Heavy metal contamination in rivers across the globe: an indicator of complex interactions between societies and catchments

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Abstract Metal contamination (i.e. a deviation from the natural content) of river particulates is closely associated with human history. Natural contents of Cd, Cr, Cu, Hg, Ni, Pb, Sn and Zn in pristine streams depend on basin lithology. Their quantile distributions ($C_{10\%}$, $C_{50\%}$, $C_{90\%}$, in parts per million) in French pristine streams are similar to those observed for 178 pristine large rivers, whose medians are very close to average shale composition. In another set of 400 rivers of unknown status or under human pressure, $C_{90\%}$ values are close to levels observed in very contaminated water bodies (harbours, sewers), a confirmation of the metal issue severity at the global scale. In Western Europe, metal contamination history as archived in river sediments, shows: (i) a similar order of metal sensitivity to human pressures (Hg = Cd > Pb = Zn > Cu > Cr > Ni); (ii) a maximum contamination state from 1950–1970, and; (iii) an effective decontamination for sensitive metals since 1980 or earlier, as a result of technological changes, metal recycling, decreased use of coal and environmental measures. Current state indicators, contents and enrichment factors, are favourable compared to 1940, and depend on the dilution by river sediment loads. Leakage rates of metals, which define the pressure/driver ratio, range in the River Seine between 0.1% and 10%, depending on the metal and time periods. *Per capita* excess loads, expressing the pressure, were found to be similar for a given metal, in Western Europe, the Danube and Mississippi river basins and were highest around the 1970s. Meanwhile, contamination is increasing in newly-industrialised countries (e.g. the Yangtze River, China). World rivers have entered the Anthropocene era. Regional surveys performed within short periods should now be preferred to the traditional approach of reporting global averages, and these new surveys should encompass pristine, degrading and recovering river basins.

Key words metal contamination; river basins; fluvial sediment; leakage rate; per capita excess load; Anthropocene

ASSESSMENT OF METAL CONTAMINATION AND ITS DIFFICULTIES

For 40 years, heavy metal contamination has been a major environmental issue in river basins, and much work has been undertaken illustrating the origins, dispersal and fate of the contaminants and the associated interactions with society. Previous work in this area has addressed fundamental questions such as: Is this river contaminated? What are the causes of contamination? Are environmental regulations successful? This paper synthesizes knowledge of these issues at different scales by taking examples including streams and rivers from France, Western Europe and across the world.

Out of the 50 elements that can now quantified by current analytical techniques, only a few are potentially toxic, sensitive to human impacts and well documented, namely; Cd, Cr, Cu, Hg, Ni, Pb, Sn and Zn. All of these elements are preferentially associated with sediment particles in the aquatic environment (Horowitz, 1995). Their natural variations have been investigated using three novel databases: (a) pristine monolithologic streams in temperate regions (Prismet); (b) medium to large pristine river basins of the world ($Glomet_{BGR}$); and (c) other rivers ($Glomet_{Polluted-unknown}$), severely contaminated and/or with unknown status. These three databases are used to define natural background contents, used as references, to assess global contamination and to rank metals by their natural variability and sensitivity to human impacts. The history of metal contamination issues in impacted basins is illustrated using the example of the Seine River in France. Finally, river contamination is considered at the regional to global scale.

As for any water quality issue, the assessment of metal contamination requires appropriate fieldwork, reliable laboratory analyses and sound interpretation based on the assembled scientific evidence. Prior to the mid-1960s, metal contamination of the aquatic environment could not be addressed as analyses, performed by polarography, were rare, expensive and delicate, and the toxicity and fate of metals in the aquatic environment were poorly understood. In addition, sample contamination, in the field and the laboratory, was common although not widely detected. Two

critical events changed the situation for metal analysis: first, the advent of Atomic Absorption Spectrometry (AAS) in the 1960s, and secondly, the development of ultra-clean methods from field to laboratory by Clair Paterson (1922–1995). These ultra-clean techniques were first used by oceanographers, then by continental water geochemists, and finally they were recommended and adopted by environmental agencies. For example, the dissolved lead decline observed in USA rivers during the 1980s by the US Geological Survey (USGS), although first attributed to the ban of leaded gasoline, was later recognized as an artefact related to relatively cleaner techniques on the basis of a challenge from oceanographers (Windom *et al.*, 1991). Consequently, the USGS shifted to the analysis of suspended and/or deposited river material to characterise metal contamination in rivers, and this approach has been shown to produce very reliable results on the basis of infrequent site visits (Horowitz, 1995). Similarly, the first background reference levels established for fluvial sediment were often overestimated, by an order of magnitude, as for mercury and cadmium in the Seine River (Meybeck *et al.*, 2007), or lead in world pristine rivers, which was originally estimated at 250 ppm (Martin & Meybeck, 1979), but which is now estimated at around 22 ppm using current procedures. Given the above historical developments, most sediment analyses used in this synthesis were produced after 1980 and sedimentary archives have been used to reconstruct contamination prior to the 1970s.

Indicators of metal contamination and dispersal in river basins

The state of particulate metals contamination is expressed by the comparison of metal *contents* (Me in mg/kg or ppm) with background or reference levels from the river basin. Fine particles (clay and fine silt) are generally enriched with metals (Horowitz, 1995) meaning that when mixed with quartz sand and/or calcite minerals, which do not contain heavy metals, particulate metal content decreases accordingly. This grain size effect is generally minimized by geochemists by sieving sediment samples at 63 or 100 μm. In addition, metal contents are also normalized to Al, or to another poorly soluble element that reflects the fine fraction, to take into account the dilution effect by silica or calcite. Normalization to Al is often lacking, however, and is not required by all environmental agencies.

The *Enrichment Factor* is then used to scale the level of contamination relative to the reference level: $EF = (Me/Al)_{sample} / (Me/Al)_{reference}$. When $EF > 1.5$, contamination is probable. The reference metal content can be determined or estimated in many ways, using pre-industrial dated sediment archives, the combination of a set of non-impacted sub-basins, regional averages from pristine basins with similar rock types, or global pristine river averages and shale average composition, as this rock originates from fine riverborne sediments. The average Upper Continental Crust, used by some geochemists, does not account for the actual distribution of surficial rocks (sedimentary rocks are minimized). Other state indicators include the *excess content* ($Me_{sample} - Me_{reference}$) which, multiplied by the river sediment load, determines the *excess load* (t year^{-1}), which in turn, can be normalized to the basin area and expressed as *excess yield* in t km^{-2} year^{-1}.

