



Target and suspect screening analysis reveals persistent emerging organic contaminants in soils and sediments

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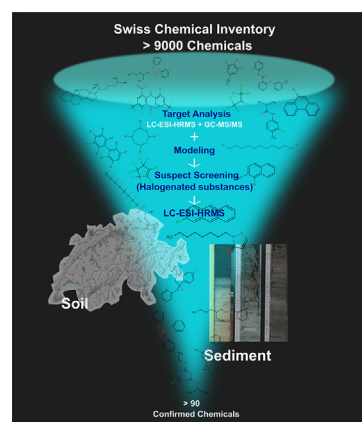
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HIGHLIGHTS

- > 500 halogenated compounds were screened in soils and sediments
- The applied approach resulted in the confirmation of 96 compounds
- Soils and sediments are long-term reservoirs of persistent contaminants
- Agriculture and wastewater impacted sites were the most contaminated sites
- Azoles and triazines are the most common groups detected

GRAPHICAL ABSTRACT



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ABSTRACT

An approach to identifying persistent organic contaminants in the environment was developed and executed for Switzerland as an example of an industrialized country. First, samples were screened with an in-house list using liquid chromatography high-resolution mass spectrometry (LC-HRMS/MS) and gas chromatography tandem mass spectrometry (GC-MS/MS) in 13 samples from the Swiss National Soil Monitoring Network and three sediment cores of an urban and agricultural contaminated lake. To capture a broader range of organic contaminants, the analysis was extended with a suspect screening analysis by LC-HRMS/MS of >500 halogenated compounds obtained from a Swiss database that includes industrial and household chemicals identified, by means of fugacity modeling, as persistent substances in the selected matrices. In total, the confirmation of 96 compounds with an overlap of 34 in soil and sediment was achieved. The identified compounds consist generally of esters, tertiary amines, trifluoromethyls, organophosphates, azoles and aromatic azines, with azoles and triazines being the most common groups. Newly identified compounds include transformation products, pharmaceuticals such as the flukicide niclofolan, the antimicrobial cloflucarban, and the fungicide mandipropamid. The results indicate that agricultural and urban soils as well as sediments impacted by agriculture and wastewater treatment plants (WWTPs) are the most contaminated sites. The plausibility of this outcome confirms the combination of chemical

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inventory, modeling of partitioning and persistence, and HRMS-based screening as a successful approach to shed light on less frequently or not yet investigated environmental contaminants and emphasizes the need for more soil and sediment monitoring in the future.

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1. Introduction

The increasing amount and number of synthetic chemicals in use over the last decades has led to a corresponding increase in the numbers and amounts of contaminants reaching the environment. National and international environmental programs since the 1970s have performed a continuous monitoring of persistent organic pollutants (POPs) and further chemicals with persistent, bioaccumulative and toxic characteristics (PBT) are continuously added to the list (Muir and Howard, 2006). While these monitoring programmes are highly important, many chemical substances in wide commercial use are still not measured in environmental samples, and their environmental fate is still unknown (Muir and Howard, 2006). Until now most of the studies on emerging contaminants have been performed on surface water samples (Moschet et al., 2014; Ruff et al., 2015) often linked to the EU's water framework directive or other national directives while soils and sediments, which are long-term reservoirs of PBT substances, have rarely been included in monitoring campaigns due to their complexity but also to the lower regulatory requirements (Borja et al., 2004).

The number and distribution of contaminants in natural systems can vary due to different natural transport processes and reaction mechanisms according to their physicochemical properties and chemical partitioning to water, air, soil and sediment. Therefore, if a compound persists over time, it can potentially be transported on suspended solids to locations far away from the source and/or bioaccumulate. For example, it has been shown that POPs can be deposited in marine and freshwater ecosystems due to their low water solubility and strongly bond to particulate matter and, because of their persistence and volatility, can be found in remote areas, far away from their initial emission sources (Hung et al., 2010). Moreover, banned pollutants can still be found in aquatic ecosystems at high frequency and levels due to the slow continuous release from soils (Hvězdová et al., 2018). Thus, persistent contaminants may form environmental reservoirs for long periods of time and reintroduced into the ecosystem and food chain, becoming potentially a source of local and even global contamination (Jones and de Voogt, 1999). The presence of organic contaminants in soils and sediment with highly hydrophobic characteristics (e.g., legacy compounds) as well as polar contaminants (e.g., pharmaceuticals, household chemicals, pesticides) has been demonstrated in different studies (Chiaia-Hernández et al., 2017a; Chiaia-Hernandez et al., 2013; Lara-Martín et al., 2015; Peck et al., 2006). The use of soils and sediment matrices to study chemical contamination throughout time is a significant advantage compared to water samples, where usually no historical samples are available and contaminants have not been recorded and studied in the past.

The analysis of organic pollutants in natural archives is challenging due to their occurrence in low concentrations, typically in the pg/g to the µg/g range, interference with natural organic matter (NOM), and the spatial variability observed from place to place. Recently, analytical instrumentation such as high-resolution mass spectrometry (HRMS) has been developed to screen for a wider range of organic contaminants at trace levels using wide-scope target, suspect, and non-target screening approaches (Hollender et al., 2017). So far, suspect screening has been the more established and successful approach to detect emerging compounds, mainly due to the different suspect lists available nowadays (e.g. NORMAN SusDat). However, "smart" suspect screening of a selected compound list with an appropriate analytical method is

becoming a key for compound identification since the identity confirmation is very time consuming and sometimes only a small fraction of compounds screened can be identified. Thus, the way forward is to integrate additional information such as physico-chemical properties and persistence specific for each matrix or location beyond consumption data or mass libraries. Some of these challenges have been addressed by Muir and Howard, who called for a novel strategy to find substances of relevance using a data compilation of compounds on the market and estimation of physico-chemical properties (Howard and Muir, 2010). Their approach resulted in long lists of chemicals of potential concern which are persistent and bioaccumulative, including hundreds of chemicals never measured in environmental samples (Howard and Muir, 2010; Muir and Howard, 2006).

More recently, Singer et al., 2016 combined a model-based prioritization using consumption data, fate properties and a generic mass balance to detect active pharmaceutical ingredients. The combined approach resulted in the detection of 27 new compounds not covered in previous monitoring campaigns. Furthermore, Gago-Ferrero et al., 2018 prioritized 160 potential organic contaminants from ~23,000 chemicals from the National Swedish Product Register by using information on market availability, usage and exposure index. The prioritization led to the identification of >30 substances not previously reported. Although insightful prioritization helps to reduce the number of suspect candidates and can lead to a higher compound identification rate, additional challenges such as analytical instrumentation, extraction techniques, selection of adequate matrices and site location to detect relevant organic contaminants are still critical.

