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Fine-particle Mn and other metals linked to the introduction of MMT into gasoline in Sydney, Australia: Results of a natural experiment

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Abstract

Using a combination of accelerator-based ion beam methods we have analysed $PM_{2.5}$ particulates for a suite of 21 species (H, C, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br, Pb) to evaluate the contribution to Sydney (New South Wales, Australia) air associated with the introduction of MMT as a replacement for lead. MMT was discontinued in 2004. Teflon filters representing continuous sampling for a 7 year period from 1998 to 2004 were analysed from two sites: one from Mascot, a suburb close to the Central Business District [CBD ($n = 718$)] and a high trafficked area, and the other, a relatively rural (background) setting at Richmond, ~20 km west of the CBD ($n = 730$). Manganese concentrations in air at the background site increased from a mean of 1.5–1.6 ng m^{-3} to less than 2 ng m^{-3} at the time of greatest MMT use whereas those at Mascot increased from about 2 to 5 ng m^{-3}. From the maximum values, the Mn showed a steady decrease at both sites concomitant with the decreasing use of MMT. Lead concentrations in air at both sites decreased from 1998 onwards, concomitant with the phase out of leaded gasoline, attained in 2002. Employing previously determined elemental signatures it was possible to adjust effects from season along with auto emissions and soil. A high correlation was obtained for the relationship between Mn in air and lead replacement gasoline use (R^2 0.83) and an improved correlation for Mn/ Al+Si+K and lead replacement gasoline use (R^2 0.93). In addition, using Mn concentrations normalized to background values of Al+Si+K or Ti to account for the lithogenically derived Mn, the proportion of anthropogenic Mn was approximately 70%. The changes for Mn and Pb detected in the particulates are attributed to the before-during-after use of MMT and decreasing use of lead in gasoline. The values measured in Sydney air are well below the reference concentration of 50 ng Mn m^{-3}. The incremental increases in air, however, are larger than expected given the limited use of MMT only in lead replacement gasoline and high quality monitoring should be undertaken in countries where MMT is used in all gasoline.

Keywords: Mn; Pb; Automobiles; Air; Soil; Ion beam methods; Sources

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1. Introduction

Fine materials in the atmosphere comprised of micron and sub-micron particles may be derived from anthropogenic sources such as motor vehicles, biomass and fossil fuel combustion, and natural sources such as windblown soils and sea spray (Cohen 1998; Cohen et al., 1996, 2002). Characterisation of the fine airborne particulates is becoming increasingly important to governments, regulators and researchers due to their potential impacts on human health (Dockery et al., 1993), transnational migration and influence on climate forcing and global warming (IPCC, 2001).

Motor vehicles are a ubiquitous source of airborne emissions that can potentially result in widespread contamination of the environment and have direct and indirect impacts on human health, especially that of young children. Two metals of specific concern in motor vehicle emissions are lead (Pb) and manganese (Mn). Lead was first added to gasoline as tetraethyl lead in the 1920s. Although subsequently used worldwide, Pb in gasoline has been phased out in recent years or is in the process of being phased out in many countries. The Ethyl Corporation, a major manufacturer of tetraethyl lead, also developed the octane enhancer methylcyclopentadienyl manganese tricarbonyl (MMT) in the 1950s and, as of 2003, was marketing the additive in 30 countries (Ethyl Corporation, 2003). In Canada it has been used extensively in gasoline, including unleaded gasoline, since the 1970s (Zayed, 2001; Health Canada, 2003) and was phased out in April 2004.

In contrast to the non-physiological role of Pb, several human enzyme systems are either activated or require Mn, and Mn plays an important role in metabolism, the nervous system and other key systems and functions (Davis, 1998). Nevertheless, excessive Mn exposure in the workplace has led to development of a neurodegenerative syndrome resembling idiopathic Parkinson's disease, and subtle nervous system deficits, consistent with Mn activity in the brain, were observed in environmentally exposed adults (Mergler et al., 1999). Recent studies of young children (up to 6 years of age) have suggested that environmental exposure to Mn in utero could affect early psychomotor development (Takser et al., 2003). In response to a petition from Ethyl Corporation to allow the use of MMT in the United States the US EPA (1994) found there was inadequate data on Mn exposure directly related to MMT, and thus it was necessary to construct estimates of potential exposure using several inferential arguments and assumptions (Davis et al., 1998).

Upon combustion, the Mn component is converted to a mixture of oxides (e.g., Mn_3O_4), phosphate ($Mn_3[PO_4]_2$) and sulphate ($MnSO_4$) (Colmenares et al., 1999). The size of the emitted particulate matter ranges from 0.1 to 10 μm diameter with >99% in the respirable fraction (<5 μm) and 86% <1 μm (Zayed et al., 1999a) although other studies by Ethyl Corporation indicate some variability in the particle size of the emissions. It has been estimated that about 12% Mn is emitted from the exhaust system with about 87% remaining in the engine (Ardeleanu et al., 1999).

