

Trace-Elements in Sheep Grazing near a Lead-Zinc Smelting Complex at Port Pirie, South Australia

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In South Australia, several studies have shown that heavy metal pollution of soils and plants occurs in the vicinity of a lead-zinc smelter at Port Pirie (Tiller et al. 1975; Cartwright et al. 1977). With about 470,000 tonnes of lead concentrates and ores treated in 1983 (The Broken Hill Associated Smelters Pty. Ltd., Works Production List 1983), the metal-refining complex at Port Pirie incorporates the world's largest Pb smelter. Since its operation in 1889, the smelters have produced about 12 million tonnes of Pb (South Australia Department of Mines and Energy, 1984). Data on soil analysis indicates that at least 3,400 km² of land near these smelters has been contaminated by the fallout of Pb, Zn and Cd (Tiller et al 1975). These workers estimated that the total Pb fallout was equivalent to about 40,000 tonnes, with most of it being deposited prior to 1925-30.

It is possible that contamination of soil and pasture by heavy metals may adversely affect the health of livestock grazing near the smelters. In sheep, Pb toxicity causes anorexia, abdominal pain and diarrhoea (Neathery and Miller 1975) whilst Zn or Cd supplementation reduces the Cu status (Mills and Dalgarno 1972; Lee and Jones 1976). This study was undertaken to investigate the effects of heavy metals on the trace-element status of sheep grazing at selected distances from the Port Pirie smelters.

MATERIALS AND METHODS

Based on the findings of Cartwright et al (1977), six properties from 6 to 40 km south-south east of the smelters were selected (Figure 1). The area generally has dry summers and wet winters. An average annual rainfall of 510 mm was recorded during the present study. One-year old Merino wethers, crossbred wethers and crossbred ewes with an average liveweight of 40 kg were obtained from a region free of major industrial activity. These sheep were stratified by liveweight within breed and sex and allocated at

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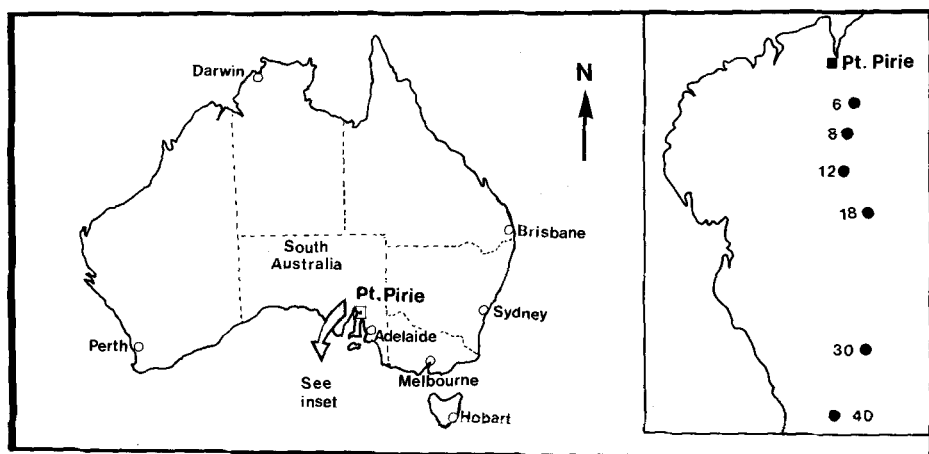


Figure 1. Distance (km) of sampling sites from a lead-zinc smelting complex at Port Pirie, South Australia.

random to one of six properties, each stocked with 14 sheep. Over a period of two years (1978-1979), blood and fecal samples were collected every 3 months and every 6 months, 3 sheep were killed on each property and samples of liver, kidney cortex, muscle, brain and bone were taken for chemical analysis.

Tissue and fecal samples were dried at 100°C for 48 h prior to chemical analysis. Fecal samples were ashed at 750°C for 2 h for ash content. The fecal ash was treated with 11.3 M HCl and 0.72 M LaCl_3 and assayed for Ca by atomic absorption spectroscopy (AAS). Samples of dried bone were defatted using an ether-soxhlet extraction procedure (Official Methods of Analysis, 1980).

