

Target and Suspect Screening Analysis Reveals Persistent Emerging Organic Contaminants in Soils and Sediments

Aurea C. Chiaia-Hernández^{1,2*}, Martin Scheringer³, Adrian Müller², Greta Stieger³, Daniel Wächter⁴, Armin Keller⁴, Marina G. Pintado Herrera⁵, Pablo A. Lara-Martin⁵, Thomas D. Bucheli⁴, and Juliane Hollender^{2,3}

¹Institute of Geography & Oeschger Centre for Climate Change Research, University of Bern, Bern, Switzerland

²Eawag, Swiss Federal Institute of Aquatic Science and Technology, Switzerland

³Institute of Biogeochemistry and Pollutant Dynamics, ETH Zürich, Switzerland

⁴Agroscope, Zurich, Switzerland

⁵Department of Physical Chemistry, Faculty of Marine and Environmental Sciences, CEI-MAR, University of Cadiz, Spain

*Corresponding author

Hallerstrasse 12 3012 Bern, Switzerland; phone +41 (0) 31 631 5518;

Email: aurea.hernandez@giub.unibe.ch

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 more than 500 halogenated compounds obtained from a Swiss database that includes industrial and household chemicals identified, by means of fugacity modelling, 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,

31 organophosphates, azoles and aromatic azines, with azoles and triazines being the most common
32 groups. Newly identified compounds include transformation products, pharmaceuticals such as the
33 flukicide niclofolan, the antimicrobial cloflucarban, and the fungicide mandipropamid. The results
34 indicate that agricultural and urban soils as well as sediments impacted by agriculture and
35 wastewater treatment plants (WWTPs) are the most contaminated sites. The plausibility of this
36 outcome confirms the combination of chemical inventory, modelling of partitioning and
37 persistence, and HRMS-based screening as a successful approach to shed light on less frequently
38 or not yet investigated environmental contaminants and emphasizes the need for more soil and
39 sediment monitoring in the future.

40

41 **Highlights**

- 42 • > 500 halogenated compounds were screened in soils and sediments
- 43 • The applied approach resulted in the confirmation of 96 compounds
- 44 • Soils and sediments are long-term reservoirs of persistent contaminants
- 45 • Agriculture and wastewater impacted sites were the most contaminated sites
- 46 • Azoles and triazines are the most common groups detected

47

48 **Keywords:** Persistent compounds, monitoring, fugacity modelling, LC-HRMS/MS, GC-MS/MS,
49 lakes

50

51 **1. Introduction**

52 The increasing amount and number of synthetic chemicals in use over the last decades has led to a
53 corresponding increase in the numbers and amounts of contaminants reaching the environment.
54 National and international environmental programs since the 1970s have performed a continuous
55 monitoring of persistent organic pollutants (POPs) and further chemicals with persistent,
56 bioaccumulative and toxic characteristics (PBT) are continuously added to the list (Muir and
57 Howard, 2006). While these monitoring programmes are highly important, many chemical
58 substances in wide commercial use are still not measured in environmental samples and their
59 environmental fate is still unknown (Muir and Howard, 2006). Until now most of the studies on
60 emerging contaminants have been performed on surface water samples (Moschet et al., 2014; Ruff
61 et al., 2015) often linked to the EU's water framework directive or other national directives while

62 soils and sediments, which are long-term reservoirs of PBT substances, have rarely been included
63 in monitoring campaigns due to their complexity but also to the lower regulative requirements
64 (Borja et al., 2004).

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

84 The analysis of organic pollutants in natural archives is challenging due to their occurrence in low
85 concentrations, typically in the pg/g to the µg/g range, interference with natural organic matter
86 (NOM), and the spatial variability observed from place to place. Recently, analytical
87 instrumentation such as high-resolution mass spectrometry (HRMS) has been developed to screen
88 for a wider range of organic contaminants at trace levels using wide-scope target, suspect, and non-
89 target screening approaches (Hollender et al., 2017). So far, suspect screening has been the more
90 established and successful approach to detect emerging compounds, mainly due to the different
91 suspect lists available nowadays (e.g. NORMAN SusDat). However, “smart” suspect screening of
92 a selected compound list with an appropriate analytical method is becoming a key for compound
93 identification since the identity confirmation is very time consuming and sometimes only a small

94 fraction of compounds screened can be identified. Thus, the way forward is to integrate additional
95 information such as physico-chemical properties and persistence specific for each matrix or
96 location beyond consumption data or mass libraries. Some of this challenges have been addressed
97 by Muir and Howard, who called for a novel strategy to find substances of relevance using a data
98 compilation of compounds on the market and estimation of physico-chemical properties (Howard
99 and Muir, 2010). Their approach resulted in long lists of chemicals of potential concern which are
100 persistent and bioaccumulative, including hundreds of chemicals never measured in environmental
101 samples (Howard and Muir, 2010; Muir and Howard, 2006).

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

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

122

123

124

125 **2. Experimental Section**

126 **2.1 Sampling collection and preservation**

127 **2.1.1 Soil.** Soils were selected based on land use, geography, known exposure and spatial
128 distribution pattern of pollutants, and were complemented by a few semi-urban controls and one
129 remote site. Currently known exposure patterns based on existing data on persistent organic
130 pollutants such as PCBs were used as indicators for diffuse input of contaminants, influence of
131 land use and geography to account for elevated pollutant emissions (Schmid et al., 2005). In total,
132 13 locations were selected as illustrated in Figure S1 and Table S1. The soils were provided by the
133 NABO, which operates about 100 long-term monitoring sites throughout Switzerland and
134 maintains a comprehensive archive of soil samples (Gubler et al., 2015). The samples were taken
135 between 2005 and 2009, with the exception of an additional sample from site H that dated back to
136 1994 and received domestic waste (H-2). Sampling took place in a standardized way on an area of
137 100 m² as described by Hämman and Desaulles, 2003. The investigated soil samples are composite
138 samples (0–20 cm soil layer; 25 subsamples taken by a gouge auger of 2.5 cm diameter)
139 representing an area of 10 m by 10 m. Information about the NABO monitoring network and
140 detailed information on sample preparation is provided by Desaulles and Dahinden, 2000 and Meuli
141 et al., 2014.

