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Spatial Heterogeneity of Soil DTPA-extractable Copper as Affected by City Pollution and Land Use in Cultivated Fields of Shenyang, China

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Abstract: Using the methods of soil analysis and geostatistics combined with GIS, this paper determined and mapped the spatial distribution of soil DTPA-extractable copper (Cu) in cultivated fields of Shenyang suburbs of China, aimed to assess the roles of industries and agricultural managements in affecting the spatial heterogeneity of soil Cu in this region. The results showed that the soil DTPA-extractable Cu fitted normal distribution after logarithm transformation and its semivariogram fitted a spherical model. The semivariogram indicated that the spatial dependence of soil DTPA-extractable Cu was moderate, with a spatial dependence range of 4.07 km. Stochastic factors contributed to 26.6% of the spatial variability. The spatial heterogeneity of soil DTPA-extractable Cu was deeply influenced by city pollution and land use. The common sources of soil Cu other than metalworking pollution were manure, wastewater sludge and pesticide over crops. The average concentrations of DTPA-extractable Cu in vegetable garden and in paddy soils were 2.0-2.5 and 1.2-1.8 times as much as in its originated soils, respectively. The areas with a higher concentration of soil DTPA-extractable Cu appeared in Shenyang near suburbs and in the riverside along Hunhe River and the wastewater drainage of Xihe River. The extremely high values in the near suburbs of the city's residential area and in the vicinity of two metalworking factories and a cable manufacturer were a striking feature, indicating the key role of industrial pollution in the spatial heterogeneity of soil DTPA-extractable Cu in the city.

Key words: City pollution . geostatisics . land use . soil copper . spatial heterogeneity

INTRODUCTION

Copper is an essential element for all life and soil is the primary source of Cu in plant, animal and human nutrition, but, high concentration of soil Cu may induce phytotoxicity and affect the biological transformation of other soil nutrients such as P, Zn and Fe [1]. Though Cu is not a cumulative systemic poison, its large dose (>100 mg) is harmful to human beings and might cause central nervous system disorder, failure of hair pigmentation and adverse effects on Fe-metabolism that results in liver damage. Excess Cu may also be deposited in eyes, brain, skin, pancreas and myocardium [2]. Many researches have been investigated the soil and plant factors affecting the dietary supply of both essential and toxic Cu [3]. While mapping the spatial distribution of soil available Cu should contribute to the sustainability of agricultural and livestock production, the improvement in diet quality and a better understanding of the nature and the extents of plant, human and animal Cu deficiencies [4] and be also useful in considering the consequences of applying Cu-containing solid wastes from agriculture and sewage sludge.

Soil is characterized by a high degree of spatial variability, even in intensively managed ecosystems [5-7] and hence, the spatial distribution of soil properties should be monitored for the effective management of farm fields. Of great concern, is to approach the most effective way to analyze and interpret the existing soil survey data to extract useful information for further study [8, 9]. It is possible to map the soil survey data to delineate the areas that would benefit for us, or to identify the areas of particular concern such as nutrients deficiency or environmental pollution. The inherent thing in this process is the assumption that a soil property measured at a given point represents that of the surrounding unsampled neighborhood. The validity of this assumption depends on the spatial variability of the soil property. Geostastistics combined with Geographic Information System (GIS) has been proved to be useful in predicting

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the spatial distribution of soil properties that are very spatially dependent in fields and regions with a limited number of soil samples. The interpolation technique usually used is kriging [10, 11].

In the last decades, human activity continuously increased the level of heavy metals circulating in the environment. Because of their toxicity to terrestrial and aquatic organisms, heavy metals contamination of ecosystems becomes a hotspot of investigations [12]. City pollution and land use were considered as the two of the main contributors to heavy metals enrichments in cultivated soils of city suburbs [13-16]. Researches made by Manta *et al*. [17] in Italy and by Sharma *et al*. [18] in India demonstrated that Cu could be inferred to be the tracers of anthropogenic pollution. Copper was found to accumulate in topsoil and decrease with soil depth [12, 19]. In the vicinity of a copper smelter, the Cu concentration was 7-115 times higher in topsoil than in subsoil [19]. Industries such as tool and cable manufacturing along with the combustion of carbons, oils, wood and certain waste products contribute to the Cu pollution of the environment. The common sources of Cu other than smelters are manure, wastewater sludge and antifungal or antialgal fumigation over crops [20]. Mapping the spatial heterogeneity of soil DTPA-extractable Cu by geostatistics combined with GIS should be helpful in assessing the influences of city pollution and agricultural practice on soil Cu distribution.