The objectives of this work were i) to investigate the presence of known and emerging persistent contaminants in 13 representative soils from the Swiss National Soil Monitoring Network (NABO) and in sediment cores from an urban and agricultural lake (Greifensee, Switzerland) based on wide-scope target analysis, ii) to further identify persistent compounds based on suspect screening analysis by liquid chromatography (LC) – HRMS/MS using a suspects list of halogenated chemicals that are likely to persist in the environment and reside predominantly in these two matrices, and iii) to highlight the utility and the need of inclusion of these two matrices in future monitoring campaigns. The present study, to the best of our knowledge, is one of the first extensive screening studies in soil and sediment samples reporting a wide range of organic contaminants barely or never reported before.

2. Experimental section

2.1. Sampling collection and preservation

2.1.1. Soil

Soils were selected based on land use, geography, known exposure and spatial distribution pattern of pollutants, and were complemented by a few semi-urban controls and one remote site. Currently known exposure patterns based on existing data on persistent organic pollutants such as PCBs were used as indicators for diffuse input of contaminants, influence of land use and geography to account for elevated pollutant emissions (Schmid et al., 2005). In total, 13 locations were selected as illustrated in Fig. S1 and Table S1. The soils were provided by the NABO, which operates about 100 long-term monitoring sites throughout Switzerland and maintains a comprehensive archive of soil samples (Gubler et al., 2015). The samples were taken between 2005 and

2009, with the exception of an additional sample from site H that dated back to 1994 and received domestic waste (H-2). Sampling took place in a standardized way on an area of 100 m² as described by Hämman and Desaulles, 2003. The investigated soil samples are composite samples (0–20 cm soil layer; 25 subsamples taken by a gouge auger of 2.5 cm diameter) representing an area of 10 m by 10 m. Information about the NABO monitoring network and detailed information on sample preparation is provided by Desaulles and Dahinden, 2000 and Meuli et al., 2014.

2.1.2. Sediments

Sediment cores were collected on November 2014 from three different locations around Greifensee. Sampling point 1 (P1, 8.678105078° N, 47.351545874° E) was located at the deepest part of the lake (depth of 32 m) to minimize direct influences of waste water treatment plant (WWTPs) effluents and agriculture, as well as used as a reference point since it has been studied extensively (Chiaia-Hernández et al., 2017a; Chiaia-Hernandez et al., 2013; Chiaia-Hernandez et al., 2014). Sampling points 2 and 3 were located near the outlet of the Uster WWTP (P2, 8.687325778° N, 47.352453944° E) and Mönchaltorfer WWTP at Aaspitz (P3, 8.697792119° N, 47.328196292° E) to cover the impact of WWTP effluents and agricultural inputs to the catchment. Twelve layers were analyzed from core P1 (1870–2014) and P3 (1981–2014) and 13 samples from core P2 (1958–2014) for validation of the findings and to identify possible false positives since time series analysis can help to identify artifacts to confirm or reject a compound (Chiaia-Hernández et al., 2017a). Details on the collection, dating and geochemical analysis are provided in the SI.

2.2. Chemical analyses

Soils and sediment samples were freeze-dried and extracted by pressurized liquid extraction (PLE) using an in-cell cleanup technique employing either Florisil or neutral alumina as a sorbing phase as reported in the SI and elsewhere (Chiaia-Hernández et al., 2017a; Pintado-Herrera et al., 2016). Detection of analytes was mainly performed on an LC system connected to a QExactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer (Thermo Fisher Scientific, San Jose, U.S.A.) equipped with an electrospray ionization (ESI) source, as described in previous publications (Chiaia-Hernandez et al., 2014; Chiaia-Hernández et al., 2017a). Gas chromatography (SCION 456-GC, Bruker) and mass spectrometry (SCION TQ, Bruker Co.) were operated in multiple reaction monitoring (MRM) mode using an electron ionization (EI) source to analyze 21 additional compounds as reported in SI, Appendix B and elsewhere (Pintado-Herrera et al., 2016).

The target analysis performed in this work consist in a list of substances relevant to surface water from former studies as well as some well-known POPs relevant to soil and sediment (*Eawag database* or *Eawag-DB*). The *Eawag-DB* list encompassed registered pesticides, pharmaceuticals and some organophosphorus flame-retardants, musk fragrances and UV stabilizers as reported elsewhere (Chiaia-Hernandez et al., 2014; Moschet et al., 2013; Pintado-Herrera et al., 2016). Target analysis in this work was used as a complementary tool to the fugacity model to show the coverage of the analytical method (e.g., identification of suspect contaminants that share similar physico-chemical properties) and to validate the developed approach.

Target analysis and further screening of additional compounds by LC-HRMS was performed with the aid of the TraceFinder 3.3 software (Thermo Fisher Scientific Corp., USA) by extracting the exact mass of the expected ion from the HR full scan chromatogram with a mass window of ±5 ppm and matching automatically their isotopic pattern. In addition, >50 internal standards were used for the quantification of selected compounds as well as a quality control in the target and suspect screening. Blank subtraction was performed automatically with uncontaminated soils from remote sites collected in 2008 and sediment layers

from ~100 years ago since contamination was not likely to be present in these samples. The output list of suspect candidates was manually evaluated for correct peak shape, plausibility of ionization in the positive and negative mode (based on different functional groups), retention time (RT) matching factor and fragmentation as described elsewhere (Chiaia-Hernandez et al., 2014). Compound identification was assigned according to Schymanski et al., 2014 where level 1 corresponds to a structure confirmed by a reference standard, level 2 corresponds to a structure candidate using library spectrum match or diagnostic evidence, level 3 is assigned to tentative candidates where multiple structures are possible (e.g. different isomers of a substance class) and level 4 and 5 correspond to unequivocal molecular formula and just an exact mass of interest, respectively. Details of the screening steps and analysis for target analysis and compound identification are provided in the SI.

Data analysis by GC-MS/MS was processed using the Bruker MS Workstation 8 software.

