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The assessment of point and diffuse metal pollution of soils from an urban geochemical survey of Sheffield, England

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Abstract. A model of soil variability as a continuous background process with superimposed point contamination was applied to 569 measurements of metal concentrations (Cr, Ni and Pb) in the topsoils of Sheffield, England. Robust estimators of the variogram were shown to be required to describe spatial variation of the metal concentrations at most sampled locations. This is diagnostic of the presence of a contaminant process. Values of the standardized kriging error from the cross-validation of each datum were used to identify spatial outliers for each metal. The ordinary kriged estimates of Cr, Ni and Pb were mapped after removing the outliers to estimate the background variation. Each of the 35 spatial outliers that occured in gardens have concentrations exceeding their Soil Guideline Value for residential land use with plant uptake, highlighting a potentially significant exposure pathway. The frequent observation of coal and furnace waste at these sites suggests that their dispersal, following domestic use and industrial processes, respectively, represents a significant point contaminant process. There was no evidence for spatial clustering of the point process. However, the spatial outliers of Cr and Ni showed a significant association with disturbed sites identified from historical land use maps, in part due to their prevalence in areas of historical steel manufacture. The magnitude of diffuse pollution for each metal in the urban soil was estimated by removing the spatial outliers and comparing robust measures of location with those from a survey of soils developed over the same parent materials in adjacent rural and peri-urban environments. The Winsorized mean Pb concentrations in urban topsoil ($203\,mg\,kg^{-1}$) were twice the value in the rural environment ($101\,mg\,kg^{-1}$), highlighting a very substantial diffuse Pb load to urban soils. The equivalent estimated diffuse components in urban soils for Cr and Ni were, respectively, 25% and 14% higher than the rural soils.

Keywords: Robust, geostatistics, spatial outlier, contaminant, land use, metal

INTRODUCTION

There is increasing interest in the quality and management of urban soils, including the implications of elevated concentrations of metals. Geochemical surveys have been undertaken in cities throughout the world (Lux 1993; Birke & Rauch 2000), and in the UK by the British Geological Survey (Rawlins 2002). The management of contamination in urban soils requires estimates of concentrations at unsampled points or over blocks of land, which can be done by geostatistics where sampling and analytical methods are consistent and there is a sufficient number of samples.

Data on metal concentrations in urban soil typically show very complex variation. In particular, there are spatially continuous variations arising from parent material and the effects of diffuse pollution. Superimposed on this is point contamination at hotspots. Sites influenced by point contamination are likely to be spatial outliers in data on metal concentration. By spatial outliers we mean observations where the concentration of a metal in the soil is unusually large (or small) in its spatial context (Laslett & McBratney 1990). Such variability may cause problems for conventional geostatistical analysis using Matheron's estimator of the variogram (Matheron 1965). For this reason we considered some robust methods proposed by Lark (2002). The objective was to model the continuous spatial variation of a variable as a realization of a random function, and to estimate the variogram of this random function from the data using a robust estimator. We then identified which observations in the data were not consistent with this modelled random function, and investigated the possibility that they represented some quasi-point process of contamination.

Such an approach to the analysis might have advantages. First, the identification of spatial outliers in the data may give insight into sources and processes of pollution. Once identified, further interpretation of the source of the contamination can be aided by assessment of the soil samples and historical map data. This would include the visual appearance of the soil (such as the presence of any unusual

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particles or material), and historical map data (including information on land use) that show the history and development of the area. This may provide information on the point processes that have influenced soil chemistry. Second, if we can identify data most likely to represent point pollution, then the best approach to spatial estimation of the variable in question is to estimate the continuous background variability separately (either from an edited data set (Lark 2002) or by robust kriging (Hawkins & Cressie 1984). Where an estimate of the natural geochemical composition of the soil is available from soil surveys in rural and peri-urban areas over the same parent material types (e.g. Rawlins *et al.* 2002), it may be possible to estimate the magnitude of the diffuse contribution to the urban soil after removal of outliers.

We suggest that our approach has advantages over simpler data editing, as might be used in non-spatial statistics, that would only identify outliers which appear unusual relative to the overall distribution of the data, so-called marginal outliers. First, a contaminant observation from a process other than the continuous background variation is likely to appear unusual in its spatial context but might not be a marginal outlier. By contrast a large value that genuinely reflects the continuous variation (e.g. as a result of diffuse pollution) is likely to be surrounded by other large values, and so will not appear to be a spatial outlier. We wished to identify the spatial outlier in the first instance, and not the marginal outlier. The second advantage of our approach is that it proposes a model of the data as a contaminant process, and a method based on robust statistics to decide whether or not this model holds. We therefore evaluated evidence that spatial outliers were present using all the data, and only proceeded to edit the data when this evidence supported it. This avoided the risk, attendant on all simple data editing methods, that we biased our inferences from data as a result of excessive trimming of unusual values (Omre 1984; Genton 1998a).

In this paper we used robust geostatistics to identify contaminant hotspots (spatial outliers) for three metals (Pb, Cr and Ni) from a soil survey of Sheffield (England) – a city with a long history of metal manufacturing and processing. We mapped these metals by kriging, after removing the outliers. We investigated the outliers to highlight significant historical factors contributing to point pollution, looking particularly at whether the spatial outliers were more closely associated with historical disturbance than the other sample sites. Finally, we used data from a previous study to estimate the typical contribution from diffuse pollution to soils in the urban area of Sheffield.

