What are the key factors influencing sediment quality along Western European rivers?

Quels sont les facteurs clefs qui influencent la qualité des sédiments le long des fleuves d'Europe occidentale?

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RÉSUMÉ

La composition des sédiments des rivières et grands fleuves fournit des indicateurs sur de nombreux processus de la zone critique comme l'état de contamination des milieux. Depuis 1945, une grande quantité de données a été produite en Europe par les gestionnaires et les chercheurs afin d'évaluer et surveiller la qualité des masses d'eau. Dans le cadre du projet Interpol, une base de données de plus de 12000 échantillons a été rassemblée pour étudier les facteurs clefs intervenant dans la variabilité des concentrations en métaux dans les sédiments entre 1945 et 2020 le long de 7 corridors fluviaux européens (Rhône, Seine, Lot-Garonne, Loire, Escaut, Meuse et Rhin). L'exploitation de ces données a permis de déterminer que les facteurs spatiaux (localisation le long du corridor, en lien avec la lithologie locale) et temporels (période critique de pollution) étaient les plus significatifs. A cette échelle, le protocole analytique ou le type de matrice analysée influencent secondairement la variabilité des concentrations. L'analyse des tendances en Cd, Pb et Zn a montré que les sections moyennes et aval des corridors sont affectées par les « hotspots » urbains et industriels, alors que la contamination en amont est surtout influencée par des secteurs historiques d'exploitation minière. Ce travail a permis de mettre à disposition de la communauté scientifique et des gestionnaires l'ensemble des données compilées et apporte de nouveaux résultats concernant l'efficacité du suivi et de la réglementation sur le temps long.

MOTS CLEFS

Sédiments, métaux, Fleuves Européens, analyses spatio-temporelles, facteurs clefs

ABSTRACT

The composition of sediments in rivers and large streams provides indicators on many processes in the critical zone such as chemical pollution. Since 1945, a large amount of data was produced in Europe by managers and researchers to assess and monitor the quality of water bodies. Within the framework of the Interpol project, a database of 12,000 samples was implemented to study the key factors involved in the variability of metal concentrations in sediments between 1945 and 2020 along 7 European river corridors (Rhone, Seine, Lot-Garonne, Loire, Scheldt, Meuse and Rhine). The exploitation of these data allowed us to determine that spatial (location) and temporal (critical pollution period) factors were the most significant. At this scale, factors such as the analytical protocol or the type of matrix have a secondary influence on the variability of concentrations. Trend analysis of Cd, Pb and Zn showed that the middle and downstream sections of the corridors are affected by urban and industrial hotspots, while upstream contamination is mostly influenced by historical mining areas. This work has made all the data compiled available to the scientific community and managers and provides new results concerning the effectiveness of regulations

KEYWORDS

Sediments, metals, European rivers, spatio-temporal analyses, key factors

1 INTRODUCTION

The industrial and urban development along European Rivers after 1945 led to major impacts and deteriorations of water and sediment quality (Meybeck, 2013). Trace metals (Cd, Cr, Cu, Hg, Ni, Pb, and Zn) have been largely released into rivers by human activities such as agricultural soil erosion, mining and industrial releases, waste waters, road and urban runoff. In Europe, river sections, especially those located downstream of major urban-industrial centres, are still affected by highly polluted sediments, mainly inherited from the past as a legacy. This long-term pollution is one of the largest issue complicating river management and restoration, especially to evaluate the improvement of the quality of water, sediment, aquatic and riverine habitats. To assess metal pollution in river sediments, monitoring programs which have been implemented since the late 1960s on watercourses have generated a large amount of data that are currently under-exploited at the river scale. Indeed, metal pollution surveys have been set up heterogeneously in space and time on different solid matrices sampled in many river environments (main stream, secondary channels, backwater areas, dam reservoirs or floodplain). A great variability of sampling and analytical protocols was also used across countries and even in various watersheds within a country (Dendievel et al. 2022). By compiling and analysing a sediment database based on past monitoring and research actions (1950s–2010s) along seven major rivers in Western Europe, the objectives of this research are (1) to decipher the variability of metal pollution in sediments along the rivers, and (2) to reconstruct and intercompare the long-term evolution of sediment quality between rivers at a European scale. This work especially aims to assess the effects of the main factors influencing the variability of metal concentrations in river sediments (matrix, sampling and analytical effects, anthropogenic and geological influence).

2 MATERIAL AND METHODS

2.1 Database of sediment contamination

Seven rivers of Western Europe were selected based on the data availability (Fig. 1): it includes four French rivers (Loire, French Rhône, Seine, Lot-Garonne River systems) and three transboundary rivers flowing from France to Belgium, Germany and the Netherlands (Rhine, Meuse and Scheldt Rivers). Major and trace metal concentrations (Al, Fe, Cd, Cr, Cu, Hg, Ni, Pb, Zn), as well as ancillary data (total organic carbon, grain-size) from bed and flood deposits (BFD), suspended particulate matter (SPM), dated sediment cores (DSC) were assessed by compiling a large dataset (>12,000 samples). A critical effort was made to gather and treat information from academic publications and regulatory monitoring provided by governmental agencies or stakeholders at a European scale (France, Belgium, Germany, the Netherlands). The validated datasets were categorised according to the river section, decades, extraction protocols and sediment type.