142

143 **2.1.2 Sediments.** Sediment cores were collected on November 2014 from three different locations
144 around Greifensee. Sampling point 1 (P1, 8.678105078° N, 47.351545874° E) was located at the
145 deepest part of the lake (depth of 32 m) to minimize direct influences of waste water treatment
146 plant (WWTPs) effluents and agriculture, as well as used as a reference point since it has been
147 studied extensively (Chiaia-Hernández et al., 2017; Chiaia-Hernandez et al., 2013; Chiaia-
148 Hernandez et al., 2014b). Sampling points 2 and 3 were located near the outlet of the Uster WWTP
149 (P2, 8.687325778° N, 47.352453944° E) and Mönchaltorfer WWTP at Aaspitz (P3, 8.697792119°
150 N, 47. 328196292° E) to cover the impact of WWTP effluents and agricultural inputs to the
151 catchment. Twelve layers were analyzed from core P1 (1870 - 2014) and P3 (1981- 2014) and 13
152 samples from core P2 (1958 – 2014) for validation of the findings and to identify possible false
153 positives since time series analysis can help to identify artifacts to confirm or reject a compound
154 (Chiaia-Hernández et al., 2017). Details on the collection, dating and geochemical analysis are
155 provided in the SI.

156

157 2.2 Chemical Analyses

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

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

176 Target analysis and further screening of additional compounds by LC-HRMS was performed with
177 the aid of the TraceFinder 3.3 software (Thermo Fisher Scientific Corp., USA) by extracting the
178 exact mass of the expected ion from the HR full scan chromatogram with a mass window of ± 5
179 ppm and matching automatically their isotopic pattern. In addition, more than 50 internal standards
180 were used for the quantification of selected compounds as well as a quality control in the target and
181 suspect screening. Blank subtraction was performed automatically with uncontaminated soils from
182 remote sites collected in 2008 and sediment layers from ~100 years ago since contamination was
183 not likely to be present in these samples. The output list of suspect candidates was manually
184 evaluated for correct peak shape, plausibility of ionization in the positive and negative mode (based
185 on different functional groups), retention time (RT) matching factor and fragmentation as described
186 elsewhere (Chiaia-Hernandez et al., 2014a). Compound identification was assigned according to
187 Schymanski et al., 2014 where level 1 corresponds to a structure confirmed by a reference standard,
188 level 2 corresponds to a structure candidate using library spectrum match or diagnostic evidence,

189 level 3 is assigned to tentative candidates where multiple structures are possible (e.g. different
190 isomers of a substance class) and level 4 and 5 correspond to unequivocal molecular formula and
191 just an exact mass of interest, respectively. Details of the screening steps and analysis for target
192 analysis and compound identification are provided in the SI.

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

194

195 **2.3 Chemical Databases**

196 Suspect screening of additional compounds was based on a chemical inventory to identify
197 compounds outside of the scope of our target analysis (*Eawag-DB*). This additional database was
198 created based on information extracted from several lists of chemicals like primarily customs
199 statistics and product registers of the Swiss authorities. For the substances included in these lists,
200 CAS numbers were collected directly, when available, or from publicly available databases (e.g.
201 <https://pubchem.ncbi.nlm.nih.gov/>, www.echemportal.org, www.chemicalize.org,
202 www.chemspider.com). In cases where a substance had several CAS numbers, all available CAS
203 numbers were compiled and later on eliminated through different filter steps as described in detail
204 under results and discussion. Evaluation of the chemical inventory led to a list of 18,349 individual
205 CAS numbers. Due to the extensive list of compounds, the collected database list was compared
206 with an earlier database developed by Stempel et al., 2012 which includes 91,699 industrial
207 chemicals on the market worldwide to identify chemicals also used abroad. Comparison of both
208 databases showed an overlap of 50% (9,187) with 13% (2,371) of these CAS numbers being
209 halogenated. For the subsequent steps, we focused on the 50% (9,187) of the substances that were
210 included in the list by Stempel et al., 2012 because for these substances, SMILES codes are
211 available. The compilation or generation of SMILES codes for several additional thousands of
212 chemicals just from their CAS numbers is a challenging, non-trivial task that was beyond the scope
213 of this work. Physicochemical properties and degradation half-life estimates for the chemical
214 structures, when possible, were calculated via quantitative structure-activity relationships (QSARs)
215 from EPI Suite (EPA, 2016) and according to approaches described by Stempel et al., 2012.

216 The filter approach used to identify substances likely to be persistent in the environment and
217 distribute predominantly in soils and sediments was implemented by calculating the distribution of
218 the selected substances in air, water, soil and sediment by using a multimedia fugacity model
219 (Mackay levels I and III (Mackay, 2001)) set up for Switzerland as described in the SI and by
220 Glüge et al., 2016. Importantly, the environmental fate models were used here as filters that identify

221 substances with certain physicochemical properties, but not to simulate a realistic situation of
222 substance use and emissions. Briefly, the level-I model used consists of the compartments soil,
223 water and air as a closed system with exchange between compartments at equilibrium and steady-
224 state. This model was used to identify chemicals that reside predominantly (i.e., more than 90%)
225 in the soil, which is, in a level-I model, solely driven by their partition coefficients. The level-III
226 model includes the compartments sediment, soil, water and air in an open system with exchange
227 between compartments and not at equilibrium but at steady-state. The level-III model was used to
228 identify chemicals that reside predominantly in soil after emission to air and in sediment after
229 emission to water. In a level-III model, this is driven by a chemical's partition coefficients and
230 degradation half-lives in combination. Emission to air was used because in this case the chemicals
231 first have to "survive" deposition from air to soil before they can build up a reservoir in the soil. In
232 the identification of substances in the sediment, emission to water was used because this is the only
233 emission scenario that leads to accumulation of more than 90% of a chemical's inventory in the
234 sediment (except direct emission into the sediment, which was not considered). The three model
235 versions, level-I, level-III with accumulation in soil and in sediment, were used in combination to
236 "cast a net" that covers a wide range of chemical properties that cause a preference of chemicals
237 for soil or sediment. All chemicals with a fraction of 0.9 or more in soil or sediment in any of these
238 model versions were selected and used for further screening. Due to the very high number of CAS
239 numbers obtained (3,500) and to explore the utility of the suspect chemical list, only CAS numbers
240 of halogenated substances were further considered as explained later under results and discussion,
241 forming the Swiss halogenated database (*Swiss-HDB*).

