



# Compositional dynamics of suspended sediment in the Rhine River: sources and controls

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## Abstract

**Purpose** Information on the geochemical composition of suspended sediments in rivers is crucial to identify sediment source type or area. In large river basins, however, the relation between sediment composition and its controlling factors is often obscured. This study aims to assess and improve the conceptual understanding on the factors and mechanisms that control the composition of suspended sediments in the River Rhine, one of the large European rivers, and to identify the dominant source types of elements.

**Materials and methods** We performed log-linear regression analysis and principal component analysis (PCA) on bi-weekly monitoring data of suspended sediment composition, supplemented with daily measurements of suspended sediment concentrations (SSC) and discharge at the Lobith monitoring station near the German-Dutch border for the period 2011–2016.

**Results and discussion** The statistical analyses show a consistent grouping of elements that display contrasting temporal variation or different responses to increased discharge. The contrasting behaviour also becomes manifest in the results from the PCA. A first component that explains about the half of the total variance in the entire dataset reflects the variation in clay content in the suspended sediment. A second component reflects anthropogenic pollution and explains about a quarter of the total variance. A third component probably reflects variation in sediment provenance.

**Conclusions** The majority of the temporal variation in suspended sediment composition can be attributed to variations in grain size (clay content), organic matter content, and anthropogenic pollution. Only a minority of the variation can be attributed to variations in the contributions from different upstream source areas. This variation represented by the third and higher components from the PCA can potentially be used for sediment provenance analysis.

**Keywords** Concentration-discharge relationships · Principal component analysis · Rare earth elements · Suspended sediment

## 1 Introduction

The transport of sediment through the river system to seas and oceans is a fundamental process in the denudation of continents and the formation of deltas and coasts (Walling 2006). In

the past decades, the sediment loads in many rivers across the globe have substantially decreased as a consequence of the construction of reservoirs and dams and sediment mining (Syvitski et al. 2005). This has led and leads to severe sediment shortage problems in downstream areas including drowning of deltas and loss of coastal land because the sediment supply is insufficient to compensate land subsidence and sea level rise (Syvitski et al. 2009).

Sediment transported by rivers comprises resistant primary minerals (e.g. quartz, zircon), secondary minerals (e.g. clays, oxyhydroxides and carbonates) produced from physical and chemical weathering of bedrock, and terrestrially derived or internally produced organic matter (Eisma 1993; Viers et al. 2009). The majority of sediment transported in rivers consists of suspended sediment, which is finer than sediment in the bed load modes of transport. As fine sediments generally contain a

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variety of elements other than silicon, the transport of fine suspended sediments contributes significantly to global elemental cycles and the transfer of pollutants from terrestrial to coastal and marine systems (Owens et al. 2005; Walling 2006). The load of sediments and associated substances in rivers is strongly controlled by discharge, not only because the load is the product of concentration and discharge, but also because the sediment concentration generally increases with discharge (Van der Perk 2013). Therefore, discharge events are very important for sediment transport and geochemical fluxes. For example, Ollivier et al. (2015) found that discharge events that represent less than 12% of the time were responsible for 69 to 91% of the annual sediment-associated element fluxes in the Rhône River in France.

Information on the elemental composition of suspended sediments in rivers has demonstrated to be crucial to identify sediment source type or source area (Förstner and Salomons 1980; Collins et al. 1997; Belmont et al. 2011; Haddadchi et al. 2013; Smith and Blake 2016; Collins et al. 2017) or to assess anthropogenic contamination of sediments (Salomons and Förstner 1980; Benson et al. 2016; Zhao et al. 2017). Geographic differences in the element concentrations in suspended sediment are mostly related to differences in parent material, weathering types and rates, river discharge, organic matter content, and additional natural or anthropogenic sources, including inputs of aerosols and diffuse and point source contaminant inputs, between catchments or river basins (Martin and Meybeck 1979; Savenko 2007). The elemental composition of suspended sediment shows generally less variability in time than in space (Nasrabadi et al. 2018; Rügner et al. 2019), although the sediment composition may change considerable in response to individual discharge events (e.g. Vale 1990; Schleichert and Keller 1997; Coynel et al. 2007; Berner et al. 2012; Pulley et al. 2016). Both long- and short-term temporal variations in the suspended sediment composition are mostly linked to variations in sediment supply from different source areas with different bedrock and associated weathering types and rates, variations in direct inputs of anthropogenic contaminants, remobilisation of previously deposited polluted sediments and variations in particle size and organic matter content of the suspended sediment (Van der Weijden and Middelburg 1989; Zwolsman and Van Eck 1999; Quinton and Catt 2007; Ma et al. 2015; Van der Perk 2013; Hamers et al. 2015; Rügner et al. 2019). Thus, to reliably quantify contaminant transport, detailed information on the temporal variation in sediment composition is essential.

The variability of sources of sediments and contaminant inputs into rivers and the transient and intermittent nature of sediment transport cause the relation between observed sediment composition and its controlling factors and processes to become obscured and complex. This particularly applies to large river basins, because of their large variability in sediment and contaminant inputs and relatively long transport distances

along which physical and chemical transformation of the sediment may take place. As a result, the identification of sediment sources becomes complicated. Hence, the selection of appropriate fingerprints and tracers of sediment (e.g. Collins et al. 2010; Smith and Karam Lennard 2018) requires a fundamental insight in the factors and processes that control the composition of sediment in large river basins.

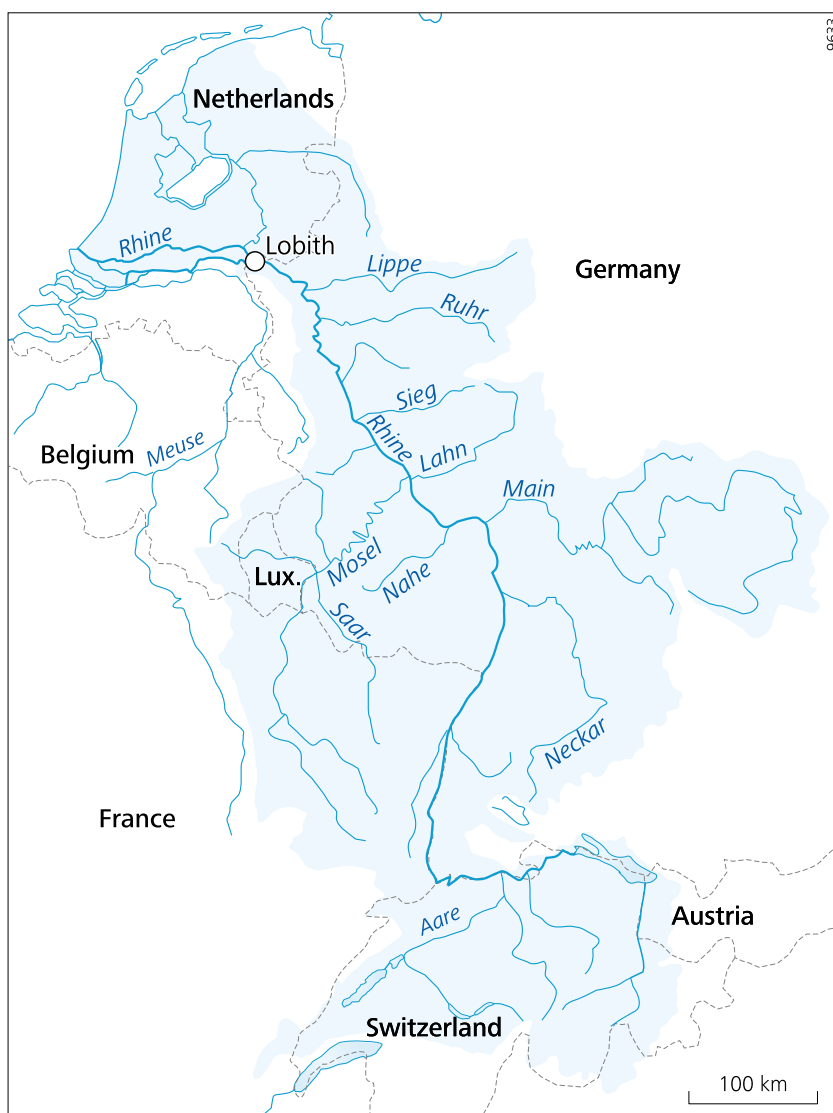
This study aims to assess and improve the conceptual understanding on the factors and mechanisms that control the element composition of suspended sediments in one of the large European rivers, the River Rhine, and to identify the dominant source types of elements (i.e. anthropogenic vs. geogenic sources). For this, we used existing monitoring data on suspended sediment composition in the Rhine River at the Lobith monitoring station in the Netherlands near the German-Dutch border for the period 2011–2016. We related the chemical composition of suspended sediments to discharge and physical sediment parameters including organic carbon and clay content and examined its seasonal variation.

