Journal of Zhejiang University SCIENCE B
ISSN 1673-1581 (Print); ISSN 1862-1783 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Spatial distribution of Cd and Cu in soils in Shenyang Zhangshi Irrigation Area (SZIA), China*

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Received Dec. 24, 2007; revision accepted Jan. 11, 2008

Abstract: Heavy metal contamination of soils, derived from sewage irrigation, mining and inappropriate utilization of various agrochemicals and pesticides, and so on, has been of wide concern in the last several decades. The Shenyang Zhangshi Irrigation Area (SZIA) in China is a representative area of heavy metal contamination of soils resulting from sewage irrigation for about 30 years. This study investigated the spatial distribution and temporal variation of soil cadmium (Cd) and copper (Cu) contamination in the SZIA. The soil samples were collected from the SZIA in 1990 and 2004; Cd and Cu in soils was analyzed and then the spatial distribution and temporal variation of Cd and Cu in soils were modeled using Kriging methods. The results show that long-term sewage irrigation had caused serious Cd and Cu contamination in soils. The mean and the maximum of soil Cd are markedly higher than the levels in second grade standard soil (LSGSS) in China, and the maximum of soil Cu is close to the LSGSS in China in 2004 and is more than the LSGSS in China in 1990. The contamination magnitude of soil Cd and the soil extent of Cd contamination had evidently increased since sewage irrigation ceased in 1992. The contamination magnitude of soil Cu and the soil extent of Cu contamination had evidently increased in topsoil, but obviously decresed in subsoil. The soil contamination of Cd and Cu was mainly related to Cd and Cu reactivation of contaminated sediments in Shenyang Xi River and the import of Cd and Cu during irrigation. The eluviation of Cd and Cu in contaminated topsoil with rainfall and irrigation water was another factor of temporal-spatial variability of Cd and Cu contamination in soils.

Key words: Cadmium (Cd), Copper (Cu), Contamination of soils, Spatial distribution, Shenyang Zhangshi Irrigation Area (SZIA)
doi:10.1631/jzus.B0710629 **Document code:** A **CLC number:** X82

INTRODUCTION

The heavy metal contamination of soils, derived from sewage irrigation, inappropriate utilization of pesticides and chemical fertilizer in farmlands, mining, waste discharge, and so on, has caused the security problems of ecological systems and foods. The Shenyang Zhangshi Irrigation Area (SZIA) located in the west suburb of Shenyang, which is one of the most important heavy industry cities in China and the political and cultural centre of Liaoning Province, takes up 28000 ha area, and has come through sewage irrigation of 35 years since 1954 (Chen *et al*., 1980). The heavy metals have accumulated in soils in irrigation areas due to long time sewage irrigation. Cd and Cu concentration in soils rose and the Cd concentration of rice grain rose since 1990 (Chen *et al*., 1985). The land was partly rezoned from crop planting to industry use in 1992 because of the high Cd concentration detected in rice grain, however currently there are still many areas used for planting vegetables and crops.

Some studies on heavy metal contamination of soils in SZIA had been carried out, but most studies focused on micro-interface processes, the contamination mechanism of Cd and appraisal of the ecological effects of Cd contamination in soils (Wu *et al*.,

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[*] Project supported by the Item of Shenyang Xi River Geochemistry Evaluation, China

1986; 1992; Yu, 1991), and those studies were only based on individual samples.

For evaluating the environmental impacts of heavy metals, it is important to determine spatial distribution of heavy metals in the soils initially. The spatial distributions of Cd and Cu contamination in soils can be determined by geostatistical methods based on sampling at different times (Atteia *et al*., 1994; Barabás *et al*., 2001; Bierkens, 1997; Carlon *et al*., 2001; Goovaerts *et al*., 1997; von Steiger *et al*., 1996). These techniques provide methods to estimate either the value of a soil attribute at locations between samples, or the probability that the attribute value will exceed a given threshold at a particular location. Such information is essential for mapping potential risks to the environment or on human health. Based on the archival information and data in 1990 and 2004, our present study aimed to (1) estimate the spatial distributions of soil Cd and Cu in SZIA, (2) compare variability of Cd and Cu in soils after ceasing sewage irrigation, and (3) elucidate the cause of variability of Cd and Cu in soils.

