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Assessing pesticide residues occurrence and risks in water systems: A Pan-European and Argentina perspective

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A R T I C L E I N F O

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A B S T R A C T

Freshwater ecosystems face a particularly high risk of biodiversity loss compared to marine and terrestrial systems. The use of pesticides in agricultural fields is recognized as a relevant stressor for freshwater environments, exerting a negative impact worldwide on the overall status and health of the freshwater communities. In the present work, part of the Horizon 2020 funded SPRINT project, the occurrence of 193 pesticide residues was investigated in 64 small water bodies of distinct typology (creeks, streams, channels, ditches, rivers, lakes, ponds and reservoirs), located in regions with high agricultural activity in 10 European countries and in Argentina. Mixtures of pesticide residues were detected in all water bodies (20, median; 8–40 min-max). Total pesticide levels found ranged between 6.89 and 5860 ng/L, highlighting herbicides as the dominant type of pesticides. Glyphosate was the compound with the highest median concentration followed by 2,4-D and MCPA, and in a lower degree by dimethomorph, fluopicolide, prothioconazole and metolachlor(-S). Argentina was the site with the highest total pesticide concentration in water bodies followed by The Netherlands, Portugal and France. One or more pesticides exceeded the threshold values established in the European Water Framework Directive for surface water in 9 out of 11 case study sites (CSS), and the total pesticide concentration surpassed the reference value of 500 ng/L in 8 CSS. Although only 5 % (bifenthrin, dieldrin, fipronil sulfone, permethrin, and terbutryn) of the individual pesticides denoted high risk (RQ > 1), the ratios estimated for pesticide mixtures suggested potential environmental risk in the aquatic compartment studied.

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1. Introduction

Freshwater ecosystems represent the terrestrial phases of the global hydrological cycle, including streams, rivers, ponds, lakes, wetlands and groundwaters. These water bodies constitute only 0.01 % of the water on Earth and less than one-tenth of the global land surface area, but are the habitat of approximately 10 % of all recorded species including 30 % of all vertebrates (Suring, 2020). A large proportion of these water systems are currently ecologically threatened with high losses of biodiversity (Beketov et al., 2013). The ongoing biodiversity decline is caused by a variety of anthropogenic stressors, being the chemical contamination derived from the pesticide use an important driver of this environmental impairment (Malaj et al., 2014; Wolfram et al., 2021). Pesticides applied as plant protection products (PPPs) in agricultural farms to safeguard crops can mainly reach the adjacent water bodies by surface runoff, subsurface drainage systems, groundwater inflow, spray drift, soil erosion or deposition (Adriaanse et al., 2017; Suciu et al., 2020; Vera-Candioti et al., 2021). The magnitude of pesticide transport is determined by several factors such as physical and chemical properties of soil, topography, weather (the amount and intensity of rainfall events), hydrology, agricultural management practices and physicochemical properties of pesticides (Gramlich et al., 2018).

In the European Union (EU), agricultural areas cover 38 % (157 million hectares) of the total land area (Eurostat, 2023a) and pesticide agricultural use estimated for 2021 was around 355,000 t (Eurostat 2023b). On the other hand, in Argentina, pesticide agricultural use estimated for 2021 was around 241,500 t, with an average approximately of 5.6 Kg/ha (FAOSTAT, 2023). The environmental fate of these contaminants is currently a major concern, among others, because of their increasing detection in waters of different European countries (Schreiner et al., 2016; Masiol et al., 2018; Belles et al., 2019; Casado et al., 2019; Herrero-Hernández et al., 2020; Wijewardene et al., 2021; Fingler et al., 2021; Casillas et al., 2022; Konečná et al., 2023; Rocha and Rocha, 2023; Simon, 2023) and Argentina (Aparicio et al., 2013; De Gerónimo et al., 2014; Pérez et al., 2021; Mac Loughlin et al., 2022; Peluso et al., 2022). Their presence in water bodies could pose a risk to aquatic organisms, but also to humans through the consumption of contaminated fish and drinking water (El-Nahhal and El-Nahhal, 2021; Baran et al., 2022; Harmon O'Driscoll, 2022; Rohani, 2023). For this reason, the EU Commission under the European Water Framework Directive (WFD) establishes the bases to regulate the chemical and ecological surface water quality in order to preserve, protect and improve the aquatic ecosystem and human health, defining environmental quality standards (EQS) for inland surface waters (i.e. rivers, lakes, related artificial or heavily modified water bodies), other surface waters and biota. In October 2022 a proposal of a Directive was released for amending previous European water legislation: the Water Framework Directive (Directive 2000/60/EC), the Groundwater Directive (GWD, Directive 2006/118/EC), and the Directive on Environmental Quality Standards (EQSD, Directive 2008/105/EC) (European Commission, 2022). In general, small basins and catchments are not well reflected in most WFD surface water monitoring programs (Szöcs et al., 2017; Weisner et al., 2022) although those represent around 80–90 % of the European hydrographic network (Spycher et al., 2018), and due to their direct proximity to fields, may be especially susceptible to agricultural diffuse pesticide pollution. The chemical and ecological status of small water bodies is to a great extent unknown because most of the studies in the literature and surface water monitoring programs have been focused on larger river basins. Furthermore, the risk to these aquatic ecosystems can substantially be underestimated since large part of these works deal with only a limited number of pesticide residues. Therefore, in the present research, the occurrence of a wide range of pesticide residues (156 active substances and 37 metabolites) and mixtures was investigated in small water bodies from areas with high intensity agricultural activity in 10 European countries and in Argentina. Furthermore, the compliance with threshold values in surface water and the potential environmental risk, considering both individual and pesticide mixtures, for the aquatic ecosystem was examined, offering valuable insights into the ecological implications of pesticide exposure in different regions.

2. Material and methods

2.1. Sample collection

In this study, a total of 64 grab samples were collected during the pesticide application period of the 2021 growing season from water bodies of distinct typology (creeks, streams, channels, ditches, rivers, lakes, ponds and reservoirs), located in regions with high agricultural activity across 11 case study sites (CSS). The samples were carefully taken at a representative time of the production system, without immediate application, when about 50 % of the pesticides were applied at the fields to produce crops. The study design included sites related to fields with the main European crops, or some notably imported and used in Europe. The distribution of samples across CSS was as follows Spain (case study site 1, CSS1, $n = 7$), Portugal (CSS2, $n = 8$), France (CSS3, $n = 6$), Switzerland (CSS4, $n = 5$), Italy (CSS5, $n = 6$), Croatia (CSS6, $n = 3$), Slovenia (CSS7, $n = 6$), Czech Republic (CSS8, $n = 8$), the Netherlands (CSS9, $n = 6$), Denmark (CSS10, $n = 3$) and Argentina (CSS11, $n = 6$) (Fig. 1). Water bodies characteristics are provided in the supplementary material (SM, Table S1). Water samples were collected sub-superficially using 2 L precleaned polypropylene bottles, frozen at −20 °C and sent refrigerated (−20 °C) to CIEMAT labs (Alaoui et al., 2021). Once arrived at the laboratory, samples were stored at −20 °C until pesticide analysis.

