Use of the dynamic technique DGT to determine the labile pool size and kinetic resupply of pesticides in soils and sediments

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ABSTRACT

The diffusive gradients in thin films (DGT) technique has been successfully and widely applied to investigate the labile fractions of inorganic contaminants in soils and sediments, but there have been almost no applications to organic contaminants. Here we developed and tested the approach for the pesticide Atrazine (ATR) in a controlled soil experiment and in situ in an intact lake sediment core. The soil study explored the relationships between soil solution, DGT measured labile ATR and solvent extractable ATR in dosed soils of different organic matter, pH status and incubation times. The results are further interpreted using the DIFS (DGT-induced fluxes in soils and sediments) model. Re-supply of ATR to the soil solution was partially sustained by the solid phase in all the soils. This was due to small labile pool size and slow kinetics, with soil pH being an important controlling factor. The in situ sediment study successfully used a DGT probe to examine labile ATR distribution through the core on the sub-cm scale. It demonstrated – for the first time – an easy to use in situ technique to investigate the effects of redox on re-supply kinetics and biogeochemical processes of trace organic contaminants in sediments.

Keywords: Passive sampling, in situ sampling, pore water, desorption, sediment profile, fine scale, Atrazine
INTRODUCTION

The availability of pesticides for transport and degradation processes in soils and sediments is determined by adsorption-desorption interactions with the solid phase.\textsuperscript{1} Several factors, such as moisture, pH, organic matter (OM) content, contact time with the solid phase, soil type and initial applied concentrations, have been reported to affect their availability in soils.\textsuperscript{2-6} In sediments, the redox state could be the controlling factor for exchange processes of pesticides between pore-water and solid phases.\textsuperscript{7} Interactions of the solution and solid phases are traditionally characterized by a distribution coefficient ($K_d$), which is the ratio of the amount of chemical adsorbed to the solid phase to that in the solution phase.\textsuperscript{8} However, not only the pesticide in the solution, but also that readily desorbed from the solid phase could be potentially available.\textsuperscript{9} When the pesticide concentration in the solution phase is depleted, following uptake by plants or organisms in soils or reactions in sediments, that adsorbed on the solid phase may be released to resupply the available pool. The dynamic sorption-desorption processes can be characterized by the capacity (labile pool size) for re-mobilization and the rate of re-supply of the pesticide from the solid phase.

Traditional approaches used for adsorption/desorption studies of pesticides in soils and sediments (sequential extraction, batch experiments)\textsuperscript{10,11} do not represent \textit{in situ} conditions, nor provide any dynamic information. Some extractants are unrealistically harsh, while batch experiments disturb the soil system with unrealistic physical and chemical conditions. However, recently developed diffusive gradients in thin-films (DGT) techniques for organic chemicals can measure the concentrations and fluxes of compounds in soils.\textsuperscript{12-15} DGT is a dynamic technique (i.e. it perturbs the equilibrium system and induces re-supply) and its measurements in soils and sediments depend on labile (i.e. species that can be easily dissociated and re-supplied) concentrations in the solution and their re-supply from the solid phase. To further interpret the information obtained by DGT, a numerical model simulating DGT uptake and
soil/sediment dynamic systems has been developed, known as DIFS (DGT-induced fluxes in soils and sediments). It has been successfully used for studying exchange kinetics of metals and nutrients\(^{16-18}\) and to interpret DGT measurements in soils and sediments in terms of labile pool size and resupply kinetic parameters. Only two studies have been published, using DGT and the DIFS model for organic compounds and both of them investigated antibiotics in soils.\(^ {13, 19}\) These studies on inorganics and antibiotics lay the foundation for our use of DGT to assess pesticide availability, resupply kinetics and labile pool size in soils and sediments. Depending on the scientific questions and objectives, environmentally realistic and elevated concentrations can be studied with DGT, either in field soils brought to the laboratory or in spiked systems. Controlled conditions (e.g. solid/solution ratios, temperature) should be used and the influence of experimental variables (e.g. pH, redox, soil composition, ageing) can be tested.

