Research article

Effects of Lead and Other Metals from Historical Smelting on Sustainable Fruit and Vegetable Cultivation

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Abstract Wollongong, located in the Illawarra region of NSW Australia, contains the industrial complex of Port Kembla. Lead in Port Kembla soils, ~2.5 km from a former copper smelter (1908-2003), have exceeded soil contamination guidelines for human health (HIL) and ecological (EIL) investigation levels. Previous studies regarding heavy metal contamination from the industrial complex, do not include comparisons to HIL and EIL guidelines. This study re-examines the risk of legacy (historic) heavy metals in urban soils to residents in proximity to the Port Kembla industrial complex. This was accomplished by reviewing: (i) resolution of heavy metal dispersion data from the copper smelter, in historic soil concentration data (n=95 top soil samples) collected by Jafari (2009) and reviewed by Noller (2020a); (ii) providing a new comparison of historic percentile data to current Australian soil contamination guidelines (NEPC, 2013) and German atmospheric pollutant guidelines; and (iii) re-evaluating treatments to soil data by Jafari (2009), in the context of bioaccessibility and bioavailability to humans and plants. At 75th percentile, arsenic, cadmium, copper, lead and zinc concentrations exceeded HIL Level A guidelines. When detection limit values (52 out of 95) were removed (n=22 samples), median cadmium concentrations exceeded HIL Level A guidelines. Dietary exposure to cadmium, lead, zinc and copper is a risk to residents through the consumption of vegetables grown in urban gardens in proximity to the Port Kembla industrial complex. Copper in vegetables sampled from soils in the vicinity of the Port Kembla copper smelter was greater in comparison to sampling completed at other smelter sites. Port Kembla urban garden vegetables showed exceedance of food guidelines for both cadmium and lead, highlighting the health risks of growing vegetables in proximity to industrial areas.

Keywords heavy metals, arsenic, smelting, sustainable, fruit and vegetable cultivation

INTRODUCTION

The Wollongong local government area (LAG) is located in the Illawarra region of New South Wales (NSW), Australia (Fig. 1), 80 km south of Sydney. The Wollongong LAG contains the industrial complex at Port Kembla; a feature which has remained in place for over 100 years (Chiaradia et al., 1997; Jafari, 2009). A copper smelter, formerly Southern Copper ERS Ltd (SC in Fig. 1), commenced operations at Port Kembla (1908-2003) and demolished in 2014. A considerable body of literature exists on the nature, extent and distribution of heavy metals and arsenic in soils in Wollongong and Port Kembla (Noller, 2020a). The current Australian guidelines for human health (HIL) and ecological (EIL) investigative levels are risk-based approaches used to examine and interpret soil, air, water and food environmental data. Existing guidelines (HIL and EIL) had yet to be implemented at the time of previous data collection and analysis (Noller, 2020a). Previously, lead (Pb) was mainly investigated at Port Kembla, yet cadmium (Cd), zinc (Zn), copper (Cu), and arsenic (As) also exceeded Australian National soil contamination guidelines (HIL and EIL) (NEPC, 2013; Noller, 2020b). In the absence of Australian air pollutant guidelines, German air pollutant controls (TA LUFT standards) for metal fallout were used (TA LUFT, 1990, 1999; Noller, 2020b).

