

OXALIC ACID AND OXALATE IN THE ATMOSPHERE

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Abstract

Oxalic acid gas and particulate concentrations have been measured at a number of locations from remote areas such as the Burrup Peninsula, WA to rural in the Hunter Valley in NSW and an site urban in Melbourne, all in Australia, and Petaling Jaya, near Kuala Lumpur, Malaysia.

The concentrations of oxalic acid gas at the remote and rural sites range from about 700 ng m⁻³ to 4000 ng m⁻³ and have a very strong annual cycle, with high concentrations during the summer periods. At the urban site in Petaling Jaya concentrations of oxalic acid gas are higher than at the remote sites, ranging from about 8000 ng m⁻³ to 30,000 ng m⁻³ and up to about 60,000 ng m⁻³ during episodic events, and they do not display a distinct annual cycle.

Oxalate particulate concentrations were measured concurrently with oxalic acid gas concentrations at some sites and the data show that at least 85% of the total is in the gas phase, which is consistent with the high vapour pressure of oxalic acid at ambient temperatures. The data presented here show a widespread occurrence of oxalic acid gas in the atmosphere. The seasonal variation in concentrations at remote sites exhibit a summer maximum and a winter minimum, suggesting that either plants or photochemistry may be the dominant source of oxalic acid in remote and rural continental atmospheres. The only previously clearly defined source of oxalic acid is motor vehicle exhaust.

The data from Petaling Jaya show that concentrations of particulate oxalate and oxalic acid were high during periods of intense forest fires in Asia indicating that biomass burning is probably a significant source of oxalic acid gas concentrations observed in the atmosphere. The mass of oxalic acid emitted from biomass burning worldwide is calculated to be 28 Tg y⁻¹ ± 20 Tg y⁻¹, including 2.8 Tg y⁻¹ ± 2 Tg y⁻¹ particulate phase oxalic acid.

Keywords: Oxalic acid, gas, particulate matter

1. Introduction

In a recent review paper it was suggested that little is known about many organic compounds which exist in the atmosphere (Goldstein & Galbally 2007). Oxalic acid, the simplest organic diacid, is present in the atmosphere in gas, particulate and rainwater phases. Little is known about the sources, concentrations or fate of this compound; in urban air the only clearly defined atmospheric source is from motor vehicle emissions (Kawamura & Kaplan 1987, Chebbi & Carlier 1996). This paper presents concentrations of oxalic acid in gas and particulate phases from a number of locations in Australia and Malaysia covering oceanic, remote continental, rural and urban environments. It suggests that other sources such as biomass

emissions, particularly in remote areas, and from biomass burning may be significant sources of oxalic acid.

2. Experimental

2.1. Sampling and analytical techniques

Gas phase oxalic concentrations were measured with passive samplers over periods ranging from one week to one month. Passive samplers have several advantages over other techniques; the main one is that can be used in remote areas, since they require no power. CSIRO has extensive experience with these samplers and has validated

them for SO₂ and NO₂ against active sampling techniques (Ayers et. al. 1998).

Particulate samples were collected either with low volume Ecotech Micro-vol samplers at a flow rate of about 3 l min⁻¹ on stretched teflon filters or on hivol samplers.

The filters used in the passive samplers, and the stretched teflon filters were extracted in Milli-Q (18 Mohm) water. Chemical analysis to determine oxalate concentrations in extracts was carried out by suppressed ion chromatography using a Dionex Ion Chromatograph with an AS11 separator column and sodium hydroxide gradient eluent.

2.2. Site descriptions

Samples were collected at a number of sites, both in Australia and Malaysia. The Burrup Peninsula is a remote area to the northeast of Dampier, Western Australia in an area bounded by latitude 20.42°S and 20.65°S and longitude 116.71°E and 116.90°E.

The Cape Grim Baseline Pollution Station is located on the north west tip of Tasmania at 40.68°S, 144.69°E. Samples were collected by a high volume sampler during baseline conditions when the wind direction was between 190° and 280°, and the condensation nucleus count was <600 cm⁻³. At this site particulate samples are collected after air has a fetch of several thousand kilometers over the ocean.

Samples of gaseous and particulate phase oxalic acid were also collected at six sites about 150 km north of Sydney in the Hunter Valley. This is a rural area, bounded by latitude 32.15°S and 32.24°S and longitude 151.61°E and 151.89°E and the concentrations measured there are representative of a rural area with some influences from motor vehicles and other emissions.

