

Solute geochemical mass balance and forest biomass in small Appalachian Blue Ridge watersheds

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Weathering rates of rock-forming silicate minerals in natural forested catchments of the US Department of Agriculture - Forest Service Coweeta Hydrologic Laboratory (North Carolina, USA) are calculated using a system of geochemical mass-balance equations to calculate mineral weathering rates from solute fluxes. The equations are constructed and constrained by petrologic, mineralogic, hydrologic, botanical, and aqueous geochemical data. The number of mineral-weathering rates that can be determined is limited by the number of elements for which solute mass-balance equations can be written. Where simplifying assumptions can reduce the number of mineral reactions that need to be considered to a number less than the number of mass-balance equations, the rate of element transfer into or out of biomass can be solved as one of the unknowns. Uptake of major cations by aggrading forest vegetation can act as an intracatchment sink for at least some mineral-derived elements, producing mineral weathering rates higher than would be estimated from solute fluxes alone.

Biomass has the least influence on weathering rates of minerals whose rate is determined by the mass balance for botanically unimportant elements (e.g., sodic plagioclase). The largest biotic effects on weathering rates are for minerals that supply important nutrients to the forest biomass (e.g., biotite mica). Six of seven Coweeta control watersheds aggraded deciduous forest biomass during the solute-flux period-of-record. In the best-constrained, the annual increment of biomass uptake of Ca and Mg equalled the rate of atmospheric deposition of these nutrients. Forest demand for K exceeded atmospheric inputs and required uptake of K released by mineral weathering. The seventh Coweeta control watershed lost biomass and nutrients due to natural infestation by defoliating organisms and consequent decay of defoliation products, which acted as a non-mineral source of alkalis and alkaline earths to streams. The magnitude of the biotic effect on silicate weathering rates in Coweeta control watersheds depends on the history of natural disturbance of the forest ecosystem in each individual control watershed, and the botanical significance of specific elements in the mass-balance equations from which weathering rates of specific minerals are calculated.

Solute behavior in agricultural vs forested watersheds during storm events: Implications for DOC sources

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Background

Two paired watersheds were monitored during storm events to use perturbations in solute concentrations to help understand the source of dissolved organic carbon (DOC) to the stream system. To test the effect of land use, one watershed is forested and the other is under cultivation, primarily for corn. The two Southeast Pennsylvania watersheds have similar characteristics of slope, aspect, and bedrock geology.

Results and Discussion

Streamwater chemistry evolves in the agricultural watershed following hysteresis loops according to the contributions of endmember water sources, most likely defined as throughfall, shallow soil water, and groundwater. During the rising limb of the hydrograph, the sequence of solute concentration maxima is (from earliest to latest arrival): potassium, turbidity, DOC, iron and manganese. At the peak of the hydrograph, minima of sodium, silica and conductivity are observed. On the falling limb, potassium and turbidity return to pre-event conditions followed by sodium, and silica. After the event, DOC remains lower than pre-event concentrations for at least several days. Potassium, turbidity, DOC, iron, and manganese all follow clockwise hysteresis loops, while conductivity, sodium, silica, and calcium follow counterclockwise loops. The forested watershed stream pattern is similar, though solutes follow more similar pathways on the rising and falling limbs of the hydrograph, creating narrower hysteresis loops. The forested watershed also takes longer to return to pre-event chemical conditions.

Geochemical mass balances and weathering rates in forested watersheds of the Southern Blue Ridge: Solving more equations in more unknowns through incorporation of rare earth elements

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Watershed solute-based geochemical mass balance methods are considered the most accurate means of quantifying elemental transfers and weathering rates at the Earth's surface. However, such calculations often suffer from the limitation that the number of unknowns exceeds the number of mass-balance equations, either yielding a system of equations that cannot be solved mathematically, or requiring less-realistic approximations to solve for a reduced number of unknowns.

New solute-based mass balance calculations for low-order watersheds at the Coweeta Hydrologic Laboratory, western North Carolina, include solute fluxes of rare earth elements (REE), yielding enough equations to calculate eight unknowns (rates of primary mineral weathering and secondary mineral formation). Weathering of garnet and accessory allanite are the major contributors of REE to Coweeta stream waters. Inclusion of REE in Coweeta watershed mass balance calculations yields mineral weathering rates that are more geochemically reasonable (e.g., garnet weathering rates are up to approximately 90% slower) than previous studies.

Use of REE in watershed solute mass balances is in its infancy. Stream REE fluxes are from one-time samples that have been converted to approximate long-term fluxes using stream SiO₂ chemistry. Also, no data have been collected on REE in precipitation. Despite these potential limitations, sensitivity analysis of the new mass balance results, and the more geochemically reasonable results, encourage further work to overcome these limitations.

