Environmental Studies of Iron in Sediments by Means of X-ray Absorption Spectroscopy

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ABSTRACT: X-ray Absorption Fine Structure (XAFS) spectroscopy was used to identify directly the metal speciation and local bonding environment of Fe in sediments originated from Dobczyce reservoir (Poland); special attention was paid to analysis of samples collected from points situated at different distances from the land. The combination of traditional approach to data analysis as well as usage of multivariate techniques provided reliable information on the local Fe structure. The obtained average oxidation state for Fe species in all samples was found to be at about +3. The number, nature, and proportion of Fe species in sediments samples were calculated by a coupled Principal Component Analysis (PCA) and Least-Squares Fitting (LSF) procedure. Results indicate for a high similarity among analyzed data collected for various points from Dobczyce reservoir. Among different forms of amorphous oxyhydroxides and various iron oxides commonly present in lake sediments, hematite (Fe₂O₃) and goethite (α-FeOOH) were found to be the dominant crystalline structures in analyzed samples. Based on that finding it can be concluded that Fe is principally bound to oxygen in sediment samples, therefore its (re)mobilization to the water may be neglected.

Key words: Sediments, XAFS, Multivariate analysis

INTRODUCTION

According to the definition sediments are naturally occurring materials, crushed by processes of weathering and erosion, transported by wind, water, or ice. Sediments may consist of organic matter, insoluble substance (soil particles or rock) and remains of water organisms. Sediments can vary in composition and physical characteristics as a function of water depth, distance from land, and the physical, chemical, and biological characteristics of their environments. Sediments play a fundamental role in the distribution of toxic compounds in aquatic systems - they can act as sinks but also as sources of contaminants. Due to their variable physical and chemical properties of sediments, they are important factors in changes taking place in the environment (Abraham et al., 1999; Ottesen et al., 1989).

Despite more than six decades of research, sedimentation is still probably the most serious technical problem faced by the dam industry (McCully, 1996). As the sediments accumulate in the reservoir, the dam gradually loses its ability to store water, and, what is even more important, quality of the stored water can be considerably deteriorated. It can be carried out by significant contribution to accumulation or release of metals and anions in aquatic systems by various processes occurring in sediments, including adsorption-desorption, oxidation-reduction or biological activities. These products may adversely impact the health of the aquatic environment. Thus, there is an urgent need to examine the composition of the sediments found in reservoirs being the source of potable water.

The Dobczyce Reservoir with an area covering 9.7 km², mean depth 11 m (max. approximately 30 m) is one of the main dams in Poland, built on the Raba River in 1985, to supply the city of Cracow (with a
population of 780k in 2012), with potable water (Amirowicz, 2000). No large industrial plant in the vicinity of the Raba basin, surrounded mainly by suburban areas with small towns like Myslenice and Dobczyce, may suggest that the main water contaminants originate from agriculture and municipal activities, connected with untreated sewage release, washed-out from dumping grounds, settlement of atmospheric dust as well as use of the plant protection agents in agriculture.

Great amounts of heavy metals are discharged by rivers and concentrated in bottom reservoir sediments. Metals present in sediments can be found in a number of different forms, what can affect their mobility. Molecular or atomic-scale studies of environmental sciences have grown in importance recently because of the need of understanding the speciation or chemical form of environmental pollutants and the basic chemical and biological processes determining their effects on human health. The input of heavy metals in water environment can significantly damage the water resources and distribution of various living organisms. Assessing the risk associated with heavy metals presence is a prerequisite for designing recovery techniques of contaminated sites and preventing future contamination.

XAFS spectroscopy is an element-specific technique and hence it is an extremely important tool in identifying the nature of metals found in sediments (Singh, 2010; O’Day et al., 2000; Isaure et al., 2002; Van Damme et al., 2010; Caroll et al., 2002). By data refinement, local structural information of the measured element, such as coordination number, atomic distance and structural disordering, as well as local geometry and electronic structures can be extracted. The obtained information is localized, limited to one or several coordination shells of the measured element. However it is necessary to mention that XAFS has proved its usefulness for samples characterization in which the absorbing atom had been found within only a single species, what seems to be rather unlikely that the environmental samples are truly composed of such simple systems. Environmental data are usually characterized by high variability, caused by variety of natural (hydrological, meteorological, geological), artificial and anthropogenic influences. The uncertainties can be introduced to final results at every step of performed experiments starting from sample preparation and ending on analysis of collected spectra. Moreover in environmental samples absorbing atom is located in several chemical environments, very often not known a priori. The best approach to avoid incorrect interpretation of environmental data and obtain information on the number of distinct species that are present within the samples, is the application of chemometric methods for data processing such as Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) (Wasserman, 1997; Beuchemin et al., 2002; Ressler et al., 2000).

