SPATIAL AND TEMPORAL TRENDS OF THE CONTAMINATION IN AN URBAN CATCHMENT: COUPLING METAL ISOTOPE GEOCHEMISTRY AND RADIONUCLIDE CHRONOMETERS

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Keywords: Maximum five keywords separated by; semi-colons

Introduction

The urban growth of the last decades exacerbated the release of numerous contaminants into the environment, which may disturb ecosystems. Understanding the origin and fate of contaminants in the environment constitutes a major societal challenge. In urbanized regions, rivers are the main sinks of contaminants, mainly through runoff on impervious surfaces and erosion of contaminated soils (Taylor and Owens, 2009). At the watershed scale, numerous pathways and sources of contamination exist, and their respective contribution is often difficult to assess when measuring pollutant concentrations alone. This study makes part of a project addressing the environmental persistence of anthropogenic pollutants (including organic and inorganic, legacy and emerging substances) in the critical zone at the scale of an urbanized catchment. This study of pollutant dynamics along the entire atmosphere-soil - aquifer-river continuum, including dissolved and particle-bound transfers, combined measurements of elemental and isotope geochemistry (e.g., Le Pape et al., 2012, 2013; Viers et al., 2008) and the use of environmental radionuclides (^{137}Cs, ^{7}Be, ^{210}Pb) to trace the spatial and temporal dynamics of the particles (e.g., Evrard et al., 2016). The objective is at identifying both sources and bio-physico-chemical processes. This study takes place in the Orge River, a sub-catchment of the Seine River watershed, chosen for its contrasts in land uses and population densities in Paris suburbs.

Methods

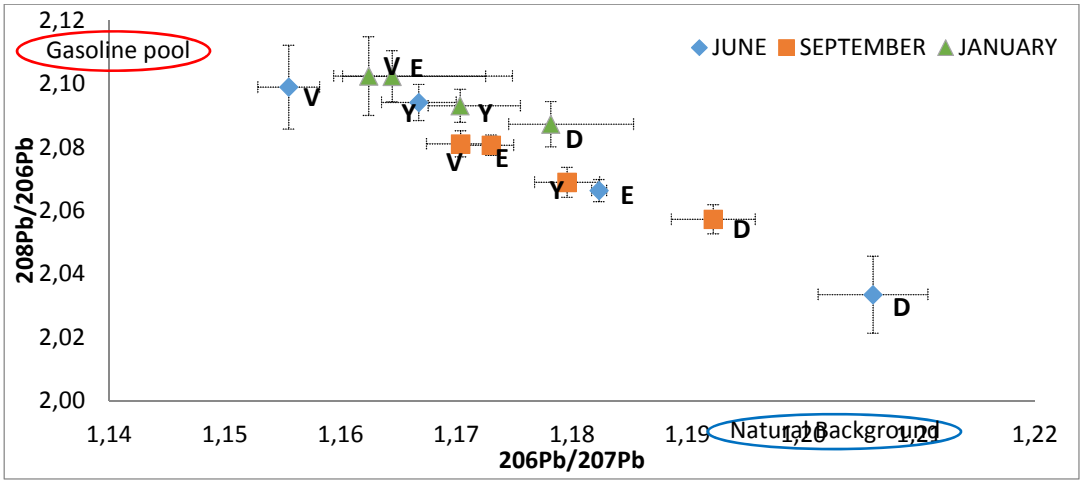
Four seasonal sampling campaigns were performed along the Orge River located 30 km southern of Paris city. The four sampling sites were chosen to describe an increasing urbanization gradient from up to downstream: D (Dourdan) in a rural area, E (Egly) with sparse urbanization, Y (Yvette, a moderately urbanized tributary), V (Viry-Châtillon) in a very dense urban area. Water and suspended particulate matter (SPM) were trapped for 4-days period and the river parameters (temperature, pH, EC, SPM content, flow, …) were measured. Water was analyzed for major, minor and trace elements by AAS and ICP-QMS. SPM were analyzed for radionuclides and for cation contents including lead isotopes ratio by ICP-QMS, after total digestion.

Results

The results show the distinct impacts of hydrological conditions and land-use changes on the concentrations and behavior of the particle-bound contaminants. Sediment contents in elements such as Cu, Pb, Sb and Zn strongly increased from headwaters to downstream locations, whereas Co and Cr concentrations remained stable across space. This spatial trend was not much affected by changes in hydrological conditions. During high flow conditions (January 2016), a four-fold increase was shown in Zn concentration from the rural upstream areas to outlet. During low flow conditions (June 2015), the upstream to downstream concentration ratio was slightly lower, i.e. 3. For most elements, the

concentration at the upstream rural site remained unchanged whatever the flow conditions. Conversely, the transfer time and the relative contribution of contaminant sources were strongly affected by rainfall and hydrological conditions. Radionuclide data showed that the particle transfers from the soil to the river were faster during high flow conditions and in urban areas than in rural areas. This may explain the highest contribution of the traffic markers to the river contamination during rainy periods as shown by the variation of the lead isotopic ratio, that switch from a "natural" lead pool, characterized by high $^{206}Pb/^{207}Pb$ and low $^{208}Pb/^{206}Pb$ ratios, to a gasoline pool (low $^{206}Pb/^{207}Pb$ and high $^{208}Pb/^{206}Pb$ ratios). The results of lead isotopic ratio for three campaigns conducted in June, September 2015 and January 2016 (Fig. 1) do demonstrate this trend. A pattern from natural background signature upstream towards a gasoline signature downstream was shown, in agreement with the urbanization gradient. Furthermore, the results tend also to demonstrate that seasonal variations may play an important role in the sources and dynamics of the contamination, illustrated by the shift in Pb isotopic signatures between low flow periods (June and September) showing a wide range of signatures ($^{206}Pb/^{207}Pb$ varying between 1.15–1.21) and high flow period (January) with much more stable values ($^{206}Pb/^{207}Pb$ ~1.16–1.18).

Figure 1. $^{208}Pb/^{206}Pb$ ratio versus $^{206}Pb/^{207}Pb$ ratio in the suspended particulate matter of the Orge River. D, E, Y and V: see text.



Moreover, the transfer time and the residence time in the riverine corridor, as revealed by the radionuclides ratio, are also keys for understanding the change in speciation and thus of the toxicity of the elements in the river.

Conclusion

Our results demonstrate the potential of combining radionuclide and isotope geochemistry measurements to understand and quantify the behavior of the contaminants and their persistence in urbanized catchments.

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