The data from Mt Isa (20.73°S, 139.49°E) was collected from 12 sites located north west of the city and the Aspendale site is in suburban Melbourne at 38.03°S, 45.10°E.

Petaling Jaya is located at 3.04°N, 101.42°E, near Kuala Lumpur, Malaysia in an area that is heavily impacted with anthropogenic emissions including from motor vehicles and industry.

3. Results

The results presented show oxalic acid gas and particulate oxalate concentrations. The gaseous oxalic acid fraction of the total oxalate/oxalic acid is presented where both phases were measured at the one location.

Figures 1 and 2 show the concentrations of oxalic acid gas phase and particulate oxalate phase respectively, at the Burrup Peninsula, and the gas fraction of the total. The concentrations are shown

as averages of gas and particulate measured at seven sites on the Burrup Peninsula for one year over monthly integrated periods. Figure 2 shows the proportion of oxalic acid gas as a proportion of the total of the gas and particulate concentrations.

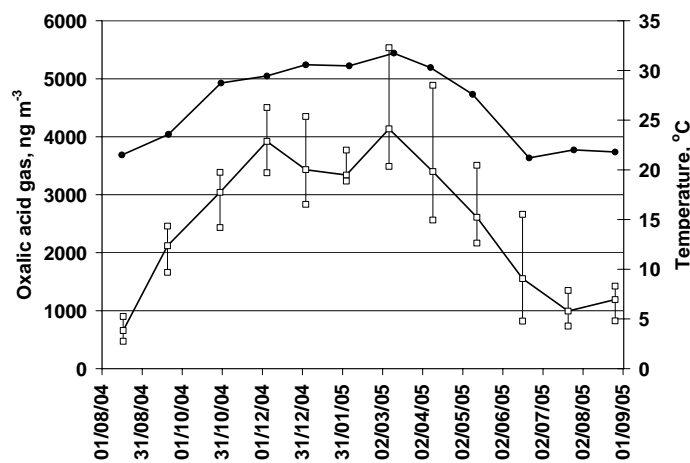


Figure 1. Average oxalic acid gas concentrations at 7 sites, and maximum and minimum concentrations on the Burrup Peninsula; open squares, and maximum ambient temperature, filled circles.

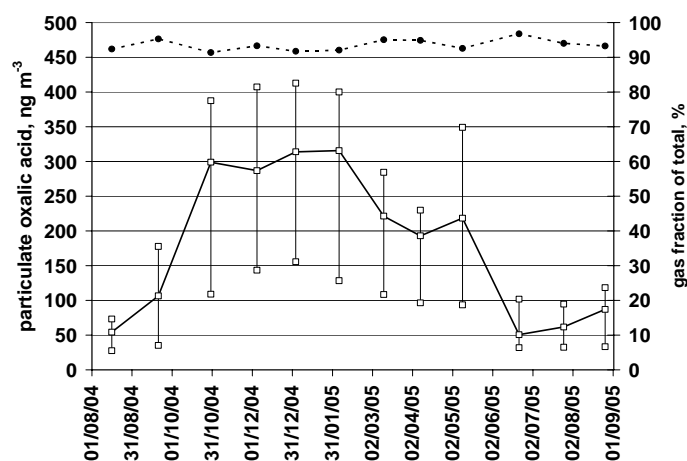


Figure 2. Average particulate oxalate concentrations at 7 sites, and maximum and minimum concentrations on the Burrup Peninsula; open squares. Filled circles are gas as a fraction of total particulate plus gas concentrations.

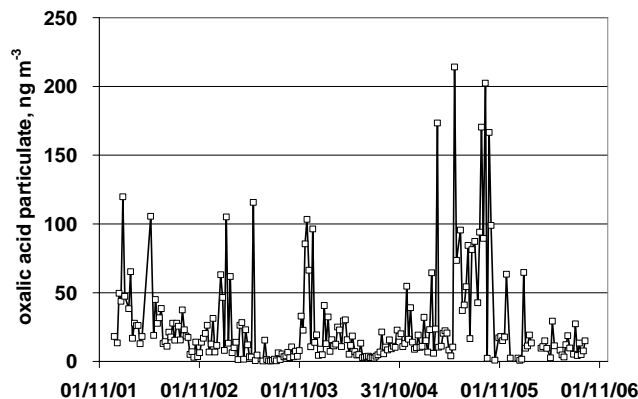


Figure 3. Particulate oxalate concentrations at Cape Grim Baseline Air Pollution Station from December 2001 until September 2006.

