Mapping of heavy metal loadings in soils by means of magnetic susceptibility measurements

M. Hanesch · R. Scholger

Abstract Contamination of soils with heavy metals is an issue all industrial and urban regions have to deal with. Generally, chemical methods are chosen to monitor soil pollution but measurements of magnetic susceptibility proved to yield additional information at low cost and consuming less time. We measured the magnetic susceptibility of soils which had been analysed chemically during the soil surveys of three Austrian provinces. Each anomaly of susceptibility either coincided with geogenic anomalies or indicated anthropogenic input of pollutants. Regional comparisons of susceptibility with chemical analyses revealed that susceptibility can be used as an indicator for the contents of individual pollutants in soils. This calibration of susceptibility has been successfully applied to an industrial region as well as to an urban environment. Two powerful applications of susceptibility measurements of soils are shown: the identification of polluted areas, and the detailed mapping of these areas to reveal the extent of pollution.

Keywords Soil pollution · Heavy metals · Magnetic susceptibility · Environmental magnetism · Austria

Introduction

During recent years, measurements of magnetic susceptibility have become a generally accepted method to map pollution. The interest in this method is rising because the promptness of the single measurement makes it possible to establish dense grids of sampling sites. Susceptibility measurements have been used to assess the spatial distribution of pollution, for example, around power plants (Kapička and others 1999) or along roads and highways (Hoffmann and others 1999). They have also proved useful to assess transport of pollutants by air (Strzyszcz 1999) or water (Scholger 1998; Petrovský and others 2000). Additional measurements of other magnetic parameters make it possible to differentiate the particles (Oldfield and others 1985) and to identify sources (Hunt and others 1984). An overview of applied studies is given by Petrovský and Ellwood (1999).
The use of magnetic measurements as a proxy for chemical methods is possible because pollutants and magnetic particles are genetically related. The most important source is the burning of fossil fuels. Magnetite and hematite are often found in fly ash. They are formed as a result of the oxidation of iron sulphides during high-temperature combustion (Flanders 1994). An analysis of fly ash specimens from coal-burning power plants revealed that the first row transition elements were concentrated in the magnetic phase of the ash (Hulett and others 1980).
The close relationship of magnetic susceptibility with heavy metal contamination has been proven by combined analyses of chemical and magnetic data (Heller and others 1998; Bityukova and others 1999). In most cases, magnetic particles and heavy metals may be produced together but forming separate particles, as was found by Kapička and others (2001) for dusts from a coal-burning power plant. In this study, the ferrimagnetic fraction constituted 9.1% of the dust collected on top of the chimney. In the case of roadway dusts, magnetic particles were found to be agglomerated with lead (Olson and Skogerboe 1975; Hopke and others 1980). The significance of the results of magnetic measurements is underlined by the fact that susceptibility of air filters was shown to be correlated to the mutagenic potency of the polycyclic aromatic compounds (Morris and others 1995).
The relationships between magnetic particles and pollutants are complex and they are different for each industrial process. In cement production, for example, additives turned out to influence the amount of magnetically susceptible material in the dusts (Goluchowska 2001). The complexity of the relations between pollutants and magnetic particles, and the fact that they have a common source but are usually separate particles make it

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impossible to derive a single function to calculate pollutant concentrations from susceptibility measurements. For each new area of investigation, new ways of interpretation have to be found. It is difficult to judge in how far susceptibility on its own is providing us with information on pollution. This study aims at assessing the potential of pollution mapping by means of susceptibility measurements at a large scale as well as at a regional scale.
The starting point of the investigation is the database provided by the soil surveys of the Austrian provinces. For each grid point of these surveys, susceptibility was measured and maps were created for an area of 39,500 km^2. A similar data set which exists for England was evaluated by Hay and others (1997). These authors found high susceptibility values around major urban and industrial areas. In the present study, susceptibility maps of Austria are used to pinpoint potentially contaminated areas which should be investigated more thoroughly. The available geochemical data serve as a quality control as well as for the regional calibration of the method. Applications for a pollution-intensive region and a first test of the method in an urban environment are shown.

Materials and methods

Samples

The soil samples collected during the soil survey programs of the Austrian provinces are used to create the large-scale susceptibility maps. The data of three provinces are put together in this study: Lower Austria, Burgenland and Styria. A geological overview of the investigated area is given in Fig. 1.
Samples were taken in a grid of 4 by 4 km to ensure a systematic investigation. In Lower Austria, topsoils were additionally sampled in a denser grid of 2.75×2.75 km (Fig. 2). The samples of the base grid were taken in several layers which are different for the provinces. For our analyses, we calculated weighted means of the measured parameters for the topsoil (0–20 cm) and the subsoil (20–50 cm).
At each grid point, four samples of each layer were taken at distances of 2 to 10 m from the grid point towards the cardinal directions. These samples were mixed to a bulk sample of approximately 1 kg, dried at a temperature of less than 30 °C and passed through a 2-mm sieve. The parts of the samples which were not used for chemical analyses were stored in soil archives in cool, dark rooms. The sampling procedures are described in detail in the soil survey reports of the provinces (Bundesanstalt für Bodenwirtschaft Wien 1994; Bundesamt und Forschungszentrum für Landwirtschaft 1996; Amt der Steiermärkischen Landesregierung 1998).
Sampling for the Vienna case study was done by the City of Vienna, Municipal Department 22 (Environmental Protection). Sampling sites were chosen to cover several zones for each district of Vienna: parks, residential areas, road sections, playgrounds for children. Mixed samples were taken from a depth of 0–10 cm, dried and sieved. The procedures are described by Kreiner (2001).

Susceptibility measurements

Two types of susceptibility measurements were carried out. For the large-scale study of the three provinces and for the Vienna case study, laboratory measurements on

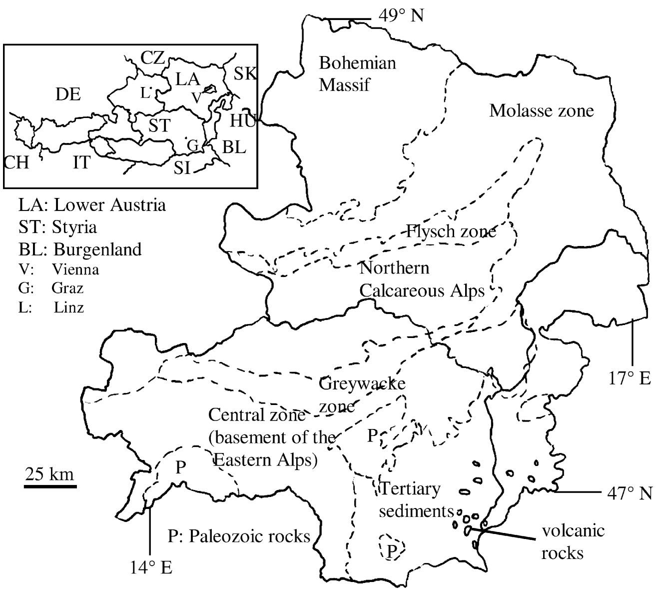


Fig. 1
The main geological units in the investigated area. Inlay: the Austrian provinces and the surrounding countries

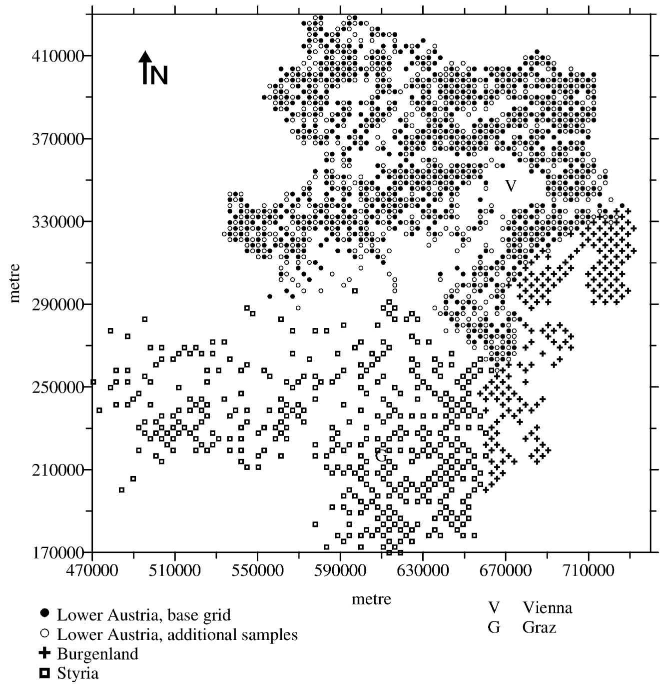


Fig. 2
Sampling grids of the three provinces. The number of sites is 1,449 in Lower Austria (725 samples in the base grid), 174 in Burgenland and 392 in Styria. The Austrian co-ordinate system (BMN), Central zone (meridian 31), is used

archived soil samples were performed. The Leoben case study is based on field measurements directly at the sampling sites.

