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Speciation of Heavy Metals in Sewage Irrigated Pastures

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Domestic sewerage contains significant concentrations of potentially toxic contaminants, including heavy metals (e.g. cadmium, zinc, cobalt, nickel, lead, mercury, boron), other metal ions (e.g. sodium, potassium, magnesium, calcium), pesticide residues (e.g. atrazine and its degradation products), other endocrine disrupting organic compounds such as PCBs, PCDD/PCDFs, polycyclic aromatic hydrocarbons (PAHs), alkyl phenols, phthalates, phyto- and synthetic estrogens, and pathogenic micro-organisms. Toxic metal contamination of soils result in major environmental and human health concerns. The ecotoxocologicol risk is dependent on the specific form of the metal and its reactivety with the soil. Estimation of ecological effect of plant and prediction of long-term impacts on soil and ground water quality should therefore be based on the proportion of the potentially "active species" of the heavy metals.

Australia's oldest sewerage Farm, the Western Treatment Plant (WTP) is located 35 km southeast of Melbourne, Victoria. The WTP has been in operation for more than 100 years and currently covers some 11,000 ha of land. The population of metropolitan Melbourne and surrounds is almost 3 million people and the WTP treats about 50% of discharged domestic sewage at an average rate of 500 ML/d. A recent reconnaisance survey focusing on total concentration of heavy metals accumulation in the Land Filtration (LF) paddock in WTP was reported by Xiong et al. (2001). This paper examines the speciation of heavy metals at this site. The objective of this paper is to explore the solid-state speciation of heavy metals in LF paddock in WTP and is part of an on-going investigation of remediation and management of the lands in the WTP.

MATERIALS AND METHODS

The details of location and description of WTP, local climate, soil characteristics, pasture, livestock grazing have previously been reported in Xiong et al. (2001). A brief description of the Land Filtration (LF) site is presented here. Land filtration is one of three methods of sewage treatment currently used to treat sewage at the WTP. The land filtration strategy involves irrigation of raw sewerage on permanent pasture paddocks during the months of high evaporation (Oct-Apr). The LF system covers 3633 ha of the WTP site (see Figure 1). Each paddock in the LF operates on a 21 day cycle consisting of one or two days of irrigation with an average seasonal

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hydraulic loading of 0.055 ML/ha/day, followed by 5 days drying and 14 days livestock grazing. About 40% of the applied volume of sewage is collected by sub-surface drains and discharged into the Port Phillip Bay. The remainder is lost through evapotranspiration. From the survey conducted by Xiong et al. (2001), the paddocks in land filtration can be divided into three groups: light, medium and heavy contamination; these are termed LF1, LF2 and LF3 respectively. The length (years) of sewage irrigation at LF3 is longer than that at LF1 and LF2 and LF2 is longer than LF1 and is indicated in Figure 1. Control paddocks that do not receive sewage are denoted as Control or Ck. The soil pH, organic matter content, CEC, total P and N at various depths were reported in Xiong et al. (2001). For the surface soils, the mean values for these were : pH 6.8; OrgC 11.8%; TotN 1.17%; TotP 0.13%; and CEC 27.5 Cmol.kg^{-1}. The mean concentration (digestion by mixture of 3:1 HCl: HNO_3 and determined by AAS) of common heavy metals found in the soil horizon A (0 to 20 cm) for each of LF1, LF2, LF3 and control paddocks are listed in Table 1.

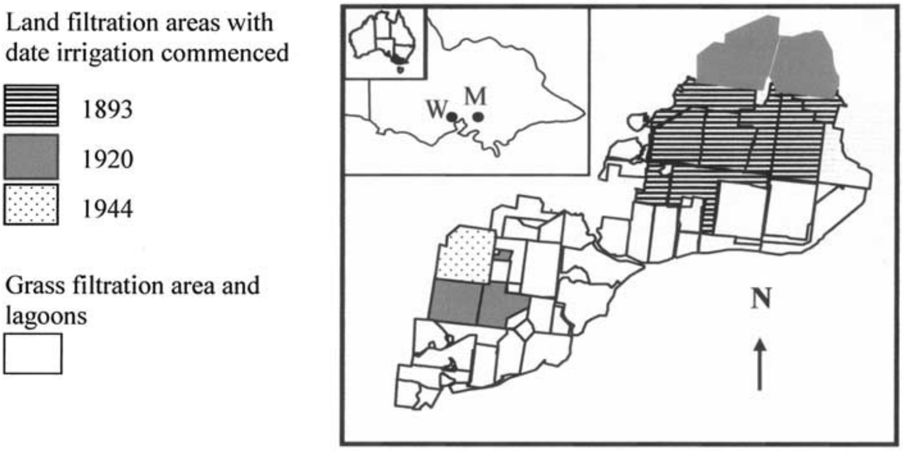

Figure 1. The land filtration and control areas at Werribee Sewage Farm, Australia.

