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Pesticide residues in European sediments: a significant concern for the aquatic systems?

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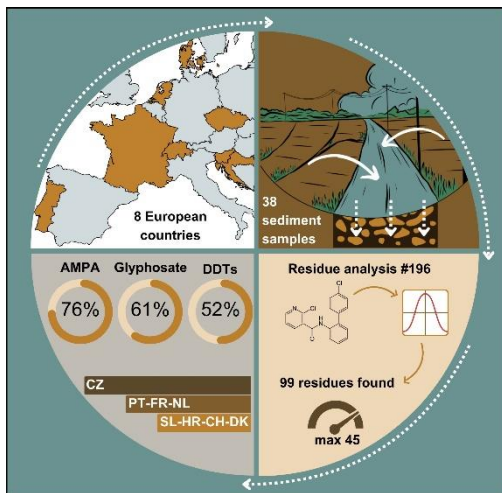
34 **Abstract**

35 The presence of pesticide residues in waterbed sediments poses a significant concern for
36 aquatic ecosystems' health. This study examined pesticide contamination in sediments of 38
37 water bodies, embedded in agricultural-dominated regions, across eight European countries.
38 Three indicators were targeted: occurrence, type, and concentrations of multiple pesticide
39 residues in sediments. 196 pesticide residues (including degradation products) were tested in
40 the sediment samples. The analytical results showed that only one sample was 'pesticide-
41 free', three samples contained a single pesticide residue, and the remaining 34 samples
42 contained mixtures of residues. Overall, 99 different residues were found in the sediments,
43 with a maximum of 48 in a single sample. Twenty-seven out of the 99 detected residues were
44 not approved for agricultural use at the time of sampling. The numbers of detected residues
45 and pesticide levels varied among countries. AMPA, glyphosate and DDTs were the most
46 common residues in sediment samples with frequencies of 76, 61, and 52%, respectively. The
47 sediments from the Czech Republic had the highest pesticide concentrations, with total
48 pesticide concentrations ranging between 600 and 1 200 $\mu\text{g kg}^{-1}$. The lowest total pesticide
49 concentrations were found in Slovenia, Switzerland, Croatia, and Denmark, ranging between
50 80 and 120 $\mu\text{g kg}^{-1}$. Sediments presented a mix of non-persistent and persistent compounds.
51 Twelve of the detected pesticides are very persistent/stable in sediments, raising concerns
52 about the long-term impacts of pesticides. Our study on the distribution of pesticide residues
53 in European sediments provides valuable insights into the extent of pesticide contamination
54 and possible risks of pesticides to water bodies' health. It also underlines the need for
55 monitoring, research, and policy efforts to mitigate the impacts of pesticides, and to evaluate
56 potential risks of re-use of dredged sediments.

57

58 **Keywords:** SPRINT project, monitoring program, agricultural diffuse contamination, waterbed
59 sediments, persistency of pesticide residues

60

61 **Graphical abstract**

62

63

64

1. Introduction

Pesticides play a vital role in modern agriculture by safeguarding crops from pests. The use of pesticides is linked to higher crop yields which helps meet the growing global demand for food [1,2]. By reducing crop damage, and avoiding the need for manual weed control, pesticides save farmers significant production costs and labour efforts [3]. While these products offer several benefits [4], their use may also pose serious risks to environmental and human health. Pesticide residues contaminate soil, water bodies, air, and affect non-target organisms such as beneficial insects, birds, and aquatic life [5]. Exposure to high levels or prolonged contact with certain pesticide residues may also lead to acute or chronic health issues for farm workers, and consumers [6].

When pesticides are applied in agricultural fields, they undergo several processes that can facilitate their transport to and accumulation in areas other than the treated fields. Nearby water bodies are particularly vulnerable to pesticide contamination [7,8]. Pesticide residues can be transported off-field through different pathways during or after application, especially via aerial dispersion, surface runoff, and leaching [9, 10]. Some pesticide residues can volatilize into the air and be carried by wind currents, and in wind-eroded particles. Monitoring data in the air is rather limited but available data have corroborated the aerial transport of DEET, transfluthrin, piperonyl butoxide, and of other contaminants namely PCBs [11]. A recent study in Germany has reported that glyphosate, chlorothalonil, metolachlor, pendimethalin, and terbuthylazine were rather common in air [12]. Recent research indicates that there has been an underestimation of the atmospheric transport and persistence of pesticides, emphasizing the necessity for enhancing their risk assessment [13]. Rainfall or irrigation can cause pesticide residues to be transported with the runoff water over the soil surface into rivers, lakes, and ponds. This is known to happen with e.g. atrazine, acetochlor, and metolachlor [14, 15]. Pesticide residues can also infiltrate into the soil and reach groundwater sources. Atrazine and its metabolites, and bentazone are amongst the most problematic ones [16]. Over time, groundwater sources may discharge into surface water bodies and contribute to sediment contamination [17, 18]. It is important to note that the movement of pesticide residues from fields to water bodies varies depending on factors like soil type, landscape characteristics, pesticide properties, and management practices [19].

