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Surveying the anthropogenic impact of the Moldau river sediments and nearby soils using magnetic susceptibility

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Abstract Measuring magnetic susceptibility is a method which is used to estimate the amount of magnetic particles in soils, sediments or dusts. Changes in magnetic susceptibility can be due to various reasons: input from different sources of sediments, e.g. from different soils or rocks, atmospheric fallout of anthropogenic dusts containing magnetic particles produced by fossil fuel combustion, steel production or road traffic. In the case of river sediments, input from the catchment is of primary significance. The main aim of this investigation was to test the potential of magnetic susceptibility screening in identifying the effect and significance of anthropogenic activities in an area with complex geological conditions. We investigated the magnetic susceptibility of riverbed sediments of the largest river of the Czech Republic, the Moldau river. Besides that, the magnetic signal of nearby topsoils as well as of outcropping bedrocks in the vicinity of the river was examined. In the upper 300 km of the river, the magnetic enhancement of the river sediments can be linked to anthropogenic activities. Positive correlations were found in the river sediments between the contents of Cu and Zn and magnetic susceptibility, while Fe, Mn and Ni did not show a correlation with magnetic susceptibility. However, the major geogenic magnetic anomaly in the area around the Slapy dam has made it impossible to unambiguously interpret the magnetic signal in terms of anthropogenic impact in the last 80 km downstream.

Introduction

The mass-specific magnetic susceptibility (χ) indicates the amount of magnetic particles in materials like soils, sediments or rocks. Magnetite is of particular importance because of its high χ value (5–10×10^{-4} m^3kg^{-1}) and its widespread occurrence in nature. It can be found in many different kinds of rocks, modern soils and sediments. Magnetic particles can originate from weathered bedrocks, biogenic activity, volcanic ashes or extraterrestrial particles.

Magnetite can also be of anthropogenic origin, mainly being produced by combustion processes and emitted together with pollutants such as heavy metals or PAH along similar transport pathways (Hunt 1986; Flanders 1994). Therefore, under certain conditions the amount of magnetic particles may correlate with the content of heavy metals (Beckwith et al. 1986; Georgeaud et al. 1997; Knab et al. 2001; Jordanova et al. 2003a, b) Recently, measurements of χ have been used as an additional method for detecting the extent of anthropogenic pollution (Petrovský and Ellwood 1999). Investigations along the river Mur (Austria) show a positive correlation between χ and the slag of iron production in river sediments and a significant positive correlation of χ to some heavy metals like Pb, Cr and Zn (Scholger 1998). Another study of river sediments by Chaparro et al. (2003, 2004) proved that magnetic susceptibility is able to reflect industrial input into river sediments. Desenfant et al. (2004) tested the magnetic susceptibility of river sediments in terms of anthropogenic pollution in an area with negligible lithogenic contribution and reported on the until now highest correlation between the concentration of magnetic particles and lead and zinc in river sediments. Wehland et al. (2002) and Jordanova et al. (2003, 2004a, b) report results of detailed magnetic susceptibility screening and profiling of the Theiss and Danube river sediments in Romania and Bulgaria. In this way the passage of the pollution front along the Danube in NW Bulgaria after the Baja Mare dam breakage disaster in January 2000 could be detected by magnetic means. It is now obvious that fast in-situ magnetic measurements, supported by laboratory magnetic analyses, can be used in estimating the anthropogenic vs. lithogenic contribution to river sediments.

The aim of this paper is to test how magnetic measurements of river sediments are affected by complex geological settings. Compared to the study of the Arc river (France) by Desenfant et al. (2004) where the catchment is based on limestones, poor in magnetically significant minerals, the area examined in this study comprises both magnetically weak and strong rock formations. Therefore, it would be useful to investigate to what extent magnetic contributions from the basement biases, or even overcomes, the contribution due to anthropogenic activities. During our first investigations of the Moldau river we found that χ can be linked to some anthropogenic activities like sewage treatment, sawmills, run-off waters and technical constructions (Petrovský et al. 2000) (Fig. 1). Following these results we extended the measurements along the Moldau river from its source to the mouth into the river Elbe north of Prague. We expected some positive correlations between the χ values and concentrations of some heavy metals like in other environments (Strzyszcz et al. 1996; Knab et al. 2001; Petrovský et al. 1998; Kapička et al. 1999) or as found by Desenfant et al. (2004) in the case of river sediments. Therefore, in addition to magnetic analyses, the sediment samples were analysed for the content of Cu, Fe, Mn, Ni and Zn.

Additionally, magnetic susceptibility of the outcropping rocks was measured in order to estimate the geological influence on the χ values in the river deposits. Especially in the region of the dams such intact outcropping rocks were difficult to find in the close vicinity of the river because of the straightening and fortification of riverbanks.

