Ambient Air Quality Research Project (1996–2001)

Internal working paper no. 4

Ambient concentrations of heavy metals in NSW



Department of Environment and Conservation (NSW) This report was prepared by staff of the Atmospheric Science Section of the Department of Environment and Conservation, Sydney

For further information about this report, phone Director Atmospheric Science on (02) 9995 5000.

This is an internal working paper and has not been reviewed by experts in the field who are independent of the study or the Department of Environment and Conservation.

The original research contained herein is being submitted to a peer-reviewed scientific journal for publication.

The EPA is a statutory body with specific powers under environment protection legislation. In September 2003, the EPA became part of the Department of Environment and Conservation (NSW).

Department of Environment and Conservation (NSW) 59–61 Goulburn Street, Sydney PO Box A290 Sydney South NSW 1232 Phone: (02) 9995 5000 (main switchboard) Phone: 131 555 (NSW only—information and publication requests) Sydney Air Pollution Index: 1300 130 520 Fax: (02) 9995 5999 TTY: (02) 9211 4723 Email: info@epa.nsw.gov.au Website: www.environment.nsw.gov.au

EPA 2003/75 ISBN 1 7413 7003 5 December 2003 Printed on recycled paper

Executive summary

The EPA is a statutory body with specific powers under environment protection legislation. In September 2003, the EPA became part of the Department of Environment and Conservation (NSW).

The NSW EPA conducted a screening survey of ambient metal concentrations in the Sydney, lower Hunter and Illawarra regions. This study was one of four studies on groups of air pollutants that form the Ambient Air Quality Research Project (1996–2001) (NSW EPA 2002).

While heavy metals occur naturally in the urban environment, anthropogenic sources are considered to make the most significant contribution to concentrations of heavy metals.

Regional ambient concentrations of metals were measured at eight monitoring sites in the Sydney–lower Hunter–Illawarra area:

- Blacktown (Sydney region)
- Earlwood (Sydney region)
- Richmond (Sydney region)
- Rozelle (Sydney region)
- Sydney CBD (Sydney region)
- Newcastle CBD (lower Hunter region)
- Albion Park (Illawarra region)
- Wollongong CBD (Illawarra region).

Samples were collected on four days from mid-August to early September 2000. Metals were collected on glass fibre filter paper using a high-volume sampler to collect particulate matter with an aerodynamic diameter of less than 10 microns (with a PM_{10} inlet), then, following nitric acid digestion, were quantified by inductively-coupled plasma-mass spectroscopy. The filter papers were analysed for the presence of twelve metals:

- antimony*
- arsenic*
- beryllium*
- cadmium*
- cobalt*
- copper
- lead*
- manganese*
- nickel*
- selenium*
- vanadium
- zinc.

The nine metals marked with an asterisk above have been nominated as 'hazardous air pollutants' by the US EPA. The three additional metals—copper, vanadium and zinc—were also analysed for.

The study provides preliminary data on regional ambient concentrations of these twelve metals in Metropolitan Sydney and the Illawarra and lower Hunter regions.

Table 1 overleaf summarises the average ambient concentration of the metals measured across all eight sites as well as the range in 24-hour levels and compares them with current international goals. The concentrations are reported in nanograms per cubic metre (ng/m³). A nanogram is 1 x 10^9 grams or 0.000000001 grams.

Beryllium was not detected in any study samples. There are no relevant international ambient air goals for cobalt and selenium, but these metals were found at very low concentrations (<1 ng/m³) and given their relatively low toxicity, should not represent a concern at a regional level. Similarly, while there are no relevant international goals for copper and zinc in ambient air, the measured concentrations of these relatively low toxicity metals were not elevated. The measured concentrations of antimony were also low.

All regional samples for lead, vanadium and manganese were well below current Australian and international goals. Although conforming with the appropriate goal, the manganese concentration in Newcastle was elevated with respect to other regions. It is likely that these concentrations were associated with dust containing manganese from remediation of the former steelworks next to the monitoring site. Further investigation of the source of these emissions will be undertaken.

The measured concentrations of arsenic, cadmium and nickel were lower than or at concentrations comparable with contemporary international goals. These results are consistent with overseas measurements.

Metal	Average of samples (24-hour: ng/m ³)			Source
Antimony	1.2	0.04–4.6	None available	
Arsenic	0.60	0.09–2.5	6	EC ¹
Beryllium	not detected (i.e. below the detection limit)	not detected (i.e. below the detection limit)	0.4	US EPA
Cadmium	0.17	0.03–1.0	5	EC ¹
Cobalt	0.19	0.10–0.39	none available	
Copper	8.2	2.4–28	none available	
Lead	30	2.4–99	500	NEPM ² & WHO
Manganese	18	3.7–119	150	WHO [#]
Nickel	3.5	0.86–20	20	EC ¹
Selenium	0.20	0.10-0.65	none available	
Vanadium	2.6	0.16–49	1000 (daily average)	WHO [#]
Zinc	33	11–71	none available	

Table 1: Heavy metals—study results and internationally recognised goals

¹ European Commission 2003: recommends measurement of the PM₁₀ fraction. Note: *Ambient Air Quality Research Project (1996–2001) Dioxins, Organics, Polycyclic Aromatic Hydrocarbons and Heavy Metals* (NSW EPA 2002) was published before the European Commission's 2003 goals were finalised. As a result, that report contains the draft goals and this report (Table 7) contains the current goals.

²NEPC 1998: this is the Australian goal for lead set in the National Environment Protection (Ambient Air Quality) Measure (NEPM). Measurement is based on Total Suspended Particulates

[#]WHO 2000: goals are based on guidelines for the risk of health impacts.

It is considered that the average 24-hour results shown in Table 1 are likely to represent the peak concentrations for these heavy metals, as sampling occurred during winter. As a consequence, annual average concentrations calculated from data across the whole year are likely to be lower than these levels and below current (annual average) international goals.

