

Contaminants in Aquatic and Terrestrial Environments

A high-resolution historical record of plant protection products deposition documented by target and nontarget trend analysis in a Swiss lake under anthropogenic pressureAurea C. Chiaia-Hernández, Paul Zander, Tobias Schneider,
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1 **A high-resolution historical record of plant protection products**
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4

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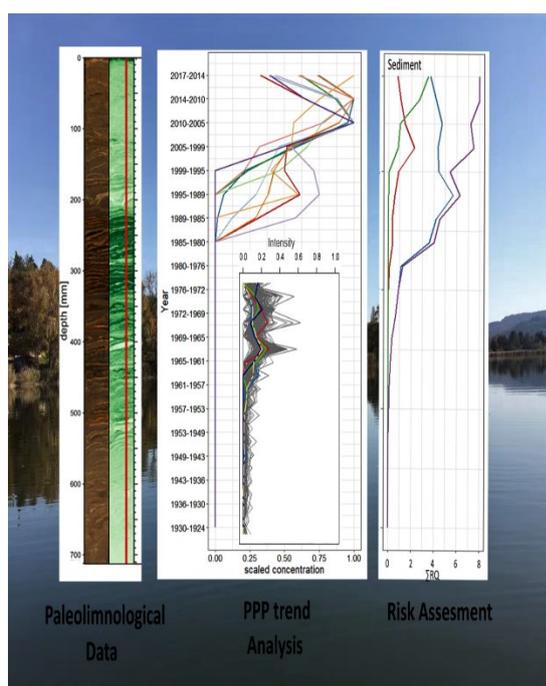
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23

24 **Abstract**

25 A multiproxy-workflow was used to assess > 60 plant protection products (PPP) in sediment
26 samples from a Swiss lake under heavy agricultural pressure. The results show the appearance
27 of PPP for the first time in the early 1960s with an overall detection of 34 PPP and with
28 herbicides and fungicides found in equal proportions. Paleolimnological data (e.g., chronology,
29 hyperspectral imaging of sedimentary green pigments and semi-quantitative elemental
30 composition (μ XRF scans)) suggest that PPP concentrations and fluxes to the sediment over
31 time are not related to land surface processes such as soil erosion or lake biogeochemistry but
32 are attributed mainly to PPP application (inferred from sales) or regulatory measures (bans).
33 Additional compounds with similar sources of contamination as the target PPP captured by
34 nontarget trend analysis (≥ 2000 unknown profiles), reveal significant inputs of contaminants
35 to the lake starting in the 1970s, followed by a decrease of contamination at the beginning of
36 the 1990s and a constant increase by $\sim 28\%$ of the unknown compounds since the year 2000.
37 An ecological risk assessment conducted on detected PPP indicates that since the 1980s the
38 sediment quality is insufficient with risk quotients values displaying maximum levels in the
39 most recent sediments (~ 2010), despite bans of specific PPP and environmental regulations.

40

41 **Introduction**

42 Since the 1960s, application of plant protection products (PPP) increased significantly with the
43 introduction of synthetic insecticides such as organophosphate insecticides in the 1960s,
44 carbamates in 1970s, pyrethroids in 1980s, and the introduction of herbicides and fungicides in
45 the late 1960s–1980s.¹ For instance, the proportion of herbicides in PPP consumption rapidly
46 increased from 20% in 1960 to 48% in 2005.² Prior to the 1980s, there was relatively little
47 concern that water resources could be contaminated with PPP.³ While significant advances have
48 been made in controlling point-source pollution (e.g., wastewater treatment plants (WWTP)),
49 less progress has been made regarding non-point-source pollution (e.g., land runoff, drainage,
50 seepage, spray drift, atmospheric deposition) due to challenges related to the seasonality,
51 inherent variability and multiplicity of origins of non-point sources.^{3, 4} Assessing the fate of
52 PPP in the environment is challenging due to the large variety of properties and applications of
53 PPP across space and time, different transport mechanisms through environmental
54 compartments and depositional processes. Once released into the environment, PPP may
55 undergo different courses (e.g. sorption or degradation) or persist due to their very slow
56 degradation, or “pseudo-persist” due to their continuous release into the environment at rates
57 exceeding degradation rates.⁵ PPP have been studied for decades in different matrices (e.g.,

2

58 plants, food and water)⁶⁻⁸ but surprisingly, not much is known about PPP contamination of lake
59 sediments, largely due to the complexity of sediment analysis and the missing link to
60 paleolimnological methods to obtain good chronologies and to investigate depositional changes
61 over time. Equally, information on toxic effects of organic contaminants in sediments and
62 sediment quality assessments at the international level are lacking, even though sediments serve
63 as habitats and spawning sites for many organisms.

64 Recently, advances in analytical instrumentation like high-resolution mass spectrometry
65 (HRMS) have opened opportunities to provide a comprehensive overview of the occurrence of
66 organic contaminants and their trends over time by using full spectrum mass spectrometry and
67 nontarget MS analysis.^{9, 10} So far, few studies have investigated systematically different PPP
68 classes simultaneously, nor documented the time when PPP appeared in the environment, or
69 explored their change over time as a response to different management practices or
70 environmental changes. Therefore, the objectives of this work were i) to develop an analytical
71 method to study PPP in lake sediments and to reconstruct sedimentary PPP contamination
72 patterns over the last ~90 years in a lake under strong agricultural pressure, ii) to use
73 paleolimnological methods as a complementary tool to better understand the depositional
74 system and provide context for the sedimentary records, iii) to assess the ecological risk posed
75 by the detected PPP, and iv) to use nontarget trend analysis to investigate additional
76 contaminants with similar physicochemical characteristics and input sources of contamination
77 as target PPP.

78

79 **Methods**

80 ***Study site and sampling collection and preservation***

81 Lake Moossee (47.0238°N, 7.4775°E) is an eutrophic and dimictic postglacial lake located 8
82 km north of the city of Bern, Switzerland (Fig. S1). The lake surface is 21.1 ha with a maximum
83 depth of 22 m. The catchment area of Lake Moossee covers 22% forest, 6% settlement, 11%
84 unproductive area, 2% lake, and 59% agriculture.¹¹ The most important crops grown around
85 the area are (in decreasing order): cereals, corn, sugar beet, potatoes, oilseed rape, orchards,
86 vegetables and vines.⁸ Moreover, Lake Moossee is surrounded by a golf course and swimming
87 recreational area (Fig. S1) located east and west of the lake, respectively.

88 In October 2017, a 72 cm (MOOS-17-D) and an 84 cm (MOOS-17-B) long sediment core were
89 retrieved using a free-fall UWITEC gravity corer from a water depth of 18.7 m (Fig. S1).
90 Afterwards, the cores were immediately stored vertically in the dark at 4°C. Before analysis, the
91 sediment cores were split lengthwise, and sectioned at different intervals using stainless steel

92 slicers and transferred to airtight containers. Core MOOS-17-B was used exclusively for dating
93 and was sampled continuously at 2 cm resolution. Core MOOS-17-D was used for quantification
94 of PPP and geochemical analysis and was sampled continuously at 2.6 cm resolution to cover
95 approximately 3 year intervals. After the wet-sediment weight was gravimetrically determined,
96 the samples were lyophilized (Alpha 1-2 LD, Christ GmbH, Germany).

