upper reaches of the Huaihe River (Liu et al., 2016), but are higher than in the Pearl River (Li et al., 2022). Generally, the distribution of PAHs in China's major rivers shows higher levels in the north than the south. Generally northern China has higher PAH emissions from combustion sources and greater industrialization of river catchments than the south (Guo et al., 2012; Zhang et al., 2019). The distribution of PAHs is mainly related to urban economic infrastructure, chemical industry configuration, and climate conditions. The northern region of China is a traditional heavy industrial area, where the combustion of fossil fuels such as coal are the main sources of PAHs (Sun et al., 2018; Yu et al., 2021). The demand for winter heating in the northern parts of China (generally north of the Yangzte), with the extensive combustion of coal and other biomass is a major source of PAHs in China (Zhang and Tao, 2009). In contrast, southern China has higher temperatures, higher humidity, and stronger ultraviolet radiation, which can promote the photodegradation and microbial degradation of PAHs (Zhang and Chen, 2017). These factors collectively lead to higher concentrations of PAHs in the air, waters and soils of north China compared to the south (Han et al., 2019; Zhang et al., 2019).

Levels in this study are generally comparable to the River Nile (Haiba, 2017), although the concentrations of 4-ring PAHs appear to be higher in the Nile than in this Nanjing/Yangzte study. Our study also gives levels comparable to those in the Mississippi River (Zhang et al., 2007).

3.6. Source analysis

Based on the earlier calculation of mass flows of PAHs in the Yangtze River upstream and downstream of the Nanjing conurbation, flows from the city itself via the Qinhuai and Jiuxiang Rivers make a minor contribution to the total load in the Yangtze (see Table 1). Some of the sources to the Yangtze upstream of Nanjing were briefly mentioned earlier, namely industrial and wastewater discharges upstream, diffusive inputs and runoff from the many large cities and conurbations further upstream, atmospheric deposition to the vast catchment of the Yangtze and its tributaries, soil erosion and sediment re-working.

A method that has been widely used in the literature to gain clues about the sources of PAHs in environmental samples is to consider compound isomer mixtures and ratios (Soclo et al., 2000; Yunker et al., 2002; Tobiszewski and Namiesnik, 2012). Of course, compounds/isomer ratios will change over time, if compounds are selectively degraded. LMW PAHs are generally more unstable and degrade faster than heavier ones. This will undermine the use of ratios as source apportionment tools. As discussed earlier in the section on seasonality, there is evidence in this dataset that some of the DGT measured labile LMW compounds are prone to degradation/losses from the river surface waters. So, discussion and interpretation of isomer ratios needs to be done cautiously.

Fig. S5 shows the ratios of Ant/Ant + Phe and Fla/Fla + Pyr; these have been used previously by Tobiszewski and Namiesnik as a tool for identifying and assessing pollution emission sources. (Tobiszewski and Namiesnik, 2012). This highlights clear differences in the isomer ratios of the DGT samples taken in winter and summer. Overall, the ratios suggest that sources to the rivers in Nanjing in winter and summer are mixed, caused by petroleum and combustion. However, in winter, there is a significant increase in coal and biomass combustion sources. Different from northern China, Nanjing is not a mandatory centralized heating area in China and has less indoor heating demands of residents in winter. But some factory heating exists in winter and small-scale residential heating has been attempted since 2019. Research has found that there was a phenomenon in the suburbs where coal and biomass combustion emit a large amount of gaseous PAHs (Li et al., 2018). Unfavorable climate conditions for pollutant dispersion occur in winter, resulting in differences in the distribution of pollutants between winter and summer.