Our sediments study was focussed on obtaining the aforementioned information at different depths \textit{in situ} in undisturbed sediment cores. In most previous studies of organics in sediments, the sediments were either treated as soils and samples mixed and stirred to obtain the bulk concentrations of pesticides or by slicing the sediment core, followed by drying and extraction of the sediment to obtain pesticide distribution at depth.\(^ {20}\) Only one \textit{in situ} profile of pesticide (Dichlorodiphenyltrichloroethane - DDT) in sediment pore-water at 2 cm resolution was reported.\(^ {21}\) Based on successful applications of the DGT technique for measuring metals and nutrients distributions directly \textit{in situ} in sediments at mm resolution,\(^ {22-24}\) this is the first study to determine the \textit{in situ} fine scale distribution of a trace organic, which is crucial for determining its potential release to the overlying water.

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, ATR) was chosen as the target pesticide. It is one of the most frequently detected and well researched pesticides. It has been used since 1958 and is registered in more than 70 countries worldwide.\(^ {25}\) It is applied to
control broad-leaf weeds during the cultivation of corn, sorghum, sugarcane, rangeland and other crops pre- and post-emergence. The soil concentration of ATR after application may typically be ~3-6 mg kg\(^{-1}\) as a result of a normal application rate of 1.12 - 2.24 kg ha\(^{-1}\). However, in some contaminated soils, following handling, spillages, accidents etc., the concentration of ATR could be 100s-1000s mg kg\(^{-1}\), requiring remediation. Its half-life in soils is usually reported as weeks to months, but it has also been detected in soils >20 years after application. Validated DGT methods have been developed previously for this compound.

The purpose of this paper was to use DGT to investigate the in situ kinetic exchange of organic pollutants between solution phase and solid phase in two different environments. In the soil experiments, realistic agricultural treatment levels and reported contaminated levels of ATR were used, while an intact sediment core from a natural lake was used for in situ fine scale DGT measurements. The labile pool size and the ability of soils/sediments to re-supply ATR induced by depletion were assessed. The DIFS model was used to show how the dynamic processes of ATR in soils and sediments can be further understood quantitatively, by estimating response time and kinetic rate constants of the desorption processes.

**MATERIALS AND METHODS**

**Chemicals**

ATR standard was purchased from Sigma-Aldrich (https://www.sigmaaldrich.com/). Its physico-chemical properties are given in Table S1. ATR product was stored as 38% suspension liquid. Stock solutions were dissolved in pure methanol (MeOH). ACN (Acetonitrile) and MeOH were purchased from Fisher (Poole, U.K.).

**Soil sample treatments**

Four typical UK agricultural soils were collected and used for the experiments. They were selected to represent varying pH (4.8 - 7.7) and organic matter content (3.9% - 8.1%) of...
agricultural land. Details of soil sites and properties are listed in Table S2. All soils were collected from the sub-surface (10-20 cm), air-dried and passed through a 2 mm sieve.

ATR was added into 500 g soils at 2 doses, to give soil ATR concentrations of 5 (normal agricultural level)\textsuperscript{25} and 100 (reported in contaminated soil)\textsuperscript{26-29} mg kg\textsuperscript{-1}. The soils were then wetted to 15-20% maximum water holding capacity (MWHC), They were kept in plastic bags and stored in the dark at room temperature for the experiments.

**Sediment sample collection**

The sampling site in the northeast of Lake Chaohu, Anhui Province, China was selected because it has been studied previously and the intact core could be efficiently transferred to the laboratory. Routine agricultural use of ATR had occurred in the catchment previously, so ATR was found in the sediments. Sediment cores were collected as described previously\textsuperscript{35} by gravity corer (Ke Fan, China) with PVC sampling tubes (length: 60cm, diameter: 8cm), then kept in an incubator (15°C) in the dark for 4 days before and then during DGT deployment.

**DGT deployment in soil and sediment**

In the soil experiment, standard DGT devices (DGT Research Ltd, UK) with HLB resin gels, agarose diffusive gels and GH Polypro (GHP) filters were used. After 1, 3, 6, 10, 15 and 23 days of incubation (from the time of ATR addition), soils were wetted to 80-100% MWHC and well-mixed to obtain a soil paste, 24 h before DGT deployment. Up to 23 days was selected to observe possible aging effects over the typical half-life of ATR in soils. For DGT deployment, small amounts of soil paste were carefully smeared onto the DGT filter, then the DGT device was gently pressed into the soil with twist and turn actions to ensure maximum contact between the soil surface and the device.\textsuperscript{13,16} All deployments were triplicated and maintained at room temperature for 22 h.