97

98 ***Dating and geochemical analysis***

99 The sediment chronology was established with ^{226}Ra , ^{210}Pb and ^{137}Cs radionuclide dating¹² on
100 the sediment core MOOS-17-B. The isotope activity profiles were measured with gamma
101 spectrometry at the University of Bern. Details about the equipment, background and sample
102 treatment are provided in Tu et al., 2020.¹³ Unsupported ^{210}Pb activities were calculated by
103 subtraction of background activity from the total activity ($^{210}\text{Pb}_{\text{unsup.}} = ^{210}\text{Pb}_{\text{tot}} - ^{226}\text{Ra}$).¹⁴
104 Different age-depth models were tested (CIC, SIT, CRS)^{14, 15} with and without missing
105 inventory (MI) corrections¹⁶ to estimate the effects of the age-depth model selection on the
106 results.¹⁷ Detailed description is provided in Supplementary Information (SI). Additionally, the
107 age-depth models were validated with the ^{137}Cs activity profile, whose peaks were used as
108 independent chrono markers (Fig. S2). The 'CRS-1954 noMI'-model (constrained to the onset
109 of ^{137}Cs at 1954 CE, Fig. S2) performed best regarding the independent ^{137}Cs chrono markers
110 at 1963 CE (nuclear weapon fallout peak) and 1986 CE (Chernobyl fallout peak).^{14, 18}
111 Sedimentary Mass Accumulation Rates (MAR; $\text{g}/(\text{cm}^2 \cdot \text{yr})$) were calculated by multiplying the
112 sedimentation rates (obtained from the CRS age-depth model) by the dry bulk density ((cm/yr)
113 $\cdot (\text{g}/\text{cm}^3)$) and were used for substance-flux calculations. The age-depth model, as well as the
114 MAR, were projected from sediment core MOOS-17-B to sediment core MOOS-17-D
115 following stratigraphic correlation of marker layers (Fig. S3). Additional information about the
116 age-depth modeling can be found in SI.

117 Total carbon (TC), nitrogen (N) and sulfur (S) were measured using an elemental analyzer
118 (Vario EI Cube CNS). Total organic carbon (TOC) was calculated by $\text{TOC} = \text{TC} - \text{TIC}$ where TIC
119 is the total inorganic carbon and was calculated by loss on ignition (LOI, Heiri et al.¹⁹). Values
120 of TC, N, S, LOI, TIC and C/N ratios are provided in Table S1.

121 Semi-quantitative elemental composition was determined using a μXRF core scanner
122 (Avaatech XRF)²⁰ equipped with a rhodium tube. Two scans were conducted at 0.5 mm
123 resolution - one with 10 kV and 10 s exposure, and one with 30 kV and 40 s, to increase the
124 elemental sensitivity.

125

126 ***Hyperspectral Imaging***

127 Hyperspectral measurements of green pigments (defined here as chlorophyll *a* and *b*, and their
128 degradation products) were done using a Specim linescan camera (PFD-CL-65-V10E)
129 following a modified method described in Butz et al.,²¹ (SI). Hyperspectral data were processed
130 using ENVI 5.4 (Exelisvis ENVI, Boulder, Colorado) and the absorption trough associated with
131 green pigments was quantified using a Relative Absorption Band Depth index (RABD)²² in a
132 technique similar to Schneider et al.²³ The RABD_{655-685max} index is reported here as the relative
133 abundance of green pigments and has been linearly correlated with concentrations of
134 chlorophyll *a* and its derivatives in Lake Moossee and other lacustrine sediments, indicative of
135 lacustrine productivity.^{24, 25} Additional details on the hyperspectral measurements are provided
136 in SI.

137

138 ***Clean-up and Enrichment of Sediment Extracts***

139 Sediments were extracted by pressurized liquid extraction (PLE) applying two extraction
140 methods used previously for the extraction of pesticides in soils.²⁶ In brief, around 4 g of
141 homogenized lyophilized sample material combined with ~1 g of diatomaceous earth (Biotage,
142 Sweden) were extracted first with ethyl acetate and acetone at a ratio of 70:30 (v/v) at 80°C and
143 at 130 bar using an ASE 200 (Dionex) to extract neutral compounds. In a second ASE run the
144 same samples were again extracted with 1% phosphoric acid and acetone in a ratio 70:30 (v/v)
145 at 120°C for the extraction of acidic compounds. The extracts were combined and spiked with
146 a mixture of 19 internal standards (absolute amount of 125 ng of each compound) and
147 evaporated to 500 µL using a TurboVap evaporator (Biotage, Sweden) using nitrogen (~8 psi)
148 and at 40°C. The evaporated extracts were mixed with 4.5 mL of ultra-pure water (MilliQ,
149 Millipore) and 5 mL of acetonitrile. The sediment matrix was removed using QuEChERS with
150 C₁₈ as a dispersive solid phase extraction (250 mg Endcapped C₁₈, BGB Analytik).

151

152 ***Liquid Chromatography Tandem Mass Spectrometric (LC-MS/MS) Detection***

153 Compound separation was performed at 35°C on a 3.0 X 2.0 mm X 3.5 µm particle size C₁₈
154 security guard cartridge connected to a 2.1 X 50mm X 3.5 µm particle size XBridge C₁₈ column
155 using an Agilent 1260 Infinity II HPLC system (Santa Clara, CA) by injecting 10 µL of extract.
156 The mobile phase consisted of 100% MilliQ water (A) and methanol (B) with formic acid, 4.5
157 mM ammonium formate and 0.5 mM ammonium fluoride added to the eluents. System
158 parameters, elution and gradient details are provided in Table S2 and S3 in SI.

159 Detection and quantification of analytes were carried out using a 6460 Agilent Triple Quad
160 system with positive and negative electrospray ionization (ESI, JetStream) in different runs
161 using dynamic multiple reaction monitoring (dMRM). In total, 215 transitions were acquired to
162 quantify 66 PPP, 5 transformation products (TP) and 19 internal standards.

163 Substance selection was based on PPP registered and sold in Switzerland that have been
164 reported to be applied to Swiss soils or detected in sediment samples from other Swiss lakes.²⁶
165 ²⁷ Internal standards used for quantification were selected by best fit to retention time, structure
166 similarity as well as method performance. Details on the sources of reference standards,
167 reagents, dMRMs, and specifics on parameters are provided in the SI.

168

169 *Accuracy and Precision*

170 First, sediment extracts of homogenized blank sediments (here older than 100 years) were
171 spiked after PLE extraction with a mix of pesticide standards (absolute amount of 200 ng of
172 each compound) in quadruples to evaluate the clean-up (liquid-liquid extraction (LLE) -
173 QuEChERS) performance. Furthermore, the whole method performance (PLE and LLE) was
174 assessed on homogenized blank sediments (n=4) spiked with the same concentration of
175 pesticide mix and stored in closed containers at 4°C for 24 hours. The sediments were then
176 immediately extracted by PLE followed by LLE clean-up. All the samples were spiked with an
177 internal standard pesticide mix solution after extraction for quantification.

178

179 *Limits of Detection and Quantification*

180 Method limits of detection (LOD) and quantification (LOQ) were calculated using the signal to
181 noise ratios (S/N). LOD values were defined as the lowest concentration in a matrix matched
182 calibration curve with a $S/N \geq 3$. LOQ values were defined as the lowest point in a matrix
183 matched calibration curve with a S/N ratio of 10 and MS/MS fragmentation.

