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Elemental and organic carbon in aerosols over urbanized coastal region (southern Baltic Sea, Gdynia)

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ABSTRACT

Studies on PM 10, total particulate matter (TSP), elemental carbon (EC) and organic carbon (OC) concentrations were carried out in the Polish coastal zone of the Baltic Sea, in urbanized Gdynia. The interaction between the land, the air and the sea was clearly observed. The highest concentrations of PM 10, TSP and both carbon fractions were noted in the air masses moving from southern and western Poland and Europe. The EC was generally of primary origin and its contribution to TSP and PM 10 mass was on average 2.3% and 3.7% respectively. Under low wind speed conditions local sources (traffic and industry) influenced increases in elemental carbon and PM 10 concentrations in Gdynia. Elemental carbon demonstrated a pronounced weekly cycle, yielding minimum values at the weekend and maximum values on Thursdays. The role of harbors and ship yards in creating high EC concentrations was clearly observed. Concentration of organic carbon was ten times higher than that of elemental carbon, and the average OC contribution to PM 10 mass was very high (31.6%). An inverse situation was observed when air masses were transported from over the Atlantic Ocean, the North Sea and the Baltic Sea. These clean air masses were characterized by the lowest concentrations of all analysed compounds.

Obtained results for organic and elemental carbon fluxes showed that atmospheric aerosols can be treated, along with water run-off, as a carbon source for the coastal waters of the Baltic Sea. The enrichment of surface water was more effective in the case of organic carbon (0.27 ± 0.19 mmol m^{-2} d^{-1}). Elemental carbon fluxes were one order of magnitude smaller, on average 0.03 ± 0.04 mmol m^{-2} d^{-1}. We suggest that in some situations atmospheric carbon input can explain up to 18% of total carbon fluxes into the Baltic coastal waters.

1. Introduction

The properties of aerosols depend on their chemical composition. Carbonaceous particles (TC = EC + OC + IC) are one of the most important components of atmospheric aerosols. They account for 35–50% of PM 10 mass. Carbonaceous particles are composed of organic (OC), elemental (EC) and inorganic carbon (IC). Elemental carbon is emitted into the atmosphere, as a primary aerosol, mainly during incomplete combustion of fossil fuels (traffic, industry, domestic heating, and refuse burning) and biomass, and is therefore treated as a direct indicator of urban pollution and traffic intensity (Ryall et al., 2002). Organic carbon can be present in both primary and secondary aerosols. Primary OC is formed during combustion processes, including unleaded gasoline combustion, biomass burning and agricultural activity (Duan et al., 2004). Primary aerosols containing organic carbon can also be emitted into the atmosphere as plant spores, pollens or soil organic matter. Secondary OC originates from oxidation and gas-to-particle conversion of volatile organic compounds (VOC) (Fermi et al., 2006).

In the global carbon cycle both elemental and organic carbon present in aerosols play an important role (Krivácsy et al., 2001; Dachs et al., 2005). Organic fraction of atmospheric carbon, as is the case with sulphate aerosols, influences the scattering of solar radiation whereas elemental carbon is the major species responsible for light absorption in the atmosphere (Tang, 1996; Ebert et al., 2004). It is estimated that, if elemental carbon dominates the composition of aerosols on a global scale, the aerosol albedo (when the global average optical thickness is 0.125) will decrease from 0.95 to 0.75. The resultant influence of aerosols on the radiation will then change from cooling by 1.2 °C to warming by 0.5 °C. On the other hand, if sulphates and organic carbon dominate the composition of aerosols, the climate will cool and the impact of CO_2 (-1 W m^{-2}) on global climate warming may be balanced (Houghton, 1995).

Another very important reason to carry out research on the carbon fractions in aerosols is human health. Epidemiological studies increasingly point to a strong connection between incidence of

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tumorous diseases, for example, mortality related to such diseases and concentrations of atmospheric anthropogenic aerosols, which enter the human body with every breath, especially in large urbanized agglomerations (Bundke and Hänel, 2003).

Published information on the variability of organic and inorganic carbon in small aerosols is still scarce and such studies have never been performed in the Polish coastal zone before. However, several authors have already shown that the spatial and temporal variations of PM10 are governed mainly by synoptic, local meteorological conditions (Augustin et al., 2006; Gupta and Kumar, 2006), and local sources, especially in urban and industrial areas (Aldrin and Haff, 2005; Artinano et al., 2004). The main purpose of this paper is to point out the physical and chemical factors which determine the variability in concentration levels of both elemental and organic carbon, which are present in total suspended particles (TSP) and in aerosols with a diameter of less than 10 μm, in the Polish coastal zone of the Baltic Sea. Coastal sites display specific meteorological patterns, like onshore/offshore breeze phenomena, and play an important role in the dispersion, transformation, removal or accumulation of air pollutants (Gariazzo et al., 2007). Therefore, identifying the sources and transport mechanisms of organic and elemental carbon present in PM 10 in urbanized Gdynia, which is located in the coastal zone, can also be considered very important.

