

ELEMENTAL COMPOSITION OF FINE PARTICLES IN FOUR MAJOR AUSTRALIAN CITIES

Olga Hawas¹, Eduard Stelcer¹, David Cohen¹, David Button¹, Lyn Denison², Neil Wong², Andrew Chan³, Rod Simpson⁴, Elizabeth Christensen⁵, Gary Golding⁵, Mary Hodge⁵, John Kirkwood⁶, Rob Mitchell⁷, David Wainwright⁸, and Fred Ardern¹.

¹ANSTO Environment, PMB 1, MENAI, NSW 2234, Australia

²EPA Victoria, G.P.O. Box 4395QQ, Melbourne, Victoria 3001

³Environmental Science Department, Griffith University, Nathan, Queensland 4111

⁴Faculty of Science, University of Sunshine Coast, Maroochydore DC, Queensland 4558

⁵Queensland Health Scientific Services, 39 Kessels Road, Coopers Plains, Queensland 4108

⁶NSW EPA, PO Box 29, Lidcombe, NSW 1825

⁷SA EPA, Level 7, 77 Grenfell Street, Adelaide, South Australia 5000

⁸Queensland EPA, Old Botany Block, 80 Meiers Road, Indooroopilly, Queensland 4068

Summary

The investigation of the chemical composition of PM₁₀ and PM_{2.5} has been carried out since February 2003 in Melbourne, Sydney, Brisbane and Adelaide. 24-hour aerosol samples are collected from a typical urban and suburban monitoring site operated by the state EPA in each city. ANSTO performs gravimetric analysis, accelerator-based ion beam analysis and integrating plate laser absorption analysis to determine the elemental composition of the aerosols. Preliminary results including quality assurance, aerosol concentrations and chemical composition including the levels of heavy metals in the samples collected up to April 2003 are discussed in this paper. The study is coordinated by Griffith University, EPA Victoria and University of the Sunshine Coast, and funded by the Commonwealth Government's Natural Heritage Trust.

Keywords: PM_{2.5}, PM₁₀, IBA techniques, elemental composition, heavy metals.

1 Introduction

Studies worldwide have found that ambient levels of PM₁₀ and PM_{2.5} are associated with adverse health effects including increase in premature deaths, hospital admissions and emergency attendances for respiratory and cardiovascular disease and exacerbation of asthma (e.g. Pope III, 2000, Dockery, 2001). The potential of adverse health effects of particle pollution has triggered extensive research on concentrations and composition of urban aerosols over the past decade. The chemical and elemental composition of aerosols is of particular interest as the adverse health effects of aerosols may be due to other pollutants adsorbed on particles. Also, by knowing the elemental composition of aerosols their emission sources and their fingerprints can be quantified and appropriate regulation policies developed.

In Australia, apart from ANSTO's comprehensive data on the composition of fine particles in NSW (Cohen, 1998) data on the composition of particles is limited. The project *Fine Particle Composition in Four Major Australian Cities* is 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 national health study funded by the Commonwealth Government's Natural Heritage Trust which is an expansion of a larger study funded by the Australian Research Council.

The project will generate a comprehensive dataset on the composition of the particle and VOC samples. Apart from providing crucial data for the national health study, data from this project together with the data from the existing monitoring networks operated by the state EPAs can also be employed in other uses including: source apportionment of particles and inter-comparison of results of particle levels from different monitoring equipment.

In this paper we describe the IBA techniques applied to determine elemental composition of PM_{2.5} and PM_{2.5-10} aerosols, and report preliminary results on quality assurance, concentrations and elemental composition of aerosols in Melbourne, Sydney and Brisbane.

2 Sampling regime and analyses methods.

2.1 Sampling regime and sites.

In this project one urban and one suburban site were selected in each city. The chosen sites are listed in Table 1 below.

Table 1. Location of sampling sites for this project.

