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# Particle bound pollutants in rivers: Results from suspended sediment sampling in Globaqua River Basins

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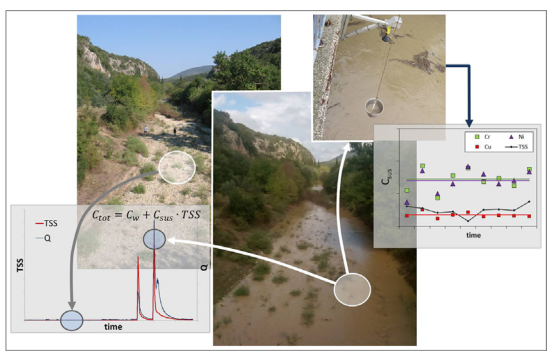
## HIGHLIGHTS

- Suspended sediments deliver an integral signal of particle-bound pollutant concentrations.
- Particle-bound pollutant concentrations in contrasting catchments differ largely for organic compounds but only moderately for heavy metals.
- The proportion of particle-bound versus dissolved pollutant fluxes depend – in the long-term – on distribution coefficients and mean suspended sediment concentrations.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Transport of hydrophobic pollutants in rivers such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals is often facilitated by suspended sediment particles, which are typically mobilized during high discharge events. Suspended sediments thus represent a means of transport for particle related pollutants within river reaches and may represent a suitable proxy for average pollutant concentrations estimation in a river reach or catchment. In this study, multiple high discharge/turbidity events were sampled at high temporal resolution in the Globaqua River Basins Sava (Slovenia, Serbia), Adige (Italy), and Evrotas (Greece) and analysed for persistent organic pollutants such as PAHs (polycyclic aromatic hydrocarbons) or PCBs (polychlorinated biphenyls) and heavy metals. For comparison, river bed sediment samples were analysed as well. Further, results are compared to previous studies in contrasting catchments in Germany, Iran, Spain, and beyond. Overall results show that loadings of suspended sediments with pollutants are catchment-specific and relatively stable over time at a given location. For PAHs, loadings on suspended particles mainly correlate to urban pressures (potentially diluted by sediment mass fluxes) in the rivers, whereas metal concentrations mainly display a geogenic origin. By cross-comparison with known urban pressure/sediment yield relationships (e.g. for PAHs) or soil background values (for metals) anthropogenic impact – e.g. caused by industrial activities – may be

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identified. Sampling of suspended sediments gives much more reliable results compared to sediment grab samples which typically show a more heterogeneous contaminant distribution. Based on mean annual suspended sediment concentrations and distribution coefficients of pollutants the fraction of particle facilitated transport versus dissolved fluxes can be calculated.



## 1. Introduction

Pollutants in river water and river bed sediments, in particular in highly urbanized or industrialized regions, are still a concern in Europe (Liu et al., 2013; Grathwohl et al., 2013; Navarro-Ortega, 2014). Besides industrial direct spills and accidents, urban pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and heavy metals may enter the rivers untreated via stormwater sewers or combined sewer overflows during intense rain events (Menzie et al., 2002; Gardner and Carey, 2004; Rule et al., 2006; Zgheib et al., 2012; Rossi et al., 2013; Mahler et al., 2012; Watts et al., 2010; Selle et al., 2013). In particular in combined sewer systems, the suspension of materials deposited during dry weather periods may lead to increased mobilisation of urban pollutants (Metadier and Bertrand-Krajewski, 2012). Legacy pollution in river bed sediments, e.g. caused by former industrial activities, is still a source of persistent organic pollutants (POPs) and heavy metals and may, if mobilized during floods, also impact downstream regions of catchments (Quesada et al., 2014). For many POPs, allowable maximum and mean concentration in bulk water samples are regulated by Environmental Quality Standards (European Union, 2013).

Transport of strongly hydrophobic organic pollutants and heavy metals in rivers is often related to transport of suspended particles (Meyer et al., 2009; Schwientek et al., 2013). As particles are typically mobilized during high discharge events, total pollutant concentrations in water increase with increasing discharge. This has been shown for transport of PAHs, e.g. by Ko and Baker (2004), Meyer and Wania (2008), Schwarz et al. (2011), Rügner et al. (2013, 2014), Schwientek et al. (2017), PCBs and DDT (Dichlordiphenyltrichlorethan, Quesada et al., 2014, Herrero et al., 2018), phosphorus and nitrogen (Grayson et al., 1996; Stubblefield et al., 2007; Spackman Jones et al., 2011; Skoulikidis et al., 2017), UV stabilizers and sunscreens (Parajulee et al., 2018; Molins-Delgado et al., 2017), mercury (Kirchner et al., 2011; Schaefer et al., 2006) and other heavy metals (Chebbo and Gromaire, 2004; Nasrabadi et al., 2016, 2018).

