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Behaviors of major and trace elements during single flood event in the Seine River, France

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Abstract

This study examines for the first time the characteristics of suspended particulate matter (SPM) and geochemical behaviors of major and trace elements during one single flood event of the Seine River, France. Source contribution, dilution by silicates and carbonates are the main scenarios consecutively occurring during the flood event, as can be inferred from the geochemical behaviors for major and trace elements. This study confirms the importance of flood events for the flux of materials transported by rivers to the ocean and emphasizes the need of systematic studies on the chemical variability of elements transported during flood events.

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Keywords: single flood event, major and trace elements, sediments, Seine River.

1. Introduction

Rivers transport up to 90% of the flux of materials from the continent to the ocean, with the suspended particulates being the main vector relative to the dissolved phase [1-5]. In many large rivers, a great part of annual flux of these materials is carried by extreme flood events, and thus only in a short period (e.g. a few days) [6-8]. The geochemical behaviors of many elements usually differ during floods compared to drought season, due to the highly

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dynamic and strongly turbulent hydraulic conditions at high water stage [9,10]. This highlights the importance of studying the geochemistry of elements during flood events [11-13]. Consequently, characterizing the properties of transported materials and the geochemical behaviors of elements in exceptional flood event is important for 1) obtaining the most complete picture of the global cycles of elements; 2) calculating the flux of elements transported to the ocean; 3) assessing the impact of floods on the riverine and coastal ecosystems; also 4) designing the most suitable measuring and monitoring strategy [14-16]. However, only few studies existed in the literature reporting the geochemical behaviors of elements in river sediments during single flood events [8, 11, 13, 14].

Here, we present the first study on both major and trace element concentrations in suspended particulate matter (SPM) collected from one single flood event of the human-impacted Seine River, France. The specific objectives are 1) to systematically investigate the variations of major and trace element chemistry during a single flood event; 2) to compare the geochemical behaviors of elements mainly impacted by human activities with those having mainly natural sources; and 3) to calculate the contribution of the flood to annual element fluxes.

2 Setting and method

The Seine River in Paris drains a basin area of about 43,800 km^2 in the northwest part of France. The basin is mainly covered by sedimentary rocks (93%), with 78% of carbonates and 15% of silicates; igneous rocks (7%) are limited to the headland region (Morvan) of the Yonne River. Except for the pristine forested region of the Seine, Yonne and Aube headwaters, most of the Seine watershed is intensively cultivated. Industrial activities are concentrated mostly in Paris conurbation and downstream from Paris.

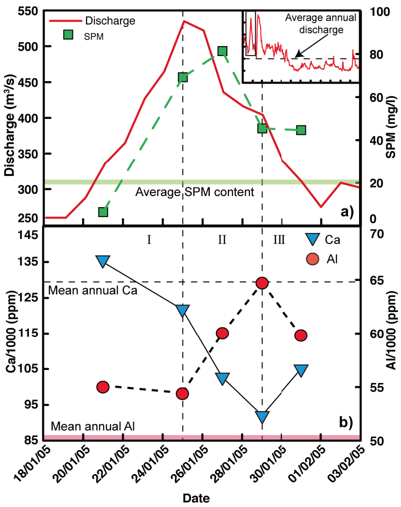
Sampling was carried out from the 21st to the 31st of January 2005 near the Jussieu University campus in Paris during the first flood event of the year. This flood had almost the same discharge (535 m^3/s) as the largest one (566 m^3/s, on 16 February) of the year 2005 and lasted for about 10 days. Five samples were collected. The water samples were filtered (0.2 μm-porosity PSE membranes) and the SPM was carefully collected from both the filters (fine) and the bottom (coarse) of the containers used. The sediments were dried and then digested using distilled HNO_3 and HF [17]. Major and trace element concentrations were analyzed by ICP-AES and ICP-MS, with precision better than 3% and 10%, respectively. The analytical quality was improved by internal standard addition (In and Re) and controlled through regular measurements of the international standard SLRS-4.

3. Results and discussion

3.1. Geochemical characteristic of the flood

In 2005, the Seine River is characterized by a relatively lower annual discharge (average 203 m^3/s) in Paris, compared to the long-term average value of about 400 m^3/s [17]. The five samples that cover almost the whole flood peak have discharge from 260 to 535 m^3/s, higher than the annual average value (Fig.1a). The SPM content of these samples varies from 6.3 to 81.4 mg/L, with most of them being higher than the average annual value of 20 mg/L (see section 3.3 for the calculation) (Fig. 1a). Both discharge and SPM show bell-shaped crests during the flood, with the discharge peak arriving two days before the SPM peak. Except for the first sample (13.6%) collected at the beginning of the flood, Ca concentrations (9.2% to 12.2%) are lower than the annual average value of 12.9% (Fig. 1b). Al concentrations (5.4 to 6.5%) of these samples are generally higher than the mean annual value of 5% (Fig. 1b). Interestingly, Al and Ca concentrations are anti-correlated during the flood, with the highest value for Al and the lowest value for Ca found on 29th Jan. 2005, two days after the SPM peak. Therefore, this flood is characterized by three successive peaks for discharge, SPM and Al content.