Exploring the effects of urban and agricultural land use on surface water quality

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Approach

This research is based on the hypothesis that the influences of land use on water quality are unique and can be quantified. In this study we investigate the influence of urban land use on nutrient cycles and trace elements and attempt to validate the applicability of previously developed biogeochemical fingerprints. (Wayland, et al., 2003)

Samples were analyzed for nutrients, major ions, and trace metals. Sites were selected representing surface watersheds with a variety of dominant and mixed land use types. Factor and cluster analysis were used to investigate the processes controlling the effects of land use on river chemistry.

Discussion of Results

Biogeochemical fingerprints of land use were referenced to the natural environment aiding in the identification of the unique contributions of urban and agricultural land uses to surface water chemistry. Similar biogeochemical fingerprints are found between the two watersheds (Urb: Na, K, Cl / Ag: Ca, Mg) and additional correlations were found for nutrients (Ag: N & Urb: N, P) and for selected trace metals (Urb: Rb, Mo, Mn, Sr and Ba / Ag: U).

Conclusions

The higher correlations of urban than agricultural land uses with nutrients were not expected and may reflect the effects of fertilization and wastewater or the season the samples were taken. More study in different geologic and urban settings is needed to help quantify these fingerprints. These studies could lead to a rapid assessment tool for the quality and sources for degradation of urban environments.

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The coprostanol/sterol ratio as indicator of organic matter provenance in soils and rivers

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This study presents the potentiality of organic markers to trace the impact of pig slurry in soils and rivers after their land disposal as organic amendment.

As described by Gruau and Jardé (abstract in this session), the analysis of long term records of dissolved organic matter (DOM) in four watersheds in western France shows divergent trends which cannot be explained by global changes solely. One alternative explanation could be that long-term record of DOM in rivers are controlled by human activities, and notably by agricultural practices. In order to test this hypothesis, a molecular analysis has been developed. This methodology is based on the molecular markers concept. Potential sources of organic matter have been studied and molecular markers or specific distributions have been evidenced. In this study we focused on the analysis of pig slurries because of the importance of pig production in the studied region. Each animal specie is characterised by one specific sterol profile. The analysis of pig slurry evidenced the presence of coprostanol (5β -cholestan- 3β -ol or 5β) as a specific marker, originating from the bio-hydrogenation of cholesterol in their gut by anaerobic bacteria, and by the presence of C_{29} -sterol. The difference with other animal or human wastes has been evidenced by comparison with cow and poultry manures and human wastes. Two ratios have been used in order to differentiate pig slurry from the others: $5\beta/C_{27}$ and C_{29}/C_{27} -sterols. Moreover, different amended soils with pig slurry have been analysed in order to test the preservation of this potential molecular marker. The presence of coprostanol has been evidenced in amended soils, even in the deepest layers (40-60 cm). The validation of the ability of this compound to be a molecular marker of pig slurry made, our analysis has been centered on DOM of the four watersheds with divergent evolutions. The results show a systematic relation between the C_{29}/C_{27} and $5\beta/C_{27}$ ratios and the type of animal breeding in each watershed. This study allows us to evidence the impact of animal breeding activities in DOM of the analysed rivers. Such a study supports the view that DOM export by rivers is not solely under the control of global, climatic parameters, but also under the control of local land-use factors.

Human impacts on boron geochemistry of the Seine River, France

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Boron concentrations and isotopic compositions have been measured in the dissolved load of the Seine basin rivers, France. Hydrology and chemistry of the Seine River and its tributaries are highly influenced by human activities as the anthropogenic pressure on the Seine catchment is one of the highest in Europe. The samples were collected between 1994 and 1996 during various hydrological regimes, complemented by a time-series of the Seine River in Paris for one year. In particular, the decennial flood event of winter 1994 was sampled. Boron appears to be conservative in rivers and not influenced by riverine processes such as adsorption onto suspended matter and/or consumption by micro-organisms. To a first order, the origin of the dissolved boron can be traced using boron isotopes in spite of the complexity of the Seine river system and boron is a suitable tracer of contamination in rivers. The total dissolved boron of the Seine River at Paris can be explained by the contribution from three distinct components: Urban effluents constitute 65 % of the boron discharge measured in the Seine River whereas agriculture-affected waters contribute to less than 10 % with a more marked influence during high water discharges. Rainwater contribution is important (25 % mean) and can reach 30 % of dissolved boron during high flood events.

Boise Valley groundwater geochemistry – Origin, infiltration rate and transport characteristics

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Ground water/ aquifer interrelationships and estimates of vertical infiltration rates and horizontal flow rates are estimated. Groundwater chemistry of the Boise Valley aquifer is apparently inverted from what is commonly found in most large intermontane groundwater basins with highly dilute groundwater at depth. Highly dilute groundwater underlies higher TDS groundwater in the aquifer.

