

Measuring and Zoning of Heavy Metals Pollution in Soil Using GIS for Fields to the South of Tehran

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Abstract

South lands of Tehran are the main source of agricultural productions in which some kinds of vegetables, legumes, cereals and other crops are growing. This research measured and zoned heavy metal soil pollution in 1500 ha of these cultivated fields south of the city of Tehran in Iran. In this study, 128 samples were collected using the systematicrandom method from 64 areas at depths of 0-30 cm and 30-60 cm and the concentrations of cadmium, chromium, nickel, lead and zinc were measured. The parameters of pH, electrical conductivity, and phosphate were also recorded. Zoning maps were developed using the inverse distance weighted method. The results showed that concentrations of heavy metals, with the exception of nickel, were higher at the shallower depth than at the lower depth. The zoning map shows that cadmium, chromium, lead and zinc occurred in greater concentrations in the northern areas and nickel in the southern areas. A comparison of these results with Iranian soil resource pollution standards indicates that the levels of chromium, nickel and zinc exceeded the standards in some parts of the study area.

Key words: Heavy metals, Soil pollution, Cultivated fields, Pollution zoning.

اندازهگیری و پهنهبندی آلودگی فلزاتسنگین در خاک با استفاده از سیستم اطلاعات جغرافیایی اراضی جنوب شهر تهران ملیحه جمالی^{۱۵}، کورس خوشبخت^۲، رضا دیهیمفرد^۲ و رضا مومنی وصالیان[†] ادانشجوی کارشناسی ارشد، گروه آلایندههای محیطزیست، دانشکده کشاورزی و منابع طبیعی، علوم و تحقیقات یزد، دانشگاه آزاد اسلامی، یزد آدانشیار گروه اگرواکولوژی، پژوهشکده علوممحیطی، دانشگاه شهید بهشتی،

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چکیده

این تحقیق با هدف اندازه گیری و پهنه بندی آلودگی فلزات سنگین در خاک زمینهای کشاورزی جنوب شهر تهران به مساحت ۱۵۰۰ هکتار انجام شد. در این مطالعه در ۶۴ مثاورزی جنوب شهر تهران به مساحت ۱۵۰۰ هکتار انجام شد. در این مطالعه در ۶۳ نقطه تعداد ۱۲۸ نمونه خاک به روش سیستماتیک-تصادفی از دو عمق صفر تا ۳۰ و ۳۰-۶۰ سانتی متری برداشت شد و غلظت پنج عنصر کادمیم، کروم، نیکل، سرب و روی اندازه گیری گردید. همچنین پارامترهایی مانند pH و فساعات نیز اندازه گیری شد. نقشههای پهنهبندی با روش وزن دهی عکس فاصله تهیه گردید. نتایج به دست آمده نشان داد که غلظت عناصر سانگین به جز نیکل در عمق اول بیشتری بیشتری بیشتری منطقه غلظت بیشتری دارند. مقایسه نتایج به دست آمده با استانداردهای آلودگی منابع خاک ایران نشان داد که در برخی از نواحی منطقه در دو عمق نمونه برداری شده عناصر کروم، نیکل و که در برخی از نواحی منطقه در دو عمق نمونه برداری شده عناصر کروم، نیکل و روی از میزان استاندارد تخطی داشتند.

کلمات کلیدی: فلزات سـنگین، آلودگی خاک، زمینهای کشــاورزی، پهنهبندی آلودگی.

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1. Introduction

Pollution primarily occurs in response to the exploitation of natural resources and the use of fossil fuels; this trend strongly increases as societies industrialize and modernize [1]. Soil is a component of the environment that is a major recipient of industrial and agricultural waste. These materials enter the soil and become a part of a cycle which affects other forms of life. Knowing the nature of pollutants and their chemical behaviors in soil is requisite to applying scientific methods to remove them [2].

Heavy metals are elements that are common soil pollutants [3]. The sources of these metals are primarily weathered parent material or industrial and agricultural activities [4, 5, 6]. Investigating the concentration and distribution of heavy metals is crucial for monitoring soil pollution and maintaining the quality of the environment. It is necessary to determine a pattern for spatial change to improve management recommendations for preventing and controlling the accumulation and removal of these pollutants [7].

Zoning for soil pollution is one way to investigate environmental pollution. This method, allows the survey of pollution distribution in different areas to decrease pollution. Mitsios et al. [8] studied maps of heavy metal distribution in Athens to determine the usefulness of GIS for mapping and management. They showed that the GIS system has good potential for zoning soil pollution when combined with other methods.