## 2 Materials and methods

### 2.1 Study area

The Rhine River rises in the Swiss Alps and flows through Switzerland along the Swiss-Liechtenstein, Swiss–Austrian, Swiss-German, German-French borders through Germany and the Netherlands into the North Sea (Fig. 1). It has an approximate length of 1230 km (Görgen et al. 2010) and a drainage basin of about 185,000 km<sup>2</sup>. The Rhine River basin covers five geologic-tectonic zones (Preusser 2008; Frings et al. 2014a, b): the Alps, the High Rhine, the Upper Rhine Graben, the Rhenish Massif, the Lower Rhine Embayment and the Rhine Delta. The Alps are primarily made up of Palaeozoic crystalline and metamorphic rocks and Mesozoic and Cenozoic sedimentary (mostly calcareous) rocks which were folded and uplifted during the Alpine orogeny (Cretaceous-Eocene) as a result of the collision of the Adriatic and the European plates. The Upper Rhine Graben and Lower Rhine Embayment were formed due to tectonic subsidence resulting from compressional stresses in relation to the alpine uplift and belong to the European rift System (Preusser 2008). In these areas, the surface geology is characterised by unconsolidated Quaternary sands and gravels. The Upper Rhine Graben is predominantly flanked by Palaeozoic crystalline rocks and Triassic sedimentary rocks. In between the Upper Rhine Graben and Lower Rhine Embayment, the Rhenish Massif forms an upland range largely built up by sedimentary rocks (mostly shales, schists and sandstone) of Devonian and Carboniferous age and which was uplifted following the Alpine orogeny (Preusser 2008).

**Fig. 1** The Rhine River basin



The Rhine delta apex is located near the German-Dutch border. In the Rhine delta zone, the river splits into three major distributaries (Waal, Nederrijn-Lek, and IJssel). The Rhine River has an average discharge of  $2300 \text{ m}^3 \text{ s}^{-1}$  at the German-Dutch border (Uehlinger et al. 2009). Its main tributary rivers are the rivers Aare, Ill, Neckar, Main, Lahn, Moselle and Ruhr. The alpine Rhine represents 19% of the catchment area, but delivers nearly half of the discharge on average (Hartmann et al. 2007); and its discharge is characterized by a snowmelt regime. The discharge regime in mid-mountain ranges and lowland regions feeding the Rhine River downstream the Swiss-German-French border is rain-dominated.

Today, about 58 million people live in the Rhine River basin, of which 60% lives in Germany and 20% in the Netherlands (Uehlinger et al. 2009). Large urban and metropolitan areas and associated industries are located around Basel (Switzerland), Mannheim, Frankfurt/Mainz, between

Cologne and Duisburg (Ruhr area) and around Rotterdam (the Netherlands).

## 2.2 Monitoring data

For this study, we used bi-weekly monitoring data of suspended sediment composition, supplemented with daily measurements of suspended sediment concentrations (SSC) and discharge at the Lobith monitoring station near the German-Dutch border from the regular monitoring programme of Rijkswaterstaat (the water authority of the Dutch Ministry of Infrastructure and Water Management) (Rijkswaterstaat 2019). The basic data is provided in Online Resource 1 (Electronic Supplementary Material). The Lobith monitoring station is the primary monitoring station for discharge and water quality in the Rhine River in the Netherlands. It is located about 5 km upstream from the

location where the Rhine River bifurcates into various distributaries.

Sampling, storage, preparation and analysis of suspended sediment are carried out according to standard protocols, which are summarised in Table 1 and described in further detail by Epema and Zimmelink (2017). Water samples for the measurement of SSC are collected daily from the thread of the river and transported and stored in 1000 ml polyethylene bottles under cool (about 4 °C) and dark conditions. In the laboratory, the water samples are filtered through a 0.45-µm membrane filter and dried at 105 °C. Bi-weekly suspended sediment samples for physico-chemical analysis are collected using a continuous flow centrifuge (17,000 rotations per minute; flow rate 1000 ± 40 L s<sup>-1</sup>). The suspended sediment samples are transported and stored in 800-ml glass bottles under cool and dark conditions. In the laboratory, the samples are freeze-dried and homogenised. Aliquots are taken for the determination of the grain size distribution and organic carbon content, and elemental analysis using ICP-MS (see Table 1). The aliquot for elemental analysis is milled and about 250 mg is subsequently, digested using 10 ml ultrapure nitric acid in a microwave at 150 °C. Grain size analysis is performed after removal of organic matter, carbonates and free iron oxide.

The compositional data used in this study included clay (< 2 µm) and organic carbon content and concentrations of the following 53 elements including trace metals and rare earth elements (REEs): Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U, Ti, Zr, V, Nb, Cr, Mo, W, Mn, Fe, Co, Ni, Cu, Ag, Zn, Cd, Hg, Al, Ga, Tl, Ge, Sn, Pb, P, As, Sb and Te. We used the available data for the period 2011–2016 (*n* = 153), since 2011 the chemical composition analysis of suspended sediments has been extended to include REEs and other trace elements. This period is hydrologically characterised by the occurrence of five discharge events with peak discharges greater than 6000 m<sup>3</sup> s<sup>-1</sup> (recurrence time approximately 2 years (Hegnauer et al. 2014)), of which one had a peak discharge of greater than 8000 m<sup>3</sup> s<sup>-1</sup> (recurrence time approximately 9 years)

(Fig. 2), and a mean discharge of 2190 m<sup>3</sup> s<sup>-1</sup>, which is slightly lower than the long-term mean discharge.

### 2.3 Concentration rating curves

The response of the elemental composition of suspended sediment to discharge variations was explored using a rating curve approach. A rating curve represents a concentration–discharge relationship, which generally take the form a power-law function

$$C = \alpha Q^\beta \tag{1}$$

Where *C* = concentration (usually expressed in mg l<sup>-1</sup>); *Q* = river discharge (usually expressed in m<sup>3</sup> s<sup>-1</sup>),  $\alpha$  and  $\beta$  are the rating curve parameters.