184

185 *Data Analysis of Target PPP*

186 PPP fluxes were calculated from sediment concentrations (pg/g_{dw}) multiplied by MAR (g/
187 (cm²·yr¹)). Identification of trends was performed using agglomerative hierarchical cluster
188 analysis (HCA) with the linkage method of Ward.²⁸ The distance matrix was based on the
189 Euclidean distance of the standardized concentrations (mean = 0 and standard deviation = 1).
190 The statistical analysis was executed with the open-source software R including the package
191 "*cluster*".^{29, 30} PPP sales volumes used in this work were reported by the Federal Office for
192 Agriculture (FOAG-BLW) and the Federal Department of Economic Affairs, Education and

193 Research (EAER-WBF) and cover the period from 2008 to 2018. Although, the local use of
194 PPP is documented in agricultural diaries, the data are not publicly available. Therefore, sales
195 data used here represent all of Switzerland.

196

197 ***Ecological Risk Assessment***

198 An ecological risk assessment (ERA) was conducted based on ecotoxicity data from freshwater
199 organisms since not enough ecotoxicity data for sediment-dwelling organisms are available.
200 Risk quotients (RQ) were calculated based on chronic environmental water quality standards
201 (AA-EQS) and measured concentrations. The AA-EQS values were derived in accordance with
202 the Technical Guidance Document of the European Union.³¹ AA-EQS values were taken from
203 the proposal for acute and chronic quality standards from the Swiss Center for Applied
204 Ecotoxicology³² or from Environmental Quality Criteria (EQC) values derived from different
205 literature as detailed in SI. For transformation products, the AA-EQS values of the parent
206 compounds were considered for the risk assessment since no EQC values were available. RQ
207 values for sediment and predicted pore water concentrations (C_{ipw}) were calculated by using the
208 organic carbon sorption coefficient values (K_{oc}), sediment concentration (C_{ised}), and the fraction
209 of organic carbon (f_{oc}) of the lake as described in detail in SI. Mixture toxicity (ΣRQ) was
210 evaluated using a concentration addition model by adding individual RQs for each sample as a
211 first tier assessment irrespective of the modes/mechanisms of action of the mixture
212 components.³³ Furthermore, ΣRQ were calculated according to PPP classes as performed by
213 Moschet et. al.,⁸ in order to determine which substance classes contributed the most to the total
214 environmental risk. Details on the ERA, equations, values used, and RQ values description are
215 reported in Table S6, S7 and S9 and in SI.

216

217 ***Visualization of Nontarget Trend Analysis***

218 Nontarget trend analysis was used as an exploratory tool to investigate the overall
219 contamination of Lake Moossee and was performed by a high resolution mass spectrometer
220 (HR-MS) using a quadrupole Orbitrap (Q-Exactive Plus, Thermo Fisher Corp., USA) at the
221 Bernese cantonal laboratories. Full scan accurate mass spectra were acquired from 100 to 800
222 Da with resolving power of 140000 reference to 200 m/z and mass accuracy of ± 5 ppm using
223 electrospray ionization (ESI) in positive and negative ionization in independent injections.
224 Details of chromatographic separation and detection have been described in details elsewhere.¹⁰
225 Temporal trends were detected by sorting identical exact masses into time series using
226 enviMass version 4.0 using configurations as described by Chiaia-Hernández et al., 2017.¹⁰

227 Mass recalibration, global intensity correction, RT alignment and blank subtraction were
228 included within the enviMass workflow. The profiles obtained were not grouped further to
229 avoid loss of information. However, ~20% of the total masses are expected to be isotopes and
230 adducts from the detected profiles.¹⁰ Blank subtraction was performed automatically with
231 homogenized blank sediment samples (~100 years old). Nontarget trend detection to identify
232 compounds of anthropogenic origin was performed using Spearman rank correlation ($\rho \geq 0.5$)
233 and agglomerative HCA with data scaling (divided by the sum of the profile), measurement of
234 similarity (Euclidean distance) and clustering (Ward's minimum variance) as described in
235 previous work.¹⁰ Identification of profiles (features) was performed by an *in-house* suspect
236 screening list using enviMass version 4.0 and > 200 reference standards and includes
237 pharmaceuticals, personal care products, industrial chemicals and pesticides.^{27, 34}

238

239 **Results and Discussion**

240 *Method Performance*

241 The accuracy and precision of the method are illustrated in Fig. 1. The results show average
242 recoveries of 80% (range from 40-120%) and method precision, indicated by relative standard
243 deviation (RSDEV %), of 8% (range from 2 to 24%). Accuracy and precision of individual PPP
244 as well as LLE recoveries are provided in Table S8. There was no correlation between
245 recoveries and log K_{ow} values ($r^2=0.288$, $p=0.018$) as shown in Fig. S4. LOD and LOQ values
246 are reported in Table S8 and range from 60 to 600 ng/kg_{dw} with an average of 80 ng/kg_{dw} and
247 from 60 to 1250 ng/kg_{dw} with an average of 220 ng/kg_{dw}, respectively. Overall, the results show
248 that a modified clean-up method originally developed for detecting pesticides in soils²⁶ can be
249 successfully applied to sediment samples to detect PPP covering different compound classes
250 and polarities (log K_{ow} -1.7 to 5.2, pKa 1 to 12). Additionally, the method shows similar or
251 significantly improved recoveries, RSDEV (%) and lower LOQ values when compared to other
252 sediment extraction methods for PPP conducted with HR-MS/MS and triple-quadrupole (QqQ)
253 instruments.³⁴⁻³⁸

254

255 *Lake sediment properties and context*

256 Sediments consist of brown organic-rich silt with light-colored endogenic calcite laminations.
257 The ²¹⁰Pb chronology (Fig. 2) indicates relatively constant sedimentation rates during the past
258 100 years. MAR vary from 0.09 to 0.23 g/(cm²·yr¹). The abundance of green pigments
259 (chlorophylls and diagenetic products) shows an increasing eutrophication trend beginning in
260 1925, with the greatest algal production occurring from 1960-1980. This period is associated

261 with better seasonal lamination preservation in the biogenic varves (indicative of anoxic bottom
262 waters), higher flux of TIC (increased calcite precipitation), and slightly reduced TOC:TN
263 ratios (indicative of a shift toward higher proportion of aquatic organic matter). We attribute
264 this period of enhanced lacustrine productivity to increased concentrations of P, which were
265 observed in many lakes across Switzerland.³⁹ The introduction of a P trapping wastewater
266 treatment plant (WWTP) in 1963, regulatory measures in the agricultural sector, and the ban of
267 phosphates in detergents in 1986 led to the reduction of external P loadings to the lake, and a
268 subsequent decline in aquatic production can be observed in decreased green pigment values
269 after 1980. The sediments above 20 cm (approximately 1981 and following years) appear to be
270 increasingly bioturbated and there is a shift towards less TIC and Ca. These changes are related
271 to reduced productivity, which led to reduced hypolimnetic oxygen consumption and decreased
272 precipitation of calcite. Overall, there is little long-term trend in Ti counts, indicating generally
273 consistently low input of detrital material from the catchment and low surface processes (soil
274 erosion) in the catchment. Sulfur (S) is consistently present throughout the record, indicating
275 that sediments remained anoxic during the study period.⁴⁰ The greater variability of the
276 elemental composition in the lower part of the sediment (prior to 1986) is related to better
277 preservation of seasonal laminae and the absence of bioturbation. Bioturbation in the upper part
278 smooths out seasonal variability of the sediment composition.

