

1 **Overlooked Highly-Volatile Persistent Organic**
2 **Pollutants in the Atmosphere**

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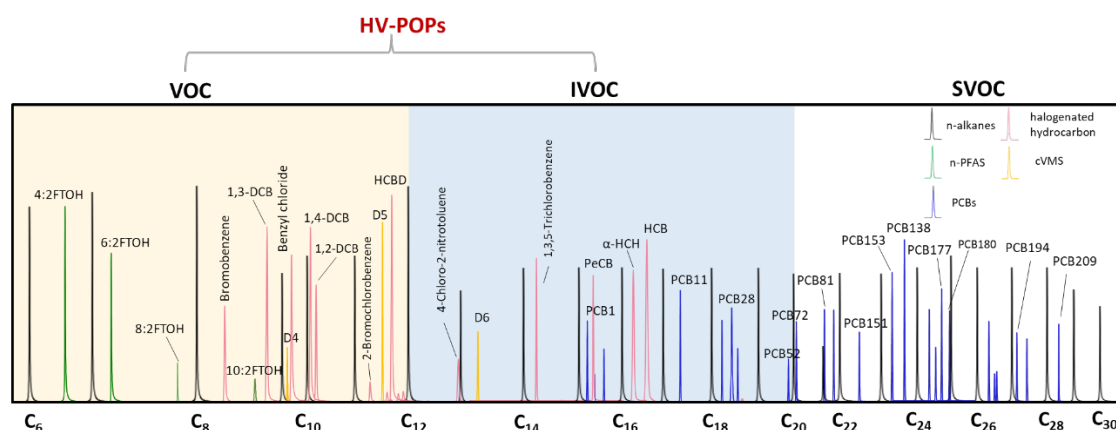
18 The atmosphere plays an important role in the cycling of persistent organic pollutants
19 (POPs) in the Earth surface system. It is also an ideal monitoring matrix as it provides
20 essential information on the distribution, sources, and transmission of POPs, to
21 support the risk assessments and the effectiveness evaluation of POPs management
22 policies. While many POPs in the atmosphere are considered 'semi-volatile', implying
23 dynamic partitioning between the gas and particle phases, and having the tendency
24 for temperature-driven air-surface exchanges, some emerging organic pollutants or
25 POPs that are newly listed in the Stockholm Convention occur in the atmosphere are
26 either highly volatile (cf. VOCs) or are with low or extremely low volatility. Currently,
27 highly volatile POPs (HV-POPs), which predominantly occur in the gas phase, are not
28 well-studied in POPs research.

29 In atmospheric chemistry, volatile components are classified on a continuum from
30 Extremely low-volatility organic compounds (ELVOCs), low-volatility organic
31 compounds (LVOCs) to semi-volatile organic compounds (SVOCs), intermediate-
32 volatility organic compounds (IVOCs), and volatile organic compounds (VOCs).¹ For
33 POPs, their volatilities actually covers a wide range from ELVOCs to VOCs, currently
34 without finer operational boundaries being adopted by the scientific community. This
35 vague boundary impedes a thorough comprehension of the atmospheric fate of POPs,
36 and their associated health risks. It also results in a disconnect between POPs and
37 secondary organic aerosols (SOA), to which the hydrophilic oxidized products of POPs
38 could contribute. Therefore, we propose to incorporate HV-POPs into the realm of
39 atmospheric chemistry, with a specific subdivision to delineate their volatility.

40 In **Figure 1**, a chromatogram map shows chromatographic peaks of several POPs
41 overlaid with homologues of normal alkanes, based on real laboratory data. For
42 instance, the effective saturation concentration (C^*) within the IVOCs range is defined
43 as $300 < C^* < 3 \times 10^6 \mu\text{g}/\text{m}^3$, with a saturation vapour pressure at 298 K ranging from 0.01-
44 10 Pa, corresponding to the saturation vapour pressures of C_{12} - C_{20} *n*-alkanes. The POPs
45 that fall within the volatility range from IVOCs to VOCs are defined as HV-POPs. This
46 includes hexachlorobutadiene (HCBD), pentachlorobenzene (PeCB), and
47 hexachlorobenzene (HCB), along with emerging contaminants such as volatile
48 methylsiloxanes (VMS) and fluorotelomer alcohols (FTOHs). In addition to the
49 identified compounds in **Figure 1**, ultrashort-chain PFAS, such as trifluoroacetic acid
50 (TFA) and its ester derivatives, and very short-chain chlorinated paraffins (vSCCPs, C6-
51 C9), could also be HV-POPs. It is noteworthy that many 'traditional' legacy POPs, such

52 as α -hexachlorocyclohexane (α -HCH) and 'light' congeners of polychlorinated
 53 biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated
 54 naphthalenes (PCNs) are also found in the HV-POPs band. Compared to legacy POPs,
 55 research on HV-POPs in the atmosphere is currently scarce and dispersed.

