Original scientific paper

Spatial distribution of copper in soils around the Mazraeh mine, north-west of Iran

Farzin Shahbazi[1], Shahin Oustan[2], Amir Khamseh[2], Naser Davatgar[3]

[1]*University of Tabriz, Faculty of Agriculture, Soil Science Dept., 5166616471. Tabriz, Iran, (shahbazi@tabrizu.ac.ir)*
[2]*University of Tabriz, Faculty of Agriculture, Soil Science Dept.*
[3]*Rice Research Institute of Iran.*

abstract
Heavy metal contamination causes serious environmental and health-related problems around the world. Mazraeh copper mine has been established since 1960 in the north-west of Iran. Thus, the garden soils around the mine may be polluted by heavy metals, particularly copper. Sampling was conducted in an area of about 1500 ha, at 30 sites in a way ahead to Ahar river. Obviously, the river is influenced by the heavy metals but not addressed in this research. Total copper concentration was determined not only at the upper 0-10 cm and 10-30 cm of soil vertical section but also at surface accumulated sediments. Statistical and geostatistical analyses were carried out using SPSS and GS+ software, respectively. According to the results obtained the spherical and Gaussian models were two best fitted approaches to interpolate copper concentration for the whole study area because of their higher R^2 and lower *RSS*. The inverse distance weighting (*IDW^2*) method was used to interpolate the concentration of copper in the whole study area due to limited data. The mean copper concentration of the samples was twice compared to the world guideline value (50 mg kg^{-1}). Collapse of tailing dam may be the main reason for copper pollution which was unfortunately occurred due to heavy rainfall on 2009, from 24 May to 27 May inclusive.

Key words: spatial distribution, pollution, Mazraeh copper mine, Iran

Introduction

Paying attention not only to contamination causes and sources but also to monitoring pathways are the main objectives in rational use of soil resources and the environment. Heavy metals diffusion is increased in the last decay due to human activities. Industrial products, mines, transport, and even uncontrolled application of pesticides are the sources to establish heavy metal contamination (Hutton and De Meeus, 2001). Theses metals may be percolated to the soil by sewage and irrigation, or scattered at the space (Salomons, 1995). Disturbance of land, either by natural processes or human activity, invention contaminations exactly in open mines whose don't feel to obey from the rehabilitation laws. Mazraeh copper mine has been established since 1960 in the north-west of Iran. It's capacity is 250 ton per day. Copper concentration process led to create waste treatment which may conduct to ponds. Numerous agricultural area and orchards located in floodplains. The poor stability of soil material not only caused to be collapsed the tailing dam but also residential and industrial wastewater discharged into sewers and are treated to the orchards. In spite of that no possibility to sample in each point, geostatistics help not only to predict the spatial and temporal distribution of a variable but also to create maps (Jiachun et al., 2006). Hooker and Nathanial (2006) created contamination and lead risk maps in England using spherical model and kriging interpolation method. Gotway et al. (1996) have reported the high accuracy of inverse distance weighting (IDW) method for studying nitrogen distribution pattern. This approach is also confirmed by others to observe the spatial distribution of heavy metals in floodplain soils around the Gule River in the Netherlands (Leenaers et al., 2003). Therefore, *IDW^2* method was solely used to interpolate the concentration of copper in the whole study area due to limited data in this research. Shahbazi and De la Rosa (2009) have reported that climate change is likely to cause severe water stress in the 21st century as water management will be increasingly important. The climate change will cause the conversion of the best agricultural lands into the marginal ones as well as bioclimatic deficiency is out of monitoring while mining and manufacturing development must be perfectly controlled.

Material and methods

This study was performed in an area extension about 1500 ha located at Mazraeh region of east Azarbaijan, Iran, between 47°02´47″ to 47°03´46″ east longitude and 38°31´56″ to 38°37´12″ north latitude. There are different kinds of parent materials including limestone, old alluvium, and volcano-sedimentary rocks.

Sampling and initial analysis

Sampling was conducted at 30 sites to determine total copper concentration not only at the upper 0-10 cm and 10-30 cm of soil vertical section but also at surface accumulated sediments. Global Positioning System was used to provide the geographical coordination of sample points. Soil samples were air dried and was then sieved via mesh 2 mm. Custom physical and chemical analyses such as texture (Gee and Bauder, 1986), EC (Bower and Wilcox, 1965) pH (McLean, 1982), CEC (Bower, 1952), OC (Nelson and Sommers, 1982), CCE (Soil Conservation Service, 1992), were performed.