Waterbed sediments are known sinks of contaminants, informing about the contamination from the watershed [20]. Since waterbeds are an integral part of the aquatic ecosystem, pollution of waterbeds may have detrimental effects on the functions and health of the ecosystem [21]. Some pesticide residues dissolve in water which allows them to remain mobile and potentially move to further locations with the water currents. Other pesticide residues have a higher affinity for organic matter and adsorb onto suspended particles, which eventually settle down and accumulate in the waterbed [22, 23]. The persistence and impacts of pesticide residues in sediments depend strongly on their chemical properties. Some pesticide residues may degrade or break down relatively quickly while others retain their

106 molecular integrity (and hence their physical, chemical, and functional characteristics) for
107 longer, leading to long-term contamination/pollution. As mentioned above, pesticide
108 residues, regardless of their persistence, can have undesired effects on non-target organisms
109 such as fish, amphibians, and invertebrates [24, 25, 26]. This can disrupt ecological balance
110 and impair ecosystem services. A short overview of recent European studies addressing the
111 contamination of sediments by pesticide residues is presented in *table SM1*. See also, for
112 example, Oubiña et al. 2006, Carazo-Rojas et al. 2018, Liu et al. 2022, San Juan et al. 2023 and
113 Damiani et al. 2023 non-European works and data.

114

115 The SPRINT project (on Sustainable Plant Protection Transition, <https://sprint-h2020.eu/>),
116 funded under the EC program H2020, focuses on the impacts of pesticide residues on the
117 ecosystem, crop, livestock, and human health, and on the transition towards more sustainable
118 pesticide use. A key project activity related to the collection of environmental and biological
119 samples is a European-wide survey for further analyses of pesticide residues and other health
120 indicators (See Silva et al. [27] for the study protocol). The primary aim of the current study is
121 to assess the presence, type, and levels of pesticide residues in European waterbeds. The
122 survey covers different regions, with different crops and pesticide regimes. The analytical
123 results will enhance our understanding of pesticides' fate, persistence and potential
124 consequences to the ecosystems. Ultimately, this knowledge may support decision-making,
125 support sustainable land management practices, and contribute to the protection of aquatic
126 ecosystem health.

127

128 **2. Material and Methods**

129 **2.1. Coverage of the assessment**

130 As mentioned above, this study is linked to a comprehensive, holistic sampling campaign
131 conducted in Europe, under the SPRINT project umbrella. This campaign, designed to assess
132 the distribution and impacts of pesticides on environmental, plant, animal and human health,
133 covered ten case study sites, all in different European countries. This was to cover the main
134 crop types in Europe, and a diversity of agricultural landscapes and practices. The campaign
135 occurred in 2021, being the exact timing of the samples' collection case study-specific;
136 sampling was aligned to the middle of the growing season for each crop) when we expect the
137 highest diversity and (bio)monitoring levels of pesticides. All samples but crop samples were
138 collected at this time. Crop samples were collected at harvest time. The middle of the growing
139 season corresponded to the end of May-begin June in almost all case studies. In the Spanish
140 and Italian case studies (no sediments originating from these – see below) it corresponded to
141 end September-begin October [27].

142 . The sediment samples were collected from small reservoirs, lakes, ponds, rivers, or
143 irrigation channels connected or in the vicinity of the sampled agricultural fields. The SPRINT
144 sampling design aimed at the collection of three to eight sediment samples per case study,
145 one per water body [27]. Due to logistical difficulties, this was not always feasible (e.g. limited

146 amount of water bodies in the study area, water bodies were too deep, etc). In the end, a total
 147 of 38 sediment samples were collected, originating from eight European countries. Details on
 148 the sediment sample locations are provided in *Table 1*. Details on the water bodies sampled
 149 in SPRINT are already presented in Navarro et al. (2024) [28].

150

151 **Table 1** General information on the case studies where the sediment samples were taken.

| Country | Country code | Covered region | Crop | Number of samples |
|-----------------|--------------|-------------------|--------------------------------|-------------------|
| Portugal | PT | Central zone | Vineyards | 8 |
| France | FR | Bordeaux | Vineyards | 5 |
| Switzerland | SH | Canton of Bern | Apple orchards | 5 |
| Croatia | HR | Istria | Olives | 3 |
| Slovenia | SL | Central zone | Maize | 6 |
| Czech Republic | CZ | All country | Oil plants | 3 |
| The Netherlands | NL | Groningen | Potatoes | 5 |
| Denmark | DK | North and Central | Spring barley and Winter wheat | 3 |

152

153 **2.2.** *Sample collection and treatment*

154 Each of the 38 samples analyzed for pesticide residues was a composite sample. Three sub-
 155 samples were collected at equidistant points along a transect representative of the water
 156 body. The sub-samples were collected with core samplers, from the top layer at a depth of 0
 157 to 10 cm. Equal quantities of each sub-sample were placed into a bucket to create the
 158 composite sample per water body. The (composite) sediment samples were then split into 2
 159 aliquots: one for the physico-chemical characterization, and the other for the determination
 160 of pesticide residues.