Parent rock mineralogy largely determines the magnetic mineralogy of soils. Extensive weathering processes may lead to the transformation of lithogenic minerals (both magnetic and non-magnetic, like different clay minerals) into weakly magnetic iron oxyhydroxides and haematite (Cornell and Schwertmann 1996) and in such cases soil susceptibility will be low. Susceptibility of the upper soil horizons may increase as a result of agricultural activities (ploughing or using fertilizers). Natural soil formation and especially production of biogenic magnetite by magnetotactic bacteria can increase χ values as well. Additionally, at least some parts of the (grass)land near rivers could have been flooded in former times and could be enriched on fine sediment load from the river which could significantly affect χ values of the soil.

River sediments represent a mixture of erosion products of rocks and soils in the catchment area. However, also inlets of anthropogenic sources like run-off from highways or water from cleaning farms can influence χ. During transportation the sediment undergoes a separation with respect to grain-size, shape and its weight. Each fraction has its own path of transportation along the river. Therefore, for measuring the river deposits and for comparison of the χ values we tried to always investigate the finest sediment fraction (<2 mm).

Geography and geology

The Moldau river is the longest river in the Czech Republic. Its source is located in the Šumava National Park in the Bohemian Massif near the border of Germany. Even here the topographic slope is less than 3% (Fig. 2). In its upper part the river flows mainly through rural areas with low population density, small villages with mostly agricultural areas and large forests. Fine sediment is rare and can be found only between gravels and boulders. The middle part of the Moldau through the geological formations of the Moldanubikum river is dominated by a chain of dams with hydroelectric power stations. The banks are straightened and fortified by boulders. Only a few larger towns like Cesky Budejovice or Cesky Krumlov are situated in this middle part. Also here, sediments are scarcely found at the banks because the dams are forming sediment traps. The lower part of the Moldau river is dominated by larger cities, with especially the area around Prague being widely urbanized. Moreover, the lower part of the Moldau river is navigable.

Along its course, the Moldau river crosses the Bohemian Massif, the high metamorphic and complexly deformed Moldanubikum and the Tepla-Barrandium (Čejchanová and Waldhausrová 1984; Mahel' et al. 1984). The Moldanubikum includes various ortho and paragneises with spacious intrusions. There are mainly migmatites of arterite and ophthalmite type and magmatites of intermediate to acid type, which are sometimes strongly deformed. Acid Palaeozoic volcanic rocks crop out in the north of Lipno Dam and in the area north of Cesky Krumlov. However, there are a few

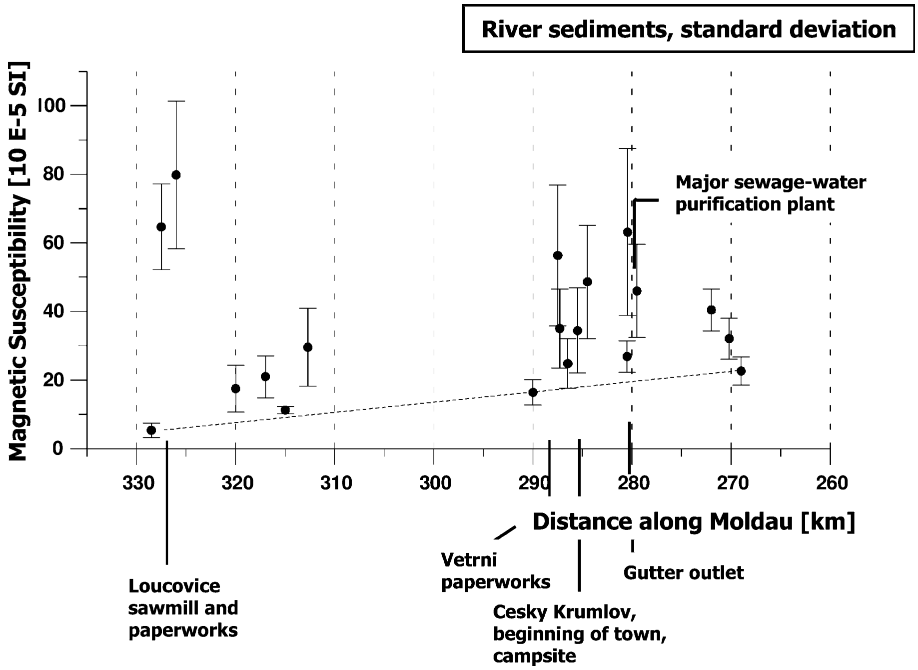

Fig. 1 Average magnetic susceptibility values (κ) of river sediments and standard deviation of the data are shown within a limited, 60 km long section of the Moldau river close to the source. Magnetic enhancement and a more pronounced data scatter can be linked to close sources of sediment pollution. The *dotted line* can be interpreted in terms of the downstream accumulation of both anthropogenic and natural contributions to the susceptibility signal of riverbed sediments. It was calculated by connecting the minimum average susceptibility values with the minimum data scatter before the next enhancement