2.2. Chemical analysis

In the present study, 193 analytes (including 156 active substances and 37 metabolites: 67 fungicides, 62 herbicides, 63 insecticides and 1 synergist), were determined in the water samples. These analytes were selected according to their occurrence in food and environmental matrices, known/possible application in the different CSS, and a pre-screening of environmental samples (Silva et al., 2021). The optimization and validation of three different methodologies were conducted for pesticide determination in the water samples. Multi-residue analysis of pesticides was carried out as described by Casado et al. (2019) with some modifications. Briefly, water samples (1 L), filtered and acidified to pH 3 with formic acid, were spiked with surrogate labeled standards and extracted by solid-phase extraction (SPE), see details at SM. The extract was divided into two aliquots for the GC and HPLC analyses. HPLC analyses were performed on HPLC-MS/MS (Varian HPLC 212–320 MS-TQ) and GC analyses were carried out in a GC–MS/MS (Varian CP-3800 GC-320 MS-TQ). For determination of glyphosate and aminomethylphosphonic acid (AMPA), 100 mL water was filtered, spiked with $^{13}C_2$, ^{15}N- glyphosate and ^{13}C,^{15}N-AMPA labeled standards, and buffered with KH_2PO_4 and $Na_2B_4O_7$ (0.1 M, pH = 9). A derivatization was carried out overnight (≈15 h) with 9-fluorenylmethoxycarbonyl chloride (FMOC—Cl; 1 mg/mL) in darkness at room temperature, and the derivatives were extracted by SPE, details are provided in SM. Instrumental determinations were conducted on HPLC-MS/MS (Varian HPLC 212–320 MS-TQ). Finally, for organochlorinated pesticide analysis, filtered water samples (250 mL) were spiked with ^{13}C labeled surrogate standards (ES-5344–50X from Cambridge Isotope Laboratories Inc.), extracted with 200 mL of dichloromethane and reconstituted in 100 μL of hexane. Instrumental analyses were performed by HRGC—HRMS (Agilent 6890 HRGC-MicroMass Autospec Ultima NT HRMS). The three different methodologies are described in more detail in the supplementary material.

2.3. Quality assurance

The analytical methodologies developed were optimized and validated in line with the SANTE/2020/12830 (SANTE, 2021a) and SANTE/11312/2021 (SANTE, 2021b) requirements, see SM for complete validation results. The limits of quantification (LOQs), defined as the lowest validated level for each analyte, ranged between 0.5 and 50 ng/L, fulfilling recovery (70–120 %) and precision (RSDr $\leq$ 20 %) criteria (Table S2). LOQs of 5 ng/L were achieved in most cases (n = 152), reaching also lower values (n = 13). It is essential to use analytical methods with LOQs below 10 ng/L in order to agree with EQS values (Moschet et al., 2014). The limit of detection (LOD) was calculated as the level at which the analyte can be detected and also identified and S/N for qualifier ion is at least 3 in water matrix spiked at LOQ level, ranging between 1 pg/L (hexachlorobenzene) and 14.6 ng/L (imidacloprid-desnitro) (Table S2). Procedural and instrumental blanks were analysed throughout the analyses to check for interferences and cross-contamination.

2.4. Environmental risk assessment calculations

The environmental risk in the aquatic ecosystem was estimated following the recommendations of the European Chemicals Bureau at Technical Guidance Document on Risk Assessment (European Commission, 2003). Risk quotients (RQ) were used to estimate the potential ecological risk of pesticides in the aquatic ecosystem at general (RQ_{50}) and worst (RQ_{max}) scenarios (Carazo-Rojas et al., 2018; Triassi et al., 2019; Royano et al., 2023) (Eq. (1)).

$$RQ_{50} \text{ or } RQ_{max} = \frac{MEC_{50} \text{ or } MEC_{max}}{PNEC} \quad (1)$$

where MEC was the measured environmental concentration of pesticides (MEC_{50}, median; MEC_{max}, maximum) and PNEC was the predicted no effect concentration. PNEC was calculated considering the most sensitive species, using the available long-term toxicity data (no-observed effect concentration, NOEC; Table S3) divided by an assessment factor (AF) (Eq. (2)). The most conservative and protective factor was applied according to the available ecotoxicological data (European Commission, 2003; Pérez et al., 2021; Li et al., 2023; see SM). When NOEC data was not available, the most sensitive acute toxicity values (median lethal, LC_{50}, and median effective, EC_{50}, concentrations) were used; this is the case of o,p'-DDD, p,p'-DDD, o,p'-DDE, p,p'-DDE, dieldrin and tetramethrin.

$$PNEC = \frac{NOEC\ (LC_{50})(EC_{50})}{AF} \quad (2)$$

Risk quotients for mixtures were also calculated at general (RQ_{mix_50}) and worst (RQ_{mix_max}) scenarios (Eq. (3)) from MEC and PNEC of each