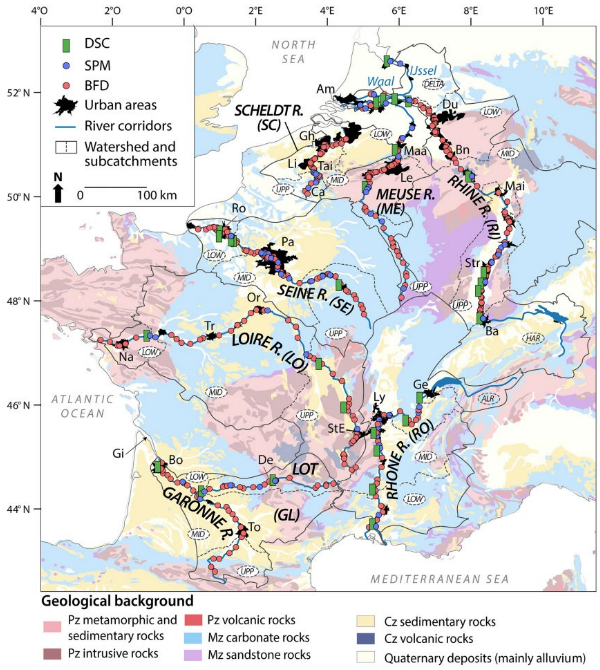

Figure 1. Map of the studied rivers with sampling sites and geology. BFD = bed and flood deposits, DSC = dated sediment cores, SPM = suspended particulate matter.

2.2 Analytical protocols

Heterogeneous sampling, treatments and digestion/extraction protocols were implemented over time, depending on technical developments and on national/international policies. Despite the systematic consultation of the laboratories involved in the metal analysis, technical information was difficult to obtain or even lacking. After sampling, three types of sieving were generally used: (i) bulk fraction or <2 mm especially for BFD and some DSC, (ii) <63 µm for other cores and recent BFD (since 2000), (iii) <20 µm on the Rhine River. Two main types of extraction protocols were used: (i) partial / pseudo-total procedure (PP hereafter) which includes *Aqua Regia*, mainly used for SPM and BFD, (ii) total extractions (TE hereafter) using a multi-acid treatment, or fluoroboric acid and borate fusion. PP and

TE procedures correspond to 22% and 52% of the data, respectively, while 26% of chemical extraction method remain undetermined. There was also a high variability of analytical equipment used for measuring metal concentrations. The detection limits were irregularly mentioned (10% to 60% according to the river). Ancillary data such as grain-size was mainly measured by using laser diffraction (>70%), the Robinson pipette method was rarely used (<5%), while the method used remains unknown for ca. 25% of the data. The TOC was most often determined by sulfochromic oxidation, dry burning, pyrolysis RockEval or other methods.

3 RESULTS AND DISCUSSION

Metal concentrations depend on the matrix characteristics such as grain-size, TOC and the period of sampling/deposit. For all metals, concentrations are generally greater in SPM and DSC than in BFD. We highlighted that the distribution of metal concentrations between SPM and DSC was similar in 54% of the cases, due to high proportion of fine sediments in these two matrices.

The processing and assessment of sediment contamination data also reveal unprecedented spatio-temporal patterns of major European Rivers:

1/ an increasing trend in metal concentrations downstream SE, RO, ME, RI Rivers (for the meaning of the acronyms, please refer to Figure 1). As an example, for Cd on the SE, the median concentrations in all fractions increased from 0.8 mg kg^{-1} in the Upper SE to 4.2 mg kg^{-1} in the Lower SE (period 1960s–1990s). Both values are higher than the geochemical background and reach the probable effect concentration (PEC) for which a severe toxicity is likely to affect sediment dwelling species, causing major concerns from the Lower Seine. Similar trends are observed for Cu, Hg, Pb, and Zn. It could be linked to emissions and releases of urban industrial zones located in the middle and lower sections of the rivers.

2/ marked increases in Cd, Cu, Hg, Pb and Zn concentrations downstream of regional pollution hotspots along GL, LO, ME, SC and RI Rivers. These increases in metals, especially in the upstream river sections, are due to historical mining/metallurgical activities and historical industrial areas.

3/ a significant temporal decrease of metal concentrations until the 2010s for most river sections. Even if it remains sometimes higher than the local geological background, it reveals a general improvement of the river quality. This is related to several factors over time: the influence of regulation on releases and potential source reduction, the increased efficiency of wastewater treatment plants as well as industrial changes in the metallurgical sector established in the river valleys (e.g. -30% of employment decline in France during the period 1990–2010).

4/ no significant variation was observed in space and time regarding Cr and Ni for several rivers (ME, RI, RO, and SC). These metal concentrations are generally considered as geogenic and remain in the UCC and local geological background ranges.

4 IMPLICATIONS

Despite the heterogeneity of the dataset, this study provides key inputs to determine that spatial (location in the corridor) and temporal (critical pollution period) factors were the most significant to explain contamination gradients. At this scale, factors such as analytical protocol or matrix type had a secondary influence on concentration variability. Trend analysis showed that the increase in Cd, Pb and Zn was closely related to the degree of anthropization and the geology of each basin. The middle and downstream sections of the corridors are affected by urban and industrial hotspots, while upstream contamination is mostly influenced by historical mining/metallurgical areas. This work has made all the data compiled available to the scientific community and managers and provides new results concerning the effectiveness of regulations and the resilience of river systems over time.

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