

Human Exposure to Metals in Groundwater Affected by Acid Sulfate Soil Disturbance

A. Hinwood · P. Horwitz · R. Rogan

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Abstract The disturbance and oxidation of sulfidic soils can cause an increase in acidity resulting in the mobilization of high concentrations of metals in groundwater or connected surface water. This is an increasing problem in urban areas of Australia and internationally. We hypothesized that the risks of exposure to contaminated water would be increased by this phenomenon. We undertook a preliminary investigation of human exposure to metals recruiting 27 residents in an acid sulfate soil-affected area, 21 residents using a bore (groundwater) for home-grown produce irrigation, and 6 residents who did not. Participants completed a questionnaire and provided a sample of urine (first morning void), toenails (from all 10 toes), hair, and borewater. Only hair metal concentrations were higher in those using bore water and ranged from below detection (<DL) to 38 mg/kg Al; <DL = 0.07 mg/kg As, 0.02–0.57 mg/kg Cd, 0.19–4.3 mg/kg Pb, 11–160 mg/kg Cu, and 99–280 mg/kg Zn. The data indicate exposure to metals in bore-water users might be occurring and further investigation is warranted even though the concentrations recorded in this study are considered low.

The impacts of disturbance and oxidation of pyritic soils are the formation of sulfuric acid, the erosion of buffering capacity of soil and water, and a subsequent increase in acidity. This has the potential to cause acidification of connected groundwater and surface water and subsequent mobilization of metals (including transition metals, heavy

metals, and metalloids). The scale of acid sulfate soil (ASS) disturbance in Australia and internationally is increasing largely due to soil disturbance in areas where rural or urban development is occurring (Appleyard et al. 2004, 2006; Fitzpatrick 2003), particularly close to or on the coast. In addition groundwater decline has exposed previously permanently wet sediments to drying and acidification. In Western Australia there are coastal areas where domestic groundwater bores now have elevated metals concentrations (Appleyard et al. 2004). Where this has occurred and where groundwater bores are used for the production of food, the potential exists for human exposure to metals with the possibility of an increased risk of health effects.

A previous study of 67 residents in Stirling, a suburb of Perth in Western Australia, confirmed the presence of elevated metals concentrations in residential groundwater bores affected by ASS disturbance, with a high proportion of residents reporting use of this water for irrigation of home-grown produce (Hinwood et al. 2006). Very high concentrations of aluminum and arsenic were reported, as well as elevated concentrations of lead and cadmium. Although not measured by Hinwood et al. (2006), copper and zinc might also be increased as a result of acidification due to their presence in soil.

Some preliminary testing of vegetable and fruit samples has been undertaken in the area to determine whether crops were taking up the arsenic from the application of groundwater or via contaminated soil. Although the results did not exceed the Food Standards Australia and New Zealand (FSANZ) Food Standards Code for arsenic, the sampling was limited to 11 households and the crops of the time, however 14 plant samples were found to exceed the FSANZ Food Standard Code value for lead of 0.1 mg/kg (Water and Rivers Commission 2002).

A. Hinwood (✉) · P. Horwitz · R. Rogan
Centre for Ecosystem Management, Edith Cowan University,
270 Joondalup Drive, Joondalup 6027 Western Australia,
Australia
e-mail: a.hinwood@ecu.edu.au

Given these preliminary investigations, high bore ownership, use of bore water for home-grown produce irrigation, the groundwater resource being affected by ASS disturbance, and the greater water usage during drying periods in this metropolitan area, we hypothesized that the potential for human exposure to metals is increased.