Contents

Executive summary Acronyms and glossary

1	Introduction	1
2	Materials and methods	2
	2.1 Sampling procedure	2
	2.2 Sampling locations	3
	2.3 Sampling dates	5
3	Results	6
4	Discussion of results	10
5	Comparison with international benchmarks	12
6	Conclusions	13
Re	eferences	14
Ap	opendices	16
	Appendix 1: Sampling and analytical procedure	16
	Appendix 2: Ambient metal concentrations measured at each monitoring site	18

List of tables

Table 1: Heavy metals—study results and internationally recognised goals	
Table 2: Details of monitoring sites	4
Table 3: Sampling schedule	5
Table 4: Average metal concentrations measured at each site	6
Table 5: Average ambient metal concentrations (ng/m ³) for the metals which	
account for >95% of the total concentration at each site	10
Table 6: Comparison of results with California	11
Table 7: Heavy metals—study results and internationally recognised goals	12
Table 8: Masses of each metal detected on the blank filters	17

List of figures

Figure 1: Monitoring sites in the Sydney region	3
Figure 2: Monitoring site in the lower Hunter region	3
Figure 3: Monitoring sites in the Illawarra region	4
Figure 4: Summary of the ambient metal concentrations measured at each site	7
Figure 5: Range of regional metal concentrations at each site	9
Figure 6: Average ambient metal concentrations (ng/m ³) which account for	
95% of the total metal concentrations at each site	11

Acronyms and glossary

AAS AECS AS As Be CBD	atomic absorption spectroscopy Analytical and Environmental Chemistry Section Australian Standard arsenic beryllium central business district
Cd Co	cadmium cobalt
CSIRO Cu	Commonwealth Scientific and Industrial Research Organisation copper
ICP-AES ICP-MS	inductively-coupled plasma atomic emission spectroscopy inductively-coupled plasma mass spectroscopy
Mn	manganese
ND	not detected (i.e. concentration below the detection limit)
ng/m³	nanograms per cubic metre
Ni	
NSW EPA Pb	New South Wales Environment Protection Authority lead
PD PM₁₀ Sb	particulate matter with aerodynamic diameter less than 10 micron antimony
Se	selenium
SCMH	standard cubic metres per hour
TSP	total suspended particulate; usually less than 50 micron aerodynamic diameter
µg US EPA	micrograms Unites States Environmental Protection Agency
V	vanadium
Zn	zinc

1 Introduction

Environment Australia (2001) defines heavy metals as:

'metallic elements with relatively high atomic mass (over 5.0 specific gravity), such as lead, cadmium, arsenic and mercury; generally toxic in relatively low concentrations to plant and animal life.'

Metals occur naturally in the environment and do not degrade. They are found in soils and rocks and thus any activity which disturbs the soil, such as mining or wind, can release these metals into the air as particulate matter. Anthropogenic sources of metals include mineral processing industries, power stations using fossil fuels, refineries, brickworks and motor vehicles. Combustion generated particles are generally smaller than geologically produced particles. Research has shown a strong association between particulate exposure and adverse health effects (Ostro and Chestnut 1997; Pope et al 2002; Lighty et al 2000; Mage et al 1999).

In 1995 the New South Wales Environment Protection Authority (NSW EPA) conducted a pilot study of toxic organics in the Sydney Region (NSW EPA 1998). As part of this study a 'desktop inventory' was developed which identified possible sources, types and quantities of emissions from different types of industries. Based on this information, the pilot study recommended that monitoring be expanded to cover a wider range of compounds including polycyclic aromatic hydrocarbons and some metals. This study was part of a more comprehensive Ambient Air Quality Research Project (1996–2001), which focused on measuring regional concentrations of air toxics across the Greater Metropolitan Region.

The NSW EPA conducted a screening survey of metal concentrations in the Sydney, Illawarra and lower Hunter regions. Regional ambient concentrations of metals were measured at eight of the NSW EPA's air quality monitoring sites. The 12 metals studied were:

- antimony*
- arsenic*
- beryllium*
- cadmium*
- cobalt*
- copper
- lead*
- manganese*
- nickel*
- selenium*
- vanadium
- zinc.

The nine compounds marked with an asterisk are included in the eleven metals nominated as 'hazardous air pollutants' by the US EPA. The other two US EPA metals (mercury and chromium VI) were not included as they could not be analysed by the method used here. The three additional metals—copper, vanadium and zinc—were also analysed for.

The results of this study are compared with current internationally recognised goals to indicate whether there is potential risk to human health or the environment.

In September 2003, the NSW EPA became part of the Department of Environment and Conservation (NSW). Since all research in this report was conducted before September 2003, the organisation is referred to as the EPA throughout.

2 Materials and methods

Currently there is no Australian Standard for analysing multiple elements in particles. Several studies in Australia have determined the ambient concentrations of some metals in particles (Ayers et al 1998; Chan et al 1997; Huo et al 1998) although the methods used for sampling and analysis vary between studies. The regional ambient concentrations measured in this study focus on the PM_{10} (particles less than 10µm) fraction of particles.

2.1 Sampling procedure

Sampling occurred during the winter months when it was expected that ambient concentrations would be highest due to stable atmospheric conditions.

A detailed description of the sampling and analytical procedures and an evaluation of the suitability of teflon and glass fibre filter papers for the sampling media is set out in Appendix 1.

Sampling for PM₁₀, particles less than 10µm in diameter, was conducted according to Australian Standard AS 3580.9.6-1990 Method 9.6: Determination of Suspended Particulate Matter—PM₁₀ High Volume Sampler with Size-Selective Inlet—Gravimetric Method (Standards Australia 1990).

The samplers were set to sample for 24 hours on a six-day cycle. PM₁₀ samples were collected on preweighed glass fibre filter papers which were transported to the NSW EPA's Analytical and Environmental Chemistry Section (AECS) for reweighing and pre-treatment prior to analysis.