After deployment, DGT devices were retrieved, the filter surface was jet washed with MQ water, the resin gels were removed and placed into 20 mL amber glass vials. Then 10 mL ACN
was added to each vial, the vials were put in an ultrasonic bath for 30 min to elute. The eluents were filtered through 0.2 μm syringe filters (PTFE, Whatman, UK) prior to analysis. The triplicate soils were combined and mixed well. Then ~50 g soil paste was placed into a 50 mL centrifuge tube and centrifuged at 3000 rpm for 40 min. The soil solution obtained from centrifuging was filtered using 0.2 μm syringe filters into 2 mL vials. About 5g of the soils remaining after centrifugation were mixed in 20 mL ACN. The mixture was shaken (rotary shaker, 2 h), then centrifuged (3000 rpm, 30 min). The supernatants were filtered (as above) into 20 mL vials. All experiments were replicated. In the sediment experiment, a standard DGT sediment probe (DGT Research Ltd. UK), containing HLB resin gel, agarose diffusive gel and a PES (polyethenesulfone) filter was carefully inserted into the intact sediment core to 10 cm depth and deployed for 48 hours (based on pilot studies and method detection limits). On retrieval, the probe was thoroughly washed with MQ water and the gels were cut from the window area with a razor blade. The binding gel was then sliced at 5 mm intervals and each slice was eluted (3 mL ACN, 30 min ultrasonic extraction). Then the sediment core was sliced at 1 cm intervals and each segment was centrifuged as described above to obtain pore-water samples; these were pre-concentrated (HLB SPE cartridges - details in SI). Finally, solvent extraction on sediment samples were carried out following the same procedure as for soils.

Chemical analysis
All samples from soil and sediment experiments were analysed by HPLC-MS/MS. Details are given in the SI.

Principle of DGT in soils and sediments
When DGT is deployed in soils and sediments, the HLB resin gel binds the compounds that diffuse through the diffusion layer, establishing a linear concentration gradient in the diffusion layer (see Figure 1). According to Fick’s first law of diffusion (Eq. 1), the flux (F(t)) is
determined. $D$ is the diffusion coefficient of the labile pesticide. $D$ of ATR at 25 °C was taken as $5.67 \times 10^{-6}$ cm$^2$s$^{-1}$, based on a previous study. With increasing deployment time, the interfacial concentration of the labile analyte, $C_i$, tends to decline due to depletion, which induces the desorption of the pesticide from the solid phase to resupply $C_i$. This contributes to the flux of pesticides measured by DGT.

![Figure 1](image_url)

**Figure 1.** Processes induced by deployment of a DGT device in soils or sediments. The analyte diffuses across the diffusion layer and is accumulated by the resin gel. Analytes in the soil solution ($C_{SS}$) become progressively depleted. Desorption from the solid phase (with labile concentration $C_{ls}$) is induced. $C_i$ is the instantaneous concentration of the analyte at the interface between DGT and the soil, $k_1$ is the sorption rate constant and $k_{-1}$ is the desorption rate constant.

The extent of re-supply (the efficiency with which analyte concentrations are sustained in soil solution relative to their initial level) is determined by the labile pool size (capacity of the available compound on the solid phase) and the kinetics of adsorption/desorption.

\[
F(t) = \frac{D C_i(t)}{A g} \quad (1)
\]

\[
C_{DGT} = \frac{M A g}{D A t} \quad (2)
\]

\[
R = \frac{C_{DGT}}{C_{ss}} \quad (3)
\]

The time averaged interfacial concentration ($C_{DGT}$) is calculated from $M$ (the mass of analyte accumulated by DGT), which is determined analytically after extracting the analyte from the binding gel (Eq. 2). $A$ is the exposed area of the diffusion layer and $t$ is deployment time. An
indicator of the extent of depletion of soil solution concentrations at the DGT interface, $R$, is
the ratio of $C_{DGT}$ to the initial soil solution concentration ($C_{SS}$) (Eq. 3). Zhang et al.\textsuperscript{36} identified
the 3 possible modes of re-supply to the DGT devices (see Figure 1), which can be determined
by $R$ values as follows:
(a) Fully sustained case: analyte taken up from the solution phase is re-supplied from the solid
phase at a rate that sustains the initial $C_{SS}$ ($R \geq 0.95$)
(b) Partially sustained case: there is some resupply from the solid phase, but insufficient to
maintain the initial $C_{SS}$ (0.1 < $R < 0.95$)
(c) Diffusion only case: there is no resupply from the solid phase to the solution phase. Supply
of the analyte is solely accounted for by diffusion ($R < 0.1$)
Case (b) is most common in the real environment. The value of $R$ is affected by analyte pool
size and kinetics of the process.\textsuperscript{37}