Table 1. The mean concentrations (mg.kg^{-1}) of heavy metals in WTP paddocks. Figures in parentheses indicate standard deviation.

	No of Paddock	Cr	Zn	Cu	Pb	Ni
Control	21	36 (1.86)	49 (3.26)	15 (0.49)	24 (1.45)	22 (1.80)
LF1	17	71 (5.92)	69 (6.12)	27 (3.08)	30 (3.00)	34 (4.05)
LF2	30	220 (32.91)	170 (22.12)	45 (3.97)	120 (17.95)	33 (4.03)
LF2	56	330 (57.03)	240 (38.58)	86 (8.89)	190 (21.18)	48 (6.30)

Key: LF1: Land filtration area - lightly contaminated; LF2: Land filtration area- medially contaminated; LF3: Land filtration area- heavily contaminated; Control: no sewage irrigated soil.

Sequential extraction procedure is useful for estimating the relative availability and/or stability of different pools of heavy metals in the plant-soil system. Zhang et al. (1998) showed for example that Zn concentrations in plants were positively correlated to Zn bound to Fe-Mn oxides in the soils. However the Cu contents in different parts of corn was not significantly correlated to the Cu species in the soil. To address this question, more information is required concerning the long-term stability of chemical species of heavy metals in continuously cultivated and sewage-irrigated agricultural soils. The procedures for the sequential extraction for particulate-bound heavy metals in sludge samples suggested by Tessier et al. (1979) were used in this study with some modification. In spite some criticism of sequential extraction procedure's ability to distinguish among discrete geochemical fractions in the soil; it is never the less widely used.

The procedure to determine the five heavy metals (Cr, Zn, Cu, Pb and Ni) and six different fractions in the soil is described now: **(I)** Exchangeable Fraction: To 2 g soil, add 40 ml of 1 M ammonium acetate, shake for 2 hours, then centrifuge. Determine metal concentration in supernatant liquid, use the residue in the next step. **(II)** Carbonate Fraction: Add 40 ml of 1 M sodium acetate, adjusted with acetic acid to pH 5. Shake for 5 hours, then centrifuge, and determine metal concentration in supernatant liquid. Use the residue in the next step. **(III)** Reducible Fraction a (e.g. Mn-oxides): Add 50 ml of 0.1 M hydroxylamine hydrochloride, adjusted to pH 2 with nitric acid. Shake for 12 hours, then centrifuge. Determine metal concentration in supernatant liquid, use the residue in the next step. **(IV)** Reducible Fraction b (e.g. Fe-oxides): Add 50 ml of 0.2 M ammonium oxalate, adjusted to pH 3 with oxalic acid. Shake for 24 hours, then centrifuge. Determine metal concentration in supernatant solution; use the residue in the next step. **(V)** Organic Fraction and sulfides: Add 5 ml of 30% hydrogen peroxide, adjusted to pH 2 with nitric acid, and heat the mixture in a water bath at 85° C until the reaction stops (i.e. no more bubbles produced). Add more H_2O_2 until no further reaction is observed. Then extract the mixture with 20 ml of 1 M ammonium acetate, shake for 2 hours, and then centrifuge. Determine metal concentration in supernatant solution; use the residue in the last step. **(VI)** Residual Fraction: digest with 14 ml of a mixture of 3:1 HCl: HNO_3 in a glass vessel. After complete digestion, add 20ml water, filter, and dilute the filtrate to 50 ml for analysis of metal concentration.

