


Sediment core data reconstruct the management history and usage of a heavily modified urban lake in Berlin, Germany

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Abstract Urban surface waters face several stressors associated with industry and urban water management. Over much of the past century, the wastewater treatment in Berlin, Germany, relied on inefficient sewage farms, which resulted in severe eutrophication and sediment contamination in the recipient surface waterbodies. A prominent example is Lake Tegel, where a multitude of management measures were applied in the last decades for the purpose of ecosystem restoration. In this study, we analyzed sediment cores of three lakes with X-ray fluorescence spectroscopy: Lake Tegel, Lake Großer Wannsee, which is environmentally similar but has a different management history, and Lake Userin, which serves as a reference located in a nature protection area. Multivariate statistical methods (principal component analysis, *k*-means clustering, and self-organizing maps) were used to assess the sediment quality and to reconstruct the management history of Lake Tegel. Principal component analysis established two main gradients of sediment composition: heavy metals and lithogenic elements. The impact of the management measures was visualized

in the lake sediment composition changing from high abundance of heavy metals and reducing redox conditions to less-impacted sediments in recent layers. The clustering techniques suggested heterogeneity among sites within Lake Tegel that probably reflect urban water management measures. The abundance of heavy metals in recent lake sediments of Lake Tegel is similar to a lake with low urban impact and is lower than in Lake Großer Wannsee suggesting that the management measures were successful in the reduction of heavy metals, which are still a threat for surface waters worldwide.

Keywords Urban lake sediment · Urban water management · Sewage farms · Heavy metals · XRF · PCA · SOM

Introduction

Until the twentieth century, German surface water pollution was dominated by industrially derived organic contaminants, heavy metals, saline effluents, acid rain, sewage as well as agriculture-derived nutrients. Nowadays, micropollutants like pharmaceuticals and their derivatives represent an additional pressure, especially in urban areas (Nützmann et al. 2011). The water cycle of Berlin, Germany, is “semi-closed” and relies on discharging treated wastewater effluents into recipient streams and lakes that also act as sources for drinking water extracted by bank filtration (Massmann et al. 2004; Gessner et al. 2014). Advancements in wastewater processing reduced nutrient loadings into Berlin’s lakes, yet in the nineteenth and twentieth century, Berlin’s water management depended on sewage farms, where—at that time state of the art—untreated sewage was deposited on constructed wetlands for purification through soil filtration. This simple technique and an input of sewage exceeding the soil infiltration capacity introduced nutrient-rich and heavy metal-contaminated waters into the

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groundwater, streams, and lakes, leading to eutrophication and long-term sediment contamination (Ginzel and Nützmann 1998). Severe water pollution problems were the consequences, e.g., contamination with sulfonamides (Richter et al. 2009) and acidification (Homer et al. 2009).

The lake sediment stratigraphy is a natural archive for environmental and anthropogenic impact and can help in evaluating past management strategies (Battarbee et al. 2005; Battarbee and Bennion 2011). For instance, heavy metals can be seen as proxies for human activities originating from industry or mining. Stratigraphically appearing heavy metal contamination often represents the beginning of such activities and, in most cases, their decline documents the introduction of modern sanitation concepts and the advent of stricter water protection standards improved industrial production processes or depletion of natural resources (Bindler et al. 2010; Thevenon et al. 2011). To evaluate vertical variation of elemental composition in lake sediment, one can either use conventional quantitative techniques (Gredilla et al. 2012), which require pre-treatment of the samples, or non-invasive analytical techniques like X-ray fluorescence spectroscopy (XRF), which allows to obtain only semi-quantitative data, yet with unprecedentedly high spatial resolution. To interpret the resulting matrices of compositional data, multivariate statistical methods can be used, for instance to achieve an assessment of past management measures. For environmental data and especially lake sediments, cluster analysis and principal component analysis (PCA) have been used for decades. Cluster analysis, e.g., *k*-means clustering, efficiently describes similarity between sets of samples but gives no information about behavior of variables in the source data. In contrast, PCA reduces the dimensions of the potentially complex original multidimensional data by extracting correlations and projecting source data on only a few latent variables. These then represent common information from variables and often align with (sometimes otherwise undetected) environmental gradients. It is a widely used technique in paleolimnology and sediment quality assessment (Arambarri et al. 2003; Borůvka et al. 2005; Reid and Spencer 2009; Comero et al. 2011; Rydberg and Martinez-Cortizas 2014; Schreiber et al. 2014; Kleeberg et al. 2015; Lin et al. 2016; Rydberg et al. 2016). An alternative approach is to use self-organizing maps (SOM), which are a type of artificial neural networks and give extended classification details (Alvarez-Guerra et al. 2008). A SOM has the profound advantage to visualize the multidimensional data on a two-dimensional plane, while to sufficiently explain most variance in a PCA model more than two PCs would have to be used. SOMs have found widespread use in sediment assessment studies (Nadal et al. 2004; Alvarez-Guerra et al. 2008; Yang et al. 2012; Subida et al. 2013; Olawoyin et al. 2013; Pandey et al. 2015) as they are able to visualize the similarities between multiple sites by further establishing their relationship to an environmental background.

One type of SOM is the “Kohonen” map, in which, expressed in a simplified way; multivariate data is sequentially presented to a grid which consists of units, each with a randomized weight vector (Kohonen 1998). The algorithm picks a random vector from the multivariate data and looks for the best matching unit in the grid. In an ensuing competitive step, the found unit and its neighbors get updated to become more similar to the input data. After presenting all input vectors from the multivariate data, the grid should converge to represent similarities between sites of the original data set. Both, PCA and SOM, are descriptive techniques, which support pattern recognition and formulation of hypotheses rather than being instruments of inductive, hypothesis-testing statistics themselves.

This study focuses on Lake Tegel, the second largest lake in the city of Berlin, Germany, which is crucial for Berlin’s water management due to drinking water production via bank filtration. In the 1950s, a linkage of upstream sewage farms into Lake Tegel was created and resulted in substantial input of nutrients and heavy metals into the lake. Ensuing eutrophication became critical in the 1970s, with oxygen depletion in the deep water, mass development of cyanobacteria (Schäuser and Chorus 2007), and a loss of the lake’s submerged vegetation and reed belts (Hilt et al. 2010). First restoration measures in this decade diverted discharge from the inflow into other surface waters and connected nearby settlements to the public sewage system (Heinzmann and Chorus 1994). The construction of the wastewater treatment plant (WWTP) Schönerlinde, in the area of the former sewage farms, and the launch of the surface water treatment plant (SWTP) Tegel, which eliminates phosphorus from the north-eastern inflow, in 1985 resulted in the restoration of the lake (Heinzmann and Chorus 1994). Furthermore, a lake pipeline was built to collect water from the lake outflow and bypass it to the SWTP Tegel to dilute influents and to maintain a minimum discharge. There are time series of water quality parameters as well as sediment investigation studies that provide further helpful insights into Lake Tegel’s history (Pachur 1989; Heinzmann and Chorus 1994; Schäuser and Chorus 2007, 2009; Kleeberg et al. 2012).