MATERIALS AND METHODS

Study area

The SZIA is located in the western suburbs of Shenyang City (Fig.1), which is one of the most important heavy industry cities in China and is political and cultural centre of Liaoning Province. The landform of the study area is even with a slope of 1:1000 and the geographical coordinates are Long. 123°11′18″ E~123°20′37″ E and Lat. 41°43′14″ N~41°48′41″ N. The main soil type is meadow brown earth paddy with high organic matter and soil viscosity-density. The clay mineral of the soil is mainly illite with a little montmorillonite. The main crops are rice, some corn and vegetables. The sewage irrigation area covered from 200 ha in 1954 to 28000 ha in 1968, and the sewage irrigation in SZIA was ceased in 1992. The irrigation water was the mixture of the Hun River water (1.0~2.0 m^3/s) and the Weigong Open Ditch sewage (3.5~4.0 m^3/s). The sewage contained a great deal of organic matter and heavy metal, and the Hun River water was almost uncontaminated. The land function in SZIA was marked out newly, and partly land changed from crop planting to industry use due to heavy metal accumulation in soils and high Cd retained in rice grain found in 1970.

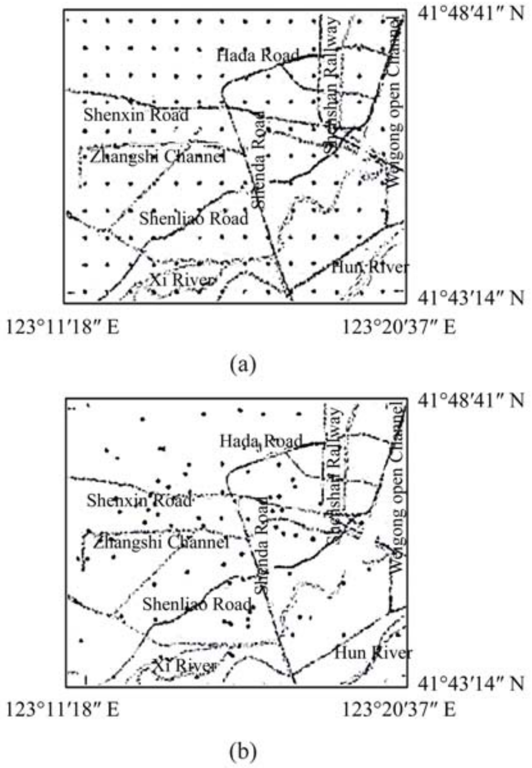


Fig.1 Location map of the study area and sampling points in 1990 (a) and in 2004 (b)

Field sampling and analysis

Soil samples for different crop cultivations of rice, corn and vegetable, etc. were collected from the topsoil (0~20 cm depth) and subsoil (20~40 cm depth) in October 2004 with a stratified random sampling design (Fig.1b). The corresponding sampling in October 1990 was from a regular grid of 100 ha spacing in an area of 15400 ha (Fig.1a). Each soil sample consisted of 4 subsamples each weighing 0.2 kg, which were distributed evenly on two diagonal lines of 100 ha grid. The soil sample located in the center of each grid. There were altogether 154 and 94 samples in 1990 and 2004, respectively. Eleven profile sections (60 or 100 cm) were selected and soil samples in these profile sections were collected every 20 cm. All soil samples collected were stored in polyethylene bags. The samples were air dried at room temperature and ground with an agate mortar and pestle to pass through a 2 mm stainless steel sieve, and then were stored at 4 °C before analyses.

The soil samples were digested in a heating block with aqua regia in polyethylene pots, and Cd and Cu analyses were conducted respectively with graphite atomic absorption spectrophotometry and flame atomic absorption spectrophotometry on a Varian SpectrAA-220 (Melbourne, Australia) with background correction. Analyses were in accordance with soil monitoring criteria (GBWO7401 and GBWO7404) according to standard methods of China (GB/T17140-1997).

Data processing

Spatial survey of the contents and distributions of Cd and Cu in SZIA soils is very important for assessing their impacts on the environment and agricultural activities. Geostatistics (Kriging in Sufer Version 6.04, Jun. 24, 1996, Golden software Inc., USA) provides tools for describing spatial variation of soil properties and for local interpolation (Kriging) to predict and map values at non-sampled locations. At present, geostatistics has been applied in the distribution and environmental behavior of soil heavy metals because it is able to treat explicitly the variables of interest as regionalized variables and demonstrate their actual spatial distribution pattern (Amini *et al*., 2005; Cattle *et al*., 2002; Wang and Liu, 2004).