The ratio between the excess metal flux carried by the river and the metal demand, or metal flow (driver of metal contamination), within the river basin, termed the *leakage ratio*, LR (%), a dimensionless factor, is a performance indicator for regulation measures (pressures/driver). Another indicator of environmental pressure, rated to the basin population, is the *per capita excess load*, EL_{cap}, expressed in g cap^{-1} year^{-1}. Both indicators can be used to compare the efficiency of environmental regulations in river basins and their trajectories, provided that past metal contents are reconstructed on the basis of dated sediment archives and past metal demands by economic history (Lestel *et al.*, 2007; Meybeck *et al.*, 2007). Per capita loads can also be derived from river reach budgets, upstream/ downstream of cities, or from sewage analyses.

SOURCES, PATHWAYS AND SEDIMENT-ASSOCIATED METAL CONTENT UNDER NATURAL CONDITIONS

River sediments originate from the erosion of soils and of surficial rocks and are deposited in floodplains and deltas (Fig. 1 (a)–(d)). Sediment deposited prior to the industrial era can be used to

establish natural levels. In some streams and small rivers it can be difficult to estimate natural reference values because ore mining and metallurgy, which began more than 4000 years ago, locally altered background levels (Coulthard & Macklin, 2003), as in the Rio Tinto (Spain) and in Dartmoor streams (UK).

Influence of lithology on sediment-associated metal contents in pristine river basins

At the stream scale (10–100 km^2) sediment metal contents are primarily controlled by catchment lithology. The *Prismet* database comprises multi-elemental analyses for more than 100 French streams located on monolithologic substrates and exposed to minimal human impacts (population density <10 p/km^2, no villages, factories or mines, minimal atmospheric pollution) in which fresh flood deposits, fine deposited river bed sediment and historical floodplain deposits at 50 cm depth, were sampled by the author in 2005/06 and sieved through a 100µm mesh.

The average contents in stream sediment originating from a given rock type (Table 1) may vary by a factor of two (Cd) to ten (Ni). Metamorphic basins are the richest in As, Pb and Sn. Basaltic basins have the highest sediment-associated contents of Co, Cr, Cu, Hg, Ni and V. Carbonate basins have the highest sediment-associated contents of Sr and the lowest concentrations of all other elements, including heavy metals. Quartz sandstone basins have the lowest sediment-associated contents of As, Co, Cu, Ni, Pb, V and Zn, an illustration of the dilution effect by geochemically inactive quartz particles. Hg cannot be related to lithology in this database, but is highly correlated to organic carbon. Shale basins export sediment with medium contents of these substances. The average elemental contents found in these pristine river basins are actually very low, particularly for Cd (0.28–0.73 ppm), Hg (0.020–0.066 ppm) and Pb (15.2–56 ppm).

Natural variability of sediment-associated metals in streams at the global scale (Prismet model)

The global distribution of sediment-associated metal contents at the stream scale (Table 1) was assessed by the extrapolation of the Prismet dataset (adjusted to 200 analyses) proportionally to the global outcrops of ten major rock types, taking into account their relative erosivity. This simple model was first tested for the major elements, particularly Al and Ca, which are most sensitive to lithology. The best fit was achieved when using the following rock proportions: granites 8%, gneiss/migmatites/schists 15.5%, basalts 12%, rhyolites 2%, trachyandesites 4.5%, quartz sandstones 5.5%, clays-rich rocks 20.5%, carbonated rocks 10%, Pre-Cambrian rocks 9% and mixed sedimentary rocks 13%. The resulting median sediment-associated contents predicted by the Prismet model are close to the shale average (see Table 1), both for major elements and heavy metals.

The 5% and 95% quantiles of the predicted Prismet distributions are assumed to represent the global range of sediment-associated contents for 90% of world streams and, in turn, the C_{95}/C_5 ratio is used as an indicator of the relative natural variability of sediment-associated heavy metals at this scale: Hg ($C_{95}/C_5 = 11.9$), Ni (9.5), Sn (9.4), Cr (9), Pb (8.6), Cu (6.3), Zn (5) and Cd (4.9). Aluminium contents are an indication of the limit of such an approach. As the Prismet dataset concerns only French streams in which sediments (<100 µm) are less weathered in comparison to the world average, due to temperate climatic conditions, and coarser than in large rivers, the modelled sediment-associated Al content in Prismet (median 64 400 ppm, average 61 400 ppm) is lower than the shale average (91 000 ppm). In the Western Europe geochemical atlas (De Vos & Tarvainen, 2006) the values for the sediment-associated Al content of "fine stream sediments" (<150 µm, basin <100 km^2) and "fine floodplain deposits" (500–6000 km^2), are also lower (respective medians 54 500 and 48 600 ppm). Horowitz & Stephens (2008) reported a median sediment-associated Al content of 59 000 ppm for USA rivers discharging to the ocean.

World average metal contents in river sediment from large pristine basins (Glomet$_{BGR}$ data set)

The Glomet$_{BGR}$ dataset (n = 178 rivers and tributaries) includes medium to large basins (0.01 to 6.4 million km^2) combining: (a) pre-anthropogenic levels determined from sedimentary archives for some European and US rivers, (b) a selection made by the author of large rivers and their tributaries

Table 1 Metal contents in pristine river sediments (mg/kg). French monolithologic streams (Prismet), distribution in world streams (Prismet model), global distribution in large rivers (Glomet$_{BGR}$), regional averages in Europe, China and USA.