2.3. Chemical databases

Suspect screening of additional compounds was based on a chemical inventory to identify compounds outside of the scope of our target analysis (*Eawag-DB*). This additional database was created based on information extracted from several lists of chemicals like primarily customs statistics and product registers of the Swiss authorities (RPC, ChemPIC, MAO). For the substances included in these lists, CAS numbers were collected directly, when available, or from publicly available databases (e.g. <https://pubchem.ncbi.nlm.nih.gov/>, www.echemportal.org, www.chemicalize.org, www.chemspider.com). In cases where a substance had several CAS numbers, all available CAS numbers were compiled and later on eliminated through different filter steps as described in detail under results and discussion. Evaluation of the chemical inventory led to a list of 18,349 individual CAS numbers. Due to the extensive list of compounds, the collected database list was compared with an earlier database developed by Stempel et al., 2012 which includes 91,699 industrial chemicals on the market worldwide to identify chemicals also used abroad. Comparison of both databases showed an overlap of 50% (9187) with 13% (2371) of these CAS numbers being halogenated. For the subsequent steps, we focused on the 50% (9187) of the substances that were included in the list by Stempel et al., 2012 because for these substances, SMILES codes are available. The compilation or generation of SMILES codes for several additional thousands of chemicals just from their CAS numbers is a challenging, non-trivial task that was beyond the scope of this work. Physicochemical properties and degradation half-life estimates for the chemical structures, when possible, were calculated via quantitative structure-activity relationships (QSARs) from EPI Suite (EPA, 2016) and according to approaches described by Stempel et al., 2012.

The filter approach used to identify substances likely to be persistent in the environment and distribute predominantly in soils and sediments was implemented by calculating the distribution of the selected substances in air, water, soil and sediment by using a multimedia fugacity model (Mackay levels I and III (Mackay, 2001)) set up for Switzerland as described in the SI and by Glüge et al., 2016. Importantly, the environmental fate models were used here as filters that identify substances with certain physicochemical properties, but not to simulate a realistic situation of substance use and emissions. Briefly, the level-I model used consists of the compartments soil, water and air as a closed system with exchange between compartments at equilibrium and steady-state. This model was used to identify chemicals that reside predominantly (i.e., >90%) in the soil, which is, in a level-I model, solely driven by their partition coefficients. The level-III model includes the compartments sediment, soil, water and air in an open system with exchange between compartments and not at equilibrium but at steady-state. The level-III model was used to identify chemicals that reside predominantly in soil after emission to air and in sediment after emission to

Table 1

List of 34 confirmed organic compounds by LC-HRMS/MS or GC-MS/MS found in soils and sediments in alphabetical order. The samples were taken between 2005 and 2009 with the exception of site H (2) which dated back to 1994 and received domestic waste. More details about the site can be found in Fig. S1, S2 and Table S1-S3. Sampling point 1 (P1) was collected from the deepest part of the lake. Sampling points P2 and P3 were collected near the outlet of the Uster WWTP and Mönchaltorfer WWTP at Aaspitz (to cover the impact of WWTP effluents and agricultural inputs to the catchment. Structures and additional information can be found in SI and Appendix B.

No.	Compound Name	CAS No.	Application	Formula	Analysis	log K _{ow}	pKa	Location Soils	Location Sediments
1	1-[(2R,3R)-2,3,8,8-Tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl]ethanone (OTNE)	54464-57-2	Personal care product	C ₁₆ H ₂₆ O	GC-MS/MS	4.20	---	A, B, H(1)	P1, P2, P3
2	2-Octyl-2H-isothiazol-3-one (OIT)	26530-20-1	Pesticide	C ₁₁ H ₁₉ NOS	LC-HRMS	3.33	---	C	P3
3	Atrazine	1912-24-9	Pesticide	C ₈ H ₁₄ ClN ₅	LC-HRMS	2.20	4.20/14.48	H (1), B, C, A	P2, P3
4	Bromochlorophene	15435-29-7	Antimicrobial	C ₁₃ H ₈ Br ₂ Cl ₂ O ₂	LC-HRMS	6.20	5.86	M	P1, P2
5	Cyproconazole	94361-06-5	Pesticide	C ₁₅ H ₁₈ ClN ₃ O	LC-HRMS	2.90	2.0/13.32	B	P3
6	Cyprodinil	121552-61-2	Pesticide	C ₁₄ H ₁₅ N ₃	LC-HRMS	3.21	3.10/13.63	B, C, H (1)	P3
7	Dichlorodiphenyldichloroethane (p,p'-DDD)	72-54-8	Pesticide	C ₁₄ H ₁₀ Cl ₄	GC-MS/MS	6.11	---	B	P1, P2, P3
8	Dichlorodiphenyldichloroethylene (p,p'-DDE)	72-55-9	Pesticide	C ₁₄ H ₈ Cl ₄	GC-MS/MS	6.11	---	A, B, D, J	P1, P2, P3
9	Difenoconazole	119446-68-3	Pesticide	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃	LC-HRMS	4.86	1.95	B	P3, P2
10	Diflufenican	83164-33-4	pesticide	C ₁₉ H ₁₁ F ₉ N ₂ O ₂	LC-HRMS	5.11	1.60/13.28	B	P3, P2
11	Dinoseb	88-85-7	Pesticide	C ₁₀ H ₁₂ N ₂ O ₅	LC-HRMS	3.24	5.08	H (1), A, B, K, M, J, I	P3
12	Diuron	330-54-1	Pesticide	C ₉ H ₁₀ Cl ₂ N ₂ O	LC-HRMS	2.53	13.18	B	P2, P3
13	Diuron-desmethyl	3567-62-2	pesticide	C ₈ H ₈ Cl ₂ N ₂ O	LC-HRMS	2.31	13.31	B	P4
14	Epoxyconazole	133855-98-8	Pesticide	C ₁₇ H ₁₃ ClFN ₃ O	LC-HRMS	3.74	2.00	A	P3
15	Ethyl hexyl salicylate (EHS)	118-60-5	Personal care product	C ₁₅ H ₂₂ O ₃	GC-MS/MS	5.35	9.72	A, B, C, D, E, F, G, H (1, 2), I, J, K, L	P3
16	Fluazinam	79622-59-6	Pesticide	C ₁₃ H ₄ Cl ₂ F ₆ N ₄ O ₄	LC-HRMS	6.93	6.69	C	P2
17	Flucifuron	370-50-3	Pesticide	C ₁₅ H ₈ Cl ₂ F ₆ N ₂ O	LC-HRMS	6.08	11.38	H (1), H (2), B, C, M, H	P1, P2
18	Fludioxonil	131341-86-1	Pesticide	C ₁₂ H ₆ F ₂ N ₂ O ₂	LC-HRMS	3.57	14.66	B, C, M, A	P2, P3
19	Galaxolide	1222-05-5	Personal care product	C ₁₈ H ₂₆ O	GC-MS/MS	4.72	---	B, H (1, 2)	P1, P2, P3
20	Hexachlorophene	70-30-4	Antimicrobial	C ₁₃ H ₆ Cl ₆ O ₂	LC-HRMS	7.08	5.15	H (1, 2), B, C, M, H, D	P1, P2
21	Homosalate (HMS)	118-56-9	Personal care product	C ₁₆ H ₂₂ O ₃	GC-MS/MS	5.00	9.72	C, D, E, F, G, H (1, 2), J, K, L	P1, P2, P3
22	Isoproturon	34123-59-6	Pesticide	C ₁₂ H ₁₈ N ₂ O	LC-HRMS	2.57	13.79	B	P3
23	N-N-diethyl-3-methylbenzamid (DEET)	134-62-3	Personal care product	C ₁₂ H ₁₇ NO	LC-HRMS	2.50	---	J, E	P2, P3
24	Oryzalin	19044-88-3	pesticide	C ₁₂ H ₁₈ N ₄ O ₆ S	LC-HRMS	2.33	9.55	A, B, C, F	P3
25	Prometryn	7287-19-6	Pesticide	C ₁₀ H ₁₉ N ₅ S	LC-HRMS	3.01	6.71/14.46	B	P1, P3
26	Propiconazole	60207-90-1	Pesticide	C ₁₅ H ₁₇ Cl ₂ N ₃ O ₂	LC-HRMS	4.33	1.95	B, C, M, H	P2, P3
27	Simazin	122-34-9	Pesticide	C ₇ H ₁₂ ClN ₅	LC-HRMS	1.78	4.23/14.75	B	P3
28	Tebutam	35256-85-0	Pesticide	C ₁₅ H ₂₃ NO	LC-HRMS	3.71	---	A, C, H (2), I	P3
29	Terbutryn	886-50-0	Pesticide	C ₁₀ H ₁₉ N ₅ S	LC-HRMS	2.88	6.72/14.31	B	P1, P3
30	Tonalide	21145-77-7	Personal care product	C ₁₈ H ₂₆ O	LC-HRMS	4.96	---	A, H (1)	P1, P2, P3
31	Triclocarban	101-20-2	Personal care product	C ₁₃ H ₉ Cl ₃ N ₂ O	LC-HRMS	4.93	11.42	H (1, 2), B, C, M, H, I	P1, P2
32	Triclosan	3380-34-5	Antimicrobial	C ₁₂ H ₇ Cl ₃ O ₂	LC-HRMS	4.98	7.68	H (1, 2), B, C, M, H, I	P1, P2, P3
33	Triisobutylphosphate (TiBP)	126-71-6	Additives	C ₁₂ H ₂₇ O ₄ P	GC-MS/MS	3.85	---	A, B, C, E, H (1, 2), J, K	P2, P3
34	Triphenylphosphate (TPP)	115-86-6	Additives	C ₁₈ H ₁₅ O ₄ P	GC-MS/MS	5.09	---	A, H (1)	P1, P2, P3