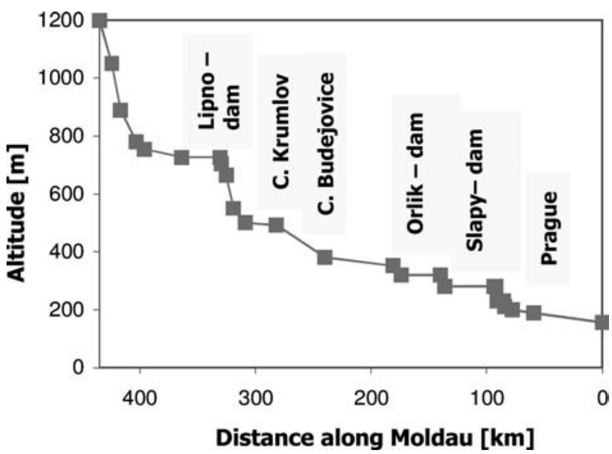

Fig. 2 Topographic diagram of the Moldau river (extreme vertical exaggeration). The slope of the river is very low; even in the upper part it is less than 3%

locations revealing undivided ultrabasites. Some diorites are explained as hypo-abyssal and subvolcanic intrusions. Ceske Budejovice is located in a basin of the Bohemian Massif. Predominantly Hercynian dykes are located in the area of the Slapy dam.

The Barrandium includes low metamorphic and partly non-metamorphic rocks of young Proterozoic and Palaeozoic age. It consists of pelitic to psammitic sediments and of basalt-spilit-keratophyry-volcanism. Near the confluence with the Elbe river, Moldau flows along mainly sedimentary rocks of the North-Bohemian Chalk Basin (Walter 1995; Mahel' et al. 1984).

The area of Slapy is known to be one of the largest positive magnetic anomalies in the Bohemian Massive. The anomaly is not connected to a specific type of eruptive rock (basic, intermediate and acid). The irregular distribution of magnetite depends on the tectonic position of the rocks and the ability to form magnetite by the migration of Fe ions (secondary minerals). Thermomagnetic curves show that all rock types contain at least two ferrimagnetic phases—one phase with a T_C of 450–500°C is interpreted as the Mg-substituted magnetite while the other phase with a T_C of 150–200°C is most probably hemoilmenite. Mg-magnetite is not the primary mineral (Čejchanová and Waldhausrová 1984).

The occurrence of this wide variety of rocks reminds us that χ can be strongly influenced by the geological background. For this reason, it was important to measure the χ values of the rocks themselves.

Methods

In-situ volume-specific low-field magnetic susceptibility (κ) was measured using a kappameter (Bartington) with a loop sensor (MS2D probe) of 18 cm diameter. We measured river sediments (preferably fine sand), rocks or boulders and non-agricultural grassland (topsoil) at each locality wherever possible. The river sediments were sampled in the riverbed or at or near the riverbanks. Topsoils were measured at sites as close as possible to the riverbank, mostly at distances of a few meters. The samples were mostly taken from outcropping rocks and/or were measured nearby the riverbank (at distances of a meter to several 10 m); in addition boulders from the riverbed were investigated. The origin of the latter was not always known; however, it has to be noted that the major aim was to control the geogenic signal at each test site. At the crucial locations of anticipated anthropogenic effect the density of measuring points was increased. In total we measured more than 1,400 single points on river sediments, 600 on topsoil and 300 on rocks at 63 sites. River sediments were sampled, dried and later sieved. The mass-specific χ of the finest fraction (<2 mm) was measured in the laboratory using a KLY-3 kappabridge (AGICO).

For heavy metal analysis part of the finest fraction was dissolved in 20 ml 2 mol HNO_3. The stock solution was analysed for the content of Cu, Fe, Mn, Ni and Zn by atomic absorption spectroscopy. Bi-plots and linear regression analysis were applied to find the potential relations between χ and the content of the investigated elements.

Results

Magnetic susceptibility of rocks

In Fig. 3 the magnetic susceptibility values of the bedrocks (geological background) are shown. For a better presentation the mean values are calculated for all sites within the 10 km "section windows", respectively.

The upper part of the Moldau river shows low mean values of less than 2.0E-4 (SI). Only the area below Cesky Krumlov reveals a higher variability [river km (R-km): 280–285].

