Temporal dynamics of stream water chemistry in the last free-flowing river draining the Sierra Nevada, California

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Abstract

Temporal patterns of stream water chemistry were analyzed across the Cosumnes River Watershed (1989 km²) from 1998-2002 to quantify hydrobiogeochemical dynamics in the last free-flowing watershed draining the western Sierra Nevada, California. The Mediterranean climate of California produces a distinct annual hydrologic pattern with three water quality seasons: baseflow, stormflow, and meltflow. The baseflow season (July – October) is dominated by groundwater chemistry that primarily originates from high elevations, and thus does not vary much across the basin. During the baseflow season discharge is negatively correlated to ionic concentration, and sediment and nutrients are generally below detection levels. The stormflow season (November – March) is separated into a flushing period (where discharge is positively correlated to river water conductivity) and a dilution period (where discharge is negatively correlated to conductivity). During average flow years, virtually the entire annual load of nutrients and sediment moves through the watershed during the stormflow season. Because stormflow hydrologically links the land with local waterways, the stormflow season shows the greatest variance among sites across the diverse landscape of the Cosumnes Watershed. Chemistry of the meltflow season (April – June) is dominated by dilute upland snowmelt, and there is little chemical variation across the watershed. Storm-scale analysis in 2001-'02 revealed that progressive flushing occurs with each storm event and that source area dynamics play an important role in chemograph response. With 19 of the 20 major rivers in the western Sierra Nevada having dams, this data set can be used by scientists and regulators as a reference to address how impoundment affects water quality.

Keywords: Water quality; Biogeochemistry; Dams; Impoundments; Cosumnes River; California;

Introduction

The Cosumnes River is the last free-flowing river draining the western Sierra Nevada, CA. Consequently, we are provided with a unique opportunity to establish the baseline water quality characteristics of an unimpounded watershed, which has numerous analogues for paired basin analysis. It is known that flow regulation by dams can greatly alter seasonal fluctuations in stream temperature (Webb and Walling, 1993a; Webb and Walling, 1996; Webb and Walling, 1997), solute chemistry (Kelly, 2001), and sediment transport (Morris and Fan, 1998). These alterations to streamflow and chemistry have frequently had deleterious effects on trophic structure and function (Cortes et al., 1998; Petts et al., 1993; Webb and Walling, 1993b). To gain a better understanding of anthropogenic impacts on the waterways of the western Sierra Nevada, it is necessary to first elucidate the characteristics of hydrochemical variability within the Cosumnes Watershed, using the system as a reference for “naturally” flowing systems.

Temporal variability in stream chemistry is controlled by a number of factors. Traditionally stream discharge was considered the master variable controlling hydrochemistry (Durum, 1953; Hem, 1948), but more recent studies have shown complex relations between discharge and stream chemistry. A study of four Norfolk, England
rivers found nitrate and sulfate concentrations to be positively correlated to discharge while other solutes where either uncorrelated or negatively correlated to discharge (Edwards, 1973). In a study of a large minimally impacted watershed in British Columbia, nitrate was the only ion positively correlated with discharge, while all other constituents, including sulfate, were diluted by increased flows (Cameron, 1996). In contrast, research at Walker Branch, TN found that nitrate concentrations were inversely related to discharge (Mulholland, 1992). Such variable results as these illustrate the need for more complex models to describe temporal variations in water quality. Other than stream discharge, water quality drivers may include nutrient cycling/retention (Soulsby et al., 2002), preferential flow (Mulholland et al., 1990), and source area dynamics (Harriman et al., 1990).

Hydrologic flowpath may be the dominant control on stream water chemistry (Harriman et al., 1990; Hill, 1993). In the Mediterranean climate of Spain, chemical variations in the waterways of the La Castanya Biological Station are controlled by soil solution chemistry during high flows, and groundwater chemistry during low flows (Avila et al., 1995). This indicates that the majority of storm flow is derived from interflow through the soil zone, while the majority of baseflow is derived from groundwater flowpaths. Findings such as these have lead to the widespread use of end-member mixing models to identify sources of streamwater in maritime (Christophersen and Neal, 1990; Creed et al., 1996) and temperate climates (Mulholland et al., 1990). Small catchment studies in the Mokelumne Watershed (adjacent to the Cosumnes) have used end-member sourcing and solute accumulation in the upper soil horizons to explain extraordinary nutrient spiking with the onset of the first winter rains (Holloway and Dahlgren, 2001; Holloway et al., 1998). In these instances, the hydrologic flowpath may be equal in importance to the amount of water in regulating stream water chemistry (Creed and Band, 1998).

