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Heavymetal contamination and spatial distribution of agricultural soil and vegetables in a village of a mining area in Guangxi, China

Zhang Xinying*, Lin Qing, Jin Mei, Wu Yufeng, Zeng Benhao
Key Laboratory of Beibu Gulf Environment Change and Resources Utilization
(Guangxi Teachers Education University), 530001, Nanning, Guangxi (CHINA)
E-mail : zxytld@sina.com

ABSTRACT

A administrative village including 13 natural villages in a mining area was selected as the study area in Guangxi. 89 vegetable samples and correspondingly 89 arable soil samples were collected. As, Cd, Pb, Zn and Cu, etc. pollutants in all the samples were detected. The results show that: the rate of As, Pb, Cd, Zn and Cu in vegetable samples exceeded the standard level are 100%, 92%, 85%, 62% and 23%, respectively. Heavy metals in almost all soil samples exceed the agricultural soil quality evaluation criteria. The main pollutants are As, Pb and Cd. This implies that local mining activities have seriously affected the local rural environment. The local rural land is unsuitable for cultivation of food crops, or health risks may conduct to the inhabitants. Geostatistical method was used to analyze the spatial distribution of various pollutants. The results show that the northwest village is polluted the most heavily, which is consistent with the distribution of pollution sources.

KEYWORDS

Northwest Guangxi; Agricultural products; Heavymetal contamination; Geostatistics; Spatial distribution.



INTRODUCTION

Many mine industries are located in rural villages. The non-ferrous metal mining activities may bring heavymetal contamination to the surrounding environment, such as air, water, soil, as well as farmland and crops. Guangxi is located in the south of China. A admnitive village in the northwest of Guangxi was studied in this paper. The land area of the village is approximately 53.39 square kilometers. It has 13 natural villages and a total population of 1,300 people. There are more than thirty industries with heavymetal discharge in it, which are mainly mining industries with seven smelters. The mines include tin, antimony, zinc, indium, lead, etc. This paper analyzes the situation in rural areas affected by heavy metal contamination, and geostatistics method was used to analyze the spatial distribution so that we can learn that how the mining activities affect the sorrounding environment. The maps of all five heavy metals showed a strong gradient of contamination around the mining sites activating in the area. The results of this study provide insight into identification of the extent and spatial variability of As, Cd, Pb, Zn and Cu pollution in the village.

MATERIAL AND METHOD

Sampling

The vegetable gardens distributed in 13 natural villages which are named from number 1 to 13 (Figure 1). The mine industries distribute mainly in the two circles. In August, 2011, 89 vegetables samples and 89 corresponding rhizosphere soil samples were collected from vegetable gardens and. Each soil sample, consisting of 3-5 subsamples (about 200g each), was collected at depths between 0-20cm, which were intended to be representative of the plough depth. All soil samples were collected using a hand auger and then stored in polyethylene bags.