Copper, Zn and Fe concentrations in blood, tissues and feces were determined using the methods described by Judson et al (1982). Blood Pb and Cd were assayed by the method of Mitchell et al (1972) with the results verified by a second method (Subramanian and Meranger 1981). Blood Se was assayed fluorometrically (Watkinson 1966) and liver Mo determined colorimetrically (Quin and Brooks 1975).

Lead and Cd in feces and in tissues were assayed by one of two methods depending on their concentrations. For samples of low metal content, 0.1 - 0.3 g sample was accurately weighed into a 5 mL plastic vial containing 1 mL of 16 M HNO_3 (Aristar grade, BDH). The mixture was heated at 100°C until the evolution of copious fumes of nitrous oxide subsided. The clear amber solution was made up to 5 mL with glass distilled water and assayed for Pb and Cd using a Varian CRA-90 carbon rod atomizer connected to a Varian AA-775 AAS. For samples of higher metal content 0.2 - 0.4 g sample was accurately weighed into a 19 x 150 mm test tube containing 4 mL of 16 M HNO_3 : 11.3 M HClO_4 mixture (4:1 v/v).

The mixture was heated to 210°C until fumes of HClO_4 appeared: the residue was made to volume with glass distilled water and the Pb and Cd were determined using a Varian AA-775 AAS.

Internal quality control materials which have been assayed by other laboratories, and U.S. National Bureau of Standards, Bovine Liver SRM 1577 and Orchard Leaves SRM 1571 were assayed with each batch of samples.

Hematocrit values were obtained using a hematocrit centrifuge.

Results were examined by one-way analysis of variance and the means were compared by the use of Duncan's multiple range test at the 5% level of probability.

RESULTS AND DISCUSSION

Throughout the study all sheep appeared clinically normal. Blood hematocrit values were similar ($P > 0.05$) for sheep at different sites, the overall mean was 38 % and the range was 26-48 %.

Selected minerals in the fecal samples were assayed as an indication of their intake by sheep (Table 1). It is evident from these results that the nearer the sheep were to the smelters, the higher the intake of Pb, Cd and Zn. Sheep 6 km from the smelters had fecal concentrations of Pb, Cd and Zn up to 110, 500 and 10 times respectively greater than values observed in sheep in the '40 km' group. Fecal Cu concentrations were not markedly altered by location (see Table 1) and Ca concentrations, not given in Table 1, was similar ($P > 0.05$) at all locations: the overall mean fecal Ca was 530 mmol/kg dry matter (D.M.) with a range of 250-1200. Seasonal variation was observed in the fecal ash content, with the highest values in the autumn-winter months (weeks 24 and 73 of the trial) and the lowest in the spring-summer months (weeks 50 and 98). This variation could be due to seasonal variation in the digestibility of the pasture or as a result of soil ingestion. There was no significant correlation ($P > 0.05$) between metal and ash content of feces.

Table 2 gives a summary of blood Pb and Cu concentrations. Generally, blood Pb concentrations decreased with distance from the smelters (Table 2). The highest mean value of 1.26 $\mu\text{mol Pb/L}$ was observed in sheep at the '6 km' site at week 87 of the trial. Ward et al (1978) reported a blood Pb value of 4.3 $\mu\text{mol/L}$ in sheep near a major highway and grazing grass containing about 300 $\mu\text{mol Pb/kg D.M.}$ Fecal values (Table 1) indicate that it is unlikely that pasture Pb values were as high as this even if the digestibility of pasture was assumed to be as low as 50%. Blood Cu levels, particularly at weeks 12 and 24, were significantly lower ($P < 0.05$) in sheep grazing near the smelters.

Blood Cd was undetected at a detection limit of 0.02 $\mu\text{mol/L}$ in all sheep. The unresponsive feature of blood Cd towards Cd intake by sheep was confirmed in a preliminary study (unpublished observations) with two sheep given a total of 16 moles of Cd as

CdCl₂ over a period of 90 days. Other elements measured in blood in the present study included Zn, Fe and Se. These elements were not affected ($P > 0.05$) by location of sheep or season and the overall mean values with their ranges were 15 $\mu\text{mol/L}$ (8.2 - 24.1) for plasma Zn, 32 $\mu\text{mol/L}$ (32 - 47) for plasma Fe and 5.2 $\mu\text{mol/L}$ (3.1 - 6.6) for blood Se.