Elemental concentrations in the six fractions (**I** to **VI**) were analyzed for metal concentrations with Atomic Absorption Spectrophotometer Hitachi 6000 calibrated with standards prepared from a 1.00 g L^{-1} stock of Cr, Zn, Cu, Pb and Ni solution from AJAX chemicals. The experimental-analytical methods were checked using certified reference material (CRM) from Analytical Products Group, Inc. Standard: Trace Metals - Order Number: 7879, Lot Number: 21921-21923. Recoveries of heavy metals obtained for certified reference materials are excellent from 95% to 103%.

RESULTS AND DISCUSSION

The concentrations of five most common heavy metals in each fraction and their sums are presented in Table 2. The results clearly show, for each of the metals examined, the accumulating heavy metal load in the soils following long periods of sewage irrigation. Total concentrations of the metals in the soils at the most heavily contaminated site (LF3) were elevated by factors ranging from 1.79 for Ni to 8.86 for Pb relative to the control site (in Table 2), with metal concentrations generally increasing with length of irrigation. However, not only does the total concentration increase, the proportions of metal found in the various fractions also change with time.

It is evident from Table 2 and Figure 2 that the dominant fraction of heavy metals in the control soil (i.e. the soil which never received sewage irrigation), except for Pb, was fraction VI. The respective percentages for each metal are Cr 59.70%, Zn 67.73%, Cu, 57.04%, Ni 79.03%; and Pb 22.14% (for Pb fraction VI is a major fraction although not the highest). The dominant fraction in the control soil for Pb was Fraction IV (34.28%). As the fraction VI of metal requires the most vigorous extraction process, metals present in this form are relatively un-bioavailable.

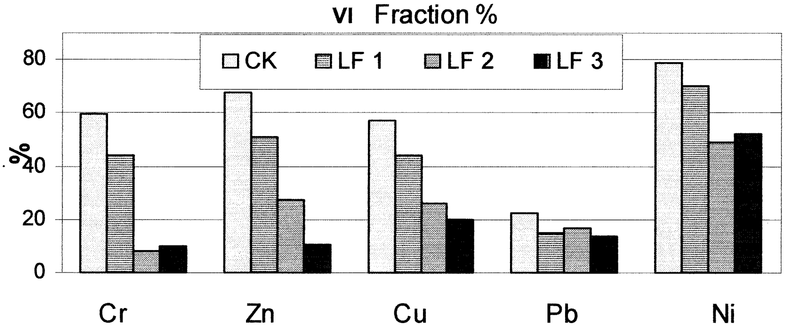

Figure 2. The proportion of fraction VI in soils at land filtration and control areas

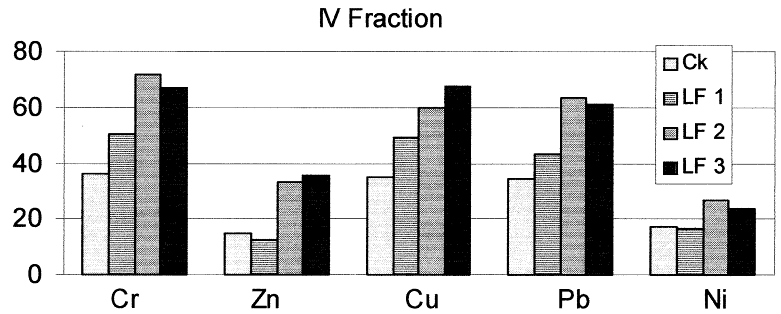

Figure 3. The proportion of fraction IV in soils at land filtration and control areas.

In soil that had been subject to irrigation with sewage i.e. land filtration area, the proportion of metal in the residual fraction becomes less significant. The proportion of Fraction VI (the residual fraction) decreased with increasing length of sewage irrigation and the trend was consistent across all metals. The highest percentage decrease (between the control soil and most often irrigated soil LF3) was Zn from 67.73 % down to 10.60 % and the least percentage decrease was for Pb from 22.14 % down to 13.9 % (in Figure 2).

Table 2. Metal fraction concentration (mg.kg^{-1}) from sequential extraction in WTP paddocks. Figures in parentheses indicate standard deviation.

