# Anthropophile elements in river sediments: Overview from the Seine River, France

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**Abstract** In contrast to larger river systems that drain relatively pristine basins, little is known about the sediment geochemistry of rivers impacted by intense human activities. In this paper, we present a systematic investigation of the anthropogenic overprints on element geochemistry in sediments of the human-impacted Seine River, France. Most elements are fractionated by grain size, as shown by the comparison between suspended particulate matter (SPM) and riverbank deposits (RBD). The RBD are particularly coarse and enriched in carbonates and heavy minerals and thus in elements such as Ba, Ca, Cr, Hf, Mg, Na, REEs, Sr, Ti, Th, and Zr. Although the enrichment/depletion pattern of some elements (e.g., K, REEs, and Zr) can largely be explained by a binary mixture between two sources, other elements such as Ag, Bi, Cr, Cd, Co, Cu, Fe, Mo, Ni, Pb, Sb, Sn, W, and Zn in SPM in Paris show that a third end-member having anthropogenic characteristics is needed to account for their enrichment at low water stage. These "anthropophile" elements, with high enrichment factors (EFs) relative to the upper continental crust (UCC), display a progressive enrichment downstream and different geochemical behaviors with respect to the hydrodynamic conditions (e.g., grain size) compared to elements having mainly a natural origin. Our findings emphasize the need for systematic studies of these anthropophile elements in other human-impacted rivers using geochemical normalization techniques, and stress the importance of studying the chemical variability associated with hydrodynamic conditions when characterizing riverine element geochemistry and assessing their flux to the ocean.

## 1. Introduction

During weathering and erosion of river catchments, the chemical elements derived from rocks and soils are distributed among river solutes, colloidal phases, suspended materials, and bed sediments following their physicochemical properties and the prevailing hydrological, chemical, geological, and climatic conditions [e.g., *Gaillardet et al.*, 2005; *Bouchez et al.*, 2011a]. River transport accounts for up to 90% of the flux of material delivered to the oceans, with the suspended particulate phase being the overwhelming vector compared to the dissolved load [e.g., *Martin and Meybeck*, 1979; *Dupré et al.*, 1996; *Canfield*, 1997; *Gaillardet et al.*, 1999; *Viers et al.*, 2009]. This highlights the importance of river-suspended sediments when studying the biogeochemical cycles at the Earth surface. Numerous studies have investigated the chemistry of suspended sediments in rivers worldwide [*Négrel et al.*, 1993; *Louvat and Allègre*, 1997; *Ludwig and Probst*, 1998; *Singh et al.*, 2008; *Marx and Kamber*, 2010; *Bouchez et al.*, 2011b]. These studies demonstrate the potential of sediment chemistry for determining weathering intensities and rates [*Yang et al.*, 2004; *Chetelat et al.*, 2013], reconstructing the composition and history of the upper continental crust [*Allègre et al.*, 1996; *Vigier et al.*, 2001; *Millot et al.*, 2004; *Dosseto et al.*, 2006], estimating fluxes of continental material transported to the oceans [*Martin and Meybeck*, 1979; *Goldstein and Jacobsen*, 1988; *Dupré et al.*, 1996; *Gaillardet et al.*, 1999; *Viers et al.*, 2009], and evaluating the riverine organic carbon flux [*France-Lanord and Derry*, 1997; *Raymond and Bauer*, 2001; *Galy et al.*, 2007; *Hilton et al.*, 2008; *Bouchez et al.*, 2010]. More recently, studies on large rivers have highlighted the importance of grain size and hydrodynamic conditions on the chemistry of elements in riverine sediment [*Benoit and Rozan*, 1999; *Singh et al.*, 1999; *Viers et al.*, 2008; *Lupker et al.*, 2012]. Hydrodynamic sorting of sediments according to their shape and density properties induces a significant chemical variability of the suspended load as a function of channel depth [*Garzanti et al.*, 2011; *Bouchez et al.*, 2011a].

However, these previous studies focus mainly on river systems that drain pristine basins or on elements having mainly natural origins, and little is known about the element geochemistry in the solid phases of smaller

rivers flowing through intensely populated and industrialized regions, where river chemistry also integrates the impact of human activities, especially for trace metals such as As, Bi, Cd, Cr, Cu, Fe, Mo, Pb, Sn, Zn, and even Gd [*Estèbe et al.*, 1998; *Elbaz-Poulichet et al.*, 1999; *Li et al.*, 2000; *Gaillardet et al.*, 2003; *Liu et al.*, 2003; *Meybeck et al.*, 2007; *Thevenot et al.*, 2007a; *Radloff et al.*, 2011]. These elements are mainly released to the environment through mining, smelting, wastewater discharge, agricultural fertilization and pesticide input, and industrial activities [*Nriagu*, 1979; *Nriagu and Pacyna*, 1988; *Lenoble et al.*, 2002; *Smedley and Kinniburgh*, 2002; *Klee and Graedel*, 2004; *Sen and Peucker-Ehrenbrink*, 2012]. For example, Cu is widely used in domestic plumbing, Cr and Cu in fertilizers, Cd, Pb, and Zn in household detergents, Fe, Pb, and Zn in sewer pipe systems, or Cr, Fe, Ni, Pb, Sn, and Zn in metal alloys [*El Samrani et al.*, 2004; *Grosbois et al.*, 2006; *Houhou et al.*, 2009; *Meybeck et al.*, 2007]. Previous studies also showed that the anthropogenic use of Mo in alloys, stainless steels, lubricants, and fertilizers may impact the Mo budget in river-suspended sediments [*Matos and Magyar*, 2005; *Neubert et al.*, 2011]. Bi is commonly used in alloys, drugs, glasses, and semiconductors, and an annual atmospheric deposition flux of about 0.4 g/ha/yr has been reported for Europe [*Senesil et al.*, 1999]. High Gd content has also been observed in river water samples and was attributed to "medical" contamination as it is injected into patients for magnetic resonance imaging (MRI) [*Elbaz-Poulichet et al.*, 2002; *Moller et al.*, 2002]. So far, the impact of sediment grain size on these "anthropogenic" trace elements in rivers remains unknown, and it is still unclear whether these elements have different behaviors compared to the elements mainly derived from natural sources (such as Al, REEs, and Th) under variable hydrological conditions. Although several studies have been conducted on elements in human-impacted rivers [*Shiller*, 1997; *Zwolsman et al.*, 1997; *Gueguen and Dominik*, 2003; *Chetelat and Gaillardet*, 2005; *Chen et al.*, 2008, 2014], most of these studies focus either on only one of the riverine phases (dissolved load, suspended particulate materials, bed sediments, or colloidal phase) or on a limited number of elements.

In this paper, we conduct the first systematic study of both major and trace elements in sediments of the human-impacted Seine River system. The Seine watershed displays two important characteristics: first, the Seine basin drains a continental area of relatively simple, carbonate-dominated lithology; second, the anthropogenic impact increases from the pristine headland toward the estuary. The specific objectives of the present study are (1) to systematically investigate the chemistry of major and trace components of the particulate load of river systems using geochemical normalization techniques, (2) to elucidate the effects of grain size and hydrodynamic conditions on both major and trace elements in the human-impacted Seine River, and (3) to compare the behaviors of elements mainly derived from human activities with those having only natural sources.

## 2. Setting, Sampling, and Analytical Methods

The Seine River, which drains an area of 79,000 km$^2$ in the northwestern part of France (Figure 1), is one of the largest rivers in Europe with a length of 780 km. Relief, climate, and variations of temporal discharge are very homogeneous throughout the basin [*Meybeck et al.*, 1998]. Due to very low relief and moderate rainfall, the long-term average suspended particulate matter (SPM) concentration of the Seine River is relatively low (44 mg/L) [*Roy et al.*, 1999; *Chen et al.*, 2009] compared to the world average of about 100 mg/L [*Gaillardet et al.*, 2005]. The Seine River and its major tributaries have similar hydrological regimes, partly controlled by human activities: discharge is the highest in winter (up to 2000 m$^3$/s) while summer flows are adjusted to about 100 m$^3$/s by regular water release from upstream reservoirs in order to maintain navigability for tourism and shipping purposes in the Paris conurbation and downstream of Paris. Geological maps show that sedimentary bedrock covers 93% of the Seine basin, of which 78% is chalk and limestone. Clays, marls, loess, loam, and sands represent the other 15%. Igneous rocks (7%, mainly granite) are limited to the upland area of the Yonne River in the southern Morvan region [*Roy et al.*, 1999]. The headwater streams of the Yonne, the Seine, and the Aube rivers drain relatively pristine forested areas, but most of the Seine basin is intensively cultivated (Figure 1). The Seine has been recognized as a human-impacted river with respect to metal contamination for both dissolved and particulate loads [*Roy et al.*, 1999; *Grosbois et al.*, 2006; *Thevenot et al.*, 2007a; *Chen et al.*, 2008, 2009; *Ayrault et al.*, 2012]. Industrial activities are concentrated mostly in the Paris conurbation and downstream from Paris. About 16 million people live within the Seine basin (average 215 persons/km$^2$), with a strong gradient of population density, from about 10 people/km$^2$ in the headwaters to about 5000 persons/km$^2$ in the Paris area.

Six sample sets were collected between 2004 and 2008 over the whole Seine basin. The first set is a time series of 44 surface river samples of the Seine River in Paris, collected monthly or bimonthly in 2004, 2005,
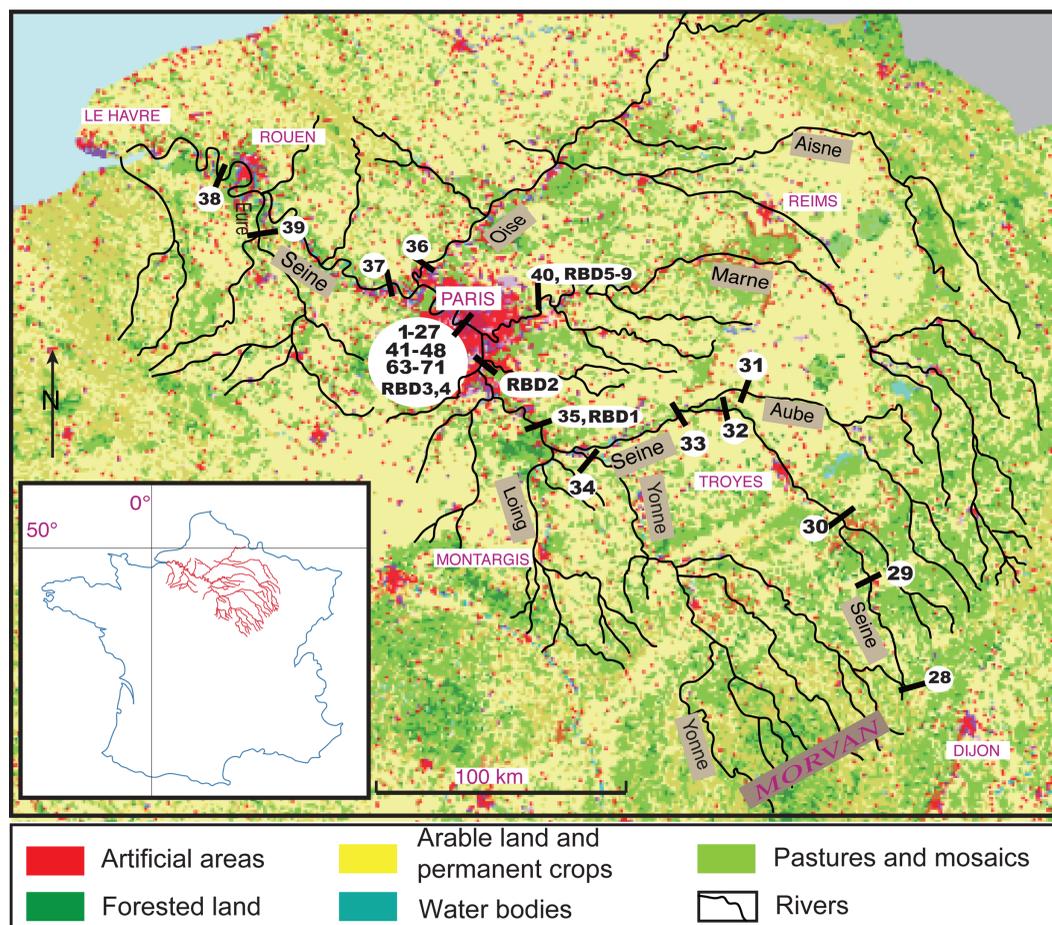
**Figure 1.** Map of land use in the Seine watershed and sampling locations. Origin of land use classification from the European Environment Agency (www.eea.europa.eu/data-and-maps/).

