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

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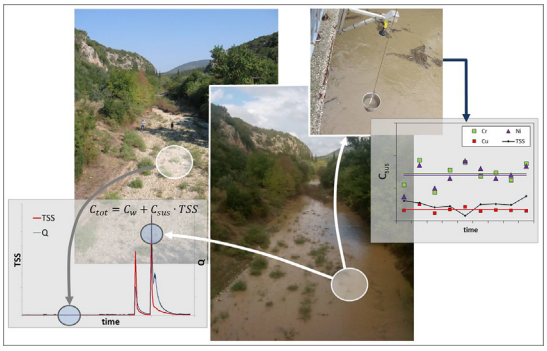
HIGHLIGHTS

- 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:

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

$C_{W,tot}$ 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

lagoon. The catchment is predominantly alpine with an altitude range of almost 4000 m. Land-use is dominated by forest (56%), followed by agricultural areas (30%). Urban land-use covers 2.2% of the catchment (Chiogna et al., 2016). The Adige in the City of Trento and the subcatchment of the Avisio River at its outlet at Lavis were chosen as event sampling locations. The Evrotas River drains a mid-altitude Mediterranean basin, located at the South-eastern Peloponnese. The catchment covers a total area of 2418 km^2. The vast majority of the river basin is covered by natural and semi-natural areas accounting for 61% of the total river basin, followed by agricultural areas that cover 38% while urban areas account for 1%. Sentenikos, located in the upstream area, and Skoura, located downstream of the City of Sparta have been selected as event sampling locations. The Sava River (945 km) is the largest tributary to the Danube River in terms of discharge. The 97,713 km^2 large catchment is extended over Slovenia, Croatia, Bosnia and Herzegovina and Serbia and comprises parts of the Alps in the west, the Dinarides in the south and the Pannonian Plain in the middle and lower course of the main stem of the river. Forest covers approximately half of the catchment, while agriculture and sealed surfaces account for 42% and 2%, respectively (Huber Garcia et al., 2017). Litija, located approx. 40 km downstream the City of Ljubljana and influenced by the Slovenian Alps, as well as Sremska Mitrovica, and Belgrade, the major city at the confluence with the River Danube were selected as event sampling locations.

In order to assess particle related pollutant concentrations on suspended sediments bulk water samples (water plus suspended sediment) were taken mainly during high discharge events at locations described above. An overview of sampled events and locations is given in Table 1. Water samples were taken 20–30 cm below water surface as grab samples or approximately 20 cm above the river bed if automated samplers were used (equipped with Teflon tubing and glass bottles; Evrotas Nov. 2016 event). For analysis of POPs (incl. PAHs) samples were transferred into amber glass bottles of 1 l. Bottles were either shipped to the University of Tübingen (UT) for analysis of total concentrations ($C_{W,tot}$) of PAHs in bulk water samples (samples were stored at 4 °C prior to analysis) or to the Institute of Environmental Assessment and Water Research, Barcelona (IDAEA-CSIC), where samples were filtered and collected particles were analysed for concentrations of POPs (C_{SUS}; samples were spiked with methanol and frozen to avoid biodegradation before shipping). For analysis of personal care products (PCPs), sample volumes up to 2.5 l were transferred into amber polyethylene (PE) bottles, frozen and shipped to IDAEA-CSIC. Samples were filtered and filtrates were analysed for concentrations of PCPs on suspended sediments (C_{SUS}). For metal analysis, water samples were filled into 2 l PE bottles, stored at 4 °C prior to analysis, and sent to the Jožef Stefan Institute, Ljubljana (JSI), where samples were filtered and collected particles were analysed for concentrations of metals (C_{SUS}). In total about 90 samples were taken (Table 1).

River bed sediment samples were also collected at the locations listed in Table 1 according to the method described in Vidmar et al. (2017) and the European Communities Technical Report 2010-041 (2010). Approximately 2 kg of the uppermost 10 cm sediment layer were taken and transferred into in 2 l plastic bottles. Samples were wet sieved over a 2 mm mesh after the collection to remove large detritus and benthic organisms. Samples were shipped to IDAEA-CSIC, Barcelona, for analysis of organic pollutants and to the JSI, Ljubljana, for metal analysis.

2.3. Laboratory treatment

2.3.1. Measurement of total suspended sediment concentration (TSS)

TSS was determined in aliquots of 250–1000 ml by weighting the dried residues after membrane filtration (in accordance to DIN 38409-2) using a 0.45 μm membrane filter in connection with heavy metal analysis or 0.7 μm glass fibre filter for POP/PAH analysis, respectively.