The area of the magnetic anomaly around Slapy shows extremely high κ values of more than 4.0E-3 (SI). Here, quite a large variability of magnetic susceptibility can be found within some hundreds of meters, as well as within one site. We found layers of sedimentary rocks with κ values of 2.2E-4 (SI) intercalated with layers with κ values of 3.0E-2 (SI) in bands of less than 1 m.

Magnetic susceptibility of topsoils

Within the uppermost 100 km from the source topsoils show lower κ values than bedrocks (Fig. 4). This reflects a rather insignificant anthropogenic effect (low enhancement in the uppermost layers due to atmospheric deposition of anthropogenic magnetic particles) in this area with mainly extensive stock farming.

More downstream the Moldau river, the rock κ values are low, but the topsoil κ values are quite high. For instance, the area around Loucovice (R-km: 330) has a median rock value of 5.0E-5 (SI) whereas the topsoil shows a more than five times higher median value of 2.8E-4 (SI), with the maximum value of 6.0E-4 (SI). This trend continues until Hluboka, that is about 10 km downstream of Ceske Budejovice (R-km: 220 km). This topsoil enhancement cannot be explained in terms of

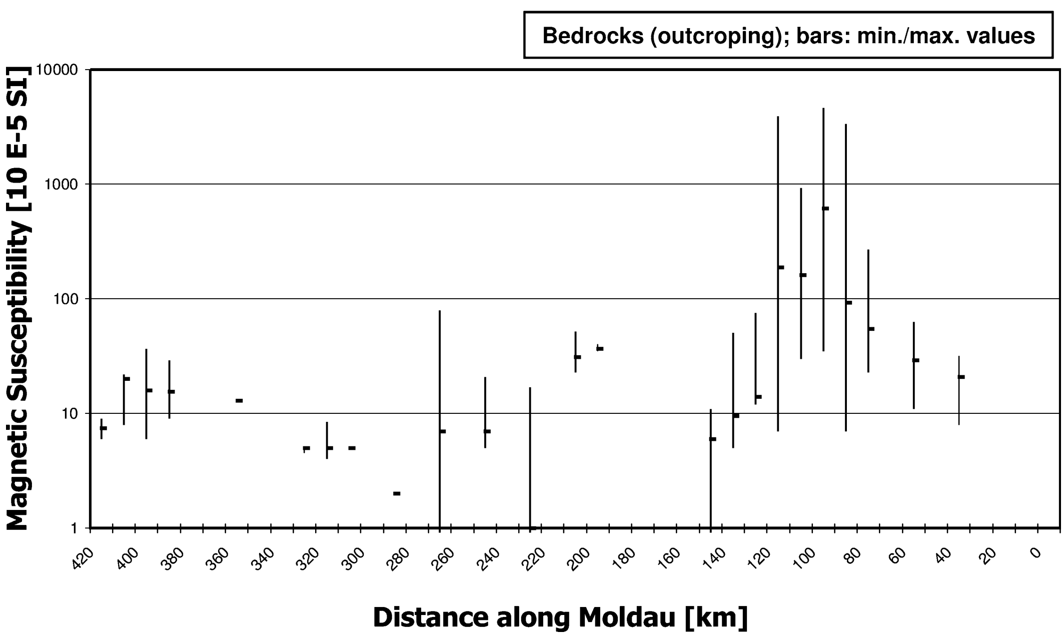

Fig. 3 Median magnetic susceptibility values of outcropping bedrocks along the Moldau river (10 km "section windows"). Between R-km 380 and 200 an area with low values and variability of κ is indicated

