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Journal of Hydrology 295 (2004) 47–63

Journal of Hydrology

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

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Received 18 July 2003; revised 2 February 2004; accepted 16 February 2004

Abstract

Temporal patterns of stream water chemistry were analyzed across the Cosumnes River Watershed (1989 km^2) for water years 1999–2002 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 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 water year 2002 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, these data provide scientists and regulators with a valuable reference to address how impoundment affects water quality.

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

1. Introduction

Temporal variability in stream chemistry is controlled by a number of factors. Traditionally discharge was considered the master variable driving stream hydrochemistry with increased flow correlated to decreased total dissolved solids (Durum, 1953; Hem, 1948), but recent studies have shown more complex

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doi:10.1016/j.jhydrol.2004.02.016

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 (Creed and Band, 1998; Harriman et al., 1990).

When differentiating stream chemistry from one season to the next hydrologic flowpath may be the primary determinant of 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, where studies have focused on the seasonal variability in stream chemistry, hydrologic flowpath may be equal in importance to discharge 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. 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, 1996, 1997), solute chemistry (Kelly, 2001), and sediment transport (Morris and Fan, 1998). These alterations to stream flow 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 basin as a reference for ‘naturally’ flowing systems.

2. The study area

The Cosumnes River Watershed, located southeast of Sacramento, CA encompasses 1989 km^2 of terrain (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

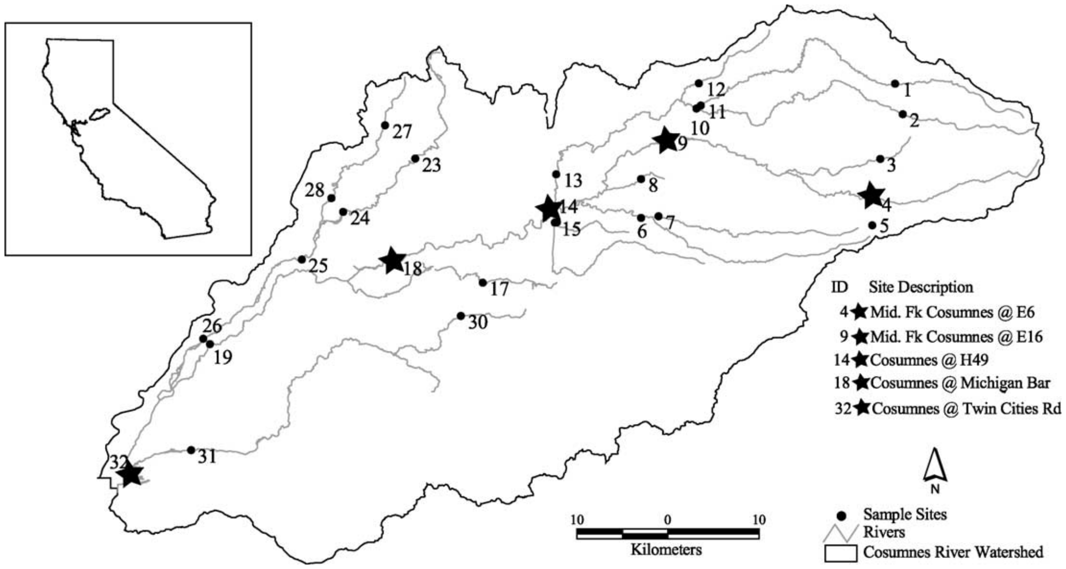

Fig. 1. Map of the Cosumnes River Watershed with locations of 28 sampling sites. This particular study focuses on the temporal dynamics of the hydrochemistry at Middle Fork at E6, Middle Fork at E16, Cosumnes at Hwy49, Cosumnes at Michigan Bar, and Cosumnes at Twin Cities; all marked with stars in the figure.

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.

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 yr^{-1} while approximately 445 mm yr^{-1} fall in the lowlands. The Cosumnes River, as gaged at Michigan Bar (Fig. 1), has a long-term (1907–2002) mean daily discharge of 14.4 $\mathrm{m}^3\,\mathrm{s}^{-1}$. This study included two dry (2001, 2002) and two wet (1999, 2000) 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 at E6 (1173 m), Middle Fork at E16 (512 m), 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.

3. 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 2001 and 2002 water years, additional storm samples were collected whenever flows exceeded 28 $\mathrm{m}^3\,\mathrm{s}^{-1}$ at the Michigan Bar gaging station (USGS gage #11335000) (Fig. 1). The sampling design resulted in approximately 37 samples/site/year. In addition, an autosampler (ISCO 6700) was placed below Twin Cities (the lowest site in the watershed) during the 2001 water year to collect storm samples. Between 12 and 24 samples were collected at variable time steps (1–2 h 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.

Each grab sample consisted of ~3 l of surface water collected from the thalweg of the river at approximately mid-depth of the water column. Electrical conductivity (EC), pH, and turbidity were measured on unfiltered subsamples using field and laboratory meters. Total suspended solids (TSS) was measured from a 500 ml subsample that was filtered through a pre-weighed glass fiber filter (Gelman), the filter was dried at 60 °C for 24 h 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 and anions were measured using ion chromatography (Dionex 500 x; CS12 cations; AS4A anions). Detection limits for cations (Ca^{2+}, Mg^{2+}, K^+, Na^+, NH_4^+) were 0.08, 0.08, 0.05, 0.05, and 0.08 ppm respectively, while for anions (Cl^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) detection limits were 0.4, 0.4, 0.5, and 0.5 μM, respectively. Dissolved organic carbon (DOC) was measured using a Dohrmann UV enhanced-persulfate TOC analyzer (Phoenix 8000) with a detection limit of 0.05 ppm. Total phosphorus (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) with a detection limit of 5 ppb. Total nitrogen (TN) was measured on a persulfate-digested split of unfiltered sample on a Carlson autoanalyzer (Carlson, 1978, 1986) with a detection limit of 50 ppb. Finally, chlorophyll-a (Chl-a) was measured from a 2000 ml sample using ethanol extraction and standard fluorometry techniques (Clesceri et al., 1998), the detection limit for the Chl-a analysis is dependent on the volume of sample filtered, in most of our analyses the detection limit was 0.1 ppb.