Significant increases ($P < 0.05$) in Pb and Cd were evident in the

Table 1: Mean concentration of lead, cadmium ($\mu\text{mol/kg D.M.}$), zinc, copper (mmol/kg D.M.) and ash (%) in faeces of sheep grazing at various distances from a lead-zinc smelting complex.

Week of trial	Test	Distance from smelters (km)						Sig. [#] of diff
		6	8	12	18	30	40	
12	Pb	257.0(5) ^a	221.8(6) ^a	181.3(6) ^a	62.8(6) ^b	11.5(6) ^b	4.5(5) ^b	***
	Cd	18.9(5) ^a	12.6(6) ^b	10.3(6) ^c	6.4(6) ^d	2.8(6) ^e	2.0(6) ^e	***
	Zn	4.9(5) ^a	2.3(4) ^b	2.5(6) ^b	1.5(6) ^c	1.2(6) ^{cd}	1.1(6) ^e	***
	Cu	0.5(5) ^e	0.4(4) ^{ab}	0.3(6) ^{bc}	0.4(6) ^a	0.3(6) ^{bc}	0.3(6) ^c	***
	ash	32.8(5)	42.1(6)	35.3(6)	38.6(6)	32.0(6)	33.0(6)	NS
24	Pb	342.6(5) ^a	228.3(6) ^{ab}	167.2(5) ^{ab}	219.7(6) ^b	26.3(4) ^c	11.6(5) ^c	***
	Cd	16.3(5) ^b	31.6(6) ^a	22.7(5) ^{ab}	23.8(6) ^{ab}	1.9(4) ^c	0.9(5) ^c	***
	Zn	5.5(4) ^c	5.2(6) ^c	5.0(5) ^c	2.9(5) ^a	1.4(3) ^b	0.8(5) ^b	***
	Cu	0.6(5) ^a	0.6(6) ^a	0.6(5) ^a	0.4(6) ^b	0.3(4) ^b	0.3(4) ^b	***
	ash	47.2(5) ^a	48.3(4) ^a	39.6(4) ^a	50.7(6) ^a	70.9(4) ^b	60.2(5) ^{ab}	*
38	Pb	470.0(6) ^a	126.8(6) ^c	236.0(6) ^b	86.5(6) ^c	16.6(6) ^d	4.3(6) ^e	***
	Cd	44.0(6) ^a	30.2(6) ^{ab}	20.5(6) ^b	25.3(6) ^b	4.1(6) ^c	2.7(6) ^c	***
	Zn	7.5(6) ^a	4.1(5) ^b	4.1(6) ^b	2.5(6) ^c	1.6(6) ^d	1.5(6) ^d	***
	Cu	0.6(6)	0.5(5)	0.6(6)	0.8(6)	0.6(6)	0.7(6)	NS
	ash	31.5(6)	26.6(6)	15.6(5)	21.5(6)	24.3(6)	22.6(5)	NS
50	Pb	222.2(9) ^b	86.5(8) ^{bc}	366.8(8) ^a	54.5(8) ^c	2.8(6) ^{cd}	0.0(5) ^{cd}	***
	Cd	38.4(8) ^a	14.4(9) ^b	34.3(7) ^a	4.7(9) ^c	3.0(6) ^{cd}	1.4(9) ^d	***