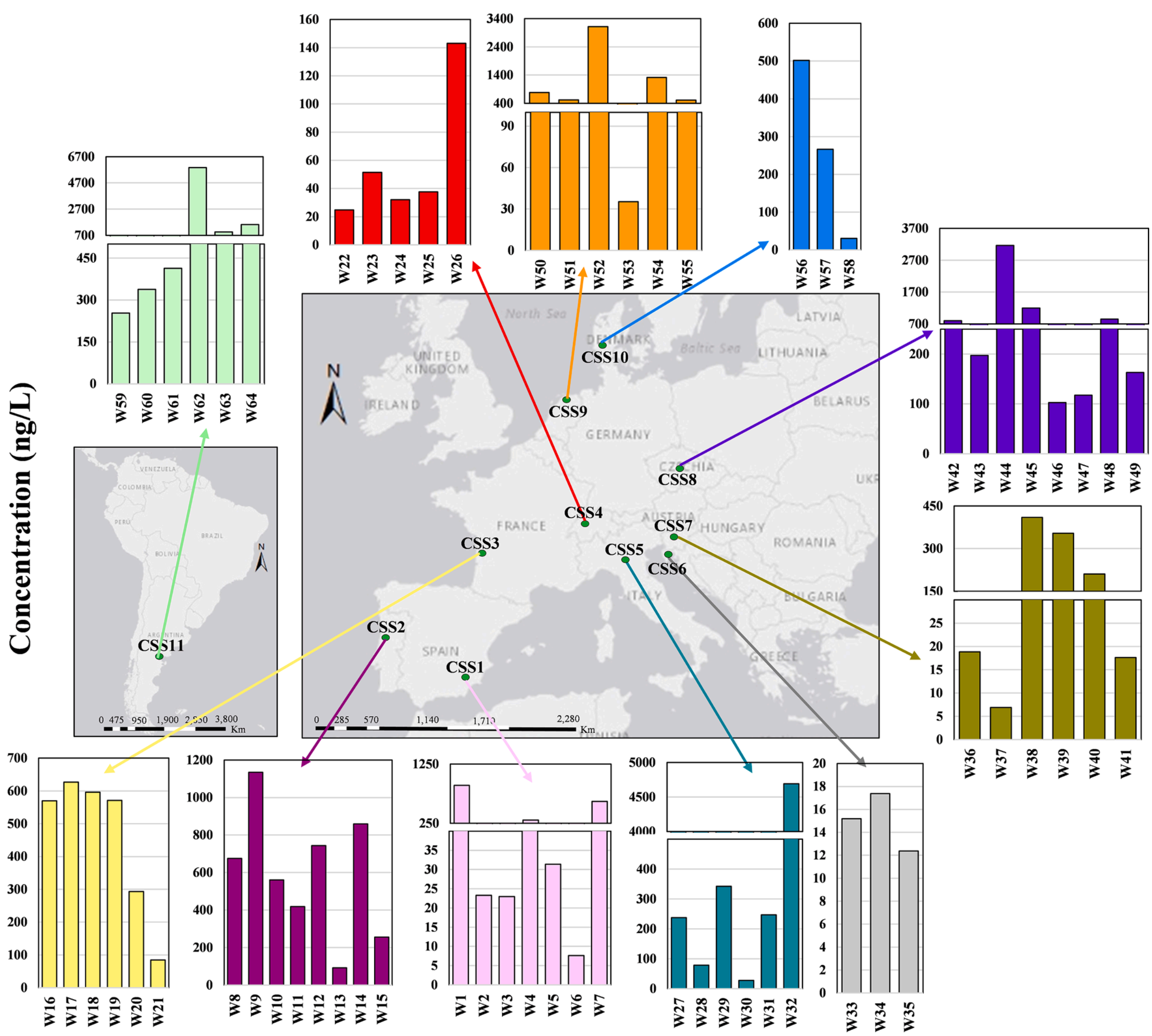

Fig. 1. Occurrence of total pesticide concentrations (∑193 pesticides, ng/L) in water at all CSS.

individual pesticide (i) (Price et al., 2012; Spycher et al., 2018). Complete details related to ecological risk assessment are included in SM.

$$RQ_{mix\_50} \text{ or } RQ_{mix\_max} = \sum \frac{MEC_{50\_i} \text{ or } MEC_{max\_i}}{PNEC_i} \quad (3)$$

In general, $RQ < 0.01$ denotes a negligible risk, $0.01 < RQ < 0.1$ reveals a low risk, $0.1 < RQ < 1$ represents a medium risk and $RQ > 1$ indicates a high ecological risk to aquatic organisms.

2.5. Statistical evaluation

Descriptive statistics (mean, median, min-max range) were calculated on positive samples (> LOD). Statistical analyses were carried out with the software SPSS 14.0 and Statgraphics Centurion XVII.I for Windows. Differences between groups (CSS, water body type, compounds, etc.) were evaluated by Mann-Whitney U or Kruskal-Wallis Tests. Spearman Rho correlations were applied to establish associations between compound concentrations. Relationships between the content of pesticides in water and their distribution (CSS, water body type, land use of the banktop) were assessed by Principal Component Analysis (PCA). In this test, only the first 25 pesticides with the highest median concentration and detection frequency (Df, sample% > LOD) > 10 % were considered, and values < LOD were replaced by the LOD divided by the square root of 2 (Fraser et al., 2013; De la Torre et al., 2020).

3. Results and discussion

3.1. Occurrence of pesticides in water bodies

All water bodies, including channels, creeks, ditches, lakes, ponds, reservoirs, rivers and streams presented comparable ($p > 0.05$) number of pesticide residues (20 pesticides per sample, median; 8–40, min-max; >LOD) and total concentrations (300 ng/L, median; 6.89–5860 ng/L, min-max) (Figure S1). The water bodies morphological features such as the adjacent land use and vegetation structure alongside are known to contribute to the quality status of the waterbody (Kiraga and Markiewicz, 2023). Therefore, the influence of land use within 5 m of the bank top of the water bodies (Table S1) was evaluated, but in general, no tendencies were observed ($p > 0.05$). Regarding the type of pesticides, there was a statistically significantly higher median concentration of herbicides (173 ng/L) in water than fungicides (31.4 ng/L) and insecticides (2.90 ng/L) (Figure S2). This tendency has been also reported in European surface waters from streams, rivers and channels (Moschet et al., 2014; Papadakis et al., 2015; Schreiner et al., 2016; Casado et al., 2019), while in Argentina there is no monitoring of surface water with such a significant number of chemical compounds as those analyzed in the present work.

The presence of 115 out of 193 pesticides (47 fungicides, 36 herbicides, 31 insecticides and 1 synergist) was detected in the small water bodies (Table S4). Most of them (88 %) showed low detection frequencies (Df < 25 %). Nevertheless, glyphosate (98 % Df), its degradation product AMPA (80 %), and terbuthylazine (70 %) were found in most water samples, highlighting their ubiquitous presence and the dominance of herbicides among detected pesticides in aquatic environments. These herbicides have been also reported with high frequency (Df of 74 % for glyphosate and AMPA, and 75–100 % for terbuthylazine) in rivers, streams, lakes and ponds from European countries (Casado et al., 2018, 2019; Wijewardene et al., 2021; Simon, 2023). At this point it must be mentioned that the low LODs achieved for organochlorine pesticides (1–20 pg/L; min-max LODs) allowed their identification in nearly all water samples at trace levels (0.03–0.66 ng/L, median). These concentrations are in agreement with those found in river water from The Netherlands (RIWA-Rijn report, 2021; Table S11) suggesting that the presence of these legacy pesticides (Table S3) should be related to their historical use and great persistence in the environment.

