

TRACE HEAVY METALS IN FINE AND COARSE AEROSOLS IN FOUR MAJOR AUSTRALIAN CITIES

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Abstract

A study, funded by Department of Environment and Heritage's Living Cities Program, collected samples of both PM_{2.5} (fine particles) and PM_{2.5-10} (coarse particles) over a 12-month period during 2003-2004 in Melbourne, Sydney, Brisbane and Adelaide. 24-hour aerosol samples were collected in six-day cycle using dichotomous samplers at two sites from a typical urban and typical suburban monitoring site operated by the state EPA in each city. ANSTO performed gravimetric analysis and accelerator-based ion beam analysis which provided information on F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, Sr, Br and Pb to determine the elemental composition of the aerosols. The overall average concentration of fine particles was 5.6 µg/m³, while PM_{2.5-10} 10 µg/m³. The concentrations of fine particles did not exceed USEPA air quality standards and proposed 24-hour and annual NEPM goal. The elemental composition of PM_{2.5-10} particles was dominated by Si, Fe, Al, K, Ca, Na and Cl, while black carbon, S, Na and Cl dominated the fine fraction. V, Cr, Ni and Co were below the minimum detection limits in most of the samples. The concentrations of Mn, Cu, Zn and Pb were measured below 0.01 µg/m³ in the coarse particles and below 0.02 µg/m³ in fine aerosols. The measured concentrations of heavy metals exhibit spatial and temporal variations.

Keywords: PM_{2.5}, PM_{2.5-10}, IBA techniques, aerosol elemental composition, trace heavy metals.

1. Introduction

Over the past decade a number of studies in Australia and worldwide found ambient levels of PM₁₀ and PM_{2.5} associated with adverse health effects (eg. Pope III, 2000, Pope et al., 2002, Dockery, 2001). The potential of adverse health effects of particle pollution has triggered further extensive research on concentrations and composition of urban aerosols as these effects were linked to differences in the sources and chemical and elemental composition of particles (Spurny, 2000).

Currently in Australia there is a national study funded through a SPIRT grant, being conducted to investigate the health effects of air pollution in Melbourne, Sydney, Brisbane and Adelaide using standardised statistical approaches. The *Fine*

Particle Composition in Four Major Australian Cities project was aimed at providing analysis of particles and VOCs, which are part of the precursors of secondary aerosols as well as air pollutants by themselves, to aid in the interpretation of the results of the health study. The objectives of this project included:

- To collect 6-daily 24-hr samples of PM₁₀, PM_{2.5} (fine particles), PM_{2.5-10} (coarse particles) and VOC samples from an urban site and a suburban site in Melbourne, Sydney, Brisbane and Adelaide over one year during 2003-2004.
- To analyse the mass concentration, elemental and ionic composition, and PAHs content in the particle samples.
- To analyse the VOCs content in the air samples.

- To investigate the trends and relationship in levels and composition of air pollutants in Australian cities.

This paper discusses the measured concentrations of coarse and fine aerosols and their elemental composition, the concentrations of trace heavy metals (V, Cr, Co, Ni, Mn, Cu, Zn and Pb) and their spatial and temporal trends in Sydney, Melbourne, Brisbane and Adelaide.

2. Sampling and analyses methods

2.1 Sampling regime

24-hr (from midnight to midnight) PM_{2.5} and PM_{2.5-10} samples were collected concurrently in Adelaide, Brisbane, Melbourne and Sydney at one urban and one suburban site in each city (see Hawas et al., 2003 for site description) on Nuclepore and Teflon filters using dichotomous samplers at the established EPA sites.

Dichotomous sampling of PM_{2.5} and PM_{2.5-10} at EPA Victoria sites used Anderson dichotomous samplers, which have 37-mm diameter filter cassettes. Dichotomous sampling at the other EPA sites used Partisol 2025 Sequential Dichotomous samplers leased from the Ecotech Pty Ltd (Rupprecht and Patashnick, 2001). The Partisol dichotomous samplers have 47-mm diameter filter cassettes. The procedures are in compliance with the Australian Standard AS3580.9.7 (Standards Association of Australia, 1990, USEPA, 1998).

