



Correlation Between Magnetic Parameters and Chemical Composition of Lake Sediments from Northern Bohemia—Preliminary Study

E. Petrovský¹, A. Kapička², K. Zapletal², E. Šebestová³, T. Spanilá³, M. J. Dekkers⁴ and P. Rochette⁵

¹Geophysical Institute, Czech Academy of Sciences, Bočni II/1401, 141 31 Praha 4, Czech Republic

²AGICO Ltd., Ječná 290, Brno, Czech Republic

³Institute of the Structure and Mechanics of Rocks, Czech Academy of Sciences, 182 09 Praha 8, Czech Republic

⁴Paleomagnetic Laboratory "Fort Hoofddijk", University of Utrecht, Budapestlaan 17, 3588 CD Utrecht, The Netherlands

⁵Universite d'Aix Marseille 3, CEREGE Europole de l'Arbois BP80, 13545 Aix-en-Provence, France

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Abstract. Recently, magnetic measurements have been used to outline areas with increased loading of toxic metals due to industrial activity. It is supposed that magnetic minerals, which are easily detectable, can carry toxic metals of anthropic origin. However, physical background of this relationship is not comprehended yet. In this study, we present our first results on statistical correlation of various magnetic parameters on one side and chemical composition on the other, obtained on sediments from the bottom of lake Nechranice, located in northern Bohemia; the captive area being typical for intensive industrial and mining activity (brown-coal basins, uranium mines, coal-burning power plants). Our results suggest, that magnetic susceptibility, which has been used in other studies as indicator of increase pollution levels due to local sources, does not actually link to any of the toxic elements in concern. This finding can be explained in terms of complex inlet due to different types of pollution sources.

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1. Introduction

In several studies, relationship between magnetic susceptibility and concentration of toxic elements in various environments was pointed out. Linear relationship between the concentration of ferrimagnetics and the Cu, Fe, Pb and Zn content in sediment samples from urban area and near highways was found by Beckwith et al. (1986). Hunt et al. (1984) observed similar relationship between saturation isothermal remanent magnetization (SIRM) and susceptibility and Pb, Cu, Zn and Cd in atmospheric particulates. Hullet et al. (1980) found that certain transition elements, like V, Cr, Mn, Co, Ni, Zn and Cu, present in fly ash from American power plants, are associated with magnetic minerals and occur mostly in the

form of substituted spinels. Similar conclusion was drawn out by Dekkers and Pietersen (1992). Positive correlation between magnetic susceptibility and concentration of Zn, Pb and Cd in Polish topsoils was found by Strzyszcz and Magiera (1993) and Strzyszcz et al. (1996). These are only few evidences that magnetic minerals, present in samples exposed to industrially derived toxic elements, are somehow related to the concentration of these elements. This relationship can be based either on incorporation of toxic elements into the lattice structure of the ferrimagnetics during combustion process, or on the adsorption onto surface of ferrimagnetics already present in the environments. The latter process is supported by findings, that goethite and haematite can adsorb e.g. Cu, Pb, Zn, Co (Rose and Bianchi-Mosquera, 1993; Rodda et al., 1993).

This study reports on our first results of statistical correlation between magnetic parameters (magnetic susceptibility, coercive force, remanent magnetization, etc.) and chemical composition of lake sediments coming from lake Nechranice, which are supposed to contain toxic elements coming from industrial activity in the lake catchment. The aim of the study was to look for thinkable relationship between the presence of specific magnetic mineral and its physical shape on one hand and the presence of toxic elements in concern on the other.

2. Samples and methods

Lake Nechranice is located on Ohře river in northern Bohemia (Fig. 1). The river catchment includes several sites of various industrial activity, e.g. brown-coal basins around Sokolovo, uranium mines close to Jáchymov, major brown-coal burning power-plants at Prunéřov, etc. Sediment samples were taken from the upper few centimeters of the lake bottom at different distance from

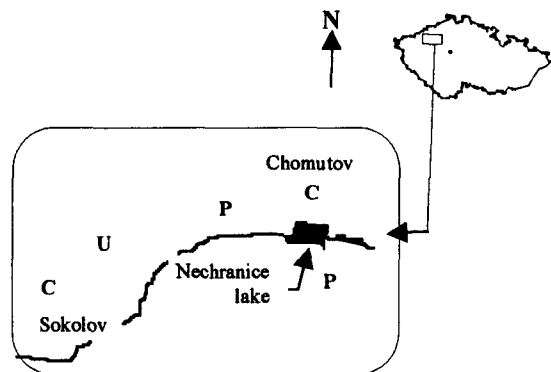


Fig. 1. Location of the Nechranice lake. C - brown-coal basins, U - uranium mines, P - coal-burning power plants.

the inlet. The samples were homogenised and dried out at moderate temperature of about 100°C. It has to be pointed out that sampling strategy was not aimed at investigating water flow patterns or sedimentation rates. The only aim was to study chemical and magnetic properties of the samples and their mutual links.