and 2006 near the Jussieu University campus with water discharge varying from 100 m$^3$/s to 1100 m$^3$/s (supporting information Table S1). The second set consists of river samples collected over a basin transect from the spring to the estuary during two cruises: one at flood stage in winter (February 2006) and another at low water stage in summer (July 2006, supporting information Table S1, Figure 1). For these two sets, all river samples were collected with an acid-precleaned 2 L PP bottle, 1.5 m below the water surface. The third set of samples was collected in March and April 2008 along two depth-profiles (down to 5 m) of the Seine River near the Austerlitz railway station in Paris using a point-sediment sampler (volume 8 L) [*Bouchez et al.*, 2012]. The fourth set consists of anthropogenic samples (urban roof runoff [RF], roadway runoff [RD], untreated sewage water [SW], and plant-treated wastewater [PTWW]), sampled between February 2005 and July 2006 in Paris. The fifth set includes nine riverbank deposits (RBD) of the Seine and Marne rivers, collected in 2006 and 2007 shortly after flood events. Finally, the sixth sample set is composed of two headland rocks: a limestone of the Cretaceous Chalk formation and a granite from the Morvan region [*Chen et al.*, 2009].

Water samples were filtered immediately for samples of the time series in Paris, and for other samples within a couple of hours after collection using polysulfone ether filter membranes (Millipore) of 142 mm diameter and 0.2 μm porosity. The suspended particulate matter (SPM) was carefully recovered by collecting sediments both retained on the filters (finest fraction) and settled at the bottom of the containers (silts) used during filtration. The sediments were dried at 60°C and powdered in an agate mortar. Samples with enough mass available (>250 mg) were separated into different aliquots. One aliquot was analyzed for major and trace element concentrations at the Service d'Analyse des Roches et des Mineraux at Nancy (SARM, France) after alkali fusion by ICP-AES and ICP-MS, respectively. The precision of these measurements was generally better than 3% for major elements and 10% for trace elements. For other samples with lower sediment amounts, about 30 mg of powdered SPM were digested in an HNO$_3$-HF mixture at IPGP [*Chen et al.*, 2009]. The
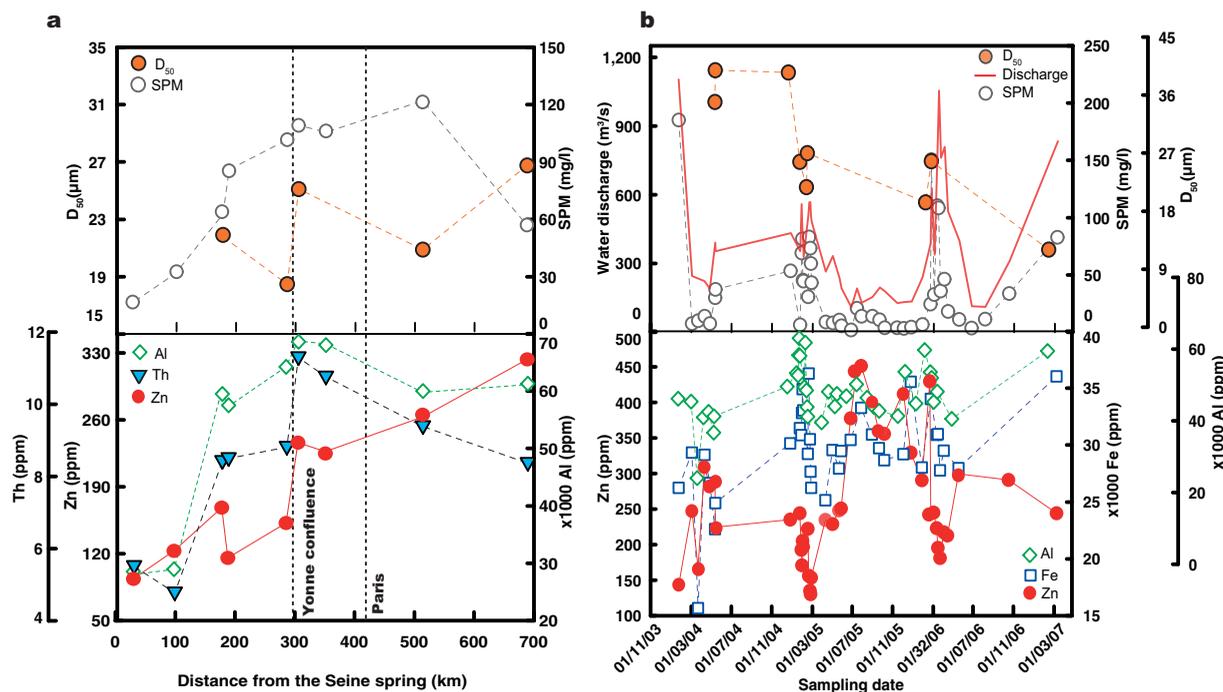
**Figure 2.** Basin-wide and temporal variations of the Seine River ((a) whole basin and (b) in Paris): (top) water discharge, suspended particulate matter (SPM) concentration, and grain size and (bottom) representative element concentrations. Zn, Al, and Th are shown as examples of variation along the source to estuary transect, and Fe, Zn, and Al concentrations are shown as examples of temporal variations in Paris.

final residue of digestion was dissolved in 2% $HNO_3$ for concentration measurement. Major elements were measured by ICP-AES with a precision better than 10%. Concentrations of trace elements were measured by ICP-MS (Thermo X-series II) at University Pierre and Marie Curie (UPMC), Paris. The analytical quality of trace element concentration data was improved by internal standard addition (In and Re) and checked through regular measurements of the international river water standard SLRS-4. Uncertainties for trace element concentration measurements were generally lower than 5%. For the basin transect samples, analyses were performed only for samples collected during the flood period, as low water stage samples did not contain enough sediment. Measurements of the same sample S40 at SARM and UPMC gave identical concentrations for almost all elements (supporting information Table S2). Particulate organic carbon (POC) content was measured, when sufficient sediment was available, by EA (Carlo-Erba NA-1500NC) after carbonate removal [*Chen et al.*, 2009]. The mineralogy of the Seine River sediment was investigated on a few samples by XRD and SEM at the Ecole Normale Superieure (Paris, France), using powdered aliquots [*Chen et al.*, 2009]. Grain size analysis was carried out by laser diffraction (Malvern Mastersizer) on aliquots of sediment samples dispersed in water.

## 3. Results

### 3.1. Concentration, Grain Size, and Mineralogy of the Seine River Sediments

Results are presented in supporting information Table S1. The samples collected in Paris over 3 years have water discharge ranging from 100 to 1013 $m^3$/s, with an average value of 380 $m^3$/s. In the following, samples collected in Paris at a discharge lower than this threshold are thus named "low water stage" samples, and others are named "high water stage" samples. The SPM content in the Seine River varies from 1.8 to 151 mg/L and increases from the headwater toward the estuary for the basin transect (Figure 2a), and with the water discharge for the Paris time series (Figure 2b, $r^2 = 0.61$). The samples from the two depth-profiles display a slight increase in SPM concentration with sampling depth. The grain size distribution of the Seine SPM has a modal size of about 50 μm. The basin transect samples show a downstream increase in grain size distribution median (or $D_{50}$, Figure 2a). In Paris, coarser grain sizes are generally observed during high water stage (Figure 2b). RBD are generally coarser than SPM samples, with modal size ranging from 50 μm to 250 μm.

The SEM observations and XRD analyses allow the identification of mineralogical compositions of SPM based on the amount of minerals contained in SPM deposited on a 47 mm diameter filter membrane. Semi-quantitative XRD analysis (using peak areas) show that Seine River sediments are composed of calcite (20–30%), clays (essentially kaolinite, 25–40%), quartz and other minerals (including feldspars, 20–40%), and organic matter (3–7%). Compared to other rivers worldwide [*Viers et al.*, 2009], the sediments of the Seine River are characterized by high carbonate contents. Significant amounts of carbonate shells were detected in RBD samples, especially in sample RBD9 (supporting information Table S1).

### 3.2. Major and Trace Element Distribution in the Seine River Sediments

Concentrations measured in the Seine River sediments are shown in supporting information Table S1. In general, Seine sediments have similar or slightly lower Al concentrations (average 5%), but much higher Ca concentrations (from 8.2 to 22%), than the suspended loads of the rivers worldwide (with average Al and Ca concentrations of 8.72% and 2.59%, respectively) [*Viers et al.*, 2009, and references therein].

Over the Seine basin, SPM of the winter transect samples have concentrations of Bi, Cd, Cu, Fe, Mg, Mo, Na, Pb, Sb, Si, Sn, and Zn that increase continuously downstream (Figure 2a shows the example of Zn). Al, K, Ti, Cr, Mn, Co, Zr, and Hf concentrations increase dramatically from the Seine spring down to the confluence of the Yonne and Seine Rivers (sample S35, Figure 2a shows the example of Al), and then remain constant or decrease slightly downstream. As, Ba, Be, Cs, Ge, REEs, Rb, Th, U, V, and W concentrations display a "bell-shaped" downstream variation, with the highest concentrations determined in sample S35 shortly after the confluence of the Yonne and the Seine Rivers (Figure 2a shows the example of Th).

