Science of the Total Environment 490 (2014) 191–198

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Monitoring of event-based mobilization of hydrophobic pollutants in rivers: Calibration of turbidity as a proxy for particle facilitated transport in field and laboratory

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HIGHLIGHTS

- Particle facilitated transport was investigated in five contrasting catchments in SW Germany.
- Turbidity is a proxy for concentrations of suspended solids and hydrophobic pollutants.
- From regressions of total PAHs vs. turbidity contamination of suspended particles are obtained.
- Contamination of suspended particles is catchment specific.

ARTICLE INFO

Article history:
Received 17 March 2014
Received in revised form 25 April 2014
Accepted 25 April 2014
Available online xxxx

Editor: D. Barcelo

Keywords:
Pollutant fluxes in rivers
Turbidity
Total suspended solids
Particle facilitated transport
Polycyclic aromatic hydrocarbons

ABSTRACT

Transport of many pollutants in rivers is coupled to mobilization of suspended particles which typically occurs during floods. Since the amount of total suspended solids (*TSS*) in rivers can be monitored by turbidity measurements this may be used as a proxy for the total concentration of particle associated pollutants such as PAHs, PCBs, etc. and several heavy metals. Online turbidity measurements (e.g. by optical backscattering sensors) would then also allow for an assessment of particle and pollutant flux dynamics if once calibrated against *TSS* and total pollutant concentrations for a given catchment. In this study, distinct flood and thus turbidity events were sampled at high temporal resolution in three contrasting sub-catchments of the River Neckar in Southwest Germany (Ammer, Goldersbach, Steinlach) as well as in the River Neckar itself and investigated for the total amount of PAHs and *TSS* in water; turbidity (NTU) and grain size distributions of suspended solids were determined as well. Laboratory experiments were performed with natural river bed sediments from different locations (Ammer) to investigate PAH concentrations, *TSS* and turbidity during sedimentation of suspended particles under controlled conditions (yielding smaller and smaller suspended particles and *TSS* with time). Laboratory and field results agreed very well and showed that turbidity and *TSS* were linearly correlated over an extended turbidity range up to 2000 NTU for the field samples and up to 8000 NTU in lab experiments. This also holds for total PAH concentrations which can be reasonably well predicted based on turbidity measurements and *TSS* vs. PAHs relationships — even for high turbidity values observed during flood events (>2000 NTU). Total PAH concentrations on suspended solids were independent of grain size of suspended particles. This implies that for the rivers investigated the sorption capacity of particles did not change significantly during the observed events.

1. Introduction

Transport of hydrophobic organic pollutants in rivers is mainly coupled to transport of suspended particles (Schwientek et al., 2013; Meyer et al., 2009). Therefore total concentrations of hydrophobic pollutants increase with increasing discharge e.g. during floods or snow melts, when sediments are mobilized. This has been proven for transport of polycyclic aromatic hydrocarbons (PAHs), e.g. by Ko and Baker (2004), Meyer and Wania (2008), Meyer et al. (2011), Schwarz et al. (2011), Rügner et al. (2013), but also for other compounds like mercury (Kirchner et al., 2011; Schaefer et al., 2006), heavy metals (Chebboa and Gromaire, 2004), polychlorinated biphenyls (PCBs) and DDT (Quesada et al., 2014), or phosphorus (Grayson et al., 1996; Stubblefield et al.,

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http://dx.doi.org/10.1016/j.scitotenv.2014.04.110
0048-9697/

2007; Spackman Jones et al., 2011; Hornsburgh et al., 2010) and particulate organic carbon and nitrogen (Slaets et al. 2014).

As suspended particles in water cause scattering of light, turbidity can be measured by optical backscatter sensors (OBSs, turbidity meters) in the field or by laboratory nephelometers. Therefore turbidity monitoring may serve as an easy to monitor proxy for particle facilitated transport. The relationship between turbidity and the amount of total suspended solids (*TSS*) depends also on the size, density, shape and type of the particles, as well as on water color (e.g.: Downing, 2006; Gippel, 1995; Gray and Glysson, 2002). However, turbidity measurements may be calibrated for *TSS* for a given catchment, and can then be used to assess the suspended particle fluxes in rivers. Rügner et al. (2013) showed that turbidity measured in NTU (Nephelometric Turbidity Units) corresponds to approx. 1–2 mg/l of total suspended solids (*TSS*).

From linear regressions of *TSS* and turbidity vs. total PAH concentrations received during a 1.5 year sampling campaign in rivers Schwientek et al. (2013) and Rügner et al. (2013) calculated mean concentrations of PAHs on suspended particles [mass/mass], which were different for different catchments depending on land-use. Higher concentrations of PAHs in suspended sediments were attributed to increased urban pressure in conjunction with low overall sediment fluxes. Urban pollutants may enter the rivers in particular via stormwater sewers or combined sewer overflows i.e. during intense rain events when large volumes of untreated waste water enter directly the rivers (Selle et al., 2013; Menzie et al., 2002; Zgheib et al., 2012). In particular in combined sewer systems, the re-suspension of materials deposited during dry weather periods may lead to increased mobilization of urban pollutants (Metadier and Bertrand-Krajewski, 2012).