Chemical composition was determined using ICP mass spectroscopy. Magnetic susceptibility was measured using KLF-3 Mini-kappabridge (Geofyzika Brno). To estimate the contribution of superparamagnetic particles, frequency-dependent susceptibility was determined on the basis of measurements by a Bartington MS2B dual-frequency susceptibility meter. Remanent and coercive parameters were evaluated following measurements of hysteresis curves performed on Molyneux vibrating sample magnetometer. The measurements were corrected for the paramagnetic contribution. Ferrimagnetic minerals present in the samples were determined on the basis of temperature dependence of magnetic susceptibility measured using CS-2 furnace attached to KLY-2 Kappabridge (AGICO Brno, Hrouda, 1994).

Relationship between chemical composition and magnetic parameters was evaluated on the basis of correlation matrices and principal component analysis using the Statgraphics™ software.

3. Results and discussion

Curie point measurements revealed that all the samples contained magnetite and all except for one another magnetic phase with transition temperature at 160-170°C. Typical behaviour of magnetic susceptibility upon heating is shown in Fig. 2. Since this transition is irreversible upon heating up to 700°C, goethite can not be considered. The temperature stability suggests the presence of a substituted spinel. However, the amount of the sample available did not allow us to carry out X-ray analysis.

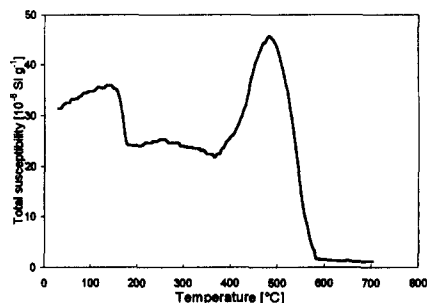


Fig. 2. Example of temperature behaviour of magnetic susceptibility, showing two magnetic transitions at 160-170°C (substituted spinel) and 575-580°C (magnetite).

Chemical composition data obtained by ICP mass spectroscopy are listed in Table 1 (only showing the questioned elements). These toxic elements show total contents much higher than background levels as reported for the northern Bohemian region by Němeček *et al.* (1995). Magnetic parameters of the same samples are shown in Table 2; κ_{lf} and κ_{hf} denote low- and high-frequency susceptibility, respectively, and f/d represents frequency dependent magnetic susceptibility (e.g., Dearing *et al.*, 1996). J_s and J_r stand for saturation and remanent saturation magnetization, respectively, and H_c means coercive force. For statistical correlation, two sets of elements were selected. Firstly, Cu, Pb, Zn, Ni and Mn were considered, the elements that were reported to be adsorbed onto the surface of goethite and/or haematite (Rodda *et al.*, 1993; Rose and Bianchi-Mosquera, 1993) or incorporated into the structure of goethite (Cornell, 1991). The other set of elements studied consists of Fe, Cd, Ti and As, the elements which were mostly found to show linear relationship with magnetic susceptibility in topsoils and atmospheric particulates (e.g., Hunt *et al.*, 1984; Beckwith, 1986; Strzyszc and Magiera, 1993; Strzyszc *et al.*, 1996).

Table 1. Chemical composition of the sediment samples (ICP Mass Spectroscopy). Only the questioned elements are listed. (Data in ppm)

Sample	Cu	Pb	Zn	Ni	Mn	Fe	Cd	Ti	As
NB1	178	94.0	639	91.6	3304	58800	5.5	6070	597
N2	161	51.6	555	173.0	1640	62350	5.4	7950	375
NB2	143	52.0	426	71.6	1464	53150	0.3	6040	358
N3	136	74.8	548	91.1	1471	55600	0.3	3930	260
NA3	173	83.2	615	79.6	1900	54200	1.8	6040	314
N5	187	81.0	680	101.0	2140	58200	5.0	6390	400
N6	211	38.7	419	89.0	893	58800	0.3	5700	321
N7	174	74.7	558	94.1	1790	55850	1.0	5565	400
N9	305	124.0	1079	100.0	1620	63800	7.5	7740	345
NA9	102	53.0	367	62.5	1240	53100	1.5	3530	97
N11	181	75.6	593	81.5	1430	60100	0.4	6430	229
N12	230	107.0	876	91.2	1380	62300	4.2	6820	384
N13	194	92.1	684	76.9	1770	62000	3.9	6045	314
N14	218	126.0	1057	88.3	1932	59900	4.4	4690	185
Average	185	81.6	650	92.2	1712	58439	2.9	5924	327
Maximum	305	126.0	1079	173	3304	63800	7.5	7950	597
Minimum	102	38.7	367	62.5	893	53100	0.3	3530	97
St. Dev.	48	26.6	218	25.6	557	3574	2.4	1245	117

Table 2. Magnetic parameters of the sediment samples; κ_f and κ_H - low- and high-frequency susceptibility, respectively, fd - frequency dependent magnetic susceptibility, J_s and J_r - saturation and remanent saturation magnetization, respectively, and H_c - coercive force.