Total pesticide (sum of 193 pesticides; 300 ng/L, median; 6.89–5860 ng/L, min-max) and individual pesticide (0.03–171 ng/L, median) content showed very high variability (Table S4). Significant differences ($p < 0.05$) in concentrations were observed between compounds (see Table S5), pointing out the organochlorines (DDT/D/Es, dieldrin, hexachlorobenzene and lindane) as the pesticides with the lowest values (0.03 - 0.66 ng/L, median). A detail of the first 25 pesticides with higher median concentration and Df > 10 % in each type of field system is shown in Fig. 2. Glyphosate was the contaminant with the highest median concentration (114 ng/L; Table S4) followed by 2,4-D (82.1 ng/L), MCPA (38.6 ng/L), dimethomorph (26.5 ng/L), fluopicolide (22.9 ng/L), prothioconazole (21.8 ng/L), metolachlor(-S) (21.3 ng/L), metalaxyl metabolite CGA 62,826 (14.9 ng/L), bentazone (12.3 ng/L) and metalaxyl-M (12.1 ng/L). The levels of glyphosate, dimethomorph and fluopicolide obtained in these water samples categorized these chemicals as priority substances of concern for the ecosystems (Silva et al., 2023). On the other hand, apart from the organochlorines, the lowest median concentration was observed for chlorothalonil (0.41 ng/L), chlorpyrifos-methyl (0.47 ng/L), chlorpropham (0.68 ng/L), piperonyl butoxide (1.00 ng/L) and epoxiconazole (1.74 ng/L). Other studies have also identified some of these pesticides in water bodies in Europe and Argentina (Table S11). Relationships between the 45 compounds with detection rates >10 % were investigated (see Table S6). Good correlations were observed between pesticides and their metabolites or degradation products, such as glyphosate and AMPA ($p < 0.01$), metalaxyl(-M) and metalaxyl CGA 62,826 ($p < 0.05$), terbuthylazine and terbuthylazine-desethyl ($p < 0.01$) or DDTs, DDDs and DDEs ($p < 0.05$). Some pesticides from the same chemical family, especially azoles ($p < 0.01$) and organochlorines ($p < 0.05$), or same type of pesticides, such as the herbicides glyphosate, bentazone, metolachlor(-S) and terbuthylazine or the fungicides azoxystrobin, cyproconazole and epoxiconazole also correlated, suggesting similar applications and/or environmental behaviour.

Possible relationships between the content of pesticides in water, considering only the first 25 pesticides with higher median concentration and Df > 10 %, and their distribution were also explored by principal component analysis (PCA) (Fig. 3 and S3, Table S7). Models depicted in three principal components (PC) 48 % of the variance. The first component (PC1, 19% of the variance) was mainly determined by the herbicides MCPA and metolachlor(-S), and to a lesser extent 2,4-D, glyphosate and the fungicide cyproconazole. The second component (PC2, 18%) included the herbicide metalaxyl(-M) and its metabolite metalaxyl CGA 62,826, and the fungicides penconazole and carbendazim. The third component (PC3, 12 %) was influenced by fluopicolide and fluopyram, and to a lesser extent by metrafenone and chlorantraniliprole. As shown in the score plots (Fig. 3c), the distribution of the different water bodies revealed higher pollutant concentrations in rivers with influence in the second component compared to ponds. Similarly, samples from channels reflected higher levels for fluopicolide and fluopyram than those collected in rivers and streams (Fig. 3c). Additionally, the lowest concentration values were observed in creeks and reservoirs for the three components. However, as described previously for total pesticide concentrations (Figure 1 and S1) no statistical significance was found for these results. The influence of land use within 5 m of the bank top of the water bodies was observed in PC3 (Figure S3b), revealing higher levels of the fungicides fluopicolide and fluopyram in samples related to vineyards compared to other land uses. Fungicides are critical for the protection of grapevine (Herrero-Hernández et al., 2016), in fact, fluopicolide and fluopyram are usually applied to control various diseases in grape cultivation (PPDB, 2023), which is in accordance with the tendency observed. Similarly, the first component determined by herbicides (including glyphosate) was mostly influenced ($p < 0.05$) by land use related to gardens (Figure S3a,b).

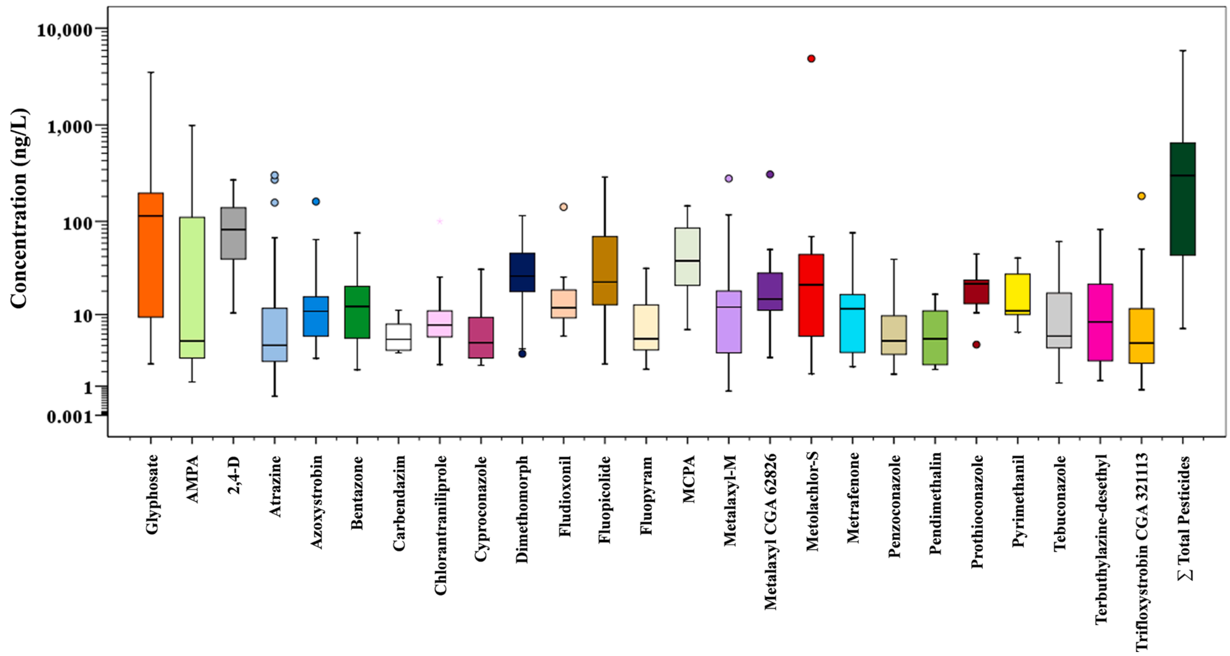

Fig. 2. Concentration (ng/L; logarithmic scale) of some pesticides in water. Only the first 25 pesticides with higher median concentration and Df > 10 % are shown. Upper edge of the box, line within the box and lower edge of the box, represents the 75th, 50th, and 25th percentiles. Vertical lines extend from the minimum to the maximum value, excluding outliers (circles) and extreme (asterisks) values.