Figure 3 displays the concentrations of particulate oxalate measured in baseline conditions at Cape Grim from December 2001 until September 2006. Samples were usually collected over 7 days, except for a few occasions when the minimum air volume was not exceeded and sampling continued for a further seven days.

Figures 4 and 5 display the concentrations of oxalic acid gas and particulate oxalate concentrations measured at Petaling Jaya, Malaysia. Gas and particulate samples were collected concurrently over weekly integrated periods from March 1994 until April 2004. During 1994, the latter part of 1997, and the beginning of 1998 large scale forest fires on Borneo and Sumarta were a major reason for the poor air quality in Petaling Jaya. The occurrence of major forest fires, caused by low rainfall and drought in the region, is closely linked to the southern oscillation index, which is plotted in Figures 4 and 5.

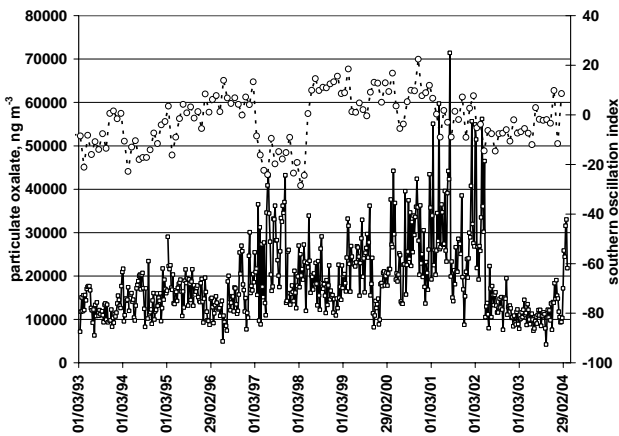


Figure 4. Oxalic acid gas concentrations measured at Petaling Jaya, Malaysia from March 1993 until April 2004. The dotted lines show the southern oscillation index.

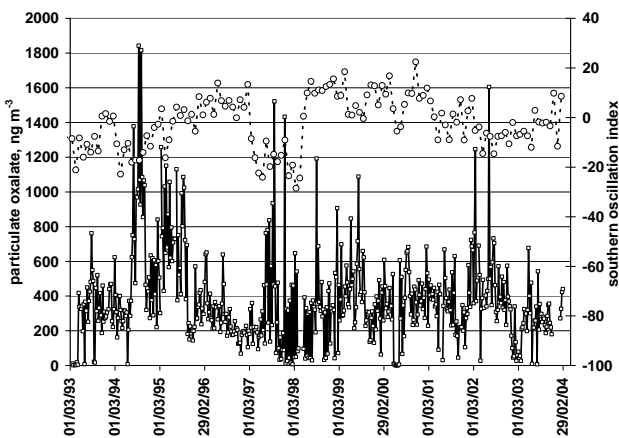


Figure 5. Particulate oxalate concentrations measured at Petaling Jaya, Malaysia from March 1993 until April 2004. The dotted lines show the southern oscillation index.

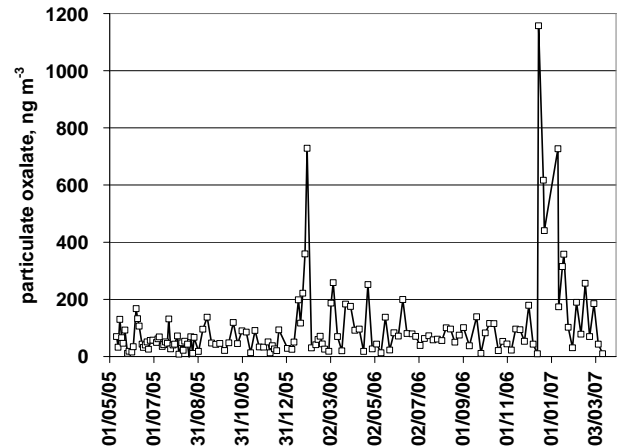


Figure 6. Particulate oxalate concentrations measured at Aspendale, Melbourne from May 2005 until April 2007.