City	Urban site	Suburban site
Melbourne	Alphington (residential/light industrial)	Footscray (residential/light industrial)
Sydney	Earlwood (residential)	Richmond (residential/semi-rural)
Brisbane	Rocklea (residential/light industrial)	Springwood (residential)
Adelaide	Netley (city/commercial)	Northfield (residential)

Dichotomous sampling of PM_{2.5-10} and PM_{2.5} is incorporated into the routine 6daily sampling programs by each of the state EPA s. Dichotomous sampling at EPA Victoria sites uses Anderson dichotomous samplers. Dichotomous sampling at the other EPA sites uses Partisol 2025 Sequential Dichotomous samplers leased from the Ecotech Pty Ltd for the sampling period. Both the Anderson dichotomous sampler and the Partisol dichotomous sampler are USEPA's reference methods for monitoring particles.

24-hour dichotomous samples are collected on Nuclepore polycarbonate filters with 2 µm pore size. Anderson samplers in Victoria are using 37 mm diameter filters and Partisols are using 47 mm filters. Nuclepore polycarbonate filters are (1) much thinner and more uniform than the Teflon filters, making them more suitable for the analysis of elemental carbon by the laser absorption technique; (2) they do not contain the fluorine element and so fluorine content in the samples can also be analysed; (3) they are also a lot less expensive than the Teflon filters, and (4) IBA detection limits are much lower on Nuclepore filters in comparison to Teflon filters.

Due to the higher pressure drop and hydrophilic properties of the Nuclepore filters, some of the Partisol samplers were found not to sample for the whole 24 hours on some sampling days due to more than 10% variation in flow rate, in particular under humid conditions in early mornings (refer to Table 3). These samples were excluded from the reported data set to ensure compliance with the USEPA sampling guidelines (USEPA, 1998). The flow rates of the Anderson samplers were also checked before and after sampling and the variation in flow rates was found to be less than 5% in all samples.

2.2 Analysis techniques

2.2.1 Ion Beam Analysis

The accelerator-based ion beam analysis (IBA) method is well established at the Australian Nuclear Science and Technology Organisation (ANSTO). The IBA methods are multi-elemental, non-destructive, sensitive, require little sample preparation and have short analysis time. The key advantage of IBA methods is their ability to analyse small milligram samples for nanogram concentrations of trace metals (Cohen, 1998).

Typically IBA methods include four simultaneous techniques, however, for this study only two were used:

- PIXE – particle induced X-ray emission
- PIGE - particle induced gamma-ray emission

An 8-mm diameter ion beam of 70-80 nA, 2.6 MeV protons from the 3 MV Van de Graaff accelerator is passed through each filter for approximately 5-6 minutes. Typical spectrum obtained through PIXE and PIGE measurements are shown in Figures 1 and 2 below.

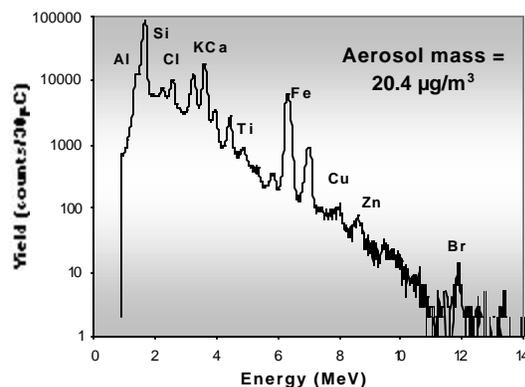


Figure 1. Typical PIXE spectrum using 30µC of 2.6 MeV protons for Nuclepore filter sample from Footscray in Melbourne.

PIXE is used to simultaneously determine over 20 different elements including Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Sr and Pb (Cohen, 1998). The X-ray spectrum above shows a characteristic peak for each element, the area of the peak is related to the concentration of that element on the filter.

The spectrum in Figure 2 shows characteristic gamma rays of sodium (gamma energy 440 keV) and fluorine (gamma energy 197keV). The 511 keV gamma ray annihilation peak is always present and is not related to concentrations of measured elements.

Determination of MDL for each element for each individual filter is part of IBA measurement techniques. PIXE detection limits vary from 1-100 ppm depending on the element, energy and total charge of incident particles (Cohen et al, 2002b). Typical PIXE sensitivities are as low as 1-10 ng/m³ (Cohen, 1998).