The dichotomous sampling of PM_{2.5} and PM_{2.5-10} at the Melbourne, Sydney and Brisbane sites started in March 2003 and ended in March 2004. This generated 12 months of mass and elemental composition data for all these sites, except for the Earlwood site in Sydney. Due to several sampler/filter problems about 9 months of data are available for the Earlwood site. Due to constraints in resources, sampling at the Adelaide sites commenced in August 2003 and ended in March 2004 generating about 8 months of data.

2.2 Ion beam analyses of aerosols elemental composition

The mass of particles and elemental composition of fine and coarse aerosol samples were determined using gravimetric analysis and the accelerator-based multi-elemental ion beam analysis (IBA) at the Australian Nuclear Science and Technology Organisation (ANSTO). The suite of IBA techniques was used to determine F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, Sr, Br and Pb (USEPA, 1999). The details of the gravimetric analysis and IBA analysis, accuracy and precision of measurement for this study were presented previously in Hawas et al., 2003. For detailed discussions on IBA methods used at ANSTO for

fine particle characterisation see Cohen et al., 1998, Cohen, 1999a, Cohen, 1999b, Cohen et al., 2002.

2.3 Detection limits and quality assurance

The Minimum Detection Limits (MDLs) for Teflon filters and Nuclepore filters are shown in Figure 1 for 37-mm filters and in Figure 2 for 47-mm filters.

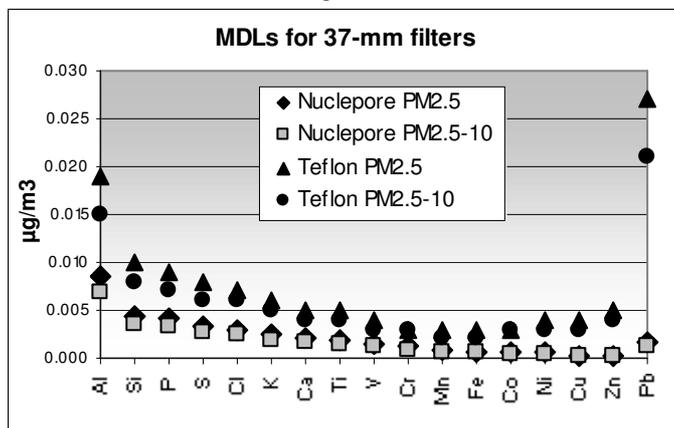


Figure 1. MDLs for 37-mm filters

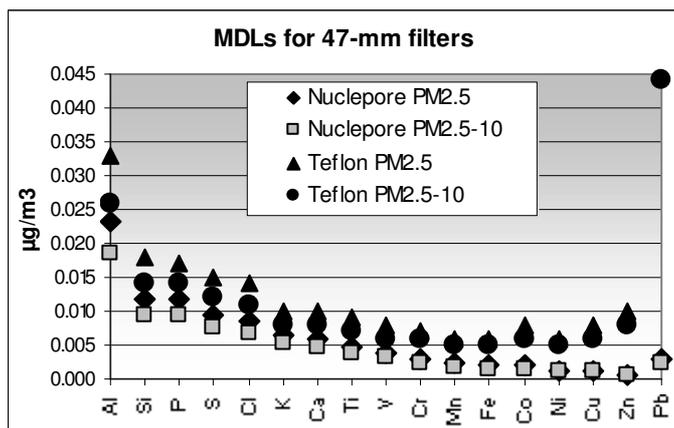


Figure 2. MDLs for 47-mm filters

As shown in Figures 1 and 2 detection limits for Nuclepore filters are much better than for Teflon, for some elements being as twice as high for Teflon filter than for Nuclepore filters. For Cr, Cu and Pb MDLs on Teflon filters were as much as 8 times higher than on Nuclepore filters. Also, as expected the 37-mm filters had lower detection limits than the 47-mm filters due to higher particle density on the filters.

The poorer MDLs for Teflon filters also were reflected in the percentage of the data above the MDLs (Figure 3).

For V, Cr, Co and Ni less than 10 % of samples collected on Teflon filters were above the MDLs. For Nuclepore filters 15-30 % of samples were measured above MDLs. For Mn, Cu, Zn and Pb twice as many samples on Nuclepore filters were

above the MDLs than those collected on Teflon filters.