log K_{ow} and pK_a values were calculated by ChemAxon (Budapest, Hungary).

--- No dissociation.

water. In a level-III model, this is driven by a chemical's partition coefficients and degradation half-lives in combination. Emission to air was used because in this case the chemicals first have to "survive" deposition from air to soil before they can build up a reservoir in the soil. In the identification of substances in the sediment, emission to water was used because this is the only emission scenario that leads to accumulation of >90% of a chemical's inventory in the sediment (except direct emission into the sediment, which was not considered). The three model versions, level-I, level-III with accumulation in soil and in sediment, were used in combination to "cast a net" that covers a wide range of chemical properties that cause a preference of chemicals for soil or sediment. All chemicals with a fraction of 0.9 or more in soil or sediment in any of these model versions were selected and used for further screening. Due to the very high number of CAS numbers obtained (3500) and to explore the utility of the suspect chemical list, only CAS numbers of halogenated substances were further considered as explained later under results and discussion, forming the Swiss halogenated database (*Swiss-HDB*).

2.4. Data analysis

A cluster analysis was carried out to group different locations and substances. The data analysis was performed using a binary variable "occurrence of a substance" at the different locations as an input. The data analysis was performed with the open-source software R using the package "pheatmap" using hierarchical clustering with complete linking (Kolde, 2019). Asymmetric distance (Jaccard) was used since only the occurrence of the same substance points to a similarity.

3. Results and discussion

3.1. Target analysis

3.1.1. Soils

The target analysis in soils confirmed the presence of 33 compounds included in the *Eawag-DB* as reported in Table S5 and S6 for LC-HRMS and GC-MS/MS analysis, respectively. The confirmed 33 compounds include mostly known pesticides reported in soil monitoring (Chiaia-Hernandez et al., 2017b) with the exception of the not previously reported plant growth retardant uniconazole. Furthermore, organophosphate esters (triisobutyl phosphate (TiBP) and triisopropenyl phosphate (TPP)) and six personal care products (ethylhexyl salicylate (EHS), galaxolide, homosalate and octahydro-tetramethyl acetophenone (OTNE)) were also detected.

3.1.2. Sediments

In total 67 compounds were detected, as shown in Table S7 and S8 for LC-HRMS and GC-MS/MS analysis, respectively. The detected compounds include mostly pesticides (39), however, antimicrobial agents, corrosion inhibitors, industrial chemicals, personal care products, and pharmaceuticals were also detected as previously reported (Chiaia-Hernandez et al., 2013). Newly confirmed substances in this lake attributed mainly due to the close proximity of the cores (P2 and P3) to WWTP outputs, include the transformation products of irgarol and fipronil, the pyrethroid permethrin and the pharmaceuticals carbamazepine, diazepam, fenofibrate, and lidocaine as shown in Table S7, and were detected mainly in the top layers of the cores. Moreover, the results also show the presence of five organophosphate esters (2-ethyl hexyl diphenyl phosphate (EHDPP), *tris-n-butyl* phosphate (TNBP), 2-ethylhexyl phosphate (TEHP), TiBP, TPP, and seven personal care products (celestolide, 2-ethyl methoxycinnamate (EHMC), EHS, galaxolide, homosalate, OTNE and taseolide). The outcomes are consistent with the slow degradation of musk fragrances, flame retardants and plasticizers in sediments (Peck et al., 2006; Zhong et al., 2018). TNBP (P1, P2 and P3), TEHP (P1), TPP (P3), OTNE (P1), and homosalate (P1, P2 and P3) show increasing concentrations over time as illustrated in Fig. S7 in the SI.