3.7. Risk assessment

PAHs can pose ecological risks to aquatic organisms in rivers. In order to evaluate the potential ecological hazards of PAHs in the rivers of Nanjing, ecological risk assessments were conducted using the data for the different sampling points in winter and summer. As explained earlier, two different approaches were used to assess the ecological risks. The first is the Risk Quotient (RQ) method. With this approach, Table S7 indicates that the levels of individual PAHs in summer are low and insufficient to warrant concern. Phe and Nap have almost no ecological risk at all the sites. For the other PAHs, their levels are classified as 'moderate'. However, with the winter levels, the ecological risk in this region significantly increased. Acy and Ace have 'high risks' at sites S1, S4, S5, and S6. These areas include ports, densely populated areas and chemical industries. The other PAHs may pose 'moderate ecological risks'. This analysis, addressing possible ecological risks for individual PAHs, indicates that although the Yangtze River Protection scheme has effectively reduced the concentration of PAHs in the Nanjing area, further measures are still needed to reduce the ecological risks caused by these pollutants.

The second method to assess ecological risks used the Species Sensitivity Distribution approach. The SSD fitting results obtained through EEC-SSD software are shown in Table S8 and Fig. S6. The smaller the HC_5 value, the greater the toxic effect of the compound. For all species, the order of toxicity effects of the 7 PAHs is Pyr > Ant > Flua > Phe > Flu > Ace > Nap. As the number of benzene rings increases, the toxic effect increases. The calculated risk quotient and the mixture risk of multiple pollutants based on the obtained PNEC values are shown in Table S9. As with the first method of risk assessment, the concentration of individual PAHs was generally at the 'low risk' level in summer. Nap and Flua were at 'moderate risk' in winter. Pyr was at 'moderate risk' in both winter and summer. For the assessment of PAH mixtures, the overall risk is 'moderate', for sites S4, S5, S6, and S7, although it was deemed as 'high risk' in winter.

The ecological risk of the Nanjing River was evaluated with both the risk entropy method and SSD method. Although the individual levels of PAH risk were slightly different, the results indicates that the overall ecological risk was higher in winter, and the risk in the downstream and the industry area of the river was significantly increased. These results indicate that although PAH concentrations seem to have generally declined in the rivers in the Nanjing area, further measures are still needed to reduce the ecological risks caused by PAHs.

4. Conclusion

A novel DGT sampler has been successfully used in situ for the measurement of hydrophobic compounds PAHs in rivers in Nanjing. The measured labile concentration of PAHs in the Yangtze River and urban rivers had a marked seasonal difference. Compared with previous studies, the concentrations of PAHs in the Yangtze River Nanjing section and other Nanjing rivers have decreased in recent years. Compared with other regions, the concentrations are generally lower than that in major rivers in northern China, and slightly higher than that in southern rivers. This study provides a new approach for effective in-situ monitoring of PAHs in aquatic environments, expanding the application of DGT technique in measuring hydrophobic organic pollutants in aquatic ecosystems.

Analysis of the sources of PAH pollution in the Nanjing region showed that PAHs in the Yangtze River mainly come from upstream accumulated loads, petrochemical enterprises along the Yangtze River, and ship transportation. The input of urban tributaries in Nanjing was small relative to the load in the main Yangtze. The risk assessment of both risk quotient and species sensitivity distribution methods showed that although PAH pollution in the Nanjing area has reduced in recent years, there are still risks in winter and in industrial areas. The government should continue to pay attention to the situation of PAH pollution in the area and maintain continuous monitoring, as well as focus on catchment governance and management.

CRediT authorship contribution statement

Qiuyu Rong: Investigation. **Hao Zhang:** Supervision. **Yanying Li:** Investigation. **Liying Yan:** Investigation. **Jun Luo:** Supervision. **Kevin C. Jones:** Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2025.125921.

Data availability

Data will be made available on request.

References

Barrado, A.I., García, S., Barrado, E., Pérez, R.M., 2012. PM2.5-bound PAHs and hydroxy-PAHs in atmospheric aerosol samples: Correlations with season and with physical and chemical factors. Atmos. Environ. 49, 224–232.