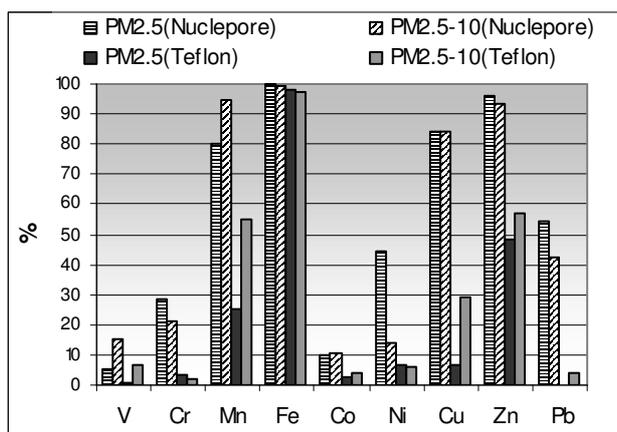


Figure 3. Percentage of samples above the minimum detection limits.

3. Results and discussion

3.1 PM_{2.5} and PM_{2.5-10} concentrations

The average concentrations of PM_{2.5} and PM_{2.5-10} in Adelaide, Brisbane, Melbourne and Sydney during the sampling period are presented in Figure 4 below.

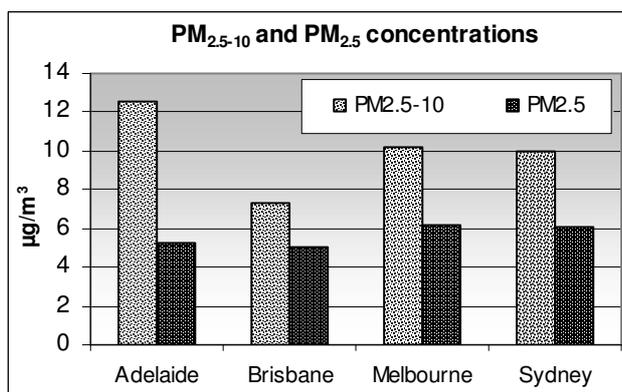


Figure 4. Average PM_{2.5} and PM_{2.5-10} concentrations in four Australian cities.

During the sampling period the average concentration of PM_{2.5} particles in Adelaide was measured at 5.2 µg/m³ (maximum at Northfield was 12.2 µg/m³ and at Netley 13.8 µg/m³). The average concentration of fine particles in Brisbane was 5.1 µg/m³ with maximum of 12.1 µg/m³ at Springwood and 16.3 µg/m³ at Rocklea. In Melbourne the average concentration of PM_{2.5} was 6.1 µg/m³ with maximum of 29.2 µg/m³ at Alphington and 20.5 µg/m³ at Footscray. The average concentration in Sydney was 6.1 µg/m³ with maximum reaching 19 µg/m³ at Earlwood and 10.8 µg/m³ at Richmond. The overall average concentration of PM_{2.5} was 5.6 µg/m³.

The average concentration of PM_{2.5-10} in Adelaide was measured at 12.6 µg/m³ (maximum 44.2 µg/m³ at Northfield and 38.4 µg/m³ at Netley). In Brisbane the average concentration was 7.4 µg/m³ (maximum of 15.4 µg/m³ at Springwood site and 18.1 µg/m³ at Rocklea site). The average concentration of PM_{2.5-10} in Melbourne was 10.2 µg/m³ reaching maximum of 77.2 µg/m³ at Alphington site and 49.6 µg/m³ at Footscray site. In Sydney average concentration of coarse particles was measured at 9.9 µg/m³ reaching maximum of 36.8 µg/m³ at Earlwood and 28.8 µg/m³ at Richmond. The overall average PM_{2.5-10} concentration was 10 µg/m³.

During the sampling time the measured PM_{2.5} 24-hour concentrations complied with US EPA 24-hour standard of 65 µg/m³. The measured PM_{2.5} concentrations also complied with the proposed 24-hour NEPM of 25 µg/m³ with only one exception when 24-hr fine particle concentration reached 29.2 µg/m³ at Alphington site in Melbourne on 6 June 2003 (dust storm day). The observed annual averages would also comply with the proposed NEPM of 8 µg/m³.