Sample	κ_f [10 ⁻⁶ SIg ⁻¹]	$\kappa_H - \kappa_f$ [10 ⁻⁶ SIg ⁻¹]	fd [%]	J_s [mAm ² kg ⁻¹]	J_r [mAm ² kg ⁻¹]	H_c [mT]
NB1	7.91	0.29	4.14	1595	316	14.3
N2	17.99	0.31	2.07	1798	312	13.1
NB2	24.51	0.35	1.34	2972	431	10.8
N3	19.66	-0.07	-0.45	1860	247	9.6
NA3	10.00	-0.15	-1.92	1319	217	12.7
N5	7.44	0.23	1.99	1082	197	13.9
N6	51.01	0.61	2.36	5458	669	11.0
N7	46.79	-0.05	-0.12	7583	1193	11.8
N9	49.06	0.15	1.92	2192	355	11.9
NA9	21.20	0.50	3.50	2404	365	11.5
N11	26.92	0.60	3.05	4608	517	8.9
N12	13.19	0.41	4.04	3204	501	10.8
N13	21.48	0.12	0.85	2469	393	11.5
N14	18.96	0.28	1.53	2573	436	10.6
Average	24.01	0.26	1.74	2937	439	11.6
Maximum	51.01	0.61	4.14	7583	1193	14.3
Minimum	7.44	-0.15	-1.92	1082	197	8.9
Stand. Dev.	14.74	0.24	1.73	1804	251	1.5

Correlation matrices of the two sets of toxic elements and magnetic parameters studied are shown in Table 3. The correlation coefficients are presented along with the corresponding levels of confidence. Two variables that have a correlation coefficient different from zero are said to be correlated. In other words, positive correlation coefficient means that both variables increase (or decrease) at the same time. Level of confidence expresses the probability that the above observation is not by chance. This parameter can reasonably serve as a measure of significance of the correlation. For more details on correlation matrices, see e.g. Wackernagel (1995). From these results one can conclude that except for manganese,

Table 3. Correlation matrix of contents of toxic elements in concern vs. magnetic parameters studied. Upper values represent correlation coefficient, while the lower ones are levels of significance. Meaningful correlations are marked in bold typeface.

	κ_f	H_c	J_r	J_s	J_r/J_s
Cu	0.3817	-0.0068	0.0732	0.0549	0.1135
	0.1781	0.9815	0.8035	0.8521	0.6993
Pb	-0.1446	0.0273	-0.1296	-0.2505	0.3925
	0.6220	0.9261	0.6341	0.3878	0.1651
Zn	-0.0158	0.0171	-0.1339	-0.2250	0.3441
	0.9573	0.9536	0.6481	0.4393	0.2283
Mn	-0.5031	0.6353	-0.2289	-0.3793	0.7917
	0.0667	0.0146	0.4311	0.1811	0.0007
	-0.0385	0.3432	-0.0876	-0.1446	0.3224
Ni	0.8960	0.2297	0.7659	0.6219	0.2610
Fe	0.1236	-0.0501	-0.0581	-0.0647	0.1514
	0.6739	0.8651	0.8437	0.8261	0.6054
	-0.1969	0.5943	-0.3608	-0.5094	0.7653
Cd	0.4999	0.0250	0.2051	0.0628	0.0014
	0.0826	0.2649	-0.0581	-0.0766	0.2438
Ti	0.7789	0.3601	0.8437	0.7947	0.4010
	-0.1280	0.5591	0.0644	-0.0422	0.5457
As	0.6627	0.0376	0.8270	0.8862	0.0436

Table 4. Coefficients of first two principal components (PC) of multivariate analysis of two sets of toxic elements and magnetic parameters in question.

Variable	PC		Variable	PC	
	First	Second		First	Second
Cu	0.092	-0.563	Fe	0.192	0.388
Zn	0.242	-0.523	Cd	0.419	0.184
Pb	0.268	-0.475	Ti	0.249	0.430
Ni	0.135	0.016	As	0.282	0.327
Mn	0.380	0.018	κ_f	-0.283	0.423
κ_f	-0.347	-0.296	H_c	0.397	0.084
H_c	0.346	0.149	J_r	-0.298	0.425
J_r	-0.328	-0.202	J_s	-0.366	0.396
J_s	-0.401	-0.178	J_r/J_s	0.430	0.015
J_r/J_s	0.436	0.011	% of variance	45.37	25.32
% of variance	40.25	25.72			

neither of the elements in concern shows significant correlation with magnetic parameters sensitive to concentration of ferrimagnetic minerals (i.e. κ_f or J_s).