		I	II	III	IV	V	VI	Sum
Cr	Control	<0.20	<0.20	0.63	12.47	0.41	20.71	34.62
				(0.07)	(1.79)	(0.05)	(3.94)	(3.68)
	LF1	<0.20	<0.20	2.57	34.14	0.68	29.69	67.48
				(0.31)	(5.90)	(0.15)	(6.60)	(12.06)
	LF2	<0.20	2.79	1.23	160.42	40.86	17.72	223.22
			(0.29)	(0.14)	(28.52)	(6.14)	(3.37)	(27.54)
	LF3	<0.20	3.38	6.99	193.97	55.64	29.37	289.55
			(0.44)	(0.65)	(27.62)	(12.85)	(4.39)	(39.12)
Zn	Control	0.80	3.10	2.91	5.70	0.20	26.62	39.33
		(0.07)	(0.25)	(0.26)	(0.65)	(0.01)	(2.66)	(3.16)
	LF1	0.69	3.71	16.85	7.12	0.03	29.78	58.18
		(0.05)	(0.42)	(1.02)	(1.01)	(0.01)	(4.45)	(5.11)
	LF2	11.03	18.29	22.94	45.70	1.70	37.20	136.86
		(0.66)	(1.22)	(1.19)	(7.34)	(0.17)	(4.25)	(4.39)
	LF3	13.69	40.97	39.17	75.00	0.94	41.38	211.15
		(1.21)	(3.61)	(5.86)	(10.71)	(0.15)	(7.36)	(14.73)
Cu	Control	0.18	0.40	<0.05	3.85	0.31	6.45	11.23
		(0.01)	(0.04)		(0.28)	(0.04)	(0.84)	(0.74)
	LF1	0.25	0.59	0.53	11.87	0.22	10.66	24.12
		(0.02)	(0.06)	(0.08)	(1.21)	(0.03)	(1.40)	(2.44)
	LF2	0.84	0.86	1.72	23.19	2.01	10.00	38.62
		(0.04)	(0.04)	(0.13)	(2.32)	(0.29)	(1.38)	(3.95)
	LF3	1.18	3.62	3.28	58.88	3.24	17.33	87.53
		(0.03)	(0.22)	(0.29)	(4.37)	(0.48)	(1.99)	(5.23)
Pb	Control	3.55	5.13	1.67	8.34	<0.20	5.38	24.26
		(026)	(0.53)	(0.19)	(1.10)		(0.93)	(2.34)
	LF1	2.92	5.53	3.13	12.13	<0.20	4.18	28.09
		(0.15)	(0.45)	(0.38)	(1.81)		(0.67)	(2.37)
	LF2	5.42	16.84	7.50	96.70	<0.20	25.38	152.04
		(0.33)	(2.19)	(1.07)	(8.58)		(5.45)	(14.25)
	LF3	5.00	18.42	30.36	131.10	<0.20	29.91	214.99
		(0.45)	(1.23)	(3.03)	(21.07)		(5.69)	(21.04)
Ni	Control	0.63	<0.10	0.30	5.82	<0.10	25.45	32.40
		(0.06)		(0.05)	(0.70)		(3.52)	(4.00)
	LF1	1.44	<0.10	4.90	8.34	<0.10	34.55	49.43
		(0.17)		(0.73)	(0.95)		(4.50)	(5.16)
	LF2	0.18	<0.10	9.26	10.62	<0.10	19.50	39.76
		(0.03)		(0.82)	(0.88)		(2.42)	(4.00)
	LF3	2.34	1.24	10.45	13.63	<0.10	30.20	57.96
		(0.19)	(0.20)	(1.51)	(1.78)		(5.17)	(6.13)

The accumulated metals in soils followed by long-standing sewage irrigation at the land filtration area are not distributed uniformly across the 6 fractions. In the land filtration soils, the Reducible Fraction b (**IV**) increasingly becomes the dominant fraction (Figure 3). In the contaminated land filtration land, most of the accumulated heavy metals were in fraction **IV**. Fraction **IV** represented up to 67.26% (at LF3), 71.86 % (at LF2) and 63.60 % (at LF2) of Cu, Cr and Pb respectively. However Zn and Ni accumulated in different fractions. Zn accumulated mainly in fractions **IV**, **III** and **VI**. Ni accumulated mainly in fraction **IV** and **VI**.

The fraction **IV** essentially represents metals adsorbed onto or otherwise associated with iron oxides. This fraction is potentially bioavailable, as these metals may be released from the iron oxides if there is a decrease in the redox potential of the soils. This may occur if the soil is moist and there is bacterial degradation of organic matter leading to the complete consumption of oxygen. Such conditions could conceivably arise in a sewage irrigation farm.

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