PIGE detection limits are typically between 10 and 100 ppm, it is less sensitive than PIXE. This reflects the atomic versus nuclear nature of the ion interactions for the two processes (Cohen et al, 2002b).

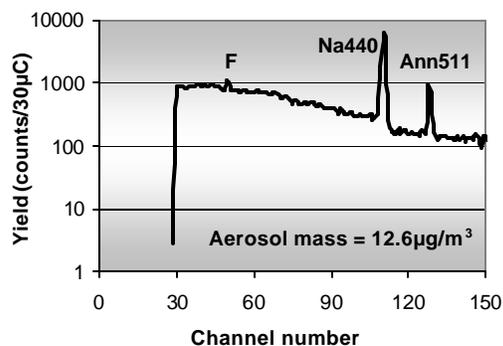


Figure 2. A typical PIGE spectrum using 30µC of 2.6 MeV protons for Nuclepore filter sample collected from Footscray in Melbourne.

The accuracy for PIXE is as low as ±1.6% for major elements with precision of ± 5-10%. PIGE accuracy is around ± 5% with precision of ± 15% (Cohen et al, 2002b).

The fine particle filters collected with the Partisol samplers were all found to have strange line features. The cause of these line features is yet unknown. Microscopic examination of the filters indicates that the line features are regions with higher particle density. In order to assess the influence of these line features on the precision of IBA analysis, replicate analysis was carried out on different sections on selected filters. No significant influence to precision was found (precision within ± 5-10% as the filters collected with the Anderson samplers which have no line features).

Calibration of the IBA analysis is part of the measurement process. The PIXE and PIGE analysis results were calibrated with certified thin (approximately 50 µg/cm²) Micromatter standards foils of Al, SiO, NaCl, CaF₂, Fe and SrF₂ (Cohen et al, 2002b).

Average detection limits for elements measured in this study are summarised in the Table 2. From Table 2, the detection limits of 37-mm filters appear to be much lower than those of 47-mm. This is probably due to higher concentration of particles collected per unit

area on smaller filters in comparison to larger 47-mm filters.

2.2.2 Weighing of samples

All clean and exposed filters were equalised to the laboratory temperature and humidity for a minimum of 24 hours. The laboratory temperature was generally between 20°C and 23°C and laboratory humidity below 50% rh at the time of weighing. The accuracy of weighing was ± 5 µg. The precision of weighing for both clean and exposed filters was ± 2 µg.

All the results of mass and elemental concentrations are converted to the standard conditions of 0°C and 760 mmHg.

Table 2. Detection limits of IBA measurements (µg/m³ std) and percentage of samples above the detection limit.

	PM _{2.5} detection limits		PM _{2.5-10} detection limits		PM _{2.5} % of samples > d.l	PM _{2.5-10} % of samples > d.l.
	37 mm	47 mm	37 mm	47 mm		
mass	0.23	0.23	0.18	0.18	100	100
BC	0.086	0.214	0.069	0.172	73	70
F	0.009	0.019	0.008	0.016	0	5
Na	0.023	0.06	0.018	0.048	73	100
Al	0.008	0.023	0.007	0.019	64	88
Si	0.004	0.012	0.004	0.009	68	96
P	0.004	0.012	0.003	0.009	30	20
S	0.003	0.01	0.003	0.008	100	98
Cl	0.003	0.009	0.002	0.007	59	100
K	0.002	0.007	0.002	0.005	100	100
Ca	0.002	0.006	0.002	0.005	98	100
Ti	0.002	0.005	0.001	0.004	36	75
V	0.001	0.004	0.001	0.003	7	14
Cr	0.001	0.003	0.001	0.002	27	25
Mn	0.001	0.002	0.001	0.002	77	93
Fe	0.001	0.002	0.001	0.002	100	100
Co	0.001	0.002	0.0005	0.002	13	20
Ni	0.001	0.001	0.0005	0.001	46	9
Cu	0.0003	0.001	0.0002	0.001	80	79
Zn	0.0003	0.001	0.0002	0.001	95	95
Br	0.001	0.002	0.001	0.002	86	86
Pb	0.002	0.003	0.001	0.002	54	41