The metals cadmium, lead, arsenic, and aluminum are well known for their health impacts in exposed populations (Jansson 2001; Jarup 2003; Jarup et al. 1998; WHO 2001). Cadmium exposure has been associated with renal disease and studies have also suggested that cadmium exposure might impact the skeleton, whereas lead is well known for its health impacts such as memory deterioration, cognitive difficulties, neurological impacts, and kidney damage (Akeson et al. 2006; Jansson 2001; Jarup 2003; Jarup and Alfven 2004; Jarup et al. 1998, 2000). Concerns have been expressed by several authors on the impacts of lower levels of cadmium on bone density (Jarup and Alfven 2004; Horiguchi et al. 2005). Inorganic arsenic is also associated with a range of health effects, including vascular disease, skin lesions at high concentrations, and cancer of the bladder and kidney (Armienta et al. 1997; Jarup 2003; Rahman et al. 2001; WHO 2001). Aluminum has the potential to impact on the central nervous system and skeletal and hemopoietic systems of humans (Jansson 2001).

Copper is an essential element for humans; however, there are some individuals susceptible to the effects of increased copper exposure, such as those with Wilson's disease, renal and liver disease, and infants (Geogopolous et al. 2001). Zinc is considered an essential element and is used frequently for therapeutic purposes (Maret and Sandstead 2006).

Traces of these metals are found in many foods. In the absence of other contaminated sources of exposure such as soil and air, the influence of occupation, or the undertaking of activities such as smoking, food is considered one of the most important sources of human exposure (Jarup 2003; Ryan et al. 2001; Wolsperger et al. 1994; Yokel and McNamara 2001). Clearly, the type of food consumed and its location influences the degree to which the population might be exposed. The concentration of metals measured in produce varies according to several factors, including the type and part of vegetable/fruit tested. It is also influenced by the chemistry, where the more acidic the environment, the greater the uptake of heavy metals (Bensryd et al. 1994). To deal with these factors, the approach taken is to use personal measures of exposure to reflect total exposure from all sources, including food, with the various potential sources of uptake assessed. This provides a practical alternative to the need to assess all fruit and vegetables in differing seasons to assess the potential for exposure.

The importance of both short-term and long-term irrigation of home-grown produce with contaminated groundwater for human exposure is largely unknown and not known in the context of ASS disturbance. There are few comprehensive studies of measured human exposure associated with consumption of home-grown produce in an acidified environment. We therefore sought to undertake a preliminary investigation of human exposure using short-term and long-term measures of exposure from an ASS-impacted environment and specifically to explore whether there was an increase in human exposure in residents using bore water affected by ASS compared with those that were not.

Methods

A cross-sectional study of human exposure of residents in an ASS-affected area was undertaken in summer 2005/2006 (following recruitment in spring 2005). Environmental and biological samples were collected along with information on demographic, lifestyle, and activity information on participants.

Study Area and Population

The Stirling area of the Swan Coastal Plain, Western Australia was selected, as it is known to be impacted by ASS with known high concentrations of metals in residential bore water that is used for the maintenance of market garden produce (Hinwood et al. 2006; Water and Rivers Commission 2002). The area of study is residential and is not impacted by industry; however, has been used for commercial market gardens in the past.

Sample Size Calculation

A sample size calculation was performed using arsenic hair data from a study of environmental arsenic exposure (Hinwood et al. 2003). These data were considered the most appropriate Australian exposure data available. On the basis of a difference of 3.16 mg/kg in hair arsenic concentration between exposed and unexposed groups, a sample size of 12 would be required to detect a difference in concentrations if one existed. To take into account that only 30% of the population might have elevated metals in groundwater bores (Hinwood et al. 2006) and the potential for misclassification and withdrawal from the study, the sample size was increased to 50. Although the aim was to recruit 50 participants in total, only 29 were recruited, with 2 later withdrawing from the study. The recruitment rate was 7% of all

households doorknocked and 22% of those that were home at the time of the visit.

Participants were recruited via doorknocking households in the target area. If no residents were present at the time of doorknocking, an information letter was left asking for participation in the study. Only participants over age 18 were included for participation in this study. Participants were excluded if they were smokers, employed in an occupation that might increase metals exposure, such as car detailing, or were residents in the area for less than 2 months. All participants were required to provide written informed consent before taking part in the study.