The target analysis performed in this work consists of a list of substances relevant to surface water from former studies. Therefore, since sediment includes mainly the aquatic environment, it is reasonable that the availability of reference standards for many of the detected compounds increased the number of confirmed compounds in the sediment (67 compounds) over soils (33 compounds).

3.1.3. Prioritization of suspect chemicals through chemical inventory and modeling

Of the 9187 CAS numbers initially included in the Swiss chemical inventory, about 3500 were present above the threshold of 90% in soil or sediment in any of the three models as explained in detail in the SI. As halogenated compounds are known to be often PBT and also easier to identify due to the characteristic isotope pattern, further efforts were concentrated on them. Chemicals without characteristic structures generally fall in the same domain as the soil and sediment matrix (e.g. natural compounds containing C, H, N, and O atoms such as fatty acids, peptides, polyphenols, carbohydrates, and humic acids), which increases the presence of interferences during identification efforts. Therefore, due to the very high number of obtained compounds and to explore the utility of the chemical inventory and modeling, only CAS numbers of halogenated substances (containing F, Cl or Br) in any of the three model runs were further considered as a first approach. Specifically, this includes 532 CAS numbers of chemicals in soil from the level-I model, 612 CAS numbers for substances in soil from the level-III model (emission to air) and 188 CAS numbers for substances in sediment from the level-III model (emission to water). Fig. 1 shows the results from the level-I model and the level-III model, emission to air. Provided are chemical-space plots spanned by the air-water and octanol-water partition coefficients, K_{aw} and K_{ow} , respectively, of the chemicals and the orange dots show chemicals residing predominantly in soil.

To each of these groups, further filters were applied and included the removal of i) CAS numbers referring to salt adducts, ii) CAS numbers referring to the same chemical structure, iii) CAS numbers of chemicals non-ionizable by ESI or chemicals with low ionization energy, and iv) CAS numbers of isomers, see Fig. S8. These filter steps led to a set of 340 CAS numbers for chemicals in soil from the level-I model and another set of 462 CAS numbers for chemicals in soil from the level-III model, with an overlap of 289 CAS numbers. In addition, there were 8 CAS numbers for chemicals in sediment that were not yet in any of the two soil sets. Overall, this gave a set of 521 CAS numbers to be screened in the instrumental analysis as shown in Fig. S9 (289 in soil, level-I and level-III model; 51 in soil, level-I model only; 173 in soil, level-III model only; 8 in sediment, level-III model). This set is called *Swiss-HDB* and contains a wide range of fluorinated, chlorinated and brominated aromatic and aliphatic substances, often with highly branched substituents, ether and tertiary amine groups, trifluoromethyl groups and phosphate ester groups. The *Swiss-HDB* with high affinity to soils or sediments (fractions of 0.9 or above) is provided in Appendix B.

3.2. Suspect screening of persistent organic contaminants

3.2.1. Soils

The prioritization of suspect chemicals from the model-based filtering resulted in the identification of 16 compounds already confirmed (level 1) using the *Eawag-DB*. Additionally 29 new compounds (6%) included in the *Swiss-HDB* were identified with three compounds identified at level 2 (e.g., by diagnostic evidence), nine compounds identified at level 3 and seventeen compounds at level 4 (Table S10). The compounds identified at levels 3 and 4 contained no characteristic fragments or their concentrations were too low to obtain representative MS/MS spectra. Therefore, the compounds with identification level ≥ 3 might not be present or at least not very relevant with regard to their concentrations. Identified compounds "likely present" (3 compounds, level 2) include two industrial chemicals (e.g. dichlorophenol) and the pharmaceutical (flukicide) niclofolan used in sheep and cattle (Ali

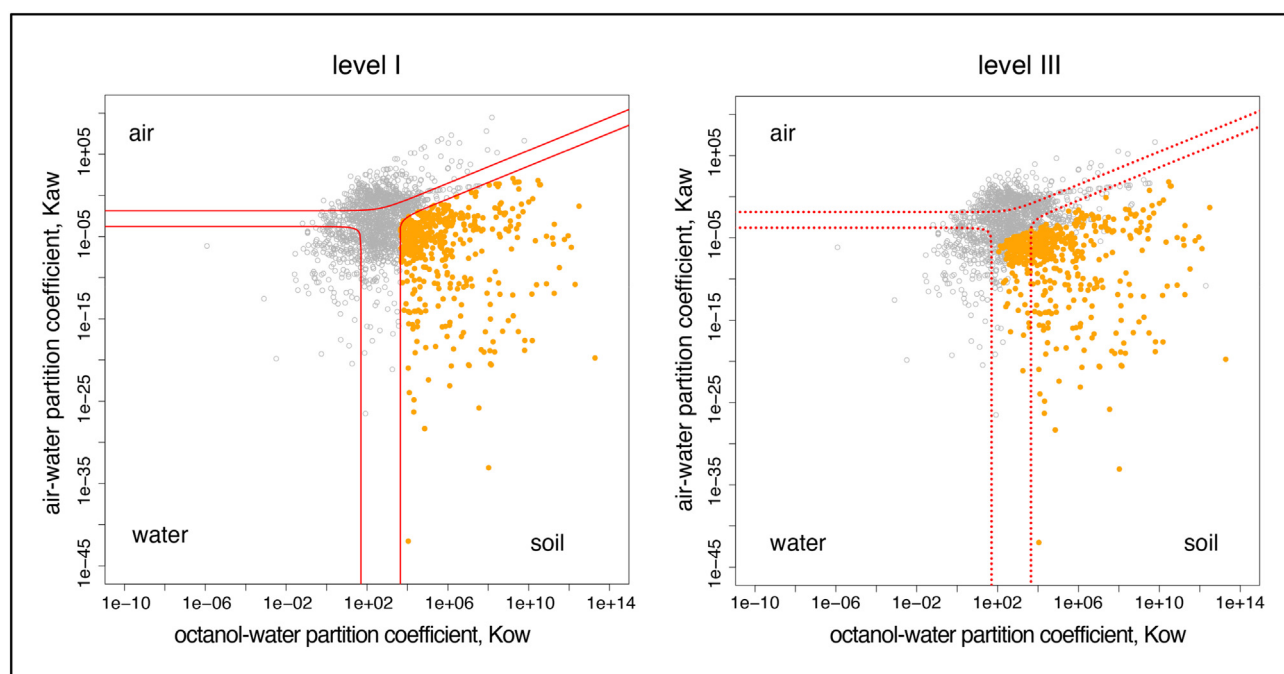


Fig. 1. Chemical space plots for 2371 halogenated substances from the Swiss chemical inventory. Left plot: Results from the level-I model; 532 substances with >90% in soil are shown in orange. Right plot: Results from the level-III model, emission scenario air, 612 substances with >90% in soil are shown in orange. Red dotted lines indicate the ratio of 0.90:0.10 between the different compartments according to the level-I model.

et al., 1990). Substituted phenols like niclofolan can be highly toxic and have low margins of safety in target species (Tuck et al., 2016). There is no toxicity data available for niclofolan and it has to the best of our knowledge never been reported before. Moreover, dichlorophenols are used as intermediates in the manufacture of different chemical compounds, including pesticides and antimicrobials, and due to their bactericidal properties can affect microflora in the environment (Jerschow et al., 2012).