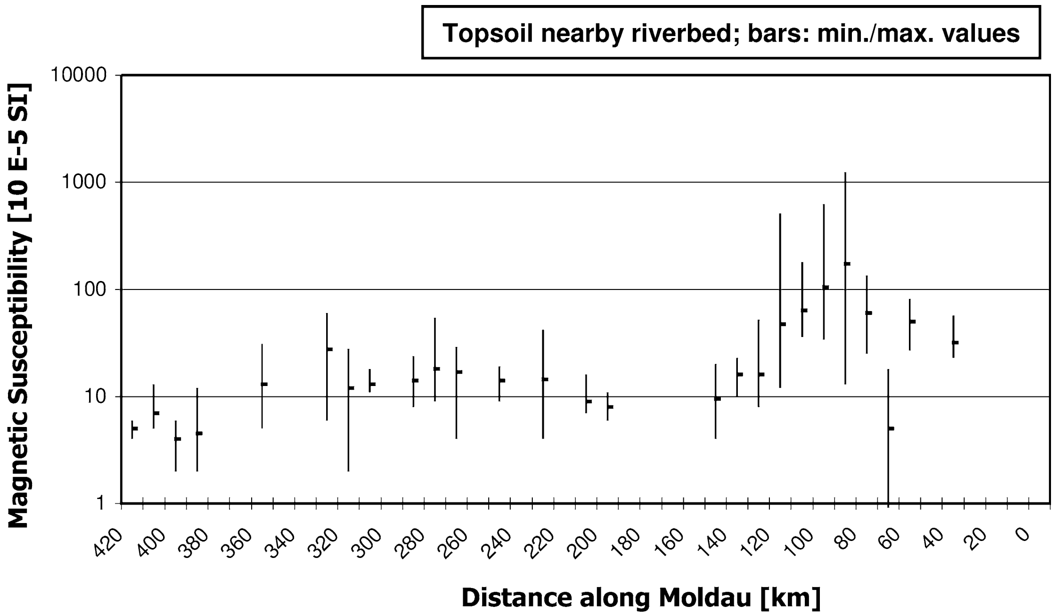

Fig. 4 Median magnetic susceptibility values (κ) of topsoils along the Moldau river (10 km "section windows"). Between R-km 350 and 210 an enhancement is observed that cannot be explained as resulting from a natural soil development

lithogenic contribution. An enlargement of this area (see Fig. 5) indicates an increase of the magnetic susceptibility near towns. However, there seems to be no relationship to the size of the towns, e.g. higher susceptibility values were observed near Cesky Krumlov (R-km: 280 km; population: 13,500) than near Ceske Budejovice (R-km: 240 km; population: 100,000).

In the area of the strong positive magnetic anomaly, the magnetic susceptibility values of soil depend on different developments of the horizons. The A horizon at

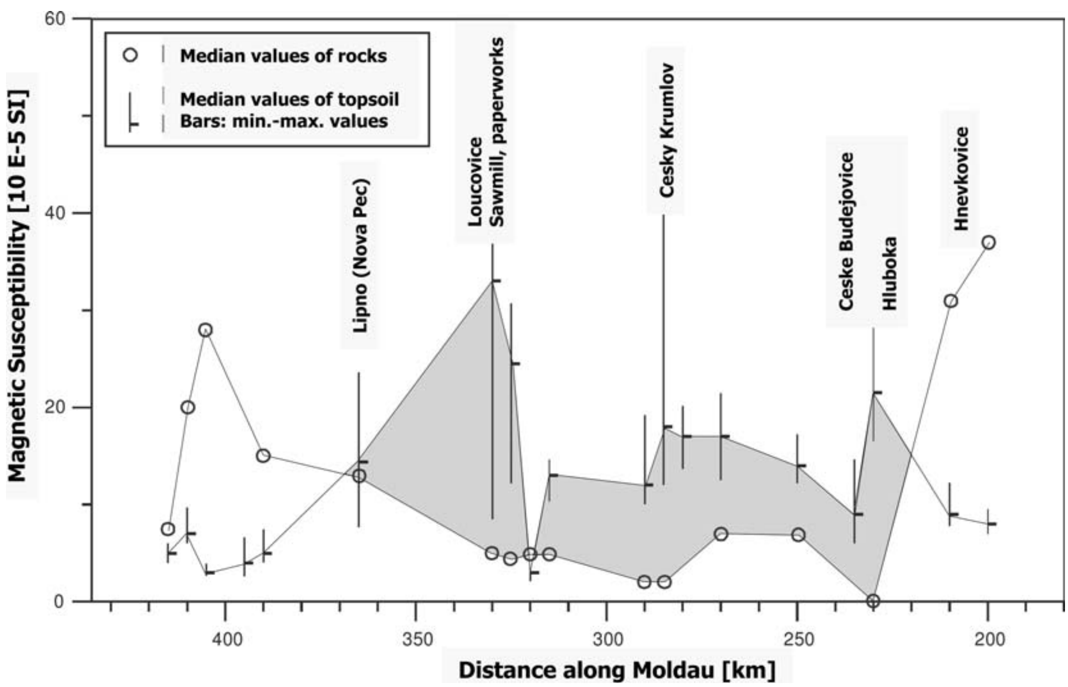

Fig. 5 Median magnetic susceptibility of topsoil (5 km sections) between 435 and 180 km (-). The κ values from the source at R-km 435 down to R-km 380 km are lower than the κ values of the bedrocks (*circle*). Between R-km 330 and 220 the topsoil reveals higher values than the rocks themselves (indicated as *grey area*). The enhancement of κ seems to originate from additional anthropogenic inputs. Locations of the larger towns are indicated