279

280 ***Plant Protection Products in Sediments***

281 Sediment analysis of Lake Moossee reveals the presence of 34 PPP, which corresponds to ~50%
282 of the investigated compounds (Fig. S5). PPP start appearing in the lake for the first time in the
283 early 1960s with 74% of the PPP showing highest concentrations between the 1980s and late
284 1990s and with 26% still on the rise. Herbicides and fungicides were equally found in sediments
285 with 16 compounds in each class and only two insecticides detected. Since 2005, fungicides are
286 the dominant class of PPP suggesting additional input sources to the lake or a change of land
287 use. Based on PPP concentrations (normalized to TOC) and fluxes patterns over the last ca. 90
288 years, detected PPP can be divided in five clusters as illustrated in Fig. 3 and S6.

289

290 ***Cluster Analysis of PPP***

291 *Cluster 1*

292 Five herbicides (atrazine, dinoseb, isoproturon, linuron, nanopramide), one fungicide
293 (metalaxyl-M), and one TP (terbuthylazine-2-hydroxy) fall into this cluster. These seven PPP
294 show the highest concentrations between the 1980s and the 1990s, followed by a systematic

295 increased between 2005 to 2010 and a constant decrease towards the sediment surface (2017).
296 These decreasing trends reflect the ban of some herbicides like dinoseb in 2002 and atrazine in
297 2012 in Switzerland or the drop in sales of these compounds. For example, sale volumes
298 obtained for isoproturon and linuron in the last twelve years have dropped between 80% and
299 100%, respectively (Fig. S7).

300 Despite the ban of dinoseb and atrazine, they can still be detected in more recent sediments,
301 revealing their persistence in the environment. This is in line with latest studies that detected
302 atrazine and its TP in more than 80% of Swiss groundwaters.⁴¹ PPP can reach groundwater and
303 lake systems by seepage from agricultural soils.^{41, 42} During this process, PPP may undergo
304 natural attenuation processes such as sorption or degradation processes.^{41, 42} Therefore, while
305 the surface water contamination usually relates to PPP application during the farming season,⁴³
306 the contamination of groundwater and sediments with PPP demonstrate the transport and
307 persistence of these substances across different compartments of the environment. In 2012,
308 isoproturon, linuron and metalaxyl-M were reported in river catchments distributed over the
309 Swiss plateau, however, additional PPP reported here were not detected.

310

311 *Cluster 2*

312 This cluster includes the herbicides chloridazon, diuron and simazine, which all show
313 increasing fluxes in the late 1960s and a sharp decrease towards the present (2017). Introduction
314 of these herbicides to the lake (before 1970) and first peak fluxes are visible earlier than the
315 other detected PPP, which is consistent with the marketing of chloridazon and simazine in the
316 1960s and diuron in the 1950s.⁴⁴ Herbicides in this cluster, along with other PPP in cluster 1
317 (e.g. atrazine, isoproturon, nanopramide and a TP of terbuthylazine), are some of the oldest PPP
318 reported.⁴⁴ The ban of simazine in 2012 and the reduced sale-volumes of chloridazon (e.g., 80%
319 since 2008) and diuron can be observed with PPP concentrations close to zero (<LOD) in recent
320 sediment layers (Fig. 3 and S7). The temporal trend of reconstructed fluxes of these three
321 herbicides in Lake Moossee are in agreement with their detection in different environmental
322 compartments such as groundwater, surface waters, soil and, to a lesser extent, in sediment
323 samples.^{8, 26, 41, 44}

324

325 *Cluster 3*

326 Six PPP are included in this cluster with highest fluxes around 2005 to 2010, followed by a
327 constant decrease towards the sediment surface, with some compounds reaching concentrations
328 below their LOD (e.g. fungicide cyprodinil). Peak fluxes from PPP included in this cluster lag

329 by 10-20 years compared to the fluxes of compounds contained in clusters 1 and 2. In cluster
330 3, orbencarb is the only herbicide detected and fungicides are the dominant pesticide class as
331 shown by high abundances of carbendazim, fenpropimorph, flusilazole, and prochloraz. The
332 findings are surprising since herbicides are usually reported as the most detected pesticide class
333 in surface waters close to agricultural catchments.^{8, 45} In 2015, fungicides were one of the most
334 widely use PPP in Europe (42%), followed by herbicides (34%).⁴⁶ Therefore, our findings could
335 suggest a higher availability and thus a higher use of fungicides in the last years. Furthermore,
336 the availability of analytical standards to detected fungicides has significantly expanded (last
337 10 years) helping to identify fungicides not studied in the past due to the lack of reference
338 materials. The increasing number of fungicides detected might be also attributed not only to
339 agriculture fields but perhaps to additional sources of contamination. In 2003, a golf course was
340 built at the east side of the lake (Fig. S1). Thus, the increased of fungicides could be linked to
341 the golf course and might explain the systematic increased of PPP in cluster 1 around the same
342 time. Fungicides (e.g., carbendazim and prochloraz) and insecticides are frequently applied to
343 golf course turfs to control surface activities of earthworms and management of fungal
344 diseases.^{47, 48} So far, water quality monitoring has focused on agriculture chemicals⁸, however,
345 pesticides applied to turfgrass systems like golf courses, home lawns and parks have rarely been
346 included in monitoring campaigns.⁴⁹ To pinpoint the specific reason for the increase of
347 fungicides in Lake Moossee further studies are needed (e.g., spatial analysis). The decrease
348 trends observed in this cluster are consistent with the bans (e.g., orbencarb since 2011 and
349 carbendazim in 2018) and sales reduction of these fungicides (Fig. S7) with the exception of
350 fenpropimorph, whose sales have been increasing in the last 10 years but its concentrations
351 have constantly decreased since the late 1990s. Moreover, carbendazim shows a surging
352 concentration towards 1980 following by a decreased around the 1990s resembling a similar
353 trend as diuron (cluster 2). The decrease in concentration might be linked to the implementation
354 of the Water Protection Act (WPA, 1991) in Switzerland, however, this pattern is not reflected
355 in any other PPP and additional trend interpretation based on PPP application, sales or soil
356 management is not possible since the data is not publicly available. From this cluster,
357 carbendazim, cyprodinil, flusilazole, and fenpropimorph have been reported in surface and
358 groundwaters in Switzerland.^{8, 41}

359

360 *Cluster 4*

361 In this cluster, PPP show a delay in peak concentrations of >15 years compared to compounds
362 in cluster 1. Cluster 4 includes ten PPP with peak concentrations in the last 12 years and

