Long term (1980- 2000) evolution of trace and crustal elements in Athens

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The aim of this work is to study the contribution of anthropogenic sources to atmospheric aerosols in Athens for a time period over two decades long. Contribution from a variety of sources is reflected in the concentration of certain trace and crustal metals.

Characteristic elements for an urban area such as Athens are Cd, V, Ni, Pb and Mn which can be considered a group of metals originating from anthropogenic sources and Fe, Cu and Cr, which originate from soil dust or mechanical abrasion processes.

The input of Saharan dust has important effects on the chemistry of the Mediterranean aerosols. These include: i) increases in atmospheric concentrations and surface fluxes of crustal trace metals over sea (e.g. Fe), ii) decreases in the Enrichment Factor (EF) values on non-crustal-contribution of certain trace metals (e.g. Cu, Zn and Pb) in the aerosols, and iii) changes in the solid state speciation of Cu, Zn and Pb. Ca, Fe, K, Mg are typical constituents of dust.

More information about the origin and the occurrence of the elements can be obtained by the calculation of the enrichment factor. The enrichment factor (EF) is defined as:

$$EF = (C_{ia}/Ca_a)/(C_{ic}/Ca_c)$$

Calcium is chosen as the reference element, where C_{ia} and Ca_a the concentrations of an element (i) and of Ca respectively, while C_{ic} and Ca_c are the equivalent concentrations in the earth's crust.

Atmospheric aerosol samples on TSP suspended particulate filters were collected at N.C.S.R. Demokritos, Agia Paraskevi, Attiki, (GAW-DEM) station. The site is partly influenced by the Urban area and partly by incoming air from the North East representative of suburban background atmospheric aerosol conditions (Eleftheriadis et al., 2014). Samples were collected, throughout the period 1980-2000 and specifically during the months January-February for winter period and June-July for summer period. TSP samples were collected at an operational flow rate of 2.35 m³h⁻¹. 24-72h samples on Cellulose filters (Whatman 41) and analysed by Electrothermal Atomic Absorption Spectroscopy for metals (Ca, Cr, Cu, Fe, Mg, Mn, Ni, V and Zn).

On the other hand Fe originates from natural sources.



<u>Figure 1</u>: Frequency of Enrichment factor with values higher than 10, for the metals Pb, V, Ni and Zn from samples collected at 1980-2000.



Figure 2: Frequency of Enrichment factor, lower than 10, for the metals Mn, Cu and Fe from samples collected at 1980-2000.

	Pb	V	Ni	Mn	Cu	Fe	Zn
Average value EF	81.2	1.12	1.3	0.49	9.01	0.89	64.5

<u>Table 1</u>: Average Value of Enrichment Factors for the metals Pb, V, Ni, Mn, Cu, Fe and Zn for the whole sampling period.

Enrichment Factors for Pb and Zn are higher than 10, which means that in their long term occurrence these metals have anthropogenic origin

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