Several studies have investigated the spatial distribution of heavy metal concentrations in the soil in Iran and other countries. Experts from Al Zahra-ACECR (2008) [9] measured and surveyed the level of petroleum hydrocarbon pollutants and heavy metals in the soil and plants around the Tehran Refinery. In this study, 50 samples of soil, water, plants and milk were collected. The high Jaccard index resulting from the high similarity coefficients for nickel, vanadium, chromium and lead with the

soil hydrocarbon distribution helped determine that the concentration of these metals is related to the activities of the Tehran Refinery. The concentration of petroleum hydrocarbons was estimated to be highest in the northern part of the study area.

Khodakaramiet al. (2011) [10] investigated the zoning of chromium, cobalt and nickel concentrations in soils of three sub-watersheds in Hamadan province (Iran) using GIS and geo-statistical techniques. They collected 135 soil samples at depths of 0-20 cm. The results showed that the distribution of chromium, cobalt and nickel conforms to the geological strata but does not comply with cultivation patterns. Fugianget al. (2008) [11] investigated the soil distribution and spatial changes of the heavy metals chromium, copper, mercury, arsenic, lead, and nickel in agricultural fields in China. They found that heavy metal concentrations decrease from cultivated fields to coastal lands; as the soil depth increased, the metal concentrations decreased. The concentration of metals had a negative correlation with soil pH, but no significant relationship with soil organic materials. They also found that the concentration of mercury, nickel and chromium had a strong relationship with land usage, but this did not hold true for arsenic.

Sun et al. (2010) [12] studied the spatial distribution, sources and risk measurement of heavy metals in urban soils in China. They collected 36 samples from six regions (suburbs, industrial areas, parks, public centers, roadsides, residential areas) to measure the concentration of Cu, Zn, Cd and Pb using the method described by Kriging. Their results show that the concentration of heavy metals in the soil was higher than their natural concentrations and industrialized areas had that the highest concentrations of heavy metals.

The present study sampled, measured and zoned heavy metal pollutants and soil chemical indicators in cultivated fields located south of the city of Tehran in the vicinity of the Tehran Refinery.

2. Materials and Methods

2.1. Study area

The study area comprised 1,500 ha of agricultural fields south of the city of Tehran, near the city of Rey. Figure 1 shows the location of the area, which was at 35°29′ to 35°33′ N latitude and 51°25′ to 51°27′ E longitude. The northern part of the study area lies near the wastewater treatment plant for south

Tehran and the western portion lies near the Tehran Oil Refinery. Agriculture is the dominant form of land use in the area; the central and northern parts grow vegetables and the southern parts grow grain (corn, hay, wheat). The difference in elevation from the lowest to the highest points is only 45 m, which represents a relatively gentle slope southward [13].

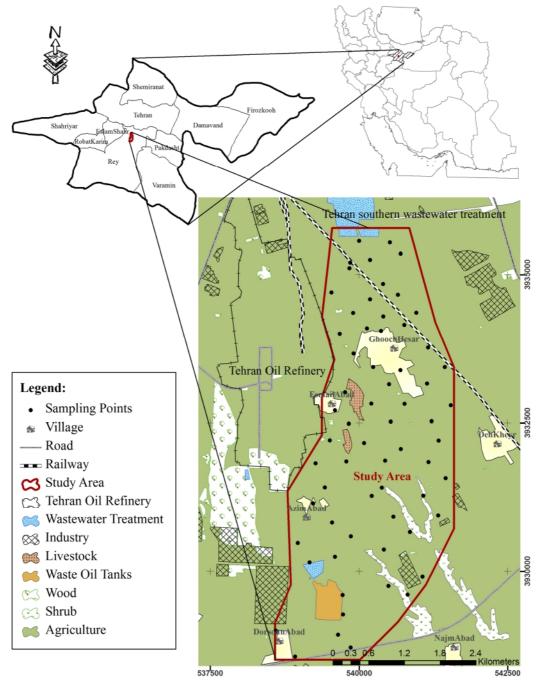


Figure 1. Geographical location of study area, distribution of sampling points and land use

2.2. Sampling

The research was a field study and the region was divided into two zones according to the severity of pollution. The area is systematically divided into 10 ha networks (317×317 m). The center of each network was selected as the sampling point. The sampling density was such that five samples were collected from the first zone and four samples from the second zone where the pollution was lower (Figure 1). In total, 64 points were selected and samples were collected from each point at depths of 0-30 cm and 30-60 cm.

