

Distribution of metals in soils from uncultivated land, soils from rice fields and in rice grown in the area of an industrial complex with metal smelting and processing facilities in Hunan Province, China

Kevin Brigden, Samantha Hetherington, Mengjiao Wang & David Santillo

Greenpeace Research Laboratories Technical Report 04/2014, April 2014

Contents

Executive Summary.....	2
1. Introduction	5
2. Sampling program.....	6
Soil samples.....	6
Water samples	7
Rice samples.....	7
3. Methodology.....	8
4. Results and Discussion	8
4.1. Uncultivated and not artificially disturbed soil.....	8
4.2. Farmed soil, irrigation water and wastewater samples.....	11
4.3. Rice.....	16
5. Conclusions	19
6. References	22
Appendix 1: Details of methodologies.....	23

Greenpeace Research Laboratories
School of Biosciences
Innovation Centre Phase 2
Rennes Drive
University of Exeter
Exeter EX4 4RN, UK

Executive Summary

Contamination of soil with a number of toxic metals, including cadmium and lead, is known to be an existing problem for many parts of Hunan Province, China. High levels of these metals have also been reported for rice grown in many parts of the province.

Metal smelters have the potential to emit significant quantities of metals to the atmosphere where adequate pollution controls are not in place, and deposition of emitted metals can result in contamination of the environment, particularly in the local vicinity of the smelter. This emission route, particularly for non-ferrous metal smelters, has been reported to be a major contribution to cadmium and lead contamination in parts of Hunan province in recent years.

This study investigated metal concentrations in surface soils, waters and rice crops in the vicinity of an industrial complex in Hunan Province, within which are situated a number of non-ferrous metal smelters and processing facilities. Samples analysed for toxic metal contaminants included:

- soils from land which was both uncultivated and not artificially disturbed (herein referred to as 'uncultivated soil'), from sites located between 200m and 2.5 km from the complex to the east, west, south and northwest, to look for signs of significant deposition of metals emitted to air;
- soils from rice fields in the same areas, together with rice grown on that land and
- surface waters used for irrigation and discharged waters of industrial origin associated with the complex, to determine their potential significance as vectors for metal contaminants.

Uncultivated soils were found to have high levels of many metals in a number of locations in the vicinity of the smelter compared to levels typically expected for soils from uncontaminated areas, most notably in the cases of cadmium, lead and arsenic, and to a lesser extent copper and zinc.

The clearest elevations in metal concentrations were observed for locations to the south of the complex, and to a lesser extent to the west of the complex. Meteorological data for the region indicate that the prevailing wind direction is from the north-east, and therefore metal deposition from emissions to air at the complex may be expected to occur predominantly to the south and west. The distribution pattern of elevated metal concentrations is consistent with atmospheric emissions from the complex making a significant contribution to elevated level of many metals in soils in areas close to the complex, including for cadmium.

However, the results also indicate the importance of other, as yet unidentified, contributory sources of metals to uncultivated soil in certain locations, most notably for cadmium, resulting in unexpectedly high concentrations in soils from some locations (e.g. W2500A/B collected approximately 2500m to the west of the complex adjacent to the Xiang Jiang River) as well as high spatial variability ('patchiness') in cadmium concentrations over relatively short distances for many locations.

For five metals (arsenic, cadmium, lead, manganese and zinc), strong correlations of concentrations in uncultivated soils indicate a common source, suggesting that emissions from the complex may be a major contributor to elevated concentrations of these five metals in uncultivated soils in this area.

The results for soil samples from fields in which rice is grown show some similarities to those from uncultivated land. High concentrations of a number of metals (especially cadmium but also zinc and lead and, at some locations, nickel and arsenic) were found in soils from some of the rice fields in the vicinity of the complex, substantially higher than concentrations found in the soil samples collected from rice fields in the two control areas located further from the complex. For all farmed soil samples, including those from the two control areas (YJ & DZ, located approximately 11km to the northwest and southeast respectively), the concentration of cadmium was equal to or exceeded the environmental quality standard in China for soils of this type (0.3 mg/kg), indicating general contamination of soils in the area. At some locations (YN, to the northeast), cadmium concentrations exceeded the standard by over 200 times.

The soils with the more elevated metal concentrations were predominantly centred on three main areas, one located less than 0.5 km to the south west of the complex (LP), another just over 1 km to the west/northwest of the industrial area (XM) and a third approximately 1 km to the northeast of the complex (YN). For two of these area (LP and XM), the patterns of metal contamination were consistent with the findings for uncultivated soils collected in the same areas indicating that emissions to air from the complex are significantly contributing to these elevated level in soils from these areas.

However, as for uncultivated soils, deposition of metals emitted to air from the complex could not explain the distribution of metal concentrations in soils from rice fields in all cases. For example, in some areas there were considerable variations in concentrations of some metals in farmed soils over relatively short distances. Furthermore, for two soil samples from one area to the northeast of the complex (YN), concentrations of certain metals were considerably higher than those for all other soils from rice field, including cadmium (65-92 mg/kg). These two soils did not have high concentrations of some other metals which were generally present at elevated levels in metal contaminated rice field soils. These anomalous results indicate that deposition from the atmosphere may not be the predominant source of metals to soils in some rice fields, most notably in YN, and that other unknown sources of metals predominate at these locations.

In addition to high levels of metals in many cases, farmed soil were also acidic, with some being highly acidic (pH 4.90 – 6.29, median 5.55), which is consistent with soil acidification that can result in the vicinity of non-ferrous metal smelters due to emission of sulphur oxides.

The study also found high concentrations of metals, including cadmium and zinc, in wastewaters discharged from the complex (up to 84 µg/l and 319 µg/l for cadmium and zinc, respectively) as well in surface water used for irrigation at some locations in the vicinity (up to 528 µg/l and 3210 µg/l for cadmium and zinc, respectively). These results indicate that, in addition to the deposition of metals emitted to the atmosphere, wastewater

discharges from the complex are contributing to inputs of cadmium and other metals to soils, including agricultural soils, in the vicinity of the complex.

Rice grown in many locations close to the complex contained high levels of cadmium, lead and arsenic. Rice from the areas surrounding the complex showed higher concentrations of cadmium and lead compared to rice from two control areas located considerably further from the complex. The cadmium levels were most notable, with all but one of the samples exceeding the maximum allowable level of cadmium in rice for human consumption in China (0.2 mg/kg), with the highest level exceeding the limit by 22 times.

The highest concentrations of both cadmium and lead were found in rice grown in an area less than 0.5 km to the south west of the complex (LP), and to a lesser extent in an area just over 1 km to the west/northwest (XM). For three rice samples from these areas, lead concentrations exceeded the allowable level of lead for rice in China (0.2 mg/kg).

Levels of cadmium and lead in rice were generally highest in areas where farmed soils had high concentrations of these metals, though this did not always follow a clear pattern. For example, rice samples with the highest cadmium levels did not originate from the area in which the highest cadmium levels were found in soil. For the data set as a whole, there was not a significant correlation ($p>0.05$) between concentrations in rice and in soil from the same locations for either cadmium or lead.

In contrast, although concentrations of arsenic were up to 3 times the maximum allowable level for rice intended for human consumptions (0.2 mg/kg) in more than half the samples, the results did not show an association between arsenic concentrations in rice samples and concentrations in soil samples from the same area, nor with distance from the complex. The underlying factors in elevated arsenic levels in rice from this area are not clear.

Consumption of rice with elevated levels of toxic metals, especially where levels exceed the national limits for human consumption in China, poses health risks. This is particularly the case for metals such as cadmium and lead which are highly toxic, able to have effects at relatively low levels of exposure, and are able to bioaccumulate such that levels can build up in the body through repeated exposure.