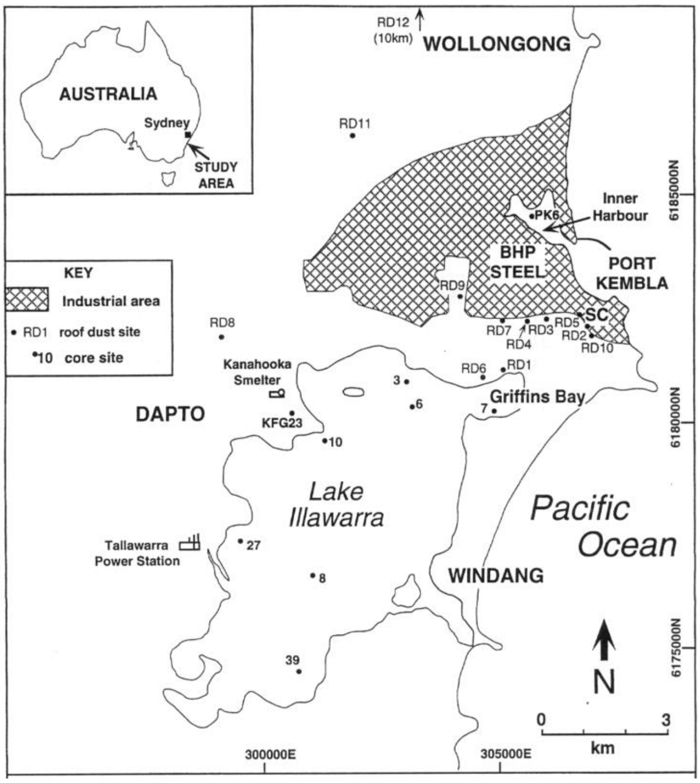

Fig. 1 Location of the historical Port Kembla industrial complex, including the southern copper smelter (SC) and other sampling sites (Chiaradia et al., 1997)

OBJECTIVE

The objectives of this study are to re-examine and evaluate the human-health risks to residents in the proximity to the Port Kembla industrial complex, based on historic heavy metal and As concentrations in soil.

METHODOLOGY

This study aims to follow three methods of re-examination and analysis: (i) to review the resolution of heavy metal and As dispersion data from the copper smelter, in historic soil concentration data (n=95 top soil samples) collected by Jafari (2009) and reviewed by Noller (2020a); (ii) to provide a new comparison of historic percentile data to current Australian soil contamination guidelines (NEPC, 2013) and TA LUFT (1990, 1999) German atmospheric fallout standards; and (iii) to re-evaluate treatments to soil data by Jafari (2009), in the context of bioaccessibility and bioavailability to humans and plants.

The Jafari (2009) study measured the total concentration of 37 elements in soil samples (n=95) by XRF-spectrometry. Soil samples were treated with 0.1M hydrochloric acid extraction and ethylenediamine tetra acetic acid (EDTA). Data from Jafari (2009) was not previously evaluated for human health or ecological risks, however extraction methods in Jafari (2009) are an analog to reflect human bioaccessibility of metals and As in soils (HCl acid extract similar to stomach acid) and indicate plant uptake (EDTA extract). The detection limit for Cd was 10-20 mg/kg (Jafari, 2009) resulting in only high values of Cd being compared with guidelines (Noller, 2020a). This study re-examines data from Jafari (2009) and Noller (2020a) and compares percentile values of As, Cd, Cu, Pb and Zn against soil guidelines (NEPC, 2013), to inform a risk assessment of potential resident exposure from historic smelter emissions.

RESULTS AND DISCUSSION

Summary results are given in percentile values in Table 1 for metals and As in soil (mg/kg), and Table 2 for mean percent extractable metals and arsenic in soil at Port Kembla.

Table 1 Percentile values for metals and arsenic in soil (mg/kg) at Port Kembla

Metal/ metalloid (n=95)	No.< Values	Mean (SD)	Median	75th percentile	Maximum	HIL[a] Level A	EIL[b] Urban-residential
Copper	0	556±1246	161	535	1999	1000	30-230
Zinc	2	373 ±417	220	432	2833	7000	25-1300
Arsenic	1	14 ±24	7	12	183	100	50-100
Cadmium	52	89 ±189	29	39	840	20	-
Lead	3	178 ±479	64	126	667	300	270-1100

Source a. HIL Level A is for urban residential with garden (Noller,2020b); and b. EIL Urban-residential includes public open spaces for both invertebrate and plant species protection level of 80% (approximated using 75% data) with upper and lower levels combining added contaminant limit with background concentration. The EIL for Cd is not available. Site specific measurements can be undertaken to derive a Cd EIL (NEPC, 2013; Noller, 2020b), but not for this study.

Examination of percentile values (Table 1) shows that concentrations of As, Cd, Cu, Pb and Zn exceeding HIL Level A investigation levels for residential soils are all greater than 75th percentile values. When the detection limit values of Cd (52 out of 95) were removed, 22 soil concentrations exceeded HIL Level A at their median (50th percentile) value.