METHODS

Study region

Soils in the city of Sheffield have developed predominantly over the Carboniferous Lower and Middle Coal Measures Formations, although part of the west of the city is over the older Millstone Grit Formation (see Figure 1). The Lower and Middle Coal Measures in this region consist of cyclothems, including mudstones, shales and inter-bedded sandstones. Soils derived from the Coal Measures in this region were shown to have naturally elevated concentrations of several trace elements including Pb, Cr and Ni in comparison to their average contents throughout England and Wales (Rawlins *et al.* 2002). There are no extensive Quaternary deposits, ensuring that all soils were derived from these two parent material types.

A resumé of industrial activity throughout the city of Sheffield has been provided by Gilbertson *et al.* (1997). The most notable features in the context of the present study are summarized here. Coal has been mined and burnt for space heating and industrial purposes in Sheffield since Roman times. The dispersal of trace elements associated with historic coal use was cited as a source for further enhancement of topsoil metal concentrations in urban areas (Rawlins *et al.* 2002). The metal working industries of Sheffield have been located in the valleys of the rivers Don, Sheaf and Porter for much of the last century (see Figure 1). In the middle of the 18th century more than 150 firms were dedicated to steel manufacture within the city and high-quality cutlery has been manufactured since that time. In the 1960s, British Steel opened a large works at Tinsley (Figure 1) to produce special steels. The dispersal of slag from locally produced stainless steel (ferrochrome) may have led to elevated concentrations of Ni and Cr in Sheffield soils. For example, recent studies have reported that slag from Swedish stainless steel production (ferrochrome) contains 2.7% Cr and 542 mg kg^{-1} Ni (Lind *et al.* 2001), while Proctor *et al.* (2002) reported total Cr contents in American slags between 132 and 3390 mg kg^{-1}.

Historically, Pb was used for the manufacture of special alloys, and more recently as an additive (alkyl-lead) in petrol. Although this practice ceased in the UK in 2000, the high density of the road network and the associated heavy traffic typical of cities in industrialized nations was evident throughout Sheffield since the 1970s. The city has a long-history of coal-mining, metal manufacturing and processing industries, resulting in both point and diffuse pollution of a range of metals, including Cr, Pb and Ni.

Soil survey

A total of 569 soil samples were collected from individual sites across the city at a density of four samples per square kilometre in June and July 1996 (Figure 1). Sample sites were selected from open ground as close as possible to the centre of each of four 500-metre squares, within each kilometre square of the British National Grid (BNG). Typical locations for sampling were gardens, parks, sports fields, road verges, allotments, open spaces, schoolyards and waste ground. Each sample was based on three samples of equal size from the corners of a triangle of side-length 2 m. Each bulked sample was collected at a depth range of 0–15 cm from the soil surface using an auger of diameter 35 mm. At each site, information was recorded on location using 1:10 000 scale Ordnance Survey maps, a description of any visible contamination (e.g. metallic, pottery, bricks, plastics etc.), Munsell colour, soil clast lithologies (e.g. sandstone, limestone, etc.), and land use. All soil samples were disaggregated following air-drying and sieved to less than 2 mm. All samples were coned and quartered, and a 50-g subsample ground in an agate planetary ball mill. The total concentration of 23 major and trace elements (including Cr, Ni and Pb at detection limits 1 mg kg^{-1}) were

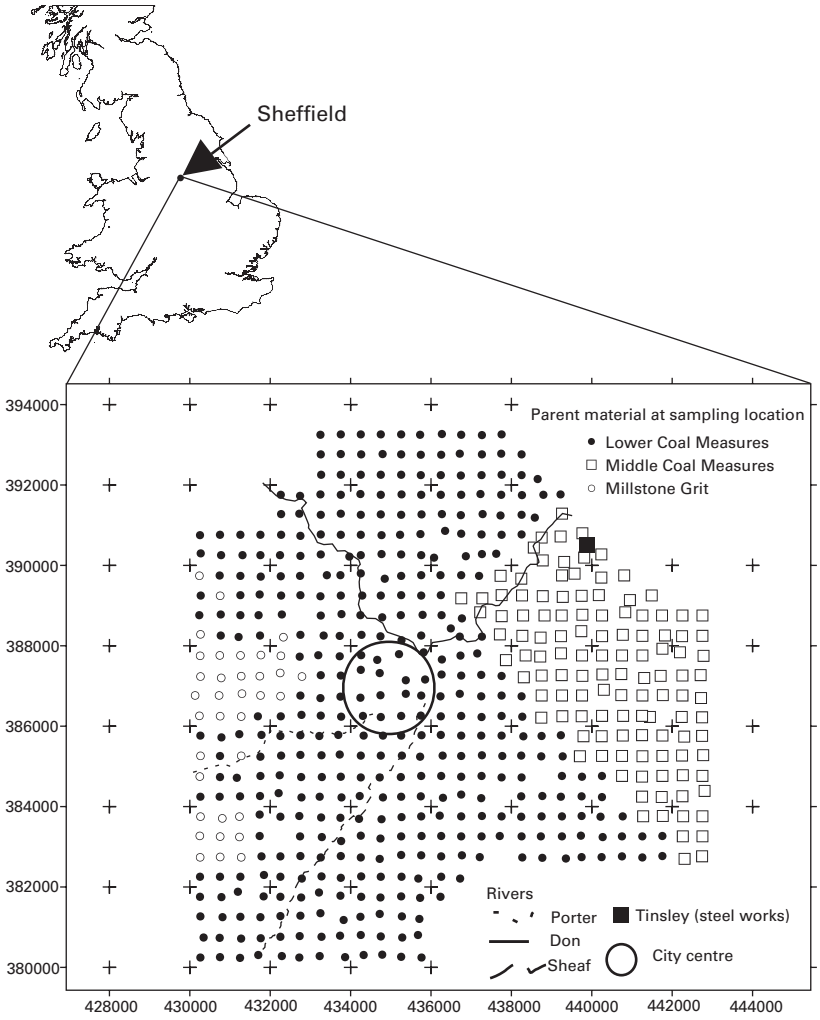

Figure 1. Location of Sheffield and soil survey sampling locations by parent material type. Cross hairs show the vertices of the 2 km grid.

determined in each sample by wavelength and energy dispersive X-ray fluorescence (XRF).

