Geophysical Research Abstracts
Vol. 12, EGU2010-15342, 2010
EGU General Assembly 2010

Water Soluble Organic Compounds over the Eastern Mediterranean: Study of their occurrence and sources

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Fine marine aerosols influence the climate system by acting as cloud condensation nuclei (CCN) in the atmosphere. The organic chemical composition and origin of the marine fine particulate matter are still largely unknown, because of the insufficient reports on in situ studies, the large variability in the emission from the sea, from the complex transfer of gases and particles at the air-sea interface, and the transport of aerosol particles from very distant sources. As important processes of formation of marine organic aerosol production we consider: transport of terrestrial particles, secondary organic aerosol (SOA) formation from the oxidation of biogenic dimethyl-sulfide (DMS), and biogenic particle emissions through sea spray. Specific compounds related to the above-mentioned processes have been proposed as molecular markers: e.g.
n-alkanoic acids and n-alkanes (terrestrial particles), levoglucosan (biomass burning aerosol), aminoacids (biological terrestrial or marine particles), methanesulphonate (MSA) (DMS oxidation), C8 and C9 dicarboxylic acids and oxo-carboxylic acids (marine SOA) and other short-chain dicarboxylic acids (marine or terrestrial SOA), and humic-like compounds (emission of marine organic carbon).
In our study, we made an effort to characterize the water-soluble organic fraction of marine aerosols collected at a background sampling site of Eastern Mediterranean (Finokalia, N35o20', E25o40', Island of Crete, Greece). The sampling period was 2007-2008. In order to identify and quantify the water-soluble organic compounds of marine aerosols determined in the present study we have used gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS) and nuclear magnetic resonance spectroscopy (NMR) and ion chromatography (IC). The origin of air masses arriving in the study area was studied by using backward trajectories calculation (NOAA HYSPLIT Model). In addition, we have used the "MODIS fire products" for fire detects. The sampling period was 2007-2008. Measurements of collective parameters such as organic/elemental carbon (OC/EC), dissolved organic carbon (DOC), and aerosol surface active substances as methylene blue active substances (MBAS) were also performed.
The concentration ranges for total suspended particles (TSP) was 12.3-61.1 microg m-3, for OC and EC 0.6-2.2 microg m-3 and 0.1-0.4 microg m-3 respectively, for DOC 0.7-1.8 microg m-3, and for MBAS 7.4-15.4 ng m-3. The average ratio OC/EC was 6.9 (+/- 3.5) and the proportion of DCO in relation to OC was 83 (+/-13) %, indicating a high degree of oxidation in the water-soluble organic matter. OC and DOC were statistically strongly correlated with the intensity of fire events in southern Europe.
The analysis of the water soluble organic extract by GC/MS, NMR and revealed the presence of 130 individual organic compounds which made the 17% of DOC. The most significant categories were:
I) Twenty (20) amino acids were determined as free (FAA) and combined (CAA) amino acids with an average concentration of 16 and 66 ng m-3 respectively. The average concentration of total amino acids (TAA) was 82 ng m-3. Glycine, glutamine, glutamic acid, aspartic acid and alanine made the 87% of the FAA fraction and glycine, alanine, glutamic acid, aspartic acid, valine and leucine the 87% of CAA. Statistically significant correlations were found between FAA and CAA, and MBAS and the intensity of fire events.
II) Twenty six (26) n-alkanoic acids (C2-C14) were detected with an average concentration of 145 ng m-3. Acetic acid, tridecanoic and heneicosanoic acids demonstrated the highest correlation with fire events.
III) Twenty two (22) saturated, unsaturated and branched dicarboxylic acids were analysed with an average concentration of 526 ng m-3. The highest statistical correlation with fire events was determined for the concentration of dicarboxylic acids with Cn larger than 6.
IV) Thirty one (31) hydroxy-, oxo- and keto- carboxylic and dicarboxylic acids were also determined. Their

average concentration was 126 ng m-3. The most significant statistical correlation with fire events were determined for the concentration of glycolic acid and keto-octanoic acid.
V) Various aromatic aromatic acids and polycarboxylic acids, such as 4-hydroxy-benzoic acid, syringic acid and trans-7-carbomethoxy-2-octendioic acid have shown the highest concentration correlation with fire events.
VI) Pinic and pinonic acids were present in relatively low concentrations (ca. 3 ng m-3). It is interesting that organosulfates of these acids were determined in the Eastern Mediterranean marine aerosol by using LC/MS.
Our results show that fire events (biomass burning) in southern Europe is a major source of water-soluble oxygenated organic compounds in the marine atmosphere. The concurrent use of mass spectrometry and NMR techniques allowed a better determination of the organic content of marine aerosols.