The archived samples are stored in different boxes for the different provinces. The sieved samples from Styria are kept in glasses whereas the unsieved samples are stored in plastic cylinders (9.5-cm diameter, 13.5-cm height), which could be measured without any sample manipulation with a Bartington MS2C loop sensor for cores (125 mm; operating frequency 565 Hz). Low-field volume susceptibility of the samples was measured using range 1 of the MS2 meter with a resolution of 1×10^{-5} SI and a measuring range of 99×10^{-3} SI. The raw data were corrected to account for sample diameters and lengths different from the standard dimensions. The sieved samples of Lower Austria and Burgenland are stored in rectangular plastic boxes (100×74×48 mm). These boxes were put on top of the Exploranium KT9 instrument which had been fixed on a table. The KT9 has a resolution of 1×10^{-5} SI and uses a 10-kHz oscillator.

Field measurements for the Leoben case study were also performed with the KT9 instrument which was pressed on the soil surface. For a control group of 37 sites in Leoben, samples of the top 5 cm were taken and measured by means of the KLY2 Kappabridge in the laboratory. The correlation coefficient for the field and laboratory measurements was 0.96, justifying the use of the faster field measurements for the mapping of the Leoben area. Mass specific susceptibility for the samples of the Vienna case study was determined with the KLY2 Kappabridge on subsamples of the dried soils which had been filled into 10-cm^3 plastic cylinders.

Calibration of the susceptibility measurements

The measurements of volume susceptibility for the soil survey samples cannot be compared directly as different instruments had been used and the samples had been treated differently. Therefore, it was decided to relate all measurements to mass specific susceptibility of the sieved samples. A representative set of subsamples was taken from each set of soil samples. These subsamples were filled in plastic cylinders of 10 cm^3, weighed, and measured with the KLY2 Kappabridge. A regression was then calculated between the mass specific and the volume specific measurements (Fig. 3), and the regression equations used to calculate mass specific values for all samples in the unit 10^{-8} m^3 kg^{-1}. The regression was calculated using the logarithmic susceptibility values because the distribution of the values is approximately lognormal (see below).

The susceptibility maps (see below) show no conspicuous features at the province boundaries. A look at a cross section through the subsoil susceptibility map (Fig. 4) confirms the effectiveness of the calibration method. It enables us to analyse the susceptibility values of the different provinces together, although the sample containers and the susceptibility meters used are different.

Definition of susceptibility anomalies

To find anomalies it is necessary to define a baseline against which values are judged. The area under investigation has a variable geology and therefore background

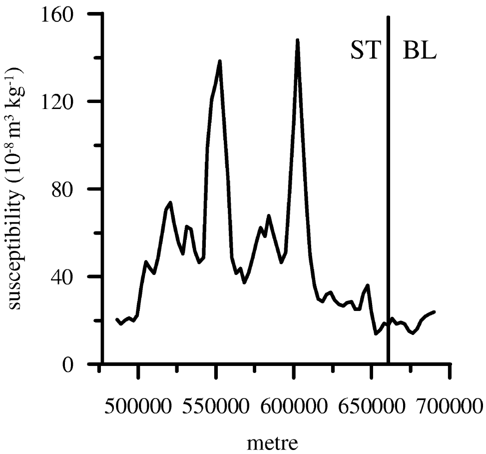


Fig. 4
Susceptibility values along a cross section through the subsoil susceptibility map (cf. Fig. 7). The level of susceptibility values stays the same at the boundary between the two provinces Styria (*ST*) and Burgenland (*BL*), although susceptibility was measured with different instruments. This proves the effectiveness of the calibration method

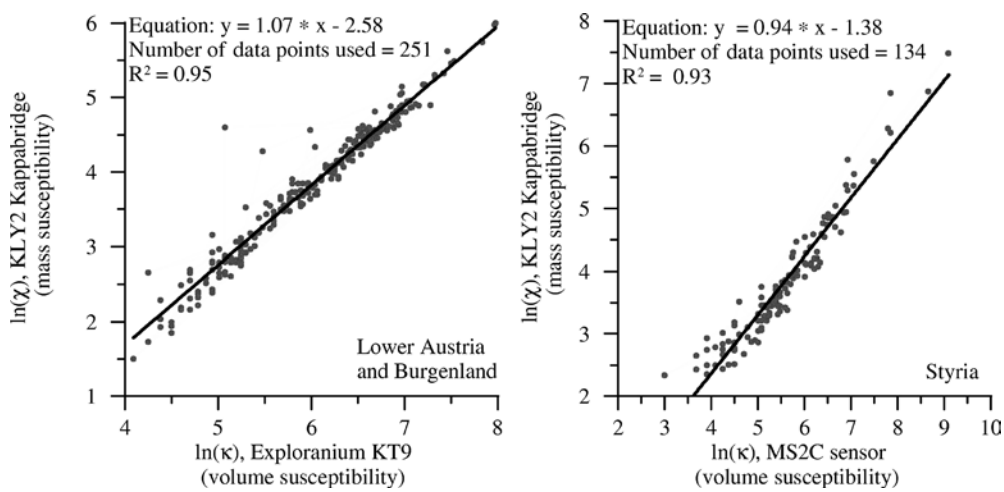


Fig. 3
Calibration curves for the calculation of mass specific susceptibility values (10^{-8} m^3 kg^{-1}) from the volume specific measurements

concentrations of magnetic particles as well as of chemical elements will not necessarily be low at all study sites (Matschullat and others 2000). In geochemical mapping, sampling different horizons in soil profiles has widely been used to distinguish natural background from anthropogenic anomalies (Selinus and Esbensen 1995). We adopt this approach and use the value of the layer between 20 and 50 cm as an approximation for the soil background. Soil processes act within this layer but anthropogenic influences are constrained to the upper horizons. The magnetic spherules typical for anthropogenic magnetic particles are usually found in the upper 5 cm of undisturbed soils (Heller and others 1998) and in the ploughed layer of agricultural soils (Hanesch and Petersen 1999). The subsoil value is not an absolute background value: the ploughed layer can reach down to a depth of 35 cm and, in excessively contaminated soils, pollutants are enriched below 20-cm depth. Nevertheless, the gradient will still be in the right direction: higher values in the upper 20 cm indicate anthropogenic influence, lower values indicate geogenic magnetic particles.

A threshold value has to be introduced because the natural development of a soil profile is usually accompanied by an increase in magnetic susceptibility of the upper horizon (Verosub and Roberts 1995), especially for well-drained soils like cambisol (Maher 1998). This natural enhancement of magnetic susceptibility is due to the in-situ formation of fine-grained ferrimagnetics by iron-reducing bacteria (Hanesch and Petersen 1999). On the other hand, solution and transport processes like those occurring in gleysol, luvisol and podzol can lead to a depletion of iron oxides and consequently to lower susceptibility values in the upper horizon. In our study area, the chernozem formed on loess showed the highest absolute enhancement values of nearly 20×10^{-8} m^3 kg^{-1}. For gleysols, the difference between topsoil and subsoil susceptibility did not exceed -15×10^{-8} m^3 kg^{-1}. A threshold of -20×10^{-8} m^3 kg^{-1} should also be sufficient for podzol and luvisol, as can be concluded from the values measured by Maher (1986) and Hanesch and Petersen (1999). Therefore, anthropogenic and geogenic susceptibility anomalies are defined as differences between topsoil and subsoil values exceeding $\pm20\times10^{-8}$ m^3 kg^{-1}.