BC – black carbon

2.2.3 Black carbon measurement

Black carbon or soot measurement is based on the measurement of optical absorption of the fine particles, which is also a measure of the black carbon content of the aerosol on the filter (Cohen et al., 2000). He-Ne Laser light of wavelength 633nm is passed through a diffuser and collimated to produce a uniform beam at the filter. The laser light transmitted through the filter is collected by a photo diode system. The laser light transmissions of each filter both before (I_0) and after exposure (I) is measured using a mass attenuation coefficient obtained from calibration measurements on acetylene

and candle flames of $\varepsilon = 7 \text{ m}^2/\text{g}$ (Cohen et al, 2000).

3 Results and discussion

3.1 Concentrations of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$

A total of 132 samples collected and validated between February 2003 and April 2003 in NSW, Victoria and Queensland. The sampling in South Australia commenced in July 2003 and not presented in this paper (Table 3).

Table 3. Number of fine and coarse particle samples analysed and validated by ANSTO from February 2003 to April 2003.

City	Site	Number of filters analysed	
		Field blanks	Exposed
Scheduled samplings		2 (a)	22
Melbourne	Alphington	2	20 (b)
	Footscray	2	18 (b)
Sydney	Earlwood	6	10 (c)
	Richmond	6	22
Brisbane	Rocklea	2	20 (d)
	Springwood	2	22
Total		20	112

Remarks:

- Field blanks are collected regularly throughout the project
- Loss of samples due to instrumental problems and damaged filters
- Loss of samples due to instrumental leaking problems and flow rate problems
- Loss of samples due to flow rate problems

The average concentrations of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ in Brisbane, Melbourne and Sydney during the sampling period are presented in Figure 3 below.

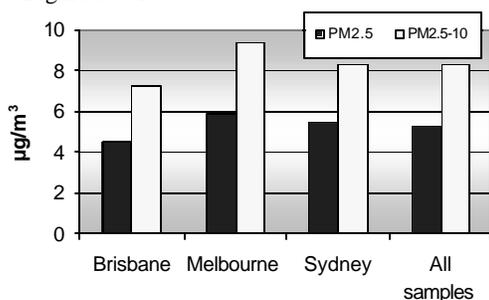


Figure 3. Average concentrations of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ samples in 3 major Australian cities during February – April 2003.

During the sampling period the average concentration of $\text{PM}_{2.5}$ particles were $4.5 \mu\text{g}/\text{m}^3$ (maximum $12.4 \mu\text{g}/\text{m}^3$) in Brisbane, $5.9 \mu\text{g}/\text{m}^3$ (maximum $11.7 \mu\text{g}/\text{m}^3$) in Melbourne and $5.5 \mu\text{g}/\text{m}^3$ (maximum $9.2 \mu\text{g}/\text{m}^3$) in Sydney. The average concentrations of $\text{PM}_{2.5-10}$ were measured to be $7.3 \mu\text{g}/\text{m}^3$ (maximum

$11.4 \mu\text{g}/\text{m}^3$) in Brisbane, $9.3 \mu\text{g}/\text{m}^3$ (maximum $20.4 \mu\text{g}/\text{m}^3$) in Melbourne and $8.3 \mu\text{g}/\text{m}^3$ (maximum $28.8 \mu\text{g}/\text{m}^3$) in Sydney.

The average concentrations of both fine and coarse aerosols appear to be similar in all cities in the samples collected.

During the sampling time the measured $\text{PM}_{2.5}$ 24-hour concentrations complied with US EPA 24-hour standard of $65 \mu\text{g}/\text{m}^3$. Moreover, the measured $\text{PM}_{2.5}$ concentrations will also comply with the proposed 24-hour NEPM of $25 \mu\text{g}/\text{m}^3$.

3.2 Elemental composition of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ aerosols

The average elemental composition (in $\mu\text{g}/\text{m}^3$) of $\text{PM}_{2.5}$ and $\text{PM}_{2.5-10}$ aerosol samples is presented in the Table 4 below.