The Australian Government phased out lead in gasoline in 2002 (NICNAS, 2003). To facilitate the transition to lead-free gasoline, the government allowed MMT to be used as a substitute for Pb for a limited period as an anti-valve seat recession additive, with its potential phase out in 2004. Sales of lead replacement gasoline (LRG) in Australia comprised about 12.6% of total gasoline sales in 2001–2002 and 5.6% in 2003–2004 (Australian Government, Department of Industry, Tourism and Resources, 2005). With such a low volume, the general provision and sale of bulk LRG by the oil refineries and terminals is uneconomical. LRG is no longer available from the major suppliers. MMT was not used in unleaded gasoline, the most widely used product, or in all LRG brands. It was added at the one refinery for 2 brands owned by that company and it was also supplied to another major under a "buy–sell" arrangement; the other two majors did not use MMT. The MMT and Mn concentrations for the major brands of gasoline using MMT ranged from 50 to 90 mg MMT L^{-1} or 13 to 23 mg Mn L^{-1}, respectively; the recommended 'treat rate' is 18 mg Mn L^{-1} (NICNAS, 2003). The Mn concentrations decreased from 23 mg L^{-1} in 2002 to about 13 mg L^{-1} in 2003 and 2004 but varied within this range. NICNAS (2003) predicted that annually around 180 t of MMT (containing approximately 45.4 t of Mn) may have been used in gasoline as an anti-valve seat recession additive within Australia. Assuming an upper figure of 20% of the Mn is released in exhaust emissions, this equates to an annual release of approximately 9.1 t of Mn to the atmosphere; further details of emissions are provided in Section 4.

The present study was initiated to take advantage of the opportunity of a 'before-during-after' trial, with the expectation of making repeated measurements over at least a four-year period. Characterisation of $PM_{2.5}$ particulates is part of wider longitudinal study begun in 2001 evaluating the potential impact on the environment and young children arising from the introduction of MMT to Australia.

2. Methods

2.1. Sampling sites

We have selected the data for 2 sites in the Sydney Basin area (approximate area 75 by 50 km) from a group of 4 that have been monitored continuously for 14 years using the same protocols. Site 23 is from Mascot and the $PM_{2.5}$ particulates have been dominated by motor vehicle emissions (Cohen et al., 2004). Site 18 is from Richmond, originally a rural area in the western part of the Sydney Basin, but it has been undergoing urban development over the past decade.

Wind rose diagrams (Davis and Gulson, 2005) show that the prevailing wind directions are from the south, with southwest to northwest breezes in the morning, changing to north east to east winds in the afternoon (Bureau of Meteorology, 1999). Calm periods are frequently experienced inland with stronger southerly winds along the coast and near the Sydney CBD. Local topographic factors also tend to give rise to local flows, especially westerly winds off the Blue Mountains escarpment, which travel eastward along river valleys to the coast. The opposite effect occurs during the late afternoon when easterly sea breezes flow from the coast up these river valleys, carrying with them pollution from the more populated areas.

2.2. Sampling methods

Atmospheric particulate matter was collected by drawing air through a filter for 24 h; usually from midnight to midnight. Samples were generally collected twice a week on Wednesdays and Sundays. A cyclone system based on the US EPA IMPROVE system collected $PM_{2.5}$ particles on a 25 mm diameter Teflon filter (Malm et al., 1994).

2.3. Sample analysis

The four IBA techniques of particle-induced X-ray and γ- ray emission (PIXE & PIGE), particle elastic scattering analysis (PESA) and Rutherford backscattering (RBS) have been applied throughout the work described here. The four techniques were applied simultaneously using 8 mm diameter beams of 2.6 MeV protons and target currents of typically10–15 nA. Each of these non-destructive methods has been described in detail elsewhere (Cohen, 1993, 1998; Cohen et al., 1996). Collectively these four techniques cover the commonly occurring elements H, C, N, O, F, Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Sr, Br and Pb with mean detection levels around 1–10 ng m^{-3} of air sampled. Typical minimum detectable limits range down to less than 1 ng m^{-3} of air sampled and experimental errors are around $\pm 7\%$ for most of the elements analysed.

These IBA techniques provide high sample throughput coupled with multi-elemental information allowing statistical analysis such as principal components analysis (Hopke, 1991) and positive matrix factorization to be used to determine source elemental fingerprints and then the source contributions to the total fine mass fraction to be quantitatively determined (Cohen, 1998; Cohen et al., 2000).

2.4. Statistical methods

The data consisted of 730 observations for the Richmond site 18 and 718 observations for the Mascot site 23. The distributions of the data for each site, which were analysed separately, were positively skewed, so the observations were $\log_e$-transformed to reduce skewness to approximately zero. Residuals were found to be approximately normally distributed. Because the data were collected sequentially from the same source (although not on consecutive days), the analyses were carried out using Prais–Winsten regression, as implemented in Stata 8.2 (Statacorp LP, College Station, Texas, USA, 2004). This form of regression estimates the autocorrelation of residuals for successive observations and produces estimates that are conditional upon this estimate. Year and month (and their interaction) were coded as orthogonal polynomials, which allowed any linear, quadratic, or cubic trends to be detected.

For other analyses such as Spearman correlations, the untransformed data were aggregated by site and year and analyses undertaken using SPSS 12.0 (SPSS Inc, Chicago, IL).

3. Results

We will only discuss the results for a 7-year period (1998–2004) covering the 'before–during–after' intervals of the use of MMT and will focus mainly on relationships of Pb and Mn.

3.1. $PM_{2.5}$ concentration in air

Particulate mass in air varied in the following way: since 1998, the maximum masses were $61\,\mu g\,m^{-3}$ at Richmond and $54\,\mu g\,m^{-3}$ at Mascot, both of which were associated with bushfires on 30/12/2001; minimum values were $1.22\,\mu g\,m^{-3}$ at Richmond on 26/07/2000 and $1.05\,\mu g\,m^{-3}$ at Mascot on 19/07/2000. The mean $PM_{2.5}$ mass concentrations were $7.4 \pm 6.4\,\mu g\,m^{-3}$ for Richmond and $8.9 \pm 6.2\,\mu g\,m^{-3}$ for Mascot. These are well below the US EPA NAAQS $PM_{2.5}$ annual standard of $15\,\mu g\,m^{-3}$.