Baz-Lomba, J.A., Harman, C., Reid, M., Thomas, K.V., 2017. Passive sampling of wastewater as a tool for the long-term monitoring of community exposure: illicit and prescription drug trends as a proof of concept. Water Res. 121, 221–230.

Cao, Y., Wang, J., Xin, M., Wang, B., Lin, C., 2024. Spatial distribution and partition of polycyclic aromatic hydrocarbons (PAHs) in the water and sediment of the southern Bohai Sea: Yellow River and PAH property influences. Water Res. 248, 120873.

Cao, Z., Liu, J., Luan, Y., Li, Y., Ma, M., Xu, J., Han, S., 2010. Distribution and ecosystem risk assessment of polycyclic aromatic hydrocarbons in the Luan River, China. Ecotoxicology 19 (5), 827–837.

Chen, C., Lin, T., Sun, X., Wu, Z., Tang, J., 2023. Spatiotemporal distribution and particle-water partitioning of polycyclic aromatic hydrocarbons in Bohai Sea, China. Water Res. 244, 120440.

Chen, C.E., Zhang, H., Jones, K.C., 2012. A novel passive water sampler for in situ sampling of antibiotics. J. Environ. Monit. 14 (6), 1523–1530.

Chen, C.E., Zhang, H., Ying, G.G., Jones, K.C., 2013. Evidence and recommendations to support the use of a novel passive water sampler to quantify antibiotics in wastewaters. Environ. Sci. Technol. 47 (23), 13587–13593.

Chen, W., Li, Y., Chen, C.E., Sweetman, A.J., Zhang, H., Jones, K.C., 2017. DGT passive sampling for quantitative in situ measurements of compounds from household and personal care products in waters. Environ. Sci. Technol. 51 (22), 13274–13281.

China, M. o. E. a. E. o. t. P. s. R. o., 2017. Yangtze River Economic Belt Ecological Environment Protection Plan.

China, M. o. E. a. E. o. t. P. s. R. o., 2020. Yangtze River Protection Law.

Daisey, J.M., Kneip, T.J., Hawryluk, I., Mukai, F., 1980. Seasonal variations in the bacterial mutagenicity of airborne particulate organic matter in New York City. Environ. Sci. Technol. 14 (12), 1487–1490.

Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature 367 (6463), 546–548.

Fang, Z., Li, K., Li, Y., Zhang, H., Jones, K.C., Liu, X., Liu, S., Ma, L.Q., Luo, J., 2019. Development and application of the diffusive gradients in thin-films technique for measuring psychiatric pharmaceuticals in natural waters. Environ. Sci. Technol. 53 (19), 11223–11231.

Fialová, P., Grabic, R., Grabicová, K., Nováková, P., Švecová, H., Kaserzon, S., Thompson, K., Vrana, B., 2023. Performance evaluation of a diffusive hydrogel-based passive sampler for monitoring of polar organic compounds in wastewater. Sci. Total Environ. 864.

Gao, Y., Zhu, N., Meng, X.-Z., Ma, W.-L., Ma, R.-S., Jin, J.-J., Ai, F.-T., Jin, L.-M., Cai, M.-H., Liu, J.-S., Zhao, J.-F., Lindner, S., 2024. Sources and ecological risk of polycyclic aromatic hydrocarbons in water and air of the Yangtze River. Environ. Sci. J. Integr. Environ. Res.: Water Research & Technology 10 (2), 389–398.

Guo, G., Wu, F., He, H., Zhang, R., Li, H., Feng, C., 2012. Distribution characteristics and ecological risk assessment of PAHs in surface waters of China. Sci. China Earth Sci. 55 (6), 914–925.

Guo, W., He, M., Yang, Z., Lin, C., Quan, X., Men, B., 2009. Distribution, partitioning and sources of polycyclic aromatic hydrocarbons in Daliao River water system in dry season, China. J. Hazard Mater. 164 (2–3), 1379–1385.

Haiba, N.S.A., 2017. Polycyclic aromatic hydrocarbons (PAHs) in the River nile, Egypt: occurrence and distribution. Polycycl. Aromat. Compd. 39 (5), 425–433.