HCA divides the analyzed data into hierarchies based on calculated similarity between samples. For cluster analysis, spectrum collected for each sample is treated as a point in an n-dimensional measurement space; hence similarity between two points is measured by the spectral distance between them. Samples within the same group are more similar to each other than samples in different groups. HCA is usually applied to data sets for which there is no a priori knowledge concerning the class membership of the samples. The results of HCA are usually displayed as a dendrogram being a tree-shaped map of the intersample distances in the data set. Interpretation of the results is intuitive, which is the major reason for the popularity of this method.

PCA - the most widely used multivariate analysis technique in science - is a method for transforming the original measurement variables into new variables called principal components (PCs). Each principal component is a linear combination of the original measurement variables. Often, only two or three PCs are necessary to explain most of the information present in the data. Dimensionality reduction is possible with PCA because spectral data sets are often redundant due to collinearity (i.e. correlations) among the measurement variables. Each principal component describes a different source of information because each defines a different direction of variance in the data. Mathematically PCA is based on an eigenvector decomposition of the covariance matrix of the variables in the data set. For samples about which there is little initial information regarding the compounds contained within, PCA can provide a significant first step in gaining insight into the nature of the samples. An implicit assumption in application of PCA in XAFS spectral data analysis is that the observed spectrum for a mixture is a linear combination of the spectra from the separate constituents. Having determined the number (n) and the type of Fe components in analyzed samples with the Target Transformation (TT) procedure, a nonlinear Least-Squares Fitting (LSF) can be applied to quantify these components in sediment samples from their normalized experimental XAFS spectra.

Sediments collected from Dobczyce reservoir have been already analyzed by means of various methods: analysis of grain size distribution and application of X-ray Diffraction method (XRD) enabled mineralogical description of sediments, the use of Atomic
Absorption Spectrometry (AAS) and Proton Induced X-ray Emission (PIXE) revealed elemental composition of the samples (Reczynski et al., 2010; Golas et al., 2005). To the best of our knowledge, no XAFS studies have been involved in analysis of local structure of selected metals found in sediments from Dobczyce reservoir. In this work special attention was paid to detect any changes in the local structure of Fe within sediments located perpendicularly and longitudinally to the main river current. Main analysis of collected XAFS spectra based on chemometric methods (HCA, PCA, TT, LSF) reveal existence of two compounds in sediments samples.

**MATERIALS & METHODS**

Sediment samples (17) were taken from three hydrologically different zones in Dobczyce reservoir: the Myslenice Basin (samples marked S01-09), the Dobczyce Basin (S13-15) and the Wolnica Gulf (S16-17); samples S10-12 come from the area between two basins. Location of samples collection points is presented in Fig.1.

All materials have been sampled by remotely activated device (Ekman grab) and transferred into pre-labeled polyethylene bags to laboratory (Cracow). Sediments were visibly coarser with depth, mainly sandy in appearance, with some bits of rock, shells, and black particulate organic matter interspersed. After 48 h of drying (36 h – air drying, 12 h in oven with temperature set to 105°C) sediments were ground and sieved (the sieve with a 2 by 2 mm² mesh screen) and in this form were sent to Singapore Synchrotron Light Source (SSLS).

At SSLS, XAFS experiments were carried out to establish chemical profiles of Fe in the sediments from each of the sampling sites. Prior to experiments the samples were prepared in form of thin layers being finely ground powder smeared on adhesive tape. The sample preparation procedure was selected based on results obtained by Reczynski and Golas (Reczynski et al, 2010; Golas et al., 2005) – concentration of Fe calculated for the samples collected from Dobczyce reservoir is in the order of thousands of ppm.

