Simulation of physical and chemical processes of polluted air masses during the Aegean-Game airborne campaign using WRF-Chem model

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The chemical and dynamic processes as well as the atmospheric composition, in the Planetary Boundary Layer (PBL) over the Aegean Sea, are investigated during an 'Etesian' event (29/8-9/9/2011) based on modeling results and a combination of airborne and ground observations. During this period atmospheric parameters, concentrations of gaseous species and size-resolved aerosol chemical composition have been measured using instrumentation flown on the UK's BAe-146-301 Atmospheric Research Aircraft operated through FAAM [1,2]. The simulations were performed by the on-line meteorological and chemical transport WRF-Chem model. Anthropogenic and on-line calculated natural (biogenic, sea-salt) emissions have been considered. Fire emissions generated by the FMI Fire Assimilation System [3] have been also included. The horizontal and vertical distribution of gaseous and aerosol species is interpreted in relation to the evolution of the PBL, and is shown that the model captures the geographical and temporal variations observed.

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Polyoxometalates and Their Effect on Tungsten Speciation and Transport

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Tungsten (W) is a toxic element with complex aqueous speciation. Tungstate, W(VI), is the dominant oxidation state of tungsten in soils, forms a variety of insoluble tungstate minerals, and often adsorbs strongly to iron oxides. This W(VI) often is significantly more readily transported than expected based on the available thermodynamic data. We have examined the role of metastable and heteropolyatomic polytungstates in enhancing the solubility of tungsten in natural systems. We have measured W concentrations following reaction with model soil minerals, and natural soils, over a variety of solution compositions and reaction periods in which a variety of polytungstate species may form in solution. In particular, we examined the effect of initial W(VI) concentration and speciation, pH, and the presence of silicate and phosphate on W(VI) sorption. The speciation and structure of adsorbed W(VI) on ferrihydrite also were examined using synchrotron-based X-ray absorption spectroscopy (XAS). Adsorption isotherms and envelopes show a complex relationship between pH and W(VI) adsorption, with more W(VI) retained at circumneutral pH. Adsorption was less extensive in solutions containing more polymeric species, suggesting that these species do not adsorb to ferrihydrite surface as strongly as does the tungstate anion. Polyoxometalate (POM) clusters form in the presence of phosphate, or persist as metastable complexes for sufficient duration to considerably enhance the solubility and transport of tungsten in natural environments. XAS confirmed that tungstate usually represents the bulk of adsorbed W(VI), but polytungstates also appear to be adsorbed to the mineral surface, particularly in systems in which W(VI) was most soluble. Equilibrium adsorption onto ferrihydrite was not achieved and takes more than one month; this unusually slow adsorption is due to the slow decomposition of weakly-adsorbing polyatomic anions to monomeric tungstate anions. The kinetic stability of metastable polytungstates thus may further enhance W solubility in natural waters and its migration in natural environments.

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