3.2. Pesticide content among case study sites

The number of residues detected in each sample (20, 8–40 pesticides/sample; median, min-max) was comparable in all CSS (Fig. 4), highlighting Croatia (CSS6) as the site with the lowest ($p < 0.05$) values (10, median, 8–12, min-max) and France (CSS3) as the highest one (28, median, 22–36 min-max; $p < 0.01$). Pesticide detection frequencies varied among CSS, see Table S4. Several compounds with high Df values (> 70 %) stood out in some CSS from the rest: Spain (CSS1; chlorantraniliprole), Portugal (CSS2; iprovalicarb, metalaxyl metabolite CGA 62,826, methoxyfenozide and penconazole), France (CSS3; fluopicolide, metrafenone and trifloxystrobin), Czech Republic (CSS8; terbutryn), The Netherlands (CSS9; azoxystrobin, MCPA and prothioconazole desthio), Denmark (CSS10; prosulfocarb) and Argentina (CSS11; 2,4-D, cyproconazole, epoxiconazole and metolachlor(-S)), providing a comprehensive understanding of pesticide contamination in the small water bodies from the diverse agricultural regions. A considerable percentage (38 %) of the pesticide residues found in water are currently not approved as PPP in the European Union (European Commission, 2023). Most of them presented low detection rates (< 15 %), except atrazine (Df of 39 %), terbutryn (38 %), epoxiconazole (20 %), pencycuron (17 %) and organochlorines (Df > 63 %). Pencycuron use was approved at water sampling time (2021 growing season). However, atrazine was not approved then and was found in water samples from 6 CSS, highlighting Slovenia (CSS7; 4.40 ng/L median, 11.8 ng/L max, 100 % Df) and France (CSS3; 2.60 ng/L median, 6.44 max, 83 % Df). In the case of Argentina (CSS11; 112 ng/L median, 302 ng/L max, 100 % Df), the application of this active substance is allowed (De Gerónimo et al., 2014) and is also frequently detected in surface water (135 ng/L max, 100 % Df; Pérez et al., 2021).

Although most of the water samples were collected very close to the farms (< 10 m; Table S1, Figure S3), no correlation ($p > 0.05$) between concentrations and the distance to the agricultural fields was found. Pesticide concentrations obtained in water samples showed very high variability among CSS (see Fig. 1 and Table S4). Argentina was the CSS with the highest median pesticide content (687 ng/L) followed by The Netherlands (654 ng/L), Portugal (618 ng/L) and France (571 ng/L). On the other hand, the lowest levels were obtained from Croatia (17.4 ng/L, median) followed by Spain (31.4 ng/L) and Switzerland (37.7 ng/L). Concentrations found in several CSS, such as Spain, Portugal, France, Switzerland, Croatia, and Argentina were lower than others reported previously in water from the respective country (Table S11; Moschet et al., 2014; Belles et al., 2019; Quintana et al., 2019; Herrero-Hernández et al., 2020; Corcoran et al., 2020; Fingler et al., 2021; Rocha and Rocha, 2023). The predominance of the herbicides was observed in all CSS except CSS3 (France), where the fungicide levels were higher (Fig. 5). Figure S5 details the first 20 pesticides with higher contribution (%) to total pesticide content and Df > 10 % in each CSS. Although differences were shown among CSS, glyphosate (18 - 50 %, min-max) and its metabolite AMPA (6–15 %) were the residues more representative. The concentration of the first 5 pesticides with higher contribution in water from each CSS is detailed in Fig. 6. Glyphosate was present in all CSS with a remarkable contribution in France (68.7 ng/L, median), Italy (95 ng/L), Croatia (8 ng/L), Slovenia (43 ng/L), Czech Republic (169 ng/L), The Netherlands (243 ng/L), Denmark (194 ng/L) and Argentina (205 ng/L) (Table S4). Other compounds were also prevalent such as fluroxypyr (in Spain, 109 ng/L), boscalid (in France, 9 %, 911 ng/L) metalaxyl metabolite CGA 62,826 (in Switzerland, 11 ng/L) and AMPA (in Italy, 118 ng/L; and Slovenia, 59 ng/L). Levels of glyphosate and AMPA obtained were in agreement with values reported in surface water from other European countries such as, France (76 ng/L and 149 ng/L, median, for glyphosate and AMPA, respectively; Ineris, 2020), Italy (170 ng/L and 180 ng/L, mean, for glyphosate and AMPA, respectively; Masiol et al., 2018), Czech Republic (37–103 ng/L; 160–481 ng/L; Konečná et al., 2023) or The Netherlands (39–71 ng/L; 207–475 ng/L; RIWA-Rijn report, 2021) and lower than others found in Argentina (1.88 μg/L; 660 ng/L; Pérez et al., 2021).

Relationships between the content of pesticides in water and their occurrence in the different CSS were also explored by PCA. The score plot distribution related to each CSS revealed that water samples from The Netherlands (CSS9) and Argentina (CSS11) presented higher levels for MCPA, metolachlor(-S) ($p < 0.05$), 2,4-D, glyphosate ($p < 0.01$) and cyproconazole compared to Spain (CSS1), Portugal (CSS2), France (CSS3), Switzerland (CSS4), Croatia (CSS6) and Denmark (CSS10) (Fig. 3a). Similarly, the score plot in Fig. 3a (right) for Portugal (CSS2) reflected higher concentrations for the herbicide metalaxyl(-M) and its