161

162 **2.3.** *Sediment physico-chemical characterization*

163 Sediment physico-chemical characterization was performed by each of the case study teams
 164 using harmonized methods (see supplementary materials for full details). In brief, pH
 165 measurements were performed following the protocol introduced by Van Reeuwijk [29],
 166 organic matter content was determined via the loss-on-ignition method at 550°C [30], and
 167 particle size distribution was measured via the hydrometer method (in HR and SL samples),
 168 laser diffraction (in NL, FR, DK, CH, CZ samples [31, 32]), or using a Coulter counter for the fine
 169 fraction (PT samples [33]). The basic characteristics of the 38 sediment samples are presented
 170 in *Table SM2*.

171

172 **2.4.** *Determination of pesticide residues*

173 Within the SPRINT project, a target list of 209 analytes was established [27]. This list was
174 targeted in all environmental samples. For sediments, the analytical methods were validated
175 and considered fit for purpose for 196 compounds. This sub-list covers 164 active substances,
176 44 degradation products, and one synergist (piperonyl butoxide; *Table SM3*). 118 out of the
177 164 active substances were approved for use in plant protection product in the EU at the time
178 of sampling, the remaining 46 were not approved (approval status refers to 01 January 2021,
179 the beginning of the year of the sampling campaign). 172 out of the 196 compounds were
180 analyzed by liquid chromatography with tandem mass spectrometry-based methods (LC-
181 MS/MS), and the remaining compounds by gas chromatography-tandem mass spectrometry
182 (GC-MS/MS; see Supplementary Material for further analytical details). The QuEChERS (quick,
183 easy, cheap, effective, rugged, and safe) approach was adopted for the multi-residues
184 methods LC-MS/MS and GC-MS/MS [34, 35, 36]. The liquid chromatography-tandem mass
185 spectrometry instrument used was a SCIEX Triple Quad™ 6500+ LC-MS/MS System. The gas
186 chromatography-tandem mass spectrometry instrument was a 7010B MS coupled to a 7890B
187 GC from Agilent Technologies [37]. Details on the chemicals and reagents involved in the
188 analyses are provided in the -supplemental materials.

189 The quality control of the analyses was performed following the SANTE/11813/2017 guidance
190 document on analytical quality control and method validation procedures for pesticide
191 analysis in food and feed [38, 39]. The method was assessed for its LOD/LOQ, linearity,
192 recovery, precision, and matrix effects. Multi-pesticide calibration standards were prepared
193 for each analytical method based on a solution that combined the reference standards of all
194 compounds included in the analysis.

195 **2.5** *Data Analysis*

196 Basic descriptives were performed at sample and matrix level. The sample-level analyses cover
197 the number of residues per sample, pesticide levels per sample, and pesticide profile per
198 sample. The matrix-level analysis included the percentage of pesticide-free and contaminated
199 samples - i.e. with pesticide residues \geq LOD (limit of detection), mixtures similarities
200 evaluation, and a correlation matrix between overall pesticide findings and sediment basic
201 characteristics. The LOD of the substances was used as the reporting limit (harmonized
202 approach among SPRINT results, see e.g., Silva et al. [40]). The LOD is the level at which signal-
203 to-noise for both quantifier and qualifier ions are at least 3. 138 of the tested residues had a
204 LOD between 0.01 and 0.5 $\mu\text{g kg}^{-1}$; 32 had a LOD between 0.50 and 1.0 $\mu\text{g kg}^{-1}$, and 24 had a
205 LOD between 1.0 and 4.4 $\mu\text{g kg}^{-1}$ (see SM excel table 1 for compound-specific information).
206 Pesticide approval status was retrieved from the EU pesticide database, and pesticide half-life
207 time in sediment and persistence class thresholds, were retrieved from PPDB - Pesticide
208 Properties DataBase (<http://sitem.herts.ac.uk/aeru/ppdb/>; see table SM3).

209 **3. Results**

210 **3.1.** *Number of pesticide residues in sediment samples, and mixtures composition*

211 The number and complexity of the mixtures in the sediment samples varied among countries
212 (*Figure 1*). The highest number of compounds was found in the sediment samples from the
213 Czech Republic, this was for the maximum number of compounds (N: 48 in sample 4, S04) and
214 the median/average number of compounds (median: 47, average: 39). The lowest number of
215 compounds was found in Slovenia (min: 0 max: 6, average and median: 2; *Figure 1*). Sample
216 15, from Slovenia, was the only 'pesticide-free' sample. Samples 16 and 19, also from Slovenia,
217 and sample 23 from Switzerland contained a single pesticide residue (S16: Imidacloprid; S19:
218 Prosulfocarb and S23: Metolachlor_S). The remaining 34 samples contained mixtures of
219 residues. 13 samples contained 2-5 residues, 7 samples contained 6-10 residues, 7 samples
220 contained 11-20 residues, 5 samples contained 21-30 residues, and the remaining 2 samples,
221 from the Czech Republic, contained 47 and 48 residues. Czech Republic has the most complex
222 mixtures (in terms of the number of residues, and type of compounds), while Croatia and
223 Slovenia present rather simple mixtures (*Figures 1, 2, and SM1*).