The Boise aquifer has a complex geohydrologic history that includes elevated concentrations of microbially generated carbon dioxide gas originating from a buried lacustrine sedimentary sequence. Thermal ground water is present at depth and also occurs along the faulted northern boundary of the basin where it interacts with natural surface water recharge from the Boise River. Large scale historical flood irrigation has created an upper alluvial groundwater system with a considerably different groundwater chemistry than the deeper ground water aquifer recharges.

Groundwater geochemistry indicates that the oxidized shallow alluvial groundwater is moving into previously reduced deeper sections of the alluvial aquifer creating an intermediate-depth oxidizing portion of the alluvial aquifer. The vertical infiltration rate of the upper aquifer, is estimated from nitrate concentrations and tritium activities sampled from water wells of various depths.

Calculated groundwater ages based on carbon-14 isotopes support the geohydrologic interpretations based on the groundwater chemistry. Remarkably, the deep ground water chemistry has almost the same chemistry as that of the natural recharge water (Boise River) even though it has moved miles horizontally through the Boise aquifer through thousands to tens of thousands of years of contact time with the aquifer mineralogy.

Geochemical indicators of natural and anthropogenic water inputs to a lake in a mixed land use watershed

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The geochemical compositions of lake waters and source water inputs are investigated to examine human impacts on the biogeochemical cycling of phosphorus in a lake and to evaluate the utility of selected chemical species as indicators of specific source types. The project is conducted in the Table Rock Lake watershed (4020 square miles) on the Missouri-Arkansas border. The lake is an 43,000 acre reservoir with a watershed that includes a diversity of land uses and an array of potentially significant phosphorus sources, which include point sources and non-point sources such as decentralized wastewater treatment systems, confined animal feeding operations, poultry litter applied to farm fields, and storm water runoff.

The project involves a coordinated plan of sampling and analysis of potential sources and lake water at sites that have been impacted by particular types of sources (source-rich surface waters). Identification of lake sampling locations was performed using geospatial data analysis techniques to relate land use patterns and other surface characteristics with areas of potentially high densities of source types. Sampling and on-site analyses were performed once per season to assess effects of seasonal variation in source loadings and lake dynamics. Samples were analyzed for dissolved and total phosphorus, a suite of anions (Br^- , Cl^- , F^- , NO_2^- , NO_3^- , PO_4^{3-} , SO_4^{2-}), major elements (Ca, Mg, K, Na), and trace elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Sr, U, V, Zn). Evaluation of the large dataset looks for patterns of dissolved species that are unique to specific source types. Multivariate statistical analysis methods, including principal component analysis, are used to identify factors that are characteristic of both natural and anthropogenic inputs. Using a web-based geographic information system (GIS), the analytical results of the present study were integrated with measurements by other groups and additional geospatial data on the watershed (e.g., land use, size and locations of permitted discharges) and made available to other parties interested in Table Rock Lake water quality.

Understanding radioactive disequilibrium in river-borne material: Dependence on colloid/particle size

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Recent studies have used U-series isotopes in river-borne material to investigate the conditions and timescale of erosion at the basin scale (e.g. Vigier et al., 2001; Dosseto et al., submitted). Because U is more soluble than Th and ²³⁴U can be preferentially ejected from the solid, ²³⁴U excess over ²³⁸U, (²³⁴U/²³⁸U) > 1, and ²³⁸U excess over ²³⁰Th, (²³⁰Th/²³⁸U) < 1, are expected in the nominally “dissolved” phase (<0.2 or 0.45 μm) and the opposite in suspended particles. However, in some cases, opposite trends have been observed (e.g. Porcelli et al., 2001). To better understand the size dependency of radioactive disequilibrium in river-borne material, U-series isotopes have been measured for different colloid/particle sizes in waters from the Murray River Basin, SE Australia. Preliminary results show that all fractions <1 μm have (²³⁴U/²³⁸U) > 1 and (²³⁰Th/²³⁸U) < 1, the extent of disequilibrium decreasing with increasing colloid/particle size. Douglas et al. (1999) have shown that the composition of colloidal matter (<1 μm) in these rivers is controlled by mixing between detrital silicate and organic material. The increasing proportion of detrital silicate may be responsible for the decrease in disequilibrium. Hence, the “true” dissolved phase (free of detrital silicate) is probably characterized by a higher disequilibrium than that observed in the nominally “dissolved” phase. This observation may have implications for the lack of complementary nature between nominally “dissolved” phase and suspended particle compositions, currently used to discuss the steady-state nature of erosion in large drainage basins (Vigier et al., 2001; Dosseto et al., submitted).