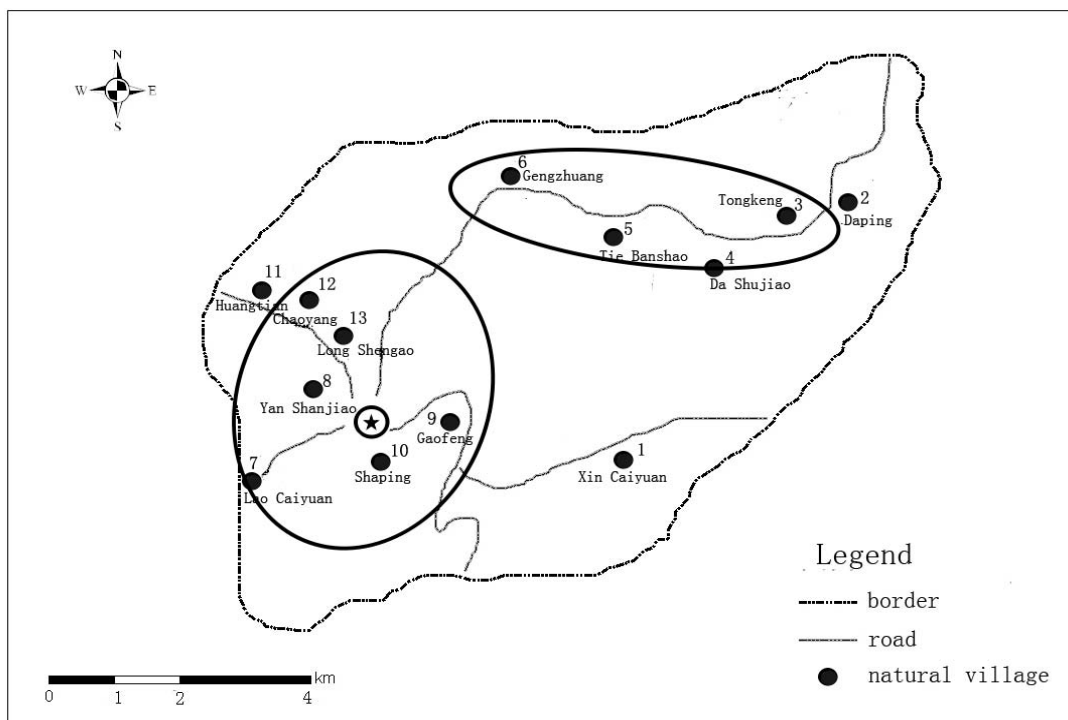


Figure 1

The edible portions of 89 most commonly grown vegetables were sampled. The vegetables sampled included *Lactuca sativa* L., *Brassicachinensis* L., *Brassica rapa* L. *Chinensis* Group., *Apium graveolens* L., *Lactuca sativa* Linn. var. *ramosa* Hort., *Cichorium endivia* L., *Brassica juncea*, *Ipomoea aquatica* Forsk., *Ipomoea atatas* (L.) Lam., *Allium tuberosum* Rottl.ex spr., *Coriandrum sativum* L.,

Allium fistulosum L. Var.giganteum Makino., Capsicum annum L., Solanum melongena L.melongena L., Dolichos lablab L., Phaseolus vulgaris L., Glycine max(L.) Merr., Ipomoea batatas [L.] Lam.[Convolvulus batatas L., Allium sativum L., Zingiber officinale Ros., etc. GPS was used for the sampling point positioning. The sample number from every natural village was listed in TABLE 1.

TABLE 1 : Sample number from every natural village

Code of the village	Total vegetables	Soil samples
1	4	4
2	9	9
3	9	9
4	12	12
5	9	9
6	20	20
7	5	5
8	5	5
9	5	5
10	7	7
11	2	2
12	1	1
13	1	1
Total	89	89

Processing and monitoring of the samples

The collected soil samples were air-dried at 20°C for 3 days and sieved through a 2 mm-polyethylene sieve to remove large debris, stones and pebbles. They were then ground in an agate grinder until fine particles (<200µm) were obtained. The prepared soil samples were analyzed for their metal concentrations using an acid digestion method (Li et al,1993). All glass and plastic ware was soaked in 10% nitric acid overnight and rinsed thoroughly with deionized water before use. The vegetables were thoroughly washed with tap water, in a fashion typical of that used by women the village prior to cooking. They were then rinsed with deionized water. The clean vegetable samples were then air-dried, weighed and placed in an oven at 60°C for 48–72 hours, depending on the sample size. Dried samples were weighed and mechanically ground and sieved (0.4 mm) before chemical analysis.

A series of 0.250 g portions of the soil samples were placed into Pyrex test tubes. 10.0 ml high-purity concentrated nitric acid and 2.5 ml high-purity concentrated perchloric acid were added. A series of 0.200 g portions of vegetative material was placed into Pyrex test tubes. 8.0 ml high-purity concentrated nitric acid and 2.0 ml high-purity concentrated perchloric acid were added. All of the samples were then gently shaken using a vortex mixer and heated progressively to 190°C in an aluminum heating block for 24 h to near dryness. After the test tubes were cool, 12.0 ml of diluted (5% (v/v)) high-purity HNO₃ were added. The solutions were thoroughly mixed using a vortex mixer and then heated at 70°C for 1 h. After cooling, the solutions were decanted into acid-cleaned polyethylene tubes for storage. Solutions were later centrifuged at 3500 rpm for 10 min, and then portions of the supernate were removed for measurement using a Themofisher iCAP 6300 Inductively Coupled Plasma (ICP-OES).

For quality control, reagent blanks, replicates, soil international standard reference materials (NIST 2709) and plant standard reference materials (NIST1515) were incorporated in the analysis to detect any contamination in the analytical materials and to assess precision and bias in the method. The analytical results showed no sign of contamination in the materials used and that the precision and bias of the analytical method were generally <10%. The recovery rates for some major elements in the international standard reference material were around 85~05%.