In Paris, Seine SPM concentrations of Al, As, Be, Cs, Ge, Li, REEs, Rb, Sc, Th, Ti, U, V, and Zr increase with increasing water discharge, and thus with increasing SPM content (Figure 2b shows the example of Al). For some elements of this group (e.g., Al, Li, and V), significant deviation from the general relationship is found for samples at extremely high water discharge (e.g., S3). In contrast, concentrations of Ag, Bi, Cd, Cu, Mo, Pb, Sb, Sn, Sr, and Zn show an inverse correlation with water discharge (or SPM content; Figure 2b shows the example of Zn). Elements such as Ba, Ca, Co, Fe, Hf, K, Mg, Mn, Na, Ni, Se, Tl, and W do not display any relationship with water discharge (Figure 2b shows the example of Fe). The geochemistry of SPM therefore shows diverse behaviors between elements at the scale of the Seine watershed.

For most elements, RBD have lower concentrations than SPM samples. Only concentrations of Bi, Ca, Hf, Na, Sr, and Zr in RBD are similar to those in SPM.

Compared to the river SPM, the suspended loads of anthropogenic samples (roof runoff, road runoff, sewage, and plant-treated wastewaters) have higher concentrations of Cd, Cu, Mo, Pb, Sn, Sb, W, and Zn, similar concentrations of Ag, As, Ba, Be, Ge, Hf, Na, Pb, Se, Sr, W, Zn, and Zr, and lower concentrations for Al, Be, Ca, Co, Cr, Cs, K, Li, Mg, Mn, Ni, Rb, REEs, Th, Ti, and U (supporting information Table S1). Among these anthropogenic samples, the roof and road runoff samples have the highest concentrations of Ba, Bi, Cd, Cu, Fe, Mo, Pb, REEs, Sb, Sc, Sn, U, W, and Zn, while PTWW are particularly enriched in Sc and Sr.

Except for two headwater samples, S29 and S30, that have a relatively high POC content (5.6% and 7.5%, respectively), the basin transect samples display a continuous increase in POC content downstream (from 2.7% for S31 to 6% for S38, close to the estuary). In Paris, POC varies from 3.6% to 7.1% and decreases with increasing water discharge ($r^2 = 0.69$), thus with SPM content. Anthropogenic samples generally have higher POC contents (from 11.3% to 26.3%), while RBD show the lowest POC concentrations (from 0.8% to 4.2%, supporting information Table S1).

## 4. Discussion

### 4.1. Enrichment Factors of Major and Trace Elements

First, we aim to establish a broad picture of the pattern of enrichment/depletion of elements in the Seine sediments relative to the geological background, before discussing the different controlling factors potentially impacting this enrichment/depletion.

The influence of different processes (e.g., weathering, hydrodynamic sorting, and human activities) affecting river sediment chemistry can be quantified using the enrichment factor (EF) [*Duce et al.*, 1975; *Meybeck et al.*, 2007; *Thevenot et al.*, 2007a; *Chen et al.*, 2009; *Viers et al.*, 2009], which involves in a double normalization of the element concentrations:

$$EF(E) = (E/Al)_{sediment} / (E/Al)_{reference} \tag{1}$$

where E is the element of interest. Concentrations of E are first normalized to that of an insoluble element (here Al) to cancel out dilution effects by the major phases such as quartz, organic matter, or carbonates. Al is well adapted to this normalization as it is not carried by heavy minerals and thus its concentration is not greatly sensitive to the presence of heavy minerals. The E/Al ratio is then normalized to E/Al in a "reference" reservoir, in order to (1) obtain comparable magnitudes of enrichment for all analyzed elements and (2) emphasize enrichment and depletion patterns due to Earth surface processes. The upper continental crust (UCC) [*Taylor and McLennan*, 1985; *Hu and Gao*, 2008] is chosen as the reference material here. Although prehistorical alluvial deposits of the Seine River could also be chosen as a reference [*Thevenot et al.*, 2007a; *Chen et al.*, 2009], data reported in the literature do not cover the whole range of elements considered in the present study.

The patterns of calculated EFs for 53 elements in suspended sediments and riverbank deposits are shown in Figure 3. Elements are ranked according to increasing mean EF values of high water stage samples in Paris (Figure 3a). In general, the basin transect samples have average EF values similar to the samples from Paris. We thus only plot the samples from the time series in Paris (both high and low water samples). In order to compare the Seine River sediments with those of a relatively pristine river system, a SPM sample (AM05–43) from the main stream of the Amazon River [*Bouchez et al.*, 2011a] was also plotted in Figure 3. This particular sample was chosen because its Zr/Al ratio (a index of heavy mineral abundance) is close to the average value of the Seine SPM. According to the large data set of *Bouchez et al.* [2011a], this sample is representative of the overall geochemistry of the Amazon River fine SPM.

Except for Cd, which is clearly enriched (due to possible contamination), and Na, Mg, K, and Sr, which are depleted (as a result of chemical weathering) [*Gaillardet et al.*, 1997], all elements have EF values close to or slightly higher than 1 in Amazon SPM. This indicates that Amazon River SPM has a geochemical composition similar to the UCC and that it may thus be used as a reference for natural geological background when assessing the geochemistry of river systems of mixed lithology.

The first overall observation that emerges from Figure 3 is that half of the analyzed elements (from Mg to Cr in Figure 3) in the Seine River SPM show EF values that are not significantly different from those of the Amazon sample, while the others are either strongly enriched or depleted in the Seine River sediments (log scale in Figure 3). The similarity between Amazon and Seine River sediments for those elements having the same range of EF is particularly noteworthy, despite the difference in geological, climatic and ecological contexts of the two river systems. The second important observation is that within the Seine River system, the high water stage SPM (Figure 3a), low water stage SPM (Figure 3b) and the RBD (Figure 3c) show different EFs, with RBD having higher values for most of the elements.

In more detail, three groups can be distinguished according to the EF values for the Seine sediment samples:

1. Na, Mg, K, Si, Sr, and Ba are significantly depleted in Seine SPM (as well as in the Amazon River SPM) compared to the UCC (EF < 1). Alkali and alkali-earth elements such as Na, K, and Mg are easily mobilized during weathering reaction, even at "mild" conditions such as those prevailing in the temperate Seine Basin. A compounding effect is that of hydrodynamic sorting, which can lead to enrichment or depletion of those elements enriched in coarse minerals (Na, Si, and Sr) in one river compared to another [*Bouchez et al.*, 2011a]. For example, it could be argued that the relatively low flow velocity of the Seine does not allow for efficient transport in suspension of dense or coarse minerals such as feldspar over most of the range in hydrological conditions. This may in turn explain the depletion in Na of the Seine SPM, Na being a main constituent of feldspar [*Garzanti et al.*, 2010]. Finally, such differences could also result from lithological variability, if the silicate bedrocks of the Seine River are rich in weathered clays, as shown for other basins [e.g., *Dellinger et al.*, 2014].

2. Co, Fe, Ga, Ge, Hf, Ni, Rb, most REEs (except Eu and Gd), Sc, Ti, Th, U, V, and Zr have an EF value close to or slightly higher than 1 (e.g., EF < 1.5) and therefore have UCC-like abundances, similar to those of the Amazon River. The simplest explanation for this similarity is that these elements are insoluble, mostly concentrated in the solid weathering residues and not significantly influenced by human activities.

3. Elements such as As, Be, Bi, Cs, Cd, Cr, Cu, Eu, Gd, Li, Mn, Mo, Pb, Sb, Sn, Tl, W, and Zn are enriched (e.g., EF > 1.5) in the Seine SPM relative to UCC and the Amazon River SPM. For example, Zn and Pb are
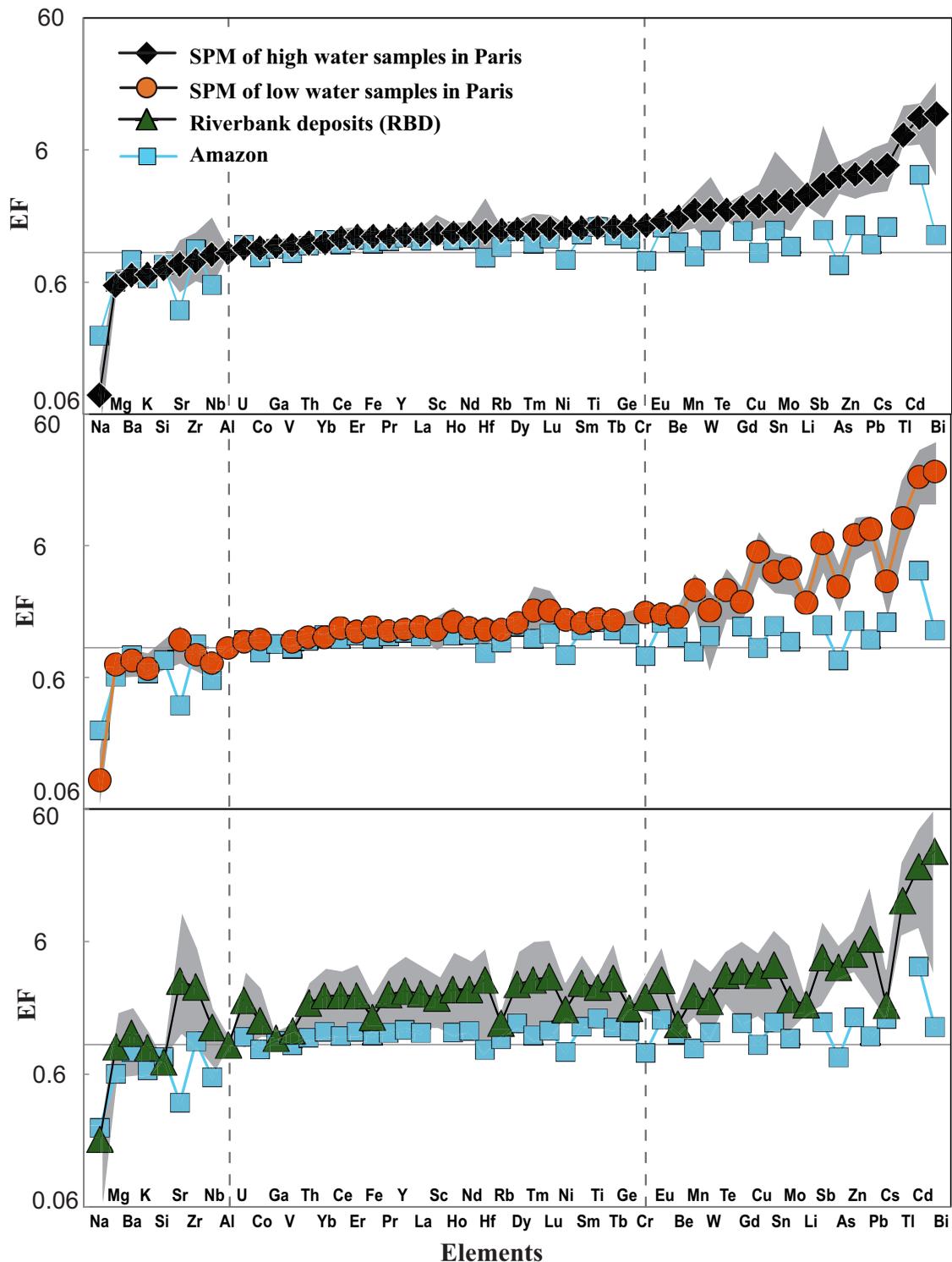
**Figure 3.** Enrichment factors (EFs) of 53 elements in both (a) high and (b) low water stage suspended particulate matter (SPM) of the Paris temporal series and (c) the riverbank deposits (RBD). The EFs are calculated relative to values for the upper continental crust (UCC) (equation (1)). Elements are ranked according to increasing EF values of high water stage samples. Ca is not shown because of its extremely high EF value. One SPM sample representing the overall composition of the suspended sediments of the Amazon River [*Bouchez et al.*, 2011a] is shown for comparison to a pristine watershed. Gray areas show the variability of the entire sample set.

typically 4–6 times enriched in the Seine sediments. The variability (the gray zone in Figure 3, defined by two standard deviations of EFs calculated over a whole set of available samples) of these elements is also more important than for other elements. While the enrichment of certain elements of this group is clearly

due to human activities (as demonstrated by the increasing EF values downstream for most of these elements), the EF > 1.5 observed for some REEs (e.g., Eu) may also indicate the role of natural processes in creating these enrichments. For example, the enrichment of Eu (and Sm and Tb to a lesser extent, Figure 3) in Seine SPM may indicate a MREE bulge effect as sometimes observed in river-suspended sediments [*Garzanti et al.*, 2010, 2011]. The enrichment of Gd probably results from anthropogenic input (see section 4.5).

