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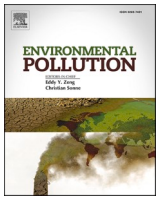

Trends in mercury, lead and cadmium concentrations in 27 European streams and rivers: 2000–2020☆

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ABSTRACT

Temporal trends for concentrations of mercury (Hg), lead (Pb) and cadmium (Cd) were evaluated from year 2000–2020 in 20 (Hg), 23 (Pb) and 11 (Cd) watercourses in remote forest catchments in Europe. Decreasing trends were observed in 15% (Hg), 39% (Pb) and 45% (Cd) of the watercourses during the period of evaluation. Decreasing trends were mainly observed between 2000 and 2005 for Hg and between 2000 and 2015 for Pb and Cd. For the last five years of the studied time period (2015–2020), more watercourses showed significant increasing, rather than decreasing Hg, Pb and Cd trends. This was interpreted as a legacy effect of metals still retained in catchment soils. The overall negative trends during the earlier part of the study period were likely driven by declining deposition of metals over Europe, especially for Pb and Cd. Other changes related to metal transport and chemistry may have contributed to the observed trends as well, including recovery from acidification and the ongoing browning of surface waters at northern latitudes. Here we found that organic carbon could explain the seasonal variation in Hg and Pb, but was not related the interannual trends. This study highlights the need for long-term monitoring and robust statistical methods that can detect multidirectional, long-term change in water chemistry.

1. Introduction

Anthropogenic emission and deposition of mercury (Hg), lead (Pb), and cadmium (Cd) have increased globally since the start of the industrialization period (Pacyna et al., 2007). Anthropogenic emission of these metals originates from energy production, combustion of fossil fuels, industrial processes and products, incineration of waste products, production and use of various metals and artisanal gold mining (for Hg) (Pacyna et al., 2009; Johansson et al., 2001; Pacyna et al., 2006). Based on agreements within the UN Convention on Long-range Transboundary Air Pollution (CLRTAP) as well as other regulatory instruments (i.e. Aarhus Protocol, Industrial Emissions Directive and the Minamata

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Convention), measures were implemented in order to reduce emissions of harmful elements such as Pb, Cd and Hg. Because these metals are all long-range, transboundary air pollutants, emissions have resulted in elevated concentrations in soils, water and biota, even in remote areas far from the original sources (Johansson et al., 2001).

Hg and Pb have been shown to have negative effects on soil microbial processes, and laboratory experiments have found reduced microbial activity, especially for Pb, already at levels currently present in e.g. mor layers in southern Sweden (Johansson et al., 2001; Bringmark and Bringmark, 2001a; Bringmark and Bringmark, 2001b). Hg, Pb and Cd can biomagnify in food webs and are often found at high concentrations in top consumers. Human exposure to these metals occurs mainly through ingestion of contaminated food (Rebelo and Caldas, 2016), including e.g. fish with high concentrations of Hg. Hg concentrations in fish are well above the Environmental quality standard set by the Water Framework Directive (0.02 mg g-1 wet weight, Directive, 2008/105/EC) in large parts of the northern hemisphere. Furthermore, Hg is often found at levels that the World Health Organization (WHO) deems potentially harmful for human consumption (0.5 mg kg-1), e.g. in 25% of Fenno-Scandian inland lakes (Åkerblom et al., 2014; Braaten et al., 2019).

Emission of these metals in Europe peaked around the 1960s for Cd, 1970s for Pb and 1980s for Hg, and has declined in recent decades (Pacyna et al., 2007; Pacyna et al., 2009; Streets et al., 2011). In EU member states, metal emissions declined by 47% (Hg), 42% (Pb), and 37% (Cd) between 2005 and 2021 (annual declines of 2.7%, 2.5%, and 2.1%, respectively) (European Environment Agency, 2023). Concentrations in precipitation over Europe are estimated to have decreased by around 3 % per year for Pb and Cd during the time period of 1990–2005 (Pacyna et al., 2009), and by 1.5–2.3 % per year for Hg between 1990 and 2013 (Zhang et al., 2016; Obrist et al., 2018). The reduction in metal deposition in northern Europe, however, has not been sufficient to prevent continued accumulation of Hg and Pb in catchment soils, whereas Cd concentrations in top soils in Sweden were found to have decreased as a result of declining deposition (Johansson et al., 2001).

Metal mobility in soils, vertically within the profile as well as laterally towards receiving waterbodies, is controlled by different soil specific factors such as acidity (especially for Cd) and organic carbon mobility (especially for Cd and Hg) (Nelson and Campbell, 1991; Bergkvist et al., 1989; Kobler et al., 2010; Huser et al., 2012; Eklöf et al., 2012). Due to the strong affinity of Hg and Pb for organic matter, the mobility of these metals tends to be lower in organic soils compared to Cd (Nelson and Campbell, 1991; Bergkvist et al., 1989).

Cycling of metals is complex because many factors influence their behavior, including biotic and abiotic chemical processes. The solubility of many metal ions is affected by pH, which acts as a general regulator of mobility. Metals like Cd, for example, are more soluble at low pH and can easily leach under acidic conditions (Christensen, 1989). Organic matter (OM) mineralization and chemical processes (e.g. changes in ionic strength) can also alter the solubility and mobility of metals (Huser et al., 2012; Landre et al., 2009; Porcal et al., 2009). Under low redox potential (i.e. reduced conditions) that may occur when groundwater level is elevated, formation of metal sulfides and coprecipitation may restrict the mobility of many trace elements. The reverse can occur when these soils turn oxic again, especially if the oxidation process produces quantitatively important amounts of protons, lowering soil pH (Borch et al., 2010; Lydersen et al., 2002). The metal form (e.g. dissolved, colloidal, or particulate) is also an important factor affecting soil mobility and concentrations in surface waters (e.g. Pb) (Ross and Sherrell, 1999; Sherrell and Ross, 1999).