	Zn	4.1(7) ^a	2.7(9) ^a	3.6(5) ^b	2.0(9) ^c	0.7(7) ^d	0.9(8) ^d	***
	Cu	0.3(8)	0.3(9)	0.3(5)	0.3(9)	0.3(7)	0.3(9)	NS
	ash	18.5(7) ^a	16.0(8) ^a	14.2(6) ^a	16.3(9) ^a	13.7(8) ^a	23.8(7) ^b	**
61	Pb	219.0(6) ^a	116.7(7) ^b	88.2(5) ^b	63.7(7) ^b	11.0(6) ^c	4.9(6) ^c	***
	Cd	105.2(6) ^a	26.2(6) ^b	11.3(5) ^c	17.6(7) ^d	2.0(6) ^e	0.2(6) ^f	***
	Zn	10.0(6) ^a	2.4(6) ^b	1.5(5) ^c	2.1(7) ^b	0.8(6) ^d	1.0(6) ^{cd}	***
	Cu	0.6(7) ^a	0.4(6) ^b	0.2(5) ^c	0.2(7) ^c	0.3(6) ^c	0.4(6) ^b	***
	ash	24.7(7)	31.2(6)	27.0(5)	29.6(7)	26.8(6)	26.6(6)	NS
73	Pb	135.8(8) ^a	137.0(7) ^a	115.3(3) ^a	52.7(6) ^b	11.0(6) ^c	9.8(5) ^c	***
	Cd	48.3(8) ^a	38.1(7) ^a	26.6(3) ^b	20.1(6) ^b	3.2(6) ^c	2.1(5) ^c	***
	Zn	4.7(6) ^a	4.5(7) ^a	4.4(3) ^a	2.4(6) ^b	1.5(6) ^c	1.2(5) ^c	***
	Cu	0.6(6) ^a	0.6(7) ^a	0.6(3) ^a	0.4(6) ^b	0.5(6) ^a	0.3(5) ^b	***
	ash	46.3(5) ^{ab}	34.0(9) ^b	28.5(3) ^b	41.4(6) ^b	36.6(6) ^b	58.4(5) ^a	***
87	Pb	196.5(6) ^a	136.8(4) ^b	122.3(3) ^b	25.0(3) ^c	33.8(4) ^{cd}	5.3(4) ^d	***
	Cd	30.4(6) ^a	21.5(4) ^{ab}	24.3(3) ^a	15.0(3) ^b	2.3(4) ^c	1.6(4) ^c	***
	Zn	5.5(6) ^d	4.8(4) ^d	3.1(4) ^a	1.7(4) ^b	1.5(3) ^{bc}	0.7(5) ^c	***
	Cu	0.5(6) ^a	0.7(4) ^a	0.5(4) ^b	0.5(4) ^b	0.5(3) ^b	0.4(4) ^b	*
	ash	19.1(4) ^c	28.9(4) ^{abc}	36.5(4) ^{abc}	21.9(4) ^{bc}	41.3(3) ^{ab}	46.5(3) ^a	**
98	Pb	122.5(4) ^a	94.3(4) ^a	44.7(3) ^b	40.5(3) ^b	8.3(3) ^c	6.9(6) ^c	***
	Cd	22.7(4) ^c	20.5(4) ^c	26.1(3) ^a	17.7(3) ^c	3.3(3) ^b	1.1(6) ^b	***
	Zn	2.3(4) ^a	1.8(4) ^b	1.9(3) ^{ab}	1.6(3) ^b	1.1(3) ^c	0.5(5) ^d	***
	Cu	0.2(4)	0.2(4)	0.3(3)	0.3(3)	0.3(3)	0.3(5)	NS
	ash	22.9(3)	30.8(3)	24.2(3)	20.9(3)	21.1(4)	15.9(4)	NS

