

Study of water-soluble atmospheric humic matter in urban and marine environments

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Abstract

Recently, atmospheric humic matter or humic-like substances (HULIS) have been found in the water-soluble fraction of atmospheric aerosol sampled at different locations. Most of these locations were continental, non-urban sites. Therefore, in this work HULIS was studied in urban and marine environments. The atmospheric concentration varied over a wide range from 0.40 to 5.44 $\mu\text{g m}^{-3}$, from the clean marine air (Mace Head, Ireland) to the heavily polluted winter urban atmosphere (Christchurch, New Zealand). In terms of carbon, ratio of HULIS was 19–51% of water-soluble organic carbon, and 10–22% of total carbon. Different spectroscopic techniques were applied for the physico-chemical characterisation of HULIS including relative aromaticity and molecular weight. Specific absorbance was observed to be much less variable than specific fluorescence, and consequently UV-VIS spectroscopy at $\lambda > 330$ nm was recommended for rapid, semi-quantitative determination of HULIS in the water extracts of atmospheric aerosol. Application of a dual filter sampling system at one of the sampling sites has revealed a significant positive sampling artefact which calls for further systematic studies on this subject, and also supports the idea of a secondary organic aerosol formation mechanism of HULIS.

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1. Introduction

During the last decade the approach to characterise the organic composition of atmospheric aerosol has considerably evolved. Classical methodology using solvent extraction and GC-MS analysis was only

capable of identifying a minor fraction (5–15%) of the organic compounds (e.g. Rogge et al., 1993). However, recent studies involving aqueous extraction and other analytical techniques (e.g. HPLC) have revealed that a significant portion (30–80%) of the organic carbon is water-soluble (Zappoli et al., 1999; Decesari et al., 2001; Krivácsy et al., 2001a; Temesi et al., 2003), and furthermore, polymer-type substances of higher molecular weight, both water-soluble and solvent extractable,

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are present. For example, proteins (Zhang et al., 2002), cellulose (Puxbaum and Tenze-Kunit, 2003), long-chain wax esters (Elias et al., 1999) have been found, but the most “mysterious” organic aerosol components discovered were probably compounds of (poly)acidic nature, chromophoric and fluorescence character and a high (~39 m/m%) oxygen content. The separation and identification of individual species have failed (Krivácsy et al., 2000), and the group of these compounds resembling natural humic matter in their physico-chemical behaviour has been called “humic-like substances” (HULIS). A brief history of the studies of HULIS in atmospheric aerosol can be seen in Table 1.

In 1986 Mukai and Ambe already mentioned a “humic acid-like brown substance”. But the discovery of atmospheric HULIS can be attributed to studies in the late 1990s (Havers et al., 1998; Zappoli et al., 1999). It was a turning point when HULIS were identified in large quantities in the water-soluble fraction of atmospheric aerosol. Since then research has been focused almost exclusively on this fraction, although a portion of HULIS is known to be water insoluble and extractable only with alkaline solution (Kiss et al., 2002). First, HULIS were thought to be macromolecules (Zappoli et al., 1999). However, comprehensive work on the

estimation of their molecular size has later shown that their molecular weights are most likely in the range 200–500 Da (Kiss et al., 2003). So, atmospheric HULIS are not macromolecules in general which explains their water solubility, and also why the first studies (Mukai and Ambe, 1986; Havers et al., 1998) following the protocol of soil humic acid quantification concluded that the atmospheric aerosol had a relatively low HULIS content.

The water solubility of HULIS has raised the question as to whether these organic molecules may influence cloud condensation. Facchini et al. (1999) pointed out that up to 50% of the polyacids were transferred from the aerosol to the liquid phase during fog events. More recently it has been shown that the high surface activity of HULIS might have a significant effect on the critical droplet size and supersaturation through the Kelvin term in the Köhler equation (Facchini et al., 2000; Mircea et al., 2002; Kiss et al., 2005). These findings indicate that HULIS may play a global role in the atmosphere by influencing indirect aerosol climate forcing.

Another exciting question is addressed to the origin of HULIS. Since during the first studies HULIS were observed in total suspended matter, soil dispersion could

Table 1
Summary of the study of HULIS in atmospheric aerosol

Site and date	Environment	Type of sample	Analytical method	Contribution to carbon content ^a	Reference
Tsukuba, Japan September 1983–September 1984	rural	total aerosol	solvent and alkaline extraction; isolation by acid precipitation; carbon measurement	0.6–3% of TC	Mukai and Ambe (1986)
Sauerland, Germany Dortmund, Germany spring and summer 1995–1996	rural urban (industrial)	total aerosol (dust)	alkaline extraction; isolation on anion exchange column; carbon measurement	1.8–1.9% of TC	Havers et al. (1998)
Po Valley, Italy	rural (polluted)	PM1.5	water extraction; size exclusion chromatography with UV-VIS detection	21–55% of WSOC	Zappoli et al. (1999)
K-pusztá, Hungary June–September 1996	rural (background)	PM1.5	water extraction; size exclusion chromatography with UV-VIS detect	40–67% of WSOC	Facchini et al. (1999)
Po Valley, Italy November 1996–March 1997	rural (polluted)	PM1.5 (interstitial)	water extraction; isolation by solid-phase extraction; carbon measurement	54% of WSOC	Krivácsy et al. (2001b)
Jungfrauoch, Switzerland summer 1998	high-alpine	PM2.5	water extraction; isolation by ion exchange chromatography; carbon measurement	40% of WSOC	Decesari et al. (2001)
Po Valley, Italy January 1998–May 1999	rural (polluted)	PM1.5	water extraction; isolation by ion exchange chromatography; carbon measurement	26% of WSOC	Mayol-Bracero et al. (2002)
Amazon region, Brazil October 1999	rural (burning season)	PM2.5	water extraction; isolation by ion exchange chromatography; carbon measurement	38–72% of WSOC	Kiss et al. (2002)
K-pusztá, Hungary January–September 2000	rural (background)	PM1.5	water and alkaline extraction; isolation by solid-phase extraction; carbon measurement	22% of WSOC and 27% of WSOC	Cavalli et al. (2004)
Mace Head, Ireland April–June and late September–October 2002	marine	PM1.5 and >PM1.5	water extraction; isolation by ion exchange chromatography; carbon measurement		

TC — total carbon, WSOC — water-soluble organic carbon.

^a Single figure means the average value.

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