2.3. Chemical analysis

Soil samples were prepared for chemical analysis by being dried at room temperature away from sunlight and then being passed through a 2 mm sieve. Extraction was conducted by the digestion of hydrofluoric, perchloric, nitric, and hydrochloric acids to determine the total concentration of heavy metals (Cd, Cr, Ni, Pb & Zn) in the soil. The instrument used for measurement was an ICP-OES [14]. The Soil and Plant Analysis Laboratory Manual [15] was the basis for analysis of the chemical parameters of the soil. Electrical conductivity (EC) was measured using an EC meter and the pH of the samples was determined from saturated soil using a pH meter. Phosphate was measured using the Olsen method and a spectrophotometer.

2.4. Statistical analysis

Analysis was carried out using Excel and SAS software [16] for statistical testing. The statistical indices for mean, standard deviation and the coefficient of variation were measured using the Spearman and t-test methods to investigate the relationships between parameters.

2.5. Geo-statistical analysis

ArcGIS Software (ver. 9.3) was used to prepare the zoning maps of the elements using the inverse distance weighting (IDW) method. Known points were used for interpolation of unknown places;

higher values were calculated for points closest to the known point and lower values for those that were farther away [17] as:

Equation (1)
$$Z(xi) = \frac{\sum_{i=1}^{n} \frac{1}{d_i^{\alpha}} Z(x)}{\sum_{i=1}^{n} \frac{1}{d_i^{\alpha}}}$$

Where d_i is the distance of each point to the estimated point, $1/d_i^{\alpha}$ is the point value, Z(xi) is the estimated value for each point, Z(x) is the measured value for point x, and α is the square of the inverse distance. The number of estimation points and squared parameters are the factors that affect the precision of estimation for the inverse distance [17].

3. Results and Discussion

3.1. Statistical description of data

Table 1 shows the statistical descriptions of concentrations of heavy metals and chemical parameters of the soil samples from the study area. The mean pH value at the shallow depth was 8.34 and for the lower depth was 8.31, indicating that the soil was alkaline. The mean concentrations of all parameters except nickel were higher for the shallow depth (0-30 cm) than for the lower (30-60 cm), although there was no significant difference for pH, EC, cadmium, chromium and nickel at both depths based on the t-test results (not reported). The results showed a significant difference for concentrations of phosphate, lead and zinc at both depths.

The results of the Spearman correlation test (not reported) between the parameters at both depths show that EC had a positive correlation with pH; this correlation was negative for pH and positive for phosphate. Phosphate, chromium, lead and zinc had positive and significant correlations with each other at both depths; this indicates that, when one parameter increased, the also other increased.

The coefficient of variation for pH was the lowest and for EC was highest at both depths. The variation coefficients for EC and phosphate were >50% at both depths, indicating high variability in the concentrations of these variables across the study area. The coefficient of variation was <50% for heavy metals, indicating the lack of wide variation for these elements.

Table 1. Statistical description and t-test results of case study parameters in soil

| | | ш | EC | P | Cd | Cr | Ni | Pb | Zn |
|----------------------------|--------------------------|-------|---------|---------------------|---------|---------|---------|---------|-------------------------|
| | | pН | (ms/cm) | 1253 0.26 45 0.2 | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | $\langle mg/kg \rangle$ |
| | Average | 8.34 | 2.27 | 1253 | 0.26 | 96 | 45.66 | 32.63 | 120.53 |
| pth n) | Minimum | 7.6 | 0.6 | 45 | 0.2 | 58 | 37 | 16 | 71 |
| First Depth (0-30 cm) | Maximum | 8.7 | 12.8 | 3914 | 0.6 | 168 | 59 | 62 | 246 |
| First Depth (0-30 cm) | Standard error | 0.03 | 0.29 | 107 | 0.01 | 3.81 | 0.69 | 1.68 | 4.88 |
| | Coefficient of Variation | 2.98 | 100.98 | 68.25 | 18.38 | 31.71 | 12.02 | 41.28 | 32.37 |
| | Average | 8.31 | 1.99 | 805.5 | 0.26 | 87.72 | 46.56 | 27.23 | 102.83 |
| epth m) | Minimum | 6 | 0.2 | 61.5 | 0.2 | 56 | 38 | 9 | 61 |
| Second Depth (30-60 cm) | Maximum | 9 | 15.2 | 2879 | 0.5 | 178 | 55 | 63 | 189 |
| econ (30- | Standard error | 0.05 | 0.26 | 78.8 | 0.01 | 3.44 | 0.67 | 1.51 | 3.66 |
| Δ. | Coefficient of Variation | 4.56 | 103.58 | 78.22 | 18.71 | 31.39 | 11.54 | 44.26 | 28.5 |
| t-test | t value | -0.06 | 0/06 | 3/32 | 1/23 | 1/7 | -0/97 | 2/43 | 2/85 |
| | p-value | 0.951 | 0/949 | 0/001* | 0/221 | 0/091 | 0/335 | 0/016* | 0/005* |
| | Freedom degree | 123 | 123 | 126 | 121 | 126 | 126 | 126 | 126 |

