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DETERMINING CRITICAL WATER QUALITY CONDITIONS FOR INORGANIC NITROGEN IN DRY, SEMI-URBANIZED WATERSHEDS¹

Arturo A. Keller, Yi Zheng, and Timothy H. Robinson²

ABSTRACT: Traditional approaches to establishing critical water quality conditions, based on statistical analysis of low flow conditions and expressed as a recurrence interval for low flow conditions (e.g., 7Q10), may be inappropriate for drier watersheds. The use of 7Q10 as a standard design flow assumes year-round flow, but in these watersheds, 7Q10 is zero or very small. In addition, the increasing use of multiple year dynamic water quality models at daily time steps can supercede the use of steady state approaches. Many of these watersheds are also under increasing urbanization pressure, which accentuates the flashiness of runoff and the episodic nature of critical water quality conditions. To illustrate, the conditions in the Santa Clara River, California, are considered. A statistical analysis indicates that higher inorganic nitrogen concentrations correlate strongly with low flow. However, peaks in concentrations can occur during the first storms, particularly where nonpoint source contribution is significant. Critical conditions can thus occur at different flow regimes depending on the relative magnitude of flow and pollutant contributions from various sources. The use of steady state models for these dry semi-urbanized watersheds based on 7Q10 flows is thus unlikely to accurately simulate the potential for exceeding water quality objectives. Dynamic simulation of water quality is necessary, and as the recent intense storm event sampling data indicate, the models should be formulated to consider even smaller time steps. This places increasing demand on computational resources and datasets to accurately calibrate the models at this temporal resolution.

(KEY TERMS: TMDL; watershed modeling; low flow; runoff; loads; storm water; inorganic nitrogen.)

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INTRODUCTION

As part of the development of watershed management plans, whether as a response to a total maximum daily load (TMDL) action or as part of proactive watershed management, the critical water quality conditions need to be determined. Critical refers to a possibility for impairing a beneficial use of a particular stream, river, or lake. The beneficial uses might be targeted towards human activities (e.g., drinking water supply, recreation, fishing), ecological uses (e.g., fisheries, wildlife habitat) or both. In most cases, the concern is the potential rise in concentrations of pollutants that can result in an exceedance of water quality standards or criteria during a long enough event to cause observable effects. The traditional approach has been to consider the low-flow conditions (e.g., Durrans, 1996; Chapra, 1997; Smakhtin, 2001) as the critical condition, using the 7Q10 (seven-day flow average with a 10-year recurrence interval) to determine the conditions to be simulated. Since in the past most water quality regulatory actions were focused on point sources, the intent was to determine the appropriate minimum flow (e.g., 7Q10) to continue diluting point source effluent and meet water quality objectives. This approach is common when employing a steady state model for evaluating water quality (Dilks and Pendergast, 2000). Although the use of 7Q10 does not require a steady state analysis, it is very common to do so. It is appropriate to use low flow conditions for streams or rivers where there is perennial flow, as occurs in most eastern, midwest, and northwestern U.S. regions or in northwestern

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Europe (Young *et al.*, 2000), where precipitation and snowmelt are sufficient in most instances for year round flow (Wolock *et al.*, 1997).

A mass balance for any reach along a river or creek is given by

$$\frac{dVC}{dt} = Q_i C_i - Q_o C + \sum_{p=1}^{P} Q_{PS,p} C_p + \sum_{n=1}^{N} Q_{NPS,n} C_n$$

$$\pm V \sum_{i=1}^{J} k_{r,j} C$$
(1)

where V is the volume of reach (m^3) ; C is the concentration (g/m^3) ; Q is the flow (m^3/s) ; k_r is the rate of source or sink process such as reactions, adsorption, etc., assuming first order with respect to concentration (per second); *i* is the inflow to reach; *o* is the outflow from reach; *PS* is the Point Source; *NPS* is the nonpoint source; *p* is the index for *PS*; *P* is the total number of *PS* in reach; *n* is the index for *NPS*; *N* is the total number of *NPS* in reach; *j* is the total number of source/sink processes; and *J* is the total number of source/sink processes considered in reach. If a steady state assumption is used for the critical condition

 $\left(\frac{dVC}{dt}=0\right)$, then the concentration could be determined from

$$C = \frac{Q_i C_i + \sum_{p=1}^{P} Q_{PS,p} C_p + \sum_{n=1}^{N} Q_{NPS,n} C_n}{Q_o \mp V \sum_{j=1}^{J} k_{r,j}}$$
(2)

However, when considering drier watersheds such as much of the southwestern U.S. or similar conditions in other parts of the world (Clausen and Pearson, 1995; Khan and Khan, 1997; Smakhtin et al., 1998a,b; Devlin et al., 2001), the standard approach to low flow conditions might not be appropriate, since the 7Q10 (= Q_o) and V might be zero or almost zero, leading to unreasonable results for Equation (2). In addition, with the availability of dynamic models such as HSPF (Codner, 1991; Fielland and Ross, 1991; Becknell et al. 1993; Chen et al., 1995; Laroche et al., 1996; Al-Abed, 2002; Munson et al., 1998), SWAT (Arnold et al., 1998; Saleh et al., 2000; Arnold et al., 2001; Eckhardt and Arnold, 2001; Neitsch et al., 2001; Santhi et al., 2001a,b; Di Luzio et al., 2002), WARMF (Chen et al., 1996; EPRI, 1998; Systech Engineering, Inc., 2000) and others, it is unclear whether using a 7Q10 approach is necessary. These models simulate streamflow and water quality dynamically as a function of precipitation inputs, and thus the need to select a particular averaging time (3Q10, 7Q10, 30Q3) is not as clear.