3.2 Seasonal variations in PM_{2.5} and PM_{2.5-10} concentrations

The concentrations of PM_{2.5} and PM_{2.5-10} measured during the study period exhibit strong seasonal trends. The concentrations of coarse aerosols in Adelaide were the highest in autumn (21 µg/m³ on average), the second highest were the concentrations in summer (13.8 µg/m³), there was no difference between concentrations measured in spring and winter (7.4 vs 10.5 µg/m³). The concentrations of PM_{2.5-10} in Brisbane were the lowest in winter (average 4.6 µg/m³) with no apparent trend for other seasons. In Sydney, the concentrations of coarse particle were the highest in summer (average 13.6 µg/m³) and the lowest in winter (average 4.9 µg/m³) with no difference between spring and autumn. Summer concentrations of PM_{2.5-10} in Melbourne (average 12.9 µg/m³) were higher than during other seasons, however these concentrations were only significantly different from spring concentrations (average 8.3 µg/m³).

Fine particle concentrations in Adelaide were also the highest in autumn than during other seasons of the year (average 7.4 µg/m³), spring concentrations were lower than in autumn and summer but not different than in winter. Winter concentrations were also not different from summer concentrations. In Brisbane again the winter concentrations were the lowest (average 4 µg/m³), there was no difference in PM_{2.5} concentrations during other seasons of the year. Summer fine particle concentrations in Sydney (average 7.3 µg/m³) were higher than in spring when the fine

aerosols had the lowest concentrations (average $4.8 \mu\text{g}/\text{m}^3$). There was no difference between fine aerosol concentrations in winter and autumn in Sydney. The concentrations of fine particles in Melbourne did not exhibit any significant seasonal trend.

3.3 Elemental composition of aerosols and trace heavy metals

The elemental composition of $\text{PM}_{2.5-10}$ particles (Figure 5) was dominated by Cl and Na from sea salt, crustal elements Al, Si, K, Ca and Fe and black carbon (3%). All other measured elements contributed less than 1% to the mass of particles. These elements and elements not measured by IBA (eg. hydrogen, oxygen, and nitrogen) are presented in Figure 5 and 6 as "Other".

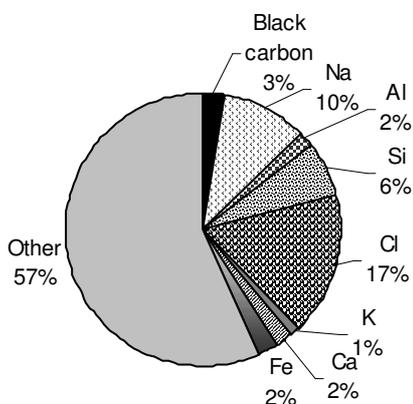


Figure 5. Elemental composition of $\text{PM}_{2.5-10}$ aerosols.

The elemental composition of $\text{PM}_{2.5}$ (Figure 6) was dominated by black carbon, S, Na and Cl, Si and Fe.

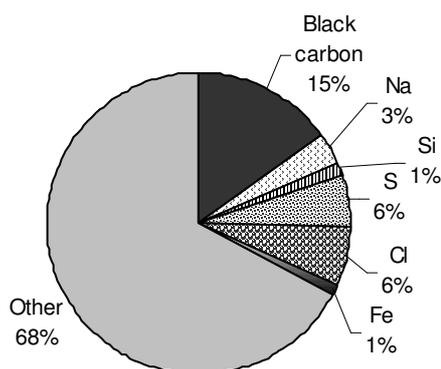


Figure 6. Elemental composition of $\text{PM}_{2.5}$ aerosols.

3.3.1 V, Co, Cr, Ni

V, Co, Cr and Ni usually associated with anthropogenic activities (Cohen et al., 2002) were measured above the detection limits in less than 30% of the collected samples across all sites. The

average concentrations in samples above the detection limits (the <MDL values are assumed to be 0.5 MDL when calculating the averages) are shown in Figures 7 and 8 for fine and coarse particles respectively. All values were blank subtracted and expressed in equivalent $\mu\text{g}/\text{m}^3$ air under standard condition (ie. 0°C and 760 mmHg).

As shown in Figure 7 the average concentrations of V in fine particles were below $0.003 \mu\text{g}/\text{m}^3$, the concentrations of all other above mentioned metals were $0.002 \mu\text{g}/\text{m}^3$ in Sydney, Brisbane and Adelaide. The concentrations of these metals in Melbourne were $0.001 \mu\text{g}/\text{m}^3$.

