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Anthropogenic rare earth element fluxes into floodplains: Coupling between geochemical monitoring and hydrodynamic sediment transport modelling

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ABSTRACT

As all rare earth elements (REEs) have an increasingly important role in high tech industries, they are now recognized as emergent pollutants in river systems impacted by anthropogenic activity. Over the past 20 years, significant anthropogenic contributions were reported for Gd, La and Sm, and we may expect that REE contamination in rivers is to further increase in a near future. Despite the work done to assess the environmental impact of REE pollutions in larger river systems, we are still lacking information on the dynamics of these anthropogenic compounds in relation to hydrological changes. Here, we observed for the first time particulate Ce originating from local industrial activities in Luxembourg and we quantified the anthropogenic contribution to the REE fluxes at the river basin scale during a single flood event.

1. Introduction

The use of rare earth elements (REEs) in new technologies increased drastically over the last decades (Du and Graedel, 2011; Haxel et al., 2002; Humphries, 2012). As a result, anthropogenic REEs (AREEs) are regularly detected in many polluted river systems of the northern hemisphere (Kulaksiz and Bau, 2013) and they are now also increasingly studied in the southern hemisphere (Merschel et al., 2015). Since the first report on the existence of AREEs in the dissolved loads of rivers (Bau and Dulski, 1996; Tricca et al., 1999), Gd anomalies have been documented through multiple studies. Wastewater treatment plants (WWTP) that receive hospital and domestic effluents are now recognized as the principal sources of Gd in polluted rivers (Bau and Dulski, 1996; Kümmerer and Helmers, 2000; Verplanck et al., 2010). The anthropogenic Gd (Gd_{ant}) is not particle-reactive due to the high stability of the Gd-based chemical complex in waters. It will preferentially remain in the effectively dissolved REE pool. More recently, Kulaksiz and Bau (2013) and Klaver et al. (2014) have shown that AREEs can also be detected in the colloidal and particulate fractions of river waters. New candidates for emerging micropollutants are now La and Sm (Kulaksiz and Bau, 2013). Both may originate from the industrial production of catalysts for petroleum refining. However, due to their strategic importance for new technologies, each REE becomes a potential contaminant in water bodies. One might suggest that the composition of the AREE pool is site dependent on and, for a given river system, controlled by the different anthropogenic contributions to the river.

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Since 1996, many studies on REE pollution have allowed one to identify anthropogenic sources and to assess the impact of AREEs on the environment (Klaver et al., 2014 and references therein; Kulaksiz and Bau, 2007, 2013 and references therein; Petelet-Giraud et al., 2009). Complementary studies proposed ecotoxicological assessments of a specific REE (Zhang et al., 2010). However, to the best of our knowledge, no study has characterised the dynamics of these AREEs in a given river system during different hydrological stages. Kulaksiz and Bau (2007), and more recently Hissler et al. (2014), quantified the contribution of the WWTP to the river system contamination at the basin scale. They showed that under low flow conditions, more than 95% of the Gd exported from the basin by the dissolved phase comes from the WWTP effluents and can be associated with anthropogenic activities. Moreover, Hissler et al. (2014) also demonstrated, using the REE balance calculation at the basin scale, which for the same low flow conditions Gd_{ant} contributes to more than 80% of the total dissolved REEs exported from the basin. Here, we ask about the resilience of the pollution with changing hydrological conditions and the transfer of these contaminants from the riverbed to the more remote and preserved areas of the polluted river basins.

In our study, we focus on the dynamics of AREEs carried by dissolved and suspended particulate loads during a single flood event. First, we identified the REEs that contribute to the anthropogenic pool in both the dissolved and particulate fractions. Next, we coupled the hydro-chemical monitoring with a hydrodynamic sediment transport model to present the temporal dynamics of AREEs in the river system and their dispersion in the floodplain during one important flooding event. We also demonstrated that higher-frequency sampling (Berman et al., 2009) and monitoring during more representative hydrological periods appear as prerequisites to improve our knowledge on AREE impacts in river basins.