Geochemical data are also available from topsoil surveys in rural and peri-urban areas for soils derived from the same parent materials that occur in the urban environment of Sheffield. Sampling in the rural survey was undertaken during the summer months of 1994, 1995 and 1996 – at around the same time of the urban survey (1996). The only difference between the sampling and analytical protocols was the scale of the sampling support and the number of incremental samples; the rural survey was based on five auger holes at the corners and centre of a square of side-length 20 m.

Geostatistical analysis for the identification of spatial outliers

We assumed that our data, z, was a realization of a hybrid random variable Z with normal background (b) and contaminant (c) processes (means and standard deviations μ_b, σ_b and μ_c, σ_c, respectively) superimposed. Observations drawn from a contaminant process occur with intensity π_i, so:

$$Z \sim [\pi_i N(\mu_c, \sigma_c), \{1 - \pi_i\} N(\mu_b, \sigma_b)] \quad (1)$$

We tested the plausibility of this model by robust estimation of the variogram (to characterize the background process), a comparison of robust and non-robust variogram estimators to decide whether a contaminant process seemed to exist, then the application of a robust variogram to identify those data that seemed inconsistent with the background. Here we summarize the steps in the geostatistical analysis of the soil metal data.

Exploratory analysis

We plotted empirical cumulative distribution functions (cdfs) with the equivalent normal cdf based on robustly estimated parameters of location (median) and scale (median absolute deviation) for each element. We also calculated the skew and octile skew (Brys *et al.* 2003). The octile skew is a measure of the assymetry of the first and seventh octiles of the data about the median, and so it is insensitive to extreme values.

We usually transform data if their conventional coefficient of skew is outside $[-1, 1]$. We wish to identify a corresponding interval for the octile skew to use as a rule of thumb to decide when a transformation is necessary. We considered Tukey's g distributions, which is a family of statistical distributions whose skewness depends on a continuous parameter, g, such that the variable may have

a negative skew ($g < 0$), no skew ($g = 0$) or a positive skew ($g > 0$) (see Hoaglin *et al.* 1985). We found that a variable with a distribution from Tukey's *g*-family with the conventional coefficient of skew in the range $[-1, 1]$ has an octile skew in the range $[-0.2, 0.2]$. We therefore propose that data are transformed if the octile skew is larger than 0.2 or smaller than -0.2. The octile skews of Cr, Ni and Pb were 0.45, 0.24 and 0.49, respectively, so we transformed each variable by calculating their natural logarithms. Summary statistics are presented in Table 1. The transformed data and their robustly estimated normal cdfs are shown in Figure 2.

Geostatistical characterization of the background variation

After checking that there was no significant anisotropy in the spatial data, we estimated isotropic variograms for each variable based on the natural log transformed data using Matheron's estimator (Matheron 1965) and three robust estimators due to Cressie & Hawkins (1980), Dowd (1984) and Genton (1998a). We then fitted a variogram model by weighted-least squares with the MVARIOGRAM procedure in GENSTAT (Payne 2002). The model parameters are shown in Table 2 and the variograms in Figure 3. Note that the estimates of the variogram obtained with Matheron's estimator are generally larger than those obtained with the robust estimators. This is consistent with the contaminated normal model of equation (1), because Matheron's estimator is not resistant to spatial outliers (Lark 2000). However, a proper validation of a robust variogram against a variogram based on Matheron's estimator is required, because Matheron's estimator is more statistically efficient than the robust alternatives, and the robust estimators may be biased if the background process is not bivariate-normal.

Lark's (2000, 2002) procedure to validate alternative variogram models is based on cross-validation. Each of our observations, $z(x_i)$, was excluded from the data in turn, and estimated by ordinary kriging from the remaining observations with the specified variogram model that we wished to test. This returned an estimate, $\hat{Z}(x_i)$, and the error variance of this prediction, the ordinary kriging variance $\sigma^2_{OK}(x_i)$. This latter term is particularly sensitive to the specified variogram model. If the variogram is correct, then we expected the statistic $\theta(x_i)$ to take the value 1.0.

$$\theta(x_i) = \frac{\{z(x_i) - \hat{Z}(x_i)\}^2}{\sigma^2_{OK}(x_i)} \qquad (2)$$

Table 1. Summary statistics for total and $\log_e$ concentrations (mg kg^{-1}) of metals in the soil ($n = 569$).

	Cr	$\log_e$ Cr	Ni	$\log_e$ Ni	Pb	$\log_e$ Pb
Mean	136	4.72	40	3.49	244	5.17
Median	101	4.62	32	3.47	164	5.1
MAD[a]	31	0.31	12	0.43	98	0.61
SD[b]	140	0.52	39	0.54	298	0.75
Min	36	3.58	8	2.08	19	2.94
Max	1359	7.22	473	6.16	4300	8.37
Skew	5.2	1.86	6.5	1.04	7.2	0.36
Octile skew	0.45	0.26	0.24	−0.01	0.50	0.13

[a]Median absolute deviation; [b]standard deviation.