When we compare the high water and low water stages in Paris, the same typology of elements is generally displayed in Figure 3. However, EF values of Ba, Bi, Cd, Co, Cr, Cu, Fe, Ge, Mg, Mo, Na, Ni, Pb, Sb, Sn, Sr, Ti, and Zn are higher in low water samples compared to flood samples in Paris, while EF values of As, Cs, Hf, K, Li, Rb, Si, and Rb are significantly higher in flood samples relative to the low water samples. Such variations can be due either to temporal changes in the transport of minerals, or to temporal changes in the source regions supplying the mainstream sediments.

Although RBD follow a trend of increasing EF, that is, overall, parallel to that of SPM, they are particularly enriched in Ba, Bi, Cd, Co, Cr, Fe, Ge, Hf, K, Mg, Ni, REEs, Sr, Ti, U, V, and Zr. Most of these elements are generally associated with heavy minerals (e.g., zircon for Zr, see also section 4.3.2) and/or large grain particles (e.g., carbonate for Sr), as has been documented in previous studies [*Hubert*, 1962; *Vital et al.*, 1999, *Franke et al.*, 2009; *Yang et al.*, 2009 and discussion below]. We also observe from Figure 3c that the variability of RBD is significantly higher than that of either high water or low water stage SPM.

To summarize, the elemental depletion and enrichment patterns of the Seine River SPM as compared to Amazon River SPM, as well as the comparison between low and high water stage samples and between Seine SPM and RBD, qualitatively suggest that three factors are at play in determining the Seine sediment geochemistry: (1) source rock composition, (2) hydrodynamic sorting, and (3) contamination by release from anthropogenic activities. Considering the fact that elements are mainly transported in the particulate phase relative to the dissolved load in the Seine River (e.g., up to 90% for Zn and 99% for Fe) [*Chen et al.*, 2009, 2014], the effects of in situ river processes such as adsorption would be very limited for element budgets in the Seine SPM. The factors impacting the SPM geochemistry are discussed in more detail in the following.

## 4.2. The Lithological Control

Bedrock lithology may have a major impact on the chemistry of SPM in the Seine River. Indeed, except for the headland of the Yonne River underlain by Hercynian gneissic, granitic and rhyolitic rocks [*Roy et al.*, 1999], the whole Seine basin is dominantly covered by carbonate rocks. It was shown by *Roy et al.* [1999] that Seine River waters are at saturation with respect to calcite, implying that both detrital or secondary carbonate minerals (e.g., shells) in Seine River sediments should be thermodynamically stable. In agreement with this observation, sample investigations using SEM and XRD have identified the overwhelming presence of carbonate minerals in suspended sediments of the Seine River. This explains the high Ca concentration (82,290–220,300 ppm) in all SPM samples collected in this study (supporting information Table S1, Figure 3) compared to Amazon River sediments (7000 ppm) [*Bouchez et al.*, 2011a], as well as the Mg and Sr enrichment of Seine sediments. In the Yonne River, weathering leads to the delivery of a large amount of aluminosilicate minerals to the Seine system. Accordingly, the highest concentrations of elements such as Al, Cs, K, and Rb along the basin transect are found in the Seine sample S35 collected just after the confluence of the Yonne River (Figure 2). Silicate material in the Seine mainstream might also be provided by the incongruent weathering of interbedded silicates, or of surficial loess and loam deposits also present in carbonate-dominated subcatchments [*Roy et al.*, 1999; *Thevenot et al.*, 2007b]. The EF similarity between Seine and Amazon River sediments for half of the elements analyzed here also reflects the homogeneity of the upper crust composition for these elements [*Taylor and McLennan*, 1985; *Hu and Gao*, 2008].

Figure 3 shows that the alkali elements Na and K are less abundant in Seine SPM compared to the UCC (also to Amazon River SPM), while Cs and Li are enriched in Seine SPM. The same trend was also found in large river systems such as the Amazon River [*Bouchez et al.*, 2011a] and the Mackenzie River [*Dellinger et al.*, 2014]. At this stage, we are unaware of any major anthropogenic sources of Cs and Li in river SPM, although disposal of recycled batteries could be a potential source of Li. Cs and Li are typically concentrated in the finest fractions such as clay minerals (thus enriched in SPM compared to RBD), while Na is enriched in coarse particles mainly composed of primary minerals. Therefore, the enrichment/depletion pattern of alkali elements is likely derived from the highly weathered and fine nature of particles from the Seine River. This
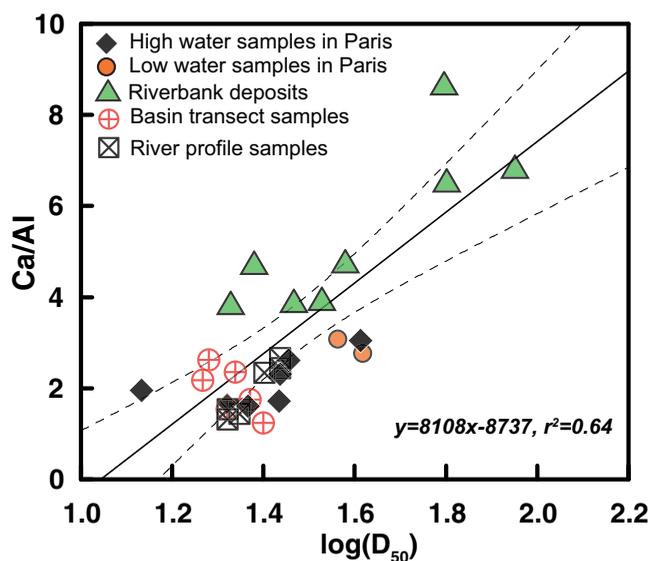
**Figure 4.** Relationship between sediment chemical compositions, as indexed by the Ca/Al ratio, and grain size median distribution ($D_{50}$) measured for some samples. High Ca/Al ratios are characteristic of carbonate-rich, coarse sediment such as riverbank deposits (RBD, excluding RBD9), while clay enrichment (Al enrichment) is observed in suspended particulate matter (SPM).

is in turn due to either (1) the hydrodynamic sorting effects (see section 4.3) that tends to preferentially enrich suspension with fine particles while leaving coarse particles on river banks and flood deposits or (2) a lithological effect, given the weathered nature of the bedrocks of the Seine watershed [*Roy et al.*, 1999; *Gaillardet et al.*, 1999]. Distinguishing between these two natural effects is beyond the scope of the paper.

Therefore, the major lithological effect observed in Seine sediment geochemistry is the supply of particulate Ca (and to a lesser extent of Mg and Sr) to the river, and the thermodynamic stability of carbonate phases. Dilution of elemental concentrations by carbonates is thus a first-order control on the geochemistry and grain size of sediments in the Seine River. Since carbonate minerals are generally coarse (as was observed through XRD and SEM analysis) and thus relatively enriched in coarse-grained sediment samples. This explains the lower concentrations observed in RBD compared to SPM for most elements.

### 4.3. The Role of Hydrodynamic Sorting of Sediment Grains

In this section, we examine the role of hydrodynamic sorting of sediment grain size, density and shape characteristics, in determining the sediment geochemistry in the Seine River. To address the grain size control, we use (1) the SPM samples collected at Paris along two depth-profiles at high water stage and (2) a comparison between SPM and RBD.

Al and Ca are major constituents in the stoichiometry of silicates (clays) and carbonates, respectively. Therefore, the Ca/Al ratio can be used as a broad indicator of the mineralogy of the Seine sediment samples that are mainly composed of silicates and carbonates. Considering SPM and RBD together, Seine sediment samples display a positive relationship between grain size distribution $D_{50}$ and the Ca/Al ratio (Figure 4), showing that river sediments rich in coarse grain particles have higher carbonate contents. We note that the two low water stage samples on which we measured $D_{50}$ are relatively coarse, which is probably due to a sampling bias (as grain size distribution was measured only for samples with enough sediment material, which are usually coarser). We also acknowledge that this correlation is less significant than that found by *Bouchez et al.* [2011b] using Al/Si in the Amazon, and is strongly driven by RBD samples. These observations suggest that in the Seine River, the mixture is slightly more complex, and for example that Ca might also be hosted, to some extent, in fine carbonate particles. Nevertheless, the correlation is significant and to first order reflects the binary mixture between coarse carbonates and fine clays. Hereafter the Ca/Al ratio is used as a chemical proxy of the grain size of particles.

### 4.3.1. SPM Geochemistry Along Depth-Profiles

Examining sediment over the two depth-profiles collected at the same location in Paris and at two close dates (March and April 2008) limits the effect of varying source contribution and hence emphasizes the effect of hydrodynamic sorting on sediment geochemistry. SPM from the depth-profile sampled in March 2008 have lower Ca/Al ratio (hence less carbonate) and finer grain size than the depth-profile sampled in April 2008. Across each of the two depth-profiles, only small chemical and grain size variations are observed. The fact that these variations are small is most likely related to the very limited spread in grain size distribution across a given depth-profiles. Such homogeneity in grain size over depth-profiles is most
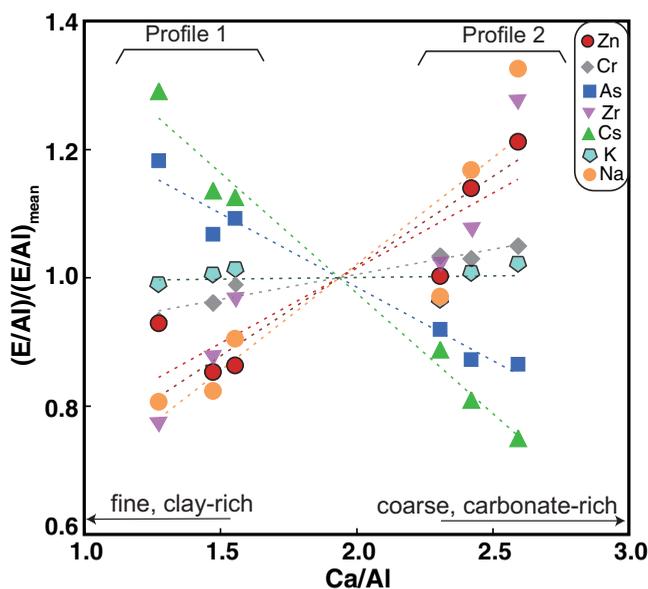
**Figure 5.** Chemical compositions of suspended particulate matter (SPM) collected over two depth-profiles in Paris. The Ca/Al ratio on the *x* axis is used here both as a mineralogical and grain size index. High Ca/Al ratios characterize coarse, carbonate-rich sediments, while low Ca/Al ratios indicate the clay-rich sediments. On the *y* axis, Al-normalized concentrations are presented relative to the average E/Al for the two profiles and indicate elemental contents that are independent from dilution by carbonate, quartz, or organic matter, and from the nature of the source material. Elements show various enrichment/depletion patterns as a function of sediment grain size, due to hydrodynamic sorting effects. Flat patterns indicate a simple dilution by the carbonates.

likely due to limited channel depth (ca. 5 m) in Paris, relatively fine size distribution ($D_{50}$ ca. 25 μm) and intense turbulent mixing at the time of sampling (March and April, corresponding to relatively high water stage).