3.2.2. Sediments

The screening of the *Swiss-HDB* in sediments resulted in the overlap of 10 compounds already confirmed with the *Eawag-DB* and the additional confirmation of 15 new compounds (level 1). The newly detected compounds found mainly in the last 10 years (top layers) and encompass three antimicrobials, ten pesticides (mainly fungicides) and one compound with a broad range of applications used in personal care products and food additives (chlorobenzhydrol). From the new pesticides detected, mandipropamid is a fungicide in the mandelamide class used to control oomycete pathogens on grapes, potatoes and other crops (PPDB). Mandipropamid has been classified as an aquatic environment hazards acute category 1 and chronic category 1 (very toxic to aquatic life with long lasting effects) (ECHA, 2011) and to the best of our knowledge, not yet been reported in environmental samples. Within the list of detected compounds, hexachlorophene, chlorophene, dichlorophene, and fluclofuron were previously identified in sediments using non-target screening approaches but were not included in our target list as a way to test the developed approach. At the time the identification of these four compounds required a lot of time and effort, thus this approach highlights the effectiveness of “smart screening” as a key for compound identification (Chiaia-Hernandez et al., 2014). Additional 8 (~2%) compounds were identified at level 2 (two compounds) and level 3 (six compounds). Compounds identified at levels 2 include the pharmaceutical cloflucarban (1-[4-chloro-3-(trifluoromethyl)phenyl]-3-(4-chlorophenyl)urea) used as disinfectant and found in antimicrobial soaps and deodorants. The complete list of identified compounds is reported in Table S11 and S12.

3.3. Linking spatial and temporal occurrence of persistent organic compounds with usage pattern and input pathways

3.3.1. Soils

Overall, the target and suspect analysis of soils shows the presence of 48 confirmed compounds (Appendix B) plus three compounds identified at level 2 (Table S10). The heatmap and cluster analysis illustrated in Fig. 2 show the presence of PFOS, EHS and homosalate as the most frequently detected compounds in soils. The results are in agreement with the high persistence and mobility of PFOS (Giesy and Kannan, 2001). However, the detection of EHS and homosalate used in sunscreen additives and their cluster with *N-N*-diethyl-3-methylbenzamid (DEET, Fig. 2), the most common active ingredient in insect repellents, raises the question of whether the presence of these compounds is mainly due to outdoor activities and their main input source should be investigated in the future. Furthermore, most contaminated places with >50% of the detected compounds were found, not surprisingly, to be agricultural areas (A and B), sites where sewage sludge had previously been applied (H), and city parks (C). Interestingly, one remote site (I) is clustered with these contaminated sites. We know from old records that at this extensive grassland site (I), sewage sludge was applied in the 1970s and 1980s. The communal WWTP is nearby and it is presumed that this grassland received quite some amounts of sludge. The collection of soils for NABO started in 1986/87, therefore, they are no records of the quantities of sewer sludge applied at this site.

Although quantification of detected compounds was not the primary goal of our study, we were able to show that some compounds showed concentration ranges up to 250 $\mu\text{g}/\text{kg}_{\text{oc}}$ with agriculture sites being the most contaminated sites followed by city parks located in urban areas as presented in Table S5 and S6 and Fig. S10. Silva et al., 2019 reported that from 317 agricultural top soils across the European Union, epiconazole and tebuconazole as well as DDT and its metabolites are among the most detected compounds, which is consistent with our results. Likewise, triazines and azole fungicides were also reported to be the most frequently detected compounds in Swiss soils and in 75 arable soils from the Czech Republic (Chiaia-Hernandez et al., 2017b; Hvězdová et al., 2018). Therefore, our results represent snapshots that are still