In Shenyang suburbs of Northeast China, cultivated fields are under city pollution and different land uses [21]. By the methods of soil analysis and geostatistics combined with GIS, this paper determined and mapped the spatial distribution of soil DTPA-extractable Cu in these fields, aimed to assess the roles of industries and agricultural managements in affecting the spatial heterogeneity of soil Cu in this region.

MATERIALS AND METHODS

Study site: Shenyang is the capital city of Liaoning Province of China, an industrial city named as one of the most polluted cities in the world by the United Nations in early 1980s, which is located on the alluvial plains of the Liaohe and Hunhe Rivers, with 5.68 million populations living in the urban area. It is in the continental temperate monsoon zone, with dry and cold winters and warm and wet summers. The annual mean temperature is 7.0 °C; annual mean precipitation is 700 mm, 70% of which occurs from May to September; and annual non-frost period is around 150 days. Our survey was conducted in four suburb districts of Shenyang (41°28'-42°10' N, 123°1'-123°48' E), with Dongling District in the east, Sujiatun District in the south, Yuhong District in the west and Xinchengzhi District in the north. Their total area is 3299 km^2, of which, 1.63 × 10^5 ha is cultivated field. According to the Chinese Soil Taxonomy [22], the soil is classified as brown soil (*Typic Hapli-Udic Argosols*) in the east, paddy soil (*Stagnic Anthrosols*) and meadow soil (*Typic Hapli-Udic Cambosols*) in the west and vegetable garden soil (*Orthic Anthrosols*) in the near suburbs. The main crops in the near suburb are vegetables and in the far suburbs are corn (*Zea mays* L.) and rice (*Oryza sativa* L.). Figure 1 shows the parent materials, rivers and soil types in the survey region.

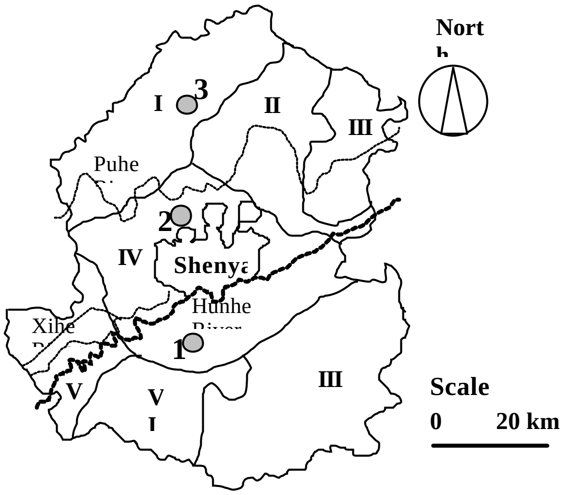


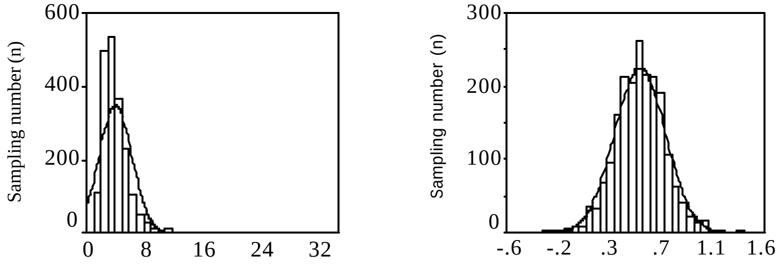
Fig. 1: Parent materials, rivers and soil types of survey region: I. Alluvial deposit of Liaohe River (meadow soil); II. Mesa from slope deposit (brown soil and meadow soil); III. Slope deposit (brown soil); IV. Alluvial deposit of Hunhe River (meadow soil and paddy soil); V. Alluvial deposit between Liaohe and Hunhe Rivers (meadow soil and paddy soil); VI. Flat fields from alluvial deposit (paddy soil and meadow soil). The three gray cycled sites are factories, of which, No. 1 and 2 are metalworking factories and No. 3 is a cable manufacturer

Soil sampling and analysis: 1994 soil samples were collected and all the samples were taken from 0-20 cm surface layer were geo-referenced by latitude and longitude with Global Positioning System (GPS) and each sample represented 70-90 ha of cultivated fields. The samples were air-dried, sieved through a 2 mm nylon screen and split into two aliquots, one for DTPA-extractable Cu determination and the other stored as reference for later investigation.

