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A parsimonious approach to estimate PAH concentrations in river sediments of anthropogenically impacted watersheds

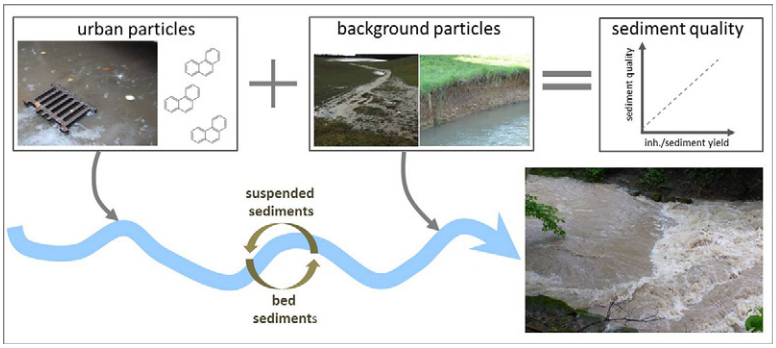
Marc Schwientek [a,*], Hermann Rügner [a], Ulrike Scherer [b], Michael Rode [c], Peter Grathwohl [a]

[a] Center of Applied Geoscience, University of Tübingen, D-72074 Tübingen, Germany
[b] Engler-Bunte-Institut, Water Chemistry and Water Technology, Karlsruhe Institute of Technology – KIT, D-76131 Karlsruhe, Germany
[c] Department Aquatic Ecosystem Analysis, Helmholtz Centre for Environmental Research-UFZ, D-39114 Magdeburg, Germany

HIGHLIGHTS

- A parsimonious model can predict PAH concentrations in suspended sediment
- PAH loading of suspended particles is watershed-specific
- Sediment quality is governed by population and sediment yield of watershed
- Landscapes with low sediment yield are vulnerable to sediment contamination

GRAPHICAL ABSTRACT



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ABSTRACT

The contamination of riverine sediments and suspended matter with hydrophobic pollutants is typically associated with urban land use. However, it is rarely related to the sediment supply of the watershed, because sediment yield data are often missing. We show for a suite of watersheds in two regions of Germany with contrasting land use and geology that the contamination of suspended particles with polycyclic aromatic hydrocarbons (PAH) can be explained by the ratio of inhabitants residing within the watershed and the watershed's sediment yield. The modeling of sediment yields is based on the Revised Universal Soil Loss Equation (RUSLE2015, Panagos et al., 2015) and the sediment delivery ratio (SDR). The applicability of this approach is demonstrated for watersheds ranging in size from 1.4 to 3000 km^2. The approach implies that the loading of particles with PAH can be assumed as time invariant. This is indicated by additional long-term measurements from sub-watersheds of the upper River Neckar basin, Germany. The parsimonious conceptual approach allows for reasonable predictions of the PAH loading of suspended sediments especially at larger scales. Our findings may easily be used to estimate the vulnerability of river systems to particle-associated urban pollutants with similar input pathways as the PAH or to indicate if contaminant point sources such as sites of legacy pollution exist in a river basin.

1. Introduction

Sediments in rivers may act as storage for anthropogenic contaminants such as polycyclic aromatic hydrocarbons (PAH). The transport of such hydrophobic pollutants in rivers occurs primarily associated to

* Corresponding author.
E-mail address: marc.schwientek@uni-tuebingen.de (M. Schwientek).

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suspended particles. Highest concentrations in the water body and also the highest transport rates of PAH occur during flood events when the hydraulic energy is sufficient to mobilize contaminated particles (Owens et al., 2001; Sicre et al., 2008). Rivers represent the major pollutants transport pathways from terrestrial to marine environments (Lin et al., 2016; Sicre et al., 2008). Polluted river bed and suspended sediment may have significant impact on local riverine ecosystems.

Polycyclic aromatic hydrocarbons (PAH) are a group of widespread organic compounds that are representative for other semi-volatile, lipophilic, toxic, and persistent pollutants in terms of urban and industrial sources and environmental behaviour. Besides of natural origins (wildfire, geogenic sources), PAH are widely emitted by anthropogenic activities such as combustion of fuels, coal, and biomass or the use of bitumen and petroleum containing products (e.g. Cheruyiot et al., 2015). Atmospheric PAH partition between the gaseous and the particle phase (sorption to dust and soot particles), the latter leading to removal from the atmosphere by dry or wet deposition (Gocht et al., 2007; Gschwend and Hites, 1981). Although long-range atmospheric transport exists and may be an important input pathway to remote areas (Burkow and Kallenborn, 2000), deposition rates are highest close to emission point sources (Gschwend and Hites, 1981; Hafner et al., 2005; Liang et al., 2016). As a result, urban particles are often highly contaminated with PAH (Jartun et al., 2008; Wang et al., 2011). These particles may be mobilized by surface runoff and are introduced into receiving water bodies either by storm water sewers or via combined sewer overflows (Ollivon et al., 1995; Walker et al., 1999; Zgheib et al., 2012). In the absence of point sources or spills, the input of untreated urban storm water was and is likely the dominating input pathway of PAH into river systems. Within the river channel, a redistribution of PAHs (or other hydrophobic pollutants such as PCB, heavy metals, etc.) between contaminated urban particles and more or less clean background particles may occur, i.e., the supply of a large flux of sediment from uncontaminated areas may dilute concentrations of urban particles (Schwientek et al., 2013). As an example, the closure of several dams along the Missouri River and the associated retention of large amounts of relatively clean sediments led to a pronounced degradation of sediment quality in the receiving Mississippi River (Van Metre and Horowitz, 2013; Walling, 2006) and demonstrates the dilution potential of sediments. Schwientek et al. (2013) proposed to predict suspended sediment quality (C_{sus}, in this case concentration of PAH) as a function of the population (P) in a watershed divided by the sediment yield (SY):

$$C_{sus} = \beta \cdot \frac{P}{SY} \tag{1}$$

The factor β is a proportionality factor which implies societal and technical standards such as emissions from traffic and heating and the technical standard of sewer systems and waste water treatment.

The present study aims at the validation of this concept, a further analysis of governing parameters, leading to a more physical interpretation of the factor β, and a strategy to provide sediment yields also for ungauged watersheds to make the concept transferrable to other regions. For this purpose, suspended sediment from 19 partly nested sub-watersheds of the upper River Neckar basin in Southwest Germany and four sub-watersheds of the River Bode basin in Central Germany was sampled and analyzed for PAH concentrations. Sediment yield data are typically rare in regions where soil erosion or reservoir siltation is not a critical problem. To overcome this lack of data, sediment yields were calculated using a conceptual model based on the Revised Universal Soil Loss Equation (RUSLE2015, Panagos et al., 2015) in combination with a spatially lumped approach to estimate the sediment delivery ratio (SDR) to surface water bodies.