363 decreasing trends over the recent years, except for the herbicides diflufenican, metolachlor and
364 pendimethanil and the insecticide fipronil (Fig. 3). Additional PPP in this cluster are the
365 fungicides cyproconazole, propiconazole, tebuconazole, fenpropidin and fludioxonil, and the
366 herbicide ioxynil. In Switzerland, the application of ioxynil has been prohibited since 2018.
367 However, decreasing fluxes of ioxynil can be observed already before the ban (from 2005
368 onwards; Fig. 3). The reconstructed PPP fluxes in this cluster are consistent with their sales
369 patterns except for the insecticide fipronil. Fipronil has been banned in Switzerland since 2011
370 due to its high toxicity to bees.⁵⁰ Thus, its detection in recent sediment layers could be attributed
371 to a delay from fipronil last application or for other additional sources. Fipronil was also used
372 for seed treatment in low amounts and as biocide. However, data on these application are not
373 available.⁵¹ Fipronil has been detected in surface waters⁸ and its TPs have been recently
374 reported to occur in sediment samples and in groundwater with direct influences of agriculture,
375 which is in agreement with our results.^{27, 41} Similar to our findings, a recent study reported a
376 wide distribution of antifungal azoles chemicals (e.g., cyproconazole, propiconazole,
377 tebuconazole) in aquatic and terrestrial ecosystems.⁵² Besides fipronil, only the herbicide
378 metolachlor and the fungicide fenpropidin have been reported in groundwater and surface
379 waters, respectively.^{8, 41}

380

381 *Cluster 5*

382 Eight PPP are included in this cluster (the fungicides azoxystrobin, difenoconazole,
383 epoxiconazole, fluazinam; the herbicides flufenacet, fluopicolide, prosulfocarb; the insecticide
384 chlorpyrifos) with constantly increasing fluxes since the 1990s (Fig. 3). PPP in this cluster show
385 a delay in peak concentrations of >19 years against compounds in clusters 1. In this cluster,
386 sales volumes do not always compare with the trends observed. The increasing trends of PPP
387 in this cluster might suggest a preference of the farmers for these substances in recent years, a
388 change in land use and/or additional contribution from other sources (e.g., golf course since
389 2003). In 2012, cereals were reported as the most important crops in the lake catchment,⁸ which
390 is in agreement with the use of fungicides detected and their usual application to control
391 diseases in cereals. The PPP detected are also applied to other crops such as root crops, legumes,
392 and fruit trees, in addition to cereals, which might indicate a shift in land use. The increase in
393 fungicides could be also attributed to the use of fungicides in the golf course as in the case of
394 carbendazim and prochloraz in cluster 3, cyproconazole, propiconazole, tebuconazole and
395 fludioxonil in cluster 4, and azoxystrobin in cluster 5, which are fungicides usually applied to

396 turf grasses.^{48, 49} However, additional studies are needed to identify the main reason for the
397 increase of fungicides in Lake Moossee in the last ~12 years.

398 With the exception of fluopicolide all the PPP in this cluster have been reported to occur in
399 surface waters but not yet in groundwater.⁸

400

401 ***Risk Assessment***

402 Since 2010, concentrations of individual sedimentary PPP range from <1 to 300 $\mu\text{g}/\text{kg}_{\text{oc}}$ with
403 the fungicides difeconazole and epoxiconazole, the herbicides prosulfcarb, diflufenican, and
404 phedimethanil having the highest concentrations (Fig. S5). Single substance risk assessment,
405 which is the least conservative risk assessment scenario, resulted in good sediment quality for
406 most of the detected PPP with RQ values <1. However, the herbicides diflufenican and dinoseb
407 show values of $1 \leq \text{RQ} \leq 2$ (moderate) and the organophosphate insecticide chlorpyrifos display
408 values of $\text{RQ} \geq 4$ (insufficient). RQ values >1 indicate impaired sediments that may pose a risk
409 to aquatic organisms. Studies carried out at sites NAWA SPEZ in Switzerland in 2017
410 demonstrate that chlorpyrifos showed the highest concentrations among the target PPP in
411 stream sediment samples, which is consistent with our results.⁵³ Chlorpyrifos, banned in
412 Switzerland as 2020, is known for its high toxicity to fish, aquatic invertebrates, bees and
413 bumblebees.⁵⁴

414 PPP do not occur as single substances in the environment; thus, organisms are usually exposed
415 to mixtures of substances. In this work, mixture toxicity was assessed as the worst-case scenario
416 (ΣRQ). Following this approach, the results show that ΣRQ values started from $\Sigma\text{RQ} \leq 1$ (good)
417 in the 1970s to $2 \leq \Sigma\text{RQ} \leq 8$ (insufficient; Fig. 3) starting in the 1980s. The high toxicity risk
418 quotients are mainly attributed to herbicides and insecticides with calculated $\Sigma\text{RQ} \geq 3.5$
419 (insufficient), accounting each for more than 40%. Even though, in this work, only two
420 insecticides were detected, the ΣRQ values are mainly attributed to chlorpyrifos. The high EQS
421 obtained for chlorpyrifos can be ascribed mainly to a combination of higher concentrations
422 found in the sediments ($\geq 28 \mu\text{g}/\text{kg}_{\text{oc}}$) and high predicted K_{oc} values used when compared to
423 other detected PPP. Subsequently, fungicides contribute only 10% to the toxicity risk even
424 though they were equally abundant as herbicides. Lake Moossee is used as a recreation area
425 with swimming facilities in the summer. The risk assessment performed in this work does not
426 evaluate the risk posed to humans. Therefore, our findings call for studies to evaluate the
427 exposure of people who frequently use these recreational areas.

428 Porewater is a major route of exposure of many benthic organisms to contaminants since
429 contaminants in this matrix are more bioavailable.⁵⁵ Thus, pore water concentrations were

430 predicted based on sediment concentrations between 2014-2017 (top layer). Pore water
431 concentrations range from non-detectable to 130 ng/L with the TP of the herbicide
432 terbuthylazine, the fungicide carbendazim, and the herbicides prosulfocarb, atrazine and
433 dinoseb as the top five PPP in decreasing order. Sedimentary concentrations of up to 5 ng/kg_{oc}
434 were measured for the banned compounds atrazine and dinoseb (banned in 2012 and 2002,
435 respectively) in the most recent sediments. While their \sum RQ values are lower than 2 (moderate),
436 atrazine and dinoseb detection emphasize their persistence and their lagged contamination of
437 the lake.

438 Previous studies conducted in Lake Moossee, report high stability of pesticides and TPs at
439 different water depths under anaerobic conditions with TP strongly outweighing parent
440 compounds.⁵⁶ In our study, only a few TP were included as a proof of concept. However, the
441 detection of the terbuthylazine TP in sediments reveals the persistence and mobility of TP and
442 the need to include them in future studies. Calculated RQ values, pore water predicted
443 concentrations and physico-chemical properties are reported in Appendix A and in SI Table S8
444 and S9.

445

446 *Nontarget Trend Analysis of Lake Moossee Sediments*

447 Nontarget trend analysis was used in this work to capture additional anthropogenic organic
448 contaminants not covered in the PPP target analysis. Profiles captured by sorting identical exact
449 masses into time series, reveal >2,000 profiles of unknown compounds in positive ionization
450 and >900 in negative ionization. The profiles were grouped by HCA and divided in six clusters
451 as illustrated in Fig. 4. The nontarget clusters display similar trends obtained by target analysis
452 as demonstrated for cluster A and E for selected targeted substances and unknown compounds
453 (profiles shown in grey, Fig. 4). Only cluster A and B (\leq 28% of the unknown compounds)
454 show increasing concentrations until today as revealed by the higher color intensities in the heat
455 map. Examples of targeted PPP in cluster B encompass the fungicides prosulfocarb and
456 difeconazole which show constant increasing concentration since the 1990s (cluster 5 in Fig 3
457 and S8).