The pre-treatment was performed according to an internal laboratory method, 'Digestion of Total Suspended Particulates (TSP) in ambient air for metal analysis by Atomic Absorption Spectroscopy (AAS), Inductively-Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) or Inductively-Coupled Plasma Mass Spectroscopy (ICP-MS) Method'. This internal method is based on AS 2800-1985 'Determination of Particulate Lead—High Volume Sampler Gravimetric Collection— Flame Atomic Absorption Spectrometric Method' (Standards Australia 1985). The filter papers were halved or quartered, and one half/quarter digested in nitric acid according to the standard. The remaining portions of the papers were retained by the laboratory for further or repeat analysis if required.

The digested samples together with similarly prepared blanks of each filter type, were then sent to the Commonwealth Scientific and Industrial Research Organisation (CSIRO) Centre for Advanced Analytical Chemistry at Lucas Heights NSW. The samples were analysed by CSIRO using Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS).

The concentrations are reported in nanograms per cubic metre (ng/m³). A nanogram is 1 x 10⁻⁹ grams or 0.000000001 grams.

2.2 Sampling locations

 PM_{10} samplers were located at selected NSW EPA ambient air quality monitoring network sites. Figures 1–3 show the locations of the monitoring sites and Table 2 describes these locations. The stations are located according to AS 2922-1987, the Australian Standard for the siting of sampling units (Standards Australia 1987).

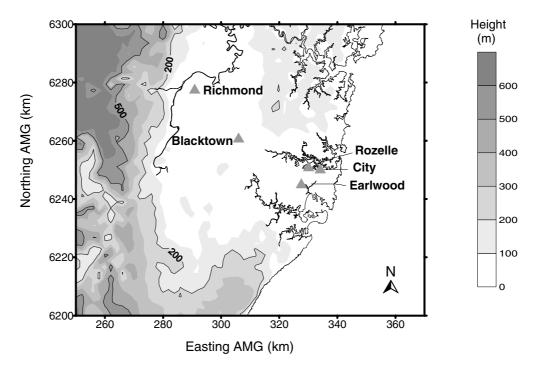


Figure 1: Monitoring sites in the Sydney region

Figure 2: Monitoring site in the lower Hunter region

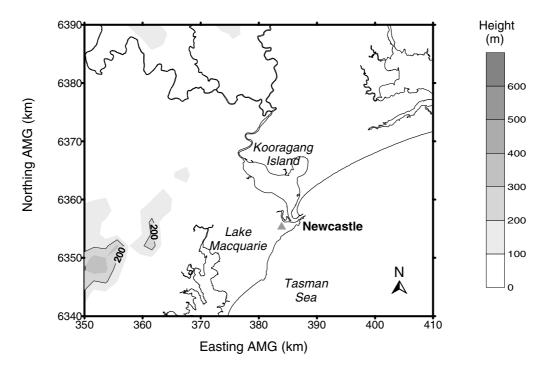


Figure 3: Monitoring sites in the Illawarra region

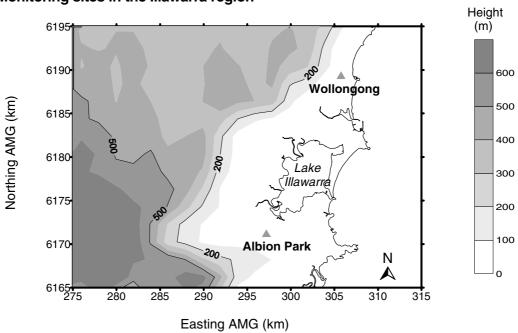


Table 2: Details of monitoring sites

		Address
Sydney Metropolitan	Blacktown	This site is in the Sydney Water depot on Flushcombe Road, Blacktown. It is situated on a ridge in the centre of the Sydney basin, in a residential area and is at an elevation of 75 metres
	Earlwood	This site is in Beaman Park, off Riverview Road, Earlwood in a residential area in the Cook's River valley and is at an elevation of 7 metres.
	Rozelle	This site is in the grounds of Rozelle Hospital on Balmain Road. Monitoring is at the north-western end of the hospital grounds, with Victoria Road and Balmain Rd/Darling St some 300 m distant. Traffic on Victoria Road becomes congested in the morning and afternoon peak hours.
	Richmond	This site is in the campus of the University of Western Sydney, Hawkesbury in the north of the Hawkesbury basin in a residential/semi- rural area and is at an elevation of 21 metres.
	Sydney CBD	This site is on the corner of George and Market streets, either on the awning of the Gowings Building (until May 2000) or the awning of the Grace Brothers building (opposite side of Market Street, after May 2000), above a very high-traffic area intersection.
Lower Hunter	Newcastle	This site is in the grounds of the Athletics Field on Dumaresq St, Hamilton South in a residential area approximately 2 km from the Newcastle city centre.
Illawarra	Albion Park	This site is in the Croom Sporting Complex on Croom Road, Albion Park in a semi-rural area in the south of the Illawarra basin and is at an elevation of 28 metres.
	Wollongong	This site is in the Australian Army Depot on Gipps St in a residential area, approximately 1 km north-west of the Wollongong city centre.

2.3 Sampling dates

Sampling at all sites occurred during August and early September 2000. Sample dates are shown in Table 3.

Table 3: Sampling schedule

	15 Aug 00	21 Aug 00	27 Aug 00	2 Sep 00
Blacktown	\checkmark	\checkmark	\checkmark	\checkmark
Earlwood	\checkmark	\checkmark	\checkmark	\checkmark
Richmond	✓	✓	\checkmark	\checkmark
Rozelle	\checkmark	\checkmark	✓	\checkmark
Sydney CBD	\checkmark	✓	✓	\checkmark
Newcastle	\checkmark	✓	\checkmark	\checkmark
Albion Park	\checkmark	\checkmark	\checkmark	\checkmark
Wollongong	✓	✓	~	\checkmark

3 Results

The ambient metal concentrations measured in each *sample* at each monitoring site are summarised in Figure 4 and Appendix 2. Table 4 summarises the average metal concentrations measured at each *site*.