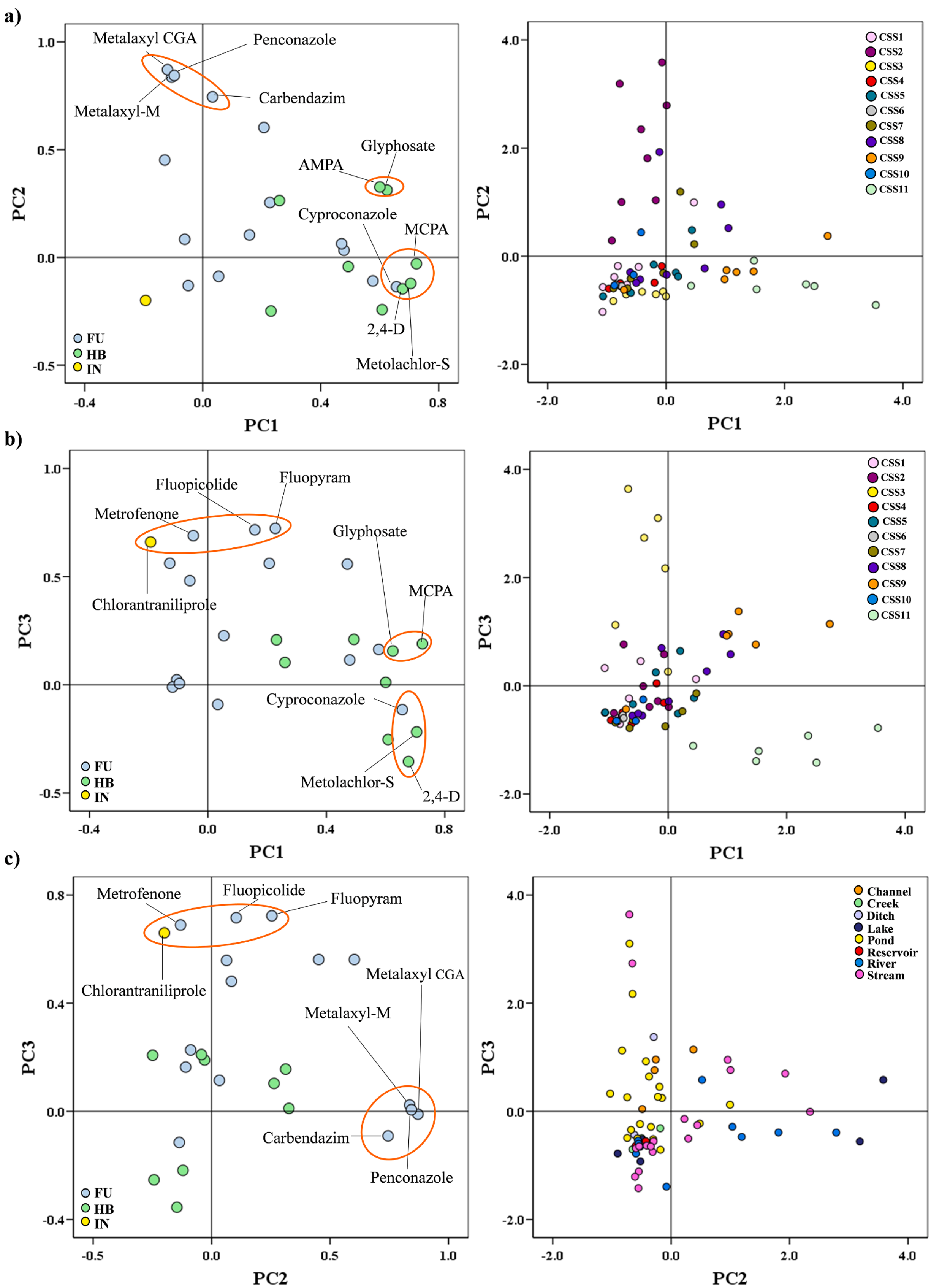

Fig. 3. Diagrams of dispersion related to the three components resulting from a principal components analysis (PCA) derived from the content of pesticides in water and pesticide distribution (type of water body and CSS): a) PC1 and PC2, b) PC1 and PC3, and c) PC2 and PC3. Loading plots (left) contribution of each variable to each component; FU: fungicide, HB: Herbicide, IN: insecticide. Score plots (right), markers set by CSS (a and b) and water body type (c), of all samples on each component.

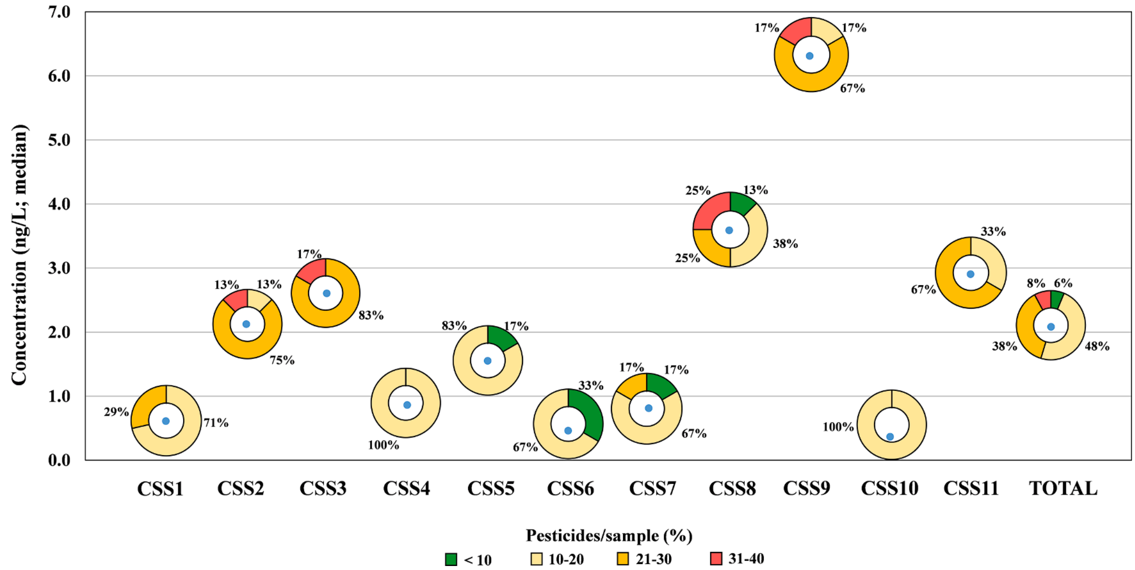

Fig. 4. Total concentration (ng/L; median; blue circles) and number of pesticides found per water sample (%) in each CSS. CSS1: Spain, CSS2: Portugal, CSS3: France, CSS4: Switzerland, CSS5: Italy, CSS6: Croatia, CSS7: Slovenia, CSS8: Czech Republic, CSS9: The Netherlands, CSS10: Denmark, CSS11: Argentina.

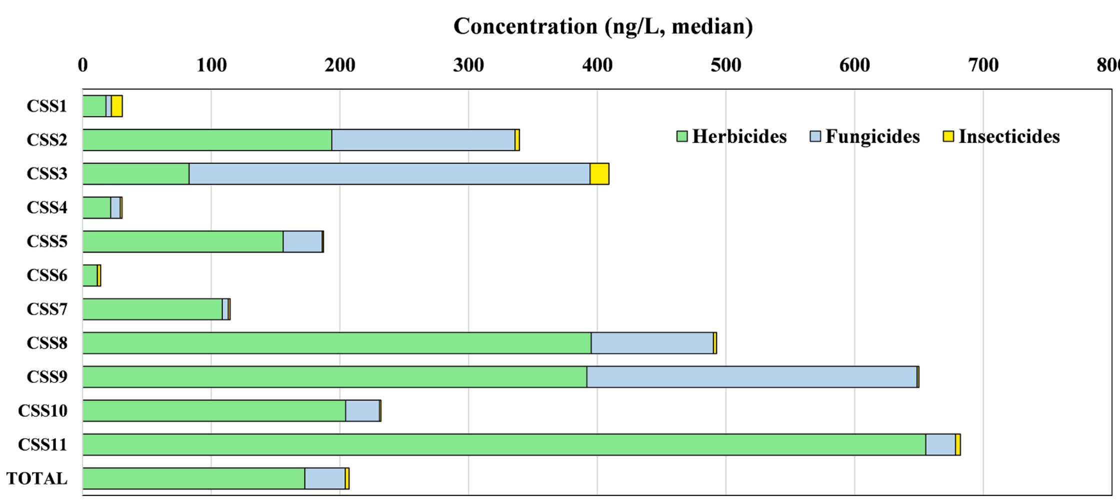

Fig. 5. Total concentration (ng/L; median) of fungicides, herbicides and insecticides in water in each CSS. CSS1: Spain, CSS2: Portugal, CSS3: France, CSS4: Switzerland, CSS5: Italy, CSS6: Croatia, CSS7: Slovenia, CSS8: Czech Republic, CSS9: The Netherlands, CSS10: Denmark, CSS11: Argentina.

metabolite metalaxyl CGA 62,826, and the fungicides penconazole and carbendazim than other CSS (CSS1, 3, 4, 6, 9 and 11). As shown the Fig. 3b water samples related to France (CSS3) and The Netherlands (CSS9) were distributed on the positive side of PC3, indicating higher values for fluopicolide and fluopyram than those observed for CSS4, 6, 7, 10 and 11. It is important to remark that the score plot distribution showed lower ($p < 0.01$) concentrations from Switzerland (CSS4) and Croatia (CSS6) samples, for the three components compared to the other sites.