458 Input of many more substances than identified with the target analysis start appearing in the
459 1970s, followed by a decrease of contaminants at the beginning of the 1990s and a constant
460 increase of different types of contaminants (\leq 28%) since the year 2000. The observations can
461 be related to the increase in agriculture and PPP production as well as the construction of a
462 highway in the catchment in the 1970s.³ Between the 1960s and late 1980s implementation of
463 environmental policies and water protection initiatives helped to stop some organic

464 contaminants reaching the lake, as seen in Fig. 4 (dotted line) with the disappearance of some
465 profiles. However, the removal of contaminants in Lake Moossee after the 1980s was not as
466 significant as observed for other lakes (e.g., Lakes Greifensee and Lugano) in Switzerland,¹⁰
467 indicating that contaminants originated from WWTP effluents have little or no substantial
468 presence in the lake. The constant increase of additional contaminants since the year 2000 as
469 seen in Fig. 4 (Cluster A, dash-point line,) is consistent with the construction of a golf course
470 built at the east side of the lake in 2003. However, further studies are needed to find the specific
471 reason of this increase. Due to the coverage of the analytical method employed (e.g., log Kow
472 -1.7 to 5.2, pKa 1 to 12, nonvolatile), the nontarget visualization and the description of the
473 catchment, the unknown compounds are most likely compounds (including TP) with similar
474 physicochemical characteristic as the target PPP entering the lake by diffuse input sources (e.g.,
475 turfgrass, agriculture, livestock systems). Additional sources of contamination are compounds
476 (e.g., biocides) released by urban environments, such as compounds leaching from the adjacent
477 highway ($\geq 33\text{m}$) and material protection agents on facades and roofs. As a proof of concept and
478 to support our assumptions, suspect screening was performed to capture additional organic
479 contaminants not covered by the target analysis. The suspect screening resulted in the
480 confirmation of four additional compounds which include i) the herbicide chlorotoluron (cluster
481 A, Fig. 4) used for controlling grass weeds in cereals, cotton and fruit production,⁵⁷ ii)
482 propazine-2-hydroxy a TP of the herbicides prometon, prometryn, and propazine (cluster E, fig
483 4), and iii) the biocides irgarol and 2-octyl-2H-isothiazol-3-one (OIT). The identified PPP and
484 biocides support our assumptions. The nontarget trend analysis highpoints that the target
485 analysis of >60 prioritize PPP falls too short for a comprehensive assessment of organic
486 pollutants and risk assessment. In this work, only ~2% of nontarget time series with increasing
487 concentrations (intensities) until today are known (600 profiles - cluster A and B in Fig.4 and
488 S8). Thus, further efforts need to be put on the identification of major sources of contamination
489 to the lake as well as on the identification of unknown substances using much larger databases
490 (e.g NORMAN SusDat)⁵⁸ which could allow the tentative identification of many more
491 compounds.

492

493 ***Insights and Future Research***

494 The applied analytical method helped to identify more polar and mobile compounds than
495 previously reported in PPP sediment analysis. Our findings confirm that PPP embedded in
496 sediments are often quite stable, especially under anaerobic conditions. By adopting
497 paleolimnological methods (e.g., chronology, hyperspectral measurements of sedimentary

498 green pigments and XRF) and applying a multiproxy-workflow, our work reveals that PPP
499 fluxes are not related to sedimentological processes such as soil erosion (Ti counts, XRF) or
500 lake biogeochemistry like precipitation of calcite or lake productivity (green pigments, HSI).
501 While there is some evidence for less anoxic conditions after the 1980s with poorer varve
502 preservation, there is no strong effect from this change in the PPP data. As a result, post-
503 depositional processes or variations in sediment binding do not majorly influence PPP fluxes
504 over time and PPP behavior can be related mainly to sales (used as a proxy for PPP application)
505 or bans.

506 Sediment records indicate PPP start appearing in the lake for the first time in the early 1960s
507 with herbicides and fungicides being equally found in sediments. The detection in recent
508 sediment layers of PPP that are not yet reported in other environmental compartments (e.g.
509 groundwater) can help identify possible persistent compounds in the future. The nontarget
510 analysis reveal significant inputs of contaminants to the lake starting in the 1970s, followed by
511 a decrease of contaminants at the beginning of the 1990s and a constant increase of different
512 type of contaminants since the year 2000. Based on suspect screening additional PPP
513 (chlorotoluron and propazine-2-hydroxy) and two biocides (irgarol and OIT) were confirmed.
514 The risk assessment on targeted PPP indicates that since the 1980s the sediment quality is
515 insufficient. RQ values displayed maximum levels in the most recent sediments, despite bans
516 of specific PPP and environmental regulations. Until today, there are no legal regulations in
517 place concerning sedimentary PPP concentrations. Neither exists any harmonized approach to
518 assess sedimentary quality regarding PPP. Thus, due to the absence of AA-EQS for sediments,
519 the risk assessment conducted in this work for detected PPP is only a rough estimation but
520 overall the true risk is much higher since >2000 unidentified compounds were not included in
521 the assessment.

522 Lake systems like Lake Moossee are abundant in the Swiss plateau and Europe and are often
523 used as freshwater supplies. Therefore, our findings are likely representative of many
524 agriculturally influenced lakes in Europe. The present study calls for further studies to
525 investigate the mechanisms of organic contaminants in sediments, particularly, how PPP and
526 other organic contaminants are reaching the lake and the lake sediments, and if these
527 compounds can be remobilized. Equally, there is an urgent need to establish AA-EQS for
528 sediments and to understand how sedimentary PPP affect lacustrine ecosystems.

529

530 **Supporting Information**

531 Additional information on site description, chronology, analytical methods, method
532 performance, fluxes, concentrations and temporal patterns, and risk assessment of PPP.

533 **Appendix A**

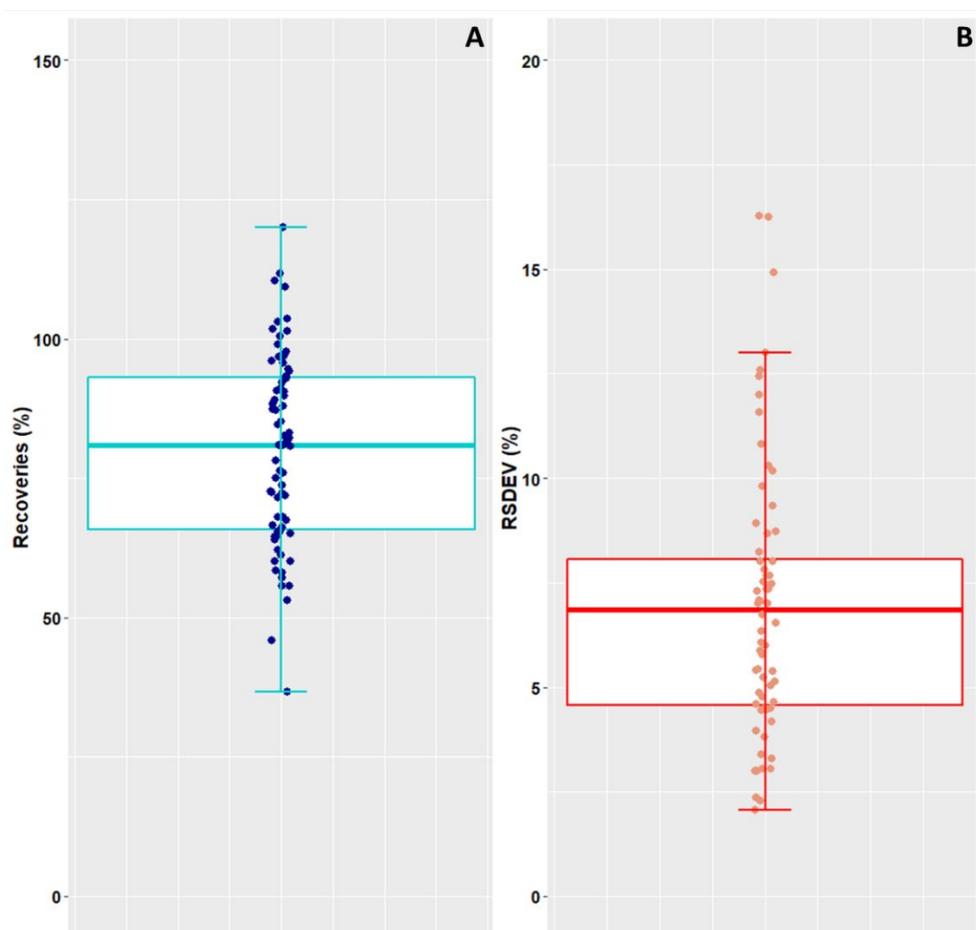
534 Fluxes, concentrations, risk quotients and pore water concentrations. Raw files of HR-MS
535 data are available on request.

