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Keywords

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Abstract

Fishponds are man-made shallow water bodies that are still little studied because of their small size. They represent high value ecosystems, both environmentally (biodiversity hotspot) and economically (fish production). They can have a high place on the hydrographic network, so their influence on water quality is of first importance for rivers and water bodies located downstream and monitored under the Water Framework Directive. These small water bodies can be a source of contaminants during draining period or an efficient buffer for pesticides. We wanted to evaluate whether these ponds could also be a remediation tool against metals by following the annual evolution of upstream/downstream flows. Cadmium, copper, lead and zinc concentrations were quantified in the dissolved phase upstream and downstream of three ponds, each one having a specific agricultural environment (traditional or organic). Metal concentration was quantified in sediments and water. For the dissolved phase, the predictive non-effect concentration was often exceeded, suggesting an environmental risk. Results highlighted also greater quantity of metals at the downstream of the pond compared to the upstream, suggesting remobilization into the ponds or direct cross-sectional contributions from the watershed (e.g. runoff from crops) or even remobilization. Regarding sediments, minimal contamination was shown but a high mineralogical variability. No buffer effect of ponds, which could reduce the risk of acute or chronic toxicity, was detected.

1. Introduction

Historically, France has been exposed to metal contamination from various anthropogenic activities, such as metallurgy (Sterckeman et al. 2000; Douay et al. 2008), mining (Audry et al. 2004; Escarré et al. 2011), intensive agriculture (Chopin et al. 2008; Banas et al. 2010) and livestock production (L'Herroux et al. 1997), hunting activities (Pain and Amiard-Triquet 1993) and also world wars (Bausinger et al. 2007; Gorecki et al. 2017). Concerning agriculture, the Lorraine region (North-eastern France) is largely occupied by agricultural lands, which represent 48.6% of the total region's surface (Ministère de l'Agriculture et de l'Alimentation 2015). However, it is well known that this activity is a source of metal pollution induced by the use of mineral fertilizers, such as phosphate fertilizers (Nziguheba and Smolders 2008). Then, world wars are also significant sources of metal contaminants in the Lorraine region. The two world wars have sustainably transformed landscapes and ecosystems. If we only consider the First World War, 1 billion shells and ammunitions were fired in Europe (Gorecki et al. 2017), and about 1.7 billion tons of unfired ammunitions were left at the Armistice (Hubé 2017). These amounts represent an important source of metal pollution. Yet, one of the main sources remains industrial activities since the industrial revolution (beginning of the nineteenth century). According to the INERIS (French National Institute for Industrial Environment and Risks), there is a 300%

increase in metal requirements in the last 50 years and a threefold increase in the environmental contaminations by metal such as cadmium, copper, lead or zinc since the industrial era (INERIS 2006). However, the metal contamination began largely before the industrial revolution. In Lorraine, the coal mining basin was exploited between the 18th and 20th centuries but there are evidences of steel activities dating from the Middle Age during the fourth century (Leroy et al. 1990). From this period and until the Steel Crisis in the 1970s, this region was the place of a high production of steel (Sinou 1977).

The toxicity of Cd, Cu, Pb and Zn, their high productions (extraction/production volume) and uses, their occurrence in the aquatic environment and resulting human exposure led to their mention in substance priority lists established by environmental or public health agencies such as the US Environmental Protection Agency (2014) or the Agency for Toxic Substances and Disease Registry (2017). The European Water Framework Directive (WFD) was set to coordinate actions of the European Union members to preserve and improve the good status of surface waters and groundwaters. It also considers Cd, Pb and their associated compounds as priority substances presenting a real risk to, or through, the aquatic environment (The European Parliament and the Council 2008). Both metals are non-essential. They do not have a known biological role and their toxicity increases with their concentration. On the contrary, Cu and Zn have biological functions at certain concentrations. They are, for example, involved in numerous biological activities and process such as proteins or enzymes functioning (Ruel and Bouis 1998; Grotz and Guerinot 2006; Osredkar and Sustar 2011). For this kind of metals, biological impairments can be observed when an organism suffers from a lack of these elements or is exposed to high concentrations. Numerous toxic effects of Cd, Cu, Pb and Zn have been reported on aquatic organisms. For example, review articles described that they are all recognized to cause deformities (Sfakianakis et al. 2015), disturbances in haematology and glycogen reserves (Javed and Usmani 2014) in fishes or to alter reproductive or developmental parameters in amphibians (Slaby et al. 2019).

The Lorraine region is characterized by a high density of barrage ponds (Le Queré and Marcel 1999). These man-made water bodies support an economic activity through fish production. Unlike intensive aquaculture systems, as trout farming, which engender large amount of waste and influence ecosystem quality (Sidoruk and Cymes 2018; Sid oruk 2019), fish production in the studied site is performed in an extensive way. This traditional fishery is characterized by the absence of supplementary food and a lower fish density. By preventing the landscape closure, maintenance of these shallow waters contributes to wetland conservation (Blayac et al. 2014). At the landscape level, they constitute privileged habitats with a wide species diversity (Scheffer et al. 2006; Broyer and Calenge 2009). For example, a comparison between river, stream, ditch and pond diversity, in an agricultural landscape in Britain, showed that ponds supported higher plant and macroinvertebrate diversities and more uncommon species compared to other waterbodies types at a regional level (Williams et al. 2004). Concerning bird diversity, there is a positive impact in agricultural area of the Lublin region in Poland regarding fishpond complexes (Nieoczym 2010). However, fishponds have negative effects on the environment and are considered as disruptors of the ecological continuum and responsible for greater water evaporation (Blayac et al. 2014). Also, fish management practices consisting to discharge the whole pond water volume, in order to catch fish, can be a source of nitrogen and phosphorus for downstream systems (Banas et al. 2002a, 2008).