**DIFS model**
The DIFS model\textsuperscript{38-40} was developed to quantify the above processes. It uses $K_{dl}$ (Eq. 4) and the
response time ($T_c$ - Eq. 5) to describe labile pool size and kinetics of adsorption (rate constant $k_1$) and desorption (rate constant $k_{-1}$). $K_{dl}$ is the distribution coefficient based on labile solid-phase components that can exchange with the solution phase and represents the labile pool size in the solid phase. $T_c$ is the response time to depletion and directly related to the rate constant of the supply process from solid phase to solution ($k_{-1}$). The model quantifies the relationship between $R$, $K_{dl}$ and $T_c$. $T_c$ and $k_{-1}$ can be obtained if $R$ and $K_{dl}$ are known. $P_c$ is the particle concentration of the soil or sediment ($P_c = m/V$, where $m$ is the total mass of all solid particles; $V$ is the pore-water volume in a given total volume of soil or sediment).

\[ K_{dl} = \frac{C_{ls}}{C_{ss}} = \frac{k_1}{P_c k_{-1}} \quad (4) \]

\[ T_c = \frac{1}{k_1 + k_{-1}} = \frac{1}{k_{-1}(1+K_{dl} P_c)} \quad (5) \]
10 The concentration of labile ATR ($C_{lb}$) was measured by ACN extraction as $C_{SE}$, so the value of $K_{dl}$ was represented with $K_d$, estimated by measuring the concentrations of ATR in soil solution or pore-water and extracted by ACN. $T_c$ was obtained from the model when $R$ and $K_d$ values were used as input parameters and the desorption rate constant $k_{-1}$ was calculated using Eq.5.

**RESULTS AND DISCUSSIONS**

**ATR distribution in soils**

The four soils varied in pH (4.8-7.7) and OM (3.9-8.1%) (Table S2). Soil Malpas (MAL) had the lowest pH (4.8) and OM (3.9%), Dares (DAR) was acidic (pH 5.7) with more OM (5.4%), Reddish (RED) had neutral pH (6.7) with low OM (4.8%) and Kettering (KET) had the highest pH (7.7) and OM (8.1%). ATR data quality was good, as shown by error bars on replicates (e.g. see Figure S1, Figures 2, 3).

Concentrations of ATR in soil solution ($C_{SS}$) and the solid phase obtained by solvent extraction ($C_{SE}$) are presented in Figure 2 and Table S4. The masses of ATR in solution and the solid phase were calculated using the concentrations from Table S4, soil solution volumes and the weight of solid phase. Results of ATR distribution between solution and solid phase are presented in Figure S1. The proportion of ATR in the solution phase for all soils showed no marked changes after the first 10 days, showing the added ATR had approached equilibrium with the soils in this time.

The results of soil solution show different orders between soils at the two different doses (Figure 2, a and b). In 5 mg kg$^{-1}$ dosed soils, the concentrations slightly decreased with time in the first 10 days, as expected.\textsuperscript{41} Soil MAL had the highest concentration. In 100 mg kg$^{-1}$ dosed soils, MAL and DAR had the lowest soil solution concentration. Previous research has shown that i) OM may reduce the release of ATR to soil solution as sorption is greater in soils enriched with OC\textsuperscript{2,4,8,41} and ii) high H$^+$ concentration (low pH) also enhances ATR sorption in soils.\textsuperscript{30,31} Interactions between ATR and OM and between ATR and H$^+$ play different roles in different
situations. Soil MAL with the highest H\(^+\) and lowest OM, displayed two opposite effects on ATR sorption. It is possible that the sorption process is mainly controlled by OM in low dosed soils and by pH in high dosed soils, due to ATR saturation on OM. Therefore, soil MAL (with lowest OM) had the highest soil solution concentration (lowest sorption) for 5 mg kg\(^{-1}\) dosed soils and soils MAL and DAR with low pH had the lowest soil solution concentrations (highest sorption) for 100 mg kg\(^{-1}\) dosed soils.

