Airborne *in situ* measurements of HDO/$H_2{}^{16}O$ confirm strong influence of convection on isotopic composition of upper tropospheric humidity

EMANUEL CHRISTNER*[1] CHRISTOPH DYROFF[1], SHAHROKH SANATI[1] AND ANDREAS ZAHN[1]

[1]KIT – Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research, Karlsruhe, Germany (*correspondence: emanuel.christner@kit.edu)

Atmospheric water is an enormously crucial trace species. It is responsible for ~75% of the natural greenhouse effect [1] and carries huge amounts of latent heat. The isotopic composition of atmospheric water vapor is an elegant tracer for a better understanding and quantification of the extremely complex and variable hydrological cycle in Earth's atmosphere, which in turn is a prerequisite to improve climate modeling and predictions.

In this context, water-isotopologues (here the isotope ratio HDO/$H_2{}^{16}O$) can be used to study the atmospheric transport of water, as $H_2{}^{16}O$ and HDO are fractionated during several transport-related processes (evaporation, cloud condensation, rainout, re-evaporation, formation of ice).

During more than 20 long-distance flights across or close to the equator, HDO/$H_2{}^{16}O$ of convectively lofted air was measured *in situ* in the upper troposphere (UT). These measurements confirm the large impact of tropical strong convection on the isotopic composition of atmospheric water. In comparison to a Rayleigh model we find on average an enhancement of δD by more than 100 ‰ above three continents (Africa, South America, East Asia, Fig. 1). A meridional profile illustrates the transport of convectively lofted air to higher latitudes by Hadley circulation.

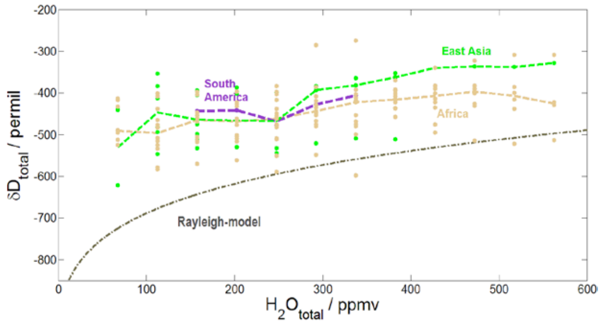

Figure 1: Enhanced tropical δD shows impact of convection on isotopic composition of humidity in the UT. Black line: Rayleigh model.

[1] Schmidt *et al*. (2010), *JGR*, **115**, D20106.

An integrated approach to build surface complexation models for chromate on iron oxides

MARIA CHRYSOCHOOU[1]* NADINE KABENGI[2] MICHAEL MACHESKY[3] CHAD JOHNSTON[1] AND JAMES KUBICKI[4]

[1]University of Connecticut, Storrs, CT 06268, USA (correspondence*: maria.chrysochoou@uconn.edu)
[2]Georgia State University, Atlanta, GA 30303, USA
[3]Illinois State Water Survey, Champaign, IL 61820, USA
[4]Pennsylvania State University, University Park, PA 16802, USA

This study presents Surface Complexation Models (SCMs) for chromate ($CrO_4{}^{2-}$) adsorption on ferrihydrite and hematite that were formulated and calibrated using complementary techniques to investigate the mechanisms and energetics of adsorption. Specifically, Attenuated Total Reflection – Fourier Transform Infrared (ATR-FTIR) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopies were applied to investigate the surface species formed under different pH, surface loading and ionic strength conditions; Flow Adsorption Calorimetry (FAC) analyses determined the enthalpies of adsorption and provide additional evidence for surface speciation; Density Functional Theory (DFT) calculations provided bond lengths, vibration frequencies and comparative enthalpy values. SCMs were formulated using the CD-MUSIC framework and calibrated taking both proton adsorption data and observed surface species distributions into account.

The results indicate that ferrihydrite and hematite present similar behavior in terms of the type of species formed, with some differences in the relative distribution and adsorption energetics that can be traced back to the mineral structure and properties. Monodentate complexes are dominant on both minerals at low chromate loadings and pH>5, while bidentate complexes are favored at acidic pH and high surface loading. No protonation of the surface complexes was observed under any conditions. More total heat of adsorption was observed on the ferrihydrite surface compared to the hematite.

The conditions at which bidentate complexes take over are dependent on ionic strength and on the presence of carbonate, as indicated by the ATR analyses and the SCMs, respectively. The calibration of the model also indicated that the distribution of the two species as a function of pH is very sensitive to the log K values. Overall, an improved fit to adsorption edges was obtained for both minerals compared to previously published models.

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