Shallow lakes and small impounded waterbodies (i.e. surface area lower than 0.5 km2) are not taken into account by the WFD, and few studies were interested in their ecological role or their environmental quality. Nevertheless, in France, small water bodies represent the majority of the lacustrine area surface (Bartout et al. 2015). At the national scale, among the estimated 4,239,003 km2 covered by lakes, up to 1,818,100 km2 correspond to waterbodies smaller than 1 km2 (Downing et al. 2006). In this context, the study was conducted not only to better understand pond impacts on the global environment but also to assess the quality of these aquatic habitats located at the very beginning of the hydro-graphic network (1st-order streams; Strahler 1952). Previous results obtained in our laboratory showed the potential of fishponds to decrease pesticide peak concentrations between the upstream station (UP) and the downstream station (DO) of the ponds (Gaillard et al. 2014). The aims of the present work were to assess UP and DO metal flows. For this purpose, Cd, Cu, Pb and Zn concentrations in water and sediment matrices, obtained from the sampling campaign realized in the previous study, were analysed in the same three ponds located in the Lorraine region (Gaillard et al. 2014). This work could bring us insights about potential beneficial buffer effect of ponds, as observed in our previous study on organic pollutants, and information about water quality in headwater streams.

2. Material and Methods

2.1. Sampling sites

Study sites were located in the Lorraine region (FR) on the Seille river watershed (Fig. 1). These shallow lakes are a part of the landscape since the thirteenth century, when they were built by monks to produce fish (Billard 2010). Today, they provide around 130 kg of fish per hectare (Banas et al. 2008). This region is characterized by an annual air temperature of 10.7 °C, with an average minimum of 2.2 °C in January and an average maximum of 19.7 °C in July. Regarding precipitation, the zone is in the average (775 mm/year) of France (800 mm/year), but it increased during the studied period (2013–14) with 946 mm and 29 heavy rainfall events (above 10 mm; 30-year average, meteorological station of Château-Salins, Météo-France).

Three fishponds were selected following these main criteria: (a) a single tributary is identified to be the main water source of each pond, (b) water sampled during the whole year characterizes the catchment and (c) different kinds of land use are identified (forests and agricultural fields). Table 1 sums up the study site characteristics. Watershed areas were 0.64 km2 for FP0, 3.45 km2 for FP1 and 0.86 km2 for FP2. Catchments of FP1 and FP2 were mainly agricultural (respectively 82 and 88% of pastures and arable lands), whereas FP0 was characterized by a forest type catchment (64%) with few arable lands

(34%). The biggest pond was FP1 with 0.316 km2, followed by FP2 with 0.044 km2 and FP0 with 0.011 km2. Due to their locations, the sub-catchments drained to UP were estimated to 81, 51 and 50% of the total catchment for FP0, FP1 and FP2, respectively (Billiard 2010). Concerning the outflow rates, the annual averages were 494 ± 44 m3/day in FP0, 3191 ± 313 m3/ day in FP1 and 419 ± 54 m3/day in FP2. Nominal water residence time estimations, calculated as the pond's volume divided by the mean outflow, were 37, 178 and 95 days for FP0, FP1 and FP2, respectively (Gaillard et al. 2014). Physicochemical parameters (temperature, pH, dissolved oxygen and conductivity) measured at UP and DO of each pond are given in Table 1. Regarding the functioning of the ponds, according to the fishery practices or the season, the flow at DO was greatly reduced. Indeed, after the fish harvest, resulting from the opening gate located on the dam to discharge the entire water volume into the downstream river, the gate was closed and the flows decreased drastically at DO (Nov. 2013 in FP0 and FP1 and Dec. 2013 in FP2). The persistence of a slight flow was due to low leaks through the dams. Then, the ponds were filled with inlet water carried by upstream rivers, which a large part was recorded at UP. We also observed a large decrease of the flows due to summer weather which could bring this value to 0 m3/day (for example at the DO of FP0).

In the Lorraine region, shallow water bodies are still used for fish production, mainly in an extensive way (no additional feed given). During the experimentation time, FP0, FP1 and FP2 were filled with four main species: common carp (Cyprinus carpio), tench (Tinca tinca), roach (Rutilus rutilus) and rudd (Scardinius erythØphthalmus). Carps and tench will feed on macroinvertebrates of the sediment while roach and rudd will feed on pelagic macroinvertebrates.