The ATR extractable from the solid phase declined slightly with time, but did not differ significantly between soils (Figure 2, c and d), except for soil MAL at the higher dosage. For both doses solvent extractable ATR constituted $>60\%$ of the ATR in all soils (Figure S1). There was a small proportion of non-extractable residues, the environmental and regulatory significance of which has been discussed elsewhere.\(^{42, 43}\)
Figure 2. ATR concentration measured by 3 approaches (a, b: soil solution; c, d: solvent extraction; e, f: DGT) over incubation time in 4 soils dosed at 2 levels (a, c, e: 5 mg kg\(^{-1}\); b, d, f: 100 mg kg\(^{-1}\))

DGT measured labile concentration

DGT gives the available concentration from both soil solution and weakly adsorbed on the solid phase. The \(C_{DGT}\) results showed decreases in low dosed soils and variations in high dosed soils for the first 10 days of the incubation (Figure 2, e and f), similar to the trend and the order of \(C_{ss}\). Soil MAL again displayed different behaviours for the two different doses, with the highest \(C_{DGT}\) of the 4 soils at the low dose and the lowest \(C_{DGT}\) at the high dose. The same explanation presented above for the soil solution results can be used here for the DGT results. \(C_{DGT}\) values were much less than the corresponding \(C_{SS}\), implying that the supply from the solid phase to the soil solution could not be fully sustained to the depletion of the pesticide by DGT (see below).

Resupply of ATR in soils

The \(R\) value reflects ATR resupply from the solid phase to soil solution, in response to the depletion by DGT. The \(R\) values varied between 0.09-0.18 for all the soils and doses, indicating ATR was partially resupplied in all cases (Figure 1). If there was no supply of ATR from the solid phase at all and only supply from diffusion, \(R\) would range from 0.06 to 0.07 (obtained from DIFS as \(R_{diff}\)). This suggests that ATR resupply from the solid phase in the 4 soils was significant and would play an important role in its bioavailability. The \(R\) values did not change
significantly with incubation time, indicating that ATR resupply was not affected markedly by aging up to 23 days. The differences of $R$ values between soils were more obvious at higher doses. Higher values were found for soils MAL and DAR which have low pH, so there is more ATR on the solid phase (see Figure 2d) and more resupply from the labile ATR pool (see Figure 3d) at the higher dose. The differences of $R$ values between soils were much smaller in lower dosed soils, averaging $0.12\pm0.01$ (RSD 8%). However, in contrast with the high dosed soils, soil MAL had the lowest $R$ value, due to the dominating influence of its low OM, with consequent low sorption of ATR and less resupply from MAL’s smallest labile pool size (Figure 3c).

**Figure 3.** $R$ values (Figures a and b) and labile pool size $K_d$ (Figures c and d) of ATR at two dosed levels (a,c: 5 mg kg$^{-1}$; b,d: 100 mg kg$^{-1}$) in 4 soils plotted with incubation time.

**Labile pool size of ATR ($K_d$) in different soils**

ATR in the labile solid phase pool will desorb during DGT deployment, to resupply the ATR depleted from the soil solution. The distribution coefficient ($K_d$) (the ratio of the concentration
of labile ATR in the solid phase extracted by ACN and the \( C_{\text{ls}} \) has been used to indicate the compound’s labile pool size in soils. Reported \( K_d \) values have ranged from 0.01-64 cm\(^3\) g\(^{-1}\), with most \(<10\).\(^{44-46}\) Values obtained in this study were between 1.3-4.0 cm\(^3\) g\(^{-1}\) (Figure 3c and 3d), within the published range.

\( K_d \) in the lower dosed soils increased slightly with incubation time for soils RED and DAR and remained constant for soils MAL and KET (See Figure 3c). In higher dosed soils, \( K_d \) varied slightly in the first 6 days of incubation and remained stable thereafter for all soils. This suggests that the ATR labile pool size was not affected significantly by the incubation time used in this study. \( K_d \) decreased with time in the 100 mg kg\(^{-1}\) treatment, while it increased slightly with time for the 5 mg kg\(^{-1}\) treatment. This is an interesting and important observation. Possible factors that may influence/cause this effect are dose-dependent differences in: i. strength of binding to the solid phase; ii. losses from the system over time, such as ATR degradation or formation of non-extractable residues. At the higher dose, the soils binding capacity may be approached or exceeded (see discussion below).

