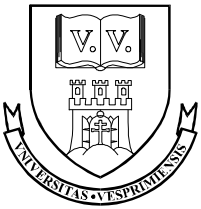
INVESTIGATION ON THE WATER SOLUBLE ORGANIC CONTENT OF ATMOSPHERIC AEROSOL BY LIQUID CHROMATOGRAPHIC METHODS

PHD THESES



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2005

INTRODUCTION, AIM OF STUDY

Atmospheric aerosol which is usually hidden from the eyes of most people is a very important constituent of Earth's atmosphere. If there was no aerosol in the atmosphere only the curvature of the Earth's surface would limit the visibility, most likely there would be no clouds and no precipitation either. Atmospheric aerosol influences our weather and climate through various effects. Direct effect of the aerosol on the radiative transfer of the atmosphere implies scattering and absorption of incoming solar radiation by aerosol particles. On the other hand aerosol particles may become cloud condensation nuclei on which the cloud droplets are formed. The indirect effect of atmospheric aerosol on the radiative transfer is derived from the considerable scattering of clouds. Concerning the interaction with solar radiation the limitation of visibility by aerosol should also be mentioned. Through its role played in cloud condensation processes aerosol influences precipitation formation and the hydrological cycle, furthermore it has a role in biogeochemical cycles via the deposition of various materials included in aerosol particles.

It was shown that aerosol is of great importance in the regulation of atmospheric processes. To explain its exact role in atmospheric processes the knowledge of its physical and chemical properties is essential. The chemical constituents of the aerosol have been investigated for several decades. In the first time the research was focused on the inorganic components. This portion is composed largely of a few inorganic ions which can relatively easily be determined, thus our knowledge on the inorganic constituents is quite precise. The situation is different concerning organic constituents. Our information on this portion is rather incomplete, while this fraction may represent up to 50 % of the total aerosol mass. This fraction is constituted by a complex mixture of a vast number of different compounds, the analysis of which is a great challenge especially when the limited sample amount is considered. The determination of all the individual compounds in this fraction cannot be accomplished at the present time. For methodological reasons

the organic solvent soluble apolar and semipolar organic constituents were analysed by GC-MS at first. This way thousands of individual compounds were identified and determined quantitatively, however these compounds added up only 10-30% of the total organic carbon altogether. Later it was found that a considerable amount of organic matter in atmospheric fine aerosol is water soluble and this fraction may influence the hygroscopic properties of aerosol particles and play a role in cloud condensation processes. Then it was shown that a part of the water soluble organic compounds resembles humic acids in numerous aspects. However the presence of humic substances having molecular weight of several thousand in atmospheric fine aerosol is difficult to explain. From mechanical attrition and disintegration processes of Earth's surface humic material can only get directly into coarse aerosol which is less important in the aspect of atmospheric processes than the fine aerosol constituted by particles smaller than 2μm in diameter. In order to find the source of humic like substances in atmospheric aerosol it is important to get information on their average molecular weight and molecular weight distribution.

The primary objective of this work was the estimation of average molecular weight and molecular weight distribution of water soluble organic compounds in atmospheric fine aerosol. During the study of organic matter it became obvious that the presence of inorganic ions in the aqueous extracts of aerosol samples interferes with the analytical techniques applied. Thus the second aim was the isolation of water soluble organic matter in dry form separated from inorganic constituents. The isolation allowed the application of physical and chemical methods of examination (e.g. UV and IR spectroscopy, elemental analysis, mass spectrometry, analysis of hygroscopicity etc.) which were not possible or not efficient before. It was also a goal to characterise the isolated organic fraction and in general the water soluble organic content of atmospheric fine aerosol by liquid chromatographic and spectroscopic techniques without the individual determination of its components.

NEW SCIENTIFIC ACHIEVEMENTS

1.: On he basis of the similarities between the gel chromatograms of samples from different fog episodes it was found that the fog and the aqueous extract of simultaneously collected interstitial aerosol contained similar compounds. This finding indicates that the UV-VIS absorbing and fluorescing humic like substances having similar chromatographic and spectroscopic properties as humic acids are distributed between fog and interstitial aerosol. Scavenging ratio calculated from chromatograms recorded with UV and fluorescence detection was approximately 0.5 which shows good agreement with the scavenging ratio of organic carbon and major inorganic ions. The similarity of scavenging ratios might be an evidence for the important role that organic constituents may play in atmospheric processes.

2.: A solid phase extraction (SPE) method was developed by which on an average 58 % of the water soluble organic carbon from aerosol samples collected at K-Puszta (rural background site, Hungary) could be isolated. The isolated fraction contained less than 0.5 % of the inorganic ions originally present in the aqueous extract. The organic matter isolated by the novel SPE method can now be examined by such chemical and physical methods as mass spectrometry, IR spectroscopy, elemental analysis, surface tension and hygroscopicity measurements which could not be applied efficiently before.

3.: By the SPE method the water soluble organic fraction of atmospheric aerosol was divided into two groups having greatly different properties. The isolated fraction contained compounds bearing polyconjugated structures, mostly acidic in character, having many oxygenated groups, less hydrophilic at pH = 2, absorbing UV-VIS radiation and fluorescing. The other fraction which passed through the SPE column without retention similarly to inorganic ions was consisted of compounds not fluorescing, weakly absorbing UV-VIS radiation,

bearing much less polyconjugated structures, very hydrophilic at pH = 2 and having many polar functional groups.

4.: The UV, fluorescence and mass spectra of organic matter isolated from aerosol samples collected in 1999-2000 at K-puszta and in the summer of 1998 at Jungfraujoch were very similar and they resembled the spectra of reference fulvic acid. This suggested that the isolated fraction contained the so called humic like substances (HULIS). The share of the isolated humic like fraction in water soluble organic carbon content of different aerosol samples varied between 38 and 72 % which indicated the relative change of the source strength of HULIS. Seasonal trend in the variation of the share of this fraction could not be revealed. Since this fraction could be isolated from samples collected in greatly different sampling sites it seems to be very likely that the HULIS are essential constituents of continental aerosol spread over large geographical areas.

5.: An analytical method involving reversed phase liquid chromatography coupled to atmospheric pressure electrospray ionization mass spectrometry was developed. The method was applied to estimate the average molecular weight of isolated organic matter. By the statistical evaluation of LC-MS spectra the average molecular weight of the isolated fraction was found to be between 200 and 300. These values have a good agreement with the results between 215 and 345 Da obtained by vapour pressure osmometry. The results of mass spectrometry were also supported by ultrafiltration, which revealed that at least 95 % of the water-soluble organic carbon passes through a filter having 500 Da cut of size. The latter result indicates that the share of macromolecular compounds in the water-soluble fraction of atmospheric fine aerosol is negligible.

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