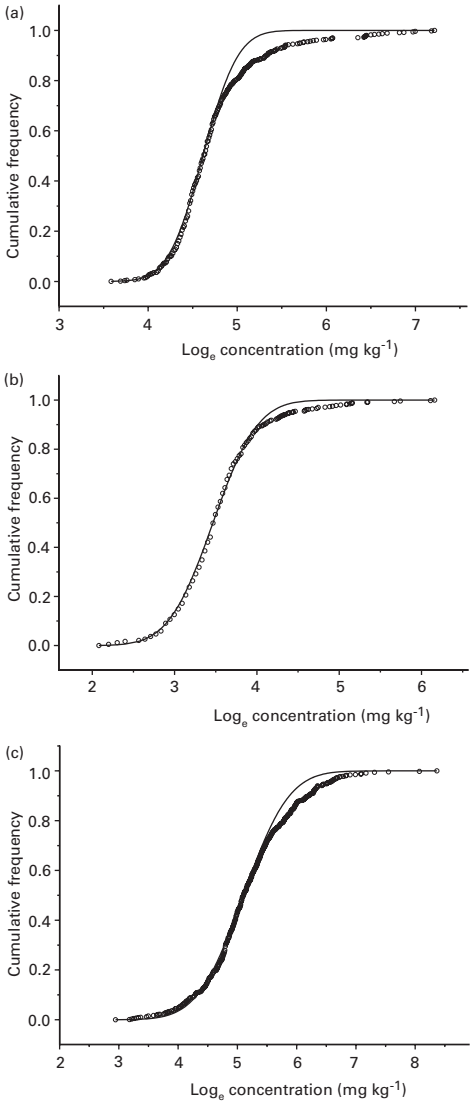

Figure 2. Log transformed cumulative frequency plots of concentrations (symbols) and Gaussian cumulative density functions (solid trace) based on robustly estimated parameters for Cr (a), Ni (b) and Pb (c).

However, the mean value of this statistic over our data is a poor diagnostic because the numerator in equation (2) is itself not robust to outliers. For this reason Lark (2000) proposed that the median over the data, $\tilde{\theta}$, be used instead. This has an expected value of 0.455 when the variogram is correct. Lark (2002) presented a method for bootstrapping a confidence interval for an estimate of $\tilde{\theta}$. If the confidence interval includes 0.455 for a variogram model based on Matheron's estimator, then this should be used and we do not have evidence for the presence of a contaminant process. If, on the other hand, $\tilde{\theta}$ for the variogram based on Matheron's estimator is significantly smaller than 0.455, then this is evidence for the presence of a contaminant process, and a robust estimator of the variogram can be used. An appropriate robust estimator could be selected by the same cross-validation process. Provided that the intensity of the contaminating process, π_i in equation (1), is smaller than the spatial breakdown point (Genton 1998b)

Table 2. Parameters of the variogram models (shown in Figure 3) for the variogram estimators.[a]

	Cr				Ni				Pb			
	Ma	CH	Do	Ge	Ma	CH	Do	Ge	Ma	CH	Do	Ge
Model	Sph	Sph	Sph	Sph	Sph	Sph	Sph	Sph	Exp	Exp	Exp	Exp
c_0 [b]	0.0338	0.0206	0.0156	0.0175	0.0313	0.019	0.0131	0.0166	0.0839	0.0706	0.0638	0.0213
c_1 [c]	0.0271	0.0161	0.0119	0.0151	0.0284	0.028	0.0273	0.0269	0.0507	0.0459	0.0464	0.0117
a [d]	6923	5883	5436	6139	6256	5454	5035	6153	7691	3885	3265	4105

Ma = Matheron (Matheron 1965) CH = Cressie–Hawkins (Cressie & Hawkins 1980), Do = Dowd (Dowd 1984) and Ge = Genton (Genton 1998) for each of the three metals. Sph = spherical; Exp = exponential; [b]nugget; [c]sill; [d]range (m) – range values for the exponential model are the effective range.

of the robust variogram estimators (which is about 0.3 for the Dowd and Genton estimators), then these estimate the variogram of the background process.

Results for the cross-validation are presented in Table 3. In each case, the value of $\tilde{\theta}$ for variogram models based on Matheron's estimator were significantly smaller than 0.455, as judged by bootstrap estimates of the confidence interval based on the variogram for which $\tilde{\theta}$ was closest to 0.455. The best variogram models for each of the three metals, judged by the closeness of $\tilde{\theta}$ to 0.455, were based on robust estimators, namely Cr (Cressie-Hawkins), Ni (Genton) and Pb (Dowd). This is evidence for the presence of a continuous background variation in the concentrations of these metals contaminated by a distinct spatial process.

Identification of spatial outliers

We wished to identify those observations most likely to represent the contaminant process, so we computed the normalized deviation or standardized kriging error (SKE),

$$\mathrm{SKE} = \frac{z(x_\mathrm{i}) - \hat{Z}(x_\mathrm{i})}{\sigma_{\mathrm{OK}}(x_\mathrm{i})} \tag{3}$$

A datum was classified as a spatial outlier (large) if its standardized kriging error was less than -1.96, that is, if it fell below the lower 95% confidence interval for a standard normal variate. This approach is similar to the Absolute Normalized Deviation that Bárdossy & Kundzewicz (1990) proposed as a diagnostic for outliers. Our procedure differs firstly in the inferential approach (above) which indicates that outliers are present in the data, and secondly, we are specifically interested in large outliers arising from contamination, so we wish to retain the sign of the deviation.

Spatial analysis of the outliers

Having identified spatial outliers in the data, we investigate whether their distribution in space appears to be an independent random process – complete spatial randomness (csr) (Cressie 1993) or show spatial dependence, such as clustering, at some scale. We treat the distribution of outliers as a quasi-point process (Lark 2002); that is to say, we recognize that the extent of any local contamination is finite, but patches are small enough so that any given patch would only be represented at one sample site under our scheme. There are many statistics for investigating spatial-point processes (Cressie 1993) but these are usually for analysing events that are exhaustively mapped on continuous coordinates over a region. By contrast, we observe spatial outliers only at a subset of our predetermined sample sites: we are investigating a sampled quasi-point process.