242
243 **2.4 Data Analysis**
244 A cluster analysis was carried out to group different locations and substances. The data analysis
245 was performed using a binary variable "occurrence of a substance" at the different locations as an
246 input. The data analysis was performed with the open-source software R using the package
247 "pheatmap" using hierarchical clustering with complete linking (Kolde, 2019). Asymmetric
248 distance (Jaccard) was used since only the occurrence of the same substance points to a similarity.

249
250
251

252 **3. Results and Discussion**

253 **3.1 Target Analysis**

254 **3.1.1 Soils.** The target analysis in soils confirmed the presence of 33 compounds included in the
255 *Eawag-DB* as reported in Table S5 and S6 for LC-HRMS and GC-MS/MS analysis, respectively.
256 The confirmed 33 compounds include mostly known pesticides reported in soil monitoring (Chiaia-
257 Hernandez et al., 2017) with the exception of the not previously reported plant growth retardant
258 uniconazole. Furthermore, organophosphate esters (triisobutyl phosphate (TiBP) and triisophenyl
259 phosphate (TPP)) and six personal care products (ethylhexyl salicylate (EHS), galaxolide,
260 homosalate and octahydrotetramethyl acetophenone (OTNE)) were also detected.

261
262 **3.1.2 Sediments.** In total 67 compounds were detected, as shown in Table S7 and S8 for LC-HRMS
263 and GC-MS/MS analysis, respectively. The detected compounds include mostly pesticides (39),
264 however, antimicrobial agents, corrosion inhibitors, industrial chemicals, personal care products,
265 and pharmaceuticals were also detected as previously reported (Chiaia-Hernández et al., 2017).
266 Newly confirmed substances in this lake attributed mainly due to the close proximity of the cores
267 (P2 and P3) to WWTP outputs, include the transformation products of irgarol and fipronil, the
268 pyrethroid permethrin and the pharmaceuticals carbamazepine, diazepam, fenofibrate, and
269 lidocaine as shown in Table S7, and were detected mainly in the top layers of the cores. Moreover,
270 the results also show the presence of five organophosphate esters (2-ethyl hexyl diphenyl
271 phosphate (EHDPP), *tris-n*-butyl phosphate (TNBP), 2-ethylhexyl phosphate (TEHP), TiBP, TPP,
272 and seven personal care products (celestolide, 2-ethyl methoxycinnamate (EHMC), EHS,
273 galaxolide, homosalate, OTNE and taseolide). The outcomes are consistent with the slow
274 degradation of musk fragrances, flame retardants and plasticizers in sediments (Peck et al., 2006;
275 Zhong et al., 2018). TNBP (P1, P2 and P3), TEHP (P1), TPP (P3), OTNE (P1), and homosalate
276 (P1, P2 and P3) show increasing concentrations over time as illustrated in Figure S7 in the SI.

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

282

283 **3.1.3 Prioritization of suspect chemicals through chemical inventory and modeling**

284 Of the 9,187 CAS numbers initially included in the Swiss chemical inventory, about 3,500 were
285 present above the threshold of 90% in soil or sediment in any of the three models as explained in
286 detail in the SI. As halogenated compounds are known to be often PBT and also easier to identify
287 due to the characteristic isotope pattern, further efforts were concentrated on them. Chemicals
288 without characteristic structures generally fall in the same domain as the soil and sediment matrix
289 (e.g. natural compounds containing C, H, N, and O atoms such as fatty acids, peptides, polyphenols,
290 carbohydrates, and humic acids), which increases the presence of interferences during
291 identification efforts. Therefore, due to the very high number of obtained compounds and to explore
292 the utility of the chemical inventory and modeling, only CAS numbers of halogenated substances
293 (containing F, Cl or Br) in any of the three model runs were further considered as a first approach.
294 Specifically, this includes 532 CAS numbers of chemicals in soil from the level-I model, 612 CAS
295 numbers for substances in soil from the level-III model (emission to air) and 188 CAS numbers for
296 substances in sediment from the level-III model (emission to water). Figure 1 shows the results
297 from the level-I model and the level-III model, emission to air. Provided are chemical-space plots
298 spanned by the air-water and octanol-water partition coefficients, K_{aw} and K_{ow} , respectively, of the
299 chemicals and the orange dots show chemicals residing predominantly in soil.

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

313

314

315 **3.2 Suspect Screening of Persistent Organic Contaminants**

316 **3.2.1 Soils.** The prioritization of suspect chemicals from the model-based filtering resulted in the
317 identification of 16 compounds already confirmed (level 1) using the *Eawag-DB*. Additionally 29
318 new compounds (6%) included in the *Swiss-HDB* were identified with three compounds identified
319 at level 2 (e.g., by diagnostic evidence), nine compounds identified at level 3 and seventeen
320 compounds at level 4 (Table S10). The compounds identified at levels 3 and 4 contained no
321 characteristic fragments or their concentrations were too low to obtain representative MS/MS
322 spectra. Therefore, the compounds with identification level ≥ 3 might not be present or at least not
323 very relevant with regard to their concentrations. Identified compounds “likely present” (3
324 compounds, level 2) include two industrial chemicals (e.g. dichlorophenol) and the pharmaceutical
325 (flukicide) niclofolan used in sheep and cattle (Ali et al., 1990). Substituted phenols like niclofolan
326 can be highly toxic and have low margins of safety in target species (Tuck et al., 2016). There is
327 no toxicity data available for niclofolan and it has to the best of our knowledge never been reported
328 before. Moreover, dichlorophenols are used as intermediates in the manufacture of different
329 chemical compounds, including pesticides and antimicrobials, and due to their bactericidal
330 properties can affect microflora in the environment (Jerschow et al., 2012).