2.3.2. Measurement of $C_{W,tot}$ PAH15 in bulk water samples

Bulk water samples (1 l) were spiked with a mixture of isotope-labelled standards for quantification purposes (10 μl, 5 perdeuterated PAH according to DIN 38407–39, in toluene, each perdeuterated PAH 20 ng μl^{-1}) and liquid/liquid extracted with cyclohexane. Extracts were dried with anhydrous sodium sulfate and concentrated to 100 μl for analysis by gas chromatography with mass spectrometer detection (GC/MS) (HP GC 6890 directly coupled with a mass selective detector Hewlett Packard MSD 5973). Quantification was done by isotope dilution (Boden and Reiner, 2004). The detection limit for each compound equalled 0.001 μg l^{-1}. PAHs are reported throughout this paper as the sum of PAH15, representing the 16 US EPA (United States Environmental Protection Agency) priority PAH excluding naphthalene. For details we refer to Schwientek et al. (2013).

Table 1
Compilation of high discharge/flood events sampled for suspended sediments (in bulk water samples) during the Globaqua project.

GARB	Location	MQ (m^3 s^{-1})	Sampling date	Q_{max} (m^3 s^{-1})	No. of samples	TSS range (mg l^{-1})	Pollutants analysed	Method
Sava, SLO	Litija	165	Sept. 03–10, 2014	360	2	31–32	PAHs	(1)
					1	47	Metals	(2)
			May 01–23, 2016	450	6	2–63	PAHs	(1)
			May 15–17, 2016		7	34–102	Metals	(2)
			Sep. 15–17, 2017	600	5	21–249	POPs	(3)
					5		PCPs	(3)
					7		Metals	(2)
Sava, SRB	Sremska Mitrovica	1600	Sept. 03–10, 2014	3300	1	96	Metals	(2)
			Mar. 18–25, 2016	–	9	23–114	Metals	(2)
	Belgrade	–	Sept. 03–10, 2014	–	1	90	Metals	(2)
			Mar. 18–25, 2016	–	13	25–174	Metals	(2)
Evrotas, Greece	Sentenikos	1.2	Sept. 07, 2016	77.5	1	3960	PAHs	(1)
	Skoura	4.8		98.4	2	5714–6792	PAHs	(1)
	longitudinal profile	1.1–4.9	Nov. 28–29, 2016	64–112	6	94–1198	POPs	(3)
					6		PCPs	(3)
					6		Metals	(2)
Adige, Italy	Trento	186	Nov. 20, 2014	398	2	53–150	PAHs	(1)
			Sept. 14–15, 2015	359	1	560	PAHs	(1)
Avisio, Italy	Lavis	23	Nov. 20, 2014	44	1	47	PAHs	(1)
			Sept. 14–15, 2015	84	8	78–150	PAHs	(1)

(1) Bulk water samples analysed at UT; (2) suspended particles from whole water samples collected on filters analysed at the JSI; (3) suspended particles from whole water samples collected on filters analysed at IDAEA-CSIC. Validity of MQ-values (mean discharge): Litija: 1993–2005; Sremska Mitrovica: 1926–1984; Sentenikos and Skoura: 1983–2016; Trento/Lavis: 1995–2005.

2.3.3. Measurement of C_{SUS} of POPs (PAH15, PCBs, DDX) in suspended sediments collected on filters

Filter cakes from TSS determination were dried (desiccator) and spiked with 15 μl of the surrogate solution at 1 ng g^{-1} and extracted by pressurized liquid extraction (PLE) using a Dionex ASE 350 accelerated solvent extractor. A mixture of hexane:dichloromethane (1:1) was used as extraction solvent. The simultaneous extraction and clean-up of the analysed compounds were briefly optimized according to Navarro-Ortega et al. (2010). Extracts were evaporated at room temperature to nearly dryness and reconstituted with hexane to a final volume of 100 μl into glass amber vials for gas chromatography. Analysis was performed with gas chromatography-tandem mass spectrometry (GC–MS/MS). To increase the sensitivity and selectivity of organochlorine pollutants (DDX, PCBs), the analysis was performed using GC–MS/MS employing a Trace GC-Ultra coupled to a triple quadrupole (QqQ) mass spectrometer TSQ Quantum (ThermoFischer Scientific). For details we refer to Quesada et al. (2014) and Martinez et al. (2004). In reported results PCBs correspond to ∑ PCB18 to PCB194, DDX corresponds to ∑ 2,4 DDE, 4,4 DDE, 2,4 DDD, 4,4 DDD, 2,4 DDT, 4,4 DDT.