XAFS experiments were performed at X-ray Demonstration and Development (XDD) beamline at SSLS with synchrotron ring energy of 700 MeV and a stored current of 350 mA. XDD is supplied with synchrotron radiation from one of the two superconducting dipoles of the Helios 2 storage ring. The photon energy is tunable from 3 to 10 keV using a channel-cut Si(111) monochromator and its flux is of the order of 10⁹ photons/s at energies of several keV. The beam size is about 4 mm horizontally and 3 mm vertically at the sample position. The photon energy scan is enabled via the rotation of the monochromator crystal driven by a motor-driver-controller system built on VME bus and controlled by the “Spec” package under the UNIX operating system (Spec User Manual, 2012). A comparison of single scans of the same sample showed an accuracy of better than 0.3 eV. Optical layout of the XAFS facility at the XDD beamline is presented in Fig.2.
Sufficient concentrations of Fe in sediments enabled to carry out experiments in transmission mode using ionization chambers to detect the incident and transmitted beam intensities, Ii and It, respectively. The samples were scanned at room temperature with the monochromatic beam in the photon energy range from 90 eV below to 750 eV above the absorption edge for metallic Fe (7.112 keV) edge in order to allow an accurate subtraction of the pre- and post-edge absorption profiles. A fine energy step of 0.1 eV was used around the edge. At absorption edge of an element, the X-ray absorption exhibits resonant and oscillating phenomena, that is used in collection of local atomic structural information. The fine structure results from the local diffraction of the excited core photoelectrons, and the strength of the oscillations is a function of the back-scattering power of the atomic matrix and the thermal and static disorder in the atomic positions.

Fe foil (standard) was repeatedly analyzed during the experiment in order to verify the stable calibration of the energy scale. Spectra were also collected from a series of reference materials: FeO, goethite (α-FeOOH), lepidocrocite (α-FeOOH), akaganeite (β-FeOOH), hematite (Fe₂O₃), magnetite, (Fe₃O₄) pyrite (FeS₂), mackinawite (Fe,Ni)₁+ₓS (where x = 0 to 0.11), ferrihydrite (Fe₂O₃•0.5H₂O), siderite (FeCO₃). Magnetite, Fe₃O₄ was selected as a standard as it is a common mineral in soils and sediments, formed by a range of microbial reactions or inherited from weathering of parent rocks (Roh et al., 2003).

RESULTS & DISCUSSION

XAFS data pre-analysis followed a standard procedure using the WinXAS code (Ressler, 1997). The data processing comprised: calibration of the energy scale, removal of the pre-edge absorption by straight-line fitting and the post-edge atomic absorption profile by fitting with a third order polynomial, normalization of an edge-step (this normalization allowed the comparison of samples with different absorber content). All spectra collected during experiments were calibrated against a position of K-edge in Fe metal-foil (7.112 keV). Threshold energy was taken as the first maximum of the first derivative of the spectra and the zero-crossing of the second derivative of the spectra. Normalized data were interpolated as needed to obtain a common energy scale for all spectra for further statistical (PCA and HCA) analysis.

XANES study. The energy position of the edge is correlated with the valence state of the atom in the sample: with increasing oxidation state the edge is shifted to higher energies. In order to make a further quantitative determination of the average oxidation state for Fe in sediments samples, the method suggested by Wong (Wong et al., 1984) was used to analyze the XANES data. A linear correlation was obtained based on the selected reference compounds (metallic Fe, FeO, Fe₂O₃, Fe₃O₄). The obtained average oxidation state for Fe species in all samples was found to be at about +3.

The pre-edge transition superimposed on the tail of the main absorption edge and edge region of the XANES spectra comprise a number of features which may be attributed to transitions between bound electronic states. Pre-edge feature in X-ray absorption spectrum is very useful to discriminate also the oxidation state and coordination number of Fe. This peak represents s-d like transition and is thus dipole forbidden, but it becomes partially allowed by mixing of the d-states of the transition metal with the p-states of the surrounding oxygen atoms (Drager et al., 1988). In our work pre-edge peaks were extracted from XANES spectra by subtracting the contribution of the edge jump which was modeled using a spline function several eV before and after the pre-edge feature. The positions
and amplitudes (intensities) of the pre-edge peaks were determined by fitting with Gaussian components.