Rating curves are traditionally used to estimate suspended sediment concentrations (Colby 1956; Walling 1977; Asselman 2000; Syvitsky et al. 2000), solute concentrations from discharge measurements (Carling 1983; Moatar et al. 2017; Rose et al. 2018), but the same approach can also be used to predict the concentrations of substances on suspended sediment (Droppo and Jaskot 1995; Rondeau et al. 2005), which are usually expressed in mg kg<sup>-1</sup>.

The rating curve parameters  $\alpha$  and  $\beta$  were estimated using linear regression between the log-transformed (base 10) concentrations and the log-transformed discharge. Parameter  $\alpha$  was bias-corrected according to Ferguson (1986):

$$\alpha = 10^a \times \exp(2.65 s^2) \tag{2}$$

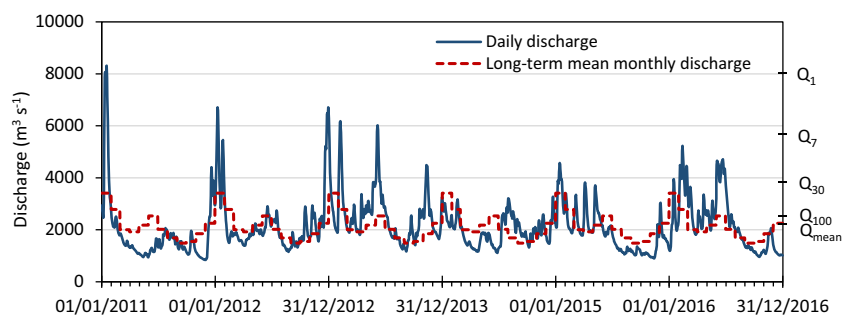
Where *a* = the intercept of the regression line (log *C* = *a* +  $\beta$  log *Q*) and *s* = standard error of the regression.

The residuals of the rating curve were related to the sediment physical parameters including organic matter and clay content and were monthly averaged to examine the seasonal variation in the concentration–discharge relation.

**Table 1** Short description of measurement and analysis methods of discharge and suspended sediment concentration and composition in the Rhine River at the Lobith monitoring station. For a detailed description of

the procedures of sampling, storage, preparation and analysis, see Epema and Zimmelink (2017) and references therein

Parameter	Unit	Protocol	Short description
Discharge	m <sup>3</sup> s <sup>-1</sup>		Discharge–stage relationship
Suspended sediment concentration (SSC)	mg l <sup>-1</sup>	NEN 6484	Filtration through a 0.45 µm membrane filter
Clay (< 2 µm) content in suspended sediment (SS)	%	NEN 5753	Determination of grain size distribution by pipet method
Organic C in SS	%	NEN 5756	Measurement of carbon dioxide formation after dry combustion after removal of carbonates
Element concentrations including trace metals (except Hg), REEs, and Total P in SS	mg kg <sup>-1</sup>	ISO 17294-2	Inductively coupled plasma mass spectrometry (ICP-MS)
Hg concentration in SS	mg kg <sup>-1</sup>		Cold-vapour–isotope dilution-ICP-MS



**Fig. 2** Daily and long-term mean monthly discharge at the Lobith monitoring station for the period 2011–2016. For reference, the following long-term (1901–2016) statistics are plotted on the secondary y-axis: average discharge ( $Q_{\text{mean}}$ ) and the discharge with an exceedance

frequency of  $100 \text{ d y}^{-1}$  ( $Q_{100}$ ) (corresponding to an exceedance probability of 27.4%),  $30 \text{ d y}^{-1}$  ( $Q_{30}$ ) (8.2%),  $7 \text{ d y}^{-1}$  ( $Q_7$ ) (1.9%) and  $1 \text{ d y}^{-1}$  ( $Q_1$ ) (0.3%)

## 2.4 Principal component analysis

To identify the primary processes controlling the temporal variation in the chemical composition of suspended sediment and their relative contribution to the total variation in the data, a principal component analysis (PCA) was conducted using the R-stats package (version 3.4.3) princomp function (R Core Team 2017). The PCA based was performed on the correlation matrix, which is equivalent to a PCA on the Z-normalised concentrations (i.e. with zero mean and unit variance). At first instance, we performed the PCA on the untransformed element concentrations. This approach implicitly assumes that the sediment composition is primarily controlled by linear mixing of different sediment sources and that geochemical transformation processes during transport including weathering, which may give rise to non-linear deviations from the linear mixture, play a minor role. Transformation of the concentration data, e.g. by taking their natural logarithm or by Al-normalisation would violate this assumption. As concentration data are essentially compositional (closed) data (Aitchison 1986), the application of statistical methods to untransformed concentration data may be problematic. In order to apply any statistical method, the data should fulfil the conditions of scale invariance and subcompositional coherence (Pawlowsky-Glahn et al. 2007). In our study, these conditions are largely met because the concentration data were obtained using standard protocols and expressed in standard units of measure, i.e. dry-weight concentrations in the entire suspended sediment sample. Furthermore, closed concentration data are subject to simplex constraints, which makes the concentrations of mutually dependent. A preliminary evaluation of the concentrations data used for our study shows that the oxides of all above elements only represent a minor proportion ( $23.3\% \pm 1.9\%$  of the total weight) of the sediment. This implies that the effect of this constraint on the mutual dependence of the concentrations is limited.

For comparison, we also performed a PCA on the concentration data normalised to Al and organic C. Normalisation to Al was achieved by calculating the dimensionless element/Al ratio. Normalisation to organic C was achieved by calculating:

$$C_{\text{norm}_{OC}} = \frac{(100 - 2 \times \overline{OC}) \times C}{(100 - 2 \times OC)} \quad (3)$$

Where  $C_{\text{norm}_{OC}}$  = organic-C-normalised concentration ( $\text{mg kg}^{-1}$ ),  $\overline{OC}$  = average organic C content of all sediment samples (%),  $OC$  = average organic C content (%), and  $C$  = element concentration ( $\text{mg kg}^{-1}$ ).

## 3 Results

### 3.1 Monitoring data

Table 2 shows the means, standard deviations and correlation matrix of the monitoring data including the element concentrations (arranged according the columns of the periodic table of elements), river discharge, SSC, and the clay and organic C of the suspended sediment. For comparison, the mean and standard deviations of the element concentrations (except Be and Ag) in the world rivers (Viers et al. 2009) are also listed. A limited selection of bivariate scatter plots of element concentrations is presented in Online Resource 2 (Electronic Supplementary Material).

The scatter plots displayed in Online Resource 1 (Electronic Supplementary Material) show that the elements are approximately linearly related, particularly those elements that are mutually positively correlated. The correlation matrix reveals a number of visually distinct groups of elements that display mutually positively correlated patterns of temporal variation. The most notable group consist of the elements Li, K, Rb, Cs, Be, Mg, Y, Ce, Br, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Th, U, V, Fe, Co, Ni, Al, Ga and Tl, which are traditionally linked to clay minerals. These elements are



moderately to strongly positively correlated with clay content and moderately to strongly negatively correlated with organic C content. Furthermore, they are moderately to strongly negatively correlated to Ca and Sr. A second group of elements is characterised by a similar, but weaker correlation to clay and organic C content (Na, Ba, La, Sm, Ti, Zr, Nb and Cr). A third group consists of the elements Mo, W, Mn, Cu, Ag, Zn, Cd, Hg, Sn, Pb, As, Sb, Te, which are usually associated with pollution. These elements are generally weakly negatively correlated with the clay content of the suspended sediment. The fourth group, which consists of the mutually strongly correlated elements Ca and Sr, which are, in turn, moderately negatively correlated with clay content and the above group of elements linked to clay minerals. P forms a fifth group characterised by a strong positive correlation with organic C.