Because of their small scale, process-based studies in headwater catchments are able to identify the biogeochemical drivers that dictate the water chemistry of streams. Yet such spatially concentrated studies are limited in their capacity to scale up to regional patterns in water quality. Scaling results from small watersheds to larger watersheds often proves difficult as complexities arise from the inevitable variations in climate, geology/geography, land use, and land cover. Consequently, there exists a need for the analysis of large minimally-impacted watersheds, which play an intermediary role in the linkage between the hydrobiogeochemical dynamics of headwater streams and regional river networks. It is the purpose of this paper to describe the temporal variations in stream chemistry of the Cosumnes Watershed with implications for inter- and intra-basin management. Annual, seasonal, and storm-event hydrochemistry were analyzed at multiple sites throughout the watershed in an effort to further define criteria for best management practices in the western Sierra Nevada. In particular, the data provide valuable information for developing effective water quality monitoring protocols to address nonpoint source constituents (e.g. total maximum daily loads – TMDL’s). These data are especially important for use in comparison to rivers with dams/reservoirs where overall water quality and temporal variations in water quantity and quality have been altered by impoundment.
The Study Area

The Cosumnes River Watershed, located southeast of Sacramento, CA encompasses 1989 km² of terrain and 2101 km of waterways (Fig. 1). The headwaters emerge at an elevation of 2200 m in a subalpine ecosystem underlain by granitic bedrock. The human population is sparse in the uplands and some logging of the coniferous forest is the only significant land use. The middle reaches of the Cosumnes River wind their way through oak woodland habitat developed on metamorphic bedrock dominated by schists and shales. These intermediate elevations are less rural with the dominant land uses being cattle grazing and viticulture. Valley sediments and annual grasslands dominate the lower Cosumnes Watershed as the river descends to its confluence with the Mokelumne River and the important aquatic habitat of the Bay-Delta ecosystem. Land use in the lower reaches is dominated by production agriculture (e.g., row crops and viticulture) with some suburbanization (Fig 2a, b).

In the Mediterranean climate of central California there is a strong seasonal cycle with virtually all of the annual precipitation occurring between December and March. Average precipitation in the upper watershed is 804 mm y⁻¹ while approximately 445 mm y⁻¹ fall in the lowlands. The Cosumnes River, as gauged at Michigan Bar (Fig. 1), has a long-term (1907-2002) mean daily discharge of 510 cfs (http://cdec.water.ca.gov/cgi-progs/queryLonger?989). This study included two dry (2000-'01, 2001-'02) and two wet (1998-'99, 1999-'00) water years. Because the headwaters extend only to 2200 m, the Cosumnes Watershed receives less precipitation as snow than do its neighboring watersheds.

Water sampling stations were located at 28 sites throughout the Cosumnes River Watershed. This study focuses on five representative sites from the mainstem of the Cosumnes (Fig. 1). The sites, from high elevation to low, are: Middle Fork Cosumnes at E6 (1173 m), Middle Fork Cosumnes at E16 (512m), Cosumnes at Hwy 49 (239 m), Cosumnes at Michigan Bar (52 m), and Cosumnes at Twin Cities (4 m). By selecting these sites along an elevational transect of the basin, temporal variation in water quality parameters can be examined from a spatial perspective.

Methods

Grab samples were collected from 28 sites every 2 weeks from October 1998 to September 2002. In California, the water year is defined as October 1 through September 30 to coincide with the onset of the rainy season in late-October to early-November. During the 2000-'01 and 2001-'02 water years, additional storm samples were collected whenever flows exceeded 1000 cfs at the Michigan Bar Gauging station (Fig. 1). The sampling design resulted in approximately 37 samples/site/year. A pump autosampler was placed below Twin Cities (the lowest site in the watershed) during the 2000-'01 water year. Between 12 and 24 samples were collected at variable time steps (1 – 2 hr intervals) for all five storms that occurred during this below average precipitation year. Year-round data collection was not possible at the lowest site (Twin Cities) because the river ceased to flow in the summer, likewise the highest site (Middle Fork at E6) was snowed-in during the winter and not accessible. A parallel study encompassing the entire central valley included sample collection at 35 sites along the Sacramento-San Joaquin
river system. Data from the central valley study were used to compare the Cosumnes River to other major rivers flowing from the western Sierra Nevada.

Electrical conductivity (EC), pH, and turbidity were measured on unfiltered subsamples. Total suspended solids (TSS) was measured from a 500 ml sample collected from the thalweg of the river and at approximately the mid-depth of the water column. The 500 ml subsample was filtered through a pre-weighed glass fiber filter, the filter was dried at 60 °C for 24 hours and weighed again, the difference being the mass of sediment in the water sample. A separate 125 ml sample was filtered through a 0.2 µm polycarbonate membrane (Nuclepore) and stored at 4 °C through completion of analysis. Major cations (Ca, Mg, K, Na, NH₄) and anions (Cl, NO₃, PO₄, SO₄) were measured using ion chromatography (Dionex 500x; CS12 cations; AS4A anions). A Dohrmann UV enhanced-persulfate TOC analyzer (Phoenix 8000) was used in the analysis of dissolved organic carbon (DOC). Total phosphorous (TP) was analyzed from a persulfate-digested split of unfiltered sample (Yu et al., 1994), the digested sample was measured with the ammonium molybdate method using a Hitachi U-2000 spectrophotometer (Clesceri et al., 1998). Total nitrogen (TN) was measured on a persulfate-digested split of unfiltered sample on a Carlson autoanalyzer (Carlson, 1978; Carlson, 1986). Finally, chlorophyll-a (CHL) was measured from a separate 2000 ml sample using standard fluorometry techniques (Clesceri et al., 1998).