Jafari (2009) noted a positive correlation between Cu ($P < 0.001$), As ($P < 0.001$), Pb ($P < 0.001$) and Zn ($P < 0.01$) concentrations and distance from the smelter stack. Concentrations in soil in proximity (< 1.5 km) to the smelter stack contained higher amounts of total Cu (>1500 mg/kg) and As (> 10-15mg/kg), Pb (> 150-200mg/kg) and Zn (> 400-600mg/kg) (Jafari, 2009). Highest concentrations of As, Cd, Cu, Pb, and Zn were attributed to samples from slag heaps (Jafari, 2009). Contamination of heavy metals and As in soils surrounding the Port Kembla smelter, range at a distance of 1-4km, but higher concentrations are observed <1km from the smelter stack.

Percentile values depicted in Table 1, shows that except for Cu, 75th percentile values for metals and As do not exceed EIL standards. Readers should note that there is no current EIL guideline for Cd. Some effects on terrestrial species in garden soil from Cu may be expected as the EIL urban-residential guideline is exceeded for concentrations greater than median (Table 1).

Single extraction technique data used to determine 0.1M Hydrochloric acid and 0.05M EDTA concentrations of elements (Table 2) show that Cu, Pb and Zn concentrations decreased with increasing distance from the stack (Noller, 2020a). The heavy metal and As extraction technique of 0.1M hydrochloric acid, can be utilized as a gastro-intestinal simulation, to predict human bioavailability (Table 2). More accurately, 0.1M hydrochloric acid extractable metals and arsenic provides an indication of their bioavailability during the gastric phase (Table 2); however, this method likely overestimates their bioaccessibility, as the intestinal phase (functions at ~ pH 7 conditions) is not considered (Noller, et al. 2017). It is important to distinguish that the human intestine is where heavy metal and As absorption takes place, while the stomach (gastric phase) is where solubilization of food (heavy metals and As) occurs. The 0.05M EDTA extractable concentrations of heavy metal and As represent the relevant concentrations of plant uptake from soil (Table 2).

Table 2 Mean percent extractable metals and arsenic in soil at Port Kembla

Extractant	Arsenic (%)	Copper (%)	Lead (%)	Zinc (%)	Cadmium (%)
0.1M HCl	35.7	22	28	43	4.27
0.05M EDTA	42.9	32	37	33	4.5

The mean 0.1M hydrochloric acid extractable Pb concentration (Table 2) of 28.0% in Wollongong soil indicates that bioaccessibility is low (compared with < 100%). This bioaccessibility (BAc) level is similar to soil at other mining centres in Australia (Noller et al., 2017). The HIL Level A 300 mg/kg for Pb and 0.1M hydrochloric acid extractable Pb is equivalent to a site-specific level of 1,071 mg/kg (BAc-adjusted site-specific concentration = HIL A (300 mg/kg) / 0.28), i.e., by assuming that the bioaccessibility is conservatively 28.0%. The HIL Level A 100 mg/kg for As and 0.1M hydrochloric acid extractable As is equivalent to a site specific level of 280 mg/kg (BAc-adjusted site specific concentration = HIL A 100 mg/kg/ 0.36); The HIL Level A 6000 mg/kg for Cu and 0.1M hydrochloric acid extractable Cu is equivalent to a site specific level of 27,300 mg/kg (BAc-adjusted site specific concentration = HIL A 6000 mg/kg/ 0.22), i.e. assuming BAc is 22.0%. If 'bioaccessibility-adjusted' concentration is utilized, no exceedances of HIL A from metals and As in soil occurs. The HIL Level A 20 mg/kg for Cd and 0.1M hydrochloric acid extractable Cd is equivalent to a site-specific level of 468 mg/kg (bioaccessibility-adjusted), assuming bioaccessibility is 4.27%. This shows 'BAc-adjusted' concentrations (n=22) do not exceed HIL A for Cd.