This study has demonstrated widespread contamination of soils in the vicinity of the industrial complex with a range of toxic metals, including agricultural soils, as well as metal contamination of rice grown in the area. The distribution of metals in soils around the industrial complex is consistent with the deposition of metals emitted to the atmosphere from the complex being a major contribution to soil metal levels, as may be expected in the vicinity of non-ferrous metals smelting activities. Furthermore, discharged wastewaters from the industrial complex are also releasing toxic metals to the immediate environment at a number of locations. At the same time, other unidentified sources and factors appear to be important influences of metal concentrations at some locations, and further research would be necessary to investigate such factors in more detail.

While ongoing releases of metals from facilities within the complex continue, both to air or *via* wastewater discharges, elevated metal levels in the surrounding environment can be expected to persist and most likely increase, with the associated accumulation of certain

metals in rice grown in the contaminated area. A reduction, and ultimate cessation, of emissions and discharges will be required to prevent further inputs of metals to this already contaminated environment. Reductions could be achieved to a large extent through the use of adequate pollution control devices, with the appropriate recycling or disposal of captured materials, though measures will also be required to reduce the demand for materials produced within the metal smelting facilities located within the industrial complex.

Conversely, the installation of additional metal smelting facilities with similar levels of pollution control to those employed at the existing facilities, can be expected to result in even greater inputs of metals to the surrounding environment, and the likelihood of increased impacts on crops grown in the area.

1. Introduction

Widespread contamination of soil with a number of metals is known to be an existing problem in many parts of Hunan Province, China (Huang et al. 2004, Wei et al. 2009). This includes cadmium and lead which have been found at levels above the national standard for agricultural soils in numerous locations within the province, with reported concentrations of over 90 mg/kg and 1800 mg/kg for cadmium and lead respectively (Huang et al. 2004). Cadmium and lead are toxic even at low levels of exposure, which are able to enter food chain, and for which levels can build up in the body through repeated exposure and have irreversible effects (ATSDR 2007, 2012). Furthermore, high levels of these metals have been reported in rice grown in Hunan province, often exceeding maximum allowable level of cadmium in rice for human consumption (Huang et al. 2004).

Numerous studies have demonstrated that metal smelters can emit significant quantities of metals to the atmosphere, and that deposition of emitted metals can result in elevated metals concentrations in surface soils in the vicinity of the smelters (Douay et al. 2009 and references therein, Kozlov & Zvereva 2007). This has also been observed in the vicinity of such facilities in Hunan Province (Wei et al. 2009). Data for Hunan province for the period from 1996 to 1999 indicate that the majority of emissions of cadmium and lead during that time resulted from metal smelting and processing, particularly for non-ferrous metals (Huang et al. 2004). Similarly, it has been reported that data gathered under official monitoring programmes indicate that a large proportion of agricultural irrigation water in Hunan Province was polluted with metals during the same period, including cadmium and lead, as well as other metals including arsenic, zinc and copper. Concentrations reportedly often exceeded national standards (Huang et al. 2004).

It has long been known that rice plants grown in metal contaminated soils can take up certain metals, particularly cadmium, but also other metals including lead (Williams et al. 2009), resulting in elevated levels in the grain. The presence of rice with elevated concentrations of these metals has been previously reported in other parts of Hunan Province (Huang et al. 2004).

This study was carried out to investigate the concentrations of metals in surface soil from land which was both uncultivated and not artificially disturbed (herein referred to as 'uncultivated soil') and regularly cultivated soils in the vicinity of an industrial complex in Hunan Province within which are situated a number of non-ferrous metal smelters and

processing facilities, as well as concentrations of metals in rice grown in areas close to the complex. Samples of surface water used for irrigation and of discharged waters of industrial origin were also analysed in order to determine the potential significance of water as a vector for metal contaminants.

2. Sampling program

Samples of surface soil from rice growing fields and from uncultivated / not artificially disturbed land, surface water and industrial wastewater were collected in July and August 2013. In addition, samples of rice grown in the same locations as some of the soil samples were collected over the same period.

Soil samples

Samples of surface soil from the top 2 cm of soil were collected from two types of location. 21 samples of soil were collected from farmed fields in the vicinity of the industrial complex in which rice was being grown. Samples of rice were also collected from some of these locations. In addition, 32 samples of surface soil were also collected from areas which were not cultivated, located at various distances from the complex along 4 transect lines radiating from the complex. These samples were collected to determine the concentrations of metals in uncultivated soils in areas around the industrial complex, and to provide insight as to whether deposition of metals which had been emitted to the air from the industrial complex was a significant factor in elevated metal levels in soils in the vicinity of the complex. The locations from which all samples were collected are given in Figure 1.

The soils from cultivated land were collected from rice fields in five areas with close proximity to, and surrounding, the industrial complex (referred to as LP, XM, SQ, YN and YQ). In addition, samples of soil were collected from rice fields in two areas located further from the industrial complex, to provide an indication of metal concentrations in 'control' locations, which are likely to be considerably less impacted by atmospheric releases or discharges to water of metals from the complex. These were collected from an area approximately 11 km northwest from the industrial complex (YJ) and another area approximately 11 km to the southeast (DZ). For each of the seven areas, three samples of cultivated soil were collected (S1-S3). The sample codes for individual samples of cultivated soil, the area from which each sample was collected, together with the dates on which they were collected, is given in table 1a.

The samples of uncultivated soil were collected from locations to the east (E), west (W), south (S) and northwest (NW) from the industrial complex, at locations approximately 200m, 500m, 1000m and 2500m in each of the four directions. For each location, two samples of soil were collected in close proximity to each other.

The sample codes for the individual samples of uncultivated soil (which include the direction (E, W, S or NW) and approximate distance in metres from the complex from which each sample was collected), are given in table 2a, together with the dates on which they were collected.

Water samples

Samples of water were collected from different location in the vicinity of the industrial complex. Water used to irrigate farmed land was collected from some of the areas from which samples of cultivated soil and rice were also collected, to determine whether irrigation water was contributing at the time to elevated metals levels in farmed land and crops in the both test (SQ, XM, YQ and YN) and control areas (YJ and DZ).

In two areas (LP and SQ) located close to the perimeter of the complex, samples of wastewater were collected from discharge pipes/channels (LPW2, SQW2), and from reservoirs connected to them (LPW1, SQW1), as well as from an adjacent wastewater holding tank (LPW3). Details of all water samples are provided in Table 3.