2. Background

For details regarding the conceptual background refer to Schwientek et al. (2013). The total contaminant concentration in water, C_{tot} [M L^{-3}], comprises the “freely” dissolved fraction, and the amount associated with suspended particles and dissolved organic carbon (DOC). The freely dissolved PAH fraction as well as potentially DOC associated PAH may be combined in the dissolved concentration C_w [M L^{-3}], while the particle associated fraction of PAH depends on the contamination of the particles, C_{sus} (loading of particles) [M M^{-1}], and the amount of suspended particles, SSC (suspended sediment concentration) [M L^{-3}]:

$$C_{tot} = C_w + C_{sus} \cdot SSC \tag{2}$$

Thus, the total concentration of PAH in water is a linear function of the suspended sediment concentration, the intercept denoting the dissolved concentration, the slope indicating the loading of the particles with the contaminant. This conceptual model assumes that water is in equilibrium with suspended particles. If C_{sus} does not change in the course of a flood event, it may easily be determined from a small number of water samples with varying concentrations of suspended sediment (e.g. at the rising limb, the peak and the falling limb of a flood event) by measurement of the bulk concentrations C_{tot} of any particle associated compound in turbid samples (e.g. during a flood event) and linear regression of C_{tot} vs. SSC. Furthermore, an obvious advantage of this method is, that C_{sus} is an integral measure for the sediment quality of a stream network and much more robust than local sediment samples that can only represent particles settled down at a particular spot and, thus, typically exhibit a considerable heterogeneity (e.g. Chiffre et al., 2016). Thus, a relatively simple sampling procedure is sufficient to determine the contamination of suspended sediments. The feasibility of this approach has been shown by a number of recent studies (Rügner et al., 2013, 2014; Schwientek et al., 2013).

3. Materials and methods

3.1. Field sites

The River Neckar in Southwest Germany is the fourth largest tributary of the River Rhine. The upper River Neckar basin, upstream of the gauge in Kirchentellinsfurt (close to the City of Tübingen) has an area of 2319 km^2. It is embedded into a hilly landscape between the Black Forest in the West and the Swabian Alb in the Southeast. A series of Triassic and Jurassic sedimentary rock formations dip at 1–2° to the Southeast and forms a number of escarpments, the most prominent one formed by the limestones of the Upper Jurassic which constitutes the Swabian Alb. The relief features elevations that range between 300 m and 1000 m a.s.l.. The climatic conditions are characterized by annual precipitation between 700 and >1200 mm and mean air temperatures between approximately 6 and 9 °C. From a hydrological point of view, the Neckar features a pluvial runoff regime with a maximum in February and a minimum in July. The mean discharge at the basin outlet is 26.5 m^3 s^{-1} while a flood event with a return period of 2 years peaks at 268 m^3 s^{-1} (data available online: http://www.hvz.baden-wuerttemberg.de/). The nine most important sub-watersheds sampled including their hydrological characteristics are compiled in Table 1. Land use (Fig. 1), as obtained from the CORINE land cover database which results from remote sensing surveys in 2006 (UBA, 2009), is dominated by agriculture (54%), approximately half of it made up by arable land, followed by forest (36%) and urban area (10%). The population density of the watershed is approximately 280 inh. km^{-2}.

The River Bode in Eastern Germany is a tributary of the River Saale which drains into the River Elbe. The Bode watershed (3300 km^2) is part of the hydrological Harz/Central German Lowland Observatory, in the Helmholtz Association Terrestrial Environmental Observatories (TERENO) network (Zacharias et al., 2011). It is divided into a

Table 1
Main sub-watersheds of the upper Neckar and Bode Rivers with area (A), mean discharge at outlets (MQ) and population density. Some of the rivers were sampled at more than one location, resulting in a total of 23 sampling locations.

	A [km^2]	MQ [$m^3 s^{-1}$]	inh. km^{-2}
Neckar watershed			
Eschach	218	2.5	134
Prim	141	1.26	341
Schlichem	108	1.1	101
Glatt	234	4.5	204
Eyach	350	3.3	243
Starzel	178	1.7	200
Steinlach	142	1.84	352
Ammer	238	1.4	499
Goldersbach	72.9	0.5	69
Neckar at Kirchentellinsfurt	2319	26.5	282
Bode watershed			
Bode at Hadmersleben	2758	13.8	100
Selke	456	1.73	82

mountainous, mostly forested, southern part in the Harz Mountains with elevations up to 1100 m a.s.l. and an almost flat northern part in the agriculturally used lowlands of the Magdeburger Börde. The Bode watershed covers large gradients in topography, climate, geology, soil, and land use, and all combinations of these landscape features are represented in the 456 km^2 watershed of the Selke tributary (Wollschläger et al., 2017). The River Selke shows a similar bisectioning as the total Bode basin with the mainly forested Harz Mountains in the southwest and agricultural lowland areas in the northeast (Fig. 1). The Sauerbach watershed is a small sub-watershed in the northern lowland part of the Bode basin. It is uninhabited, almost exclusively agriculturally used and covers an area of 1.4 km^2 (Musolff et al., 2016). The population densities of the total Bode and Selke watersheds are 100 and 80 inh. km^{-2}, respectively.

3.2. Sampling campaigns

Water samples were taken during flood events at the Rivers Steinlach (2014–2016), Ammer, Goldersbach, Neckar (various locations) and remaining tributaries (2015–2016) and in the Bode watershed (Rivers Bode, Selke and Sauerbach, 2012–2014). Data are complemented with results from regular monthly and flood-related campaigns conducted in the sub-watersheds Ammer, Goldersbach, and Steinlach and the River Neckar at Tübingen from 2010 to 2013 (Schwientek et al., 2013 and Rügner et al., 2014). In total, 257 samples from published and recent campaigns were used for a comprehensive analysis. Either grab sampling or automated samplers (Rivers Steinlach, Ammer, Goldersbach, Bode, Selke, Sauerbach) were used. In general, samples were taken close to the river bank at some distance below the water table and were carefully transferred to the lab in amber glass bottles and stored at 4 °C until further processing and analysis.

3.3. Lab procedures

3.3.1. Analysis of 15PAH in turbid water

Bulk water samples were spiked with a mixture of isotope-labeled 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 then 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 equaled 0.001 μg L^{-1}. PAH are reported throughout this paper as the sum of 15 PAH, representing the 16 U.S. EPA priority PAH excluding naphthalene.