Results and Discussion

Annual Patterns - Water Quality Seasons

The Mediterranean climate of California contributes to the formation of three distinct water quality seasons within the Cosumnes River Watershed: (1) Baseflow season, where chemistry is controlled by groundwater inflow, (2) Stormflow season, where chemistry is controlled by lateral flow through the landscape via overland flow, interflow, and shallow groundwater routes, and (3) Meltflow season, where the majority of the flow in the stream is derived from melting snow in the uplands. Each of these seasons exhibits a unique and predictable chemistry, thus differentiation among them for scientific and management purposes becomes important. In contrast, watersheds with major dams and reservoirs have their temporal water chemistry patterns buffered by the large volume of water impounded in their reservoirs.

Baseflow Season

The baseflow season at Michigan Bar (the one gauged site in the watershed) was characterized by median flows of 28 cfs between 1998 and 2002. Due to groundwater pumping and multiple diversions for irrigation below Michigan Bar, the river typically dries completely in the lower reaches for 2-4 months each summer. Thus we have limited baseflow data for the lowest elevation site at Twin Cities. Electrical conductivity (EC) reaches a seasonal low at the beginning of the baseflow season as the last snowmelt waters move through the system. This annual minimum is followed by a steady increase in EC until the end of the summer when groundwater is the primary source of
streamwater (Fig. 3). This pattern creates a negative correlation between EC and discharge during this season (Fig 4a, 4b). Median EC values for the baseflow season range from 38.8 µS cm\(^{-1}\) at MF at E6 to 116.6 µS cm\(^{-1}\) at Twin Cities. For all sites, both TSS and NO\(_3\)-N have median values lower than the detectable limit (MDL = 1 mg l\(^{-1}\) and 0.05 mg l\(^{-1}\), respectively) during the baseflow season as flow velocities are low, and nutrient removal by periphyton, phytoplankton, riparian vegetation, and hyporheic denitrification is at a seasonal maximum. Though concentrations of certain constituents may be high during this period (e.g., DOC, CHL, major anions and cations), discharge is low resulting in negligible baseflow fluxes of these constituents (Fig. 5).

**Stormflow Season**

In an average water year the stormflow season is marked by high discharges carrying elevated concentrations of DOC, CHL, TSS, and NO\(_3\) (Fig. 6). The chemistry of stormflows is dependent on the timing of the first large flushing flow(s). In 1998-‘99 and 1999-‘00 there were large flushing storms (above 5000 cfs at Michigan Bar) in late December or early January, storms after these events tended to create a dilution effect (Fig. 3). With records dating back to 1907, these flushing flows arrive in December or early January about 50% of the time, and the remaining 50% of the years experience flushing flows in February or March, if at all (http://cdec.water.ca.gov/cgi-progs/queryLonger?989). As a result, the stormflow season has two distinct chemical patterns: (1) the flushing pattern which occurs before the first large storm(s), when discharge is positively related to solute concentration, and (2) the dilution pattern after the first large storm(s), when discharge is negatively correlated with solute concentrations.

During 1998-‘99 and 1999-‘00, the dilution pattern dominated the stormflow seasons, and dissolved salts were inversely related to discharge (Fig. 4a). The flushing pattern dominated the stormflow season during 2000-‘01 and 2001-‘02, years when flows did not exceed 2700 cfs at Michigan Bar (Fig. 4b), which created a somewhat positive relation between discharge and solute concentration. Median EC values for the storm season (1998-2002) ranged from 39.5 µS cm\(^{-1}\) at MF at E6 to 101.6 µS cm\(^{-1}\) at Twin Cities.

DOC and chlorophyll data were only collected during the two dry years (2000-‘01 and 2001-‘02). As a result it is difficult to fit these constituents into our model for water quality trends during normal flow years. The water stored in upper soil horizons is rich in DOC due to the large amount of organic matter present in these horizons. The elevated DOC levels in streamflow are indicative of the hydrologic flowpath the water took to get to the stream. DOC spiked with each stormflow in 2000-‘01 and 2001-‘02 (Fig. 6) most likely because there was no single storm large enough to flush the upper soil horizons of soluble organics.

Because the Cosumnes is a flow-through system without any significant dams to buffer storm fluxes we saw that, in 1999-‘00, 72.5% of the annual flow moved past Michigan Bar in the months of January and February alone (Table 1a). The major anions and cations follow this same trend with, on average, 75% of the annual flux occurring during January and February. What distinguishes the stormflow season from the others is
the fact that nearly 100% of the annual flux of NO₃ and TSS occurs during these few months (Fig. 5).

