

A dust-soil-groundwater-dust cycle, Southwestern United States

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Dust inputs to arid southwestern U. S landscapes strongly influence soil particle size, which affects infiltration rates in the unsaturated zone, as well as soil chemical composition, which may affect groundwater chemistry. Our recent work demonstrates the active role that wet playas (depth to groundwater <10 m) play in dust emissions. Long-term monitoring (20 years) in the eastern Mojave and southern Great Basin reveals cyclic fluctuations in deposited dust that are controlled in part by the amount and seasonal distribution of rainfall and by the behaviour of different source types (wet playas, dry playas, and alluvium).

Deposition rates (fluxes) of silt-and clay-sized dust vary annually from about 2 to 20 g/m²/yr. Sites throughout the study area respond to ENSO-related precipitation cycles; peaks in dust flux occur during consecutive dry years and also during very wet years. However, soluble-salt flux (~0.8 to 2.0 g/m²/yr) increases only during periods of high winter-dominated rainfall that are preceded and accompanied by strong summer rains. A major control on dust emissions is the hydrologic condition of surface sediments. The silt-clay and soluble-salt fluxes increase during wet years at sites close to wet playas, whereas only silt-clay flux increases during drought periods at sites downwind of alluvial sources and "dry" playas with deeper groundwater (>10 m)

The presence of ground water just below playa surfaces (wet playas) creates efflorescent-salt rich, fluffy sediment that easily becomes airborne with gentle winds. As long as the water table remains below, but near, the playa surface, efflorescent salt production mixes with silt and clay to produce large quantities of dust. This process also enriches dissolved metal concentrations well above that found in the groundwater because huge quantities of ground water are continuously lost to evaporation. Trace metals such as As, U, Sb, and Li (As and U largely from salts, Sb and Li largely from silicates) are commonly enriched in both surface samples and dusts derived from wet playas we have examined, including Owens (dry) Lake, Soda Lake, and Franklin playa, Calif. Soluble anion contents of dust samples fluctuate over three orders of magnitude (Cl and NO₃: 10⁰-10² ppm, SO₄: 10²-10⁴ ppm). Seasonal (6-month) deposition rates of these anions suggest that dust inputs may be a significant source of solutes (Cl and NO₃: 10⁻²-10¹ g/ha, SO₄: 10⁻¹-10² g/ha).

Solute sources in a tropical granitoid watershed, Luquillo, Puerto Rico

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Weathering reactions in soil, saprolite, and bedrock impart distinct signatures, which can be used to determine sources of solutes in natural waters. We are studying weathering and water flowpaths in the Rio Icacos watershed in the Luquillo Mountains, Puerto Rico, a USGS WEBB research site. Thick saprolites (up to 8 meters) are developed on early Eocene quartz diorite bedrock. Primary bedrock minerals (plagioclase, quartz, hornblende, biotite) weather at disparate rates and have widely differing Ge/Si and Sr isotope ratios. For example, plagioclase has Ge/Si=1.5 (μmol/mol) and ⁸⁷Sr/⁸⁶Sr=0.7042 and is rapidly converted to kaolinite at the sharp bedrock/saprolite interface. In contrast, biotite, which survives the bedrock/saprolite interface, has Ge/Si= 6.1 (μmol/mol) and ⁸⁷Sr/⁸⁶Sr=0.7827, and weathers more slowly within saprolite and the thin (~50 cm) overlying ultisol.

Ridgetop soil and saprolite pore waters, sampled by suction lysimeters installed at depths between 15 and 750 cm, show compositional differences that vary as a function of depth, reflecting predominant weathering reactions. Pore waters at depths approaching the bedrock/saprolite interface have low Ge/Si ratios (1.0-1.4) and ⁸⁷Sr/⁸⁶Sr (0.7052-0.7063), largely reflecting dissolution of plagioclase. Shallower pore waters have higher Ge/Si (2.3 – 4.0 μmol/mol) and increasingly radiogenic ⁸⁷Sr/⁸⁶Sr (up to 0.712), reflecting dissolution of biotite and secondary (Ge-enriched) kaolinite.