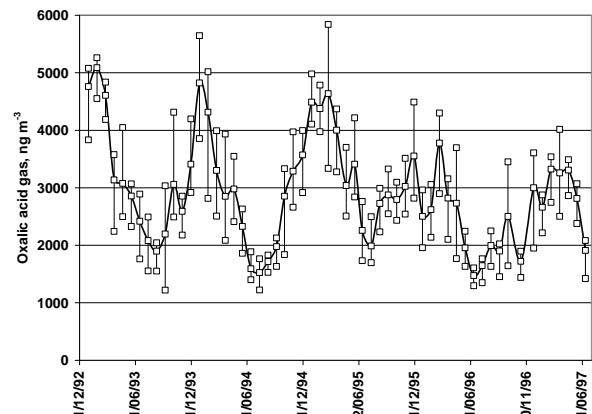


Figure 7. Oxalic acid gas concentrations at six sites in the Hunter valley, NSW from December 1992, until June 1997 with maximum and minimum concentrations, open squares.

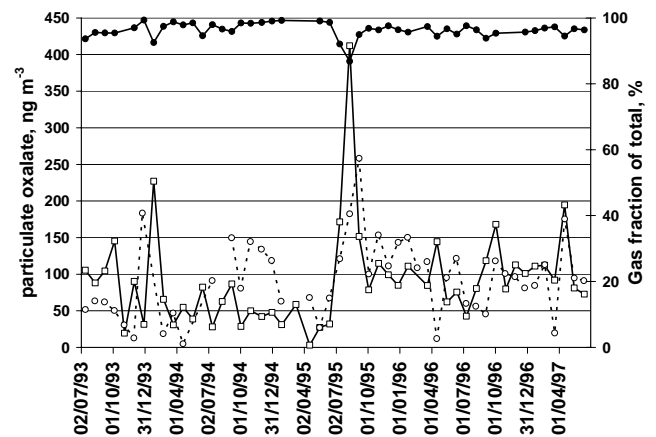


Figure 8. Particulate Oxalate concentrations at two sites in the Hunter valley, NSW from December 1992, until

June 1997, round and square open symbols, and the fraction of gas, filled circles.

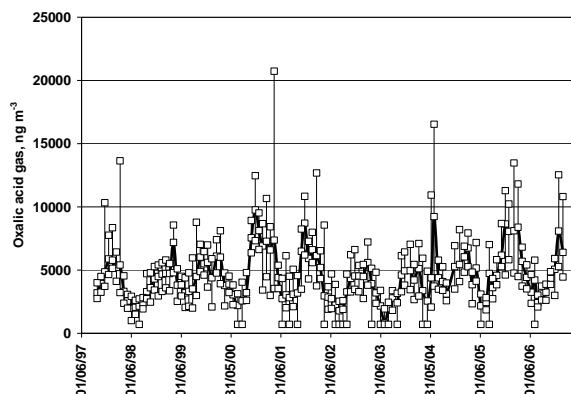


Figure 9. Oxalic acid gas concentrations measured at 12 sites near Mt. Isa from September 1997 until January 2007. The open squares are the maximum and minimum concentrations.

4. Discussion

4.1. Distribution of oxalic acid and oxalate

The mean concentrations of oxalic acid in the gas phase and oxalate in the particulate phase are presented in Table 1. Two trends are detectable. The warmer locations have higher oxalate concentrations, and there are higher concentrations over the continent compared to the oceans. This suggests a substantial widespread continental source of oxalic acid and oxalate.

Table 1. The mean concentrations of oxalic acid gas and particulate oxalate at various locations from this study. Units are ng m^{-3} .

Location	Environment	Oxalic acid	Oxalate
Cape Grim	Remote marine 41°S		26
Burrup	Remote continental 20°S	2500	185
Mt. Isa	Remote continental 21°S	4500	
Hunter Valley	Rural 32°S	2900	92
Aspendale	Suburban 38°S		100
Petaling Jaya	Urban 3°N	13,600	380

4.2. Seasonal Cycles

Figures 1 and 2 present gas and particulate phase oxalic acid concentrations that show a clear increase in concentration during the summer periods and a decrease in concentration during the cooler months. Figure 1 includes the average

maximum temperature for each month, and this shows a very good correlation with the oxalic acid gas concentrations. A similar seasonal cycle in oxalic acid gas concentrations can be seen in the Hunter Valley sites shown in Figure 7, although no discernable seasonal cycle is obvious in the particulate concentrations at two of the sites. Figure 9 shows gas concentrations of oxalic acid measured for several years around Mt. Isa, and summer maximum are quite obvious, except for the elevated concentrations during June 2004.