Basin lithology	n	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn	Al
Prismet-Granites	16	0.70	37.7	10.3	0.046	14.2	52	11.4	63	65700
Prismet-Gneiss/migmatites	13	0.59	72.4	22.4	0.051	30.0	56	18.4	118	76300
Prismet-Rhyolite	4	0.41	44.5	9.2	0.028	13.2	42.3	7.3	67	71000
Prismet-Trachyandesites	6	0.73	32	16	0.031	16	25	4.5	146	84000
Prismet-Basalts	6	0.52	392	29	0.066	109	34	3.8	143	72200
Prismet-Quartz Sandstones	12	0.53	46.7	7.1	0.022	11.3	15.2	2.3	36	29400
Prismet-shales/clay	10	0.34	89.6	23.8	0.061	40.2	31.4	4.3	84	71500
Prismet-Precambrian	12	0.28	72.1	14.5	0.042	21.0	18.2	2.55	81	56900
Prismet-Carbonated rocks	12	0.32	51.2	12.1	0.020	29.8	16.2	2.2	54	31900
Prismet-Mixed sedimentary	17	0.66	62	14	0.063	20	30	3.5	78	43900
Prismet model C$_{90}$	200	0.81	138	32.9	0.97	62.7	61.4	9.2	145	86600
Prismet model C$_{50}$	200	0.45	64	15.4	0.041	24.7	24.3	3.3	82	64400
Prismet model C$_{10}$	200	0.19	31	7.3	0.011	10.9	13.9	2.1	40	29000
Glomet $_{BGR}$ C$_{90}$		0.7	147.0	57.5	0.12	83.0	38	4.50	143	102600
Glomet $_{BGR}$ C$_{50}$		0.27	72	24.5	0.040	40	22.5	2.20	90	72000
Glomet $_{BGR}$ C$_{10}$		0.100	40	5.6	0.010	19.0	13	1.50	53	44000
Glomet $_{BGR}$ C$_{90}$/C$_{10}$		*7.0*	*3.7*	*10.3*	*12.3*	*4.4*	*2.9*	*3.00*	*2.7*	*2.3*
n		154	229	263	85	257	243	21	247	175
EU streams (1) C$_{50}$		0.28	63	17	0.038	21	20.5	2.25	71	54400
EU floodplain sediments (1) C$_{50}$		0.3	59	17		22	22	2	65	48600
E. China alluvium (2) min. avg.	10	0.066	44	18	0.026	14.8	15.9		51.7	
E. China alluvium (2) max. avg.	10	0.15	81	27.1		31.7	41.6		95	
US rivers background (3) C$_{50}$		0.4	58	20	0.04	23	20	2.5	91	59000
Mississippi background 1893 (4)		0.125	71	22	0.70	40	25	2.4	132	84600

(1) De Vos & Tarvainen (1998), (2) Wang & Chen (1995), (3) Horowitz & Stephens (2008), (4) Presley *et al.* (1998).
n: number of analyses.

with minimal human impacts, i.e. from the least developed areas of the world (Amazon, Orinoco, Upper Niger, Congo, Middle Irrawaddy, Mekong, Upper Yangtze, Upper Colorado, Yukon, Mackenzie, Lena, Patagonia and British Columbia rivers), mainly from academic studies which cannot be listed in full here (e.g. Gaillardet *et al.*, 1999, 2003; Rachold, 1999; Gaiero *et al.*, 2002; see also references in Savenko, 2006, and Viers *et al.*, 2009). Regional studies for highly erosive basins are included and are based on those for the Upper Amazon (Elbaz-Poulichet *et al.,*1999), Alaska (analyses from Art Horowitz, pers. comm., 2005), Taiwan and New Zealand, plus specific surveys for sediment-associated Hg (e.g. Cossa *et al.*, 1996), as well as unpublished personal data.

The pristine state of these basins has been checked through an iterative process. After an initial selection (population density <10 people/km^2, limited mining, expert judgment), river metal contents, Me$_i$, were compared with the upper decile of the Prismet distributions (C$_{90Prismet}$, see Table 1) for at least three of the most sensitive elements (Cd, Cr, Cu, Hg, Pb, Zn). If the Me$_i$/C$_{90Prismet}$ ratio exceeded 0.8, the river analysis was re-qualified as of unknown status and mixed with another set of rivers of known contamination into the Glomet$_{Polluted-unknown}$ data set.

The resulting world pristine composition is first compared to the shale average for Al and Ca (Table 1). The average Glomet$_{BGR}$ sediment-associated contents, weighted by river sediment discharges, for 58 major rivers plus Taiwan and New Zealand rivers, totalling half of the exorheic area and 45% of world fluvial sediment discharges, are 83 000 ppm for Al and 24 500 ppm for Ca, i.e. very close to the shale averages, 91 000 and 22 000 ppm, respectively. This suggests that both soil weathering intensity and parent rock lithology are properly taken into account in the

Glomet$_{BGR}$ dataset. The median sediment-associated Al content for Glomet$_{BGR}$ is lower than the weighted average (72 000 ppm). When corrected by the Al$_{shale}$/Al$_{river}$ ratio (e.g. 91 000/64 400 = 1.4 for the Prismet model), the Prismet model and Glomet$_{BGR}$ median contents are very similar to the average shale for most sediment-associated heavy metals (see Table 3).

Sediment-weighted average levels have not been calculated for heavy metals due to the uneven distribution of analyses. The most frequently analysed elements in the Glomet$_{BGR}$ database (n = 85 to 263 analyses) are: Co (87%), Cu (79%), Al (75%), Ni (71%), Cr (66%), Pb (63%), Zn (61%), Cd (50%), As (54%), V (48%), Hg (33%) and Sn (13%). A similar ranking is found in the Glomet$_{Polluted-unknown}$ database. The distribution of sediment-associated metals in Glomet$_{BGR}$ (C$_{10\%}$, C$_{50\%}$, C$_{90\%}$), is similar to that of the Prismet model established at the stream scale (Table 1). Median values are also close to European Union (EU) stream medians (De Vos & Tarvainen, 2006; Table 1). An earlier global average calculated by Martin & Meybeck (1979), although still used as a pristine state reference value, is questionable for these heavy metals, because some samples may have been contaminated (e.g. Congo River). The sediment-associated averages (Salomons & Förstner, 1984), based mostly on sedimentary archives, which proposed much lower figures, close to the shale averages, are more reliable (see Table 3).

PAST AND CONTEMPORARY SEDIMENT-ASSOCIATED METAL CONTENTS IN IMPACTED BASINS

The specific objectives driving metals analyses for samples collected from river basins are various. Geochemists focus on large pristine rivers and their tributaries to determine the controlling factors of rock weathering at the global scale (Gaillardet *et al.*, 1999, 2003). Geochemical atlases map streams and small rivers with variable human impacts (Salminen, 2003; De Vos & Tarvainen 2006). Environmental agencies focus on streams (Rice, 1999), or on river discharges to the oceans (Horowitz *et al.*, 2011) with variable states of contamination. Other studies aim to understand the origins, transfers and state of metal contamination, e.g. for the River Seine basin (Meybeck *et al.*, 2007; Thevenot *et al.*, 2007). Historical metal contamination can be reconstructed from dated cores taken along river networks (e.g. Bricker, 1993; Presley *et al.*, 1998; Winkels *et al.*, 1998; Grousset *et al.*, 1999; Audry *et al.*, 2004).