Deposition of aerosols containing the refractory form of carbon (EC) enriches surface seawater with carbon, which is unavailable to heterotrophic bacterioplankton but which changes the optical properties of the water. On the other hand, deposition of organic carbon in aerosols can supply the seawater with biodegraded dissolved substrates, DOC precursors. Results obtained during the final decades of the 20th century indicated that about half of the OC is water soluble (Cadle and Groblicki, 1982; Mueller et al., 1982; Sempere and Kawamura, 1994; Zappoli et al., 1999). There are three main mechanisms of OC exchange between the ocean and the atmosphere; i) diffusive exchanges by volatilization (sea to air) and absorption (air to sea) of gas phase OC, ii) dry deposition of atmospheric aerosol OC, and iii) by wet deposition of aerosol and gaseous OC. The few existing reports assessing these mechanisms are limited to estimations of fluxes associated with wet and dry aerosol OC deposition (Willey et al., 2000; Durrieu de Madron et al., 2000; Kieber et al., 2002). In this paper the first results of studies into organic and elemental carbon fluxes in Gdynia, located in the Polish coastal zone of the Baltic Sea, will be presented.

2. Materials and methods

2.1. Sampling

Measurements of aerosols were performed in Gdynia on the roof of the Institute of Oceanography building ($\varphi = 54°31'$ N, $\lambda = 18°48'$ E), where a coastal atmospheric chemistry station and a meteorological station have existed together for several years (Fig. 1). The height of the building (20 m a.s.l.) enables measurements to be taken from above the levels of neighboring tree canopies and buildings. The Institute is located in an urbanized area of Gdynia which is just a few hundred meters from the sea coast (Gulf of Gdansk). Gdynia is a city with a population of around 250,000 people, located close to agricultural and industrial centres (e.g. shipyards, food-processing and chemical plants, port facilities — Fig. 1), and two other large cities – Gdańsk and Sopot – are in close proximity. Altogether, the population of the so-called "Tri-city" agglomeration is nearly 1 million.

The measurements of PM 10, total particulate matter (TSP), organic, elemental and total carbon were performed between 3 September and 1 October 2007 in 24-hour cycles from Monday to Friday. Samples were also taken at weekends (Friday afternoon–Monday morning). All PM TOT samples were collected by means of a system consisting of a suction pump, gas flow meter and filter holder. Air flow through the system was maintained at 2.5 $m^3 h^{-1}$ by the critical orifice. PM 10 samples were collected by means of a Low Volume Sampler (LVS-3) with PM 10 inlet produced by ATMOSERVICE (Poland) and INGENIEURBÜRO NORBERT DERENDA (Germany). The inlet corresponds with the European standard CEN EN 12341, as well

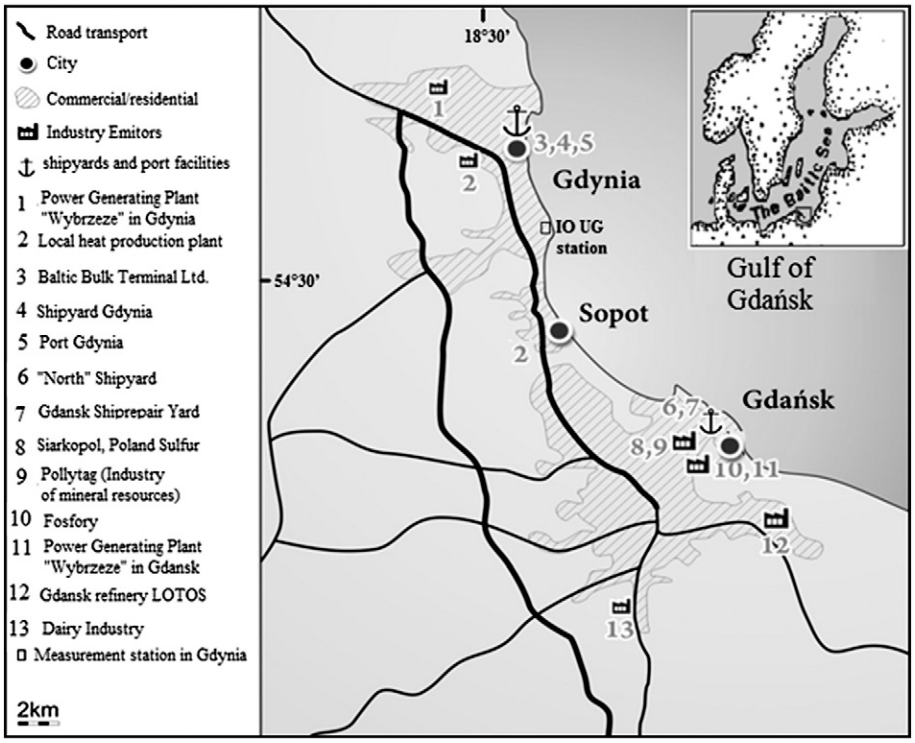

Fig. 1. Map of Tri-city with Gdynia station and major source location.