Asynchrony within nutrient cycles occurs in California’s Mediterranean climate (Holloway and Dahlgren, 2001). Instead of a continuous nitrogen feedback among senescing plants, their soils, and new growth, nitrogen is mineralized and accumulates in soils during the dry summer and fall months. With the onset of winter rains, water begins to flow through the upper soil horizons, mobilizing the accumulated nitrate and transporting it to the stream channel. Each storm progressively flushes this nitrogen pool so that by March there is little if any nitrogen found in stormflows (Fig 10). When the rains stop and hydrologic flowpaths switch from interflow to groundwater flow this nitrogen pool is no longer leached. Thus, in an average water year, we measure very low nitrate concentrations in streamwater during the meltflow and baseflow seasons.

During the winter, precipitation washes free sediment into local waterways and high-energy channel flows carry this sediment through the system scouring and entraining more sediment along the way. By the end of the stormflow season much of the easily suspendable material within the channel has been moved out of the system. Though the meltflow season has occasional high flow events, they are generally not sufficient to increase levels of suspended sediments.

**Meltflow Season**

The meltflow season is characterized by elevated discharges carrying low concentrations of solutes and suspended materials. Though monthly flow during the meltflow season (median = 3.4 x 10¹⁰ L month⁻¹) was not statistically different from the stormflow season (median = 2.5 x 10¹⁰ L month⁻¹), chemical and particulate loading was, on average, an order of magnitude lower (Fig. 5).

EC was not correlated with discharge during the meltflow season (Fig. 4a, 4b). During the meltflow season, waters from groundwater, surface and subsurface lateral flow, and melt water combine in varying amounts to determine stream water chemistry. Early in the season, snowmelt is the dominant component between storms, surface and subsurface lateral flow is the majority of the flow during storm events, and groundwater contributions dominate late in the melt season. Stormflow chemistry may vary depending upon whether the rain falls on snow or bare ground. As a result, some storms cause an increase in conductivity (rain on soil), while others cause a decrease in conductivity (rain on snow). Additionally, as flow decreases and groundwater inflow begins to dominate, there occurs a marked increase in EC. Because all these factors occur simultaneously and to different degrees during the snowmelt season, there is little correlation between discharge and solute concentrations.

**Inter-annual Patterns - Dry-year vs. Wet-year Chemistry**

During an “average” water year (those years where flushing flows occur during the stormflow season), the timing of flow though the channel and upper soil horizons is very predictable. The amount of flow may vary if there is an especially wet year but the same temporal chemical pattern will result. Similarly, an average versus a heavy
snowpack will not change the chemical patterns we see in the meltflow season; it may change the intensity of late spring rain-on-snow events but the snowmelt will still produce dilute within-channel flows below the snowline. In contrast, during dry years the timing and low volume of precipitation events can delay the flushing of chemical pools in the soil. This delay and related chemical variation alters our temporal model.

An inverse relationship between solute concentration and stream discharge is observed in many watersheds (Edwards, 1973; Melack and Sickman, 1995). Yet for a brief period each year, when rains come after an extended dry season, there is a solute flushing effect (Creed and Band, 1998; Creed et al., 1996; Fenn and Poth, 1999; Muscutt et al., 1990). In the Cosumnes River Watershed this flushing period, when solute concentration is positively correlated with discharge, is often brief and is truncated by a large storm. Apparently, the large storm effectively leaches the solute-rich water from the soil horizons into streams. Subsequent storms then drain through soil horizons that have already had accumulated solutes flushed out, creating a negative relationship between discharge and solute concentration.

In the 2000-'01 and 2001-'02 water years (dry years), the flushing period lasted from November to March (Fig 3). There were no large storms similar to those evidenced in 1998-'99 and 1999-'00; instead numerous small storms only partially leached high-solute waters from soils. These storms were not large enough to appreciably dilute the soil solute pool and instead may have acted to push high solute waters into streams in a piston-flow manner (McGuire et al., 2002). During this extended flushing period, stream water EC reached the highest levels seen in the study (up to 149 \( \mu \text{S cm}^{-1} \) at Twin Cities). Due to this extended flushing period, the water quality characteristics of the stormflow season were dominated by repeated, small flushing events.

In Figs. 4a and 4b conventional discharge-solute regressions are separated into data collected in each of the three water quality seasons. What become apparent are trends within the annual pattern that elucidate the seasonality of stream and solute flow dynamics in the watershed. Comparing Figs. 4a and 4b, it can be seen how the driest years (2000-'01 and 2001-'02) have a slightly positive correlation between discharge and EC for the stormflow seasons, while the average flow years have a negative correlation during this same season. These data clearly show how the numerous small flushing flows that occurred during 2000-'01 and 2001-'02 altered the chemical patterns seen during average flow years.