However, when the two sampled depth-profiles are considered together, significant correlations are observed between the Ca/Al ratio and other element E/Al concentration ratios (Figure 5). In this plot, the E/Al ratios are normalized to the average E/Al ratio of the two depth-profiles: $(E/Al)_{sample}/(E/Al)_{mean}$. These doubly normalized ratios highlight the sorting effects at play in the river channel at the sampling location. This approach is similar to that developed in the Amazon River by *Bouchez et al.* [2011b].

Figure 5 shows three types of elements with distinct geochemical behaviors. First, Bi, V, and K (Figure 5 shows the example of K) have a flat pattern, indicating that their abundances are controlled by the dilution of a single carrying phase (here this dilution occurs because of carbonates). However, other elements in Figure 5 do not define flat patterns and are thus not simply controlled by carbonate dilution. In this group, elements such as Cd, Co, Cr, Cu, Hf, Mg, Mo, Na, Ni, Pb, Sb, Si, Sn, Sr, Zn, and Zr and to a lesser extent Ba and REEs (Figure 5 shows the examples of Cr, Na, Zn, and Zr) are depleted in low Ca/Al, fine sediments from the depth-profiles. By contrast, As and Cs and to a lesser extent Mn, Be, and Rb (Figure 5 shows the examples of As and Cs) are enriched in those fine sediments. Interestingly, such patterns of enrichment and depletion as a function of grain size (here indexed with the Ca/Al ratio) are strikingly similar to those found by *Bouchez et al.* [2011b] for the Amazon River. It is noteworthy that these enrichment/depletion patterns affect almost all elements, even those which are known to be significantly affected by anthropogenic activities in the Seine River, such as Zn, Cu, or Fe [*Buzier et al.*, 2006; *Chen et al.*, 2008, 2009, 2014; *Rocher et al.*, 2004; *Thevenot et al.*, 2007a]. Therefore, these elements are sensitive to hydrodynamic sorting effects as well, and part of their enrichment/depletion in river sediments might thus result from the grain size effects. However, we note that the linear correlation coefficients ($r^2$) between $(E/Al)_{sample}/(E/Al)_{mean}$ and Ca/Al ratio are generally smaller for those elements (e.g., Cu, Cr, Cd, Fe, Ni, Pb, Sb, Sn, and Zn) known to be affected by anthropogenic activities, especially for transition metals Cu, Zn, and Ni. This observation suggests that their mode of transportation is at least partially decoupled from that of elements (i.e., REEs and Th) mostly influenced by natural processes.

### 4.3.2. Comparison Between Suspended Particulate Matter (SPM) and Riverbank Deposits (RBD)
The mineralogical analysis of our nine RBD samples shows that these deposits are significantly different from SPM and are characterized by coarse minerals and higher carbonate content. Enrichment factors (Figure 3) show that RBD are enriched in a large number of elements such as Ag, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Hf, Ga, K, Mg, Na, Ni, REEs, Sc, Sn, Sr, Ti, U, W, and Zr compared to SPM. The fact that most EFs are high in RBD reflects the depletion of Al in those coarse samples that contain less clay mineral. Previous studies on river sediments showed that most of these elements (e.g., Fe, Hf, REEs, Sc, Sn, Th, Ti, W, and Zr and to a lesser extent Co and Cr) are generally contained and enriched in heavy minerals, for example Zr in zircon,
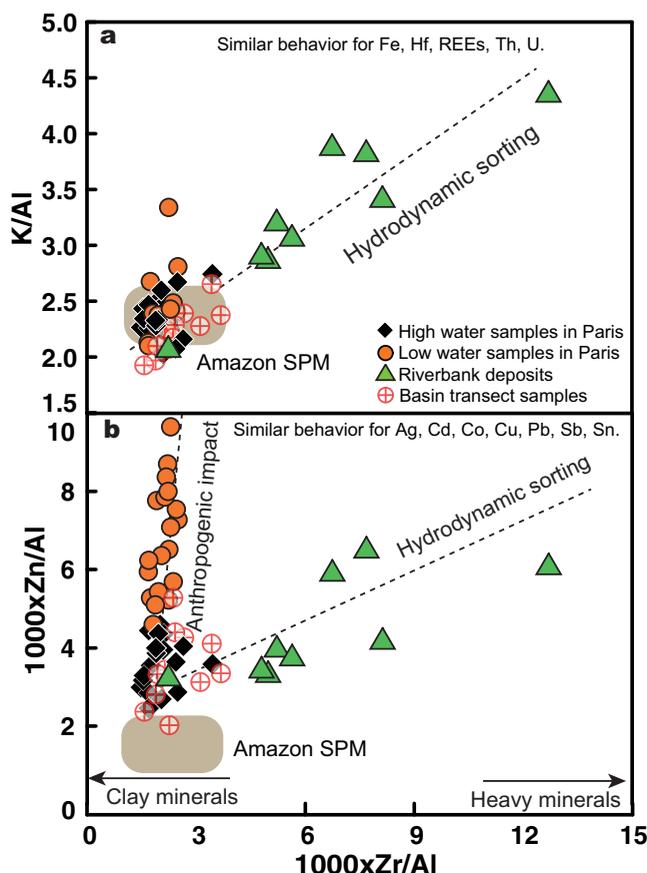
**Figure 6.** Chemical composition of suspended particulate matter (SPM) and riverbank deposits (RBD). The Zr/Al ratio on the *x* axis indexes enrichment in coarse and dense minerals such as zircons. High Zr/Al ratios characterize coarse, heavy minerals-rich sediments such as RBD. On the *y* axis, Al-normalized K and Zn concentrations are independent from dilution by carbonate, quartz, or organic matter. (a) K/Al versus Zr/Al shows a single trend, attesting to a binary mixture and highlighting hydrodynamic sorting, (b) while a third end-member (anthropogenic inputs) with a prominent contribution at low water stage is required to explain the pattern of Zn.

Cr in chromite, Ti in rutile, Ti and Fe in ilmenite, Ba in barite, REEs and Th in titanite or monazite, Sn in cassiterite, and W in scheelite [*Hubert*, 1962; *Vital et al.*, 1999; *Yang et al.*, 2009; *Garzanti et al.*, 2010]. These heavy minerals are generally present in coarse river sediments such as RBD because of their high specific density and resistance to weathering [*Hubert*, 1962; *Vital et al.*, 1999, *Franke et al.*, 2009, and references therein]. The correlation of E/Al and Zr/Al (quantifying the abundance of heavy minerals) shows that enrichment of heavy minerals occurs in both RBD and SPM, especially at high water stage. This is true for K (Figure 6a) and other elements such as Fe, Hf, REEs, Th, and U (figures not shown). The enrichments of Ca, Mg, Sr, and possibly U in RBD are linked to the abundance of carbonate phases as discussed above. The enrichments of Na and K in RBD suggest the contribution of unweathered feldspar minerals, as was already reported in the Amazon bed load [*Bouchez et al.*, 2011b].

To summarize, our results clearly illustrate the importance of grain size effects on the chemistry of the Seine River sediments. In particular, RBD (and thus also bed loads) are clearly different from SPM from a geochemical point of view and therefore cannot be used as surrogates of suspended sediments to assess weathering conditions and contamination in a river system [*Albarede and Semhi*, 1995; *Horowitz et al.*, 1999; *Grosbois et al.*, 2006; *Thevenot et al.*, 2007a, 2007b; *Franke et al.*, 2009; *Priadi et al.*, 2011, 2012].

### 4.4. The Imprint of Anthropogenic Sources

For other elements such as Zn, Bi, Cd, Cu, Mo, Pb, Sb, and Sn and to a lesser extent Fe, Mn, and Mg, Al-normalized concentrations display two distinct trends when plotted against Zr/Al (Figure 6b shows Zn/Al). For these elements, low water stage SPM samples display a trend that is clearly different from that described by RBD and most high water stage samples. This shows that the enrichment of these Zn-like elements in low water stage samples is not due to heavy minerals but more likely results from anthropogenic input.

#### 4.4.1. Differences Between Low and High Water SPM Caused by Anthropogenic Inputs

According to Figure 3, Cu is one of the most enriched elements in Seine River sediments. Therefore, in the following we examine the potential sources of Cu and possible processes affecting its transport, and later extrapolate our findings to other elements showing similar behavior in the Seine River. Using Ca/Al as a grain size proxy, the plot of Cu/Al ratio as a function of Ca/Al (Figure 7) clearly shows that particles of the Seine River define two trends, as observed in Figure 6 for Zn. The RBD and the SPM collected at high water
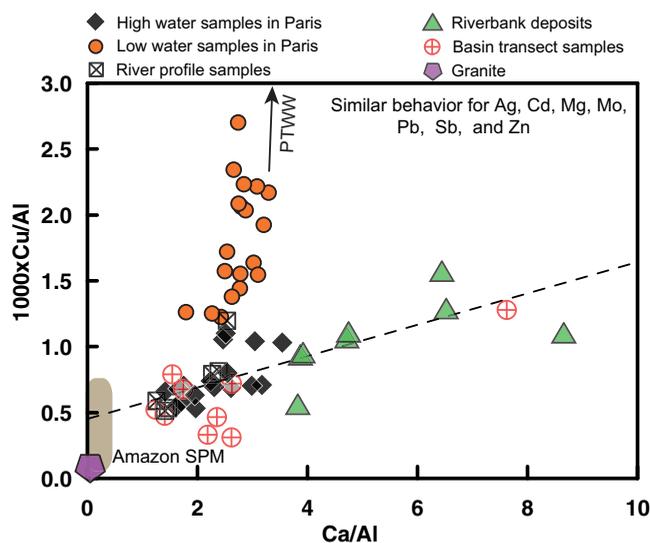
**Figure 7.** Cu/Al versus Ca/Al for all sediments, anthropogenic, and 2 bedrock samples of the Seine basin. Gray areas represent the range (average ± 2SD) of Cu/Al and Ca/Al ratios in Amazon River SPM [data from *Bouchez et al.*, 2011a]. The riverbank deposit RBD9 was not included because of its extremely high and most likely unrepresentative carbonate (shell) content.