The resultant data were grouped by site and season and a one-way ANOVA was conducted between each site within each season and between each season within each site (the highest and lowest elevation sites were excluded for this latter analysis due to incomplete temporal data). Significant differences between data distribution means for each site and season were determined using a Tukey–Kramer HSD pair-wise comparison test. In order to determine chemical variance between sites across multiple seasons, F ratios and Prob $> F$ were calculated for the three sites with year-round data (Middle Fork at E16, Cosumnes at Hwy 49, and Cosumnes at Michigan Bar). F statistics were also reported for the three seasons at Middle Fork at E16, Cosumnes at Hwy 49, and Cosumnes at Michigan Bar. Constituents were chosen for statistical analysis based on three factors, (1) the data were continuous and complete for all sites and collection dates, (2) the constituents were not highly correlated, and (3) the constituents were relevant to the analysis and aided in the interpretation of the data set.

Chemical fluxes were calculated for the one site in the watershed with a gage, Cosumnes at Michigan Bar, by multiplying the mean daily flow by linearly interpolated daily concentration data.

4. Results

4.1. Seasonal patterns

4.1.1. Baseflow season

The baseflow season at Michigan Bar (the one gaged site in the watershed) was characterized by median flows of 0.79 $m^3\,s^{-1}$ between 1999 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 incomplete 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. 2b–f). This pattern creates a negative correlation between EC and discharge during the baseflow season (Fig. 3a and b). Median EC values for the baseflow season increase from 38.8 μS cm^{-1} at Middle Fork at E6 in the upper

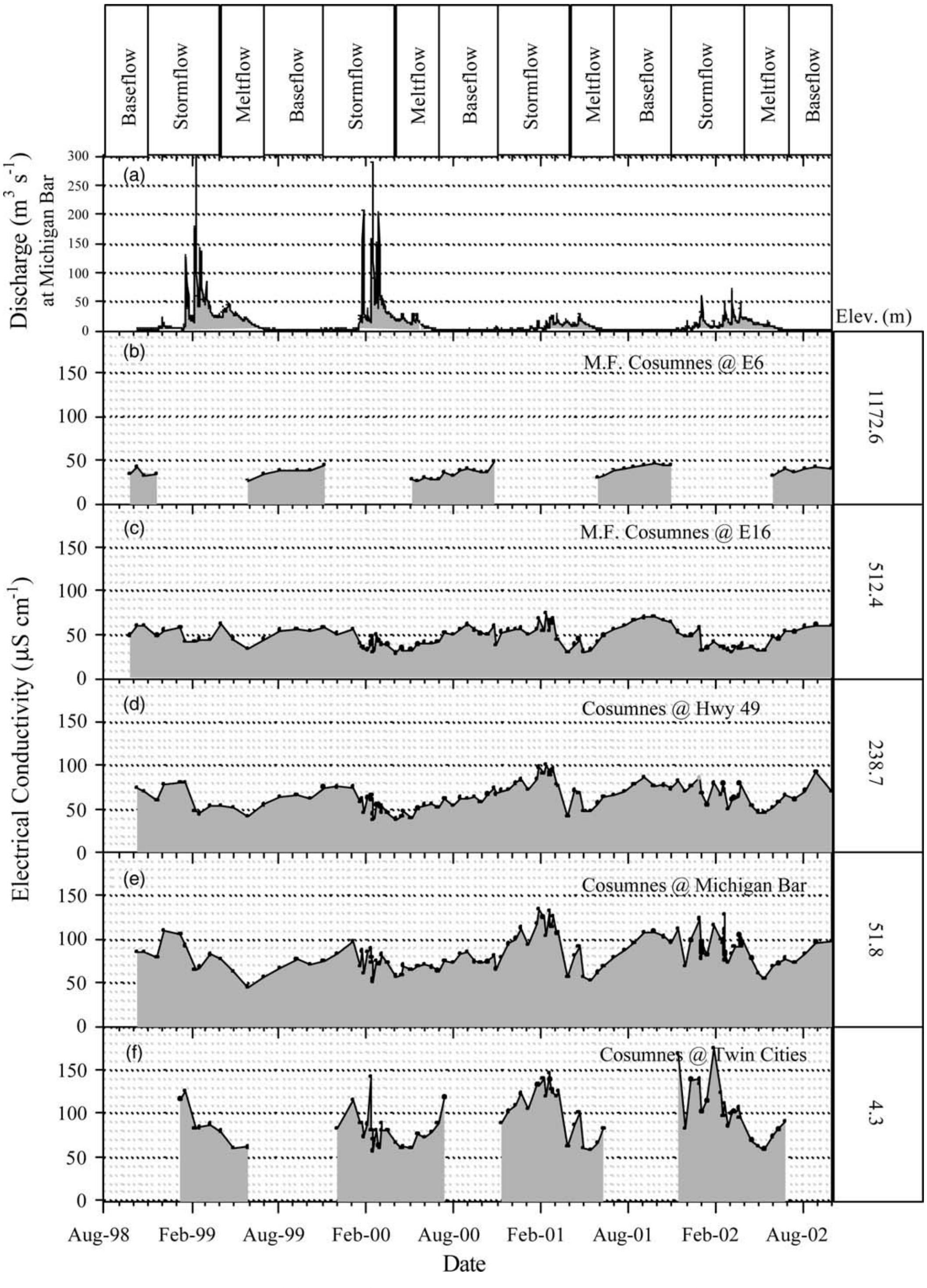

Fig. 2. Temporal variation in electrical conductivity at the five study sites. Chemographs are accompanied by the Michigan Bar hydrograph (a), hydrologic season markers, and the elevation for each site. Stormflow season 1999 has poor resolution due to lack of storm sampling.