Han, J., Liang, Y., Zhao, B., Wang, Y., Xing, F., Qin, L., 2019. Polycyclic aromatic hydrocarbon (PAHs) geographical distribution in China and their source, risk assessment analysis. Environ. Pollut. 251, 312–327.

He, H., Hu, G.J., Sun, C., Chen, S.L., Yang, M.N., Li, J., Zhao, Y., Wang, H., 2011. Trace analysis of persistent toxic substances in the main stream of Jiangsu section of the Yangtze River, China. Environ. Sci. Pollut. Res. Int. 18 (4), 638–648.

He, J., Fan, S., Meng, Q., Sun, Y., Zhang, J., Zu, F., 2014. Polycyclic aromatic hydrocarbons (PAHs) associated with fine particulate matters in Nanjing, China: distributions, sources and meteorological influences. Atmos. Environ. 89, 207–215.

Jia, T., Guo, W., Liu, W., Xing, Y., Lei, R., Wu, X., Sun, S., 2021. Spatial distribution of polycyclic aromatic hydrocarbons in the water-sediment system near chemical industry parks in the Yangtze River Delta, China. Sci. Total Environ. 754, 142176.

Kalf, D.F., Crommentuijn, Trudie, Plassche, E.J.v. d., 1997. Environmental quality objectives for 10 polycyclic aromatic hydrocarbons (PAHs). Ecotoxicol. Environ. Saf. 36 (1), 89–97.

Kim, K.H., Jahan, S.A., Kabir, E., Brown, R.J., 2013. A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. Environ. Int. 60, 71–80.

Kot, A., Zabiegała, B., Namieśnik, J., 2000. Passive sampling for long-term monitoring of organic pollutants in water. TrAC, Trends Anal. Chem. 19 (7), 446–459.

Li, B., Wu, S., Zhou, S., Wang, T., Wang, C., 2018. Spatiotemporal distribution and dynamic modeling of atmospheric gaseous polycyclic aromatic hydrocarbons in a rapidly urbanizing city: Nanjing, China. Environ. Geochem. Health 40 (6), 2603–2616.

Li, H., Wang, X., Peng, S., Lai, Z., Mai, Y., 2022. Seasonal variation of temperature affects HMW-PAH accumulation in fishery species by bacterially mediated LMW-PAH degradation. Sci. Total Environ. 853, 158617.

Li, R., Tang, X., Guo, W., Lin, L., Zhao, L., Hu, Y., Liu, M., 2020. Spatiotemporal distribution dynamics of heavy metals in water, sediment, and zoobenthos in mainstream sections of the middle and lower Changjiang River. Sci. Total Environ. 714, 136779.

Li, Y., Chen, C.L., Chen, W., Chen, J., Cai, X., Jones, K.C., Zhang, H., 2019. Development of a passive sampling technique for measuring pesticides in waters and soils. J. Agric. Food Chem. 67 (22), 6397–6406.

Liang, Y., Li, H., Li, S., Chen, S., 2023. Organic diffusive gradients in thin films (o-DGT) for determining environmental behaviors of antibiotics: a review. J. Hazard Mater. 459, 132279.

Liu, J.L., Zhang, J., Liu, F., Zhang, L.L., 2014. Polycyclic aromatic hydrocarbons in surface sediment of typical estuaries and the spatial distribution in Haihe river basin. Ecotoxicology 23 (4), 486–494.

Liu, M., Feng, J., Hu, P., Tan, L., Zhang, X., Sun, J., 2016. Spatial-temporal distributions, sources of polycyclic aromatic hydrocarbons (PAHs) in surface water and suspended particular matter from the upper reach of Huaihe River, China. Ecol. Eng. 95, 143–151.

Manzetti, S., 2013. Polycyclic aromatic hydrocarbons in the environment: environmental fate and transformation. Polycycl. Aromat. Compd. 33 (4), 311–330.