								Wollongong ng/m ¹
Antimony	0.40	1.4	0.11	2.2	2.2	2.8	0.22	0.28
Arsenic	1.3	0.84	0.40	0.44	0.51	0.84	0.18	0.22
Beryllium	nd							
Cadmium	0.10	0.14	0.06	0.16	0.28	0.41	0.04	0.11
Cobalt	0.21	0.16	0.13	0.15	0.26	0.12	0.10	#
Copper	4.2	11	3.9	8.3	22	6.2	3.1	4.9
Lead	28	68	8.9	28	48	30	3.4	24
Manganese	7.4	5.6	4.4	7.0	6.4	66	5.9	4.6
Nickel	0.98	0.95	5.2	#	6.2	1.6	#	#
Selenium	0.29	0.20	0.16	0.14	0.22	0.16	0.10	0.34
Vanadium	0.46	0.46	0.26	0.58	13	1.0	0.48	0.66
Zinc	29	30	26	27	46	47	11	19

Table 4: Average metal concentrations measured at each site

Ambient concentration is less than half that attributable to the blank filter paper, therefore the results are not reported

nd not detected, i.e. below the detection limit

Due to the limited number of samples no conclusions can be drawn regarding the sources of the metals, however several points can be made:

- beryllium concentrations were below the detection limit in all samples at all sites
- the remaining eleven metals were detected at all sites
- nickel was detected at Rozelle, Albion Park and Wollongong although the ambient concentrations were less than half that attributed to the blank filter paper, therefore the results were not reported.

The ambient manganese concentration measured at Newcastle is elevated relative to all the other sites. Elevated concentrations of manganese were found in a previous study, which sampled particles less than 2.5 μ m (Huo et al 1998) at Mayfield (a suburb of Newcastle). This was attributed to a source from steel making.

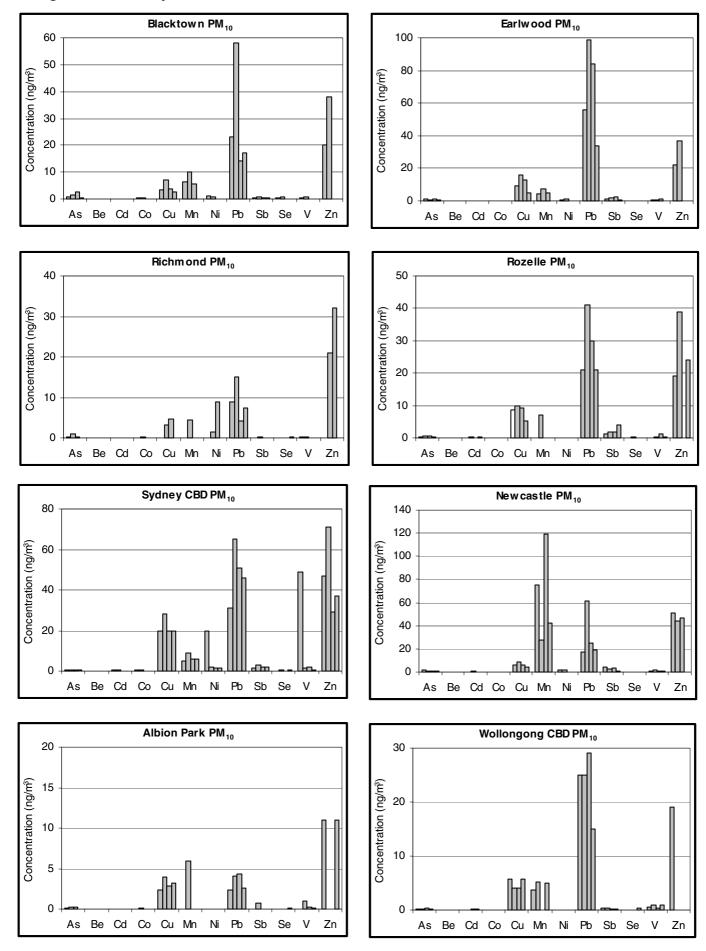


Figure 4: Summary of the ambient metal concentrations measured at each site

Figure 5 presents the average, minimum and maximum concentrations of each metal at each monitoring site. These results are based on the four samples collected at each site.