### 3.2 Relation with discharge

Table 3 lists the rating curve parameters and the coefficient of determination ( $R^2$ ), standard error and the  $p$ -value of the regression between the log-transformed concentration and log-transformed discharge. Figure 3 depicts the concentration–discharge relations including the fitted rating curves, for the elements that show a significant positive relationship (i.e. a positive value of  $\beta$  that significantly deviates from zero at a significance level of 0.05) (Fig. 3a), a significant negative relationship (Fig. 3b), and a non-significant relationship with discharge (Fig. 3c). The elements that show a positive value of  $\beta$  belong in most cases to above group of elements that are traditionally linked to clay minerals. The clay content of suspended sediment also shows a positive value of  $\beta$  (i.e. clay content increases with discharge), whereas the organic matter content shows a negative value of  $\beta$ . The elements that show a negative value of  $\beta$  belong in most cases to above group of elements that are traditionally associated with pollution.

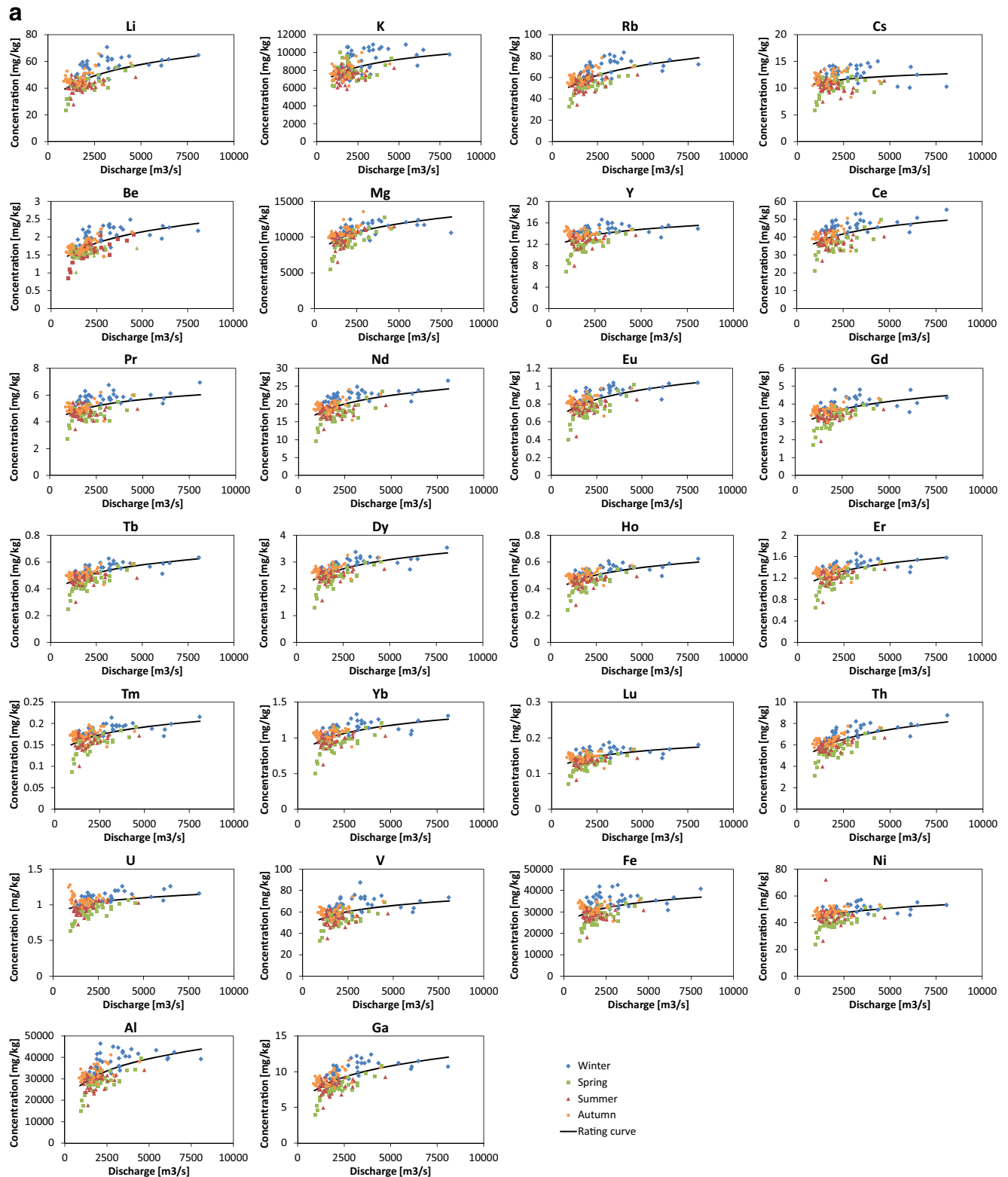
In general, the residuals of the relation between the elemental concentration and discharge (see Fig. 3) display a seasonal pattern with positive residuals (i.e. predicted concentrations using the power-law rating curve greater than the observed concentrations) during spring and summer months (April–September) and negative residuals during autumn and winter (October–March). Especially for group of the elements that are linked to clay minerals, the residuals are negatively correlated to clay ( $< 2 \mu\text{m}$ ) content (correlation coefficients generally between  $-0.25$  and  $-0.5$ ) and positively correlated to organic C content (correlation coefficients generally between  $0.4$  and  $0.6$ ). The rating curve residuals of the Ca and Sr show a different seasonal pattern and are generally positive between January and April and negative during the rest of the year.

**Table 3** Rating curve parameters  $a$  and  $b$  and the coefficient of determination ( $R^2$ ), standard error (S.E.) and the  $p$ -value of the regression between the log-transformed concentration and log-transformed discharge