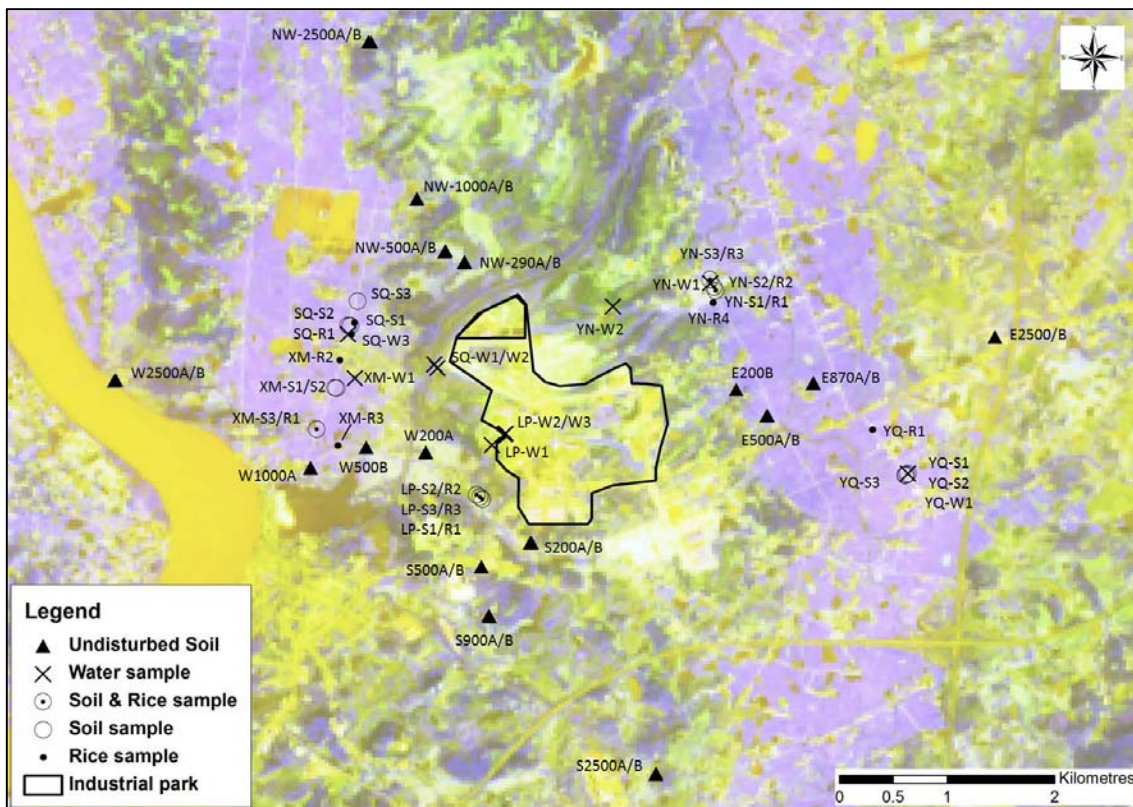


Figure 1 – Map showing the locations of samples of soil from field where rice was being grown, uncultivated soil from uncultivated land, surface water and rice. Samples collected in the YJ and DZ areas are not shown as these are outside the area shown on this map

Rice samples

Where possible, samples of rice were collected from the same location as samples of soil from farmed land, in an attempt to determine whether, and to what extent, the metal concentrations in the rice samples were correlated with concentrations in the corresponding soils in which the rice was grown. However, this was not possible in all cases, in part because the maturity of the rice plants varied from location to location. In these cases, some samples of rice that had been grown in the area, but perhaps not in the same

precise location as a soil sample, were collected to provide an indication of metal concentrations in rice from the area in general. See Table 4 for details.

As for farmed soils, samples of rice were also collected from the two control areas located further from the industrial complex; YJ (approximately 11 Km northwest from the industrial complex) and DZ (approximately 11 Km southeast from the industrial complex). For each of these two areas, a sample of rice was collected from three locations from which a sample of soil was also collected. In addition, a single sample of rice was collected at an earlier date from the DZ area, though the precise growing location is not known (DZ04).

3. Methodology

Heavy metal concentrations were determined for all soil and water samples by ICP atomic emission spectroscopy (AES) following acid digestion and using appropriate certified reference materials in addition to intra-laboratory standards. For water samples, reported concentrations are of dissolved forms determined for filtered samples.

Concentration of arsenic, cadmium, lead and mercury were determined in rice samples at an independent laboratory employing the following methods; GB/T 5009. 11-2003, 15-2003, 12-2010 and 17-2003, Chinese National Food Safety Standards for the determination of arsenic, cadmium, lead and mercury in foods respectively.

4. Results and Discussion

Results are presented below in three sections; 1) for samples of uncultivated soil, 2) for samples of soil from land on which rice is grown, as well as samples of irrigation water and industrial wastewaters, and 3) rice samples. Concentrations of metals (mg/kg dry weight) in uncultivated soils and cultivated soils are given in Tables 1a & 2a respectively, with concentrations in all water samples ($\mu\text{g/l}$) in Table 3, and in rice samples in Table 4.

4.1. Uncultivated and not artificially disturbed soil

There was good agreement between the concentrations of the majority of metals determined in the two adjacent samples of uncultivated soils collected at the 16 locations. However, there were examples where the concentration of certain metals in one sample was more than double the concentration in the other sample from the same location. This was most notable for cadmium, where such differences were found for 8 of the 16 locations. These data indicate that concentrations of cadmium in surface soils vary significantly over relatively short distances in many areas surrounding the industrial complex. Such variations were less commonly encountered for other metals.

In absolute terms, a number of metals were found at high concentrations at some locations compared to levels typically expected for uncultivated soils from uncontaminated areas, most notably in the cases of cadmium, lead and arsenic, and to a lesser extent copper and zinc.

The clearest elevations in metal concentrations were observed in samples of uncultivated soil collected from locations to the south of the complex, and to a lesser extent to the west of the complex. This pattern is consistent with meteorological data for the region, which indicate that the prevailing wind direction is from the north-east (Hengyang 2012), such that metal deposition from emissions to air at the complex may be expected to occur predominantly to the south and west.

For samples collected to the south, concentrations of cadmium were highest in samples at 500m and generally decreased with distance from the complex. Concentrations were, nonetheless, still elevated above expected background values in samples collected approximately 2500m from the complex (1.2-1.7 mg/kg, S2500A/B). A similar pattern was found for concentrations of arsenic, lead and, to some extent, zinc.

For samples collected along the transect to the west, the pattern was less clear. One sample collected approximately 500m from the complex had a particularly high cadmium concentration (4.7 mg/kg, W500A), though the second sample from this area had a considerably lower level (0.7 mg/kg, W500B). Though cadmium levels decreased at around 1000m, concentrations increased again in samples collected 2500m from the complex (W2500A/B). The concentrations of zinc with distance from the complex followed a similar pattern to those of cadmium.

The two samples collected approximately 2500m west from the complex (W2500A/B) also contained higher levels of other metals than all other samples on the west transect, most notably arsenic, copper, lead and manganese. Information collected since sampling indicates that the adjacent Xiang Jiang River is known to flood the area at times, though whether this could explain the higher concentrations of metals in the soils is not known.

Compared to samples collected to the south and west from the complex, concentrations of metals were generally lower for samples collected to the east, and particularly to the northwest of the complex. For samples collected to the northwest, there were no noticeable pattern between metal concentrations and distance from the complex. Furthermore, the metal concentrations across all samples were amongst the lowest for the samples of uncultivated soils.

Correlations between concentrations of individual metals

There were significant correlations between the concentrations of many metals ($p < 0.01$) in samples of uncultivated soils from all locations, as shown in Table 1b.

Concentrations of arsenic, cadmium, lead, manganese and zinc were all correlated with one another, suggesting that concentrations of these five metals are all predominantly influenced by inputs from a common source. Given the proximity of the industrial complex and the potential for atmospheric emissions from metal smelters such as those located in the complex to impact soils in their vicinity, it seems likely that emissions from the complex are a significant contributor to the elevated concentrations of these five metals detected in many of the uncultivated soils in this area.