224 Thirty-one different mixtures were detected among the sediment samples. A two-
225 compound glyphosate-AMPA mixture was found in 4 samples, the remaining mixtures were
226 unique (in their full composition, *Figure SM1*). There were however common combinations
227 among mixtures, i.e. "mixture root, MR". Fourteen "2-compound-MR" were detected in ten
228 or more samples (Glyphosate+AMPA root appears in 23 samples – 19 in combination with
229 other compounds, AMPA+DDE p,p' root in 17 samples, etc; *Figure 3a*). Eight "3-compound-
230 MR" were detected in ten or more samples (Glyphosate+AMPA+DDEpp root in 14 samples;
231 glyphosate+DDDpp+DDEpp in 13 samples, etc; *Figure 3b*). Glyphosate and/or DDT residues
232 (i.e. glyphosate/AMPA and/or DDDpp/DDEpp) were present in all of the most common MR.

233

234

235 **3.2.** *Type of pesticide residues identified in the sediments*

236 A total of 99 different pesticide residues were found above the respective LOD (*Table SM3*).
237 72 of the 99 were either approved active substances or degradation products of approved
238 substances; remaining 27 were (related to) not approved substances. Glyphosate (approved
239 herbicide) and its main metabolite AMPA were the two most frequently detected compounds.
240 Glyphosate was present in 23 samples, originating from 7 countries (all countries except
241 Croatia). AMPA was detected in 29 samples out of the same 7 countries. DDE p,p' (metabolite
242 of the long-banned DDT) was the third most common compound, detected in 19 samples from
243 7 countries (in this case only not detected in Slovenian samples). These top 3 substances have
244 very different profiles. According to PPDB, glyphosate and AMPA have high solubility in water
245 and low bioaccumulation potential (octanol/water partition coefficient, $Kow < 2.7$), DDE has
246 low solubility in water and a higher tendency to accumulate in sediments ($Kow > 3.0$).
247 Glyphosate is expected to undergo fast degradation in sediments, AMPA slow degradation
248 and DDE is a rather stable compound, with very slow degradation. The remaining compounds
249 had been detected mostly occasionally; 59 residues had frequencies of detection below 10%,

250 31 residues had frequencies of detection between 10 and 25%, and the remaining 6 residues
251 had frequencies of detection between 25 and 50% (*Figure 2*). See also table SM2 for
252 interpretation on compound detections based on application information collected in the case
253 studies.

254 The correlation matrix in *table 2* provides insights into the strength and direction of the
255 associations between overall pesticide findings (number and total levels) and sediment
256 characteristics. Despite the different origins of the samples, different numbers of samples per
257 case study site/country, and other inherent variability factors linked to the samples, a strong
258 and positive association exists between pesticide load and organic matter content. And, as
259 somehow expected, samples with more residues present higher total pesticide contents.

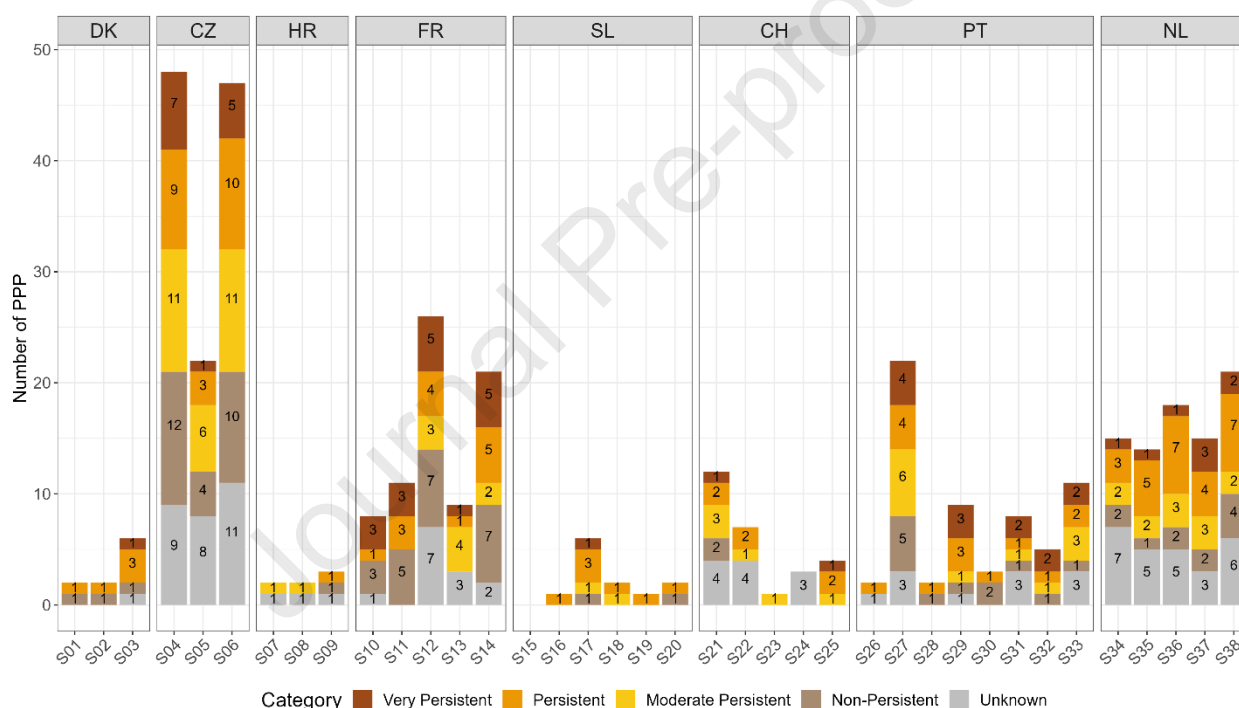
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262 **3.3. Pesticide concentrations in the sediment samples**