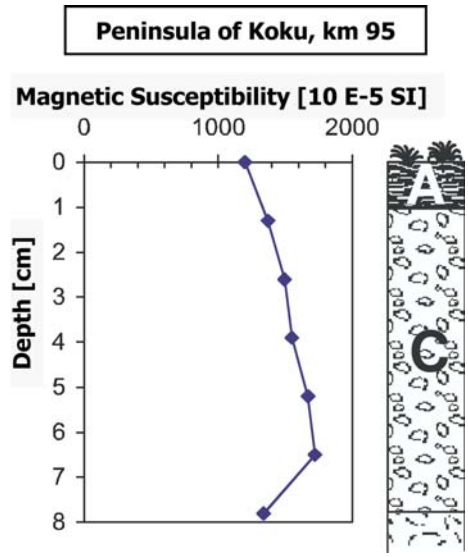

Fig. 6 Depth profile of the magnetic susceptibility (field measurements) of soil with A and C horizons, covered by grass at the peninsula Koku, R-km 95

the peninsula "Koku" shows an average κ value of about 3.8E-3 (SI), some sites have extremely high values of up to 1.2E-2 (SI). A depth profile reveals that below the A horizon (~1 cm thickness) the C horizon has increased κ values up to 1.7E-2 (SI) at 6 cm depth. Below this horizon, the κ value decreases down to 1.3E-2 (SI) at about 8 cm depth, at the surface of the bedrock (see Fig. 6).

River sediments

River sediments show a similar behaviour as the topsoil, but it obviously reflects local enhancements better (Fig. 7). This, however, can be also caused by a separation of magnetic/ non-magnetic fractions during transportation and re-sedimentation. This can be recognized by the large variation within each 10 km "section window". Nevertheless, the downstream trend of the mean values is quite smooth.

The region around Slapy (R-km: 95 km) with the anomaly of κ dominates the plot. However, a clear increase in κ can be observed in the first 100 km from the source of the Moldau river. It reaches its maximum in the region between Lipno (R-km: 325 km) and Cesky Krumlov (R-km: 280 km). As stated above, the geological background cannot be considered as a significant source of magnetic particles. The κ values of the bedrocks decrease whilst those of the sediments increase. After this maximum, the κ values of river sediments decrease rapidly while rocks show a high variability of mean values in this section.

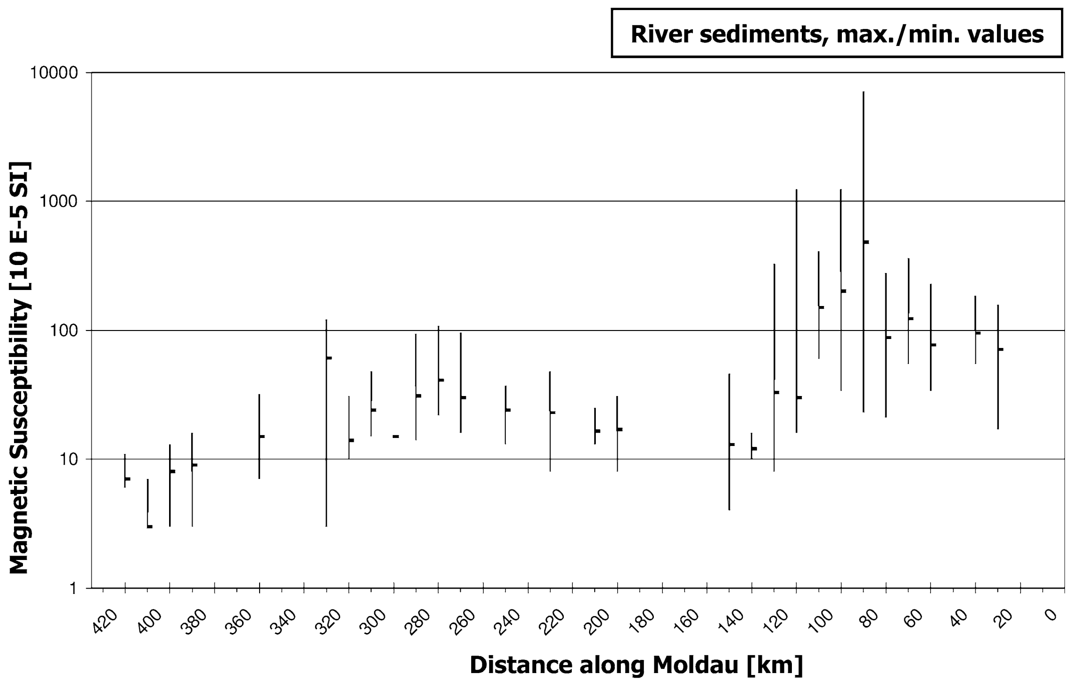

Fig. 7 Magnetic susceptibility of the river sediments along the Moldau river (10 km "section windows"). A large variability of κ can be recognized. In the first 100 km from the source of Moldau river κ increases continuously. It reaches its maximum in the area between Lipno (R-km 330) and Cesky Krumlov (R-km 280). Further downstream the κ values decrease up to the beginning of the magnetic anomaly around Slapy followed by very high values and variability up to the mouth into the Elbe river Northern of Prague