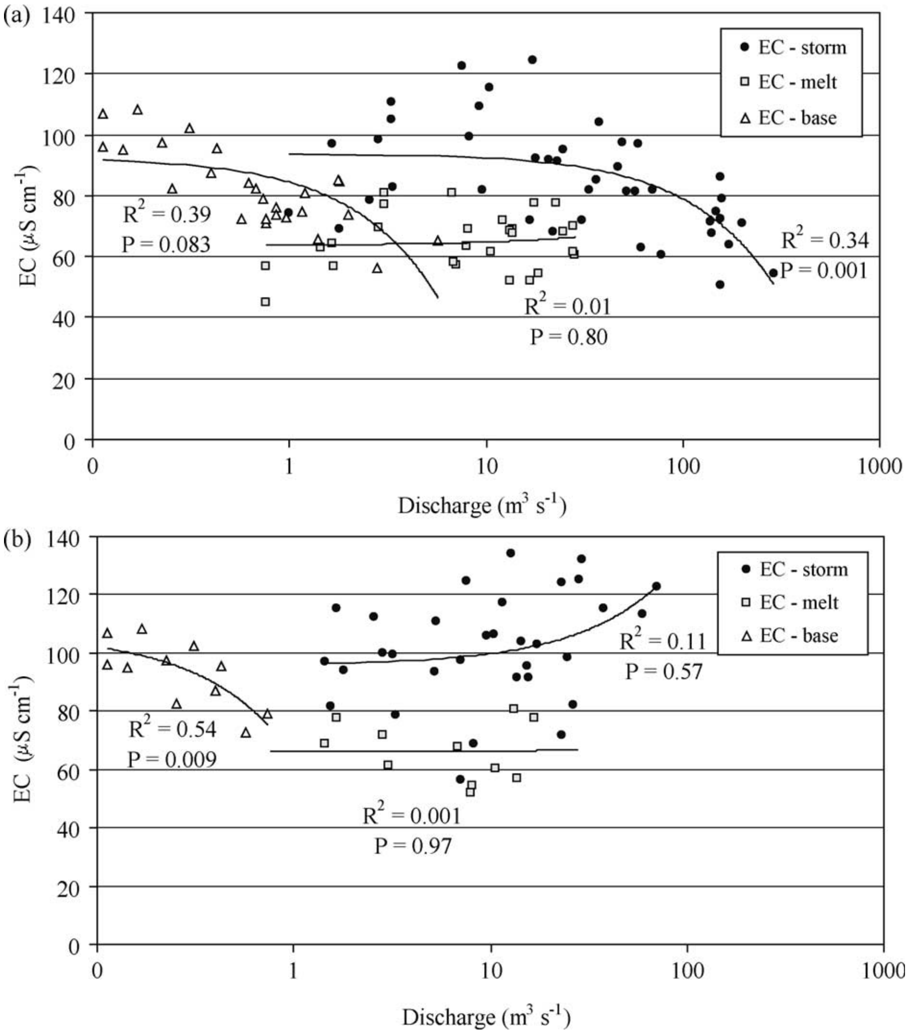

Fig. 3. Discharge–electrical conductivity (EC) rating curves for the Michigan Bar site for the three hydrologic seasons. (a) Data from 1999 and 2000, two 'average' flow years. (b) Data from 2001 and 2002, two dry water years. Note: trend lines are linear while the discharge axis is logarithmic.

watershed to 116.6 μS cm^{-1} at Twin Cities in the lower watershed. For all sites, both TSS and NO_3-N have median values lower than the detectable limit (MDL = 1 mg l^{-1} and 0.005 mg l^{-1}, respectively) during the baseflow season. Though concentrations of certain constituents may be high during this period, discharge is low resulting in negligible baseflow fluxes of these constituents (Fig. 4).

4.1.2. Stormflow season

In an average water year the stormflow season is marked by high discharges carrying elevated concentrations of DOC, Chl-a, turbidity, and nitrate (Fig. 5b–f). The chemistry of stormflows is dependent on the timing of the first large flushing flow(s). In w.y. 1999 and 2000 there were large flushing storms (above 142 m^3 s^{-1} at Michigan Bar) in late December or early January, storms after these events tended to create a dilution effect (Fig. 2c–f). 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