3.2. Temporal variation of $PM_{2.5}Mn$

For the Richmond site 18, the index of autocorrelation of the residuals, ρ, was -0.063, which was not significantly different from zero, according to the Breusch–Godfrey test of autocorrelation (Godfrey, 1978) [$\chi^2(1) = 2.68$, $p = 0.1019$]. Thus, the data would have met the assumption of the independence of residuals, even without the adjustment made by the Prais–Winsten procedure. There was a significant interaction effect [$F(66, 646) = 1.47$, $p = 0.012$]. Inspection of graphs and data suggested that this interaction was at least in part due to unusually high readings in May, October and November of 2002, rather than to any systematic trends. Tests of the effects of year and month in a main effects model showed a significant effect of year [$F(6, 712) = 14.95$, $p < 0.001$] and no effect of month [$F(11, 712) = 1.40$, $p = 0.168$]. The orthogonal polynomial coefficients for year showed significant linear, quadratic and cubic trends over time. Deviation contrasts, which compared each year with the overall mean, indicated that the Mn results for 1998 and 1999 were significantly lower than the mean, while those for 2001–2003 were significantly higher than the mean.

For Mascot site 23, the autocorrelation of the residuals was significant [$\rho = -0.127$, $\chi 2\ (1) = 10.80$, $p = 0.001$], so that the Prais–Winston adjustment played an important part in ensuring the validity of the analysis. The interaction between year and month was not significant [$F(66, 634) = 1.08$, $p = 0.323$]. A main effects model was therefore tested. There were significant effects for both year [$F(6, 700) = 13.99$, $p < 0.001$] and month [$F(11, 700) = 19.98$, $p < 0.001$]. There were significant linear, quadratic and cubic effects for year, but only the quadratic and cubic effects were significant for month. Deviation contrasts indicated that the Mn means for 1998 and 2000 were lower than the overall mean, while those for 2001 and 2002 were higher. Deviation contrasts for month indicated that the Mn means for January and February, and October and November, were lower than average, while those for April–August were higher.

Other results are presented graphically as box plots over time and scatter plots for elements of interest to our specific problem. Spearman correlation coefficients for most of the elemental pairs, except for Ni, V and Co, were robust with p-values < 0.0001 and provide minimal useful information.

The temporal variations of Mn and Pb are shown in Figs. 1 and 2. Although a relatively rural setting, the Mn data for the Richmond site show the same increase from 2001 that is so clear for the Mascot site. However, the range of variation for the Richmond site is much smaller than for Mascot and may indicate a more homogeneous source for Mn. The Pb values show a decrease over time consistent with the cessation of Pb use in gasoline. With this trend also obvious in the Richmond site, the increase in Mn from 2001 may well reflect a small contribution from gasoline. The gasoline-derived Mn may be either from direct sourcing in this area or windborn from the main area of Sydney metropolitan area as described in an earlier section.

Manganese values between those for the Richmond and Mascot sites are found for the Liverpool site, about 50 km south west of the CBD, where traffic is also a major contributor to air particulates (Cohen, unpublished data).

3.3. Source characterization

Principal component analysis and positive matrix factorization of long-term data from the Mascot site have been used to identify inter-element associations and generate source fingerprints which, for

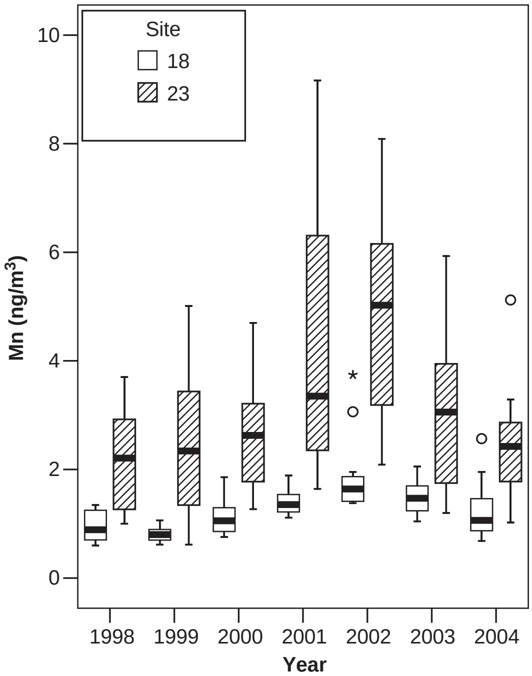

Fig. 1. Temporal variation of Mn concentration in air from 1998 to 2004 at Mascot (site 23, suburban) and Richmond (site 18, rural). The exact date of MMT introduction is uncertain but was at least by 2000.