Suspended sediments in rivers represent an integral signal of particles (Walling, 2005) and thus provide information on particle related pollution within a river reach. The latter was demonstrated by Rügner et al. (2014) and Schwientek et al. (2017) for PAHs in catchments in southwest- and central Germany and by Nasrabadi et al. (2018) for heavy metals in southwest German and Iranian catchments. In particular, the studies showed that pollutant concentrations on suspended sediments in small to intermediate sized catchments were stable over time at a given location and likely reflect the urban/industrial pressure and/or geological background in the respective upstream area. For hydrophobic organic contaminants such as PAHs, Schwientek et al. (2013, 2017) showed that concentrations in suspended sediments are positively correlated with population density in the catchment and negatively correlated with specific sediment yields. Many heavy metals, however, are immanent constituents of minerals and thus often reflect the metal concentrations of the surrounding geological setting (including soils and sediments).

### 1.1. Objectives

In this study, high discharge events in the Globaqua River Basins (GARBs, http://www.globaqua-project.eu/en/home/) Sava (Slovenia and Serbia), Adige (Italy), and Evrotas (Greece) were sampled and analysed for the presence of PAHs, a range of other POPs and heavy metals. Results are then compared with previous studies in contrasting catchments in Germany, Iran, and Spain and beyond. In particular, pollutant concentrations on suspended particles sampled at different stages of a high discharge event or at different locations within a catchment are evaluated. Data are further compared to results from river bed sediment samplings. The overall goal of the study was to demonstrate that suspended sediment sampling delivers an integral signal of particle-bound pollutant concentrations in rivers and to quantify and compare particle related pollutant concentrations in European catchments representing different typological, climatic and land-use settings.

## 2. Materials and methods

### 2.1. Pollutant transport by suspended sediments

Suspended sediments in a river represent a mixture of particles from different sources (i.e. urban areas, agricultural land, river bed sediments). Bulk (turbid) water samples may be analysed for total suspended sediment (TSS) and total pollutant concentrations. The total concentration of pollutants consists of both, the dissolved and particle-associated fraction:

$$C_{W,tot} = C_W + C_{SUS}\,TSS \qquad (1)$$

$C_{W,tot}$ and $C_W$ denote the total and dissolved concentrations of the compound in river water (e.g. in mg $l^{-1}$), $C_{SUS}$ the concentration on suspended particles (e.g. in mg $kg^{-1}$) and TSS the total suspended sediment concentration in river water (e.g. in kg $l^{-1}$), respectively. If total concentrations analysed from bulk water samples are plotted versus TSS, a linear relation is generally obtained where $C_{SUS}$ corresponds to the slope while $C_W$ denotes the intercept (Schwientek et al., 2013; Nasrabadi et al., 2018). TSS can be replaced by turbidity measurements provided the relationship between turbidity and TSS has been established (roughly 1 turbidity unit corresponds to 1 mg $l^{-1}$ TSS, Rügner et al., 2013). These relationships are valid if the dissolved and particle-bound concentrations of pollutants remain stable during an event or different seasons. Alternatively, $C_{SUS}$ and $C_W$ in bulk water samples may also be determined directly by filtering and analysing solid and liquid fractions. The ratio of $C_{SUS}/C_W$ may be interpreted as distribution coefficient ($K_d$, e.g. in l $kg^{-1}$). Particle facilitated transport dominates if the distribution coefficient is larger than the water to solids ratio in the river (i.e. the inverse of TSS). If the $K_d$ equals the water to solids ratio, 50% of the pollutant flux occurs bound to particles.

### 2.2. Sampling locations and sampling campaigns

For catchment characterization and evaluation of pollutant based stressors within the catchments we refer to Chiogna et al. (2016) for Adige; Milačič et al. (2017) for Sava; and Tzoraki et al. (2015), Gamvroudis et al. (2015) and Karaouzas et al. (2018) for Evrotas. An overview on locations of GARBs is provided at http://www.globaqua-project.eu/en/content/Case-studies.2/. In brief, the Adige River is the second longest river in Italy, with a length of 410 km and a drainage area of 12,000 $km^2$. Its source is near the Italian border with Austria and Switzerland and it flows into the Adriatic Sea south of the Venice