There are also locations where seasonal cycles in either gas or particulate concentrations are not evident. This is obvious both in polluted locations, such as the Petaling Jaya in Figures 4 and 5, and at Cape Grim BAPS in Figure 3. The cause of the lack of seasonal cycles at these two locations is unclear, but may be due to smaller annual temperature variations, and oxalic acid emissions from motor vehicles at the Petaling Jaya site and low temperature variations at Cape Grim.

4.3. Gas phase/particulate phase partitioning

The data presented in the Figures 2 and 8 show that oxalic acid gas concentrations were typically 85% to 99% of the sum of the oxalic acid gas and particulate oxalate concentrations. This is true for unpolluted sites such the Burrup Peninsula (Figures 1 and 2), and for sites such as the Petaling Jaya that is heavily impacted by anthropogenic pollution (Figures 4 and 5).

Figure 8 shows the proportion of oxalic gas to the total of gas and particulate concentrations measured concurrently at the Hunter Valley sites is usually more than 90%.

Figure 10 shows the saturation vapour concentration of gas phase of oxalic acid calculated at standard atmospheric pressure of 1013 hPa against the corresponding temperature. This shows that the saturation concentration of oxalic acid is $172 \mu\text{g m}^{-3}$ at 10°C and increases to $6188 \mu\text{g m}^{-3}$ at 40°C .

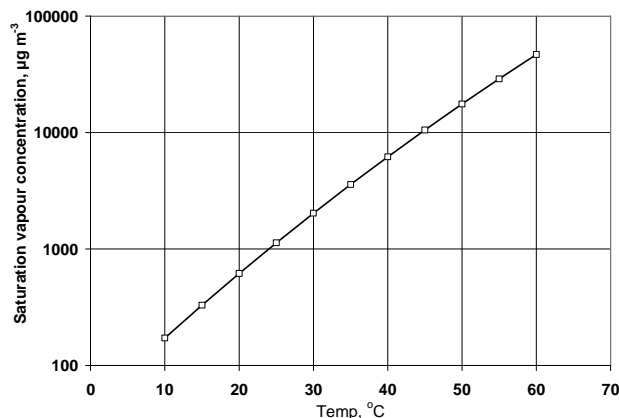


Figure 10. Saturation vapour pressure of oxalic acid

The maximum oxalic acid gas concentrations were measured at the Petaling Jaya site and were about 80,000 ng m⁻³ (Figure 4). At a temperature of 30° C the saturation vapour pressure of oxalic acid is about 3600 µg m⁻³, so that at a polluted site, such as Petaling Jaya, oxalic acid gas is only about 4% of the saturation concentration. In contrast, the maximum oxalic acid gas concentration at the unpolluted Burrup Peninsula sites is about 5500 ng m⁻³ which is about 0.2% of the saturation concentration at 35 °C. This explains the high proportion of oxalic acid present in the gas phase compared with the particulate phase.

4.4. Sources of Atmospheric Oxalic Acid

There are several potential sources of atmospheric oxalic acid including primary sources, such as emissions from motor vehicles (Kawamura & Kaplan 1987), from biomass and from biomass burning, and secondary sources such as oxidation of acetylene and ethylene in maritime clouds (Warneck 2003).

Particulate oxalate concentrations measured at Cape Grim (Figure 3) had average and median concentrations of 26 ng m⁻³ and 14 ng m⁻³ respectively with a maximum of 214 ng m⁻³. Other measurements have been made in maritime regions; for example Kawamura and Usukura (1993) measured particulate oxalate concentrations of 19.7 ± 7.2 ng m⁻³ in the central Pacific Ocean, and Kawamura and Sakaguchi (1999) measured 6.5 ng m⁻³ to 161 ng m⁻³ in the equatorial Pacific Ocean. The concentrations measured at Cape Grim are consistent with predicted concentrations of 10 ng m⁻³ to 72 ng m⁻³ arising from the oxidation of acetylene and ethylene in maritime clouds by hydroxyl radical (Warneck 2003).

The concentrations in the Burrup Peninsula, Mt. Isa and the Hunter Valley indicate that oxalic acid and oxalate are widespread in the remote continental areas at concentrations about 3 times those of oceanic regions, indicating a widespread continental source of oxalic acid and oxalate.