To illustrate the point, the conditions in the Santa Clara River (SCR) are presented. It is located in Southern California (Figure 1) and although parts of it are urbanizing rapidly, it is the last major river in this region that is not heavily channelized, with over $4,000 \text{ km}^2$ of catchment area. Much of the lower watershed was originally Spanish land grants used for grazing cattle and dry land farming. Urbanization since the late 1940s has continuously modified the land use, resulting in discharge of imported water and municipal wastewater. Since the 1950s, agriculture has been also transforming from seasonal dry land farming to predominantly year round irrigated farming of citrus, avocado, and row crops.

The climate in this region is Mediterranean, typical of the Southern California coast. Average annual precipitation varies from 0.36 m along the coast, to about 0.43 m near Santa Paula in the intermediate altitudes, and more than 0.63 m in the surrounding mountains. Precipitation is concentrated in a short rainy season with a few strong storms delivering the majority of the natural input (Figure 2). Temperatures range from above 30°C in the higher elevations in summer to slightly below freezing during the winter. Although there is minor snowfall in the higher elevations, it provides no significant water storage.

The basin drains from the east through the SCR and its major tributaries, Castaic, Piru, Hopper, Sespe, and Santa Paula Creeks (Figure 1). The mountains are composed of marine and terrestrial sedimentary and volcanic rocks. The basins are filled with a mixture of deposits of sands, silts, and clays interspersed throughout the region, representing the exposure of several of the underlying formations. Natural flow in all the major streams and tributaries in the basin is intermittent and ephemeral, with most of the streamflow related to floodflows. Under very high flow conditions, the river is continuous from the headwaters to the discharge at the estuary. This surface flow does not persist year round, as the surface water percolates to the underlying ground water within a relatively short distance downstream of the Los Angeles-Ventura County line. Water from Northern California is imported by United Water Conservation District through Pyramid Lake and Lake Piru, and periodically released down Piru Creek and the lower portion of the SCR, in Ventura County. Water is also imported by the Castaic Lake Water Agency for municipal use in the Santa Clarita Valley. Some of this imported water enters the river or land surface as treated effluent, irrigation return flow, or via

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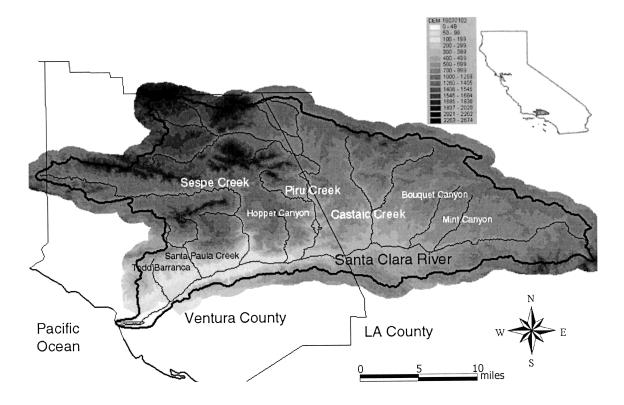


Figure 1. Location and General Topography and Hydrology of the Santa Clara River.

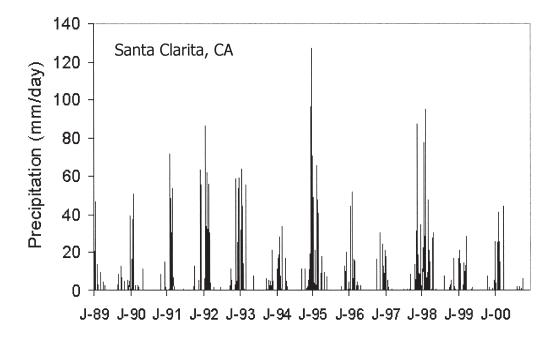


Figure 2. Measured Precipitation in Santa Clarita, California, From January 1989 (J-89) to December 2000.

ground water, providing a significant fraction of the flow (Hanson *et al.*, 2003; Izbicki, 2003).

The SCR watershed presents an interesting combination of land uses, where the upper SCR (nearest to Los Angeles) is urbanized and expanding rapidly, while the central and lower SCR is still dominated by agriculture and smaller cities with less development and growth (Figure 3). Thus, the flow of the SCR has been modified due to land use changes, climatic conditions, drawdown of the aquifers from decades of pumping, and water imports. Discharges from wastewater treatment plants, and nonpoint source discharge in the watershed have changed the flow and concentration of nutrients and other contaminants in receiving waters. These conditions are typical of the developing southwestern U.S., which relies heavily on imported water to continue growing.

For this study, the conditions that lead to high concentrations of inorganic nitrogen species (i.e., ammonia, nitrite, and nitrate) in different reaches and tributaries of the SCR watershed were evaluated. The analysis was divided into three sections: (1) an analysis of the low flow conditions and the correlation between low flow and high concentrations of these nitrogen species; (2) an evaluation of the timing of point and nonpoint source discharges of these nitrogen species to the river and tributaries to determine the possibility of high concentration peaks during the initial storm events (first-flush effect); and (3) conditions where rising ground water might be a significant contribution to total loading. This paper investigated the dependence of critical conditions on different flow regimes depending on the relative magnitude of flow and pollutant contributions from various sources.