Compared with many other geostatistics methods, Kriging provides a more accurate description of the data spatial structure and produces valuable information about estimation error distributions because Kriging provides optimal estimates by interpolation (theoretically without bias and with minimal variance) for tracing out pollution of unrecorded sites, based on the theory of regionalized variables (Liu *et al*., 2002; Zhang and Fan, 2002; Zhang *et al*., 2002). Therefore we used Kriging analysis to estimate the spatial distribution pattern of Cd and Cu in SZIA. The levels of the interpolation curves were determined at (1) 0.11 and 33.3 mg/kg (background levels of soil Cd and Cu in the studied district, respectively), (2) 0.60 and 67 mg/kg (the levels in the second grade standard soil (LSGSS) of Cd in China according to GB15618-1995 and the threshold of soil Cu, respectively) and (3) 1.5 and 100 mg/kg (2.5 times the LSGSS of Cd and the LSGSS of Cu in China according to GB15618-1995, respectively).

RESULTS

Statistical features of soil Cd and Cu

The statistical distributions of soil Cd and Cu were examined, statistical parameters were calculated with geostatistics methods (Table 1), and statistical distributions were plotted (Figs.2 and 3). The results indicate that the logarithmic frequency distributions of soil Cd and Cu were clearly non-normal. For topsoil and subsoil, the Cd means were respectively 2.83 times and 1.24 times the LSGSS in China, and the maxima were respectively 16.92 times and 12.62 times the LSGSS in China in 2004. The Cu means go near to background level of soil Cu in SZIA, and the maxima were more than the threshold of soil Cu, but less than the LSGSS in China in 2004. The Cd means were respectively 1.71 times and 0.55 times the LSGSS in China, and maxima were respectively 15.67 times and 5.26 times the LSGSS in China in 1990. The Cu means respectively go near to background level and the threshold of soil Cu for subsoil and topsoil. In topsoil, the maxima of Cu were respectively 0.908 times and 2.56 times the LSGSS in China in 2004 and 1990. The variation coefficients and variances of Cd and Cu were relatively high in 1990 and 2004, either in the topsoil or in the subsoil, which reveals heterogeneity of the soil Cd and Cu.

Table 1 Statistical parameters of soil Cd in SZIA

Stratum (cm)	Year	Element	Mean (mg/kg)	Range (mg/kg)	Variation coefficient	Variance
0~20	1990	Cd	1.023	0.179~9.400	1.916	1.217
		Cu	64.900	11.000~256.00	19.740	1281
	2004	Cd	1.698	0.000~10.150	1.637	1.547
		Cu	45.100	16.700~90.800	6.590	297
20~40	1990	Cd	0.331	0.100~3.156	5.915	1.217
		Cu	33.400	1.700~75.800	10.150	339
	2004	Cd	0.741	0.000~7.567	4.735	1.983
		Cu	36.500	6.600~72.900	6.960	254