Sample code	W200A	W200B	W500A	W500B	W1000A	W1000B	W2500A	W2500B	E200A	E200B	E500A	E500B	E870A	E870B	E2500A	E2500B	NW290A	NW290B	NW500A	NW500B	NW1000A	NW1000B	NW2500A	NW2500B	S200A	S200B	S500A	S500B	S900A	S900B	S2500A	S2500B	
Sampling date	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	23/8	
Arsenic	10	12	<10	13	12	21	148	111	11	13	<10	<10	14	10	29	14	<10	<10	11	14	<10	14	<10	<10	11	<10	22	31	15	18	10	11	
Barium	91	101	1100	361	125	274	1110	1000	167	120	95	79	662	1000	1320	384	80	90	66	69	76	159	100	73	3100	3590	1230	1590	1660	1120	155	143	
Cadmium	<0.2	0.3	4.7	0.7	0.4	1.2	12.3	12.2	0.9	0.3	<0.2	0.3	0.7	0.9	1.0	0.5	0.5	0.3	<0.2	<0.2	<0.2	0.6	0.6	<0.2	1.3	1.2	2.0	5.4	2.9	1.4	1.2	1.7	
Chromium	39	41	27	30	35	26	37	30	38	40	33	31	36	37	29	34	40	40	31	40	37	49	45	29	38	36	42	40	42	35	48	36	
Cobalt	6	6	10	15	10	6	13	11	10	10	5	4	11	9	14	11	5	4	3	5	7	10	9	9	6	6	5	6	31	11	29	20	
Copper	14	14	17	17	13	17	60	46	26	21	13	11	21	22	23	49	18	16	15	21	14	16	10	10	42	44	27	48	35	37	20	18	
Lead	17	18	28	34	23	35	162	123	38	23	23	19	27	34	35	20	27	25	18	30	17	38	24	15	54	57	57	175	74	83	31	51	
Manganese	79	72	363	414	219	300	2130	1525	161	172	81	90	520	431	549	413	80	71	44	73	187	258	161	149	67	58	79	192	472	253	572	617	
Molybdenum	<1	<1	<1	<1	<1	<1	2	1	<1	<1	<1	<1	<1	<1	2	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	1
Nickel	15	14	13	20	12	10	33	26	15	15	10	9	14	15	24	21	13	13	9	13	14	12	13	12	13	13	12	15	28	14	43	27	
Vanadium	46	48	27	31	39	29	50	38	44	43	35	31	31	34	32	38	45	44	35	48	37	46	33	29	41	41	46	46	43	34	40	40	
Zinc	63	72	213	78	59	97	408	352	89	64	46	43	84	102	83	71	63	53	39	53	49	67	57	44	113	119	114	202	418	100	137	108	

Table 1a. Concentrations of metals (mg/kg dry weight) in samples of soil from uncultivated land in the vicinity of the industrial complex, collected at different distances to the west (W), east (E), northwest (NW) and south (S) from the complex.

	Arsenic	Barium	Cadmium	Chromium	Cobalt	Copper	Lead	Manganese	Molybdenum	Nickel	Vanadium	Zinc
Arsenic	1.000											
Barium	0.214	1.000										
Cadmium	0.954*	0.225	1.000									
Chromium	-0.212	-0.045	-0.212	1.000								
Cobalt	0.012	0.044	0.102	0.223	1.000							
Copper	0.667*	0.651*	0.647*	-0.006	0.145	1.000						
Lead	0.729*	0.461*	0.809*	0.046	0.157	0.790*	1.000					
Manganese	0.918*	0.105	0.858*	-0.152	0.389	0.564*	0.625*	1.000				
Molybdenum	0.063	0.027	-0.275	-0.439	0.425	-0.249	-0.524	0.196	1.000			
Nickel	0.430	0.075	0.445	0.195	0.825*	0.403	0.379	0.685*	0.522*	1.000		
Vanadium	0.220	0.056	0.197	0.685*	-0.008	0.334	0.335	0.083	-0.311	0.193	1.000	
Zinc	0.740*	0.417	0.840*	-0.004	0.504*	0.665*	0.751*	0.749*	-0.218	0.595*	0.221	1.000

Table 1b. Pearson correlations between different metals in samples of uncultivated soil samples, (*) showing correlations significant at the 0.01 level (two tailed)

Although additional correlations are shown in Table 1b, these tend to be between individual pairs of metals rather than for groups where each member is correlated with all others in the group, and therefore the factors affecting these other correlations are less clear. For example, concentrations of chromium and vanadium are correlated with one another but not with any of the other quantified metals. This could indicate that the chromium and vanadium contents of the soils in the area arise from the minerals naturally present in the soil, rather than from inputs from industrial activities

4.2. Farmed soil, irrigation water and wastewater samples

The results for soil samples from fields in which rice is grown show some similarities to those from uncultivated land. A number of metals (especially cadmium but also zinc and lead and, at some locations, nickel and arsenic) were found at high concentrations in some of the rice fields in the vicinity of the complex, substantially higher than concentrations found in the soil samples collected from rice fields in the two control areas (YJ and DZ).

The samples with elevated metal concentrations were predominantly centred on three main areas; LP (less than 0.5 km to the south west of the complex), XM (just over 1 km to the west/northwest of the industrial area) and YN (approximately 1 km to the northeast of the complex). Samples from the SQ area, located to the northwest of the industrial area and adjacent to the XM area, also contained somewhat elevated levels of cadmium.

For samples of soil from cultivated fields in the LP and XM areas, located to the south and west of the complex respectively, the patterns of metal contamination are consistent with the findings for uncultivated soils collected in the same vicinity.

For cadmium, zinc, lead and arsenic, higher concentrations were found in samples from LP compared to XM. Within each of these two areas, the concentrations of metals other than cadmium were comparable between the three individual samples, with concentrations varying by up to a factor of 2. In the case of cadmium, concentrations were more variable for samples from XM (0.9 – 5.6 mg/kg) compared to LP (2.5 – 6.9 mg/kg). The reason for such variations in farmed soil over relatively short distances in the XM area is not clear, including tilling, addition of fertilisers or other materials and irrigation.

High levels of certain metals were also found in samples of water collected from the LP area. Wastewater from a discharge pipe on the perimeter of the complex (LPW2) contained high concentrations of both cadmium (84 µg/l) and zinc (319 µg/l) compared to concentrations typically found in uncontaminated surface waters. Even higher concentrations of cadmium (528 µg/l) and zinc (3210 µg/l), as well as high concentrations of lead, manganese and to a lesser extent nickel, were found in water collected from an adjacent reservoir (LPW1) which is used at times for irrigation. These results indicate that cadmium and other metals are released to the environment in wastewaters from the industrial complex, in addition to releases to the atmosphere. A sample of water from a holding tank in the same area (LPW3) did not contain high metal concentrations.

A sample of irrigation water was collected from the XM area close to where the soil and rice samples were collected. Concentrations of cadmium, zinc and vanadium in the irrigation

water were somewhat higher than those in irrigation waters from other areas in the vicinity, including from the two control areas (YJ and DZ), though lower than in the water samples from the LP area.

Although irrigation water collected from the SQ area (SQW3) did not contain elevated metal concentrations, reasonably high concentrations of cadmium and zinc were found in water (SQW2) collected from a drain originating from a facility within the complex, with even higher concentrations of these metals present in water from an adjacent reservoir (SQW1). Water from the drain (SQW2) also had a high vanadium concentration, though this was not reflected in the reservoir water. One of the facilities within the industrial complex is known to manufacture vanadium based materials, and this would seem to be a likely source of the vanadium found in the water within the drain. According to available information, water from the drain, does not flow into the reservoir, although water from both sources subsequently flow to cultivated land via a single channel. The absence of vanadium at a detectable concentration in the reservoir water indicates that cadmium and zinc detected in the reservoir and drain arise from separate sources.

The results for samples from the YN area to the northeast indicate that the situation is somewhat different. Two of the three soil samples (YNS1 and YNS2) contained considerably higher concentrations of cadmium (65-92 mg/kg), as well as zinc (517-566 mg/kg), nickel (61-63 mg/kg) and molybdenum (3-5 mg/kg) compared to all other soil samples in this study. In other areas in which high levels of zinc and cadmium had been found, these were generally accompanied by high concentrations of other metals, including lead and arsenic; this was not the case for YNS1 / YNS2. Similarly, the elevated nickel and molybdenum concentrations were unique to these two samples amongst the cultivated soil samples.

In contrast, the third sample of cultivated soil from the YN area (YNS3), collected approximately 100m from the other two samples, did not contain such high metal concentrations. Cadmium was present at a level (1.7 mg/kg) above typical background for uncontaminated soils, but still far lower than in YNS1 and YNS2.

The reasons for the very high levels of metals, including cadmium, in two of the three samples from this area is not known. However, the far lower levels in the adjacent sample (YNS3) as well as the inconsistency between the very high concentrations in YNS1/YNS2 and the general pattern of metal distribution in soils in the vicinity of the complex indicate that deposition from the atmosphere is not the predominant source of metals to soil in the locations where YNS1 & YNS2 were collected.