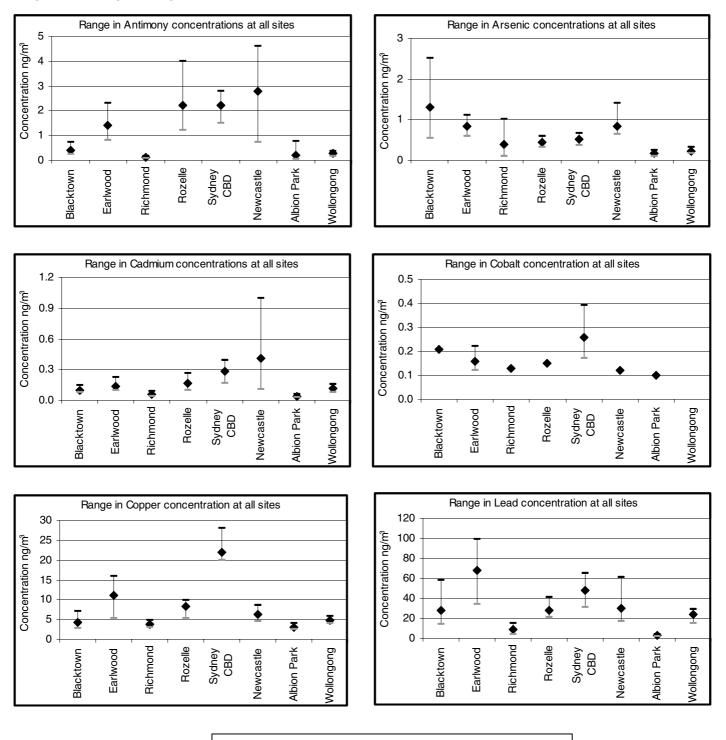
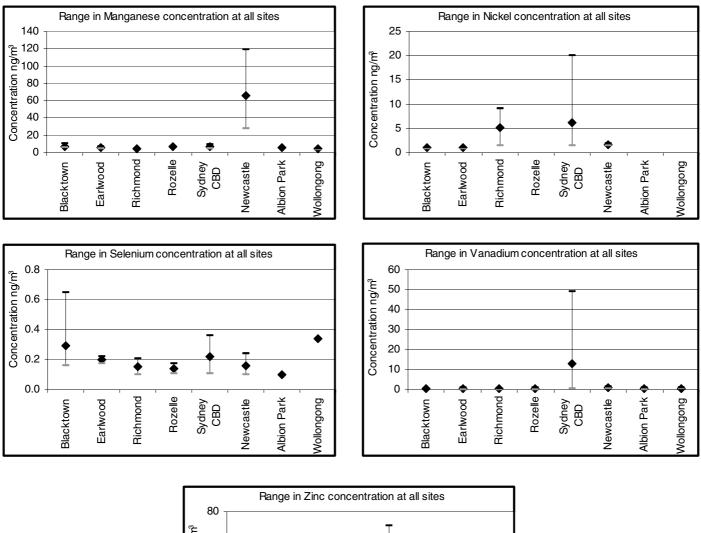
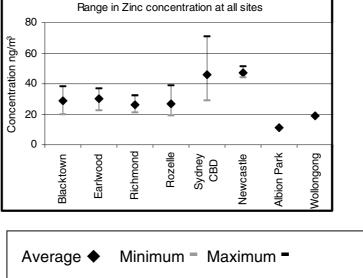


Figure 5: Range of regional metal concentrations at each site

Average
Minimum
Maximum





The results show that the average ambient concentration of each metal remains fairly constant across all sites. The only exception is elevated manganese concentrations at the Newcastle site and elevated vanadium concentrations at the Sydney CBD site. Cadmium, selenium and cobalt are less than 1 ng/m³ and arsenic and antimony are less than 5 ng/m³ in all 24-hour samples across all sites.

4 Discussion of results

The concentrations of each metal detected, from highest to lowest, at each site are given below. The set in bold represent 95% of the total concentration of metals found at each site:

- Blacktown—**zinc, lead, manganese, copper,** arsenic, nickel, vanadium, antimony, selenium, cobalt, cadmium
- Earlwood—lead, zinc, copper, manganese, antimony, nickel, arsenic, vanadium, selenium, cobalt, cadmium
- Richmond— zinc, lead, nickel, manganese, copper, arsenic, vanadium, selenium, cobalt, antimony, cadmium
- Rozelle—lead, zinc, copper, manganese, antimony, vanadium, arsenic, cadmium, cobalt, selenium
- Sydney CBD— **zinc, lead, vanadium, copper, nickel, manganese**, antimony, arsenic, cadmium, cobalt, selenium
- Newcastle—manganese, zinc, lead, copper, antimony, nickel, vanadium, arsenic, cadmium, cobalt
- Albion Park—**zinc, manganese, lead, copper,** vanadium, antimony, arsenic, cobalt, selenium, cadmium
- Wollongong lead, zinc, copper, manganese, vanadium, selenium, antimony, arsenic, cadmium

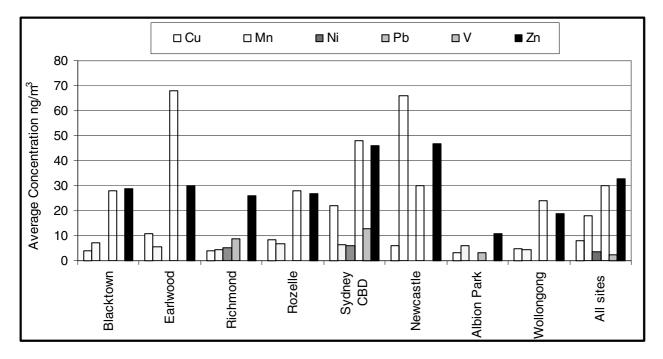
The concentrations of the metals which account for >95% of the total concentration at each site are summarised in Table 5 and Figure 6.

Table 5: Average ambient metal concentrations (ng/m³) for the metals which account for >95% of the total concentration at each site

						Average Zn
Blacktown	4.2	7.4	~	28	~	29
Earlwood	11	5.6	~	68	~	30
Richmond	3.9	4.4	5.2	8.9	~	26
Rozelle	8.3	7.0	~	28	~	27
Sydney CBD	22	6.4	6.2	48	13	46
Newcastle	6.2	66	~	30	~	47
Albion Park	3.1	5.9	~	3.4	~	11
Wollongong	4.9	4.6	~	24	~	19
All sites	8.2	18	3.5	30	2.6	33

~ Not in the top 95%

Figure 6: Average ambient metal concentrations (ng/m³) which account for >95% of the total metal concentration at each site



This variation in the relative ambient metal concentrations at each site has also been found in other overseas studies (CARB 2001). Table 6 compares the range in the concentrations found in this study to the average annual concentrations found in California for the year 2000. The ambient metal concentrations measured in this study are comparable with those measured in California. The Californian measurements demonstrate the large range in concentration for all metals as demonstrated in the limited number of samples in this study.

