Using total suspended solids (TSS) and turbidity as proxies for evaluation of metal transport in river water

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ABSTRACT

The present study was carried out in Haraz basin (Iran) that is located in south of the Caspian Sea. The goal of this study was to establish correlations amongst total suspended solids concentration (TSS) and turbidity with total pollutant concentrations to evaluate the dissolved and particle-bound concentrations of major toxic metals. It also aimed to validate TSS and/or turbidity measurements as proxies to monitor pollutant fluxes. Eight metals, namely nickel, lead, cadmium, copper, zinc, cobalt, arsenic and strontium were analyzed for dissolved and total concentrations in water at ten locations within the catchment. TSS and turbidity were also measured. Sampling campaigns were designed to cover both the rainy (December) and the dry (May) season within the basin. The robust relationship between TSS (202 ± 1212 mg/l) and turbidity (63 ± 501 NTUs) in both seasons warranted their interchangeable potential as proxies within the observed ranges. Total element concentrations were plotted in separate attempts versus TSS and turbidity for all locations and both events. Very good linear correlations were attained where the slopes represent the metals concentration on suspended solids and the intercept the dissolved concentration in water. The results achieved by these linear regressions were in very good agreement with independently measured values for dissolved concentration and concentrations on river bed sediments taken at the same locations. This demonstrates that turbidity and/or TSS measurements may be used for monitoring of metal loads if once calibrated against total concentration of metals. The results also revealed that in the lower Haraz catchment metal concentrations on suspended and river bed sediment were homogeneously distributed along the investigated river stretch. This is assumed to be due to intensive gravel and sand mining activities in the upper and middle part of the catchment.

1. Introduction

Heavy metals/metalloids are among the most notorious threats for water and soil ecosystems. Transfer of such pollutants from solid to aqueous phase at the interface of sediments/particles facilitates their entry into the food chain and further bioaccumulation in neighboring fauna and flora (Fabure et al., 2015; Nasrabadi et al., 2015; Karbar et al., 2012; Biati et al., 2010; Ogundiran et al., 2012; Conceicao et al., 2013; Bu-Olayan and Thomas, 2013). A vast variety of geogenic (rocks weathering and soil erosion) and anthropogenic sources (mining activities, urban and agricultural run-offs, industrial and municipal sewer overflows, etc.) may cause toxic metals discharge into water bodies. The metals can be dissolved in the water column, absorbed/adsorbed to the sediments/particulates or accumulated in biota. Accordingly, during recent years a great attention has been paid to studies where the behavior of metals in different media is discussed (La Colla et al., 2015; Hejabi et al., 2011; Adekola and Eletta, 2007; Li et al., 2006; Jain et al., 2005; Chow et al., 2005; Olivares-Rieumont et al., 2005; Hope, 2006). In comparison with other media, river bed and suspended sediments play a more significant role in overall pollution and environmental risks (Poerstner and Muller, 1973; Foster and Hunt, 1975; Throne and Nickle, 1981; Sakai et al., 1986; Karbassi et al., 2007; Nasrabadi and Shirani Bidabadi, 2013). A remarkable number of relevant studies focus on concentrations associated with suspended or bed sediments, but only few try to assess the
speciation of different metals in these matrices. In the last few
decades, researchers have followed a variety of sequential extrac-
tion techniques to estimate the fractionation of metals in sediments
(Chester and Hughes, 1967; Tessier et al., 1979; Forstner and
Wittmann, 1981; Horowitz et al., 1999; Stamatis et al., 2006;
Tessier et al., 1980; Elsokkary and Muller, 1990; Korfali and
Davies, 2000; Rauret, 1998; Pardo et al., 1990). Dozens of
methods for determining several forms of metals in sediments are
described in literature (Kersten and Foerstner 1991; Lopez-Sanchez
et al., 1993; Das et al., 1995; Li-Jyur et al., 2003). The most wide-
spread methods are based on sequential extraction schemes where
different reagents are utilized consecutively to extract defined solid
phases (Nasrabadi et al., 2010a). Such methods are all time-
consuming, labor-intensive and expensive. Thus generating
continuous or at least semi continuous temporal/spatial data sets is
hardly possible. Focusing on dissolved and adsorbed phases and
consideration of proxies might be a feasible substitution for the
above mentioned complex speciation schemes. Proxies that are
easy and cheap to measure would be very valuable to monitor
pollutant concentrations and loads. A vast range of organic pol-
lutants as well as nitrogen and phosphorus has been proved to be
transported by suspended solids in river systems (Meyer and
Wania, 2008; Meyer et al., 2011; Schwarz et al., 2011; Rügner
et al., 2014; Quesada et al., 2014; Spackman Jones et al., 2011;
Hornsburgh et al., 2010; Sluets et al., 2014). Ruegner et al. (2013,
2014) and Schwientek et al. (2013) showed that concentrations of
polycyclic aromatic hydrocarbons (PAHs) in rivers correlate very
well with turbidity and TSS in a number of small catchments in
southern Germany (Neckar at Tuebingen: 2,300 km²; tributaries:
39–139 km²). Not many studies considered toxic metals. Kirchner
et al., 2011 for example, studied the dependence of total Hg concen-
trations on total suspended solids in a river downstream of
Gambonini mine, San Francisco in order to quantify the remedia-
tion effectiveness by comparing contaminant rating curves.
Chebboa and Gromaire (2004) determined the fractions of Pb, Zn
and Cu associated to suspended solids in surface runoff in Paris and
attributed high concentrations to local roofing materials.