Element	$a$	$b$	$R^2$	S.E.	$p$ -value
Li	8.6	0.224	0.316	0.062	$< 0.001$
Na	2809	$-0.220$	0.254	0.071	$< 0.001$
K	2866	0.137	0.193	0.053	$< 0.001$
Rb	13.2	0.198	0.288	0.059	$< 0.001$
Cs	6.45	0.075	0.045	0.065	0.008
Be	0.32	0.222	0.343	0.058	$< 0.001$
Mg	3089	0.158	0.285	0.048	$< 0.001$
Ca	1034640	$-0.367$	0.373	0.090	$< 0.001$
Sr	1898	$-0.302$	0.496	0.058	$< 0.001$
Ba	4682	$-0.333$	0.328	0.091	$< 0.001$
Y	6.23	0.101	0.120	0.052	$< 0.001$
La	658	$-0.337$	0.389	0.080	$< 0.001$
Ce	13.7	0.142	0.201	0.054	$< 0.001$
Pr	1.92	0.127	0.173	0.053	$< 0.001$
Nd	5.60	0.163	0.245	0.054	$< 0.001$
Sm	5.66	$-0.005$	0.000	0.094	0.896
Eu	0.23	0.168	0.263	0.053	$< 0.001$
Gd	1.07	0.159	0.220	0.057	$< 0.001$
Tb	0.15	0.159	0.275	0.049	$< 0.001$
Dy	0.77	0.164	0.279	0.050	$< 0.001$
Ho	0.16	0.147	0.236	0.050	$< 0.001$
Er	0.42	0.147	0.226	0.052	$< 0.001$
Tm	0.06	0.142	0.223	0.050	$< 0.001$
Yb	0.34	0.145	0.217	0.053	$< 0.001$
Lu	0.05	0.136	0.172	0.057	$< 0.001$
Th	1.50	0.188	0.318	0.052	$< 0.001$
U	0.53	0.086	0.100	0.049	$< 0.001$
Ti	1885	$-0.160$	0.158	0.070	$< 0.001$
Zr	8.2	$-0.008$	0.000	0.145	0.904
V	21.7	0.130	0.153	0.058	$< 0.001$
Nb	0.64	0.038	0.005	0.099	0.376
Cr	157	$-0.106$	0.099	0.061	$< 0.001$
Mo	3.09	$-0.142$	0.072	0.097	0.001
W	1.35	$-0.241$	0.133	0.117	$< 0.001$
Mn	6345	$-0.165$	0.182	0.066	$< 0.001$
Fe	12231	0.123	0.137	0.058	$< 0.001$
Co	13.5	0.017	0.003	0.054	0.471
Ni	21.1	0.103	0.116	0.054	$< 0.001$
Cu	458	$-0.261$	0.295	0.077	$< 0.001$
Ag	14.0	$-0.431$	0.454	0.090	$< 0.001$
Zn	6265	$-0.351$	0.425	0.077	$< 0.001$
Cd	149	$-0.632$	0.523	0.114	$< 0.001$
Hg	506	$-0.923$	0.725	0.108	$< 0.001$
Al	5847	0.224	0.297	0.065	$< 0.001$
Ga	1.60	0.224	0.303	0.065	$< 0.001$
Tl	0.40	0.025	0.004	0.077	0.445
Ge	0.06	0.088	0.004	0.255	0.422
Sn	124	$-0.552$	0.310	0.156	$< 0.001$
Pb	1638	$-0.412$	0.444	0.087	$< 0.001$
P	7172	$-0.179$	0.064	0.130	0.002
As	78.2	$-0.208$	0.297	0.061	$< 0.001$
Sb	2.98	$-0.286$	0.239	0.097	$< 0.001$
Te	0.63	$-0.259$	0.204	0.097	$< 0.001$

### 3.3 Principal component analysis

Table 4 summarises the results of the principal component analyses on the untransformed element concentrations (Table 4a), the Al-normalised concentrations (Table 4b) and the organic C-normalised concentrations (Table 4c). The PCA



**Fig. 3 a** Concentration-discharge relations of elements showing a significant positive relation with discharge. The different colours represent the seasons during which the samples were collected: winter (January–March), spring (April–June), summer (July–September) and autumn (October–December). **b** Concentration-discharge relations of elements showing a significant negative relation with discharge. The different colours represent the seasons during which the samples were

collected: winter (January–March), spring (April–June), summer (July–September) and autumn (October–December). **c** Concentration-discharge relations of elements showing neither a significant positive relation nor a significant negative relation with discharge. The different colours represent the seasons during which the samples were collected: winter (January–March), spring (April–June), summer (July–September) and autumn (October–December)



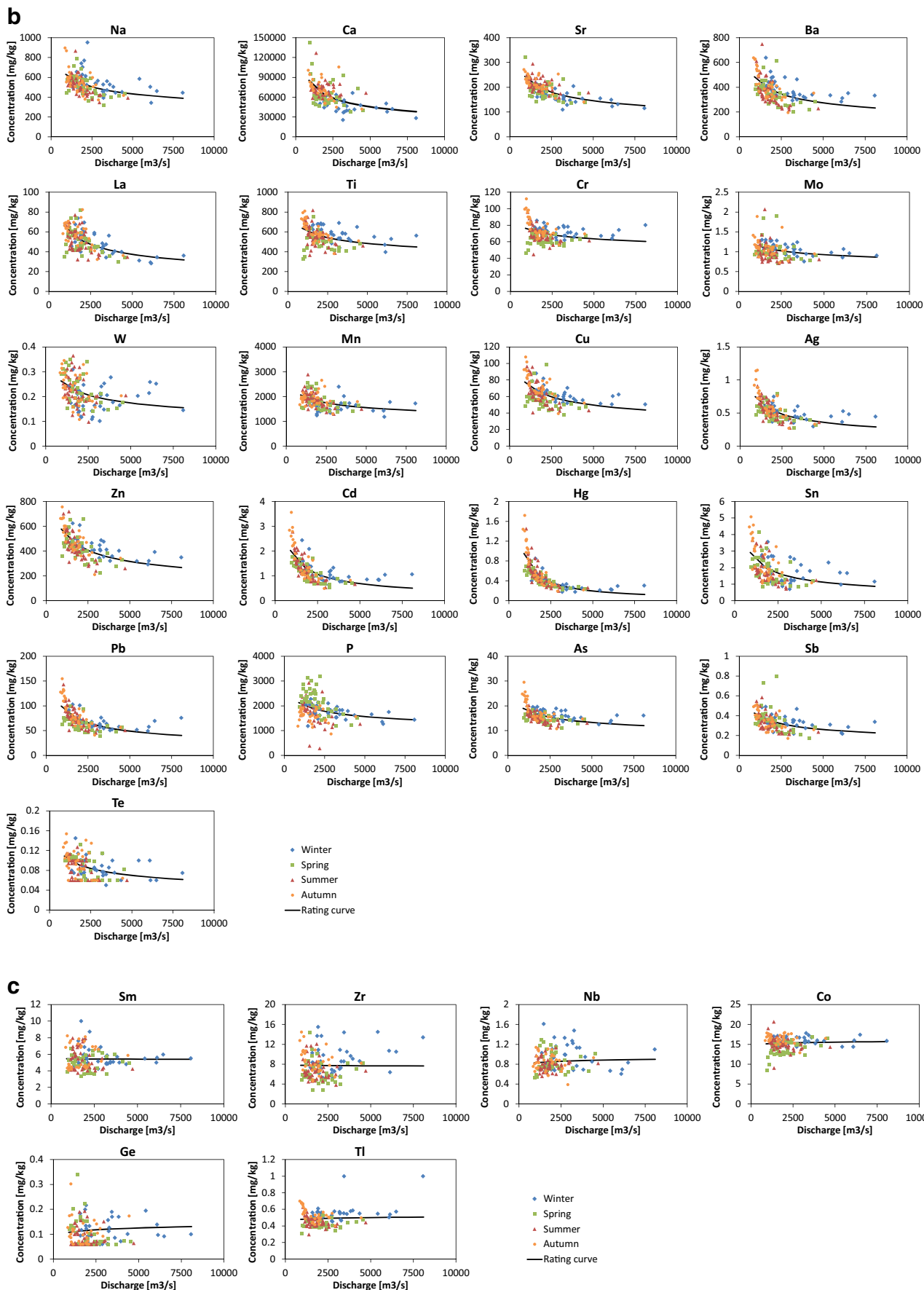


Fig. 3 (continued)