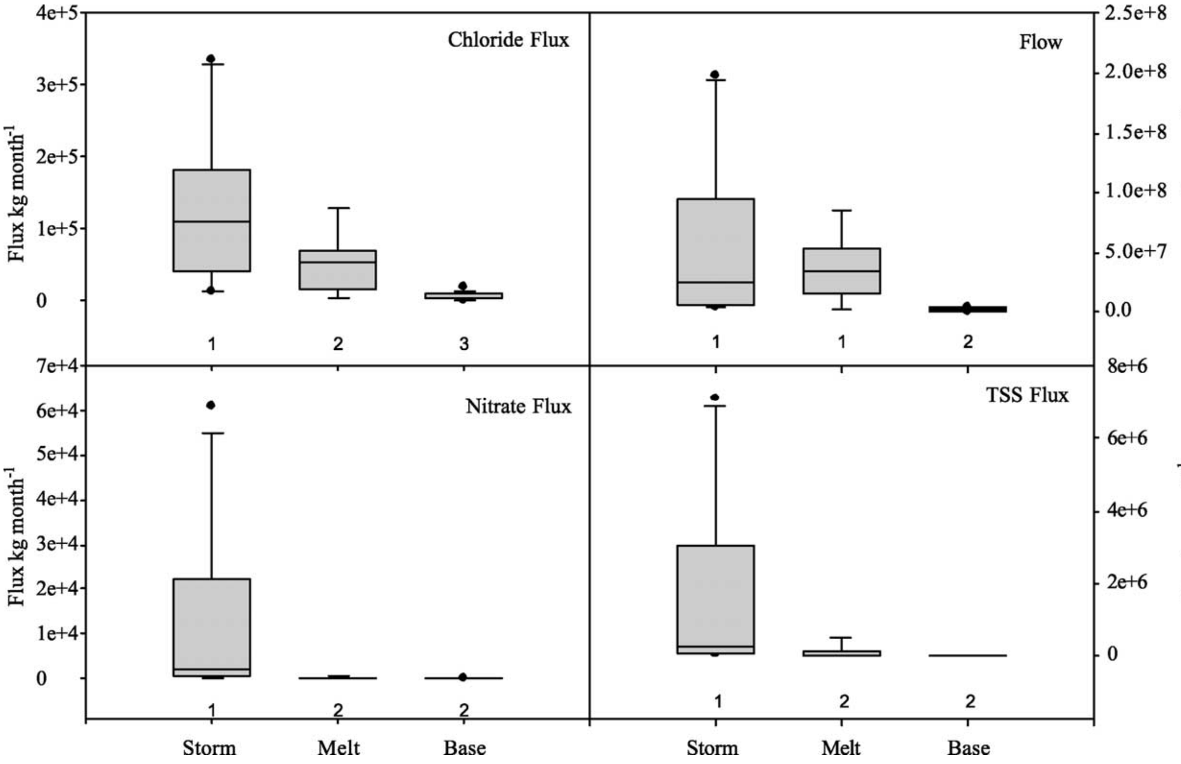

Fig. 4. Boxplots representing the distribution of monthly flux data for chloride, nitrate, total suspended solids (TSS), and flow, as measured at Michigan Bar. Distributions represent monthly fluxes calculated from October 1998–September 2002. Monthly data are grouped into three major hydrologic seasons (Storm, Melt, Base). Numbers below boxplots represent significance of differences between distributions. 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.

correlated with solute concentrations as indicated by EC. 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.

During w.y. 1999 and 2000, the dilution pattern dominated the stormflow seasons, and dissolved salts were inversely related to discharge (Fig. 3a). The flushing pattern dominated the stormflow season during w.y. 2001 and 2002, years when flows did not exceed 77 $m^3 s^{-1}$ at Michigan Bar (Fig. 3b), which created a positive but weak relation between discharge and solute concentration. Median EC values for the storm season (1999–2002) ranged from 49 $\mu S cm^{-1}$ at Middle Fork at E16 to 101.6 $\mu S cm^{-1}$ at Twin Cities (Fig. 2).

Because the Cosumnes is a free-flowing system without any significant dams to buffer storm fluxes, 72.5% of the annual flow in w.y. 2000, moved past Michigan Bar during January and February (Table 3). 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 NO_3 and TSS occurs during these two months (Fig. 4, Table 3). The greatest variability between sites occurred during the stormflow season with DOC, EC, K, NO_3, and pH all explainable by position in the watershed (Table 2).

4.1.3. Meltflow season

The meltflow season is characterized by elevated discharges carrying low concentrations of solutes and suspended sediments (Figs. 4 and 5). Though monthly flow during the meltflow season (median $= 3.4 \times 10^7$ $m^3 month^{-1}$) was not significantly different (as measured by student's *t*-test) from the stormflow

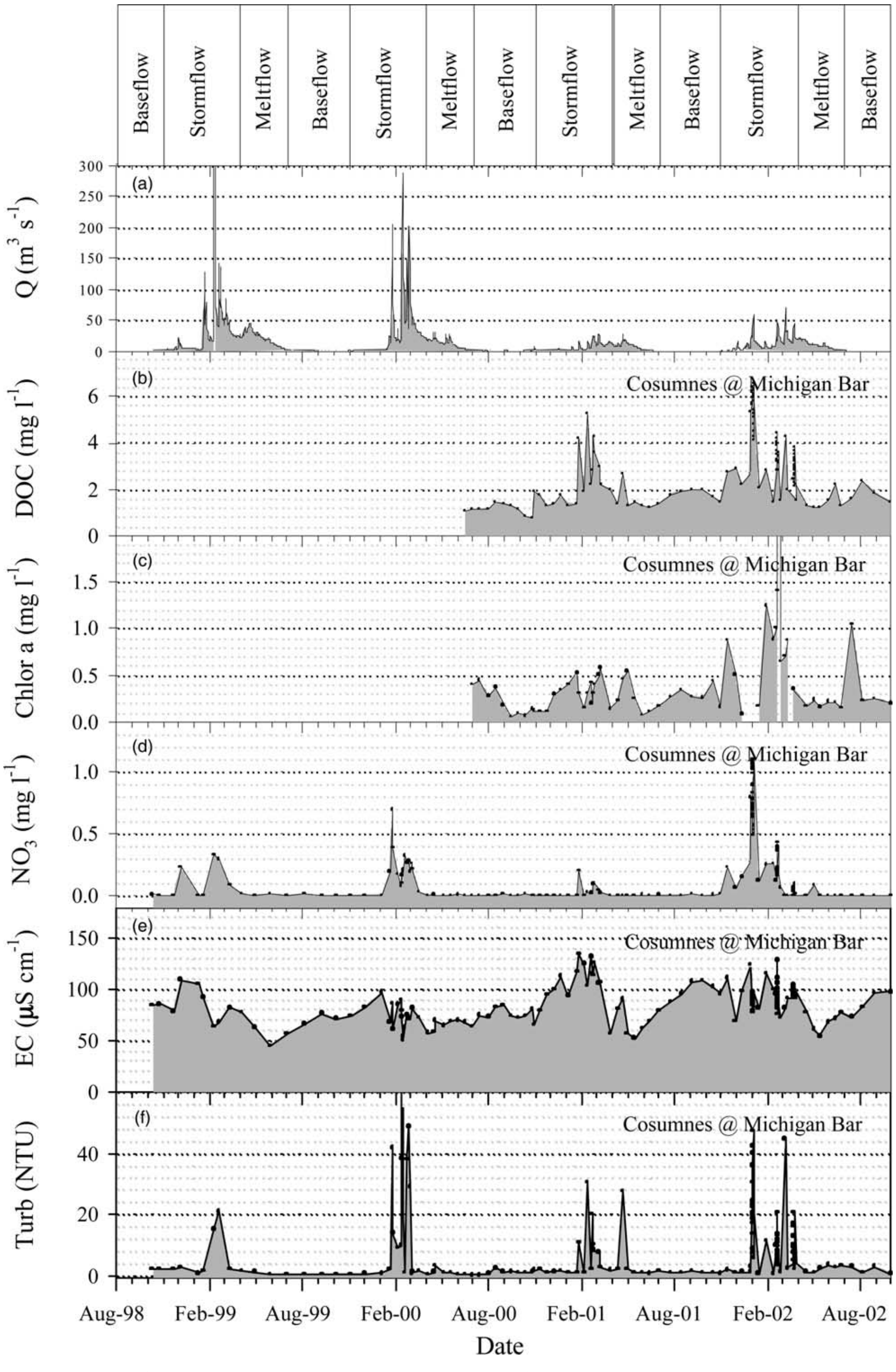

Fig. 5. Temporal variation in (a) flow, (b) DOC, (c) Chl-a, (d) NO_3, (e) EC, and (f) turbidity at Michigan Bar. Turbidity data were used in place of TSS for the figure because the data were more continuous.

season (median $= 2.5 \times 10^7$ m^3 month^{-1}), sediment and solute loading was, on average, an order of magnitude lower (Fig. 4).