Data Collection

All participants were asked to complete a brief questionnaire about use of their groundwater bore, application of water to home-grown produce, and consumption of home-grown produce. Each questionnaire also requested demographic information, as well as information on exposure to cigarette smoke and the use of specific products such as termiticides, as these products and activities might confound the results.

Participants were requested to provide a first morning void urine sample in a 60-mL prelabeled acid-washed polyurethane container. Participants were asked to provide toenail clippings from all 10 toes (Hunter 1990) and provide a sample of hair cut from the nape of the neck, placed into separate polyethylene labeled plastic bags.

Participants were requested to take a sample from an operating bore water tap into an acid-washed, rinsed 500-mL polyethylene container. pH was measured in the laboratory after collection using a calibrated portable CyberScan 510 pH meter.

All bore water and urine samples were analyzed for inorganic arsenic and lead by inductively coupled plasma-atomic electron spectroscopy (ICP-AES; Varian Vista Pro), including aluminum measured using inductively coupled plasma-mass spectrometry (ICP-MS Agilent 7500 ICP-MS with Collision Cell). The analytical limit of detection for analysis of cadmium in urine was too high for use in this study. Toenail samples were digested in nitric acid and metals detected by ICP-MS. Hair was washed with deionized water and methanol to remove external contaminants, dried, and digested in nitric acid, and metals were detected using ICP-MS. Aluminum concentration in hair was detected and quantified using ICP-MS. All samples were analyzed by the Chemistry Centre of Western Australia. Standard QA/QC procedures were employed for all matrices. The “SRM-1640” trace elements in freshwater reference standards was utilized for water samples. For urine samples, the Bio-RadUrine metals Level 2 control was used. Hair and toenails were compared with

GBW07601 (human hair), DORM (dogfish muscle tissue), and DOLT (dogfish liver tissue). Mixed-element standards were used to spike selected samples in each batch. Blanks, duplicates, and recoveries were also run for each batch.

All questionnaire and environmental and biological analyte data were entered into a database and analyzed (using SPSS version 13 for Windows) to generate descriptive statistics and graphical displays.

Results

The demographic characteristics of the study population are shown in Table 1. Noting the small numbers in this preliminary study, there were some major differences between the groups. The length of time lived in the area was lower in the non-bore-water-use group and this group had a much higher percentage of participants living with a smoker in the house and were exposed to smoking more frequently (Table 1). Both groups consumed home-grown produce and spent time gardening, with the non-bore-water-use group growing and consuming less home-grown produce (Table 2).

The water metal concentrations were generally low, with few samples with low pH (Table 3). Few samples exceeded the NHMRC drinking water guidelines or ARMCANZ recreational water quality guidelines for metals (ARMCANZ, 2000; NHMRC, 2004) (Table 3). Both aluminum and lead water concentrations were

Table 1 Demographic characteristics of study population

	Bore water users (<i>n</i> = 21)	Non-bore-water users (<i>n</i> = 6)
Age years (mean)	52.4	46.5
Range	36–86	29–74
Males (%)	45.0	16.7
Mean months lived in area	192	66.7
Range	2–419	5–157
Smoker in residence (%)	28.6 ^a	86 ^a
Frequency of smoking (%)		
Daily	85.7	50
Few days per week	0	50
< Few days per week	14.3	0
Medication unspecified (Y)	42.9	50
Diet (%)		
No special diet	90.5	100
Fat modified	0	0
Lower blood fat	9.50	0
Other		0

^a All smoking reported to occur outdoors

Table 2 Activities related to bore water use in the study population

Activity	Exposed group (<i>n</i> = 21)	No use of bore water group (<i>n</i> = 6)
Home-grown produce (Y)(%)	71.4	50
Consume home-grown produce (Y) (%)	83.3	60
Frequency of consumption home-grown produce (%)		
Daily	7.7	0
Few days per week	46.2	66.7
Few days per month	30.8	33.3
< Few days per month	15.4	0
Wash fruit and vegetables always (Y) (%)	100	100
Peel fruit and vegetables (Y) (%)		
Always	61.5	100
Often	23.1	
Never	15.4	
Use termaticides (Yes) (%)	38.1	33.3
Don't know	42.9	50.0
Use fertilisers (Y) (%)	90.5	100
Current use bore water		N/A
Every day	4.8	
2–3 times per week	61.9	
4–5 times per week	23.8	
None	9.5	
Time spent gardening (Y) (%)	81.0	100
Hour	58.8	50
1–5 hours	41.2	50

significantly correlated with pH (Spearman correlation coefficients of -0.822 and -0.700 , respectively).

