

Influence of Drought and Total Phosphorus on Diel pH in Wadeable Streams: Implications for Ecological Risk Assessment of Ionizable Contaminants

Theodore W Valenti,^{*†,‡,§,#} Jason M Taylor,^{‡,||} Jeffrey A Back,^{‡,||} Ryan S King,^{‡,||,#} and Bryan W Brooks^{‡,§,#}

[†]National Research Council, US Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division, 6201 Congdon Boulevard, Duluth, MN 55804, USA

[‡]Center for Reservoir and Aquatic Systems Research, Baylor University, Waco, Texas, USA

[§]Department of Environmental Science, Baylor University, Waco, Texas, USA

^{||}Department of Biology, Baylor University, Waco, Texas, USA

[#]The Institute of Ecology, Earth and Environmental Sciences, Baylor University, Waco, Texas, USA

(Submitted 15 December 2010; Returned for Revision 7 February 2011; Accepted 7 April 2011)

ABSTRACT

Climatological influences on site-specific ecohydrology are particularly germane in semiarid regions where instream flows are strongly influenced by effluent discharges. Because many traditional and emerging aquatic contaminants, such as pharmaceuticals, are ionizable, we examined diel surface water pH patterns (i.e., change in pH over a 24-h period) at 23 wadeable streams in central Texas, USA, representing a gradient of nutrient enrichment during consecutive summers of 2006 and 2007. The years of our study were characterized by decidedly different instream flows, which likely affected production:respiration dynamics and led to distinctions in diel pH patterns between 2006 and 2007. Site-specific ambient water quality criteria for NH₃ and the aquatic toxicity of the model weak base pharmaceutical sertraline were predicted using continuous water quality monitoring data from the sites. Drought conditions of 2006 significantly increased ($p < 0.05$) diel pH changes compared to high instream flows of 2007, and the magnitude of diel pH variability was most pronounced at nutrient-enriched sites in 2006. Differences in diel pH change patterns between 2006 and 2007 affected predictions of the environmental fate and effects for model weak base pharmaceuticals and NH₃. Overall, site-specific diel pH was more variable at some sites than the difference in mean surface water pH between the 2 summers. Diel pH variability affected regulatory criteria, because 20% of the study sites in 2006 experienced greater than 5-fold differences in National Ambient Water Quality Criteria for NH₃ over 24-h periods. Our study emphasizes the potential uncertainty that diel pH variability may introduce in site-specific assessments and provides recommendations for environmental assessment of ionizable contaminants. *Integr Environ Assess Manag* 2011;7:636–647. © 2011 SETAC

Keywords: Ionizable contaminants Potency Site-specific pH Climate change Water quality

INTRODUCTION

Climate change models predict further reductions in future water availability in semiarid regions of the southwest United States. This region already experiences substantial variability in natural stream flow exemplified by prolonged periods of drought (Hurd et al. 1999; Sun et al. 2008). Drought events can limit the assimilation capacity of systems receiving point-source discharges or cause deviations in site-specific water chemistry due to altered transient pathways of water. These types of system level effects may have direct consequences on biological and geochemical processes (Brooks et al. 2006; Boxall et al. 2009). In some instances, low flow conditions may lead to the complete elimination of lotic habitat. The most extreme scenario includes suppressed hydrologic regimes in which effluent-dominated streams are losing systems with instream flows strongly influenced by or completely comprised of return flows from effluent discharges (Brooks et al. 2006). The effect that reduced flow will have on the aquatic risks of contaminants is difficult to predict

and presents a considerable challenge for integrated environmental assessment and management efforts of aquatic systems in semiarid regions.

In addition, population growth, urbanization, and the intensification of agricultural operations in some semiarid regions have increased nutrient inputs to surface waters (Boxall et al. 2009; Heathwaite 2010). Altering nutrient availability can cause shifts in community composition and standing biomass (Marti et al. 2004), which may affect critical ecosystem functions and related services, such as production and respiration dynamics (Grimm et al. 2004; Walsh et al. 2005). Other contaminants, including pharmaceuticals and personal care products and agrochemicals, are often associated with the same sources responsible for eutrophication of surface waters (e.g., wastewater treatment plants [WWTPs], livestock rearing facilities, and agricultural fields; Brooks et al. 2008). The combination of these stressors makes it difficult to infer environmental hazards, because site-specific conditions can alter the physicochemical properties, bioavailability, and toxicity of contaminants (Farrington 1991; Van Wezel 1998; Walsh et al. 2005).

More than 75% of the essential drugs described by the World Health Organization and approximately one-third of modern pesticides have ionizable groups (Manallack 2007; Franco et al. 2010). Ionization state is important for

* To whom correspondence may be addressed: valenti.ted@epa.gov

Published online 27 April 2011 in Wiley Online Library

(wileyonlinelibrary.com).

DOI: 10.1002/ieam.202

ecological risk assessment, because it influences environmental fate and biological effect of some contaminants (Van Wezel 1998). Ionization state and lipophilicity of a chemical are directly related, which is exemplified by pH influence on partitioning of drugs in the body (Kwon 2001). Such relationships are further evidenced by differing log D (i.e., the pH-dependent octanol–water distribution coefficient) and bioconcentration factors for ionizable compounds over ranges of environmentally relevant surface water pH (Hernandez and Rathinavelu 2006). For example, as surface water pH approaches and surpasses the logarithmic acid dissociation constant (pK_a) value of a weak base, the compound will increasingly exist in the un-ionized form, which is often regarded as more toxic because of its greater propensity to cross cellular membranes (Hernandez and Rathinavelu 2006).

The importance of ionization state for ecological hazard is emphasized by the integration of site-specific pH adjustment factors into the US Environmental Protection Agency (USEPA) National Ambient Water Quality Criteria (NAWQC) for some contaminants. One important example is ammonia (NH_3), a weak base with a pK_a value of 9.2. To account for differences in pH between sites that can affect ionization state and potency, criteria adjustment factors were determined by relating site-specific pH to toxicity data derived from laboratory experiments completed over pH gradients (USEPA 2009). Consequently, acceptable concentrations of NH_3 in the water column may vary appreciably between sites. For example at 24 °C, the criterion maximum concentration (CMC) for surface waters is 31.4 mg total N/L at a site assuming no freshwater Unionidae present and a pH of 6.5, whereas a comparable value for a site with a pH of 9 is only 0.85 mg/L (USEPA 2009). If freshwater Unionidae are present, CMC values would be even lower to ensure adequate protection for this highly sensitive family of bivalve mollusks (USEPA 2009).

A practical constraint of implementing criteria based on pH-dependent toxicity is defining site-specific conditions. Surface water pH culminates from fluctuating interactions that vary on different spatial and temporal scales among the atmosphere, hydrological system, climate, geological substrate, and physical morphology of watersheds over longitudinal gradients. Bedrock mineralogy, soil compression, till depth, elevation gradient, precipitation patterns, and vegetation may cause appreciable differences in surface water geochemistry among watersheds (Allan 1995; Fitzhugh et al. 1999). At smaller spatial scales within watersheds, distinctions among surface water pH at sites is realized because of additional factors, such as transfers of allochthonous nutrient subsidies, groundwater and tributary inputs, proximity to wetlands, availability of acid-neutralizing materials, and both point and nonpoint pollution.

Although there is an understanding of how environmental heterogeneity contributes to spatial variability in surface water pH between sites, less information is available to regulators regarding factors that influence temporal variability at sites. For example, seasonal and annual variability in precipitation may influence ionic composition of surface waters by controlling inputs of groundwater, subsurface water, and overland flow. At an hourly time scale, inorganic C in surface waters may become uncoupled with concentrations of CO_2 in the atmosphere if rates of biological transformation exceed rates of physicochemical transfer between environmental compartments (Maberly 1996). For

instance, assimilation of organic C driven by photosynthesis can cause elevated pH during light hours as CO_2 is removed from the water column, limiting the formation of carbonic acid (Odum 1956). Diel oscillations in pH, referring to changes in pH over a 24-h period including both day and night, will likely have correlates to seasonality, because successional shifts of phytoplankton and macrophyte communities, coupled with changes in standing biomass, can influence the potential CO_2 demand of aquatic systems (Maberly 1996). This effect may be especially true for effluent-dominated systems in the southwestern and south central United States that commonly experience low flow hydrologic regimes (Brooks et al. 2006). Increased ecosystem biomass can cause high rates of respiration, whereas subsidies of organic material from WWTPs, pasture lands, or other terrestrial sources may enhance heterotrophic production in surface waters. Therefore, eutrophication may facilitate high rates of primary production and cause extreme diel pH oscillations at sites (Halstead and Tash 1982; Maberly 1996; Guasch et al. 1998; Kent et al. 2005).