Stream water compositions in the Rio Icacos vary as a function of flow regime. At baseflow, which we interpret to reflect groundwater discharge to streams, stream compositions are similar to the deepest saprolite pore waters. During storm events, stream water Ge/Si increases with discharge to a maximum of about 2.2 μmol/mol, reflecting contributions of soil and saprolite water pushed out of pore spaces by infiltrating precipitation. A hydrograph separation model based on Ge/Si and [Si] suggests that stormflow is dominated by the soil water component, with groundwater contributing <10% of water flux at peak stormflow. We are currently testing these ideas with analyses of oxygen isotopes to constrain water sources, and U-series disequilibrium isotopes as an additional solute tracer.

**Carbonate and plagioclase
weathering rates in Pleistocene
glacial drift deposits:
Solute fluxes from soils to shallow
groundwater systems**

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Thick Pleistocene glacial drift deposits mantle large portions of the upper Midwestern U.S.A.. In lower Michigan, high permeability of soils and underlying glacial drift produce unusually close chemical linkages among soil, ground and surface waters. This region also provides an ideal natural laboratory with abundant organic matter and freshly eroded, reactive minerals in which to determine sequence and mass balances of carbonate and silicate mineral weathering and the evolution of soil waters into shallow groundwaters.

Sites were instrumented for soil water chemistry in vertical profile to 4 meters depth (UM George Reserve). Water and solute budgets were determined by Br tracer introduction to instrumented soil monoliths at the LTER site at the MSU Kellogg Biological Station.

Soil water Na concentrations derived from plagioclase dissolution (corrected for atmospheric inputs) typically attain concentrations between 30-120 μM within the upper 25-50 cm and show little increase thereafter, implying that the reaction is largely completed within the rooting zone. Carbonate dissolution (DIC, divalent cations) is localized in deeper soil horizons where carbonate minerals are still abundant. Dolomite and calcite appear to dissolve at similar rates (Mg/Ca ratio of 0.4) and soil waters are near equilibrium with respect to dolomite which is more soluble than calcite at these relatively low temperatures (<15°C).

Taken together, these data demonstrate the rapid and early nature of solute acquisition and the importance of root respiration and dissolved organic matter flux.

**Origin of radiogenic Sr in surface
waters of central Texas, USA**

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Stream waters from the four tributaries in the Lake Waco drainage basin in central Texas were analyzed for their Sr isotopic composition in order to investigate the origin of the solutes in the lake and the extent of weathering of limestones in the basin. All of the stream waters have Sr isotope ratios that are more radiogenic than the Cretaceous limestones (maximum of 0.7076) that underlie the watershed (Table 1).

Table 1. Sr isotopic composition of Lake Waco drainage basin surface waters

Sample	⁸⁷ Sr/ ⁸⁶ Sr
Up-basin North Bosque River	0.70885
Mid-basin North Bosque River	0.70853
Lower-basin North Bosque River	0.70837
Hogg Creek	0.70910
Middle Bosque River	0.70894
South Bosque River	0.70852
Lake Waco	0.70846

The North Bosque is the largest of the four streams and becomes less radiogenic downstream. The smallest of the subbasins, Hogg Creek, has the most radiogenic Sr of any of the surface waters. The most likely source of the radiogenic Sr in the stream waters is dust that contains high Sr ratios which has accumulated in the soils of the drainage basin. This idea is consistent with the higher Sr ratios observed in streams that receive abundant soil water or shallow groundwater such as the shallowly incised upstream North Bosque and Hogg Creek.

If Sr can be used as a proxy for the origin of Ca, then the amounts of externally derived Ca in the stream waters can be estimated. Using a typical Sr ratio for Saharan or Gobi desert dust of 0.715, it appears that between 10 to 20% of the calcium in the streams may be derived from weathered dust that has been deposited in the soils.

REE in Konza Prairie LTER Site (USA) Soil — Allochthonous?

