# Monitoring "Air Particulate Matter"

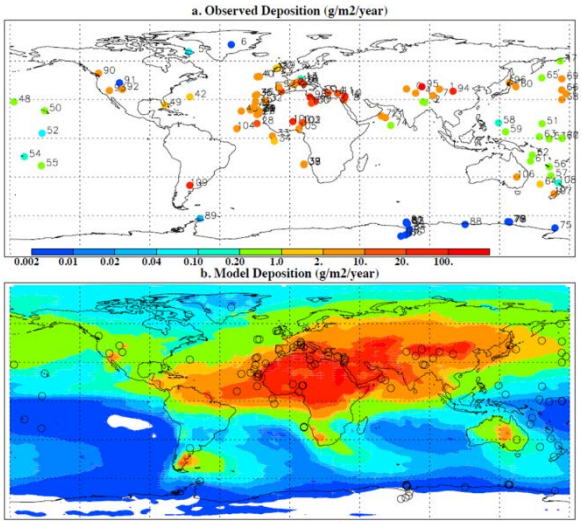


***Figure 1:*** **Observed and modelled global dust deposition.** The correlation coefficient between modelled and observed dust deposition is 0.86. The median of model to observation ratio is 1.15.

**Reproduced from Figure 12 of Zhang *et al*, *Biogeosciences* 2015**

Air pollution from aerosols impacts the earth system in several ways including the modification of the earth's radiative balance, and its influence on biogeochemical cycles. Friberg *et al* (*TellusB* 2014) [1] is an extensive IBA study of stratospheric aerosols directly relevant to the radiative balance. A basic study of the role of iron and black carbon in aerosol light absorption is by Derimian *et al* (*Atmospheric Chemistry & Physics* 2008 [2]), and on the biogeochemistry see the massive recent reviews of secondary organic aerosols by Hallquist *et al* (*Atmospheric Chemistry & Physics* 2009) [3] and atmospheric iron deposition by Mahowald *et al* (*Annual Review of Marine Science* 2009) [4]; all of these three papers summarise many data collected by IBA.

These effects profoundly affect our understanding of global warming and the correlated huge changes in the biosphere. Of course, air pollution also immediately and directly affects human health, and is now subject to regulations which are progressively becoming both stricter and more strictly enforced. Putaud *et al* (*Atmospheric Environment*, 2010) [5] summarises European data collected under the COST programme, significant parts using IBA.

***Figure 1*** shows a very large study (Zhang *et al, Biogeosciences* 2015 [6]) which models aerosol deposition at a global level, work based on large experimental datasets collected over many years at multiple sites by nine different groups using a large number of analytical methods, including IBA methods with accelerator facilities at Sydney (ANSTO: Cohen *et al, Atmospheric Pollution Research* 2011 [7]) and Florence (LABEC: Fomenti *et al, J. Geophysical Res.* 2008 [8]).

Every analytical technique has its limitations, and in almost all cases it is desirable to use one or more complementary technique. For aerosol analysis it is essential to measure "black carbon" (soot) separately as well as the total deposited mass on the filters. Volatiles are measured in various ways and

of course cannot be measured by IBA. Alternatives to IBA (as used for example by Carpenter *et al, Journal of Atmospheric Chemistry* 2010 [9]) for measuring the elemental composition include ion chromatography (IC), high performance liquid chromatography (HPLC), inductively-coupled-plasma mass spectrometry (ICP-MS) and total-reflection X-ray fluorescence (TXRF). But IBA remains a highly competitive technique with the following advantages:

1. IBA has high sensitivity (typically of order 10 mg/kg) to elements from H to Pb simultaneously.
2. IBA has a high absolute accuracy (with a standard combined systematic uncertainty near 5%).
3. IBA usually has over 80% mass closure, with the residue being largely volatiles (this is regarded as excellent for PMF methods). That is, IBA measures major (matrix), minor and trace elements, and also (incidentally) measures the filter itself. These give self-consistency measures for the data which validate the claims of high accuracy.
4. IBA requires no sample preparation.
5. IBA has a very high throughput, capable of multi-elemental analyses of hundreds of samples per day.
6. IBA has a sensitivity and spatial resolution enabling high time resolution measurements.
7. IBA is non-destructive.

Note that IC, HPLC, ICP-MS and TXRF are all destructive techniques, and none of them have the extended multi-elemental sensitivity of IBA. Of course, the sensitivity of each technique for particular elements can be much better than IBA, but where higher sensitivity is needed these techniques can generally be applied to the same samples measured by IBA.

The ANSTO group has been collecting comprehensive aerosol data using IBA from many Australian and Asian sites for well over twenty years and systematically does a source apportionment analysis using positive matrix factorisation (PMF) methods together with back trajectory estimates of aerosol origin. ***Figure 2*** shows data from an important paper (Cohen *et al, Atmospheric Pollution Research* 2011 [7]) summarising 11 years data collection at one site. Raw elemental concentrations for 20 elements in over a thousand samples can be represented by just seven "factors". This sort of analysis is very powerful, allowing a very complete understanding of aerosol composition and origin.

It is also possible to collect time resolved information from "streaker" samples using the spatial resolution of the focussed and scanned ion beam to evaluate areas on the streaker sample corresponding to specific collection times, as is done by the LABEC group (Nava *et al, Science of the Total Environment* 2015 [10]) as a part of a much wider study. Time resolved measurements are only feasible with IBA methods.