Nitrate and suspended sediment fluxes during January and February were calculated for both the 1999-'00 and 2000-'01 water years. The results (Tables 2a, b) indicate that although only 72.5% of the annual flow occurred during January and February 2000 (as measured at Michigan Bar), it carried nearly 100% of the annual flux of NO\(_3\)-N and sediment. The last row of Table 2b compares the fluxes seen in the two wettest months of the year for 1999-'00 and 2000-'01. During January and February of 2001 there was 20% as much flow as in 2000, there occurred a proportional reduction in each of the constituents except for sediment and nitrate, which decreased by 96.2% and 99.3%, respectively. This lack of correlation indicates that sediment and nitrate fluxes are not a function of total discharge alone. In order for thorough nutrient flushing and efficient sediment transport to occur there needs to be not only a large volume of water, but also that volume needs to move through the system in a short amount of time (\textit{i.e.}, during a big storm). To compare nutrient and sediment transport between wet and dry
year we should then look at storm intensity, not flow volume. By comparing the variance in flow between the wet and dry year we can calculate a value representing the change in flow intensity between the two years. Discharge in January – February 2001 had 1.7% the variance (interpreted as flow intensity) of January – February 2000, a number much closer to the fraction of sediment (3.8%) and nitrate (0.7%) transported in that dry year. Thus, at Michigan Bar, we have indirect evidence that inter-annual comparisons of nitrate and sediment fluxes are more a function of flow variance than flow volume.

Storm-Scale Analysis

High resolution water chemistry data were collected for five storms during 2001. Four of the storms were during the stormflow season (Figs. 7a – d) and one was during the meltflow season (rain-on-snow) (Fig. 7e). The chemographs for each storm varied as progressive flushing caused a general decrease in most constituents. In the first storm, total phosphorous (TP), EC, and TSS spiked on the rising limb of the hydrograph creating a strong clockwise hysteresis (Fig. 7a). This pattern is indicative of flushing storms (Muscott et al., 1990). EC spiked early in the storm from a background level of 143 $\mu$S cm$^{-1}$ to 222 $\mu$S cm$^{-1}$ and then decreased as the mass of dilute rainwater began to overwhelm the higher ionic strength waters being flushed from the terrestrial environment. TP and TSS did not reach a maximum until just before the peak discharge of the storm. TP shows a strong correlation with TSS because much of the phosphorous that is transported in streams is sorbed to sediment particles or exists as particulate organic matter (Jordan-Meille et al., 1998). When stream energy is at a maximum (near the peak discharge of the storm) the stream has a greater sediment carrying capacity as reflected in the TSS and TP responses seen in the first storm.

In the second storm of the season TP concentrations showed no distinct pattern linked to changing discharge (Fig. 7b). The storm still appears to be a flushing event because TSS and EC both increased with increasing discharge. The third storm of the season was more complex as there were two hydrograph peaks to the storm, both with different chemistries (Fig. 7c). The first hydrograph peak resulted in a small decrease in TP concentration, no response in EC, and a slight rise in TSS. This pattern appears to represent a transition between flushing and diluting storm characteristics. In contrast, the second hydrograph peak of the storm only 13 hours later showed all the signs of being a flushing flow: TSS, EC, and TP all reached a maximum with increasing discharge. It is very likely that this storm demonstrates the effect that multiple watershed source areas have on downstream hydrograph and chemograph response. Analysis of rain gauges across the watershed revealed that the first spike (diluting) of this storm was derived primarily from upland sources while the second spike (flushing) was caused by rain in the lower watershed. Because land use and land cover in the lower watershed are dominated by grasslands and agriculture, and because 2000–‘01 was a relatively dry water year, stormflows originating from the lowlands had a prolonged flushing pattern. Conversely, because the uplands are sparsely populated, underlain by granitic bedrock, and dominated by undisturbed conifer forests, a dilution pattern was expected with stormflows.

The last storm in the stormflow season was caused by heavy rains across the entire watershed (Fig. 7d). There was a slight flushing effect evident on the rising limb
of the hydrograph, followed by declining EC, TSS and TP as the storm progressed. EC declined to levels below background with the peak of the storm, indicating that this was the first dilution storm of the season. TP declined steadily and reached stable levels of about 200 $\mu$g l$^{-1}$ just after the storm peak. TSS steadily declined through the entirety of the storm.

The one large storm during the meltflow season was characterized as a rain-on-snow event. The streamflow originated in the uplands with the bulk of the precipitation falling in the upper watershed. This event caused a large pulse of dilute water to move through the watershed with little contribution from the lower watershed. The result was a clear dilution pattern during the rising limb and a recovery in TP and EC levels during the falling limb (Fig. 7e). In contrast, TSS levels showed a progressive decrease suggesting depletion of sediment sources.

**Upper and Lower Watershed Temporal Variability**

In the upper reaches of the watershed (M.F. at E6, M.F. at E16, and Cos. at Hwy 49), solute concentrations and temporal variability of concentrations for most constituents were minimal in comparison to the lower watershed. The highest variances in solute concentrations occur during storm events when interflow and overland flow hydrologically connect the terrestrial and aquatic environments. In the Cosumnes River Watershed the uplands have closed canopy forests, soils with low cation exchange capacities, relatively insoluble country rock (e.g., granite), and minimal human impacts. These factors all contribute to the low solute concentrations and variances seen for most chemical constituents in the upper reaches.