2.2. Sampling design and quantification of metals in water

UP and DO of each pond were equipped with automatic water samplers (SD-900 Sigma) (Fig. 1). At DO, water samplers exclusively took water coming out of the ponds. Water was sampled approximately every 15 days at UP and DO from March 25, 2013 to March 14, 2014 (this period is rounded to 1 year in the manuscript). For each pond, two automatic water samplers were used (one at the UP and one at DO) to collect 24 h composite samples (each sample is a mix of 24 aliquots). The 1-year sampling campaign leads to the collection of 150 samples, regardless of weather conditions and water flows (time based sampling strategy). All samples were filtered (GF/A filters; 0.45 μm) on site and stored in 50-mL polypropylene Falcon tubes at 4 °C quickly to avoid the sorption of metals. Within 24 h, samples were acidified with HNO3 (3%) at the laboratory. Cd, Cu, Pb and Zn concentrations were determined in dissolved phase by inductively coupled plasma mass spectrometry (ICP-MS) performed by the Centre de Recherches Pétrographiques et Géochimiques (CRPG, Nancy, FR). Cd, Pb, Cu and Zn were detected in all samples. Limits of quantification of Cd, Cu, Pb and Zn were 0.006, 0.017, 0.04 and 1 μg/L, respectively. UP and DO flows were intermittent, so sample numbers could be different between the sampling locations. Samplers collected 19, 17 and 19 water samples at UP and 19, 18 and 19 at DO for FP0, FP1 and FP2, respectively. In the same time, the water flow was continuously monitored with recording every 15 min over the studied period at each sampling point.

2.3. Sampling design and quantification of metals in sediment

Sediment samplings were performed with a standard Eckman grab at four sites in each pond in May 2014. Sampling sites were all located in high sedimentation zones (Banas et al. 2001, 2002b) and equally distributed between the right and left banks of the main channel in UP (UP-R and UP-L) and DO (DO-R and DO-L) (Fig. 1). UP-R and UP-L were located at 3 m of the helophytic vegetation while DO-R and DO-L were in open water at equal distance from the main channel and the banks of the pond (riparian zone). At each point, the sampling was made twice. Homogenized mixtures were washed off the biggest particles (rocks, leaves, branches ...) using a sieve with a 2-mm mesh before being ground, freeze dried and stocked at room temperature. Cd, Cu, Pb and Zn concentrations were assessed by inductively coupled plasma optic emission spectroscopy (ICP-OES) according to the method described by Carignan and collaborators (Carignan et al. 2001) at the CRPG (Nancy, FR). For each fishpond, metal concentrations at the four sampling points (UP-R, UP-L, DO-R and DO-L) were averaged to obtain a representative metal concentration in the sediment and compared to sediment Predicted No Effect Concentration (PNEC) values of each metal (INERIS 2005a, b, 2011, 2016).

Enrichment factors (EF) of sediment were obtained using average metal contamination in the same geographic area and aluminium concentration as reference. EF were assessed using the following equation:

$$\mathrm{EF} = ([\mathrm{M}]/[\mathrm{Al}])_{\mathrm{sediment}}/([\mathrm{M}]/[\mathrm{Al}])_{\mathrm{re\,ferencearea}}$$

where [M] referred to metal concentration (Cd, Cu, Pb or Zn; μg/g) and [Al] referred to Al concentration (g/100 g) both measured either in the sediment of each fishpond and in the soil (30–50 cm depth layer) of reference area. A significant enrichment from anthropogenic activities was considered when the value was higher than 2; otherwise, a natural variability of the mineralogical composition of the sample was admitted (Sutherland 2000; Hernandez et al. 2003).

Al is often used to normalize metal data because it is the major component of fine-grained aluminosilicates to which an important part of trace metals is associated (Loring 1991; Sutherland 2000). Metal concentration references were measured in soils at 30–50 cm deep in the closest areas to the drainage basin of each pond by a French soil quality monitoringnetwork (INRA, Unité INFOSOL 2014). We expected low anthropogenic perturbations at this depth, thus representing natural pedo-geochemical background. For FP0, soil surrounding the pond is a silty soil type occupied by deciduous forest. Regarding FP1 and FP2, a Keuper marl soil surrounds both ponds and it was occupied by a 3-year crop rotation (mainly rape, corn, barley).

2.4. Statistical analysis

Differences between annual average concentrations of each metal in water at UP and DO of FP0, FP1 and FP2 were determined using paired samples t tests. Student's t tests for one sample were performed to compare the average concentrations contained in freshwater to the PNEC of each metal (INERIS 2005a, b, 2011, 2016). From metal concentrations in water assessed along the year approximately every 2 weeks and daily averaged water flows, we estimated a daily flux for each metal. For that purpose, we assumed that concentrations were constant during a period around the measure. One period corresponded to the half time between the concentration assessment moment from the preceding and the following measures. For each sampling stations, 355 daily fluxes were estimated for Cd, Cu, Pb and Zn from March 25, 2013 to March 14, 2014. Paired samples t tests were used to assess differences between UP and DO in FP0, FP1 and FP2 concerning metal flux. All over the document, results are expressed as mean ± standard error of the mean (SEM). All statistical analysis and graphical representations were obtained with R software (version 3.5.1—The R Foundation for Statistical Computing, 2018).