Prior research has focused on how diel pH fluctuations can affect the bioavailability of metals and nutrients in aquatic systems (Crumpton and Isenhardt 1988; Jones et al. 2004; Gammons et al. 2005; Morris et al. 2005; Nimick et al. 2007; Tercier-Waeber et al. 2009). In this study, we expand upon this concept and examine how discharge rates may affect diel pH oscillations at wadeable stream sites in central Texas during summers of unusually low and high flow. Furthermore, we explore the importance of total P on diel pH patterns, because Scott et al. (2008) and King et al. (2009) previously suggested that primary production in these streams is strongly limited by P. We then demonstrate how variations in site-specific pH on both daily and yearly scales affects the potency of weak bases, using NH_3 and pharmaceuticals as model contaminants, by relating measured surface water pH to previously defined pH-dependent toxicological relationships.

MATERIAL AND METHODS

Study sites

Data were collected from 23 wadeable streams in the Brazos River Basin, Texas, USA, within the Cross Timbers Level III Ecoregion. These sites were selected to span a gradient of P enrichment, yet still capture a full range of natural variability in geology, drainage networks, stream size, and other physiographic factors (King et al. 2009). The permitted wastewater outfalls, land use for the catchment, and total P for each stream site are presented in Table 1. Several sites (e.g., BLUF-01, HARR-01, MBOS-01, SBOS-01) had >10% crop land. Some sampling stations were located directly downstream of WWTP discharges (e.g., LEON-02, NBOS-01, NBOS-05, NOLC-01, NOLR-01), whereas others likely had at least a portion of flow composed of WWTP effluent (e.g., COWH-01, NBOS-02, NBOS-03, NBOS-04, MERI-01, MBOS-01, SBOS-01, LEON-01). The spatial orientation and flow rates of the sites are shown in Figure 1.

Diel water quality monitoring

Diel changes in dissolved oxygen (DO), pH, and temperature were determined by deploying YSI 600 XLM and YSI

Table 1. The start of the sampling date, drainage area, wastewater outfall, land-use breakdown, and potential nutrient inputs for the 23 sites sampled in 2006 and 2007

Site	Start date		Area (km ²)	Outfalls (MGD)	Water (%)	Dev. (%)	Forest (%)	Shrub (%)	Grass (%)	Pasture (%)	Crop (%)	Wetland (%)	Imp. (%)	Total P (μg/L)	
	2006	2007												2006	2007
STEE-01	19-Sep	22-Sep	127	0	0.8	0.5	14.7	52.4	26.8	2.6	2.1	0.5	0.1	19	13
LAMP-02	26-Sep	18-Sep	1571	0	0.2	0.7	14	53.6	29.2	1	1.1	0.3	0.1	12	12
NEIL-01	23-Sep	24-Sep	357	0	0.2	0.2	35.6	1.4	57.7	0.7	2.2	1.8	0.2	6	11
PALU-01	19-Sep	22-Sep	933	0	0.4	1.1	32.9	11	49.8	3.1	0.8	1	0.2	10	13
ROCK-01	26-Sep	18-Sep	221	0	0.1	1.3	24.3	39.9	34	0.1	0.1	0.3	0.2	10	9
CORY-01	28-Sep	20-Sep	220	0	0	1.5	26.9	5.3	59.2	1.5	3.5	2	0.2	31	17
DUFF-01	19-Sep	22-Sep	157	0	0.2	0.4	22.4	13.1	57.1	1.5	4.1	1.1	0.2	24	25
LAMP-01	26-Sep	18-Sep	720	0	0.3	0.6	10.9	56.6	28.8	1.5	0.9	0.3	0.1	20	13
COWH-01	28-Sep	18-Sep	1180	0.06	0.1	0.7	18.8	43	33.8	1.6	1.5	0.4	0.1	12	10
NBOS-02	19-Sep	22-Sep	489	3.5	0.6	6.5	10.7	20.1	43.9	8.5	7.8	1.9	1.3	221	97
NBOS-03	21-Sep	22-Sep	925	3.5	0.5	4.3	13.3	22.6	44.6	7.1	6	1.6	0.8	46	47
NBOS-04	21-Sep	24-Sep	1890	3.75	0.5	3.1	18.4	13.5	55.1	4.1	3.5	1.7	0.6	8	38
MERI-01	21-Sep	24-Sep	480	0.04	0.4	0.3	32.3	0.4	63.7	0.5	1	1.4	0.2	18	10
BLUF-01	3-Oct	26-Sep	68	0	0.1	0.6	8.8	0	69.1	1.4	17.2	2.9	0	63	135
HARR-01	30-Sep	26-Sep	77	0	0.1	12	1.6	0	42.6	3	38.6	2.1	2	17	13
MBOS-01	3-Oct	24-Sep	478	0.09	0.1	1.6	10.5	0	63.2	2	19.9	2.7	0.1	30	13
SBOS-01	30-Sep	26-Sep	220	1.1	0.2	6.7	3.7	0	48.5	4.9	33.9	2.2	0.9	34	15
LEON-01	21-Sep	20-Sep	4705	3	0.8	3.1	12.2	33.1	33.3	8.4	8.5	0.8	0.3	25	18
LEON-02	28-Sep	20-Sep	6180	6.08	0.7	2.7	13.5	30.6	37.6	6.8	7.2	0.9	0.3	2027	164
NBOS-01	3-Oct	20-Sep	257	3.5	0.6	8	11	17.6	36.8	12.1	12	1.9	1.6	654	984
NBOS-05	23-Sep	24-Sep	3097	5.28	0.5	2.5	23.8	8.5	56.2	3.4	3.1	2	0.5	21	24
NOLR-01	19-Sep	22-Sep	275	6.73	1.6	12.3	3.2	0.1	65.7	8.8	5.9	2.3	2.5	1860	1333
NOLC-01	26-Sep	18-Sep	451	33.77	0.5	32.4	24	7.9	30.2	1.4	1.3	1.6	11.7	2053	895

Dev. = developed land (commercial + residential); Imp. = impervious surface; MGD = million gallons per day.

6600 (YSI Instruments, Yellow Springs, OH, USA) multi-parameter datasondes at each site for 48 h. Data were collected from 23 wadeable streams in September and October of 2006 and September of 2007. Data collected during 2006 was during a near-record drought, and flow was minimal or absent at nearly all sites, except effluent-dominated streams (Figure 1). For example, annual departures from normal precipitation in the studied watershed areas in 2006 were between -102 and -406 mm, whereas comparable values in 2007 were between 102 and 508 mm (NOAA National <http://www.weather.gov/climate/index.php?map=2>; Brooks et al. 2011). Exceptional high stream flows occurred during the summer of 2007 and data were collected during a brief period of stream-flow recession. Instruments were placed in the central channel in areas of discernable flow, if possible. Values for each parameter were collected at 15-min intervals, and data was transferred to a computer at the completion of deployment. All instruments

were calibrated with all reagents at room temperature within 24 h prior to data collection (TCEQ 2003). Quality assurance postcalibration checks were completed using error limits for pH, DO, and temperature of 0.5 standard units, ±5% error at saturation, and ±1 °C, respectively (TCEQ 2003).

Nutrient measurements

Water samples for total P and total N were collected from each site on the day of datasonde deployment (Table 1) in 2006 and 2007 and transported back to the laboratory for analysis. Total P concentrations were determined using the molybdate-blue method on persulfate-digested samples (EPA 365.1). Total N concentrations were determined using the sulfanilamide method on persulfate-digested samples (EPA 353.2). Total P and N concentrations were measured colorimetrically with a Lachat Quickchem 8500 Flow Injection Autoanalyzer (Loveland, CO, USA).