Chemical analyses

The chemical analyses of the dried and sieved soils were performed by the Agricultural Research Centre Styria for the province of Styria, including the case study Leoben. Humus content, defined as nonliving organic matter, was determined by wet oxidation. The iron content was measured in an extract of ethylenedinitrilotetracetatic acid (EDTA). This procedure yields the iron content which is available for plants, that is, mostly iron bound in complexes or adsorbed to the surface of soil particles. The determination of fluorine also aimed at finding the proportion easily available for plants. Fluorine is extracted by water and measured with an ion selective electrode. Heavy metals were extracted by aqua regia and then measured by flame atomic absorption spectrometry (AAS) (for Mo, Cd, and As by graphite furnace AAS). Mercury was determined by cold-vapour AAS. The content of polycyclic aromatic hydrocarbons (PAH) is defined as the sum of fluoranthene, pyrene, triphenylene and chrysene. After extraction with acetone, PAH contents are measured by coupling gas chromatography to mass spectrometry.

The heavy metal analysis for the Vienna case study was performed by the City of Vienna, Municipal Department 22 (Environmental Protection). After extraction by aqua regia, the content of several metals was determined by inductively coupled plasma mass spectrometry (ICP-MS).

Statistical and graphic analyses

Statistical calculations were performed with the SPSS 10.0 software. Contour plots were created with Surfer 7.00. The survey maps were produced in the Austrian co-ordinate system, central zone, meridian 31. Co-ordinates for the Leoben case study are given in the Austrian co-ordinate system, eastern zone, meridian 34. Point kriging was used for the surface estimation, with a search radius of 12 km in four sectors. Grid points are empty if less than three data points are within the search region or more than two sectors are empty. The susceptibility scales on the maps are not equidistant, due to the logarithmic distribution of the values.

Results

Distribution of susceptibility values

Table 1 lists the distribution parameters of the measured susceptibility values for the total area of the soil surveys as well as for the individual provinces. The values are given separately for the topsoil (0–20 cm) and the subsoil (20–50 cm). Susceptibility varies over three orders of magnitude. This large variation was also found in soils of the United Kingdom (Maher 1986; Dearing and others 1996) and California (Fine and others 1992). Variations are caused by differences in geology, soil-forming processes and by anthropogenic input of magnetic material. Only in Styria, the median value (37×10^{-8} m^3 kg^{-1}) reaches approximately the value found in English topsoils by Hay and others (1997; 38×10^{-8} m^3 kg^{-1}). For the other provinces, the median value is lower by about 10×10^{-8} m^3 kg^{-1} (Lower Austria: 26×10^{-8} m^3 kg^{-1}, Burgenland: 27×10^{-8} m^3 kg^{-1}). The higher values in Styria are due to the occurrence of large ore bodies. Histograms and box plots of the distributions for the individual provinces are shown in Fig. 5 for the topsoils and in Fig. 6 for the subsoils. The histograms are given for the natural logarithms of susceptibility because the distributions are more similar to a lognormal than to a normal distribution. For the province of Burgenland, the distributions of topsoil as well as of subsoil values are bimodal. Higher values are concentrated in the northeastern part of Burgenland where the main soil type is chernozem on loess which tends to have higher susceptibility values than other soil types. In the topsoil, the difference to the values in the rest of the province is amplified by an anthropogenic anomaly (anomaly no. 5, see below). To get a first idea about anthropogenic influences, the difference between topsoil and subsoil susceptibility was

Table 1
Susceptibility values (10^{-8} m^3 kg^{-1}) for the total area and the individual provinces

	Total area	Lower Austria	Burgenland	Styria
Topsoil				
Number of samples	2,014	1,448	174	392
Minimum	4	4	4	5
Maximum	1,147	301	136	1,147
Median	29	26	27	37
Lower quartile	18	17	17	24
Upper quartile	53	50	60	57
Subsoil				
Number of samples	1,254	714	174	366
Minimum	2	3	2	6
Maximum	389	356	122	389
Median	24	21	22	29
Lower quartile	15	14	15	20
Upper quartile	47	44	53	52
Difference between topsoil and subsoil[a]				
Number of samples	1,253	713	174	366
Minimum	–135	–67	–14	–135
Maximum	814	68	41	814
Median	3	3	3	5
Lower quartile	0	1	0	–2
Upper quartile	8	8	7	11

[a]Differential susceptibility values are positive for higher values in the topsoil

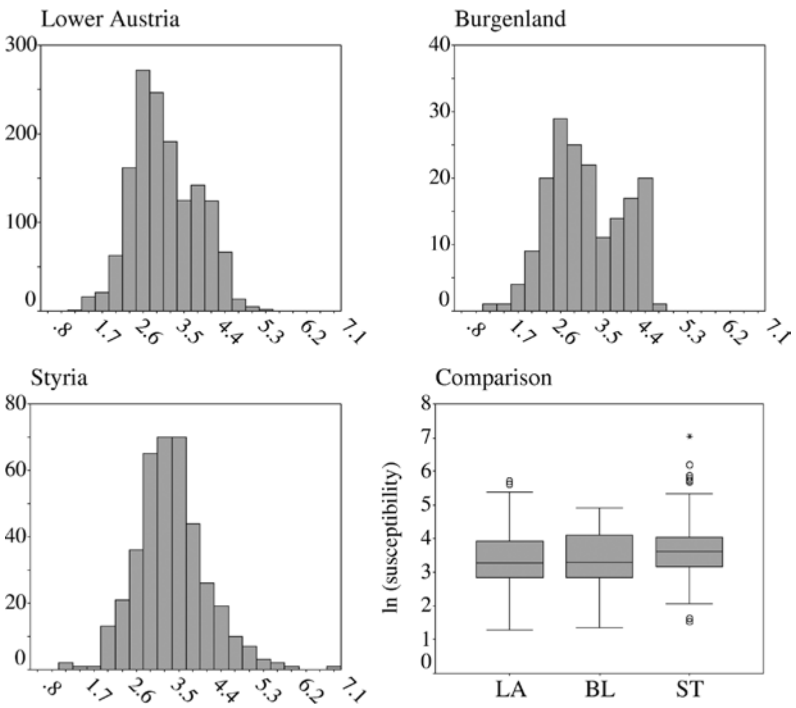


Fig. 5
Histograms and box plots of susceptibility in the topsoil for the three provinces. The natural logarithms of the mass specific susceptibility values are shown on the *x*-axes. The y-axes of the histograms have different scales due to the highly differing number of samples available for the three provinces. The *boxes* in the box plot give the interquartile range of the values, the *lines* in the boxes the median values. *Circles* outside the boxes indicate outliers (more than 1.5 box lengths from the edge of the box), and *asterisk* represents extreme value (more than three box lengths from the edge of the box)

calculated (Table 1). Positive values indicate higher values in the topsoil. The median values of the difference are slightly positive in the investigated area, which may be explained by pedogenic enhancement. If the values exceed the values reached by natural enhancement in soils, they indicate input through the air or by human activities (application of sewage sludge, pesticides, etc.). Styria shows the most extreme values in the negative as well as in the positive direction. In this province, geogenic anomalies are widespread as well as anthropogenic enhancement due to mining and industry.

Susceptibility mapping

Geogenic anomalies

Susceptibility maps of the subsoil and topsoil as well as the contour map for the copper values in the study area are shown in Figs. 7, 8 and 9. In the region of the Northern Calcareous Alps (see Fig. 1), some sites have no subsoil. This causes the larger gap in the subsoil map. At sites in which elevated susceptibility values in the subsoil coincide with high values in the topsoil or even surpass them, magnetically susceptible material will be of geological

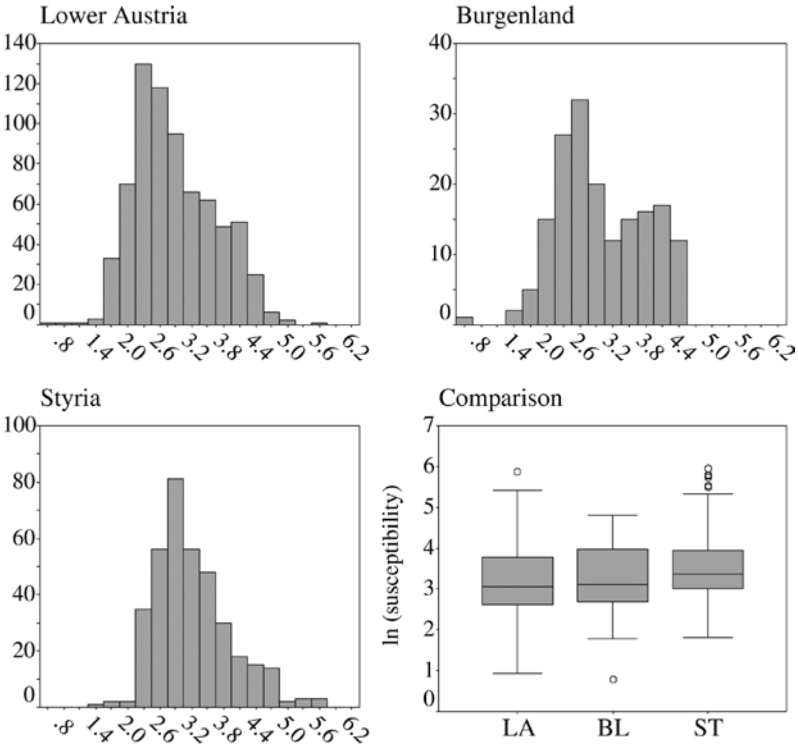


Fig. 6
Histograms and box plots of susceptibility in the subsoil (for explanations, see Fig. 5)

