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QUANTIFYING RESPIRABLE CRYSTALLINE SILICA IN THE AMBIENT AIR OF THE HUNTER VALLEY, NSW – SORTING THE SILICA FROM THE SILICON

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Abstract

Crystalline forms of silica are known to cause lung damage for which there is no effective treatment. Silicon is abundant in crustal material and silicates are the single largest mineral grouping, with silica (SiO_2) being the most abundant crustal compound. Media reports of high levels of silicon in particles in the air in the vicinity of Hunter Valley open-cut coal mines have caused community anxiety and concerns about potential health impacts on local populations.

An extensive sampling campaign using continuous air quality monitoring and targeted collection of particles has been carried out in an area close to mining operations. It was determined that silicon as silica was present in the ambient air, although the concentrations of crystalline silica measured suggest that it should not should cause health problems even for sensitive individuals within the general population. The results of the research should inform more rigorous discussions of air quality management plans for fine particles in the Hunter Valley and aid discussions of community concerns over the potential health impacts of coal mining.

Keywords: Silica, health impacts, coal mining, Hunter Valley

1. Introduction

Silica can occur both in crystalline and amorphous forms. There are several crystalline forms, quartz, cristobalite and tridymite, while the amorphous form occurs mainly as diatomaceous earth resulting from deposition of the exoskeletons of living organisms. It is generally only the crystalline forms which are fibrogenic (NEPC, 2001), while inhalation of amorphous silica has been found to cause only transient lung damage but not to induce pneumoconioses (respiratory diseases caused by inhalation of inorganic dusts). Fibrogenic crystalline silica inhalation can cause inflammation resulting in scarring and progressive reduction in lung capacity for which there is no effective treatment (Castranova and Vallyathan 2000; AIOH 2009).

The role of silica is undisputed as a cause of silicosis. The International Agency for Research on Cancer concluded in 1997 that crystalline silica is carcinogenic to humans but the evidence for this is disputed by some researchers (Pelucchi et al. 2006; Peretz et al. 2006). One recent Australian study, suggests that a concentration limit of 3 $\mu g/m^3$ of crystalline silica in ambient air is necessary in order to protect vulnerable communities (Bridge 2009).

As a result of its crustal abundance, silicon is ubiquitous in atmospheric particulate samples, particularly in those areas where crustal disturbance has and is occurring from both natural (e.g. wind and water erosion) and human intervention (e.g. mining and agriculture). An earlier SEM study of airborne particles in the close vicinity to an open cut coalmine, reported that the contribution of crystalline silica (as quartz) made up 2.5-16.2% of the mineral content collected (Jones et al. 2002).

2. Experimental Programme

2.1. Monitoring particulate matter concentrations

The current field study employed two OSIRIS samplers (Turnkey Instruments Ltd) to monitor particulate matter (PM) concentrations. The sampler utilises the principle of low angle forward scattering of light to determine particle concentration and used a heated inlet to

precondition the particle sample and minimise moisture derived artefacts. The instrument can be set to classify particles in the TSP, PM_{10}, $PM_{2.5}$ and PM_1 size fractions. A 25 mm dia. exit filter (Pall Teflo) captures the PM following measurement.

The samplers were placed at two near-mine rural sites (Glenville and Rix's Creek) in the open cut mining region of the NSW Hunter Valley. Each sampler was operated on a continuous basis during the period January – November 2010. To capture short-term particle exposure peaks, each instrument was operated at relatively high temporal resolution (15 mins) with these high resolution data averaged to provide longer term concentration data.

Samples were also collected using the Micro Orifice Uniform Deposit Impactor (MOUDI) which allowed comparison of the OSIRIS with a gravimetric PM measurement technique (Marple et al. 1991). The MOUDI allows size selected PM deposition samples to be collected on a range of substrates which can then be examined optically, chemically as well as gravimetrically.

Given the prevailing Hunter Valley meteorological conditions (predominant NW winds in winter and SE winds in summer), opportunistic samples were obtained using the MOUDI in both seasons for further chemical and microscopic examination.