Metal dispersal in contemporary impacted river basins

Metal dispersal for a typical Western European or North American river basin is presented in schematic form in Fig. 1. Even in the absence of metal inputs from human activities, changes in water budgets (Fig. 1, right A, B, C, K, M) and sediment budgets (A, B, C, K, L) may affect *metal fluxes*, for example, after the construction of a major reservoir (G). In impacted river basins, *metal contents* can be altered in many ways. When there is mining (E), this is the primary source of metal, through the inputs of wastewaters, weathering and erosion of tailings; it is often associated with smelting (F), which generates considerable metal emissions into the atmosphere (H). Contaminated fallout can be observed locally (J$_2$) or outside the emitting river basin (J$_1$). Mining and associated smelting can occur in remote basins that could otherwise be regarded as pristine (e.g. Arctic basins, New Guinea, Australia). Rural areas (D) are much less impacted than river reaches downstream of mega cities and/or industrial areas where metal use is considerable.

The dispersal of metals in the anthroposphere starts with their transformation into metal products (e.g. pipes, building materials, cables, railroads) and metal-containing products (pigments, glass, tires, cars, batteries, etc.) (N). The first category does not leak significantly into the aquatic environment, but it is responsible for a gradual build-up of metals within infra-structures. After use (O), metal-containing products and some metal products (car batteries) can be recycled through secondary fusion *(P)*, before being re-processed (N) and used again (O). Numerous re-use loops also exist within industries (Q). When there is no mining, the flow of metals within river basins is maintained by external imports of ore, refined metals and metal-containing products, while river basins can also export these materials *(R)*. Metal recycling
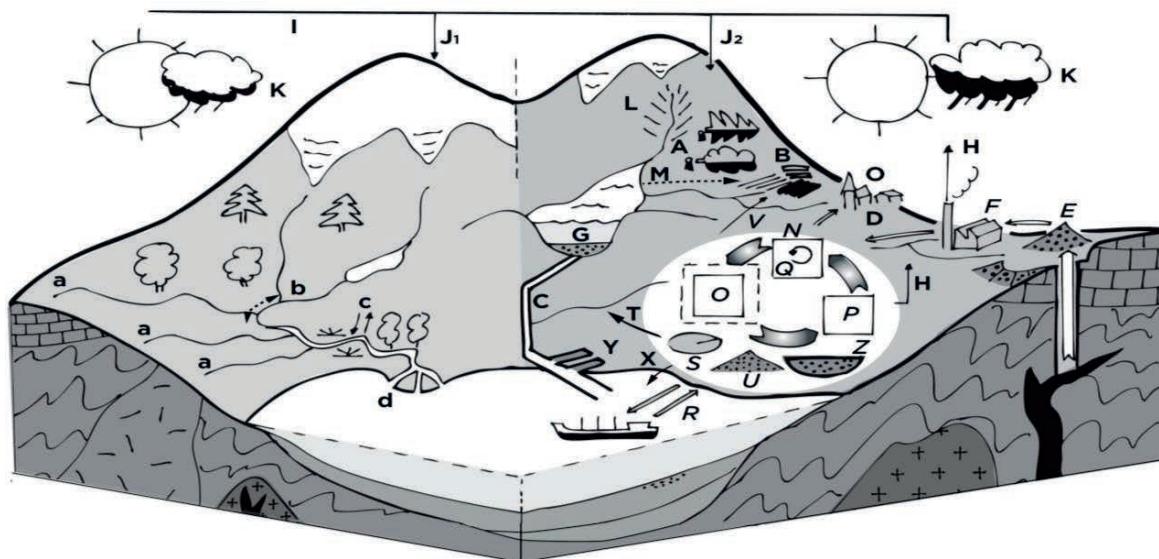
Fig 1 Metal dispersal within pristine river basins (left) and impacted basins (right). (a) weathering of various types of surficial rocks, (b) dissolved–particulate exchange, (c) sorting and settling of sediment, (d) sediment deposition. A: deforestation and enhanced soil erosion, B: agriculture, C: wetland filling and channelization, D: domestic waste waters, E: mining, F: smelting, G: reservoir construction, H: atmospheric emissions, I: long-range atmospheric pollution, $J_{1,2}$: atmospheric fallout, K: hydroclimatic change , L: enhanced erosion, M: water diversion, *N*: metal transformation, *O*: metal use, *P*: metal product recycling and second fusion, *Q*: metal re-use within industries, *R*: imports–exports of metal ores, refined metals and metal-containing products, S: treatment of waste waters, T: urban wastes waters inputs, U: non-secured waste dumps, V: re-use of treated sludge in agriculture, X: direct waste discharge to the coast, Y: harbours, Z: final wastes depositories (*N to R*: material flows of metals in the Anthroposphere).

(*N-O-P*) is now a major circular flow, much greater in many river basins than primary smelting and river metal fluxes to the ocean. Secondary smelting (*P*) may be externalized outside the river basin or outside the country (Lestel, 2011, and pers. comm.). Metal leakages should now, in theory, be minimized: wastewaters are treated (S), organic-rich treated sludge, which should not contain significant levels of metals, is recycled on agricultural land (V) or stored in final secured depositories (Z) that also receive metal-containing ashes and dust from the treatment of solid wastes and smoke discharges (H).

This ideal picture has gradually become commonplace in the last 20 to 30 years in North America and Western Europe. Before this period, metals were discharging into the environment at each step of the circulation summarised in Fig. 1: into the atmosphere, the soils (past industrial soils are often very contaminated), surface water and groundwater, and from non-secured urban and industrial waste dumps (U). Also, many coastal cities used to discharge their wastes directly to harbours (Y), estuaries or the coastline (X), a contamination pathway rarely taken into account in land to sea contaminant budgets. Such types of metal circulation probably still occur in many newly developing countries, although these environmental problems are not necessarily documented in detail. Metal dispersal through the environment can be used as a marker of economic development and environmental management efficiency.