From Table 4, $\text{PM}_{2.5}$ fraction of aerosols was dominated by black carbon, sulphur, sodium and chlorine. On average, the concentrations of black carbon in $\text{PM}_{2.5}$ were $0.72 \mu\text{g}/\text{m}^3$ (16% of the average mass of $\text{PM}_{2.5}$) in Brisbane samples, $0.32 \mu\text{g}/\text{m}^3$ (5.4%) in Melbourne samples and $0.83 \mu\text{g}/\text{m}^3$ (15%) in Sydney samples. Black carbon or soot is a product of combustion processes from anthropogenic sources and therefore is mainly present in the fine fraction of the aerosol (Seinfeld and Pandis, 1998).

On average, sulphur concentration in $\text{PM}_{2.5}$ particles in Brisbane samples was 4.4% of the mass, 5% in Melbourne samples and 6% in Sydney samples. The average concentration of sulphur in all samples was $0.27 \mu\text{g}/\text{m}^3$ or 5% of the mass of $\text{PM}_{2.5}$. Sodium and chlorine were the second most abundant element in this fraction. On average, sodium contributed 4.5% ($0.24 \mu\text{g}/\text{m}^3$) to the mass of $\text{PM}_{2.5}$ in all samples, while chlorine 2% ($0.11 \mu\text{g}/\text{m}^3$).

The $\text{PM}_{2.5-10}$ particle mass was dominated by silicon, sodium, chlorine and iron. Sodium was the most abundant element in this fraction. On average, sodium concentrations in $\text{PM}_{2.5-10}$ samples were 17% of the mass of $\text{PM}_{2.5-10}$ in Brisbane samples, 12% in Melbourne samples and 8.7% in Sydney samples. Chlorine was the second most abundant element in this fraction. It contributed as much as 15% to the mass of coarse aerosol in Brisbane samples, 9% in Melbourne samples and 6.4% in Sydney samples. Sea salt is main source of sodium and chlorine in aerosol samples (Cohen, 1998). The relative abundance of these elements in collected samples indicates that sea salt was one of the major sources of both fine and coarse particles at selected sites as a result of the coastal location of the major Australian cities.

On average, silicon contributed 4% to the mass of PM_{2.5-10} particles in Brisbane samples, 5% in Melbourne samples and 8% in Sydney samples.

The average concentration of iron in coarse particles was 1.5% in Brisbane samples, 2.8% in Melbourne samples as well as in Sydney samples

Table 4. Average elemental composition of PM_{2.5} and PM_{2.5-10} (µg/m³ std) aerosol samples in 3 major Australian cities during February – April 2003.

	Brisbane		Melbourne		Sydney	
	PM _{2.5}	PM _{2.5-10}	PM _{2.5}	PM _{2.5-10}	PM _{2.5}	PM _{2.5-10}
BC	0.715	0.179	0.316	0.099	0.829	0.239
F	<0.019	<0.016	<0.019	<0.016	<0.019	<0.016
Na	0.201	1.244	0.357	1.138	0.134	0.725
Al	0.027	0.095	<0.023	0.127	0.052	0.227
Si	0.033	0.299	0.034	0.497	0.112	0.682
P	<0.012	<0.009	<0.012	<0.009	<0.012	<0.009
S	0.201	0.052	0.289	0.082	0.328	0.039
Cl	0.095	1.059	0.195	0.805	0.011	0.532
K	0.028	0.064	0.03	0.058	0.043	0.086
Ca	0.014	0.076	0.022	0.152	0.025	0.13
Ti	<0.005	0.012	<0.005	0.018	<0.005	0.02
V	<0.004	<0.003	<0.004	<0.003	<0.004	<0.003
Cr	<0.003	<0.002	<0.003	<0.002	<0.003	0.002
Mn	0.005	0.004	0.002	0.006	0.004	0.005
Fe	0.039	0.112	0.052	0.261	0.076	0.23
Co	<0.002	<0.002	<0.002	0.002	<0.002	0.002
Ni	0.001	0.001	<0.001	<0.001	0.001	0.001
Cu	0.002	0.002	0.002	0.013	0.004	0.004
Zn	0.018	0.007	0.018	0.02	0.008	0.005
Br	0.016	0.012	0.002	0.002	0.015	0.01
Pb	0.005	0.003	0.004	0.005	0.004	0.003

Silicon and iron are two key elements known as crustal elements in aerosol (Chan et al, 1997). The concentrations of the elements were found to be significantly correlated (R²=0.8) indicating a common source such as soil. Therefore soil is another likely sources of coarse aerosols in these three cities.