There were marked differences in labile pool size between soils for both doses. In the lower dosed treatments, \( K_d \) values in soils RED and DAR were higher than in soils KET and MAL. \( K_d \) in soil MAL was the lowest, indicating the smallest labile pool. Soil MAL is lowest in OM, which is a dominant sorbent for ATR.\(^{47}\) As a slightly basic herbicide, the adsorption of ATR would be weakened with increasing pH, explaining the lower \( K_d \) value in soil KET, despite its higher OM content. The labile pool size was not affected by the ATR dose for soil KET and DAR as the \( K_d \) values were similar for both doses. It was significantly reduced for soil RED and much increased for soil MAL in higher dosed soils. This demonstrates that the effect of the higher dose on the labile pool size was different between soils. The results suggest that the sorption sites might be saturated in soil RED and more ATR adsorption occurred on weaker binding sites in acidic soil MAL. McGlamery et al.\(^{48}\) reported that the degree of adsorption...
and desorption was independent of concentration in a clay loam and increasing application of ATR over ‘reasonable limits’ (0.37–40 mg kg$^{-1}$) appeared to not saturate the adsorption sites. This is true for soils KET and DAR, but not for the other two soils. The 100 mg kg$^{-1}$ dose used here may be beyond ‘reasonable limits’ and soil properties are also important.

**Resupply kinetic characteristics of ATR in different soils**

The labile pool size ($K_d$) determines the capacity of a chemical to be re-supplied by the solid phase. The response time ($T_c$) and desorption rate constant ($k_{-1}$) directly relate to the rate of its resupply to solution.$^{37}$ The kinetic information obtained from DIFS model calculations for ATR in the 4 soils is presented in Figure 4 and Table S5.

The incubation time had no significant influence on the kinetics of ATR resupply in these soils at both doses as $T_c$ was in the similar order of magnitude, as were the $k_{-1}$ values, except for some fluctuations in soil DAR (Figure 4). The $T_c$ values were $>10^3$ sec in soils RED and KET, indicating that ATR was supplied slowly from the solid phase to the solution phase in these soils. These two soils also had relatively low $K_d$ values (Figure 3), particularly for higher dosed soils. Kinetics of resupply is normally important when there is a large labile reservoir on the solid phase (high $K_d$).$^{13}$ In the case of small labile pool size, $T_c$ has little effect on the uptake of analyte by DGT, since the pool will be depleted rapidly.$^{49}$ Hence soils RED and KET had little capability to resupply ATR to the solution phase. Both soil RED and KET had much higher pH (2-3 units higher) than MAL and DAR; pH is probably the major factor controlling the labile pool size and resupply kinetics of ATR in soils (see below).

$T_c$ values in soils DAR and MAL were lower (by several orders of magnitude) than the other soils with exception for MAL at high doses, indicating shorter response time and faster resupply kinetics for ATR in lower pH and lower OM soils.

There were several extreme values (outliers) of $T_c$ or $k_{-1}$ obtained by the model at different incubation times, despite the minor differences between other parameters. Lehto et al.$^{50}$ used
an error function ($E$) for the quantitative assessment of $K_{dl}$ and $T_c$ using 2D DIFS model. It was suggested that the estimation of $T_c$ could sometimes have large uncertainty. Therefore, we do not intend to over-interpret these extreme values. Instead, we use $T_c$ and $k_{-1}$ information cautiously, as relative values to make comparison between different soils and incubation times and to assess their kinetic resupply of ATR relatively.

Figure 4. log$T_c$ and log$k_{-1}$ values of ATR at different incubation time up to 23 days for two dosed levels (5 mg kg$^{-1}$ and 100 mg kg$^{-1}$) in four different soils. (a) log$T_c$ vs time in 5 mg kg$^{-1}$ dosed soils; (b) log $k_{-1}$ vs time in 5 mg kg$^{-1}$ dosed soils; (c) log$T_c$ vs time in 100 mg kg$^{-1}$ dosed soils; (d) log $k_{-1}$ vs time in 100 mg kg$^{-1}$ dosed soils.