2.2. Collection techniques

Samples for analysis were collected from both the MOUDI impaction substrates and the OSIRIS exit filters. Stretched Teflon filters (Pall Teflo®) were used both as MOUDI substrates and as OSIRIS exit filters, while specially prepared 30 mm dia. × 2 mm thick polycarbonate discs were used as MOUDI substrates to collect samples for SEM and QEMSEM analysis.

2.3. Measurement of silica and silicon

2.3.1. Ion Beam Analysis (IBA)

OSIRIS exit fiters [1] and MOUDI samples collected during the sampling period were analysed by the Australian Nuclear Science and Technology Organisation (ANSTO). Filter samples were analysed by ANSTO using a multi-element IBA technique. The IBA technique is well suited to elemental analysis of filters as it is non-destructive and can detect a broad range of elements at minimum detection limits as low as 1 ng/m³ of air sampled. The use of the two IBA techniques, particle induced X-ray and gamma ray emission (PIXE and PIGE) allowed the determination of the following commonly occurring elements; Na, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Br and Pb. (Cohen 1998; Cohen et al. 2004).

2.3.2. XRD analysis of α-quartz and crystobalite(SiO2)

Exit filters [1] from the OSIRIS measurements and MOUDI samples collected during the sampling period were subsequently analysed by the Workcover NSW laboratories for crystalline silica (both α-quartz and crystobalite). Both of these compounds of silicon have known deleterious effects on most mammals. The crystalline silica was measured by X-Ray diffractometry (NHMRC 1984).

2.3.3. SEM and QEMSCAN determination of silica and silicates

QEMSCAN® (Quantitative Evaluation of Minerals by SCANning electron microscopy) is an automated scanning electron microscopy and energy-dispersive x-ray spectroscopy (SEM-EDS) solution by FEI which allows quantification of mineral phases. Gottlieb et al.(2000) and Pirrie et al. (2004) give general descriptions of the system.

SEM and QEMSCAN were used provide an alternative method for the quantification of the proportion of quartz in the PM samples and to identify other silicon containing species present, as a possible clue to their source.

Polycarbonate substrates coated with sized PM deposited in the MOUDI were carbon coated, providing a conductive layer to prevent charging of the sample surface. Samples examined by QEMSCAN were placed into sample block holder (holding 16 substrates at a time), with measurements made using an accelerating e-beam voltage of 20 keV. The energy-dispersive X-ray (EDX) spectra were collected across regular grids at a 1 micron stepping interval, individually mapping the particle by particle chemistry. The background (defined by a backscatter electron (BSE) threshold <25 was not mapped. EDX spectra are based on 1,000 photon total counts collected at 5nA. Mineral identification and classification of phases in the PM was based on a Spectral Analysis Engine developed for clay identification (Haberlah et al. 2011).

[1] The OSIRIS exit filters contain particles which are above the respirable range (ie greater than 10µm) as well as the respirable particles. However, the analyses provide some guidance as to the quantity of silicon (as crystalline silica) as a proportion of the total silicon in the air sampled.

3. Measurements and Results

3.1. PM10 and PM2.5

Comparison of the OSIRIS data from the two sampling sites showed them to be well linked, this outcome was consistent with results from previous projects which monitored PM at these sites (Nelson et al. 2007; Nelson et al. 2008). The finer PM2.5 material can be seen as a more "regional" pollutant than PM10 and was much more closely correlated (Figure 1).

Although the OSIRIS data in Figure 1 appears to show compliance with the 24 hr NEPM guideline there is some evidence that the OSIRIS underestimates PM2.5 when compared to a gravimetric device (such as the MOUDI). Were this to be the case then some values would approach the 24 hr NEPM Guideline. Annual averaged data is unavailable, although based on the period sampled, it would appear likely that the NEPM PM2.5 annual advisory level of 8 µg/m³ would be exceeded.

