

Nanoparticle contribution to elemental concentration in atmospheric particulate matter

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Several epidemiological studies suggest that health diseases due to the exposure to atmospheric particulate matter (PM) are mainly associated with the inhalation of particles able to penetrate deeply into the respiratory tree. Among these, particular attention has been recently paid to particles smaller than 100 nm in diameter (nanoparticles, NPs). Because of their peculiar morphology, chemical composition, minute size and high surface area NPs are very reactive towards their environment and able to penetrate living cells. Moreover, they are able to adsorb and carry heavy metals and other carcinogenic compounds.

Due to their high surface area, atmospheric NPs easily aggregate to form large clusters; when in contact with biological systems, however, clusters may disaggregate again releasing free NPs able to translocate across the respiratory epithelium and enter the lymphatic and the circulatory system. For this reason, the quantitative relevance of aggregated NP contribution to PM is of great importance in air quality and health studies.

Instruments measuring atmospheric NP concentration select incoming particles on the basis of their physical characteristics (optical diameter, electric mobility or aerodynamic diameter). When using these techniques, aggregated NPs are fatally neglected, as clusters physically behave as a single, wider particle (generally between 0.1 and 1 μm). Environmental studies would thus benefit from the availability of a chemical method able to evaluate the contribution of insoluble NP contained in aggregates to atmospheric PM.

We have developed a method able to fractionate the total elemental concentration in atmospheric PM into three contributes: the water-soluble fraction, the insoluble non-nanometric fraction and the fraction due to insoluble NPs, both individual and contained into larger clusters. The application of the method to size-segregated real atmospheric PM samples is described.

The method consists in the following procedure. PM samples are dispersed in deionized water, exposed to ultrasounds and then filtered to separate the insoluble coarser particles from the suspended fraction, which contains elements both as suspended solid NPs and in water-soluble form. The insoluble fraction is subjected to microwave-assisted acid digestion and analysed by ICP-MS. The suspended fraction is divided into two aliquots: one is directly analysed by ICP-MS, the other one is injected into a chromatograph equipped with an anion

exchange cartridge and then analysed by ICP-MS. NP contribution to the total elemental concentration is evaluated as the difference between the results obtained before and after the elution from the cartridge.

The application of the method to size-segregated atmospheric samples collected in the urban atmosphere of Rome, Italy, has highlighted three possible behavior of the analyzed elements.

For some elements, which show a dimensional distribution almost completely in the coarse range (e.g.: Na, Li, Mg, Ba, Mn, Sr), the ICP results obtained before and after passing the chromatographic pre-column agreed well, indicating that the suspended fraction contained only soluble species of these elements. A second group (e.g.: Rb, Tl, K) was mainly confined in the fine fraction; again, the ICP results obtained before and after the elution were in quite good agreement. These elements were thus contained in fine particles as soluble species, not retained by the chromatographic pre-column. A third group of elements (e.g.: Sb, Cd, V, As, Sn, Pb) also exhibited a relevant fine contribution, but the values obtained after the elution were markedly lower than those obtained from the direct analysis. All these elements are likely contained in a NP fraction that is analyzed by ICP-MS, as well as the soluble fraction, but is retained by the chromatographic pre-column. The latter behaviour is shown by most of the elements typically emitted from combustion sources, which are considered as the main responsible for NP emission in the atmosphere.

Although the proposed method needs a wider field application, these results are of environmental and toxicological relevance because the health and environmental effects of the elements identified in the NP fraction (As, Cd, Sb, V, Pb) could be considerably different from the effects caused by the same elements in soluble forms or contained in coarser particles (Cho et al., 2012; Mukhtar and Limbeck, 2013) Furthermore, this fractionation scheme may allow an increase of elemental selectivity as tracers of PM sources responsible for emission of inorganic NPs, as waste incineration.

Cho, W.S., Duffin, R., Thielbeer, F., Bradley, M., Megson, I.L., MacNee, W., Poland, C.A., Tran, C.L., Donaldson, K. (2012) *Toxicol. Sci.* **126**, 469–477.

Mukhtar, A., Limbeck, A. (2013) *Anal. Chim. Acta*, in press, doi:10.1016/j.aca.2013.02.008.