331
332 **3.2.2 Sediments.** The screening of the *Swiss-HDB* in sediments resulted in the overlap of 10
333 compounds already confirmed with the *Eawag-DB* and the additional confirmation of 15 new
334 compounds (level 1). The newly detected compounds found mainly in the last 10 years (top layers)
335 and encompass three antimicrobials, ten pesticides (mainly fungicides) and one compound with a
336 broad range of applications used in personal care products and food additives (chlorobenzhydrol).
337 From the new pesticides detected, mandipropamid is a fungicide in the mandelamide class used to
338 control oomycete pathogens on grapes, potatoes and other crops. Mandipropamid has been
339 classified as an aquatic environment hazards acute category 1 and chronic category 1 (very toxic
340 to aquatic life with long lasting effects)(ECHA, 2011) and to the best of our knowledge, not yet
341 been reported in environmental samples. Within the list of detected compounds, hexachlorophene,
342 chlorophene, dichlorophene, and flucofuron were previously identified in sediments using non-
343 target screening approaches but were not included in our target list as a way to test the developed
344 approach. At the time the identification of these four compounds required a lot of time and effort,
345 thus this approach highlights the effectiveness of “smart screening” as a key for compound
346 identification (Chiaia-Hernandez et al., 2014a). Additional 8 (~2%) compounds were identified at

347 level 2 (two compounds) and level 3 (six compounds). Compounds identified at levels 2 include
348 the pharmaceutical cloflucarban (1-[4-chloro-3-(trifluoromethyl)phenyl]-3-(4-chlorophenyl)urea)
349 used as disinfectant and found in antimicrobial soaps and deodorants. The complete list of
350 identified compounds is reported in Table S11 and S12.

351 352 **3.3 Linking spatial and temporal occurrence of persistent organic compounds** 353 **with usage pattern and input pathways**

354 **3.3.1 Soils.** Overall, the target and suspect analysis of soils shows the presence of 48 confirmed
355 compounds (Appendix B) plus three compounds identified at level 2 (Table S10). The heatmap
356 and cluster analysis illustrated in Figure 2 show the presence of PFOS, EHS and homosalate as the
357 most frequently detected compounds in soils. The results are in agreement with the high persistence
358 and mobility of PFOS (Giesy and Kannan, 2001). However, the detection of EHS and homosalate
359 used in sunscreen additives and their cluster with *N-N*-diethyl-3-methylbenzamid (DEET, Figure
360 2), the most common active ingredient in insect repellents, raises the question of whether the
361 presence of these compounds is mainly due to outdoor activities and their main input source should
362 be investigated in the future. Furthermore, most contaminated places with >50% of the detected
363 compounds were found, not surprisingly, to be agricultural areas (A and B), sites where sewage
364 sludge had previously been applied (H), and city parks (C). Interestingly, one remote site (I) is
365 clustered with these contaminated sites. We know from old records that at this extensive grassland
366 site (I), sewage sludge was applied in the 1970s and 1980s. The communal WWTP is nearby and
367 it is presumed that this grassland received quite some amounts of sludge. The collection of soils
368 for NABO started in 1986/87, therefore, they are no records of the quantities of sewer sludge
369 applied at this site.

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

378 2018). Therefore, our results represent snapshots that are still representative of the situation today,
379 with the exception of banned compounds.

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

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

397
398 **3.3.2 Sediments.** The analysis of sediment cores allows us to go back in time and study the different
399 trends of organic contaminants inputs with 82 confirmed compounds and two additional
400 compounds identified at level 2. In this study, the close proximity of the cores (P2 and P3) to
401 WWTPs outputs and agricultural inputs led to the detection of additional contaminants such as
402 different pharmaceuticals and personal care products never reported before in this lake and in other
403 sediments. We have shown that compounds embedded in sediments are often quite stable,
404 especially under anaerobic conditions, with degradation frequently happening in the water phase
405 and not in sediment layers as revealed by the similar water ratios of parent compound to
406 transformation products reported in previous studies (Chiaia-Hernandez et al., 2013). Moreover,
407 the outcomes of sediment analysis is in accordance with recent soil monitoring campaigns (Chiaia-
408 Hernandez et al., 2017; Hvězdová et al., 2018; Silva et al., 2019) which emphasizes the utility of
409 lake sediments as a complementary tool in soil monitoring. For selected pesticides, patterns over

410 time are shown in Figure 3, where a rapid increase in concentrations is observed for the fungicide
411 difeconazole while other pesticides show a decreasing concentration over time. For example, the
412 fungicide fenpropimorph, the herbicide diuron and its demethylation product diuron-desmethyl
413 exhibited their highest concentrations around the 1980s, followed by a reduction either of their use
414 in the catchment or due to their higher elimination rates due to the upgrade of WWTPs in
415 Switzerland more recently (Chiaia-Hernández et al., 2017). Fluctuating concentrations are
416 observed for diuron and diuron-desmethyl in the 1970s to the 1980s. To pin point the individual
417 processes for the decrease and increase of diuron and diuron-desmethyl is an impossible task since
418 no application records of diuron around the catchment are available for that time, neither water
419 samples from WWTP effluents. Additionally, diuron and diuron-desmethyl show similar trends
420 over time but with higher concentrations of the transformation product. The results are consistent
421 with the higher stability of diuron-desmethyl over diuron and the almost no transformation of
422 diuron in sediments (Field et al., 2003). Additional increase over time is observed for the antifungal
423 agents climbazole and propiconazole (Figure S11). In 2018, the European Commission (EC)
424 published a proposal to restrict the use of climbazole as a preservative in hair, skin and foot care
425 products (Commission, 2018a). Now, the EC has not renewed the approval of propiconazole for
426 the use in cosmetic products (Commission, 2018b; ECHA, 2020). It remains to be shown how
427 quickly the effects can be seen and whether such actions will lead to a decrease of climbazole and
428 propiconazole in top sediments layers. Because of large fluctuations in concentration of different
429 organic contaminants in water and soils, sediments can offer an additional tool or alternative
430 technique to study chemical contamination throughout time and space to prioritize relevant
431 contaminants as have been shown here for selected compounds.