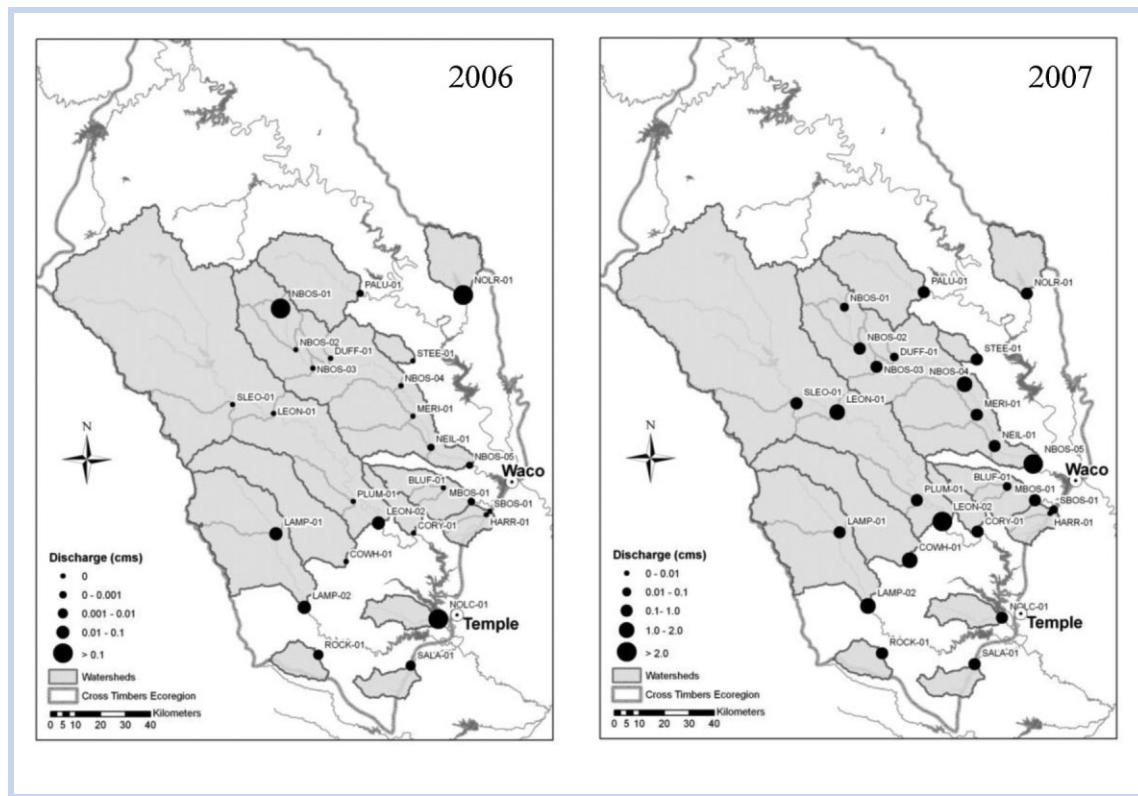


Figure 1. The map shows the location and discharge (in cubic meters per second [cms]) rates for study sites during the low flow conditions of 2006 and high flow conditions of 2007. The scale for discharge rates is different on each figure.

pH Influences on aquatic toxicity

The mean, minimum, and maximum daily pH values as well as the measured values at 8 AM, 11 AM, 2 PM, and 5 PM were determined for each wadeable stream site. These time intervals were selected to represent the typical work day when discrete samples are most likely to be collected for regulatory monitoring purposes (e.g., streams listed under section 303(d) of the Clean Water Act). In addition, cumulative frequency distributions of daily instream pH measurements were created to quantify the likelihood of observing a given pH value at each site. The pH data for discrete measures (mean, minimum, maximum, specific time points) and the values for each cumulative frequency distribution were then used to examine site-specific NAWQC for NH₃ using Equation 1, where $T = ^\circ\text{C}$ (refer to USEPA 2009 for a more detailed description of the equation variables).

$$\text{CMC} = 8.26 \times \left(0 \cdot \frac{0489}{1 + 10^{7.204 - \text{pH}}} + 6 \cdot \frac{95}{1 + 10^{\text{pH} - 7.204}} \right) \times \text{MIN}(12.09, 6.018 \times 10^{0.036 \times (25 - r)}) \quad (1)$$

Similar approaches were used for the model weak base pharmaceutical sertraline, which Valenti et al. (2009) demonstrated had pH-dependent potency over environmentally relevant surface water pH gradients. The mean, minimum, and maximum daily pH values were used to predict fathead minnow (*Pimphales promelas*) median lethal

concentration (LC50) values by solving Equation 2.

$$\text{Log LC50} \frac{\mu\text{g sertraline}}{\text{L}} = (-0.27 \times \text{pH}) + 4.34 \quad (2)$$

Site-specific potency ratio

Site-specific potency ratios (SSPRs) were developed to assess the magnitude of change in potency of contaminants due to daily fluctuations in pH. The novel SSPR metric (unitless) was derived by dividing the predicted endpoint for the lowest daily pH by the respective endpoint for the highest observed pH during a day at a site. Essentially, the SSPRs accounted for the slope of a pH-dependent relationship of a contaminant and places it in a relative site-specific context by bracketing the pH gradient observed at a site. For example, if a site has a daily minimum pH of 7.2 and a daily maximum pH of 8.4, the CMC NH₃ values for both these pH values at 24 °C with no mussels present are 19 and 2.5 mgN/L, respectively (USEPA 2009). The SSPR would then be calculated by dividing the higher CMC value by the lower CMC value. The CMC NH₃ values for the site in this scenario would thus be 7.6. The difference in hazard for a contaminant due to diel pH variability cannot be inferred solely on pH change, because pH-dependent toxicological relationships are seldom linear. In the case of NH₃, the CMC at 24 °C would differ by 2.4-fold between pH 6.5 and 7.5, whereas there would be a 6.2-fold difference between pH 7.5 and 8.5 (USEPA 2009).

Statistical analysis

Separate unbalanced 2-factor analysis of variance (ANOVA) analyses using year (2006, 2007), total P (TP) class (either $<20 \mu\text{g/L}$ and $>20 \mu\text{g/L}$ or $<800 \mu\text{g/L}$ and $>800 \mu\text{g/L}$), and their interactions were completed to assess how these factors influenced mean pH. We selected $20 \mu\text{g/L}$ as a threshold, because King et al. (2009) observed a structural periphytic community response at this concentration. The substantially higher threshold of $800 \mu\text{g/L}$ was selected based on regulatory thresholds in Texas (TCEQ 2007). Similar analyses were completed for daily pH change at sites. Additional 2-factor ANOVAs using the same factors of year and TP class were completed to examine their effects on mean NH_3 NAWQC, mean sertraline LC50 values, and SSPRs for NH_3 and sertraline. Balanced ANOVA analyses were completed by comparing the mean CMC NH_3 values at 8 AM, 11 AM, 2 PM, and 5 PM for all sites separately by year ($\alpha = 0.05$). As noted above, these times were selected to span

the typical work day when discrete sampling events would likely occur for regulatory monitoring purposes. Tukey's multiple comparisons test was used to assess significant differences among the mean CMC NH_3 values for each discrete time point. All statistics were performed with the R Statistical Program (R Foundation 2011).

RESULTS

Continuous water quality monitoring and nutrients

Results from continuous monitoring efforts of water quality at stream sites indicated appreciable differences in daily mean values between the 2 study years (Table 2). In 2006, daily mean DO, pH, and temperature at the sites ranged from 3.1 to 10.2 mg/L, 7.3 to 8.9, and 19.2 to 28.4 °C, respectively. Daily averages varied considerably less among the sites in 2007, with DO, pH, and temperature ranging from 6.3 to 8.8 mg/L, 7.5 to 8.1, and 23.6 to 26.7 °C,

Table 2. Mean dissolved oxygen (mg/L, \pm SD), pH, and temperature at wadeable stream sites in the Brazos River Watershed, Texas, during low flow (2006) and high flow (2007) conditions