We analysed the spatial outliers as a sampled point process following Lark (2002) and computed the mean distance between each observed spatial outlier and its nearest neighbouring sample site, also identified as a spatial outlier, $\bar{\omega}$. We computed the sample distribution of $\bar{\omega}$ under a null hypothesis of csr, conditional on the positions of all the sample points and the overall proportion at which a spatial outlier was observed. This was done by Monte Carlo simulation, generating 10 000 realizations of the csr process and estimating $\bar{\omega}$ for each. The quantiles of the 10 000 values of $\bar{\omega}$ gave us estimates of points of the sample distribution of the statistic under the null hypothesis. We did this for each metal.

Identification of historical sources of contamination

The positions of the sample sites were superimposed over a series of digitized historical Ordnance Survey maps for Sheffield dating from 1855, 1906, 1924, 1948 and 2004. Each site was investigated to see whether it had had some historical disturbance that could result in locally elevated concentrations of metal in the soil, such as the presence of works (e.g. steel, railway, forge, industrial units, depots), quarries, railway embankments and roads.

We proceeded to test null hypotheses that the occurrence of spatial outliers for a metal and the occurrence of an historical disturbance are mutually independent events (so spatial outliers are no more likely on a disturbed site than an undisturbed one). We undertook this analysis by calculating contingency tables. The columns of these tables corresponded to the presence or absence of spatial outliers for a metal. The rows corresponded to the presence or the absence of an historical disturbance. We assumed that the observations for each category are independent (given the results of the spatial point process analyses) and so we tested the null hypothesis for each table by computing

$$\sum \frac{\{O - E\}^2}{E} \tag{4}$$

over the four cells of the table, where O and E are the observed and expected counts respectively. The resulting statistic was tested against χ^2 with one degree of freedom. Given the large values of O and E in all cells, a Yates correction was not applied.

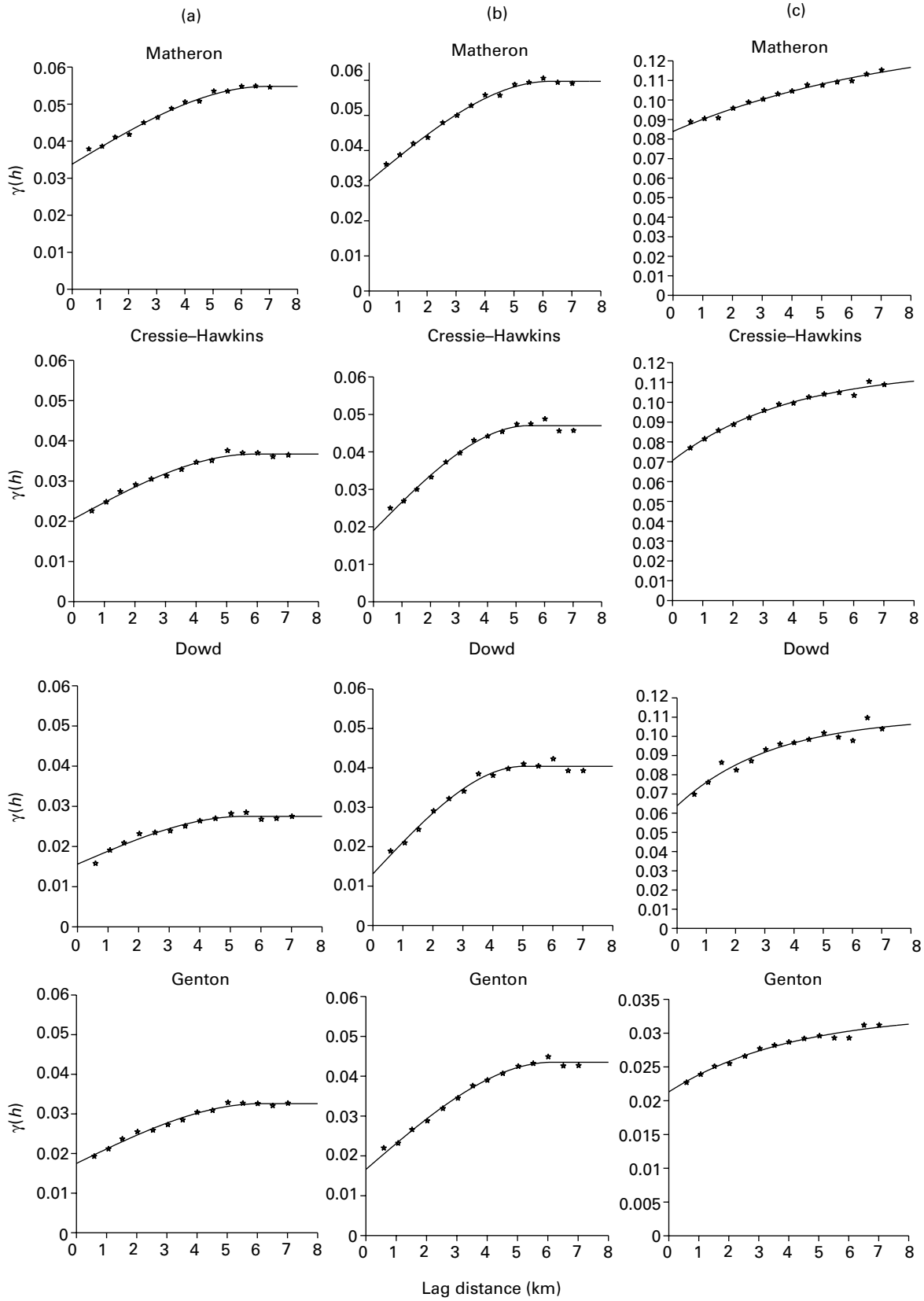

Figure 3. Estimates (symbols) and fitted models (curves) for the four variogram estimators for Cr (a), Ni (b) and Pb (c).