Inverse distance weighting method

(IDW) is a type of deterministic method for multivariate interpolation with a known scattered set of points. The assigned values to unknown points are calculated with a weighted average of the values available at the known points.

In order to study the spatial distribution, IDW was used.

Assessment method

The single factor index method

The calculation formula is as follows:

$$P_i = C_i/S_i$$

In this formula, P_i represents the environment quality index of the pollutant i in soil or vegetables; C_i is the on-the-spot survey concentration of the pollutant i ; and S_i denotes on behalf of the assessment standard of the pollutant i . If $P_i \leq 0.7$, the heavy metals content stands under the warning limit; if $0.7 < P_i \leq 1$, the heavy metals content does not exceed the environment quality standard, the farm crops develop normally and have no harm to human health, but heavy metals pollution has already been in the warning condition; and if $P_i > 1$, the heavy metals content goes beyond the environment quality standard, which would influence the growth of farm crops, and affect human health. If $1 < P_i \leq 2$, light pollution; $2 < P_i \leq 3$, moderate pollution; and $P_i \geq 3$, heavy pollution.

The synthetic pollution index method.

N. L. Nemerow's synthetic pollution index method was adopted to calculate synthetic pollution index of soil and vegetable heavy metals and evaluate the pollution degree of them. The formula is expressed below:

$$P = \sqrt{[(\bar{p}_i)^2 + [\max(p_i)]^2] / 2}$$

where P stands for the synthetic pollution index; \bar{p}_i represents the mean of various pollutant indices; and the $\max(p_i)$ is the maximum pollution index of single-factor pollutant. The detailed evaluation standards are the same as the single factor index method.

RESULTS AND DISCUSSION

Concentration of heavy metals in soil samples

89 soil samples were collected, As, Cd, Pb, Zn, Cu were analyzed. Farmland environmental quality evaluation standards for edible agricultural products (HJ 332-2006) was used to calculate the synthetic pollution index.

From TABLE 2, we can observe that As concentration varies from 0.08 to 1578 mg.kg⁻¹ in the soil, Cd varies from 1.62 to 271.8 mg.kg⁻¹, Pb varies from 90.9 to 1318 mg.kg⁻¹, Zn varies from 104 to 2130 mg.kg⁻¹, Cu varies from 18.6 to 85.6mg.kg⁻¹. All the pollutants varies greatly and show their heterogeneity which implies that all the pollutants come from human activities. Cd and Pb in all soil samples are over the standard level. As is over the standard level in 84.6% of the soil samples, Zn is over standard level in 69.2% of the samples, Cu is over standard level in 53.9% of the samples. All the synthetic pollution index are over 3 and show heavy contamination. The maximum ratio exceeding the standard value is 52.6, 906.0, 26.4, 10.7, 1.71 for As, Cd, Pb, Zn, Cu, respectively.

Concentration of heavymetals in vegetable samples

89 vegetable samples were collected, As, Cd, Pb, Zn, Cu were also analyzed for all samples. The results were listed in TABLE 3. Limits of eight elements in cereals, legume, tubers and its products (NY 861-2004) was used to calculate the pollution index.

TABLE 2 : avymetal content in agricultural soil; Unit: mg.kg⁻¹

Sample site	As	Cd	Pb	Zn	Cu	synthetic pollution index
1	0.08	8.14	580	719	63.9	20.1
2	31.6	1.62	90.9	104	27.4	7.96
3	120	35.6	632.8	518	61.0	86.8
4	111	35.9	140	158	28.1	86.4
5	1578	18.9	1284	1582	85.6	59.8
6	392	6.43	374	504	29.4	18.6
7	500	4.94	276	406	34.9	15.2
8	64.2	2.96	184	171	36.5	10.3
9	220	8.66	454	941	50.8	24.9
10	572	10.1	860	1079	74.4	26.5
11	49.0	1.84	97.6	126	18.6	4.59
12	277	5.74	324	528	22.0	14.5
13	3.91	272	1319	2130	63.4	654
Standard	30	0.30	50	200	50	
Exceeding standard ratio	84.6%	100%	100%	69.2%	53.9%	
Max. ratio¹	52.6	906.0	26.4	10.7	1.71	