**Table 4** Results of PCA of element concentrations in suspended sediment in the Rhine River

	Component 1	Component 2	Component 3	Component 4	Component 5
<b>a. Not-normalised concentrations</b>					
Proportion of variance explained	0.460	0.234	0.059	0.046	0.024
Elements with positive loadings Values > 0.20	–	Ba, Ti, Cr, Cu, Ag, Zn, Cd, Hg, Sn, Pb, As, and Sb	Nb (+0.36)	K, Nb, Mo, Mn, P (+0.47), Sb	Sm (+0.54), W, Mn, Co, Ni
Values between 0.15 and 0.20	–	Na, La, W, Mn, and Te	Co	–	Mo
Elements with negative loadings Values < -0.20	–	–	Na, K, Sm, Zr (-0.39), W, and Sn (-0.30)	Mg, Ca (-0.37), and Sr (-0.31)	K, Ti, and Nb
Values between -0.15 and -0.20	Li, K, Rb, Cs, Be, REEs (except La and Sm), Fe, Co, Ni, Al, Ga, Tl	–	–	–	Rb, V, Tl, and Sb
Relations with component scores	–	–	–	–	–
Q	$r = -0.48; p < 0.001$	$r = -0.59; p < 0.001$	n.s. ( $p > 0.10$ ), but scores seem to show a delayed negative response	n.s. ( $p > 0.10$ )	n.s. ( $p > 0.10$ )
Clay (<2 µm) Org. C	$r = -0.63; p < 0.001$ $r = 0.61; p < 0.001$	$r = -0.28; p < 0.001$ $r = 0.14; p < 0.1$	n.s. ( $p > 0.10$ ) n.s. ( $p > 0.10$ )	$r = 0.21; p = 0.008$ $r = 0.68; p < 0.001$	n.s. ( $p > 0.10$ ) n.s. ( $p > 0.10$ )
Remarkable trends in component scores	–	–	Jumpwise increase in early 2013	–	Jumpwise decrease in early 2014
Long-term trend	–	–	–	–	–
Seasonality of monthly averaged scores	Strong seasonality with negative values between October and March and positive values between April and September with a peak in May	Weak, but clear seasonal pattern with generally negative values from January through August and positive values from September through December	–	Weak, but clear seasonal trend with positive values from January through June with a peak in April and negative values in the second half of the year	Weak seasonal trend with negative values from January through May and positive values from August through December
<b>b. Al-normalised concentrations</b>					
Proportion of variance explained	0.523	0.137	0.058	0.041	0.035
Elements with positive loadings Values > 0.20	–	Zr and Sn	Li, K (0.37), Rb, Mg, Ca, Sm, and P	Ca, Sr, Nb (0.31), and Mn	Mg (0.33), Ca, Sr, U
Values between 0.15 and 0.20	–	Ba, W, Sb, and Te	Sr, Th, and W	Mg, La, P, and Sb	K, Hg, and Ga
Elements with negative loadings Values < -0.20	–	–	–	–	Nb, Mo, Ge, P (-0.32), and Sb
Values between -0.15 and -0.20	majority of metals	REEs except La, Pr, and Sm	Contaminant metals Cr, Cu, Ag, Zn, Cd, Hg, Pb	Nd, Th, and Sn	K, Be, Ce, and Pr

Table 4 (continued)

	Component 1	Component 2	Component 3	Component 4	Component 5
Relations with component scores					
Q	$r = 0.60; p << 0.001$	$r = -0.33; p << -0.001$	$n.s. (p > 0.10)$	$r = -0.21; p = 0.009$	$r = -0.23; p = 0.004$
Clay (<2 $\mu\text{m}$ )	$r = 0.49; p << 0.001$	$r = -0.23; p = 0.004$	$n.s. (p > 0.10)$	$r = -0.31; p << 0.001$	$n.s. (p > 0.10)$
Org. C	$r = -0.44; p << 0.001$	$r = 0.30; p << 0.001$	$r = 0.31; p << 0.001$	$r = 0.26; p = 0.001$	$r = -0.58; p << 0.001$
Remarkable trends in component scores					
Long-term trend	–	Jumpwise decrease in early 2013	Slightly decreasing trend	Slight jumpwise increase in April 2014	–
Seasonality of monthly averaged scores	Strong seasonality with large positive values during January and February and generally negative values between April and September	–	Weak but clear seasonal trend with positive values from March to August and negative values from September to February	Weak but clear seasonal trend with positive values from April to August and generally negative values from September to March	Weak but clear seasonal trend with negative values from January through June and positive values during the second half of the year
<b>c. Organic-C-normalised concentrations</b>					
Proportion of variance explained	0.440	0.244	0.055	0.063	0.044
Elements with positive loadings	–	Ba, Ti, V, Cr, Cu, Ag, Zn, Cd, Hg, Sn, Pb, As, and Sb	Nb	Nb, Mo, Mn (0.33), P (0.48), and Sb	Sm (0.44), W, Ni, and Ge
Values > 0.20	–	Na, La, W, Mn, and Te	Co	K	Co
Values between 0.15 and 0.20	Ca	–	–	–	–
Elements with negative loadings	–	–	Na, K (-0.33), Sm, Zr (-0.39), and Sn	Ca	K, Rb, La, Ti, and Nb
Values < -0.20	Li, Rb, Cs, Be, Y, majority of REEs (except La and Sm), V, Fe, Al, and Ga	–	Li, W, and Te	Mg, Sr, U, Cr, and Hg	V, Al, and Sb
Relations with component scores					
Q	$r = -0.48; (p << 0.001)$	$r = -0.59; (p << 0.001)$	$n.s. (p > 0.10)$	$n.s. (p > 0.10)$	$r = 0.18; (p = 0.02)$
Clay (<2 $\mu\text{m}$ )	$r = -0.65; (p << 0.001)$	$r = -0.26; (p < 0.001)$	$n.s. (p > 0.10)$	$n.s. (p > 0.10)$	$n.s. (p > 0.10)$
Org. C	$r = 0.41; (p << 0.001)$	$r = 0.28; (p < 0.001)$	$n.s. (p > 0.10)$	$r = 0.71; (p << 0.001)$	$n.s. (p > 0.10)$
Remarkable trends in component scores					
Long-term trend	–	–	Increase in second half 2012 / early 2013	–	Jumpwise decrease in April 2014
Seasonality of monthly averaged scores	Strong seasonality with negative values between November and March and positive values between April and October	–	–	Weak but clear seasonal trend with positive values from February to June and negative values during the rest of the year	–

of the untransformed concentrations yields five components that explain 82.4% of the total variance in the dataset. The remaining components explain less than 2.5% of the total variation each; the sixth component (2.4% explained variance) is mainly determined by La (loading 0.47). The PCA of the Al-normalised concentrations yields five components that explain together 79.4% and the PCA of organic C-normalised element concentrations five components that explain 81.7% of the total variance in the respective data sets.

The PCA results show a consistent pattern of components representing similar behaviour with groups of elements and different behaviours between these groups. The similar components are indicated by different colour shadings in Table 4 and are described and explained in further details below.

The first component for all PCA analyses, which explains between 44 and 53% of the total variance in the data sets, represents the variation in the concentrations of especially REEs (except La and Sm) and other metals that are significantly positively related to discharge and clay content and significantly negatively to organic matter content. The concentrations of these metals show a strong seasonal trend with lower concentrations during summer than during winter. The Al-normalised concentrations of these metals show opposite relations with discharge, clay content, organic matter content, and season.

A second component (third component for the Al-normalised concentrations) represent the variation in the contaminant metals Cr, Cu, Ag, Zn, Cd, Hg, Sn and Pb. Other elements that have relatively high loadings on this factor include Ba, La, Ti, Sb, and As. This component explains about 24% of the total variance in the data sets for the not-normalised and organic-C-normalised concentrations, but only about 6% for the total variance in the data set for Al-normalised concentrations. The component scores for the not-normalised and the Al-normalised concentrations show a weak seasonal trend whereas the scores for the organic-C-normalised do not show any seasonal variation.