METHODS

For this work, the WARMF model was used, although any one of a number of other available watershed models would produce comparable simulated output. The watershed model implementation was carried out by Systech Engineering, Inc., as part of a stakeholder led approach facilitated by the authors. WARMF was selected by the stakeholder group based on its comparable scientific strength vis-à-vis SWAT or HSPF, and its superior ability to analyze stakeholder concerns and develop TMDLs. The watershed was discretized into more than 190 catchments ranging from a few km² to several hundred km² in size, depending on the resolution of land use data and impact on the overall calibration (Figure 4). Some regions contribute little to degrade water quality, since they are mostly natural vegetation managed by

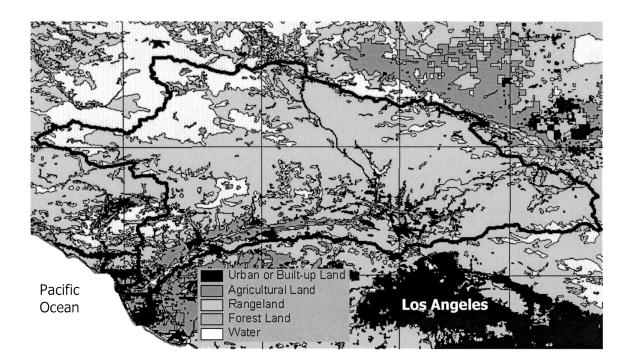


Figure 3. Major Land-Use Categorization of the Santa Clara River Watershed (watershed outline in black).

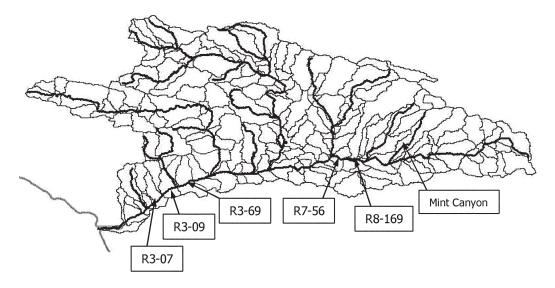


Figure 4. Watershed Delineation Used in WARMF Model. The segments of the Santa Clara River discussed in detail are highlighted.

federal or state agencies, and/or they have limited flow and chemical data. Other regions have several stream gages and/or water quality sampling locations, allowing discretization of the catchments into smaller subcatchments. As with similar models, soil properties and other land use parameters are considered as a weighted average for the subcatchment. Water coming from precipitation, as rainfall or snowfall, is routed through the canopy, land surface, shallow subsurface flow, and deep ground water flow to the receiving water bodies, namely streams, rivers, or lakes, with losses due to evapotranspiration, irrigation, or other extractive uses that do not return it to the system. Chemicals are (1) in the system initially (e.g., nitrogen in vegetation, ground water, and/or soil minerals); (2) applied to the land surface (e.g., fertilization, irrigation water, atmospheric deposition, septic system discharge, animal waste), and/or (3) discharged directly into a waterbody (e.g., discharge of treated effluent). Assimilation and transformation among N species is simulated, on the soil surface or in the various water compartments. The model was run at a daily time step, given that most of the input and calibration data were only available in that timeframe.

The WARMF model was implemented using data for water years 1989 to 2000, obtained from local agencies (e.g., United Water Conservation District, Ventura County Flood Control District, Los Angeles County Department of Public Works, Ventura County Farm Bureau, four large wastewater treatment plants, city governments, agricultural associations, environmental organizations, and land developers), regional/state agencies (e.g., Southern California Association of Governments, Regional Water Quality

Control Board, State Water Resources Control Board, and the California Air Resources Board), and national agencies (e.g., U.S. Environmental Protection Agency, U.S. Geological Survey, National Oceanic and Atmospheric Administration, and the U.S. Fish and Wildlife Service) for meteorology, land use, fertilizer application rates, atmospheric deposition, point source flow and concentrations, water quality, gauged flow, etc. Although WARMF can simulate ground water flow and subsurface chemical transport, it is done at a low spatial resolution (similar to HSPF and SWAT). Given that ground water models were available from the United Water Conservation District for the lower SCR and a combination of stakeholders in the upper SCR, they provided monthly flows (to or from the river) for each subcatchment of the SCR during the 11-year simulation period. Monitoring data from wells near the SCR were used to determine the initial chemical concentrations in ground water. Documentation used for the TMDL, which details at length the source analysis, input data, and ground water interactions (Herr, 2003a,b), and calibration and validation (Keller and Zheng, 2003), is available (Los Angeles Regional Water Quality Control Board, 2004). The model was validated using more recent data. Examples of calibration results for flow and chemistry are presented in Figure 5 for Reach R7-56 of the SCR; and in Figure 6 for Mint Canyon, a tributary in the upper SCR watershed. The stream gage in Reach R7-56 was moved further downstream in 1996. There are no calibration data for water quality in Mint Canyon. WARMF does not calculate a concentration when flow goes near zero, resulting in a discontinuous line for the nitrogen compounds.

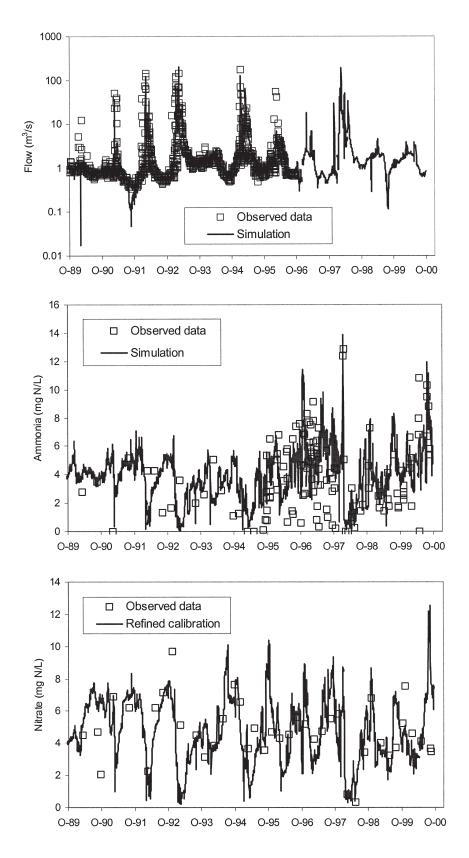


Figure 5. Comparison of (a) Observed Flow and Water Quality Data for (b) Ammonia and (c) Nitrate, and WARMF Model Simulation Results for Reach 7-56 of the Santa Clara River, From October 1, 1989 (O-89), to September 30, 2000 (O-00).