536

537 **Acknowledgements**

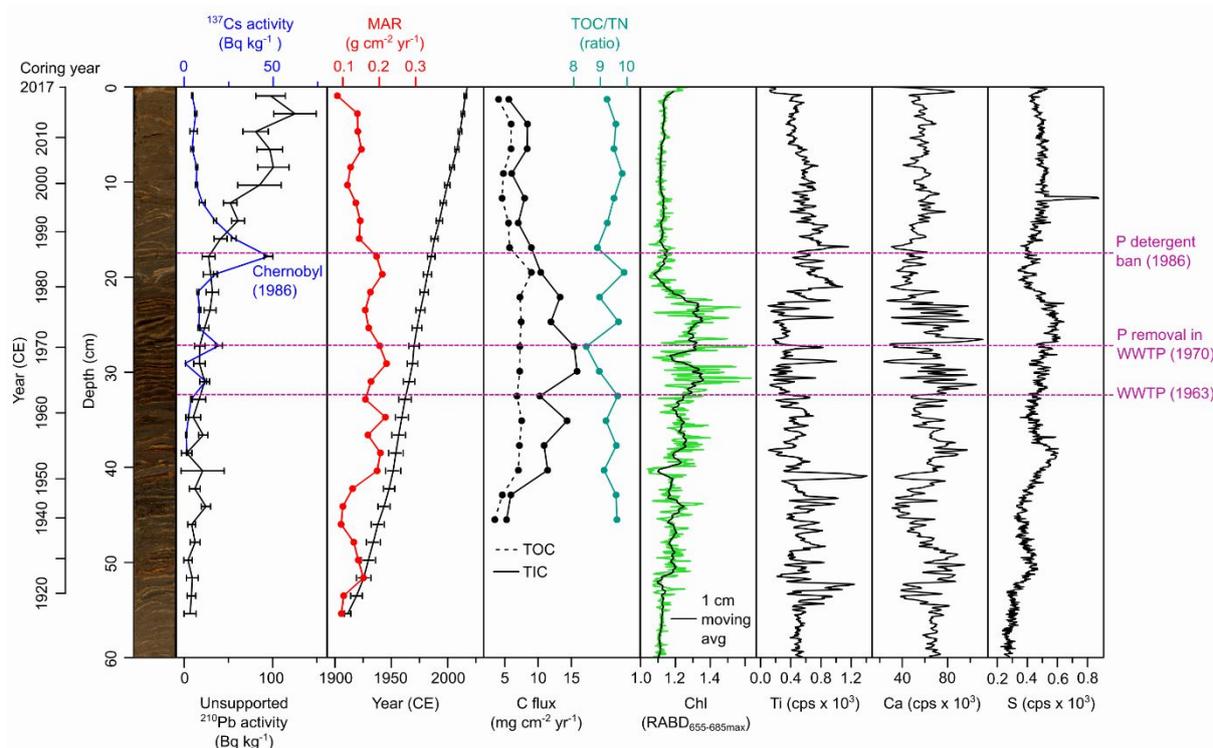
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546