In this study, the recent and historical composition patterns in urban lake sediments are investigated using a multivariate assessment of sediment data obtained by a fast non-invasive analytical technique. Sediment cores from heavily impacted Lake Tegel were collected and analyzed via XRF. For comparison, further sediment cores were taken in an additional urban lake (Lake Großer Wannsee) and a lake with low urban impact (Lake Userin). Using PCA and SOM, the sediment stratigraphy of each core is analyzed and should serve as a basis for a sophisticated sediment quality assessment. In addition, these data may help to evaluate the threat of future remobilization of heavy metals from the sediments of lakes used for drinking water abstraction like Lake Tegel and Lake Großer Wannsee. The hypotheses are that (1) management measures

such as those that were applied at Lake Tegel are successful in reducing the abundance of heavy metals both in the water and in the sediment phase and (2) the recent sediment of urban lakes is less contaminated with heavy metals than in the past but still has a higher contamination than a lake with low urban impact. Here, the main question remaining is whether the recent sediments of Lake Tegel feature a lower abundance of heavy metals than in the past. Finally, (3) urban water management causes spatial heterogeneity in the sediment composition within and between urban lakes in the same catchment. Distinct hot-spots that differ vastly from other locations in the same lake should be recognized and handled by urban water management strategies.

Material and methods

Study sites

All investigated lakes (Fig. 1) are connected to River Havel and are roughly the same size (Table 1). Lake Tegel and Lake Großer Wannsee, in contrast to Lake Userin, can be considered as bays to the River Havel. Along the River Havel, the catchment is strongly changing from rural to urban dominance, here represented by the three lakes: Lake Userin as the less-affected lake close to the source of the River Havel, Lake Tegel as the first lake the River Havel enters during its passage through Berlin, and Lake Großer Wannsee as the final lake the River Havel passages as it leaves Berlin.

Lake Tegel (52.5761° 13.2533°) is a lowland urban lake situated in North-Western Berlin. It borders densely populated urban areas at the eastern, southern, and western shores as well as harbors and industrial sites at the eastern shore while the northern shore consists mainly of forests. Seven islands divide the lake into a northern main basin and a southern more river-like part integrated with the River Havel. The main inflows are the River Havel at the south-western boundary of the lake basin and the composite inlet of Nordgraben and Tegeler Fließ in the north-east, which receives the treated effluents of a wastewater treatment plant and, in the past, discharges from a sewage farm. The mixing of the River Havel into the lake—the lake enters the basin either via a northern or a southern passage—depends on wind circulation and river discharge itself which is controlled by a downstream watergate (Schimmelpfennig et al. 2012).

Lake Großer Wannsee (52.4275° 13.1730°) is a bay of the River Havel in the south-west of Berlin. It has two main inflows: in the north, the River Havel and in the South, the artificial Teltow channel entering via the Lake Kleiner Wannsee. The southern inflow can also act as outflow depending on the hydraulic regime. Just like Lake Tegel, Lake Großer Wannsee is used for drinking water abstraction by the Berlin water works. The Teltow channel is infamous for high

sewage loads and pollution originating from shipping and industry. About half of its discharge enters Lake Großer Wannsee over the passage by Lake Kleiner Wannsee (Heberer 2002). Increased concentrations of pharmaceuticals sourced from industry are documented for Lake Kleiner Wannsee (Heberer et al. 2002).

Lake Userin (53.3411° 12.9694°) is a lowland lake situated in Southern Mecklenburg-Western Pomerania near the town Userin. The lake is part of the Müritznational park and belongs to a nature protection area with the aim to keep the surface waters in their original state with low anthropogenic impact. The River Havel has its spring approximately 12 km upstream from Lake Userin and crosses the lake from north to south.