Copper concentrations in both soil samples and surface sediments were measured using Aqua-Regia method (Chen and Ma, 2001). Copper Pollution Index (PI) is defined as the ratio of copper concentration at the sample to the background (Fagbote and Olanipekun, 2010). It is divided to 4 classes (<1, low; 1-3, medium; 3-6, high; and >6, very high).

Statistical and geostatistical analysis

Statistical analysis was performed using the Statistical Package for Social Science (version 16.0; SPSS Inc., Chicago, IL, USA) program. Descriptive statistics for selected properties of soils and sediment were calculated.

The geostatistical analysis was performed with the GS+ package program for the environmental sciences, version 5.1. Data models require nugget (C_0), sill (C_0+C), range of parameter (A_0) whose are derived parameters excessive R^2 and reduced sums of squares (*RSS*) to decide and to present the appropriate model. The nugget effect, representing the undetectable experimental error and field variation within the minimum sampling space, was quite large relative to the sill, which represents total spatial variations. In the next step, models fitted according to hypothetical of IDW which assumes that each measured point has a local influence that diminishes with distance. Interpolation with IDW was being selected by the Geostatistical Analyst Wizard tool to digitize and mapping soil pollution. Although Inverse distance weighting and kriging are the two most widely employed interpolation tools, IDW was used due to limited number of data points while Kriging works well when data is abundant (>50 data points) and the collection points are well distributed across the study area (McKenzie et al., 2008). IDW is relatively fast and easy to compute, and straightforward to interpret. It's general idea is based on the assumption that the attribute value of an unsampled point is the weighted average of known values within the neighborhood, and the weights are inversely related to the distances between the prediction location and the sampled locations.

Geographical information system (GIS)

A file of data transferred to a congenial program (e.g. ArcGIS 9.3) that is popular package with excellent graphics. The main application in ArcGIS, ArcMap, is being used for all mapping and editing tasks in the present study. Interpolation with IDW was being selected by the Geostatistical Analyst Wizard. In digital soil mapping (DSM) the soil variables such as soil biological indices are increasingly mapped using regression-kriging to produce a typical map based on geostatistics (Shahbazi et al., 2013). Area extension of each mapping unit is then calculated to find the spatial variability of copper concentration in the field scale.

Results and discussion

Statistical descriptive analyses are summarized in Table 1. All parameters except organic carbon have normal distribution.

Table 1. Descriptive statistics for selected properties of soils at two depths (n=30)

Soil Properties	Depth (cm)	Mean	Min.	Max.	S_d	CV (%)	Skewness	Kurtosis
Sand (%)	0-10	53.8	22.1	83.5	12.3	22.8	0.1	1
	10-30	57.7	40.6	80.6	11.2	19.4	0.3	1
Silt (%)	0-10	32.4	8.7	50.8	9	27.7	0.3	0.6
	10-30	28.7	13.9	47.9	9	31.2	03	0.4
Clay (%)	0-10	13.8	6	27.1	5.6	40.4	0.6	0.5
	10-30	13.6	5.5	24.7	5.9	43.3	0.5	1.1
CCE (%)	0-10	5.3	0	13.8	3.4	64.2	0.5	0.15
	10-30	4.5	0	10.1	2.57	57.1	0.1	0.3
pH	0-10	8.1	8.4	7.7	0.2	2	0.5	0.3
	10-30	8.3	7.6	8.6	0.2	2.4	1.4	2.6
EC (dS m^{-1})	0-10	1.09	0.37	2.67	0.5	42.2	1.4	3.4
	10-30	0.9	0.5	2.1	0.4	43.9	1.8	3.3
OC (%)	0-10	1.92	0	13.16	2.3	118.7	4.3	21.9
	10-30	1.4	0	12.3	2.1	149.3	4.9	25.8
CEC ($cmol_c$ kg^{-1})	0-10	26	15.8	54.8	6.9	26.4	2.5	10.1
	10-30	23.2	12.7	36.7	5.6	30.7	0.3	0.02

Sd, standard deviation; CV, coefficient of variations; CCE, carbonate calcium equivalent; pH, soil reaction; EC, electrical conductivity; OC, organic carbon; CEC, cation exchange capacity.