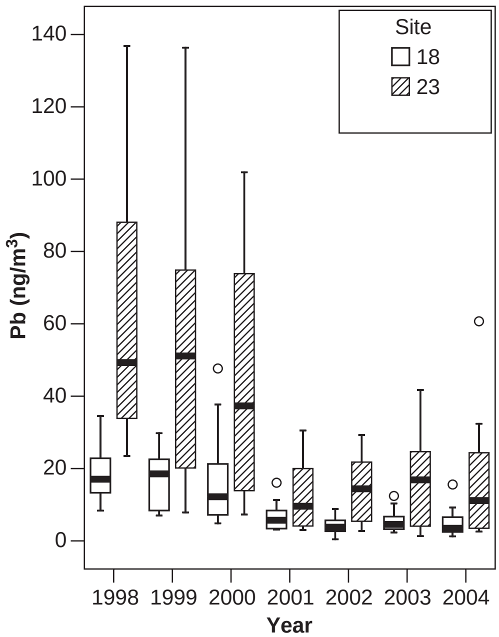

Fig. 2. Temporal variation of Pb concentration in air from 1998 to 2004 at Mascot (site #23, suburban) and Richmond (site #18, rural).

motor vehicle emissions include Cu, Zn, Fe, Mn, Ti, Pb, Cr, Br and black carbon (BC) (Cohen et al., 2004).

Investigations focused on annual trends in the Sydney Basin have shown there to be strong seasonal trends in many elements, especially Pb, with higher values in winter compared with summer (Figs. 3 and 4; and Cohen et al., 2004). The time series plot in Fig. 3 shows the increase in Mn probably associated with the introduction of MMT in 2000 and subsequent decrease to 2004 along with the 4:1 seasonal variations in Mn concentration in air. Fig. 4 shows the 1:5 season variations for Pb over time along with the decrease in Pb from 1998–2002, the variable nature in 2002–2004 and an increase in the winter peaks of 2003 and 2004.

To overcome the seasonal variability, ratios of elements that have the same seasonal variability and originate from different sources are used. Lead, Mn, Zn and black carbon all have higher values in winter compared with summer and at Mascot are all strongly associated with automobiles.

Since the overall nature of emissions from motor vehicles in Sydney would have not changed significantly from 1998 to 2004, ratios of elements such as Zn/BC (Fig. 5) should be constant over time. By normalizing Pb (Fig. 6) and Mn (Fig. 7) to the same black carbon or Zn values on the same day, any changes in these gasoline additives should be discernible. The marked decrease in Pb/BC ratios (Fig. 6) is consistent with the decreasing use of Pb in gasoline whereas the variable trends for Mn/BC are consistent with the introduction and then cessation of the use of MMT.

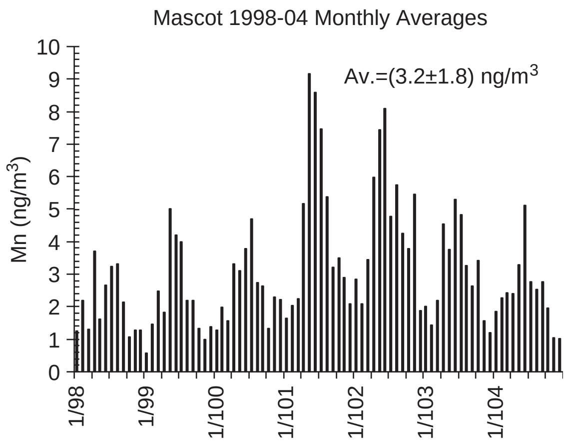

Fig. 3. Monthly variation of Mn concentration in air from 1998 to 2004 at the Mascot (suburban) site.

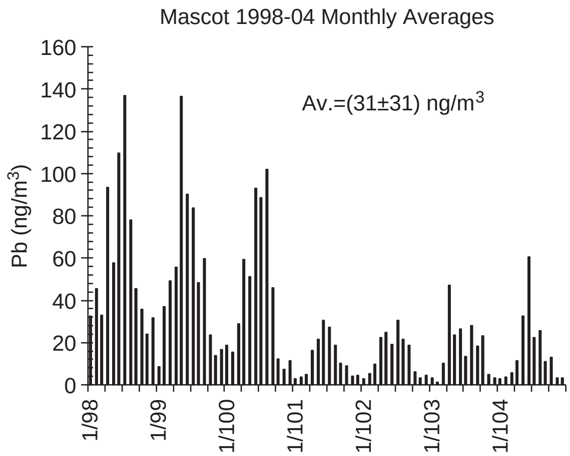

Fig. 4. Monthly variation of Pb concentration in air from 1998 to 2004 at the Mascot (suburban) site.

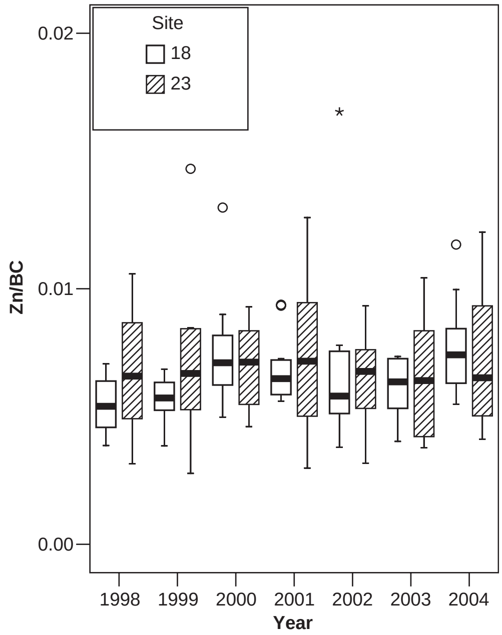

Fig. 5. Temporal variation of Zn/BC for the Mascot (#23, suburban) and Richmond (#18, rural) sites showing the limited change over time that allows for correction for seasonal effects.