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Diel cycles in stable isotopes of dissolved O₂ and dissolved inorganic carbon in the Big Hole River, Montana

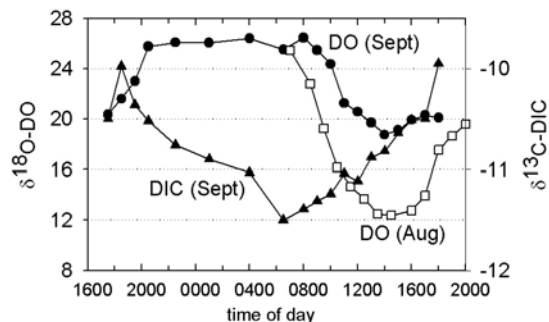
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Large diel changes in the isotopic composition of dissolved oxygen ($\delta^{18}\text{O}$ -DO) and dissolved inorganic carbon ($\delta^{13}\text{C}$ -DIC) were measured in the Big Hole River, SW Montana. $\delta^{18}\text{O}$ -DO showed a diel range of 14‰ in August 2004, and 8‰ in September 2004. $\delta^{13}\text{C}$ -DIC showed a diel range of 1.4‰ in September 2004.



The results are explained by daytime photosynthesis with the net production of isotopically light O₂ and net consumption of isotopically light CO₂, and by night-time respiration which consumes isotopically light O₂ and produces isotopically light CO₂, together with gas transfer between the river and the atmosphere. Other measured river parameters (such as pH, DIC and DO concentrations) were consistent with this interpretation. The greater diel range of $\delta^{18}\text{O}$ -DO in August vs. September is consistent with a higher rate of biological productivity during August (warmer), and by the higher DO concentrations during September (cooler).

This study is one of the first to document diel changes in $\delta^{18}\text{O}$ -DO and $\delta^{13}\text{C}$ -DIC in a river, and is consistent with the preliminary data of Tobias and Bohlke (2004). The use of $\delta^{18}\text{O}$ -DO and $\delta^{13}\text{C}$ -DIC has potential to advance our understanding of the biological, chemical, and physical processes that take place in rivers and lakes.

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Ecohydrochemical studies in the Achankovil River basin, Western Ghats, South India

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Preliminary studies on the nutrient and water chemistry of the high altitude river basin with relatively homogeneous lithology with pristine ecosystem in Western Ghats region has been carried out. A time series survey has been carried out to understand the natural and anthropogenic hydro geochemical processes controlling the water chemistry in the Achankovil River of the Western Ghats. The water is neutral with pH and EC ranges from 6.32-7.56 and 24 – 54 $\mu\text{S/cm}$. Chloride and sodium are the dominant anion and cation in the water respectively. Correlation analysis of the chemical parameters of the water shows that some ions have additional sources such as sea spray, soil conditioners and evaporates. This study shows that the majority of carbonate is derived from carbonate weathering followed by silicate weathering. Cation concentrations show decreasing trend from upstream to downstream in contrast to the increasing trend in the major world rivers. Dissolved silica in premonsoon water is low. This is due to the silica uptake by diatoms. The Gibbs plot indicates that the river chemistry is dominated by rock weathering induced by precipitation. The partial pressure of CO_2 in water is high and is in equilibrium with the atmosphere. Thermodynamic plots show that dolomite, kaolinite, albite and chlorite are in equilibrium with the river water. The additional sources which influence the water chemistry are sea spray leaching of evaporates and anthropogenic inputs. Chemical weathering is predominant here compared to physical weathering. The annual discharge of the Achankovil River is $1.48 \text{ km}^3/\text{yr}$ and transports a significant amount of solute flux ($1389 \times 10^6 \text{ t/yr}$) and suspended flux ($27 \times 10^6 \text{ t/yr}$) to the Vemband estuarine lake. The overall material transport seems to be lower compared to the other Indian rivers nevertheless the solute loads are comparable to certain large rivers like Cauvery in the south India. The concentration of PO_4 , NO_3 and Carbon are very high due to the contribution from multiple sources. The solute flux including the nutrient flux is very high among the Western Ghats Rivers in comparison to its size, which will certainly supplement the productivity of the lake/estuary and the coastal waters. Since this study is restricted to limited period, long-term data procurement and analysis along with micro nutrients studies are needed, which are lacking in the present study, to gain insight into the material flux by this river into the Arabian Sea.