Urinary metals concentrations were only detected for arsenic and lead (Table 4). The concentrations of arsenic are reflective of seafood intake, with all inorganic metal concentrations recording less than 1 ($\mu\text{g/L}$). The urinary lead concentrations were similar for both groups (Table 4). There was no correlation between the bore-water metal and urinary metal concentrations.

Metal toenail concentrations were higher in the non-bore-water users compared with bore-water users, noting the very small sample size in the former group (Table 4). A Spearmans rho correlation matrix using data across all

participants showed significant correlations between aluminum and arsenic; lead and aluminum, and lead and cadmium toenail concentrations.

The mean metal hair concentrations in the bore-water users were generally higher for aluminum, cadmium, and lead hair concentrations than those found for non-bore-water users (Table 4). Median concentrations were also higher in bore-water users for cadmium, lead, and copper. Hair cadmium and lead concentrations were significantly correlated.

The influence of participant demographics and activities on the measures of exposure were explored. Males had higher toenail metals concentrations and females had higher hair metals concentrations; however, because of the small numbers in this study, significance testing was not undertaken. There was no difference in urinary metal concentrations between bore-water users and nonusers. Having a smoker in the residence and consuming home-grown produce had little influence on metal concentrations other than for aluminum (Table 5). Mean and median toenail metal concentrations were slightly higher in participants reporting time spent gardening compared with those who do not garden (Table 5). Time spent gardening also increased mean and median hair aluminum, cadmium, and lead concentrations (Table 5). Participants using bore water four to five times a week had higher hair metal concentrations for aluminum, cadmium, and lead than those using water two to three times or week or not using water; given the small numbers in each category, statistical analyses have not been presented here.

Discussion

The bore-water metals concentrations in this study were lower than those previously detected in the Stirling area (Hinwood et al. 2006; Water and Rivers Commission 2002). However, there were indications that participants in this study had a low pH in their bore waters, which could lead to mobilisation of metals.

There was no difference in urinary metal concentrations for bore-water users compared with nonusers, suggesting for most metals that short-term exposure is not occurring. This is consistent with the low concentrations of metals in

Table 3 Water metal concentrations of participants using bore water ($\mu\text{g/L}$)

	pH	Al-water	As-water	Cd-water	Pb-water
<i>N</i>	19	19	19	19	18
Median	6.38	<DL (0.5)	<DL (0.5)	<DL (0.1)	0.400 (DL 0.1)
Mean	6.07	760	0.800	1.00	1.30
Range	4.09–7.14	0.5–9000	<0.5–3.00	<0.1–7.10	<0.1–13.0
SD	0.87	218	0.8	2.00	3.00

Note: <DL = less than detection limit

Table 4 Urinary, toenail, and hair metal concentrations of bore water and non-bore-water users