Analyses of copper concentration at soils and sediments are fully presented in Table 2. Frequency distributions of all measured parameters are normal. The results revealed that the mean of copper concentration at upper 10 cm, 10-30 cm and sediments were 105.3 mg kg^{-1}, 86.4 mg kg^{-1} and 1116 mg kg^{-1}, respectively. Therefore, according to world guideline value (Kabata-Pendias and Pendias, 1994), 50 mg kg^{-1}, the mean copper concentration of the study soils was approximately twice. Decreasing of standard deviation related to soil depths show that soils have been polluted from surface to subsurface. There is significant difference between copper concentrations at two sampled depths where the same observations had been previously resulted (Fageria et al., 2002; Wenqing et al., 2005).

Table 2. Point by point copper concentration in soils and sediments

Sample No.	Longitude (m)	Latitude (m)	Copper concentration (mg kg^{-1})		
			0-10 cm	10-30 cm	sediment
1	679598	4276699	98.1	87.95	1698.45
2	679590	4276677	257.88	154.31	1854.8
3	679238	4276080	123.98	101.49	1659.02
4	679080	4275710	101.82	87.23	1566.05
5	679020	4275687	94.29	81.75	1248.83
6	678486	4574631	87.18	71.17	1351.68
7	678240	4273948	120.89	93.29	1116.94
8	678318	4273550	72.58	74.54	982.7
9	678248	4273193	87.13	62.42	1182
10	678380	4272730	119.19	100.62	973.06
11	678441	4272332	88.31	59.23	1148.83
12	678497	4272188	155.04	82.66	1006.16
13	678563	4271946	121.41	99.84	1140.7
14	678558	4271790	102.73	81.43	1031.95
15	678679	4271437	99.72	89.3	1033.65
16	678778	4270918	73.49	76.18	792.33
17	678606	4270814	90.07	71.25	964.76
18	678435	4270667	72.93	83.72	1057.52
19	678230	4270461	74.77	69	714.78
20	678211	4270172	99.92	90.93	877.13
21	678156	4269882	86.87	64.42	1034.59
22	678285	4269552	80.97	74.95	971.09
23	678265	4269307	94.88	88.56	1229.62
24	678192	4270594	102	109.25	1221.27
25	678334	4268143	121.2	80.98	998.36
26	678330	4267954	114.89	87.68	444.4
27	678381	4267200	92.46	74.78	1102.8
28	678340	4267477	111.09	98.7	973.9
29	678269	4268719	92.54	85.81	986.48
30	678248	4266931	120.71	108.84	1118.01

There is no correlation between carbonate calcium equivalent and total copper concentration on contrary there is positive correlation between total concentration copper and EC, OC, silt and clay as Chen et al. (2009) had been reported copper concentration and its distribution relation with silt and clay contents. The results are also revealed that the pollutant index in the samples near to the source of dam is high and very high as well as it is briefly diminished at surface 0-10 cm of land. This result equal to the previous research work outputs (Ahiamadjie, 2011).

There are some mines in Morocco such as Atlas and also in China such as Dabaoshan where the copper concentration in Dabaoshan mine is 1486 mg kg^{-1} (Zhou et al., 2007) while in Mazraeh mine is 5870 mg kg^{-1}. The orders of representative heavy metals are following as:

Fe>Ca>Cu>Na>K>Mg>Mn>Zn>Ni>As>Pb>Co>Cd

The mean value of PI in blank soils is about 2 but in 15 surface (0-10 cm) and subsurface soils (10-30 cm) are 4.36 and 3.36 respectively. It means that pollution is being led from vertical section of the soils as well as it more appears near the tailing dam source. Statistical analyses revealed that PI has significant differences ($p<5$) at two depths (Figure 1).