2.3.4. Measurement of C_{SUS} of PCPs in suspended sediments collected on filters

River water samples of the Litija Sept. 2017 and Evrotas Nov. 2016 events were analysed following the methods described by Gago-Ferrero et al. (2011) and Molins-Delgado et al. (2017). 22 PCPs – mainly sunscreens – were analysed. In summary, filters containing the suspended particles from 2.5 l were extracted by PLE using the same Dionex ASE 350 accelerated solvent extractor as for POPs analysis. In this case, methanol and water were used as extracting solvents. The obtained PLE extracts, around 20 ml, were diluted to 25 ml. Three aliquots of 2 ml of each extract were filtrated using nylon syringe filters of 0.45 μm pore size. Then, 1 ml of methanol was used to ensure the complete transfer of the sample. The filtrated extracts were collected and evaporated until dryness in a nitrogen stream. The residues were reconstituted with 1 ml of methanol containing the corresponding isotopically labelled internal standards and further analysed by high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS) on a Symbiosis™ Pico (Spark, Holland) liquid chromatograph coupled to a hybrid quadrupole-linear ion trap 4000 QTRAP mass spectrometer (Applied Biosystems-Sciex; Foster City, CA, USA) using an electrospray ionization source (ESI).

2.3.5. Measurement of C_{SUS} of metals in suspended sediments collected on filters

For the determination of the total metal concentrations on suspended particles, 1 l of a whole water sample was filtered through a 0.45 μm membrane filter. The filter was transferred to Teflon vessels and a microwave digestion of the mineral phase as described in Vidmar et al. (2017) applied. Element concentrations on suspended particles were determined by ICP-MS (7700×, Agilent Technologies, Tokyo, Japan). A CEM Corporation (Matthews, NC, USA) MARS 5 Microwave System was used for sample digestion.

2.3.6. Measurement of heavy metals and POPs in river bed sediments

For the determination of the metal concentrations in sediments, approximately 0.25 g of the sample (fraction < 63 μm) was added to Teflon vessels and microwave-assisted digestion as described in Vidmar et al. (2017) was applied. Concentrations were determined as described above for suspended sediment samples. The method based on Navarro-Ortega et al. (2010) and Quesada et al. (2014) was applied for determination of POPs in sediments. In brief, samples were freeze-dried and sieved through a 120 μm mesh. One gram of sample was extracted by accelerated solvent extraction (ASE). A mixture of hexane:dichloromethane (1:1) was used as extraction solvent. Instrumental analysis was performed as described above for suspended sediment samples.

3. Results and discussion

3.1. C_{SUS} PAH15 on suspended particles determined from $C_{W,tot}$ – TSS relationships

Bulk (turbid) water samples from the Sava, Evrotas and Adige catchments were analysed for $C_{W,tot}$ PAH15 and TSS concentrations (see Tables 1 and 2). Concentrations on suspended particles (C_{SUS} PAH15) were calculated from linear regression of $C_{W,tot}$ vs. TSS (Eq. (1)) as shown for the examples in Fig. 1. Regressions were forced through the origin, assuming that C_W might be neglected for the strongly sorbing PAH15, and to account for uncertainty in $C_{W,tot}$ at low TSS concentrations. C_{SUS} values correspond to mean values during the respective events. Previous studies in German rivers showed high concentrations on suspended sediments up to several mg kg^{-1} in densely populated areas and low values (minimum: 0.1 mg kg^{-1}) in unpopulated regions (Schwientek et al., 2017).

In principle, C_{SUS} PAH15 values are low to very low in all GARBs. In the Sava (Litija), C_{SUS} PAH15 is slightly higher in 2014 than in 2016 (higher discharge). Also in the Adige concentrations were higher during lower turbidity events (2014, compared to 2015). C_{SUS} PAH15 in the Evrotas during the flood in Sept. 2016 were the lowest (<0.01 mg kg^{-1} at Skoura). Despite the very low concentrations and the limited number of samples and associated uncertainties, a catchment-specific behaviour (Sava at Litija > Adige at Trento > Evrotas/Avisio) can clearly be identified. Standard errors for linear regressions are 2%, 60%, 86% for Evrotas at Skoura 2016, Sava at Litija 2016, and Avisio at Lavis 2015, respectively.