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The Konza Prairie NSF-LTER Site is a 35 km² tallgrass prairie located in the central USA with a mid-continental temperate climate. Most of the site has never been plowed, making it a rare remnant of once extensive grasslands in North America. The early Permian-aged bedrock has eroded into a bench (limestone)-and-slope (mudstone) type landscape. Bedrock is overlain by thin (2m or less) Pleistocene-aged loess or patchy alluvium/colluvium. Soils are mature, with thin O-, variable A-, and thick B- (or Bt-) horizons. Aeolian dust flux at the site is at least 50 kg/hc/mo [1] and weathering of this modern flux may be evident in shallow ground water in the limestone aquifers [2]. We investigated REE in sequential chemical leaches of soil profiles to characterize the REE distribution, evaluate effects of soil processes, and explore the possibility that dust imparts a REE signature different from the loess-based soils. Results show that the chemically resistant, oxidizable, reducible, and acid-leachable fractions of the soil at all depths (to 38 cm) have similar normalized REE patterns resembling UCC, although abundances vary over more than two orders of magnitude. The normalized REE pattern of the exchangeable fraction is significantly different from other fractions, suggesting that there is addition of labile material with recognizable REE signature or that fractionation during ion exchange has occurred. If fractionation has occurred, it differs from REE fractionation documented in similar environments. We suggest that the REE pattern in the exchangeable fraction of the Konza Prairie soils reflects input of allochthonous material.

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Variability of nitrate sources in a regional aquifer: Role of soil processes and land use

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Understanding sources of nitrate in regional aquifer systems (>50,000 km²) is complicated by spatial variability in the controlling factors inherent in regional studies and by temporal variability that may span thousands of years, as indicated by ground-water age distributions. On the other hand, spatial and temporal variability at these scales provides an opportunity to observe systematic changes in the relative importance of controlling factors that otherwise may not be apparent at smaller scales of investigation. The unconfined High Plains aquifer underlies an area of about 450,000 km² in the western United States and supports one of the largest areas of irrigated agriculture in the country. Radiocarbon dating indicates that the aquifer contains a stratified sequence of ground-water ages spanning Holocene time.

Investigations of the soil zone, deep vadose zone, and aquifer indicate that nitrate in the aquifer was related to soil processes and land use that varied spatially and temporally. Prior to the widespread development of irrigated agriculture in the late 1950's, nitrate in ground water was derived from natural soil nitrogen. Volatilization and leaching of nitrogen in the soil zone produced systematic regional variations in the $\delta^{15}\text{N}$ composition of nitrate in recharge. The relative importance of volatilization and leaching in the soil zone, evaluated on the basis of $\delta^{15}\text{N}[\text{NO}_3]$ values in paleorecharge, was related to climate, with volatilization being more predominant in warmer, drier regions. A clear shift in the sources and larger fluxes of nitrate to the aquifer were apparent after the onset of irrigated agriculture. The new sources included applied fertilizer, manure, and naturally-accumulated nitrate stored in the vadose zone that was mobilized by irrigation. The greatest potential for irrigation-driven mobilization of natural nitrate was in warmer, drier regions because leaching was a relatively minor sink for soil nitrogen in those areas during the Holocene. Results from this study demonstrate the value of regional investigations in understanding linkages between soil-zone processes and ground-water chemistry.

Redox controls on denitrification at the soil–aquifer interface

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The onset of large-scale groundwater abstraction in the 1960s for drinking water production has resulted in a significant lowering of the watertable, at the study site in the eastern part of the Netherlands. Here, zones with upward seepage of anoxic groundwater the decreased and the surface load of nitrate increased due to intensified agricultural activities.

This study focuses on the effects of this increased oxidant loading on the chemistry of the subsurface and the controlling redox processes. So far, oxygen and nitrate concentrations are being buffered by the reductive properties within the soil and aquifer matrix within the upper fifteen meters of the subsurface. In this zone, the decline in nitrate is mirrored by a decrease in soil-derived dissolved organic matter (DOM) and nitrite concentrations, pointing to active denitrification. However, DOM alone cannot account for the observed oxidant decrease.

An unsuspected source of additional reduction capacity was found in the presence of a shallow ferrous iron-bearing carbonate phase [1]. Isotopic and elemental investigation of this phase indicated that it precipitated from alkaline Fe(II)-containing groundwater. The well-known and widespread occurrence of ironhydroxide accumulations in the sandy soils of the this area originated from the source of upward seeping deeper anoxic groundwater.