*p<0.05

3.2. Comparison of results with soil standards

Table 2 compares the mean and range of concentration of the parameters with soil pollution standards. These standards include those approved by the Environmental Protection Agency of Iran in 2013 and the United States Environmental Protection Agency (USEPA) in 1993. The chromium concentrations

exceeded the standards at both depths for protecting the environment and agricultural lands and the nickel concentrations exceeded the standards of USEPA and protecting the environment at both depths. The zinc concentration for the shallow depth exceeded the standards for protecting the environment.

Table 2. Standard values for heavy metals and means obtained for these elements in the study area

| Depth 1 | | Dept | th 2 | Environmental Pro | | | | | |
|---------|---------|---------|---------|-------------------|--------------------------|-------------------|-------------|-----------|--|
| Average | | Range | Average | Range | Environmental Protection | Agricultural land | Protection | USEPA1993 | |
| | Average | Kange | Avelage | Range | Environmental Frotection | Agriculturar land | Groundwater | | |
| Cd | 0.3 | 0.2-0.6 | 0.3 | 0.2-0.5 | 3.9 | 5 | 20 | 19 | |
| Cr | 96 | 58-168 | 87.7 | 56-178 | 64 | 110 | 3000 | 1500 | |
| Ni | 45.7 | 37-59 | 46.6 | 38-55 | 50 | 110 | 600 | 9 | |
| Pb | 32.6 | 16-62 | 27.2 | 9-63 | 300 | 75 | 300 | 210 | |
| Zn | 1205 | 71-246 | 102.8 | 61-189 | 200 | 500 | 3000 | 1400 | |

3.3. Zoning maps

Figures 2 and 3 show maps of the spatial distributions of heavy metals and other parameters, respectively. The highest concentrations for cadmium (>26.0 mg/kg) were recorded at both depths in the northern region; most part of area had a concentration of 0.24-0.26 mg/kg for cadmium at both depths.

Based on the zoning maps of chromium at both depths, 90% of the area shows high concentrations of >64 mg. At both depths, the highest concentration for chromium (>110 mg) was recorded in the northern

part of the area and chromium concentration decreased in the southern part. The coefficient of variation of chromium concentration was 31.7 at the shallow depth and 31.4 at the lower depth (<50%), which indicates the absence of very high change in the concentration in the study area. Since agriculture is the dominant usage of area land, the application of fertilizers and other chemical materials in these areas has led to an increase in the concentration of heavy metals such as chromium, cobalt, cadmium, arsenic,

lead, copper and zinc [18, 19]. The results of Spearman test confirm this.

Luoet al. [20], Micoet al. [21], Inácioet al. [19], and Ladoet al. [22] determined the source of heavy metals in soil and concluded that the chromium concentration was controlled by the igneous bedrock. Shi et al. [23] claimed that chromium and arsenic showed moderate spatial dependence on human factors in addition to soil parent material. In the present study, the presence of fine sediment in the alluvial plain and major changes in land use mean that human factors have played a significant role in the dramatic increase in the concentration of these elements in the soil.

A comparison of the results with those obtained by Al Zahra University experts in 2008 [9] and by Hani et al. in 2010 [24] showed that chromium contamination in the area has increased and that this increase is higher as the depth increases. One reason for this increase is the lack of degradation and the accumulation of heavy metals in the soil. The Al Zahra University experts reported that oil and heavy metal pollution from Tehran Oil Refinery are being released into the soil of this area. They have demonstrated that the reason for the high chromium content of the soil is related to the high similarity coefficients for oil hydrocarbon distribution in the soil, which is again strongly related to the activities of Tehran Refinery. Hani et al. noted that the concentrations of heavy metals in the soil also increased in response to the use of raw sewage water for irrigation in nearby fields. Irrigation mixed with sewage, and water from wells and aqueducts are all contaminated with different types of oil and is the cause of heavy metal contamination of the soil.