The concentrations of particulate and gaseous oxalic acid measured at Petaling Jaya (Figures 4 and 5) probably result from a combination of emissions from biomass burning and motor vehicles. Figures 4 and 5 have the southern oscillation index (SOI) plotted with the oxalic acid concentrations. The SOI is calculated in equation (1) and sustained negative values indicate an El Nino event with a decrease in the strength and lower rainfall over northern Australia and south east Asia.

$$SOI = 10 \times \frac{pdiff - pdiffav}{SD(Pdiff)} \quad (1)$$

Where:

Pdiff = (average Tahiti MSLP for the month) - (average Darwin MSLP for the month)

Pdiffav = long term average of Pdiff for the month in question

SD(Pdiff) = long term standard deviation of Pdiff for the month in question.

Figures 4 and 5 show that two low SOI episodes occurred during the sampling period at Petaling Jaya; one for most of the calendar year 1994 and the other from about February 1997 until about June 1998. During 1997 intense fires raged on the islands of Borneo and Sumatra destroying about 10 million hectares of forest (Barber & Schweithelm, 2000).

4.5. Particulate Oxalate Emissions from Biomass burning

The particulate oxalate concentrations presented in Figure 6 are measured at an urban site in suburban Melbourne. Several samples were collected during December 2006 and January 2007 when the site was heavily impacted with smoke from large forest fires burning out of control to the east and north east of Melbourne. Figure 6 shows that elevated concentrations were recorded for particulate oxalate during this period. In addition to oxalate, potassium concentrations were measured and non sea-salt potassium concentrations were calculated from the molar ratios of sodium and potassium, assuming the sodium ion has a marine origin (Millero 1976).

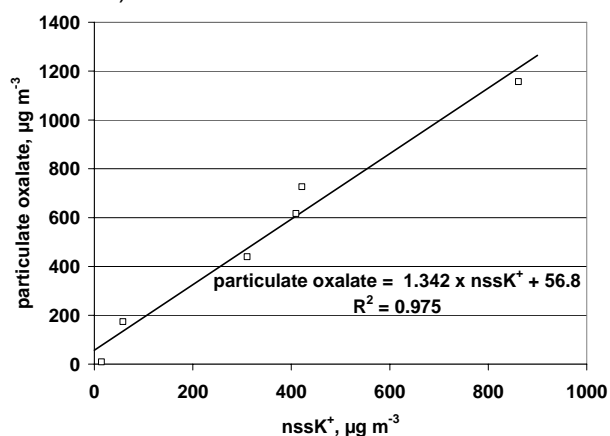


Figure 11. Correlation of particulate oxalate and non sea-salt potassium during a smoke impacted period at Aspendale, Melbourne during summer 2006/2007.

Figure 11 shows relationship between particulate oxalate and non sea-salt potassium during these smoke impaction events. The Figure shows the two species are highly correlated, and that particulate oxalate can be estimated from non sea-salt potassium using a slope of 1.3. Scholes et al. (2003) provide emission factors for potassium from biomass burning from savanna and grassland, tropical forest and extra tropical forest, and the

average emission factor is about $0.3 \text{ gm kg}^{-1} \pm 0.2 \text{ gm kg}^{-1}$ of dry fuel. Scholes et al. (2003) estimate the dry mass of fuel burnt each year to be $7000 \text{ Tg} \pm 2 \text{ Tg}$. This data, taken together, provides a method to calculate the annual emission of particulate oxalic acid from biomass burning.

From the results of this calculation it is estimated that $2.8 \text{ Tg y}^{-1} \pm 2 \text{ Tg y}^{-1}$ of particulate oxalic acid is emitted to the boundary layer from all biomass burning sources. The data presented in Figures 2 and 8 implies the ratio of the distribution of gaseous and particulate oxalic acid is about 9:1. We assume that a similar ratio applies in smoke plumes, given the physical/chemical basis of the gas/particulate partitioning. The corollary to this is that biomass burning may contribute about $28 \text{ Tg} \pm 20 \text{ Tg}$ of oxalic acid annually to the boundary layer, and that this is made up of about $2.8 \text{ Tg} \pm 2 \text{ Tg}$ of particulate oxalate and $25.2 \text{ Tg} \pm 18 \text{ Tg}$ of gaseous oxalic acid.