263 Cyprodinil and dicamba were the compounds with the highest (median) concentrations, of
 264 116 and 83 $\mu\text{g kg}^{-1}$, respectively (Figure 2). Spinosyn A, AMPA, difenoconazole, glyphosate,
 265 tebuconazole, penconazole, and deltamethrin, represent the group with the second-highest
 266 levels, with median concentrations ranging from 10 to 32 $\mu\text{g kg}^{-1}$. The remaining 90
 267 compounds had median concentrations below 10 $\mu\text{g kg}^{-1}$. The sediments from the Czech
 268 Republic presented also the highest total pesticide concentrations, ranging from 600 to 1200
 269 $\mu\text{g kg}^{-1}$. This was followed by Portuguese, French, and Dutch samples, with total pesticide
 270 concentrations ranging between 200 - 800 $\mu\text{g kg}^{-1}$. The lowest total pesticide concentrations
 271 were found in Slovenia, Switzerland, Croatia and Denmark, ranging between 80-120 $\mu\text{g kg}^{-1}$
 272 (Figure 2).

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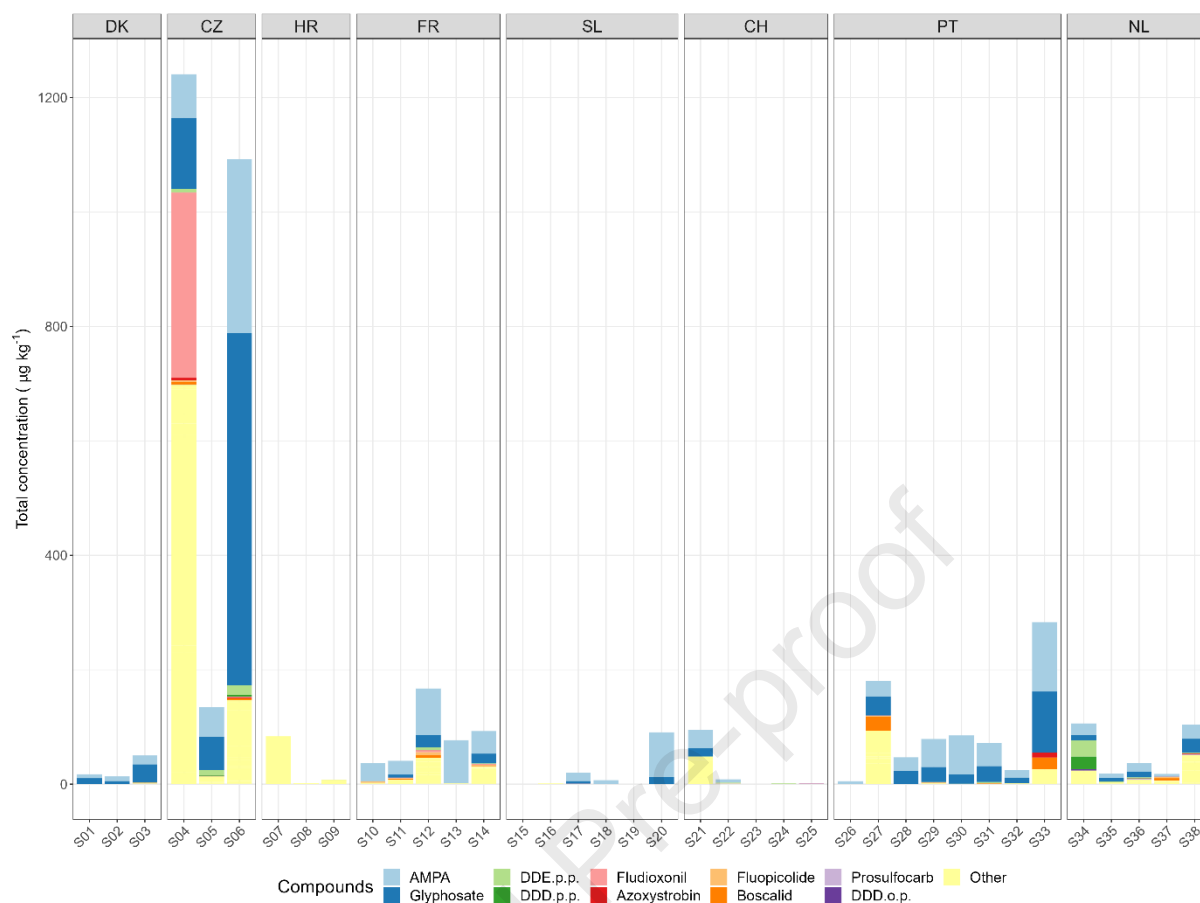