Monitoring stations may pick up very different contamination levels, depending on their positions on the river network (Fig. 1). As a result, in a given river basin, metal contents may range over one (Cr, Cu, Pb, Ni, Zn) to two (Cd, Hg) orders of magnitude, illustrating the spatial variability of human impacts, as recorded in the River Seine (Horowitz *et al.*, 1999). It is therefore difficult to assess metal contamination without intensive environmental surveys and without knowing the likely key metal discharges within river basins. Maximum impacts are found downstream of mining and smelting facilities and of big cities. River size is also important: for a similar pressure, small rivers are more contaminated due to the lack of dilution. In the Quinnipiac

River, Connecticut, USA (480 km^2) impacted by silver plating industries (Rozan *et al.*, 1994) and in Narragansett Bay, Rhode Island, USA (850 km^2) impacted by many industries for more than 100 years (Bricker, 1983), past metal enrichment factors are orders of magnitude higher than in the Mississippi Delta (3.2 million km^2; Presley *et al.*, 1998). Canals and harbours (Y), are typically not considered in river or coastal surveys, but are frequently very contaminated (see Table 3).

The retention of contaminated particles in soils, lakes, floodplains (Fig 1, left) and in reservoirs (G), often with a 99% sediment trapping efficiency, reduces metal loads and minimizes metal discharges at downstream stations. Such storage of contaminated sediment may last for decades to millennia, long after the cause of contamination has ceased. Many of these contaminated sites are still not registered. In some instances, the risks of their potential environmental impacts are not addressed (orphan pollution). Other important issues include the fate of dredged sediment, from lower river reaches and harbours, or of contaminated reservoir sediment. In the River Lot (France), sediment contaminated by cadmium and zinc, due to a former zinc mine, now closed, and stored in small reservoirs for decades, was re-mobilized after a big flood and transported to the Gironde estuary where particulate Cd can be re-solubilized, jeopardizing coastal biota (Audry *et al.*, 2004). Some agricultural soils that received urban sludge can now be considered as contaminated and improper for cropping. These unaddressed contamination issues will be more difficult to deal with as environmental criteria become increasingly constraining in the drive to improve protection of valuable water and soil resources with a growing global population.

Contamination history of the Seine, Western European and North American rivers

The River Seine (France) provides an illustration of the progressive understanding of metal contamination in a typical Western European river over the last 40 years. Major sources of metal emissions are the megacity of Paris (10 million people and many metal processing workshops) and its metal industries (automobiles, etc.). The dilution capacity of the River Seine is very low due to the typical sediment loads (700 000 t year^{-1} for 65 000 km^2; low suspended sediment concentrations, TSS = 20 mg/L^{-1}), thus maximizing the metal contents of particulate material. Metal contamination analysis using the Driver-State-Pressure-Impact-Response approach (DPSIR), recommended by the European Environmental Agency, was attempted by Meybeck *et al.* (2007). The metal survey work on the River Seine started in the early 1970s when the first analyses of Hg, then Cd, were provided by academic studies, at the request of the recently established Seine River basin authority (now AESN). The first natural references to help set the contamination level were overestimated by a factor of 5 to 10 for Cd and Hg. Despite extreme levels of Cd and Hg (>10 ppm), no special warnings were issued to river and/or estuarine users, due to a lack of widespread evidence for contamination and of sediment quality criteria. In the late 1970s, the first measures to control metal use were promoted by AESN, particularly in plating workshops (Cd recycling), but mercury anodes were still used by chemical industries. The metal survey of Paris sewer sludge started in 1979 and in river sediments a few years afterwards. The first contamination assessment did not identify a critical issue: sewage sludge that was spread onto agricultural land for decades always complied with the quality criteria, first established in the 1980s. Since 1979, a 10-fold decontamination trend has been observed at the Seine-Aval treatment plant (8 million equivalent people in the 1970s and 1980s). National criteria for agricultural soil and for dredged sediments and sediment contamination levels were lacking, as a result of discussions between the six French river basin authorities and different ministries. National criteria were subsequently established during the 1990s and revised in the 2000s (Oudin, 2000), following the EU Water Framework Directive (WFD) (Quevauviller *et al.*, 2008).

By 2000, the decontamination trend of the Seine basin had started to be established, but the state of the contamination peak (level, period, metal) and its relation with key drivers and pressures remained unknown. Before 2000, the assessment of pressures, i.e. loads from urban or industrial wastewaters, was not possible for individual metals. France used two aggregated indicators to fund river basin authorities; the *metox* load (a theoretical assemblage of As, Cd, Cr,

Cu, Hg Ni, Pb and Zn, with different weights calculated from industrial production) and the *equitox* test, the *Daphnia* exposure to all toxic substances. In the mid-2000s, the first sedimentary record of metals near the river mouth revealed an unknown long-term contamination history (Meybeck *et al.*, 2007). It showed that the River Seine has been extremely contaminated since World War I by Cd, Cr, Cu, Hg, Pb and Zn, with a contamination peak from 1955 to 1965. The maximum enrichment factors (EF) ever measured in some River Seine sediment samples were of the order: Hg (EF max 850), Cd (130), Cu (35), Pb (25), Zn (20), Ni (10) and Cr (10). Current metal EFs (2008–2010) are now orders of magnitude lower. Severe impacts on aquatic biota, and on people using river water and/or estuarine sources of protein, are likely for the period 1920 to 1980, but are difficult to isolate from other water quality issues. For example, before 1970, the river was hypoxic in summer for more than 100 km, ammonia was very high and bacterial contamination was also severe due to limited collection and treatment of wastewaters. The legacy of metal pollution downstream of Paris is important for dredged sediment management, and is evident in contaminated agricultural soils, including floodplain soils at depths of 30 to 100 cm.