stage in Paris and along the basin transect plot along one trend of increasing Cu content with increasing Ca/Al ratio (or increasing grain size). This trend defines a mean Cu/Ca ratio of about 0.0004, lower than that of the river sediments of the Amazon River (average 0.0054) [*Bouchez et al.*, 2011b], which also plot on this line (Figure 7). This likely implies that the RBD and SPM transported during high water stage are largely influenced by a natural silicate component (see the granite shown in Figure 7), although the contribution of an anthropogenic component to this end-member cannot be ruled out. By contrast, the SPM samples collected at low water

stage in Paris define a very different trend in Figure 7, crossing the previously defined line at Ca/Al of 2.8 and Cu/Al of 0.73, which is the average Cu/Al ratio of the flood SPM samples. In other words, the Cu content of RBD and high water stage SPM of the Seine River is well accounted for by a binary mixture between two end-members, whereas at low water stage, a third, Cu-rich end-member is necessary to explain the composition of Seine River sediments. Cu in low water samples is up to 2.5 times enriched relative to the flood samples at a given Ca/Al ratio (or a given carbonate content, or a given grain size). Al-normalized Ag, Cd, Mg, Mo, Pb, Sb, and Zn concentrations display similar trends as Cu in the E/Al versus Ca/Al diagrams (examples shown for Zn, Pb, and Mg in Figures 8a, 8b, and 8c for SPM samples in Paris, respectively). By contrast, Cs, Cr, REEs, Sc, Th, Y, U, and V define a single trend in the E/Al versus Ca/Al diagrams (Figures 8d, 8e, and 8f show the examples for Cs, Nd, and Y in SPM samples in Paris, respectively). For these elements, a simple binary mixture is sufficient to explain the chemical composition of the Seine River sediment regardless of the water stage. The two end-members of this binary mixture are likely to be distinct lithological entities, being aluminosilicates (as shown by the Seine basin granite in Figure 7) and carbonates or heavy minerals, which contain also Cu-rich phases.

A first possibility to explain the difference between low and high water stages for some elements (e.g., Cu, Pb, and Zn, Figures 7 and 8) would be that the hydrodynamic conditions favor their transport during low water stage. For example, in this scenario, a fine Cu-rich phase would be transported at low water stage, and this form would be different from the phases transported at high water stage. This pattern would be expected if, during low water stage, flocculation of colloidal-bound Cu would occur, or if dissolved Cu would sorb onto very fine organic particles. However, no correlation between Cu enrichment and grain size was observed, and SPM of low water stage has a grain size distribution comparable to SPM of high water stage (supporting information Table S1).

The alternative is a temporal variation in the sources supplying elements such as Cu and Zn to the Seine. Except for the Yonne River watershed, the lithology of the Seine basin is fairly homogeneous and no tributary seems to be able to account for such large enrichments as those observed in low water stage SPM (Figure 7). As low water stage SPM samples tend toward the composition of integrative anthropogenic samples such as plant-treated wastewaters (PTWW in Figure 7, with Cu/Al ratio of about 0.035), anthropogenic input is likely the other source. The anthropogenic overprint of such elements (e.g., Cu, Pb, and Zn) has already been suggested by numerous monitoring studies on the Seine basin [*Buzier et al.*, 2006; *Rocher et al.*, 2004; *Thevenot et al.*, 2007a, 2007b], and was demonstrated recently using Fe and Zn isotopes [*Chen et al.*, 2009, 2014].

**Figure 8.** Al-normalized concentrations of various elements versus Ca/Al for the temporal series of suspended particulate matter (SPM) collected in Paris. Ca/Al is used as a proxy of grain size. Elements such as (a) Zn, (b) Pb, or (c) Mg display two distinct trends, while elements such as (d) Cs, (e) Nd, and (f) Y plot on a single trend for both low and high water stage SPM. The enrichments of the former elements at low water stage are attributed to human activities. The arrows in Figure 8a illustrate the method for calculating additional anthropogenic flux of elements at low water stage in Paris by subtraction of the high water stage trend (see Appendix A). Gray histograms represent the distribution of E/Al ratios in Amazon River sediments [data from *Bouchez et al.*, 2011b], and should be compared to the E/Al ratio of the high water SPM linear trend at Ca/Al = 0.

Isotopic arguments confirm that the enrichment of these elements in the SPM is of anthropogenic origin and that this contribution is more visible at lower water stage [*Chen et al.*, 2009, 2014].

Based on the previous isotope studies of *Chen et al.* [2008, 2009], we can use Zn as a proxy for the anthropogenic end-member. Unlike Nd having mainly natural origin (Figure 9a), Al-normalized concentrations of a number of elements such as Bi, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Sb, Sn, Ti, V, and W correlate well with Zn/Al across the whole SPM dataset at Paris (Figures 9b–9h). This demonstrates unambiguously that the concentration of these elements in Seine SPM is controlled by a mixture between natural and anthropogenic sources and that this anthropogenic source is more prominent at low water stage.

### 4.4.2. Potential Processes for an Anthropogenic Contribution to Seine River SPM Geochemistry

The nature and origin of the anthropogenic sources are beyond the scope of this paper, but we can formulate hypotheses here. In large cities such as the Paris conurbation, a dominant part of the anthropogenic effluents is collected in the sewer systems. Plant-treated wastewater is then rejected into the rivers, while treated sediments are incinerated or spread on farmland. The wastewater treatment plants deliver fairly constant volumes of treated water to the Seine River across the year [*Thevenot et al.*, 2007a]. Given the
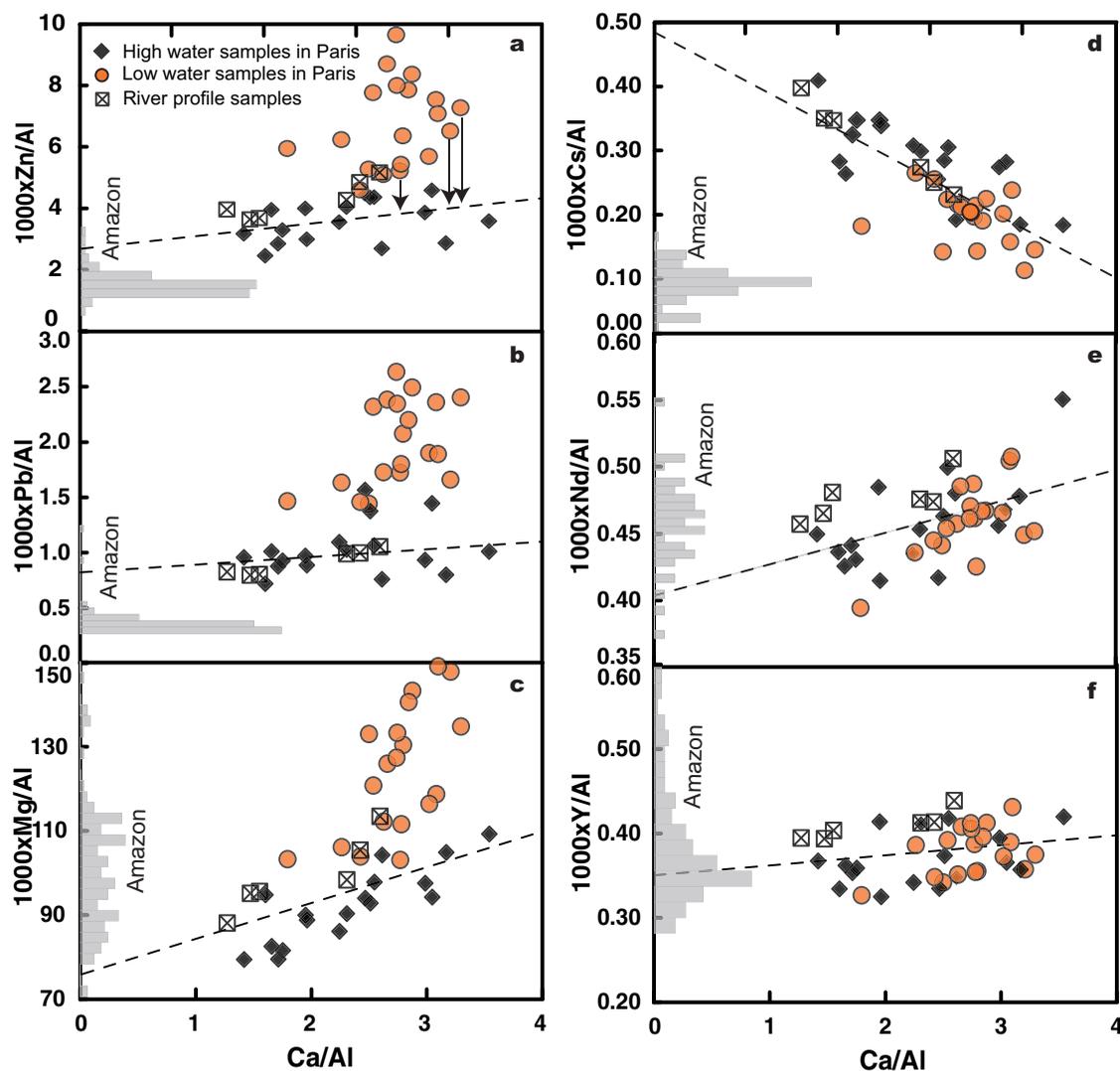
**Figure 9.** Al-normalized concentrations of various elements versus Zn/Al for the temporal series of suspended particulate matter (SPM) collected in Paris. Zn/Al is used here as a proxy of anthropogenic contamination. Elements mainly originating from natural sources, such as (a) Nd, do not show any correlation with Zn, while elements such as (b–h) Cd, Cu, Cr, Mo, Pb, Sb, and Sn, displaying a correlation with Zn in this diagram, are also affected by anthropogenic inputs. Gray areas represent the range (average ± 2SD) of E/Al ratios in the Amazon River SPM [data from *Bouchez et al.*, 2011b].