3. Results

3.1. Metal concentrations

Statistical analysis did not reveal significant differences between UP and DO metal concentrations in dissolved phase of all fishponds (Fig. 2). For Cd, concentrations were approximately similar at UP and DO (for UP and DO, respectively: 0.02 ± 0.001 and 0.02 ± 0.003 µg/L for FP0; 0.01 ± 0.002 and 0.01 ± 0.002 µg/L for FP 1; 0.01 ± 0.001 and 0.01 ± 0.002 µg/L for FP2). These values, as well as the maximum concentrations observed during the whole study period, never reached the PNEC of Cd (0.19 µg/L; Fig. 2a). Cu concentrations were 2 ± 0.3 and 2.3 ± 0.2 µg/L, 0.8 ± 0.1 and 0.9 ± 0.2 µg/L for FP1 and 1.4 ± 0.2 and 1.5 ± 0.3 µg/L for FP2, at UP and DO, respectively. The maximum concentration measured at UP and DO in FP0 (UP 4.4 µg/L, DO 4.3 µg/L), FP1 (UP 2.4 µg/L, DO 3.3 µg/L) and FP2 (UP 3.5 µg/L, DO 5.9 µg/L) always exceeded the PNEC (1.6 µg/L). These values were recorded during the spring of 2013, except in DO of FP0 where the highest Cu concentration was recorded in November 2013. In addition, for FP0, the average Cu concentrations also exceeded the PNEC at UP and DO (only in a significant way at DO; $p < 0.01$; Fig. 2b). Pb was assessed at concentrations of 0.3 ± 0.1 and 0.3 ± 0.1 µg/L for FP0, 0.1 ± 0.02 and 0.1 ± 0.03 µg/L for FP1 and 0.1 ± 0.02 and 0.3 ± 0.1 µg/L for FP2, at UP and DO, respectively. The mean concentrations of Pb never reached the PNEC (0.41 µg/L). The Pb maximum concentrations at UP (0.8 µg/L) and DO (1 µg/L) from FP0, as well as DO (2.4 µg/L) from FP2, were above this threshold during the spring of 2013 (Fig. 2c). At last, concerning Zn, concentrations were 6.7 ± 0.8 and 9.6 ± 2.6 µg/L for FP0, 6.2 ± 1.6 and 6.2 ± 0.7 µg/L for FP1 and 6.3 ± 1 and 7 ± 1 µg/L for FP2 for UP and DO, respectively. All the Zn maximal concentrations measured exceeded the PNEC estimated at 7.8 µg/L during spring 2013 (FP0, UP 14.8 µg/L, DO 53.1 µg/L; FP1, UP 29.1 µg/L, DO 10.2 µg/L; FP2, UP 18 µg/L, DO 18.4 µg/L). Average concentration assessed in DO of FP0 also reached the PNEC but not significantly (Fig. 2d).

3.2. Metal flux

Comparisons between UP and DO of each fishpond highlighted a significant greater amount of metal assessed in dissolved phase at DO than at UP, except for FP1 concerning Cd ($p = 0.067$; Fig. 3). In that case, Cd fluxes were 0.02 ± 0.001 g/day at UP and 0.02 ± 0.001 g/day at DO. In other ponds, Cd fluxes were 0.004 ± 0.0004 and 0.01 ± 0.001 g/day for FP0 ($p < 0.01$) and 0.003 ± 0.0002 and 0.01 ± 0.001 g/day in FP2 ($p < 0.01$), at UP and DO, respectively (Fig. 3a). Cu fluxes were 0.6 ± 0.04 and 1.1 ± 0.1 g/day for FP0 ($p < 0.001$), 1.7 ± 0.1 and 2 ± 0.1 g/day for FP1 ($p < 0.05$) and 0.4 ± 0.04 and 0.7 ± 0.1 g/day for FP2 ($p < 0.01$), at UP and DO, respectively (Fig. 3b). Then, Pb fluxes calculated were 0.1 ± 0.01 and 0.2 ± 0.03 g/day in FP0 ($p < 0.001$), 0.1 ± 0.01 and 0.4 ± 0.03 g/day in FP1 ($p < 0.001$) and 0.03 ± 0.003 and 0.2 ± 0.03 g/day in FP2 ($p < 0.001$), at UP and DO, respectively (Fig. 3c). At last, Zn fluxes were 1.6 ± 0.1 and 3.2 ± 0.3 g/day in FP0 ($p < 0.001$), 11.4 ± 0.6 and 16.9 ± 1.3 g/day in FP1 ($p <0.001$) and 1.6 ± 0.1 and 2.9 ± 0.4 g/day in FP2 ($p < 0.001$), at UP and DO, respectively (Fig. 3d). The highest flux was always assessed during spring 2013 for all metals, except in FP2 for Cd in UP (Nov. 13) and Zn in UP and DO (Dec. 13/Jan. 14).

3.3. Enrichment factor and metal concentrations in sediment

Enrichment factors, calculated from average concentrations in pond sediments and in surrounding soils for Cd, Cu, Pb and Zn for each fishpond, are given in Table 2. A significant enrichment from anthropogenic activities of Cd in FP0, FP1 and FP2 was highlighted. Regarding Cu, Pb and Zn enrichment factors, values suggested no or minimal contamination but a natural variability of the mineralogical composition. The estimated PNEC for Cu (0.8 mg/kg) and Zn (37 mg/kg; INERIS 2005a, b) were exceeded by the determined concentrations in the sediment of all fishponds (Table 2). Conversely, the PNEC of Cd (2.3 mg/kg) and Pb (53.4 mg/kg; INERIS 2011, 2016) were not reached.

