

River Chemistry as a Monitor of Yosemite Park Mountain Hydroclimates

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High-frequency, high-altitude measurements of water chemistry provide insights into processes relating to the hydrology, climate, and geochemistry of mountain catchments. When such observations are combined with stream stage, temperature, snow, weather, and other surface hydroclimate measurements, they are particularly useful in allowing connections between climate, river discharge, river chemistry, and ecosystems to be discerned.

Climate is the major source of variability in U.S. and global water resources. For example, large-scale variations in the global atmosphere and the Pacific Ocean are responsible for much of the variability in river discharge in Hawaii, Alaska, the U.S. Pacific Northwest, and the U.S. Southwest [Cayan and Peterson, 1989], and thus are closely linked to water and energy resources of the western United States [Cayan *et al.*, 2003].

Long-term observations to define these connections are limited at alpine elevations above 1,200–1,500 meters, partly because the observations are difficult to make, even though much of the water for lower elevation human needs is delivered (as snow) to the high elevations. A hydroclimate monitoring network in Yosemite National Park in the Sierra Nevada of California was started in 2000 to complement monitoring efforts in other parts of the Sierra Nevada and to better understand watershed responses to atmospheric forcing [DiLeo *et al.*, 2004].

Hydroclimate linkages are known from long-term stream gauge and meteorological observations, but these observations are largely from settings below 1,500 meters, and generally are not informed by river chemistry information. A first goal of the Yosemite monitoring network was to determine the degree of the association between these continuing, long-term observations and observations of stream water chemistry in natural, unmanaged watersheds.

This was accomplished by monitoring river chemistry with continuous sensors at some of the long-term observation sites.

Examples of river conductivity, nitrate, and dissolved silica, and watershed primary production are shown to illustrate how river chemistry and remotely sensed observations may be used to augment the information provided by conventional hydrological and meteorological observations.

Monitoring Results: The Value of Multiple Observations

Hydroclimatic Variability. Key monitoring stations of the Yosemite hydroclimate monitoring network (note that there are several other instruments in Yosemite as well) are shown in Figure 1a. Geochemists recognize the importance of both geology and climate in alpine river chemistry research. In the impervious granitic watersheds of Central Sierra Nevada, geology (soil thickness) perhaps discerns hydrologic differences in alpine watersheds better than climate, and climate (large-scale snowpack and air temperature) defines hydrologic similarities in alpine watersheds better than geology. Thus, both lines of research are essential.

This study, as part of a hydroclimate network, is starting with the climate connections to river chemistry. For this reason, it is important to sample the variables at the same rates, which is unusual.

Examples of linkages in snow water content, air and water temperatures, river discharge, conductivity (a measure of total dissolved solids), nitrate, and dissolved silica concentrations are shown for 2003, a year with a strong peak in both snow melt discharge and rain events. Figures 1b–1h illustrate covariations between the stream chemistry and traditional hydrologic measures on hourly, daily, and longer timescales during spring and summer, when the system is undergoing large diurnal and seasonal changes. The steep decline in daily snow water equivalents (the depth of liquid water that is obtained when the snowpack is melted) is in response to the steep rise in daily air temperatures in mid-April, which in

turn generates a rise in daily discharge with increasing amplitudes of the hourly snow melt discharge (SMD) deviations.

Conductivity. In the Yosemite's Merced River at Happy Isles, conductivity varies inversely as river discharge (i.e., as river discharge increases, or as time per unit discharge decreases, conductivity decreases), until river conductivity approaches the conductivity of melted snow ($<10 \mu\text{S cm}^{-1}$), in mid-June (Figure 2a). By the time the lowest conductivities are achieved (Figure 2b), soil salts have been well flushed from the watershed above the gage. This relatively complete flushing within a span of a few months is possible because the soils above the gage were severely thinned and cleaned out by the most recent Pleistocene glaciation that ended about 10,000 years ago.

Rain Pulse Response. High-resolution sampling captures the Merced River's chemical response to rain. Dissolved silica concentrations roughly follow conductivity variations during SMD and the dry seasons, as the source of conductivity and dissolved silica is from dissolution (weathering) of soil. However, although the lowest riverine conductivity values are similar to snowmelt, correspondingly low concentrations of dissolved silica [Brown and Skau, 1975] are never observed. This is probably because when the soil salts are flushed from the watershed, the flushing flows are in contact with silica including silicates, a major component of the soil and river sediment.