Irrigation water (YNW1) and water from a reservoir (YNW2) from the YN area did not contain high levels of those metals which were found at elevated levels in cultivated soil samples, suggesting that these water sources do not significantly contribute to contamination of the farmed fields with cadmium or other metals.

The possibility that other contaminated liquid or solid materials have been deposited on these fields at some time in the past cannot be evaluated.

In addition to high levels of metals in many cases, the samples of farmed soil also had reasonably high acidity, with pH values ranging from 4.90 – 6.29 (median 5.55). Atmospheric emission from non-ferrous metal smelters, predominantly sulphur oxides, can result in considerable acidification of soils in the vicinity of the smelter, and this may be a significant contribution to the soil acidity observed. Due to their composition, soils in Hunan province are some of the more vulnerable in China to acidification due to acid deposition (Tao et al. 2002).

The mobility of many metals, as well their uptake into crops, is generally increased in soils with higher acidity. For this reason, Chinese national standards for concentrations of metals in agricultural soil depend on the soil pH, with lower limits for more acidic soils (those with lower pH). The most stringent limit is set for soils with pH below 6.5, which applies to all farmed soils in this study. For such soils, the regulation sets an environmental quality standard of 0.3 mg/kg for cadmium (MEP 1995).

For all farmed soil samples, including those from the two control area (YJ & DZ), the concentration of cadmium was equal to or exceeded this standard, indicating general contamination of soils in the area. Cadmium concentrations in some areas far exceeded the limit, most notably for two samples from YN (YNS1 & YNS2) where concentrations were over 200 times higher. For these two samples, the zinc concentrations also exceeded the standard (200 mg/kg), though to a lesser extent. In the LP and XM areas, cadmium concentrations exceeded the standard by up to approximately 20 times in each area. Though higher lead and arsenic concentrations were found in soils from some areas compared to others, no samples exceeded the limit for lead (250 mg/kg) or arsenic (30 mg/kg) in this type of soil.

Correlations between concentrations of individual metals

For the soils from farmed land, the pattern of correlations between concentrations of individual metals was less clear compared to those for the uncultivated soils samples. This may be due to the diversity of soil amendments and disturbances arising from farming activities, including tilling, addition of fertilisers or other materials and irrigation.

As was the case for uncultivated soils, concentrations of cadmium in farmed soils were correlated with those of zinc. In contrast, cadmium was not correlated with arsenic, copper or lead for farmed soils. Similarly, concentrations of arsenic in farmed soils were correlated with those of copper and lead, as in uncultivated soils, though not with zinc.

Although concentrations of molybdenum in farmed soils were correlated with all other metals, this is an artefact of molybdenum concentrations being below detection limits in all but three samples rather than indicative of a common source.

area	YJ*			DZ*			LP			SQ			XM			YQ			YN			EQS
Sample code	YJ S1	YJ S2	YJ S3	DZ S1	DZ S2	DZ S3	LPS1	LPS2	LPS3	SQS1	SQS2	SQS3	XMS1	XMS2	XMS3	YQS1	YQS2	YQS3	YNS1	YNS2	YNS3	
Sampling date	22/08	22/08	22/08	22/08	22/08	22/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08	24/08
pH	5.16	5.52	4.90	5.36	5.03	4.96	5.47	5.90	5.72	5.83	5.84	6.14	5.96	5.74	5.55	5.83	6.29	6.12	5.25	5.46	5.30	<6.5
Arsenic	<10	<10	<10	<10	<10	<10	21	14	19	11	<10	<10	11	13	10	12	11	10	10	11	12	30
Barium	95	92	92	85	85	79	2470	1200	2310	1400	520	636	1060	789	2840	725	1680	737	1290	301	414	
Cadmium	0.3	0.3	0.3	0.3	0.4	0.3	5.5	2.5	6.9	0.7	0.5	1.4	1.0	0.9	5.6	0.4	0.4	0.3	92	65	1.7	0.30
Chromium	40	37	37	71	74	72	39	37	42	37	35	33	33	38	23	43	50	44	39	40	42	
Cobalt	11	11	9	13	13	13	6	5	6	7	7	8	8	8	7	12	11	11	8	7	6	
Copper	21	22	18	31	32	30	26	24	26	21	19	17	20	20	24	22	25	22	24	23	21	50
Lead	21	22	19	33	32	29	108	82	94	29	30	30	38	38	41	27	30	29	23	26	26	250
Manganese	227	176	141	217	151	179	94	73	63	95	76	198	123	143	127	258	146	175	161	130	136	
Molybdenum	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	5	3	1	
Nickel	20	20	18	18	18	17	13	11	14	15	15	13	14	15	11	19	21	19	63	61	17	
Vanadium	39	39	37	47	49	46	43	34	46	41	42	34	40	45	27	45	49	45	54	47	47	
Zinc	68	70	61	70	73	67	191	118	245	91	88	73	109	107	130	60	68	65	566	517	73	200

Table 2a. Concentrations of metals (mg/kg dry weight) in samples of soil from land where rice is grown in areas surrounding the industrial complex. * control village located further from the complex. The Environmental Quality Standards (EQS) for certain metals for Class II soils with soil pH < 6.5 (MEP1995)

	Arsenic	Barium	Cadmium	Chromium	Cobalt	Copper	Lead	Manganese	Molybdenum	Nickel	Vanadium	Zinc
Arsenic	1.000											
Barium	0.472	1.000										
Cadmium	-0.225	0.063	1.000									
Chromium	0.161	-0.451	-0.127	1.000								
Cobalt	-0.489	-0.564	-0.219	0.703*	1.000							
Copper	0.608*	0.065	0.044	0.800*	0.395	1.000						
Lead	0.917*	0.654*	-0.127	-0.108	-0.560	0.277	1.000					
Manganese	-0.481	-0.518	-0.037	0.324	0.759*	0.039	-0.582	1.000				
Molybdenum	-0.966	0.806*	0.977*	-0.988	0.999*	0.992*	-0.917	0.757*	1.000			
Nickel	-0.325	-0.158	0.950*	-0.002	-0.016	0.042	-0.307	0.116	0.884*	1.000		
Vanadium	0.028	-0.215	0.438	0.545	0.286	0.403	-0.120	0.116	0.851*	0.526	1.000	
Zinc	-0.016	0.212	0.960*	-0.179	-0.372	0.082	0.098	-0.213	0.910*	0.885*	0.399	1.000

Table 2b. Pearson correlations between different metals in samples of soil samples from cultivated field in which rice is grown, (*) showing correlations significant at the 0.01 level (two tailed)

Area	YJ*	DZ*	LP			SQ			XM	YQ	YN	
Sample code	YJ W1	DZW1	LP W1	LP W2	LP W3	SQ W1	SQ W2	SQ W3	XMW1	YQW1	YNW1	YNW2
Description	irrigation water	irrigation water	water from reservoir (almost dry)	wastewater pipe discharging into reservoir	waste water tank	reservoir water	drain between reservoir & factory CD	irrigation water	irrigation water	irrigation water	irrigation water	reservoir water
Arsenic	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Barium	12	<5	91	40	29	44	13	113	122	436	50	19
Cadmium	<2	<2	528	84	<2	9	4	<2	2	<2	<2	<2
Chromium	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
Cobalt	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Copper	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20	<20
Lead	<50	<50	121	<50	<50	<50	<50	<50	<50	<50	<50	<50
Manganese	<2	<2	1080	46	5	891	3	24	<2	<2	<2	70
Nickel	<10	<10	21	<10	<10	13	<10	<10	<10	<10	<10	<10
Vanadium	<10	<10	<10	<10	<10	<10	599	<10	24	<10	<10	<10
Zinc	19	33	3210	319	92	792	111	53	84	16	31	32