4. Discussion

The aim of this work was to better understand the impacts of lentic aquatic systems on the quality of running water. We determined if an improvement of water quality between UP and DO occurred regarding metals. Our previous study highlighted a buffer role of barrage fishponds resulting in a reduction of pesticide peak concentrations (Gaillard et al. 2014). In this former study, based on the same sampling campaign, despite the fact that only the main entry was considered, because of logistical limitations, we could still observe a significant buffer effect. The results were totally different for metals, and the buffer effect was not shown (Fig. 2). A greater quantity of metal was observed at DO compared to UP, regardless of the kind of element or the studied fishpond. The samplers at UP were located to avoid ebb of the pond while optimizing the sampled catchment area. On the contrary, at DO, the entire catchment was monitored as lateral waters were collected too. It could explain partially the higher quantity of dissolved metals in the output flows (Fig. 3). Metals can also reach DO from all around the ponds by runoff from agricultural fields. This limitation might as well influence the difference between UP and DO in metal concentrations (Fig. 2). In addition, the sampling strategy, which was fitted to follow 3 different ponds simultaneously during a complete year, may be lacking of accuracy to reflect the variability of concentrations between UP and DO. Nevertheless, former studies demonstrated that fishponds could also be reservoirs for different components, such as nitrogen and phosphorus which are released during the emptying of the pond (Banas et al. 2002b, 2008). In the present work, maximum concentrations of metals were observed mainly during spring season while draining of the ponds for fish production happens during late winter. We can explain the decreasing concentrations of nutrients and pesticides at DO because these compounds can be partly assimilated or metabolized through physical processes (e.g. photodegradation) or biological processes (e.g. bacterial activity). Since metals are conservative contaminants, these processes cannot induce degradation of the compound. Only a modification of the metal speciation could be induced by the pond and would require a specific study.

In our study, atmospheric inputs were not estimated, but it is well known that metals can be transported over very long distances and impactenvironment far from their emission points (Steinnes and Friedland 2006). Another study, which took place 200 km from our study sites, showed that particles (< 10 µm) from the atmosphere could be contaminated to Cd and Pb (Malherbe et al. 2017). Globally, in the 1990s, the Pb concentrations were higher than the quality threshold (0.25 µg/m3) but decreased until the end of the study in 2012. Concerning Cd, concentrations never reached the quality threshold (5 ng/m3) and decreased until 2012. Yet, regarding watershed sizes compared to fishpond areas, it seems unlikely that direct atmospheric depositions explained alone the observed difference between UP and DO. Indeed, even for the largest pond (FP1, area of 0.316 km2) and with significant annual precipitation (i.e. 946 mm recorded during the study), assuming that Pb and Cd reached these thresholds (i.e. 0.25 µg/m3 and 5 ng/ m3, respectively), the direct contribution of the rain on the pond would be at most 0.07 g of Pb and 0.0015 g of Cd. These maximum annual contributions are lower than intakes recorded during a single day at UP.

It is well known that pH influences the release and the bioavailability of metals release from particulate phase in waters or from sediments (Bourg and Loch 1995). It has been proved that adsorption of Cd, Cu and Zn increases in alkaline conditions due to binding to suspended particles as hydroxides (Serpaud et al. 1994; Cappuyns and Swennen 2008). In the studied ponds, during the sampling campaign, no pH variation was observed (or detected) between UP and DO (Table 1). Thus, in that case, we cannot conclude that the bioavailability of metal increased at DO due to pH. In the same way, no high variation in dissolved oxygen explaining metal desorption was observed during the study period. However, as previously mentioned, the largest downstream releases of metals were measured mainly during spring season which corresponds to the phytoplankton bloom period. During this period, decomposition of organic matter settling on the sediment results in a large depletion in dissolved oxygen in the deepest water layers and in the sediment which are likely to induce desorption of metals from sediments (Banas et al. 2002b, 2010). This hypothesis and the processes involved in the release of metals from the sediments in the ponds would need to be studied in further works. Globally, during the entire study period, our pH conditions might account for the low Cd concentrations in spite of many sources of contamination in the Lorraine region (i.e. metallurgic and agricultural activities). However, in contrary to Cd, Pb and Zn, the Cu mobility can also increase (Cappuyns and Swennen 2008) and could explain the quantified concentrations in our water samples.

Comparison of metal concentrations in water to PNEC values also suggested a high contamination of certain elements and significant environmental risks. In fact, in dissolved concentrations in water, not only all maximum Pb and Zn concentrations, but also the average Pb concentration in DO of FP0, exceeded the PNEC. This suggests that at least once a year, a potential environmental risk could have occurred (Fig. 3). In the same way, Cu maximum concentrations were higher than the PNEC in FP0 and at DO of FP2. Fishponds are often recognized as biodiversity hotspots at the landscape scale (Williams et al. 2004; Scheffer et al. 2006; Nieoczym 2010). Nevertheless, it is necessary that environmental management applied to these small water bodies is in accordance with potential ecological services. The studied sites showed a high metal contamination from anthropogenic activities, leading to poor ecological status. Located in the same region but closer from industrial activity, the Fensch river in the Lorraine region (FR) was considered in the 1980s as the most contaminated French river due to urbanization, high steel industry and mining activities (Montarges-Pell etier et al. 2007). However, concentrations encountered in the studied ponds could be higher than the concentrations measured in the Fensch river (Cu 3.4 µg/L, 02/2005; Pb 0.36 µg/L and Zn 41.51 µg/L, 06/2005; Montarges-Pelletier et al. 2007). Figure 3 shows that the maximum concentrations determined in our study often exceeded these values.