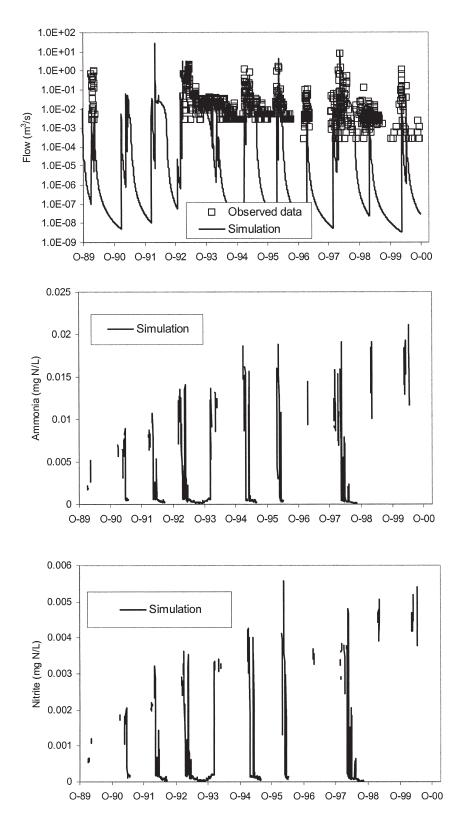


Figure 6. Comparison of (a) Observed Flow and Water Quality Data for (b) Ammonia and (c) Nitrate, and WARMF Model Simulation Results for Mint Canyon.

RESULTS AND DISCUSSION

Low Flow Analysis

The analysis focused on three reaches and a number of tributaries of the SCR where the Los Angeles Regional Water Quality Control Board has determined that the water quality objectives have been exceeded in the past, resulting in potential impairment of the designated beneficial uses. The low flow conditions were characterized using two different criteria: (1) 7Q10 – the lowest seven-day flow with a recurrence of 10 years; and (2) 30Q3 – the lowest 30day flow with a recurrence of three years.

Although the most common criterion for low flow conditions is 7Q10, given the climatic conditions of the SCR watershed, the 30Q3 was considered as an additional criterion, since many of the tributaries have no flow for a considerable part of the year. For this study, the 11-year period between Water Year (WY) 1989 and WY 2000 was considered. Daily flow data were available at a number of gaging stations in the SCR reaches. However, there were little or no flow data for a number of the tributaries. Thus, simulation results from the WARMF model were used to estimate the daily flows for these tributaries, as well as for those time periods where the flow gauges were not operational in the SCR reaches.

The results of the low flow analysis are presented in Table 1. Most of the watershed has no flow conditions at some point of the 11-year period, and only the main segments of the SCR have some flow under the 7Q10 criterion. Even the 30-day average flows in the tributaries are very low or zero.

TABLE 1. Low Flow Conditions in the Santa Clara River Watershed (m^3/s) .

River Segment	7Q10	30Q3	
SCR R3-09	0.17	0.798	
SCR R7-56 (below Valencia WWTP)	0.02	0.501	
SCR R7-137 (at Valencia WWTP)	0.05	0.642	
SCR R7-129 (above Valencia WWTP)	0.39	0.472	
SCR R8-169	0.0002	0.145	
Mint Canyon Creek	0.0	0.0	
Wheeler Canyon Creek	0.0	0.0008	
Todd Barranca Creek	0.0	0.0026	
Brown Barranca Creek	0.0	0.0	

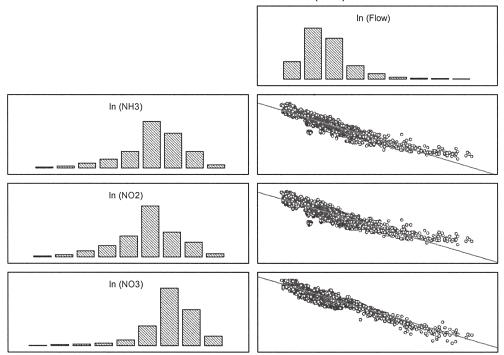
Figure 7 presents a graphical representation of the correlation of simulated natural logarithm of water quality versus natural logarithm of flow for SCR R3-09, which is in the lower SCR between Sespe Creek and Todd Barranca Creek (Figures 1 and 4). For the analysis, simulated data were used, after calibration, since the original data sets are sparse, and in particular since samples for water quality analysis were not collected regularly during low flow conditions or storm events, which are important for the analysis. The preliminary analysis indicated that there is a much stronger correlation between log(flow) and log(concentration) than between flow and concentration (Figure 8, for SCR R3-07 immediately below R3-09). Flow and water quality in these two segments is influenced to some extent by the discharges of the Santa Paula and Fillmore waste water treatment plants (WWTP), although there is an important contribution from agricultural nonpoint sources and rising ground water, as discussed later.