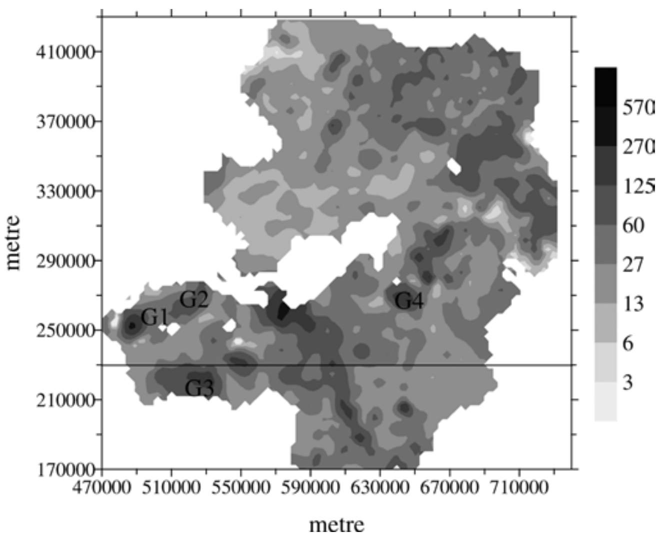


Fig. 7
Contour plot of susceptibility (10^{-8} m^3 kg^{-1}) measured in the subsoil (20–50 cm). Geological susceptibility anomalies are marked with *G1* to *G4*. The *line* marks the cross section displayed in Fig. 4

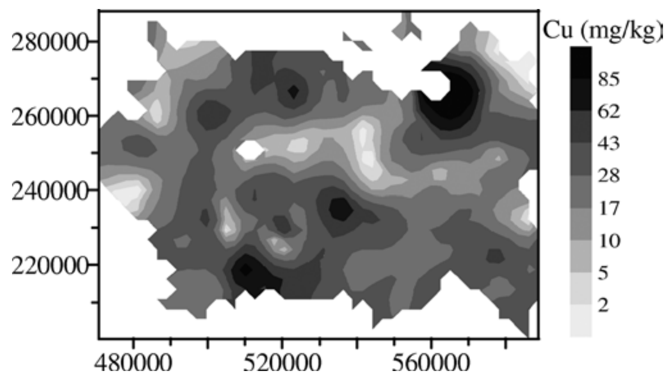


Fig. 8
Contour map of copper values in the subsoil in western Styria. Susceptibility anomalies in this region (compare Fig. 7) are mainly caused by ore bodies

origin. The bedrock material has a considerable influence on the susceptibility of the soil (Fontes and others 2000). In a previous study on the Styrian topsoil data set, multivariate analysis has been applied to define groups of soils which are similar in their heavy metal loading and magnetic susceptibility (Hanesch and others 2001). A fuzzy cluster analysis showed the dominant role of geology in the building of the groups.

A first approximation to divide topsoil anomalies into geogenic and anthropogenic anomalies is the analysis of the difference between the topsoil and the subsoil. Anomalies of susceptibility which are more pronounced in the subsoil than in the topsoil are marked on the susceptibility map for the subsoil (Fig. 7): G1: the upper Ennstal with many ore bodies (especially copper, lead, zinc); G2: iron ores near Lassing and arsenic and copper anomalies; G3: Paleozoic body of Murau with iron deposits, copper and arsenic anomaly; G4: strong arsenic anomaly in the region of the Wechsel pass (sulphidic ore). The anomaly between G2 and G4 was defined as an anthropogenic anomaly (no. 7) due to the much higher topsoil values (see below).

In the whole region of western Styria where anomalies G1, G2 and G3 are located, susceptibility values are related to Cu, Co and Ni values. Figure 8 shows the contour map for the copper values in this part of the investigated area. A comparison to Fig. 7 (contour map of susceptibility) reveals the

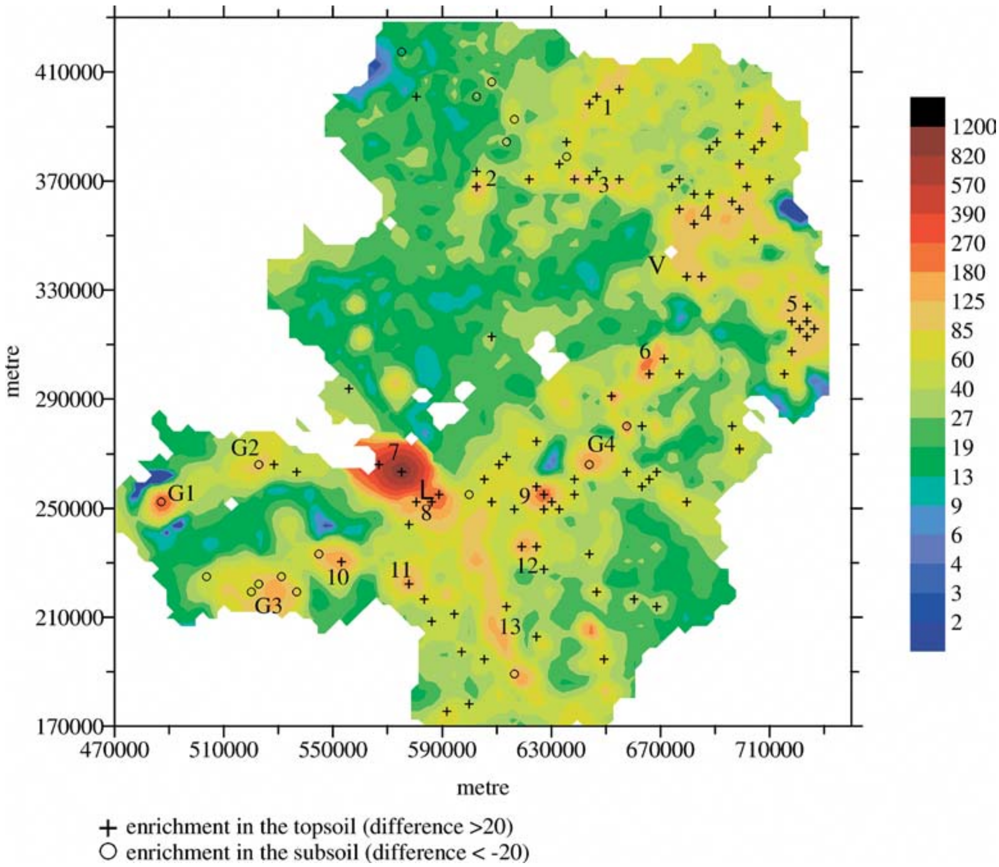


Fig. 9
Contour plot of susceptibility (10^{-8} m^3 kg^{-1}) measured in the topsoil (0–20 cm). The *numbers* mark regions with elevated susceptibility values combined with a considerable difference between topsoil and subsoil (>20×10^{-8} m^3 kg^{-1}). The gap next to the *V* is the location of the city of Vienna where no grid samples were taken. The other gaps are regions in the Alps where no samples are available

Table 2
Correlation coefficients forsubsoils in western Styria (corresponding region shown in Fig. 8; n=145; correlation coefficients shown are significant at the 0.01 level)

	Co	Zn	ln(Cu)[a]	ln(Ni)	Silt (%)	pH
ln(κ)	0.64	0.42	0.64	0.62	0.42	0.50

[a]Logarithmic values are used for those variables which show lognormal distributions

relation between copper and magnetic susceptibility in the subsoil. Even in the topsoil, high correlations exist between susceptibility and Cu, Co and Ni (Table 2). The correlations with pH and the grain-size parameter silt demonstrate the additional influence of pedological parameters.