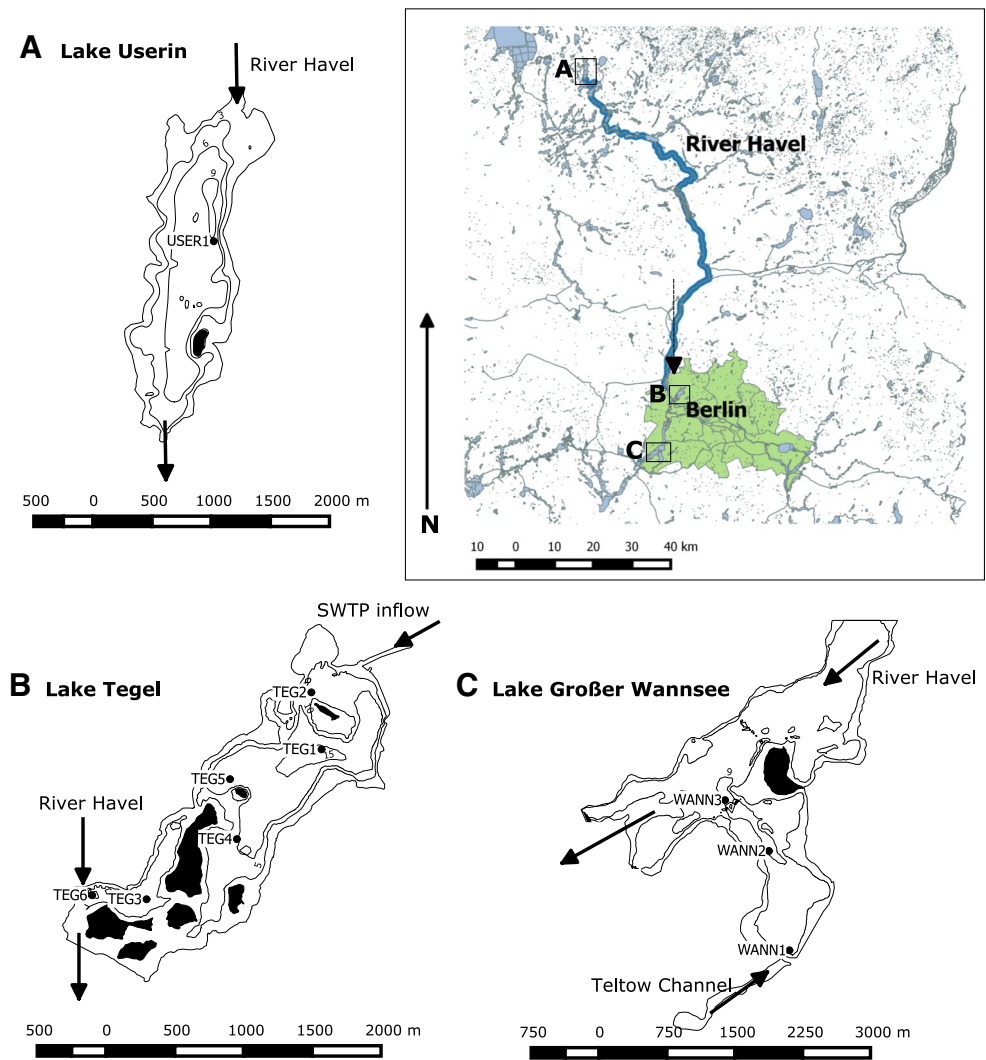
Sampling

Sediment cores were taken at various locations (Table 2, Fig. 1) between September 2015 and March 2016 with a modified Kajak sampler (inner diameter 6 cm, UWITEC®) and were split in halves vertically before transport to the laboratory for XRF analysis at GEOPOLAR, University of Bremen. An additional sediment core was taken at the position of Lake Tegel's deepest site (TEG1), vertically subdivided into 1-cm layers, freeze-dried, and prepared for radioisotopic sediment dating at the Institute of Environmental Physics, University of Bremen.

Analytical methods

All sediment cores were scanned in sections for major and trace elements with an ITRAX XRF-core scanner, COX analytical systems (Croudace et al. 2006). Scanning was done with a Mo-tube with a step size of 1 mm and a count time of 30 s per step; tube settings were kept constant for all cores using a voltage of 40 kV and a current of 25 mA. Element data produced by the scanner are semi-quantitative and are expressed as total counts (cnts), i.e., integrated peak area. In addition to the scanning, high resolution photographs (256 dpi) and 16-bit radiographs of the sediment cores were produced. To minimize bias resulting from matrix changes and tube aging and to increase comparability between cores from different sites, the data were normalized by division with the measured coherent scatter. Therefore, data are expressed as total element counts to coherent scatter ratios (cnts/coherent). As proxy for organic carbon and water content, the ratio of incoherent to coherent scatter measured by XRF was used (Phedorin and Goldberg 2005; Liu et al. 2013; Davies et al. 2015). We further used the ratio of normalized Fe to Mn total counts as proxy for redox conditions (Naehrer et al. 2013; Davies et al. 2015; Rothwell and Croudace 2015). High/low ratios of Fe:Mn point to reducing/oxidizing redox conditions. The non-processed XRF data are available in Online Resource 1.

Fig. 1 Location of the sampling sites (SWTP surface water treatment plant), black patches represent islands



Radioisotopic sediment dating was achieved by analyzing abundance of ^{210}Pb , ^{226}Ra , ^{214}Bi , ^{137}Cs , ^{40}K , and ^7Be by γ -spectroscopy using an n-type coaxial Ge-detector (Canberra Industries). Using a constant flux:constant sedimentation (CF:CS) model, in which the flux of ^{210}Pb is assumed to be constant, the chronology for TEG1 was formulated (Sanchez-Cabeza and Ruiz-Fernández 2012; Bonotto and García-Tenorio 2014).

Data analysis

XRF data were pre-processed as follows: (1) discarding of element data due to unreliable measurement, noisy signals, or intensities close to background level and (2) discarding of all elements with ubiquitously low intensity. Furthermore, only those elements complying with these restrictions in all ten sediment cores were considered. Valid

Table 1 Morphological parameters of investigated lakes

	Lake Tegel, Berlin	Lake Großer Wannsee, Berlin	Lake Userin, Mecklenburg-Western Pomerania
Area [km ²]	3.9 ^a	2.8 ^a	3.3 ^b
Volume [Mio. m ³]	26.1 ^a	15.4 ^a	17.2 ^b
Maximum depth [m]	15.9 ^a	9.8 ^a	9.9 ^b
Mean depth [m]	6.6 ^a	5.5 ^a	4.6 ^b

^a Jahn et al. (2002)

^b Provided by the state departments for agriculture and environment, Mecklenburg Lake Plateau

Table 2 Assessment of the different sites regarding their location and urban impact (SWTP surface water treatment plant, WWTP wastewater treatment plant)

Site	Location	Core length [mm]	Anticipated urban impact
USER1	Middle of Lake Userin	346	Weak: nature protection area
TEG1	Deepest site of Lake Tegel, main lake basin	790	Strong
TEG2	Inflow of treated wastewaters	652	Strong: inflow of SWTP and WWTP, close to harbor
TEG3	Close to inflow of River Havel	572	Moderate
TEG4	Southern edge of main lake basin	730	Moderate
TEG5	Northern edge of main lake basin	401	Moderate
TEG6	Inflow of River Havel	235	Weak: inflow with agricultural impact
WANN1	Inflow/outflow of/to Lake Kleiner Wannsee and Teltow Channel	234	Strong: receives discharges of treated wastewaters and industry
WANN2	Deepest site of Lake Großer Wannsee	342	Strong
WANN3	Inflow/outflow of/to River Havel	316	Strong: River Havel catchment area now includes the city of Berlin

elements for statistical analysis were K, Ca, Ti, Rb, Zr, Sr, Mn, Fe, Cr, Cu, Zn, and Pb.

To efficiently describe patterns in the multivariate dataset, we used PCA based on data from all depth layers of all cores. Data were logarithmically transformed to improve linear relationships between the elements, and scaled to a mean of zero and a standard deviation of one to ensure equal weight of all variables. We further computed the correlation of each element to the respective PCs. For clustering, we used the k -means method with the Hartigan-Wong algorithm, 25 random starts, and a maximum amount of 1000 allowed iterative runs (Hartigan and Wong 1979). The pre-processed (logarithmically transformed) data were used to differentiate between a total number of five clusters, which were chosen visually by the “elbow method”. Here, the sums of squared errors for k from 1 to 20 were calculated and plotted (Everitt and Hothorn 2009). The interpretation of the clusters was done using box-and-whisker-plots. For filtering and smoothing, we either used a moving average filter implemented by convolution kernel or the Savitzky-Golay algorithm (Savitzky and Golay 1964). For the latter, the smoothing was established by fitting a first order polynomial model on the data set with a set window size of 31 data points.

