



Chemical composition and mass closure of ambient PM₁₀ at urban sites

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ABSTRACT

The chemical composition of PM₁₀ was studied during summer and winter sampling campaigns conducted at two different urban sites in the city of Thessaloniki, Greece (urban-traffic, UT and urban-industrial, UI). PM₁₀ samples were chemically analysed for minerals (Si, Al, Ca, Mg, Fe, Ti, K), trace elements (Cd, Cr, Cu, Mn, Pb, V, Zn, Te, Co, Ni, Se, Sr, As, and Sb), water-soluble ions (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺) and carbonaceous compounds (OC, EC). Spatial variations of atmospheric concentrations showed significantly higher levels of minerals, some trace metals and TC at the UI site, while at the UT site significantly higher levels of elements like Cd, Ba, Sn, Sb and Te were observed. Crustal elements, excepting Ca at the UI site, did not exhibit significant seasonal variations at any site pointing to constant emissions throughout the year. In order to reconstruct the particle mass, the determined components were classified into six classes as follows: mineral matter (MIN), trace elements (TE), organic matter (OM), elemental carbon (EC), sea salt (SS) and secondary inorganic aerosol (SIA). Good correlations with slopes close to 1 were found between chemically determined and gravimetrically measured PM₁₀ masses for both sites. According to the chemical mass closure obtained, the major components of PM₁₀ at both sites were MIN (soil-derived compounds), followed by OM and SIA. The fraction unaccounted for by chemical analysis comprised on average 8% during winter and 15% during summer at the urban-industrial site, while at the urban-traffic site the percentages were 21.5% in winter and 4.8% in summer.

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1. Introduction

Ambient particulate matter is a mixture of organic and inorganic constituents formed by a large variety of mechanisms associated with both natural and anthropogenic sources. Airborne particles with an aerodynamic diameter of <10 μm (PM₁₀) have been found to be widely associated with health problems. They can also influence climate and degrade visibility by participating in a number of important atmospheric processes.

Concerns on the levels of PM have led to the establishment of daily and annual limit values for PM₁₀ starting from 2001 (European Directive EU/1999/30, 1999). Currently, research on the physico-chemical properties of airborne particulate matter is intense and toxicological studies attempt to identify which particle characteristics are responsible for which adverse biological responses (e.g. particle number, size, surface, chemical composition), and suggest

that the chemical composition of PM (which reflects differences in source contributions) plays an important role in these responses (Sandström et al., 2005). There is great scientific interest in the chemical composition of atmospheric particulate matter, which may vary largely depending on the sources of particles, the season of the year, the prevailing weather conditions and the chance for dispersion (Rööslé et al., 2001). Several components of air particles including heavy metals, trace elements, organic compounds, ions, etc., may have detrimental effects on human health. Thus, the question is raised whether the legislation of PM levels alone is enough to protect the population from the exposure to hazardous atmospheric pollutants, or whether the levels of specific PM components should also be legislated (Viana et al., 2007). The European Union has established ambient air quality standards for certain toxic elements, such as lead (EC, 1999), cadmium, arsenic, nickel, mercury and the carcinogenic benzo[a]pyrene (EC, 2004). Air quality guidelines have also been recommended by the World Health Organization for other elements (WHO, 2000).

The current study presents a comparative analysis of the aerosol chemical composition at two sites located in Thessaloniki.

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Identified species embrace minerals and trace metals, ionic components, and carbonaceous material. Seasonal and spatial variations are also investigated. Furthermore, we have applied a mass closure model to PM₁₀ samples to test whether the gravimetrically determined mass can be reconstructed by the chemically determined constituents.

2. Experimental

2.1. Sampling sites description

Thessaloniki (40°62'E, 22°95'N) is one of the most densely populated cities in Greece and Europe (16 000 inhabitants km⁻²). It is a coastal city surrounded by several stable residential communities. An extended industrial zone is located northwesterly including oil refining, petrochemical facilities, metal scrap incineration, non-ferrous metal smelting, iron and steel manufacturing, truck and auto painting, metal recovery facilities, electrolytic MnO₂ production, and lubricating oil recovery. In addition, cement production, lime production and quarry works producing materials for the metro construction operate north of the city. Since winds of the north sector are most prevalent throughout the year, there is great concern for potential transport of pollutants from industrial sources to residential areas.

The locations of the sampling sites are shown in Fig. 1. The urban-traffic site (UT) was selected in central Thessaloniki at a place surrounded by commercial shops and residential houses. The sampling system was situated on the roof (~3.0 m above ground level) of an air quality monitoring station situated in a small green traffic island adjacent to a busy street with a traffic density ~11 000 vehicles day⁻¹. The urban-industrial site (UI) was located in the western part of the city, at a residential area in short distance from a heavily trafficked road (>30 000 vehicles day⁻¹). The sampling equipment was placed about 3 m off a crossroad, 1.5 m above ground level.