432

433 **4. Conclusions**

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

441 The results obtained in this study overlap with identified PBT substances (e.g., triclocarban, TPP,
442 hexachlorophene and different trazines) and compound classes (e.g., organophosphates, sulfates
443 and azoles) reported in other studies which validate the used approach (Gago-Ferrero et al., 2018;
444 Howard and Muir, 2010). Moreover, this study shows that smart screening and spatial sampling
445 (soils and sediments from different origins) might become essential for the successful identification
446 of additional relevant compounds as well as give insights into types of contaminants never reported
447 before or not frequently reported in the environment. Our results also highlight the need to include
448 these neglected matrices in monitoring campaigns since they not only are reservoirs of persistent
449 contaminants but also serve as habitats and spawning sites for different organism. Studies carried
450 out in 2015 and 2017 under the National Surface Water Quality Monitoring Program in Switzerland
451 (NAWA SPEZ) demonstrate that pesticides in stream sediments can cause adverse effects in
452 benthic organisms, with some pesticides exceeding effect thresholds. Little is known about the
453 concentration or toxic effects of organic contaminants in sediments and sediment quality
454 assessments at the international level are lacking. Similar is the case of soil monitoring, where large
455 soil surveys (e.g. with a number of sites and compounds exceeding 10) of agricultural soils are
456 surprisingly rare (Hvězdová et al., 2018). Therefore, this study calls for more inclusion of soils and
457 sediments to determinate environmental quality standards as well as develop quality assessments.
458 In the future, additional screening of all the compounds obtained from the environmental fate
459 model (3,500 compounds with fractions above 90% in soil or sediment) should be performed with
460 the aid of different analytical and extraction techniques and instrumentation to identify new
461 persistent organic contaminants since the results show that, for the small subset of halogenated
462 compounds (521) screened, this strategy was effective. However, differentiation from matrix
463 components and identification for non-halogenated compounds without characteristic structural
464 elements might be demanding and not always successful. Likewise, quantification of all
465 compounds detected is needed to link the findings with risk assessment.

466

467 **Acknowledgements**

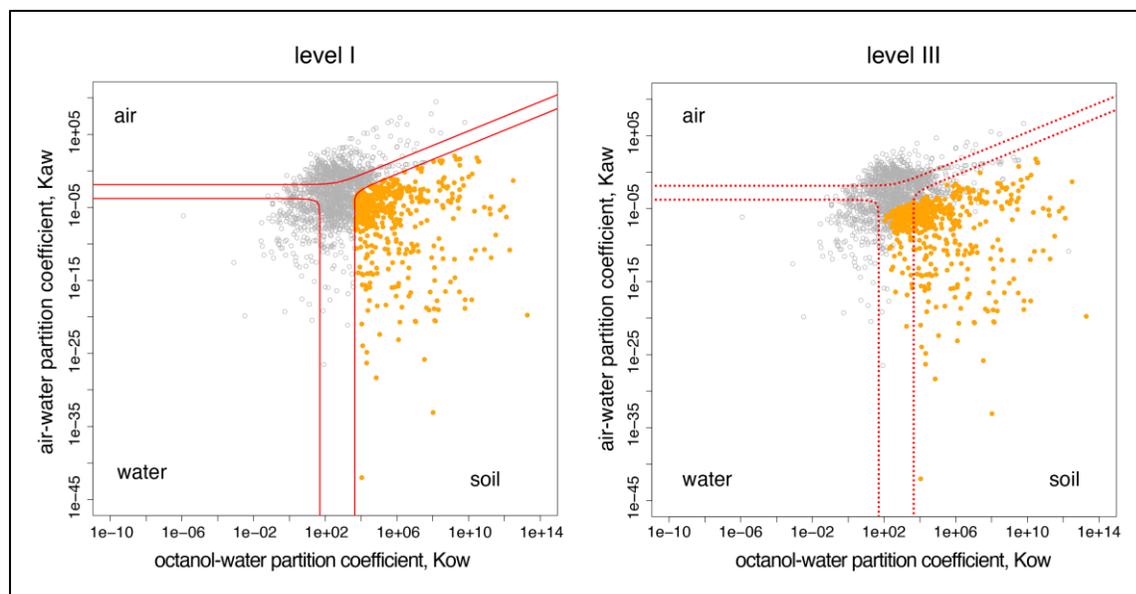
468 The authors thank Andreas Maccagnan for his work in the laboratory (Eawag), Martin P. Frey
469 (ZHAW) for his advice in R, the Sedimentology Group at Eawag for their help in the collection of
470 cores and inorganic analysis of the samples, and the Paleolimnology group at the University of
471 Bern from their thoroughly discussions. Funding by the Federal Agency of the Environment

472 (FOEN) and by the University of Bern through the Interfaculty Research Cooperation One Health
473 are gratefully acknowledged.

474
475 **Appendix A.** Supplementary data in this sections are descriptions of analytical methods, site,
476 chemical analysis and additional Figures and Tables.

477 **Appendix B.** Swiss halogenated database (Swiss-HDB) with high affinity to soils or sediments
478 (fractions of 0.9 or above) and a list of the 96 compounds found in soil and sediments.