For data visualization and further clustering, we additionally used a SOM as implemented in the “kohonen” package (Kohonen 1998; Wehrens et al 2007) in R (R Core Team 2016). We provided a hexagonal grid of six times six units. This total number of 36 nodes was iteratively chosen to ensure that the amount of empty nodes in the final grid is low. As training data, the sediment data from sites of all lakes up to a depth of 150 mm were used. For training, the default algorithms of the package were applied (complete data was presented to the network 100 times, learning rate vector (0.05 0.01), circular neighborhood shape). The algorithm converged the grid into a map with clustered units after 40 iterations. The

amount of clusters was determined by k -means clustering and the “elbow method.”

Results

Sediment characteristics of Lake Tegel

Sediment cores of Lake Tegel were mainly composed of mud and, in deeper layers, sapropel-like material. The sediment core photographs and respective radiographs display that brighter, brownish colored zonations in deeper sediment layers appear in conjunction with dark grayscale values referring to denser material, especially in TEG2 and TEG4 (Fig. 2). This agrees with a change in the visible sediment stratigraphy changing from a brownish to a black sediment color in the middle of most sediment cores together with a white grayscale value and therefore less-dense material. This indicates two general zonation types for most sediment cores: either denser material visible by a brownish sediment color or less-dense material with a black sediment color.

PCA model

The first two principal components capture 39 and 23% of the overall variance, which totals to 62% (eigenvalues and eigenvectors of the PCA are given in Appendix Table 3). The distance bi-plot (Fig. 3a) displays a strong heterogeneity of Lake Tegel’s sites with points scattered across bivariate space, while Lake Großer Wannsee shows dominant dispersion along PC1 and Lake Userin is constricted to relatively limited location in the top left side. The clustering divided the data points into five groups, plotted on the bivariate space of the first two components. Clusters 2, 3, and 5 mainly consist of data points from sites of Lake Tegel as well as Lake Großer Wannsee,

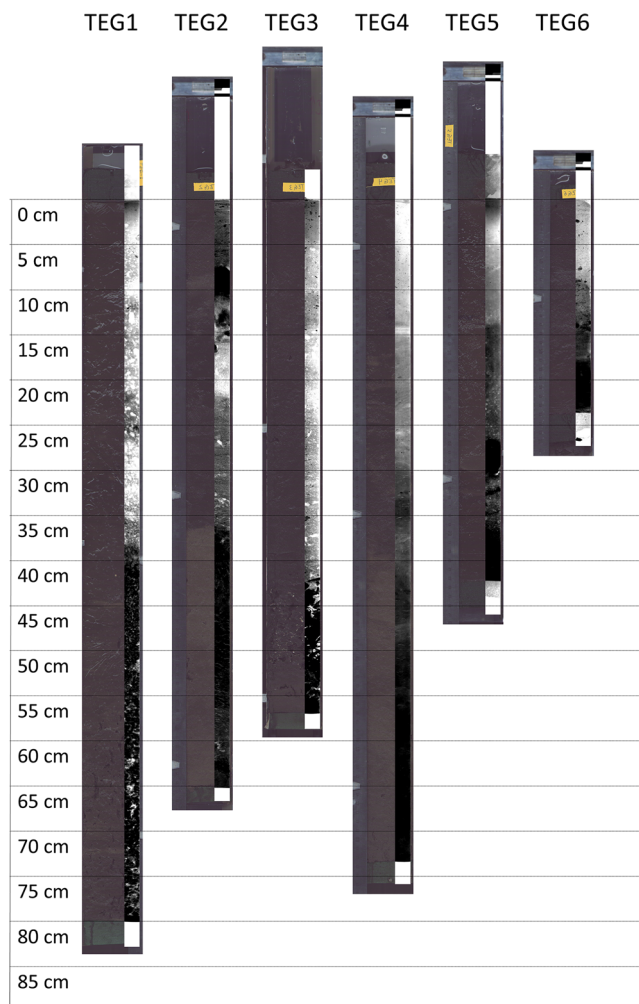


Fig. 2 High resolution photographs of all sediment cores from Lake Tegel and the respective grayscale radiographs: darker grayscale values correspond to a visibly lighter sediment color, indicating the settling of a brown, dense material, e.g., visible in TEG2 and TEG4

whereas cluster 1 incorporates data from all three lakes and cluster 4 only data from Lake Tegel and Lake Userin. The elements Cr, Pb, Zn, Cu, and Fe correlate positively with PC1 relating this axis to heavy metals, whereas Ti, Rb, K, Sr, Mn, and Ca are negatively correlated to PC2 (Fig. 3b). The latter elements are predominantly lithogenic in origin (Rb, Zr as well as Sr, in clay minerals or aluminosilicates) (Boës et al. 2011; Schreiber et al. 2014). Further support for PC2 being a proxy for the geological background of the respective catchment areas comes from Mn and Ca, which mostly originate from sedimentary rock, e.g., carbonates like rodochrosite or from calcareous mud (Pachur 1989). Masking Lake Großer Wannsee and Lake Userin, the heterogeneity among individual sites of Lake Tegel becomes obvious (Fig. 3c). The sites in or close to the main basin (TEG1, TEG4, TEG5) disperse along an axis from the upper left side to the lower right side indicating a simultaneous increase of heavy metals and lithogenic elements. The inflow site TEG2 displays the highest horizontal

dispersion indicating pronounced changes in the abundance of heavy metals while lithogenic elements remain constantly high in abundance. In contrast, the inflow site of River Havel, TEG6, displays only a vertical dispersion. The chronology of TEG1 by radioisotopic dating suggested the 1950s as the timeframe for the observed maximum abundance of heavy metals which coincides with the start of intensified wastewater discharge originating from sewage farms. Furthermore, we established clusters using the data of all Lake Tegel sites, which overlap and are close to identical with the previously formulated five clusters are as follows:

- Clusters 1, 2, and 3 mainly include data points that show the transition from deeper sediment layers to more recent layers of sites from the main basin
- Cluster 4 contains the recent sediment layers of the sites TEG2, TEG3, and TEG4, which are situated either close to the inflow of the SWTP or are at the edge of the main basin
- Cluster 5 incorporates recent sediment layers of sites from the main basin (TEG1, TEG5) and the River Havel inflow TEG6, as well as deep layers from the SWTP inflow site TEG2