	As-urine* µg/L	Pb-urine µg/L	Al-toenail mg/kg	As-toenail mg/kg	Cd-toenail mg/kg	Pb-toenail mg/kg	Al-hair mg/kg	As-hair mg/kg	Cd-hair mg/kg	Pb-hair mg/kg	Cu-hair mg/kg	Zn-hair mg/kg
	Users											
<i>N</i>	21	21	21	21	21	21	17	17	17	17	17	17
Median	20.0	5.00	25.0	0.05	0.05	1.2	5.5	0.001	0.130	0.99	41.0	170
Mean	103	8.00	28.6	0.07	0.07	1.39	8.39	0.008	0.180	1.30	54.0	168
Range	<DL (1.0)–103*	<DL (0.1)–20.0	11.0–60.0	0.05–0.3	0.01–0.22	0.50–3.5	<DL–38.0	<DL–0.07	0.02–0.57	0.19–4.30	11.0–160	99–280
SD	0.29	5.00	14.9	0.06	0.06	0.75	9.41	0.020	0.150	1.14	41.9	46.4
	Bore-											
<i>N</i>	5	5	3	3	3	6	5	5	5	5	5	5
Median	20.0	10.0	49.0	0.05	0.14	2.87	5.7	0.001	0.060	0.680	30.0	150
Mean	32.0	8.00	64.3	0.06	0.10	2.87	5.44	0.0168	0.17	0.710	57.6	160
Range	2–50	<DL (0.1)–10.0	45.0–99.0	0.05–0.1	0.01–0.33	0.20–5.8	2.9–8	0.001–0.08	0.05–0.22	0.350–1.30	28.0–150	140–210
SD	16.0	3.00	30.1	0.029	0.167	2.80	2.4	0.035	0.090	0.370	52.5	29.2

* Total arsenic

Table 5 Mean toenail and hair metal concentrations for selected participant activities (mg/kg)

Factor	Al-toenail	As-toenail	Pb-toenail	Cd-toenail	Al-hair	As-hair	Pb-hair	Cd-hair	Cu-hair
Smoker in residence	Yes	40.7 (n = 9)	0.06 (n = 9)	0.07 (n = 9)	10.8 (n = 8)	0.01 (n = 8)	1.26 (n = 8)	0.20 (n = 8)	53.1 (n = 8)
	No	28.5 (n = 15)	0.08 (n = 15)	1.43 (n = 15)	6.0 (n = 14)	0.01 (n = 14)	1.13 (n = 14)	0.14 (n = 14)	56.3 (n = 14)
Consume home-grown produce	Yes	32.4 (n = 17)	0.06 (n = 17)	1.59 (n = 17)	9.63 (n = 15)	0.01 (n = 15)	1.06 (n = 15)	0.16 (n = 15)	56.1 (n = 15)
	No	31.5 (n = 4)	0.06 (n = 4)	1.13 (n = 4)	4.5 (n = 4)	0.02 (n = 4)	0.94 (n = 4)	0.09 (n = 4)	58.5 (n = 4)
Spend time gardening	Yes	30.8 (n = 18)	0.08 (n = 18)	1.38 (n = 18)	8.23 (n = 15)	0.006 (n = 15)	1.29 (n = 15)	0.17 (n = 15)	57.8 (n = 15)
	No	23.7 (n = 3)	0.05 (n = 3)	0.87 (n = 3)	6.8 (n = 3)	0.02 (n = 3)	0.35 (n = 3)	0.043 (n = 3)	45.3 (n = 3)

the bore water in this study. The urinary concentrations reported in other population studies are comparable or higher than those reported in this study, with the exception of the concentration of lead in urine in this study, which was much higher (Seifert et al. 2000; Wilhelm et al. 2004). It should also be noted that the urinary measures are not necessarily appropriate for all metals. Aluminum, lead, and cadmium in blood are considered more reliable measures (Wilhelm et al. 2004).

There was no association between bore-water concentrations and toenail metal concentrations. The toenail concentrations found for all participants appear to be reflective of soil concentrations, given the strong correlations between the metals in toenails and the relationship with time spent gardening. Natural levels of cadmium in Australian soils range up to 1 mg/kg, 2–200mg/kg for lead, 10–300mg/kg for zinc, and up to 100 mg/kg for arsenic, noting that geography might have a significant influence on these levels (NEPC 1999).

Hair metal concentrations were, however, higher in those using bore water with elevated concentrations of aluminum, cadmium, and lead compared with non-bore-water users. These results might also be reflective of exposure to soil where the washing process might not have removed exogenous metals. However, the relationship between gardening and hair metals was not strong and there was a clear relationship between increases in hair metals and increased frequency of bore-water use, as well as an increase in those consuming produce.