**Figure 10.** Particulate organic carbon (POC) content versus Cu/Al ratio. The increase of Cu/Al ratio with POC implies that Cu is mostly associated with organic matter in flood samples, while for the low water stage samples the different trend may indicate other major Cu carriers such as sulfides. Element/Al ratios for Bi, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Pb, Sb, Sn, W, and Zn show similar relationships with POC.

higher SPM content (from 28 to 49 mg/L) [*Chen et al.*, 2009] in treated water compared to the Seine waters (from 2 to 45 mg/L, supporting information Table S1), the relative contribution of PTWW to the Seine sediment flux is the highest at low water stage, when the Seine discharge is artificially maintained at about 100 m$^3$/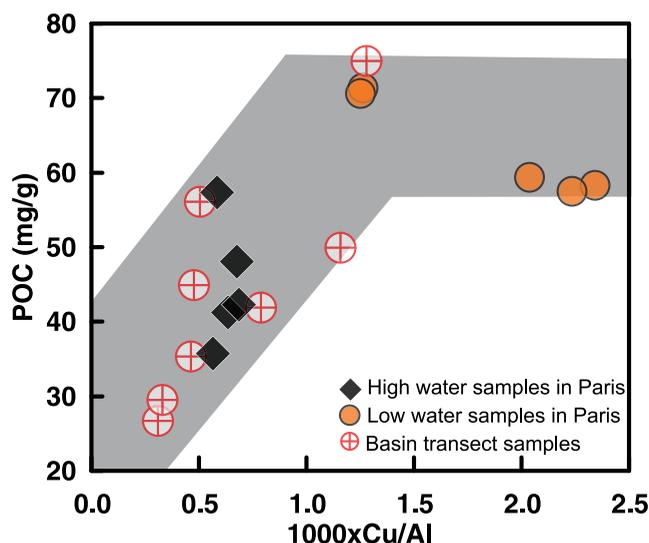s in summer. The anthropogenic inputs constitute a significant source of metals such as Zn, Cu, Fe, and Pb to the Seine River at lower water stage. The sediments delivered to the Seine in PTWW are substantially enriched in Zn and Cu-bearing sulfide minerals, representing up to ~40% of heavy metal carriers [*Houhou et al.*, 2009], and organic matter (POC

concentrations between 19.5% and 26.3%, supporting information Table S1) formed under anaerobic conditions in the sewer system [*Herbert et al.*, 1998; *Jong and Parry*, 2003; *Seidl et al.*, 1998b]. The anthropogenic contribution to these two components in the Seine River is apparent from the dramatic increase in amorphous ZnS particles and POC contents from upstream to downstream of Paris city [*Meybeck et al.*, 1998; *Seidl et al.*, 1998a; *Priadi et al.*, 2012]. Cu is an essential bio-element assimilated by organisms and has also a strong affinity for sulfides. Figure 10 shows that in high water samples, POC concentration increases with Cu/Al ratio, indicating that Cu is mostly associated with organic matter. In contrast, the rather constant POC concentration with increasing Cu/Al ratio observed in low water samples suggests that an excess of Cu, decoupled from organic matter, could be carried by sulfides, and that POC-bound Cu cannot explain the Cu enrichment at low water stage (Figure 7). Element/Al ratios for Bi, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Pb, Sb, Sn, W, and Zn show the same relationship as Cu/Al with POC. Although more work is needed to decipher the speciation of these elements, our results suggest that two main anthropogenic components are contributing to the Seine River sediment budget of these elements: (1) sulfides in the low water samples and (2) metals associated with organic carbon in the high water samples. It is for the moment impossible to identify the exact pathway through which anthropogenic elements are enriched in the Seine River sediments. For example, Cu, Zn, and other metals might be initially released into the environment in dissolved form, and then sorb onto organic and mineral surfaces, or complexed with colloids and finally be transferred to the particulate phase by flocculation.

The fact that Mg is enriched in SPM at low water stage (Figure 8c) is surprising, since it is not expected that anthropogenic activities would affect the particulate concentration of this major lithogenic element. The source of this Mg enrichment at low water stage remains unknown; one possible explanation could be that it is derived from the weathering of urban concrete buildings, in which case it should also be observable for other elements (such as Sr). More work is thus needed to identify the source and processes affecting Mg in the Seine River, and to clearly test whether anthropogenic activities contribute to the Mg particulate budget.

### 4.4.3. Increase of River Particulate Elemental Fluxes by Human Activities

Although we cannot identify the exact source of some elements enriched in Seine SPM during low water stage, it is interesting to quantify the contribution of this input to the elemental particulate fluxes of the Seine River. Elemental fluxes carried by the Seine SPM at Paris can be calculated from measured discharge, SPM concentration and element concentrations in SPM for the years 2004, 2005, and 2006 (Table 1,

**Table 1.** Elemental Particulate Fluxes (in Tons) for the Seine at Paris in the Years 2004, 2005, and 2006[a]

| | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | As | Sn | Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| *2004* | | | | | | | | | | | | |
| Total flux | 2798 | 77 | 74 | 782 | 29,226 | 9.9 | 31 | 40 | 190 | 13 | 8.9 | 236 |
| Corrected flux | 2802 | 78 | 74 | 749 | 29,251 | 9.8 | 31 | 36 | 178 | 14 | 8.2 | 229 |
| Relative difference (%) | −0.1 | −0.2 | 0.6 | 4.2 | −0.1 | 0.7 | −0.2 | 11.4 | 6.2 | −3.9 | 7.9 | 3.1 |
| Relative difference (%)[b] | 0.0 | −0.6 | 0.6 | 5.1[c] | −0.1 | −0.2 | −0.2 | 12.3[c] | 6.9[c] | −1.8 | 11.1[c] | 3.1 |
| Standard deviation[b] | 1.3 | 1.9 | 1.9 | 3.9 | 1.3 | 2.0 | 2.1 | 5.5 | 4.6 | 2.1 | 6.0 | 3.7 |
| *2005* | | | | | | | | | | | | |
| Total flux | 434 | 10 | 11 | 119 | 4147 | 1.4 | 4.6 | 7.3 | 29 | 1.6 | 1.2 | 35 |
| Corrected flux | 434 | 10 | 11 | 119 | 4147 | 1.4 | 4.6 | 7.3 | 29 | 1.6 | 1.2 | 35 |
| Relative difference (%) | 0.3 | −0.3 | 3.9 | 8.1 | 1.3 | 2.9 | 2.7 | 23.6 | 18.5 | −3.0 | 14.2 | 4.3 |
| Relative difference (%)[b] | 0.3 | −1.0 | 3.5[c] | 8.2[c] | 1.6[c] | 0.3 | 2.7[c] | 30.2[c] | 22.5[c] | −3.4 | 14.4[c] | 4.3 |
| Standard deviation[b] | 1.3 | 2.2 | 2.4 | 3.0 | 1.1 | 2.0 | 2.2 | 6.7 | 5.8 | 2.7 | 4.3 | 2.3 |
| *2006* | | | | | | | | | | | | |
| Total flux | 1387 | 32 | 33 | 335 | 13,919 | 4.6 | 15 | 22 | 102 | 6.2 | 3.8 | 99 |
| Corrected flux | 1386 | 34 | 33 | 337 | 13,734 | 4.7 | 15 | 16 | 85 | 6.7 | 3.2 | 103 |
| Relative difference (%) | 0.1 | −7.9 | 0.1 | −0.5 | 1.3 | −1.3 | −1.5 | 27.1 | 17.3 | −8.5 | 14.8 | −3.7 |
| Relative difference (%)[b] | 0.0 | −6.7 | −0.5 | −0.4 | 1.1 | −5.4 | −1.3 | 38.5[c] | 20.3[c] | −9.9[c] | 15.5 | −4.9 |
| Standard deviation[b] | 3.3 | 8.4 | 9.4 | 5.8 | 2.7 | 9.4 | 8.2 | 17.3 | 12.3 | 8.8 | 16.4 | 9.4 |
| *Total over 3 years* | | | | | | | | | | | | |
| Relative difference (%) | 0.1 | −2.8 | 1.6 | 3.9 | 0.8 | 0.8 | 0.3 | 20.7 | 14.0 | −5.2 | 12.3 | 1.2 |

[a]Instantaneous fluxes were first calculated for each sample using the discharge and SPM of the sampling day, along with the measured elemental concentrations, to obtain "total fluxes" (Appendix A). These fluxes were then multiplied by the number of days up separating the sampling day and the mid-dates between the previous and next sampling dates. All fluxes obtained for 1 year were then summed. The "corrected fluxes" correspond to fluxes calculated (a) for SPM at high water stage using measured concentrations and (b) for SPM at low water stage, using chemical projected (at a given Ca/Al) onto the relationship describing the high water stage composition (Figure 8a, Appendix A). The latter thus corresponds to the concentration that low water stage sample would have if the anthropogenic source active at low water stage did not exist. Relative difference between the two fluxes is given in % for each year and averaged over the 3 years. Although the calculation of fluxes is affected by significant uncertainties (due for example to irregular sampling and missing or over-representation of large events), the relative differences are both affected by these systematic offsets and some of this uncertainty cancels out.
[b]Uncertainty on the relative difference as obtained using a Monte Carlo simulation (Appendix A).
[c]Significant relative contributions at the 68% confidential level.

Appendix A). This represents a total flux encompassing both natural and anthropogenic inputs. The chemical composition of high water stage samples provides a baseline to which we can compare the additional flux supplied by the anthropogenic source at low water stage.

Using Figure 8, we can fit the data of high water stage samples by a linear relationship between element E/Al ratio and Ca/Al ratio:

$$\left(\frac{E}{Al}\right)_{HWS} = a^E \times \left(\frac{Ca}{Al}\right)_{HWS} + b^E \tag{2}$$

where $a^E$ represents the slope and $b^E$ is the intercept with the y axis. Then, we can use the coefficients ($a^E$ and $b^E$) of this relationship to calculate a "corrected" elemental ratio of the low water stage samples, $\left(\frac{E}{Al}\right)_{LWS,corr}$, for each Ca/Al ratio of the low water stage sample (example shown in Figure 8a):

$$\left(\frac{E}{Al}\right)_{LWS,corr} = \left(a^E \times \left(\frac{Ca}{Al}\right)_{LWS} + b^E\right) \tag{3}$$

The particulate flux of the element E corrected for the low water stage anthropogenic end-member can then be computed using the Al flux (see Appendix A). For each year, the contribution of the additional flux from the anthropogenic input can be calculated (Table 1).

Elements exhibiting a single trend in Figure 8 (for example K, Na, and Nd) do not have a significant anthropogenic contribution of sources at low water stage. Interestingly, Fe displays different trends between low- and high water stage [*Chen et al.*, 2014], but the relative increase in concentration observed at low water stage is fairly small compared to the total Fe budget of sediments, resulting in a relatively small anthropogenic contribution at low water stage (Table 1). However, for elements such as Cu, Zn, Mo, or Pb, the contribution is at least 20%, confirming the importance of anthropogenic inputs at low water stage. It is noteworthy that this calculated anthropogenic contribution on these element fluxes represents a minimum value, as anthropogenic inputs likely impact the high water stage SPM and RBD [*Thevenot et al.*, 2007b;

*Chen et al.*, 2009]. This is for example visible in Figures 6 and 7, where many high water stage SPM have Zn/Al and Cu/Al ratios above the silicate-carbonate (here the chalk) mixing trends.

### 4.5. Amazon River Sediments as a Proxy of the Natural End-Member of Human-Impacted Rivers

The whole data set from *Bouchez et al.* [2011a] for the Amazon River sediments has also been plotted in the three-element diagrams (Figures 6–9) for comparison: with gray areas (average ± 2SD) in Figures 6, 7, and 9, and with histograms (data point distribution) in Figure 8. The Amazon River drains the world's largest basin with various geological settings (from Paleozoic shale to modern igneous rocks) and various weathering regimes, and thus likely has a SPM chemistry representative of continental weathering under pristine conditions [*Gaillardet et al.*, 1997; *Vital et al.*, 1999; *Bouchez et al.*, 2011b]. These data also account for the natural heterogeneities inherited from the geomorphic and geological diversities within the river. Interestingly, most data points of the Amazon River also plot on the linear relationships defined by the Seine flood samples (RBD and high water stage samples, Figures 6–9). This implies that the natural end-member of the Seine SPM has E/Al ratios similar to that of the Amazon River for most elements. Based on the above discussion (also section 4.1), we suggest that the Amazon River can serve as an analogue of the natural end-member for most elements in the SPM of human-impacted rivers.