The lowest conductivities measured during this 4-year study occurred during the meltflow season (Fig. 2). However, EC was not correlated with discharge during the meltflow season (Fig. 3a and b). Both nitrate and turbidity were near or below detection during this season while DOC and Chl-a were significantly lower than in either of the other hydrological seasons (Fig. 5).

The meltflow season witnessed the least variation between the chemistries of the sites analyzed (Tables 1a and 2). During the meltflow season the only constituent which could be explained by position in the watershed was EC (Table 2).

4.2. Storm-scale analysis

High resolution water chemistry data were collected for five storms during 2001 at the lowest site in the watershed (Cosumnes at Twin Cities). Four of the storms were during the stormflow season (Fig. 6a–d) and one was during the meltflow season (rain-on-snow) (Fig. 6e). The chemographs for each storm varied as progressive flushing caused a general decrease in most constituents. In the first storm, TP, EC, and TSS spiked on the rising limb of the hydrograph creating a strong clockwise hysteresis (Fig. 6a). This pattern is indicative of flushing storms (Muscutt et al., 1990). EC spiked early in the storm from a background level of 143–222 μS cm^{-1} and then decreased as the mass of dilute rainwater began

Table 1

Analysis of variance for selected constituents between five contiguous sites: Middle Fork at E6 (1), Middle Fork at E16 (2), Cosumnes at Hwy 49 (3), Cosumnes at Michigan Bar (4), and Cosumnes at Twin Cities (5), during the three separate seasons (a). Additionally, ANOVA with *F* statistics (b) is reported for the three seasons: Storm (S), Melt (M), and Base (B), at the three sites with year-round data (2, 3, and 4)

a. Constituent	Season		
	Storm	Melt	Base
Chl-a	$2_{(a)}3_{(ab)}4_{(a)}5_{(b)}$[*]	$2_{(a)}3_{(ab)}4_{(a)}5_{(b)}$	$1_{(a)}2_{(a)}3_{(a)}4_{(a)}$
DOC	$2_{(a)}3_{(b)}4_{(b)}5_{(b)}$	$2_{(a)}3_{(ab)}4_{(ab)}5_{(b)}$	$1_{(a)}2_{(a)}3_{(b)}4_{(b)}$
EC	$2_{(a)}3_{(b)}4_{(c)}5_{(d)}$	$2_{(a)}3_{(b)}4_{(c)}5_{(c)}$	$1_{(a)}2_{(b)}3_{(c)}4_{(d)}$
K	$2_{(a)}3_{(b)}4_{(b)}5_{(c)}$	$2_{(a)}3_{(a)}4_{(a)}5_{(a)}$	$1_{(a)}2_{(b)}3_{(c)}4_{(c)}$
NO_3^-	$2_{(a)}3_{(ab)}4_{(b)}5_{(b)}$	$2_{(a)}3_{(a)}4_{(a)}5_{(a)}$	$1_{(a)}2_{(a)}3_{(a)}4_{(a)}$
pH	$2_{(a)}3_{(ab)}4_{(b)}5_{(b)}$	$2_{(a)}3_{(a)}4_{(a)}5_{(a)}$	$1_{(a)}2_{(a)}3_{(b)}4_{(b)}$
Turbidity	$2_{(a)}3_{(a)}4_{(a)}5_{(b)}$	$2_{(a)}3_{(a)}4_{(a)}5_{(b)}$	$1_{(a)}2_{(a)}3_{(a)}4_{(a)}$

b. Constituent/statistic	Site		
	2	3	4
Chl-a	$S_{(a)}M_{(a)}B_{(a)}$	$S_{(a)}M_{(a)}B_{(a)}$	$S_{(a)}M_{(a)}B_{(a)}$
F ratio (*Prob* > F)[†]	0.649 (0.53)	2.079 (0.14)	0.815 (0.45)
DOC	$S_{(b)}M_{(a)}B_{(a)}$	$S_{(b)}M_{(a)}B_{(a)}$	$S_{(b)}M_{(a)}B_{(a)}$
F ratio (Prob > *F*)	6.124 (<0.01)	9.318 (<0.01)	10.71 (<0.01)
EC	$S_{(a)}M_{(a)}B_{(b)}$	$S_{(b)}M_{(a)}B_{(b)}$	$S_{(b)}M_{(a)}B_{(b)}$
F ratio (Prob > *F*)	25.02 (<0.01)	17.76 (<0.01)	20.39 (<0.01)
K	$S_{(a)}M_{(a)}B_{(b)}$	$S_{(a)}M_{(a)}B_{(b)}$	$S_{(b)}M_{(a)}B_{(c)}$
F ratio (Prob > *F*)	13.44 (<0.01)	18.82 (<0.01)	21.43 (<0.01)
NO_3^-	$S_{(a)}M_{(a)}B_{(a)}$	$S_{(b)}M_{(a)}B_{(a)}$	$S_{(b)}M_{(a)}B_{(a)}$
F ratio (Prob > *F*)	3.595 (0.03)	13.54 (<0.01)	16.90 (<0.01)
pH	$S_{(a)}M_{(b)}B_{(b)}$	$S_{(a)}M_{(a)}B_{(b)}$	$S_{(a)}M_{(ab)}B_{(b)}$
F ratio (Prob > *F*)	9.715 (<0.01)	17.91 (<0.01)	10.54 (<0.01)
Turbidity	$S_{(a)}M_{(a)}B_{(a)}$	$S_{(b)}M_{(a)}B_{(a)}$	$S_{(b)}M_{(ab)}B_{(a)}$
F ratio (Prob > *F*)	1.957 (0.15)	5.273 (<0.01)	4.703 (0.01)

[*] Values followed by the same lower case letter are not significantly different ($p = 0.05$).