Within the International Cooperative Programme on Integrated Monitoring of Air Pollution Effects on Ecosystems (ICP IM), Hg, Pb, and Cd have been monitored in natural or semi-natural catchments in Europe during the last two decades, allowing for the comparison of spatial and temporal patterns of these metals over Europe. Monitoring under the ICP IM programme aims to inform CLRTAP on the resulting effects of emission reduction policies. These three metals were noted as particularly harmful in the 1998 Aarhus Protocol on Heavy Metals and the emission, and use of the highly toxic Hg is also regulated in the UN Minamata Convention on Mercury.

The aim of this study was to evaluate temporal trends of Hg, Pb and Cd concentrations in 28 European streams and rivers from 2000 to 2020 that may have been affected by emission reduction policies in Europe. This was done using statistical methods that can determine the magnitude and direction of trends, as well as changes in trend direction. Potential drivers for changes in temporal trends of Hg, Pb and Cd in the studied systems were evaluated as well.

2. Methods

2.1. Data selection

This study included water chemical data from European streams and rivers within the ICP IM (n = 11) and the Swedish national monitoring program (n = 16) (Fölster et al., 2014) (Supplementary information, Table S1). The number of sites included in this study that had sufficient data for each metal was 20 for Hg, 23 for Pb and 11 for Cd (Fig. 1). The sites were located in Austria (n = 1), Czech Republic (n = 1), Finland (n = 3), Lithuania (n = 1), Norway (n = 1), Spain (n = 1), and Sweden (n = 19) (Supplementary information, Table S1). Water samples from the streams and rivers were collected for a minimum 13 years and maximum 21 years, between January 2000 and December 2020, with 20 years as the mean time series length (Supplementary information, Figs. S1–S6).

The ICP IM sites are located in natural or semi-natural areas, with minimal to no anthropogenic land uses in their catchments, allowing for evaluation of long-term trends in water chemistry due to changes in air pollution and climate alone. The source of metals deposited in these catchments may still be anthropogenic, although mainly entering the system via diffuse, atmospheric emissions of these long-range transboundary air pollutants. The Swedish monitoring sites within the program "trend watercourses" generally have larger catchments (0.93–9827 km^2, mean: 1478 km^2) compared to the ICP IM catchments (0.19–1052 km^2, mean: 97 km^2), and therefore the Swedish monitoring sites include more land use in the form of forest management. Watercourses included in this study were those with a minimum of 13 years of data with at least 50 measurements for each variable. The watercourses also had to have less than 4% agriculture and less than 4% urban/built areas in their catchments to be included.

Chemical variables monitored included Hg, Cd and Pb, as well as pH, total or dissolved organic carbon (TOC or DOC), absorbance at 420 nm (Abs420), and sulfate (SO_4). Because samples were collected in different countries, different laboratories were used for analysis of the study variables. The analytical methods, detection limits, and analytical uncertainty for Hg, Pb, and Cd are provided in Supplementary information, Table S3.

Data below detection limit were set to half the value of the detection limit. In most sites, no data were below detection limit, but site 168, 169, 170, 181, ES02 and AT01 had 0.4%–44% Pb data below detection limit and site 191 and ES02 had 2% and 20% Cd data, respectively, below detection limit. No Hg data were below detection limit. We do not expect that the data below their associated detection limits had any major effects on the trend analyses results, as long as the detection limit is constant over time. In Sweden, the detection limit for Hg, Pb and Cd decreased over time due to improved laboratory methods and equipment in some of the laboratories. To avoid detection of trends due solely to improved accuracy of analytical methods, all values below detection limit were set to half of the highest detection limit value in the studied time series. The highest detection limits were 0.06 ng/l for Hg, 0.02 μg/l for Pb, and 0.006 μg/l for Cd in the Swedish sites. Previous to June 2006, however, values below detection limit were reported simply as 0.02 μg/l (Pb) and 0.005 μg/l (Cd), with no "<" symbol being used. It was therefore impossible to determine if the values were at or below the