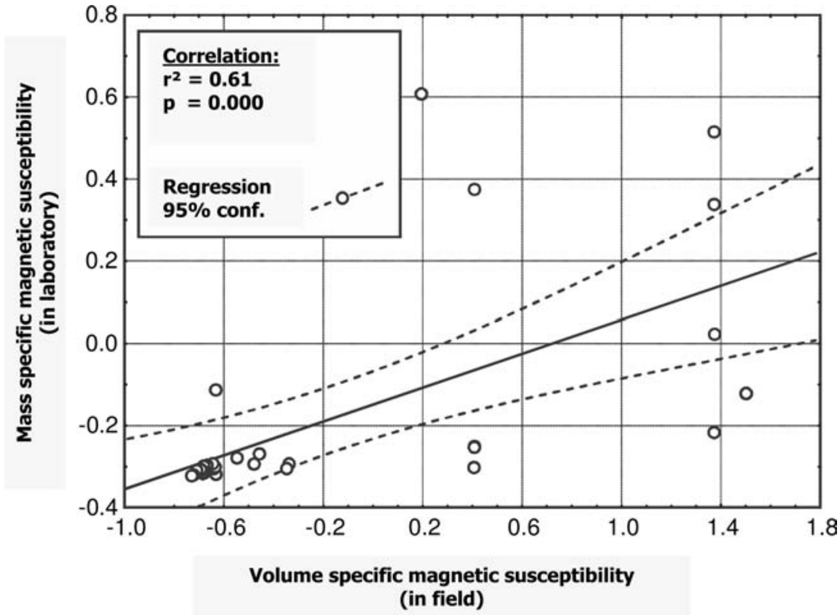

Fig. 8 A comparison of the mass-specific susceptibility (measured on river sediment samples) versus the volume-specific susceptibility (measured in field, both standardized, $N=32$). The relatively low correlation-coefficient is at least partly influenced by the different integration volumes. Especially the thin layered sediments cause significant inhomogeneities within the samples and field measurements

Comparison between field and laboratory measurements

The loop sensor used for the field measurements is positioned at the surface of the material. For non-conductive material the penetration depth is about 8 cm corresponding to 95% of the recorded signal (by a depth of 1.5 cm: 50%) (Lecoanet et al. 1999). Especially, because of the lack of fine river sediments we do not exactly know the homogeneity of the material measured within the depth of penetration. The sandy layer may be less than 10 cm in thickness. In this case, a sublayer of a different material will influence the κ values. In order to control our field measurements, we considered river sediment samples. After drying and sieving, the finest fraction was measured (<2 mm). Field measurements cannot be directly compared to their laboratory counterparts because of the inhomogeneity in river sediments and the difference in investigated volumes (at a ratio of ~135:1). Nevertheless, there is a significant linear correlation with the coefficient of correlation $R^2=0.61$ (Fig. 8). In the case of soils, R^2 was found to be 0.77 by Kapička et al. (1997). For further investigations, information about the thickness of the sediment layer would help to interpret the results.

Comparison between magnetic susceptibility and heavy metals

The variation of the magnetic susceptibility of river sediments near some villages encouraged us to investigate their relationship to some selected pollutants, in this case a set of heavy metals. The content of Ni, Cu and Zn is obviously increased in two areas. One of the two areas lies downstream of Ceske Budejovice until the mouth of the Otava river. This section is about 90 km long. The other area is the last 80 km of the Moldau river, starting from the mouth of the Sázava river, passing the area of Prague, until the confluence with Elbe river.

One sample was taken from the sediments in the area of the strong magnetic anomaly. It reveals an extremely high χ value, but the content of heavy metals was within the normal range for this lithology. This sample was considered as an outlier and was excluded from further statistical calculations. Linear regression analysis reveals significant positive correlations ($p<0.05$) of Cu and Zn with the magnetic susceptibility, with correlation-coefficients r^2 of 0.81 and 0.69, respectively (Fig. 9a, b). Fe, Mn and Ni did not show a significant relationship with κ.