2. Theory

By causing light to be scattered, suspended particles concentra-
tion may have a meaningful correlation to turbidity. Using lab-
oratory nephelometers and optical backscatter sensors offers the
capability to easily detect the turbidity in the lab and in-situ,
respectively. Although a variety of parameters like density, size
and shape of particles as well as water color may affect the rela-
tionship between the values of TSS and turbidity (Downing, 2006),
turbidity may be considered as a reliable and feasible proxy for
suspended sediment and thus pollutant concentrations within a
given basin if once a precise and meaningful correlation between
TSS and turbidity was established. Such correlations have been
discussed in detail over a wide range of case studies. A common and
routine linear relationship may be defined as:

Fig. 1. Major land use within the study area (adapted from Nasrabadi et al., 2011): B bared land, DF dry farming, OC outcrop, F1 high density forest, F2 Medium density forest, FO mixed forest/orchard, FP fish pond, I1 agricultural area with low limitation, I2 agricultural area with limitation, IO mixed agriculture/orchard, L2 reservoir, O orchard, Of mixed orchard/agriculture, R1 grazing land high density, R2 grazing land medium density, RD grazing land/dry farming, U Urban area, U1 installations.
Ruegner et al. (2013) found linear relationships between TSS and turbidity with \( m = 2.28 \) mg L\(^{-1} \) NTU\(^{-1} \) for naturally suspended sediments in rivers in S-Germany. Other studies report slightly lower or higher \( m \) values (e.g. 1.1 mg L\(^{-1} \) NTU\(^{-1} \) for particles from karstic springs or up to 3 mg L\(^{-1} \) NTU\(^{-1} \) for suspended sediments in the Lake Tahoe basin, respectively; Schwarz et al., 2011; Stubblefield et al., 2007).