Nitrate chemistry is different from dissolved silica and conductivity in that the atmosphere is the major source of nitrogen. Thus, a summer storm (circle insets in Figures 1e–1g) produced a decrease (dilution response) in conductivity and dissolved silica and an increase in nitrate concentrations. Mechanisms for the increase of nitrate include nitrification by lightning and wash-off of atmospheric deposition and mineralized organic matter from the dry summer landscape and soils.

Chemical Signatures of Runoff From Snowmelt Versus Soil Water. The Merced River at Happy Isles and the Stanislaus River at Clark Fork (in the neighboring basin north of the Tuolumne River) have similar runoff rates (river discharge per unit area) and climate-driven daily and hourly SMD variations. However, the two watersheds differ geologically, with sparse soil in the Merced (low mean soil thickness) compared with the Stanislaus (high mean soil thickness). The difference is that while all of the glaciations, including the most recent, "cleaned out" the Merced above the gage, the watershed above Clark Fork, on the Stanislaus, was not

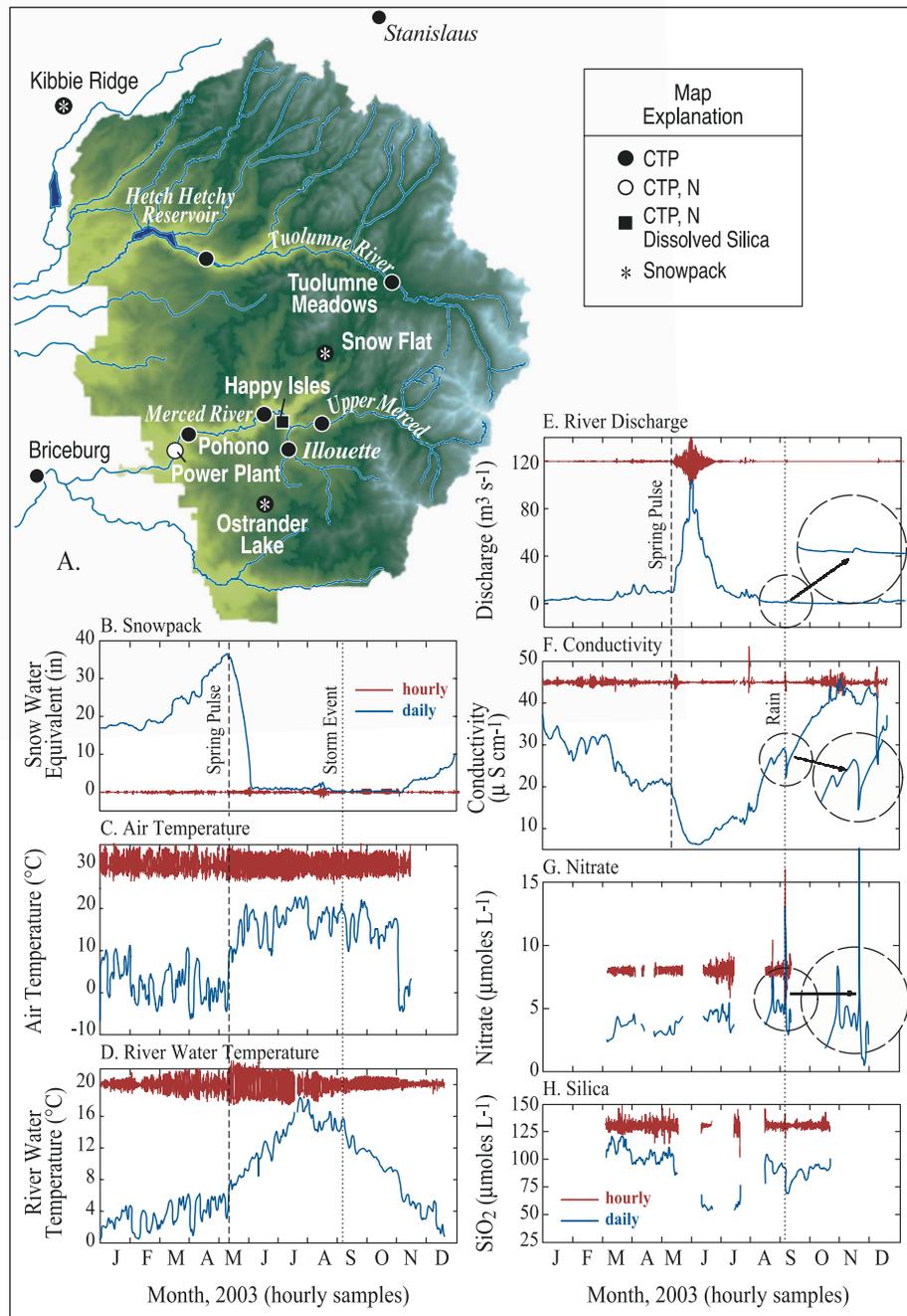


Fig. 1. Examples of the monitoring results for 2003: (a) instrument locations within and near Yosemite National Park for the data presented; (b) snowpack at Ostrander Lake; (c) air temperature at Kibbie Ridge; (d) Merced River water temperature at Happy Isles; (e–h) Merced River discharge at Happy Isles, conductivity, nitrate, and dissolved silica, respectively. The hourly deviations (red) from the daily mean (blue) vary around zero and may be offset to avoid overlap. Note the transition associated with the spring pulse and the fall rainstorm response.