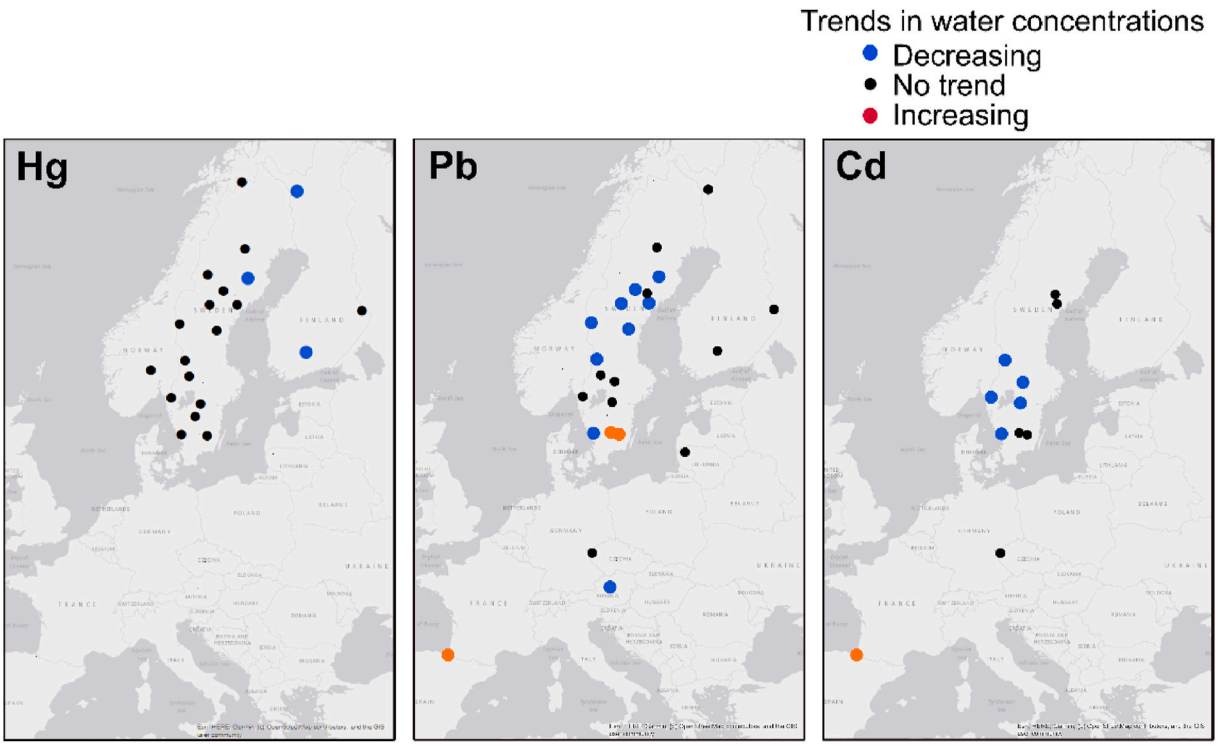

Fig. 1. Trends for mercury (Hg), lead (Pb), and cadmium (Cd) concentrations in European watercourses determined with Seasonal Mann-Kendall tests. Significant ($p < 0.05$) decreasing (blue) or increasing (red) trends for concentrations during 2000–2020 are noted in the map. The watercourses with no significant trends are marked in black. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

detection limit. Watercourses with >30 values at or below 0.02 μg Pb/l and 0.005 μg Cd/l before June 2006 were therefore excluded from analysis. If < 30 values were at or below the detection limit before June 2006, those values were set to half the detection limit (i.e. 0.001 μg/l for Pb and 0.003 μg/l for Cd), as described above. We excluded one site for Pb, and 14 sites for Cd from the Swedish dataset for the reason stated above. There were no data below detection limit for Hg.

TOC and DOC are comparable only in waters with low suspended particles. Because the trends were based on either TOC or DOC for a single watercourse (i.e. no mixing of TOC and DOC at one site), however, we considered the comparison of TOC or DOC trends between the watercourses acceptable as long as the measurements were consistent over time within each watercourse. The same is true for sample frequency, which varied between sites. Sample frequency was generally monthly for Cd and Pb, and bimonthly for Hg. However, some watercourses were sampled at a greater frequency; as often as monthly for Hg (n = 3) and up to twice a month for Pb (n = 7) and Cd (n = 4). In other watercourses, sampling frequency was lower. Some watercourses were sampled less than 5 times per year for Hg (n = 3) and less than 11 times per year for Pb (n = 4) and Cd (n = 2). Whether the samples were filtered or not before analyses of Hg, Pb, and Cd also differed between sites. In Sweden, Norway, Finland, and Czech Republic, the particulate fraction of Hg, Pb, and Cd were considered low and analyses were conducted on unfiltered samples. In Spain, Lithuania and Austria, samples were filtered through a 0.45 μm filter before Pb and Cd analyses. The difference in pretreatment of the samples makes it challenging to compare the absolute concentrations between sites, but still allow for comparison of overall trends between the watercourses.

Flow was measured at most of the ICP IM watercourses, except for ES02, FI01, FI03 and FI06. For the Swedish monitoring sites, flow was sometimes measured by the Swedish Hydrological and Meteorological Institute (SMHI) at the location for water sampling. When there were no flow measures being taken at the sampling site, we made use of the rather dense network of hydrological measurement stations from SMHI to identify a downstream, upstream or nearby location with active flow measures (Supporting Information, Table S9). As only average monthly flow was reported from the hydrological stations within ICP IM, flow was not used to calculate exports but to evaluate the trends in flow to be related to metal trends.

2.2. Statistical analyses

Long-term trends for Hg, Pb and Cd, and associated water chemical variables (pH, SO_4 and DOC or TOC), were analyzed using the nonparametric Seasonal Mann-Kendall test (Loftis et al., 1991) and generalized additive mixed models (GAMM) (Hastie and Tibshirani, 1986; Wood, 2017). The seasonal Mann-Kendall test is robust, can handle outliers and only requires trends to be monotonic but not linear. Monthly mean values were used if several observations were available for one month. Change over time was calculated using the Theil slope (Loftis et al., 1991). However, seasonal Mann-Kendall and Theil slope can only determine the magnitude and direction of a trend over a predefined time-period, and give no information on variation in trend within that time-period. We therefore also analyzed the data using GAMM, which allows for evaluation of time series without prior definition of the shape of the trend curve.

Each time-series was analyzed individually with a model that included a thin plate spline function to evaluate the long-term time trend, and a cyclic cubic regression spline to express the seasonal variation in the data. The error term in the model was assumed to follow a continuous, autoregressive process of lag 1 to account for the observations' dependence in time that is typically present in time series data. Such a structure for the error term also works if observations are unequally spaced in time, which is often the case.