[†] A low *F* ratio (relative for each constituent) indicates that the chemistry does not vary much between the three seasons, while a (Prob > *F*) less than 0.05 indicates that the three seasons can be used to explain variation in a given constituent for a particular site.

Table 2

F ratio and (Prob $> F$) values for selected constituents between Middle Fork at E16, Cosumnes at Hwy 49, and Cosumnes at Michigan Bar within each of the hydrological seasons

Constituent/statistic	Season		
	Storm	Melt	Base
Chl-a			
F ratio (Prob $> F$)	1.38 (0.262)	1.07 (0.356)	0.18 (0.840)
DOC			
F ratio (Prob $> F$)	8.10 (0.001)	3.08 (0.057)	8.08 (0.001)
EC			
F ratio (Prob $> F$)	115.13 (<0.001)	45.92 (<0.001)	43.74 (<0.001)
K			
F ratio (Prob $> F$)	10.18 (<0.001)	2.00 (0.144)	9.17 (<0.001)
NO_3^-			
F ratio (Prob $> F$)	4.70 (0.011)	0.03 (0.966)	0.18 (0.839)
pH			
F ratio (Prob $> F$)	8.01 (<0.001)	2.07 (0.135)	9.37 (<0.001)
Turbidity			
F ratio (Prob $> F$)	2.11 (0.127)	0.09 (0.917)	0.36 (0.362)

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. 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. 6b). 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. 6c). 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 h 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 gages 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 (data not shown).

The last storm in the stormflow season was caused by heavy rains across the entire watershed (Fig. 6d). 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 as discharge increased, 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. 6e). In contrast, TSS levels showed a progressive decrease suggesting depletion of sediment sources.

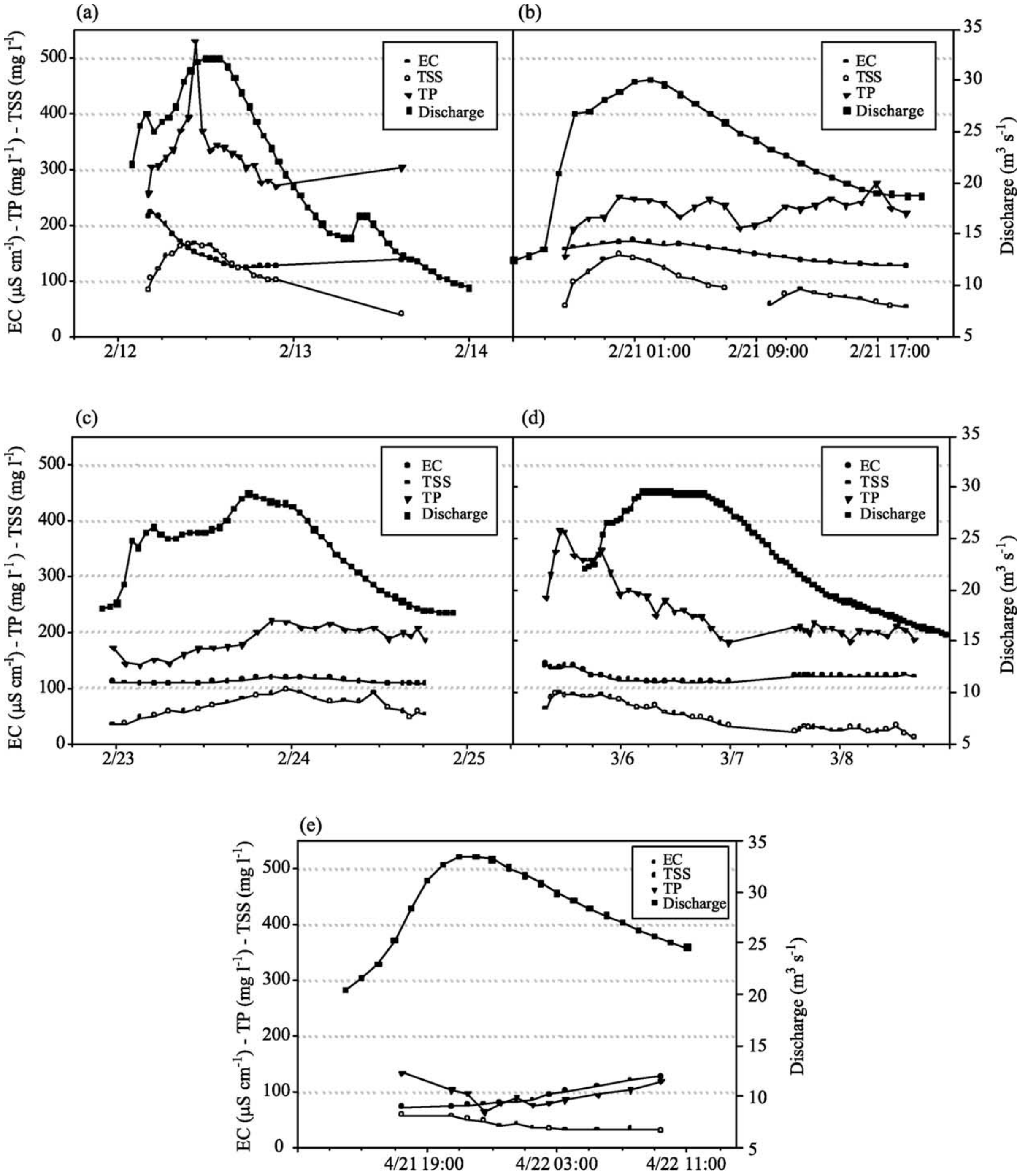

Fig. 6. High resolution autosampler data were collected below Cosumnes at Twin Cities for five storms during the w.y. 2001 stormflow season. Chemographs for TP, EC and TSS are plotted along with flow estimates from the Michigan Bar gaging station. Plots a–c depict a flushing pattern, while plots d and e show dilution patterns.