Anthropogenic anomalies

The main interest of our study is the detection of anomalies caused by anthropogenic influences. These anomalies are distinguished not only by high susceptibility values in the topsoil but also by a considerable difference between topsoil and subsoil. The most marked anomalies are numbered on the topsoil susceptibility map (Fig. 9). At each of these locations, high susceptibility values were found to coincide with increased heavy metal values.
The anomalies 1, 2, and 3 in the northern part of the study area and anomaly 9 in Styria are close to deposits of industrial minerals or pyrrhotite and pyrite. At these locations, a more refined mineral analysis would be necessary to distinguish between the contribution of the natural minerals and phases produced by technical processes. Natural minerals can be accumulated in the soil due to mining activities. The processing of the natural minerals, industrial processes in general and traffic cause the accumulation of the newly produced phases. This distinction would require a separate analysis for each anomaly.
Anomalies 4 and 13 are regions where various influences are mixed. Northeast of Vienna (no. 4) crude oil and natural gas is extracted from the ground. Refineries and other industry cause emissions as well as heavy traffic in this area. The heavy metals showing anomalies in this region are Cu, Cr, Mo, Ni, Pb and Cd. In the valley of the river Mur between Bruck/Mur and Graz (no. 13), the situation is similar. Traffic is canalised within the valley and different industries settled there. High values occur for Pb, Cd, Cu, Zn and Co. Magnetic susceptibility indicates the sum of anthropogenic stresses on the environment in these regions. This mixture of various influences is the reason why correlations between susceptibility and individual heavy metals tend to be poor within these areas. The amount of individual heavy metals can not be deduced from susceptibility values.
Anomaly 5 is near the highway A4 south-east of Vienna, and anomaly 6 coincides with the industrial region around Ternitz and Wiener Neustadt. The highest susceptibility values are found in the industrial regions of Styria: Erzberg – Vordernberg (7: iron mining and processing), Leoben (8: steelworks and other industry), Fohnsdorf (10: steel and

metal industry), Voitsberg (11: glass, ceramics, metal industry) and Weiz (12: electrical industry). The Styrian soil surveys revealed elevated values for different metals in these regions which are caused by human activities. High-resolution information on the spatial extent of these contaminants can quickly be found by measuring susceptibility around the suspect areas using a denser grid of measurement points. Samples which already have been analysed chemically can be used to estimate metal contents from these susceptibility measurements. This procedure is illustrated below for the region around Leoben (anomaly 8).

Regional analysis of contamination (case study Leoben)

For several centuries, Leoben has been a centre of mining, metallurgy and heavy industry. Steel production and processing still plays an important role in the economic life of the city, nowadays together with wood processing and the production of printed circuit boards. The express roadway from Vienna to Klagenfurth in Carinthia passes through the city as well as the railway line connecting Vienna to Italy. Therefore, soil samples may have accumulated heavy metals and magnetic materials over a long time span, and a mixture of several sources has to be expected.

Field measurements of volume susceptibility were performed in an area of 6 by 16 km in and around the city of Leoben. The grid of measuring points was 500×500 m around the city, and 250×250 m within the city. The measuring points are marked on the map of Leoben (Fig. 10) which also shows the contour plot of susceptibility. The direction of the valley of the river Mur is mirrored by the direction of the anomaly. The migration of contaminants to the north and south is limited by the morphology. The Mießriegel, for example, has a height of 1,213 m above sea level, whereas the city of Leoben lies at a height of about 540 m above sea level.

Twenty-two soil profiles of the Styrian soil survey lie within or near the measured area. Each of these profiles was sampled at two or three depths and analysed chemically. Susceptibility of the dried samples was measured in the Styrian soil archive. The susceptibility of the samples from the uppermost horizon agrees well with the field measurements of surface susceptibility. For further statistical analyses, the samples of all horizons were pooled, yielding a database of 62 cases. Susceptibility as well as most of the other analysed parameters within this database are lognormally distributed (Kolmogorov-Smirnov test).

Table 3 lists the median values for susceptibility, heavy metals and PAH for all cases together as well as for the different horizons. Susceptibility and PAH lie high above the Styrian median for topsoils. Pb and Cd fall to the median of the province at depths of 5–20 cm, Hg, Mo, F and Zn even below 20 cm. These are the parameters related to anthropogenic pollution. On the other hand, values do not change much for As, Cu and Co and even rise in the subsoil for Cr and Ni. These elements will be mostly of geogenic origin. A comparison with the world mean values for cambisols (Kabata-Pendias and Pendias 1992) shows the difficulty of an overall mean value for soils. For some elements, it differs significantly from the local median, as geological differences are not accounted for by the world mean and there are a number of different soil types mixed in this study.

Significant correlations between susceptibility and other soil parameters are listed in Table 4 . The highest coefficients are found for Hg, Zn and Cd. During the chemical analysis, the following metals showed a considerable enrichment in the topsoil: Zn, Pb, Mo, Cd and Hg. Of these metals, only Mo has no significant correlation to the susceptibility. Anthropogenic pollution is the dominant factor influencing soil susceptibility in this area. The role of susceptibility as an indicator of pollution is emphasised by the high correlation coefficient for the PAH content. This correlation of susceptibility with PAH was also found in a lake sediment core (Morris and others 1994). PAH are the product of combustion processes. Industry, heating of houses, traffic and natural fires are sources of these substances, and they are generally regarded as an indicator of environmental pollution.

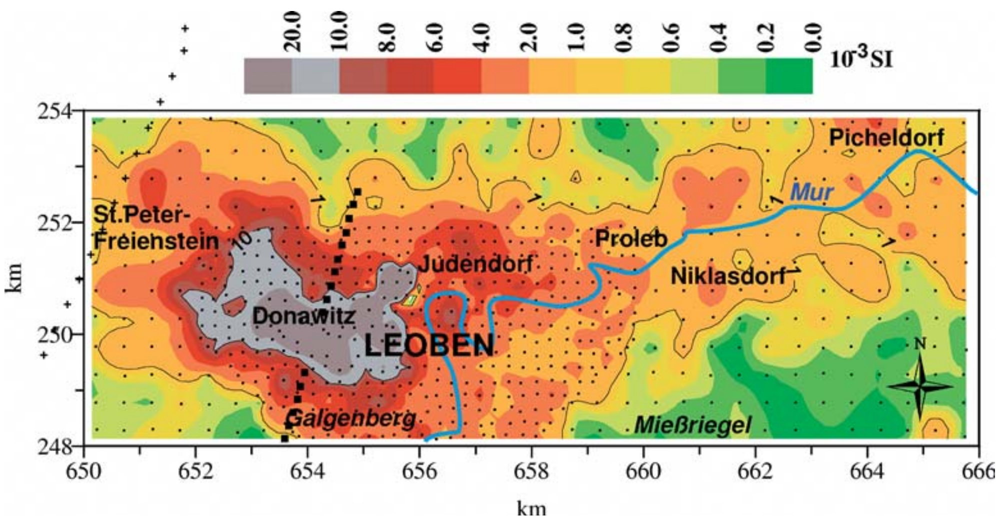


Fig. 10
Contour plot of volume susceptibility around the city of Leoben. The closed *circles* mark the measurement points. The steelwork is located at Donawitz. Transport of magnetic particles occurs dominantly along the valley of the river Mur. *Squares* mark the profile Donawitz (cf. Fig. 12), small *crosses* the profile Trofaiach (cf. Fig. 13)

Table 3
Median values of the soil survey samples in the area of the Leoben case study (all values in mg kg^{-1}, except for susceptibility in 10^{-8} m^3 kg^{-1} and PAH in ppb)

	Median of all cases (*n*=62)	Median for 0–5 cm (*n*=20)[a]	Median for 5–20 cm (*n*=20)	Median for 20–50 cm (*n*=17)	Median for Styrian topsoils (*n*=392)[b]	World mean for cambisols[c]
χ	169	259	160	81	37	
Pb	24.1	39.9	22.7	13.8	24.2	28
Cd	0.27	0.40	0.24	0.12	0.24	0.45
Hg	0.24	0.40	0.24	0.10	0.12	0.1
Zn	112	134	111	88	95	60
PAH	109	163	(101)	(20)	46	
Mo	1.06	1.46	0.96	0.85	0.80	2.8
Cr	46.8	46.1	44.9	52.4	40.9	51
As	16.9	17.8	18.0	17.4	11.5	8.4
F	1.00	1.53	1.09	0.55	0.51	0.39
Cu	30.0	30.9	29.1	28.5	25.4	23
Ni	39.5	33.9	38.2	47.0	27.3	26
Co	14.2	13.8	14.3	15.1	13.0	10