3.2. C_{SUS} of POPs (PAH15, PCBs, DDX, and PCPs) measured in suspended sediments collected on filters

Results for C_{SUS} PAH15 in the Sava high discharge event in Sept. 2017 showed low but fairly constant concentrations on suspended particles ranging from 0.14 mg kg^{-1} to 0.21 mg kg^{-1} at the end of the event. The average value was 0.17 mg kg^{-1}, which is in good agreement with the data from the Sept. 2014 and May 2016 events in Litija (see Fig. 2) and indicates that concentrations are relatively stable over time (2014–2017). Note, that despite a large variation in TSS the pollutant concentration (C_{SUS} PAH15) varies only slightly indicating quite stable conditions during an event (e.g. same source of PAHs).

Results for C_{SUS} PAH15 in Evrotas (Nov. 2016 event) show low concentrations on suspended particles along a longitudinal profile ranging from Sentenikos (upstream region) over Achouria, upstream Spartis (US Spartis), downstream the waste water treatment plant of Sparta (DS WWTP) to Zagana and finally to Skoura (downstream region; see Fig. 2). No pronounced influence of the City of Sparta and its wastewater treatment plant (WWTP) can be identified. The average concentration along the Evrotas profile in Nov. 2016 is 0.22 mg kg^{-1} (see Table 2) and thus slightly higher than during the Sept. 2016 high discharge event. Again, no pronounced influence of the suspended sediment content on the concentration of PAHs on solids was observed.

For the Sava high discharge event in Sept. 2017 and for the Evrotas longitudinal profile (Nov. 2016) also C_{SUS} of PCB and DDX as well as PCP have been measured in suspended sediments. C_{SUS} of PCB and DDX were very low (<0.01 mg kg^{-1}; Table 2) and thus much lower than PAHs. Similarly, very low C_{SUS} of PCP were observed. In the Evrotas, EHMC (Ethyl hexyl methoxy cinnamate) was determined in 4 out of 6 samples at a concentration range of 0.002–0.004 mg kg^{-1}, and OC (Octocrylene) in all samples at concentrations levels of 0.04–0.13 mg kg^{-1}. In the Sava, C_{SUS} of PCP were below detection limits, also because collected mass on filters was partly too small.

Table 2
Average concentrations of PAH15, PCBs, DDX, and metals in suspended sediments and river bed sediments including a comparison to literature data. All concentrations in mg kg^{-1}, lod = limit of detection.