Table 3. Values of $\tilde{\theta}$ from cross-validation based on the four variogram models[a] and the bootstrapped confidence intervals (CIs) for the selected estimator.

	Ma	CH	Do	Ge	CIs
Cr	0.28	0.48[b]	0.71	0.61	0.367–0.557
Ni	0.25	0.39	0.54	0.48[b]	0.372–0.551
Pb	0.34	0.39	0.42[b]	1.27	0.368–0.558

[a]For model key, see Table 2. [b]Model selected and that upon which bootstrapped confidence intervals were estimated because of the four models; it has the smallest difference from 0.455, the value of $\tilde{\theta}$ we expect when the variogram is correct in accordance with Lark (2002).

RESULTS

Geochemical maps and spatial outliers

There were between 29 and 48 high-value spatial outliers for each of the three metals. There were 127 unique sample locations classified as high-value spatial outliers, of which 110 samples were so-classified for only one of the three metals, 15 samples for two of the three metals, and 2 samples for all three metals. We removed the spatial outliers from each of the variates of the three metals and generated kriged estimates of their concentrations on a regular grid at intervals of 200 m and threaded contours through the values (Figures 4, 5 & 6).

The distributions of the high-value spatial outliers for Cr (Figure 4) and Ni (Figure 5) have broad similarities. A large proportion occur in areas of current and historical steel manufacturing to the northeast of the city centre in close proximity to the River Don, and to a lesser extent along the River Sheaf towards the southwest. The contour maps show that the highest concentrations (representing the background process) of Cr (140 mg kg^{-1}) and Ni (70 mg kg^{-1}) also occur to the northeast of the city. The elevated concentrations may reflect a strong regional trend in aerial particulate deposition of Cr and Ni originating from the centres of steel manufacturing to the northeast of the city. This is supported by unpublished data from a survey of the inorganic composition of 642 tree bark samples collected throughout Sheffield. In contrast, there are considerably more Pb outliers close to the city centre, and along a corridor stretching towards the southwest along the River Sheaf (Figure 6). Although the highest Pb concentrations (> 350 mg kg^{-1}) reflecting the background process are generally confined to the south and west of the city, we do not have sufficient knowledge of the location and magnitude of historical, diffuse sources of Pb to give a detailed interpretation. To provide a comprehensive interpretation of the metal distributions presented in Figures 4–6 would also require further understanding of the local distribution and geochemistry of the different components of Coal Measures cyclothems and how these relate to the native metal concentrations in the soils derived from them.

Table 4 shows $\bar{\omega}$ for the spatial outliers for each metal, and for historical disturbances at the sample site. Also shown are confidence intervals for this statistic under a null hypothesis of complete spatial randomness, obtained by the Monte Carlo procedure described above. These show that

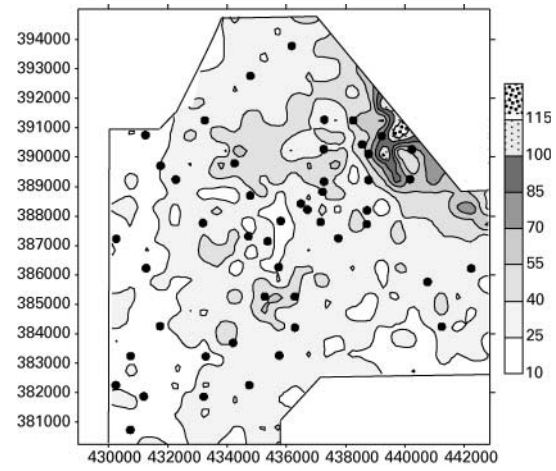

Figure 5. Contour maps of Ni concentrations (mg kg^{-1}) based on punctually kriged estimates with spatial outliers (•) removed from the original data.

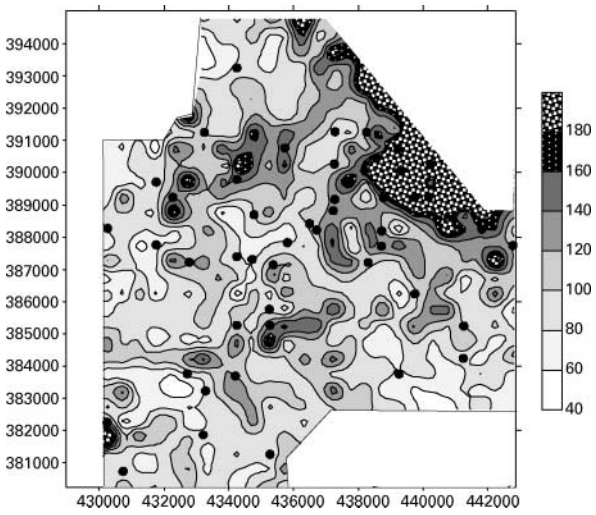

Figure 4. Contour maps of Cr concentrations (mg kg^{-1}) based on punctually kriged estimates with spatial outliers (•) removed from the original data.