The average concentrations in $\text{PM}_{2.5-10}$ particles (Figure 8) were below $0.0025 \mu\text{g}/\text{m}^3$ for Cr and Co. the concentrations of V were $0.002 \mu\text{g}/\text{m}^3$ in all four cities while the concentrations of Ni below $0.0015 \mu\text{g}/\text{m}^3$.

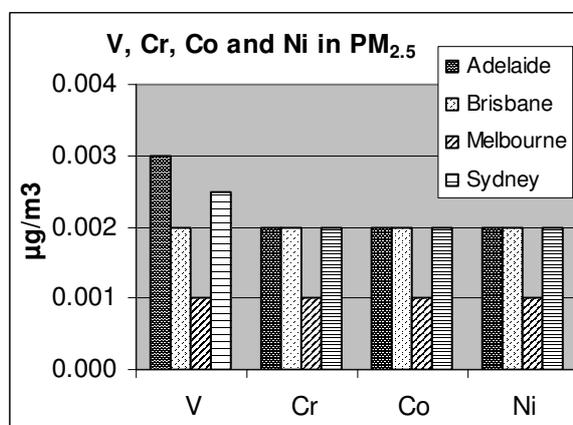


Figure 7. $\text{PM}_{2.5}$ concentrations of V, Cr, Co and Ni in four Australian cities.

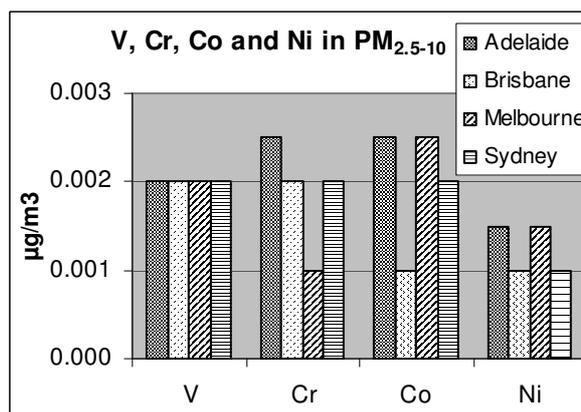


Figure 8. $\text{PM}_{2.5-10}$ concentrations of V, Cr, Co and Ni in four Australian cities.

3.3.2 Mn, Cu, Zn, Pb

The concentrations of Mn, Cu, Zn and Pb in $\text{PM}_{2.5-10}$ and $\text{PM}_{2.5}$ are shown in Figures 9 and 10 respectively. These metals are generally related to anthropogenic activities such as industry and motor vehicle pollution (Mn is part of new petrol additives)

and of interest due to their environmental and health related impacts (Environment Australia, 2000, Cohen et al., 2002).

As shown in Figure 9 the average concentrations of Mn in $PM_{2.5-10}$ were below $0.01 \mu\text{g}/\text{m}^3$. The concentrations in Adelaide and Melbourne were higher than in Sydney and Brisbane ($p < 0.005$). The concentrations measured in autumn across all four cities were significantly higher than concentrations measured in spring and winter.

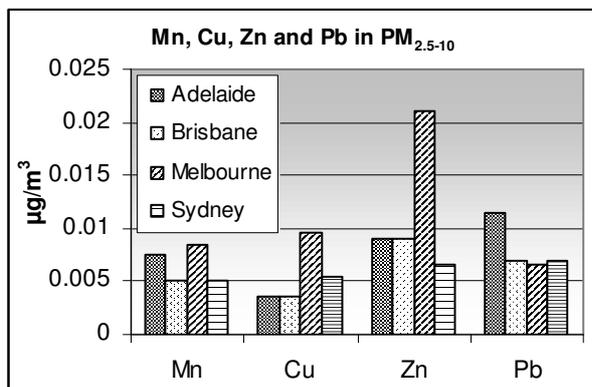


Figure 9. Mn, Cu, Zn and Pb in coarse particles in four Australian cities.

Cu concentrations were also below $0.01 \mu\text{g}/\text{m}^3$, with the highest average observed in Melbourne ($p < 0.005$). The seasonal variations of Cu concentrations were observed in Adelaide where concentrations measured in autumn were higher than during other season and in Sydney where coarse Cu concentrations were higher in summer.