In the upper watershed baseflow DOC concentrations were low and relatively stable around 1 mg l$^{-1}$ (Fig. 8). The first significant storms of the season in Jan and Feb of 2000-'01 and 2001-'02 were reflected in the chemograph by sharp DOC spikes with concentrations as high as 4 mg l$^{-1}$. Late season storms, though hydrologically similar to earlier events, carried lower concentrations of DOC (~2 mg l$^{-1}$). With the onset of snowmelt-dominated flow DOC concentrations decreased to ~1 mg l$^{-1}$. Elevated concentrations of DOC occur at higher flows when hydrologic flowpaths short-circuit the lower soil horizons and move preferentially as subsurface lateral flow through the organic-rich surface horizons.

Chlorophyll-a levels during the summer were stable and low (~0.2 $\mu$g l$^{-1}$) (Fig. 9). Our storm-sampling regime did not include chlorophyll splits so there are data gaps during high flow periods. M.F. at E16 CHL concentrations spiked in the melt season (2 $\mu$g l$^{-1}$) and with the first flushing flow of 2001-'02 (3 $\mu$g l$^{-1}$). This flushing pulse was seen throughout the watershed and most likely was related to the entrainment of periphyton that accumulated in the stream channel during the summer months. Chlorophyll-a patterns at Hwy 49 showed a different pattern with concentrations spiking during winter storms (7 $\mu$g l$^{-1}$), as well as during the melt season.

Figure 3 illustrates how M.F. at E16 does not have a distinct flushing period and Cosumnes at Hwy 49 shows only a weak EC response to early rains in 1998-'99, 1999-'00, and 2001-'02 (note there is no storm season data for M.F. at E6). This same phenomenon is seen in tributaries from similar elevations and may reflect the fact that the
upper watershed does not foster conditions favorable for early winter solute flushing. Nitrate flushing in particular was not evident above Hwy 49 (Fig. 10). The perennial vegetation (coniferous forests) in the upper watershed has the ability to uptake nutrients all year round, including during the fall when soil moisture becomes available. As a result, nutrient uptake and availability are better synchronized in coniferous forests than in the deciduous oak/annual grasslands found at lower elevations. Deciduous oaks and annual grasses have little capacity to take up nutrients after senescence allowing nutrient pools, especially nitrate, to accumulate to high levels. These nutrients are rapidly leached with the onset of the fall/winter rain season.

In contrast to the upper portions of the watershed, early winter solute flushing is evident at all the lower watershed sites. Though EC peaks during the baseflow season at Michigan Bar (110 µS cm⁻¹) an even greater peak occurs during the storm seasons with conductivities as high as 170 µS cm⁻¹ at Twin Cities. The Michigan Bar subwatershed is dominated by oak woodlands and grazing while the Twin Cities subwatershed is dominated by grasslands and agriculture, with some suburban influence. The impact that these various land use and land cover types have on the water chemistry of the stream is best observed when the landscape is hydrologically connected with local waterways. During the baseflow and meltflow seasons when this hydrologic connection is broken the chemistry throughout the watershed does not vary much in form or degree. But during the winter when precipitation connects the landscape to the streams we see a wide fluctuation in all of the measured constituents. This fluctuation is greatest in the lower watershed where agriculture and grazing dominate. In this way it can be seen how the uplands are an important source of dilute waters for the more heavily used lowlands.

The data clearly show that stream water from the high elevation has no detrimental affects on overall water quality and that it acts primarily as a source of water for dilution. Thus, projects to enhance water quality should be applied primarily to the lower portions of the watershed, which are the source of the greatest amounts of pollutants (nutrients, sediments). In addition, the disproportionate transport of constituent fluxes during stormflow is an important consideration when designing a watershed monitoring program to evaluate water quality (e.g., total maximum daily loads – TMDLs). It is necessary to collect several samples during storm events when many pollutant concentrations and discharge volumes are highest (Tate et al., 1999). The combination of high pollutant concentrations and discharge volumes creates a large flux. As demonstrated in the Cosumnes River Watershed, greater than 90% of the sediment, nitrogen and phosphorus fluxes occur over the period of a few weeks during the first major storm events of the water year. In contrast, many pollutant concentrations are low and do not vary during the baseflow season (about 6 months long), and thus require a minimal sampling effort during the summer months.

**Implications for Impounded Systems**

Research has shown that the presence of a major dam on the course of a waterway acts to thermally and chemically buffer the river downstream of the impoundment. In Kelly’s (2001) analysis of inputs and outputs from 14 major reservoirs in the Western United States, the wide range in seasonal dissolved solids seen upstream of the
impoundments was essentially reduced to a constant value downstream. The reservoirs impounding flow from the western Sierra Nevada function primarily as flood control and water supply facilities. Efficient operations of such facilities include the curtailment of high flows so that lowland communities are not flooded during the winter and have ample water during the dry summer. The “homogenization” of the hydrograph and associated chemographs results in the elimination of the water quality seasons.

Reservoirs in a watershed sever the hydrologic flowpaths present before impoundment and reset water quality parameters (Kelly, 2001; Ward and Stanford, 1995). The differences in hydrologic flowpaths and water source areas that affect temporal stream chemistry dynamics are not applicable below an impoundment because all flow is routed through the reservoir and mixed before continuing downstream. Reservoirs alter stream chemistry in a number of ways including: (1) increasing residence times from days to months, (2) buffering solute concentrations, (3) mixing inflow with unique lake conditions that are dependent on climate, depth, wind conditions, etc., (4) releasing waters from varying depths and at varying discharges, and (5) trapping coarse particulate matter. Because of factors such as these, hydrologic flowpaths and water source areas no longer dictate water chemistry below a reservoir.