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275

276 *Figure 1 Number of compounds detected in sediment samples across European Countries.*
 277 *Different colors represent different persistency classes in sediment, in line with PPDB*
 278 *classification (very persistent: $DT_{50 \text{ WaterSediment}} > 365$ days; persistent: $100 \text{ d} < DT_{50 \text{ WS}} \leq 365 \text{ d}$;*
 279 *moderate persistent: $30 \text{ d} < DT_{50 \text{ WS}} \leq 100 \text{ d}$; non-persistent: $DT_{50 \text{ WS}} \leq 30 \text{ d}$; unknown: $DT_{50 \text{ WS}}$*
 280 *not known). DK: Denmark; CZ: Czech Republic; HR: Croatia; FR: France; SL: Slovenia; CH:*
 281 *Switzerland; PT: Portugal; NL: Netherlands*

282



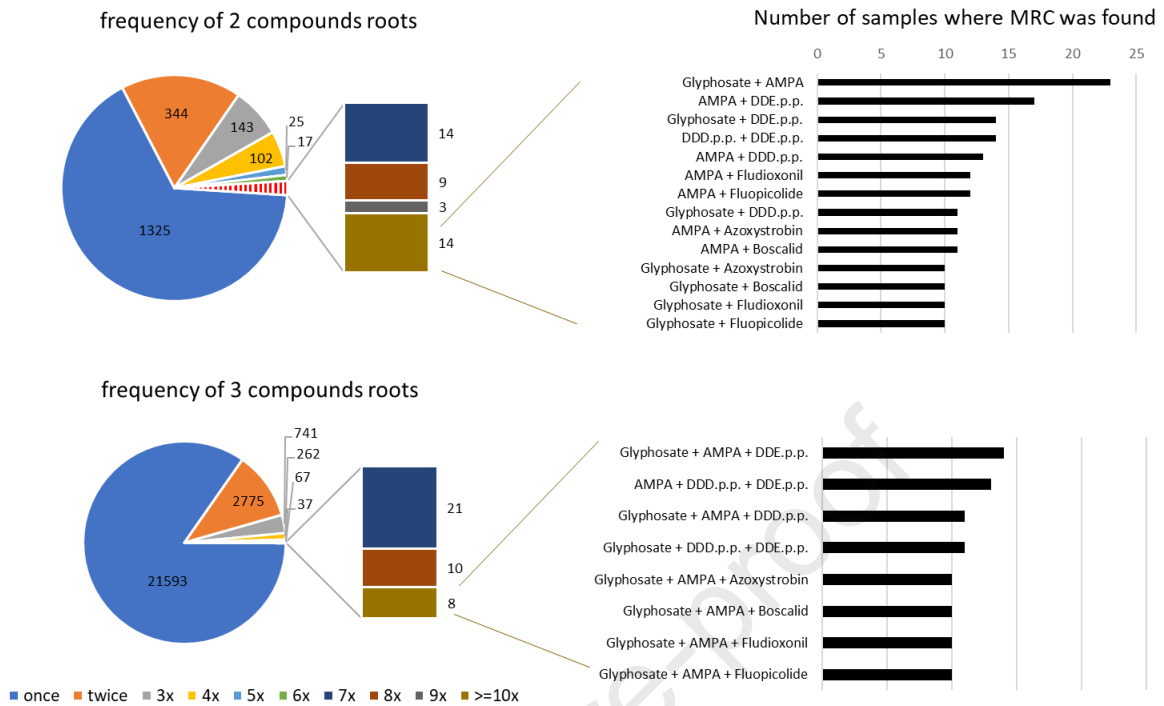
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285 Figure 2 Pesticide concentrations in the sediment samples ($\mu\text{g kg}^{-1}$). The 10 pesticides with
 286 highest concentrations are specified in the graph. The category 'others' reflects the sum of
 287 pesticide concentrations not included in the top 10. DK: Denmark; CZ: Czech Republic; HR:
 288 Croatia; FR: France; SL: Slovenia; CH: Switzerland; PT: Portugal; NL: Netherlands

289

290



291

292 *Figure 3 - Overview of similarities among pesticide mixtures. The pie charts on the left indicate*
 293 *how often a 2 or 3 compound combination was found among all 2 or 3 compounds possible*
 294 *combinations (from the pool of 196 tested compounds). The bar graphs on the right highlight*
 295 *the most common 2-/3-Mixture Root Compounds (MRC).*