Total concentration in river water includes the dissolved and particulate-bound fraction of a contaminant:

\[
C_{w,\text{tot}} = C_w + C_{\text{sus}}
\]

\[ TSS = m \text{Turbidity [NTU]} \]  

\[ y = 2.28x \quad R^2 = 0.96 \]

Ruegner et al. (2013) found linear relationships between TSS and turbidity with \( m \) values of 1–2.8 mg L\(^{-1} \) NTU\(^{-1} \) (average 1.9 mg L\(^{-1} \) NTU\(^{-1} \)) for naturally suspended sediments in rivers in S-Germany. Other studies report slightly lower or higher \( m \) values (e.g. 1.1 mg L\(^{-1} \) NTU\(^{-1} \) for particles from karstic springs or up to 3 mg L\(^{-1} \) NTU\(^{-1} \) for suspended sediments in the Lake Tahoe basin, respectively; Schwarz et al., 2011; Stubblefield et al., 2007).

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corresponds to $C_{\text{sus}} \text{m}$ (in $\text{mg L}^{-1} \text{NTU}^{-1}$).

The aim of this study is to establish correlations of TSS with turbidity and with total pollutant concentrations to (1) estimate dissolved and particle-bound concentrations and (2) to make use of TSS and/or turbidity measurements as proxies to estimate major toxic metals transport in lower Haraz basin south of the Caspian Sea.

3. Materials and methods

The lower part of the Haraz River basin located south of the Caspian Sea, Iran was considered as the study area. The drainage area and the length of main stem are around 4060 km² and 185 km, respectively. The mean discharge of the river in the lower Haraz basin was approximately 30 m³ s⁻¹ during the last fifty years while the annual means varied between 15 and 55 m³ s⁻¹ (Mohseni-Bandpei and Yousefi, 2013). Generally, the study area is mainly covered by dense forests, rice paddies and urban space. A major anthropogenic activity is given by sand mining installations (see Fig. 1). These intensive sand and gravel mining activities usually take place close to or directly within the river channels. Once a location is exploited activities move to the next suitable location such that numerous locations within the river stretch are affected over time. Jurassic passive-margin deposits are represented by the clastic (sandstone-shale) Shemshak Formation, and the Lar and Delichi carbonates. Comprising largely submarine tuffs, the eocene Karadj formation is suggestive of the onset of active continental-margin magmatism (Davidson et al., 2004). A detailed description of the geology may be found in Nasrabadi et al. (2010a).

Considering the information on pollution by metals within the basin gained during recent years (Karbassi et al., 2008; Biati and Karbassi, 2010; Nasrabadi, 2015; Nasrabadi et al., 2010a), eight elements namely nickel, lead, cadmium, copper, zinc, cobalt, arsenic and strontium were selected for further analysis. Sampling of water

![Fig. 4. Linear regressions of total concentration of elements in water and total suspended solids (TSS) during two December (dry, open rectangles) and May (wet, open triangles) sampling campaigns.](image-url)
and suspended sediments were executed within two distinct campaigns – one in May and the other in December 2012. May and December have the lowest and highest amount of average monthly precipitation by 34.5 and 121.2 mm, respectively (Nasrabadi et al., 2011). So the campaigns were designed to cover both rainy and dry seasons within the basin. Ten sampling locations were selected in order to cover variability in land use (agricultural, industrial and urban activities), geology and hydrology within the catchment area. Locations largely coincide with locations selected in former studies to allow for comparison of results.

Samples were collected in 500 ml high density polyethylene (HDPE) bottles, which had been carefully washed and rinsed in advance. Water was collected at a certain distance from the riverbed and sufficiently far from the banks, natural or artificial obstacles and turbid water zones. The bottles were first rinsed with river water before being filled. The samples designed for determination of dissolved metal concentration (C_{\text{diss}}) were filtered through 0.45 μm filters, while the ones for determination of total concentrations were not filtered. Filtered samples were then acidified to pH 2 with 1% Merck nitric acid and transported to the laboratory for analysis.