In contrast, in the River Loire basin (France) metal mines (for Sb, Sn, Pb and Zn) and coal mines (for As, Bi, Cd and Hg) were the major causes of severe contamination before 1950, then metal industries, when mining declined after 1950. Maximum EFs were 53 (Hg), 23 (Cd), 6.2 (Zn), 6.0 (Cu), 5.6 (Sn), 4.8 (Pb), 3.4 (Cr) and 2.8 (Ni) (Grosbois *et al.*, 2012). Since 1980, a rapid reduction in metal contamination has been observed in the River Loire, as in the River Seine. Similar contamination trajectories are also observed in many Western European rivers in sedimentary archives: Rhine (Middlekoop, 1997; Winkels *et al.,* 1998), Mersey (Harland *et al.,* 2000), Scheldt (Zwolsman & van Eck, 1999), Garonne (Grousset *et al.*, 1999) (Fig. 2). The period of most severe metal contamination typically extends from 1920 to 1990, with two common peaks (1930–1940s and 1950–1960s). In these low-turbidity (TSS <30 mg/L) middle-sized river basins, with high population pressures (100 to 400 p/km^2), enrichment factors at peak contamination were typically between 10 and 50 for the most sensitive elements (Hg and Cd > Pb, Zn > Cu > Cr and Ni). De-contamination is sometimes observed before the mid-1970s, i.e. before any metal regulation was in place, e.g. for Pb and Zn in the River Rhine and for Pb, Cu, Cd in the River Seine. In large and/or turbid rivers (Mississippi), or rivers with sediment retention in reservoir (Volga), the metal contamination levels are much lower (Fig. 2). Dilution by high sediment loads, limiting the excess metal contents in particles, is also observed in the turbid River Rhône with a maximum EF of 13 (Pb), 11 (Cd), 7 (Hg), 5 (Cu) and 2 (Zn), even though the Rhône valley historically was the home of numerous industries; for almost all metals anthropogenic inputs decreased at the end of the 1960s, except for Hg which decreased after 1980 (Ferrand *et al.*, 2012).

The general de-contamination trend in Europe (Vink *et al.*, 1999) is notable, while the demand for metal (the driver) continues to rise, as in France (Meybeck *et al.*, 2007). Causes of the observed de-contamination vary with river basin, the type of economy and environmental policies. De-industrialisation and changes in industrial processes (e.g. declining use of mercury anodes), declining use of coal as in France after 1970, are likely causes for the observed decline of sediment-associated metal contents, before any metal regulation was in place. The recycling of metals within industries, e.g. in the automobile industry, recycling of metal-containing products such as batteries, are other potential causes of declining metal contamination in rivers of the western world. Metal use regulations including the gradual Hg ban since the 1970s and the Cd use limitation from 1995, seem to have been effective mostly after 1980.

Leakage ratios, LRs, an expression of the pressure/driver relation, can be taken as an indicator of environmental efficiency. For the River Seine, LRs have continuously decreased from 1950 to 2005 for Cd, Cu, Cr, Ni, Pb and Zn, despite the continuous increase in metal demand (except for Cd demand, which declined after 1995). For the 1950s, LRs have been estimated at 20% (Cd), 4% (Zn), 2% (Pb) and 0.8% (Cu), with these estimates subsequently decreasing exponentially by 5 to 10 times (Meybeck *et al.*, 2007). The trend for Hg differs in that the demand has declined by a factor of 100 since the 1950s, but LR_{Hg} is still high, exceeding 10%.
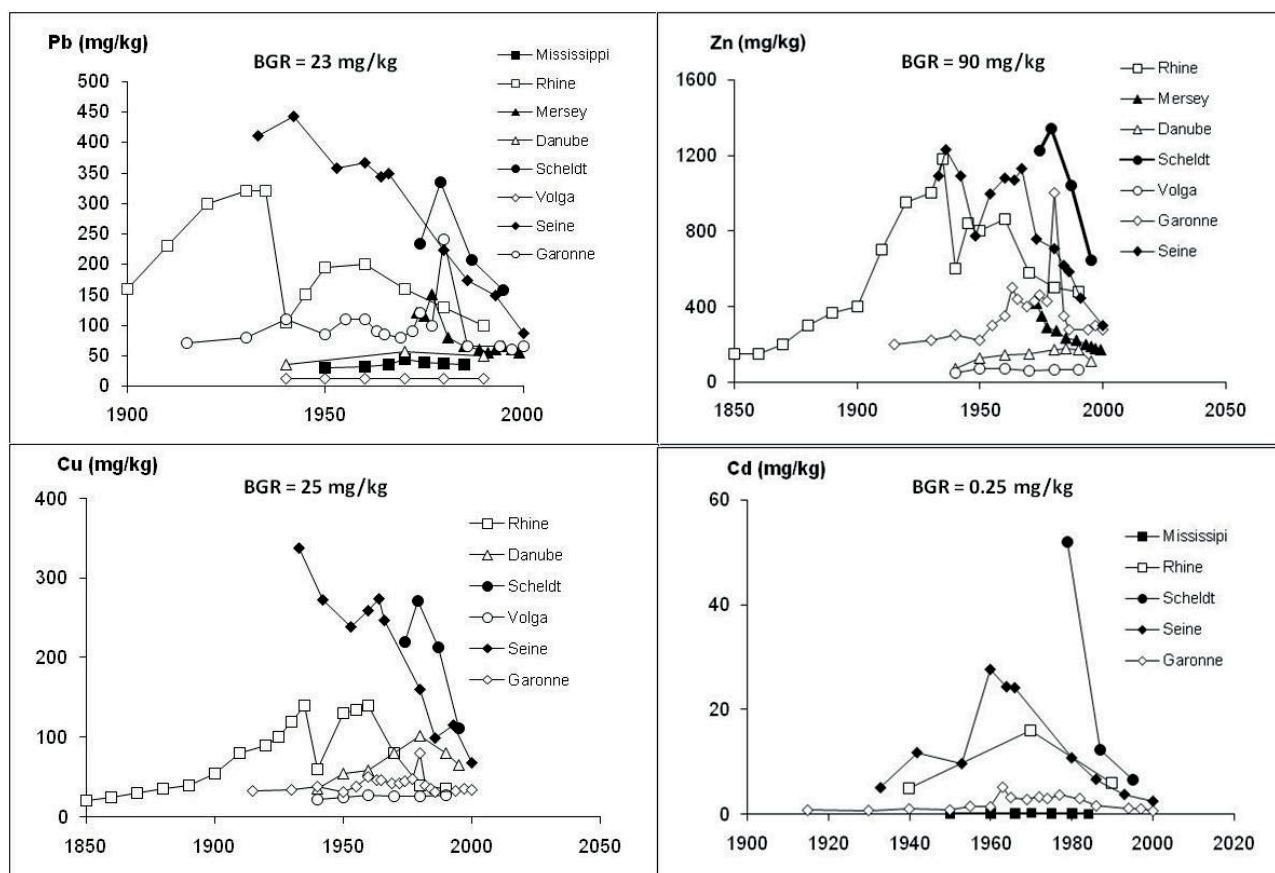
Fig 2 Trends in sediment-associated metal contents (Pb, Zn, Cu, Cd) in various European rivers and the Mississippi (mg/kg). BGR: average pre-anthropic background values.