Trend significance was determined using first derivatives of the temporal smooth, i.e. with the seasonal variation removed. Uncertainty was computed according to Monteith et al. (2014) and Simpson (2018). Whereas denser monitoring frequency will not affect the estimate of the

trend curve itself, the corresponding uncertainty will be smaller when more data are available. Station-wise analyses were summarized by compiling the individual information in common plots, e.g. by counting the number of significant changes at specific time points or by plotting the information of when significant changes occurred for individual series in a combined plot, following methods in von Brömssen et al. (von Brömssen et al., 2021). Because the main goal for this analysis is combined visualization of several stations and variables and not traditional hypothesis testing, the significance level was set to 0.2. For Hg, Cd and Pb, combined trends were estimated for all stations together using a GAMM, with a common smooth trend curve that also allowed individual station-wise deviations from this curve (Pedersen et al., 2019).

To test the relationship between metal concentrations and organic carbon (OC) and pH, a generalized linear mixed model (GLMM) was constructed for each watercourse with OC and pH as fixed factors. A repeated structure was used for the error term in the GLMM to account for repeated sample occasions at each site in the same way as done for the GAMM.

3. Results and discussion

In this study, long-term trends for Hg, Pb, and Cd were evaluated using data from remote, minimally impacted, mainly forested catchments. This is evident when comparing the concentrations of Hg, Pb, and Cd in the watercourses in this study (Supplementary information, Table S4) with the substantially higher concentrations of these elements from catchments influenced by point-sources and substantial, anthropogenic land-use in Portugal (Couto and Ribeiro, 2022), Poland (Juśkiewicz and Gierszewski, 2022), Romania (Bravo et al., 2014) and Greece (Karaouzas et al., 2021). Instead, the concentrations presented herein were similar to studies from other remote surface waters in Sweden (Huser et al., 2012; Eklöf et al., 2012; Klaminder et al., 2006), France (Cavalheiro et al., 2016), and across Europe (Bravo et al., 2018).

3.1. Concentrations and trends (Mann-Kendal) for Hg, Pb and Cd

The mean concentration of Hg for the full time series 2000–2020 varied from 0.9 ng/l (site 170) to 6.2 ng/l (site FI01) in the studied watercourses (Supplementary information, Table S4). Hg concentration trends between year 2000 and year 2020 decreased in 3 watercourses (15%) and did not increase in any (Fig. 1, Supplementary information, Table S5). Relative to the mean concentrations of Hg calculated using the first three years of the data series in each watercourse, the significant trends during 2000–2020 (Supplementary information, Table S5) corresponded to total decreases of up to 2.6% (mean: 1.5%, n = 3) over the study period. A previous evaluation of Hg concentration trends in 19 Swedish watercourses showed no significant trend for most sites (n = 18) between 2000 and 2010 (Eklöf et al., 2012). In this study, using a more geographically disperse dataset including an additional decade of data, slightly more declining trends were found. However, in 17 (85%) of the watercourses included herein, there was no significant trend.

The mean concentration of Pb for the full time series (2000–2020) varied between 0.03 μg/l (site FI06) and 1.82 μg/l (site LT03) in the studied watercourses (Supplementary information, Table S4). Trends for Pb concentration decreased in 9 watercourses (39%) and increased in 3 (13%), but had no significant change in 11 (48%) of the watercourses. Relative to the mean concentration of Pb calculated using the first three years of each data series, the significant trends during 2000–2020 (Supplementary information, Table S6) corresponded to total decreases of up to 3.4% (mean: 1.5%, n = 9) and increases of up to 8.8% (mean: 3.5%, n = 3) over the study period. A previous study on Pb concentration trends detected a north-south gradient across Sweden, with decreasing trends in northern regions and increasing trends in southern Sweden (Huser et al., 2011). This north-south gradient was not obvious in this study, with increasing trends being observed in southern Sweden and Spain. Even though there were few significant, positive trends for Pb, the trends in Spain were relatively strong (+8.8 % from 2007 to 2019).

The mean concentration of Cd for the full time series (2000–2020) varied between 0.013 μg/l (site 191) and 0.238 μg/l (site CZ02) in the studied watercourses (Supplementary information, Table S4). Concentrations of Cd had decreasing trends in 5 of the sites (45%), and increased in only one (9%) of the watercourses (Fig. 1, Supplementary information, Table S7). Relative to the mean concentrations of Cd calculated using first three years of data for each watercourse, the significant trends during 2000–2020 (Supplementary information, Table S7) corresponded to total decreases of up to 5.3% (mean: 2.0%, n = 5) and one increase of 21.6% (n = 1) over the study period.

The temporal trends for the Spanish site ES02 are noteworthy, with strong, increasing trends for both Cd (21.6%) and Pb (8.8%). The mean concentration of Cd from this site (0.104 μg/L) is also high in comparison to the other study sites (Supporting information, Table S4). Despite being a remote area with a minimally impacted catchment, previous studies have also detected high levels of Cd and Pb in topsoils in this area (González-Miqueo et al., 2009). These relatively high concentrations may be caused by consistent winds that pass through the neighboring region of the Basque Country, which is a heavily industrialized area with an abundance of refineries and steel mills. High concentrations may also be attributed to the soils in the catchment that consist of Paleozoic schists and slates that are rich in these metals (González-Miqueo et al., 2010).

3.2. GAMM trend testing

Mann-Kendall trend tests identified which watercourses had significant trends, and the Theil slope was used to determine the magnitude of overall change in concentrations of Hg, Pb and Cd. When generating GAMM models for these time series, however, we found that the trends were often non-monotonic. Before 2005, more than 50% of the watercourses had decreasing trends for Hg. Since 2010, however, only around 10% of the watercourses had decreasing trends. While the trends generally decreased in the beginning of the study period, the concentrations of Hg started to increase again towards the end of the time series (Figs. 2 and 3).