Conclusions

The magnetic susceptibility of the Moldau river sediments varies due to different sediment inputs from different sources. Additionally, the transportation and the sorting of sediments depends on the hydrological regime of the river. In terms of potential magnetic enhancement processes, the geological background should be considered locally as the source of primary significance. However, other local sources affecting magnetic susceptibility, such as soil developments, run-offs from highways or other anthropogenic activities, are clearly reflected by enhanced magnetic susceptibility values in areas of minor or negligible lithogenic contribution. This

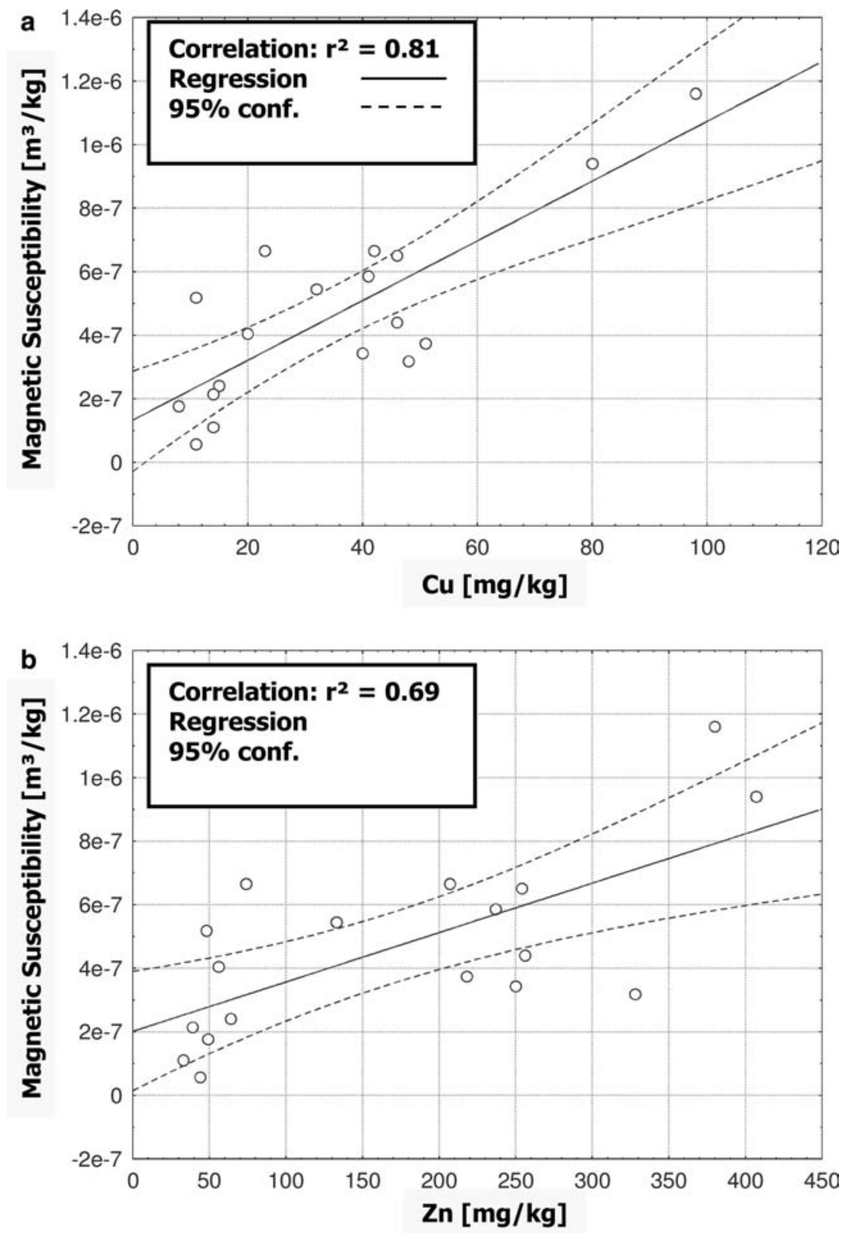

Fig. 9 a, b Correlation diagrams of Cu and Zn versus magnetic susceptibility of the sediment samples. Cu and Zn show a significant positive correlation with χ

anthropogenic effect can be observed mainly in the first 100 km along the river. In the other part of the Moldau river, the variation of the magnetic susceptibility of the bedrocks is too large to allow an unambiguous interpretation. Actually, in the case of the magnetic anomaly in the Slapy region and downstream, it was impossible to link magnetic susceptibility to anthropogenic activities. Here the susceptibility values are almost two orders higher than any expected anthropogenic input.

Bi-plots of the magnetic susceptibility and the concentration of Cu and Zn show a significant positive linear correlation, with a coefficient of correlation of $r^2 = 0.81$ and 0.69, respectively. This proves the potential of the magnetic method in monitoring the contents of these heavy metals in the Moldau river sediments. The contents of Cu, Ni and Zn reach maximum values in the area downstream of Ceske Budejovice and in the last 80 km around Prague.

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