Key words: Achankovil River; Nutrient concentrations, seasonal variation; solute acquisition

Export of DOM by rivers: Assessing the relative effects of climate change and human activities using long-term records

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This study presents long-term records of dissolved organic matter (DOM) as indicated by oxydability measurements that were constructed for four watersheds in western France as back as 1979. Observations show contrasted evolutions with three watersheds exemplifying large increases in DOM concentrations over the period of study (a doubling of the concentration over a period of 25 years is observed in one case), while the fourth shows DOM concentrations that decrease with time. All watersheds show common inter-annual control on DOM concentration in response to a succession of dry and wet periods with a cyclicity of 5-7 years. The same cyclicity in DOM concentrations is apparent in the long term records of DOM for rivers located in northern England. The evidence support the view that this cyclicity is climatic in origin being likely a consequence of the North Atlantic Oscillation that controls the yearly amount of precipitation that falls over Western Europe.

As regards the significance of long-term trends, we note that the onset of DOM increase in those rivers showing positive long-term DOM trends is in phase with an increase in average annual temperature. This might suggest that the change in temperature is the key mechanism that causes these trends, suggesting that the climate is also the driving force of long-term DOM trends in river. However, such an hypothesis is faced with the problem of explaining why one of the studied watershed shows a divergent evolution, i.e. a long-term DOM decrease. Alternative explanations must thus be found. One such alternative explanation could include changes in land management and agricultural practices. A survey of agricultural practices in the four studied watersheds reveals that the watershed showing a long-term decrease of DOM is marked by massive spreading of pig manure, a process that does not occur in the other three watersheds. Spreading of pig manure may acidify watershed soils, thereby promoting the adsorption of organic matter on soil minerals which could ultimately limit the export of DOM by rivers. The evidence supports a view that DOM export by rivers is under the control of global, climatic factors mediated by local land-use factors which can cause divergent long-term evolutions in the DOM export capacity of rivers on relatively short spatial scale.

Chemical weathering and erosion in New Zealand monitored by bedload and suspended sediments

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Chemical and physical erosion processes have been investigated in a wide range of high sediment yielding rivers from New Zealand using major and trace element data from suspended sediments and fluvial bedload grain size fractions. Average fluvial particulate compositions from New Zealand are similar to estimates of average upper continental crust (UCC) composition. Recalculation of global fluvial elemental fluxes using average New Zealand suspended and bedload sediment compositions as a proxy for sediment derived from all high standing islands (HSIs, 30% of total) results in world average compositions that more closely resemble the UCC than previous estimates using major world rivers alone.

Weathering of the Southern Alps is strongly partitioned(?) between the chemical weathering of carbonates and physical weathering of silicates. The similarity of sediments from rivers draining both sides of the drainage divide indicates minimal climatic control on weathering intensity of fluvial sediments. Rather, bedload geochemistry is controlled primarily by mechanical attrition and hydrodynamic fractionation, both of which depend on sediment residence time within the fluvial system. Combined with suspended sediment data from rivers throughout New Zealand, these findings suggest that HSI fluvial sedimentary evolution is dominated by physical weathering processes and that several cycles of sedimentary recycling may occur without production of a silicate chemical weathering signature.

Impact of storm runoff from subtropical watersheds on coastal water quality and productivity

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Runoff from storms occurring in subtropical watersheds in Hawaii leads to sediment and freshwater pulses to coastal waters that rapidly affect water quality. This is particularly true in semi-enclosed embayments with relatively long residence times. The response of coastal waters to such inputs has often been evaluated by synoptic sampling that only provides snapshots of the evolution of these highly dynamic environments. In contrast, continuous in-situ measurements, when combined with synoptic sampling, are better able to reflect the short-term biogeochemical response of these systems. Our approach facilitates the characterization of impacts of storm runoff from watersheds on coastal waters and is better suited to evaluating overall ecosystem responses over extended periods of time following storm events.

In this presentation we discuss data from several extreme rain events during the winter seasons of 2003-2004 and 2004-2005 acquired by our Coral Reef Instrumented Monitoring Platform (CRIMP). We discuss the response of Kaneohe Bay to storm sediment and nutrient inputs, the relationships between physical, biological, and chemical processes in the watershed and the bay, and the evolution of the aquatic community structure during and following phytoplankton blooms.

Elevated DIN:DIP (25) in storm runoff changes significantly the proportion of dissolved nutrients available for biological uptake. Increases in Chl-a in the bay shortly after storms and changes in the plankton community structure reflect an evolving biological response stimulated by the inputs of excess nutrients.

An approach to interpreting contaminant deposition fluxes from dated sediment cores

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Background

Detailed interpretation of trends in particle-associated contaminant fluxes to sediment often requires modeling to resolve the effects of drainage basin holdup and post-depositional mixing. Modeling is especially necessary for constraining flux estimates for atmospherically deposited contaminants. We apply simple models of drainage basin holdup and post-depositional mixing to the interpretation of ¹³⁷Cs and other tracer profiles in dated cores collected from lakes and reservoirs in New York State.