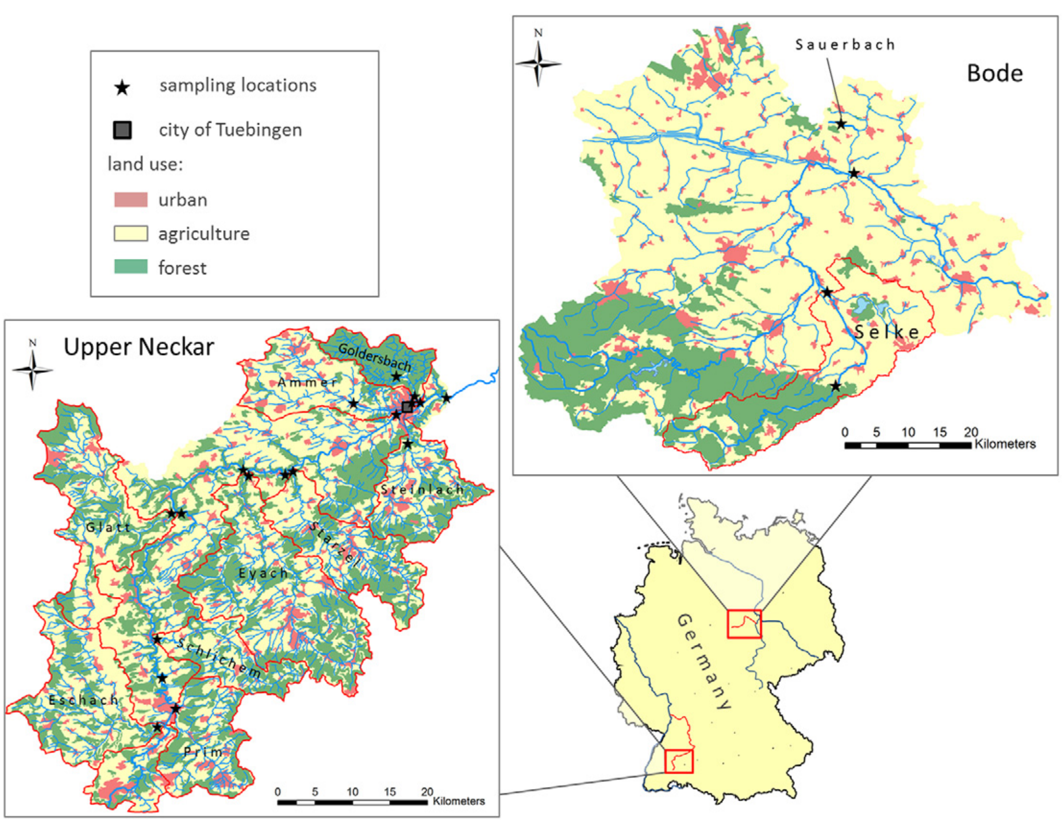

Fig. 1. Upper Neckar (left) and Bode (right) basins with sub-watersheds, sampling locations and land use (data from UBA, 2009).

3.3.2. Measurement of suspended sediment concentration

SCC was determined in aliquots by weighting the dried residues after membrane filtration (Whatman 934-AH glass microfiber 1.5 μm).

3.4. Measurement of sediment yields

Sediment fluxes and yields were measured for the Neckar sub-watersheds of the Rivers Steinlach (local watershed area $A_{local} = 127\ km^2$), Ammer ($A_{local} = 134\ km^2$) and Goldersbach $A_{local} = 37.2\ km^2$, based on continuous monitoring of turbidity. Gauging stations in the watersheds were equipped with online probes (UIT GmbH, Dresden, Germany) recording flow (Q, water levels converted by rating curves) and turbidity at 15-min intervals. Each turbidity probe was calibrated versus SSC according to the watershed-specific conversion factors determined by Rügner et al. (2014). The suspended sediment flux $\dot{m}$ can then be computed by

$$\dot{m}\ \left[g\ s^{-1}\right] = Q\ \left[m^3\ s^{-1}\right] \cdot SSC\ \left[g\ m^{-3}\right] \quad (3)$$

and the annual sediment yield (SY) by integration of the flux over annual periods

$$SY = \int \dot{m}\ dt \quad (4)$$

3.5. Modelling of sediment yields

For most of the sampled catchments no sediment yield data were available. Thus, the sediment yields were predicted using the data base of the RUSLE2015 model (Panagos et al., 2015) which provides long-term average annual soil loss rates by sheet and rill erosion for Europe on a high resolution (100 m grid size) for the reference year 2010. The soil loss rates were modeled with a modified version of the Revised Universal Soil Loss Equation (RUSLE, Renard et al., 1997) on the basis of recently available pan-European datasets to account for the input factors of the RUSLE model (rainfall erosivity, soil erodibility, cover management, slope length/slope steepness and support practices) (Panagos et al., 2015).

The percentage of the total annual soil loss (RUSLE2015) that reaches surface waters was estimated by deriving an empirical spatially lumped approach for the sediment delivery ratio (SDR). To adapt the empirical parameters of the SDR approach to the data basis of the RUSLE2015, 13 independent watersheds located in highland regions of Germany for which long-term monitoring data series of suspended sediment concentrations (preferably 30 years) are available were selected. Since most of the soil loss is produced on arable land, only watersheds with a high proportion of agricultural areas were chosen. Table 2 presents the characteristics of the 13 watersheds.

The total annual soil loss of the RUSLE2015 was summed up in a GIS for each watershed. Then the sediment delivery ratio was quantified from the total soil loss produced in the watersheds and the sediment yield transported in the rivers at the watershed outlet (Eq. (5)):

$$SDR = \frac{\sum_{i=1}^{n} BA_i \cdot A_i}{SY} \cdot 100 \quad (5)$$

where SDR is the sediment delivery ratio in %, BA_i the average annual long-term soil loss rate on the area i in $t\ ha^{-1}\ year^{-1}$, A_i the size of the area i in ha (hectare), and SY the average annual long-term sediment yield at the watershed outlet in $t\ year^{-1}$. In the next step the calculated SDRs of the watersheds (Table 2) were correlated to watershed properties in order to explain the variation of the SDR. The sediment input into surface waters is mainly controlled by the location of the main sediment source areas and the morphology along the flow pathways. Venohr et al. (2011) derived an approach for the SDR based on the variables 'mean gradient' (determined from a digital elevation model (DEM), 1000 m grid size) and 'percentage of arable land' for mesoscale watersheds in Germany. The latter was used as a substitutional measure to estimate how much of the arable land is in direct vicinity to the surface waters. However, we found for the 13 test watersheds that the percentage of arable land is not suitable to estimate the vicinity of arable land to surface waters (see Table 2) since the land use pattern strongly depends on landscape characteristics. We therefore considered the flow distance from arable areas to the surface water bodies. As the flow path can significantly differ from the beeline due to the topography, the length of the flow paths was calculated for each cell of a digital elevation model (DEM, 50 m grid size, BKG, 2007) in a GIS. Flow directions were defined in the DEM along the largest gradient. Then a watercourse network was generated from the depression lines of the DEM with the help of an algorithm for calculating flow accumulations, whereby the generated drainage density in the watersheds was adapted to the actually existing watercourse network. Finally, the flow lengths were calculated for each cell. After this, a grid data set was created which only contained the flow lengths for arable land. The proportion of arable areas which are located in a flow distance of < 500 m was quantified for each watershed (see parameter AL_{SF} in table 2). The 'mean gradient' and the 'proportion of arable land located in a flow distance of less than 500 m' (Table 2) showed a linear coefficient of determination r^2 of 0.58 and 0.28, respectively, to the SDR. A multiple linear regression based on these two variables was derived by adapting the empirical factors with the method of the smallest squared difference (Eq. (6)).

$$SDR = 0.2988 + 1.7401 \cdot S + 0.1189 \cdot AL_{SF} \quad (6)$$

Table 2
Characteristics of the 13 watersheds used to calibrate the approach for quantification of the sediment delivery ratio (SDR). A is watershed area, MQ is mean discharge, SSC_M is mean suspended sediment concentration, AL_{SW} is share of arable land in close vicinity to surface water bodies and S is large scale gradient.