A similar pattern was found for Cd. Before 2010, concentrations decreased in approximately 30% of the watercourses. The number of watercourses with decreasing trends by the end of the dataset, however, was <15%. This pattern was also similar for Hg, where there were more watercourses with increasing than decreasing trends during the last five years of the study period.

It should be noted that some of the watercourses had a few values with exceptionally high concentrations during the studied period. Trend estimation in GAMM is quite robust to single outliers, as long as the outliers are not located in the very beginning or the very end of the time series dataset. We thus expect that these high concentrations have not influenced the direction and magnitude of the GAMM trends for most sites. At three sites, however, unusually high concentrations occurred in the beginning or at the end of the time series, and thus may have artifically driven trend direction, e.g. Hg concentrations at site 170, Pb concentrations at LT03 and Cd concentrations at site 191 (Supplementary information, Figs. S2, S4, and S6).

Trend analyses generally showed that the decreasing metal concentrations detected during the beginning of the 21st century do not continue to the same extent 20 years later (Fig. 3, Supplementary information, Figs. S1–S6). The results also illustrate that the trends over the whole time period, detected using the seasonal Mann-Kendall test (Fig. 1), are strongly influenced by the declining concentrations in the beginning of the time series. Hence, the results in Fig. 1, when Hg and Cd decrease in some (Hg) or around half (Cd) of the watercourses, are not relevant for the latter part of the data set (2015–2020). The proportion of watercourses with increasing or decreasing concentrations over time was more stable for Pb than for Hg and Cd (Fig. 2), but the overall trend

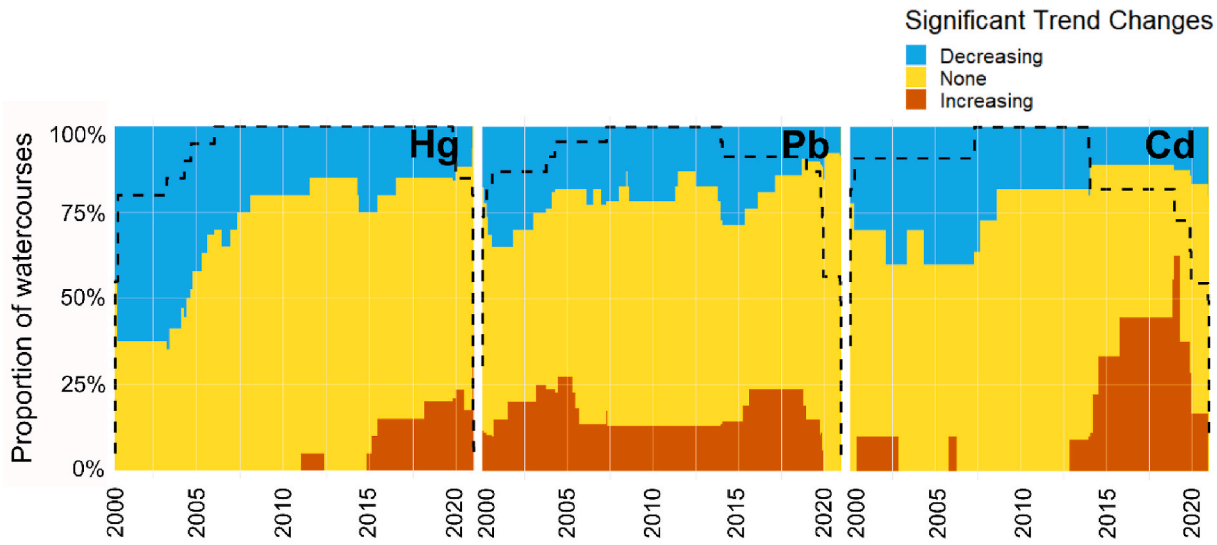

Fig. 2. The proportion of watercourses showing a significant increasing (red), decreasing (blue) or no trend (yellow) for mercury (Hg), lead (Pb), and cadmium (Cd) concentrations during the period 2000–2020. Trends were analyzed using generalized additive models (GAMM). The dashed lines show the annual proportion of the total number of stations with data. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

of Pb also had a slight increase in concentration towards the end of the time series (Fig. 3).

3.3. Trends in relation to deposition

Concentration trends are not linear over the time series, and the information on when and where the trends occur is important for assessing which factors may drive these trends. The deposition of Hg, Pb and Cd has decreased over Europe during the last few decades as a result of emission control via reductions in release from e.g. combustion of coal and oil, production of iron and steel, and waste incineration (Pacyna et al., 2009; European Environment Agency, 2023). The decreasing deposition of these metals likely affected trends in at least some of the watercourses. The recovery of forested catchments, however, is a slow process and annual exports of Hg, Pb and Cd in runoff have seldom been found to exceed the total annual input of these metals via wet and dry deposition (Aastrup et al., 1991; Ukonmaanaho et al., 2001; Grigal, 2002; Bringmark et al., 2013; Hsu-Kim et al., 2018). This is especially true for Hg, where mass-balance studies show that Hg runoff generally accounts for only 5–10% of the total annual Hg deposition on forested catchments (Hsu-Kim et al., 2018; Bishop et al., 2020).