Discussion of results

Dated cores collected from two New York City drinking water reservoirs are well described by a 3–4 year half-time of delayed delivery followed by simple, complete mixing of sediments to a fixed depth. Model results for the reservoir cores are consistent with delayed delivery of atmospheric ¹³⁷Cs indicated by historical measurements in reservoir-derived tapwater.

Modeling of a core collected from Central Park Lake, Manhattan, suggests that a substantial portion (ca. 40–85%) of recent contaminant flux is due to indirect inputs from the drainage basin, and cannot be attributed to direct atmospheric input.

Conclusions

A small set of simple models constrained by geochemical tracers can comprise a workable approach to the interpretation of local and regional atmospheric contaminant depositional fluxes from well-dated sediment cores. This is in contrast to recent efforts to model less-ideal cores using models which are markedly more complex and less constrained by geochemical evidence.

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Factors controlling tufa deposition at waterfall sites

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Study on calcite precipitation has major implications for both the hydrochemical evolution of river systems and the global carbon cycle. The precipitation of calcite generally requires the water to be 5 to 10 times supersaturation with respect to calcite, which is usually achieved by the removal of CO₂. Formation of waterfall tufa has been often simply described as the result of water turbulence in fast-flowing water. In this paper, the formation mechanisms of waterfall tufa are discussed and a series of laboratory experiments are designed to simulate the hydrological conditions at waterfall sites. The influences of the air-water interface, the water flow velocity and the solid-water interface on CO₂ outgassing and calcite precipitation are compared and evaluated quantitatively. The results show that the principal cause of waterfall tufa formation is the enhanced inorganic carbon dioxide outgassing resulted from the sudden hydrological changes occurring at waterfall sites, rather than organisms, evaporation or the solid-water interface. The air-water interface area and the water flow velocity are greatly increased at waterfall sites as a result of the “aeration effect”, “low pressure effect” and “jet-flow effect”, which greatly accelerate CO₂ outgassing. Inorganic CO₂ outgassing drives the waters to become highly supersaturated with respect to calcite, and consequently results in much calcite deposition. The solid-water interface is less important as the air-water interface in affecting calcite precipitation at waterfall sites. Field measurements showed that conductivity, Ca²⁺ and HCO₃⁻ concentrations along Tianhe Creek and Hot Creek decrease downstream while pH rises. Field observations also showed that tufa deposition occurred mainly at waterfall sites.

Soil contamination of heavy metals in Katedan industrial area, Hyderabad, Andhra Pradesh, India

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Studies on quantitative soil contamination due to heavy metals were carried out in Katedan Industrial Development Area, south of Hyderabad, Andhra Pradesh, India under the Indo-Norwegian Institutional Cooperation Programme. The geology of the study area consists of granites and pegmatite of Archaean age with residual soil from granite. The area falls under a semi-arid type of climate with average rainfall of 800 mm per year. The industrial area is having about 325 industries manufacturing batteries, chemicals and dealing with cloth dying, metal plating and edible oil production. Many industries discharge their effluents either on the open land, ditches or creeks. Solid waste from some of the industries is randomly dumped along roads contaminating the soil and water in the area.

Soil samples were collected during two hydrological cycles and were analyzed for major, minor and trace elements by XRF spectrometry. Comparing the results with the Soil Quality Guidelines (SQGL), it was observed that almost whole of the industrial area is heavily contaminated by high concentrations of lead, arsenic, chromium, copper, nickel and zinc. By and large, the residential area is not heavily contaminated except some of the pockets where high concentrations of Pb, As and Cr are observed. The pre and post monsoon studies indicate that As, Cd and Pb contaminants are more mobile and may reach the groundwater while the other contaminants seem to be more stable. The source of high concentrations of heavy metals like Cr, Cu, Pb etc seem to be anthropogenic and it is not possible to derive these concentrations from surrounding rocks which are predominantly granite.

Correlation diagram were plotted to find out the relationship between various trace metals. There is a well-defined relationship between As vs. Pb with extraordinary linear correlation.

Studies were carried out on surface water samples also, which indicate high concentration of toxic elements. Geochemical maps showing the distribution of many metals are prepared for the whole area and results will be presented in this paper.

Measurements of oxygen and hydrogen isotopes in the Skagway River catchment, Alaska

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This work investigated the seasonal variations in oxygen and hydrogen isotopes in the Skagway River, a medium-sized catchment (375 km²) fed by moderately high precipitation and glacial meltwater. Nearly weekly samples of river flow were gathered from August 2000 through November 2001 and again in the summers of 2002 and 2003. During the summer periods, samples of glacier ice, precipitation, and groundwater were also collected.