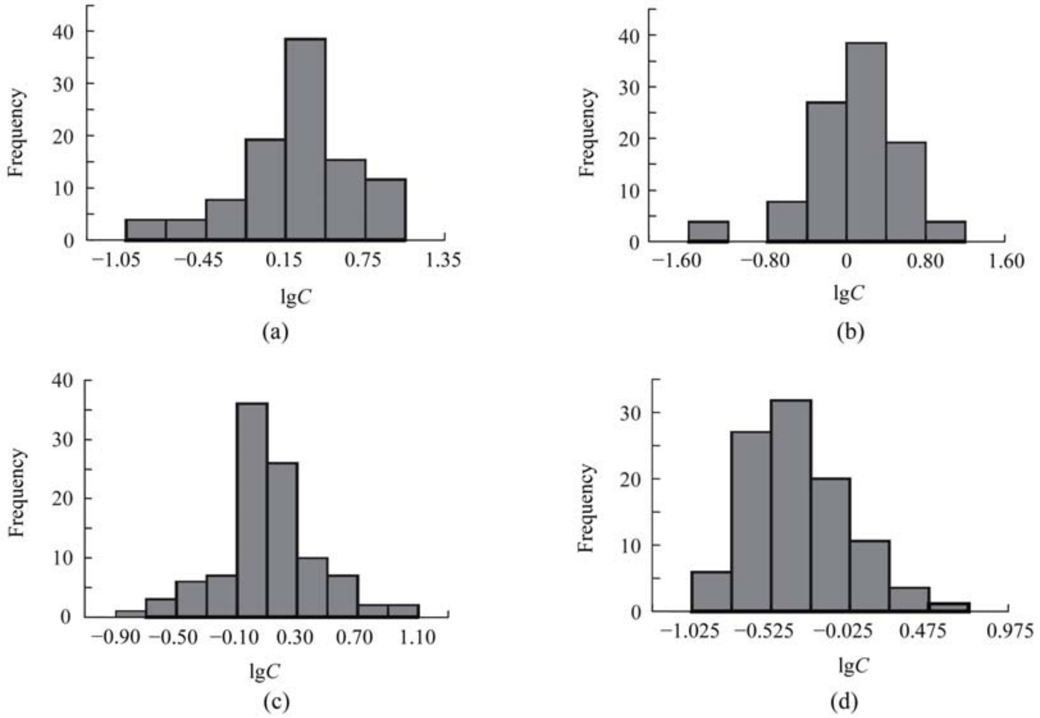


Fig.2 Logarithmic frequency distribution of soil Cd. (a) Topsoil, in 2004; (b) Subsoil, in 2004; (c) Topsoil, in 1990; (d) Subsoil, in 1990

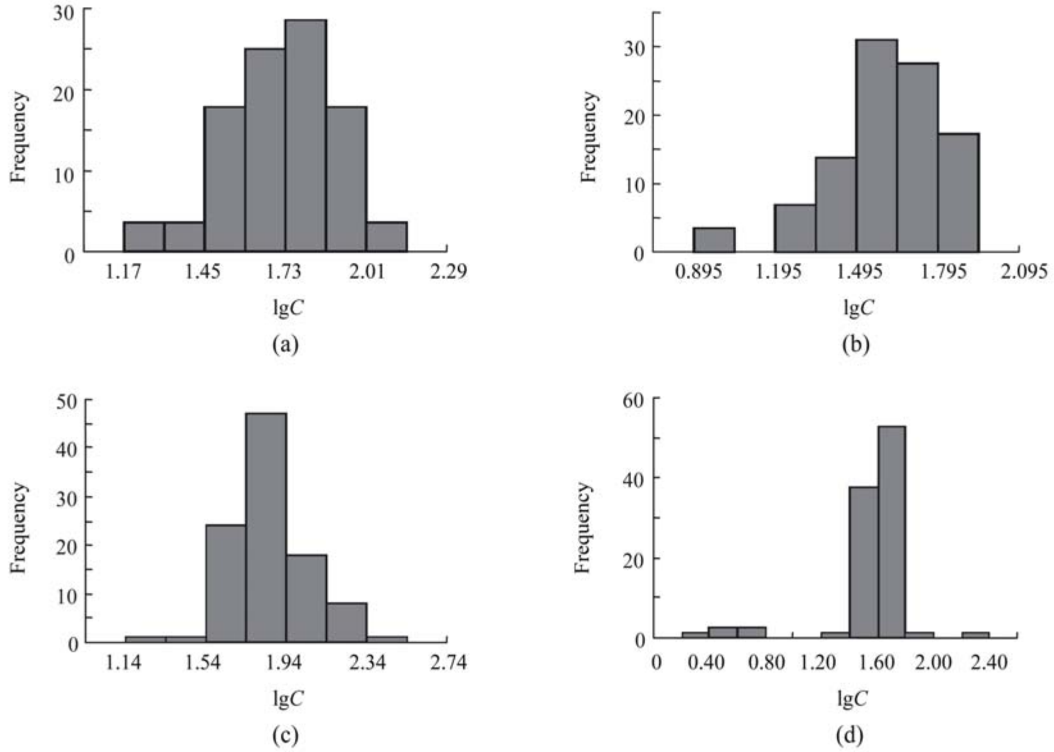
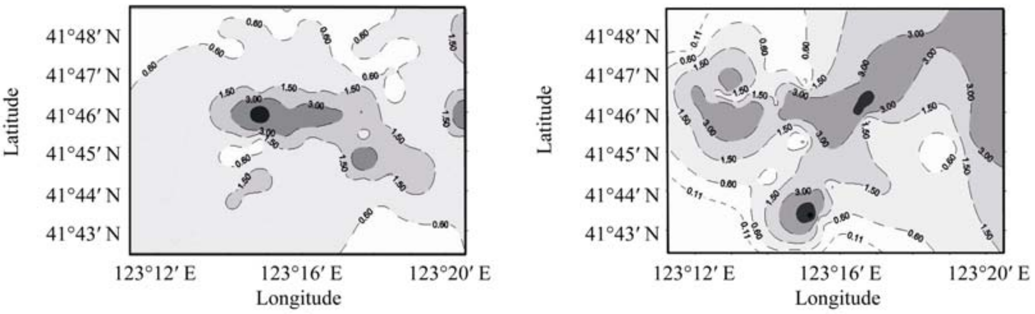


