The transportation, time-dependent distribution of heavy metals in paddy crops

C.X. Wang ^{a,*}, Z. Mo ^a, H. Wang ^a, Z.J. Wang ^a, Z.H. Cao ^b

^a State Key Laboratory of Aquatic Environmental Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China

^b Institute of Soil Sciences, Chinese Academy of Sciences, Nanjing 210000, China

Abstract

Sixteen experimental plots ($5\text{ m} \times 6\text{ m} = 30\text{ m}^2$) were designed with four different levels of heavy metals (HMs) concentration in soil. The concentrations of heavy metals in soils, and paddy plant during the different periods of growth were investigated. A relationship between the total HM content in plants and the HM level in soil was found for a wide range of concentrations. The exchangeable fraction of HMs extracted with 1 M MgCl_2 solution according to Tessier's method increased correlation with the dosage of supplemented HMs, then decreased as time went on. The time-related variation of exchangeable HMs in soil demonstrated that the amount of effective HMs taken up by paddy differed at various growth phases. The amount of HMs accumulated in different parts of paddy followed the order of root > stem > grain, leaf. The transportation potential of the HMs in paddy in present study followed the order of Zn, Cr > Cd, Cu > Pb. The HM content in root, stem and leaf of paddy plant (dry weight) was low at time of seedling. The concentration in the root increased sharply at time of tillering, decreased thereafter. The concentrations in stem and leaf reached the highest at time of tillering, then decreased, while rose slightly at following time.

© 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Heavy metals; Transportation; Distribution; Paddy; Soil

1. Introduction

One of the potential risks ascribed to soil is the consumption by men of crop plants grown on heavy metal (HM) contaminated soils. A major pollution source of HMs to soil in China is sewage irrigation (Zhen and Chen, 1990), which can result in complex pollution by HMs. The effect of complex pollution by HMs is associated with many factors, such as interaction of the elements, crop species, ratio of element concentrations, soil character and environmental conditions (Xia and Mu, 1984; Petruzzelli, 1989). The HMs from anthropogenic sources usually enter the environment in

bioavailable forms, then they can transform to other speciations. To understand the joint effects of combined HMs and to forecast, evaluate, prevent and cure HM pollution, well-designed studies are needed to determine the extent of HM accumulation in soil and crops, and to study the responses and uptake of HMs by crops.

The reported studies (Suzuki and Iwao, 1982; Rivai et al., 1990) on the transportation, distribution and accumulation of HMs in plants are mostly limited to the comparison of HM amounts and speciation in different parts of plants at the time of harvesting, focusing on the endpoint of growth, ignoring the time-dependent processes during whole growth phases. However, the transportation, distribution and accumulation of HMs in different parts of plants varies at different growth stages (Xu and Xu, 1993). The endpoint at harvesting cannot alone illustrate clearly the HM behavior in plants. Research on the time-dependent distribution and

* Corresponding author. Tel.: +86-10-62849107; fax: +86-10-62923543.

E-mail address: chunxia@mail.rcees.ac.cn (C.X. Wang).

accumulation of HMs in plants will provide information relating to the growth, metabolism and clearance activity of plants under the stress of HM compounds. This present study will give a preliminary description of the effects of HMs on plants.

In this study, the relationship between the HM content in agricultural soils and the HM content in paddy plants was investigated. The possibility of using HMs level in soil to infer the risk to human consumers of these crops was evaluated, as was the uptake of different HMs by different paddy organs. The exchangeable forms of HMs in soils, and total HM concentrations in different parts of paddy at different growth phases was also examined.

2. Materials and methods

2.1. Experiment design

The study was carried out at NianYu Farm, AnZhen, Wuxi, Jiangsu province, in the delta of Changjiang river, an important agricultural zone in China. The soil type was *cultivated hydromorphic paddy soil* (Chinese soil classification). The properties of the soil were: pH 7.2–7.4, organic content 25–30 g/kg, CEC 7.5–8.2 cmol/kg. The background HM content in the soil is listed in Table 1. The soil had been cultivated for years and was sufficiently fertile before planting. The experimental plots were treated in the same way as the local fields, carbamide fertilizer was applied and the soil was irrigated as usual during experiment. The experimental plots (5 m × 6 m = 30 m²) were completely randomized, with four groups, each group with four replicates, one group was set as control, the other three were supplemented with different dosages of HMs before planting the paddy.