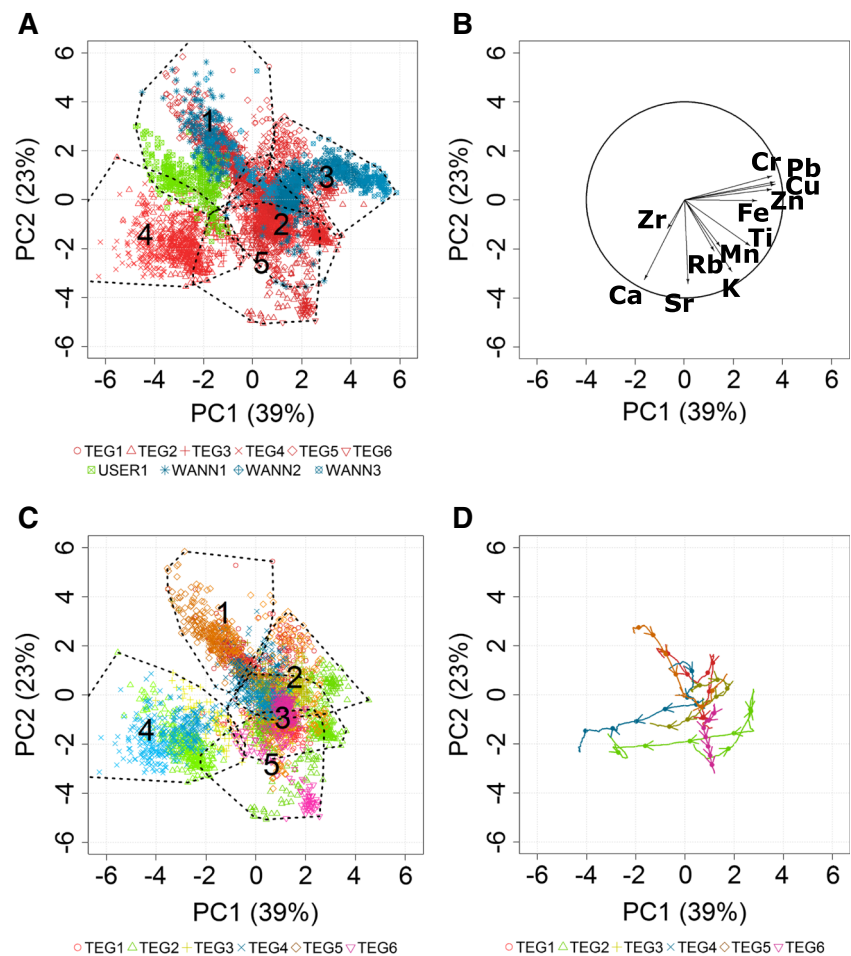
To show simplified stratigraphic patterns, a moving average filter over 100 data points (equal to 10 cm) was applied to the scores of each core ordered along the depth axis (Fig. 3d). In the deeper layers, the development of most sites is marked by a sharp U-turn at times of heavy metal contamination. In recent layers, most sites move towards the lower left edge characterized by low heavy metal contamination.

Clustering with *k*-means

The spatial distribution of the established five clusters (Fig. 4a) over Lake Tegel as well as over the sediment depth visualizes for TEG1, TEG2, TEG3, TEG4, and partially TEG5 a sequence mostly changing from cluster 1 in deep layers over cluster 2 and cluster 3 to cluster 4 in the upper sediment layers. Cluster 5 occurs in recent sediment layers of TEG5 and TEG6, as well as in the deep sediment of TEG2. The box-and-whisker-plots (Fig. 4b) characterize the clusters as follows (due to the negative correlation of lithogenic elements to PC2, high/low PC2 scores represent a low/high abundance of lithogenic elements):

- Cluster 1: high organic carbon content, high Fe/Mn ratio, low abundance of Zn, Fe, Ca, and K, low PC1 score, and highest PC2 score
- Cluster 2: high abundance of Zn and Fe, high PC1 score, high Fe/Mn ratio, high content of organic carbon, high PC2 score, and low abundance of Ca and K

Fig. 3 Distance bi-plots for the PCA. **a** Scores of the first and second principal component. **b** Arrows show structural coefficients of various elements on the PCA axes with unit circle, PC1 correlates with Cr, Pb, Zn, and Fe (heavy metals) whereas PC2 correlates mainly with Sr, Ca, Rb, Mn, K, and Ti (lithogenic elements). **c** Sites of Lake Tegel are visualized separately; hereby, deeper to recent layers are represented by the transition from dark to lighter colors. **d** Filtered lines (moving average of 10 cm) illustrate the historical change in sediment composition of Lake Tegel's sites, arrows represent the direction from deeper to recent sediment layers



- Cluster 3: high abundance of Zn and Fe, high PC1 score, low Fe/Mn ratio, moderate PC2 score and content of organic carbon, and low abundance of Ca and K
- Cluster 4: high abundance of Ca, low PC2 score, low abundance of Zn, Fe, and K, low PC1 score as well as a low Fe/Mn ratio and organic carbon content
- Cluster 5: high abundance of K, high PC1 score and lowest PC2 score, high Fe/Mn ratio, similar abundance of Zn, Fe, and Ca like the clusters 2 and 3, and lowest content of organic carbon

Vertical distribution of redox zonations

For the sites TEG2, TEG3, and TEG4, a relationship between the abundance of heavy metals (represented by PC1) and the Fe/Mn ratio can be established (Fig. 5). Deep layers feature a low Fe/Mn ratio probably related to oxidizing redox conditions. In the vertical course of the sediment cores, we observed an increase of the Fe/Mn ratio concomitant with increasing abundance of heavy metals. The uppermost, recent sediment

layers still display an increased abundance of heavy metals, compared to deeper layers, but mostly decreased Fe/Mn ratios. The development of TEG1 begins with an already increased abundance of heavy metals probably due to higher sedimentation rates at this site. Afterwards, the stratigraphy is similar to previously described ones. Both TEG5 and TEG6 also feature the decrease of heavy metals resulting in lower Fe/Mn ratios.

Classification with SOM

We clustered the converged SOM into 11 groups (Fig. 6a). Lake Tegel is stretching from the lower left side of the map, representing the inflow sites, to the upper right side, where the edges of the main basin (TEG3, TEG4, and TEG5) are located. The deepest site is at the center of the map close to Lake Userin, which is located on the left side of the map close to the SWTP inflow of Lake Tegel and next to Lake Großer Wannsee's Teltow channel inflow site. The remaining sites of Lake Großer Wannsee are situated at the lower right corner of the map. The scaled segment plots of each unit reveal different weighting towards the respective elements (Fig. 6b). The heavy metal contamination consisting of Cr, Cu, Zn,

and Pb is mainly related to the Havel inflow on the lower right corner. The lithogenic elements like K, Ca, Ti, Rb, and Sr as well as Zr are located at the lower left edge of the map. This is the location of Lake Tegel’s SWTP inflow site as well as the Havel inflow into Lake Tegel. For Lake Tegel, the part close to the SWTP inflow shows increased loadings of the lithogenic elements, whereas the sites near the River Havel are related to an increased weighting to heavy metals. The recent layers in the main basin of Lake Tegel still have a slightly increased abundance of heavy metals in contrast to Lake Userin. But nonetheless, the map converged to a close neighborhood between Lake Tegel’s deepest site and Lake Userin. The sites of Lake Großer Wannsee can be divided in the southern site with only an increased weighting to Mn and Fe, and the northern river-influenced sites showing higher contributions by heavy metals.