Re-emission of Hg from terrestrial land can account for up to one third of the total Hg deposition on peat soils, but it is assumed to be low from Podzols (Jiskra et al., 2015). With this large and still growing soil pool of Hg, it could be expected that changes in the Hg deposition rate might have a relatively weak effect on Hg concentrations in runoff, at least in catchments with a low share of open water surfaces. A study in North America, however, has found rather rapid Hg concentration decreases following declines in Hg deposition (Gerson and Driscoll, 2016). The authors suggested catchments can be more responsive to Hg deposition declines than expected from mass-balance studies. That is to say, recently deposited Hg may be more active and mobile in the ecosystem compared to historically imported Hg. Mass-balance data from three of the Swedish catchments in this study showed that runoff contained 13–70% and 20–56% of the total annual Cd and Pb deposition, respectively (Eklöf et al., 2020). Internal sources and fluxes, such as vegetation uptake (primarily Cd), volatilization (primarily Hg), and weathering, however, complicate the interpretation of mass-balance budgets (Starr et al., 2003).

3.4. Drivers of detected trends

Previous studies investigating Hg, Pb, and Cd in European surface waters and sediments have generally linked temporal changes in concentration to land use activities such as mining, agriculture, and industry (Couto and Ribeiro, 2022; Dendievel et al., 2022). The catchments in the present study, however, were located in remote areas and other drivers than land use are likely to have influenced the trends for Hg, Pb and Cd concentrations observed in this study.

Both Hg and Pb generally correlate positively with the concentration of OC in surface waters (Huser et al., 2012; Eklöf et al., 2012; Tarvainen et al., 1997; Mannio et al., 1990). This was the case herein as well, where OC concentration was a significant variable that correlated positively with the variation in Hg and Pb concentrations in 14 of the watercourses for both variables (Table 1, GLMM, $p < 0.05$). This supports previous work that showed that Hg and Pb correlate on the short-term or seasonal scale, as Hg and Pb are often complexed with OC and follow the same seasonal patterns, including high concentrations during high flow events (Huser et al., 2012; Schuster et al., 2008). Over longer periods, however, temporal trends for metals and OC patterns were not consistent. The largest number of watercourses with declining Hg concentrations were found between 2000 and 2010 (Fig. 2), whereas this decade had the largest number of watercourses with increasing concentrations of OC (Fig. 4). Supporting this, TOC concentrations generally increased in 164 Swedish watercourses during 1990–2020, with the largest increases being detected before 2005 and trends generally levelling out after 2010 (Eklöf et al., 2021). Hence, when OC concentrations were increasing, Hg and Pb concentrations were decreasing in most watercourses.

When normalizing metal concentration with OC concentration, the ratios of Hg/OC, Pb/OC and Cd/OC varied substantially over time (Supplementary information, Fig. S7). Between 2000 and 2010, these ratios decreased significantly in >70% (Hg/OC), >30% (Pb/OC), and >40% (Cd/OC) of the watercourses, indicating less mobilization of metals relative to changes in OC over time. Thus, OC does not seem to be the major driver for the long-term trends of Hg and Pb, even though they are generally positively correlated with each other at a seasonal scale. This is in agreement with Eklöf et al. (2012) who found that despite an increase in TOC in most of the watercourses between 2000 and 2010, concentrations of Hg did not increase. This could be related to not only the quantity but also the quality of OM, which may have changed over time (Eklöf et al., 2012; Worrall and Burt, 2010). We found the OC quality trends, expressed as absorbance normalized with OC

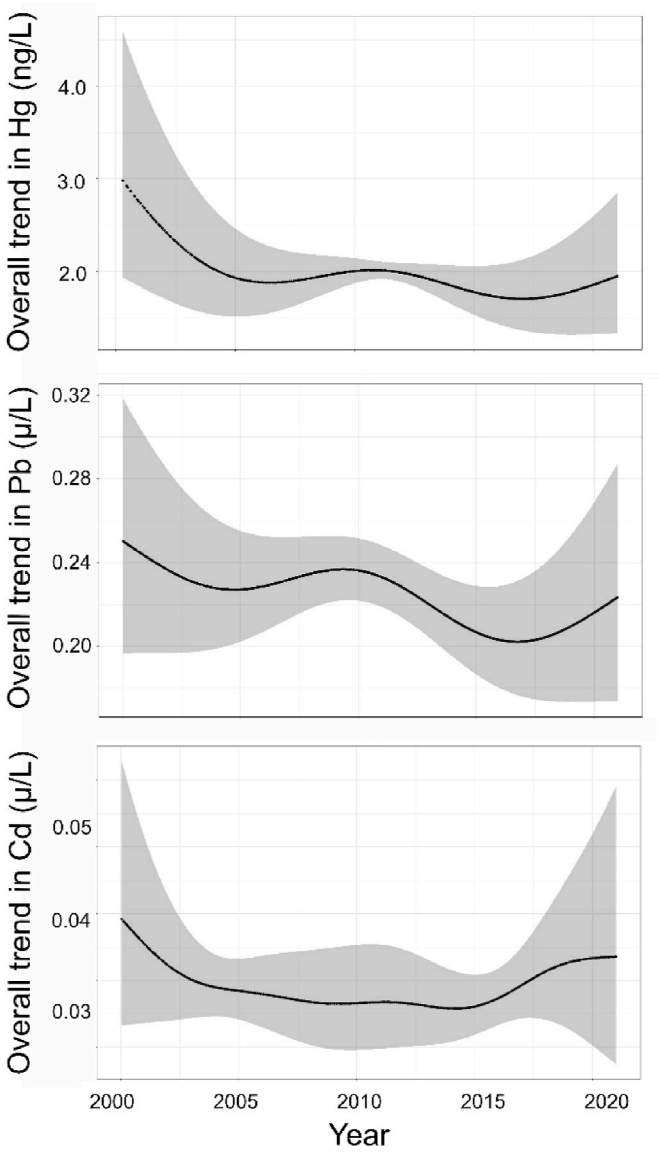

Fig. 3. The average Hg (upper), Pb (middle) and Cd (lower) concentration trends (black line) in the studied watercourses between 2000 and 2020 from all watercourses based on a GAMM including a common trend and individual stationwise deviations show non-monotonic trends and their pointwise confidence intervals (gray shade).