3.3. Compliance with reference values in water

The Water Framework Directive (WFD) establishes annual average environmental quality standards (AA-EQS) and maximum allowable concentrations (MAQ-EQS) for inland surface water (European Commission 2013, 2022) which should not be exceeded in order to protect human health and the environment. Only 22 out of 193 pesticides investigated in the present study have EQS set in the WFD, so regulatory acceptable concentrations (RAC) provided by the Federal Environment Agency of Germany (UBA, 2020) covering 57 % of the targeted pesticides were also considered (Table S11). This fact stands out that most of the pesticide residues applied in the fields and found in the European surface waters are still unregulated under the WFD. The total concentration (sum of 193 pesticides) obtained was very close (615 ng/L, mean, 300 ng/L, median) to the AA-EQS of 500 ng/L established for the sum of all individual pesticides, metabolites and degradation products detected and quantified in the monitoring procedure (European Commission 2022). The compliance with the reference values at each CSS is summarized in Table S8, mean values obtained in water were compared to AA-EQS and maximum values with MAC-EQS and RAC (Argentina has been also included for comparative purposes). Several compounds exceeded the reference values established in water: acetamiprid (>AA-EQS in CSS1-Spain, CSS5-Italy and CSS9-The Netherlands, and >RAC in CSS5-Italy, CSS8-Czech Republic and CSS9-The Netherlands), bifenthrin (> AA-EQS and RAC in CSS11-Argentina), chlorpyrifos (>AA-EQS and RAC in CSS3-France), clothianidin (>AA-EQS and RAC in CSS2-Portugal), fipronil (>RAC in CSS8-Czech Republic), imidacloprid desnitro (>AA-EQS in CSS11-Argentina), methiocarb (>RAC in CSS5-Italy), nicosulfuron (>AA-EQS in CSS9-The Netherlands), permethrin (>AA-EQS in

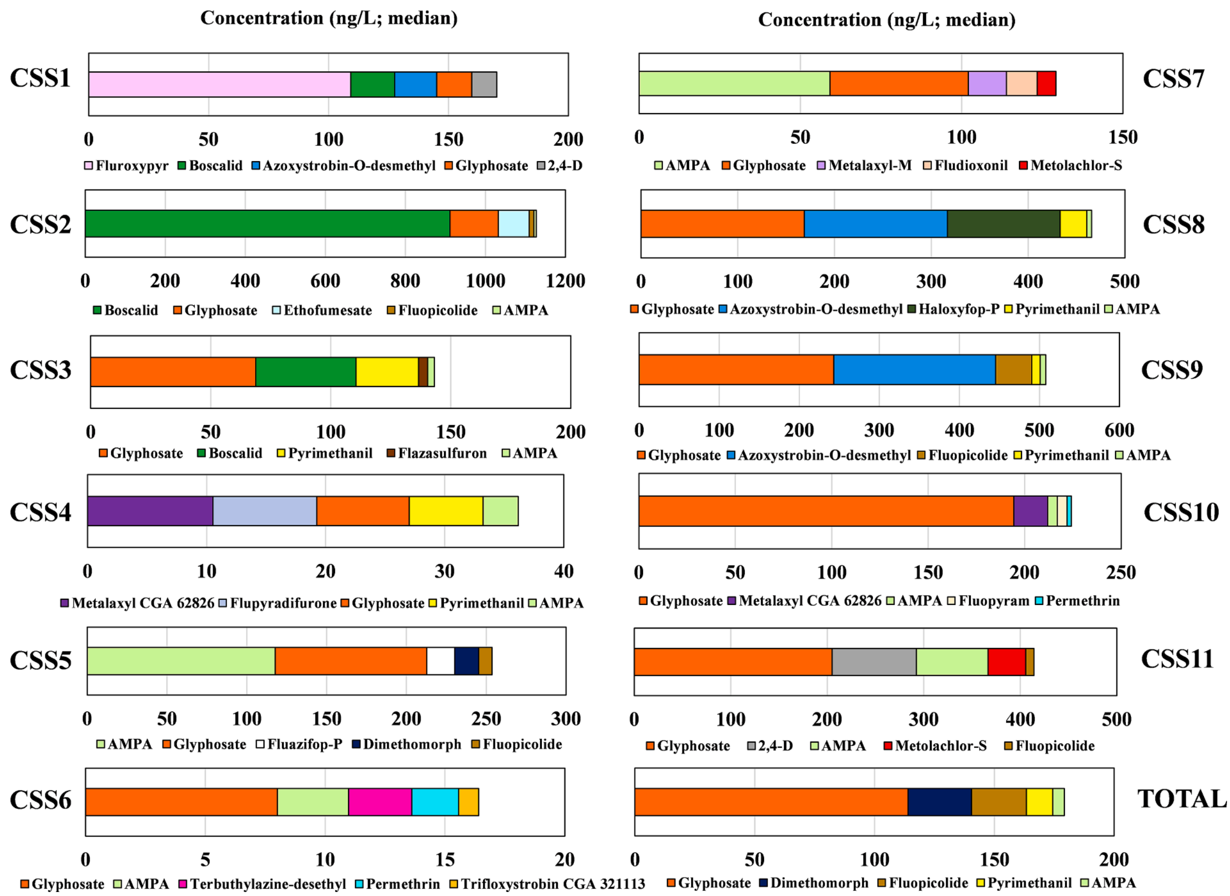

Fig. 6. Concentration (ng/L; median) of some pesticides in water from each CSS. Only the first 5 pesticides with higher contribution and Df > 10 % are shown. CSS1: Spain, CSS2: Portugal, CSS3: France, CSS4: Switzerland, CSS5: Italy, CSS6: Croatia, CSS7: Slovenia, CSS8: Czech Republic, CSS9: The Netherlands, CSS10: Denmark, CSS11: Argentina.

CSS6-Croatia and CSS10-Denmark), spinosyn A (>RAC in CSS5-Italy), and the total concentration (>AA-EQS in 5 CSS and >MAC-EQS in 8 CSS) (Figure S6). Some of them were already banned when the sampling was carried out (Table S3). Nevertheless, their presence raises high concern since ecotoxicological effects have been reported even at lower concentrations (Schulz, 2004; Cruzeiro et al., 2017; Norman et al., 2020). Concentrations of clothianidin, fipronil, and methiocarb exceeding the RAC have been previously measured in streams from Germany (Weisner et al., 2022) and have also shown a relevant pressure on the invertebrate toxicity (Siddique et al., 2020; Leiss et al., 2021). Similarly, Szöcs et al. (2017) also found RAC exceedances and high risk quotients for neonicotinoids, chlorpyrifos and nicosulfuron in small streams. It is worth mentioning that the WFD thresholds are based on water surface monitoring strategies conducted in large rivers while small streams are surveyed less frequently, despite the latter receive substantially higher inputs of pesticides due to their adjacent connection to agricultural fields. However, it is important to recognize that small stream ecosystems serve as biodiversity hotspots, playing a decisive role in ecological conditions and habitats (Weisner et al., 2022). Results obtained in the different small water bodies related to agricultural fields reflect a possible negative ecological impact and risk due to pesticide exposure in surface waters, and reveal the need to include these water masses in the monitoring schemes.