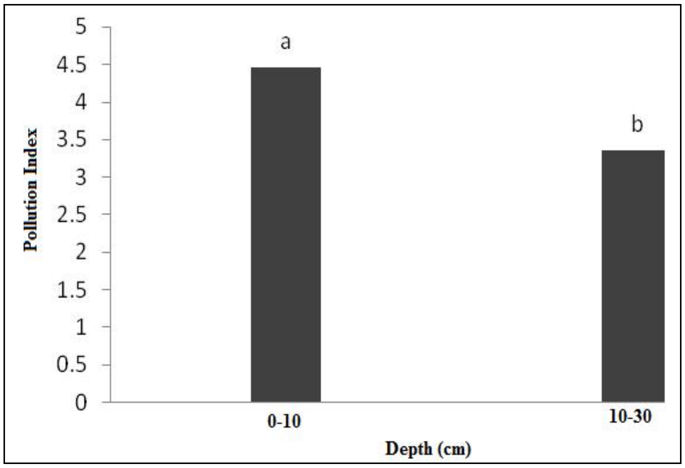

Figure 1. Depth effect on pollution index in the soils

According to the best fitted models (highly R^2 and low RSS) resulted by geostatistical analyses (Table 3 only represents for the upper 10 cm of the soil) showed that the ratio of nugget variance to sill was lower for the sediments compared to the soils. Additionally, this ratio for the upper 10 cm of the soils was lower than the next 20 cm, resulted in more spatial dependence of copper distribution in sediments and upper 10 cm than to the next 20 cm.

Table 3. The best fitted models to variograms of studied indices (0-10 cm)

Indices	Model	C0	C0+C	A0 (m)	C0/C0+C (%)	R^2 (%)	RSS
Sand	Spherical	66.85	139.32	5049	48	99.9	0.866
Silt	Spherical	69.1	255.7	4200	27	74.3	2.29
Clay	Exponential	0.01	28.01	1154	0	94.2	11.8
CCE	Guassian	4.8	6.8	2300	70.6	70.8	0.609
pH	Spherical	0.0118	0.2336	11670	5.1	98.4	0.00001
EC	Spherical	0.071	0.744	12180	9.5	95.3	0.0007
OC	Guassian	0.0093	0.0956	13140	11.8	97	0.000006
CEC	Guassian	16.1	63.2	7070	25.5	95.5	15.3
Cu[a]	Spherical	0.018	0.06	6500	30	84.5	0.0001

a, total copper concentration

Figure 2 illustrates variogram of fitted models for copper concentration estimation in the study area at two soil depths and sediments too. The Gaussian model is distinguished as the best fitted model for sediment estimation (R^2=96). ME, RMSEn, S_d and S_e of IDW approach for estimating of copper concentration at two depths are following as (0-10 cm: 1.04, 0.39, 33.94, 6.2; 10-30 cm: -0.82, 0.2, 18.6, 3.39). Created georeferenced continuous thematic maps of copper concentration are presented in Figure 3.

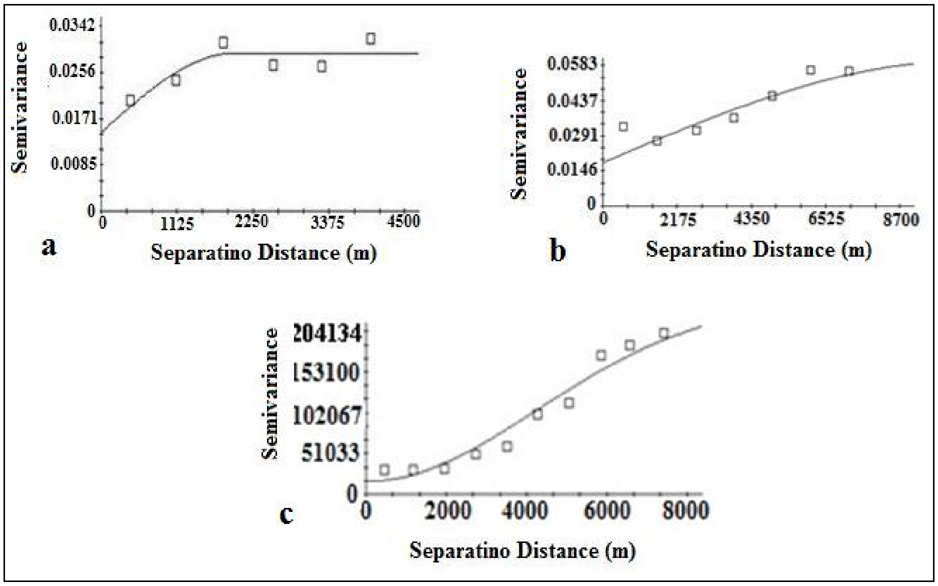

Figure 2. Isotropic model variogram fitted to copper concentration. (a) Surface soils. (b) Subsurface soils. (c) Sediment.