Table 1
A summary of the results from General Linear Mixed Models (GLMM) with cadmium, lead and mercury as the dependent variable and pH and OC as fixed factors. A repeated structure is included to account for the sampling date. One model is constructed for each watercourse, and the numbers of watercourses with significant positive and negative interactions between the fixed factors and the dependent variable are given in the table.

	pH	TOC or DOC
Mercury (n = 20)	1 (+)/10 (−)	14 (+)/0 (−)
Lead (n = 21)	3 (+)/8 (−)	14 (+)/0 (−)
Cadmium (n = 10)	0 (+)/7 (−)	5 (+)/2 (−)

(Abs420/OC), to vary over the study period in this study as well (Supplementary information, Fig. S7). The Abs420/OC ratio decreased significantly in 25–75% of the watercourses between 2000 and 2010, and in <25% of the watercourses between 2010 and 2020. It has been suggested that a higher Abs420/OC ratio tends to represent a greater proportion of aromatic, hydrophobic and larger molecular size fractions in OC (Eklöf et al., 2012). OC-fractions measured as Abs420 have been suggested to be more important for Hg mobilization than other OC-fractions (Eklöf et al., 2012). The concentrations of Hg and the Abs420/TOC ratio were highest in most watercourses in the beginning of the study period, which could imply that the colored (Abs420) OC fractions mobilized more Hg. The temporal trends for Hg and Abs420/OC did, however, not fully follow the same pattern, as the declining trends for Hg peaked in 2000 and for Abs420/OC around 2007.

Changes in catchment hydrology may influence ground water flow paths and redox status, factors that in turn influence metal solubility and mobilization. More superficial groundwater flow paths commonly mobilize OC and attached metals from upper soil horizons (Bravo et al., 2018; Schuster et al., 2008; Laudon et al., 2011). For the watercourses where flow was measured on site or in nearby location, average monthly flow decreased in a few watercourses in Sweden (199) and Czech Republic (CZ02). Flow increased in one watercourse in Lithuania (LT03). In most watercourses, however, no trends were detected (Supplementary information, Table S9 and Fig. S9). It is, however, not only the average monthly flow that may change, but previous research has shown that more frequent drought periods have occurred in southern Europe over time as well (Peña-Angulo et al., 2022). Temporal variation in hydrology may influence the concentrations of metals in surface waters, especially with respect to seasonal variation. Unfortunately, the available data for this study did not allow us to determine if the long-term trends for Hg, Pb, and Cd were influenced by changes in hydrology in the catchments.

The deposition of acidifying compounds and most of the metals included in this study both reached a maximum in the 1970s in Europe, and thereafter started to decline (Rühling and Tyler, 1984). The spatial patterns and temporal trends of many metals follow the pattern for acid deposition, but acid deposition can also increase metal mobility and transport from soils to surface waters (e.g. Cd), alter metal speciation in the water (e.g. Hg, Pb, Cd) and affect the sedimentation rate in surface waters (e.g. Pb, Cd) (Nelson and Campbell, 1991; Lydersen et al., 2002; Steinnes, 1990). The deposition of sulfate (SO_4) can further affect the bioavailability of Hg via enhanced methylation of Hg by sulfate reducing bacteria (Rask et al., 2007). The effects from acidification recovery are illustrated in this study by changes in pH and the concentrations of SO_4 (Fig. 4, Supplementary information, Fig. S8). In the beginning of the time series, when most watercourses had increasing pH and decreasing SO_4 concentrations, we found the strongest decreasing trends for Hg, Pb and Cd. After 2015, rather few (<25%) watercourses had continued, declining concentrations of SO_4. This may indicate that acidification in many catchments had reached its apex before 2015, and other drivers, such as those related to climate, may have become more important after 2015. However, the covariation between declining deposition of SO_4 and of Hg, Pb and Cd makes it difficult to determine whether the metal trends in the watercourses are due to declining metal deposition or the recovery from acidification, or both. There were likely multiple drivers of the observed trends and at least for the acid sensitive Cd, the recovery from acidification was the most probable driver of the detected trends.

The GLMM analysis partially supported this, with pH relating negatively to Cd concentration in 7 of the 10 watercourses (Table 1). There were also significant relationships between Cd and OC, positive in 5 and negative in 2 of the watercourses (Table 1 and Supplementary information, Table S8). Only the more acidic watercourses had data for Cd. Stream water acidity, may be related to stream order/size, with the acidic watercourses (pH $\leq$ 6) tending to be headwater streams with small watersheds (mean 4 km^2). In these small streams, the stream water was likely influenced more by terrestrial sources of OC and acidic compounds, and the metals were likely mobilized from soil to water along with terrestrial OC and/or influenced by soil acidity. In the larger rivers, in-stream processes such as microbial processes, sedimentation and re-mobilization of metals from sediments may have had a larger,