1 Maximum exceeding the standard ratio

TABLE 3 : Heavy metals in vegetable samples Unit: mg.kg⁻¹

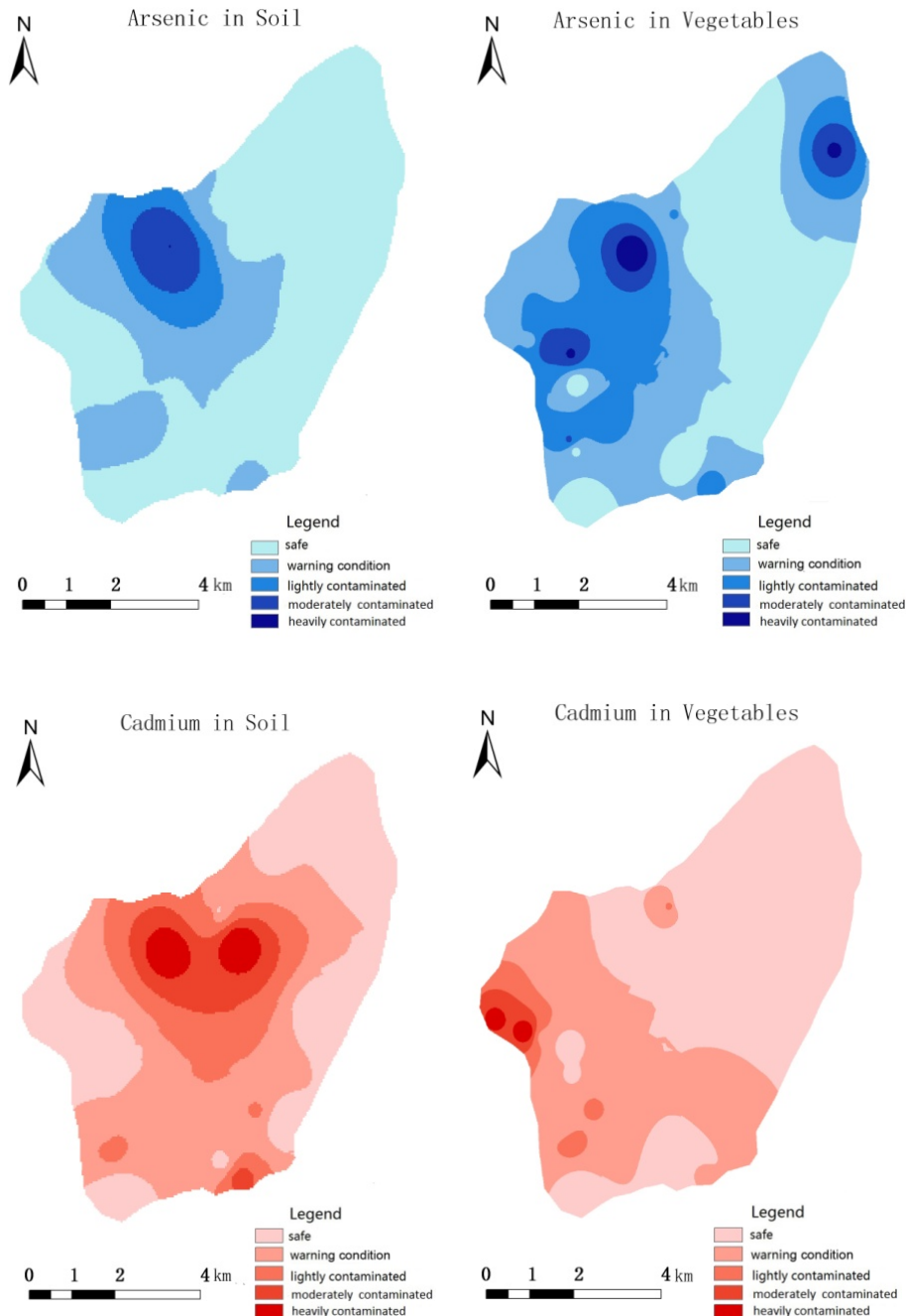
Sample site	As	Cd	Pb	Zn	Cu	synthetic pollution index
1	1.17	0.86	3.21	6.57	6.91	12.1
2	0.21	0.00	0.14	17.2	0.31	1.33
3	6.98	0.37	1.69	26.0	6.45	36.7
4	0.70	1.08	8.27	89.8	5.23	22.7
5	5.72	2.68	12.6	122	11.2	51.5
6	3.42	1.56	4.55	107	9.24	22.9
7	4.57	0.88	2.45	64.4	0.14	22.8
8	1.00	1.69	1.88	86.9	0.14	9.45
9	1.16	0.42	2.76	42.2	0.10	10.9
10	10.5	2.21	8.39	112	0.16	57.0
11	3.20	3.90	5.43	7.93	6.90	54.5
12	7.59	1.35	10.0	10.8	10.9	112
13	8.16	0.16	11.8	12.4	11.2	129
Standard	0.15	0.20	0.20	20.00	10.00	
Exceeding standard ratio	100%	85%	92%	62%	23%	
Max. ratio	69.9	19.5	63.2	6.13	1.12	