Site	Dissolved oxygen (mg/L)		pH (units)		Temperature (°C)	
	2006	2007	2006	2007	2006	2007
STEE-01	7.5 \pm 1.9	6.7 \pm 0.7	7.7 \pm 0.1	7.5 \pm 0.1	25.2 \pm 1.7	26.2 \pm 0.7
LAMP-02	8.4 \pm 1.9	7.4 \pm 1.1	8.7 \pm 0.1	8.0 \pm 0.1	21.9 \pm 1.9	24.8 \pm 0.7
NEIL-01	8.0 \pm 1.3	7.7 \pm 0.7	8.4 \pm 0.1	7.9 \pm 0.1	23.7 \pm 2.2	26.2 \pm 0.7
PALU-01	8.1 \pm 2.1	7.2 \pm 1.1	8.0 \pm 0.3	7.8 \pm 0.1	21.9 \pm 0.9	24.3 \pm 0.5
ROCK-01	8.8 \pm 0.9	8.4 \pm 1.4	8.1 \pm 0.1	7.7 \pm 0.1	24.3 \pm 1.6	25.6 \pm 0.9
CORY-01	5.3 \pm 4.2	7.7 \pm 1.1	7.6 \pm 0.3	7.9 \pm 0.1	23.5 \pm 2.1	24.6 \pm 0.9
DUFF-01	8.9 \pm 3.1	7.3 \pm 1.9	8.1 \pm 0.2	7.6 \pm 0.1	19.7 \pm 1.6	26.0 \pm 0.7
LAMP-01	3.1 \pm 1.2	7.5 \pm 1.9	7.3 \pm 0.1	7.7 \pm 0.1	25.0 \pm 0.9	25.0 \pm 1.1
COWH-01	4.7 \pm 1.7	7.8 \pm 0.9	7.7 \pm 0.1	7.7 \pm 0.1	19.2 \pm 0.7	23.6 \pm 0.6
NBOS-02	7.4 \pm 2.2	7.7 \pm 2.9	8.0 \pm 0.1	7.9 \pm 0.2	24.3 \pm 0.7	25.4 \pm 0.6
NBOS-03	5.4 \pm 3.0	8.8 \pm 2.4	8.1 \pm 0.2	8.1 \pm 0.1	21.6 \pm 1.8	24.4 \pm 1.3
NBOS-04	7.9 \pm 5.3	8.4 \pm 1.7	8.9 \pm 0.6	8.0 \pm 0.1	27.8 \pm 2.9	24.4 \pm 1.2
MERI-01	10.2 \pm 3.7	4.9 \pm 1.3	7.4 \pm 0.2	7.7 \pm 0.1	27.3 \pm 2.0	23.8 \pm 0.9
LEON-01	7.8 \pm 2.4	6.4 \pm 1.1	7.9 \pm 0.1	8.1 \pm 0.1	23.3 \pm 2.4	26.6 \pm 0.9
MBOS-01	9.2 \pm 2.7	7.2 \pm 0.3	8.2 \pm 0.3	8.0 \pm 0.0	21.7 \pm 1.0	25.9 \pm 0.4
BLUF-01	5.5 \pm 1.2	7.8 \pm 0.8	7.8 \pm 0.1	8.0 \pm 0.1	21.5 \pm 1.6	26.0 \pm 1.5
HARR-01	9.0 \pm 2.0	7.3 \pm 1.4	8.6 \pm 0.2	7.9 \pm 0.2	23.2 \pm 1.7	26.3 \pm 1.1
SBOS-01	10.0 \pm 2.7	7.1 \pm 1.1	8.2 \pm 0.2	7.9 \pm 0.0	23.7 \pm 3.7	27.1 \pm 1.3
LEON-02	7.6 \pm 1.9	7.2 \pm 0.2	7.3 \pm 0.1	7.6 \pm 0.1	23.7 \pm 1.4	26.1 \pm 0.2
NBOS-01	8.6 \pm 2.8	7.0 \pm 1.1	8.2 \pm 0.3	7.6 \pm 0.1	28.4 \pm 2.3	26.1 \pm 1.0
NBOS-05	8.8 \pm 2.1	7.5 \pm 0.8	7.8 \pm 0.2	7.9 \pm 0.1	25.9 \pm 1.5	26.7 \pm 1.0
NOLC-01	8.5 \pm 2.3	7.9 \pm 0.5	8.2 \pm 0.2	7.8 \pm 0.0	22.1 \pm 4.5	25.4 \pm 1.2
NOLR-01	6.9 \pm 0.5	6.3 \pm 0.6	8.1 \pm 0.1	7.7 \pm 0.1	21.9 \pm 1.2	26.1 \pm 0.8

respectively (Table 2). Daily oscillation patterns of these variables were apparent in both years; examples for 4 sites in the watershed with different land use and varying degrees of WWTP inputs are shown in Figure 2. In general, DO, pH, and temperature values all shifted upward during daylight hours, followed by decreases in these variables during the night (Figure 2).

Concentrations of surface water TP at the study sites were similar for 2006 and 2007 (Table 1). In 2006, 10 of the 23 sites had TP concentrations $<20 \mu\text{g/L}$, whereas 5 had TP concentrations $<800 \mu\text{g/L}$. In 2007, 12 of the 23 sites had TP concentrations $<20 \mu\text{g/L}$, whereas 3 had TP concentrations $<800 \mu\text{g/L}$.

Influence of hydrology and total P on daily mean pH and pH change

Year significantly influenced pH change ($p=0.01$) such that the mean (\pm standard deviation [SD]) pH change was significantly higher in 2006 (0.7 ± 0.4 pH units) than in 2007 (0.3 ± 0.2 pH units). TP was not significantly different regardless of whether thresholds of either 20 ($p=0.2$) or $800 \mu\text{g TP/L}$ ($p=0.97$) were considered. Furthermore, no statistically significant interactions were observed between hydrology and TP ($p>0.4$). Interestingly, mean pH change was highest for sites with TP concentrations exceeding either the 20 or $800 \mu\text{g/L}$ threshold under low flow conditions,

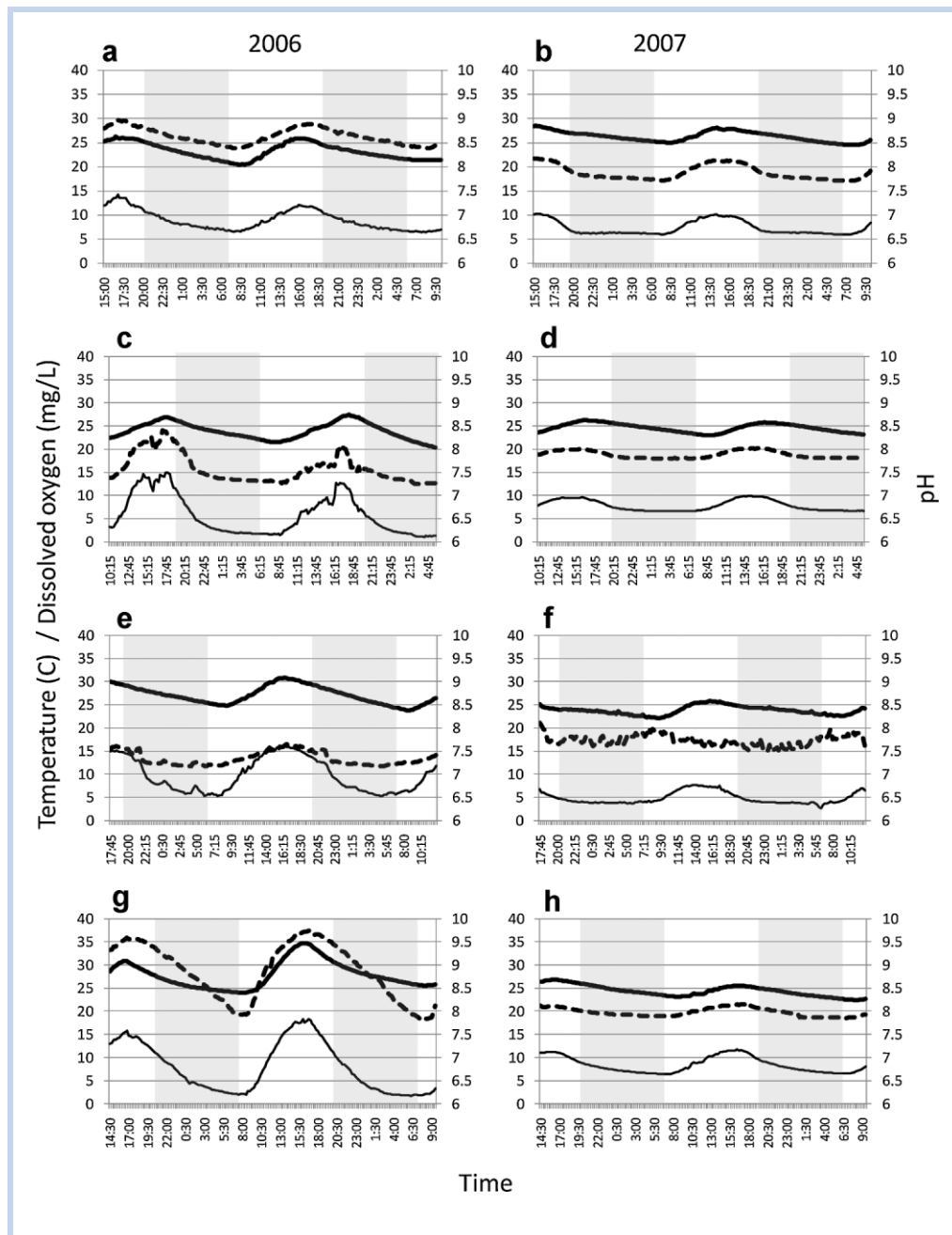


Figure 2. Daily patterns in measured temperature (thick solid line) and dissolved oxygen (thin solid line) on the left axis and pH (dashed lines) on the right axis sampled under low (2006) and high (2007) flow conditions. The lightly shaded gray areas represent night, whereas no shading represents daytime. (a, b) DUFF-01: $<5\%$ crop and pasture land, no wastewater treatment plant (WWTP) input; (c, d) BLUFF-01: 17% crop land; (e, f) MBOS-01: 20% crop land and minor WWTP input; (g, h) MBOS-02: 8% cropland, 9% pasture land, and substantial WWTP input.