A major problem, however, in characterizing different sources of Mn is the ubiquitous levels in soils that may range up to thousands of $\mu g\,g^{-1}$ Mn. Titanium, Si, K and Al are commonly used to characterize uncontaminated soils so that any increase above background levels of these elements by a potential contaminant element, expressed as a ratio, may be indicative of anthropogenic contamination (enrichment factor). Several recent papers

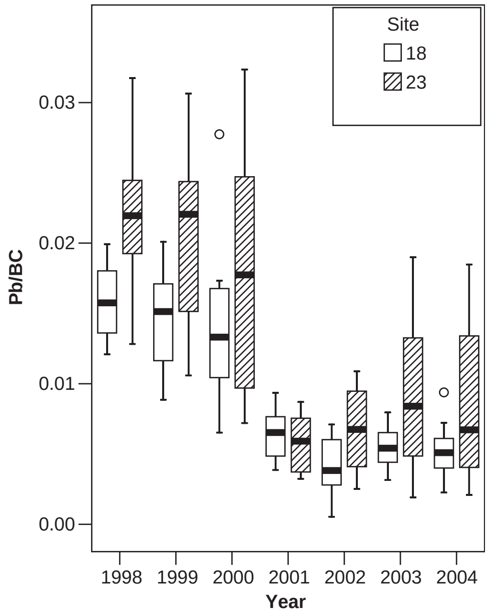

Fig. 6. Temporal variation of Pb/BC for the Mascot (#23) and Richmond (#18) sites showing the changes over time when corrected for seasonal effects.

(e.g. Rasmussen, 1998; Hamon et al., 2004; Reimann and de Caritat, 2005) have expressed concern over the use of "global" crustal or lithogenic values for estimating enrichment factors and recommended use of local background values for this purpose or other approaches such as relationships with Fe and Mn contents in soils. In our case, we can use the "local" values from the background Richmond site for Si, K, Al and often Ti with which to normalize the Mn values. In pollution and geochemical studies, the elements Al, Si and K are often grouped. We have not added Ti to the grouping because of the potential for derivation of Ti from anthropogenic sources such as automotive, mentioned above. Nevertheless, scatter plots of Ti vs. Al or Ti vs. Si show a very high correlation ($p<0.001$), or alternatively, minimal temporal change when plotted as ratios, for the background site of Richmond, similar to those for Zn/BC in Fig. 5. A plot of Mn/(Al+Si+K)1000 (or Mn/Ti) versus years (Fig. 8) shows a significant increase in the Mn/(Al+Si+K)1000 (or Mn/Ti) ratio from 1999 to 2001–2002 for the Mascot site (#23) and then a gradual decline to 2004. In contrast, these ratios for the Richmond site (#18) exhibit small variations over time, although there are statistically significant differences as described earlier in Section 3.2.

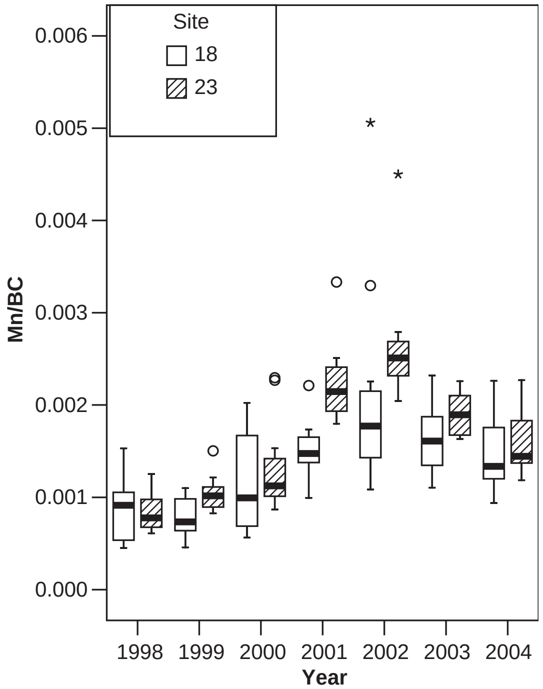

Fig. 7. Temporal variation of Mn/BC for the Mascot (#23) and Richmond (#18) sites showing the changes over time when corrected for seasonal effects.

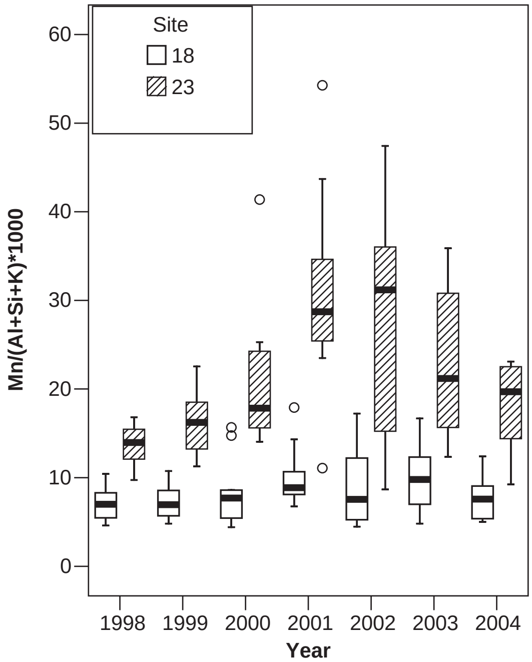

Fig. 8. Temporal variation of Mn/Al + Si + K versus time for the Mascot (#23) and Richmond (#18) sites showing the changes over time when normalized to local crustal ('soil') values.