The zoning maps for nickel indicate that the highest concentrations of nickel (>50 mg) occur in the southern part of the area at both depths. The coefficient of variation for nickel concentration is very high, 12 at the shallow depth and 11.5 at the lower depth (< 50%), which indicates the lack of extreme change in concentration in the study area.

Since the study area is agricultural, it is possible that the increase in concentration of heavy metals is the consequence of agricultural activities and the high use of fertilizers [25].

Lin et al. [26] stated that soil pollution by heavy metals (nickel, cadmium, copper, lead, zinc, arsenic and chromium) in Greece has a direct relationship with local and urban-industrial activities. To determine the source of heavy metals in soil, Facchinelliet al. [27], Luoet al. [22], Micoet al. [20] and Ladoet al. [19] concluded that nickel concentrations are controlled by the bedrock. A comparison of the results obtained from Al Zahra University [9] and from Hani et al. [24] shows that chromium contamination in the study area increased, and this increase was greater by depth in one area. One reason for this increase is the failure of heavy metals to degrade or accumulate in soil.

The Al Zahra University [9] study showed that, for groundwater sources, the highest mean values for nickel (8.5 ppb) and lead (10.7 ppb) were in aqueduct samples and the maximum concentration of oil compounds in the aqueduct samples occurred in western Ismail Abad. The large amount of petroleum contaminants in this aqueduct is probably the result of considerable leakage of oil from a pipeline in this area. The zoning maps of the area show the highest concentration of nickel occurred in the southern part of Ismail Abad. The Al Zahra University research, as mentioned, stated that the increase in the nickel concentration in the soil is not surprising and is itself a result of pollution of the aqueduct by oil. Moreover, irrigation of agricultural lands with sewage primarily occurs in nearby fields, as based on wholesale observation and the results from Hani et al. [24].

The results taken of lead analysis of the samples has shown that this element decreased significantly as the depth increased. Lead showed similar behavior at both depths and the northern part of the area had a higher overall concentration of this element. At the shallow depth, half of the study area had concentrations of >30 mg/kg. Zoning maps of the

lower depth show that 30% of the total area has a concentration >30 mg/kg of lead. Furthermore, as the lead concentration decreased, the depth increased; concentrations of >40 mg/kg were recorded in the northern part of the area.

As mentioned, as the depth increased, the zinc content decreased significantly. Although zinc is an important micronutrient for growing plants and crops, but in high concentrations it is toxic for plants, animals and humans [28]. The zoning maps indicate that this element reaches amounts >200 mg in the western part of the study area (Ismail Abad) at the shallow depth. The increase in zinc concentration clearly occurs in the western and northwestern study area at both depths. Lin *et al.* have stated that soil pollution from zinc is highest where there is local and urban-industrial human activity [26].

Since the study area is agricultural, it is possible that the increase in zinc concentration is a result of agricultural activity and the high use of fertilizers. The coefficient of variation for zinc concentration at the first depth is 32.4 and at the second depth is 28.5 (<50%) indicating the absence of great change for this element. A comparison of the results with those obtained by Al Zahra University and from Hani *et al.* shows that zinc pollution in the area has decreased and was higher at the lower depth. Zinc dissolves in slightly acidic soil and can easily enter groundwater from the soil. One way of stabilizing and controlling the zinc in soil is to increase the soil acidity.

The results of pH analysis of samples show that the soil of the study area is alkaline, as are most areas in Iran. The pH decreased as depth increased. Camacho-Tamayo *et al.* investigated the chemical properties of soil in Columbia and concluded that samples of surface soil were more alkaline [29]. Patil*et al.* examined soil samples in India and reported that the surface soil of the area was alkaline [30]. Zoning maps for pH show that most parts of the area have pH values of 8-8.5 in both depths and that the central and northern soils of the study area were more alkaline than the southern soil at both depths.

One reason for high soil pH is the use of untreated sewageto irrigate crops. Long-term sewage irrigation of fields was shown by Rusan*et al.* to increase soil pH [31]. In Jordan, Al-Nakshabandi*et al.* [32] reported the similar results using the same approach.

Zoning maps show that EC increased from north to south in the study area. On maps for the the lower depth, EC sharply but sporadically increased around the villages of Durson Abad and Azim Abad. The maps also show that most of the area has a conductivity of <3 m/S. The results of EC testing in the study area soil showed that as the depth increased, the EC decreased.