							Zn ng/m³
Blacktown	Average	4.2	7.4	~	28	~	29
	Min	2.7	5.6	~	14	~	20
	Max	7.0	10	~	58	~	38
Earlwood	Average	11	5.6	~	68	~	30
	Min	5.2	4.4	~	34	~	22
	Max	16	7.4	~	99	~	37
Richmond	Average	3.9	4.4	5.2	8.9	~	26
	Min	3.1	4.4	1.5	4.3	~	21
	Max	4.7	4.4	9.0	15	~	32
Rozelle	Average	8.3	7.0	~	28	~	27
	Min	5.3	7.0	~	21	~	19
	Max	9.9	7.0	~	41	~	39
Sydney CBD	Average	22	6.4	6.2	48	13	46
	Min	20	5.1	1.4	31	0.67	29
	Max	28	8.9	20	65	49	71
California, USA ¹	Average	29.8	26.7	4.2	10.8	8.0	71.4
	Min	1	1	1	2	5	5
	Max	350	130	34	180	32	4800

~ Not in top 95%

¹ Californian data was sampled using a Xontech 920/cellulose filter (measured as PM_{10})

5 Comparison with international benchmarks

There are few international goals for heavy metals against which the concentrations found in this study can be compared. The World Health Organisation's *Guidelines for Air Quality* (2000) and the European Commission's 2003 standards for certain heavy metals are based on annual averages. Given that this study is based on a limited number of 24-hour average samples, only general inferences are possible.

Table 7 compares the results of this study with those available international goals. For beryllium, an assessment based on available US EPA risk factors was used rather than a goal.

Metal	Average of samples (24-hour: ng/m³)	Range of samples (24-hour: ng/m³)	Ambient air goals (annual average: ng/m³)	Source
Antimony	1.2	0.04–4.6	none available	
Arsenic	0.60	0.09–2.5	6	EC ¹
Beryllium	not detected, i.e. below the detection limit	not detected, i.e. below the detection limit	0.4	US EPA
Cadmium	0.17	0.03–1.0	5	EC ¹
Cobalt	0.19	0.10–0.39	none available	
Copper	8.2	2.4–28	none available	
Lead	30	2.4–99	500	NEPM ² & WHO [#]
Manganese	18	3.7–119	150	WHO [#]
Nickel	3.5	0.86–20	20	EC ¹
Selenium	0.20	0.10–0.65	none available	
Vanadium	2.6	0.16–49	1000 (daily average)	WHO [#]
Zinc	33	11–71	none available	

¹ European Commission 2003: recommends measurement of the PM₁₀ fraction. Note: *Ambient Air Quality Research Project (1996–2001) Dioxins, Organics, Polycyclic Aromatic Hydrocarbons and Heavy Metals* (NSW EPA 2002) was published before the European Commission's 2003 goals were finalised. As a result, that report contains the draft goals and this report (Table 7) contains the current goals.

²NEPC 1998: this is the Australian goal for lead set in the National Environment Protection (Ambient Air Quality) Measure (NEPM). Measurement is based on Total Suspended Particulates.

[#]WHO 2000: goals are based on guidelines for the risk of health impacts.

If it is assumed that the maximum concentrations recorded in this study remain constant for all days of the year, the ambient PM_{10} metal concentrations measured at general urban sites (regional) would be well below current international (annual average) goals. It must also be noted that samples have been taken during the winter months (when it was expected that ambient concentrations would be highest due to stable atmospheric conditions) and therefore are not indicative of year-round emissions.

6 Conclusions

The study provides valuable preliminary data on regional ambient concentrations of heavy metals in Metropolitan Sydney and the Illawarra and lower Hunter regions.

Beryllium was below its detection limit in all samples. There are no relevant international ambient air goals for cobalt and selenium, however all the results for these metals were at very low concentrations (<1 ng/m³) and given their relatively low toxicity, should not represent a concern at a regional level. Similarly, while there are no relevant international goals for copper and zinc in ambient air, the measured concentrations of these relatively low toxicity metals were low. The measured concentrations of antimony were also low.

All regional samples for lead, vanadium and manganese were well below current Australian and international goals. Although conforming with the appropriate goal, the manganese concentration in Newcastle was elevated with respect to other regions. It is likely that these concentrations may be associated with dust containing manganese from remediation of the former steelworks next to the monitoring site. Further investigation of the source of these emissions will be undertaken.

The measured concentrations of arsenic, cadmium and nickel were lower or at concentrations comparable with contemporary international goals. These results are consistent with overseas measurements.

References

Ayres G, Keywood M, Gras J, Cohen D, Garton D and Bailey G 1998, *Chemical and Physical Propoerties of Australian Fine Particles: A Pilot Study*, Final Report to Environment Australia from CSIRO Division of Atmospheric Research and Australian Nuclear Science and Technology Organisation

CARB (California Air Resources Board) 2001, *Annual Toxics Summaries*, http://arbis.arb.ca.gov/aqd/toxics/toxics.html

Chan Y, Simpson R, McTanish G, Vowles P, Cohen D and Bailey G 1997, 'Characterisation of Chemical Species in PM₂₅ and PM₁₀ aerosols in Brisbane, Australia', *Atmospheric Environment*, 31

Environment Australia (Department of the Environment and Heritage) 2001, *State of Knowledge Report: Air Toxics and Indoor Air Quality in Australia*, Canberra, ISBN 0642547394

European Commission 2003, *Proposal For a Directive of The European Parliament and of the Council Relating to Arsenic, Cadmium, Mercury, Nickel and Polycyclic Aromatic Hydrocarbons in Ambient Air,* Brussels, 16.7.2003 COM (2003) 423 Final, 2003/0164 (COD)

Huo X, Crisp P and Cohen D 1998, 'Elemental Composition of Fine Aerosol Particles around Sydney during 1992 and 1993', *Clean Air*, 32 (4)

Lighty J, Veranth J M and Sarofim A F 2000, 'Combustion Aerosols: Factors governing their size and composition and implications to human health', *Journal of Air and Waste Management*, 50, 1565–1618