3.4. Source of Mn

Is most of the Mn in the $PM_{2.5}$ particulates coming from motor vehicle emissions or other sources such as soil? The forgoing discussion indicates a significant contribution from MMT. Another approach to address this query is to compare the Mn values with the use of LRG as MMT was used in this product by only 2 major suppliers. In Fig. 9 the air Mn values are plotted against LRG use by the major suppliers in NSW. There is a good correlation with Mn concentration in air of R^2 0.83 and the correlation with Mn/Al + Si + K ratio, which effectively removes the soil component of Mn, is even higher (R^2 0.93). The intercept of the line for Mn vs. LRG of 1.6 ng m^{-3} is consistent with the background value of Mn in air of about 1.5 ng m^{-3} for the Richmond site.

It is possible to obtain an estimate of the extra Mn added to Sydney air over time at the Mascot site using an enrichment factor approach. Here enrichment factors (EF) for Mn at Mascot were calculated using a ratio of either Mn/Al + Si + K or Mn/Ti with the crustal or lithogenic factors of Al, Si, K, Ti and Mn coming from the Richmond site, taken to be background. As there is potentially a small contribution of Mn from MMT for the Richmond site (Figs. 1, 8), the lithogenic factors are based on the values from 1998 to 2000. The annual Mn/Al + Si + K (or Mn/Ti) values for Mascot are referenced to the same ratios at Richmond to obtain the Mn EF. Lithogenic contributions to the total Mn air values were calculated as the product of the Al + Si + K or Ti concentrations and the Mn/Al + Si + K or Mn/Ti lithogenic abundance. Anthropogenic Mn was then calculated from the difference of total Mn and lithogenic Mn (e.g. Shotyk et al., 2002; Jackson et al., 2004). A summary of the enrichment of Mn in air at the Mascot site is given in Table 1. The results for both lithogenic factors indicate a maximum increase in 2001–2002 of about 2.5 ng Mn m^{-3} ('Mn anthro' in Table 1) or a doubling in the Mn concentration in air for the $PM_{2.5}$ fraction.

The good correlations for Mn in air and LRG usage over time are comparable to the decreasing trends over time observed for Pb in air and gasoline (Fig. 10). Similar trends for Pb have been reported earlier (e.g. US EPA 1986).

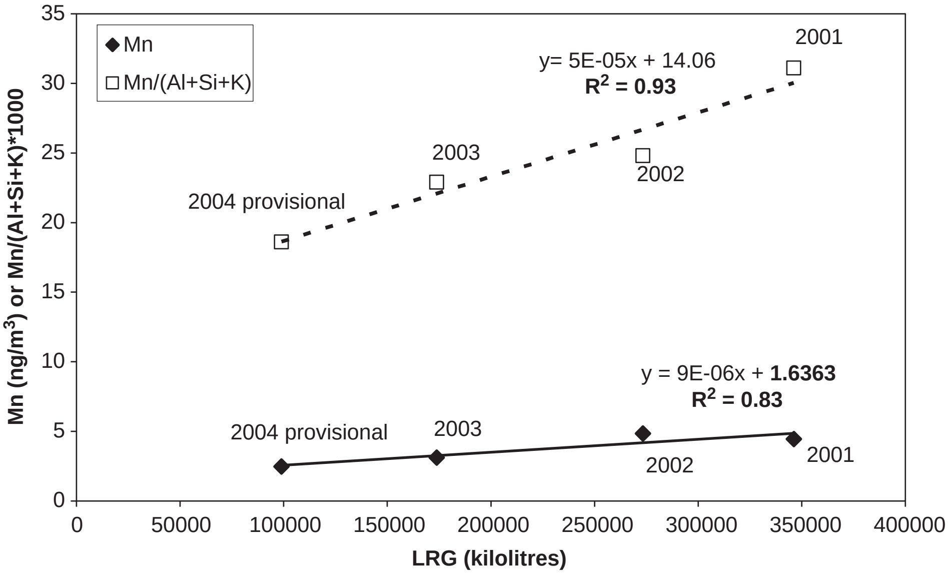

Fig. 9. Temporal variation of Mn concentration ($ng\,m^{-3}$) and Mn/Al + Si + K ratios in air as a function of volume of gasoline sold by two suppliers in NSW between 2001 and 2004.

4. Discussion

Our results show that using highly sensitive IBA methods it is possible to detect changes in Mn and Pb in $PM_{2.5}$ particulates in spite of the limited use of MMT only in unleaded gasoline and by not all major suppliers. Furthermore, using other elements measured simultaneously with the Pb and Mn, it is possible to make allowances for seasonal effects and other sources such as from crustal rocks (soils).

The changes in Mn concentration in air, as well as ratios such as Mn/Al + Si + K or Mn/Ti, track the changes in use of LRG in NSW and are consistent with the hypothesis that the increased amounts of Mn in the air derive largely from MMT. The ability to track the changes has been facilitated by the introduction of MMT at a specific time and then its phase out after 4 years. It has not been possible to ascertain the exact date of introduction of MMT to Sydney but, from the changes shown in Fig. 8 and estimations in Table 1 of the Mn anthropogenic component, it would appear that some MMT was already in use in 1999.