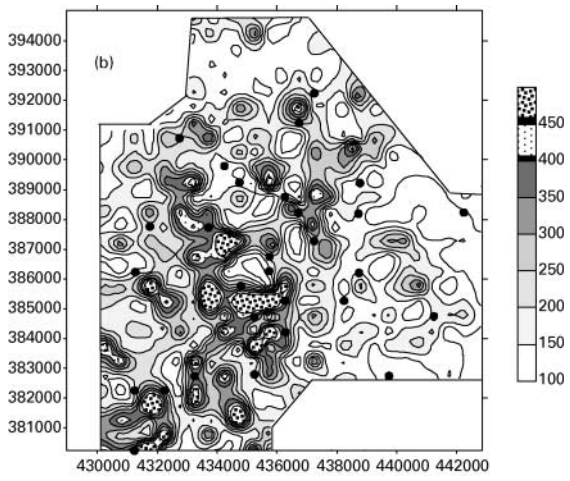

Figure 6. Contour maps of Pb concentrations (mg kg^{-1}) based on punctually kriged estimates with spatial outliers (•) removed from the original data.

in no case can we reject a null hypothesis of complete spatial randomness, and so we can regard the observations for any one of these point processes as independent.

High-value outlier sites occurred in 35 residential gardens, highlighting a widespread and potentially significant exposure pathway to these three metals in the soil. The Soil Guideline Values (SGVs) for residential land use with plant uptake (Department of the Environment Food and Rural Affairs and the Environment Agency 2002a–c) are ($mg\,kg^{-1}$): Cr (130), Ni (50) and Pb (450). At each of these residential sites, the metal concentrations exceeded these published values. Of the residential garden sites that were classified as outliers, there were 18 and 19 observations, respectively, associated with coal waste particles and slag or furnace waste recorded during sample collection (see Table 5). The prevalence of waste material related to coal and coal-burning is unsurprising in the residential soils of Sheffield given that coal was the dominant domestic energy source for more than a century. Both domestic coal ash and the contents of coalbunkers may have been spread on gardens during both the 19th and 20th centuries. The frequent observation of slag or furnace waste suggests that this material has been dispersed widely throughout gardens in the urban area and may have had a significant impact on soil metal concentrations.

The other sites with no clear historical local source of contaminants were dominated either by recreational land uses, such as parks, golf courses and school playing fields, or by the verges of roads and car parks. Of this series of locations, the metal spatial outliers were dominated by Ni (20 samples) and Cr (12 samples), with relatively few occurrences of Pb (5 samples). The contaminants observed during soil sampling at these sites included eight instances of coal waste particles and eleven instances of slag/furnace waste.

Table 4. Observed values of $\bar{\omega}$ and confidence limits under the null hypothesis of complete spatial randomness.

		Confidence interval of $\bar{\omega}$ under the null hypothesis		
Event	$\bar{\omega}$	95%	99%	99.9%
Historical disturbance	570.6	561–619	553–627	543–639
Spatial outlier				
Cr	968.8	851–1126	808–1166	756–1229
Ni	1002.8	843–1112	795–1157	743–1204
Pb	1306.5	1022–1494	940–1571	858–1694

Table 5. The number and type of solid contaminants observed at a total of 94 high-value outlier sites during soil sample collection.

Contaminant type	Count
Bricks	35
Coal waste	26
Slag/furnace waste	24
Plastics	23
Bulk industrial waste	17
Clear glass	13
Coloured glass	8
Metal	6
Iron/steel wire	4
Ceramics	3
Tiles	3
Galvanized iron	2
Rubber	2
Solid fertilizers	1

Assessment of the point process

We plotted the SKEs for pairs of metals (Figure 7) indicating for each point whether the sites are likely to have been disturbed. These plots show that the sites with the smallest SKE values for Ni and Cr are dominated by the disturbed sites, but a close look at Figure 7b suggests no such relationship for Pb.

We present in Table 6 a set of three contingency tables. The first number in each cell is the count of our sample sites corresponding to each contingency. The expected counts for each cell under the null hypothesis are shown in parentheses; these were computed from the marginal totals of the table. Note that for Cr and Ni we observe substantially more sites with historical disturbance and spatial outliers than is expected under the null hypothesis, which is rejected with a small P-value. By contrast, the observed and expected counts are very similar for Pb, and the null hypothesis is accepted.

The association of the spatial outliers in Ni and Cr with historically disturbed sites is interesting and supports the inference that these points are sites where the metal concentration results from local contamination. We find Cr and Ni hotspots in the northeast of the city (see previous section) where the steel manufacturing industry dominated land use for much of the 20th century. By contrast the occurrence of Pb hotspots is less clearly associated with our disturbed land use categories.

Estimates of diffuse pollution

A previous study comparing topsoil metal concentrations in peri-urban and rural environments demonstrated significant differences in median concentrations of Ni and Pb in soils developed over Lower and Middle Coal Measures lithologies (Rawlins *et al.* 2002). In such circumstances it is necessary to compare topsoils within the same parent material class to avoid any differences due to natural, pedo-geochemical variation. A greater proportion of the soil samples in the urban survey are derived from the Lower Coal Measures ($n = 390$) than from to the Middle Coal Measures ($n = 118$; Figure 1). For the purpose of assessing the magnitude of diffuse pollution in the urban area (over and above that in peri-urban and rural areas), we chose to limit our comparison to urban and rural soils developed over the Lower Coal Measures. We removed 76 spatial outliers from the urban soil samples over the Lower Coal Measures; the remaining samples represent the natural soil composition plus the diffuse component. We calculated median and Winsorized mean values for the three metal concentration distributions representing robust measures of location in each distribution. We calculated the same statistics for 415 samples from the rural and peri-urban survey over the same parent material. The statistics are presented in Table 7.