To quantify the importance of the identified oxidant buffering reactions, oxidation studies were performed on sediments and groundwater from various depths. It was found that 90% of DOM was oxidized within the soil zone, that 10% of the remaining fraction did not degrade in the aquifer. Excitation–emission fluorescence spectroscopy on DOM samples indicated a largely humic/fulvic composition with only little changes with the various degradation extents. Sediment incubations confirmed that the identified carbonate phase was sufficiently reactivity to contribute to the observed denitrification.

This study is a clear illustration of the how the interplay between chemical processes in aquifer and soil control the chemistry of groundwater.

Reference

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Evapoconcentration not an indicator of nitrate in Kansas ground water

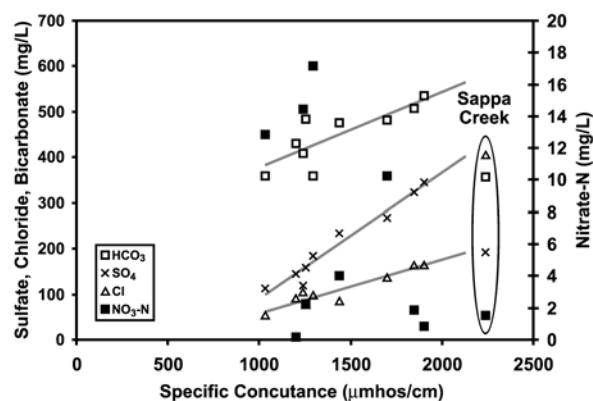
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Nitrate source determination in an area with a calcareous silt/clay vadose zone and high salinity groundwater due to evapoconcentration precludes the use of NO_3/Cl ratios for quantifying denitrification processes or identifying animal waste sources. In northwest Kansas, groundwater was evaluated using SO_4/Cl ratios, anion trends, and the $\delta^{15}\text{N}$ natural abundance isotope method to identify sources of heightened nitrate concentrations in drinking water.

An increasing trend of anion concentration with specific conductance is typical of evapoconcentration enrichment of ground water as is shown in the figure below. SO_4/Cl ratios and mixing curves also suggest that evapoconcentration occurred. Sappa Creek, which flows through the study area, shows the impact of increased salinity possibly due to water softeners, sewage treatment outfall, or runoff from adjoining farmland and a golf course.



Nitrate-N values do not appear to be related to evapoconcentration enrichment processes (see figure). Nitrate sources included primarily fertilizer with some animal waste. Possible enrichment in ^{15}N associated with processes involving calcareous silt/clay soils and/or denitrification enrichment affected observed isotope values at wells where no apparent animal waste sources exist. The presence of a very depleted $\delta^{15}\text{N}$ value, low nitrate, and reducing water chemistry suggests that areas of limited biological activity exist even when the general water chemistry is impacted with measurable nitrate.

Reversible sorption of phosphate anions by sediments of Lake Baikal

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Results of experimental studies of the adsorption of phosphate by sediments of Lake Baikal are described. It was believed earlier that inorganic phosphate is buried in the sediments of Lake Baikal as hydroxyl apatite (Mizandrontsev, 1990). A similar mechanism was proposed for Lake Michigan (Brooks and Edginton, 1994). Our studies showed that in case of Lake Baikal this is not true. Modern sediments from the Southern Basin of Lake Baikal were sterilized by gamma-irradiation. Samples of wet sediments (~0.1 g dry mass) were stirred with Baikal water (~100 mL; pH 7.8). Portions of carrier-free [³²P]-orthophosphate were added, radioactivities of the supernatant and the sediment found, and distribution coefficient K_D calculated (Fig. 1).

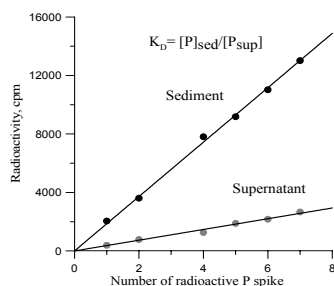


Figure 1. Adsorption of [³²P]-phosphate by Baikal sediment.

Addition of alkali liberated part of radioactive phosphate, whereas addition of acid resulted in its stronger binding.

Similar experiments were performed with carrier-free [³⁵S]-sulfate; this anion was not bound by sediments at all. After Baikal sediment was stripped of iron-hydroxous film by treatment with 1% oxalic acid, K_D for phosphate dropped from 6000 to 600.