Before transplanting paddy seedling, a mixture of CdCl₂, Pb(NO₃)₂, ZnCl₂, Cu(NO₃)₂, and CrCl₃ solution was added to soil in the designated dosage. The HMs mixture was supplemented by means of sprinkling and stirred with irrigation water on the topsoil. The composition and concentration of the added HMs in the experimental plots is listed in Table 2. The high dosage supplement of HMs was selected so as to be close to the limit of soil quality, one third and one ninth of the limit was designated as medium and low dosage respectively (Wu and Yu, 1998a).

Table 1

The background heavy metal content in the soil of the experimental plots (mg/kg)

Metals	Cu	Pb	Zn	Cr	Cd
Concentration (mg/kg)	26.3	36.4	68.5	17.1	0.6

Table 2

Supplemented heavy metal concentrations selected (mg/kg)

Treatment	Cu	Pb	Zn	Cr	Cd
Control	0	0	0	0	0
Low dosage	10	30	10	10	0.15
Medium dosage	30	90	30	30	0.5
High dosage	90	270	180	90	1.5

2.2. Sample preparation and chemical analysis

Soil and plant samples were collected at different times during paddy growth. Soil samples were air-dried and ground gently to pass through 100-mesh sieve. For determination of the total metal concentration, 0.1 g homogenized soil sample was put into a 50-ml Teflon vessel and wetted by drops of deionised distilled water. Two ml of concentrated HNO₃, 1 ml of concentrated HClO₄ and 0.5 ml of HF were added respectively. The mixture was heated at 100 °C for 4 h with the cap closed, and then heated until no smoke appeared with cap open. 1 ml HNO₃, 1 ml HClO₄ and 1 ml deionised distilled water were added, and heated until a transparent solution was obtained. The exchangeable fraction of metals was extracted according to Tessier method (Tessier et al., 1979). Four g soil sample was extracted using 40 ml 1 M MgCl₂ (pH = 7.0) for 2 h, then centrifuged at 3000 r/min for 20 min, the supernatant solution was then passed through a 0.45 µm membrane, and the filtrate used.

Whole-plants were sampled just before transplanting, at the time of tillering, jointing, booting and harvesting, separately. The plants were washed with tap water thoroughly to remove the soil and then washed with distilled water three times, root, stem, leaf and grain were separated and oven dried. The plants sample were digested using HNO₃ and 30% H₂O₂ according to Jones (1991). The metal concentrations of all the resulting solutions were measured by HITACHI Z-6100 flame AAS or PERHIN-ELMER 3100 Graphic AAS, depending on the HM concentration level in solutions.

3. Results and discussion

3.1. Relationship between HM concentrations in soil and in plants

The concentrations of Pb, Cu, Zn, Cr and Cd supplements added to the soil is listed in Table 2. After transplanting of paddy seedling, the HM concentrations in the soils ranged from 30 to 166 mg/kg for Cu, 40 to 210 mg/kg for Pb, 90 to 500 mg/kg for Zn, 30 to 90 mg/kg for Cr, and 0.84 to 2.2 mg/kg for Cd, respectively, showing distinct differences among runs of different dosage. From the beginning to the end of the experi-

ment, the total HM concentrations in the topsoil decreased gradually (data not shown), the reduced HMs might be due to paddy plant uptake, runoff wash out, and leaching.

At maturity, the concentration of HMs in different parts of the paddy crop is illustrated in Fig. 1. The HMs accumulated by the paddy plant were related to the HM content in soil showing a positive correlation, but not a linear relationship, which might be related to the inhibition mechanism of root assimilation to HMs (Wang and Wu, 1998).

Fig. 1. The concentration of heavy metals in paddy at maturity (mg/kg).