Since most of the pollutant fluxes in rivers occur at high turbidities (Gippel, 1995; Rügner et al., 2013) the objective of this study was to extend previous findings towards distinct events and laboratory experiments with high suspended sediment concentrations (up to 2000 and 8000 NTU, respectively). Further development aims for online turbidity measurements using in situ probes, which allow monitoring the dynamics of particle fluxes in rivers directly.

2. Background

The fraction of suspended solids is often represented by turbidity measurements based on optical backscattering; results are reported as Nephelometric Turbidity Units (NTU) or Formazine Turbidity units (FTU) depending on the standards used. Mostly simple linear relationships are reported:

$$TSS = m\ \text{Turbidity[NTU]} \quad (1)$$

with slope m varying usually in a range from 0.5 to 3 (see review in Rügner et al., 2013). Previous studies in Southern Germany resulted in robust and reasonably linear relationships of turbidity [NTU] and *TSS* with slopes of approximately 0.9–2.4 (see Rügner et al., 2013).

The total concentration $C_{w,tot}$ of a pollutant in a water sample (e.g. in mg l^{-1}) comprises the concentration of pollutants dissolved in water (C_w) as well as the amount associated with suspended particles:

$$C_{w,tot} = C_w + C_{sus}TSS \quad (2)$$

C_{sus} denotes the pollutant concentration on suspended particles (e.g. in mg kg^{-1}), whereas *TSS* corresponds to the fraction of suspended particles in water (in kg l^{-1}). Eq. (2) represents a linear relationship between total concentration ($C_{w,tot}$) and *TSS* with slope C_{sus} and intercept C_w.

3. Material and methods

3.1. Water sampling campaigns

Water samples were taken during distinct flood events from the Rivers Ammer, Goldersbach, Steinlach and Neckar in November 2012 and July/August 2013 with automated samplers (ISCO 3700; equipped with Teflon tubing and glass bottles) at distinct locations (Ammer: gauge Pfäffingen, Goldersbach: gauge Bebenhausen, Steinlach: upstream of waste water treatment plant). In addition, grab samples were taken during the declining periods of the flood events. At the River Neckar grab samples were taken during a pronounced flood (location: City of Tübingen). Sampling intervals varied between 2 h during phases with steep increase/decrease of discharge to several hours during the recession of the hydrograph. Water samples were taken approx. 20 cm above the river bed (automated samplers) or approx. 20 cm below water level (grab samples), filled into brown glass bottles (0.5 or 1 l for PAHs; 1 l for *TSS* determination; 250 ml for measurements of turbidity, dissolved organic carbon (*DOC*), grain size distribution) and stored at 4 °C prior to analysis. In total about 100 samples were taken during flood events.

For the characteristics of the catchments see Grathwohl et al. (2013). In brief, Ammer, Goldersbach and Steinlach are relatively small catchments of approx. 100–150 km^2 which tribute to the Neckar River in SW Germany and which differ in land-use and hydrology. The Ammer catchment features a mainly urban and agricultural land-use with a city (Herrenberg) located in the upper part of the catchment; the Goldersbach catchment is a nature reserve which is – at least upstream of the gauge Bebenhausen – completely forested; the Steinlach catchment is characterized by a mixed land-use, but a more dynamic hydrograph, as it is located close to the mountain region of the Swabian Alb with elevations up to 900 m. These streams converge at the River Neckar at Tübingen. Locations of the sampling stations are displayed in Fig. 1.

3.2. Laboratory experiments

To cover even larger turbidity ranges than in flood events a set of laboratory experiments was performed where natural river sediments and river water from 5 different locations along the Ammer main stem were taken (see Table 1). Sediment samples were well-mixed and suspended in 10 l tin cans followed by sampling of supernatant water after distinct time periods of sedimentation. In total 20 water samples (four for each sediment) covering a turbidity range from 41 NTU up to several thousand NTU were received. These samples were analyzed for *TSS*, turbidity, total PAHs, and grain size distribution.

3.3. Chemical analysis

3.3.1. Water analysis

TSS was determined by weighing the dried residues after membrane filtration (cellulose nitrate 0.45 μm) according to DIN 38409-2. Turbidity was quantified by a nephelometer (Hach 2100N Turbidimeter) and reported in Nephelometric Turbidity Units (NTU). Calibration was based on formazin, which is an aqueous suspension of hydrazine sulfate and hexamethylenetetramine. For *DOC* measurements filtered samples were acidified to pH 2, purged with nitrogen gas and *DOC* determined using a TOC analyzer (Elementar High TOC; thermal oxidation at 680 °C and CO_2 quantification using an IR detector).

3.3.2. Total organic carbon (TOC)

For determination of organic carbon content (TOC) filters from *TSS* determination (filter plus solids) were dried, pulverized in a mortar, decarbonized (using 16% hydrochloride acid), neutralized with distillated water and centrifuged (8–10 steps). Remaining solids were re-dried (60 °C) and TOC was measured with an elemental analyzer (Elementar