The estimation of the EF is often used to determine if trace metals come from anthropogenic activities or natural sources (Sutherland 2000; Hernandez et al. 2003). Our results showed a significant anthropogenic influence for Cd (Table 2). EF values oscillated between 2.87 and 4.92 depending on the fishpond, suggesting a moderate enrichment according to literature (Sutherland 2000). Phosphorus fertilizers, frequently spread on agricultural fields, were sources of contamination by Cd. Cd contents in mineral fertilizers remain unaddressed across the European Union (Ulrich 2019). Former practices in fishpond exploitation consisting to apply slag, a by-product obtained from metallurgic activity, could also be a source of contamination to metals including Cd. A few decades ago, slag treatment was common in fishponds and, even if we do not have evidence, it might occur in our study sites and could explain the Cd enrichments. Concerning other metals, a natural variability of the mineralogical composition could be admitted. However, we can notice that Cu concentrations in sediments were higher than the PNEC in all the studied sites, as Zn concentration in FP0 and FP1 (Table 2). Nevertheless, EF values for Cu did not reveal any anthropogenic input. So, we could not explain this result by past Cu treatments which were common to limit cyanobacterial blooms in fishponds (Sevrin-Reyssac and Pletikosic 1990).

Despite the importance of headwater streams, few studies provided baseline data on contamination by assessing their quality status. Most of the time, they focused on downstream systems (Kreuger 1998; Meybeck et al. 2007). There is no reference value concerning contamination of headwater stream regarding metals. Only particular ecosystems were considered such as mountains (Claveri et al. 1995; Zaharescu et al. 2009). However, headwater streams remain an important part of the hydrographic system by influencing the downstream water quality (Alexander et al. 2007) and thus should be more considered. This work is in continuity of Gaillard and collaborators' work showing the high contamination of the beginning of hydrographic networks by phytopharmaceutical products (Gaillard et al. 2016). The present results bring novel data on the status of agricultural headwater streams, aiming to understand ecosystem services or disservices provided by ponds. They should help improving management practices to avoid downstream metal contaminations. As example, previous work proved the ability of stormwater basin to avoid downstream Cu contamination by runoff water from vineyards, inducing sequestration (Banas et al. 2010). The system could also be improved with protections all around it to prevent meteorological disturbance (such as wind) leading to metal contaminant remobilization.

5. Conclusion

It has been previously showed that barrage fishponds are singular ecosystems. They are considered as biodiversity hotspots, buffer zones for organic pollutants and also an important part of economic activity of many regions. The present work has shown that headwater streams located in agricultural plain are contaminated not only by pesticides but also by metals. However, and keeping in mind that particulate phase was not taken into account, this study highlighted that ponds located on these streams might not be a remediation tool to improve water quality regarding metals but as an accumulation reservoir, as well as a funnel, releasing past or present metal contamination.

Table 1. Study site characteristics

	FP0		FP1		FP2	
Watershed						
Area (km^2)	0.64		3.45		0.86	
Land use	Forest (64%)		Arable land (82%)		Arable land (84%)	
Pond						
Area (km^2)	0.011		0.316		0.044	
Outflow rate (m^3/day)[a]	494 ± 44		3191 ± 313		419 ± 54	
Nominal residence time (day)	37		178		95	
GPS position	48° 45′ 42.808″ N 6° 49′ 31.7643″ E		48° 44′ 52.152″ N 6° 42′ 19.534″ E		48° 45′ 17.543″ N 6° 44′ 17.974″ E	
	UP	**DO**	**UP**	**DO**	**UP**	**DO**
Streams						
Temperature (°C)[a]	10.8 ± 2.2	12.4 ± 2.8	11.9 ± 2.4	13.7 ± 2.9	11.6 ± 2.3	12.5 ± 2.5
pH[a]	7.8 ± 1.6	8 ± 1.6	7.8 ± 1.5	8.2 ± 1.7	7.8 ± 1.5	7.7 ± 1.5
Dissolved oxygen (mg/L)[a]	8.7 ± 1.7	8.6 ± 1.7	8.3 ± 1.6	8.7 ± 1.8	8.5 ± 1.7	7.4 ± 1.4

[a] Expressed as mean ± SEM

Table 2. Concentrations of Cd, Cu, Pb, Zn (mg/kg) and Al (g/100 g) measured in sediment (N = 4) of FP0, FP1 and FP2 and associated enrichment factors