Table 1: Summary statistics of soil DTPA-extractable Cu (mg kg^{-1}) in Shenyang suburbs

Number (n)	Mean*	Minimum	Maximum	Median	S.D	Skewness	Kurtosis
1994	3.64	0.24	34.28	3.22	1.65	4.70	45.28

*The mean and median were used as the primary estimation of central tendency and the standard deviation (S.D.), variation coefficient (C.V.%) and the maximum and minimum values were used as the estimation of variability



a. DTPA-extractable Cu (mg/kg)

b. After log transformation

Fig. 2: Histogram (bars) and theoretical normal distribution (lines) of soil DTPA-extractable Cu before and after logarithm transformation

Wastewater samples were collected from Xihe River in May and June of 2000 and each time, five samples were taken along the coastwise of Xihe River.

Soil extractable Cu was extracted by DTPA (diethylenetriamine penta-acetic acid) at pH 7.3, while the total Cu both in soil and in wastewater was digested by HF-HNO_3-$HClO_4$. Both DTPA-extractable and total Cu were measured by AAS, with flame or graphite furnace when required [23].

Geostatistics analysis: The spatial variability of DTPA-extractable Cu was characterized by the semivariogram that graphed the variances between spatially separate data points as a function of the distance or lag separating them. A modeled semivariogram was then used in kriging, a weighted linear interpolation with weights determined by semivariogram and variance minimization.

Semivariogram analysis was based on the theory of regional variables and on the assumptions of a) the data must be a continuous distribution and this distribution should be normal for parameter estimation; and b) the semivariance exists and is a unique function of the lag distance independent of location [10, 24].

Experimental semivariogram was obtained from omnidirectional semivariances, $\gamma(h)$, of a set of spatial observations, $z(x_i)$, which was calculated as:

$$\gamma(h)=\frac{1}{2N(h)}\sum_{i=1}^{N(h)}\left[z(x_i)-z(x_i+h)\right]^2 \qquad (1)$$

where $N(h)$ is the number of observations separated by a lag distance h. Semivariance estimations may depend on the parameters as lag interval, lag number and anisotropy, *etc.* and experimental semivariograms are fitted by theoretical models with well known parameters nugget C_0, sill ($C_0 + C$) and range of spatial dependence a.

The traditional statistical parameters and the distribution frequency of DTPA-extractable Cu were calculated by SPSS (Statistics Package for Social Sciences, 10.0, SPSS inc., 1999). In this study, the data exhibited positive skewness and kurtosis statistics indicated that the data of DTPA-extractable Cu were basically fitted normal distribution after log transformation (Table 1 and Fig. 2). The geostatistical parameters and the map for DTPA-extractable Cu were obtained by using grid functions of Arc/Info software.

RESULTS AND DISCUSSION

Summary statistics: The data in Fig. 2 shows that soil DTPA-extractable Cu fitted normal distribution after logarithm transformation. Its main distribution interval was from 2.0 to 6.0 mg kg^{-1}. 16.4% of test samples had a DTPA-extractable Cu concentration less than 2.0 mg kg^{-1} and 10.7% of them had the concentration greater than 6.0 mg kg^{-1}. It can be seen from the results in Table 1 that the mean value was much higher than the median value, indicating the central tendency dominated by the outliers in the distributions. The difference in mean and median values and the high variation coefficient in this study should be attributed to the extremely high values of soil DTPA-extractable Cu in the near suburbs and some point-polluted sites of Shenyang.