***Figure 3*** shows hourly-resolved data collected in Tuscany for one whole week in January 2006. Sophisticated PMF methods confirmed that the coarse potassium fraction correlates with crustal elements (airborne soil particles), but the fine fraction is from biomass burning: the correlated Na-Cl signals are sea-spray markers and the transition metals are traffic markers.

To use the PMF techniques essential for reliably determining the factor fingerprints needed to understand aerosol behaviour, large quantities of raw data are indispensible. The more elements in the

dataset, and the higher the accuracy and sensitivity of the measurements, the more information can be extracted from the analysis.

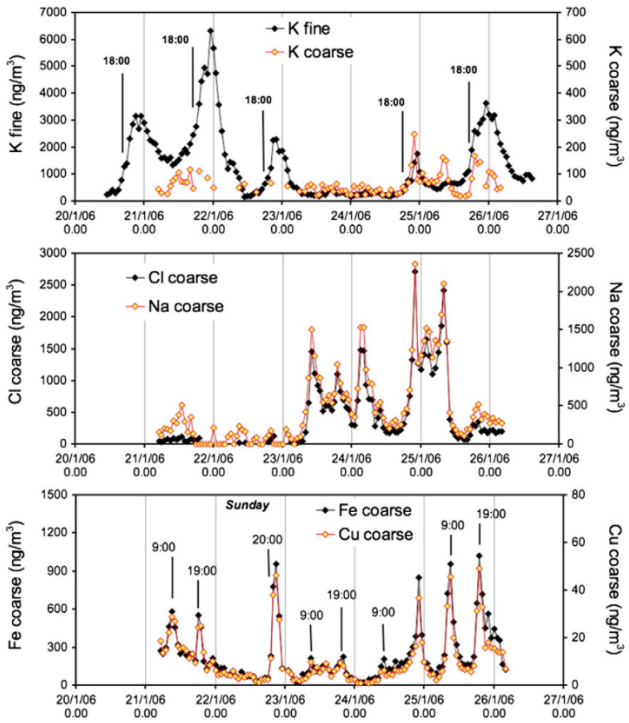


***Figure 3:* Short term variation of elements in aerosols from Florence correlated and uncorrelated with biomass burning**

***Left:*** Elemental composition (halogen, alkali and transition metals) for two fractions collected over one week with one hour time resolution at a site in Capannori (50 km west of Florence).

Complementary methods: total carbon (TC) was measured and organic and elemental carbon (OC and EC) estimated. The soluble component was measured with ion chromatography (IC) and inductively-coupled-plasma atomic emission spectroscopy (ICP-AES). In this study the only IBA technique used was PIXE.

**Reproduced from Figure 5 of Nava *et al*, *Science of the Total Environment* 2015.**

IBA sensitivity from H to Pb is given by the use of different techniques: elastic (usually non-Rutherford) backscattering (EBS or RBS) with a particle detector at a backscattering angle, particle-induced X-ray emission (PIXE) with an X-ray detector, particle-induced $\gamma$-ray emission (PIGE) with a gamma detector (usually high purity germanium, HPGe), and particle elastic scattering analysis (PESA) with a particle detector at a forward scattering (recoil) angle. These are described in some detail in Cohen *et al* (2004) [11] and Cohen (1993) [12] and should be considered as a form of Total-IBA [13].

For most of the periodic table (Z>10) the sensitivity is given by PIXE (a good review of PIXE analysis of aerosols is given by Maenhaut, 2015 [14]), but PIGE is indispensible for Li, F and valuable for Na and other light elements. EBS gives high sensitivity to C, N, O and is also valuable for characterising the filter (for data self-consistency purposes). PESA gives sensitivity to H but must be used in a vacuum to avoid artefacts due to adsorbed water. All of these techniques are multi-element.

The ANSTO (Sydney) group makes measurements in vacuum with all four detectors used simultaneously. The LABEC (Florence) group makes measurements in air using mainly PIXE and PIGE (see Chiari *et al, J. Aerosol Science* 2015 [15] for in-vacuum PESA). The particle technique EBS is complicated in air by the large energy loss corrections that are hard to calibrate; it has therefore not yet been used in air in large studies, but the feasibility of external beam EBS has been demonstrated for cultural heritage applications (for example Pascual-Izarra *et al*, 2007 [16]).

IBA is fast enough to compete with synchrontron X-ray fluorescence (sy-XRF): 30 sec measurement times have been demonstrated by Lucarelli *et al* (2014) [17]. We should note that Total-IBA (that is at

least PIXE + EBS analysed self-consistently) is an absolute (standard-less) technique where XRF is a relative one. We can also remark that faster data collection is possible in air since beam damage to the filters is suppressed by much better cooling.

IBA has a high absolute accuracy. Cohen *et al* (2002) [18] have demonstrated a long-term reproducibility (system uncertainty) of about 4% for both PIXE and PIGE, where these long term measurement PIGE data are for Li, Rb, F, K, Si, Fe in thick ceramic samples. In any particular dataset of course the precision in PIGE and for trace elements in PIXE will usually be dominated by counting statistics, which for this application are usually better than 15% in the worst cases. 1% absolute (traceable) accuracy for routine standard-less and model-free RBS has recently been demonstrated (Colaux *et al, Analysis* 2015 [19]), and EBS and PESA analyses are also capable of the same accuracy given the scattering (non-Rutherford) cross-sections, which for most important cases are known to 5% or better. However, Nguyen & Martinsson (2007) [20] only claim 10% accuracy for their EBS.

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