Similar correlations are observed in other regions of the watershed (Figures 9 and 10). There are two other WWTP, the Valencia WWTP above R7-56 and Saugus WWTP in R8-169. These have an impact on both flow and water quality levels. A power law can be used to represent the observed relationship between flow, Q, and concentration of solute, X, where X is NH₃, NO₂⁻ or NO₃⁻

$$[X] = a \ Q^b \tag{3}$$

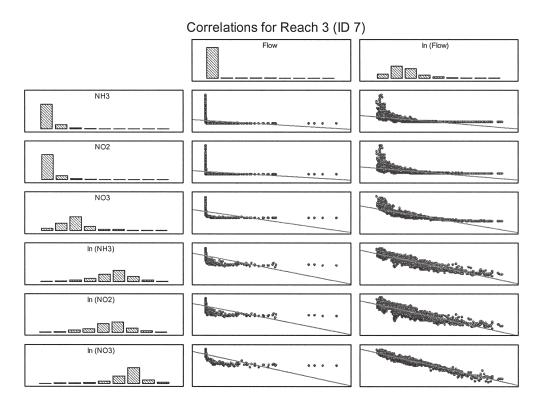
The coefficients a and b for the various reach segments are presented in Table 2, as well as the regression coefficient, R². The strongest correlation is for nitrate, followed by ammonia and nitrite. The higher the mean concentration of a compound, the stronger the correlation. Concentrations for all three compounds, in general, decrease with flow, indicating that the highest concentrations are typically found at the low flow conditions for the SCR, except for NH₃ and NO₂⁻ in SCR R3-69 (Figure 11), discussed in more detail below. The dilution effect of higher flows (a high negative value for the exponent b) is strongest in the vicinity of a WWTP, where, in general, there is more urbanization that results in stormwater flow from impervious surfaces.

This analysis is not meaningful for the tributaries (e.g., Mint Canyon) and headwaters of the SCR, since flow is limited to a few days a year where there is sufficient precipitation to generate surface runoff that does not immediately disappear in the dry streambed. In these streams, the critical condition is during the episodic flows (Figure 6), since there is no flow during the rest of the year.



Correlations for Reach 3 (ID 9)

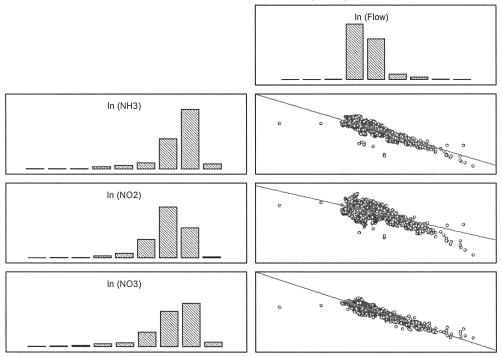
 $\begin{array}{l} \mbox{Figure 7. Statistical Analysis of Simulated ln(water quality) Versus ln(flow) for Reach 3-09 of the Santa Clara River. \\ \mbox{Range for flow = } 0.238 - 974 \ m^3/day, for NH_3 = 0.0062 - 5.67 \ mg \ NH_3 - N/L, for NO_2 = 0.0020 - 1.07 \ mg \ NO_2 - N/L, \\ \mbox{for NO}_3 = 0.0887 - 4.53 \ mg \ NO_3 - N/L. \\ \mbox{Nine categories are considered for each parameter.} \end{array}$



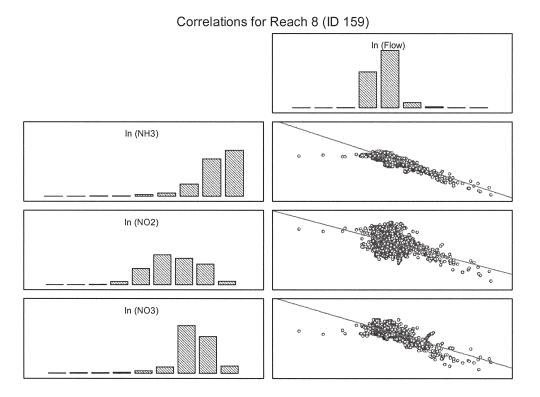
 $\begin{array}{l} \mbox{Figure 8. Statistical Analysis of Simulated Water Quality Versus Flow for Reach 3-07 of the Santa Clara River.} \\ \mbox{Range for flow} = 0.238 - 986 \ m^3/day, for NH_3 = 0.0043 - 3.65 \ mg \ NH_3 - N/L, for NO_2 = 0.0018 - 1.27 \ mg \ NO_2 - N/L, \\ \mbox{for NO}_3 = 0.0751 - 4.95 \ mg \ NO_3 - N/L. \ Nine categories are considered for each parameter.} \end{array}$

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 $\begin{array}{l} \mbox{Figure 9. Statistical Analysis of Simulated ln(water quality) Versus ln(flow) for Reach 7-56 of the Santa Clara River. \\ \mbox{Range for flow = } 0.0206 - 141 \ m^3/day, for NH_3 = 0.0457 - 13.9 \ mbox{mg NH}_3 - N/L, for NO_2 = 0.0043 - 0.940 \ mbox{mg NO}_2 - N/L, \\ \mbox{for NO}_3 = 0.203 - 12.6 \ mbox{mg NO}_3 - N/L. \\ \mbox{Nine categories are considered for each parameter.} \end{array}$



 $\begin{array}{l} \mbox{Figure 10. Statistical Analysis of Simulated ln(water quality) Versus ln(flow), for Reach 8-159 of the Santa Clara River. \\ \mbox{Range for flow} = 0.0024 - 77.1 \mbox{ m}^3/\mbox{day, for NH}_3 = 0.0472 - 19.5 \mbox{ mg NH}_3-\mbox{N/L, for NO}_2 = 0.0037 - 1.04 \mbox{ mg NO}_2-\mbox{N/L}, \\ \mbox{ for NO}_3 = 0.297 - 8.17 \mbox{ mg NO}_3-\mbox{N/L}. \\ \mbox{Nine categories are considered for each parameter.} \end{array}$

Segment	NH ₃			NO ₂ -		NO ₃ -			
	a	b	\mathbf{R}^2	a	b	\mathbf{R}^2	a	b	\mathbf{R}^2
SCR R3-07	0.31	-0.76	0.75	0.10	-0.72	0.70	1.7	-0.44	0.88
SCR R3-09	0.73	-0.85	0.84	0.14	-0.79	0.79	2.0	-0.43	0.86
SCR R3-69	0.0016	0.14	0.01	0.0004	0.25	0.02	1.7	-0.31	0.48
SCR R7-111	0.48	-0.26	0.13	0.090	-0.080	0.0085	5.5	-0.65	0.84
SCR R7-56	3.9	-0.72	0.72	0.21	-0.43	0.33	4.7	-0.72	0.83
SCR R7-137	6.1	-0.86	0.74	0.090	-0.18	0.030	5.1	-0.64	0.67
SCR R7-129	0.47	-0.48	0.28	0.15	-0.39	0.16	2.8	-0.45	0.64
SCR R8-169	2.9	-0.83	0.75	0.095	-0.47	0.18	2.4	-0.36	0.46

TABLE 2. Power Law Coefficients for Various Segments of the Santa Clara River.