The third component (second component for the Al-normalised concentrations) represents the variation of the concentrations of Zr, Sn, Nb and Co in particular. This third component explains about 5.5% of the total variance in the data sets for the not-normalised and organic-C-normalised concentrations and about 14% for the total variance in the data set for Al-normalised concentrations. The component scores for the not-normalised and organic C-normalised concentrations are not statistically significantly related to discharge, clay and organic matter. However, the component scores of the Al-normalised concentrations are significantly related to these variables. Furthermore, this component is characterised by a ‘jumpwise’ shift in early 2013, which represents an increase in Nb concentrations and a decrease in Zr and, to a lesser extent, Sn concentrations.

The fourth component (fifth component for the Al-normalised concentrations) represents a large part of the variation in P concentrations and explains between 3.5 and 6.3% of the total variance in the data sets. The component scores are relatively strongly related to the organic C content of the suspended sediment and show a weak but clear seasonal trend with high values from January through June, with a maximum in April, and relatively low values during the second half of the year.

The remaining fifth component for the not-normalised and the organic-C-normalised concentrations represents the variations in Sm, W, Ni, Co, K, Ti, Rb, Nb, V and Nb concentrations. This component explains only 2.4% and 4.4% of the total variance in the respective data sets. The component scores are characterised by a jump-wise decrease in early 2014. Although scores of the fourth component for the Al-normalised concentrations are also characterised by a shift in early 2014, the elements contributing to this fourth component are different from the elements contributing to the fifth component for the other data sets.

## 4 Discussion

In general, the average elemental concentrations in Rhine suspended sediment are generally well within the range reported for the world rivers (Viers et al. 2009), although they are slightly lower than the average concentrations in the world rivers. Exceptions are Zn and Pb, which have higher average concentrations in the Rhine River than in the world rivers, which may likely be attributed to legacy and current anthropogenic pollution in the Rhine catchment (Middelkoop 2000; Vijver et al. 2008). Ti, Zr, and Nb are also exceptions, but these elements have substantially lower concentrations in the Rhine River than in the world rivers. The precise reason for this deviation is unknown, but it might be due to the difference in analytical method and the digestion procedure in particular. The Rhine suspended sediment samples are digested using nitric acid, which may not dissolve the total amount of these elements in the sample. The digestion procedures in the database of the chemical composition of suspended sediments in the world rivers is not reported by Viers et al. (2009).

The results of our data analyses on the elemental concentrations in suspended sediment shows a consistent grouping of elements that display contrasting temporal variation reflected in different seasonal or long-term variations or different responses to increased discharge. This contrasting temporal behaviour becomes manifest in the results from the PCA. The first component from the PCA represents the variation in the concentrations of elements that are generally associated with fine-grained inorganic mineral fraction of suspended sediment (Luoma and Rainbow 2008; Van der Perk 2013). This becomes manifest in a moderate-to-strong positive correlation

between these elements and clay content (particle size < 2  $\mu\text{m}$ ) and a moderate-to-strong negative correlation with organic C content. Note that the correlation of the component scores with clay and organic matter content have the opposite sign. The elements represented by this first component show a positive relation between their concentration in suspended sediment and discharge, which may be attributed to an increased supply of fine-grained clastic matter to and mobilisation in the river channel network during periods of increased discharge. The elements thus likely originate from diffuse, primarily geogenic sources. The negative correlation of the element concentrations with organic C and the seasonal variation of the residuals of the concentration-discharge relation is probably caused by primary production of organic C, which dilutes the inorganic fraction and associated elements in the suspended sediment (Winkels et al. 1998; Hamers et al. 2015). Assuming the organic matter content of suspended sediment is twice the organic C content, the dilution factor due to variations in organic C varies between about 1.09 and 1.15. Moreover, the concentrations of clay-associated elements are negatively correlated to the Ca and Sr concentrations, which may be explained by dilution of the clay-associated element concentrations by calcite precipitation. This process may contribute to the above seasonality in concentrations and residuals.

Notably, normalisation of the element concentrations to Al or organic C—and the subsequent Z-normalisation of the Al and organic C normalised concentrations—does not result in a substantial decrease in the proportion explained by the first component associated with variations in clay-associated elements. Apparently, the variations in Al and organic C do not fully represent the variation in metal concentrations due to the content of clay minerals and the clay effect remains persistent in the normalised concentrations.

The second component for the not-normalised concentrations represents the variation in the concentrations of contaminant elements including Cr, Cu, Zn, Cd, Hg and Pb, which are adsorbed to both organic and inorganic fractions of suspended sediment (Luoma and Rainbow 2008; Kulaksız and Bau 2011; Van der Perk 2013). These contaminant elements are largely derived from point source discharges into the river network (Vink and Behrendt 2002). Their concentrations generally show a negative relation with discharge, a weak negative relation to clay content, and a weak positive relation to organic C content. This opposite response compared with the above first group of elements may also be attributed to inputs of relatively uncontaminated clastic material during periods of increased discharge. These inputs dilute the contaminant concentrations in suspended sediments. The fact that the relation to organic C is only weak is likely the result of variation in the organic C content of suspended sediments due to internal primary production.

The third component is characterised by a jump-wise shift in concentrations in early 2013 indicating a breakthrough of sediment relatively rich in Nb and relatively poor in Na, K, Sm and Zr. The origin of this breakthrough event is more difficult to interpret. It could be the result of a sudden input of sediment due to a past hydrologic event or human intervention in the river system, for example the recurrent addition of sediment in the upstream German reach of the Rhine River to counteract channel incision (Frings et al. 2014a, b). Although the added sediment consists of coarse material, abrasion of this sediment could lead to a shift in the elemental composition of the fine fraction that is transported in suspension. To test the above hypothesis requires information on the geochemical composition of the artificially added sediment and its derivatives.

The fourth component for the not-normalised concentrations is dominated by the variation in P concentrations and is characterised by a strong positive correlation with organic C content and a weak but significant positive correlation with clay content. The seasonal pattern of the PCA scores with high values during spring together with the absence of a significant correlation with discharge suggests that this component represents the inputs of P-rich terrestrial organic matter through soil erosion processes rather than P inputs from sewage treatment plants or sewage overflows. During spring, the supply of sediments and particulate P to the River Rhine reaches its maximum value because of the high soil moisture levels and bare fields (Van Dijk 2001; Schulz and Bischoff 2008). The concomitant inputs of inorganic and organic soil particles may explain the positive correlation with clay content. Furthermore, the negative loadings of Ca, Mg and Sr on the fourth component indicate that during winter and spring, the supply of the P-rich terrestrial organic matter coincides with a decreased contribution of sediments from the Swiss part of the Rhine basin, where the concentrations of these elements in stream sediment are higher than in the German part of the basin. This suggests that the terrestrial organic matter is mainly derived from the German part of the catchment. Calcite dissolution during winter and precipitation during summer may also contribute the seasonal pattern of the PCA scores (Van der Weijden and Middelburg 1989), although the peak and trough of the PCA scores are three months later than the expected maxima of calcite dissolution and precipitation.