glaciated in the most recent glaciation.

In early spring 2001, the phase of the diurnal cycle of conductivities in the Merced shifted from peaking after to peaking before the diurnal river discharge. In the Stanislaus, the same conductivity shift happened, but much later in the season, at higher levels of discharge, and only briefly. This difference is thought to be related to a more complete flushing of soil water and salts in the Merced than in the Stanislaus.

A simple two-component (snow and soil water) mixing model was applied to flow and conductivity observations on the two rivers

to help understand this difference [Peterson *et al.*, 2004]. The mixing model suggests that the observed conductivity phase transition over a five-day period can be explained by an increase in the fraction of snow water in the river compared with that of soil water, early in the spring in the Merced and later in the Stanislaus. Thus, the difference in timing was because the Stanislaus requires much higher snowmelt flows to dilute the greater fraction and salinity of soil water. A repeat of this phase transition is illustrated here (Figures 2c and 2d) for the Merced River at Happy Isles in 2003.

Remote Sensing

Remote sensing supports studies of the alpine nitrogen sources and sinks. From in situ surface samples, atmospheric input of nitrogen (nitrate + ammonium) is estimated at 2 kg N ha⁻¹ yr⁻¹ (averaged over 1984–2000 [Clow *et al.*, 2003]), while from stream sensors, the river output or flux of nitrogen (nitrate) at Happy Isles is estimated at only 0.2 kg N ha⁻¹ yr⁻¹ (averaged over 2000–2003). Using the products from the Moderate-Resolution Imaging Spectroradiometer (MODIS) instrument onboard NASA's Terra