Fig.3 Logarithmic frequency distribution of soil Cu. (a) Topsoil, in 2004; (b) Subsoil, in 2004; (c) Topsoil, in 1990; (d) Subsoil, in 1990

Spatial distributions of Cd and Cu in soils

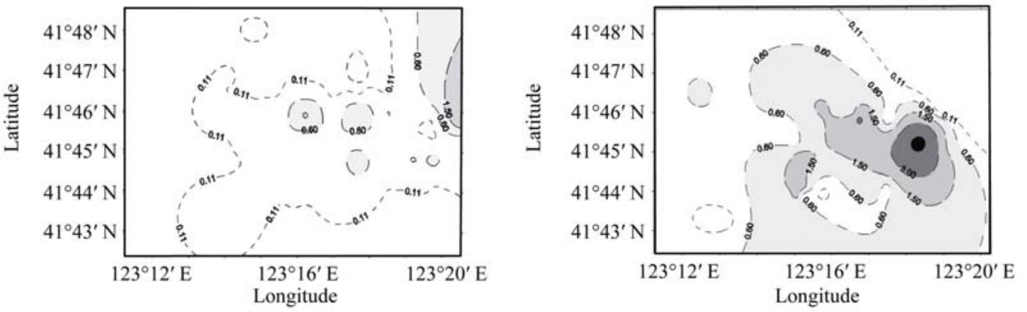
The Kriging interpolation maps of the Cd and Cu data in the study area for 1990 and 2004 are shown in Figs.4~7. The contour maps in Figs.4 and 5 show that Cd contamination of the topsoil was severer. The topsoil area with Cd level more than 0.6 mg/kg was 12579 ha (81.6%) in 1990 and 12186 ha (79.1%) in 2004, and the subsoil area with Cd level more than 0.6 mg/kg was 1272.4 ha (8.3%) in 1990 and 6389 ha (41.5%) in 2004. Compared with those in 1990, the mean and the maximum of Cd in soils were augmented, and the soil extent with Cd level more than 0.6 mg/kg evidently increased too in 2004.

Cu contamination of soils was less than Cd contamination of soils. The topsoil area with Cu level more than 100 mg/kg was 1666 ha (5.95%) in 1990 and 3096 ha (11.05%) in 2004 (Fig.6). The subsoil area with Cu level more than 100 mg/kg was 459.3 ha (1.64%) in 1990 and there was no subsoil with Cu level more than 100 mg/kg in 2004 (Fig.7). Compared with those in 1990, the mean and the maximum of Cu decreased in topsoil, but the mean of Cu was augmented in subsoil in 2004. The topsoil extent with Cu level more than 100 mg/kg evidently increased in 2004 compared with that in 1990, and it was on the contrary for the subsoil.



