Chemical weathering fluxes through a coastal aquifer, the Pingtung Plain, southwest Taiwan

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Tracing groundwater offshore has resulted in a wide range of submarine groundwater discharge (SGD) estimates for specific marine locations, but complementary, similarly-focused studies measuring potential throughput on land are few. We analysed the waters from 43 wells at varying depths through a 264 m window in the Pingtung Plain for major dissolved cations, anions, dissolved SiO_2, and stable isotopic composition of oxygen and hydrogen of water, and used Darcy's Law to compute their subsurface fluxes. Compared to chemical flux estimates from the adjacent Kaoping River, results show that 1.1 to 12.3 % of combined surface runoff and potential subsurface discharge to the ocean can be attributed to groundwater-derived weathering fluxes. Estimated propagated errors at 2σ on subsurface fluxes are ± 30 % assuming the hydraulic conductivity is known by ±10 %. Multi-year daily hydraulic head data gives the direction of groundwater flow through the plain, and indicates that pumping has led to episodic reversals of flow, facilitating seawater intrusion in the near-coast aquifer. Hydrological connectivity exists throughout the drilled depth of the basin, whereas chemical gradients suggest that stratified flow is in operation, with up to a two-fold increase in silicate-derived Na^+ seen in deeper horizons as compared to the near surface. For all ions except Ca^{2+} and SO_4^{2-}, the average concentrations of dissolved species in the distal groundwaters exceed those of the river, ranging from a factor of 1.2 in the case of Li^+, K^+ and Mg^{2+} to 5.4 in the case of Ba^{2+}. At 12.3 %, the relative groundwater flux of Ba^{2+} exceeds that of all other elements by at least a factor of two. Furthermore, Ba^{2+} concentrations in the near surface coastal aquifer exceed those in deeper horizons by up to a factor of 7.9. The observation of increasing Ba^{2+} in the shallow subsurface could be accounted for by a desorption mechanism. However, the correlation of Ba^{2+} and ionic strength is poor, requiring an additional mechanism that could affect Ba, (additional dissolution of Ba-bearing phases), and/or the ionic strength (~Na^+), such as reverse weathering. Results suggest that, with the exception of Ba^{2+}, submarine groundwater chemical fluxes into the Taiwan Strait are modest in comparison to those related to surface runoff. If reverse weathering is promoted in seawater-intruded aquifers, the silicate weathering fluxes in the Pingtung Plain would still be underestimated after the incorporation of SGD.

Isotopic insight into volcanic sulfate formation in the troposphere.

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We present analyses of oxygen and sulfur isotopic composition of sulfate extracted from volcanic ash collected near volcanoes few hours or days after eruptions. This study is based 10 volcanic eruptions that occurred from the equator to 65°N.

Very significant variability is observed in the dataset with SO_4 concentration ranging from 350 to 7500ppm, $\delta^{18}O$ from 0.2 to 13.2‰, $\Delta^{17}O$ from -0.14 to 0.35‰ and $\delta^{34}S$ from 3.9 to 10.5‰.

While $\delta^{34}S$ of volcanic sulfate is expected to reflect processes that mainly occurred in the volcanic plume, the O-isotopes clearly trace the oxidation pathways of volcanic SO_2 in the atmosphere and more specifically in the troposphere for our samples.

Assuming that $\Delta^{17}O = 0‰$ and $\delta^{18}O = 5\text{-}7‰$ in SO_2 coming out from the volcanoes, the resulting sulfate $\Delta^{17}O$ would be significantly different from 0‰ only if a substantial fraction of SO_2 was oxidized via mass-independent fractionating oxidation pathways (reaction with O_3 or H_2O_2). On the other hand, the $\delta^{34}S$ of sulfate was expected to fall within the initial volcanic SO_2 range, which is $\delta^{34}S = 6\text{-}8‰$. The fluctuations of about 2‰ outside this range in the measured sulfate may reflect some Rayleigh distillation processes in the volcanic plume.

The different volcanic events analysed here correspond to different environmental conditions (latitude, season…) for the oxidation of volcanic SO_2. We analyse, via 3-D chemistry-transport model calculations, the expected levels of SO_2 oxidants in the atmospheric column above the studied volcanoes. For each eruption, we are able to compare the measured $\Delta^{17}O$ with the $\Delta^{17}O$ estimated in sulfate produced by SO_2 oxidised in model-calculated background conditions.

Our results indicate that, for the vast majority of the cases, the main oxidant for volcanic SO_2 in the troposphere is OH radicals or, at least, that SO_2 is not significantly oxidised via a mass-independent fractionating channel. OH in the very dry stratosphere carries a substantial mass-independent isotopic anomaly while in the humid troposphere this anomaly is thought to be lost through isotopic exchanges with H_2O. It is likely that the low pH of volcanic aerosol clouds could reduce very significantly the heterogeneous oxidation via the mass-independent O_3 and H_2O_2 in the troposphere.