[a]Two profiles were excluded from the analysis per horizon because the depths were defined differently there. PAH values for 5–20 cm and 20–50 cm were measured for one profile only
[b]For comparison, the median value for the uppermost horizon of the Styrian grid points is given (Amt der Steiermärkischen Landesregierung 1998)
[c]The world mean value for cambisols was taken from Kabata-Pendias and Pendias (1992). Enrichment in the topsoil can be seen for susceptibility, Pb, Cd, Hg, Zn, Mo and F, whereas Cr, As, Cu, Ni and Co do not change too much with depth or even show a higher median value in the deepest horizon

Table 4
Correlation coefficients (r) with susceptibility for the soil survey samples located around Leoben (all shown coefficients are significant at the 0.01 level)

Component	r
ln(Pb)	0.503
ln(Cu)	0.385
ln(Cd)	0.565
ln(Hg)	0.769
ln(Fe)	0.438
ln(Zn)	0.672
ln(F)	0.541
ln(Cr)	0.428
ln(PAH)[a]	0.560
ln(humus)	0.543

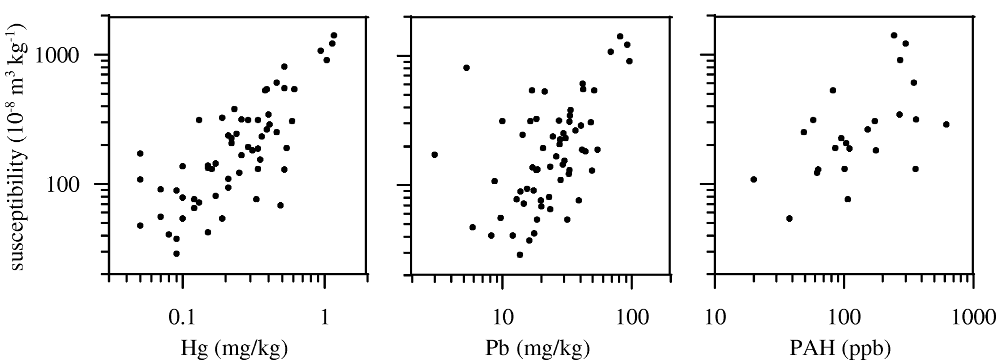
[a]PAH were determined for 24 topsoil samples

Scatter plots of susceptibility versus Hg, Pb and PAH are shown in Fig. 11.

In addition to the grid measurements of susceptibility covering the investigated area, profiles were chosen along which prospecting holes were dug to depths of 60 cm. The two profiles Donawitz and Trofaiach are marked in Fig. 10. For these prospecting holes, volume susceptibility was measured in the field at the surface, in the upper layer of the soil (0–5 cm depth) and in the subsoil (40-cm depth). Between the prospecting holes, surface susceptibility was measured every 10 m.

Figure 12 shows the results for the Donawitz profile which crosses the region of highest susceptibility values. The gap in the surface profile is the area of the steelworks. Subsoil susceptibility values lie far below the topsoil values for all prospecting holes. Even the margin of the investigated area is considerably affected by industrial emissions. Near the centre of the anomaly, the subsoils also show elevated susceptibility values. The surface susceptibility measurements show a dependence on the height above sea level. The highest values (>30×10^{-3} SI) north of the plant are restricted to heights below 720 m. The same is valid for the southern part of the profile where the highest values lie below a height of 720 m above sea level. However, even the lowest values along this profile lie well above susceptibility

Fig. 11
The scatter plots of susceptibility versus Hg, Pb and PAH demonstrate the correlation between susceptibility and these parameters over three orders of magnitude for the Leoben study area. Susceptibility measurements allow a rough estimation of the content of these pollutants in the individual soils. The two outstanding values in the lead graph (lead content low in comparison to susceptibility value) are two subsoil samples (20–50 cm). The elevated susceptibility will be caused by the parent material in these cases, as the samples have high values in Cr, Co and Cu but exceptionally low values in the anthropogenic variables Pb, Mo and Cd



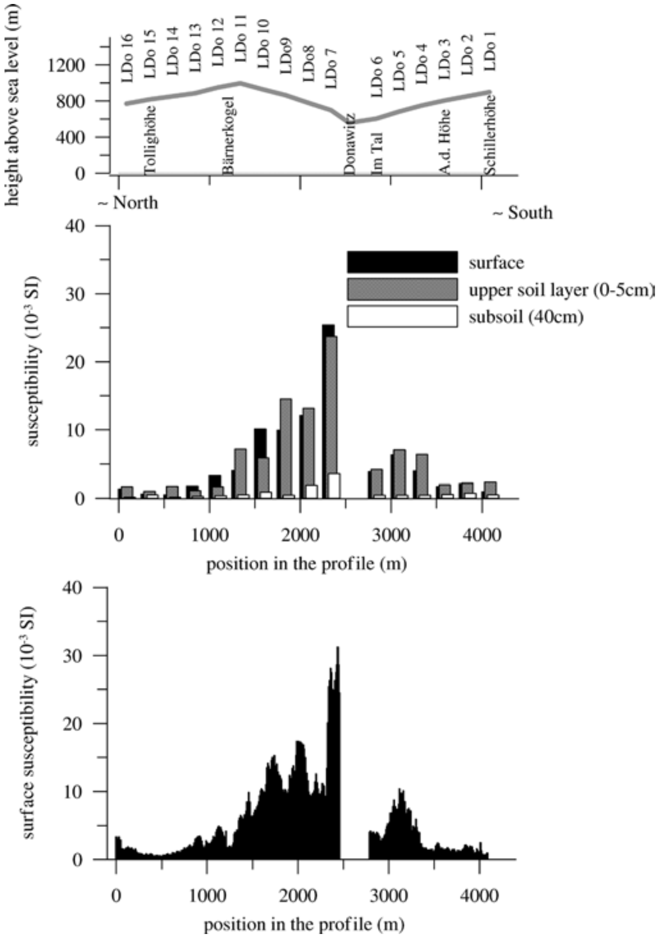


Fig. 12
Height above sea level, susceptibility measured in prospect holes (every 250 m) and surface susceptibility measured every 10 m along the profile Donawitz (cf. Fig. 10, *squares*)

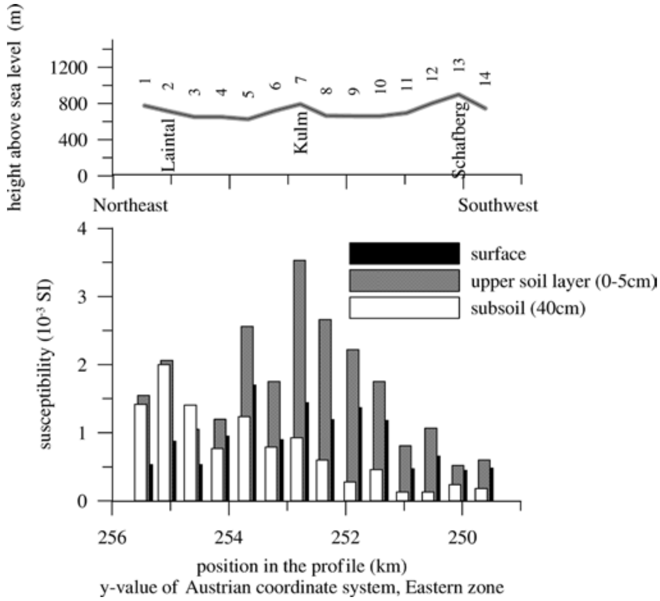


Fig. 13
Height above sea level and measurements of volume susceptibility in prospect holes (every 500 m) for the profile Trofaiach (cf. Fig. 10, *crosses*). Note that the scale for the susceptibility values differs by a factor of 10 from the scale in Fig. 12

values which would be expected for unpolluted soils. This confirms the results of the analysis of the soil survey samples which revealed susceptibility values far above the median value of Styria (Table 1).
The second profile (Trofaiach) is shown in Fig. 13. The absolute values are ten times smaller than in the centre of the anomaly. Nevertheless, the enrichment in the topsoil is still clearly visible from the centre of the profile to the south-west. Surface values tend to be lower than the values for the upper soil layer because of the lower density at the surface.