because respective mean values (\pm SD) were 0.7 (\pm 0.5) and 0.7 (\pm 0.4) pH units, whereas the lowest mean pH change occurred at sites with TP concentrations below thresholds under high flow conditions (e.g., TP < 20 μ g/L = 0.3 \pm 0.2 and TP < 800 μ g/L = 0.3 \pm 0.4 pH units). During the drought conditions of 2006, daily pH change was >0.5 units at more than 60% of the sites, and some sites oscillated >1.0 pH units over the course of a day. There was no significant effect of year ($p=0.07$), TP class (< 20 μ g/L, $p=0.98$; < 800 μ g/L, $p=0.83$), or their interactions on mean site pH (< 20 μ g/L, $p=0.98$; < 800 μ g/L, $p=0.83$). However, pH was slightly higher in 2006 at sites, because respective means (\pm SD) in 2006 were 8.0 (\pm 0.3, $n=10$) when TP was <20 μ g/L and 8.0 (\pm 0.5, $n=12$) when TP was >20 μ g/L, whereas respective means for 2007 were 7.8 (\pm 0.16, $n=12$) and 7.9 (\pm 0.13, $n=10$). In addition, the 2006 and 2007 means for site pH were similar to those mentioned above, when a threshold of 800 μ g TP/L was considered.

pH Influences on NAWQC for ammonia

Appreciable variability was observed in allowable NH₃ concentrations based on USEPA NAWQC CMC values (USEPA 2009) due to shifts in pH at the sites, particularly during the low flow conditions of 2006. Some sites had higher recommended allowable NH₃ criterion values in 2006, whereas others had higher values for 2007 (Figure 3). However, neither year ($p=0.31$) nor TP ($p=0.27$) significantly influenced predicted NAWQC values for NH₃. Sites with TP concentrations of <20 μ g/L during low flow conditions had the lowest mean (\pm SD) NH₃ NAWQC value (7.8 \pm 3.6 μ g/L), whereas all other groups of sites had mean values >11.5 μ g/L.

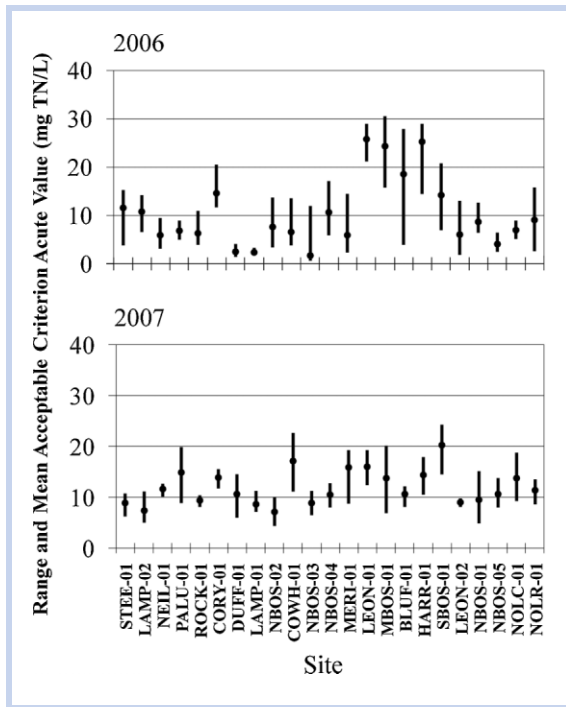


Figure 3. The allowable water column concentrations of total N (TN) at sites based on pH-dependent relationships reported in ambient water quality criteria for ammonia (USEPA 2009). The dot represents the daily average and the lines represent the range in predicted values based on daily pH fluctuations at sites.

Interestingly, in 2006 (a drought year) NH₃ CMC values were significantly higher ($p < 0.05$) near sunrise (8 AM), than during afternoon observations at 2 PM and 5 PM, respective mean NH₃ CMCs (\pm SD) were 14.0 (\pm 1.5) compared to lower total N (TN) values of 8.4 (\pm 1.6) and 7.3 (\pm 1.3) mg/L. Because of differences in acceptable NH₃ CMC values over the course of the day, 5 sites had measured TN concentrations that would have exceeded allowable levels (Table 3). It is important to note that these exceedances only occurred in the afternoon. In contrast during 2007 (a high flow year), no significant differences in NH₃ CMC values were observed over the course of the day; mean NH₃ CMC values for 8 AM, 2 PM, and 5 PM were 7.8 (\pm 0.2), 7.9 (\pm 0.2), and 7.9 (\pm 0.2) mg TN/L, respectively.

Table 3. The mean measured total N concentration and calculated ammonia NAWQC (total N, mg/L) for stream sites during the drought conditions of 2006 based on discrete pH measurements at 8 AM, 11 AM, 2 PM, and 5 PM^a

Site	Measured total N (mg/L)	NAWQC CMC (Total N, mg/L)			
		8 AM	11 AM	2 PM	5 PM
STEE-01	2.1	15.2	12.4	9.9	8.9
LAMP-02	1.1	13.7	12.4	9.4	9.4
NEIL-01	0.2	8.9	5.2	3.7	3.6
PALU-01	0.2	8.7	8.6	7.2	6.4
ROCK-01	0.1	9.8	5.5	4.4	4.3
CORY-01	0.7	15.7	15.4	11.9	12.4
DUFF-01	0.6	4.0	2.9	2.1	1.6
LAMP-01	0.2	2.9	2.7	2.1	1.8
NBOS-02	0.8	13.7	11.1	4.9	3.5
COWH-01	0.2	10.5	6.6	4.1	3.9
NBOS-03	1.6	9.6	1.6	0.7	0.6
NBOS-04	0.3	14.7	11.9	7.8	6.6
MERI-01	0.9	9.6	6.9	3.3	2.7
LEON-01	1.3	28.5	27.9	26.2	23.3
MBOS-01	19.4	29.9	25.6	20.8	16.5
BLUF-01	0.5	25.9	23.6	15.4	8.3
HARR-01	0.4	24.6	25.9	25.6	23.6
SBOS-01	0.4	20.5	17.0	11.3	7.2
LEON-02	8.1	13.0	9.6	2.1	2.2
NBOS-01	4.6	12.4	10.3	6.7	7.2
NBOS-05	0.6	6.2	4.5	3.6	3.0
NOLC-01	8.9	8.9	7.8	6.1	5.5
NOLR-01	13.7	14.7	5.5	3.2	5.6

^aNumbers highlighted and italics indicate that the mean measured total N concentration exceeds regulatory acceptable concentrations. CMC = criterion maximum concentration; NAWQC = National Ambient Water Quality Criteria.

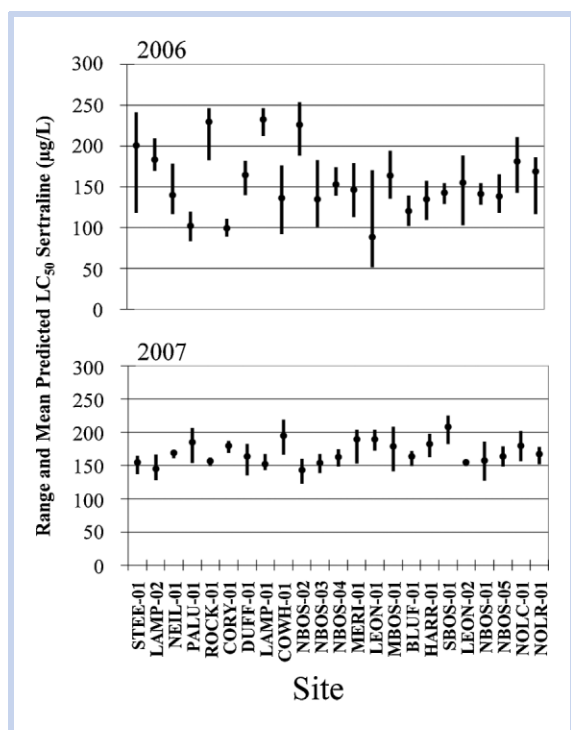


Figure 4. Predicted median lethal concentration (LC50) value for sertraline based on pH-dependent toxicological activity reported by Valenti et al. (2009). The dot represents the daily average and the lines represent the range in predicted values based on daily pH fluctuations at sites.

pH-Dependent potency of sertraline

In general, there was more variability in predicted sertraline LC50 values during periods of low versus high instream flows (Figure 4). There was not a consistent relationship in calculated responses for sites between years, because some had lower predicted values in 2006 whereas others had lower values in 2007. Respective daily mean predicted sertraline LC50 values (\pm SD) were 156 (\pm 39) and 169 (\pm 17) μ g/L in 2006 and 2007, respectively. Results of the 2-way ANOVA indicated that neither year, TP, nor their interactions significantly influenced predicted LC50 values for the study sites ($p > 0.4$).