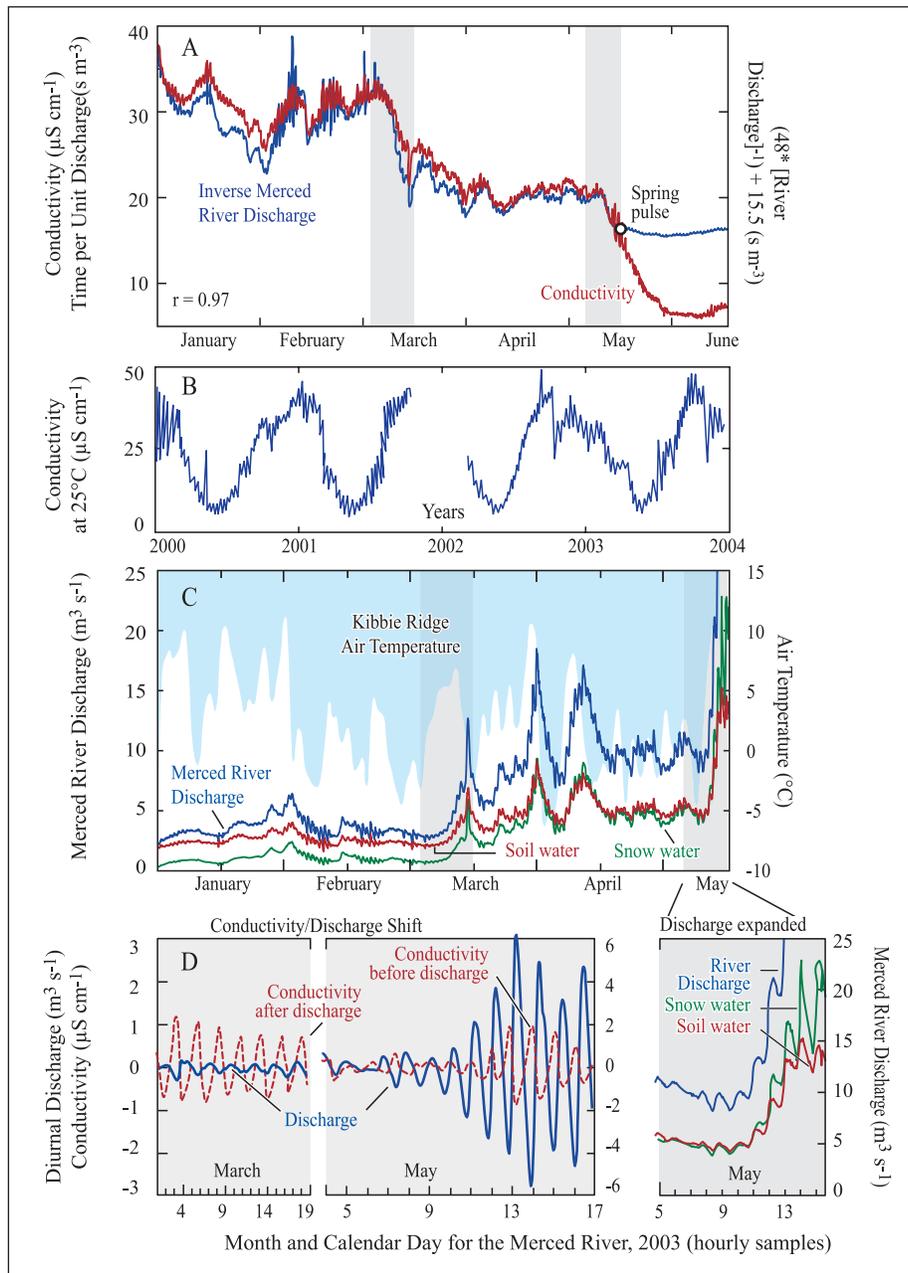


Fig. 2. Merced River discharge and conductivity at Happy Isles, 2003: (a) conductivity and the scaled inverse of water discharge; (b) annual cycles of conductivity, Merced River at Happy Isles, 2000–2004; (c) Kibbie Ridge air temperature and Merced River discharge with snow water and soil water estimated from a simple conductivity mixing model; (d, left) blowup of observed conductivity phasing when soil water discharge is greater than snow water discharge, (d, middle) blowup of transition when observed conductivity phasing changes from after to before discharge, and (d, right) blowup of the estimated soil and snow water during the phase transition.

satellite, it has been found that net primary production is $3000 \text{ kg C ha}^{-1} \text{ yr}^{-1}$ (averaged over the watershed for 2000–2003, approximately $20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$).

Because the river flux output is small compared with the atmospheric input, it can be concluded that the system is undersaturated with nitrogen and that the atmospheric nitrogen is recycled and transformed by biotic processes. Further, remotely sensed estimates of daily gross primary productivity above Happy Isles decreased from 3100 to $2700 \text{ kg ha}^{-1} \text{ yr}^{-1}$ from 2002 to 2003; and from the stream sensor at Happy Isles, the nitrate flux increased from 0.2 to $0.4 \text{ kg N ha}^{-1} \text{ yr}^{-1}$. These differences were

probably due to the earlier snowmelt/greening (longer growing season) in 2002 compared with 2003 (Figure 3).

Alpine Hydroclimatology Research

A framework that links atmosphere, river discharge, river chemistry, ecosystems, and geology is helpful because of the large-scale influences that affect alpine hydrologic and chemical variability. Accounting for these largescale climate variations, and also regional ecosystem processes, is not only crucial to understanding local stream chemistry, but also simplifies the understanding of how water chemistry varies over a family of regional watersheds. Traditional alpine

hydroclimate variables, such as air temperature, snowpack, and river discharge, have long observational records, which can be used to interpret a much more limited set of observations of river, soil, and groundwater chemistry.