Applicability of the method in an urban area (case study Vienna)

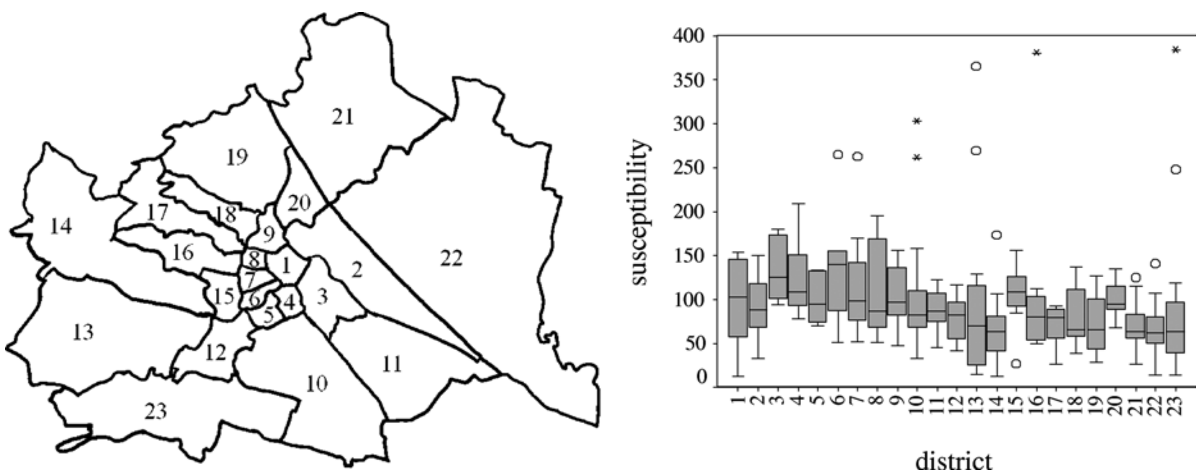
The city of Vienna covers an area of 415 km^2 and has more than 1.5 million inhabitants. Vienna is a metropolitan area with mixed contributions to the susceptibility signal. Unlike the situation in Leoben, there is no dominant industrial sector which most of the emitted particles can be attributed to. Table 5 shows the susceptibility values for the total area and for the 23 city districts of Vienna. The distribution of the districts is shown in Fig. 14, together with the box plots of the susceptibility values. The median value for all 282 samples is 80.7×10^{-8} m^3 kg^{-1} which agrees well with the values around Vienna measured for the soil survey samples of Lower Austria (compare Fig. 9).
The box plots in Fig. 14 show that several outliers and extreme values occur. It has to be taken into account that urban soils are hardly ever formed by soil processes. Anthropogenic substrates like construction waste, slags and ashes form a considerable part of the soil matrix. These substrates have influences on pedological parameters like the pH value as well as on the content of pollutants (Hiller and Meuser 1998). Therefore, the content of pollutants is much more influenced by the parent material than in natural soils.
Figure 14 also shows that the districts in the inner part of the city tend to have higher susceptibility values than the outer districts which include more green spaces. This relation between the area usage and the susceptibility values is shown more clearly in Fig. 15. The larger the amount of green space in a district, the smaller the median of susceptibility. The highest rank correlation coefficient (r=0.83) with the median of susceptibility per district is found for the percentage of the area used by traffic.
The Municipal Department 22 (Environmental Protection) of the City of Vienna analysed the following elements: As, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Pt, Se, V, and Zn. Only 22 samples were above the detection limit for Pt, and one sample for Se. These elements were not further analysed. The highest rank correlation coefficients with susceptibility were calculated for Cd (0.518), Cu (0.619), Pb (0.596) and Zn (0.580). These elements were found to show the same trend as magnetic susceptibility during an investigation of roadside soils along a highway in Germany (Knab and others 2000). Copper is commonly found in

Table 5
Susceptibility values (10^{-8} m^3 kg^{-1}) measured in the city districts of Vienna. *N* Number of samples per district

District	*N*	Minimum	Lower quartile	Median	Upper quartile	Maximum
1	7	12.0	49.7	103.3	148.2	154.1
2	12	32.3	67.0	88.1	120.7	150.3
3	8	93.6	100.3	124.9	174.8	179.4
4	7	77.8	89.7	108.7	187.6	209.2
5	6	70.5	72.5	95.4	132.3	133.5
6	6	50.9	77.8	140.3	182.2	264.9
7	7	52.2	60.1	98.0	169.9	261.7
8	6	51.0	64.0	87.0	175.4	195.2
9	10	47.0	77.8	96.7	139.5	155.4
10	20	33.0	66.9	82.0	110.6	302.3
11	14	45.0	74.2	87.4	107.5	121.7
12	11	41.5	51.6	82.4	100.8	116.5
13	18	14.9	25.0	69.6	117.8	364.9
14	15	12.9	27.1	63.3	80.1	173.3
15	10	26.1	89.5	108.2	127.4	156.0
16	10	49.4	52.8	80.8	104.8	380.6
17	10	26.1	53.3	79.4	89.1	92.2
18	8	38.6	56.9	65.9	113.7	136.7
19	16	28.6	41.8	65.8	100.5	127.1
20	9	67.3	85.8	95.0	124.0	134.6
21	20	26.3	55.7	62.8	83.3	124.7
22	32	13.9	47.6	62.5	79.6	139.7
23	20	13.6	38.3	63.0	96.7	384.1
Total	282	12.0	55.7	80.7	106.0	384.1

soils affected by road dusts (Nriagu 1979). Car exhaust and tire wear lead to an enrichment of Pb, Zn and Cd in roadside dust particles, and Pb was found to be concentrated in high-density magnetic particles (Hopke and others 1980). The correlation analysis of susceptibility and heavy metals thus confirms the results drawn from analysing the area usage in the different districts – traffic is the dominant source of pollutants in the city of Vienna. The same conclusion had been drawn from the chemical analysis of the soil data (Kreiner 2001). Scatter plots of susceptibility vs. Cu, Pb and Zn are shown in Fig. 16. Some of the sample sites have been further classified by the city administration as lying directly at main roads (35 samples), within parks with children playgrounds (36 samples) and within larger, green recreational areas (26 samples). The susceptibility values in parks within the city do not differ significantly from the values measured near the main roads (Fig. 17). The pollutants are distributed into the city parks. A significant reduction of susceptibility can only be found in the large recreational areas. However, the elements correlated with susceptibility are the same for sites near roads and for sites within recreational areas (Table 6). It can be concluded that the pollutants are diluted during their transport into the recreational areas. New influences on susceptibility are not found but the correlation coefficients are smaller for the recreational areas.

Fig. 14
The districts of Vienna and box plot of susceptibility values (10^{-8} m^3 kg^{-1}) measured for the samples from the different districts. The *boxes* mark the interquartile range, the *lines* in the boxes the median value. *Circles* are outliers (more than 1.5 box lengths from the edge of the box), *asterisks* mark extreme values (more than three box lengths from the edge of the box). The *whiskers* are the minimum and maximum values without outliers and extremes. Districts in the inner (more populated) part of the city tend to have higher susceptibility values. The western boundary of districts *21* and *22* is formed by the river Danube