Mage D, Wilson W, Hasselblad V and Grant L 1999, 'Assessment of Human Exposure to Ambient Particulate Matter', *Journal of the Air and Waste Management Association* (49), November 1999

NEPC (National Environment Protection Council) 1998, National Environment Protection Measure for Ambient Air Quality, 26 June 1998

NSW EPA 1998, *Pilot Air Toxics Project*, Technical Report EPA 98/21, New South Wales Environment Protection Authority, Sydney, NSW, Australia

NSW EPA 2002, Ambient Air Quality Research Project (1996-2001) Dioxins, Organics, Polycyclic Aromatic Hydrocarbons and Heavy Metals, New South Wales Environment Protection Authority, 2002/35 http://www.epa.nsw.gov.au/air/dopahhm

Ostro B and Chestnut L 1997, 'Assessing the Health Benefits of Reducing Particulate Matter Air Pollution in the United States', *Environmental Research*, Section A, 76, 96–106

Pope C, Burnett R, Thun M, Calle E, Krewski D, Ito K and Thurston G 2002, 'Lung Cancer, Cardiopulmonary Mortality and Long-Term Exposure to Fine Particulate Air Pollution', *Journal of the American Medical Association*, Volume 287 (9), 1132–1141

Standards Australia 1984, AS 2724.3–1984 – Australian Standard – Ambient Air – Particulate Matter – Determination of Total Suspended Particulates (TSP) – High Volume Sampler Gravimetric Method

Standards Australia 1985, AS 2800–1985 – Australian Standard – Ambient Air – Determination of Particulate Lead – High Volume Sampler Gravimetric Collection – Flame Atomic Absorption Spectrometric Method

Standards Australia 1987, AS 2922–1987 – Australian Standard – Ambient Air – Guide for the Siting of Sampling Units

Standards Australia 1990, AS 3580.9.6–1990 – Australian Standard – Methods for Sampling and Analysis of Ambient Air – Determination of Suspended Particulate Matter – PM_{10} High Volume Sampler With Size-Selective Inlet – Gravimetric Method

WHO (World Health Organisation) 2000, *Guidelines for Air Quality*, Published by the World Health Organization, Geneva http://www.who.int/environmental_information/Air/Guidelines/AQGUIDEpref.pdf

Appendices

Appendix 1: Sampling and analytical procedure

Sampling for PM_{10} , particles less than 10µm in diameter, was performed according to AS 3580.9.6–1990 Method 9.6: Determination of Suspended Particulate Matter – PM_{10} High Volume Sampler With Size-Selective Inlet – Gravimetric Method (Standards Australia 1990).

Samples were collected using an Ecotech model 2000 high volume air sampler, the PM_{10} sampler being fitted with a size-selective inlet. The samplers were set to sample for 24 hours on a six-day cycle. Sample flow rates were set at 68 standard cubic metres per hour (SCMH) in accordance with the standard. The PM_{10} samplers were located at selected NSW EPA ambient air quality monitoring network sites where calibration of flow rates occurred on a routine three-monthly basis using an orifice plate and manometer.

PM₁₀ samples were collected on pre-weighed glass fibre filter papers. As soon as practical after the sampler had finished collecting the sample, the filter paper was removed from the sampler, placed in a clean plastic envelope and transported to the NSW EPA's Analytical and Environmental Chemistry Section for reweighing and pre-treatment prior to analysis.

The pre-treatment was performed according to the Analytical and Environmental Chemistry Section's internal laboratory method, Digestion of Total Suspended Particulates (TSP) in Ambient Air for Metal Analysis by AAS, ICP-AES or ICP-MS Method. This method is based on AS 2800–1985 Determination of Particulate Lead – High Volume Sampler Gravimetric Collection – Flame Atomic Absorption Spectrometric Method (Standards Australia 1985). The filter papers were halved or quartered, and one half/quarter digested in nitric acid according to the standard. The remaining portions of the papers were retained by the laboratory for further or repeat analysis if required.

The digested samples together with similarly prepared blanks of each filter type, were then sent to CSIRO Centre for Advanced Analytical Chemistry at Lucas Heights NSW. The samples were analysed by CSIRO using Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS).

The volume of air sampled was calculated according to AS 2724.3–1984–AS 3580.9.6–1990 using the duration and volume flow-rate of the sample (Standards Australia 1984; Standards Australia 1990). The duration of the sample was known from the hours run meter fitted to the high volume sampler. The average flow-rate during sampling was estimated by noting the flow-rates from the instrument's digital readout when the sample filter was installed and when the sample filter was removed and averaging the two measurements. The total sample volume was then corrected to standard conditions of 101.3 kPa and 273 K using average monthly temperature data for the sampling period.

Two types of unexposed (blank) filter papers (glass fibre and teflon) were analysed to test for concentrations of metals. Table 8 summarises the concentration of each metal detected on the blank filter papers.

Table 8: Masses of each metal detected on the blank filters

			Teflon	Teflon		
	Mass present on blank	Equivalent concentration	Mass present on blank	Equivalent concentration		
	(µg/filter)	(ng/m ³)	(µg/filter)	(ng/m ³)		
As	< 0.04–0.56	< 0.02–0.31	1.0	0.7		
Be	0.12-0.24	0.07–0.13	0.87	0.6		
Cd	0.008-0.15	0.004-0.08	0.4	0.3		
Со	0.10-0.30	0.05-0.16	1.6	1		
Cu	3.3–7.8	1.8-4.2	NA	NA		
Mn	1.6–20	0.9–11	17	11		
Ni	< 0.40–13	< 0.22 –7	8.7	5.6		
Pb	0.12–4.8	0.06 - 2.6	6.6	4		
Sb	0.04–0.13	0.02-0.07	0.38	0.2		
Se	< 0.20–4.0	< 0.11–2.2	51	33		
V	0.41–0.77	0.22-0.42	51	32		
Zn	33–64	18–35	NA	NA		

NA Not available

µg micrograms

Because of the high blank concentrations detected on the teflon papers, glass fibre filter papers were used during this study.