There are limited data available for atmospheric particulates in Australia. An investigation using the same sampling and analytical protocols as in the present study was undertaken in Adelaide, Brisbane, Canberra, Launceston, Melbourne and Sydney during 1996–1997, prior to introduction of MMT (Ayers et al., 1999). In 4 of the 6 cities (Adelaide, Brisbane, Melbourne, Sydney), the Mn concentrations were ~3 $ng\,m^{-3}$, based on a maximum of eight 24-h samples. The values of Mn in the PM_{10} fraction were 2–4 times higher than those in the $PM_{2.5}$ fraction.

NICNAS (2003) modeled two environmental exposure scenarios for Mn, one for a present use of MMT and the other for a 'wind-down' phase in 2004. They determined a long-term average estimate (AVE) and a reasonable maximum exposure estimate (RME). In the modeling, NICNAS assumed that MMT had 100% market share of lead replacement gasoline, a treat rate of 18 mg Mn L^{-1}, 20% emission from the exhaust, and 20% of the predicted 180 t of imported MMT was used in Sydney. However, as mentioned previously, lead replacement gasoline only represented from 5.6% to 12.6% of the total market for Australia (not just NSW) for 2001–2004. For the AVE Mn concentration in air at ground level, modeling under the present use scenario, the Mn concentrations would be 4.9 $ng\,m^{-3}$. For the 2004 scenario with MMT use declining to 14.5 t (3.7 t Mn) and a 20% emission rate, NICNAS estimated that 0.74 t of Mn would be released into the Sydney atmosphere; the AVE air value would be 2.0 $ng\,m^{-3}$.

These estimates for air are based on a 100% market share for MMT in LRG. Given the use of other additives by 2 of the major companies, these estimates would appear to be maximum. How

Table 1
Al, Si, K, Ti and Mn concentration (in $ng\,m^{-3}$), Mn enrichment factors and relative lithogenic and anthropogenic Mn contribution to total Mn for $PM_{2.5}$ particulates at Mascot site 23

Year	Al	Si	K	Ti	Mn	Mn/(Al + Si + K)	Mn EF (Al + Si + K)	Mn litho	Mn anthro	Mn anthro (%)	Mn/Ti	Mn EF Ti	Mn litho (Ti)	Mn anthro (Ti)
1998	27.1	65.5	66.3	4.30	2.19	0.0138	1.89	1.16	1.03	47	0.51	1.16	1.89	0.30
1999	21.3	59.1	61.6	4.49	2.46	0.0174	2.38	1.04	1.43	58	0.55	1.25	1.97	0.49
2000	18.5	52.5	62.7	3.92	2.62	0.0196	2.69	0.97	1.65	63	0.67	1.52	1.73	0.90
2001	13.4	53.5	76.1	3.82	4.45	0.0311	4.27	1.04	3.41	77	1.17	2.65	1.68	2.77
2002	27.4	92.1	76.6	5.00	4.85	0.0248	3.39	1.43	3.42	71	0.97	2.21	2.20	2.65
2003	16.4	63.8	55.8	3.58	3.11	0.0229	3.13	0.99	2.12	68	0.87	1.97	1.58	1.53
2004	17.6	60.1	55.2	3.97	2.47	0.0186	2.54	0.97	1.50	61	0.62	1.41	1.75	0.72

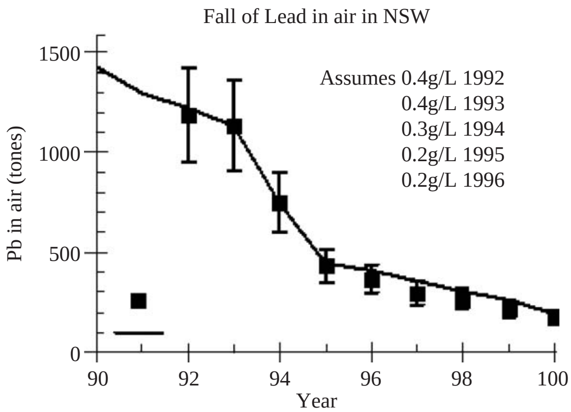

Fig. 10. Temporal variation of Pb in Sydney air (in tonnes) and Pb from gasoline (redrawn from Cohen et al., 2004).

realistic are the estimates? Precise figures of LRG use are confidential but sales figures for NSW were provided by the major supplier. Using the NICNAS values of a treat rate of $18\,mg\,L^{-1}$, a 20% emission rate, that 80% of the use is in Sydney, and that the other major supplier using MMT has sales about half of the main supplier, then about 1 t Mn would be emitted to Sydney air for the year 2001, 0.79 t for 2002, 0.50 t for 2003 and 0.28 t for 2004. These estimates of Mn emitted to air in Sydney are of a similar magnitude to those estimated by NICNAS for 100% market share. However, the maximum atmospheric levels of $4.9\,ng\,m^{-3}$ are almost the same as the mean levels measured at Mascot for 2002. This assumes that the overwhelming majority of Mn in air at Mascot is from motor vehicle exhaust.

These values are considerably lower than the values measured in Canada and some other countries. For example, ambient air $PM_{2.5}$ concentrations of approximately $5–50\,ng\,m^{-3}$ were reported by Wood and Egyed (1994) in a range of Canadian cities with most having $PM_{2.5}$ concentrations in the range of $10–20\,ng\,m^{-3}$; they concluded that MMT use did not contribute significantly to ambient air respirable Mn concentrations. Loranger and Zayed (1997) estimated the average air concentration of respirable Mn (PM_5) in a low traffic urban site in Montreal of approximately $15\,ng\,m^{-3}$. In a follow-up study, Zayed et al. (1999b) measured respirable Mn (particles $<5\,\mu m$), using a 36-h sampling protocol of 12 h for each of three consecutive days, taken at several sites in Montreal. The results were of a similar magnitude: a petrol station ($35\,ng\,m^{-3}$), an underground car park

(30 ng m^{-3}), the centre of Montreal (44 ng m^{-3}), the vicinity of an expressway (53 ng m^{-3}) and the vicinity of an oil refinery (18 ng m^{-3}).