Martins de Barros, R., Lissalde, S., Guibal, R., Guibaud, G., 2023. Adaptation of the o-DGT for the sampling of 12 hormones: calibration, performance evaluation, and recommendation. Environ. Sci. Pollut. Res. Int. 30 (26), 68177–68190.

Moon, H.B., Kim, H.S., Choi, M., Choi, H.G., 2010. Intake and potential health risk of polycyclic aromatic hydrocarbons associated with seafood consumption in Korea from 2005 to 2007. Arch. Environ. Contam. Toxicol. 58 (1), 214–221.

Net, S., Dumoulin, D., El-Osmani, R., Rabodonirina, S., Ouddane, B., 2014. Case study of PAHs, Me-PAHs, PCBs, phthalates and pesticides contamination in the Somme River water, France. Int. J. Environ. Res. 8 (4), 1159–1170.

Rizzi, C., Villa, S., Waichman, A.V., de Souza Nunes, G.S., de Oliveira, R., Vighi, M., Rico, A., 2023. Occurrence, sources, and ecological risks of polycyclic aromatic hydrocarbons (PAHs) in the Amazon river. Chemosphere 336, 139285.

Rong, Q., Li, Y., Luo, J., Yan, L., Jones, K.C., Zhang, H., 2024. Development of a novel DGT passive sampler for measuring polycyclic aromatic hydrocarbons in aquatic systems. J. Hazard Mater. 470, 134199.

Rougerie, J., Martins de Barros, R., Buzier, R., Devillers, D., Fondaneche, P., Lissalde, S., Leblanc, J., Saut, M., Rebillard, J.P., Mazzella, N., Guibaud, G., 2021. Diffusive gradients in thin films (DGT): a suitable tool for metals/metalloids monitoring in continental waterbodies at the large network scale. Sci. Total Environ. 754, 142147.

Soclo, H.H., Garrigues, P.H., Ewald, M., 2000. Origin of polycyclic aromatic hydrocarbons (PAHs) in coastal marine sediments: case studies in Cotonou (Benin) and Aquitaine (France) areas. Mar. Pollut. Bull. 40 (5), 387–396.

Sun, J., Pan, L., Tsang, D.C.W., Zhan, Y., Zhu, L., Li, X., 2018. Organic contamination and remediation in the agricultural soils of China: a critical review. Sci. Total Environ. 615, 724–740.

Sun, J.H., Wang, G.L., Chai, Y., Zhang, G., Li, J., Feng, J., 2009. Distribution of polycyclic aromatic hydrocarbons (PAHs) in Henan reach of the Yellow River, Middle China. Ecotoxicol. Environ. Saf. 72 (5), 1614–1624.

Sun, K., Song, Y., He, F., Jing, M., Tang, J., Liu, R., 2021. A review of human and animals exposure to polycyclic aromatic hydrocarbons: health risk and adverse effects, photo-induced toxicity and regulating effect of microplastics. Sci. Total Environ. 773, 145403.

Tang, N., Hattori, T., Taga, R., Igarashi, K., Yang, X., Tamura, K., Kakimoto, H., Mishukov, V.F., Toriba, A., Kizu, R., Hayakawa, K., 2005. Polycyclic aromatic hydrocarbons and nitropolycyclic aromatic hydrocarbons in urban air particulates and their relationship to emission sources in the Pan–Japan Sea countries. Atmos. Environ. 39 (32), 5817–5826.

Tobiszewski, M., Namiesnik, J., 2012. PAH diagnostic ratios for the identification of pollution emission sources. Environ. Pollut. 162, 110–119.

Uddin, M.M., Xu, F., 2024. Sources, occurrences, and risks of polycyclic aromatic hydrocarbons (PAHs) in Bangladesh: a review of current status. Atmosphere 15 (2).