As the Seine basin is mainly underlain by carbonate rocks, the variable amount of carbonate in SPM is a first-order control on the geochemistry of elements in SPM. When SPM concentrations are normalized to an immobile element (here Al, mainly of natural origin), this major dilution effect is canceled out and a better description of the element geochemistry of river sediments could be obtained. Since Al and Ca are major constituents of silicates (fine particles such as clays) and carbonates (coarser minerals), the Ca/Al ratio is used here as indicator of the mineralogy of the Seine SPM and a proxy of the grain size [17,18]. Ca/Al ratio is strongly impacted by the flow rate during the flood. In a previous study, we distinguished elements in the Seine SPM into different groups according to their geochemical behaviors at variable hydrological conditions [19]. The following discussion is based on Al-normalized concentrations in SPM samples and systematically investigates the geochemical behaviors of elements representative of different groups relative to the Ca/Al ratios.



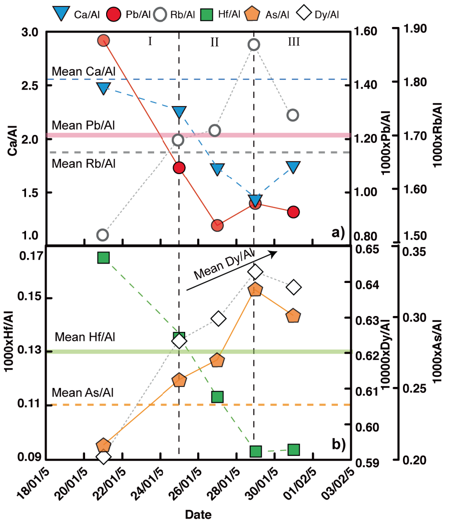


Fig. 1 (left) Temporal variations of discharge, SPM, Ca and Al contents. The calculated average annual values are also given for the year 2005. Fig. 2 (right) Temporal variations of major and trace elements (normalized to Al). Mean annual values for element/Al ratios are also plotted for comparison.

3.2. Sequence of sediment transport events during the flood

Fig. 2 shows element/Al ratio variations during the flood event, as well as annual average values. Two groups of elements can be distinguished: in the first group E/Al ratios decrease for the first four samples and increase for the fifth (e.g Ca and Pb in Fig. 2a; Hf in Fig. 2b); while in the second group E/Al ratios increase for the first four samples and decrease for the fifth one (e.g. Rb in Fig. 2a; As and Dy in Fig. 2b). The first group includes carbonate-related elements Ca, Mg, Sr (e.g. Ca in Fig. 2a), elements associated to heavy-minerals such as Hf, Nb, Zr (e.g. Hf in Fig. 2b), and “anthropophile” elements (that are generally associated to human activities) such as Ag, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Sn, W, and Zn (e.g. Pb in Fig. 2a) [17,19, 20]. The second group is composed of elements such as As (Fig. 2b), Be, Se, alkali elements (Li, Na, Rb – Fig. 2a, K, Cs), REEs (e.g. Dy in Fig. 2b), Sc, Th, Ti, U, V, and Y. Since the elements of a same group display similar geochemical behaviors, we discuss in the following only of the elements representative of each group, which are illustrated in the figures.

During the flood, both SPM content and Ca/Al ratio describe a hysteresis loop, while Rb/Al, Pb/Al, Dy/Al, and Hf/Al show almost no hysteresis. Based on the geochemical characteristics of SPM samples and behaviors of elements during the flood event (Fig. 3), three consecutive events (I to III) can be distinguished.

• The first event (I) covers the first increase limb of the discharge peak (Samples 1 and 2, Fig. 1a). During this period, Ca/Al slowly decreases from the highest value of 2.5 down to 2.25. The first sample displays relatively higher Pb/Al and Hf/Al ratios compared to their annual averages (Fig. 2). Anthropophile elements Ag, Bi, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Sb, Sn, W and Zn display similar patterns as Pb. These anthropophile elements are generally associated to organic matters or sulfides in anthropogenic wastewaters [17], which are generally mobile, as demonstrated by Zn isotopes [20]. The first sample is also enriched in Nb and Zr relative to Al, indicating enrichment in heavy minerals (e.g. zircon for Zr). The dramatic increase in SPM content (Fig. 1a and 3a) during this period indicates a strong hydrodynamic forcing, leading to the re-suspension of heavy minerals, that had been deposited on the riverbank during previous flood events. Therefore, the observed Ca/Al decrease is likely due to increased inputs of organic matter or sulfides derived from urban (sewage) systems, and/or of heavy minerals previously deposited on the riverbanks and riverbed.