Discussion

Reconstruction of the management history of Lake Tegel

PCA identified two main gradients of sediment composition: heavy metals and geological background elements. This is in accordance to similar studies that used XRF analysis and PCA to assess the sediment composition of surface water systems, in which the first two principal components were also mainly correlated to either heavy metals or lithogenic elements (Schreiber et al. 2014; Kleeberg et al. 2015). Lake Tegel’s sites are especially heterogeneous; while main basin sites show a high dispersion along the vertical axis and thus a change of the abundance of lithogenic elements, the site close to the north-eastern inflow features a horizontal dispersion implying a change of the abundance of heavy metals. Nonetheless, all

Fig. 4 Clustered vertical profiles of the sediment cores at Lake Tegel. **a** Map of Lake Tegel, rotated about 45°, the color profiles at each site represents the respective cluster established by *k*-means for the vertical sediment layers. **b** Box-and-whisker-plots for the respective elements, scores or proxies, the colors represent again the respective clusters established by *k*-means (here the organic carbon is presented by the ratio of incoherent to coherent scatter)

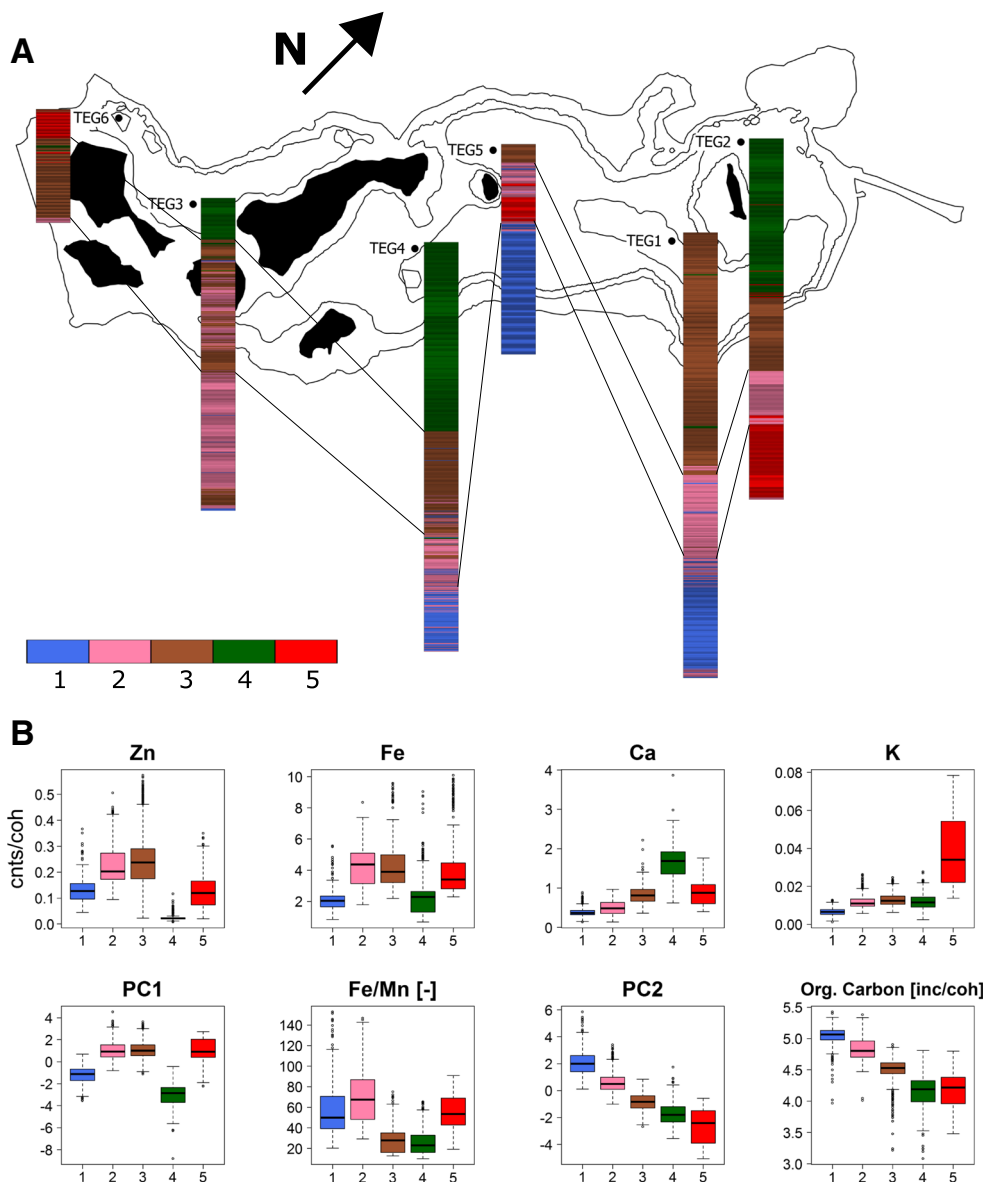
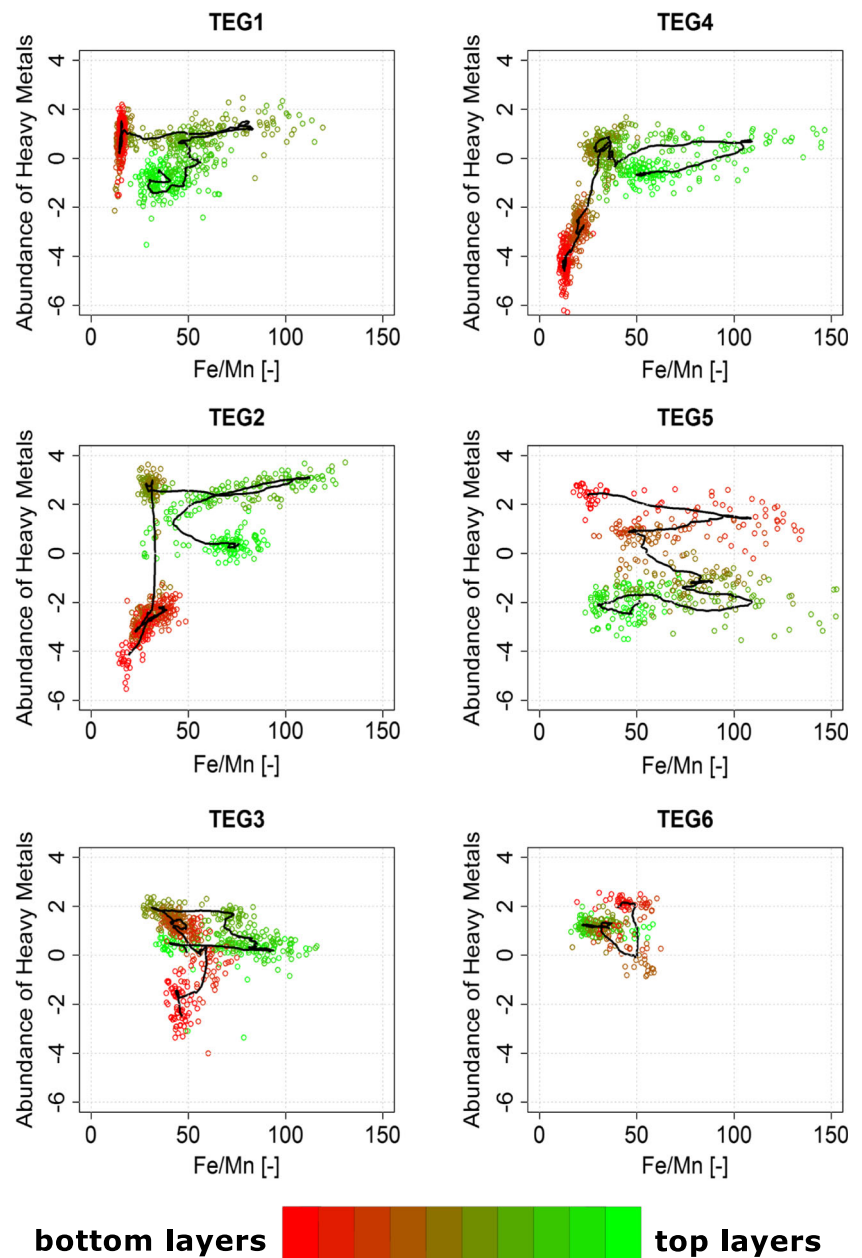