To determine total concentration of metals in water samples (C_{\text{tot}}) a digestion process according to US EPA, Method 3005 (1999) was considered. Each sample was first well shaken for homogenization before a 50 mL sub-sample was taken for digestion and added to a mixture of concentrated (70%) nitric acid and concentrated (40%) hydrochloric acid (1.0 ± 0.1 mol conc. HNO₃ and 0.50 ± 0.05 mol conc. HCl). The samples were then digested for 2–2.5 h at 95 ± 5 °C. Details are well described in US EPA Method 3005.2. Method blank, laboratory control sample and lab duplicates were considered according to the mentioned reference. For each metal, average accuracy values laid within 90–110%. The analysis of metals in final solutions was carried out by an inductively coupled plasma atomic emission spectrometer (ICP-AES) according to EPA – 3005 method. Accuracy was determined by measurement of standards and of duplicates and deviation from standards was less than ±4% for each metal.

The concentration of total suspended solids (TSS) was determined according to Standard methods 2540 D by filtering a defined water volume through a membrane filter (cellulose nitrate 0.45 μm) and weighing the dried residues. Turbidity was analyzed by a nephelometer (Hach 2100N Turbidimeter) and reported in Nephelometric Turbidity Units (NTU). Calibration was based on formazin, which is an aqueous suspension of hydrazine sulfate and hexamethylenetetramine.

For linear regressions in TSS vs. turbidity plots catchment specific slopes (m values) were calculated. For C_{\text{wet}} vs. TSS or turbidity plots element specific intercepts and slopes (C_{0} and C_{\text{wet}} values, respectively) were calculated. For all regression coefficients (slopes and intercepts) standard errors were calculated according to algorithms used in Excel 2013 software. Details of calculations can be found e.g. in Sachs and Hederich (2006).

### 4. Results and discussion

**TSS-turbidity relationships**: Besides the slope value of linear regression (m) and standard errors of the regressions, mean values and standard deviation of TSS/turbidity ratios (m Mean) were also calculated. The overall results (Table 1) are in good agreement with literature data on turbidity-TSS correlations for suspended sediments (e.g. Rüegner et al., 2014), in particular with sampling campaigns which cover a comparable turbidity range and which were performed in catchments with comparable land-use (Ammer and Steinlach in S-Germany as well as the Haraz catchment in Iran were all characterized by a mix of agricultural/urban land-use and forest; Grathwohl et al., 2013; Nasrabadi et al., 2011, respectively).

Table 1 – TSS vs. turbidity relationships from this and similar studies (No.: number of samples; m ± standard error and $R^2$ from...
**Fig. 5.** Linear regressions of total concentration of elements in water and turbidity during two December (dry, open rectangles) and May (wet, open triangles) sampling campaigns.

**Fig. 6.** Comparison of measured (from laboratory analysis) and regression based (intercept from plots) dissolved metal concentrations; *Sr values divided by 10 to fit into scales shown.