Number of samples assayed in parentheses. [#] Significance of difference:*** ($p < 0.001$), ** ($p < 0.01$), * ($p < 0.05$) and NS (not significant). For each row, mean values with a different superscript differ ($p < 0.05$).

Table 2: Mean concentration ($\mu\text{mol/L}$) of blood lead and plasma copper of sheep grazing at various distances from a lead-zinc smelting complex.

Week of trial	Test	Distance from smelters (km)						Sig [#] of diff
		6	8	12	18	30	40	
12	Pb	1.03 ^a	0.73 ^{ab}	0.69 ^{ab}	0.47 ^{bc}	0.27 ^{cd}	0.22 ^d	***
	Cu	10.70 ^a	8.60 ^a	11.90 ^{ab}	13.60 ^{abc}	15.50 ^{bc}	16.40 ^{bc}	**
24	Pb	0.82 ^a	0.61 ^{ab}	0.41 ^b	0.32 ^b	0.42 ^b	0.31 ^b	**
	Cu	7.10 ^{ab}	4.70 ^a	9.40 ^{bc}	14.70 ^{cd}	15.50 ^d	16.30 ^d	***
38	Pb	0.79 ^a	0.52 ^{ab}	0.38 ^b	0.36 ^b	0.29 ^{bc}	0.19 ^c	***
	Cu	19.50 ^{ac}	15.80 ^b	21.60 ^a	20.10 ^{ac}	17.90 ^b	18.00 ^{bc}	*
50	Pb	0.87 ^a	0.34 ^{bc}	0.72 ^a	0.53 ^b	0.22 ^{cd}	0.14 ^d	***
	Cu	18.10	18.30	17.70	19.20	18.50	19.90	NS
61	Pb	0.92 ^a	0.62 ^b	0.74 ^b	0.54 ^b	0.53 ^b	0.23 ^c	**
	Cu	19.20	14.20	18.40	18.90	16.00	17.30	NS
73	Pb	0.80	0.71	0.89	0.82	0.69	0.76	NS
	Cu	13.70	10.40	12.20	15.90	17.70	14.00	NS
87	Pb	1.26 ^a	0.52 ^b	0.53 ^b	0.47 ^b	0.43 ^b	0.20 ^c	***
	Cu	18.20	16.30	14.00	17.90	18.00	18.10	NS
98	Pb	0.82 ^a	0.63 ^{ab}	0.63 ^{ab}	0.53 ^b	0.43 ^{bc}	0.34 ^c	**
	Cu	16.80	18.30	17.30	15.30	16.30	16.00	NS

Each value represents the mean of 6 determinations except at 12 km (week 73) where each value represents 3 determinations. # Refer to Table 1 for explanatory note.

Table 3: Mean concentration of copper, zinc (mmol/kg D.M.), lead and cadmium ($\mu\text{mol/kg D.M.}$) in livers of sheep grazing at various distances from a lead-zinc smelting complex.

Week of trial	Test	Distance from smelters (km)						Sig [#] of diff
		6	8	12	18	30	40	
24	Cu	0.1 ^a	0.2 ^a	0.3 ^a	0.8 ^b	3.0 ^c	2.9 ^c	***
	Pb	20.1 ^a	24.7 ^a	9.2 ^b	6.5 ^b	2.1 ^c	3.1 ^c	**
	Cd	17.0 ^a	18.3 ^a	10.1 ^b	8.8 ^b	2.3 ^c	1.8 ^c	***
	Zn	2.0	2.3	2.2	1.9	1.7	2.1	NS
50	Cu	1.8 ^a	1.5 ^a	2.7 ^{ab}	3.0 ^{ab}	7.1 ^c	3.8 ^b	**
	Pb	29.5 ^a	19.2 ^b	25.0 ^a	23.2 ^{ab}	4.8 ^c	6.2 ^c	***
	Cd	18.4 ^{ac}	24.0 ^a	45.4 ^b	10.6 ^c	2.2 ^d	2.7 ^d	***
	Zn	1.9	1.9	2.0	2.1	2.2	2.3	NS
73	Cu	3.6 ^b	1.0 ^a	-	2.0 ^{ab}	4.8 ^c	4.9 ^c	*
	Pb	13.1 ^a	17.7 ^a	-	17.1 ^a	5.1 ^b	5.8 ^b	***
	Cd	14.5 ^{ab}	35.2 ^a	-	20.0 ^b	1.9 ^c	1.8 ^c	***
	Zn	1.8	1.6	-	2.1	1.8	1.9	NS
98	Cu	1.1 ^a	1.0 ^a	2.1 ^{ab}	5.4 ^c	7.5 ^c	3.1 ^b	**
	Pb	34.1 ^a	21.7 ^{ab}	15.0 ^b	18.6 ^b	6.6 ^c	4.5 ^c	**
	Cd	22.4 ^{ab}	21.5 ^b	33.9 ^a	12.2 ^c	3.9 ^d	1.4 ^d	***
	Zn	1.7	1.8	2.3	1.7	1.7	1.7	NS

Each value represents the mean of 3 determinations. # Refer to Table 1 for explanatory note.