5. Discussion

The Mediterranean climate of California contributes to the formation of three hydrological seasons each with distinct water quality characteristics: (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 stream chemistry is largely influenced by melting snow in the uplands. The stormflow season can be further divided into flushing and dilution periods. This seasonal chemical pattern, noted in the Cosumnes, has also been witnessed in tributary studies in nearby watersheds (Holloway and Dahlgren, 2001; Lewis et al., 2000), but has never been explicitly reported. Each of the water quality seasons exhibits a unique and predictable chemistry, thus differentiation among them for scientific and management purposes becomes important.

Due to the scale of this study end-member mixing analysis was impossible, instead source areas and hydrologic flowpaths for each hydrologic season were evaluated by hydrograph analysis and supporting statistical analysis. For instance, the onset of the meltflow season was marked by a diel fluctuation in the hydrograph accompanied by dilute chemistries that did not vary much between sites. We inferred that this low variation in chemistries between sites (Tables 1a and 2) was caused by dilute snowmelt originating in the uplands and traveling downstream with relatively little input from local groundwater sources. Similarly, the onset of the baseflow season was marked by the end of the diel pattern in the hydrograph and the beginning of more variance between the study sites (Tables 1a and 2). Though we expected baseflow season variability between sites to be greater, we attribute the lack of variability to the fact that the lower reaches of the river are losing during the baseflow season. Due to this, chemistry across the basin is being controlled by upper watershed groundwater inputs. The source areas and hydrologic flowpaths of the stormflow season were determined by analysis of rain gages, autosampler data, and chemical variation between sites. Not surprisingly the stormflow season exhibited the highest variability in chemistry between the sampling sites (Tables 1a and 2). We attribute this variability to the fact that during the stormflow season rainfall across the watershed in draining through a highly variable landscape and into local waterways.

Nitrate transport within each of these seasons varies dramatically. Asynchrony within nutrient cycles in California's Mediterranean climate causes marked nitrate spiking during the flushing season (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 (Hart et al., 1993). With the onset of winter rains, water begins to flow through the upper soil horizons, mobilizing the accumulated nitrate (Holloway and Dahlgren, 2001) 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. 7).

Turbidity, an indicator of suspended sediment, follows a similar pattern. During the winter, precipitation washes 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 (Fig. 5f). Though the meltflow season has occasional high flow events, the waters constituting these flows are derived from upland sources and have low levels of TSS.

The TSS and nitrate patterns witnessed in the Cosumnes stand in stark contrast to those analyzed in the neighboring Mokelumne watershed (data not shown). In the Mokelumne two large low elevation dams effectively dilute and attenuate stormflow season flushing flows. The sediment settles out behind the dams while the nitrate becomes incorporate in the nutrient dynamics of the Reservoirs. The result is that downstream reaches never receive nutrient and sediment rich flushing flows during the early winter.

5.1. Spatial considerations in watershed temporal analysis

In the upper reaches of the watershed, solute concentrations and temporal variability of concentrations for most constituents were minimal in comparison to the lower watershed (Table 1b).