Watershed	Monitoring station	A [km^2]	MQ [$m^3\ s^{-1}$]	SSC_M [$g\ m^{-3}$]	Cultivated areas [%]	AL_{SW} [%]	S [%]	SDR [%]
Spree[1]	Cottbus	2328	21.7	11	39	20.7	1.2	4.3
Leine[2]	Herrenhausen	5151	52.4	39	76	23.2	3.3	12.5
Fulda[3]	Hann.-Münden	6915	64.3	36	38	24.7	3.8	6.4
Werra[3]	Hann.-Münden	5457	51.6	66	39	24.5	4.5	13.2
Lahn[4]	Kalkofen	5298	45.6	24	48	22.5	3.4	7.9
Regnitz[5]	Pettstadt	6980	54.5	43	41	22.3	2.1	8.2
Main[5]	Kemmern	4424	44.7	40	61	20.9	3.5	8.0
Main[5]	Marktbreit	13,974	111.0	40	47	22.0	2.6	6.8
Naab[6]	Duggendorf	5487	51.3	24	47	22.5	2.8	5.7
Gr. Laber[6]	Schönach	419	2.5	51	71	11.2	1.2	4.1
Gr. Vils[6]	Vilsbiburg	347	2.8	78	66	19.4	1.0	5.1
Rott[6]	Ruhstorf	1195	9.4	98	66	24.1	1.6	6.3
Amper[6]	Inkhofen	3204	47.3	26	51	18.9	2.6	6.2

German water resources yearbook: [1] Elbe basin (LfU Brandenburg, 2004); [2] Weser basin (NLWKN, 2011)); [3] Weser basin (NLWKN, 2015); [4] Rhine basin (LANUV, 2011); [5] Main basin (LfU Bayern, 2014a); [6] Danube basin (LfU Bayern, 2014b).

where SDR is the sediment delivery ratio in %, S is the mean gradient in % and AL_{SF} is the share of arable land located in a flow distance of <500 m from surface water bodies in %.

Fig. 2 presents the comparison between the long-term average annual sediment yields observed at monitoring stations and the predicted yields calculated by applying the SDR approach (Eq. (6)) for the 13 watersheds. The predicted sediment yields correlate well with the observed ones, the systematic error (BIAS) is −13,682 t (relative BIAS −1.8%), the mean absolute error (MAE) is 11,231 t, the mean absolute percentage error (MAPE) is 18%, and the root mean square error (RMSE) is 15,364 t (relative RMSE 2.1%).

Thus, Eq. (6) is suitable to estimate the SDR from agricultural areas to surface waters, since most of the total annual soil loss in the 13 test watersheds was produced on cultivated land (> 95%). According to the RUSLE2015 the average annual soil loss rate on naturally covered areas is 0.07 t ha^{-1} $year^{-1}$ in Germany, whereas the soil loss on cultivated land is 1.7 t ha^{-1} $year^{-1}$. Since the soil loss from naturally covered areas is low in comparison to the soil loss from agricultural areas, it was assumed that most of the eroded material from naturally covered areas is transported to surface waters and no retention within the watershed was considered for eroded soil in these areas.

The procedure derived for the 13 test watersheds was then applied for the tributaries of the Neckar and Bode to estimate the sediment yields from agricultural and naturally covered areas.

3.6. Statistical procedures and evaluation of uncertainty

A key parameter of the applied approach, the particle loading C_{sus}, was derived as the slope of a linear regression of total PAH and suspended sediment concentrations (Eq. (2)). The slope was calculated as follows:

$$C_{sus} = \frac{\mathrm{cov}(\mathrm{SSC}, \mathrm{PAH})}{\mathrm{var}_{\mathrm{SSC}}} \quad (7)$$

where cov(SSC,PAH) denotes the covariance of the SSC and PAH concentration data series and $\mathrm{var}_{\mathrm{SSC}}$ the variance of the SSC concentrations of a certain sampling location.

The uncertainty of the determined C_{sus} values arises from two sources: i) the conceptual error of the attempt to explain the data by a linear regression model, expressed by the residual (in y direction) of the data points scattering along the regression line. This error $\sigma_{C_{sus}}$ was quantified by

$$\sigma_{C_{sus}} = \sigma_{\mathrm{PAH}} \sqrt{\frac{1}{\sum\left(\mathrm{SSC_i} - \overline{\mathrm{SSC}}\right)}} \quad (8)$$

with σ_{PAH} being the standard deviation of the total PAH concentrations relative to the regression line; ii) the uncertainty of the slope of the fitted regression line due to analytical errors of PAH and SSC concentration measurements, $\Delta_{C_{sus}}$, which was determined by Monte Carlo simulations. 10,000 realizations were run for each regression while the data values were randomly varied within the analytical error margins conservatively estimated to be ±10%. $\Delta_{C_{sus}}$ is reported as the coefficient of variation of the 10,000 calculated slopes per sampling location.

4. Results

4.1. PAH and SSC concentrations

Total PAH concentrations in turbid water samples are strongly correlated with particle concentrations for all sampled watersheds. Fig. 3 shows an exemplary linear regression for the River Steinlach in the upper Neckar basin. In addition to samples taken from 2014 to 2016, data published in Schwientek et al. (2013) and Rügner et al. (2014) are included and confirm exceptionally well the trend found in the former studies. The slope of the regression line to all data points indicates, according to Eq. (2), a loading C_{sus} of suspended particles with PAH of 1.2 mg kg^{-1}. It is noteworthy that C_{sus} values are not only fairly invariable in the course of single events, but they are stable over timescales of years. C_{sus} is thus an integral watershed specific measure for bed sediment contamination with hydrophobic pollutants that behave similarly as the PAH do.