It is important to note that Rawlins *et al.* (2002) also reported statistically significant elevated concentrations of Pb and Ni in areas of high, compared to low, population

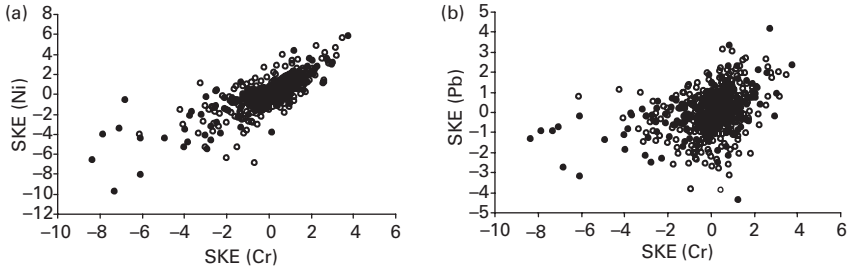

Figure 7. Scatter plots of the standardized kriging error (SKE) for disturbed (•) and undisturbed (o) sites: (a) Cr vs Ni and (b) Cr vs Pb.

density for the rural topsoil samples over the Coal Measures. Therefore, any significant difference between the urban and rural distributions should be dominated by the magnitude of diffuse pollution in the urban and rural environments.

For each of the three elements, the urban survey median and Winsorized mean values were greater than those from the rural survey. By far the largest difference was observed for Pb, the two measures having 83 and 102% higher concentrations in the urban environment, respectively. This estimate represents a very significant diffuse load to topsoils in the urban, relative to the rural, environment. Although there are several potential point-sources of Pb in the urban environment (e.g. solder, paints, alloys and batteries), diffuse pollution is likely to have been dominated by atmospheric deposition of aerosols from sources such as coal burning and vehicle exhaust emissions. Previous research based on soil Pb isotopic composition from sites in Switzerland identified vehicle exhaust emissions related to the use of leaded petrol and fly-ash from waste incineration as significant contributory sources of Pb in polluted soils (Hansmann & Koppel 2002). The authors of this study observed that in soils subject to significant pollution ($66\,mg\,kg^{-1}$) of anthropogenic Pb, the Pb isotopic composition could not clearly identify pollutant sources due to there being several possiblities. Given that the magnitude of the diffuse load to the urban soils of Sheffield ($73–102\,mg\,kg^{-1}$; differences between urban and rural median and Winsorized mean concentrations, respectively) is comparable to that in the Swiss study, we presume that given the likely plethora of diffuse Pb sources throughout urban Sheffield, particularly over the last 150 years, the same difficulties in defining sources would be observed if Pb isotope data were available.

By contrast, the magnitude of the diffuse pollution components for Ni and Cr in the urban environment were relatively small. The two measures of location demonstrated that diffuse pollution gave Ni concentrations in the urban topsoils that were 25% greater than in the rural environment, and between 11 and 14% higher for Cr.

DISCUSSION

We noted that hotspots of both Cr and Ni were strongly associated with historically disturbed sites, and this was most likely explained by their occurrence in areas of former steel manufacturing. By contrast, Pb was less clearly associated with our disturbed land use categories. This may in part be accounted for by the variety of small-scale historical uses of Pb (e.g. paint, batteries and solder) leading to frequent contaminant hotspots.

This finding contributes to our general understanding of the circumstances in which historical land use maps can help inform (or misinform) our decisions at the desk study stage of the investigation of potentially contaminated land (British Standards Institution 2001). One problem with our reliance on historical land use maps to assess the likely presence or absence of contaminant hotspots is that they cannot account for the unrecorded removal and replacement of topsoil (or soil-dominated material). This may result from natural processes or anthropogenic activities, or the deliberate removal of contaminants from site (waste disposal) across the city.

Although we have identified a substantial historical load of diffuse Pb pollution to urban soil throughout much of Sheffield, we know nothing of its current chemical form. In terms of risk assessment, it would be valuable to

Table 6. Three contingency tabulations for the association of spatial outliers for each metal and the historical occurrence or otherwise of a local source of disturbance.[a]

Historical disturbance	Spatial outlier						
	Cr		Ni		Pb		Row total
	No	Yes	No	Yes	No	Yes	
No	392 (378.9)	21 (34.1)	387 (378.1)	26 (34.8)	392 (391.9)	21 (21.1)	413
Yes	130 (143.1)	26 (12.9)	134 (142.8)	22 (13.2)	148 (148.1)	8 (7.9)	156
Column total	522	47	521	48	540	29	
P-value	7.5e−06		2.7e−03		0.98		

[a]In each cell the first number is a count, the second number is the expected count under a null hypothesis that the row and column categories are independent and so the cell probabilities are determined entirely by the marginal probabilities for the table. The *P*-values reported are for this null hypothesis.

Table 7. Median and Winsorized[a] mean metal concentrations (mg kg^{-1}) in soils developed over Lower Coal Measures in the urban survey (outliers removed) and a rural survey reported in Rawlins *et al.* (2002).

	Cr	Ni	Pb
Rural median ($n = 415$)	85	23	88
Urban median ($n = 316$)	94	29	161
Difference (urban/rural)	11%	26%	83%
Rural Winsorized mean ($n = 415$)	87	24	101
Urban Winsorized mean ($n = 316$)	100	30	203
Difference (urban/rural)	14%	25%	102%

[a]Based on 5th and 95th percentiles.

have some quantitative measure of Pb bioavailability or bioaccessibility, to improve our understanding of Pb exposure to both human (Ruby *et al.* 1999) and ecological (Cook & Hendershot 1996) receptors. In undertaking such measurements, it would be beneficial if the bioavailability of Pb in these urban soils were compared to that of native Pb. The latter could be determined from soils developed over the same parent material in rural areas subjected to minimal historical diffuse pollution. We would then be able to quantify the relative importance of the diffuse and native Pb in terms of current exposure, and establish the environmental significance of the historical diffuse load.

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