Site-specific potency ratio

The NH_3 SSPR values exhibited much greater variability during drought conditions of 2006 compared to higher instream flow conditions of 2007. For example, NH_3 SSPR values ranged from 1.7 to 20.7 in 2006, compared to a range of 1.2 to 3.1 in 2007 (Table 4). Similar to observations for pH swings between study years, a significant main effect of year also significantly affected NH_3 SSPR values ($p = 0.05$); however, no statistically significant main effects of TP ($p = 0.18$) or an interaction ($p = 0.31$) between year and TP were observed. The mean (\pm SD) SSPR value for NH_3 was 4.1 (\pm 4.1) in 2006, yet just 1.9 (\pm 0.5) in 2007 (Table 4). Nevertheless, the magnitude of difference among SSPR values is considerably greater than the differences in means between 2006 and 2007 (Table 4).

Sertraline SSPR values were smaller than those calculated for NH_3 , ranging from 1.2 to 3.3 in 2006 and 1.1 to 1.5 in 2007. The main effect of year significantly affected sertraline

SSPR values ($p = 0.01$); however, similar to SSPR values for NH_3 , effects of TP ($p = 0.15$) and interactions between year and TP ($p = 0.31$) were not observed.

DISCUSSION

Site-specific pH and analysis of effects

A synergy between our current understanding of the factors that influence surface water quality at sites, and toxicokinetic and pharmacokinetic principles is needed to better guide water quality managers and regulatory agencies in decisions concerning the potential hazard of ionizable compounds and other contaminants with pH-dependent potencies. In the traditional risk assessment paradigm, hazard of a contaminant is inferred by establishing an exposure distribution that summarizes the predicted environmental concentration based on either modeled or measured concentrations in the environment, which is then related to dose–response curves for biological entities. By integrating these 2 distributions, a joint probability curve is created that estimates the likelihood of observing adverse effects in the environment. Although site-specific pH conditions can influence both exposure and effects, the focus of this study was to emphasize how ignoring site-specific pH considerations may alter analysis of effects and therefore cause uncertainty in ecological risk assessment. We specifically focused on environmental effects, because various experiments have demonstrated that aquatic potencies of ionizable traditional contaminants (Brooks et al. 2011), pharmaceuticals (Nakamura et al. 2008; Valenti et al. 2009; Kim et al. 2010), antimicrobials (Orvos et al. 2002), and harmful algal toxins (Valenti et al. 2010) are influenced by ambient pH.

In our study, we describe NH_3 as a model contaminant under the assumption that physicochemical variables governing its ionization state in the environment would be similar to those affecting the bioavailability and potency of other ionizable contaminants of emerging concern (e.g., pharmaceuticals, agrochemicals). Our focus was on weak bases, because some of the central Texas streams we studied experienced elevated ambient surface water pH during the day under drought conditions. In future studies, similar considerations may be warranted for weak acids, such as pentachlorophenol, for example, because their potencies may also be affected by site-specific pH (USEPA 1995), especially in circumneutral or more acidic surface waters. It is important to emphasize that generalization related to ionization state and toxicity are based on toxicological effects that are not mode-of-action-specific, and that additional considerations may be pertinent on a case-by-case basis for certain contaminants (Berninger and Brooks 2010).

Although pH-dependent considerations are embedded in guidelines for establishing NAWQC for some ionizable contaminants, such as NH_3 (USEPA 2009) and pentachlorophenol (USEPA 1995), as well as other contaminants with known pH-dependent potency (e.g., the biotic ligand model for Cu), neither federal nor state regulatory guidelines are in place for many contaminants of emerging concern (e.g., pharmaceuticals, agrochemicals) (Daughton and Brooks 2011). As considerations related to ionization become more prominent, it is highly likely that pH-dependent potency relationship will be identified for other contaminants of emerging concern. In our study, we used sertraline as a model contaminant to demonstrate how site-specific pH could

Table 4. The ratio of mean NAWQC for ammonia and predicted toxicological responses to sertraline between 2006 (low flow) and 2007 (high flow) at stream sites in the Brazos River Watershed, Texas^a

Site	Ammonia			Sertraline		
	2006/2007	2006 SSPP	2007 SSPP	2006/2007	2006 SSPP	2007 SSPP
BLUF-01	1.8	7.2	1.5	1.2	2.0	1.1
CORY-01	1.1	1.7	1.3	1.0	1.2	1.1
COWH-01	0.4	3.6	2.0	0.7	1.5	1.3
DUFF-01	0.2	2.9	2.4	0.6	1.4	1.3
HARR-01	1.7	2.0	1.7	1.3	1.3	1.2
LAMP-01	0.3	1.9	1.6	0.7	1.2	1.2
LAMP-02	1.5	2.2	2.2	1.1	1.3	1.3
LEON-01	1.6	1.4	1.6	1.2	1.2	1.2
LEON-02	1.8	7.2	1.2	0.9	1.9	1.1
MBOS-01	0.4	1.9	3.0	1.3	1.3	1.5
MERI-01	0.9	6.1	2.2	0.7	1.8	1.3
NBOS-01	1.1	2.0	3.1	1.0	1.3	1.5
NBOS-02	0.2	4.0	2.3	1.0	1.6	1.3
NBOS-03	1.0	20.7	1.8	0.6	3.3	1.2
NBOS-04	0.4	2.9	1.6	1.0	1.4	1.2
NBOS-05	0.5	2.6	1.7	0.7	1.4	1.2
NEIL-01	0.5	3.1	1.2	0.8	1.4	1.1
NOLC-01	0.8	1.7	2.0	0.8	1.2	1.3
NOLR-01	0.5	6.1	1.6	0.9	1.8	1.2
PALU-01	0.7	1.8	2.2	0.8	1.2	1.3
ROCK-01	0.7	2.8	1.3	0.9	1.4	1.1
STEE-01	1.3	4.1	1.7	1.1	1.6	1.2
Mean	0.9	4.1	1.9	0.9	1.5	1.2
SD	0.5	4.1	0.5	0.2	0.5	0.1

^aVariability associated with daily fluctuations in surface water pH are demonstrated by site-specific potency ratio (SSPP) for the weak bases ammonia and sertraline. NAWQC = National Ambient Water Quality Criteria.

influence its potential to cause adverse biological effects because a clear pH-dependent toxicological relationship was already demonstrated with the commonly used test organism fathead minnow (*P. promelas*) (Valenti et al. 2009). In this research, there was a significant shift in the dose–response curve between pH 6.5 and 8.5, with LC50 values nearly 9 times lower at the higher pH. We related the pH-dependent toxicological relationship developed in this prior study to our pH monitoring efforts reported in this study to demonstrate how site-specific conditions could substantially alter the potency of weak bases (Figures 3 and 4). From an ecological risk assessment perspective, it is probable that differences in ambient surface water pH may affect dose–response curves for other ionizable contaminants. Figure 5

illustrates how a shift in the dose–response due to changes in exposure pH could substantially change the likelihood of observing adverse effects in the environment.

Influence of diel pH variability on derivation of NAWQC

Daily oscillations in surface water pH at some sites may confound the derivation of NAWQC and increase uncertainty if site-specific pH is based solely on discrete sampling events. Daily fluctuations in NAWQC for NH₃ based on mean surface water pH compared to the variability observed over the course of the day are shown in Figure 3. The importance that sampling time has on defining site-specific pH and consequential NAWQC for some contaminants is further

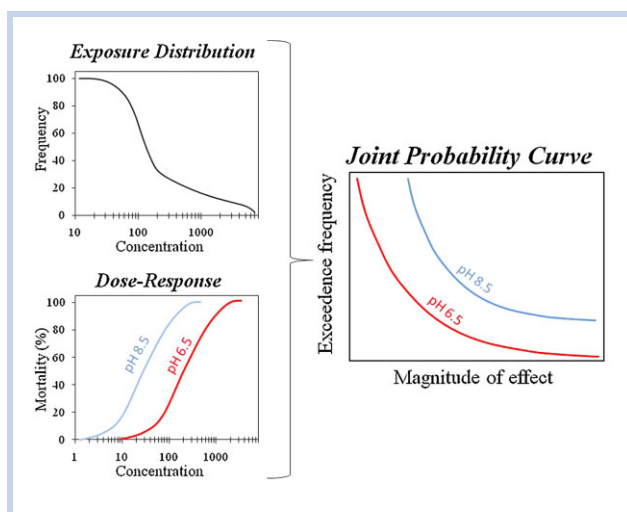


Figure 5. An illustration that demonstrates a hypothetical scenario in which site-specific pH conditions affect risk characterization for weak bases.

emphasized by the substantial daily fluctuations in allowable total N concentration at some sites (Table 3). In a hypothetical scenario examining pH measurements at 8 AM, 11 AM, 2 PM, and 5 PM to represent the typical work day when discrete samples would be collected by field monitoring efforts, we demonstrate that the lower pH values observed in the morning would indicate that water quality standards are maintained, whereas the heightened pH of the later afternoon would cause exceedances at some sites. The aforementioned scenario assumes that the mean TN concentration measured at these sites is representative of concentrations observed throughout the day at these sites. However, we did not analytically confirm TN at each time interval and thus we cannot confirm that such scenarios came to fruition in the environment. Nevertheless, other researchers describe NH_3 concentrations peaking at midday and then declining throughout the night at sites in close proximity to WWTPs (Crumpton and Isenhardt 1988), which would suggest that our assumptions are potentially conservative. Regardless of the validity of our assumption concerning TN concentrations throughout the day, the growing concerns of N pollution in surface waters makes it important to consider the implications of this hypothetical scenario, because it demonstrates a potential regulatory concern that has received surprisingly little attention and emphasizes the need for a more in-depth examination of diel pH dynamics and their potential effect on water quality monitoring for NH_3 .