Location	PAH15	PCBs	DDX	Cu	Pb	Ni	Cr	Zn	Co
Globaqua River Basins: suspended sediments, for metals in Sava see also[a,b]									
Sava, Litija, Sept. 2014/May 2016/Sept. 2017	0.4/0.2/0.2	–/–/0.01	–/–/0.008	17/20/41	33/24/35	36/34/52	35/59/90	123/91/185	6.8/7.1/15
Sava, Sr. Mitrovica, Sept. 2014/Mar. 2016	–	–	–	39/51	34/123	182/210	186/217	138/316	25/26
Sava, Belgrade, Sept. 2014/Mar. 2016	–	–	–	47/52	34/110	167/204	157/231	140/278	22/26
Evrotas, Sentenikos, Sept./Nov. 2016	<0.03/0.2	–/0.001	–/0.001	–/50	–/22	–/149	–/191	–/149	–/22
Evrotas, Skoura, Sept./Nov. 2016	<0.03/0.3	–/0.01	–/0.002	–/58	–/32	–/154	–/203	–/136	–/27
Adige, Trento, Nov. 2014/Sept. 2015	0.2/0.05	–	–	–	–	–	–	–	–
Avisio, Lavis, Nov. 2014/Sept. 2015	0.2/0.03	–	–	–	–	–	–	–	–
Globaqua River Basins: bed sediments < 0.063 mm; for metals in Sava see also[a,b]									
Sava, Litija, Sept. 2014/Sept. 2015	0.7/2.2	0.004/0.003	0.005/0.003	34/14	68/27	34/18	153/34	293/54	–
Sava, Sr. Mitrovica, Sept. 2014/Sept. 2015	0.7/8.2	0.005/0.007	0.005/0.006	36/22	34/52	190/90	273/136	129/172	–
Sava, Belgrade, Sept. 2014/Sept. 2015	0.8/4.4	0.006/0.005	0.007/0.007	87/19	56/26	237/76	287/88	155/78	–
Evrotas, Sentenikos, Jul. 2015	0.03/0.2	<lod/0.003	<lod/0.002	27	12	93	154	58	12
Evrotas, Skoura, Jul. 2015	0.04/1.2	0.003/0.004	0.002/0.01	40	32	52	122	100	14
Adige, Trento, Mar. 2015/Jul. 2015	0.6/2.0	0.004/0.003	0.004/0.01	–	–	–	–	–	–
Similar studies: suspended sediments									
Cinca, Monzon/Fraga (2017)[c]		0.1/0.3	0.09/0.04						
Ammer, GER (2011–2014)[d,e]	5.8			45	23	15	8.2	160	4.9
Steinlach, GER (2011–2014)[d,e]	1.3			28	19	23	16	104	9.4
Goldersbach, GER (2011—2013)[d,e]	0.1			15	22	17	7.3		5.8
Haraz River, Iran (2012–2016)[e]	–			33	24	34		37	14
Previous studies: bed sediments									
Sava, Litija (2005/2006)[f,g]	0.2			34	42	27	73	142	
Sava, Sr. Mitrovica (2005/2006)[f,g]	0.9			45	79	177	276	275	
Sava, Belgrade (2005/2006)[f,g]	0.3			46	97	82	151	173	
Ammer, GER (2012)[d]	8.6	0.04							
Haraz River Estuary, Iran[h]				32	26	44	28	74	10
Yangtze River Estuary, China[i]				25	24		72	83	
Buyuk Menderes River, Turkey[j]				137	54	315	165	120	29
St. Lawrence River Harbor, Canada[k]				108	58	43	69	306	
Baden-Württemberg State, GER: soils[l]	0.5			19	27	27	36	60	
Upper Continental Crust[m]				28	17	47	92	67	17

[a] Vidmar et al. (2017).
[b] Milačič et al. (2017).
[c] Herrero et al. (2018).
[d] Rügner et al. (2014).
[e] Nasrabadi et al. (2018).
[f] Milačič et al. (2010).
[g] Heath et al. (2010).
[h] Nasrabadi et al. (2010).
[i] Wang et al. (2015).
[j] Akcay et al. (2003).
[k] Pourabadehei and Mulligan (2016).
[l] LABO (2003).
[m] Rudnick and Gao (2014).

3.3. C_{SUS} of metals measured in suspended sediments collected on filters

Concentrations of metals on suspended particles (C_{SUS} of metals) in the Sava during the high discharge events in March 2016 (Sremska Mitrovica, Belgrade) and May 2016 (Litija) and along a longitudinal profile of the Evrotas between Sentenikos and Skoura during the Nov. 2016 event are shown in Fig. 3. In general, average concentrations for single metals on suspended particles are distinct at different locations (see also Table 2), showing e.g. lower concentrations of Ni and Cr at Litija (Sava), while 3–5 times higher concentrations are observed for these metals at Sremska Mitrovica and Belgrade (Sava) and also at the Evrotas. C_{SUS} of metals vary only slightly during a single event: in the Sava less than approx. 50% around average values in Litija and Sremska Mitrovica and slightly more in Belgrade. Deviations from average are

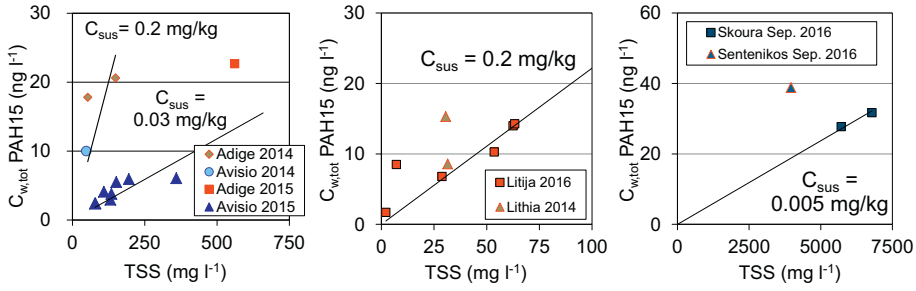

Fig. 1. $C_{W,tot}$ PAH15 vs. TSS relationships for samples from Adige/Avisio (left, Nov. 2014 and Sept. 2015), Sava (middle, Sept. 2014 and May 2016) and Evrotas (right, Sept. 2016). Linear regression lines are displayed for Adige at Trento 2014, Avisio at Lavis 2015, Sava at Litija 2016 and Evrotas at Skoura Sept. 2016.