Table 2: Parameters for best-fitted semivariogram model of soil DTPA-extractable Cu

Model	Nugget C_0	Sill C_0+C	Nugget/Sill $C_0/(C_0+C)$, (%)	Range a, (km)
Spherical	0.417	1.565	26.60	4.07

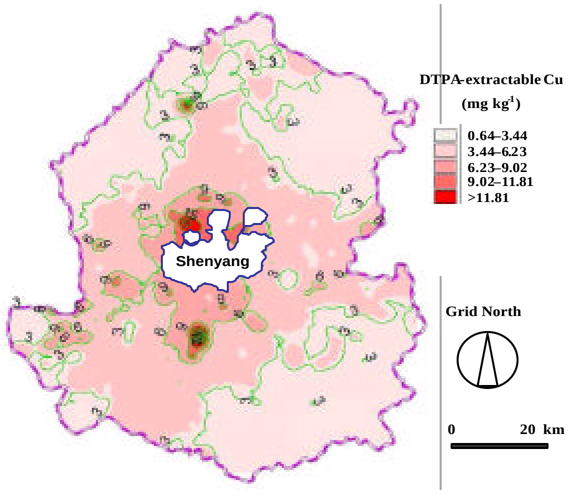


Fig. 3: Map obtained with kriging, showing soil DTPA-extractable Cu distribution in cultivated fields of Shenyang suburbs

Semivariogram analysis and interpolation via kriging: The best-fitted semivariogram model of DTPA-extractable Cu was spherical model and the corresponding parameters were shown in Table 2. Nugget semivariance expressed as the percentage of the total semivariance enables the comparison of the relative size of the nugget effect among soil properties [24]. In this study, the ratio of C_0 to C_0+C was 26.6%, indicating that the soil DTPA-extractable Cu was moderately spatially dependent [25].

In this study, the Range value (*a*) was only 4.07 km, indicating the short distance over which soil DTPA-extractable Cu was spatially dependent and some important ecological processes having deeply affected the heterogeneity of soil DTPA-extractable Cu.

The map in Fig. 3 shows that the northwest, northeast and southeast parts of the study region had a lower average value of soil DTPA-extractable Cu (areas III and I), while the near suburbs around the city and the riversides along the Hunhe River and the wastewater drainage of Xihe River had a higher average value (areas IV, V and VI). The distribution of soil DTPA-extractable Cu in the study area exhibited a strongly heterogeneous characteristic, with its concentration gradients decreased with the distance from the city center and the potential point-polluted sites, which was in line with Murray *et al.* [26] who reported that the Cu detected at elevated concentrations decreased in its concentration with the distance from the urbanized and industrialized center of an urban watershed.

Effects of soil types and land use patterns: It is shown in Fig. 4 that different soil types and land use patterns had a marked influence on the soil DTPA-extractable Cu concentration. Vegetable garden soil, either derived from brown soil or meadow soil, had extremely high values of DTPA-extractable Cu, about twice as much as those in its originated soils. The average values of the two vegetable soils were 5.76 mg kg^{-1} (n=18) and 5.58 mg kg^{-1} (n=134), respectively. Paddy soil had a higher average concentration of DTPA-extractable Cu than its derived soils, *e.g.*, the paddy soil derived from meadow soil had an average concentration of 4.76 mg kg^{-1} (n=579), while its originated meadow soil with sandy, loamy and clay texture had an average concentration of 2.66 mg kg^{-1} (n=33), 3.00 mg kg^{-1} (n=18) and 2.63 mg kg^{-1} (n=399), respectively.

The high value of DTPA-extractable Cu in vegetable garden soil could be attributed to the high application rate of chemical fertilizers and pesticides and the use of manure and city sludge [16]. Pietrzak and McPhail [27] observed that the use of Cu-based fungicides increased the total copper concentration up to 250 mg kg^{-1} in some vineyard soils, compared to the background level of approximately 10 mg kg^{-1}. Murray, *et al.* [26] found that soil Cu concentration was significantly different among different land use categories, with the mean concentration several times greater in industrial areas than background levels. Our results showed that different land use practice did induce the spatial heterogeneity of soil DTPA-extractable Cu in cultivated fields of a certain region.

Effects of city pollution: Table 3 shows that the soil total Cu concentrations in some vegetable fields in near suburbs of Shenyang were 1.34-6.09 times as much as the background value [24] and, although there was no significant correlation between soil total Cu and DTPA-extractable Cu, the latter was much higher in test vegetable garden soils than in the whole suburbs (Table 1 and 3), indicating the effect of anthropogenic pollution.