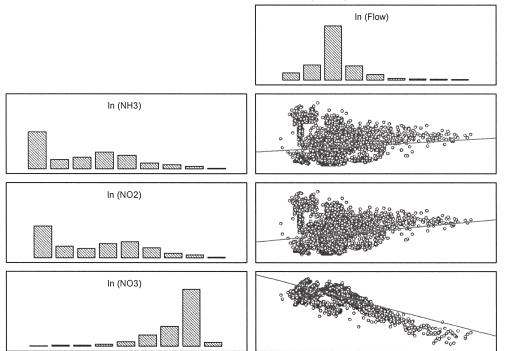


Figure 11. Statistical Analysis of Simulated ln(water quality) Versus ln(flow) for Reach 3-069 of the Santa Clara River. Range for flow = $0.238 - 974 \text{ m}^3$ /day, for NH₃ = $0.0062 - 5.67 \text{ mg NH}_3$ -N/L, for NO₂ = $0.0020 - 1.07 \text{ mg NO}_2$ -N/L, for NO₃ = $0.0887 - 4.53 \text{ mg NO}_3$ -N/L. Nine categories are considered for each parameter.

TIMING OF POINT AND NONPOINT SOURCE LOADS

Although the previous analysis indicates that there is a strong negative correlation between flow and concentration (i.e., the highest concentrations occur during the lowest flows), the timing of the point source (PS) and nonpoint source (NPS) loads is important. Figures 12, 13, and 14 present an analysis of PS and runoff NPS load timing, as well as the ground water contribution. This analysis was done using the WARMF model, first zeroing out the nutrient load from PS to the river, and, subsequently, the NPS to the land surface and/or river, and comparing the mass loading in the river for the various cases. Only the nitrate load is presented, since the ammonia and

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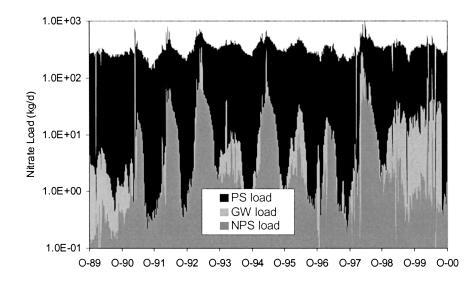


Figure 12. Point Source (PS), Nonpoint Source (NPS) and Ground Water (GW) Load in kg Per Day in SCR R7-56, From October 1, 1989 (O-89), to September 30, 2000 (O-00). Note the logarithmic scale for the y-axis.

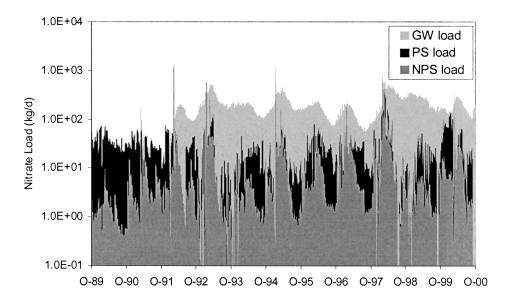


Figure 13. Point Source (PS), Nonpoint Source (NPS) and Ground Water (GW) Load in kg Per Day in SCR R3-69, From October 1, 1989 (O-89), to September 30, 2000 (O-00).

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nitrite load in the river is almost entirely from PS discharges. Ammonia from fertilizer application converts relatively rapidly to nitrate on the land surface or assimilated in plants, resulting in very small loading to the river in most segments. Figure 12 presents the analysis for SCR R7-56, which is dominated by PS loading and has a significant urban and suburban contribution via storm water. The timing of PS and NPS loading peaks generally coincides in this segment, and exhibits sharp peaks during each storm event, generating a critical condition at a high flow. For SCR R3-69 (Figure 13), a segment dominated by agriculture with no major nearby point sources and a dry gap separating it from the upper reaches most of the time, the nitrate load in the river is dominated by ground water contributions most of the year. Thus, this segment of the river is atypical in that higher concentrations of NH_3 and NO_2^- occur generally during higher flow rates (Figure 11) (i.e., when a strong storm event washes the land surface). Late fall and winter storms result in NPS nitrate load peaks, particularly during the first important storms (Figure 13). For Mint Canyon (Figure 14), a long subcatchment in the upper watershed with rapidly increasing sub-urbanization, the loading is expected to be dominated by NPS, with only sporadic ground water contributions. There are no significant point sources in this catchment.

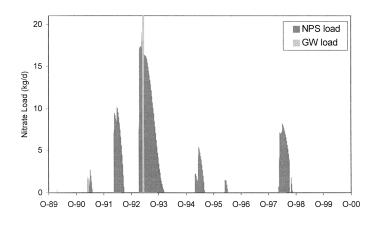


Figure 14. Nonpoint Source (NPS) and Ground Water (GW) Load in kg Per Day in Mint Canyon, From October 1, 1989 (O-89), to September 30, 2000 (O-00).