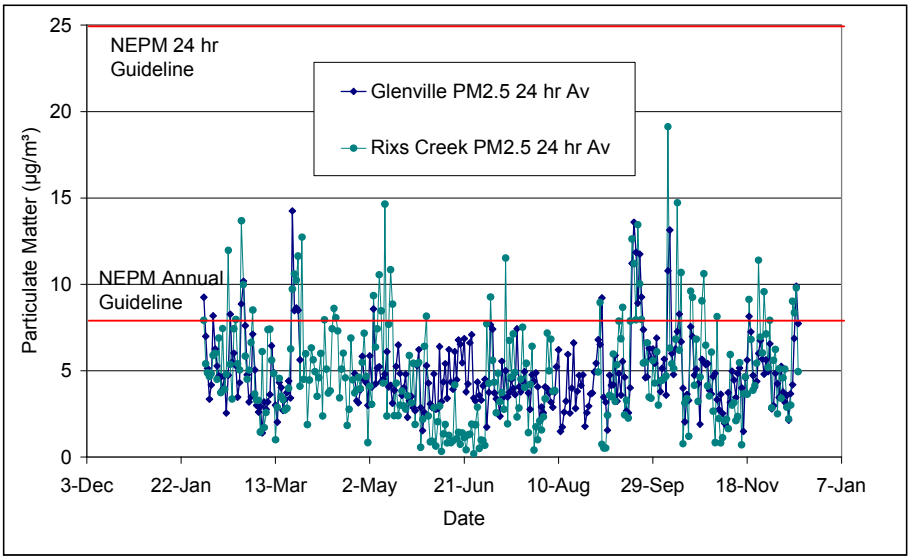


Figure 1. 24hr averaged OSIRIS PM2.5 data for the Glenville and Rixs Creek sampling sites from January – December 2010.

3.2. Total silicon (IBA)

Because the MOUDI sampler does not uniformly deposit the PM across the impactor surface, analysis using the ANSTO IBA technique has required some modification. These modifications are described in detail elsewhere in the proceedings of this conference. Results for silicon measured by IBA using an 8mm beam have been estimated using the methods described in that paper (Stelcer et al. 2011).

Table 1 shows the total silicon estimated by IBA for MOUDI Stages 1-8 and the inlet and exit stages for two sampling periods of five days during May 2010 (M8) and August/September 2010 (M14). The distribution of silicon across the sized PM (Figure 2) shows that the majority is found in the larger sized PM (dominated by wind blown dusts) with only ~8-15% of the silicon mass in the PM2.5 fraction.

3.3. α-Quartz (XRD)

Table 1 shows the α-Quartz estimated in the MOUDI filters by the use of XRD. The minimum detection limit of the method used was ~0.06 µg/m³

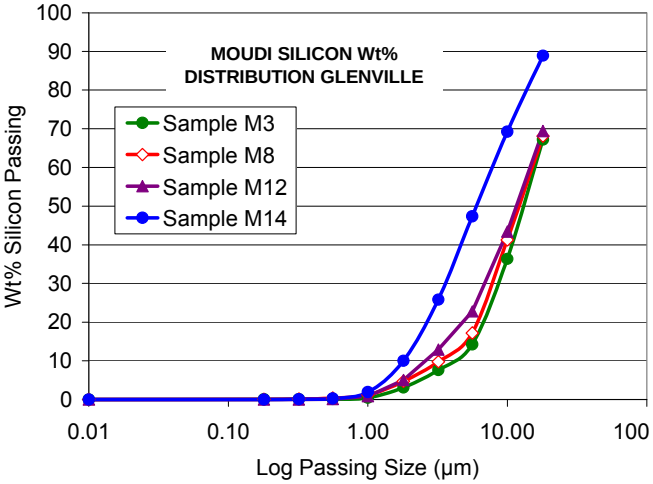


Figure 2. Wt % distribution of silicon in MOUDI samples

as a consequence α-Quartz was not detectable in the MOUDI stages 6-8 and the exit filter (E) i.e. below a particle size of about 1 µm. This is the result of the minor amount of silicon in the PM in these smaller sizes (Fig 2.), where PM from organic sources and secondary particles formed as a result of atmospheric chemical processes dominate

(Finlayson-Pitts and Pitts 2000). XRD failed to detect crystobalite in any of the samples.

Overall levels of respirable crystalline silica were estimated in the PM2.5 fraction (mid-way between MOUDI stages 3 and 4) as 0.61 µg/m³ (M8) and 0.53 µg/m³ (M14). In the PM10 fraction (below MOUDI stage 1) crystalline silica is estimated to be 1.9 µg/m³ (M8) and 1.1 µg/m³ (M14).