The DIFS model can simulate profiles of ATR concentrations in soil solution and solid phase through the soil layer and diffusion layer, with respect to distance. The profiles were modelled at incubation times of 1 and 23 days with DGT deployment for 5, 11, 16 and 22 h. The results are shown in Figures S2 and S3 (lower and higher dosed soils, respectively). ATR concentrations in soil solution and solid phase were normalized to their maximum concentrations. At the lower dose, soils MAL and DAR showed less depletion into soil solution.
and significant depletion from the solid phase with DGT deployment time. The opposite trends were demonstrated for soils RED and KET, where more ATR was depleted from soil solution and much less from the solid phase. There was no significant difference between profiles at 1 and 23 days incubation. Similar profiles with similar characteristics for each soil and case were obtained for higher dose soils (Figure S3), indicating total concentration did not affect the relative distribution of ATR in soils in response to a sink (e.g. DGT samplers or plant roots).

Soils RED and KET have higher pH than soils MAL and DAR. The results suggest that soil pH is the controlling factor for depletion and resupply of ATR and its distribution in soil solution and solid phase.

**Comment on mechanism of pH and OM effects**

Within the limits of this study with just 4 soils, the influence of pH can be interpreted mechanistically. ATR is a weakly basic herbicide with a pKa of 1.68. In near neutral pH environments (e.g. soil RED), ATR stays in its neutral form, with adsorption mainly via van der Waals forces or hydrogen bonding. Under acid conditions (soils MAL and DAR), ATR will be protonated to the cationic form and its affinity to negatively charged soil colloids becomes stronger. Ion exchange then dominates the binding process. Maximum adsorption of ATR on soils normally occurs at pH close to its pKa, when cationic and neutral ATR forms both exist. At higher pH values (soil KET) the cationic fraction of ATR declines and the protonation effect weakens. Higher soil pH will also enhance hydrolysis of carbonyl, hydroxyl and other functional groups on the soil surface and promote dissolution of SOM, leading to less adsorption of ATR. Note that the differences in the order of $C_{ss}$, $C_{DGT}$ and $R$ values between soils can therefore be understood in terms of the differences in labile pool size and re-supply kinetic characteristics, which are themselves controlled simultaneously, but not equally, by pH and OM.
ATR availability and resupply in sediments

As we have demonstrated above, the combination of the DGT technique and DIFS modelling can provide useful information about interactions between solution and solid phases, kinetics and lability of ATR resupply in soils. Application of DGT and DIFS in sediment is therefore a potentially very valuable approach to obtain in situ information and advance understanding of biogeochemical processes of pesticides and other trace organics.

DGT sediment probes were deployed in the top 10 cm of the sediment core, as it is normally the most reactive part of the sediment.\(^5\) The results of DGT measured concentrations, \(C_{\text{DGT}}\), together with porewater concentrations, \(C_{\text{PW}}\), and the extracted solid phase concentrations, \(C_{\text{SE}}\), at different depth are shown in Figure 5 (a-c). A sharp peak appeared at -2 cm for all three profiles. For DGT, the labile concentration of ATR initially decreased with depth until -1.5 cm, then increased to its maximum (0.23 \(\mu\)g L\(^{-1}\)) at -2.0 cm. It subsequently decreased to its minimum (-0.05-0.06 \(\mu\)g L\(^{-1}\)) and stayed relatively constant below. The \(C_{\text{PW}}\) and \(C_{\text{SE}}\) profiles were very similar, with lower concentrations at -1.0 cm and increasing to a maximum at -2.0 cm. The concentrations in both phases then declined to their minimum values at -3.0 cm depth.