To corroborate the hypothesis that storm events can in some cases lead to higher temporary concentrations, high frequency sampling data from nearby creeks during storm events were analyzed (described in more detail in Robinson *et al.*, 2002). For a semiurbanized segment of the creek, nitrate concentrations rise early during the storm and then become diluted as runoff from other areas reaches the creek (Figure 15). In contrast, another creek with agricultural land use exhibits higher concentrations after the storm event, due to shallow ground water contributions (Figure 16). This on-going project will serve to establish more conclusively the need to consider high frequency sampling during storm events to monitor for critical conditions, particularly in semi-urbanized watersheds.

CONCLUSIONS

The analysis indicates that for the generally dry conditions in this region, the traditional approach of characterizing critical water quality conditions using 7Q10 or even 30Q3 is not appropriate, for the sources of water and pollutants are constantly shifting in SCR, a common condition for urbanized or semiurbanized watersheds. In addition, increasing urbanization of these watersheds leads to faster runoff during storm events. The use of a steady state model for a single flow condition and a fixed source of water and pollutants is unlikely to accurately represent the critical condition.

In this case study using the Santa Clara River data, there is no single time when critical conditions occur, because the flow and water quality of SCR changes with time due to dynamic shifts of water and pollution loads among storm water, ground water, and point source discharges. Critical conditions occur in situation at low flows during large storm events that wash nonpoint source loads, and in areas where ground water contributions are significant.

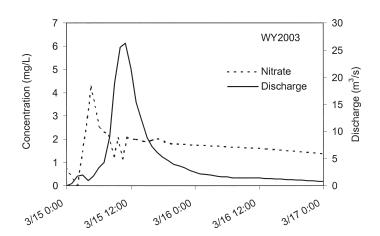


Figure 15. Observed Hydrograph and Nitrate Concentration in Lower Carpinteria Creek, California, in March 15 to 16, 2003.

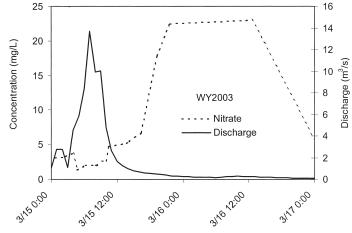


Figure 16. Observed Hydrograph and Nitrate Concentration in Lower Franklin Creek, California, in March 15 to 16, 2003.

Dynamic simulation of water quality is necessary, and as the recent intense storm event sampling data indicate, the models may have to be run at very small time steps, on the order of 15 to 60 minutes. This will place increasing demands not only on computational resources but also datasets to accurately calibrate the models at this temporal resolution. The analysis also indicates the importance of ground water contributions in some subcatchments, and the need to incorporate surface and ground water exchanges in the evaluation of critical water quality conditions.

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LITERATURE CITED

- Al-Abed, N.A. and H.R. Whiteley, 2002. Calibration of the Hydrological Simulation Program Fortran (HSPF) Model Using Automatic Calibration and Geographical Information Systems. Hydrol. Process 16: 3169-3188.
- Arnold, J.G., R. Srinivasan, R.S. Muttiah, and J.R. Williams, 1998. Large Area Hydrologic Modeling and Assessment – Part I: Model Development. Journal of the American Water Resources Association (JAWRA) 34(1):73-89.
- Arnold, J.G., P.M. Allen, and D.S. Morgan, 2001. Hydrologic Model for Design and Constructed Wetlands. Wetlands 21(2):167-178.
- Becknell, B.R., J.C. Imhoff, J.L. Kittle, A.S. Donigian, and R.C. Johanson, 1993. Hydrological Simulation Program: FORTRAN. User's Manual for Release 10, Report No. EPA600R93174 667.
- Chapra, S., 1997. Surface Water-Quality Modeling. McGraw Hill, New York, New York.
- Chen, C.W., J. Herr, R.A. Goldstein, F.J. Sagona, K.E. Rylant, and G.E. Hauser, 1996. Watershed Risk Analysis Model for TVA's Holston River Basin. Water, Air and Soil Pollution 90:1-2.
- Chen, Y.D., S.C. Mccutcheon, R.F. Carsel, A. Donigian, J.R. Cannell, and J.P. Craig, 1995. Validation of HSPF for the Water Balance Simulation of the Upper Grande Ronde Watershed, Oregon, USA. IAHS Publication (230):3-13.
- Clausen, B. and C. Pearson, 1995. Regional Frequency-Analysis of Annual Maximum Streamflow Drought. J. Hydrology 173 (1-4):111-130.
- Codner, G.P., 1991. Tale of Two Models: SWMM and HSPF. Natl. Conf. Publ. Inst. Eng. Aust., IE Aust, Barton 2(91):569-574.
- Devlin, M., J. Waterhouse, and J. Brodie, 2001. Community and Connectivity: Summary of a Community Based Monitoring Program Set Up to Assess the Movement of Nutrients and Sediments Into the Great Barrier Reef During High Flow Events. Water Science And Technology 43(9):121-131.
- Di Luzio, M., R. Srinivasan, and J.G. Arnold, 2002. Integration of Watershed Tools and SWAT Model Into BASINS. Journal of the American Water Resources Association (JAWRA) 38(4):1127-1142.