• The second event (II) covers most of the recession limb of the discharge crest (Samples 2 to 4), and is characterized by a strong increase in Al concentration (Fig. 1 to 3), probably due to important proportions of clay minerals. Clays (silicates) are fine and generally have natural origin. The dilution by silicates is thus a dominant scenario of this period. In this event, SPM content increases to its maximum (81.4 mg/L, sample 3). Ca/Al ratio dramatically decreases to the lowest value (1.5), indicating a progressive enrichment in silicate minerals. While Rb/Al, As/Al and Dy/Al increase to the highest value (Fig. 2), an abrupt drop of Hf/Al is observed. These trends reflect a decreasing relative contribution of heavy minerals at low water stages. The fact that anthropophile element/Al ratios are relatively lower than the annual averages (Fig. 2) indicates a decreasing supply of these elements (e.g. from sewage systems) after their strong delivery at the beginning of the flood (possibly from combined sewage overflows).

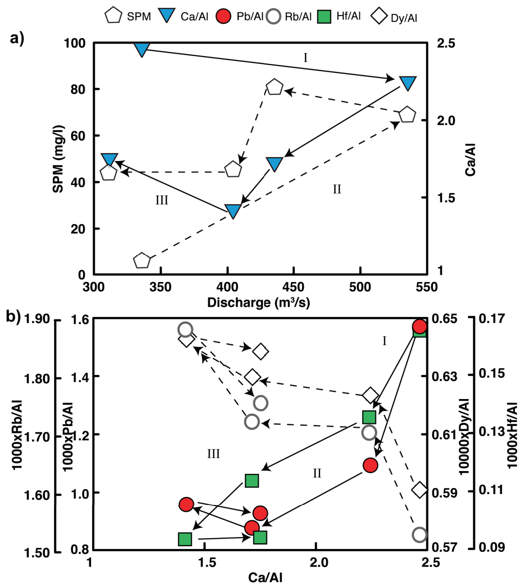


Fig. 3 Hysteresis loops for SPM and Ca/Al ratio (a) and three-element diagrams of selected major and trace elements (b) showing the variability during the three main scenarios of the flood event.

• During event III (Sample 4 and 5), the water discharge continues to decrease, while the SPM content remains almost constant (Fig. 1a). During this event, Ca/Al increases, Hf/Al is stable, while Rb/Al, Dy/Al, As/Al, and Pb/Al decrease (Fig. 2). The increase in Ca/Al (Fig. 1b) indicates the renewed importance of carbonate input to the river, relative to other sources. As a result, the dilution by carbonates is an important characteristic of this period. The sharp decrease in Rb/Al (Fig. 3) likely indicates a stronger contribution of silicates for the alkali elements. The almost unchanged Pb/Al and Hf/Al ratios (Fig. 2 and 3) during this period may indicate that these elements are not principally controlled by silicates (nor carbonates) in the Seine SPM.

3.3. Flux of elements transported by the flood event

Using the discharge Q and the particle content [SPM] of day i, the flux of SPM over a given period of time of n days ($F_{(SPM)}$) can be calculated as:

$$F_{SPM} = \sum_{i=1}^{n}[SPM]_i \times Q_i \quad (1)$$

The measured SPM content is interpolated between sampling dates. The flux of element F_E can be also calculated:

$$F_E = \sum_{i=1}^{n}[SPM]_i \times Q_i \times [E]_i \quad (2)$$

Both the annual fluxes (n = 365) and the flux of the flood event (n = 5) can be calculated using these two equations. In addition, we can also calculate the average annual SPM content and element concentration by normalizing the above fluxes to the sums of annual discharge ΣQi and $\Sigma Qi \times [SPM]_i$, respectively. Although the studied flood is not extreme, it transports 20% of the annual (2005) SPM flux to the Ocean. Regarding the elemental fluxes, this flood event carried 17% to 35% of the annual fluxes, with 26%, 19%, 27%, 24%, 24% and 22% for Al, Ca, Rb, Dy and Pb, respectively.

4. Conclusion and perspectives

During a single flood on the Seine River, France, the water discharge, SPM concentration and fine silicate sediment content displayed three consecutive peaks. Accordingly, major and trace elements behave differently at these variable stages, depending on their sources, physico-chemical properties and the hydrodynamic conditions of the river. In general, alkali elements, REEs and As, Be, Se, Sc, Th, Ti, U, V, and Y are mostly controlled by silicates, while anthropophile elements such as Pb, Cu and Zn and the elements associated to the heavy minerals follow coincidently the carbonate variation. This study confirms the importance of flood events for estimating the flux of materials transported by rivers to the ocean. Our findings emphasize the importance of systematic monitoring studies on the chemical variability of sediments transported during flood events in order to properly characterize riverine elements geochemistry and assessing the fluxes of elements to the ocean.

Acknowledgments

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