Riverwater showed the most depleted $\delta^{18}\text{O}$ near the river's mouth in early summer. Similar values were found in meltwaters sampled at the toe of Laughton Glacier. The precipitation samples were gathered from three sites of varying elevations: at sea level, at 825 meters, and at 1025 meters near the valley summit. The $\delta^{18}\text{O}$ values ranged from -8.2 ‰ at the lowest elevation site to -20.3 ‰ at the highest. Measured groundwater $\delta^{18}\text{O}$ value was -17.3 ‰, and the mean for surface glacier ice was -17.5 ‰.

The fractional components of water sources in the river were determined by using mass balance and by establishing isotopically derived endmembers of river baseflow and glacial meltwater. The baseflow $\delta^{18}\text{O}$ was computed from groundwater values taken by sampling a nearby well. Glacial runoff, measured in late June and early July at the toe of Laughton Glacier, yielded a mean meltwater value for $\delta^{18}\text{O}$ of -19.7 ‰. Rainfall contributions to the river have greatest influence in the fall, the typically rainy season, and during winter storms when temperatures are above freezing to allow for isotopically heavier rain, rather than snow, to fall. During these occasions, the riverwater may exhibit an isotopic signature more enriched than the groundwater endmember.

The δD values for a few of the river samples ranged from -125 ‰ to -137 ‰. A plot of these results and their corresponding $\delta^{18}\text{O}$ values, $\delta\text{D} = 7.7 \delta^{18}\text{O} + 4.9$ with $R^2 = 0.97$, shows a good fit with Craig's meteoric water line.

A 4 ‰ shift in $\delta^{18}\text{O}$ to more negative values occurred around mid-May. This shift corresponds with atmospheric temperature increases that result in lower $\delta^{18}\text{O}$ and δD from upper elevation snowpack and glacial melt becoming the major contributor to runoff. Isotopic analysis determined that up to 87 % of water in the riverbed during June is derived from glacial melt.

Riverine particulate organic carbon from the western Southern Alps, New Zealand

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The flux of particulate organic carbon (POC) from small mountainous rivers draining active orogens accounts for a large proportion of the global riverine POC flux [1]. Their importance in atmosphere-ocean carbon dynamics may be disproportionately large due to their high-sediment production, small storage potential and tendency to discharge sediment at extremely high concentrations [2]. It is therefore important to constrain the type and amount of carbon mobilised.

Suspended load, bedload and sediment samples from landslide debris fans were taken from catchments draining the rapidly eroding, densely vegetated western Southern Alps, New Zealand. The samples allow estimates of the POC yield and determination of the main sources of organic carbon (C_{org}) using C/N as a mixing proxy.

POC yield estimates range from $280\text{--}4600 \times 10^6 \text{ mol.yr}^{-1}$ – which are high globally and similar to previous estimates [1]. C_{org} decreases with increased suspended sediment concentration (SSC). At mean annual SSC C_{org} concentration $\sim 0.4\%$ and C/N ~ 13.5 , which is characteristic of the clay/silt fraction measured in landslide deposits. This may be the main POC source during mean flow and is related to breakdown and re-sorption of non-kerogen carbon onto mineral grains during soil processes (c.f. [3]). During higher flow events, when these rivers may transport the majority of their POC yields to the ocean, the source of carbon (and its C/N) may be significantly different.

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Geochemical evolution of Pleistocene glacial meltwaters within regional carbonate aquifer systems, Midcontinent, U.S.

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Pleistocene glacial meltwaters recharged regional aquifer systems along the margins of the Illinois, Michigan, and Appalachian basins, significantly suppressing freshwater-saline water mixing zones to great depths and reorganizing drinking water resources. Importantly, dilute water recharge into Silurian-Devonian carbonate aquifers migrated into overlying fractured, organic-rich shales and generated economic deposits of microbial gas. New elemental and isotope analyses of Sil.-Dev. groundwaters and overlying glacial drift, along the margins of the three basins, were integrated with previously published data on basinal fluids to investigate the impact of Pleistocene glaciation on regional-scale groundwater flow and geochemical evolution of glacial meltwaters within confined aquifers.