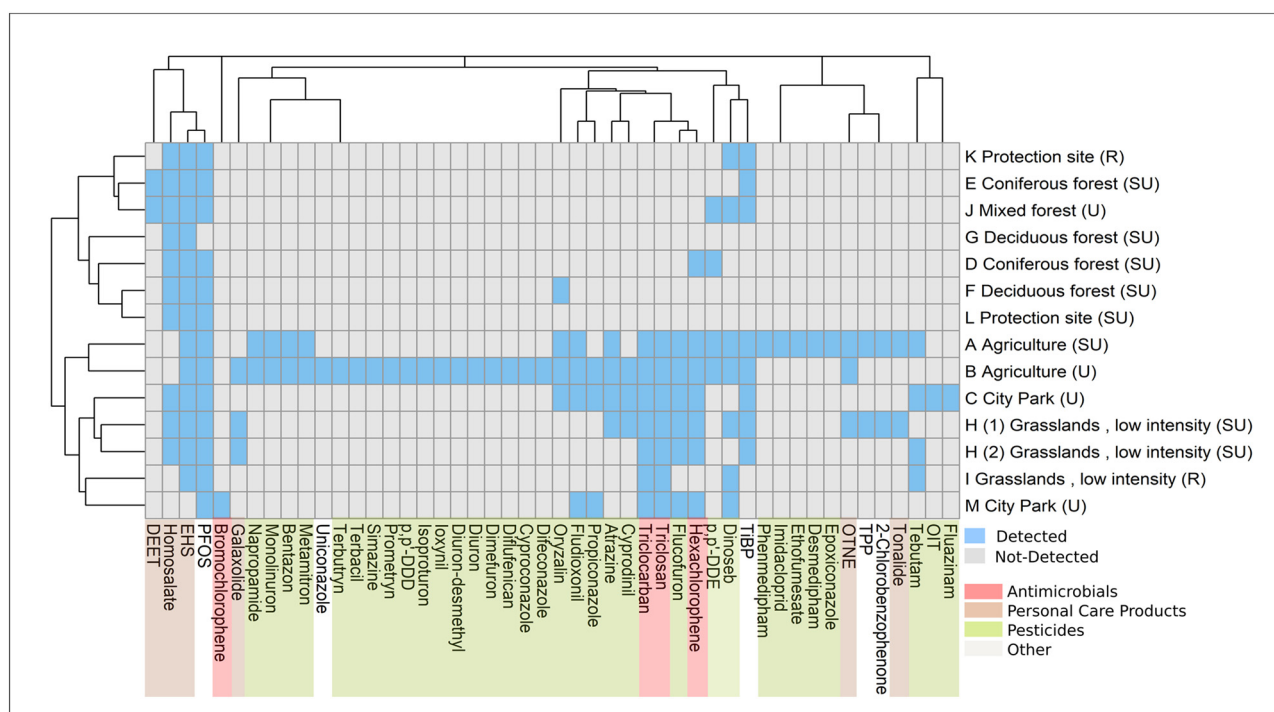


Fig. 2. Heat map of 48 organic contaminants confirmed in soils from the Swiss Soil Monitoring Network (NABO) from 13 different locations. The samples were taken between 2005 and 2009, with the exception of an additional sample at site H (H (2)) which dated back to 1994 and received domestic waste. Compound classification is presented with green (pesticides), pink (antimicrobial), brown (personal care products), and white (other). The classification "other" represents additives, industrial chemicals and growth retardants. Compound specifics are described in Table 1 and under SI. Letters in parenthesis represent location: U = urban, SU = semi urban, R = remote. Specific location and soil details are provided in SI and in Fig. S1 and Table S1.

representative of the situation today, with the exception of banned compounds.

Agricultural soils are the primary receivers of pesticides and the primary sink and key reservoirs of pesticides. Therefore, it is surprising that pesticides are excluded from existing soil monitoring networks which focus mainly on soil organic matter and soils contaminated with trace metals or POPs (e.g., PCB, PAHs, DDT and HCH) (Morvan et al., 2008; Saby et al., 2008). Furthermore, the detection of several pollutants in city parks calls for studies to evaluate the exposure to these substances for people frequently using these recreational areas (e.g. children).

Our outcomes emphasize the persistence of different organic contaminants that in some cases can be detected more than a decade after they were used or applied (site H (2), 1994) and include plastic additives (TiBP), antimicrobials (hexachlorophene, triclocarban and triclosan), personal care products (EHS, galaxolide, homosalate), and pesticides. Furthermore, our results show that protection sites and forests in semi urban sites, although not free of contaminants, are still mostly pristine as depicted in Fig. 2. The application of sewage sludge to agricultural fields was terminated in Switzerland in 2005 and, thus, the analysis of only two soils in this study where sludge was applied in previous years can only provide a glimpse on the occurrence of pharmaceutical and personal care products, to name a few, in this matrix. Still, the situation in other countries where sludge is still being applied to soils might be different and calls for more extensive soil monitoring.

3.3.2. Sediments

The analysis of sediment cores allows us to go back in time and study the different trends of organic contaminants inputs with 82 confirmed compounds and two additional compounds identified at level 2. In this study, the close proximity of the cores (P2 and P3) to WWTPs outputs and agricultural inputs led to the detection of additional contaminants such as different pharmaceuticals and personal care products never reported before in this lake and in other sediments. We have

shown that compounds embedded in sediments are often quite stable, especially under anaerobic conditions, with degradation frequently happening in the water phase and not in sediment layers as revealed by the similar water ratios of parent compound to transformation products reported in previous studies (Chiaia-Hernandez et al., 2013). Moreover, the outcomes of sediment analysis is in accordance with recent soil monitoring campaigns (Chiaia-Hernandez et al., 2017b; Hvézdová et al., 2018; Silva et al., 2019) which emphasizes the utility of lake sediments as a complementary tool in soil monitoring. For selected pesticides, patterns over time are shown in Fig. 3, where a rapid increase in concentrations is observed for the fungicide difeconazole while other pesticides show a decreasing concentration over time. For example, the fungicide fenpropimorph, the herbicide diuron and its demethylation product diuron-desmethyl exhibited their highest concentrations around the 1980s, followed by a reduction either of their use in the catchment or due to their higher elimination rates due to the upgrade of WWTPs in Switzerland more recently (Chiaia-Hernández et al., 2017a). Fluctuating concentrations are observed for diuron and diuron-desmethyl in the 1970s to the 1980s. To pin point the individual processes for the decrease and increase of diuron and diuron-desmethyl is an impossible task since no application records of diuron around the catchment are available for that time, neither water samples from WWTP effluents. Additionally, diuron and diuron-desmethyl show similar trends over time. The results are consistent with the higher stability of diuron-desmethyl and the almost no transformation of diuron in sediments (Field et al., 2003). Additional increase over time is observed for the antifungal agents climbazole and propiconazole (Fig. S11). In 2018, the European Commission (EC) published a proposal to restrict the use of climbazole as a preservative in hair, skin and foot care products (Commission, 2018a). Now, the EC has not renewed the approval of propiconazole for the use in cosmetic products (Commission, 2018b; ECHA, 2020). It remains to be shown how quickly the effects can be seen and whether such actions will lead to a decrease of climbazole and propiconazole in