Data from the Cosumnes Watershed show that nutrient concentrations depend upon the season of the year and antecedent meteorological conditions. If the Cosumnes River were to be dammed this variability would be greatly reduced and the timing of nutrient pulses to the lowlands would change. Presently, nutrient transport out of the Cosumnes Watershed is relegated to just a few months out of the year (Fig. 5). During these two or three winter months the demand for nutrients and food resources by the aquatic ecosystem is at a seasonal low. In contrast, a combination of impoundment and nutrient enrichment from agriculture has created an exactly opposite temporal nutrient pattern in a number of other rivers draining the Western Sierra (Fig. 11). Nitrate in groundwater has elevated the baseflow nitrate levels in the Tuolumne and Merced Rivers. During the winter when the dams on these nutrient enriched rivers release dilute waters, nitrate levels decrease. This pattern continues into the San Joaquin River and eventually into the Sacramento – San Joaquin Delta. Pristine watersheds, like the adjacent Mokelumne Watershed, exhibit a pattern more similar to the Cosumnes, with increased winter flows causing a slight nitrate and TN elevation. Yet, the nutrient release exhibited in the Mokelumne is completely flow dependent, when the utility which operates the upstream dam decides to release no water (e.g. Fig. 11, 2001), there is no nutrient spike. Using the Cosumnes as a model for a free-flowing system, it can be seen how the presence of dams on Sierra Nevada Rivers has altered temporal water quality patterns and nutrient budgets for the downstream Bay-Delta ecosystem. This change has most likely created a major shift in primary production and thus ecosystem function in the lowlands.

**Summary**

These data suggest that hydrologic flowpath exerts a strong control on water chemistry in the Cosumnes River Watershed. As hydrologic flowpath changes throughout the year, three water quality seasons develop (stormflow, meltflow, baseflow). This pattern, noted in the Cosumnes, has also been witnessed in tributary
studies in nearby watersheds (Holloway and Dahlgren, 2001; Lewis et al., 2000). During an average water year in the Western Sierra Nevada, precipitation falls between November and March, upland snow melts between April and June, and the rest of the year receives virtually no precipitation. Because the hydrometeorology is partitioned in this manner a parallel segregation of water chemical patterns occur in the streamwaters. The stormflow season consists of a flushing period followed by high flows carrying elevated sediment and nitrate and low levels of other major dissolved constituents. The meltflow season frequently has flows as high as those seen during the storm season, yet these flows are derived from melting snow in the uplands and are depleted of nutrients, sediment and major solutes. Lastly, the baseflow season is controlled by groundwater chemistry primarily from upland sources; these low flows have elevated solute concentrations, low sediment and nutrients, and median levels of chlorophyll and DOC.

This four year study was fortuitous enough to encompass two dry and two average flow years. The contrast was striking, as solute rating curves during the stormflow seasons had opposite trends. During the two dry years, the rainy season was delayed until January and even then only small storms occurred; these storms did not fully flush the upper soil horizons until late in the season resulting in a positive correlation between flow and EC during the stormflow season. This is in contrast to average precipitation years when storms began in November and culminated in a large flushing storm in early January. All subsequent storms during these years caused the dilution of stream water solute concentrations. Thus, the determination of the chemical patterns within the stormflow season depends upon the timing and intensity of the first large flushing storm(s) of the season.

High resolution sampling of storm events in 2000-‘01 revealed that progressive flushing of solutes occurred with each successive storm. The storms were flushing-type storms until early March when the first dilution-type storm occurred. A two peak storm in February revealed the complexities which arise when multiple source areas in the watershed contribute to different sections of the hydrograph; such storms that show both a dilution and flushing effect can confound the conceptual model we have presented.

Solute flushing was evident at all lowland sites, but upland sites showed little if any flushing effect. The coniferous forest in the upper watershed provides greater ground cover and more efficient nutrient retention than the lower elevation oak woodlands and annual grasslands. A simple spatial analysis of chemical concentrations throughout the watershed indicates the importance of the uplands for delivering diluting waters to the more heavily populated and farmed lowlands.