Venkatraman, G., Giribabu, N., Mohan, P.S., Muttiah, B., Govindarajan, V.K., Alagiri, M., Abdul Rahman, P.S., Karsani, S.A., 2024. Environmental impact and human health effects of polycyclic aromatic hydrocarbons and remedial strategies: a detailed review. Chemosphere 351, 141227.

Vijayanand, M., Ramakrishnan, A., Subramanian, R., Issac, P.K., Nasr, M., Khoo, K.S., Rajagopal, R., Greff, B., Wan Azelee, N.I., Jeon, B.H., Chang, S.W., Ravindran, B., 2023. Polyaromatic hydrocarbons (PAHs) in the water environment: a review on toxicity, microbial biodegradation, systematic biological advancements, and environmental fate. Environ. Res. 227, 115716.

Wang, C., Zhou, S., Wu, S., Song, J., Shi, Y., Li, B., Chen, H., 2017. Surface water polycyclic aromatic hydrocarbons (PAH) in urban areas of Nanjing, China. Water Sci. Technol. 76 (7–8), 2150–2157.

Wang, R., Biles, E., Li, Y., Juergens, M.D., Bowes, M.J., Jones, K.C., Zhang, H., 2020a. In situ catchment scale sampling of emerging contaminants using diffusive gradients in thin films (DGT) and traditional grab sampling: a case study of the River Thames, UK. Environ. Sci. Technol. 54 (18), 11155–11164.

Wang, R., Jones, K.C., Zhang, H., 2020b. Monitoring organic pollutants in waters using the diffusive gradients in the thin films technique: investigations on the effects of biofouling and degradation. Environ. Sci. Technol. 54 (13), 7961–7969.

Wang, X.-H., Wang, X., Huppes, G., Heijungs, R., Ren, N.-Q., 2015. Environmental implications of increasingly stringent sewage discharge standards in municipal wastewater treatment plants: case study of a cool area of China. J. Clean. Prod. 94, 278–283.

Wang, X., Shi, W., Wu, J., Hao, Y., Hu, G., Liu, H., Han, X., Yu, H., 2010. Reproductive toxicity of organic extracts from petrochemical plant effluents discharged to the Yangtze River, China. J. Environ. Sci. (China) 22 (2), 297–303.

Wang, X., Yuan, K., Chen, B., Lin, L., Huang, B., Luan, T., 2016. Monthly variation and vertical distribution of parent and alkyl polycyclic aromatic hydrocarbons in estuarine water column: role of suspended particulate matter. Environ. Pollut. 216, 599–607.

Wang, Z., Liu, Y., Zhang, A., Yang, L., Wei, C., Chen, Y., Liu, Z., Li, Z., 2024. Occurrence characteristics, environmental trend, and source analysis of polycyclic aromatic hydrocarbons in the water environment of industrial zones. Environ. Res. 245, 118053.

Wong, C.M., Williams, C.E., Collier, U., Schelle, P., Pittock, J., 2007. World's top 10 rivers at risk.

Xie, H., Chen, Q., Chen, J., Chen, C.L., Du, J., 2018. Investigation and application of diffusive gradients in thin-films technique for measuring endocrine disrupting chemicals in seawaters. Chemosphere 200, 351–357.

Xu, S., Liu, W., Tao, S., 2006. Emission of polycyclic aromatic hydrocarbons in China. Environ. Sci. Technol. 40 (3), 702–708.

Yan, L., Rong, Q., Zhang, H., Jones, K.C., Li, Y., Luo, J., 2022. Evaluation and application of a novel diffusive gradients in thin-films technique for in situ monitoring of glucocorticoids in natural waters. Environ. Sci. Technol. 56 (22), 15499–15507.

Yan, Z., Yang, H., Dong, H., Ma, B., Sun, H., Pan, T., Jiang, R., Zhou, R., Shen, J., Liu, J., Lu, G., 2018. Occurrence and ecological risk assessment of organic micropollutants in the lower reaches of the Yangtze River, China: a case study of water diversion. Environ. Pollut. 239, 223–232.