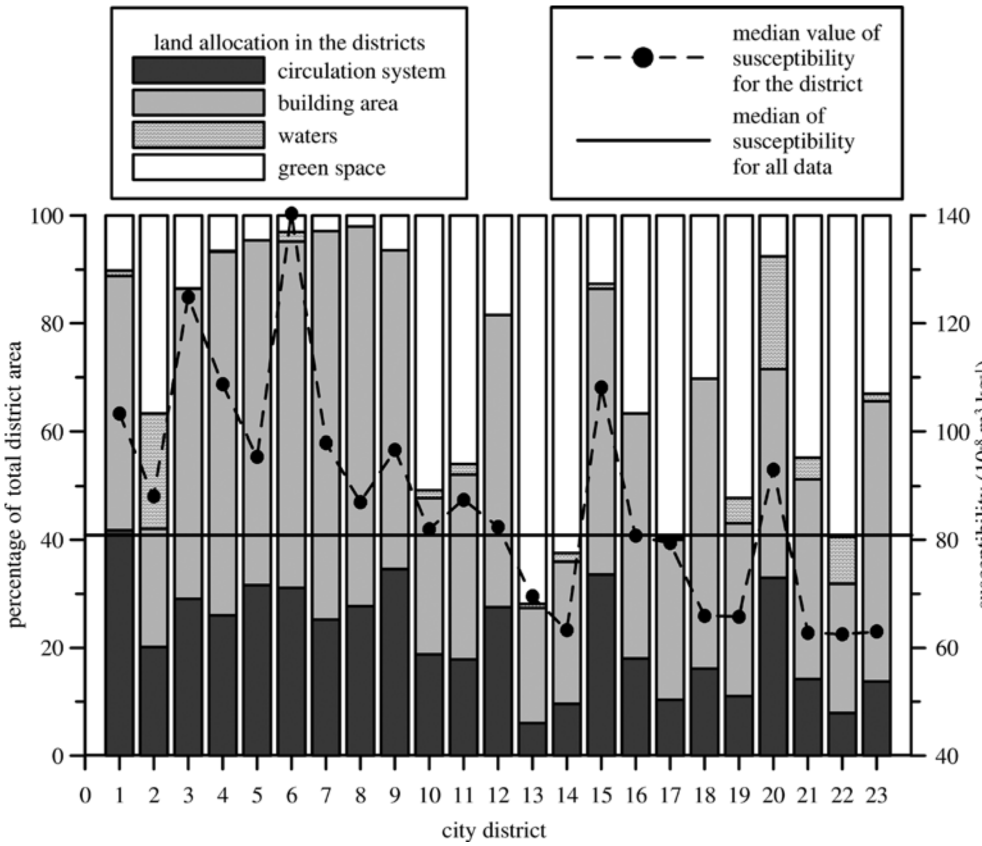


Fig. 15
Comparison of land use in the districts of Vienna, with the median value of susceptibility measured in the district (land-use data taken from the official web site of the city of Vienna)

Discussion

The aim of the study was to test the potential of magnetic susceptibility measurements for pollution monitoring. For a start, the distribution of susceptibility within a large area has been investigated. The anomalies appearing on the susceptibility maps are a good indicator for pollution as long as some knowledge of the underlying geology is available. Then, geogenic anomalies can be sorted out. A more reliable method to distinguish anthropogenic and geogenic anomalies is the additional measurement of subsoil susceptibility. Elevated values in the topsoil together with a considerable enrichment ($>20\times10^{-8}$ m^3 kg^{-1}) in the topsoil proved to be a reliable indicator of anthropogenic stresses on the soil. Thus, susceptibility measurements on their own can yield valuable information on the distribution of potential contaminants. It is then possible to designate areas which should be further investigated.

An example how to obtain detailed information about a polluted area was given for the industrial city of Leoben. Volume susceptibility measurements at the soil surface yield a detailed picture of the spatial distribution of pollutants. The preferred direction of propagation can be seen in this picture. It was found that the pollutants reach a defined height above sea level.

Information on the nature of the pollutants cannot be provided by susceptibility measurements. For the Leoben case study, chemical analyses were available from the Styrian soil survey at 22 sites and at up to three depths in the soil. Susceptibility was measured for these soil samples and correlations with the metals were calculated. Hg, Zn, Cd and PAH had the highest correlations with susceptibility, and it

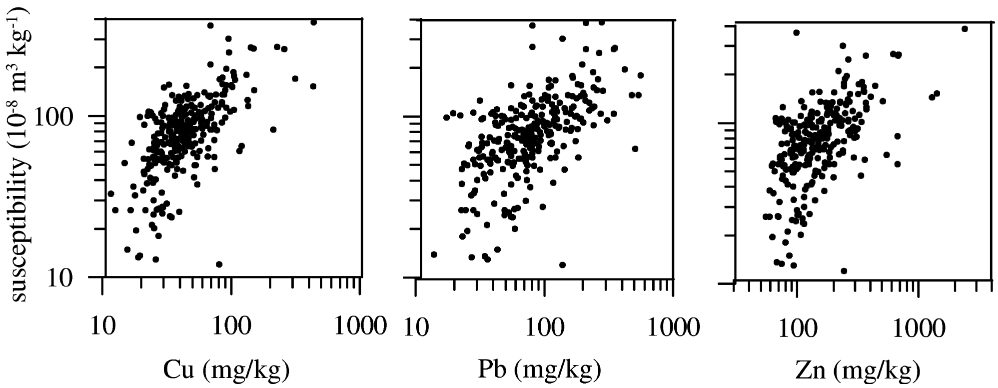


Fig. 16
Scatter plots of susceptibility vs. Cu, Pb and Zn for the 282 Vienna soil samples

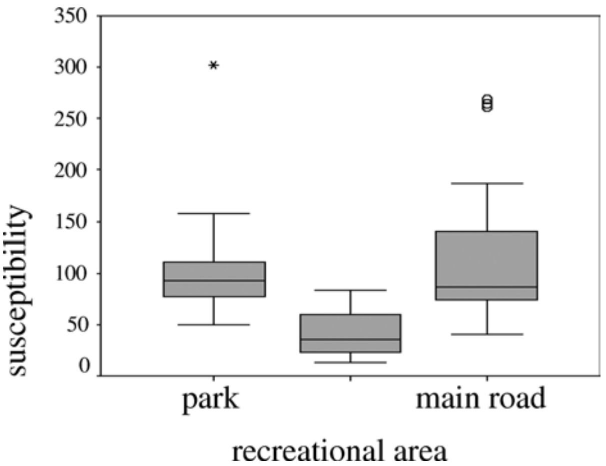


Fig. 17
Box plots for susceptibility values (10^{-8} m^3 kg^{-1}) measured in parks with children playgrounds, within recreational areas and at main roads. The parks within the city do not differ significantly from the main roads

Table 6
Rank correlation coefficients with susceptibility (all shown correlations are significant at the 0.01 level; the only correlation which disappears in the recreational areas is the one with molybdenum)

	Cd	Cu	Mo	Pb	Zn
Main roads	0.73	0.71	0.67	0.64	0.67
Green spaces	0.54	0.68		0.63	0.66

was possible to estimate their contents in the soil from the susceptibility values. A restricted number of chemical analyses combined with susceptibility measurements can thus be used to estimate the distribution of certain pollutants in a region. This approach is less time consuming and at the same time less expensive than a chemical analysis using a dense grid of sites. It is especially promising for regions where one source dominates the pollution pattern.
The applicability of susceptibility measurements should also be tested in a more complex environment. The city of Vienna was chosen where no dominant source was expected. Correlation analysis of susceptibility and heavy metals showed, however, that the dominant source in Vienna is the pollution by traffic. The highest correlations were found with Cd, Cu, Zn and Pb. The main difference to Leoben is the spread of the source of pollutants over the city area of Vienna, in contrast to the point source in Leoben which produces much higher peak values.
The urban soils of Vienna had been expected to produce a susceptibility signal which would be hard to interpret. The background of the signal is highly variable due to anthropogenic substrates forming a considerable part of urban soils. This led to a larger number of outliers and extreme values. During the statistical analysis of these data it was necessary to change to nonparametric methods. Using these methods, however, we obtained meaningful results which prove that susceptibility measurements can be a useful complementary method in tracing pollutants in urban soils. The great advantage of susceptibility measurements is their promptness and their low cost. It would be possible to increase the density of existing grids of chemical measurements and to make repeated measurements within shorter intervals. Thus, changes can be monitored quickly. Chemical analysis could be concentrated at locations where severe pollution is to be expected from the susceptibility measurements.

Conclusions

A two-step approach for the use of magnetic susceptibility in pollution monitoring proved to be a powerful tool in this study. A grid of susceptibility measurements is analysed for anthropogenic anomalies by using either the geological information at hand or the difference of topsoil and subsoil values. Regions which are defined as suspect to being polluted in this initial step can then be investigated more thoroughly. On the one hand, surface measurements in a denser grid can yield high-resolution information on the spatial distribution of pollution. On the other hand, additional chemical analysis can be performed at selected points. Thus, the main pollutants are defined. A correlation with the susceptibility values leads then to an estimate of their distribution in the investigated area. This procedure saves time and substantially undercuts the costs for extensive chemical analysis. Therefore, the proposed susceptibility mapping makes it possible to intensify investigation in space as well as in time.

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