Table 2 Metal *per capita* loads in river basins: excess particulate fluxes, normalized to basin population (g capita^{-1} year^{-1}).

	Period	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Area (10^6 km^2)	Population (10^6 people)
W. European rivers (1)	1960–1970	2.8	63.7	31.4	0.74	5.6	33.7	175	0.53	123
St Lawrence (2)	1995–2000	0.23	24	17.2	0.05	12	7.6	64		
Mississippi (3)	1970–1990	0.58	45	10	0.175	6.2	30	47.5	3.2	67
Danube (4)	1990	/	9	30	0.6	9.5	9.5	70	0.8	81

Based on Elbe, Meuse, Garonne, Rhine, Scheldt, Seine rivers, (2) based on Montreal sewer analysis by Gobeil *et al*. (.2005), (3) based on Presley *et al*. (1998), (4) based on Winkels *et al*. (1998)

When linking the excess metal load to river basin population, the per capita excess loads (EL$_{cap}$) extend over three orders of magnitude in Western European and North American rivers, from Hg (0.1–1 g cap^{-1} year^{-1}) to Zn (100 g cap^{-1} year^{-1}) (Table 2). Metal life cycles and their trajectories remain specific for each element and for each river basin, e.g. the retention of contaminated particles in the Great Lakes limits the EL$_{cap}$ in the St Lawrence River Basin.

The interpretation of such data is challenged by various limitations and uncertainties. The metal recycling loop (Fig. 1, N-O-P) has been very dynamic over the last 60 years, e.g. in France where major transfers of metals between river basins and the Paris megacity are well-documented (Lestel, 2012). Therefore, it is difficult to compare excess river metal fluxes to the overall material flows of metals that may vary within short timeframes, e.g. when a major source of metal is established or closed (primary or secondary smelting), or when specific types of materials are no longer permitted or become obsolete (e.g. Cd cells, Hg anodes, Pb glass, Cd, Cr, Pb and Zn

pigments, leaded gasoline). An example of rapid de-contamination, due to de-industrialization and industrial transformations, was observed in the Elbe River basin after 1989 in East Germany and Czechoslovakia (Vink *et al.*, 1999). Economic statistics are not necessarily generated for environmental analysis: they are collected for spatial administrative or political entities (e.g. country level), and are therefore often not available for all metal-containing products or known with great certainty (Lestel *et al.*, 2007). Contamination legacy should also be taken into account during life cycle analysis. In northern France, cadmium levels in some canals can reach 500 ppm, i.e. more than a thousand times the natural background. This so-called "orphan pollution" was generated by one of the major metal recycling units of Western Europe, which has since closed.

Metal trends (1893–1993) in the Mississippi River basin (serving 67 million people) assessed using delta sediments (Presley *et al.*, 1998) show limited metal contents (maximum levels in 1970–1990: 0.36, 0.139, 37, and 151 ppm for Cd, Hg, Pb and Zn, respectively), corresponding to very low EFs normalized to Al (EF = 3.0, 2.3, 1.7 and 1.35 for Cd, Hg, Pb and Zn), compared to European rivers. Such limited contamination is due to the high sediment loads (currently around 170×10^6 t year^{-1}). In the River Mississippi, an excess of 1 ppm of metal corresponds to an annual excess load of 170 t, compared to 0.7 t for the River Seine in France. In contrast, calculated per capita excess loads for North American and European rivers are very similar (Table 2).

CAN GLOBAL RIVER CONTAMINATION BE ESTIMATED?

Assessing global metal contamination involves a moving target. In some regions (USA, W. Europe) overall de-contamination for most metals has been observed since 1980. In other basins, as in China, the contamination is still progressing. In the Yangtze River, a core taken before the Three Gorges Dam (TGD) closure, some 230 km downstream of the TGD in Shishou ox-bow lake (Müller *et al.*, 2008), showed a marked and continuous increase between 1982 and 2006 for Cd (×3), Cu (×1.26), Hg (×15), Ni (×1.06), Pb (×1.6) and Zn (×1.4). As in the Mississippi, enrichment factors are limited by the high sediment load of the Yangtze. When based on this record, per capita load estimates for the Yangtze population in 2005 are very similar to the European and American estimates for the 1970–1980s, meaning that the recent trajectories of rivers in western *versus* developing countries are reversed.

The last dataset, for rivers of polluted and unknown status (Glomet$_{Polluted-unknown}$, Table 3), combines analyses mostly published between 1975 and 2008 (161 to 406 rivers from all continents, depending on metals). It includes rivers from Western Europe, USA (e.g. Horowitz *et al.*, 2001), China (e.g. Chen & Wang, 1995; Chen *et al.*, 2000), many severely contaminated rivers such as the Nile Delta (Siegel *et al.*, 1995), the Culiacan River, Mexico (Ruiz-Fernandez *et al.*, 2003), Indian rivers including the Yamuna (Singh, 1999) and Ganga (Ansari *et al.*, 2000), the Paraiba Do Sul River, Brazil (Carvalho *et al.*, 1999), and rivers affected by mining and smelting (Paul *et al.*, 1994; Horowitz *et al.*, 1995; Cizewski, 1997; Prieto, 1998). Table 3 also presents average metal contents in estuaries (e.g. Kennish, 1997), harbours and urban sewers (1980–2000) from various sources.

Many other estimates have been proposed for pristine rivers on the basis of recent analyses (e.g. Chen & Wang, 1995; Savenko, 2006; Jambon & Thomas, 2009) (see Table 3), and these all converge towards the shale composition. The latest review of world rivers by Viers *et al.* (2009) summarizes an exceptional and original data set of large rivers analysed over 15 years by these authors, including many pristine basins and some more impacted ones, with different contamination stages (Table 3). Their world average content is much higher than pristine median estimates presented here (Glomet$_{BGRC50}$), for Cd (×5.7), Cu (×1.8), Ni (×1.5), Pb (×2.8), Sn (×1.6) and Zn (×1.6). Human impacts are obvious and Viers *et al.* (2008) figures should be considered as a general state, averaged for the period 1990–2005, mixing rivers of opposite trajectories.