Table 3

The heavy metals content in paddy grain (mg/kg)

Treatment	Cu	Pb	Zn	Cr	Cd
Control	4.95	0.38	40.1	10.1	0.1
Low dosage	5.7	1.1	45.3	12.1	0.1
Medium dosage	9.7	3.2	47.8	11.1	0.1
High dosage	11.4	4.7	51.3	17.6	0.3

$n = 4$.

Table 3 shows the HM concentrations in paddy grain at maturity. HM content in the grain could be an indicator for safety assessment, since it goes directly into food for human consumption. HM concentrations in grain vary with plant species, HM content of the soil, soil type, as well as the environmental and climate conditions (Wu and Yu, 1998a,b). The average HM concentrations in paddy grain consumed in China are Cu: 0.55 mg/kg, Pb: 0.075 mg/kg, Zn: 1.89 mg/kg, Cr: 0.32 mg/kg and Cd: 0.027 mg/kg, respectively (Chen, 1994). In this study, the highest concentration of HMs in paddy grain were: Cu: 11.4 mg/kg, Pb: 4.7 mg/kg, Zn: 51.3 mg/kg, Cr: 17.6 mg/kg and Cd: 0.3 mg/kg. The concentrations of Cu, Pb, Cd and Cr all exceeded the permitted limit for heavy metals in paddy grain, that is Cd: 0.2 mg/kg, Pb: 1.0 mg/kg, Cu: 10.0 mg/kg and Cr: 1.0 mg/kg (GB15201-94, GB2715-81, GB2713-81, GB5199-94, GB13106-91).

It could be seen clearly that the higher the HM content in soil, the higher the HM concentrations in plants. HMs in the soil could suggest a geographical contamination of the soil and indicate a risk for cultivation of human-edible crops.

3.2. HMs distribution and transportation in paddy plants

Fig. 1 illustrates the HM concentrations in different parts of the paddy. It shows that the concentration order of HMs in different parts of paddy was: root > stem > grain > leaf. Similar observations have been reported by Xu (1995). The translocation of HMs to the above-ground portions of plants was minimized in order to minimize the toxic effects caused by metals in soil (Foy, 1984), this observation was consistent with the common behavior of plants in their response towards environment stress.

The ratio of the HM content in grain to that in soil has been referred as uptake efficiency, which can be used to express the transport potential of HMs in plants (Wu, 1998). The general sequence of uptake efficiency for individual elements is $Cd > Zn > Cu > Pb, Cr$ (Wu and Yu, 1998a,b), the efficiency values from our field experiments using 5 HMs in combination are shown in Table 4, together with those obtained by Wu and Yu (1998a,b).

From Table 4, it can be seen that the uptake efficiency in conditions of combined heavy metal pollution was

Table 4

The uptake efficiency of paddy in conditions of individual and combined heavy metal pollution

	Individual element (potted) ^a	Combined elements (potted) ^a	Combined elements (field)
Cu	0.04–0.05	0.04–0.07	0.0982–0.1882
Pb	0.0002–0.0008	0.002–0.008	0.0104–0.0253
Zn		0.15–0.24	0.2064–0.5854
Cr			0.1643–0.5906
Cd	0.022–0.024	0.4–1.58	0.0909–0.1667

^a From Wu and Yu (1998a).

higher than that of individual heavy metal pollution; the values from the field experiment are higher than from the pot experiment (Cd was an exception). It is concluded that the transportation potentials of these 5 HMs are higher under field conditions, and under combined element pollution. The potential sequence of HM transportation in plants was $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb}$ and Cr under both individual (Wu and Yu, 1998a,b) and combined element pollution conditions. Because of the alternative effects among elements, the transportation potential of these HMs in combined condition would be increased, while the order of potential was about the same as that under individual element pollution (Wu and Yu, 1998a,b). In the condition of field contaminated by combined HMs in this study, the sequence of transportation potential was $\text{Zn}, \text{Cr} > \text{Cd}, \text{Cu} > \text{Pb}$. From the uptake efficiency and

the information of HMs distribution in plants (Fig. 1), an unusual phenomenon was that the transportation potential of Cr was elevated greatly, exceeding the degree of other elements, the reason is unknown.