The total annual biogenic and anthropogenic VOC's emissions to the atmosphere is estimated to be about 1300 Tg (Guenther et al. 1995). The total oxalic acid emission from biomass burning is then only a small fraction of the total estimated emissions. But this is only one source of oxalic acid emissions, and others such as motor vehicle exhaust emissions and vegetative emissions would be expected to be significant emission sources. For example, Andrea and Merlet (2001) estimate that 12.7 Tg of methanol are emitted annually from biomass burning, but the source from flowering plants at 100 Tg is much larger, as Galbally and Kirstine (2002) document.

5. Conclusions

This paper presents oxalic acid gas and particulate oxalate concentrations from a range of locations, including clean marine and clean continental to polluted urban sites. The gas concentrations were found to be 85% to 99% of the total of the oxalic acid gas plus particulate oxalate concentration. The concentrations of oxalic acid gas at the remote and rural sites range from about 700 ng m^{-3} to about 4000 ng m^{-3} and have a very strong annual cycle, with high concentrations during the summer periods. Gas concentrations were about $10,000 \text{ ng m}^{-3}$ to $20,000 \text{ ng m}^{-3}$ at the urban site of Petaling Jaya, and during periods of intense forest fires in south-east Asia they reached about $60,000 \text{ ng m}^{-3}$. The data suggest that emissions from biomass and biomass burning may be significant sources of oxalic acid. It is estimated that $28 \text{ Tg y}^{-1} \pm 20 \text{ Tg y}^{-1}$ is emitted from biomass burning worldwide.

Acknowledgments

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References

- Andreae M. O. and Merlet P., 2001, 'Emission of trace gases and aerosols from biomass burning', *Global Biogeochem. Cycles*, **15**:955–966.
- Ayers G.P., Keywood M.D., Gillett R., Manins P.C., Malfroy H. & Bardsley T., 1998, 'Validation of Passive Diffusion Samplers for SO_2 and NO_2 under Australian conditions', *Atmospheric Environment*, **32**:3587-92.
- Barber C. V. & Schweithelm J., 2000, 'Trial by fire: forest fires and forestry policy in Indonesia's era of crisis and reform', World Resources Institute Forest Frontiers Initiative In collaboration with WWF-Indonesia & Telapak Indonesia Foundation.
- Chebby A. & Carlier P. 1996, 'Carboxylic acids in the troposphere, occurrence, sources, and sinks: a review', *Atmos. Environ.*, **30**:4233-49.
- Galbally I. E. & Kirstine W. 2002 'The Production of Methanol by Flowering Plants and the Global Cycle of Methanol' *J. Atmos. Chem.* **43**:195–229.
- Goldstein A. H. & Galbally I.E. 2007, 'Known and Unexplored Organic constituents In the Earth's Atmosphere', *Environ. Sci. and Technol.*, **41**:1515-21.
- Guenther A. B., Hewitt C. N., Erickson D., Fall R., Geron C., Graedel T., Harley P. C., Klinger L., Lerdau M., McKay W. A., Pierce T., Scholes B., Steinbrecher R., Tallamraju R., Taylor J., & Zimmerman, P. R., 1995, 'A global model of natural volatile organic compound emissions', *J. Geophys. Res.*, **100**: 8873–92.
- Kawamura K. & Kaplan I.R., 1987, 'Motor exhaust emissions as primary source of carboxylic acids in Los Angeles ambient air', *Environ. Sci. and Technol.*, **21**:105-110.
- Kawamura K., Sakaguchi F., 1999, 'Molecular distributions of water soluble dicarboxylic acids in marine aerosols over the Pacific Ocean including tropics', *J. Geophys. Res.*, **104**:3501–3509.
- Kawamura K., Usukura K., 1993, 'Distribution of low molecular weight dicarboxylic acids in the north pacific aerosol samples', *J. Oceanography* **49**:271–283.
- Millero F.J. 1974. 'The physical chemistry of seawater', *Ann. Rev. Earth Plan. Sci.*, **2**:101.
- Scholes M. C. et al., (2003). Biosphere-atmosphere interactions. In: *Atmospheric chemistry in a changing world : an integration and synthesis of a decade of tropospheric chemistry research: the International Global Atmospheric Chemistry*

Project of the International Geosphere-Biosphere Programme. G. P. Brasseur, R. G. Prinn, and A. A. P. Pszenny (editors). New York: Springer. p. 19-71.

Warneck P., 2003, 'In-cloud chemistry opens pathway to the formation of oxalic acid in the marine atmosphere', *Atmos. Environ.*, **37**:2423–27.