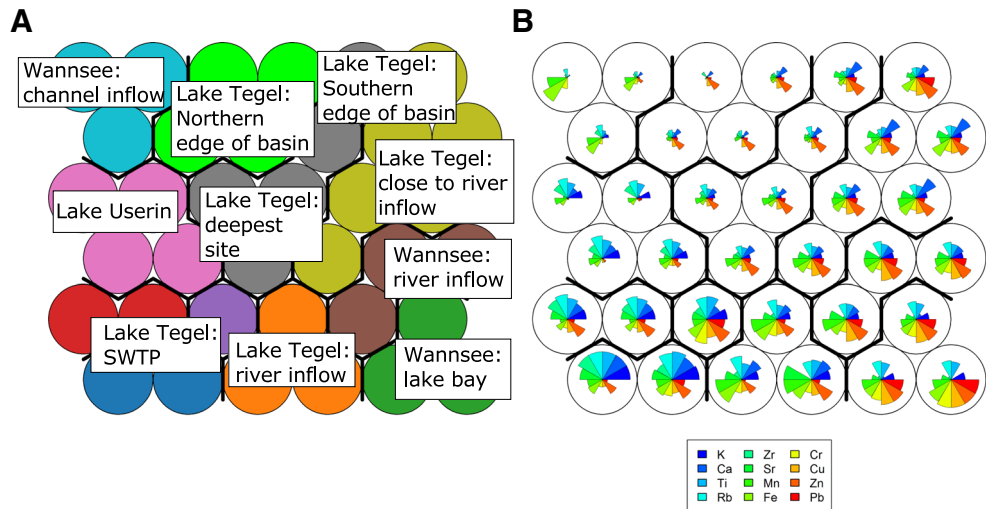
Fig. 5 Normalized Fe/Mn ratio vs. abundance of heavy metals represented by PC1, data points were filtered with Savitzky-Golay algorithm, the color gradient goes from red (lower or deeper sediment layers) to green (upper or recent sediment layers); for TEG 1, TEG2, TEG 3, and TEG4, a lower Fe/Mn ratio in the deep layers implying oxidizing redox conditions in the past. With an increase of heavy metals in upper layers, the Fe/Mn ratio increases (reducing redox conditions); recent sediment layers are mostly characterized by a lower abundance of heavy metals and lower Fe/Mn ratios



sites show a tendency towards low abundance of heavy metals and increased abundance of lithogenic elements in recent layers. In the past, the sediment of Lake Tegel was heavily influenced by an excess of heavy metals, which predominantly originated from the discharge of inadequately treated wastewaters from sewage farms. Especially the elements Zn and Pb are indicators for anthropogenic pollution (Grousset et al. 1995). The established clusters identify a sequence pattern for the sediment cores in the main basin. In deep sediment layers (cluster 1, TEG1, TEG4, TEG5), the sediment is characterized by high organic carbon content, probably already reducing redox conditions and low abundance of heavy metals and lithogenic elements. In the next step, the loading regime is changing (cluster 2, TEG1, TEG3, TEG4, and TEG5); the organic carbon content

is reduced and the abundance towards heavy metals as well as lithogenic elements is increased. A slight increase of the Fe/Mn ratio as well as higher abundance of Zn and Fe suggests that during these times, the discharges from the sewage farms reached Lake Tegel and, due to a time lag, the beginning eutrophication enforced reducing redox conditions. During this transition, the sediment color changed from brownish to black implying increased abundance of sapropel-like material probably due to eutrophication. Subsequently, in cluster 3 (TEG1, TEG3, TEG4, TEG5), the organic carbon content and the Fe/Mn ratio are decreasing, but the abundance of heavy metals stays constant and the abundance of lithogenic elements is increasing. The uppermost recent layers for the cores TEG1 and TEG5 belong to this cluster, whereas the recent layers from

Fig. 6 Self-organizing map. **a** Clustered map of the similar neighborhoods, the TEG sites in the center are bordering the less heavy metal contaminated sites on the left edge of the map (Lake Userin, Lake Großer Wannsee channel inflow) and the more contaminated sites on the right side (Lake Großer Wannsee bay and river inflow). **b** Code map showing contributions of elements as segment plots, there is a distinction between lithogenically imprinted sites on the left and heavy metal contaminated sites on the right



TEG2, TEG3, and TEG4 are part of cluster 4. Here, the loadings of heavy metals are vastly reduced and the organic carbon content as well as Fe/Mn ratio are low. The applied management measures resulted in the decrease of nutrients, especially phosphorus, and heavy metals entering Lake Tegel, therefore enabling the restoration of the lake system. Our findings contradict the apprehension by Pachur (1989) about a future remobilization of heavy metals and indicate that the applied management measures are capable of restoring lakes and reducing heavy metal abundance in the sediment. The latter is still a threat for worldwide surface water systems (Chen et al. 2015). Nonetheless, for most cores (especially TEG2, TEG3 and TEG4), the abundance of heavy metals and the tendency towards reducing redox conditions are still increased in the upper sediment layers compared to deep ones in spite of the reduction achieved by the management measures.