The elemental composition of the fine and coarse aerosols was found to be consistent with other studies, where PM_{2.5} fraction is usually dominated by elements related to combustion processes such as sulphur and black carbon, while elements related to crustal matter such as Si, Fe and Al and sea salt elements (Na and Cl) had higher contribution to the coarse aerosols (Chow et al, 1996, Chan et al, 1997).

3.3 Heavy metals (Mn, Cu, Pb, Zn)

Manganese, copper, lead and zinc and other heavy metals are generally related to anthropogenic pollution and of particular interest because of the potential adverse health and environmental impacts (Environment Australia, 2000)

The heavy metal concentrations (Mn, Cu, Pb, Zn) measured at sampling sites are shown

in Figures 5 (fine particles) and 6 (coarse particles) below.

Manganese and copper levels, usually associated with anthropogenic activities (Cohen et al, 2002a), were generally below 0.005 µg/m³ and close to their detection limits. Concentrations of zinc and lead usually associated with motor vehicle and industry emissions were close or below 0.015 µg/m³ in the samples from all selected cities. Lead concentrations were well below annual NEPM goal of 0.5 µg/m³ in all samples. Higher zinc levels in Sydney samples warrants further sampling and investigation to obtain long term averages and seasonal variations.

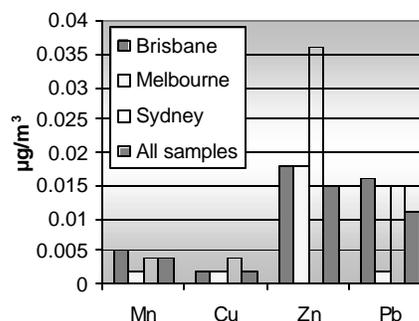


Figure 5. Concentrations of selected heavy metals in PM_{2.5} samples.

Similar trend was observed in PM_{2.5-10} samples. The concentrations of all selected heavy metals were generally below 0.005 µg/m³ and close to their detection limits.

Copper concentrations in Melbourne samples were higher, however, it was found to be highly correlated with crustal elements (Ca, Al and Fe). Higher coarse zinc concentrations on the other hand may need to be investigated further.

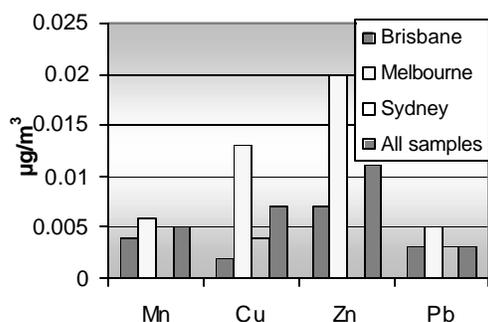


Figure 6. Concentrations of selected heavy metals in PM_{2.5-10} samples.

The other heavy metals, V, Cr, Co and Ni, were below or close to minimum detection limits.

4 Summary

In summary, accelerator based multi-elemental ion beam analysis (IBA) techniques are highly sensitive with low detection limits and high accuracy and precision. 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 used to quantify elemental composition of PM_{2.5} and PM_{2.5-10} aerosols. Gravimetric analysis determined the mass concentration of PM_{2.5} and PM_{2.5-10} particles.

The detection limits of most of the elements measured by IBA were close or below 0.01 µg/m³. The precision of IBA measurement was below 15%, while accuracy below 5%. The precision of gravimetric analysis was ± 2 µg, while accuracy ± 5 µg.

The concentrations of fine particles in collected filters did not exceed USEPA air quality standards and proposed 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. Most of the measured heavy metals were close or below their detection limits.

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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