City pollution such as atmospheric dust, vehicle exhaust and sewage sludge could increase the soil total Cu both in urban and in vicinity rural areas [28], *e.g.*, a case study showed that the soil available Cu in roadside

Table 3: DTPA-extractable and total Cu concentration of vegetable garden soil in near suburbs of Shenyang

Sampling site	DTPA-Cu (mg kg^{-1})	Total Cu (mg kg^{-1})	DTPA-Cu/total Cu (%)	Total Cu/ background value*
Changqing, Wushan Town, Dongling District	7.75	32.81	23.61	1.34
Hunhe, Wushan Town, Dongling District	5.95	83.03	7.17	3.38
Qianzhai, Hunhe Town, Dongling District	6.27	64.81	9.67	2.64
Huoyu, Hunhe Town, Dongling District	11.44	76.65	14.92	3.12
Xiyao, Lingdong Town, Yuhong District	13.07	70.79	18.47	2.88
Fangxi, Lingdong Town, Yuhong District	11.82	47.57	24.85	1.94
Dahan, Beiling Town, Yuhong District	11.71	68.10	17.19	2.77
Liutiaohu, Beiling Town, Yuhong District	10.28	42.21	24.36	1.72
Fugan, Yangshi Town, Yuhong District	5.56	62.53	8.89	2.55
Dapu, Yangshi Town, Yuhong District	11.17	149.50	7.47	6.09

*The background value of soil Cu in Shenyang suburbs was 24.57 mg kg^{-1} according to [24]

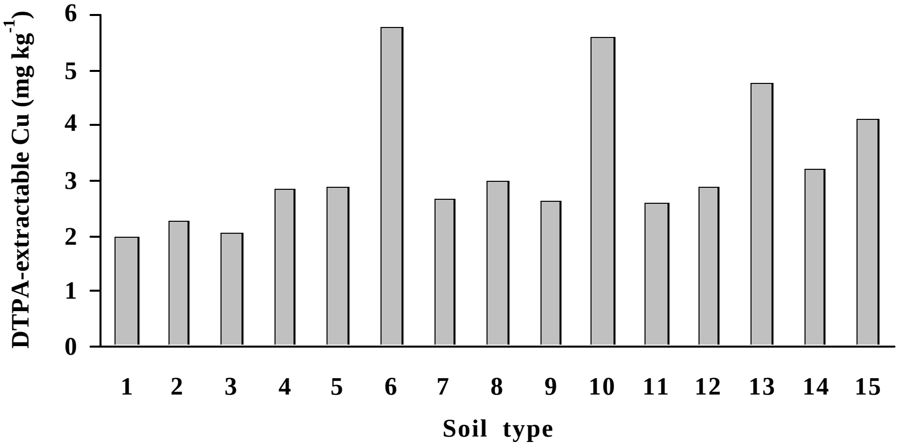


Fig. 4: Average DTPA-extractable Cu concentrations of different soil types. Soil type: 1. Brown soil derived from acidic rocks (n, 27); 2. Brown soil derived from alkaline rocks (n, 15); 3. Brown soil derived from slope deposit (n, 40); 4. Brown soil derived from loess deposit (n, 126); 5. Meadow brown soil (n, 218); 6.Vegetable garden soil derived from brown soil (n, 18); 7. Sandy meadow soil (n, 33); 8. Loamy meadow soil (n, 18); 9. Clay meadow soil (n, 399); 10. Vegetable garden soil derived from meadow soil (n, 134); 11. Carbonate meadow soil (n, 90); 12. Carbonate meadow boggy soil (n, 9); 13. Paddy soil derived from meadow soil (n, 579); 14. Paddy soil derived from carbonate meadow soil (n, 69); 15. Paddy soil derived from brown soil (n, 68)