Table 4: Mean concentration of copper, zinc, (mmol/kg D.M.), lead and cadmium (umol/kg D.M.) in kidney cortex of sheep grazing at various distances from a lead-zinc smelting complex.

Week of trial	Test	Distance from smelters (km)						Sig [#] of diff
		6	8	12	18	30	40	
24	Cu	0.2	0.2	0.3	0.3	0.4	0.3	NS
	Pb	272.0 ^a	194.0 ^{ab}	134.0 ^b	60.0 ^c	12.4 ^d	16.5 ^d	***
	Cd	23.7 ^{ab}	27.5 ^a	20.5 ^{ab}	19.3 ^b	14.2 ^c	18.3 ^{bc}	***
	Zn	2.1	2.0	2.4	1.8	1.8	2.0	NS
50	Cu	0.3	0.2	0.2	0.2	0.3	0.3	NS
	Pb	134.1 ^a	141.2 ^a	89.7 ^b	66.7 ^b	15.3 ^c	25.1 ^c	***
	Cd	62.7 ^a	120.6 ^b	168.3 ^b	54.7 ^a	27.0 ^c	21.3 ^c	***
	Zn	2.3	2.2	2.1	1.9	1.8	1.9	NS
73	Cu	0.3	0.3	-	0.3	0.4	0.3	NS
	Pb	98.0 ^a	131.5 ^a	-	141.5 ^a	18.3 ^b	13.8 ^b	***
	Cd	79.0 ^a	134.0 ^b	-	67.7 ^a	31.3 ^c	27.7 ^c	***
	Zn	2.0	2.1	-	1.9	1.9	1.9	NS
98	Cu	0.2	0.3	0.3	0.2	0.3	0.3	NS
	Pb	352.7 ^a	101.7 ^b	100.0 ^b	62.4 ^b	15.6 ^c	22.3 ^c	***
	Cd	83.0 ^a	73.5 ^a	177.3 ^b	85.0 ^a	25.7 ^c	29.0 ^c	***
	Zn	2.0	1.9	3.0	1.6	1.7	1.6	NS

Each value represents the mean of 3 determinations. [#] Refer to Table 1 for explanatory note.

Table 5: Mean concentration of lead (umol/kg D.M. fat-free) in rib bone of sheep grazing at various distances from a lead-zinc smelting complex.

Week of trial	Distance from smelters (km)						Sig [#] of diff
	6	8	12	18	30	40	
24	231 ^a	168 ^{ab}	135 ^b	36 ^c	19 ^d	12 ^d	***
50	289 ^a	142 ^{bc}	160 ^b	92 ^c	34 ^d	45 ^d	***
73	258 ^a	200 ^a	-	67 ^b	28 ^c	40 ^c	***
98	316 ^a	214 ^b	226 ^b	117 ^c	32 ^d	34 ^d	***

Each value represents the mean of 3 determinations. [#] Refer to Table 1 for explanatory note.

tissues of sheep within 18 km of the smelters (see Tables 3, 4 and 5). Overall, Pb and Cd contents in the kidney were up to about 14 and 5 times respectively greater than those in the liver. Similar observations were recorded in sheep given Cd and Pb (Lee and Jones 1976; Rolton et al. 1978). The reason for the preferential accumulation of Pb in the kidney is unknown. However, the accumulation of Cd in the kidney could have been