	Cd	Cu	Pb	Zn	Al
PNEC	2.3	0.8	53.4	37	NA
FP0					
Mean ± SEM	0.3 ± 0.01	29.4[a] ± 0.2	20.6 ± 0.4	107.1[a] ± 3.9	8.5 ± 0.2
EF	2.87	1.39	0.51	1.05	1
FP1					
Mean ± SEM	0.4 ± 0.04	16.3[a] ± 3	17.6 ± 2	64.6[a] ± 12.3	4.8 ± 0.05
EF	4.92	1.01	0.78	0.98	1
FP2					
Mean ± SEM	0.4 ± 0.01	24[a] ± 1.3	31.5 ± 1.8	94.8[a] ± 5.3	6.7 ± 0.3
EF	3.44	1.06	1.64	1.02	1

EF enrichment factor

[a] Mean concentration higher to PNEC (INERIS, 2005a, b, 2011, 2016)

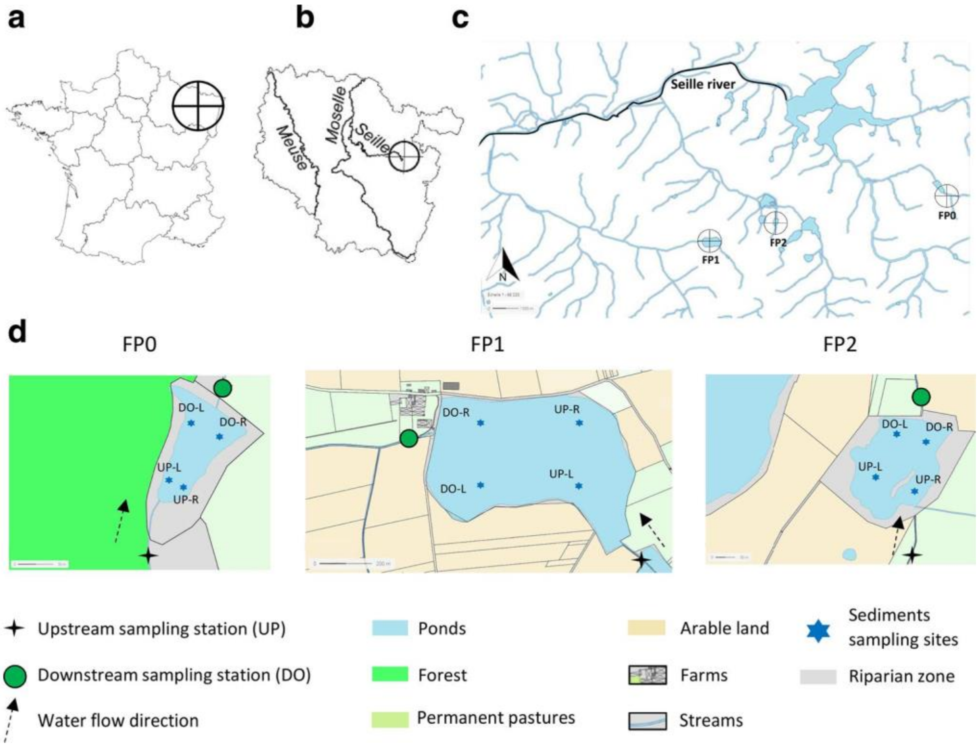

Figure 1.
Location of the studied ponds (a France, b Lorraine, c ponds positions on the Seille river catchment) and land use, water flows direction and sampling sites around the three dam ponds (d)

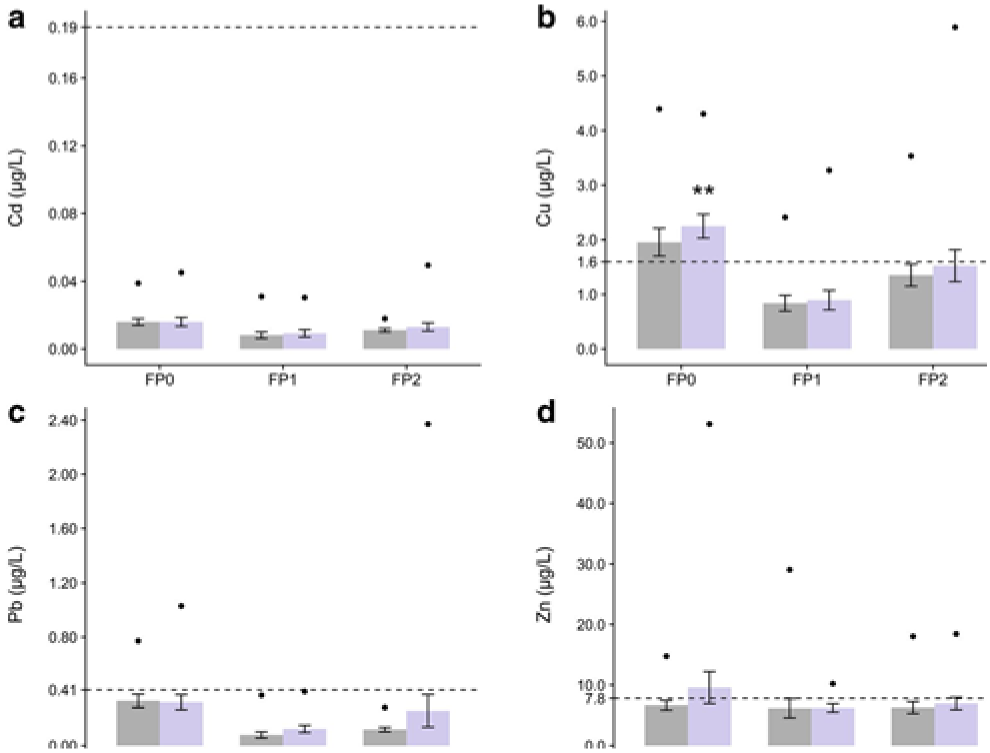

Figure 2.