Groundwaters in the recharge areas of the glacial drift and carbonate aquifers are predominately Ca-Mg-HCO₃ waters with $\delta^{18}\text{O}$ and δD values within the range of modern precipitation (-11.0 to -4.5%), and have $\delta^{13}\text{C}$ values of DIC consistent with open system carbonate mineral dissolution ($\sim -12.5\%$). Groundwaters in confined aquifers, beneath lake-bed clays and Upper Dev. black shales, have relatively low $\delta^{18}\text{O}$ and δD values (-18 to -11%), within the estimated range of Pleistocene glacial meltwater (-25 to -11%), and have low activities of ^{14}C ($<8\text{pmc}$). Since the Late Pleistocene, these glacial meltwaters have been extensively altered by water-rock interactions, biogeochemical processes, and mixing with Na-Ca-Cl brines. Confined groundwaters have high $\delta^{13}\text{C}_{\text{DIC}}$ values (-10 to -2%), and elevated Sr/Ca and Mg/Ca ratios, indicating they evolved via incongruent dissolution of carbonate minerals and anhydrite under closed system conditions. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{34}\text{S}_{\text{SO}_4}$ values are within the range of Sil.-Dev. carbonates and evaporites. Glacial meltwaters have been preserved at relatively shallow depths along the basin margins and have not been flushed out by more recent recharge, illustrating the importance of ice-induced hydraulic loading on deep circulation of meteoric waters, and the relatively long residence times of drinking water resources.

High concentrations of uranium and thorium in residual soils of Wailpalli watershed, Nalgonda district, Andhra Pradesh, India

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Environmental studies were carried out in Wailpalli watershed of Nalgonda district to find out the radiogenic elemental concentrations in soils and rocks of the area. The geology of the area comprises of Granites ranging from granodiorite to Granite, mafic dolerite dykes and pegmatite veins. These granites are of 2400 million years of age, they belong to Hyderabad granites. The granites contain quartz, orthoclase, microcline, hornblende etc., as major mineral phases and the accessory minerals are magnetite, zircon, allanite, fluorapatite and epidote etc. The concentration of radioactive elements is dependent on the presence of some of the above accessory phases.

Wailpalli watershed is located in between the latitudes 17°20'' to 17°80'', longitudes 78°48'' to 79°00'' comprising an area of 150 sq.km. Granite exposures are mostly found in western part of watershed. 600 soil samples and 195 fresh granite samples were collected covering the entire watershed and were analysed for their U & Th content by X-ray fluorescence spectrometer. The analytical data show very high concentration of U and Th. 85% of the soil samples and 80% of the rock samples show uranium above normal levels of 1 to 4.5 ppm (in residual soils and granites IAEA, 1988) and 85% of thorium concentrations in rock and soil are above the normal levels of 1 to 15 ppm (in residual soils and granites). The results demonstrate the high concentrations of U & Th in the residual soils, which are derived geogenically from the granitic rocks. Most of the area in Wailpalli watershed is under active irrigation and these radioactive elements may enter the food chain of the human beings and may be hazardous to human health.

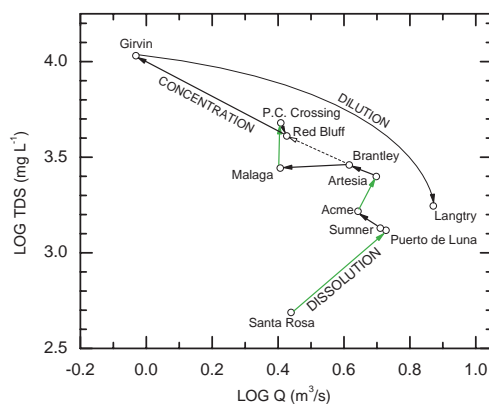
Identifying sources of total dissolved solids (TDS) in the Pecos River, USA

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The Pecos is one saline river in the desert southwest. The causes of the high salinity ($>10000 \text{ mg L}^{-1}$) need to be determined. Analysis of hydrological and chemical variables indicates that relationship between ion flux (L_i) and stream discharge (Q) can be best described by a log-linear function, $\log L_i = a + b \log Q$ (YUAN and MIYAMOTO, 2004). Here we use the USGS daily flow and major ion concentration records from 11 gauging stations along the river spanning 1959-2002 to estimate mean TDS load and therefore TDS concentration (Figure 1). The stream discharge is an arithmetic average of continuous daily flow, whilst the TDS is a weighted average of inferred daily TDS. Flowpath from the upper basin downward is indicated by solid arrows. This analysis suggests that the TDS of the Pecos is controlled by salt pick-up or dissolution, evaporative concentration and / or crystallization, and dilution. Salt dissolution occurs mainly in the upper basin, whereas the dilution occurs in the lower end of the basin. The evaporative concentration is the dominant process for the increasing TDS in the middle portion of the basin. River water seeps into underground between Brantley and Malaga and back to surface between Malaga and Pierce Canyon Crossing. The losses of flow and salts upstream are offset by the gains downstream in a long run (i.e., 44 years).

Figure 1 Logarithmic graph of stream discharge (Q) vs. TDS.



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