2. Methodological approach

2.1. The upper Alzette River basin (Luxembourg, Europe)

The Alzette floodplain has a surface of 2.2 km^2 and is located in the southwestern part of Luxembourg, at the outlet of a 290-km^2 river basin (Fig. 1). At this location, the Alzette River has a mean annual discharge of 1.78 m^3·s^{-1}. The area of interest, mainly covered by grassland, is flooded almost every year when the river discharge exceeds 25 m^3·s^{-1}. REEs found in the river have different origins and are generally derived from organic matter and soils developed on limestone and marl (Hissler et al., 2014). Moreover, anthropogenic activities have an impact on the REE concentrations of the river. Since 1875, this region has experienced a substantial trace metal pollution due to important urban and industrial developments (Hissler et al., 2008). Contemporary industrial (e.g., surface treatments) and urban (waste incineration, hospital effluents, etc.) activities continue to deteriorate the water quality of the Alzette River.

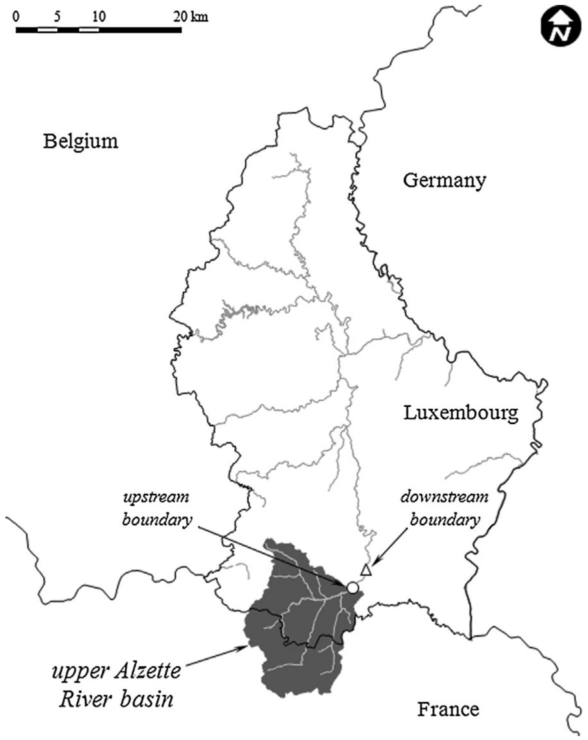

Fig. 1. Location of the area of interest, at the outlet of the upper Alzette River basin in Luxembourg, delimited by its upstream and downstream boundaries (Hostache et al., 2014).

The study area encompasses a 4-km river reach and its associated floodplain. Its upstream and downstream boundaries correspond respectively to the outlet of the upper Alzette River basin (Fig. 1) and a site located 4 km downstream from the outlet in the middle of the floodplain area (downstream boundary – Fig. 1). A little creek, which collects urban and industrial effluents, reaches the Alzette River 700 m before the downstream boundary. The discharge of this creek varies from 0.5 to 2.0 m^3·s^{-1} and can be considered as negligible, compared to the Alzette River during high water levels.

2.2. Water sampling, preparation and analysis

The upstream and downstream river boundaries are equipped for monitoring river discharge every 15 min and for sampling hourly stream water at 20 cm below the water surface using ISCO© autosamplers. Urban effluents were also sampled regularly during the flood event. About 60 water samples were collected for the determination of the REE concentration. This corresponds to an average of 10 samples per day at the two boundary locations.

The water samples were filtered using 0.45-μm Teflon filters in order to separate the particulate and the dissolved + colloidal fractions (named dissolved in the following sections). The dissolved fraction was acidified directly after the filtration, using 1% ultrapure HNO_3. The filters were dried in a desiccator to estimate the suspended sediment concentration and mineralized using