Cd (a), Cu (b), Pb (c) and Zn (d) concentrations (µg/L) in dissolved water at UP and DO in FP0, FP1 and FP2. Results are expressed as mean ± SEM. Maximum concentrations per station are represented by black dots and PNEC of metal by dotted line. Differences between metal concentrations of UP and DO of each fishpond were assessed using paired samples t tests (no significant difference found). Comparisons of the average concentrations of metals contained in freshwater to the PNEC were realized by performing Student's t tests for one sample (**p < 0.01)

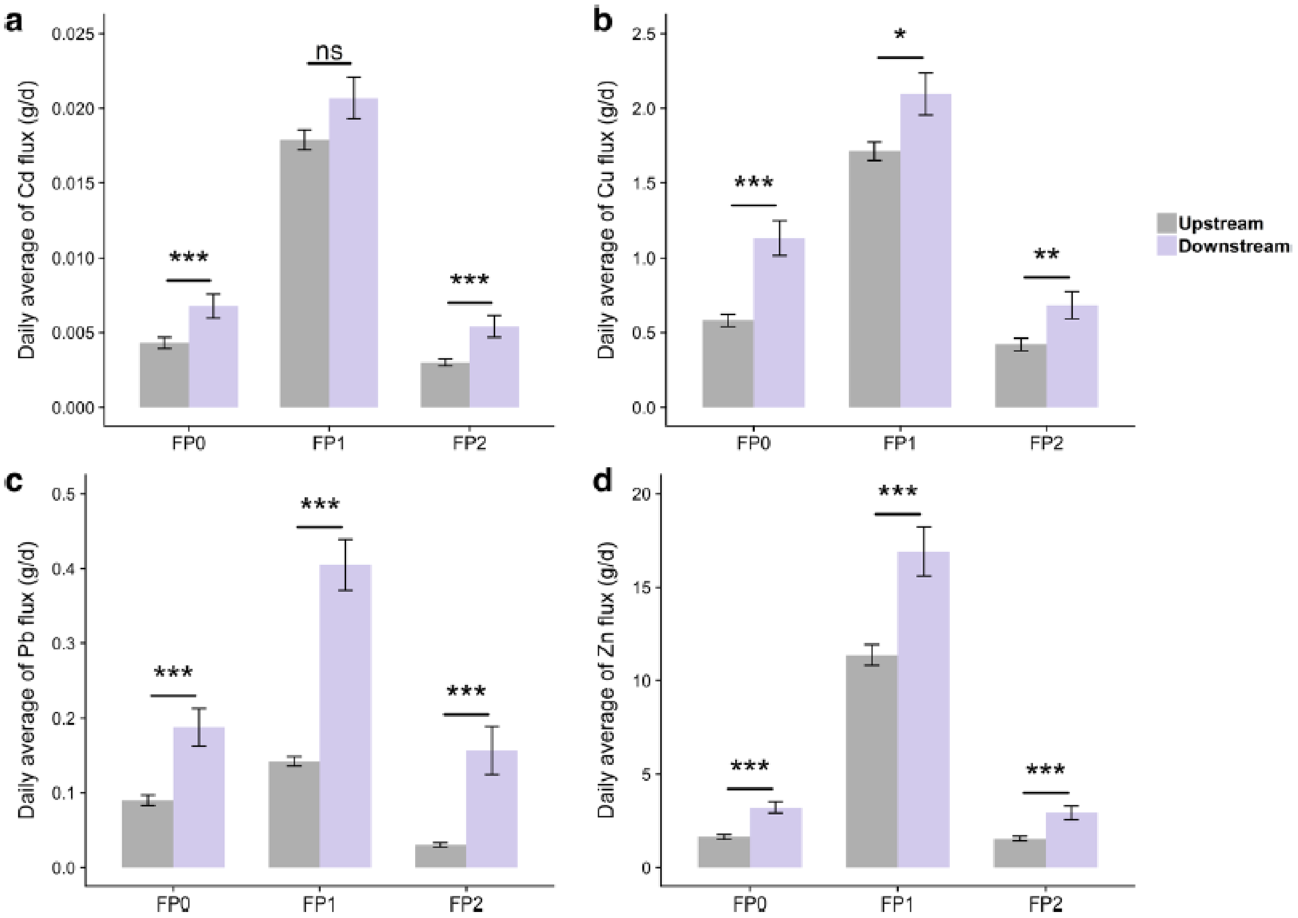

Figure 3.
Cd (a), Cu (b), Pb (c) and Zn (d) flux (g/day) at the UP and DO in FP0, FP1 and FP2. Results are expressed as mean ± SEM. Differences between metal fluxes of UP and DO of each fishpond were assessed using paired samples t tests (*p < 0.05, **p < 0.01, ***p < 0.001, ns: non-significant)

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