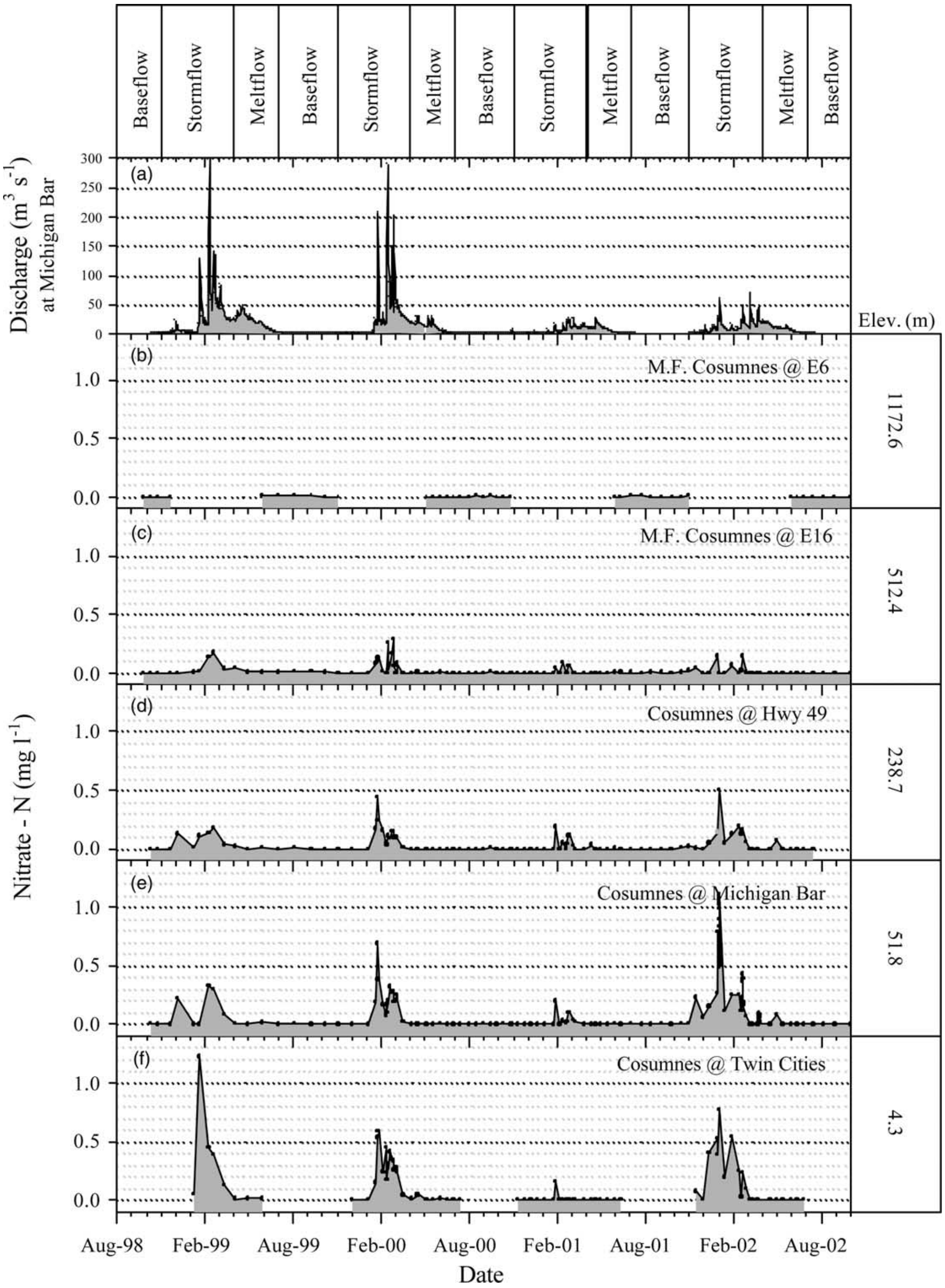

Fig. 7. Temporal variation in nitrate at the five study sites. Nitrate flushing with the onset of winter rains is most pronounced at the two low elevation sites (e and f).

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.

Figs. 2 and 7 illustrates how Middle Fork at E16 has only a weak flushing period, in these upper reaches the stormflow season is dominated by diluting storms rather than flushing, the results of this phenomenon can be seen in Table 1b as there is no significant difference in EC, nitrate and turbidity between the stormflow season and the meltflow season. 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. The perennial vegetation (coniferous forest) in the upper watershed has the ability to uptake nutrients all year round, including during autumn 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 (Hart et al., 1993). These nutrients are rapidly leached with the onset of the fall/winter rain season.

The impact that various land use and land cover types have on water chemistry of the stream is best observed when the landscape is hydrologically connected with local waterways (Basnyat et al., 1999; Lockaby et al., 1993). 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 (Tables 1a and 2). But during the winter when precipitation connects the landscape to the streams we see a wide fluctuation in chemistry between the sites in nearly all of the measured constituents (Table 2). Comparing the data from Middle Fork at E16, Cosumnes at Hwy 49, and Cosumnes at Michigan Bar we can see that each site responds differently to seasonal change (Table 1b). Middle Fork at E16 (an upper elevation site) exhibits the least chemical variability between hydrologic seasons for all constituents analyzed except EC. Meanwhile, Cosumnes at Michigan Bar (the lowest site of the three) has the most chemical variability between hydrologic seasons for the majority of the constituents analyzed. Obviously, position in the watershed affects seasonal variability in chemistry. But again this finding does not hold true in the neighboring Mokelumne Watershed where dams act to eliminate the difference in temporal response found at various elevations in the catchment.

Reservoirs in a watershed sever the hydrologic flowpaths present before impoundment and reset water quality parameters (Kelly, 2001; Ward and Stanford, 1995). The common result being that temporal response in the chemograph will not differ much between low elevation sites below a dam and high elevation site above. 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. As such, the Cosumnes survives as the last watershed draining into the Central Valley of California where temporal analysis can be conducted along a longitudinal transect of the river. Lack of impoundments on the Cosumnes gives us the opportunity to conduct meaningful analysis of temporal variations in stream chemistry on the annual, seasonal, and storm event time-scales.

5.2. Inter-annual patterns—dry-year vs. wet-year chemistry

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, 1996; Fenn and Poth, 1999; Muscutt et al., 1990). In the Cosumnes River Watershed this flushing period, 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 the main channel. 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 2001 and 2002 water years (dry years), the flushing period lasted from November to March (Fig. 2). There were no large storms similar to those evidenced in w.y. 1999 and 2000; 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 175 μS cm^{-1} at Twin Cities). Due to this extended flushing period, the dilution period of the storm season was brief, and the water quality characteristics of the stormflow season were dominated by repeated, small flushing events.

Nitrate and suspended sediment fluxes during January and February were calculated for both the 2000 and 2001 water years. The results (Table 3) 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. 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 (i.e. during a big storm). To compare nutrient and sediment transport between wet and dry years 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.

Table 3

Fluxes for selected constituents (in Mg) and discharge (in m^3) measured at Michigan Bar during a wet year (2000) and a dry year (2001). Two month totals are calculated for January and February and weighed against annual totals, and finally weighed against each other

Year		Discharge	TSS	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
2000	January–February total	350318	8075	1116	1	369	1583	4020	654	343	5	1182
	Annual total	483157	8105	1527	2	488	2075	5589	850	345	5	1492
	Percent flux: January–February vs. annual total	72.5	99.6	73.0	37.5	75.5	76.3	71.9	76.9	99.5	100.0	79.2
2001	January–February total	71853	377	304	0	67	363	667	171	3	0	355
	Annual–total	145752	892	557	0	130	642	1298	288	3	0	567
	Percent flux: January–February vs. annual total	49.3	42.3	54.6	N/A	51.3	56.6	51.4	59.5	99.2	N/A	62.5
2001 vs. 2000	Percent flux: January–February vs. January–February	20.5	3.8	27.5	N/A	18.0	23.2	16.9	26.4	0.7	N/A	30.4

6. Summary

This study suggests that hydrologic flowpaths exert 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). The stormflow season consists of a flushing period followed by diluting storms. The meltflow season frequently has flows as high as those seen during the storm season, yet these flows are largely 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, N, and P, and median levels of chlorophyll and DOC.

This 4-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 above 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 w.y. 2002 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.

Solute flushing was evident at all lowland sites, but upland sites showed little 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 cultivated lowlands.

Because the chemographs within each water quality season are strongly influenced 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 western 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.

Acknowledgements

The authors would like to thank Xien Wang, Ken Tate, Wendy Trowbridge, Jeffery Mount, Jennifer McDowell, Kai Wood, and the numerous lab assistants who aided in this project. This research was funded by the CALFED Bay–Delta Project (grant # 99-NO6).

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