One reasons for high soil EC is the use of untreated sewageto irrigate crops. Rusanet al. (2007) studied long-term sewage irrigation of fields and concluded that use of wastewater in irrigation can increase soil EC. Zemaet al. reported that, in Italy, EC increased in soil in areas where sewage also had high EC [33]. In Abarkuh in Iran, Fallahzadeh and Haj-Abbasi [33] demonstrated that EC can decrease in response to proper irrigation methods with safe water. A survey of the effect of treated sewage on soil quality by Xuet al. [34] concluded that treated sewage can increase the water EC over that of well water.

Phosphate zoning maps delineate the areas with the highest phosphate concentrations at 500-2000 mg/kg at the shallow depth and 1500-2000 mg/kg phosphate at the lower depth. The amount of phosphate was greater in the north than in the south. Some northern and central parts had values of >2000 mg/kg, although this was only recorded sporadically. Westfall and Davis (2009) classified the amount of phosphate in corn to be as low at 0-6 mg and very high at >22 [35] the level of phosphate measured was >22 mg in several parts of the study area. This increased level of phosphate increased the danger of this substance entering the surface water.

Phosphate analysis indicated that the amount of soil phosphate decreased significantly as the depth increased, which could be a result of its low mobility. Phosphate compounds are not water-soluble [36], which means that they do not leach and are not transferred into deeper levels of the soil. It was expected that the amount of phosphate would be greater at the surface than in the depths. Ben Musa *et al.* [3376] analyzed soil samples of agricultural fields at different depths and reported large amounts of phosphate at the surface level of the soil and that the concentration decreased as the depth increased.

4. Conclusion

The results show that the concentrations of heavy metals and chemical parameters have increased in the fields south of Tehran as a result of agricultural activity and long-term use of untreated sewage for irrigation. In addition, the Tehran Oil Refinery has contaminated the aqueducts and well water and increased risks to the health of farmers, consumers of their products and to the overall environment.

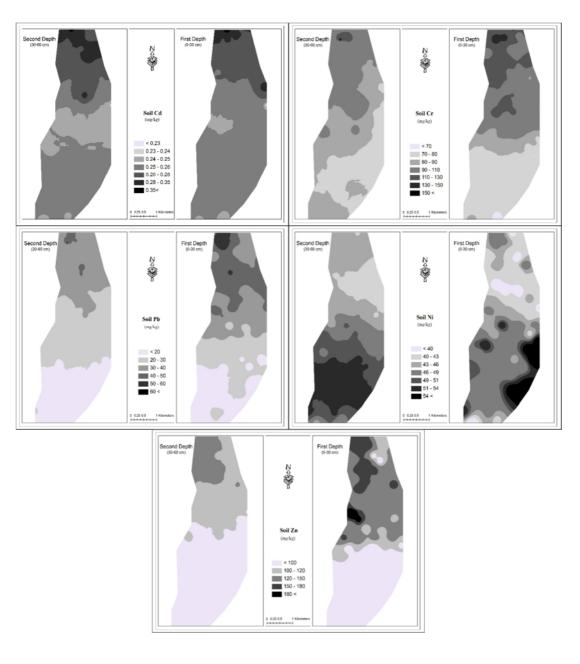


Figure 2. Map of Spatial Distribution of Cd, Cr, Ni, Pb and Zn

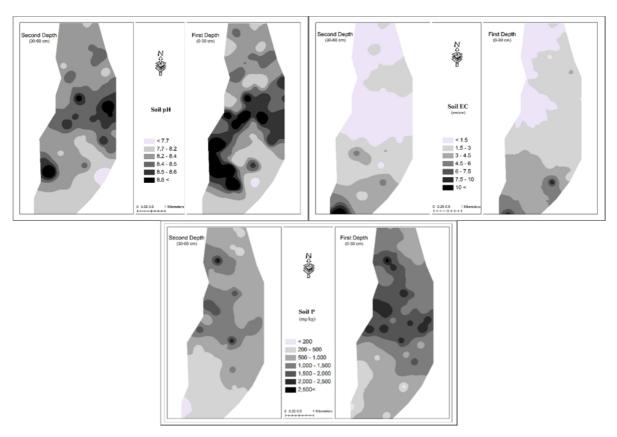


Figure 3. Map of Spatial Distribution of pH, Electrical Conductivity and Phosphate

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