Table 1. Silicon and α-Quartz in MOUDI samples

MOUDI Sample	Passing Size (µm)	α-Quartz measured by XRD (µg/m³)	Total silicon measured by IBA (µg/m³)	% of total silicon as α-Quartz
M8-0	18	0.80	2.96	12.5
M8-1	10	0.75	2.49	14.1
M8-2	5.6	1.05	2.24	21.8
M8-3	3.2	0.57	0.69	38.6
M8-4	1.8	0.18	0.47	18.0
M8-5	1.0	0.14	0.33	19.5
M8-6	0.56	ND	0.08	NA
M8-7	0.32	ND	0.02	NA
M8-8	0.18	ND	0.01	NA
M8-E		ND	0.00	NA
M14-0	18	0.14	0.35	18.6
M14-1	10	0.16	0.61	12.0
M14-2	5.6	0.39	0.68	26.9
M14-3	3.2	0.43	0.67	30.1
M14-4	1.8	0.25	0.49	24.2
M14-5	1.0	0.06	0.25	10.9
M14-6	0.56	ND	0.05	NA
M14-7	0.32	ND	0.01	NA
M14-8	0.18	ND	0.00	NA
M14-E		ND	0.00	NA

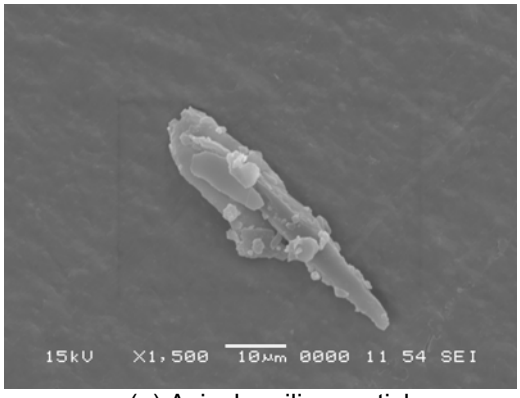
ND not detected NA not applicable

Both measurements would comply with existing health guidance. The current NSW guideline is a maximum concentration of silica in air of 100 µg/m³ for industrial exposures . Other guidance suggests that a value of 3 µg/m³ (α-Quartz) in the respirable component of ambient air would protect even sensitive individuals within the general population (Bridge 2009). EPA Victoria sets a limit for PM2.5 of 3 µg/m³ (α-Quartz) in the vicinity of mines and extractive industries.

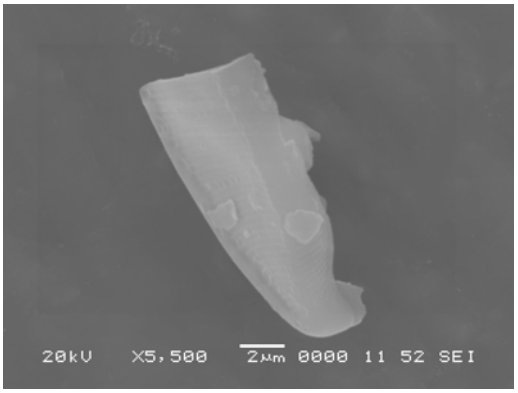
α-Quartz measured in the OSIRIS exit filters ranged from 0.8 – 3.6 µg/m³ of air sampled (although there were several samples below detection limits). These samples contain PM from above the respirable range and therefore provide further confidence that α-Quartz values in respirable PM are low and do not pose a risk to community health.

3.4. Silica and other silicates (SEM and QEMSCAN)

Examination of collected particles using scanning electron microscopy (SEM) shows that crystalline silica does form some of the mass collected [Figure 3(a) and (b)].



(a) Acicular silica particle



(b) Angular silica shard

Figure 3(a & b) SEM micrographs of silica particles collected from ambient air in the Hunter Valley, NSW showing some of the varying morphologies

Effective determination of the mineral composition of the PM by SEM/EDS is limited by the analysis volume of the EDS system to particles larger than ~2 µm, (MOUDI stages 4 and above). However, an examination of Figure 2 shows that this should encompass more than 90% of the silicon in the samples.

QEMSCAN analysis of the sized MOUDI samples confirms the diverse nature of the mineral species in the PM collected. Table 2 shows the range of silicon containing minerals determined in the MOUDI inlet substrate (-18+10 µm) for sample M5.