479



480
 481 **Figure 1.** Chemical space plots for 2,371 halogenated substances from the Swiss chemical
 482 inventory. Left plot: Results from the level-I model; 532 substances with >90% in soil are shown
 483 in orange. Right plot: Results from the level-III model, emission scenario air, 612 substances with
 484 >90% in soil are shown in orange. Red dotted lines indicate the ratio of 0.90:0.10 between the
 485 different compartments according to the level-I model.

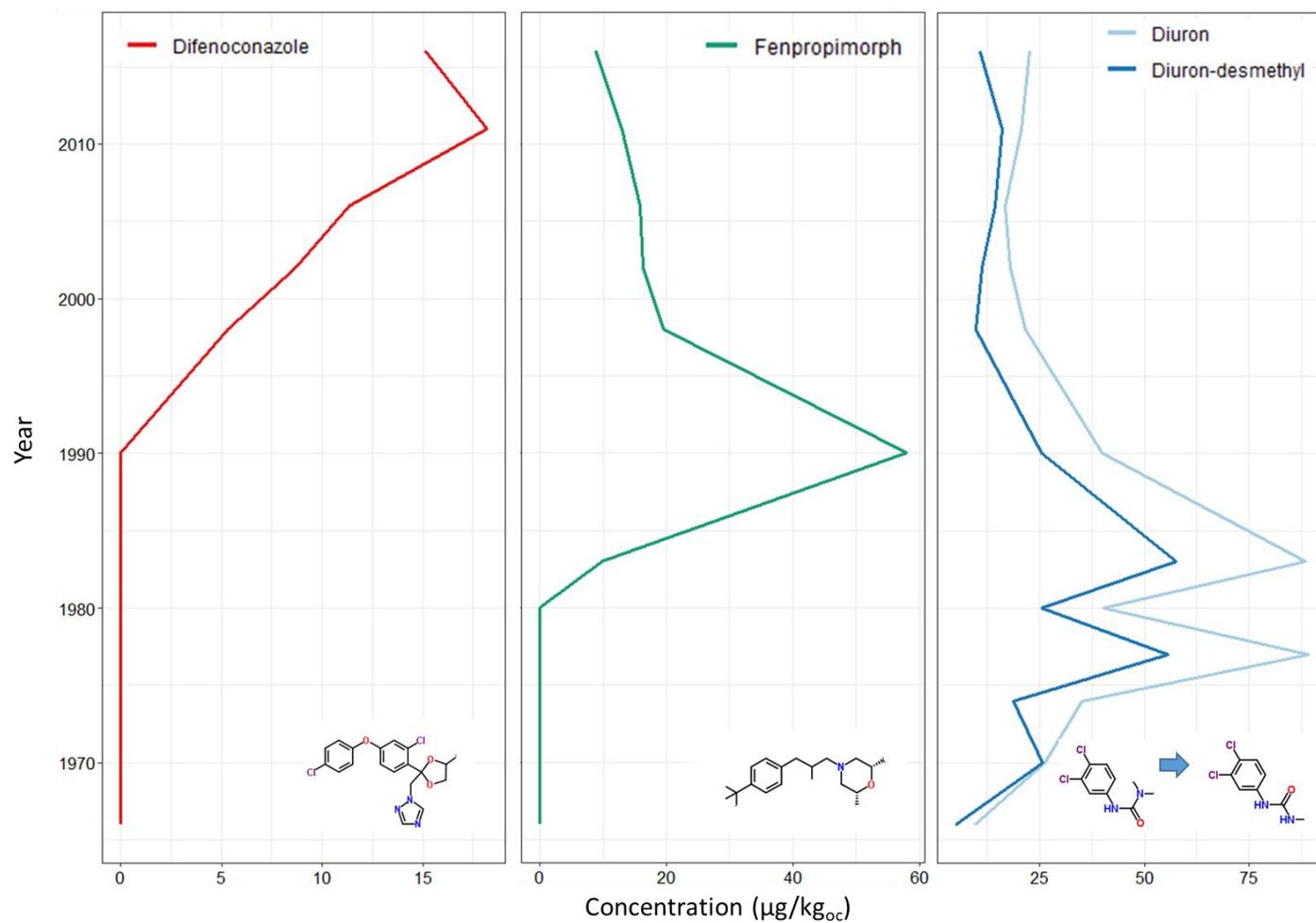


Figure 3. Temporal concentration trends of the pesticide difenoconazole, fenpropimorph, diuron, and diuron-desmethyl (transformation product of diuron) in sediments from Greifensee near Aaspitz (P3) with impact of WWTP effluents and agricultural inputs to the catchment. Map location and details of sediment cores can be found in Figure S2 and S3 and Table S3.

*Figures acquired from ChemSpider (<http://www.chemspider.com/>)

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 Figure 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-[(2 <i>R</i> ,3 <i>R</i>)-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-2 <i>H</i> -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 (<i>p,p'</i> -DDD)	72-54-8	Pesticide	C ₁₄ H ₁₀ Cl ₄	GC-MS/MS	6.11	---	B	P1, P2, P3
8	Dichlorodiphenyldichloroethylene (<i>p,p'</i> -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 ₅ 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

No.	Compound Name	CAS No.	Application	Formula	Analysis	log K _{ow}	pKa	Location Soils	Location Sediments
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	Flucofuron	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	<i>N-N</i> -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

No.	Compound Name	CAS No.	Application	Formula	Analysis	log K _{ow}	pK _a	Location Soils	Location Sediments
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