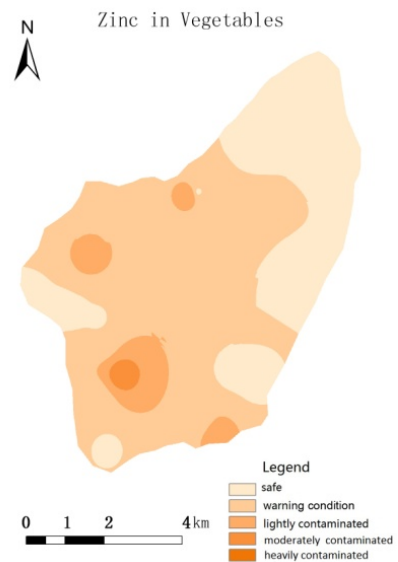
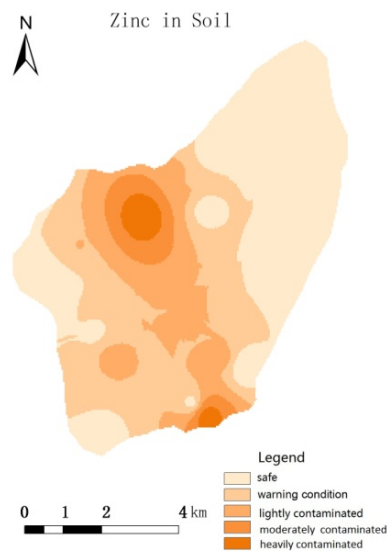
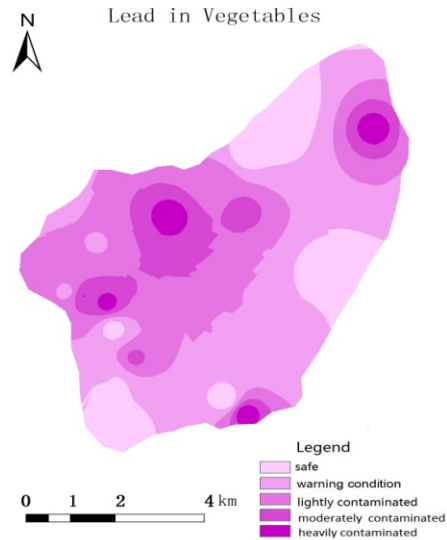
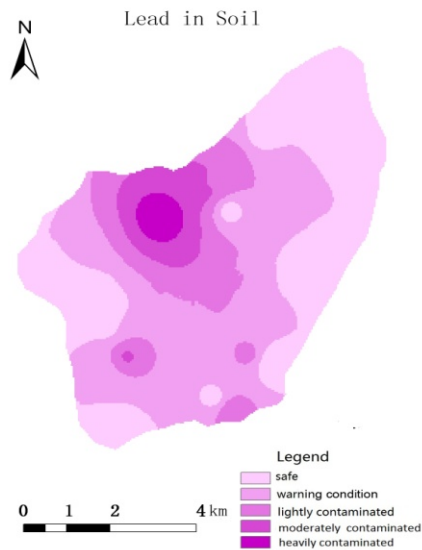
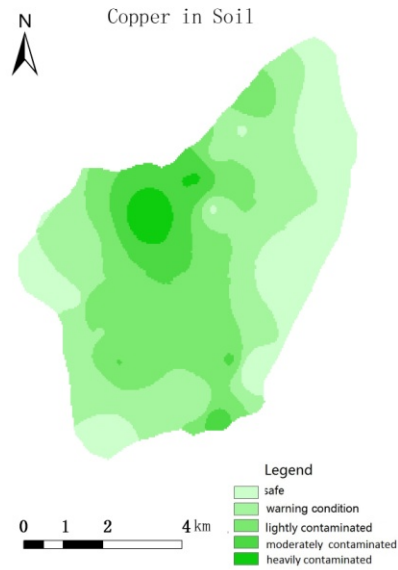
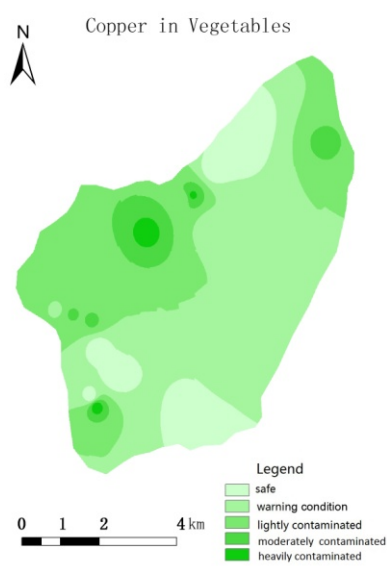
As concentration varies from 0.21 to 10.49 mg.kg⁻¹ in the soil, Cd varies from 0 to 3.90 mg.kg⁻¹, Pb varies from 0.14 to 12.6 mg.kg⁻¹, Zn varies from 6.57 to 122 mg.kg⁻¹, Cu varies from 0.10 to 11.2mg.kg⁻¹. Exceeding standard ratio of As, Cd, Pb, Zn, Cu are 100%, 85%, 92%, 62%, 23%, respectively. The maximum ratio exceeding the standard value are 52.6, 906.0, 26.4, 10.7, 1.71 respectively. The synthetic pollution index are over 3 in 12 of 13 samples which show great unsafety of the vegetables.