In order to identify key relationships in the data, that is, find similarities; assess differences among analyzed points, it is necessary to apply an appropriate statistical method such as HCA. The R platform for statistical computing and graphics was used in the calculations (package stats) (DCT, 2009). Fig. 3 presents the HCA results performed on pre-edge regions obtained from XANES spectra; as can be seen three groups can be distinguished: first group – consisting of the samples S03, S09, S15 – located in close proximity to the land, second group – samples located in the middle stream (S04, S08, S11) of the reservoir, and middle stream of Wolnica Gulf (S17) – (surprisingly sample (S05) collected very close to the land belongs also to this group) and the third group enclosing samples situated at the entrance of small gulfs (S02, S06, S13, S16) as well as samples situated close to the land from the area between two main basins (S10, S12) and S07 (from the main stream of Dobczyce reservoir) and S14 (from the central part of Dobczyce basin). As can be seen in Fig. 4 the mean pre-edge peaks

![Cluster Dendrogram](image)

Fig. 3. Cluster analysis result (dendogram) on pre-edges spectra collected from various locations from Dobczyce reservoir with cluster membership marked by the rectangles

![Mean pre-edge peaks](image)

Fig. 4. Mean pre-edge peaks characteristic for three clusters obtained by HCA
characteristic for three various groups found by HCA, differ slightly in terms of position and amplitude what may point at subtle changes in the local symmetry of iron species within sediments.

As was mentioned earlier detailed EXAFS analysis can reveal the local structural information of Fe in sediments samples. Taking into account that in environmental samples analysed element can exist in more than one chemical environment, PCA analysis was used to obtain information about the number of components (significant independent sources of variations) statistically meaningful to quantitatively reproduce the experimental data set of normalized EXAFS spectra (Manceau, 2002). Primary components refer to those, which contain the signal and, in principle, are sufficient to reconstruct each experimental spectrum by suitable linear combination. Secondary components refer to those, which contain only the noise. A major advantage of PCA approach is that no a priori assumption is needed as of the number of references and the type of reference compounds used. As default the number of components necessary to reconstruct the experimental spectra is limited to those components that show significant eigenvalues/weights. Results from the PCA performed on the spectra of 17 sediments samples collected from various locations are given in Table 1.

The number of meaningful components \( n \) was evaluated with three criteria: the indicator parameter \( \text{IND} \) (internal parameter in WinXAS software (Ressler, 1997)), the sum of the residuals times the number of components used \( S(R^*n) \) and visual inspections of the components and spectral reconstructions. It is very important to mention that more than one criterion should be used in choosing the number of significant components as the determination of \( n \) is a crucial step that may influence the solution obtained in the subsequent target analysis.

\( \text{IND} \) and \( S(R^*n) \) indicators exhibit minima at the boundary between primary and secondary components hence can be used to guide the decision as of which components are primary and which are secondary ones. If the minima in \( \text{IND} \) and \( S(R^*n) \) do not fall on the same principal component, this might indicate that the last component is only a minor constituent in the experimental spectra. In our analysis \( \text{IND} \) and \( S(R^*n) \) reached a minimum for two components, suggesting that only component 1-2 are linear combinations of real species for samples. The first component extracted by PCA using Fe K-edge EXAFS data for sediments accounted for 98.28% of the total variance within the data while the second component explained 0.97% of the total variance. XAFS spectroscopic data usually show a very high eigenvalue for the first component, the subsequent eigenvalues are relatively less significant compared to the first one.

As was mentioned earlier PCA analysis was conducted in WinXAS Version 3.11; selected first two components were used to reconstruct all EXAFS spectra to verify that in all cases reconstructed spectra superimpose with the experimental ones; plots residuals versus spectrum number were also checked for any spikes that could indicate any missing components. As was noticed adding more components beyond the first two did not improve the quality of the reproduction significantly. That visual inspection was additional step in the identification of minimum number of components describing properly experimental spectra. Fig. 5 depicts the examples of spectra collected for sediments compared with the reproduced data using the first two components, as can be seen a very good agreement with the experimental data was obtained.