Table 3: Concentrations of metals (µg/l) in filtered samples of irrigation water and wastewater. * control village located further from the complex.

area	YJ*			DZ*				LP			SQ		XM			YQ	YN				
Rice sample	YJR1	YJR2	YJR3	DZR1	DZR2	DZR3	DZR4	LPR1	LPR2	LPR3	SQR1	SQR2	XMR3	XMR2	XMR1	YQR1	YNR1	YNR2	YNR3	YNR4	LIMIT
Sampling date	22/8	22/8	22/8	08/7	07/8	07/8	01/7	22/8	22/8	22/8	08/8	01/7	01/7	08/8	24/8	01/7	24/8	24/8	24/8	01/7	-
Same location as soil sample	YJ S1	YJ S2	YJ S3	DZ S1	DZ S2	DZ S3	-	LPS1	LPS2	LPS3	Near SQS1/S2	-	-	-	XMS3		YNS1	YNS2	YNS3	-	-
Arsenic rice	0.540	0.189	0.532	0.202	0.154	0.223	0.28	0.124	0.083	0.087	0.421	0.14	0.35	0.407	0.131	0.28	0.275	0.188	0.715	0.28	0.2
Cadmium rice	<0.005	0.028	0.012	0.033	0.07	0.020	0.019	2.723	4.393	3.826	0.666	1.2	0.81	1.604	1.573	0.88	1.858	0.293	0.064	0.43	0.2
Mercury rice	0.004	0.003	0.009	0.005	0.004	0.005	<0.01	0.005	0.006	0.005	0.009	<0.01	<0.01	0.009	0.006	<0.01	0.006	0.006	0.006	<0.01	0.02
Lead rice	0.061	0.047	0.069	0.082	0.086	0.069	0.02	0.274	0.270	0.166	0.275	0.073	0.13	0.368	0.179	0.047	0.154	0.123	0.135	0.03	0.2

Table 4 Concentrations of metals (mg/kg fresh weight) in rice grown in areas surrounding the industrial complex, indicating where samples of soil were also collected from the same location.

* control village located further from the complex.

4.3. Rice

The results from the analysis of arsenic, cadmium, mercury and lead in rice samples collected in the region, including from two control areas located approximately 11 km from the industrial complex, are given in Table 4, together with a summary of the average and range of concentrations for each area in Table 5.

For each metal, Table 5 also shows the maximum allowable concentration set for rice intended for human consumption in China (Ministry of Health 2012).

area	YJR1-R3*	DZR1-R4*	LPR1-R3	YNR1-R4	SQR2-R2	XMR1-R3	YQR1	Limit in food ⁽¹⁾
# samples	3	4	3	4	2	3	1	
Arsenic	0.420 0.189-0.540	0.215 0.154-0.28	0.098 0.083-0.124	0.365 0.188-0.715	0.281 0.14-0.421	0.296 0.131-0.407	0.28 -	0.2
Cadmium	0.014 <0.005-0.028	0.036 0.019-0.070	3.65 2.72-4.39	0.661 0.064-1.858	0.933 0.666-1.2	1.329 0.81-1.604	0.88 -	0.2
Mercury	0.005 0.003-0.009	0.004-<0.01 0.004-0.005	0.005 0.005-0.006	0.006 <0.01 - 0.006	0.007 <0.01-0.009	0.007 <0.01-0.009	<0.01 -	0.02
Lead	0.059 0.047-0.069	0.064 0.02-0.086	0.237 0.166-0.270	0.111 0.03-0.154	0.174 0.073-0.275	0.226 0.13-0.368	0.047 -	0.2

Table 5. Average and range of concentrations (mg/kg fresh weight) in samples of rice from each area, * control village located further from the complex. Average values were calculated using half the detection limit for non-detect values. (1) Ministry of Health 2012 (GB 2762-2012)

Cadmium

Amongst the four metals quantified, the most notable results are those related to concentrations of cadmium in samples of rice.

For rice collected from the two control areas, cadmium concentrations were in the range <0.005-0.028 mg/kg (YJR1-YJR3) and 0.019-0.070 mg/kg (DZR1-DZR4). These data are consistent with the finding that the concentrations of cadmium in farmed soils samples from each of the two areas were the lowest amongst the areas investigated in this study (0.3 mg/kg, YJS1-YJS3 and 0.3-0.4 mg/kg, DZS1-DZS3), as well as with the absence of cadmium above the detection limit in irrigation water from both areas (YJW1, DZW1).

Concentrations of cadmium in rice from all other locations were considerably higher, exceeding the maximum allowable level of cadmium in rice for human consumption (0.2 mg/kg, Ministry of Health 2012) in all but one sample (YNR3).

The highest cadmium concentrations were found in rice collected from LP, an area less than 0.5 km to the south west of the industrial area. Concentrations were in the range 2.72-4.36 mg/kg (LPR1-LPR3), exceeding the allowable level by between 14-22 times. Soil samples from the same locations (LPS1-LPS3) had some of the highest cadmium concentrations amongst the farmed soil samples (2.5 – 6.9 mg/kg). There is also evidence of cadmium contamination of water in this area (LPW1, LPW2), with one of these water sources being used at times to irrigate fields.

However, the association between cadmium concentrations in rice and in soils from this area did not follow a clear pattern. For example, the rice sample from LP with the highest

cadmium concentration (LPR2, 4.39 mg/kg) was associated with the soil sample (LPS2) which had the lowest cadmium concentration amongst the three samples from this area (2.5 mg/kg). The reason for this is not clear.

All three samples of rice from the XM area, just over 1 km to the west/northwest of the industrial area, also had high levels of cadmium (0.81-1.604 mg/kg), exceeding the legal limit by between 4 to 8 times. One of these rice samples (XMR1, 1.573 mg/kg cadmium) was collected from a location from which a sample of soil (XMS3) was also found to contain a high cadmium concentration (5.6 mg/kg). A similar level of cadmium was also found in a second sample of rice from the XM area (XMR2, 1.604 mg/kg), while a third rice sample collected from this area earlier in the year had approximately half the cadmium concentration (XMR3, 0.81 mg/kg).

Two other farmed soil samples from the XM area (XMS1, XMS2), both collected approximately 400m to the northeast of XMS3 (but still northwest of the complex), had notably lower cadmium concentrations (0.9-1.0 mg/kg), indicating variation in the degree of cadmium contamination for farmed soils in this area, which could have an impact on cadmium level for rice grown in the soils. The reason for this degree of variation in farmed soil cadmium concentrations over relatively short distances is not clear, but may be due in part to differences in farming activities in the fields.

Somewhat elevated cadmium concentrations, though lower than at XM, were found in rice from other areas in the vicinity of the industrial area. For rice samples from the YN area, located approximately 1 km to the northeast of the complex, high levels of cadmium were found in some samples, though a large variation was found between individual samples collected from adjacent fields. For three of the four samples, the cadmium concentration exceeded the legal cadmium limit for rice (0.2 mg/kg), with concentrations ranging from 0.293 mg/kg (YNR2) to 1.858 mg/kg (YNR1). Samples of soil from a field from which two of these three rice samples were collected contained the highest concentrations of cadmium found in this study (92.3 mg/kg, YNS1 and 64.6 mg/kg, YNS2). Soil from the location of the third rice sample (YNR4) was not analysed.

For one other location in the YN area, approximately 100m to the northwest, the concentration of cadmium was considerably lower in both rice (0.064 mg/kg, YNR3) and farmed soil from the same location (1.7 mg/kg, YNS3). The reason for the different finding for this location in the YN area is not clear.

In the case of cadmium, although elevated levels in rice were generally associated with elevated levels in soil collected from where the rice was grown, the most contaminated rice samples (LPR1-R3) did not originate from the areas with the most contaminated soils (YNS1/YNS2) for which cadmium concentrations were far higher than those for all other soil samples from rice growing locations.