Because the chemographs within each water quality season are determined by hydrologic flowpath, the same patterns are not expected to be seen in watersheds containing large impoundments. Such impoundments tend to “reset” water quality parameters (Stanford and Ward, 2001) through retention and regulation, thus interrupting flowpaths and changing chemical patterns. Because the Cosumnes River is the last free-flowing watershed draining the Sierra, this study was a unique opportunity to characterize the seasonal changes in water chemistry of a large naturally flowing system in California. It is hoped that these data will be useful for scientists and regulators alike for future watershed study and planning.
Acknowledgments

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a. $R^2 = 0.0079$, $P = 0.80$

$R^2 = 0.3429$, $P = 0.001$

$R^2 = 0.3869$, $P = 0.083$

b. $R^2 = 0.0002$, $P = 0.97$

$R^2 = 0.1119$, $P = 0.57$

$R^2 = 0.5408$, $P = 0.009$

$R^2 = 0.0002$, $P = 0.97$
FIG 11

San Joaquin River below Tuolumne

Discharge (cfs)

NO3-N and TN (mg l⁻¹)
Fig. 1. Map of the Cosumnes River Watershed with locations and names of 28 sampling sites. This particular study focuses on the temporal dynamics of the hydrochemistry at sites 4 (Mid. Fk. Cosumnes at E6), 9 (Mid. Fk. Cosumnes at E16), 14 (N. Fk. Cosumnes @ H49), 18 (Cosumnes at Michigan Bar), and 32 (Cosumnes at Twin Cities Rd.); all marked with stars in the figure.

Fig. 2. Geology and land use/land cover for the Cosumnes River Watershed. The upper watershed is dominated by granite bedrock and coniferous vegetation. The middle reaches are underlain by metamorphic rocks and are used for cattle grazing and viticulture. The lower reaches are more populous with widespread agriculture on fertile valley sediments.

Fig. 3. Temporal variation in electrical conductivity at the 5 study sites. Chemographs are accompanied by the Michigan Bar hydrograph (a), water quality season markers, and the elevation for each site. Conductivity peaks during the 1999-’00 storm season occur between storm peaks. Stormflow season 1998-’99 has poor resolution due to lack of storm sampling.

Fig. 4. Discharge-solute rating curves for Michigan Bar for the three water quality seasons. (a) Data from 1998-’99 and 1999-’00, two “average” flow years. (b) Data from the 2000-’01 and 2001-’02, two dry water years. Note: trend lines are linear while the discharge axis is logarithmic.

Fig. 5. Boxplots representing the distribution of monthly flux data for chloride, nitrate, total suspended solids (TSS), and flow, as measured at Michigan Bar. Distributions represent monthly fluxes calculated from Oct. 1998 - Sept. 2002. Monthly data is grouped into three major water quality seasons (Storm, Melt, Base). Top and bottom edge of each box represents the 75th and 25th percentile respectively, the line bisecting the box represents the median, points are outliers, and the ends of the whiskers represent the 90th and 10th percentile.

Fig. 6. Temporal variation in (a) flow, (b) DOC, (c) Chl-a, (d) NO3−, (e) EC, and (f) turbidity at Michigan Bar. Turbidity data were used in place of TSS for the figure because the data were more continuous.

Fig. 7. High resolution autosampler data were collected for 5 storms during the 2001 – ’02 stormflow season. Chemographs for total phosphorus (TP), EC and TSS are plotted along with flow estimates from the Michigan Bar gauging station. Plots a – c depict a flushing pattern, while plots d and e show dilution patterns.

Fig 8. Temporal variation in dissolved organic carbon (DOC) at the five study sites. DOC data were only collected during the last two years of the study.

Fig. 9. Temporal variation in chlorophyll-a at the five study sites. Chlorophyll data were only collected during the last two years of the study.

Fig. 10. Temporal variation in nitrate at the five study sites. Nitrate flushing with the onset of winter rains is most evident at the three lower sites (d – f).

Fig 11. Nutrient export from five central valley sampling sites. The Cosumnes is the only free-flowing system shown. The Tuolumne, Merced, and San Joaquin have nutrient enriched baseflows, this in combination with impoundment has created a nutrient chemograph which is opposite of that seen in the Cosumnes.
Fluxes for 12 constituents (in Mg) and discharge (in m³) measured at Michigan Bar during a wet year (2000) and a dry year (2001). Two month totals are calculated for Jan. and Feb. and weighed against annual totals, and finally weighed against each other.

<table>
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<th>Year</th>
<th>Discharge</th>
<th>Sus. Sed.</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>PO₄³⁻</th>
<th>SO₄²⁻</th>
<th>HCO₃⁻</th>
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<td>Jan-Feb Total</td>
<td>350318</td>
<td>8075</td>
<td>1116</td>
<td>1</td>
<td>369</td>
<td>1583</td>
<td>4020</td>
<td>654</td>
<td>343</td>
<td>5</td>
<td>1182</td>
<td>20760</td>
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<td>Annual Total</td>
<td>483157</td>
<td>8105</td>
<td>1527</td>
<td>2</td>
<td>488</td>
<td>2075</td>
<td>5589</td>
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<td>345</td>
<td>5</td>
<td>1492</td>
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<td>72.5</td>
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<td>73.0</td>
<td>37.5</td>
<td>75.5</td>
<td>76.3</td>
<td>71.9</td>
<td>76.9</td>
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<td>377</td>
<td>304</td>
<td>0</td>
<td>67</td>
<td>363</td>
<td>667</td>
<td>171</td>
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<td>0</td>
<td>355</td>
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<td>557</td>
<td>0</td>
<td>130</td>
<td>642</td>
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<td>288</td>
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<td>49.3</td>
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