As the significant components defined in the PCA have no chemical or physical meaning, TT procedure attempts to determine if a chosen reference spectrum (i.e., from a given model compounds) can be considered as a legitimate “end-member” component. Mathematically, this means that it can be represented in the same mathematical space as defined by the

<table>
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<tr>
<th>Component</th>
<th>Eigenvalue (Variance explained %)</th>
<th>Cumulative variance %</th>
<th>IND</th>
<th>S(R^*n)</th>
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<td>1</td>
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<td>98.280</td>
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<td>13.00</td>
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<tr>
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<td>0.970</td>
<td>99.250</td>
<td><strong>0.605</strong></td>
<td><strong>9.16</strong></td>
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<td>99.371</td>
<td>0.627</td>
<td>9.51</td>
</tr>
<tr>
<td>4</td>
<td>0.092</td>
<td>99.463</td>
<td>0.712</td>
<td>9.63</td>
</tr>
<tr>
<td>5</td>
<td>0.036</td>
<td>99.499</td>
<td>0.832</td>
<td>10.3</td>
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</table>
components of the sample spectra. This was done by multiplying the reference spectrum by the eigenvector column and row matrix. If this resultant spectrum matches well with the reference (c.a. 1% error or experimental limits) then the reference spectrum is a possible species in the unknown data sets. Two model compounds are found to yield a sufficient match upon transformation, namely, goethite and hematite. The corresponding XANES spectra together with their transformed spectra are displayed in Fig 6 a, b; on the other hand, Fig 6 c shows TT results for akageneite, indicating that this Fe species is likely not present in the analyzed sediment samples.

The proportion of each Fe species in the various samples was determined by LSF of the experimental EXAFS spectra with linear combinations of the reference spectra. Simulations were performed using one or two Fe species out of the two references previously identified by TT. Fitting was optimized by minimizing the residue of the fit, for all accepted fits R was less than 1. Visual examination was also used to check the consistency of the fit. The best fits for sediment samples spectra were obtained with a combination of two reference spectra for goethite and hematite. In Fig. 7 the percentage contributions of each reference spectrum to the fit for various experimental
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Fig. 6. TT results indicating presence of goethite (α-FeOOH) and hematite (Fe₂O₃) in sediment samples, akaganeite (β-FeOOH) is unlikely present in analyzed spectra.

Fig. 7. Percentage contributions of hematite and goethite to the best fits for sediment samples spectra collected from various location within Dobczyce reservoir. Points are color-coded according their cluster membership established by pre-edge peaks HCA analysis. (Estimated errors of presented values are lower than 1%)
data are presented, as can be seen in all analyzed samples collected from various location, there is more hematite than goethite within collected material. Points shown in Fig. 7 were color-coded based on earlier analysis of pre-peak regions (HCA), points denoted as cluster 1 contain the highest percentage of hematite, however for point S05 classified as a cluster 2, also the similar amount of hematite was detected; what can be understood by checking the point position on the map (Fig. 1), point S05 is located near the land on the same side like point S09, which belongs to cluster 1.

For most of the points representative for cluster 2 (S04, S08, S11, S17), concentration of hematite and goethite within them seems to be at very similar level, only small differences -less than 2% for hematite (65.84-67.04%) and less than 2% (30.93-32.38%) for goethite are noticeable. Cluster 3 includes points for which mentioned earlier differences are greater – for hematite 5%(61.66-66.43%) and for goethite 12%(27.75-39.02%).

CONCLUSION

The Dobczyce reservoir is a main source of potable water for almost 1 million people. As was mentioned earlier sedimentation is an inevitable happening taking place in all water reservoirs. Quality of the potable water depends strongly on processes occurring in sediments. That is why in this paper local structure of Fe, found in sediment samples collected from various points from Dobczyce reservoir, was analyzed by XAFS. As environmental system is characterized by a plethora of influences, for proper XAFS spectra analysis also chemometric methods were used. The obtained average oxidation state for Fe species in all analyzed samples was found to be at about +3 based on the method suggested by Wong (Wong et al., 1984). PCA estimated the number of significant components-separate constituents within XAFS sediments spectra, TT analysis pointed for goethite and hematite as dominant compounds in analyzed spectra; LSF calculated their proportion for every location.

All results indicate for a high similarity among analyzed data collected for various points from Dobczyce reservoir. Based on obtained results, it can be concluded that Fe is mainly connected to oxygen in sediments samples, hence its (re-) mobilization to the water may be disregarded.

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