- Dilks, D. and J. Pendergast, 2000. Comparison of Dynamic and Steady-State Models for Determining Water Quality Based National Pollutant Discharge Elimination System Limits for Toxics. Water Environment Research 72(2):225-229.
- Durrans, S., 1996. Low-Flow Analysis With a Conditional Weibull Tail Model. Water Resources Research 32(6):1749-1760.
- Eckhardt, K. and J.G. Arnold, 2001. Automatic Calibration of a Distributed Catchment Model. J. Hydrology 251(1-2):103-109.
- EPRI (Electric Power Research Institute), 1998. Watershed Analysis Risk Management Framework: A Decision Support System for Watershed Approach and Total Maximum Daily Load Calculation. Palo Alto, California, Electric Power Research Institute.
- Fielland, C.E. and M.A. Ross, 1991. Improved HSPF Infiltration Calibration Procedure With a Linked GIS. Proc. Int. Symp. Ground Water Pract., ASCE, New York, New York, pp. 126-131.
- Hanson, R.T., P. Martin, and K.M. Koczot, 2003. Simulation of Ground-Water/Surface-Water Flow in the Santa Clara-Calleguas Ground-Water Basin, Ventura County, California. Water-Resources Investigations Report 02-4136.
- Herr, J., 2003a. Final Task 1 Report for Santa Clara River Nutrient TMDL Analysis: Source Identification and Characterization. Prepared by Systech Engineering for the Los Angeles Regional Water Quality Control Board, Los Angeles, California. Available at http://www.swrcb.ca.gov/rwqcb4/html/meetings/tmdl/ santa_clara/03_0523_NitrogenCompound/Task1Final.pdf. Accessed on April 27, 2004.
- Herr, J., 2003b. Final Task 2 Report for Santa Clara River Nutrient TMDL Analysis: Linkage Analysis, Hydrology and Water Quality. Prepared by Systech Engineering for the Los Angeles Regional Water Quality Control Board, Los Angeles, California. Available at http://www.swrcb.ca.gov/rwqcb4/html/meetings/ tmdl/santa_clara/03_0523_NitrogenCompound/Task2Final.pdf. Accessed on April 27, 2004.
- Keller, A.A. and Y. Zheng, 2003. WARMF Model Calibration Refinement for Nitrogen Compounds in the Santa Clara River. Technical report prepared for the Los Angeles Regional Water Quality Control Board, Los Angeles, California. Available at http://www. swrcb.ca.gov/rwqcb4/html/meetings/tmdl/santa_clara/03_0523_ NitrogenCompound/SCR%20N%20TMDL%20calibration%20 refinement%2006-16-03.pdf. Accessed on April 27, 2004.
- Khan, S. and M. Khan, 1997. Water Quality Characteristics of the Kabul River in Pakistan Under High Flow Conditions. J. Chemical Society Of Pakistan 19(3):205-210.
- Izbicki, J.A., 2003. Source, Movement and Age of Ground Water in a Coastal California Aquifer. USGS FS 126-96, U.S. Geological Survey, Sacramento, California. Available at (http://ca.water. usgs.gov/archive/fact_sheets/b08/intro.html). Accessed on April 27, 2004.
- Laroche, A.M., J. Gallich, R. Lagace, and A. Pesant, 1996. Simulating Atrazine Transport With HSPF in an Agricultural Watershed. Journal of Environmental Engineering 122(7):622-630.
- Los Angeles Regional Water Quality Control Board, 2004. Santa Clara River – Nitrogen Compounds TMDL. Technical Support Documents. Available at http://www.swrcb.ca.gov/rwqcb4/html/ meetings/tmdl/tmdl_ws_santa_clara.html. Accessed on April 27, 2004.
- Munson, A., S. Socolofsky, and E. Adams, 1998. HSPF Modeling of the Charles River Watershed. Int. Water Res. Eng. Conf. Proc., ASCE, Reston, Virginia, Vol. 2, pp. 1356-1361.
- Neitsch, S.L., J.G. Arnold, J.R. Kiniry, and J.R. Williams, 2001. Soil and Water Assessment Tool: User's Manual 2000. Grassland, Soil and Water Research Laboratory, Agricultural Research Service, Temple, Texas, 781 pp.

- Robinson, T.H., A. Leydecker, J.M. Melack, and A.A. Keller, 2002. Nutrient Concentrations in Southern Californian Streams Related to Landuse. *In:* Coastal Water Res., J.R. Lesnik (Editor). American Water Resources Association, Middleburg, Virginia, TPS-02-1, pp. 339-343.
- Saleh, A., J.G. Arnold, P.W. Gassman, L.M. Hauck, W.D. Rosenthal, J.R. Williams, and A.M.S. McFarland, 2000. Application of SWAT for the Upper North Bosque River Watershed. Transactions of the ASAE 43(5):1077-1087.
- Santhi, C., J.G. Arnold, J.R. Williams, W.A. Dugas, and R. Srinivasan, 2001a. Validation of the SWAT Model on a Large River Basin With Point and Nonpoint Sources. Journal of the American Water Resources Association (JAWRA) 37(5):1169-1188.
- Santhi, C., J.G. Arnold, J.R. Williams, L.M. Hauck, and W.A. Dugas, 2001b. Application of a Watershed Model to Evaluate Management Effects on Point and Nonpoint Source Pollution. Transactions of the ASAE 44(6):1559-1570.
- Smakhtin, V., 2001. Low Flow Hydrology: A Review. J. Hydrology 240(3-4):147-186.
- Smakhtin, V., K. Sami, and D. Hughes, 1998a. Evaluating the Performance of a Deterministic Daily Rainfall-Runoff Model in a Low-Flow Context. Hydrological Processes 12(5):797-811.
- Smakhtin, V., D. Watkins, D. Hughes, K. Sami, and O. Smakhtina, 1998b. Methods of Catchment-Wide Assessment of Daily Low-Flow Regimes in South Africa. Water SA 24(3):173-185.
- Systech Engineering, Inc., 2000. WARMF User's Manual. Systech Engineering, Inc., Ramon, California.
- Wolock, D., J. Fan, and G. Lawrence, 1997. Effects of Basin Size on Low-Flow Stream Chemistry and Subsurface Contact Time in the Neversink River Watershed, New York. Hydrological Processes 11(9):1273-1286.
- Young, A., C. Round, and A. Gustard, 2000. Spatial and Temporal Variations in the Occurrence of Low Flow Events in the UK. Hydrology and Earth System Sciences 4(1):35-45.