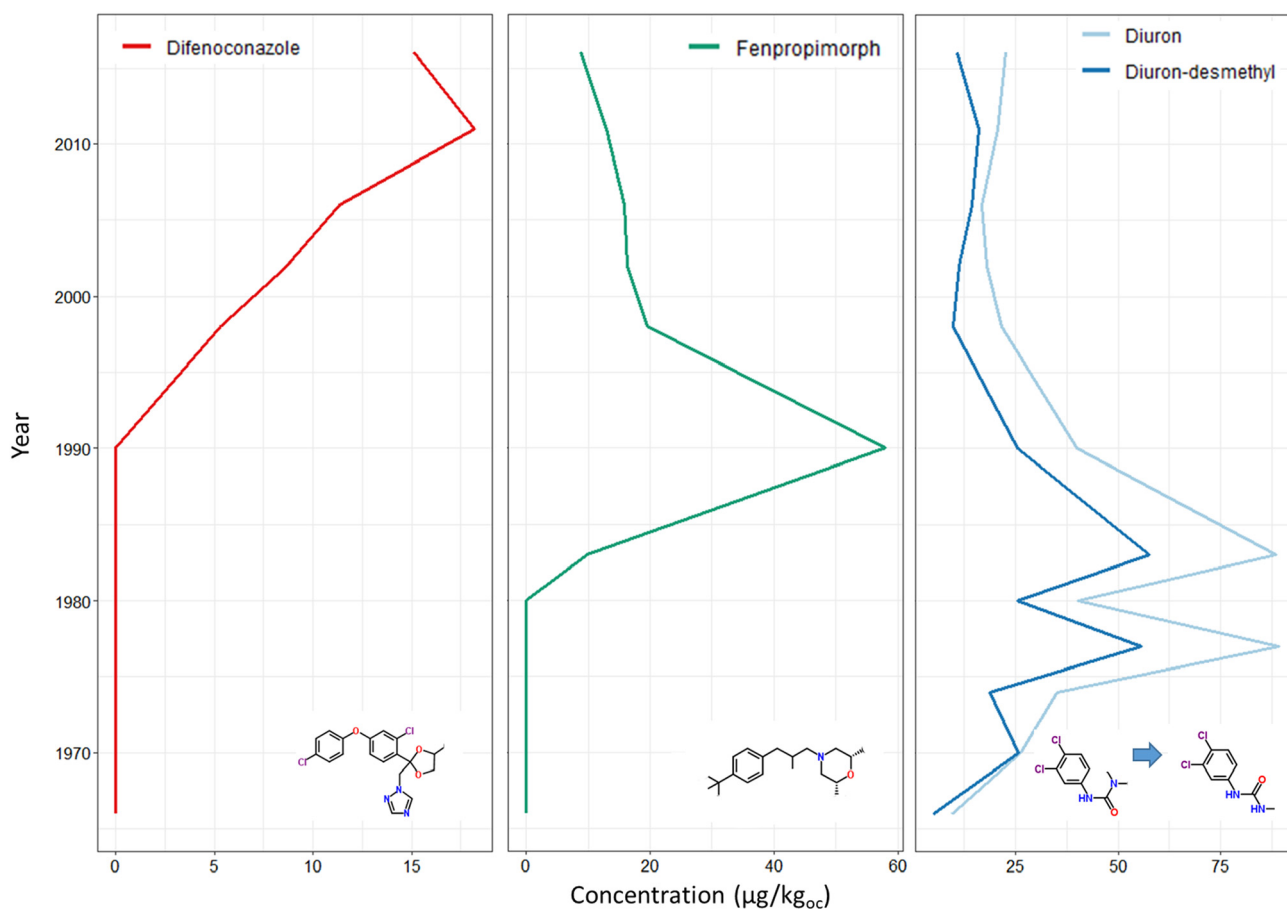


Fig. 3. Temporal concentration trends of the pesticide difenoconazole, fenpropimorph, diuron, and diuron-desmethyl (transformation product of diuron) in sediments from Greifensee near Aaspitz (P3) with impact of WWTP effluents and agricultural inputs to the catchment. Map location and details of sediment cores can be found in Fig. S2 and S3 and Table S3. *Chemical structures acquired from ChemSpider (<http://www.chemspider.com/>).

top sediments layers. Because of large fluctuations in concentration of different organic contaminants in water and soils, sediments can offer an additional tool or alternative technique to study chemical contamination throughout time and space to prioritize relevant contaminants as have been shown here for selected compounds.

4. Conclusions

Target and suspect screening of organic contaminants in soil and sediments shows that these two matrices are long-term reservoirs of persistent contaminants with the identification of 34 compounds in both matrices, 96 overall confirmed compounds and five compounds tentatively identified (level 2). The identified compounds comprise pesticides, industrial chemicals, pharmaceutical, and personal care products consisting mostly of esters, tertiary amines, trifluoromethylated chemicals, organophosphates, azoles and aromatic azines groups, with azoles and triazines being the most common groups, as summarized in Table S13 and Appendix B.

The results obtained in this study overlap with identified PBT substances (e.g., triclocarban, TPP, hexachlorophene and different triazines) and compound classes (e.g., organophosphates, sulfates and azoles) reported in other studies which validate the used approach (Gago-Ferrero et al., 2018; Howard and Muir, 2010). Moreover, this study shows that smart screening and spatial sampling (soils and sediments from different origins) might become essential for the successful identification of additional relevant compounds as well as give insights into types of contaminants never reported before or not frequently reported in the environment. Our results also highlight the need to

include these neglected matrices in monitoring campaigns since they not only are reservoirs of persistent contaminants but also serve as habitats and spawning sites for different organism. Studies carried out in 2015 and 2017 under the National Surface Water Quality Monitoring Program in Switzerland (NAWA SPEZ) demonstrate that pesticides in stream sediments can cause adverse effects in benthic organisms, with some pesticides exceeding effect thresholds. Little is known about the concentration or toxic effects of organic contaminants in sediments and sediment quality assessments at the international level are lacking. Similar is the case of soil monitoring, where large soil surveys (e.g. with a number of sites and compounds exceeding 10) of agricultural soils are surprisingly rare (Hvězdová et al., 2018). Therefore, this study calls for more inclusion of soils and sediments to determinate environmental quality standards as well as develop quality assessments.

In the future, additional screening of all the compounds obtained from the environmental fate model (3500 compounds with fractions above 90% in soil or sediment) should be performed with the aid of different analytical and extraction techniques and instrumentation to identify new persistent organic contaminants since the results show that, for the small subset of halogenated compounds (521) screened, this strategy was effective. However, differentiation from matrix components and identification for non-halogenated compounds without characteristic structural elements might be demanding and not always successful. Likewise, quantification of all compounds detected is needed to link the findings with risk assessment.

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Credit authorship contribution statement

Aurea C. Chiaia-Hernández: Conceptualization, Methodology, Formal analysis, Writing - original draft, Visualization, Project administration, Funding acquisition. **Martin Scheringer:** Conceptualization, Project administration, Writing - review & editing, Visualization, Funding acquisition. **Adrian Müller:** Formal analysis, Writing - review & editing. **Greta Stieger:** Visualization. **Daniel Wächter:** Methodology, Writing - review & editing. **Armin Keller:** Funding acquisition. **Marina G. Pintado-Herrera:** Formal analysis. **Pablo A. Lara-Martín:** Formal analysis, Writing - review & editing. **Thomas D. Bucheli:** Conceptualization, Project administration, Writing - review & editing, Funding acquisition. **Juliane Hollender:** Conceptualization, Project administration, Resources, Writing - review & editing, Funding acquisition.

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.

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