Similar linear regressions were received for samples from the other 22 locations. For the sub-watersheds of the upper River Neckar investigated in 2015 and 2016 only few data points are available due to extended drought periods. Nevertheless, two independent flood events could be sampled. Because of the remarkable temporal stability of the linear relations as shown, e.g., in Fig. 3, we are confident that this is sufficient to derive meaningful values for C_{sus}, although partly an increased uncertainty might be expected. As examples, the data of independent floods in 2015 and 2016 from the Rivers Glatt, Eyach, and Starzel are depicted in Fig. 4. The data points are typically well described by regression lines which pass near to the origin. All resulting C_{sus} values are

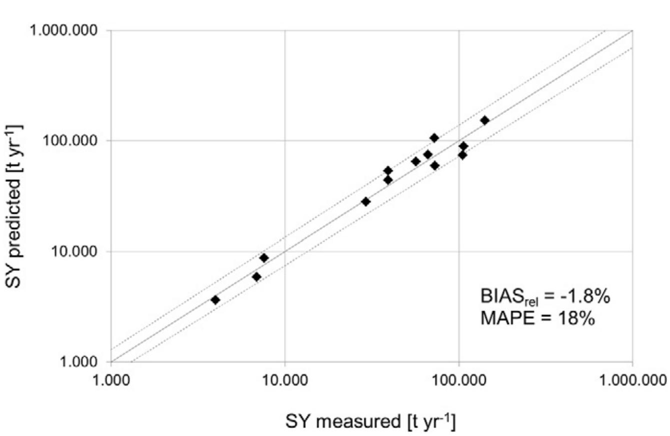

Fig. 2. Correlation of measured and predicted long-term annual sediment yields at monitoring stations for the 13 test watersheds. Where SY is sediment yield, $BIAS_{rel}$ is relative systematic error and MAPE is mean absolute percentage error. The dashed lines mark an error range of ±30%.

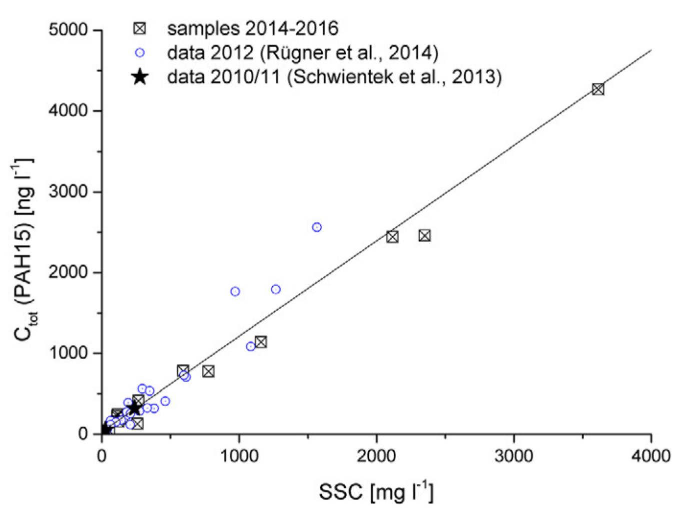

Fig. 3. Total concentrations of PAH versus suspended sediment concentrations for the River Steinlach samples from sampling campaigns from 2010 to 2016. The straight line denotes the linear regression to all data (slope 1.2 mg kg^{-1}, $r^2 = 0.96$) and is, according to Eq. (2), interpreted as PAH loading C_{sus}.

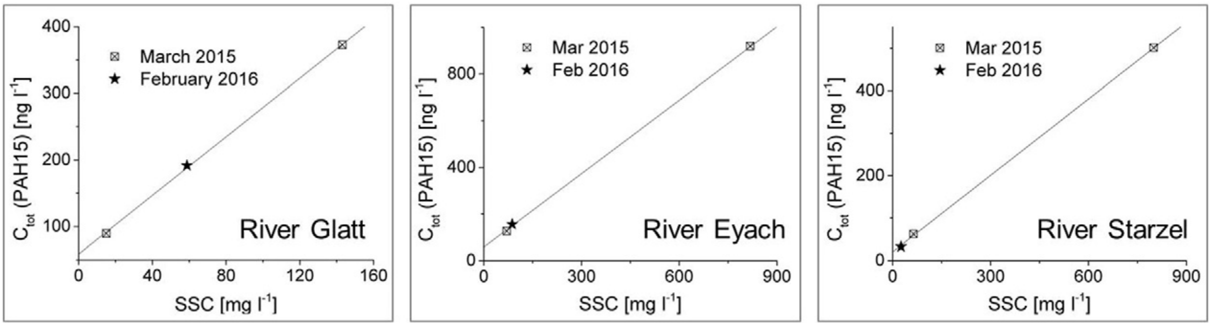

Fig. 4. Total concentrations of PAH versus suspended sediment concentrations for the Rivers Glatt (left), Eyach (middle), and Starzel (right) from sampling campaigns in 2015 and 2016.

compiled in Table 3 along with measures of uncertainty: The relative errors $\sigma_{C_{sus}}$ due to conceptual model uncertainty are in the range between 0.2% (River Schlichem) and 23% (Sauerbach creek), the average error is 7.3%. The uncertainty due to the analytical error of PAH and SSC measurements, $\Delta_{C_{sus}}$, is systematically larger for those locations with only 3 data points (up to 13%) while regressions with large n are only weakly sensitive to analytical errors. On average $\Delta_{C_{sus}}$ is 8.5%.

The number of inhabitants living in the watershed of each sampling location (determined through GIS analysis) as well as the modeled mean annual sediment yields are also displayed in Table 3.

4.2. Measured sediment yields and comparison with model results

In Germany, continuous data series of suspended sediment transport are only available for larger watersheds. Hence, the calibration of the model was based on these large-scale data. The reliability also for smaller systems has to be confirmed. In the Steinlach, Ammer and Goldersbach watersheds (areas between 37 and 238 km^2) SY were measured and could be used for the prediction of sediment quality and a further evaluation of the modeled SY data. The available data for each sampling location within these watersheds, either measured or modeled, are given in Table 4. The mean annual yield of the River Steinlach for the period 2014–2016 deviates by 3% from the modeled long-term average value of about 3500 t year^{-1}. For the River Goldersbach measurements for 2014–2016 are available for the upstream gauge at Bebenhausen only. The mean SY of the 3 years exceeds the modeled value by 116%. A likely reason for this discrepancy is the historical agricultural use of the Goldersbach watershed before it was afforested in the 19th century. Legacy colluvium and alluvial loam deposits in the flood plains are still existing and are easily erodible, i.e. the geomorphic Goldersbach system has not yet equilibrated to the recently changed land use. A clear predominance of bank erosion over surface erosion of the forested valley slopes was formerly documented by Schmidt-Witte and Einsele (1986). However, the process of bank erosion is not represented by the RUSLE which explains the underestimation of sediment yield by the model. The measured specific sediment yield (SSY) amounts to 11.3 t year^{-1} km^{-2} (period 2014–16) and is well in line with the SSY of approximately 10 t a^{-1} km^{-2} given by Schmidt-Witte and Einsele (1986) for the period 1981–82. For the total watershed the same authors found a slightly higher SSY of 13 t year^{-1} km^{-2}. This results in a total SY of approximately 950 t a^{-1}, once again exceeding the modeled yield for the same reason. For the river Ammer, on contrary, the SY measured at Pfäffingen (2014, 2016) was by 56% smaller compared to the modeled yield. The upper Ammer watershed upstream of Pfäffingen is strongly karstified and of relatively little relief. The perennial stream network density is low and surface runoff is usually not observed, hence, the model likely overestimated both soil loss and the SDR.