296

297

298 *Table 2 - Correlation matrix between variables under investigation. OM: organic matter.*

| | OM | Sand | Clay | Silt | Total_concentration | No_pesticide |
|---------------------|-------|-------|--------|----------|---------------------|--------------|
| pH | -0.13 | 0.32 | -0.19 | -0.27 | 0.00 | -0.08 |
| OM | | -0.16 | -0.19 | 0.24 | 0.63*** | 0.65*** |
| Sand | | | -0.34* | -0.95*** | 0.14 | 0.03 |
| Clay | | | | 0.03 | -0.05 | -0.17 |
| Silt | | | | | -0.13 | 0.02 |
| Total_concentration | | | | | | 0.87*** |

299 ***: $p < 0.001$; *: $p < 0.05$; no * sign: not significant ($p \geq 0.05$)

4. Discussion

In this study, we examined pesticide contamination in waterbed sediments at the European scale. Our findings corroborate off-site contamination by pesticides and that sediments can serve as sinks for pesticide residues. All sediment samples but one contained pesticide residues, in a mix of approved and non-approved substances, or metabolites. The pesticide-free sample was observed in Slovenia, in a region of maize production. This specific sample originates from the Slovenian water body with the greatest distance to agricultural fields [28]. Having information on soil types and connectivity/presence of discontinuity areas could also add to the discussion on Slovenian results. Other factors like land use, or the proportion of conventional and organic farms in the surrounding area/watershed do not seem to explain it as the water sample from this water body has tested positive for some of the analytes [28]. At the same time, it is important to stress that, although rather comprehensive, we had a targeted list of analytes. So it is possible that our pesticide free sample, like some/all the other samples in study, may present other not analysed pesticides.

Glyphosate and AMPA were dominant in terms of frequency and concentration in the sediment samples, likely a consequence of the high use of glyphosate-based herbicides across European countries and their relatively high persistence in sediments [40]. Previous studies reported high use but higher Kow compounds such as chlorpyrifos, cypermethrin and diazinon as top frequent and top concentration compounds in sediments [51, 54-56, 60]. In our study we only detected traces of chlorpyrifos, and of its metabolites, likely a consequence of its ban in the EU in January 2020. Our cypermethrin figures were also much lower than those reported by for instance Peres et al [60], in the Ebro River Delta. The difference is likely related to their lower LOD for this compound and their focus on rice cultivation where the cypermethrin is used extensively (see more below on possible causes for country/region variations). Diazinon was not tested in our study as it is non-approved for use as PPP since 2007.

Due to the widespread use of glyphosate-based herbicides, we cannot inform much on the source of contamination, if from farms connected /in the vicinity to water bodies, or from more distant farms within the watershed, where this type of herbicides may have been used. It is also important to acknowledge that pesticide use in urban areas can also contribute to the pesticide findings in the waterbodies [54], and that application information is rather often not enough to fully explain sediment findings. The hydromorphological characteristics of the water body for instance can promote either conservation/accumulation either degradation of pesticides [57]. Pesticide and sediment characteristics, as already touched upon in this paper, are also key factors. Indeed, it is known that some pesticide residues have stronger and faster adsorption to sediments, and their desorption is much less effective and incomplete even after a long equilibration time. Sediment particle size and organic matter content are known to play a crucial role in the sorption-desorption dynamics [41]. Such dynamics translate into a double role of sediments: sink and source of contaminants [60]. Our study is closely linked with the sink/accumulation aspect. Anthropogenic activities and natural events can lead to the re-suspension of contaminated sediments, and remobilization of contaminants to the liquid phase, and sediment-dwelling organisms can accumulate such

contaminants and introduce them into the aquatic food chain [62-64]. The results of this study have also illustrated that persistent residues (legacy and or of current use; $DT50_{WS} > 100$ days) were the most common compounds in the sediments. This is even though the sediment samples were collected in the middle of the growing season. DDT residues, for instance, banned in Europe decades ago [43], were still frequently found in the sediment samples. These compounds, and respective background levels, should be accounted for in risk assessments, and for the definition of environmental quality standards. It should be also recognized that some pesticides, currently approved in the EU market, and of moderate to high persistency like AMPA and azoxystrobin, can accumulate in sediments over time, potentially leading to concerning high concentrations [44, 45]. The identification of specific pesticides exhibiting prolonged persistence in sediment samples is of paramount importance. For targeted pesticide regulatory measures, to evaluate persistence models accuracy, etc. Our results highlight the presence of certain chemical compounds with high half-lives and/or concentrations, such as AMPA, glyphosate, DDT, fludioxonil, azoxystrobin, fluopicolide, boscalid, and prosulfocarb. This persistence may be attributed to the chemical properties of the pesticides, such as their molecular structure and hydrophobicity, making them less available for microbial degradation [46, 47]. Other relevant factors include sediment composition, organic matter content, and the composition of the local microbial communities. Our study underscores the need to explore these factors in greater detail to unravel the complex interactions governing pesticide fate in sediments. Additionally, the impact of land use practices on sediment contamination status requires further investigation. Indeed, the presence of (certain) pesticides in sediments, can indicate the absence of effective integrated pest management strategies, and weak or inadequate regulations regarding pesticide use and/or water bodies protection measures [48, 49, 50].