**Table 3**

Results from linear regressions shown in Figs. 4 and 5; $C_w$: concentrations of elements in water (intercept ± standard error); $C_{sus}$: concentration in suspended solids (slope ± standard error); $K_d$ is the distribution coefficient $= C_{sus}/C_w$.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Data analyzed</th>
<th>$C_w$ (µg/L)</th>
<th>$C_{sus}$ (mg/kg)</th>
<th>$R^2$</th>
<th>$K_d$ (L/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni TSS based</td>
<td>28 ± 1.1</td>
<td>34 ± 2.1</td>
<td>0.94</td>
<td>1200</td>
<td></td>
</tr>
<tr>
<td>Pb TSS based</td>
<td>5.7 ± 1.0</td>
<td>21 ± 1.9</td>
<td>0.88</td>
<td>3700</td>
<td></td>
</tr>
<tr>
<td>Cd TSS based</td>
<td>3.1 ± 0.2</td>
<td>7.0 ± 0.4</td>
<td>0.95</td>
<td>2200</td>
<td></td>
</tr>
<tr>
<td>Cu TSS based</td>
<td>17 ± 1.5</td>
<td>32 ± 2.9</td>
<td>0.87</td>
<td>1900</td>
<td></td>
</tr>
<tr>
<td>Zn TSS based</td>
<td>69 ± 1.9</td>
<td>45 ± 3.6</td>
<td>0.89</td>
<td>650</td>
<td></td>
</tr>
<tr>
<td>Co TSS based</td>
<td>12 ± 0.3</td>
<td>10 ± 0.7</td>
<td>0.93</td>
<td>830</td>
<td></td>
</tr>
<tr>
<td>As TSS based</td>
<td>78 ± 1.4</td>
<td>34 ± 2.6</td>
<td>0.91</td>
<td>430</td>
<td></td>
</tr>
<tr>
<td>Sr TSS based</td>
<td>482 ± 8.5</td>
<td>210 ± 16.3</td>
<td>0.90</td>
<td>440</td>
<td></td>
</tr>
<tr>
<td>turbidity based</td>
<td>78 ± 1.1</td>
<td>36 ± 2.1</td>
<td>0.94</td>
<td>450</td>
<td></td>
</tr>
<tr>
<td>turbidity based</td>
<td>479 ± 7.8</td>
<td>219 ± 15.0</td>
<td>0.92</td>
<td>460</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 7. Comparison of metal concentrations in suspended solids (C_{suspended}) and bed sediments from Nasrabadi et al. (2010a); *Sr values divided by 10 to fit into scales shown.

linear regressions: \( r_{\text{mean}} \pm \text{ standard deviation represents the average of all TSS/turbidity ratios.} \)

Fig. 3 indicates the good linear correlation between TSS and turbidity in water samples taken during the two events (May and December 2012). A TSS and turbidity range of 202–1212 mg/l and 63–501 NTUs was covered, respectively. Maximum turbidity and TSS values during the rainy season were only slightly increased compared to the dry season although higher rate of precipitation and consequently increased generation of urban and agricultural run-offs in December would suggest increased concentrations. However, it is noteworthy to mention that in both periods the sand mining activities in riverbanks are in progress which may insert a constant TSS concentration in the base flow of the river.

Metal concentrations: Total and dissolved concentrations of eight metals are shown in Table 2. As it is seen element concentrations in samples collected during rainy season show again only slightly higher values in comparison with the samples from the dry season campaign, as also TSS/turbidity values are only slightly increased. Stations 4, 5, 6 and 7 located in central parts of the study area show for most metals higher total concentrations (and partly also dissolved concentrations) of metals than the other locations. This is attributed to more intense riverbank mining activities in this section of the study area and possibly also to other impacts which arise from urban and industrial land use (Figs. 1 and 2).

TSS and/or turbidity - C_{tot} relationships: In a parallel approach TSS and/or turbidity vs. C_{tot} relationships were evaluated in order to calculate dissolved and particle-bound concentrations of mentioned elements through linear regressions as given by Equation (2). Total element concentration versus TSS plots for each element are shown in Fig. 5. Very good linear correlations of TSS and C_{tot} were observed for all elements (Cd, Co, As, Pb, Cu, Ni, Sr and Zn) across all selected locations (R^2 values vary from 0.87 for copper to 0.95 for cadmium). The same holds for linear correlations of turbidity and C_{tot}. These results are plotted in Fig. 6. High values for R^2 (from 0.91 for copper to 0.95 for cadmium) were achieved here. Detailed results for TSS and turbidity based data are shown in Table 3.

The observed correlations not only hold for the two investigated events but also for all locations where samples were taken. This strongly suggest that at least the smaller grain size fraction of the river sediment – which makes up the suspended particle load – shows only little heterogeneity across the middle/lower part of the catchment which was investigated here. As already mentioned, the all season sand/gravel mining activities in the river may have caused a continuous suspended sediment transport over years. Subsequent sedimentation and re-suspension of these fine sediment particles during distinct events might have caused the observed homogenous pattern in pollutant loadings of suspended particles along the lower course of the river. This finding is in contrast to the strong heterogeneity of metal concentrations typically observed in river sediments. Thus, often applied fingerprinting strategies, which use the heterogenous patterns of river sediments for the identification of the particles’ sources (e.g. Franz et al., 2013; Walling, 2013) would not be suited in this or comparable cases or would at least require a thorough proof of feasibility.