For the lower River Ammer no measurements are available and the SY for the sampling locations 'Tübingen' and 'confluence' were synthesized from the measurements in Pfäffingen and at the River Goldersbach (a tributary of the lower River Ammer) and the modeled SY from the intermediate – non-karstic - Ammer catchment. As the yield of the River Goldersbach was underestimated while the River Ammer's yield at Pfäffingen was overestimated by the model, the estimated yield at the Ammer mouth is no more than 25% below the modeled data point, which is within the error margins of the model calibration (see Fig.2).

Measured and modeled results are in good agreement for the total watersheds of Steinlach and Ammer, in particular if the short record of measurements is considered. For sub-watersheds the reliability of the model is lower. However, it has to be taken into account that the presented watersheds are somewhat special cases with influence of karst and the rather recent land use change - features that are not adequately represented by the simplistic RUSLE-based approach. In conclusion, the uncertainties of the model tend to increase in small systems, but for watersheds larger than 100–200 km^2 the approach is a promising alternative to estimate average annual long-term sediment yields if measurements are missing.

Table 3
Compiled results for all studied watersheds. $\sigma_{C_{sus}}$ denotes the error of the linear regression model according to Eq. (6) while $\Delta_{C_{sus}}$ indicates the uncertainty of the regressions due to analytical errors, determined by Monte Carlo calculations.

River/Location	n	C_{sus} [mg kg^{-1}]	$\sigma_{C_{sus}}$	$\Delta_{C_{sus}}$	Inhabitants	Modeled SY [t year^{-1}]
Eschach	3	0.8	7%	12%	29,137	2934
Prim	3	0.6	4%	11%	48,043	2302
Neckar, Neckarburg	3	1.0	7%	11%	146,419	7442
Schlichem	3	0.4	0%	11%	10,855	2182
Neckar above Glatt	3	1.2	11%	11%	200,393	12,276
Glatt	3	2.2	2%	11%	47,637	5230
Neckar above Eyach	2	1.4	0%	11%	270,418	20,225
Eyach	3	1.1	1%	9%	85,175	6927
Neckar above Starzel	3	1.1	5%	13%	359,485	27,225
Starzel	3	0.6	1%	10%	35,533	3636
Neckar above Tübingen[a]	12	1.6	13%	4%	455,058	34,588
Steinlach	40	1.2	3%	5%	50,013	3457
Ammer, Pfäffingen	30	5.6	5%	5%	68,700	2260
Ammer, Tübingen	9	4.2	11%	7%	110,000	2852
Ammer, confluence	7	3.5	19%	6%	118,684	3358
Goldersbach, Bebenhausen	26	0.1	6%	5%	0	196
Goldersbach, confluence	9	0.4	15%	6%	5000	465
Neckar, Kirchentellinsfurt[a]	10	1.6	12%	5%	654,360	41,641
Bode, Hadmersleben	18	1.3	7%	9%	274,795	15,865
Selke, Meisdorf	21	1.3	6%	6%	6090	1685
Selke, Hausneindorf	22	0.9	3%	8%	37,480	3008
Sauerbach	21	0.1	23%	6%	0	–

[a] Regression line forced through origin due to hysteresis-type data scatter and uncertainty of linear regression model.

Table 4
Available SY data in the monitored watersheds of Rivers Steinlach, Goldersbach, and Ammer (Bhs. = gauge Bebenhausen, Pf. = gauge Pfäffingen, Tü = Tübingen, upstream of confluence with Goldersbach); data in the line "avrg. (2014–16)" were used for computations in Fig. 3.

	Steinlach [t year^{-1}]	Goldersbach, Bebenhausen [t year^{-1}]	Goldersbach, confluence [t year^{-1}]	Ammer, Pfäffingen [t year^{-1}]	Ammer, Tübingen [t year^{-1}]	Ammer, confluence [t year^{-1}]
Measured year						
2014	3282	659		1163		
2015	2025	259				
2016	4718	354		873		
Avrg. (2014–16)	3342	424	950[a]	1018	(1550)[b]	(2500)[b]
Modeled	3457	196	465	2310	2852	3358

[a] Period 1980–81, data from (Schmidt-Witte and Einsele, 1986).
[b] Data extrapolated/calculated, see text for explanation.

4.3. Relationship between C_{sus}, population, and sediment yield

According to Eq. (1), a linear relationship is anticipated between C_{sus} and the ratio of inhabitants and mean SY. A linear regression model was fitted to the data of the upper Neckar basin (Fig. 5), excluding the two tributary Rivers Prim and Glatt which deviate from the general linear trend (discussed in Section 5.2). The relative root-mean-square error (RMSE) of measured data versus values predicted by the linear model for the 14 considered sub-watersheds of the upper River Neckar yields 20%. Interestingly, the regression model (River Neckar basin) works equally well for the sampling locations in the River Bode basin, with one exception: If the outlier of the Selke in Meisdorf (also discussed in Section 5.2) is ignored the relative RMSE amounts to 4%. This indicates that the linear relationships observed in former studies (Schwientek et al., 2013) are valid for watersheds up to 3000 km^2 in size that may be hundreds of kilometres apart from each other (but with comparable societal and technical standards).

5. Discussion

5.1. Mass flux-based conceptual model to predict sediment quality for meso-scale river watersheds

First, the general relation between sediment quality, sediment flux, and urbanization shall be examined more deeply: The predicted trend shown in Fig. 5 is based on two hypotheses: (i) The major source of PAH in rivers is atmospheric deposition in the urban/industrial areas;

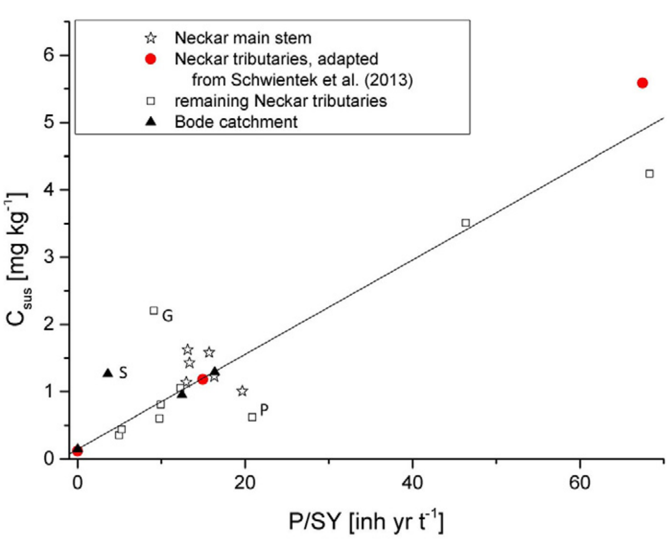

Fig. 5. PAH loading on suspended particles (C_{sus}) versus population (P) divided by the mean sediment yield (SY). The relationship is explained by a linear regression. Abbreviations refer to outliers discussed in the text: P = River Prim, G = River Glatt, S = River Selke at Meisdorf.