Spatial distribution of Heavymetals in soil and vegetable in the adminative village

Inverse distance weighted interpolation method was used to analyze spatial distribution of As, Cd, Pb, Zn, Cu. Both Single factor pollution index and synthetic pollution index were used to draw the maps. The maps are placed following.

The above maps show the spatial distribution of As, Cd, Pb, Zn, Cu in this village. Five safety classifications were used according the pollution index. From these maps we can judge the contamination degree for the vegetable or the soil everywhere of the village. The northwest of the village (7[#]-13[#]) is polluted heavily both in soil and vegetables due to many mine industries existing there. Villages (3[#]-6[#]) are also in light pollution to heavy pollution in soil in according with the industry distribution.





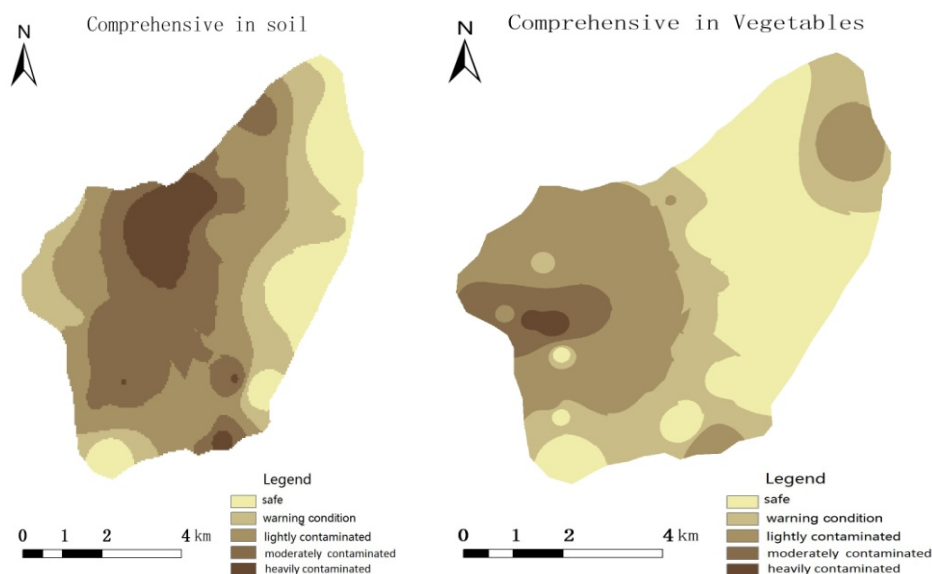


Figure 2

CONCLUSION

4.1 village was contaminated heavily both in vegetable and farmland soil. The key pollutants are As,Cd and Pb. The inhabitants was in high health risk if they eat the vegetable. The contamination was come from the mining activities.

4.2 The northwest of the village was contaminated most heavily. We can judge it by IDW method. The contamination degree is in accordance with the mine industry distribution.

4.3 In order to protect the human health, partition management can use to the garden soil. The area contaminated heavily shouldn't plant edible agricultural products.

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