3.3. The time-dependent variation of HMs concentration in paddy

Since plants take up most mineral elements from the soil solution, it is often assumed that the dissolved metals are readily available to organisms (Barber, 1984). Determination of dissolved metals may provide useful information on metal bioavailability and toxicity (Knight et al., 1998). Soluble and exchangeable fractions account for the main dissolved HMs in soil. In the present study, the soluble fraction of HMs in the topsoil was very low, nearly undetected (data was not shown). The exchangeable fraction of HMs was used to predict bioavailable HMs in soil (Petrucelli, 1989; Cheng and Jiang, 1994), therefore, a higher extractable HMs level demonstrated higher bioavailability of metals. In this study, a correlation could be established between exchangeable HMs concentration in soil and HMs in paddy plant: the higher the exchangeable fraction of HMs in soil, the higher the HMs content in paddy. As shown in Fig. 2, average levels of exchangeable HMs were very low; the largest percentage of the exchangeable form of HMs accounted for 3.8% (Cd), suggesting that the HMs in soils are mainly present as highly insoluble forms.

Fig. 2. The variation of exchangeable heavy metals concentration in soil (mg/kg).

Fig. 2 shows that the exchangeable fraction of HMs in soils varied after supplementing with different dosages. After a period of time, the concentration of exchangeable forms of HM in soils decreased to a certain level. The relatively high concentration of exchangeable HMs was reached before the paddy-jointing phase (about July 30th in this study), which suggests that the amount of HMs taken up by paddy roots during the time of tillering is more than at any other period. The time-dependent variation of exchangeable HMs indicates that the amount of HMs which can be absorbed by paddy differs at different growth phases.

Fig. 3. The variation of heavy metals concentration in root of paddy (mg/kg).

The HM concentrations in the roots of paddy seedlings were about: Pb 2.1 mg/kg, Cu 3.6 mg/kg, Zn 26.5 mg/kg, Cr 1.6 mg/kg and Cd 0.1 mg/kg, respectively before transplanting. The HM concentrations in root reached a peak at the time of tillering as shown in Fig. 3. This might have been due to the concentration of available HMs in the soil being relatively high at time of tillering, at the same time the metabolic activity in the root was intensive. This result was accordance to the

Fig. 4. The variation of heavy metals in stem of paddy (mg/kg).

observation of the study using radioisotope tracers (Xu, 1995).

The decrease of the HM content in roots as time went on may have contributed to following processes, associated with the inhibition of root metabolic activity and assimilation by the accumulated HMs (Zhao and Niu, 2000): the upward transportation of HMs away from root; increase in the biomass of root; and the decrease of the available HM fraction in soil taken up by root.

Fig. 5. The variation of heavy metals concentration in leaf of paddy (mg/kg).

Figs. 4 and 5 show the time-dependent variation of HM levels in the stem and leaf. The HM concentrations accumulated in the straw of the seedling were low, reaching a peak at the time of tillering. The HM content of the stem decreased fleetly at the time of jointing, then increased gradually at the time of booting and harvesting.

We believe that the HM concentrations peaked in stem because of the intensive metabolic activity in stem and the transportation of the HMs from root during period of tillering. The decrease of HM content (dry weight) at the time of jointing might be ascribed to the increase of stem biomass during period of jointing; intensifying of forbearance and clearance of HMs after tillering (Xia and Mu, 1984; Xu and Yang, 1995) under the stress of HM contamination. As time went on, the forbearance and clearance activity of plant to the HMs might decrease the HM accumulation in plant. The case of HMs accumulation in leaf was similar to that in stem, but the HMs content did not distinctly increase and was relatively stable after the time of jointing.

4. Conclusions

Based on the results obtained, following conclusions can be drawn:

1. A correlation existed between the HM concentrations in the soil, with concentrations in the roots, stem, and grain of the paddy. The higher the HM content in the soil, the higher the HM content in the paddy plant.
2. HM concentrations in different parts of paddy followed the order of: root > stem > grain, leaf. It has been found that the transportation potential of these 5 HMs was higher under field conditions with combined element pollution. In individual element pollution, reported transportation potentials of the HMs was $Cd > Zn > Cu > Pb$ and Cr , while in the combined HM pollution in this study, the order of transportation potentials was $Zn, Cr > Cd, Cu > Pb$.
3. The total HM concentrations in root, stem and leaf of the paddy plant was low at time of seedling. The HMs content in the root increased sharply at time of tillering, and decreased thereafter. The HMs content in stem and leaf reached a peak at the time of tillering, then decreased before finally rising slightly.