PAH deposition in rural areas is less important because rates are lower, and connectivity from the locations of deposition to rivers is very much restricted in comparison to that from urban surfaces. (ii) PAH emissions can be related to the individual consumer behaviour such as exhausts from vehicle traffic, heating systems, and small industries commonly existing also in small to medium towns.

The presented data give convincing evidence that hypothesis (i) applies: Two of the study watersheds (Goldersbach at Bebenhausen and Sauerbach) are uninhabited and both show only very small background levels of PAH in suspended sediments (Table 3). This is particularly remarkable for the Goldersbach watershed which is surrounded by agglomerations. Furthermore, so far unpublished data from an additional uninhabited sub-watershed of the River Steinlach shows similar behaviour (Weiherbach, C_{sus} = 0.1 mg kg^{-1}).

A limited spatial extend of elevated concentrations in different matrices (air, water, sediments) around PAH sources was also reported, e.g., by Bomboi and Hernández (1991), Hafner et al. (2005), Gocht et al. (2005), and Kannan et al. (2005). Additionally, Van Metre et al. (2000) propose vehicle-related emissions that are not dependent on atmospheric transport such as tire wear, crankcase oil, or roadway wear. Nevertheless, there is atmospheric transport of a certain proportion of PAH across the boundaries of urban areas which is documented e.g. in elevated PAH concentrations also in forest topsoils across the federal state of Baden-Württemberg (Gocht and Grathwohl, 2004). The data show, however, that PAH are strongly accumulated only in the top few cm of soil profiles. Any local erosion is likely to cut deeper into the surface and to mobilize mostly uncontaminated soil layers which would result in a strong dilution of the average PAH loading. Since erosion is a selective process and typically only small proportions of a watershed's area are easily erodible and deliver the major part of eroded material, an accordingly small proportion of deposited PAH in rural areas may be mobilized. In forested areas bank erosion will dominate and mobilize mainly deeper, uncontaminated soils. In agriculturally used areas, where sheet erosion is most likely to occur, ploughing leads to a homogenization of the top 30 cm of soils which has a similar dilution effect. As a result, sediments that were mobilized from surfaces in rural areas show a strongly diluted PAH signal. The degree of dilution is reflected by the small (yet larger than zero) C_{sus} values found in the uninhabited test watersheds (Table 3).

Hence, hypothesis (ii) remains to be confirmed. Data of atmospheric PAH deposition within the City of Tübingen measured by Martin et al. (2002) may be used as representative for the study area. At a sampling location adjacent to a busy road close to the city center the authors determined an average deposition rate close to 1 μg m^{-2} day^{-1} for the sum of the PAH congeners phenanthrene - benzo(g,h,i)perylene (which is commonly a close approximation to the sum of PAH15). This value corresponds to a PAH deposition of 365 g km^{-2} year^{-1} and, using the population density of 2,500 inh. km^{-2} in the urban area of Tübingen, may be scaled down again to a per capita PAH deposition of 0.15 g year^{-1}. Due to their hydrophobic nature, PAH strongly tend to sorb to particles either during their atmospheric transport or after they have settled down. A certain fraction of the PAH-laden particles will then be mobilized by precipitation and can either reach receiving waters directly via stormwater sewers or be split into a flux that is spilled into a stream via combined sewer overflows and another one that will be eliminated by the wastewater treatment plant. Hence, the proportion of PAH that reach aquatic systems after deposition is very much dependent on the local stormwater management (i.e. separate or combined sewers), the state and capacity of the sewer system, the presence of storm water treatment facilities, but also on climatic variables such as the frequency, duration, and intensity of rain storms. The PAH flux that is introduced into a stream will likely be distributed among the contaminated urban and the more or less clean background particles stemming from various natural sources of sediment in the watershed.

Based on hypotheses (i) and (ii) we derive a conceptual model which can physically explain the regression line shown in Fig. 5. The final PAH loading of the sediments (mass/mass) may be expressed as the ratio of PAH flux (mass/time) and total sediment flux (mass/time) or, as a simpler approach, annual load of PAH per annual sediment yield:

$$\mathrm{SL} = \mathrm{D} \cdot \mathrm{CF} \cdot \frac{\mathrm{P}}{\mathrm{SY}} + \varepsilon \tag{9}$$

where SL = predicted sediment loading [mg kg^{-1}]

D = per capita PAH deposition rate [g $inh.^{-1}$ $year^{-1}$]

CF = conveyance factor, determining fraction of PAH that reaches receiving water body [−]

P = population of watershed [inhabitants]

SY = sediment yield of receiving stream [t $year^{-1}$]

ε = background loading of sediment from rural areas [mg kg^{-1}]

The slope (0.0703 [g $inh.^{-1}$ $year^{-1}$]) of the regression line in Fig. 5 corresponds to the product D × CF. Assuming D = 0.15 g $inh.^{-1}$ $year^{-1}$, as calculated for the City of Tübingen (see above), CF is calculated as 0.47. Both factors include properties that may change regionally. The per capita PAH deposition is dependent on the general standard of living (number of vehicles, energy consumption, etc.), the predominant source of energy for heating (gas, oil, coal, wood, etc.), and the existence of industrial sources. For instance, in an area in the vicinity of Le Havre (France), that is additionally influenced by industrial emissions, Motelay-Massei et al. (2006) found a slightly higher per capita PAH deposition rate of 0.27 g $inh.^{-1}$ $year^{-1}$. The 'conveyance factor' sums up all effects determining the fraction of PAH that reach the receiving water body and could be further split up into factors describing, e.g., the degree of surface sealing, the density, type and capacity of sewer systems, the number of storm water retention basins, and, finally, climatic characteristics of the study area. The intercept in Fig. 5 corresponds to the background loading ε which in turn is a physical representation of the C_{sus} values found in the uninhabited test watersheds. For anthropogenically impacted watersheds, ε may be neglected (confirming hypothesis i).

5.2. Prediction validity and constraints

A number of factors introduce uncertainty and may lead to deviations from the predicted sediment quality. First of all, the sediment yield model used is based on simple empirical concepts and was developed for large scale applications. Particularly in small watersheds, model results become uncertain since the importance of local conditions which might not be well represented by the RUSLE model increases. For instance, an underestimation of the sediment yield by the model would shift data points to the right and away from the predicted trend in Fig. 5. This is a probable explanation for the outlier (River Prim) clearly below the calculated trend. The Prim watershed is characterized by large areas covered with hillside debris. The effect of a missing sediment yield of the River Prim is in line with the corresponding shift of the River Neckar data point immediately downstream of the River Prim mouth (data point neighbouring the River Prim in Fig. 5).