Several authors have made predictions of the effect of the use of MMT on airborne Mn levels in the USA. For example, Pfeifer et al. (1994) predicted that if all gasoline in the US contained MMT at the allowable level of 8 mg L^{-1} (0.03125 g Mn gal^{-1}), the incremental increase in total suspended particulates in urban areas would be about 10–20 ng Mn m^{-3}. Wallace and Slonecker (1997) suggested that use of MMT in all gasoline in the USA would increase Mn in fine airborne particulates ($PM_{2.5}$) by about 5–10 ng m^{-3} in urban areas. Data from monitoring ambient air $PM_{2.5}$ particulates from Riverside California in 1990 (Pellizzari et al., 1992) showed a 24 h median Mn concentration of approximately 10 ng m^{-3}.

In Sydney, the maximum median value was achieved in 2002 with a value of about 5 ng Mn m^{-3}, more than doubling the estimated background value of 1.5–1.6 ng m^{-3} prior to MMT introduction; but as pointed out earlier, the value of 5 ng m^{-3} includes a lithogenic component. The Sydney values may be compared with those from Toronto where $PM_{2.5}$ particulates from roof monitors showed a median value of ~10 ng Mn m^{-3}, ~15 for fixed sites and outdoor measurements of 8.6 ng Mn m^{-3} (Pellizzari et al., 1992). The limited increase in Toronto where MMT is used in all gasoline is surprising compared with the values for Sydney. In comparing the Toronto study with a similar study in Indianapolis USA, where MMT was not used, Pfeifer et al. (2004) noted that the increase in median exposure to $PM_{2.5}$ Mn of about 5 ng m^{-3} was similar to the increase predicted by Wallace and Slonecker (1997). Furthermore, Pfeifer et al. (2004) suggested that the increase would not be sufficiently large to cause exposures to be above the reference concentration (RfC) of 0.050 μg Mn m^{-3} designated by US EPA (1993) or other guidelines for Mn exposures among the general population if MMT were to be introduced into gasoline in Indianapolis.

In a number of these studies from other countries where multi-element data are lacking, the Mn values could include non-MMT sources such as wind-blown dust. For example, the US EPA (1994) concluded that approximately 75% of the $PM_{2.5}$ Mn collected in the Los Angeles basin was from automotive sources. This conclusion is consistent with our data, which accounted for the lithogenic dust, where the contribution from anthropogenic sources was about 70% at the time of maximum MMT use (Table 1). In a study using dispersion modeling adjacent to a major Canadian freeway, Loranger et al. (1995) predicted that the contribution of automotive sources to background Mn concentrations was 50% at 25 m and only 8% at 250 m from the road. Crump (2000) concluded that most of personal Mn exposure in Toronto was from non-MMT sources such as from the erosion of the steel wheels on the steel tracks in the subway. Likewise, Pfeifer et al. (1999) interpreted personal exposures in London to arise mainly from subway use. In a reinterpretation of the earlier study of Zayed et al. (1996) in Toronto on total suspended and respirable particulates from office workers and taxi drivers, Pfeifer et al. (2004) suggested that much of the difference between the two groups was from crustal sources and time spent outdoors.

From an environmental point of view, Bhuie & Roy (2001) analysed surface soil samples (0–5 cm depth) at distances of up to 40 m from the roadside in the Greater Toronto Area Canada for a suite of elements, including total and available Mn plus a number of other parameters. They concluded that although MMT has been used continuously for approximately 25 years in Canada, its contribution to the terrestrial environment has been very low and has not significantly increased Mn levels along the highways. In contrast, Mielke et al. (2002) estimated that at 1999 US highway fuel use, 8.3 mg Mn L^{-1} would yield 5000 metric t of Mn annually. If 13% of Mn were emitted via the exhaust system, 650 t Mn would become aerosols annually, while 87% or 4350 t remained in engines. Mielke et al. (2002) claim a precautionary lesson from the use of Pb as a fuel additive is that the use of Mn as a fuel additive would be associated with an increased risk for neonates exceeding the estimated total daily intake of 2.1–16.5 μg Mn (especially in urban inner-city environments). Known pharmacokinetic processes that may relate to the increases in brain Mn concentration in neonates compared with adults include: increased Mn absorption from the juvenile gastrointestinal tract, an incompletely formed neonatal blood–brain barrier, and a virtual absence of excretory mechanisms until weaning (Pfeifer et al., 2004).

In spite of the cessation of use of Pb in gasoline in Australia in 2002, the small increases in Pb in air in the winters of 2003 and 2004 are most likely due to meteorological conditions such as more calm inversions than previous years. This Pb component may be due to Pb in resuspended road dust.

Summary: Although our methods have been able to detect increases in Mn in air associated with the introduction and cessation of use of MMT in Sydney, the levels are well below the reference levels. The incremental increases in air, however, are larger than expected given the limited use of MMT only in lead replacement gasoline and high quality monitoring should be undertaken in countries where MMT is used in all gasoline.

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