The concentrations of copper in hair were considerably higher than have been reported in the international literature (Georgopoulos et al. 2001; Razagui and Ghribi 2005). The concentrations observed might be related to ASS but are also thought to be contributed to by the presence of copper pipes for provision of drinking water to homes in the study area. There is also the possibility of residual contamination in soil due to the past use of this area as a market growing area. In addition, copper in hair is not considered to be the most reliable measure of exposure, and analysis of copper in urine might be preferred (Georgopolous et al. 2001). The source of copper, exposure pathways, and health impacts in this community need further attention.

In general the hair lead and cadmium concentrations were lower than those reporting population concentrations (Anwar 2005; Razagui and Ghribi 2005; Siefert et al. 2000; Wilhelm et al. 1994). Arsenic concentrations in hair were also significantly lower than those previously measured in Australia and elsewhere (Hinwood et al. 2003). Zinc concentrations in hair in this population are comparable with other population studies (Razagui and Ghribi 2005).

Cigarette smoking is a major source of exposure and has been shown to increase blood and urinary cadmium levels, with food being the major contributor to body burden

(Ewers et al. 1999; Jarup, 2003). Antacid intake has been shown to confound urinary aluminum concentrations (Jansson 2001). In this study, urinary aluminum concentrations were all below the analytical limit of detection and smoking was shown to increase hair aluminum and copper concentrations only.

Information on soils and hair treatment types was not collected and these factors could have influenced the outcomes.

Given that the area of Stirling is a residential urban area predominantly used as a market garden growing area in the past, we regard the only significant source of metals exposure for residents in this area other than occupational and specific activities that include working with metals is the presence of metals in the environment and food. There might be some contribution of metals from the use of pesticides and fertilizers; however, the degree of use and potential influence of such use on the results is unknown.

This study is limited by its small size and the measures of human exposure selected for some metals. The study was affected by a very low recruitment rate, which might have biased the sample by self-selection of people interested in the topic, thereby not being representative of the area. However, as each participant had personal measures of exposure examined, the results will reflect exposure of the group recruited where the results cannot be generalized to other members of the community. The low recruitment rate also influenced the sample size for which the power to detect a difference between the groups was significantly compromised. For the difference of 0.7 mk/kg observed in this study based on lead, a sample size of 62 would have been required. Clearly, this has had a significant affect on the ability to draw firm conclusions on the results obtained.

Further, the metals in groundwater for this group of residents were much lower than those previously observed. It is possible the participants recruited in this study were using water at a deeper level in the aquifer beyond any plume of ASS-affected water. Given the fluctuations in groundwater levels seasonally, meaning that water will be drawn by bore-water users from slightly different parts of the aquifer, it is reasonable to predict that water quality at different times of the year will vary, and this too might have been a factor in this study. Nevertheless, some useful baseline data have been acquired for subsequent investigations.

The concentrations of metals reported in recent media releases on recent bore-water samples taken in adjacent areas to the one targeted in this study report concentrations of arsenic up to 12.8 mg/L, with other metals also being elevated in other locations on the Swan Coastal Plain (Bekele 2005). The results of this study support the need to further investigate the relationships between domestic use of bore water, the consumption of home-grown produce, and human exposure to metals.

Summary

Participants in this study have concentrations of metals in hair that are elevated in bore-water users compared with non-bore-water users, suggesting increased exposure to metals via this source. Several studies report the potential for health impacts at low levels of exposure, particularly those in sensitive subgroups.

Many areas on the Swan Coastal Plain are known to be impacted by ASS. The scale of human exposure to subsequent groundwater is not known; however, we now have two preliminary investigations indicating that activities such as growing home-grown produce and consumption patterns provide routes of exposure that warrant further investigation. This combines with recent reports of even higher concentrations of metals in groundwater in ASS-affected areas to heighten concern.

This source of exposure of metals is increasing in urbanized areas of Western Australia and its impact on the population needs to be assessed in a comprehensive way to elucidate the relationships between environmental exposure, consumption of home-grown produce, and health effects.

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