### 4.6. A New Geochemical Classification of Elements in SPM of Human-Impacted Rivers

Our systematic investigation of Seine River SPM and the comparison with the Amazon River can finally be used to classify the behavior of chemical elements with respect to anthropogenic activities for human-impacted rivers. Based on E/Al versus Ca/Al diagrams similar to those displayed in Figure 8, two groups of elements can be distinguished: the first group is constituted of elements showing a clear enrichment in SPM at the low water stage compared the high water stage. The second group is formed of elements behaving similarly at high and low water stages. When extrapolated to Ca/Al ≈ 0, elements of the second group generally display E/Al ratios close to those of the Amazon River or within the inter-basin variability, indicating that human activities have limited impact on their concentrations. Elements from both groups are influenced by hydrodynamic sorting, as traced by Ca/Al ratios.

The first group includes Ag, Bi, Cd, Co, Cr, Cu, Fe, Gd, Mg, Mn, Mo, Ni, P, Pb, Sb, Sc, Sn, Ti, and Zn. Most of these elements have relatively high EFs (e.g., > 1.5, Figure 3) and are commonly used in various human activities [*El Samrani et al.*, 2004; *Grosbois et al.*, 2006; *Houhou et al.*, 2009; *Meybeck et al.*, 2007; *Thevenot et al.*, 2007a]. We propose here to call them "anthropophile" elements as they are clearly influenced by human activities, at least in the urban context of the Paris conurbation. Although Fe and Co have EF values close to 1 (Figure 3), they do display clear enrichment at low water stage, probably due to anthropogenic inputs, as demonstrated by Fe isotopes [*Chen et al.*, 2014]. Therefore, these two elements are also classified into the "anthropophile" group. Examining group 1 closely, the slope of the E/Al versus Ca/Al relationship for high water stage samples is variable (as shown in Figures 8a and 8b). It is close to 0 (flat line, no correlation) for example for Cu, Mn, Mo, Pb, Sb, Sn, and Zn, indicating that these elements are not sensitive to hydrodynamic sorting during the high water stage and therefore that heavy minerals contribute only slightly to their budget in Seine River sediments. Other elements from this group (Cd, Cr, Fe, Mg, Ni, and Ti) are sensitive to grain size effects, as indicated by the positive slope of the relationship between E/Al and Ca/Al defined by high water stage samples (see Mg in Figure 8c).

The comparison with the Amazon River sediments (taken as a pristine reference) shows that a number of anthropophile elements are enriched not only in the sediments of low water stage but also during high water stage (e.g., Figures 8a and 8b). Distinguishing between the natural contribution of heavy minerals and anthropogenic contamination for the coarse fractions of the Seine sediments is not straightforward. Using Zn isotopes, *Chen et al.* [2009] clearly showed that, at least for Zn, the high water stage sediments are indeed contaminated by anthropogenic sources.

Unlike anthropophile elements, most REEs, Ba, Be, Ga, K, La, Na, Nb, Si, Sr, Th, U, W, Y, and Zr in Figure 8-type diagrams do not display any enrichment in low water stage samples compared to high water stage samples (Table 1 and Figures 8d–8f). This suggests that the forcing induced by the Paris conurbation does not influence their abundances. Interestingly, these elements generally have EF values close to 1 (Figure 3), which means that EF calculation is globally consistent with the three-element diagrams. In fact, the slope defined by these elements in the E/Al versus Ca/Al diagram (Figure 8) can be negative (As, Cs, Li, and Se, Figure 8d), close

to zero (Be, K, La, Na, Pr, Tb, U, V, Y, Yb, and W, Figure 8f) or positive (all others, Figure 8e). The behavior of the elements from this group is similar to that reported in the sediments of the Amazon River, as their distributions are mostly affected by hydrodynamic sorting effects related to their main natural mineral carriers. A positive slope in such figures (e.g., Figure 8e) means that they are significantly carried by heavy minerals in the coarse fraction. It is interesting to note that the E/Al ratios of these elements are generally close to those found in the Amazon River when extrapolated to Ca/Al $\approx$ 0, showing the absence of human impact in the Paris Conurbation and its watershed. A negative slope (As, Cs, Li, or Se) indicates a mixing between a clay-rich component and a coarse component depleted in these elements [*Bouchez et al.*, 2011b]. An intriguing observation is that the E/Al ratios of these elements in the Seine SPM are higher than those found in the Amazon River. This may be due to either the different nature of Seine River SPM (the particles are much finer than in the Amazon River, see section 4.2 for Cs and Li), or to the contamination of the finest fraction by human activities (as is probably the case for As and Se). This would mean that these elements are also anthropophile elements despite the fact that they do not show any enrichment in the low water stage sediments. At this stage, it is not possible to rule out the effect of natural processes, such as climatic and hydrodynamic factors, that could lead to the enrichments of these elements (including Mg) in the Seine SPM.

## 5. Conclusions

The present extensive and systematic study of sediment chemical compositions is an attempt to distinguish between the effects of lithology, hydrodynamic sorting and anthropogenic input on the elements transported in particulate phases by the Seine River in France. We show that the dilution by carbonates (thus Ca) is the first-order control on the chemistry of all trace elements, hence normalized abundances (e.g., to Al) should thus be used in order to describe the geochemistry of river sediments. Calculation of enrichment factors relative to the UCC demonstrates differences between the Seine and the Amazon SPM for many elements, and even within the Seine River under variable hydrological conditions. Nevertheless, Amazon River SPM has similar geochemical characteristics to the finer natural end-member of Seine SPM, indicating that the Amazon River has a SPM geochemistry similar to the UCC and may serve as a pristine reference for elements in human-impacted rivers. Our study highlights that grain size influences both elements mostly derived from natural sources and elements impacted by anthropogenic activities. In general, concentrations of elements such as Ag, Bi, Cd, Co, Cr, Cu, Fe, Gd, Mg, Mn, Mo, Ni, P, Pb, Sb, Sc, Sn, Ti, and Zn in sediments exhibit large variations during the hydrological cycle, with a specific enrichment in low water stage samples compared to the flood samples, due to anthropogenic inputs as demonstrated by their higher enrichment factors. These elements are commonly used by human activities and we propose to name them "anthropophile" elements. The contribution of the anthropogenic inputs (possibly plant-treated wastewater) at low water stage can represent 20% of the total particulate flux of these anthropophile elements in Paris, and one half to one third of the total anthropogenic contribution, as calculated in previous studies and from Zn isotopes. Human activities thus perturb the global biogeochemical cycle of these elements, especially in coastal oceanic environments, for example by releasing such anthropophile elements from human-derived particles to the dissolved phase upon entry into the ocean. These findings emphasize the need for systematic studies on river sediments taking into account the temporal variations and the variability with grain size. For example, unlike what was proposed by *Horowitz et al.* [1999] or *Grosbois et al.* [2006] for the Seine River, coarse floodplain deposits cannot be used as a surrogate for finer suspended sediment composition. This is especially true for elements such as Ba, Ca, Cr, Hf, Mg, Na, K, REEs, Th, U, or Zr, which are strongly influenced by coarse and heavy minerals. Overall, our results point out the need to carry out similar studies in large rivers that are undergoing increasing "chemical stress" from human activities.

## Appendix A

The contribution of the anthropogenic low water stage end-member can be assessed by quantifying elemental particulate fluxes and using E/Al-Ca/Al correlations (Figure 8). For each year, the total particulate flux of the element E during a given *year* is $F_{year}^E$:

$$F_{year}^E = \sum_{j=1}^{n_{year}} Q_j \times [SPM]_j \times [E]_j \times \delta_j \qquad (A1)$$

where $n_{year}$ is the number of samples collected during the year, $Q_j$ is the discharge measured [*Chen et al.*, 2009] when sample *j* was taken, $[SPM]_j$ is the SPM concentration of the sample *j*, $[E]_j$ is the concentration of

the element E in SPM of sample $j$, and $\delta_j$ is the time over which we assume that $Q_j$, $[SPM]_j$, and $[E]_j$ are representative (from the mid-date between sample $j-1$ and $j$ to the mid-date between sample $j$ and $j+1$). We assume for this calculation that these parameters are homogenous over the water column. This represents a total flux encompassing both natural and anthropogenic inputs.

Using equations (2) and (3) of the main text, we can calculate the particulate flux of the element E during a given *year* if the low water stage anthropogenic end-member would have been absent, $F_{year,corr}^E$:

$$F_{year,corr}^E = \sum_{j=1}^{n_{year}} Q_j \times [SPM]_j \times [Al]_j \times \delta_j \times \left(\frac{E}{Al}\right)_{j,corr} \qquad (A2)$$

where $\left(\frac{E}{Al}\right)_{j,corr}$ is the "corrected" elemental ratio (e.g., $\left(\frac{E}{Al}\right)_{LWS,corr}$ for sample $j$ taken at low water stage, as in main text equation (2); and simply $\left(\frac{E}{Al}\right)_{HWS}$ for sample $j$ taken at high water stage). We then calculate the relative difference between $F_{year}^E$ and $F_{year,corr}^E$.

In order to assess whether the calculated differences are significant, we performed an uncertainty analysis based on a Monte Carlo simulation. Equation (A1) is equivalent to

$$F_{year}^E = \sum_{j=1}^{n_{year}} Q_j \times [SPM]_j \times [Al]_j \times \delta_j \times \left(\frac{E}{Al}\right)_j \qquad (A3)$$

where $\left(\frac{E}{Al}\right)_j$ is the elemental ratio. As the term $Q_j \times [SPM]_j \times [Al]_j \times \delta_j$ featuring in both equations (A2) and (A3) is actually the flux of particulate Al associated with sample $j$, the main source of uncertainty are (i) the flux of Al, which we assume to be associated with a relative uncertainty (1 sigma) of 30% (from combined weighing errors, errors on instantaneous discharge, lack of spatial/temporal representativity of the sample); (ii) the ratio $\left(\frac{E}{Al}\right)_j$ that we consider to be associated with a relative uncertainty of 10% (from analytical uncertainties); and (iii) the ratio $\left(\frac{E}{Al}\right)_{j,corr}$ to which we associate an uncertainty stemming from the linear regression of equation (1) in the main text (e.g., uncertainty on parameters $a^E$ and $b^E$). For each year, we performed the calculation 100 times, each time with a set of parameters taken randomly following a normal distribution centered on its most likely value and with a standard deviation equal to the uncertainty as described above. We report in Table 1 the averages and standard deviations obtained over these 100 simulations. Relative contributions that differ from 0% by more than the standard deviation obtained over the 100 simulations are considered as significant (at the 68% confidence level).

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