Yang, H., Lu, G., Yan, Z., Liu, J., Dong, H., Jiang, R., Zhou, R., Zhang, P., Sun, Y., Nkoom, M., 2019. Occurrence, spatial-temporal distribution and ecological risks of pharmaceuticals and personal care products response to water diversion across the rivers in Nanjing, China. Environ. Pollut. 255 (Pt 1), 113132.

Yang, M., Xu, X., Wang, D., Liu, Q., Lyu, J., Lin, L., Wang, D., Chen, Y., Liang, W., 2022. Distribution characteristics, source and ecological risks assessment of Polycyclic Aromatic Hydrocarbons in water bodies of typical sections of the Yangtze River. China Environ. Sci. 42 (11), 5308–5317.

Yang, Y., Chen, Z., Zhang, J., Wu, S., Yang, L., Chen, L., Shao, Y., 2021. The challenge of micropollutants in surface water of the Yangtze River. Sci. Total Environ. 780, 146537.

Yin, X., Guo, C., Lv, J., Hou, S., Zhang, Y., Jin, X., Teng, Y., Xu, J., 2019. Biomimetic accumulation of methamphetamine and its metabolite amphetamine by diffusive gradients in thin films to estimate their bioavailability in Zebrafish. Environ. Sci. Technol. Lett. 6 (12), 708–713.

Yu, H., Liu, Y., Han, C., Fang, H., Weng, J., Shu, X., Pan, Y., Ma, L., 2021. Polycyclic aromatic hydrocarbons in surface waters from the seven main river basins of China: spatial distribution, source apportionment, and potential risk assessment. Sci. Total Environ. 752, 141764.

Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S., 2002. PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. Org. Geochem. 33 (4), 489–515.

Zhang, H., Davison, W., 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. Anal. Chem. (Washington) 67 (19), 3391–3400.

Zhang, K., Liang, B., Wang, J.Z., Guan, Y.F., Zeng, E.Y., 2012. Polycyclic aromatic hydrocarbons in upstream riverine runoff of the Pearl River Delta, China: an assessment of regional input sources. Environ. Pollut. 167, 78–84.

Zhang, P., Chen, Y., 2017. Polycyclic aromatic hydrocarbons contamination in surface soil of China: a review. Sci. Total Environ. 605–606, 1011–1020.

Zhang, S., Zhang, Q., Darisaw, S., Ehie, O., Wang, G., 2007. Simultaneous quantification of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals and personal care products (PPCPs) in Mississippi river water, in New Orleans, Louisiana, USA. Chemosphere 66 (6), 1057–1069.

Zhang, Y., Tao, S., 2009. Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. Atmos. Environ. 43 (4), 812–819.

Zhang, Y., Zhang, L., Huang, Z., Li, Y., Li, J., Wu, N., He, J., Zhang, Z., Liu, Y., Niu, Z., 2019. Pollution of polycyclic aromatic hydrocarbons (PAHs) in drinking water of China: composition, distribution and influencing factors. Ecotoxicol. Environ. Saf. 177, 108–116.

Zhao, Z., Gong, X., Zhang, L., Jin, M., Cai, Y., Wang, X., 2021. Riverine transport and water-sediment exchange of polycyclic aromatic hydrocarbons (PAHs) along the middle-lower Yangtze River, China. J. Hazard Mater. 403, 123973.

Zheng, B., Wang, L., Lei, K., Nan, B., 2016. Distribution and ecological risk assessment of polycyclic aromatic hydrocarbons in water, suspended particulate matter and sediment from Daliao River estuary and the adjacent area, China. Chemosphere 149, 91–100.

Ziyaei, K., Mokhtari, M., Hashemi, M., Rezaei, K., Abdi, F., 2024. Association between exposure to water sources contaminated with polycyclic aromatic hydrocarbons and cancer risk: a systematic review. Sci. Total Environ. 924, 171261.