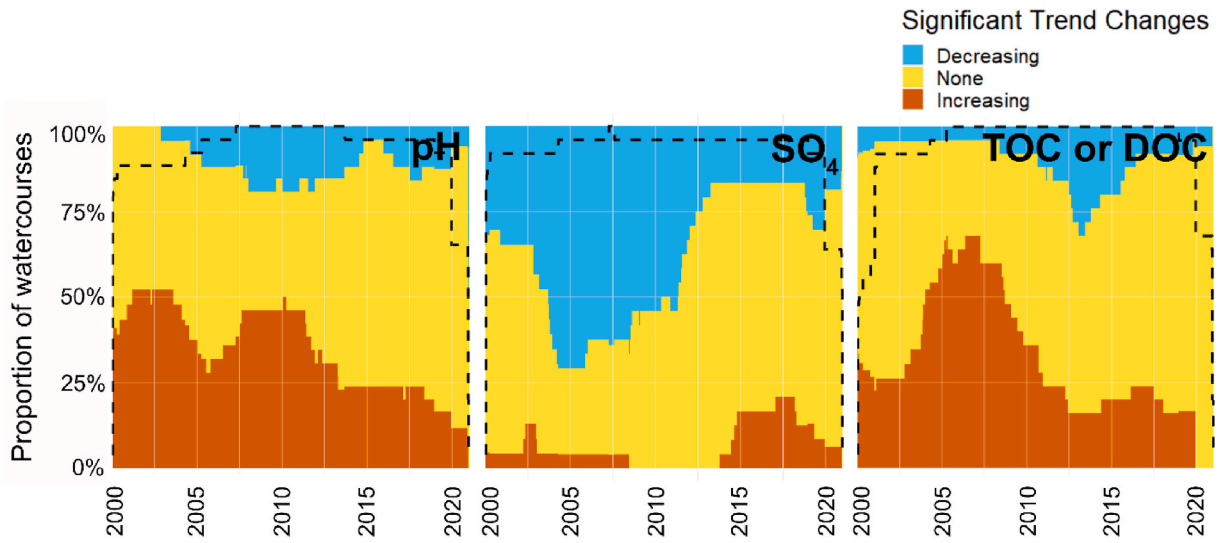

Fig. 4. The proportion of watercourses showing a significant increasing (red), decreasing (blue) or no trend (yellow) in pH, sulfate (SO_4) concentrations, and dissolved or total organic carbon (DOC or TOC) concentrations during the period 2000–2020. The trends were analyzed by generalized additive models (GAMM). The dashed lines show the proportion of the total number of stations with data for that time point. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

relative effect on metal concentration in the watercourses. It should also be noted that in many watercourses the metals correlated to both OC and pH due to the fact that high concentrations of organic acids can decrease pH values.

According to the GLMM analyses, pH was negatively correlated to Hg and Pb concentrations in 10 of 20 and 8 of 21 watercourses, respectively. Earlier studies in England and Wales (Neal et al., 1997; Tipping et al., 2003) found that recovery from acidification was a relatively minor explanatory variable in comparison to changes in DOC with respect to the transport of Pb to surface waters. However, a study from Sweden (Huser et al., 2012) found that in very acidic streams, Pb concentrations were more influenced by pH whereas at higher pH (but still acidic) concentrations were more influenced by OM. This relationship to pH was also supported by a greater fraction of dissolved Pb at low pH (<4.8) and a higher share of organically or colloid bound Pb fractions at higher pH (>4.8) (Huser et al., 2012). In the present study, we did not find similar differences in relationship between pH and/or OC, and Cd, Pb or Hg concentrations in acidic (pH < 4.8) or less acidic (pH > 4.8) watercourses (Supporting information, Table S8).

4. Conclusions

The key finding in this study was that there were significant, declining trends in many systems for the metals included in this study, but that the trends were often not monotonic and actually started to reverse in the latter part of the dataset. Significant declines were mainly detected from 2000 to 2005 for Hg, and between 2000 and 2015 for Pb and Cd. During the last five years of the study period (2015–2020), the concentration of these metals started to increase again in some watercourses, indicating a legacy effect of historic accumulation of these metals in the catchment soils. We also show the importance of long-term and continuous monitoring of surface water chemistry, as well as the use of statistical methods that do not require monotonic direction and can also identify significant, multidirectional trend changes in time series data. Finally, the detected trends in metal concentrations are likely to have been caused by temporal variations in important drivers, including anthropogenic deposition of metals and chemical variations in the watercourses related to pH and/or OC. Changes to variables such as pH and OC are related to changes in other factors such as acid deposition or climate. Future studies should continue to work with these long-term data sets to not only determine if the most recent changes we detected will continue, but should further study the interrelated effects of a changing climate, continued emission controls, hydrology and soil-water processes likely responsible for the observed trends detected in this study.

CRediT authorship contribution statement

Karin Eklöf: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Claudia von Brömssen:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Brian Huser:** Writing – original draft. **Staffan Åkerblom:** Writing – review & editing, Data curation. **Algirdas Augustaitis:** Writing – review & editing, Data curation. **Hans Fredrik Veiteberg Braaten:** Writing – review & editing, Data curation. **Heleen A. de Wit:** Writing – review & editing, Data curation. **Thomas Dirnböck:** Writing – review & editing, Data curation. **David Elustondo:** Writing – review & editing, Data curation. **Ulf Grandin:** Writing – review & editing. **Adéla Holubová:** Writing – review & editing, Data curation. **Sirpa Kleemola:** Writing – review & editing, Data curation. **Pavel Krám:** Writing – review & editing, Data curation. **Lars Lundin:** Writing – review & editing, Data curation. **Stefan Löfgren:** Writing – review & editing, Data curation. **Hampus Markensten:** Writing – review & editing, Data curation. **Filip Moldan:** Writing – review & editing, Data curation. **Gunilla Pihl Karlsson:** Writing – review & editing, Data curation. **Pernilla Rönnback:** Writing – review & editing, Data curation. **Salar Valinia:** Writing – review & editing. **Jussi Vuorenmaa:** Writing – review & editing, Data curation.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.124761.

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