Elevated cadmium levels were also found in rice grown in two other areas from which fewer samples were collected. Two rice samples (SQR1, SQR2) collected at different times from the SQ area, located northwest of the industrial area and adjacent to the XM area, contained 0.666 and 1.2 mg/kg cadmium, exceeding the allowable limit by 3 and 6 times, respectively. Soil samples from a field in the SQ area, though not one from which rice

samples were collected, contained somewhat elevated cadmium levels (0.5-1.4 mg/kg, SQS1-SQS3). In addition, water from a reservoir used to supply the SQ area (SQW1) was also found to contain an elevated cadmium level, though it is not known if these water sources are used for irrigation of the fields sampled.

In addition, one rice sample (YQR1) collected in the earlier batch of samples from the YQ area, located approximately 2 kilometres to the east of the complex, contained 0.88 mg/kg cadmium, over 4 times the maximum allowed level. The precise location from which the rice sample (YQR1) was collected is not known. Soil samples collected from farmed fields in the YQ area at a later time (YQS1-YQS3) had cadmium concentrations similar to those in the two control areas (YJ and DZ), and cadmium was not detected in irrigation water from this area. The reason for the high level of cadmium in the single rice sample is not known.

Lead

As for cadmium, the average concentrations of lead in rice samples collected from the two control areas (0.059 mg/kg, YJ and 0.064 mg/kg, DZ) were lower than for all other areas with the exception of YQ (0.047 mg/kg).

The highest average lead concentrations were found in rice samples from LP (0.237 mg/kg) and XM (0.226 mg/kg), the two areas for which the highest cadmium concentrations were also found in rice, though there was notable variation in concentrations between individual samples from XM. The precise growing location is not known for two of the three rice samples from XM.

For two samples from LP (LP01, 0.274 mg/kg and LP02, 0.270 mg/kg) and a single sample from XM (XM02, 0.368 mg/kg), the lead concentrations exceeded the allowable level for rice (0.2 mg/kg). In addition, a single sample from SQ exceeded this limit (SQ01, 0.275 mg/kg)

For LP, an area less than 0.5 km to the south west of the industrial area, farmed soils collected from the same locations as the rice samples had the highest lead concentrations amongst all areas. Similarly, farmed soils from XM had lead concentrations slightly higher than other areas. These results indicate that there may be a link between elevated levels of lead in rice and in farmed soil for these two areas which are located close to the western side of the industrial area.

For two areas, YN and SQ, rice had elevated lead levels, though there was notable variation in rice concentrations between individual samples for each area. However, concentrations of lead in farmed soils from these areas were similar to those for both the two control areas (YJ and DZ).

As for cadmium, there was no significant correlation ($p > 0.05$) between the rice and soil levels for the whole data set, when comparing the average rice and average soil lead concentrations for each area.

Arsenic

Concentrations of arsenic exceeded the maximum allowable level for rice intended for human consumptions (0.2 mg/kg) in more than half the samples. However, average concentrations in rice samples collected from areas closer to the industrial complex were

similar, and in many cases lower than, those for samples from the control areas. Furthermore, considerable variability was found in arsenic concentrations for rice samples from each area.

Overall, the data do not indicate any association between concentrations of arsenic in rice samples and concentrations in soil samples from the same area. Concentrations in farmed soil samples were similar for all areas, with the exception of LP from where soil samples had somewhat higher arsenic concentrations. However, the arsenic concentrations in rice samples from LP were the lowest of all areas, including the two control areas.

Mercury

There were no clear patterns in the concentrations of mercury in rice samples from different areas, and higher levels were not found in samples from areas closer to the complex compared to those collected from the two control areas (YJ and DZ). Concentrations in all samples were below the maximum allowable level for rice intended for human consumption (0.02mg/kg).

5. Conclusions

This study has demonstrated that there is metal contamination of soils in many areas in the vicinity of the industrial complex, and that rice grown in these areas frequently contains elevated levels of metals, including cadmium and lead.

Samples of uncultivated soil with elevated concentrations of certain metals (cadmium, arsenic, lead, and to some extent zinc) were predominantly those from locations to the south, and to a lesser extent to the west, of the complex. However, elevated concentrations were also found in some locations to the east of the complex.

These data, together with meteorological data indicate that the predominant wind direction in the area is from the northeast, are consistent with a distribution pattern due to deposition of metals emitted to the atmosphere from the industrial complex. This suggests that sources within the complex are a significant contributor to elevated concentrations of metals in soil in this area, including cadmium.

However, the data also indicate that there are other important contributory sources of metals in certain locations, such as locations approximately 2500m to the west of the complex, which are known to be flooded periodically by the adjacent Xiang Jiang River. The data also show that cadmium concentrations in uncultivated soils can vary considerably over short distances in many of the areas surrounding the industrial complex, something which was generally not the case for other metals, and which cannot be explained by deposition of atmospheric metals.

For five metals (arsenic, cadmium, lead, manganese and zinc), soil concentrations correlate between all pairs of metals in the group, suggesting that emissions from the complex are a major contributor to elevated concentrations of these five metals in uncultivated soils in this area.

Similarly, in certain areas, agricultural soil from land where rice was being grown had high concentrations of cadmium, as well as zinc and lead. This was also observed for nickel and arsenic in individual areas. Concentrations of these metals were notably higher than for soils from equivalent locations in the two control areas located further from the complex.

This situation was found predominantly in three areas. For two of these areas, to the southwest and to the west/northwest, the data are consistent with the findings for uncultivated soils, which also show elevated concentrations predominantly to the south and west of the complex and at a similar distance from the complex. Just as for uncultivated soils, cadmium concentrations were found to vary more over short distances compared to other metals in some areas.

High levels of certain metals, particularly cadmium and zinc, were also found in samples of water collected from these, and some other, areas. These results indicate that discharged wastewater may make a significant contribution to inputs of cadmium and other metals to soils, including agricultural soils, in the vicinity of the complex, in addition to inputs due to deposition of metals emitted to the atmosphere from facilities in the complex.

Other evidence for inputs to agricultural land that are specific to the individual location was found in one other area (YN), to the northeast of the complex, where the highest concentrations by far of cadmium, zinc and some other metals were found in farmed soil. These anomalous data indicate that soil concentrations in these locations may be influenced by other specific but so far unidentified sources and do not predominantly arise from deposition of metals from the atmosphere. Irrigation water in the area was not found to be the source for these metals. This localised soil contamination could perhaps have arisen from deposition of other liquid or solid wastes/materials in the past, though no specific information is available to evaluate this possibility.

Overall, correlations between concentrations of certain metals for farmed soil, including cadmium, zinc, arsenic and lead, indicate some consistency with the findings for uncultivated soil that suggest a common source for these metals at most other sites, though with less certainty.

In addition to high metal concentrations, all samples of farmed soil were also found to be acidic (pH 4.90 – 6.29) which can result in increased mobility of many metals, as well as increased uptake into crops (ATSDR 2007, 2012). Soil in Hunan Province are some of the more vulnerable in China to acidification due to acid deposition (Tao et al. 2002), and it is possible that atmospheric emissions from non-ferrous metal smelters in the complex, including of sulphur dioxide, have made a considerable contribution to the acidification of soils in this area.

Chinese national standards set the most stringent limits for agricultural soils with these levels of acidity (pH<6.5). Concentrations of cadmium in many of the farmed soil samples in the current study exceeded the national standard, in some cases to a very large extent, with the highest concentrations being over 200 times the standard (0.3 mg/kg). The two most contaminated farmed soils also had zinc concentrations 2-3 times the zinc standard.

For rice, the most notable results were those related to concentrations of cadmium. Other than for the two control areas, cadmium concentrations in rice exceeding the maximum allowable level in rice for human consumption (0.2 mg/kg, Ministry of Health 2012) for all but one sample (YNR3).