Table 3 summarizes and compares historical Pb and Cd (µg/m^2.day) fall-out data at Port Kembla and other Wollongong sites, with fallout data from the electrolytic refinery site at Hobart, Tasmania (located 1600 km south of Sydney, NSW; Fig. 1). Converting the measured fall-out in units of µg/cm^2.year to µg/m^2.day (Table 3) enabled a comparison of historical data for Pb and Cd with current German dust metal and metalloid deposition guidelines (TA LUFT, 1990 and1991). A retrospective evaluation of fallout data compared to German guidelines informs on the significance of historical Pb and Cd deposition in soil. Data in Table 3 shows: (i) Lead at sites near Port Kembla smelters exceed TA LUFT 'protection of human health and crop land integrity' and 'Grassland integrity' (May 1981) for fallout monitoring during the 1970s - 1980s; and (ii) Cadmium, at all sites at Port Kembla, exceed TA LUFT 'Protection of human health' guideline by 47 times at a value of 94µg/m^2.day except when <5.5µg/m^2.day. Contour diagrams of dust fall-out in Archibold and Crisp (1983) showed that Pb deposition extended across the north central part of the Wollongong study area in September 1980, with peak fallout occurring at the smelter, which subsequently decreased in April 1981. Table 3 shows the residents at this time could have been exposed (ingestion) to elevated Cd and Pb from fall-out.

Cd and Pb uptake from atmospheric fall-out, could have occurred in vegetable gardens, 1-2 km from smelter locations. Although current emission of Pb is not an issue in Wollongong for human health exposure from inhalation, it is possible that remobilization of Pb or Cd from surface soil is an ingestion issue today, particularly for children. The historical record of Cd and Pb fallout from the Port Kembla copper smelter and steelworks indicates the extent of dispersion of Cd and Pb was real and likely resulted in direct exposure to residents or due to ingestion of garden vegetables.

For ecological conditions soil organisms can be affected. Comparison of fallout levels of Cd and Pb in Hobart suburbs from the electrolytic zinc refinery (Table 3) show emissions were lower than for Port Kembla, but similar to Wollongong suburbs. Dietary exposure to Cd, Pb, Zn, Cu, and As is a risk to human health through consumption of vegetables, especially in urban-residential areas. The extent of Cu uptake in vegetables sampled from soils in the vicinity of the smelter at Port Kembla was greater than at other smelter sites (Kachenko and Singh, 2006). Both Cd and Pb in vegetables at Port Kembla exceeded Australian Food Standards maximum level (ML both 0.1 mg/kg fresh weight for Cd and Pb; (FSANZ 2016; Kachenko and Singh, 2006). This highlights the importance of historical investigations and retrospective evaluations. This study reveals the risk of heavy metal persistence in urban-residential soils near historic smelter operations. Local residents may be at risk from growing vegetables in soils not completely rehabilitated following decommissioning of smelters.

Table 3 Summary of historical air fallout data for lead and cadmium at Port Kembla and Wollongong, NSW and Hobart, Tasmania

Site (n)	Cadmium Mean±se (µg/m^2.day)	Lead Mean±se (µg/m^2.day)	Reference
Wollongong suburbs			
Wollongong suburbs (2)	<5.5	71.2 ±27.4	Beavington (1977)
September 1980 (13)	-	185 ±36.8	Crisp et al., (1984)
October 1980 (4)	-	725 ±323	Crisp et al., (1984)
November 1980 (9)	-	183 ±44	Crisp et al., (1984)
Port Kembla			
Port Kembla smelter/ works (5)	26.3 ±9.7	568 ±230	Beavington (1977)
September 1980(1)	-	1040	Crisp et al., (1984)
October 1980(1)	-	4870	Crisp et al., (1984)
May 1981(7)	94 ±3.0	3760 ±109	Archibold and Crisp (1983)
Rural site			
56km from SC smelter (1)	<5.5	24.7	Beavington (1977)
Hobart suburbs			
Hobart suburbs (11)	1.70 ±0.60	40 ±14	Ayling and Bloom (1976)
Electrolytic zinc refinery site (7)	6.0 ±5.0	173 ±100	Ayling and Bloom (1976)
Dust Deposition Guidelines			
Cadmium[a]	2		TA LUFT (1990, 1999)
Lead[a]			
Protection of human health[b]		100	
Protection of crop land integrity[c]		185	
Protection of grassland integrity[c]		1900	

Source a. Averaging Period 1 year; *b .TA LUFT (1990); and c. TA LUFT (1999).*

CONCLUSION

The total concentrations of heavy metals and As in 95 surface soil samples collected in 2009 as percentile values provided better resolution of dispersion distance from the copper smelter at Port Kembla. The comprehensive treatment of existing data by comparing historical data against current guidelines was not previously possible until this study. Historical fallout data compared against current heavy metal fall-out guidelines predicts past smelter emissions build-up in soil suggesting potential risks to residents ingesting vegetables grown from contaminated urban soils.

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