The SSPR approach proposed in this study could allow researchers and regulators to screen the predicted site-specific effects associated with altered potencies for NH_3 and other contaminants over a 24-h period. Use of the SSPR metric clearly demonstrated substantially more variability in predictions of NAWQC or adverse effects for ionizable compounds during drought compared to high flow conditions (Table 4). In addition, differences in SSPR values between NH_3 and sertraline indicate that diel pH oscillation is not the only causal factor affecting this variable, but rather that physicochemical properties intrinsic to the contaminant of concern must also be considered. The substantially greater SSPR values calculated for NH_3 is spurred by the fact that ambient pH values of study sites were closer to the pK_a value

of NH_3 . Therefore, changes in dissociation over the course of the day were predicted to be markedly greater for NH_3 than for sertraline. The relative importance of diel pH change on potency is therefore relative to not only the magnitude of pH change at a site but also to the specific dissociation behavior of the contaminant of concern over the range of observed pH values.

Implications of diel pH variability for monitoring water quality

In this study, we identified that drought caused daily mean pH to be markedly higher compared to pH during flood conditions at several sites in central Texas (Table 2). However, perhaps more importantly, the continuous water quality monitoring data collected during our study allowed us to identify that low flow conditions prompted significantly greater swings in pH at sites over the course of the day. In fact, variability in surface water pH was actually more pronounced when comparing observations at sites collected over the course of the day compared to the differences in mean pH values between the 2 years. It is critical to note that such distinctions would have been impossible to identify with only discrete samples. Other researchers have commented how short-term (daily, bi-hourly) variability in geochemical parameters may actually account for a majority of the variability once thought to represent fluctuations due to much coarser seasonal or yearly time scales (Nagorski et al. 2003; Tercier-Waeber et al. 2009). Consequently, the timing of discrete sampling events during the day may introduce as much or more uncertainty to ecological risk assessment as would collecting samples between seasons or years.

Accurately defining site-specific conditions for some water quality parameters may require a revisiting of how surface water quality data are collected and monitored. In our study, patterns of pH oscillation followed those of DO (Figure 2), which strongly suggests that mechanisms controlling these patterns are likely associated with primary production: respiration, a critical ecosystem function. Notably, whereas many water resource managers rely on guidance suggesting 24-h continuous monitoring dissolved oxygen (DO) profiles with data taken at hourly intervals to assess regulatory compliance, similar efforts are not required for pH. In fact, there is currently sparse guidance pertaining to suitable sampling regimes for monitoring pH in surface water, and few suggestions for minimum daily sampling frequency or specific timing of sampling events exist. For instance, the guidance document for NAWQC for NH_3 recommends that TN concentrations should be monitored simultaneously with each pH measurements (USEPA 2009) but does not specifically comment on timing or frequency of sampling. Some states have proposed probabilistic approaches to define segment-specific pH for calculating allowable instream concentrations of toxicant; however, these are again based on discrete sampling events. The current approach of the Texas Commission of Environment Quality for defining site-specific pH is an example of this approach, whereby the 15th percentile from a minimum of 30 values collected over approximately the same time period in which samples for the contaminant of concern are collected is used as a conservative estimate for defining regulatory thresholds. Although more progressive, this approach still relies on discrete sampling events to characterize site-specific pH and does not consider

the importance that time of day may have on pH measurements.

Based on observations in the present and other studies (Gammons et al. 2005; Nimick et al. 2007; Tercier-Waeber et al. 2009), we recommend employing 24-h continuous monitoring to determine diel pH dynamics at sites where contaminants with pH-dependent physicochemical properties or potency may be present in the environment at levels of potential concern. We strongly encourage researchers to be cognizant of the potential temporal variability in surface water pH at sites while designing and implementing sampling protocols, especially during low flow conditions. While defining requirements associated with characterization of site-specific pH for regulatory purposes, it would be ideal to capture both the lowest and highest observed daily pH at a site so that data could be applicable for refining risk characterization of both weak acids and bases. At a minimum, if collection of continuous water monitoring data at various time points is not feasible, then sampling efforts should target potential worst-case scenarios for the specific contaminant(s) of concern by attempting to take discrete samples at times of concern (e.g., late afternoon for weak bases or earlier morning for weak acids and/or heavy metals). Applying approaches such as these during routine water quality monitoring could enable environmental assessors and managers to reduce uncertainty and ensure that the likelihood that criteria values are not overly under- or overprotective for designated water uses.

FUTURE PERSPECTIVES

Future water scarcity associated with global climate change and altered precipitation patterns may profoundly impact instream flows in semiarid regions, which have direct implications for water resource management. A number of ecosystem alterations are already evident in arid regions of the southwest and south central United States and more are likely to become apparent in the future as the science continues to advance and anthropogenic impact increases due to population growth and altered land use patterns. Although scientists have identified the need to improve our understanding of how global climate change may influence site-specific ecosystem functions and services (Wenning et al. 2010), applying theoretical to real world scenarios has proven challenging because the environmental impacts are seldom explored at multiple levels of organizations. Consequently, conducting research during unusual weather patterns (e.g., severe droughts or floods) may provide important insight and allow scientists to more accurately predict the magnitude of system-level effects triggered by climate change in the future.

Predicting the cumulative effects of climatic variability on the risk of ionizable contaminants may require a paradigm shift in the environmental assessment and management approaches for freshwater systems. Although our study clearly demonstrates that diel pH swings occur and that patterns of daily oscillations are in part influenced by instream flow and total P, far more research is needed before a comprehensive knowledge of the causal factors contributing to these patterns are fully understood. Describing a linkage among the various interwoven dynamic environmental processes occurring at both the biological and geological time scales that influence site-specific pH will inevitably require a multifaceted interdisciplinary approach. In the future it will therefore be important for researchers to more closely study variables directly measured in surface waters (e.g., instream

flow, nutrient availability, chlorophyll-*a*, turbidity, and dissolved organic matter), as well as those in the surrounding watershed (e.g., physiogeological mineralogy, land use, and hydrology). From an ecotoxicology mindset, it will also be essential to identify how site-specific pH and patterns of diel oscillations influence not only the potency of ionizable contaminants, but also how these factors may affect the magnitude and frequency of exposure of the course of the day. For example, it is important that future research examines how diel shifts in pH may affect bioconcentration factors for ionizable contaminants. Similarly, diel pH patterns should also be the focus of speciation and bioavailability research for other inorganics (e.g., metals, nutrients) that are known to be influenced by pH.

Acknowledgment—This research was partially funded by a US Geological Survey and Texas Water Resources Institute grant to T.W.V. and B.W.B., the Glasscock Fund for Excellence in Environmental Science to T.W.V., and a USEPA grant to R.S.K. and B.W.B. (agreement CP-966137-01). The Center for Reservoir and Aquatic Systems Research (CRASR) at Baylor University provided additional analytical and logistical support.