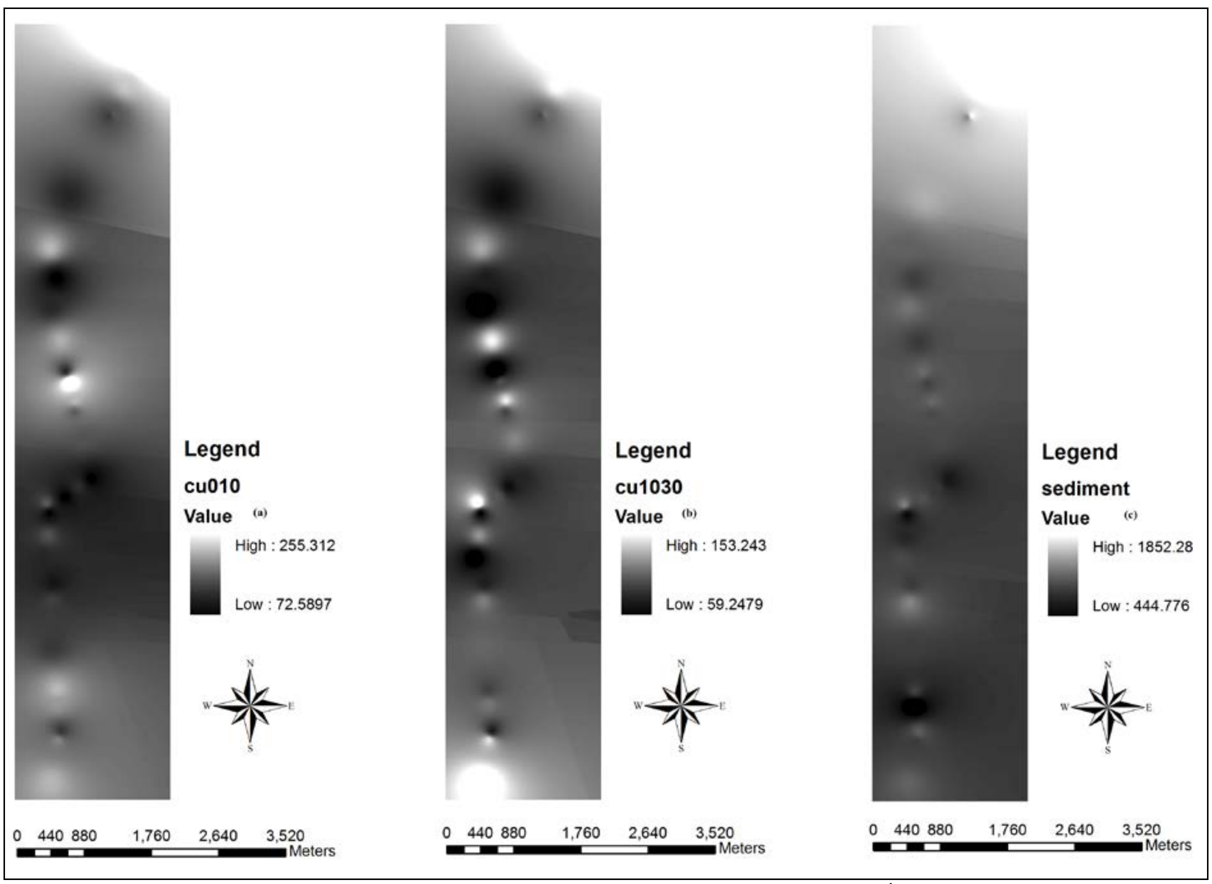

Figure 3. Raster stretching values of copper concentration /mg kg^{-1}. (a) Surface soils. (b) Subsurface soils. (c) Sediment.

Conclusions

Pollution index presents that the soils around the Mazraeh mine have been polluted.

The collapse of tailing dam is the main reason for copper pollution which was unfortunately occurred due to heavy rainfall on 2009, from 24 May to 27 May inclusive.

Copper fractionation has been studied during this research work but it is not fully addressed in this article.

IDW approach for prediction of cooper concentration at subsurface soils is over-estimation while at surface soils is under-estimation. Spherical and Guassian models are two best fitted modes. It is also understood the copper concentration decreases by increasing distances from the source. There is moderate to high spatial dependence for copper distribution in the study area.

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