Of the silicon containing minerals, silica (SiO_2) is a relatively minor component in this size fraction with the larger PM material being dominated by clays, which made up more than 70% of the identified minerals.

Table 2. The range and vol% of silicon containing minerals identified in the inlet stage of MOUDI sample M5

Mineral	Description	Vol (%)
Smectite	clay minerals – alumino silicates	38.2
Illite	micaceous clay mineral –alumino silicates	25.2
Kaolinite	clay minerals – alumino silicates	8.4
Silica	silicon dioxide	8.3
Plagioclase	(Na, Ca) alumino silicates	7.7
Chlorite	(Mg,Fe,Ni, Mn) alumino silicates	1.2
K-feldspars	(K) alumino silicates	0.7
Muscovite	micaceous mineral – (K) alumino silicates	0.4
Biotite	K (Mg,Fe) alumino silicates	0.2
Glauconite	Fe (K) alumino silicates	0.2
Serpentine	Hydrous (Mg,Fe) phyllosilicates	0.1

Figure 4 shows the changes in mineralogical makeup of the PM in MOUDI sample M5 with changing particle size. Although the proportion of silica in the size fractions appears to remain relatively static (~10 Mass%) there are observable changes in some of the other silicon containing components.

QEMSCAN also allows the determination of the degree of liberation of silica in the samples and its association with other mineral species. An examination of the degree of liberation of the silica in the samples has shown that often 30-50% of the quartz is locked into composite particles with other minerals.

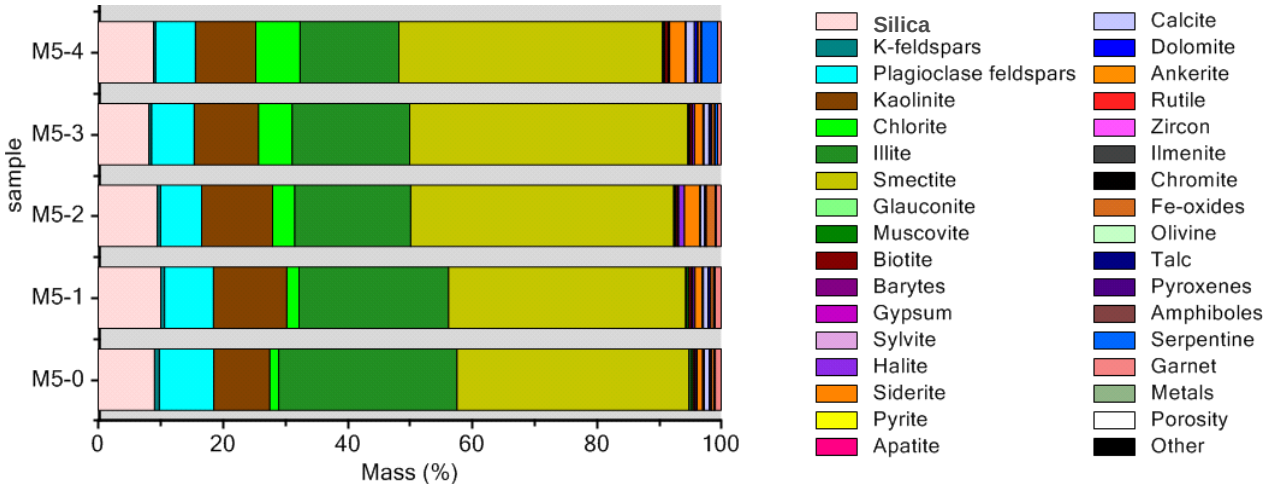


Figure 4 Stacked histogram of sample mineralogy determined by QEMSCAN for MOUDI sample M5 (Stages 0-4).

4. Conclusions

A PM sampling campaign targeted at measuring levels of silica in ambient air has been carried out in the vicinity of open cut coal mining operations in the Hunter Valley, NSW. Silica and silicon concentrations in PM samples collected using a MOUDI size selective sampler were determined by a variety of techniques including IBA, XRD and EDS. The deportment of the silicon and the mineral species in which it was contained was estimated using QEMSCAN. Measurements suggest that although silicon as quartz is present in the ambient air sampled, the levels are not such that they should cause health problems even for sensitive individuals within the general population

5. Acknowledgements

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