The concentrations of Zn in $PM_{2.5-10}$ were below $0.01 \mu\text{g}/\text{m}^3$ except for Melbourne where the average concentration was measured at $0.021 \mu\text{g}/\text{m}^3$. The seasonal trend in Zn concentrations was observed in Sydney where summer concentrations were higher than winter and in Melbourne where autumn and summer concentrations were higher than winter and spring concentrations ($p < 0.005$).

There was no difference in $PM_{2.5-10}$ Pb concentrations among the four cities ($p < 0.005$) with concentrations measured below $0.01 \mu\text{g}/\text{m}^3$. The seasonal trend was observed in Brisbane where the coarse Pb concentrations were higher in autumn and in Melbourne where concentrations were higher in summer.

The concentrations of Mn and Cu in fine particles were below $0.005 \mu\text{g}/\text{m}^3$ (Figure 10). The concentrations of Mn in Brisbane were higher than in Sydney and Melbourne but not different than in Adelaide ($p < 0.005$). Seasonally, the highest concentrations of Mn in fine particle were observed in autumn in all cities and the lowest in spring and winter.

The concentrations of Cu were higher in Sydney ($p < 0.005$). Summer concentrations of Cu were

higher in all cities except Brisbane where no seasonal trend was observed.

The concentrations of Zn in fine particles were below $0.02 \mu\text{g}/\text{m}^3$ with the concentrations in Sydney being the lowest among cities (average $0.0075 \mu\text{g}/\text{m}^3$). There was no seasonal trend in fine Zn concentrations in all cities except Melbourne where concentrations in summer and autumn were higher than in winter and spring ($p < 0.005$).

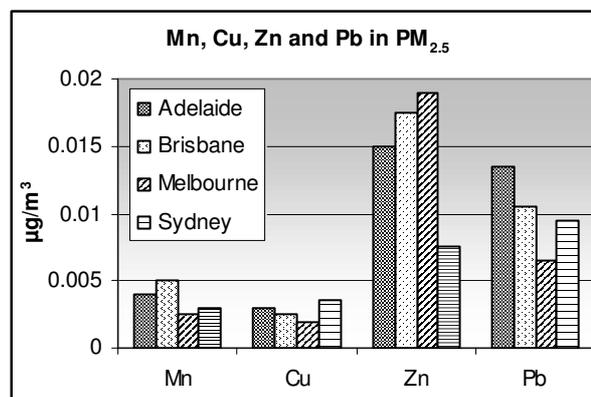


Figure 10. Mn, Cu, Zn and Pb in fine particles in four Australian cities.

The average Pb concentrations in $PM_{2.5}$ were around $0.01 \mu\text{g}/\text{m}^3$ and similar in all four cities ($p < 0.005$) with no apparent seasonal trend except for Melbourne where the fine Pb concentrations were higher in autumn.

4 Summary

In summary, accelerator based multi-elemental (IBA) techniques provided quantitative information on concentration of black carbon, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Ni, Zn, Br, Pb. Gravimetric analysis determined the mass concentration of $PM_{2.5}$ and $PM_{2.5-10}$ particles.

The overall average concentration of fine particles was $5.6 \mu\text{g}/\text{m}^3$, while $PM_{2.5-10}$ $10 \mu\text{g}/\text{m}^3$. The concentrations of fine particles did not exceed USEPA air quality standards and proposed annual NEPM goal.

$PM_{2.5}$ aerosols were found to be dominated by black carbon, sulphur, sodium and chlorine. $PM_{2.5-10}$ particles were dominated by sodium, chlorine, silicon and iron. Less than 30 % of collected samples had V, Co, Cr and Ni above the MDLs in both fine and coarse particles. The concentrations of Mn, Cu, Zn and Pb were generally below $0.01 \mu\text{g}/\text{m}^3$ in $PM_{2.5-10}$ and below $0.02 \mu\text{g}/\text{m}^3$ in $PM_{2.5}$ particles.

5 Acknowledgment

We would like to acknowledge the help of staff from state EPAs for regular filter changes throughout the study. We also acknowledge the help of all the 3 MV Van de Graaff accelerator staff at ASNTO for assistance with IBA measurements. The project is

coordinated by Griffith University, EPA Victoria and University of the Sunshine Coast, and funded by the Commonwealth Government's Natural Heritage Trust.

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