fields was 1.15 times as much as that in the fields away from roadside [29]. Heavy application of sewage sludge significantly raised the Cu concentrations in soils and in all plant parts over the whole growth season [15]. According to Warman and Cooper [30], the Cu concentrations in fresh chicken manure and compost exceeded its maximum in ordinarily used compost. In a case study carried out by Jackson *et al.* [31], the mean total Cu concentration in poultry litter could be up to 479 mg kg^{-1} and 49% of which was soluble. The average concentrations of total Cu in fresh pig and chicken manure in Liaoning Province of China were 28.4 and 36.1 mg kg^{-1}, respectively [32] and hence, the heavy application of animal wastes was thought to be one of the main contributors to the soil Cu enrichment in the near suburb of big cities [24]. Moreover, heavy application of chemical fertilizers and pesticides on vegetable fields was also thought to be the contributor to soil Cu enrichment [16]. According to Zhang *et al.* [32], the average concentrations of DTPA-extractable Cu in fresh pig and chicken manure in Liaoning Province of China were 5.3 and 8.4 mg kg^{-1}, respectively, suggesting the use of manure, especially of chicken manure could be the cause of high DTPA-extractable Cu concentration in soils of near suburbs. It could be concluded that city pollution was the dominant factor causing the heterogeneity of soil DTPA-extractable Cu in vegetable fields of near suburbs.

Table 4: Total Cu concentration in wastewater of Xihe River (n=10)

Total Cu (mg L^{-1})				
Range	Mean	Variation coefficient (%)	National irrigation standard of China (mg L^{-1})	Pollution index
8.9-15.7	11.9	23.8	≤1.0	11.9

The results in Table 4 indicated that the total Cu concentration in test wastewater of Xihe River during irrigation season was ranged from 8.9 to 15.7 mg L^{1}, with an average of 11.9 mg L^{1}, being 11.9 times as much as China's national irrigation limit. Xihe River is the main wastewater drainage in west Shenyang, which collects the industrial wastewater from dozens of factories in west Shenyang's Tiexi Industrial District and the living sewage from north Shenyang's Huanggu District, with an average daily discharge of 5×10^5 t. This river is also a channel having irrigated the fields in the riverside villages and towns for about forty years. Farmers there often use raw wastewater in irrigation due to the scarcity of fresh water in early summers [33]. In conventional wastewater treatment, considerable portions of heavy metals remain in the treated effluent if no special advanced treatment is carried out and thus, a long-term irrigation with under-treated wastewater might induce the ground water-and soil pollution by heavy metals such as Cu, Zn and Pb [34]. Al-Subu *et al*. [35] reported that irrigation with Cu-containing water had an obvious effect on soil Cu accumulation. The Cu increment in cultivated fields irrigated with wastewater was reported in some big cities of China and most results were in accordance with ours, *e.g*., the soil total Cu in wastewater irrigation area in west Beijing was 1.88 times as much as in its freshwater irrigation area and 2.64 times as much as the background value [36]. It could be concluded that the soil Cu enrichment in test area was due to the long-term irrigation with wastewater and hence, the distribution of soil DTPA-extractable Cu was more heterogeneous, compared with the nearby areas.

The extremely high values of soil DTPA-extractable Cu in the vicinity of two metalworking factories and a cable manufacturer were a striking feature in the map obtained with kriging (Fig. 1 and 3). In the vicinity of Factory No.1, the DTPA-extractable Cu was scaled as 9 mg kg^{-1} by kriging interpolation, with the highest two values of 34.28 mg kg^{-1} and 26.13 mg kg^{-1} around it; and in the vicinity of Factory No.2 and a cable manufacturer, soil DTPA-extractable Cu was also extremely high. The containment of metal factory on soil Cu enrichment has been reported by several literatures, *e.g*., the most important quantitative sources, as smelters, produce pollution as far as 1.3 km, with soil copper concentrations diminishing in an exponential fashion with distance from the smelter [37]. Levels higher than 1000 mg Cu kg^{-1} have been found in soils near a copper and nickel industrial complex in Sudbury, Canada [20].

CONCLUSION

The spatial heterogeneity of soil DTPA-extractable Cu in cultivated fields of Shenyang suburbs was deeply influenced by city pollution, sewage sludge and manure application, land use pattern and crop production. The high levels of soil DTPA-extractable Cu in the near suburb and wastewater irrigation area of Shenyang were basically induced by the city pollution from anthropogenic activities. Irrigation with under-treated wastewater was considered as one of the main sources of soil Cu, which should be forbidden in city suburbs. The map obtained with kriging shows a clear relationship between anthropogenic activities and soil DTPA-extractable Cu concentration gradients, with the peaks corresponding to the areas at the vicinity of two metalworking factories and a cable manufacturer. When recorded in the form of a soil map, the results of such a survey make it possible to identify the unusually polluted areas and also, to provide more information for precise agriculture and environmental control.

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