(a) (b)

Fig.4 Spacial distributions of Cd in topsoil in 1990 (a) and in 2004 (b)
The figures in curves are isolines in concentration (mg/kg)



(a) (b)

Fig.5 Spacial distributions of Cd in subsoil in 1990 (a) and in 2004 (b)
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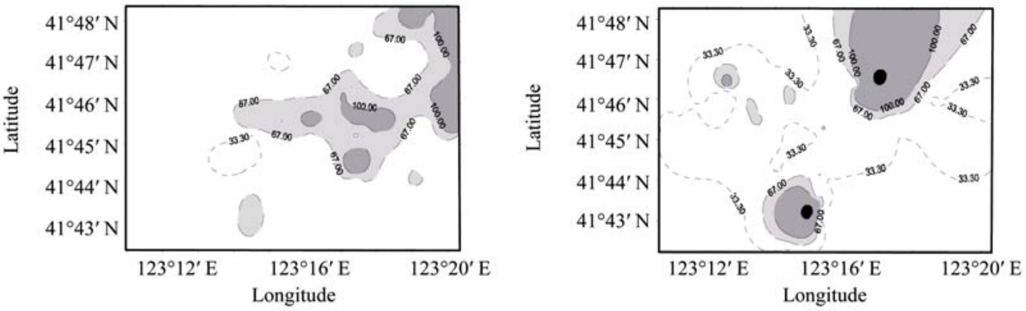
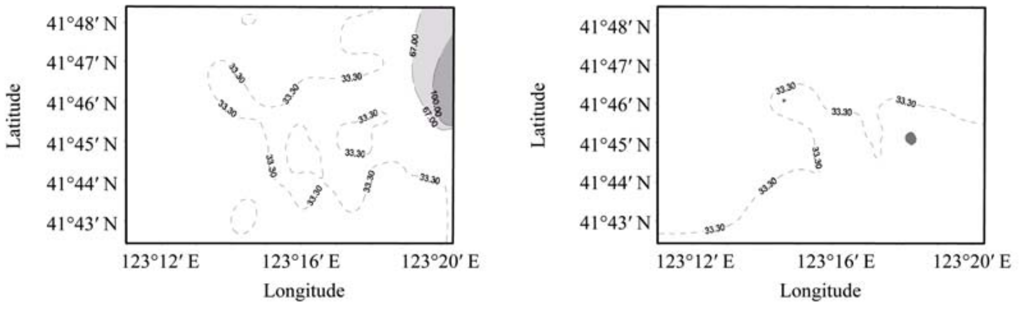


(a) (b)

Fig.6 Spacial distributions of Cu in topsoil in 1990 (a) and in 2004 (b)
The figures in curves are isolines in concentration (mg/kg)

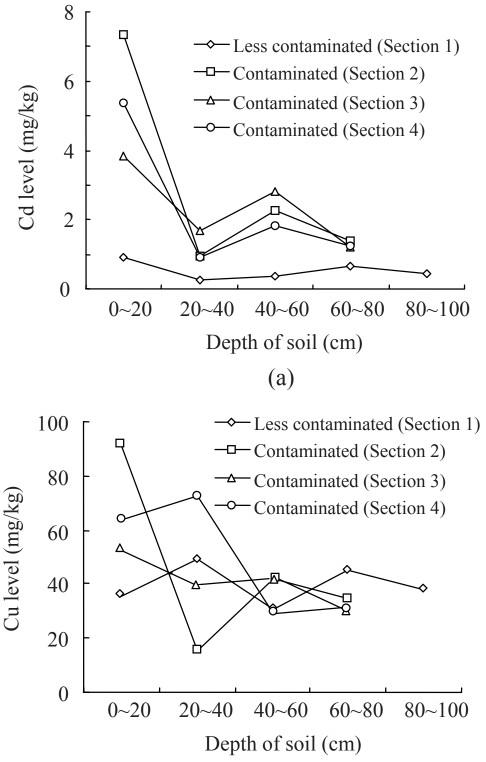


(a) (b)

Fig.7 Spacial distributions of Cu in subsoil in 1990 (a) and in 2004 (b)
The figures in curves are isolines in concentration (mg/kg)

Distribution of soil Cd in vertical profile sections

Fig.8 shows distribution curves of Cd and Cu in different vertical soil profile sections in 2004. The curves show that, for a background vertical profile section (Section 1), the Cd and Cu levels were nearly constant from top to bottom, and yet for polluted vertical profile sections (Sections 2~4), the Cd and Cu levels were markedly augmented in topsoil and evidently decreased with depth of soil.