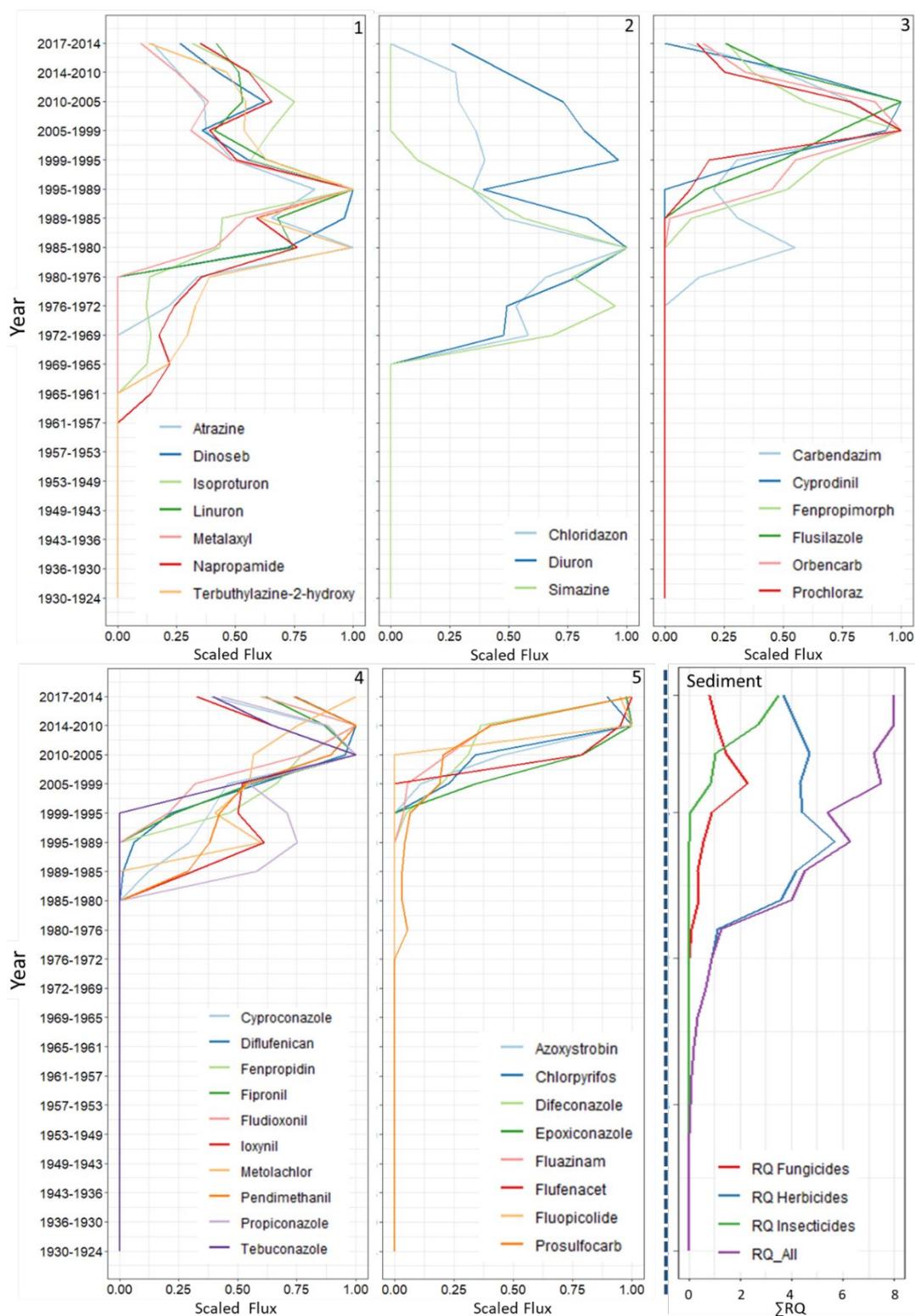


547

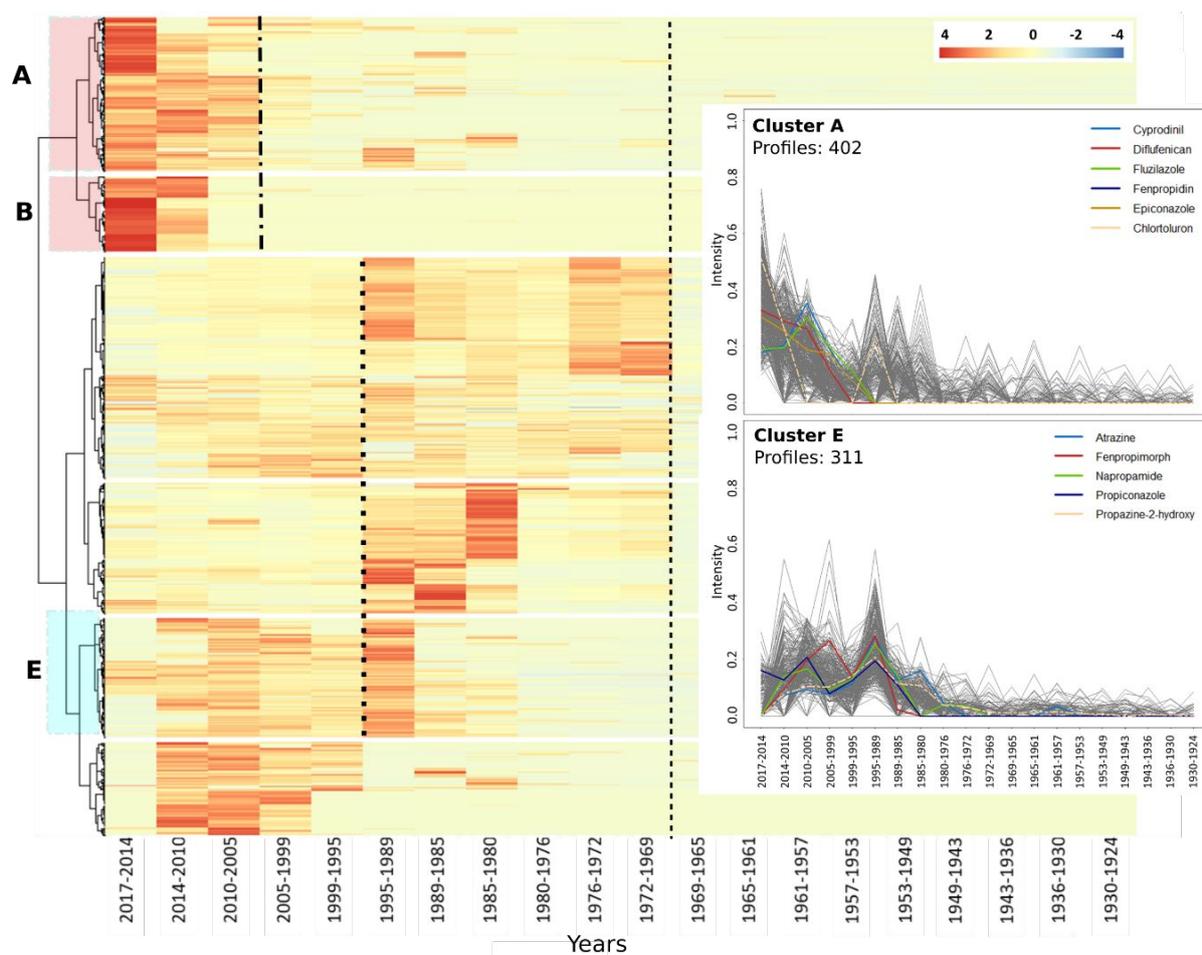
548 Fig. 1. Method accuracy and precision of 66 PPP and five transformation products with box
 549 plots showing recoveries (%), A panel in blue) and relative standard deviation (RSDEV %), B
 550 panel in red). Color points represent individual measurements. Accuracy and precision of
 551 individual PPP is provided in Table S8.
 552



553 Fig. 2. Illustrates, from left to right, a sediment core picture of Lake Moossee (MOOS-17-D),
 554 Cesium (^{137}Cs) and lead ($^{210}\text{Pb}_{\text{unsupported}}$) activity, mass accumulation rates (MAR), total organic
 555 carbon (TOC), total inorganic carbon (TIC), ratios of TOC to total nitrogen (TN), abundance
 556 of green pigments (Chl), titanium (Ti), calcium (Ca), and sulfur (S). Pink horizontal lines
 557 represent the installation of the first wastewater treatment plant (WWTP) in the catchment in
 558 1963, phosphorus removal in WWTP in 1970, and the ban of phosphorus in detergents in 1986,
 559 respectively.
 560



561
 562 Fig. 3. Vertical concentration profiles sorted by hierarchical cluster analysis of 34 PPP (panel
 563 1-5) detected in sediments of Lake Moossee showing five different clusters over time with
 564 scaled fluxes. The panel on the lower right shows mixed toxicity values (Σ RQ) for sediments
 565 with PPP total contribution (RQ_ALL) and their contribution for each PPP class (fungicides,
 566 herbicides, and insecticides).



567
 568 Fig. 4. Heat map of unknown standardized substances grouped by hierarchical cluster analysis
 569 (HCA) detected in sediments of Lake Moossee in positive ionization ($n = 2,073$). Significant
 570 inputs of contaminants are visible at the beginning of the 1970s (dash black line).
 571 Environmental policies and water protection initiatives between the 1960s and late 1980s had
 572 an effect in the lake shown by the decreased of signals of unknown profiles (point line). Cluster
 573 A and B highlight new features appearing since 2005 and still increasing until today (dash-point
 574 line). Plots of cluster A and E are plotted with the corresponding captured profiles (grey),
 575 detected target compounds and new detected compounds (dotted white lines) in same cluster.
 576
 577

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611 [ocuments/BVE/AWA/de/GBL/SeenDivers/GBL_Kleinseen_2003.pdf](https://www.bve.be.ch/bve/de/index/wasser/wasser/gewaesserqualitaet/Seen.assetref/dam/documents/BVE/AWA/de/GBL/SeenDivers/GBL_Kleinseen_2003.pdf). Accessed on
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