

## Chemical evolution of perched groundwater flowing through weathered bedrock underlying a steep forested hillslope, northern California

HYOJIN KIM<sup>1\*</sup>, JAMES K.B. BISHOP<sup>12</sup>  
WILLIAM E. DIETRICH<sup>1</sup> AND INEZ FUNG<sup>1</sup>

<sup>1</sup>University of California, Berkeley Dept. Earth and Planetary Science, 307 McCone Hall, Berkeley CA94709  
hyojin820@berkeley.edu

<sup>2</sup>Earth Science Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, MS 90-1116, Berkeley CA 94709, USA

At the ~4000 m<sup>2</sup> Rivendell study site on a 30° hillslope underlain by argillite along the South Fork Eel River, we have monitored the chemistry of rainfall and of groundwater that seasonally perches on dense, fresh bedrock (5 to 20 m below the surface) and flows through a weathered bedrock zone to an adjacent channel. This is a part of a collaborative study focused on coupling hydrologic, geochemical, ecological, and atmospheric processes. Water samples were collected every 1 to 3 days for five years from three wells: upslope (Well 10), mid-slope (Well 3), and downslope (Well 1).

At the beginning of the rainy season Well 10 groundwater is deep with a constant high concentration of major cations (Ca, Mg, and Na). New water arriving from seasonal storms causes water-table rise (4 to 6 m), and systematic dilution until rising water levels reach a new, significantly diluted constant value. Surprisingly, however, Si shows an opposite response and increases in concentration with rising water level. Well 3 response is generally similar. Well 1 behaves differently: its water-table is highly responsive to rainfall inputs, but its chemistry shows no significant change, except briefly during rainstorms.

Our data suggests that the deeper groundwater flow which is highly concentrated is in thermodynamic equilibrium with the argillite. Seasonal rainwater passes quickly through the soil and weathered bedrock where it rapidly uptakes major cations via cation exchange reactions and Si through amorphous silica dissolution. PCO<sub>2</sub> is highly elevated due to biological activity. Intensive biological activities in this layer increase the rate of mineral dissolution and thus continuously replenish exchangeable cations and the amorphous silica pool.

## Ship-plume sulfur chemistry: ITCT 2K2 case study

HYUN S. KIM<sup>1</sup>, YONG H. KIM<sup>1</sup> AND CHUL H. SONG<sup>1,\*</sup>

<sup>1</sup>School of Environmental Science and Engineering, Gwangju Institute of Science and Technology, 1 Oryong-dong, Buk-gu, Gwangju 500-712, Republic of Korea

The ship-plume sulfur chemistry was investigated for the ITCT 2K2 (Intercontinental Transport and Chemical Transformation 2002) ship-plume experiment, using the ship-plume photochemical/dynamic model developed in this study. In order to evaluate the performance of the model, the model-predicted mixing ratios of SO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> were compared with those observed. From these comparisons, it was found that the model-predicted levels were in reasonable agreements with those observed ( $0.56 \leq R \leq 0.71$ ), when the pH of sea-salt particles (pH<sub>ss</sub>) was  $\leq 6.5$ . The ship-plume equivalent lifetimes of SO<sub>2</sub> ( $\tau_{SO_2}^{eq}$ ) were also estimated/investigated for this particular ship-plume case. The magnitudes of  $\tau_{SO_2}^{eq}$  were found to be controlled by two main factors: (i) the mixing ratios of in-plume hydroxyl radicals (OH) and (ii) pH<sub>ss</sub>. The former is governed primarily by stability conditions of the marine boundary layer (MBL), when the ship NO<sub>x</sub> emission rate is fixed. The latter determines if the heterogeneous oxidation of dissolved SO<sub>2</sub> occurs via reaction with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, when pH<sub>ss</sub> < 6.5) or with ozone (O<sub>3</sub>, when pH<sub>ss</sub> > 6.5). According to the multiple ship-plume photochemical/dynamic model simulations, the estimated  $\tau_{SO_2}^{eq}$  over the entire ship plumes ranged from 10.32 to 14.32 hrs under moderately stable (E) to stable (F) MBL conditions. These values were clearly shorter than the background SO<sub>2</sub> lifetime ( $\tau_{SO_2}^b$ ) of 15.18- 23.20 hrs. In contrast,  $\tau_{SO_2}^{eq}$  was estimated to be 0.33 hrs when the pH<sub>ss</sub> remained at ~8.0 (a rather unlikely case). In addition, the SO<sub>2</sub> loss budget was further analyzed to estimate the influences of the two main factors on the ship-plume sulfur chemistry. The changes in the loss budget with pH<sub>ss</sub> clearly showed a shift in the dominant SO<sub>2</sub> loss processes from heterogeneous SO<sub>2</sub> conversion (when pH<sub>ss</sub> > ~6.5) to the gas-phase oxidation of SO<sub>2</sub> by OH (when pH<sub>ss</sub> < ~6.5).

**Acknowledgements.** This work was financially supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) grant from the Ministry of Education, Science and Technology (MEST) (2012R1A1A2041481).