There was a slight increase for \(C_{\text{PW}}\) at -6.0 cm. For labile solid phase ATR, the profile was relatively uniform below -3.0 cm. These concentration profiles are likely determined by redox conditions. Labile Fe (II) and Mn (II) concentrations were measured in situ at 5 mm resolution in the same sediment core using DGT trace metal probes. Labile Fe and Mn concentrations increased sharply from the sediment surface until -4.0 cm, with the sharpest at -2.0 cm (Figure S4). The results indicate that i) Fe and Mn oxides/hydroxides become reduced to labile Fe(II) and Mn(II) with depth; ii) the anoxic/reduction condition intensified at -2.0 cm and -4.0 cm depths. Reduction of Fe/Mn oxides greatly influences the sorption/desorption and remobilisation of other elements and chemicals. Therefore, the profiles of ATR observed above could be the result of redox conditions and the reduction of Fe/Mn oxides/hydroxides.
To assess ATR labile pool size and kinetic resupply, the $R$ value (ratio of $C_{\text{DGT}}$ and $C_{\text{PW}}$) was calculated. DGT concentrations measured at 0.5 cm resolution were averaged to 1 cm intervals for the calculations. The $R$ value depth profile is presented in Figure 5d. The $R$ value was 0.47 at -1.0 cm, then decreased to 0.19 at -2.0 cm. There was slight variation in $R$ values below -2.0 cm, but these were not significant for interpretation. The profile for labile pool size $K_d$ (obtained by $C_{\text{SE}}/C_{\text{PW}}$), was similar to the $R$ value trend, with the largest $K_d$ (8.21) at -1.0 cm depth, decreasing to <5 at -2.0 cm depth and below (Figure 5e). These results indicate ATR resupply from the solid phase to pore-water and the labile pool size were greater at the top layer of the sediment and significantly less below -2.0 cm, due to redox conditions. The DIFS model was used to obtain the response time, $T_c$, and the desorption rate constant, $k_1$ at different depths. The $k_1$ results are shown in Figure 5f and $T_c$ in Table S6. The highest rate constant was at -4.0 cm, demonstrating fastest resupply at this depth. All the results discussed above reflect that the surficial layer of sediment had a greater capability to resupply ATR, while there was less available ATR present in the sediment below -2.0 cm. All features that occurred at -2.0 cm and -4.0 cm depth for ATR concentrations, labile pool size, resupply capability and kinetics of resupply are closely linked to the redox conditions and the reduction of Fe/Mn oxides/hydroxides. This precise information can only be obtained with an in situ high spatial resolution technique, such as DGT.
**Figure 5.** ATR distribution profiles in the sediment measured by three methods (a: DGT; b: porewater extraction; c: solid phase extraction), $R$ (d), $K_d$ (e), and $\log k^{-1}$ (f) value distribution with depth.

**Environmental implications and future research directions**

This Special Issue highlights the key roles of soils and sediments as sources/sinks in the regional and global scale cycling of organic contaminants. However, detailed understanding of the kinetics of solid-solution exchange and fine scale distributions of organic chemicals that control fluxes to/from soils and sediments are still very limited. This is at least partially because we have lacked the appropriate tools and techniques to perform the necessary measurements, until now.55

There is already a large body of research and development on the use of DGT to investigate the speciation, bioavailability, dynamic solid-solution interactions and fine scale distribution of heavy metals and nutrients in soils and sediments.12,16-18,20,23,24,36,37,56-59 This paper has taken...
a first step to apply DGT and the DIFS model as tools to investigate the labile pool size and kinetic resupply of organic chemicals in soils and sediments. Although ATR was selected for this study, DGT devices have already been developed and validated to quantitatively measure ~170 different organic chemicals, including antibiotics, pesticides, personal care products, pharmaceuticals, oestrogens, flame retardants and perfluorinated compounds. So far, they have been used to monitor surface and wastewaters, but not for biogeochemical process studies in soils and sediments. There is therefore a wide range of potential future DGT applications in the fields of environmental organic biogeochemistry and ecotoxicology.

DGT can be used in controlled experiments, to investigate how environmental factors and aging influence solution-solid phase exchange. This type of systematic work has been crucial for improving our knowledge of biogeochemical processes of inorganics. Many of the same issues warrant similar attention for organic chemicals, to better understand mobility/retention in soils, their bioavailability and link to microbial processes and their influence on persistence. Knowledge of the kinetic re-supply and the labile pool size is of key importance to bioremediation of trace organics, for example, and help improve risk assessment. This approach can be useful in the fields of agrochemicals (pesticides in soils), waste management (e.g. biosolids addition to soils) and bioremediation.

This paper is the first to use the DGT sediment probe to investigate an organic chemical in situ in sediments. The probe makes it possible to obtain finely spatially resolved (mm scale) information in intact sediment cores. We achieved detection with a resolution of 5mm and for ng L⁻¹ concentrations in a lake system. Finer spatial scales can be achieved in future, to improve understanding of processes in water-sediment surface micro-layers and the role of oxic/anoxic conditions in controlling retention in sediments or resupply to the water column. DGT has been deployed to study trace elements in 2-dimensions at the sub-mm scale. This is achievable for...
organics, subject to suitable detection systems and limits, with the potential to make a step-change in fundamental understanding of trace organics biogeochemistry.

SUPPORTING INFORMATION

Supporting information is available free of charge via https://pubs.acs.org/.

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40. For DIFS software access, contact www.dgtresearch.com (see FAQs section).


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