Discussion of results: It is clear that hydroxyl apatite $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_4$ cannot be the phase of the sediments of Lake Baikal which binds phosphate, because this mineral does not dissolve in alkali, but does dissolve in acid. Data obtained with stripped sediment support the suggestion that the binding agent is Fe (III) hydroxide (Moore and Reddy, 1994). The fact that intact sediment does not bind sulfate suggests that binding of phosphate is a specific process, rather than mere anion exchange.

Conclusion: The results obtained are significant for environmental protection of Lake Baikal – they will help to estimate the permissible discharge of P.

References

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Examining water-rock interaction at the Idaho National Engineering and Environmental Laboratory using uranium and strontium isotopes as natural environmental tracers

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⁸⁷Sr/⁸⁶Sr, $\delta^{234}\text{U}$, and U and Sr concentrations of perched water and core leachates have been measured to examine water-rock interaction at the Vadose Zone Research Park (VZRP) at the Idaho National Engineering and Environmental Laboratory. U and Sr are used as proxies at the uncontaminated VZRP for water-rock interaction of radiochemical waste contamination on other laboratory property. The VZRP consists of active percolation ponds surrounded by monitoring wells, which are open at geologic contacts in the subsurface to sample perched water. Preliminary analyses of five outflow and twenty perched water samples show isotopic compositions that range between those of the outflow water and another end member(s) at depth. Uranium concentrations range from 2.01 ± 0.01 ppb at the outflow to 6.41 ± 0.02 ppb at 120 feet, and corresponding isotopic compositions decrease from 1063.2 ± 15.6 ‰ $\delta^{234}\text{U}$ to 866.8 ± 4.9 ‰ $\delta^{234}\text{U}$. Sr concentrations and ⁸⁷Sr/⁸⁶Sr isotopic ratios of most perched samples lie within the variable compositions of the outflow water, except two wells, in which the ⁸⁷Sr/⁸⁶Sr isotopic composition decreases and Sr concentration increases. Water samples taken from one depth over a period of two months during a Br⁻ tracer test show decreasing $\delta^{234}\text{U}$ that corresponds with Br⁻ breakthrough. The Br⁻ tracer test coincided with a change in the location of the outflow discharge; thus the decreasing $\delta^{234}\text{U}$ is a result of interaction with newly wetted vadose zone materials. Interestingly, these samples also show essentially no change in uranium concentration. This type of natural attenuation would be undetectable without isotopic analyses. ⁸⁷Sr/⁸⁶Sr vs. $\delta^{234}\text{U}$ for all samples gives a reaction path mixing model between two end members, the outflow water and another member. The nature of the other endmember(s) will be determined by isotopic analysis of leachate from sequential extractions of core material from the site.

Characteristics of river sediment in the light of the environmental quality standard value of Japan – A case study at the Tama, the Tsurumi, the Hino and the Kamo rivers in Japan

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Introduction

The soil contamination countermeasures law in Japan has been enforced on February 15, 2003. The responsibility of those concerned with social aspects of soil contamination management and land occupation has increased in Japan.

Our study is clarifying distinction with the natural origin and the artificial origin about the soil contamination (e.g, Matsumoto et al., 2002). And we show the geochemical and geological characteristics of stream sediments from the Tama, the Tsurumi, the Hino and the Kamo rivers, in Japan.

Results and discussion

We show research results of the degree of contamination in one of the most polluted rivers, the Tama and the Tsurumi rivers (Kanto District), the Kamo river (Shikoku District) which is very clear based on investigations of BOD, and the Hino river (San-in District) which is also relatively clear and has chromite mine at near the source. Above rivers were sampled at intervals of 2-3km over their entire stretch. The content and elution of chemical compounds was examined, and mineral composition was established by both XRD (X-Ray Diffraction) and observation under a polarization microscope.

Of the determinations of Cd, CN, Pb, Cr6+, As, and Hg only Pb content was above the environmental quality limit in one location of the Tsurumi river. However, in the down-river part Pb-concentration was 10 times higher than at the source as the result of man's production activity; for Hg the same tendency was detected at the Tama and Tsurumi rivers.

Reference

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