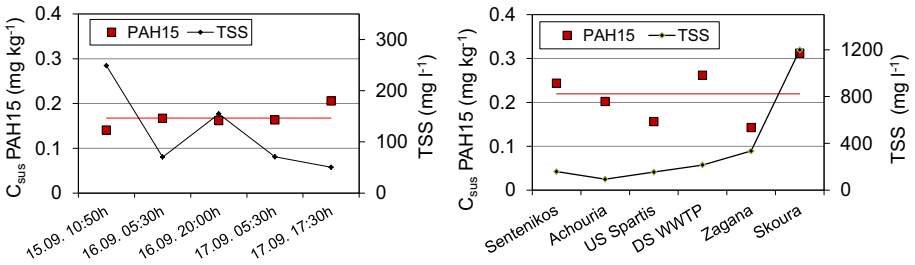

Fig. 2. Total suspended sediment (TSS) and C_{SUS} PAH15 concentrations measured during the Sept. 2017 flood event in the Sava in Litija (left), and along a longitudinal profile between Sentenikos and Skoura during the Nov. 2016 flood event in the Evrotas (right). The red lines indicate average C_{SUS}.

more pronounced at the earliest stage of the event. C_{SUS} of metals varies even less along the longitudinal profile (Evrotas) as already observed for the PAHs. Also, no clear influence of the suspended sediment concentration on metal loadings on particles is observed. In Sremska Mitrovica and Belgrade the concentrations for Pb were remarkably different (factor of 3) during the events in 2014 compared to 2016. C_{SUS} for all other metals differed less between the different events.

3.4. Comparison of pollutant concentrations on suspended particles with results from river bed sediments sampling in GARBs

Concentrations of PAH15 in river bed sediments (see Table 2) taken during two different sampling campaigns at the same or nearby locations in the Sava (at Litija), Evrotas (Sentenikos, Skoura) and Adige (Trento) showed slightly (1st campaign) to remarkably higher (2nd campaign) concentrations of PAH15 than on suspended sediments. In previous sampling campaigns of river bed sediments in 2005/2006, Heath et al. (2010) report PAH concentrations comparable to results from the 1st river bed sediment sampling campaign shown in this study. The PAH15 concentrations in suspended sediments show – at least for the low-intermediate polluted sites as Litija and Trento – less variation (50% around average value) than concentrations of PAH15 in the river bed sediments (factor of 2–5 around average values; see Table 2). This is explained by the inherent heterogeneity of local river bed sediments with respect to PAHs. PCB and DDX concentrations in river bed sediment samples were much lower than for PAHs (≤0.01 mg kg^{-1}) and in the same range as concentrations on suspended sediments.

River bed sediments from the Evrotas (one campaign) and Sava (two campaigns) were also investigated concerning metal concentrations (see Table 2; Vidmar et al., 2017; Milačič et al., 2017). The measured concentrations are comparable to concentrations on suspended sediments and also to data from previous river bed sediment sampling campaigns (Milačič et al., 2010). Also, observed concentration ranges are comparable (<factor 2–3). Exceptions are Cr and Zn (at Litija) and Cu and Cr (at Belgrade) which differed by a factor > 3 in the 2014 and 2015 sediment sampling campaigns.

3.5. Comparison with data from similar studies and data from literature

3.5.1. Hydrophobic organic contaminants

Relatively low but constant C_{SUS} PAH15 values were observed in the Sava at Litija (2014–2017). Evrotas and Adige show even lower C_{SUS} PAH15 values, partly diluted by input of fresh/uncontaminated sediments during pronounced floods, and also larger variabilities. Concentrations are much lower than most of the data found by Schwientek et al. (2017) in catchments in SW Germany (e.g. Ammer, Steinlach, see Table 2). Schwientek et al. (2017) showed that the loading of suspended particles with PAHs mainly depends on the ratio of inhabitants in the catchment to mean sediment mass flux in the river. Using population numbers in the catchments (Adige in Trento: 670,000; Sava in Hrastnik, close to Litija: 530,000) and measured annual