The climate of Thessaloniki is temperate strongly influenced by the sea breeze. Mean monthly values of relative humidity during

the sampling campaigns ranged between 40% and 75%, while those of temperature between 6 °C and 30 °C. Prevailing wind directions during the same period were S/SW (56% and 63%), N/NE (21% and 15%) and N/NW (13% and 18%) at the UI and the UT sites, respectively. Winds of southern sector were weaker than northern winds (1.7 m s⁻¹ vs 2.2 m s⁻¹) and were associated with higher relative humidity and ambient temperature.

2.2. PM sampling and mass measurement

PM₁₀ sampling was carried out concurrently at the two sites during wintertime (December 2006–March 2007) and summertime (June–September 2007). Twenty-four hour samplings were carried out according to EN-12341 using two Low Volume PM₁₀ Samplers (LVS3.2, Ingenieur Derenda, Berlin) with flow rate 2.3 m³ h⁻¹ operating in parallel at each site. PM₁₀ was collected on high purity quartz filters (Tissuquartz™, Pall) pre-fired at 500 °C for 4 h and on Teflon filters (Zefluor, Pall 2 μm); different filter types were necessary to achieve the chemical characterization of the samples as for elements, ions, elemental (EC) and organic carbon (OC). The sampling campaigns resulted in the collection of 32 (winter) and 46 (summer) valid samples at the UT site, and 39 (winter) and 42 (summer) valid samples in the UI site. Samples considered “not valid” were mostly due to technical problems with the samplers, which resulted in short sampling times.

The PM₁₀ mass was gravimetrically determined according to EN-12341. Loaded and unloaded filters were conditioned for 48 h at 20 ± 1 °C and 50 ± 5% relative humidity before weighing in a KERN 870 microbalance (*d* = 0.01 mg). Filter samples were stored in a cool and dark place until analyses (for less than two weeks).

2.3. Analytical techniques

Organic carbon (OC) and elemental carbon (EC) concentrations were determined on quartz filter sections (1 cm²) by the Thermal Optical Transmission method in a Sunset Laboratory OC/EC Analyser (Flarountzou et al., 2008). Briefly, samples were heated in a completely oxygen-free helium atmosphere, in four increasing temperature steps to remove all organic carbon on the filter. The transition from the third temperature to the fourth (from 500 °C to 700 °C) also decomposes carbonate carbon (CC). Then the pure helium eluent is switched to a 2% oxygen/helium mixture in the sample oven and the temperature is stepped up to 850 °C for EC determination. Organic and elemental carbon are detected by a flame ionization detector (FID) after oxidation to carbon dioxide that is finally reduced to methane. The detection limit of analysis was 0.5 mg cm⁻² for both OC and EC and the uncertainty better than 10%.

Concentrations of Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, SO₄²⁻ were measured using ion chromatography (IC). A quarter of each quartz filter was extracted with 10 mL of ultra-pure water–isopropanol mixture (9:1 v/v) in an ultrasonic bath for 20 min. Ions were determined in a Shimadzu system consisted of an LC-10 AD pump, a CDD-6A conductometric detector (0.25 μL flow-cell) and a CTO-10A column oven. Cations were separated on an Alltech Universal Cation column preceded by a guard column of the same material using 3 mM methanesulfonic acid. Anions were separated on an Alltech Allsep Anion column preceded by a guard column of the same material using a phthalic acid and lithium hydroxide mixture of 4 mM. Column temperature was held constant at 35 °C. Mobile phases were degassed with helium stream before IC analyses. Calibration curves (0.01–10 ppm) were constructed for each ion. The method detection limits were 0.06, 0.03, 0.09, 0.02, and 0.03 μg mL⁻¹ for Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺, respectively and 0.03, 0.07, 0.26 μg mL⁻¹ for NO₃⁻, SO₄²⁻ and Cl⁻, respectively.

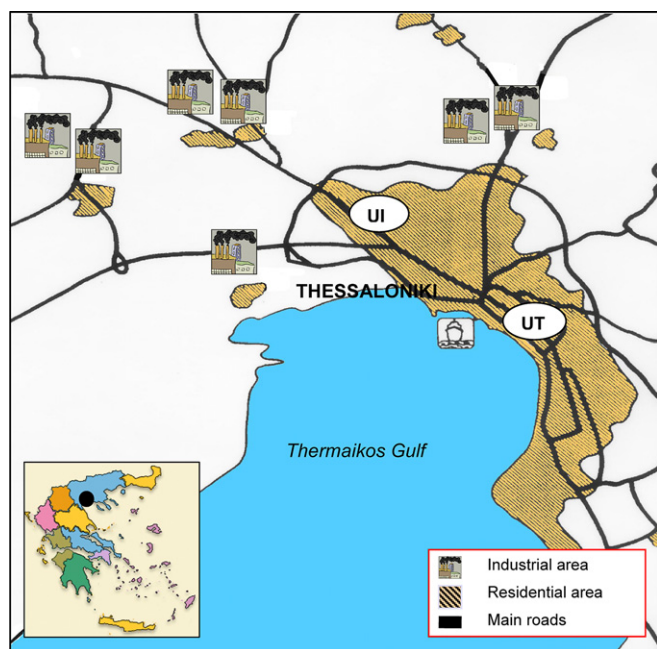


Fig. 1. Map of the sampling area and the location of the sampling sites (UI: urban-industrial site; UT: urban-traffic site).

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