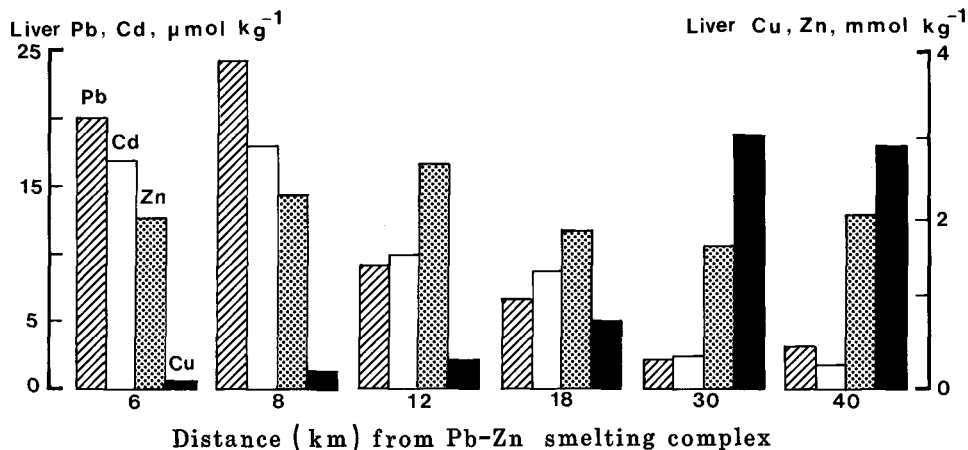


Figure 2. Mean concentration of Pb, Cd, Zn and Cu in liver of sheep at week 24.

due to the direct uptake of Cd, resulting from an increased synthesis of renal metallothionein, and the renal uptake of Cd-thionein released from the liver (Frazier 1982). The mean liver Pb and Cd concentrations in sheep in the '6 km' group were up to 8 and 16 times respectively greater than the values in sheep in the '40 km' group. Similarly, kidney Pb and Cd concentrations in sheep in the '6 km' group were higher, being up to 17 and 3 times respectively greater than values observed in sheep in the '40 km' group. The Pb content of kidney samples were the only tissues found to have metal concentrations in excess of the maximum permitted levels set by National Health and Medical Research Council of Australia. On the four properties nearest the smelters, the mean levels of Pb in the kidney cortex ranged from 60 to 350 $\mu\text{mol/kg}$ D.M., values well above the permitted limit of 9.7 $\mu\text{mol Pb/kg}$ wet weight (equivalent to 39 $\mu\text{mol/kg}$ D.M. assuming a 75 % moisture content). Muscle samples were found to contain less than 2 $\mu\text{mol Pb/kg}$ D.M. and 0.8 $\mu\text{mol Cd/kg}$ D.M.

In contrast to liver Pb and Cd concentrations, liver Cu concentration was found to be inversely related to closeness to the smelters. This situation is particularly noticeable at week 24 of the study (Figure 2). The low concentrations of liver Cu indicate that sheep closest to the smelters were at risk to Cu deficiency. The low Cu status of sheep near the smelters is likely to be an induced deficiency since intake of Cu did not appear to be markedly altered by location (see above). Although Mo and S are known to reduce the availability of dietary Cu, it is unlikely these elements contribute markedly to the lower Cu status of sheep near the smelters. Liver Mo concentrations were found to be similar ($P > 0.05$) in sheep at different locations, with values ranging from 32 to 40 $\mu\text{mol/kg}$ D.M. Although S was emitted from the smelters, this release did not appear to alter the S concentration of the pasture in the area investigated (R.

Merry, personal communication). It is more likely that the high intakes of Cd and Zn by the sheep grazing in the vicinity of the smelters (Table 1) reduced the availability of dietary Cu. The antagonistic effects of Cd and Zn on Cu metabolism in sheep under experimental conditions have been well documented (Mills and Dalgarno 1972; Lee and Jones 1976). In East Germany, it has been reported that sheep grazing in areas contaminated with Cd from industrial plants had abnormally low levels of Cu in tissues (Grun et al, 1977). The high Pb intake of sheep may also have adversely affected the Cu status of the sheep since it has been shown that Pb supplementation causes a reduction in liver Cu reserves of ewes (Chergariu 1978).

Despite the higher Zn intake of the sheep near the smelters, there was no effect of location or season ($P > 0.05$) on the Zn content of liver and kidney. Similar observations on the homeostatic control of liver Zn content were observed by Miller et al (1978) with Zn-supplemented cows. It appears that liver Zn content is an unreliable indicator of Zn intake by ruminants.

The results presented in this study indicate a complex Cu-Cd-Zn-Pb interaction in sheep grazing near the Port Pirie Pb-Zn smelters. Although the mechanisms of this interaction are not known, it is apparent that sheep near the smelters are at risk to Cu deficiency. Further, these sheep were found to have kidney Pb concentrations well above the maximum permitted level recommended for human consumption.

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