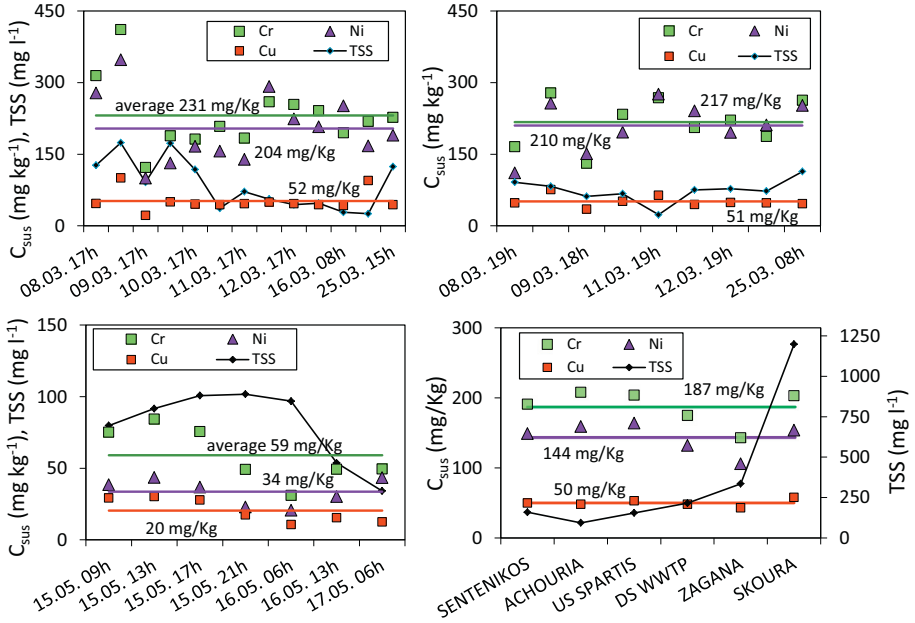

Fig. 3. C_{SUS} of metals (Cr, Ni, Co) and TSS data measured during the event in March 2016 in Belgrade (upper left graph) and Sremska Mitrovica (upper right graph), in the May 2016 flood event in Litija (lower left graph), and along a longitudinal profile between Sentenikos and Skoura during the 2016 flood event in the Evrotas (lower right graph). Only samples with particle yield >15 mg were considered.

sediment loads (Adige in Trento: 950,000 tons/year; Sava in Hrastnik: 400,000 tons/year; Sava Commission, 2013) and applying the approach proposed by Schwientek et al. (2017), a loading of sediment particles with PAH15 of 0.1–0.15 mg kg^{-1} for the Sava at Hrastnik, and 0.05 mg kg^{-1} for the Adige in Trento was obtained (for Evrotas no sediment yields were available). The calculated values are in the same range or even lower than the measurements presented in this study (see Table 2), corroborating the hypothesis that for catchments with relatively high sediment yield but only low to intermediate urban pressure only low contamination levels can be expected. As the approach does not account for inputs from legacy contaminations the slight underestimation of PAH levels may hint either to high local inputs in the past, e.g., from urban or industrial areas, or a larger proportion of PAHs that are conveyed from urban surfaces to receiving streams compared to the reference catchments in Germany where this correlation was first observed.

Increasing PAH15 concentrations in river bed sediment samplings further downstream the Sava (at Sremska Mitrovica and Belgrade) could be indicative of a more important urban pressure and/or additional inputs from industry. The latter is more likely since, e.g., PCBs which – at low concentrations – should also be associated with urbanization, do not parallel PAH15 increase along the profile. Note that, e.g., in the Ammer in SW Germany, river bed sediments with high levels of PAHs also show relatively high PCB concentrations (Schwientek et al., 2013; see Table 2).

Legacy pollution was reported as explanation of relatively high values of PCBs and DDX in suspended sediments of the River Cinca, a tributary of the Ebro river (Spain) during a pronounced flood in 2017 (Herrero et al., 2018). The Cinca catchment (approx. 10.000 km^2 in size) is characterized by many dams and reservoirs and chemical industry. Herrero et al. (2018) sampled suspended sediments along a longitudinal profile ranging from upstream Monzon to Fraga, a city located close to the confluence of the Cinca with the Segre River, a tributary to the Ebro River. Results revealed remarkably high concentrations on suspended sediments with up to 0.3 mg kg^{-1} of PCBs (in Fraga) and up to 0.1 mg kg^{-1} of DDX in upstream regions.