References

- NORMAN Substance Database – NORMAN SusDat. <https://www.norman-network.com/nds/susdat/>. Accessed on 17.07.2019.
- Ordinance on Protection against Major Accidents. Swiss Federal Council. <https://www.admin.ch/opc/en/classified-compilation/19910033/>. Accessed on 25.01.2019.
- PPDB: Pesticide Properties DataBase. Agriculture & Environment Research Unit (AERU) at the University of Hertfordshire. <https://sitem.herts.ac.uk/aeru/ppdb/en/>. Accessed on 02.07.2019.
- Proposal for Harmonised Classification and Labelling-ECHA. <https://echa.europa.eu/documents/10162/7aa96cc7-e3f7-79b1-b580-cdb1663bc9df>. Accessed on 08.01.2020.
- Swiss Ordinance on the Rotterdam Convention on the Prior Informed Consent Procedure for Certain Chemicals in International Trade (ChemPICO). <https://www.admin.ch/opc/en/classified-compilation/20021523/>. Accessed on 13.04.2018.
- Swiss product register for chemicals. <https://www.rpc.admin.ch>. Accessed on 13.04.2018.
- Ali BH, Sheikh HA, McKellar QA. Pharmacokinetics of niclofolan in desert sheep. *Journal of Veterinary Pharmacology and Therapeutics* 1990; 13: 217-219.
- Borja A, Valencia V, Franco J, Muxika I, Bald J, Belzunce MJ, et al. The water framework directive: water alone, or in association with sediment and biota, in determining quality standards? *Mar Pollut Bull* 2004; 49: 8-11.
- Chiaia-Hernandez A, Schymanski E, Kumar P, Singer H, Hollender J. Suspect and nontarget screening approaches to identify organic contaminant records in lake sediments. *Analytical and Bioanalytical Chemistry* 2014a; 406: 7323-7335.
- Chiaia-Hernández AC, Günthardt BF, Frey MP, Hollender J. Unravelling Contaminants in the Anthropocene Using Statistical Analysis of Liquid Chromatography–High-Resolution Mass Spectrometry Nontarget Screening Data Recorded in Lake Sediments. *Environmental Science & Technology* 2017; 51: 12547-12556.
- Chiaia-Hernandez AC, Keller A, Wächter D, Steinlin C, Camenzuli L, Hollender J, et al. Long-Term Persistence of Pesticides and TPs in Archived Agricultural Soil Samples and Comparison with Pesticide Application. *Environmental Science & Technology* 2017; 51: 10642-10651.
- Chiaia-Hernandez AC, Krauss M, Hollender J. Screening of Lake Sediments for Emerging Contaminants by Liquid Chromatography Atmospheric Pressure Photoionization and Electrospray Ionization Coupled to High Resolution Mass Spectrometry. *Environmental Science & Technology* 2013; 47: 976-986.
- Chiaia-Hernandez AC, Schymanski EL, Kumar P, Singer HP, Hollender J. Suspect and nontarget screening approaches to identify organic contaminant records in lake sediments. *Anal Bioanal Chem* 2014b; 406.
- Commission E. Scientific Committee on Consumer Safety (https://ec.europa.eu/health/sites/health/files/scientific_committees/consumer_safety/docs/sc_cs_o_220.pdf). Accessed on 27.05.2019. 2018a.
- Commission E. Scientific Committee on Consumer Safety (<https://eur-lex.europa.eu/legal-content/EN/TXT/PDF/?uri=CELEX:32018R1865&from=EN>).. Accessed on 28.05.2019 2018b.
- Desaules A, Dahinden R. Nationales Boden-Beobachtungsnetz. Veränderungen von Schadstoffgehalten nach 5 und 10 Jahren. Schriftenreihe Umwelt Nr. 320, Bundesamt für Umwelt, Wald und Landschaft (BUWAL), Bern: 129 S. 2000.

- ECHA. CLH Report for Mandipropamid. European Chemicals Agency.
<https://echa.europa.eu/documents/10162/e1ea06b3-6f44-4abc-98ef-d5be81c11f46>. Accessed on 10.06.2020. In: Agency EC, editor, 2011.
- ECHA. EU. Cosmetics Regulation, Annex III, Restricted Substances. European Chemicals Agency.
<https://echa.europa.eu/de/substance-information/-/substanceinfo/100.056.441>. Accessed on 10.06.2020, 2020.
- EPA U. Estimation Programs Interface Suite™ for Microsoft® Windows, v 4.11 or insert version used]. United States Environmental Protection Agency, Washington, DC, USA., 2016.
- Field JA, Reed RL, Sawyer TE, Griffith SM, Wigington PJ. Diuron Occurrence and Distribution in Soil and Surface and Ground Water Associated with Grass Seed Production. *Journal of Environmental Quality* 2003; 32: 171-179.
- Gago-Ferrero P, Krettek A, Fischer S, Wiberg K, Ahrens L. Suspect Screening and Regulatory Databases: A Powerful Combination To Identify Emerging Micropollutants. *Environmental Science & Technology* 2018.
- Giesy JP, Kannan K. Global Distribution of Perfluorooctane Sulfonate in Wildlife. *Environmental Science & Technology* 2001; 35: 1339-1342.
- Glüge J, Bogdal C, Scheringer M, Hungerbühler K. What determines PCB concentrations in soils in rural and urban areas? Insights from a multi-media fate model for Switzerland as a case study. *Science of The Total Environment* 2016; 550: 1152-1162.
- Gubler A, Wachter D, Blum F, Bucheli TD. Remarkably constant PAH concentrations in Swiss soils over the last 30 years. *Environmental Science: Processes & Impacts* 2015; 17: 1816-1828.
- Hämmann M, Desaulles A. Hämmann M., Desaulles A. 2003: Handbuch: Probenahme und Probenvorbereitung für Schadstoffuntersuchungen in Böden. Vollzug Umwelt (VU-4814-D). Bundesamt für Umwelt, Wald und Landschaft (BUWAL), Bern: 100 S.
<https://www.bafu.admin.ch/bafu/de/home/themen/boden/publikationen-studien/publikationen/handbuch-probenahme-schadstoffuntersuchungen.html>. Accessed on 03.07.2019. 2003.
- Hollender J, Schymanski EL, Singer HP, Ferguson PL. Nontarget Screening with High Resolution Mass Spectrometry in the Environment: Ready to Go? *Environmental Science & Technology* 2017; 51: 11505-11512.
- Howard PH, Muir DCG. Identifying New Persistent and Bioaccumulative Organics Among Chemicals in Commerce. *Environmental Science & Technology* 2010; 44: 2277-2285.
- Hung H, Kallenborn R, Breivik K, Su Y, Brorström-Lundén E, Olafsdottir K, et al. Atmospheric monitoring of organic pollutants in the Arctic under the Arctic Monitoring and Assessment Programme (AMAP): 1993–2006. *Science of The Total Environment* 2010; 408: 2854-2873.
- Hvězdová M, Kosubová P, Košíková M, Scherr KE, Šimek Z, Brodský L, et al. Currently and recently used pesticides in Central European arable soils. *Science of The Total Environment* 2018; 613-614: 361-370.
- Jerschow E, McGinn AP, de Vos G, Vernon N, Jariwala S, Hudes G, et al. Dichlorophenol-containing pesticides and allergies: results from the US National Health and Nutrition Examination Survey 2005-2006. *Annals of Allergy, Asthma & Immunology* 2012; 109: 420-425.
- Jones KC, de Voogt P. Persistent organic pollutants (POPs): state of the science. *Environmental Pollution* 1999; 100: 209-221.
- Kolde R. R package 'pheatmap'. R package version 1.0.12. 2019. 2019.
- Lara-Martín PA, Renfro AA, Cochran JK, Brownawell BJ. Geochronologies of Pharmaceuticals in a Sewage-Impacted Estuarine Urban Setting (Jamaica Bay, New York). *Environmental Science & Technology* 2015; 49: 5948-5955.
- Mackay D. Multimedia Environmental Models: CRC Press 2001.