Furthermore, the model uses mean precipitation characteristics of a 30-year period. Thus, the results have to be interpreted as long-term averages and the short-term variability of the sediment fluxes is not considered. In contrast, the measured data series that were used to test the model results in the Neckar tributaries (Section 4.2) are short and probably not representative of the respective mean system behaviour. The time scale of transport and mixing processes is the next debatable aspect: Fluxes of PAH-contaminated urban and low concentrated background particles are introduced and mixed in the river within timescales of hours. Is the simple approach using (average) annual fluxes (Eq. (9)) justified though? As demonstrated by Rügner et al. (2014) and Schwientek et al. (2013) and the new data presented in this paper PAH loadings at the watershed outlets did not vary tremendously over time, neither in the course of single events nor between individual events (see little scatter in Fig. 3). This is very remarkable since sediment contributions of variable quality from different subwatersheds as well as PAH-laden input pulses from urban effluents can be expected to exhibit strong temporal patterns, leading to abruptly changing compositions of the suspended sediments at the watershed outlet. As a possible explanation an important storage within the channels (and on the flood-plains) capable of the apparent strong smoothing effect during the transport in the stream network is hypothesized. Parsons et al. (2015) proposed an ever continuing exchange between particles of the river bed and those in suspension, even if critical shear velocities are exceeded. Mixing of and finally efficient exchange between stored and freshly introduced particles may lead to relatively constant PAH loadings over time. Important channel storages of fine sediments were reported e.g. by Buendia et al. (2016), Lopez-Tarazon et al. (2011), and Walling et al. (1998). The importance of this channel storage in relation to the sediment fluxes will be different for different watersheds. Thus, for single watersheds the prediction accuracy might increase if not annual sediment yields but the cumulative fluxes of a shorter period, that better represents the turnover time of the channel storage, are applied.

The conceptual framework deployed for our predictions is based on the assumption of diffuse PAH emissions mainly from combustion sources (hypothesis i). Any relevant point source, e.g., large PAH emitting industries or sites of legacy pollution, could result in predictions deviating more or less strongly in a positive direction from the calculated trend. Historical point sources such as charcoal industries and a long history of mining activities in the Black Forest and the Harz mountains could be reasons for the positive outliers in Fig. 5 (River Glatt and River Selke at Meisdorf).

It is likely that the size of the watersheds will affect the accuracy of the presented concept. At larger scales the probability increases that, during individual events, only a part of the total watershed gets activated in terms of flood generation and sediment transport. Depending on where the flood and the sediment flux is originating, variable sediment qualities are possible for subsequent flood events. Furthermore, it may be hypothesized that the factors D and CF might vary across regions (and potentially also within large watersheds), depending, e.g., on climate and standard of living.

5.3. Practical implications

The most important consequence of the presented considerations is the dependence of sediment quality not only on urban impact, but, equally important, on the delivery of fine grained sediments as 'diluting agents'. Although this concept is straightforward and easy to comprehend, the implications have rarely been reviewed so far. Soil erosion, e.g., due to poor land use management, is widely accepted to be an environmental concern (Walling, 2006), the additional input of fine sediments a threat to water management infrastructure (Alahiane et al., 2016). Moreover, various detrimental effects on ecosystems are attributed to increased concentrations of suspended sediment, among them the loss of habitat diversity (Buendia et al., 2014) or the reduction of solar energy availability for primary production (Davies-Colley and Smith, 2001). While the perception of suspended particles as transport vectors for hydrophobic pollutants such as PAH is common and fluxes of particle-associated pollutants are usually related to particle fluxes (Rügner et al., 2014; Sicre et al., 2008), it is usually overseen, that increasing sediment fluxes do not mean an increased source strength in the case of urban pollutants and that, in contrary, the chemical quality of sediments may even improve by dilution effects. Independently of the absolute input of hydrophobic pollutants, organisms living in or feeding upon sediments rather experience the ratio of pollutant and sediment fluxes. An interesting finding arising from this is that rivers draining landscapes with low sediment production are particularly vulnerable to sediment contamination. This conclusion may apply, e.g., to many karstic landscapes where little surface runoff is generated and input of sediments into surface waters is low. A recently discovered contamination of fish within the River Ammer with polychlorinated biphenyls (PCB) despite the absence of a known point source may be explained by this concept. Furthermore, a retention of natural sediment fluxes within reservoirs might increase the downstream vulnerability of rivers due to the reduced potential to dilute the input of urban particles. Concluding, the problem of sediment input into aquatic environments is not unilateral and there may also be incidents, in particular in systems with strong urban impacts that require sufficiently large fluxes of fine sediments to maintain low contaminant levels beneficial for benthic organisms and those feeding on them. At this point it has to be clarified that, from a river management point of view, an engineered input of sediment could result in diverse detrimental effects and will never be a reasonable substitute for the reduction of contaminant sources.

Besides of the due validation of these thoughts in additional independent systems and also for additional pollutant groups (e.g. PCB), it is still to be tested to which extend the concept is transferrable in terms of scales and climatic, geologic, and societal conditions. How well can factors such as D and CF be defined for regions and is a description of CF as a function of sub-factors (e.g. standard of living, technical standard, etc.) possible? The application of the proposed method in terms of sediment quality prediction will regionally result in uncertainties. But even if it cannot provide a fully quantitative measure, it may still be used as an analytical tool in the comparison of watersheds. Outliers, as also displayed by Fig. 5, can hint to irregularities within these watersheds, e.g., the existence of point sources.

Furthermore, the role of sediment and contaminant storage in the river channels is still not fully clear. To what extend are transient input patterns smoothed and what are the timescales of contaminant storage? What is the return period of a flood that erases the memory of past inputs and resets the system? Sicre et al. (2008) raised the question which effects climate change will have on the transport of particle-bound pollutants to marine environments. In the light of our conclusions, a potential increase of sediment yields will not necessarily affect the fluxes of urban pollutants and may in turn even improve the quality of riverine sediments.

6. Concluding remarks and outlook

The presented data confirm the concept that river sediment quality in terms of contamination with hydrophobic urban pollutants such as PAH, is decisively governed by the sediment yield of a watershed. The consequence is that, opposed to the common perception, river sediments in urbanized watersheds may be relatively clean if a sufficient dilution of urban particle fluxes with clean sediments from natural erosion processes exists. Even more intriguing, unexpectedly high pollution levels in river sediments may occur in areas with low population density but weak supply of suspended particles. Accordingly, also on a global scale, the vulnerability of riverine sediments to contamination will differ regionally depending on the regional specific sediment yield, which may vary by orders of magnitude (e.g. Walling and Webb, 1996). Karstic or low gradient areas or river systems that are depleted in suspended particles due to impoundments that retain the sediment supply of the upstream watershed may be particularly vulnerable. Where no measured sediment yields are available, the presented parsimonious concept may still be applicable by use of the rather simple conceptual modeling of sediment yields based on the publicly EU-wide available RUSLE2015 data. It was shown that this model is a promising opportunity for meso-scale watersheds (>100–200 km^2).

Further research should examine the applicability of this approach across regions and the variability and dependence of the D and CF factors. Climatic and technical aspects are two possible controls of urban contaminant input into aquatic systems. Further, the scale-dependence of the discussed relationships is not clear. Regarding temporal variabilities, the importance of in-stream storage of sediment and particle-associated pollutants and the interactions of storage and contaminant fluxes need further elucidation.

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