This study can be seen as an update of the study by Van der Weijden and Middelburg (1989), who performed a similar multivariate analysis on the geochemical composition of suspended sediment in the Rhine at Lobith for the period between 1975 and 1981. However, their data set was less extensive in terms of the number of elements analysed. In their 1980s study, Van der Weijden and Middelburg (1989) distinguished four factors which together explained 75% of the total variation: (1) heavy metals (47.0%), (2) clays (11.5%), (3) calcium carbonate (8.8%) and (4) manganese oxides (7.9%). The first factor identified in the 1980s study

is comparable with our second component and can mainly be attributed to variation in sediment composition due to anthropogenic inputs, i.e. pollution. This factor was explained by the dominant decreasing trend in pollution in the late 1970s and early 1980s. Nowadays, such trend is absent and the variation in contaminant metals are primarily due to discharge variations and related variations of inputs of relatively uncontaminated sediment. The second factor in the 1980s study is comparable with our first component. The fact that our first and second factor are in reversed order in comparison with the first two factors identified in the 1980s study can probably be largely attributed to the fact that during the 1970s, the contaminant concentrations in suspended sediment were subject to larger variations associated to the aforementioned pollution trend and a possibly stronger negative response of contaminant concentrations to discharge events. Furthermore, a larger number of elements associated with clay minerals and less affected by anthropogenic pollution were taken in to consideration in our analysis compared with the 1980 study. This could also contribute to the reversal of the order of the factors. The third (calcium carbonate) and fourth (manganese) factors identified in the 1980 study were not found in this study as separate principal components. The calcium carbonate and manganese factors were subject to strong seasonality and likely driven by eutrophication processes. The reason that these factors did not become manifest in our PCA may be attributed to the strong decline in eutrophication in the River Rhine since the 1980s (Hartmann et al. 2007). Thus, comparison of our results with the precursor study by Van der Weijden and Middelburg (1989) demonstrates that anthropogenic pollution strongly affects the compositional dynamics of suspended sediment in rivers. Although the contamination levels in the Rhine River have been substantially reduced since the 1970s and 1980s (Hartmann et al. 2007; Van der Perk 2013), the pollution factor (second component for the not-normalised concentrations) still accounts for a considerable proportion of the variation in suspended sediment composition.

Data presented by Le Meur et al. (2016) for various measurement locations in the French Mosel River (a major tributary of the Rhine River in France and Germany) and its tributaries generally show a similar response of element concentrations to discharge variations. The element concentrations in suspended sediment in the Mosel catchment show generally positive responses for REEs and a negative response for the contaminant metals Cu, Pb, Cd and Zn (Le Meur et al. 2016). Negative responses of Cu concentrations in the Rhine and Meuse Rivers to discharge were also reported by Hamers et al. (2015). In contrast to our results, Ba in the Mosel catchment shows generally a positive response to discharge (Le Meur et al. 2016). The negative response of the Ba concentrations in Rhine suspended sediment at the Lobith monitoring station suggests that the Ba concentrations are primarily controlled by anthropogenic inputs, whereas the Ba

concentrations in the Mosel catchment are likely largely controlled by inputs from geogenic sources. The reported Ba concentrations in suspended matter in the Mosel catchment is on average higher (Le Meur et al. 2016) than that at Lobith (this study). This can be attributed to the higher Ba concentrations in soils and stream sediments in the Mosel catchment than in the downstream parts of the Rhine catchment (Salminen et al. 2005). Furthermore, In the Mosel catchment, Cr show a shift from the more geogenically controlled, positive response to discharge in the upstream parts of the catchment to an anthropogenically controlled, negative response more downstream (Le Meur et al. 2016). This is in agreement with the negative response of Cr to discharge found in this study.

The deviating behaviour of La and Sm in the Rhine suspended sediment compared with the other REEs, which becomes manifest in the correlation matrix (Fig. 2) and the relation with discharge (Fig. 3a–c), was also reported by Kulaksız and Bau (2011). They identified the source of anthropogenic pollution of La and Sm to be an industrial discharge of waste water just north of Worms in Germany (approximately 410 km upstream from the Lobith monitoring station). The anthropogenic Gd anomaly observed by Kulaksız and Bau (2011) was not observed in our study because anthropogenic Gd is only present in dissolved phase (Klaver et al. 2014).

The effect of dilution of anthropogenically contaminated suspended sediment by sediment inputs from land surface erosion was also found by Ollivier et al. (2011) for the Rhône River in France and by Ma et al. (2015) for the Daliao River and Estuary in China. Ma et al. (2015) reported concentrations of contaminant metals in suspended sediment to be on average 2–3 times higher during the dry season than during the wet season. The seasonal variation in contaminant concentrations in suspended sediment due to interannually produced organic matter due to algal blooms was also reported by Hamers et al. (2015) for metals and organic pollutants. Previously, this seasonality in element concentrations on suspended sediment had been observed in the Scheldt estuary in the southwestern part of the Netherlands (Zwolsman and Van Eck 1999) and in freshwater lakes that are fed by the downstream distributaries of the Rhine River (Van de Meent et al. 1985; Koelmans 1998; Winkels et al. 1998).

The concentration–discharge relationships derived in this study can be used to estimate a continuous time-series of sediment-associated element concentrations in the Rhine River analogous to the rating curve method to estimate suspended sediment concentrations (Ferguson 1986). The estimation of element concentrations may be improved by the seasonal variation in residuals of the concentration–discharge relationships taking into account. The resulting estimated element concentrations can subsequently be combined with measured or rating curve-estimated suspended sediment

concentrations to obtain monthly, seasonal or annual sediment-associated element loads.

This study shows factors that do not directly relate to sediment source type or area (i.e. clay/organic C content and anthropogenic pollution) explain the majority, approximately 70%, of the temporal variation in suspended sediment composition in the Rhine River. These factors should thus be omitted in identifying the sediment provenance, which thereby also eliminates many of the issues common in sediment fingerprinting studies, including effects of grain size, geochemical transformation and internal organic matter production (Koiter et al. 2013; Laceby et al. 2017; Smith and Karam Lennard 2018). The selection of sediment tracers and fingerprints should thus be based on the other components which may be associated with sediment source areas, but only explain a minor proportion of the total variation in suspended sediment composition. To identify the sediment source areas and to quantify the contribution of these source areas to the suspended sediment load, additional information is required about the geochemical composition of the top soils in the upstream river basin. The use of geochemical databases such as the FOREGS Geochemical Atlas of Europe (Salminen et al. 2005) as a source of such information seems promising, but further study is required to evaluate the value and limitations of these data for this purpose.

## 5 Conclusions

This study examined the temporal variation of suspended sediment composition at the Lobith monitoring station in the Rhine River in the Netherlands. The analysis of a comprehensive dataset for the period between 2011 and 2016 shows that the composition of suspended sediment is for a large part controlled by the clay content. The clay content is, in turn, controlled by inputs of clastic materials during hydrologic events and seasonality. This becomes manifested in increased concentrations of geogenic elements, including Li, K, Rb, Cs, Be, REEs (except La and Sm), Fe, Co, Ni, Al, Ga and Tl, during periods of high discharges and decreased concentrations during summer when the primary production of organic matter dilutes the element concentrations.

The sediment composition is also affected by anthropogenic pollution that is mainly derived from point source discharges. Prominent anthropogenic pollutants in the Rhine River include “traditional” heavy metals such as Cr, Cu, Zn, Cd, Hg and Pb, but also Na, La, W and Te. These concentrations of these elements in suspended sediment decrease with increasing discharge due to dilution by the increased inputs of clastic material during hydrologic events. The direction of the relation between element concentrations and discharge thus reveals important information whether the elements are of anthropogenic or geogenic origin. Furthermore, the sediment

composition is also controlled by sediment provenance, but only a minority of the temporal variation can be attributed to this factor. This factor reveals itself in deviant temporal patterns of the PCA scores, which are independent from seasonality and discharge. The precise cause of these patterns is not yet fully understood.

The multi-variate analysis of the elemental composition of suspended sediment in combination with information on discharge, clay content, and organic C content, has demonstrated to be useful distinguish between the different factors controlling the suspended sediment composition, which allowed us to unravel the geogenic and anthropogenic sources of the elements.

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