To validate the approach, the dissolved concentrations in water C_{w} derived from regression data (Table 3) were compared with the mean concentrations of dissolved metals from direct measurements, both from rainy and dry seasons (Table 2). These data are in very close agreement which is shown in Fig. 6. The error between independently measured and regression based dissolved concentrations for metals are between 0.1 – 8.5% and 0.2–8% for TSS and turbidity-based test attempts, respectively.

In addition, the particulate-bound concentrations C_{suspended} derived from regression data (Table 3) were compared with bed sediments concentrations measured at the same locations in August 2007 (Nasrabadi et al., 2010a; for a grain size fraction < 63 μm). For most metals these data sets are in good agreement (Fig. 7). For As, Cu and Co the difference in reported values is below 10%, while for Pb, Ni and Cd the estimated difference is around 30%. For Zn and Sr concentrations of suspended solids are remarkably lower than concentrations in river bed sediments, 46–82 mg kg\(^{-1}\) and 220–550 mg kg\(^{-1}\), respectively (Nasrabadi et al., 2010b). Whether this is due to heterogeneities in sediment sampling or due to different grain size distributions of suspended and river bed sediments has to be further investigated.

Distribution coefficients (Kd) were calculated by dividing the C_{suspended} values from regressions by the intercept (C_{tot}). These metal specific Kd values reflect geochemical distributions between solid phases and dissolved concentrations and may be considered as an alarming parameter showing the risk level of a toxic element’s bioavailability. In particular when shifted to lower values metals may then show an affinity to be released more easily into water phase. Whether the already relatively low Kd values for elements as As, Co, Zn and Sr observed in this study may be related to increased risks has to be further investigated by geochemical modeling. Remarkably high values of As in river water up to 100 μg l\(^{-1}\) and thus ten times greater than published WHO guidelines of 10 ppb have already been reported within the area (Nasrabadi et al., 2015).

5. Conclusions

Very robust linear regressions were obtained between total element concentrations in water and total suspended solids and turbidity, respectively. Slope and intercept of these regressions correspond to the element concentrations associated with the suspended solids and the dissolved concentration in water. Both, C_{tot} and C_{w} determined form the regressions agree very well with independently measured concentrations in sediment and water samples. The correlations between total concentrations in water and TSS or turbidity hold for all sampling locations over a large spatial scale as well as for wet and dry conditions indicating that suspended solids in the river represent an integral measure of sediment quality in the total catchment. In the Haraz catchment pollutants are mostly of geogenic origin but fluxes are likely enhanced by mining activities which release particles into the river. Further anthropogenic pressures such as agriculture or urbanization were less important for the pollutant fluxes observed. Finally, this new data set confirms earlier correlations of suspended solids and turbidity over large ranges of TSS (202–1212 mg/l) and turbidity (63–501 NTUs). Thus turbidity measurements may serve as easy and low cost proxies not only to monitor suspended solids in rivers, but also to determine fluxes of particle associated...
pollutants such as heavy metals and metalloids in catchments. To our knowledge this is the first study focusing on particle facilitated metal transport at that scale and it would be interesting to compare this results with data from other catchments with different geology, hydrological dynamics and land use.

Acknowledgments

This study was possible through the fruitful collaboration between the corresponding author from University of Tehran, Iran and the research team of WESS, Eberhard Karls Universitaet Tuebingen. The connection was established by a DAAD (Deutsche Akademische Austausch Dienst) scholarship which is highly appreciated by the board of authors. The study was also supported by the EU FP7 Collaborative Project GLOBAQUA (Grant Agreement No 603629).

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