In many instances, elevated cadmium levels in soil were associated with elevated cadmium levels in rice grown in the same location. The highest cadmium levels in rice, exceeding the allowable level by up to 22 times, were grown in areas where the highest cadmium concentrations in farmed soils were found and in some cases where discharged wastewater was found to be contaminated with cadmium. However, there was not always a clear pattern between levels in individual rice samples and those found in the environment in which it had been grown.

Similarly, lead concentrations in rice were higher in samples collected closer to the industrial complex compared to the two control areas, with the lead concentrations in four samples exceeding the allowable level for rice (0.2 mg/kg) by 1-2 times. Levels were generally highest in areas where farmed soils had higher lead concentrations and from where rice also had the highest cadmium levels (LP and XM). There were, however, notable variations in concentrations in rice between individual samples from adjacent locations.

Overall, although for some individual samples there was an association between the concentration of both cadmium and lead in rice and in the soil in which it was grown, for the whole set of samples taken together there was not a significant correlation for either metal ($p > 0.05$) between the rice and farmed soil concentrations, either comparing the average rice and average soil concentrations for each area, or comparing the concentrations for those individual samples where a soil and a rice sample were collected from the same location.

Arsenic concentrations in rice exceeded the maximum allowable level for rice intended for human consumption (0.2 mg/kg) in more than half the samples, though the data did not indicate an association between concentrations of arsenic in rice samples and concentrations in soil samples from the same area, nor with proximity to the industrial complex.

Taken together, the data from this study demonstrate that there is widespread contamination of soil in this area, including agricultural soil, with a range of toxic metals, as well as metal contamination of rice grown in the majority of the locations sampled. At a number of locations, discharged wastewaters from the industrial complex are also releasing toxic metals to the immediate environment. Furthermore, the distribution of metals in soils around the industrial complex is consistent with a hypothesis that deposition of metals emitted to the atmosphere from the complex is a significant contributory factor, as may be expected in the vicinity of non-ferrous metals smelting activities. At the same time, other unidentified sources and factors appear to be important in determining metal concentrations at some locations; further research and analyses would be necessary in order to investigate such factors in more detail.

6. References

- ATSDR (2007) Toxicological profile for lead, United States Public Health Service, Agency for Toxic Substances and Disease Registry, August 2007
- ATSDR (2012) Toxicological profile for cadmium, United States Public Health Service, Agency for Toxic Substances and Disease Registry, September 2012
- Wei, C.Y., Cheng, W., Linsheng, Y. (2009) Characterizing spatial distribution and sources of heavy metals in the soils from mining-smelting activities in Shuikoushan, Hunan Province, China. *Journal of Environmental Sciences* 21: 1230–1236
- Douay, F., Pruvot, C., Waterlot, C., Fritsch, C., Fourrier, H., Loriette, A., Bidar, G., Grand, C., de Vaufleury, A., Scheifler, R. (2009) Contamination of woody habitat soils around a former lead smelter in the North of France. *Science of the Total Environment* 407(21): 5564-5577
- Hengyang (2012) Hengyang geography. Hengyang municipal bureau of land and resources. <http://www.hygt.gov.cn/gtzyyw/dzzh/dzhjbh/201210/W020131028371575543602.swf> (Chinese)
- Huang, D., Huang, X., Liu, S., Liu, Q. (2004) Situation and Countermeasures of Cd and Pb Pollution in Hunan Province, *Research of Agriculture Modernization* (25): 81-85 (Chinese)
- Kozlov, M. V. & Zvereva, E. L. (2007) Industrial barrens: extreme habitats created by non-ferrous metallurgy. *Reviews in Environmental Science and Biotechnology* 6: 231–259
- MEP (1995) GB15618-1995. Environmental quality standard for soils. Published by Ministry of Environmental Protection (MEP) of the People's Republic of China & The State Bureau of Technical Supervision (now General Administration of Quality Supervision, Inspection and Quarantine) of the People's Republic of China.
- Ministry of Health (2012) GB2762-2012. National food safety standard - The Limits of Pollutants in Foods. Published by Ministry of Health of the People's Republic of China.
- Tao, F., Hayashi, Y. & Lin, E. (2002) Soil vulnerability and sensitivity to acid deposition in China. *Water, Air and Soil Pollution* 140: 247–260
- Williams, P.N., Lei, M., Sun, G., Huang, Q., Lu, Y., Deacon, C., Meharg, A.A., Zhu, Y.G. (2009) Occurrence and Partitioning of Cadmium, Arsenic and Lead in Mine Impacted Paddy Rice: Hunan, China. *Environmental Science and Technology* 43(3): 637-42

Appendix 1: Details of methodologies

Water samples

Preparation

A portion of each sample was filtered through a 0.45 micron filter and then acidified by the addition of concentrated nitric acid to give a final concentration of 10% v/v to enable determination of dissolved metal concentrations. 50 ml of each acidified sample was digested firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding at 180°C for a further 15 minutes. Cooled digests were filtered and made up to 50 ml with deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5, 1.0, 2.5 and 5.0 mg/l respectively, and matrix matched to the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Quality control

Two samples were prepared for ICP analysis in duplicate and analysed to verify method reproducibility, along with a blank sample (10% v/v nitric acid in deionised water), and two mixed metal quality control solutions of 0.4 mg/l and 4 mg/l respectively for each meta. All control samples were prepared in an identical manor to the samples.

Calibration of the ICP-AES was validated by the use of quality control standards of 0.4 mg/l and 4 mg/l respectively prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

Soil samples

Preparation

A representative portion of each sample was air dried to constant weight, homogenised, sieved through a 2mm mesh and then ground to a powder using a pestle and mortar. Approximately 0.5 g of each dried and ground sample was digested with 2 ml concentrated hydrochloric acid and 8 ml concentrated nitric acid, firstly overnight at room temperature, then using microwave-assisted digestion with a CEM MARS Xpress system, with a temperature ramp to 180°C over 15 minutes followed by holding at 180°C for a further 15 minutes. Following cooling, digests were filtered and made up to 50ml with deionised water.

Analysis

Prepared sample digests were analysed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Varian MPX Simultaneous Spectrometer. Multi-element standards at concentrations of 0.5, 1.0, 2.5 and 5.0 mg/l respectively, and matrix matched to

the samples, were used for instrument calibration. Any sample exceeding the calibration range was diluted accordingly, in duplicate, and re-analysed.

Quality control

Five samples were prepared in duplicate and analysed to verify method reproducibility, along with an identically prepared blank. To check the method efficiency, three certified reference material (CRM) samples were prepared in an identical manner; GBW07406, soil reference material certified by the China National Analysis Centre for Iron and Steel Beijing, China. GBW07311, stream sediment certified by the China National Analysis Centre for Iron and Steel, Beijing, China. LGC6187, leachable metals in river sediment certified by the Laboratory of the Government Chemist, UK.

Calibration of the ICP-AES was validated by the use of quality control standards of 0.4 mg/l and 4 mg/l respectively prepared in an identical manner but from different reagent stocks to the instrument calibration standards.

pH

To determine the pH of each soil sample, 10 ml deionised water was added to a 10 g portion of air dried soil, the slurry was mixed well and allowed to stand to 10 minutes. The pH of the slurry was determined using a Hanna Instruments HI98129 pH meter calibrated using pH 4.01 and pH 7.01 Hanna buffer solutions. The pH meter and electrode was rinsed with deionised water between samples.

Rice samples

Samples of rice were analysed at an independent laboratory using the following methods;

Lead: GB 5009.12-2010 National Food Safety Standard Determination of lead in foods

Mercury: GB/T 5009.17-2003 Determination of total mercury and organic-mercury in foods

Cadmium: GB/T 5009.15-2003 Determination of cadmium in foods

Total arsenic: GB/T 5009.11-2003 Determination of total arsenic and abio-arsenic in foods