56 HV-POPs can be sampled from air using active and passive methodologies. The active
 57 air samplers include the low- or high-volume samplers with filters and cartridges, and
 58 the denuder samplers. The former is easy to deploy, while the denuder sampler is
 59 more efficient at trapping the gas phase of HV-POPs, reducing sampling artifacts. The
 60 passive air sampler (PAS) is easy to prepare and deploy, requiring no electricity, making
 61 it preferable for remote regions and surveys at multiple sites. The strong absorbents
 62 such as XAD, Tenax resins and activated carbon are usually employed to capture VOCs.
 63 The PAS using XAD sorbent impregnated polyurethane foam (PUF) sampler (SIP-PAS)
 64 has been adapted for sampling HV-POPs. However, it is reported that there is
 65 breakthrough of HCBd from PUF plugs, which are widely used to capture SVOC-POPs,
 66 leading to an underestimation of HCBd in Arctic air.² Specific quality control and quality
 67 assurance (QA/QC) practices are needed for target HV-POPs throughout the laboratory
 68 procedures to ensure reliable recoveries. Air sampling of HV-POPs is easily normalized
 69 with established standard operating protocols, making monitoring data from various
 70 laboratories more comparable.



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72 Figure 1. The chromatogram map overlaid by typical persistent organic pollutants
 73 (POPs) and C₆-C₃₀ *n*-alkanes using a DB-5MS GC column (60 m × 0.25 mm × 0.25 μm).

74 Several HV-POPs have served as vital raw materials and solvents for the chemical
 75 industry, with widespread applications, large production and significant disposed
 76 waste volumes. We give examples in China. First, chlorobenzenes (CBs) are used
 77 extensively in pesticide and dye manufacturing, and in the electronics industry as raw

78 materials and additives. More than half of the global production and consumption of
79 CBs is in China. Second, HCBD is used as a chemical solvent, heat transfer agent and
80 hydraulic system liquid, and can be unintentionally emitted from chlorinated solvent
81 production (e.g. chloromethane and perchloroethylene). Nearly a thousand tonnes of
82 HCBD emissions were estimated for 2016 in China. Third, methylsiloxanes, essential in
83 organic synthesis, are predominantly manufactured in China, with a global annual
84 production of 8-10 million tonnes.³

85 Because of their high volatility and large production and consumption volumes, HV-
86 POPs can occur in the atmosphere at high levels relative to other POPs, and are likely
87 to transport to remote places such as the Arctic. Our recent analysis of HV-POPs in
88 urban air samples from Guangzhou, China, revealed concentrations of CBs, HCBD,
89 FTOHs, and VMS in the ng- $\mu\text{g}/\text{m}^3$ range. This is similar to, or higher than the polycyclic
90 aromatic hydrocarbons (PAHs), a well-known group of air toxics. HCBD concentrations
91 in areas surrounding perchloroethylene production could range from μg to mg/m^3 ,
92 exceeding its occupational exposure limit of $210 \mu\text{g}/\text{m}^3$.⁴ Abundant evidence shows
93 that HCBD, HCB and α -HCH are widespread in the Arctic.

94 Their high volatility enables HV-POPs to reside in the atmosphere for a long time,
95 favoring their reactions with free radicals. This can lead to their mineralization and
96 transformation into hydrophilic oxidized products, which can be removed by
97 atmospheric deposition. For example, there is potential for HCB to be transformed to
98 more water-soluble pentachlorophenol (PCP); and for FTOH to PFOA. For VMSs at
99 higher concentrations in indoor air, the continuously produced silanol products may
100 participate in the formation of SOA. Modellers may treat HV-POPs as 'long-life' gases,
101 disregarding their multimedia exchanges. Observation-based inverse models can be
102 applied to estimate their primary emissions, thereby supporting chemicals
103 management and policy making.

104 Inhalation may be the key pathway for HV-POPs to enter wildlife and human food
105 chains. Most HV-POPs exhibit low K_{OW} ($<10^5$) and high K_{OA} ($>10^6$), making them prone
106 to bioaccumulate in respiring animals, including humans.⁵ HCBD can form toxic
107 metabolites in the human body, and the U.S. Environmental Protection Agency
108 classifies it as a potential human carcinogen (Group C). PeCB, HCB, perfluorochemicals,
109 and their precursors are widely detected in human breast milk and serum, and capable
110 of accumulating in the human placenta.

111 Future research may benefit from integrating the HV-POPs concept into the regulatory

112 frameworks of the Stockholm Convention. Robust global collaboration is essential for
113 standardized monitoring, observation-based inverse modeling, mitigation strategies in
114 the technosphere, as well as direct and indirect atmospheric transport studies at
115 regional and global scales.

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