It should be noted that e.g. TEG2, TEG5, and TEG6 show vertical zones belonging to the fifth cluster. These layers are characterized by an increased abundance of heavy metals and lithogenic elements (especially Fe and K), as well as a low organic carbon content and an increased Fe/Mn ratio. This is probably due to soil runoffs or erosion events causing the leaching of elements from clay minerals and deposition at lake sites close to the inflows. TEG5 can be considered as a special case showing a different vertical sequence of clusters than the other cores. This could be because of the hydraulic regime under east wind conditions, when water from River Havel is entering the lake over the northern passage and transported material is settling down at the north-western sites of the main basin.

Assessment of recent sediment composition at Lake Tegel

The composition of the recent sediment cores at Lake Tegel varies across the SOM encircling Lake Userin and edging sites of Lake Großer Wannsee. Here, the deepest site of Lake Tegel is located next to Lake Userin, indicating similar abundances

of heavy metals as well as lithogenic elements. The inflow site close to the SWTP of Lake Tegel has the highest abundance of lithogenic elements, whereas the sites close to the River Havel feature increased loadings of heavy metals. The higher abundance of heavy metals in the River Havel probably originates from natural and anthropogenic sources in its catchment area and appears only high in relation to the recent low heavy metal effluents from the urban area.

The bays of the River Havel, Lake Tegel and Lake Großer Wannsee, are characterized by their urban impact and applied water management measures. This becomes apparent in the gap between Lake Großer Wannsee’s channel inflow site and its northern sites, which feature very dissimilar sediment compositions. The settling of heavy metals close to inflows and near shores is in accordance with the findings of similar studies investigating the heavy metal accumulation in lake sediments (Thevenon et al. 2011; Pang et al. 2015). The Teltow channel inflow, originally assumed to have an increased heavy metal contamination by industrial runoffs, features a low abundance of heavy metals and lithogenic elements. This is probably due to the settling of most heavy metals in the channel bed upstream of Lake Großer Wannsee. Furthermore, the increased abundance of heavy metals in the sediments of the sites at Lake Großer Wannsee close to the River Havel probably originates from industrial activities in the city of Berlin. In Hoelzmann and Zellmer (2008), the authors identified high heavy metal concentrations in the sediments of the River Spree in Berlin, which discharges into River Havel downstream of Lake Tegel. Heavy metals probably accumulated in these sediments since the beginning of industrialization, with a decline in loadings only occurring after 1990 due to economic changes and a general decline of industrial production in conjunction with improved industrial processes in Berlin (Hoelzmann and Zellmer 2008). The increased abundance of heavy metals in Lake Großer Wannsee is therefore a direct consequence of urban effluent discharge.

Conclusions

Using a rapid, high resolution technique and assessing the results with multivariate methods, the management history of Lake Tegel could be visualized and interpreted. The management measures were successful in reducing the abundance of heavy metals in the sediment. In the past, the lake sediments from the different sites succeeded in a largely similar sequence pattern from low abundances of heavy metals as well as lithogenic elements over reducing redox conditions with an increased abundance of heavy metals to, again, low abundances of both heavy metals and lithogenic elements in recent sediment layers. Still, the vertical sediment composition of some sites differs vastly, especially close to the inflows and at the edge of the main basin. The cause for the heterogeneity of the sediment composition is probably the heavily modified urban water management which aims to optimize and control the water cycle for human needs. It results in altered inflow fluxes and hydraulic regimes. For instance, the SWTP at Lake Tegel artificially increases and maintains the inflow. Nowadays, the sediment composition of Lake Tegel, even if heterogeneous, shows reduced heavy metal contamination than in the past, less

than a proximate urban lake and is, at some sites, similar to the heavy metal abundance of a less-impacted lake.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Appendix

Table 3 Eigenvalues and eigenvectors for the first 12 principal components of the PCA (*PC* principal component)

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10	PC11	PC12
Eigenvalues [%]	38.6	22.4	12.5	8.6	5.7	4.3	2.5	1.6	1.3	1.1	0.9	0.4
Eigenvectors [–]												
K	0.22	–0.43	0.27	–0.03	0.16	–0.28	0.19	–0.59	0.40	0.06	0.20	0.05
Ca	–0.19	–0.48	–0.22	–0.24	0.07	0.03	–0.16	–0.05	–0.10	0.52	–0.53	–0.20
Ti	0.30	–0.28	0.33	0.02	0.19	–0.38	0.37	0.53	–0.32	–0.05	–0.15	0.00
Rb	0.13	–0.31	0.19	0.33	–0.85	0.10	–0.06	0.03	–0.02	0.05	–0.04	0.01
Zr	–0.08	–0.17	0.64	0.04	0.29	0.63	–0.25	0.06	–0.03	–0.04	0.03	–0.06
Sr	0.02	–0.51	–0.28	–0.27	0.00	–0.06	–0.43	0.14	–0.07	–0.55	0.26	0.08
Mn	0.16	–0.28	–0.46	0.35	0.17	0.50	0.48	–0.07	–0.17	–0.03	0.13	0.03
Fe	0.33	0.00	–0.17	0.53	0.25	–0.10	–0.43	0.30	0.43	0.21	–0.01	–0.03
Cr	0.40	0.15	0.01	0.19	0.11	–0.11	–0.35	–0.47	–0.63	–0.05	–0.15	–0.01
Cu	0.42	0.10	–0.04	–0.32	–0.11	0.11	0.02	0.07	0.01	0.14	0.32	–0.75
Zn	0.40	0.06	–0.03	–0.41	–0.07	0.19	–0.07	0.12	–0.04	0.42	0.21	0.62
Pb	0.42	0.11	–0.04	–0.22	–0.05	0.22	0.10	–0.05	0.34	–0.42	–0.64	0.04

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