(a)

(b)

Fig.8 Cd (a) and Cu (b) distribution in soil vertical profile sections in 2004

DISCUSSION

Data usability

Although the location and number of soil sampling were different between 1990 and 2004, soil samples were quantitatively adequate for representative of soils because soil samples were collected with the same sampling methods in the same soil stratum, and soil type was homogeneous and landform was even in the study area. The geometry means and the maxima of soil Cd and Cu were comparable. The data of soil Cd and Cu were processed by Kriging interpolation in the study area for 1990 and 2004, so the spatial distributions of Cd and Cu in soils for 1990 and 2004 were comparable.

Genetic discussion

The increase of Cd and Cu concentrations and soil extent contaminated by Cd and Cu indicated the Cd and Cu import since the sewage irrigation ceased in SZIA in 1992, which may be related to Cd and Cu reactivation of the sediments in Xi River and the transport of contaminated soils by people due to industrial development in SZIA. The Xi River, the inland river of Shenyang City, comes from the south of Weigong Open Ditch, and carries the sewage and industrial waste water at all times. The water monitoring from different section of Xi River presented that Cd contents in water were respectively 0.010~0.069 mg/kg in 1990 and 0.005~0.040 mg/kg in 2004, which were respectively 2~13.8 times and 1~8 times the criteria of agricultural irrigation water in China (0.005 mg/kg); The Cu contents were respectively 0.06~0.59 mg/kg in 1990 and 0.092~0.421 mg/kg in 2004, which were respectively 0.6~5.9 times and

0.092~4.21 times the criteria of agricultural irrigation water in China (0.1 mg/kg).

The analysis of Xi River sediments indicated that Cd was 1.13~15.73 mg/kg and Cu was 37.2~559 mg/kg in 2004. The available Cd and Cu [extracted by HOAc, 25% (v/v)] of sediments are weakly held in ion exchange sites, and easily held in soluble amorphous compounds of iron and manganese; carbonates and those metals were weakly held in organic matter (Selvaraj *et al*., 2004) and easily activated. In Xi River sediments, the available Cd is 37.4%~52.0% of total Cd, and the available Cu is 25.0%~31.6% of total Cu. These features showed that Cd and Cu in sediments may be reactivated into water, and then carried into soils by irrigation water. The transport of contaminated soils by people due to industrial development in SZIA and the exhaust gas of automobile also partly explained the variation of Cd and Cu in topsoil. The Cd and Cu abnormity in subsoil may be related to the eluviation of Cd and Cu in contaminated topsoil with rainfall and irrigation water and redeposition in subsoil because of the comparative acidity of topsoil (pH 5.79) with subsoil (pH 6.12). The eluviation test of soil column (pH 7.15 and pH 6.12, soil column height 60 cm, leach time 72 h) for soils contaminated with Cd and Cu indicated that Cd and Cu leached were larger in pH 6.12 (7%~57% for Cd and 15%~56.0% for Cu) than in pH 7.15 (5%~32% for Cd and 3%~29% for Cu) in topsoil, which explained Cd and Cu in subsoil.

CONCLUSION

Sewage irrigation over a long time had caused serious Cd and Cu contamination in soils in SZIA, China. At present, the mean and the maximum of soil Cd are markedly higher than the LSGSS in China, and the maximum of soil Cu is close to the LSGSS in China in 2004 and is more than the LSGSS in China in 1990. The contamination magnitude of soil Cd and the soil extent of Cd contamination had evidently increased since sewage irrigation ceased in 1992. The contamination magnitude of soil Cu and the soil extent of Cu contamination had evidently increased in topsoil, but had obviously decreased in subsoil. The soil contamination of Cd and Cu was mainly related to Cd and Cu reactivation of contaminated sediments in Xi River and the import of Cd and Cu during irrigation. The eluviation of Cd and Cu in contaminated topsoil with rainfall and irrigation water was another factor of temporal-spatial variability of Cd and Cu contamination in soils.

ACKNOWLEDGEMENT

The authors would like to thank the Liaoning Institute of Geology and Minerals in China for carrying out the survey of heavy metal concentrations in SZIA in 1990.

References

Amini, M., Afyuni, M., Khademi, H., Abbaspour, K.C., Schulin, R., 2005. Mapping risk of cadmium and lead contamination to human health in soils of Central Iran. *Sci. Total Environ.*, **347**(1/2/3): 64-77.