On the other hand, cadmium, arsenic and manganese show significant correlation with magnetic parameters reflecting the stability of domain structure (H_c , and/or J_r/J_s). The observed positive correlation suggests that the more of the toxic elements is present, the wider is the hysteresis loop, or, in other words, the more stabilised are the domain walls. Low values of fd (Table 2) suggest that the samples are not dominated by superparamagnetic particles; coarse multidomain grains are assumed as the dominant fraction.

Principal component analysis is one of the most widely used methods of multivariate data analysis, mainly due to its simple algebra and straightforward interpretation. A set of correlated variables is transformed into uncorrelated, orthogonal factors - principal components (Wackernagel, 1995). These are represented by linear combinations of the individual variables, explaining certain part of total variances within the data set. Variances in the data cloud can be displayed graphically by biplots in the coordinate system of the principal components, length of the vectors being indicator of the component weight (i.e. how much of the variances can be explained by this particular linear combination) and angle between each couple of vectors showing their mutual correlation. Fig. 3 shows the results of principal component analysis of the two sets of elements and magnetic parameters in concern. Coefficients of the first two principal components are listed in Table 4. Clearly, the previous results obtained by correlation matrices are confirmed. Major part of variances (40%) within the dataset consisting of the first set of elements and magnetic parameters can be explained by linear combination, dominated by Mn, H_c and J_r/J_s with approximately the same weight. Next, 26% can be explained mainly by the concurrent presence of copper, zinc and lead. Neither of the elements correlates with concentration-dependent magnetic parameters. Similar results were obtained for cadmium and arsenic from the other set of elements. Surprisingly, iron shows correlation with neither of the magnetic parameters measured.

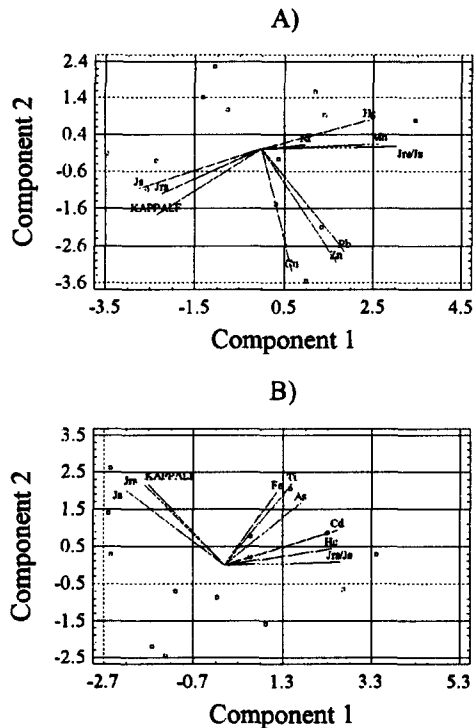


Fig. 3. Biplots of first two principal components of principal component analysis of the two sets of toxic elements and magnetic parameters studied. The principal component coefficients are listed in Table 4.

4. Conclusions

In this preliminary study, bottom-lake sediments from lake Nechanice in northern Bohemia were investigated. Captive area of the lake is largely affected by various industrial activities as brown-coal mines and power plants, uranium mines and steel industry. We focused on two sets of toxic elements present in the samples and their correlation with magnetic parameters. Except for manganese, neither of the elements exhibits positive relationship with magnetic susceptibility. On the other hand, cadmium, arsenic and manganese showed to be linked with coercive force and remanent to saturation magnetization ratio. This can be explained in terms of incorporation of these elements into the structure of ferrimagnetic minerals present. This idea is supported by observed temperature behaviour of magnetic susceptibility, displaying Curie temperatures corresponding to magnetite and a substituted spinel structure. Following the findings of Rodda *et al.* (1993) or Cornell (1991), such adsorption or incorporation is possible and can yield the increase of domain-wall pinning sites, thus resulting in the observed trend of "hardening" the hysteresis loops.

The observation that magnetic susceptibility data were practically random, independent of the contents of toxic elements, can be caused by complex effect of various pollution sources. Obviously, atmospheric particulates were

not dominant as in the case of the effect of power plants alone (e.g. Hunt *et al.*, 1994; Strzyszcz *et al.*, 1996). Moreover, effect of dissolution of atmospheric particulates in aqueous environs can certainly bias the expected observations. Therefore, in this kind of magnetic investigation of industrial pollution, clear distinction between individual types of pollution sources has to be done, which is a challenge to our further studies.

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