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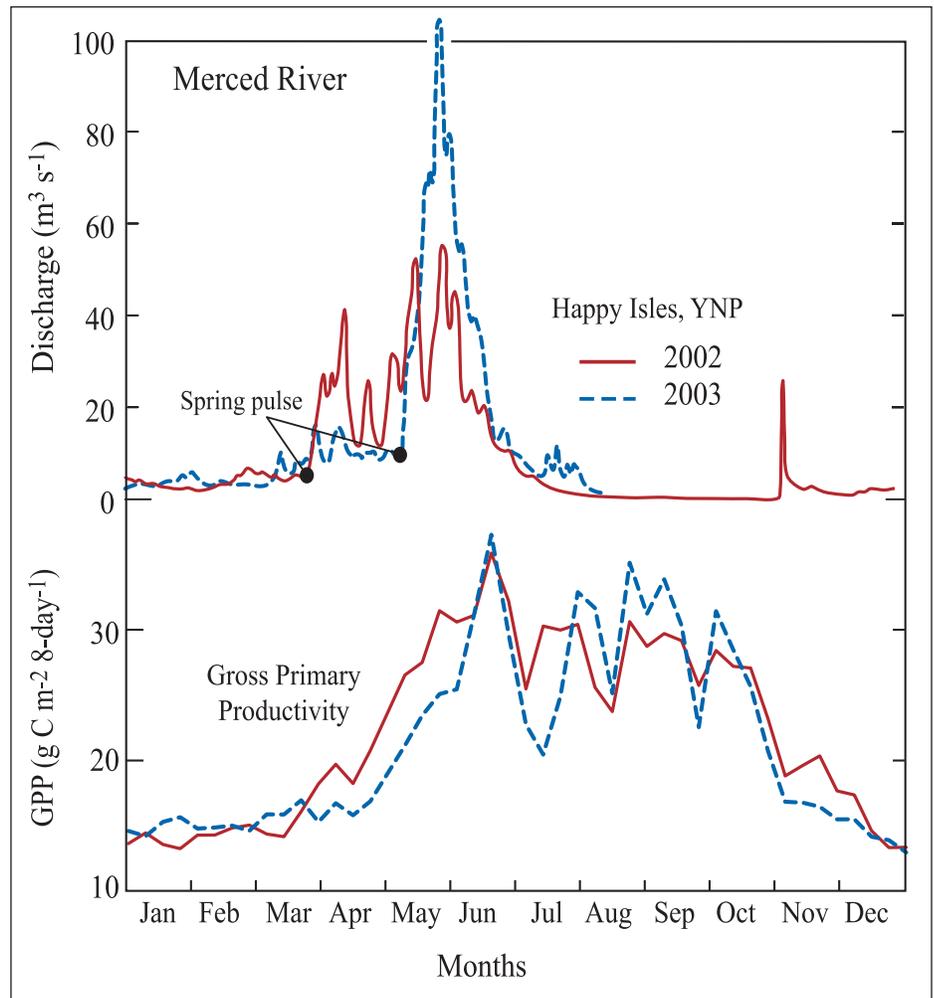


Fig. 3. Merced River discharge at Happy Isles 2002 (warm spring) and 2003 (cool spring) and MODIS-derived gross primary production for the same years.

NEWS

Experiment To Characterize Tropical Cloud Systems

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A major experiment to study tropical convective cloud systems and their impacts will take place around Darwin, northern Australia, in January and February 2006. The Tropical Warm Pool International Cloud Experiment (TWP-ICE) aims to study cloud systems and their radiative, chemical, and moisture budget impacts from the initial convection through to the decaying, convectively generated cirrus.

This broad aim is being addressed by a dense observational network that includes two sites equipped with cloud radar and lidar, a polarimetric (dual-polarization) weather radar and another operational Doppler radar in the area, wind profilers, infrared interferometers, flux stations, lightning interferometers, and oceanographic measurements. Also, an array of

five radiosonde sites arranged in a ring with a diameter of about 250 km around Darwin will conduct soundings every three hours for a period of 24 days.

In addition, a fleet of aircraft includes high-altitude aircraft for in situ cloud and chemistry sampling, aircraft for remote sensing (cloud radar, lidar, radiometry, and infrared interferometry), and an atmospheric boundary layer aircraft (Table 1). Crucial satellite data will also be gathered. The experiment design ensures that not only will an outstanding data set for cloud properties be collected, but also that this data set can be placed in a synoptic and global context with the radar and satellite coverage, soundings, and numerical weather prediction so that the results gathered here can be applied globally. Also, the data set should be ideal for heating, water, and momentum budget

studies, i.e., the impact of the convection in the area, and for providing the boundary conditions for modeling activities ranging from climate models to weather prediction, cloud resolving, and single-column models.

TWP-ICE is a collaboration of the U.S. Department of Energy's (DOE) Atmospheric Radiation Measurement (ARM) Program and the ARM-Unmanned Aerospace Vehicle (UAV) Program, NASA centers, the Australian Bureau of Meteorology, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Airborne Research Australia (ARA), and universities in Australia, Canada, Japan, the United Kingdom, and the United States. Detailed atmospheric measurements will be made through the austral summer, providing unprecedented coverage through the pre-monsoon and monsoon periods.

The timing of the experiment corresponds with the maximum in monsoonal rainfall across northern Australia. However, the large intra-seasonal variability in the region makes it likely that oceanic monsoon systems as well as continental "break" storms will be sampled.

Some of the specific science questions that will be addressed include:

- How do the cirrus microphysical characteristics vary with convective intensity and evolve as the clouds age?