Atteia, O., Dubois, J.P., Webster, R., 1994. Geostatistical analysis of soil contamination in the Swiss Jura. *Environ. Pollut.*, **86**(3):315-327. [doi:10.1016/0269-7491(94)90172-4]

Barabás, N., Goovaerts, P., Adriaens, P., 2001. Geostatistical assessment and validation of uncertainty for three-dimensional dioxin data from sediments in an estuarine river. *Environ. Sci. Technol.*, **35**(16):3294-3301. [doi:10.1021/es010568n]

Bierkens, M.F.P., 1997. Using Stratification and Residual Kriging to Map Soil Pollution in Urban Areas. *In*: Baafi E.Y., Schofield, N.A. (Eds.), Geostatistics Wollongong ’96. Kluwer Academic Pub., Dordrecht, p.996-1007.

Carlon, C., Critto, A., Marcomini, A., Nathanail, P., 2001. Risk based characterisation of contaminated industrial site using multivariate and geostatistical tools. *Environ. Pollut.*, **111**(3):417-427. [doi:10.1016/S0269-7491(00)00089-0]

Cattle, J.A., McBratney, A.B., Minasny, B., 2002. Kriging method evaluation for assessing the spatial distribution of urban soil lead contamination. *J. Environ. Qual.*, **31**: 1576-1588.

Chen, T., Wu, Y.Y., Zhang, X.X., Kong, Q.X., 1980. The mend of Cd soils and prevention and cure of Cd contamination in ripe in Zhangshi irrigation area. *Environ. Sci. Sin.*, **1**(5):7-11 (in Chinese).

Chen, T., Wu, Y.Y., Kong, Q.X., Tan, F., 1985. Cd speciations in soils in Zhangshi irrigation area. *Acta Ecolog. Sin.*, **15**(4):300-305 (in Chinese).

Goovaerts, P., Webster, R., Dubois, J.P., 1997. Assessing the risk of soil contamination in the Swiss Jura using indicator geostatistics. *Environ. Ecol. Stat.*, **4**(1):49-64. [doi:10.1023/A:1018505924603]

Liu, R.M., Wang, X.J., Zheng, Y., Li, Y., Jiang, Y.C., Zhou, X.W., 2002. The application of geostatistics in the study of water quality of Taihu Lake. *Acta Scientiae Circumstantiae*, **22**(2):209-212 (in Chinese).

Selvaraj, K., Ram, Mohan, V., Szefer, P., 2004. Evaluation of metal contamination in coastal sediments of the Bay of Bengal, India: Geochemical and statistical approaches. *Mar. Pollut. Bull.*, **49**(3):174-185. [doi:10.1016/j.marpolbul.2004.02.006]

von Steiger, B., Webster, R., Schulin, R., Lehmann, R., 1996. Mapping heavy metals in polluted soil by disjunctive Kriging. *Environ. Pollut.*, **94**(2):205-215. [doi:10.1016/S0269-7491(96)00060-7]

Wang, X.J., Liu, R.M., 2004. Spatial analysis and eutrophication assessment for chlorophyll a in Taihu Lake. *Environ. Mon. Assess.*, **101**(1/2/3):1-8.

Wu, Y., Chen, G., Zhang, X., 1986. Pollution Ecology of Cd in the Zhangshi Irrigation Area of Shenyang. *In*: Gao, Z.M. (Ed.), Studies on Pollution of Soil-Plant Systems. China Science and Technology Press, Beijing, p.339-344 (in Chinese).

Wu, Y.Y., Chen, T., Kong, Q.X., 1992. Prevention and cure of heavy metals contamination of farmland in China. *Agro-Environ. Prot.*, **11**(4):187-189.

Yu, F.L., 1991. Studies on the Change of Cadmium in Shenyang Zhangshi Irrigation Area. Centre Station of Environmental Monitory of Shenyang, Issues 3 and 4 (in Chinese).

Zhang, W.J., Fan, H.Y., 2002. Establishment of environmental criterions for Cd, Hg, As, Pb, Cu, Zn, Ni in Tianjin soils. *Urban Environ. Urban Ecol.*, **15**(3):47-48 (in Chinese).

Zhang, Z.Y., Zhan, H.L., Guo, X.P., 2002. The spatial variable analyses of salt in farmland of plage plain. *J. Hohai Univ. (Nat. Sci.)*, **7**(4):50-65 (in Chinese).