- Meuli RG, Schwab P, Wächter D, Ammann S. Ergebnisse der Nationalen Bodenbe-obachtung (NABO). Zustand und Entwicklung 1985–2004. Umwelt-Wissen Nr. 1409. Bundesamt für Umwelt (BAFU), Bern: 94 S. Accessed on 12.09.2019. 2014.
- Morvan X, Saby NPA, Arrouays D, Le Bas C, Jones RJA, Verheijen FGA, et al. Soil monitoring in Europe: A review of existing systems and requirements for harmonisation. *Science of The Total Environment* 2008; 391: 1-12.
- Moschet C, Piazzoli A, Singer H, Hollender J. Alleviating the Reference Standard Dilemma Using a Systematic Exact Mass Suspect Screening Approach with Liquid Chromatography-High Resolution Mass Spectrometry. *Analytical Chemistry* 2013; 85: 10312-10320.
- Moschet C, Wittmer I, Simovic J, Junghans M, Piazzoli A, Singer H, et al. How a Complete Pesticide Screening Changes the Assessment of Surface Water Quality. *Environmental Science & Technology* 2014; 48: 5423-5432.
- Muir DCG, Howard PH. Are There Other Persistent Organic Pollutants? A Challenge for Environmental Chemists†. *Environmental Science & Technology* 2006; 40: 7157-7166.
- Peck AM, Linebaugh EK, Hornbuckle KC. Synthetic Musk Fragrances in Lake Erie and Lake Ontario Sediment Cores. *Environmental Science & Technology* 2006; 40: 5629-5635.
- Pintado-Herrera MG, González-Mazo E, Lara-Martín PA. In-cell clean-up pressurized liquid extraction and gas chromatography–tandem mass spectrometry determination of hydrophobic persistent and emerging organic pollutants in coastal sediments. *Journal of Chromatography A* 2016; 1429: 107-118.
- Ruff M, Mueller MS, Loos M, Singer HP. Quantitative target and systematic non-target analysis of polar organic micro-pollutants along the river Rhine using high-resolution mass-spectrometry – Identification of unknown sources and compounds. *Water Research* 2015; 87: 145-154.
- Saby NPA, Bellamy PH, Morvan X, Arrouays D, Jones RJA, Verheijen FGA, et al. Will European soil-monitoring networks be able to detect changes in topsoil organic carbon content? *Global Change Biology* 2008; 14: 2432-2442.
- Schmid P, Gujer E, Zennegg M, Bucheli TD, Desaulles A. Correlation of PCDD/F and PCB concentrations in soil samples from the Swiss soil monitoring network (NABO) to specific parameters of the observation sites. *Chemosphere* 2005; 58: 227-234.
- Schymanski EL, Singer HP, Longrée P, Loos M, Ruff M, Stravs MA, et al. Strategies to Characterize Polar Organic Contamination in Wastewater: Exploring the Capability of High Resolution Mass Spectrometry. *Environmental Science & Technology* 2014; 48: 1811-1818.
- Silva V, Mol HGJ, Zomer P, Tienstra M, Ritsema CJ, Geissen V. Pesticide residues in European agricultural soils – A hidden reality unfolded. *Science of The Total Environment* 2019; 653: 1532-1545.
- Singer HP, Wössner AE, McArdell CS, Fenner K. Rapid Screening for Exposure to “Non-Target” Pharmaceuticals from Wastewater Effluents by Combining HRMS-Based Suspect Screening and Exposure Modeling. *Environmental Science & Technology* 2016; 50: 6698-6707.
- Stempel S, Scheringer M, Ng CA, Hungerbühler K. Screening for PBT Chemicals among the “Existing” and “New” Chemicals of the EU. *Environmental Science & Technology* 2012; 46: 5680-5687.
- Tuck S, Furey A, Danaher M. Analysis of Anthelmintic and Anticoccidial Drug Residues in Animal-Derived Foods. In: Kay F, MacNeil JD, Wang J, editors. *Chemical Analysis of Non-antimicrobial Veterinary Drug Residues in Food*, 2016, pp. 245-309.
- Zhong M, Wu H, Mi W, Li F, Ji C, Ebinghaus R, et al. Occurrences and distribution characteristics of organophosphate ester flame retardants and plasticizers in the sediments of the Bohai and Yellow Seas, China. *Science of The Total Environment* 2018; 615: 1305-1311.