3.4. Environmental risk assessment in the aquatic ecosystem

Up to 37 % of the pesticides quantified in the present study are included in the PAN International List of Highly Hazardous Pesticides (HHPs; PAN, 2021; WHO, 2019; Table S3), 60 % of which present acute or chronic hazards to human health and 57 % environmental toxicity. Furthermore, as mentioned previously, the concentration obtained for several compounds surpassed the threshold values set in surface water directives (WFD and RAC) suggesting a possible ecological impact in the aquatic system. To corroborate such findings, data obtained were used to perform an environmental risk assessment, considering both individual and pesticide mixtures, in the aquatic ecosystem (Tables S9, S10). Although the ratios calculated for most of the residues presented $RQ_s < 0.1$ (low risk, Table S10), ratios for mixtures presented medium ($0.1 < RQ < 1$) or high ($RQ > 1$) risk for the aquatic organisms both at general and worst scenarios in the majority of CSS. Little is known about the combined effect of pesticide mixtures, but results underline greater potential risks compared to the single compounds. The individual pesticides that pointed out for involving high risk were bifenthrin, dieldrin, fipronil sulfone, permethrin, and terbutryn (Table S9). Although several pesticide residues exceeded the threshold values set in surface water (Table S8), not all denoted high risk. Only bifenthrin and permethrin, whose values were higher than reference values, revealed high risk for the aquatic ecosystem. The pyrethroid insecticides are extremely elusive yet biologically active at low concentrations (< 5 % Df and ≤ 3 ng/L in the present study, Table S4) and define aquatic risks on a European scale (Wolfram et al., 2021). On the other hand, high risk was estimated for some compounds whose concentrations were below the threshold values and considered safe for aquatic organisms. Results were in agreement with the statement that the contribution of pesticides to the aquatic ecological status is underestimated under the current environmental exposure and protective thresholds (Stehle and Schulz, 2015; Weisner et al., 2022).

Differences in the estimation of the environmental risk assessment were observed among CSS. The CSS with the highest percentage of medium and high risk ratios (% cases with risk ratios between 0.1 and 1, and above 1, respectively) was CSS11 (Argentina) followed by CSS3 (France) and, CSS 2 (Portugal) (Table S10). Across all countries, 3 % and 5 % of the cases (RQ_{50} and RQ_{max}, respectively) denoted environmental risk in the aquatic compartment studied.

Limitations and uncertainties were found in the present risk estimation. Environmental risk assessment of some pesticides and their metabolites or degradation products is currently hampered by the lack of information related to toxicological assays. Several compounds quantified in water in the present study lack aquatic toxicological data (37 % for aquatic plants, 16 % for algae and 12 % for aquatic invertebrates and fish, Table S3), so their input has not been considered in the risk estimation. Besides, RQ_s were calculated from a conservative perspective (median and maximum concentrations) for both individual and additional (mixture toxicity) approaches (EFSA, 2013). Despite the uncertainties derived from the lack of information, results related to the addition effect among pesticide residues suggested that concentrations in water bodies studied could involve significant ecological risk for the aquatic ecosystem and remarked the necessity of integrated risk assessments that mirror the complexity of these widespread pesticide mixtures in the environment.

4. Conclusions

The occurrence of 193 pesticide residues and mixtures was investigated in 64 small water bodies located in regions with high agricultural activity across 11 CSS from Europe and Argentina. Concentrations and detection frequencies were explored to evaluate the influence of land use, water body sampled, and their distribution among CSS to provide valuable information. Glyphosate, AMPA, and terbuthylazine were frequently detected, indicating their pervasive and ubiquitous presence, and highlighting the dominance of herbicides among detected pesticides in aquatic environments. Organochlorine pesticides, with high detection frequencies, were identified at trace levels, suggesting historical use. Significant variability in pesticide concentrations and detection frequencies was observed among CSS, with Croatia showing the lowest and France the highest values. Several pesticides, including acetamiprid, bifenthrin, chlorpyrifos, and permethrin, frequently exceeded reference values, raising concerns about potential ecological impacts. The conformity of the concentrations quantified in the water masses with the threshold values established for surface water demonstrates the importance to control water quality to protect aquatic ecosystems and contribute to the progressive reduction of emissions of hazardous substances into these compartments. The study also identified a considerable percentage of pesticides categorized as Highly Hazardous Pesticides (HHPs), with potential risks to human health and environmental toxicity. The environmental risk assessment performed, considering mixtures and individual pesticides, suggested potential risks across different trophic levels in the aquatic ecosystem. The results provide evidence of potential ecological risks associated with pesticide exposure in aquatic systems and reveal the necessity to improve the measures to achieve a good chemical and ecological status for small surface water bodies, aligning with current regulations. Moreover, the study emphasizes the importance of conducting further research, particularly focusing on the effects of complex pesticide mixtures on aquatic organisms.

CRediT authorship contribution statement

Irene Navarro: Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Adrián de la Torre:** Writing – review & editing, Validation, Methodology, Investigation. **Paloma Sanz:** Writing – review & editing, Validation, Methodology, Investigation. **Nelson Abrantes:** Writing – review & editing. **Isabel Campos:** Writing – review & editing. **Abdallah Alaoui:** Writing – review & editing. **Florian Christ:** Writing – review & editing. **Francisco Alcon:** Writing – review & editing. **Josefina Contreras:** Writing – review & editing. **Matjaž Glavan:** Writing – review & editing. **Igor Pasković:** Writing – review & editing. **Marija Polić Pasković:** Writing – review & editing. **Trine Nørgaard:** Writing – review & editing. **Daniele Mandrioli:** . **Daria Sgargi:** Writing – review & editing. **Jakub Hofman:** Writing – review & editing. **Virginia Aparicio:** Writing – review & editing. **Isabelle Baldi:** Writing – review & editing. **Mathilde Bureau:** Writing – review & editing. **Anne Vested:** Writing – review & editing. **Paula Harkes:** Writing – review & editing. **Esperanza Huerta-Lwanga:** Writing – review & editing. **Hans Mol:** Writing – review & editing. **Violette Geissen:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization. **Vera Silva:** Writing – review & editing, Project administration, Conceptualization. **María Ángeles Martínez:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.watres.2024.121419.

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