3.5.2. Metals

In the Sava, concentrations of Cr, Ni, Pb and Zn, which show relatively high values in Sremska Mitrovica and Belgrade, were explained by industrial activities (Vidmar et al., 2017). High concentrations for Ni, Cr, and Zn were also found at Sremska Mitrovica in a former investigation campaign (2005/2006) by Milačič et al. (2010). Accordingly, in this study the concentrations on suspended particles for all metals investigated are higher at Sremska Mitrovica and Belgrade compared to Litija. All these concentrations in the lower Sava are much above average background concentrations in continental crust or larger rivers around the world (see Table 2). Elevated zinc and partly also copper concentrations on suspended sediments in the River Ammer, SW Germany, which were above the local background values in soils in the State of Baden-Württemberg, are due to high urban and industrial pressure in the catchment (Nasrabadi et al., 2018). Metal concentrations in Evrotas are also relatively high already in the river's headwaters in spite of lacking urban pressure. This could be due to the fact that the Peloponnese, as a very active geological region, comparable e.g. to the Menderes Region in SW Turkey (see Table 2), may reflect an elevated geochemical background. In general, data on metal concentrations on suspended sediments are in a fairly narrow range compared to the organic compounds, which, e.g., for the PAHs vary by orders of magnitude.

3.6. Implications for pollutant mass fluxes

If concentrations of pollutants on suspended sediments are known, their mass fluxes can be calculated from mean annual sediment fluxes. Schwientek et al. (2017) provided mean TSS data for SW-German catchments (Ammer River: 31 mg l^{-1}; Steinlach River: 110 mg l^{-1}). For the Sava, comparable mean annual suspended sediment concentrations in the range of 50–100 mg l^{-1} have been reported by the Sava Commission (2016) (Litija: 75 mg l^{-1}; Sremska Mitrovica: 59 mg l^{-1}). Assuming K_d values in the range of 10^5 l kg^{-1} as reported by Schwientek et al. (2013) for PAHs and a C_{SUS} PAH15 value of 0.2 mg kg^{-1}, this means for Litija, that about 90% of the average annual PAH load of about 90 kg is transported by particles. For most metals discussed here, K_d values on suspended sediments are expected to be in the range of 10^3 l kg^{-1} to 10^4 l kg^{-1}, as shown by Nasrabadi et al. (2018). Thus metal fluxes depend on both, particles and dissolved species. For instance, about 30% of the average annual Cu load of 38 t at Litija (average C_{SUS} for Cu = 0.26 mg kg^1) would be transported by particles if a log K_d value of 3.7 is assumed (Nasrabadi et al., 2018). Hence, metal transport may even be dominated by the dissolved fraction. During extreme events with very high turbidities (if TSS [kg l^{-1}] exceeds 1/K_d) particle-facilitated transport of course dominates for most compounds.

4. Conclusions

This study demonstrated that suspended and river bed sediments in the alpine regions of the GARBs (Adige, Evrotas, Upper Sava) do not show much contamination with hydrophobic organic pollutants, mainly because of high sediment fluxes and low populated catchments. With increasing industrial activities e.g. along the lower Sava, concentrations increase slightly. As observed in several earlier studies, concentrations of hydrophobic organic pollutants on suspended particles at a given location are fairly constant over time and do not much depend on the suspended sediment concentration. Transport of PAHs is bound to particles because of their high distribution coefficients. Significant concentration differences with respect to local grab sediment samples are due to the inherent heterogeneity of river bed sediment layers (in space and time).

Metal concentrations on suspended particles at a given location are also fairly stable and mostly reflect the geogenic background. Because of that all metal concentrations collected (Table 2) even in comparison with literature data are within a limited range (variable only by a factor of 3 to 4). Exceptions are e.g. Ni and Cr in the lower SAVA which show locally elevated concentrations because of industrial influence. Again, slightly more variable concentrations found in local grab samples (river bed sediments) than in suspended sediments probably reflect heterogeneities in sediment layers. In contrast to PAHs, metals are transported to a larger extend as dissolved fraction, depending on the K_d and the average particle concentration.

The catchment specific, but time-invariant behaviour of pollutants concentrations on suspended sediments may not prevail during extreme floods or dredging, mining or construction activities which mobilizes different shares of sediments from upstream regions or local inputs into the river (e.g. accidental spills). Event-based sampling of bulk water including the suspended sediments as described here is a suitable tool to compare catchments with different urban and/or industrial pressure or to separate anthropogenic influence from geogenic background of specific pollutants.

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