Acknowledgements

This work was financially supported by National Key Basic Research Science Foundation of China (G199011806). The authors wish to express the appreciation to Prof. Zhu Jianguo, Dr. Zhang Huanchao and Eng. Ping Peiliang for their assisting in the field aspects,

to Ms. Zhao Lihui and Sun Jingfang for performing the metals analysis.

References

- Barber, S.A., 1984. Soil Nutrient Bioavailability: A Mechanistic Approach. John Wiley, New York.
- Chen, H.M., 1994. The Heavy Metal Pollution in Soil–Plants Ecosystem. Sciences Publication House, Beijing (in Chinese).
- Cheng, Y.Y., Jiang, Y.G., 1994. Handbook of Biomedical Microelements Data. Tianjing Sciences and Technology Publication House, Tianjing (in Chinese).
- Foy, C.D., 1984. The physiology of plant adaption to mineral stress. *Iowa State Journal of Researches* 57, 365–391.
- Jones, J.B., 1991. Plant tissue analysis in micronutrients. In: Mortvedt, J.J., Cox, F.R., Shuman, L.M., Welch, R.M. (Eds.), *Micronutrients in Agriculture*, second ed. In: SSSA Book Series, No. 4. Soil Science Society of America, Madison WI, pp. 477–521.
- Knight, B.P., Chaudri, A.M., McGrath, S.P., Giller, K.E., 1998. Determination of chemical availability of cadmium and zinc in soil using inert soil moisture samplers. *Environmental Pollution* 99, 293–298.
- Petruzzelli, G., 1989. Recycling wastes in agriculture: heavy metal bioavailability. *Agriculture, Ecosystem and Environment* 27, 493–503.
- Rivai, I.F., Koyama, H., Suzuki, S., 1990. Cadmium content in rice and its daily intake in various countries. *Bulletin of Environmental Contamination and Toxicology* 44, 910–916.
- Suzuki, S., Iwao, S., 1982. Cadmium, copper, and zinc levels in rice and rice field soil of Houston, Texas. *Biological Trace Elements Research* 4, 21–28.
- Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation for particulate trace metals. *Analytical Chemistry* 51 (7), 844–850.
- Wang, X., Wu, Y.Y., 1998. Research on assimilation character to joint HMs pollution by different crops. *Agro-Environmental Protection* 17 (5), 193–196 (in Chinese).
- Wu, Y.Y., Yu, G.Y., 1998a. The effect to paddy growth by joint pollution of Cd, Pb, Cu, Zn and As. *Agro-Environmental Protection* 17 (2), 49–54 (in Chinese).
- Wu, Y.Y., Yu, G.Y., 1998b. The transportation of joint pollution of Cd, Pb, Cu, Zn and As. *Acta Scientiae Circumstantiae* 18 (4), 407–414 (in Chinese).
- Xia, Z.L., Mu, C.R., 1984. The effects to tobacco and corn by interactive effects of Cd, Zn, Pb. *Journal of Ecology* 4 (3), 231–235 (in Chinese).
- Xu, H.N., Xu, J.L., 1993. The effect to wheat by heavy metals pollution in soil ecosystem. *Chinese Environmental Sciences* 13 (5), 367–371 (in Chinese).
- Xu, J.L., Yang, J.R., 1995. The heavy metals in land ecosystem. Chinese Environmental Sciences Publication House, Beijing (in Chinese).
- Zhao, Z.Q., Niu, X.F., 2000. The biological mechanism of the restoration of injured plants by toxic metals in environment. *Progress of Environmental Sciences* 13 (5), 54–57 (in Chinese).
- Zhen, C.R., Chen, H.M., 1990. The transport of heavy metals from soil–water system and effect to paddy growth. *Journal of Environmental Sciences* 10 (2) (in Chinese).