This dominance of widespread use and legacy compounds (glyphosate/AMPA/DDT/DDE) was also visible in our mixture root analyses, which seems not to be the best approach to identify associations between crop type and mixtures in sediments. Nevertheless, overall, pesticide contamination was found to be country-dependent, with Czech sediments presenting the highest number of pesticide residues and the highest concentrations among sampled countries. The same pattern was observed in soils, also covered by the SPRINT campaign. Soils were collected approximately at the same time as sediments, in nearby sometimes connected agricultural fields [42]. The higher numbers and concentrations of pesticide residues in sediments of a certain country are most likely a result of more intensive and/or diverse agricultural practices in the sampled region, but also of sediment characteristics. Czech Republic samples contain the highest organic matter content among all samples which could explain at least in part the higher pesticide figures. Water analyses (from the waterbodies where sediment was collected, and sampled at the same time as sediments) show the highest total pesticide concentration in Dutch, Portuguese and French samples. Glyphosate was the compound with the highest median concentration in water, followed by 2,4-D and MCPA. The discrepancy in water-sediment-top ranks is linked with pesticide properties and soil-water partition coefficients.

Finally, alongside its wide compound and spatial coverage, the sampling design has brought some limitations to the study. The main ones are the limited number of samples and the fact we had only one sampling time. Inter- and intra-annual variations are possible due to variations in pesticide use, and seasonal natural fluctuations (e.g. rainfall regime, river flow). In this study, the relation between the residues found in the sediments and their source is not completely understood due to a lack of data, and the complexity of the problem. For future works, it is recommended to do an inventory of all farms in the watersheds, including information on the farming system, type of crop, and pesticide residues used, but also a connectivity study, exploring links and discontinuity points between the farms and the studied water bodies. Last but not least, in-situ and ex-situ impacts (re-use of dredge sediments) risk assessment, out of the scope of this paper, should be further explored. This is especially relevant for the establishment/evaluation of sediment quality guidelines and pesticide/dredge sediment life cycle assessments.

5. Conclusions

Our sampling design, covering eight European countries, highlighted the ubiquitous presence of pesticide residues in waterbed sediments. The number, type, and concentrations of the pesticides varied among countries, highlighting the need for further explanatory driving factors and comprehensive monitoring programs. Some patterns and common challenges were still identified. Glyphosate and its main metabolite AMPA were the two most frequently detected compounds and the ones with the highest concentrations in the sediment samples. These together with DDTs were included in most of the mixtures found. Indeed, almost all sediment samples presented a mix of currently used and banned compounds, stressing challenges around diffuse pollution and pesticide legacy effects. Understanding the dynamics and impacts of (mixtures of) pesticide residues is essential for the protection and conservation of aquatic ecosystems, but also to achieve the soil, air and water zero pollution vision of the European Union by 2050. By studying pesticide residues in sediments, we can also uncover valuable insights into their potential "chemical time bomb" aspect, highlighting the need to explore the acute and long-lasting effects of pesticide use on aquatic systems, and ultimately the need for more sustainable and environmentally conscious agricultural practices.

Authors contributions

Conceptualization: all co-authors;

Data curation: Case Study Site teams, Chow Khurshid, Vera Silva, Rima Osman, Hans Mol, Lingtong Gai; Formal analysis: Chow Khurshid, Vera Silva, Lingtong Gai;

Funding acquisition: Violette Geissen, Coen J. Ritsema, Chow Khurshid;

Investigation: all co-authors;

Methodology: sampling design – WP2 team (Abdallah Alaoui, Anne Vested, Vivi Schlünssen, Florian Christ) and multiple SPRINT experts involved in monitoring plan; lab analyses - Hans Mol, Rima Osman

Project administration: Violette Geissen, Vera Silva, Coen J. Ritsema,

Resources: All authors;

Software: Chow Khurshid, Rima Osman, Lingtong Gai;

Supervision: Coen Ritsema, Violette Geissen, Vera Silva;

Validation: Chow Khurshid, Rima Osman, Vera Silva, Lingtong Gai;

Visualization: Lingtong Gai, Chow Khurshid, Vera Silva, Paula Harkes

Roles/Writing: original draft - Chow Khurshid; review & editing - All authors; final draft: Chow Khurshid, Vera Silva

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Declaration of competing interest

The authors declare no conflict of interest

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Highlights

- A total of 196 pesticide residues were analyzed in 38 sediment samples.
- The sediment samples originated from 38 water bodies, from eight European countries.
- 99 different pesticide residues were found in the sediments.
- AMPA, glyphosate, and DDTs exhibited the highest levels and detection frequencies.
- Sediments presented a mix of non-persistent and persistent compounds.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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