The relatively high quantities of some of the metals detected on the blanks presented a major difficulty for the interpretation of the ambient monitoring data, especially as ambient concentrations were so low.

The concentration of each metal at standard conditions was calculated by dividing the corrected mass per filter by the total sample volume. The metal results obtained from CSIRO were corrected by subtracting a blank value corresponding to the batch of the filter papers. Where both the quantity detected in the sample and corresponding blank filter were below the limit of detection of the analytical method (i.e. reported by the analyst as a 'less than' number), the result was not reported (represented by 'ND' in this report). A blank-corrected mass per filter was then calculated taking into account the portion of the filter analysed except where relatively high blank concentrations were found which may have significantly affected accuracy of the result. In this circumstance the following rules were applied:

- where the quantity detected in the total sample (blank + air) was less than that detected in the corresponding blank, the result was not reported (represented by # in this report)
- where the quantity collected on the filter attributable to the air sample was less than half that attributable to the blank filter, the result was not reported (represented by # in this report).

	BLACKTOW	'N			
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³	
As	0.78	1.5	2.5	0.54	Α
Ве	ND	ND	ND	ND	В
Cd	0.09	0.15	0.08	0.08	С
Co	0.21	0.21	#	#	С
Cu	3.4	7.0	3.8	2.7	С
Mn	6.5	10	5.6	#	Μ
Ni	1.1	0.86	#	#	Ν
Pb	23	58	14	17	Ρ
Sb	0.36	0.72	0.26	0.25	S
Se	0.19	0.65	0.17	0.16	S
V	0.28	0.64	#	#	N
Zn	20	38	#	#	۷ Z

Appendix 2: Ambient metal concentrations measured at each
monitoring site

	RICHMOND			
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³
As	0.34	1.0	0.17	0.09
Ве	ND	ND	ND	ND
Cd	#	0.09	0.04	0.05
Co	#	0.13	#	#
Cu	#	3.1	4.7	#
Mn	#	4.4	#	#
Ni	#	1.5	9.0	#
Pb	9.0	15	4.3	7.3
Sb	0.09	0.16	0.09	0.10
Se	0.10	#	ND	0.21
V	0.18	0.34	#	#
Zn	#	21	32	#

	EARLWOO	D		
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³
As	1.0	0.65	1.1	0.60
Ве	ND	ND	ND	ND
Cd	0.13	0.22	0.11	0.1
Co	0.12	0.22	0.13	#
Cu	9.3	16	13	5.2
Mn	4.4	7.4	5.1	#
Ni	0.9	1.0	#	#
Pb	56	99	84	34
Sb	1.0	1.7	2.3	0.79
Se	0.21	0.22	0.17	#
V	0.31	0.41	0.98	0.16
Zn	22	37	#	#

	ROZELLE			
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³
As	0.39	0.58	0.50	0.31
Ве	ND	ND	ND	ND
Cd	0.1	0.26	0.13	0.16
Co	#	0.15	#	#
Cu	8.5	9.9	9.4	5.3
Mn	#	7.0	#	#
Ni	#	#	#	#
Pb	21	41	30	21
Sb	1.2	1.8	1.7	4.0
Se	ND	0.17	0.11	#
v	#	0.32	1.2	0.22
Zn	19	39	#	24

ND Not detected

Ambient air concentration less than half that attributable to the blank filter paper, therefore results not reported

	SYDNEY CBD							
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³				
As	0.60	0.67	0.42	0.36				
Ве	ND	ND	ND	ND				
Cd	0.37	0.39	0.17	0.21				
Co	0.39	0.30	0.17	0.2				
Cu	20	28	20	20				
Mn	5.1	8.9	6.1	5.7				
Ni	20	1.9	1.4	1.6				
Pb	31	65	51	46				
Sb	1.5	2.8	2.1	2.2				
Se	0.13	0.36	0.11	0.3				
V	49	1.5	2.2	0.67				
Zn	47	71	29	37				

	NEWCAST	LE		
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³
As	1.4	0.69	0.65	0.64
Ве	ND	ND	ND	ND
Cd	0.13	1.0	0.11	0.40
Со	0.12	#	#	#
Cu	6.0	8.6	5.7	4.6
Mn	75	28	119	42
Ni	1.8	1.5	#	#
Pb	17	61	25	19
Sb	4.6	2.7	3.3	0.74
Se	0.10	0.24	0.21	0.10
V	0.58	1.6	1.2	0.73
Zn	51	44	47	#

	ALBION PARK					WOLLONGONG			
	15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³		15-Aug-00 ng/m ³	21-Aug-00 ng/m ³	27-Aug-00 ng/m ³	2-Sep-00 ng/m ³
As	0.10	0.24	0.20	#	As	0.21	0.17	0.31	0.18
Ве	ND	ND	ND	ND	Be	ND	ND	ND	ND
Cd	0.04	0.03	0.06	0.05	Cd	0.08	#	0.16	0.10
Co	#	0.10	#	#	Co	#	#	#	#
Cu	2.4	4.0	2.9	3.2	Cu	5.7	4.1	4.1	5.7
Mn	#	5.9	#	#	Mn	3.7	5.1	#	5.0
Ni	#	#	#	#	Ni	#	#	#	#
Pb	2.4	4.1	4.3	2.6	Pb	25	25	29	15
Sb	0.04	0.76	0.05	0.05	Sb	0.33	0.36	0.27	0.17
Se	ND	ND	#	0.10	Se	#	ND	#	0.34
V	#	1.0	0.27	0.18	v	0.58	0.86	0.28	0.91
Zn	11	#	#	11	Zn	19	#	#	#

ND Not detected

Ambient air concentration less than half that attributable to the blank filter paper, therefore results not reported