The metal content distributions (C_{10}, C_{50}, C_{90}) generate global indicators of metal sensitivity to human impacts: C_{90}/C_{10} for Glomet$_{Poll-unknown}$ ranges from 6.8 for Cr and Ni, to 73 and 100 for Cd and Hg. Extreme contamination at the global scale is measured by $C_{90Glomet\ poll.-unknown}/C_{90Glomet\ -BGR}$ which ranges from 1.5 for Ni, to 20 for Cd. Median or average contamination is estimated by $C_{50Poll.-unknown}/C_{50BGR}$ and $C_{average-Viers}/C_{50Glomet\ -BGR}$: in both cases provides similar rankings for

Table 3 Global distributions of metals in pristine and impacted river sediments (contents in ppm). Dimensionless contamination indicators in italics.

	Cd	Cr	Cu	Hg	Ni	Pb	Sn	Zn	Al
Glomet $_{Poll-unknown}$ C_{90}	14	230	200	2.0	124	256	25.50	1015	107500
Glomet $_{Poll-unknown}$ C_{50}	0.5	83.0	39	0.12	43.5	33.7	4.80	120	72000
Glomet $_{Poll-unknown}$ C_{10}	0.19	34	11.3	0.02	18	13.7	1.70	48.0	38050
Glomet$_{Poll-unknown}$ C_{90}/C_{10}	*73.7*	*6.8*	*17.7*	*100.0*	*6.9*	*18.7*	*15.00*	*21.1*	*2.8*
n (Glomet $_{Poll-unknown}$)	293	358	406	161	318	387	45.00	397	201
Glomet$_{Poll-unknown}$ $C50$/ Glomet$_{BGRC50}$	*3.0*	*1.4*	*1.8*	*3.4*	*1.3*	*2.1*	*3.3*	*2.0*	*1.0*
Glomet $_{Poll-unknown}$ $C90$ / Glomet$_{BGRC90}$	*20.0*	*1.6*	*3.5*	*16.3*	*1.5*	*6.7*	*5.7*	*7.1*	*1.0*
Estuaries (n = 75) C_{90}	7.4	413	382.0	1.42	113	482	3.70	2150	82200
Harbours (n = 20) C_{90}	32.8	288	418.0	5	54	883	18.80	3122	51850
Urban sewers (n = 21) mean	35.7	437	586.0	2.7	67.8	105		746	17700
Median background (Glomet$_{BGRC50}$)	0.27	72	24.5	0.040	40	22.5	2.20	90	72000
World average background (?), 1979 [1]		100	100.0		90	150		350	94000
World average background, 1980s [2]	0.2	60	25.0		50	15.0		105	
World average [3]	0.2	76	50.0			15.9		107.7	67600
World average [4]	1.55	130	75.9		74.5	61.1	4.6	208	87200
World average background [5]	0.5	85	45		50	25	2.9	130	86300
Shales [6]	0.25	100	45.0	0.18	70	22	5.00	100	91000

(1) Martin & Meybeck (1979), (2) Salomons & Forstner, (1984), (3) Chen & Wang (2000), (4) Viers *et al.*, (2009), (5) Savenko (2006), (6) Reimann & De Caritat (1998). n = number of analyses.

sediment-associated heavy metal contamination at the global scale relative to natural background conditions: Cd = Hg >> Pb, Zn ,Cu >> Cr, Ni.

CONCLUSIONS

Metal contamination of the aquatic environment is ancient, severe and now a global issue. Sediment archives are gradually providing information about its trajectories at periods of time when there was a lack of scientific knowledge, analytical techniques, social awareness, environmental surveys and political will. In Western Europe and North America, where maximum environmental contamination was recorded between the 1930s and the 1980s, metal emissions into rivers have largely decreased, since 1980, while metal use increased, providing proof of improved environmental protection. The analysis of the complex interactions between societies and metal contamination of their aquatic environment can be structured using the DPSIR approach. The metal demand (D) in river basins is driven by population and economic development (internal drivers) while mining and smelting (primary fusion) are driven by global metal markets (external drivers). Pressures (P*)* correspond to emissions of metals during their use, transformation and recycling (secondary fusion). The Leakage Rate (LR), the excess loads and per capita excess loads, are specific to a given metal and a given temporal period. In river basins with a long human history, these indicators may be biased by the legacy of past pressures (contaminated soils, sediments, waste dumps, mine tailings). The state (S) of metal contamination in rivers, expressed by excess metal contents and enrichment factors (EF), is a recent concern in human history, when considering the duration of past contamination. Prior to 1970, contamination was not routinely assessed for lack of analytical techniques and survey methodologies. In the first industrialized river basins, metal contamination was present before the 1900s, severe after 1920, peaked between 1950 and 1980, and fell dramatically thereafter. In emerging countries, the state of rivers, when documented, is often comparable to those conditions some 40 years ago in western countries and is still degrading as development progresses. The State of contamination is controlled by river sediment loads: low-turbidity rivers are structurally fragile to metal contamination (e.g. Rhine,

Seine), while high-turbidity rivers (Mississippi, Yangtze) are more resilient. The impact (I) of metal contamination is the least reported item and its metrics are still evolving. Social responses (R) to contamination are recent and were often developed, in western countries, after the most severe contamination period. The Leakage Ratio (LR) can be used as an environmental performance indicator to compare the efficiency of responses to metal contamination within basins and their evolution. Thresholds or contamination criteria for river sediment, soils, sewage sludge, dredged sediments and aquatic biota are part of these responses; they have continued to evolve over the past 30 years, as in France (Meybeck *et al*., 2007) and are still often different from one country to another. Some sediments officially considered as harmless 30 years ago and thereby managed accordingly (stored on non-secured sites or recycled on agricultural land), are now regarded as toxic products.

The present global average metal content of river sediment and the associated metal fluxes to the world's oceans are now moving targets. The river contamination trajectories in western and fast developing countries have been inverted over the last 40 years: in the early industrialized world the peak contamination is over, while in emerging economies, it may not have been reached. One should also take into account the growing retention of sediment at the global scale, e.g. by major reservoirs (Vôrôsmarty *et al*., 2003; Walling & Fang, 2003). In contrast, regional surveys, which can be performed within a short time, provide a snapshot of sediment-associated metal contamination, as demonstrated for USA rivers by Horowitz *et al*.(2011). Detailed regional assessments, sediment archive studies and metal life-cycle analyses should now be promoted at the global scale to assist targeted environmental management.

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