REFERENCES

- Allan JD. 1995. Stream ecology: Structure and function of running waters. London (UK): Chapman & Hall. 388 p.
- Berninger JP, Brooks BW. 2010. Leveraging mammalian pharmaceutical toxicology and pharmacology data to predict chronic fish responses to pharmaceuticals. *Toxicol Lett* 193:69–78.
- Boxall ABA, Hardy A, Beulke S, Boucard T, Burgin L, Falloon PD, Haygarth PM, Hutchinson T, Kovats RS, Leonardi G., et al. 2009. Impacts of climate change on indirect human exposure to pathogens and chemicals from agriculture. *Environ Health Perspect* 117:508–514.
- Brooks BW, Valenti TW, Cook-Lindsay BA, Forbes MG, Scott JT, Stanley JK, Doyle RD. 2011. Influence of climate change on reservoir water quality assessment and management: Effects of reduced inflows on diel pH and site-specific contaminant hazards. In: Climate: Global change and local adaptation I, Linkov T, Bridges editors. NATO Science Series. New York (NY): Springer. p 495–528.
- Brooks BW, Ankley GT, Hobson JF, Lazorchak JM, Meyerhoff RD, Solomon KR. 2008. Assessing the aquatic hazards of veterinary medicines. In: Crane M, Barrett K, Boxall A, editors. Effects of veterinary medicines in the environment. Boca Raton (FL): CRC/Taylor & Francis. p 97–128.
- Brooks BW, Riley TM, Taylor RD. 2006. Water quality of effluent-dominated ecosystems: ecotoxicological, hydrological, and management considerations. *Hydrobiologia* 556:365–379.
- Crumpton WG, Isenhardt TM. 1988. Diurnal patterns of ammonium and un-ionized ammonia in streams receiving secondary treatment effluent. *Bull Environ Contam Toxicol* 40:539–544.
- Daughton CG, Brooks BW. 2011. Active pharmaceuticals ingredients and aquatic organisms. In: Environmental contaminants in wildlife: Interpreting tissue concentrations 2nd ed. Meador J, Beyer WN, editors. Boca Raton (FL): CRC/Taylor & Francis. p 281–341.
- Farrington JW. 1991. Biogeochemical processes governing exposure and uptake of organic pollutant compounds in aquatic organisms. *Environ Health Perspect* 90:75–84.
- Fitzhugh RD, Furman T, Webb JR, Cosby BJ, Driscoll CT. 1999. Longitudinal and seasonal patterns of stream acidity in a headwater catchment on the Appalachian Plateau, West Virginia, USA. *Biogeochemistry* 47:39–62.
- Franco A, Ferranti A, Davidsen C, Trapp S. 2010. An unexpected challenge: ionizable compounds in the REACH chemical space. *Int J Life Cycle Assess* 15:321–325.
- Gammons CH, Nimick DA, Parker SR, Cleasby TE, McCleskey RB. 2005. Diel behavior of iron and other heavy metals in a mountain stream with acidic to neutral pH: Fisher Creek, Montana, USA. *Geochim Cosmochim Acta* 69:2505–2516.

- Grimm NB, Grove JM, Pickett ST, Redman CL. 2004. Integrated approaches to long-term studies of urban ecological systems. *Bioscience* 50:571–584.
- Guasch H, Armengol J, Marti E, Sabater S. 1998. Diurnal variation in dissolved oxygen and carbon dioxide in two low-order streams. *Water Res* 32:1067–1074.
- Halstead BG, Tash JC. 1982. Unusual diel pHs in water as related to aquatic vegetation. *Hydrobiologia* 96:217–224.
- Heathwaite AI. 2010. Multiple stressors on water availability at global and catchment scales: understanding human impact on nutrient cycles to protect water quality and water availability in the long term. *Freshw Biol* 55:241–257.
- Hernandez MA, Rathinavelu A. 2006. Basic pharmacology: Understanding drug actions and reactions. Boca Raton (FL): Taylor & Francis Group. 392 p.
- Hurd B, Leary N, Jones R, Smith J. 1999. Relative regional vulnerability of water resources to climate change. *J Am Water Resour Assoc* 35:1399–1409.
- Jones CA, Nimick DA, McCleskey RB. 2004. Relative effect of temperature and pH on diel cycling of dissolved trace elements in Prickly Pear Creek, Montana. *Water Air Soil Pollut* 153:95–113.
- Kent R, Belitz K, Burton CA. 2005. Algal productivity and nitrate assimilation in an effluent dominated concrete lined stream. *J Am Water Resour Assoc* 41:1109–1128.
- Kim J, Park J, Kin PG, Lee C, Choi K, Choi K. 2010. Implications of global environmental changes on chemical toxicity-effect of water temperature, pH, and ultraviolet B irradiation on acute toxicity of several pharmaceuticals in *Daphnia magna*. *Ecotoxicology* 19:662–669.
- King RS, Taylor JT, Back JA, Fulton BA, Brooks BW. 2009. Linking observational and experimental approaches for the development of regional nutrient criteria for wadeable streams. Final Report. CP- 966137-01. US Environmental Protection Agency Region 6. 151 p.
- Kwon Y. 2001. Handbook of essential pharmacokinetics, pharmacodynamics, and drug metabolism for industrial scientists. New York (NY): Kluwer Academic/Plenum. 316 p.
- Maberly SC. 1996. Diel, episodic and seasonal changes in pH and concentrations of inorganic carbon in a productive lake. *Freshw Biol* 35:579–598.
- Manallack DT. 2007. The pKa distribution of drugs: application to drug discovery. *Perspect Med Chem* 1:25–38.
- Marti E, Aumatell J, Gode L, Poch M, Sabater F. 2004. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. *J Environ Qual* 33:285–293.
- Morris JM, Nimick DA, Farag AM, Meyer JS. 2005. Does biofilm contribute to diel cycling of Zn in High Ore Creek, Montana? *Biogeochemistry* 76:233–259.
- Nakamura Y, Yamamoto H, Sekizawa J, Kondo T, Hirai N, Tatarazako N. 2008. The effects of pH on fluoxetine in Japanese medaka (*Oryzias latipes*): Acute toxicity in fish larvae and bioaccumulation in juvenile fish. *Chemosphere* 70:865–873.
- Nimick DA, Harper DD, Farag AM, Cleasby TE. 2007. Influence of in-stream diel concentration cycles of dissolved trace metals on acute toxicity to one-year old cutthroat trout (*Oncorhynchus clarki lewisi*). *Environ Toxicol Chem* 26:2667–2678.
- Odum HT. 1956. Primary production in flowing waters. *Limnol Oceanogr* 1:102–117.
- Orvos DR, Versteeg DJ, Inauen J, Capdevielle M, Rothenstein A, Cunningham V. 2002. Aquatic toxicity of triclosan. *Environ Toxicol Chem* 21:1338–1349.
- R Foundation. 2011. R statistical program. Version 2.13.0. Vienna (AT): Wirtschaftsuniversität Wien.
- Scott JT, Back JA, Taylor JM, King RS. 2008. Does nutrient enrichment decouple algal-bacterial production in periphyton? *J N Am Benthol Soc* 27:332–334.
- Sun G, McNulty SG, Moore Myers HA, Cohen EC. 2008. Impacts of multiple stresses on water demand and supply across the southeastern United States. *J Am Water Resour Assoc* 44:1441–1457.
- Tercier-Waeber ML, Hezard T, Masson M, Schafer J. 2009. In situ monitoring of the diurnal cycling of dynamic metal species in a stream under contrasting photobenthic biofilm activity and hydrological conditions. *Environ Sci Technol* 43:7237–7244.
- [TCEQ] Texas Commission of Environmental Quality. 2007. DRAFT: 2006 Guidance for assessing and reporting surface water quality in Texas (June 27, 2007). Austin (TX): TCEQ, Monitoring Operations, Surface Water Quality Monitoring Program. 166 p.
- [TCEQ] Texas Commission of Environmental Quality. 2003. Surface water quality monitoring procedures. Vol 1: Physical and chemical monitoring methods for water, sediment and tissue Publication RG-415, December 2003. Austin (TX): TCEQ. 198 p.
- [USEPA] US Environmental Protection Agency. 1995. 1995 Updates: Water quality criteria documents for the protection of aquatic life in ambient water. EPA-820-B-96-001. Washington (DC): USEPA, Office of Regulations and Standards, Criteria and Standards Division. 114 p.
- [USEPA] US Environmental Protection Agency. 2009. Draft 2009 update aquatic life ambient water quality criteria for ammonia—Freshwater. EPA-822-D-09-001. Washington (DC): USEPA Office of Water. 153 p.
- Valenti TW, Perez-Hurtado P, Chambliss CK, Brooks BW. 2009. Aquatic toxicity of sertraline to *Pimephales promelas* at environmentally relevant surface water pH. *Environ Toxicol Chem* 28:2685–2694.
- Valenti TW, James SV, Lahousse MJ, Schug KA, Roelke DL, Grover JP, Brooks BW. 2010. A mechanistic explanation for pH-dependent ambient aquatic toxicity of *Prymnesium parvum* carter. *Toxicol* 55:990–998.
- Van Wezel AP. 1998. Chemical and biological aspects of ecotoxicological risk assessment of ionizable and neutral organic compounds in fresh and marine waters: a review. *Environ Rev* 6:123–137.
- Walsh CJ, Roy AH, Feminella JW, Cottingham PD, Groffman PM, Morgan RP. 2005. The urban stream syndrome: current knowledge and the search for a cure. *J N Am Benthol Soc* 24:706–723.
- Wenning RJ, Finger SE, Guilhermino L, Helm RC, Hooper MJ, Landis WG, Menzie CA, Munns WR, Rombke J, Stahl RG. 2010. Global climate change and environmental contaminants: A SETAC call for research. *Integr Environ Assess Manag* 6:197–198.