

Properties and processing of organic aerosol in the Po valley

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The chemical and microphysical properties of submicron organic aerosol (OA) strongly depend on sources and atmospheric processing.

OA properties were investigated in the framework of ARPA-ER Supersite project and Pegasos project. Observations were performed at an urban site (Bologna) and a rural location (San Pietro Capofiume) in fall 2011, summer 2012, fall 2013, and winter 2013. The suite of deployed measurement techniques included High Resolution Time of Flight Aerosol Mass Spectrometry (HR-TOF-AMS), Hydrogen Nuclear Magnetic Resonance (H-NMR), Fourier Transform Infrared Spectrometry (FTIR), together with thermo and thermo-optical analysis.

At both sites, OA represented about 50% of submicron particle mass during the colder seasons (winter and fall), and about 60% in summer. The oxygen to carbon ratio (O:C), an index of the oxidation level of OA, showed a clear seasonality with higher values in summer at the rural site. Different organic aerosol processing mechanisms characterized different areas and seasons. Photochemical processing was more relevant during summer. Fog processing was significant during fall experiments in the rural site, where frequent and prolonged fog events occurred. Van Krevelen diagram (H:C vs O:C) suggested that different processing mechanisms took place through different chemical oxidation pathways. We also present results from positive matrix factorization (PMF) analysis performed on the datasets collected at both sites.

Ultrafast Pump-Probe Studies of Geochemical Reactions

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Time-resolved spectroscopic methods provide new opportunities for understanding reaction mechanisms in all areas of the chemical sciences. In essence, ultrafast spectroscopy using the pump-probe approach can measure the rates of elementary reaction steps that occur on subnanosecond timescales, and provide chemical characterization of reaction intermediates with as much information content as conventional methods. Time-resolved versions of UV-vis, infrared, Raman, X-ray absorption and electron paramagnetic spectroscopy are now available. This presentation will give an introduction to ultrafast pump-probe studies of geochemical reactions, particularly discussing the opportunities and challenges of time-resolved X-ray absorption spectroscopy. TR-XAS is a major focus for all current and planned X-ray sources, and currently undergoing to a rapid growth in facility availability and data quality.

The pump-probe method achieves very high time resolution only when a reaction of interest can be initiated by a fast trigger pulse (the "pump"), typically a laser pulse. Thus, photochemical reactions, such as the photolysis of ferrioxalate or mineral photoreductive dissolution, are naturally suited for ultrafast studies. In addition, the photoreduction or photooxidation of organic and inorganic adsorbates at semiconductor mineral surfaces are also now being studied by ultrafast spectroscopic techniques. However, most geochemical reactions are not naturally light driven, and a major challenge is the development of strategies for reaction initiation. Photoactive dye molecules can be used to efficiently transfer electrons to iron and manganese oxide minerals, and may also permit the study of metal redox reactions in homogeneous solution.

Interpretation of spectroscopic signatures from reaction intermediates can be difficult because their nature precludes the preparation of stable reference species. Thus, simulation can play an important role in the interpretation of TR-XAS. For example, model calculations of the XAS of iron(II) sites in iron(III) oxides revealed that both valence state change and lengthening of the iron-oxygen bond length contributed to the spectral changes observed at the near-edge, confirming the polaronic nature of this reactive site.