



# Geochemical and hydrodynamic controls on arsenic and trace metal cycling in a seasonally stratified US sub-tropical reservoir

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## Abstract

The phase distribution of trace metals and oxyanions, including U and As, in 2 surface water bodies was investigated within a South Texas watershed hosting a high density of surface U mine pits and tailings. The objectives of the study were to evaluate the environmental legacy of U mining, with particular emphasis on the spatial and temporal variability of water quality in Lake Corpus Christi, a downstream reservoir that serves as the major water resource to a population of ~350,000 people in the region. Lyssy Pond, a livestock pond bordered by U mine tailings, was used as a model case-study site to evaluate the cycling of U mine-derived oxyanions under changing redox conditions. Although the pond showed seasonal thermal and chemical stratification, geochemical cycling of metals was limited to Co and Pb, which was correlated with redox cycling of Mn mineral phases, and U, which suggested reductive precipitation in the pond's hypolimnion. Uranium levels, however, were too low to support strong inputs from the tailings into the water column of the pond. The strong relationships observed between particulate Cr, Cs, V, and Fe suggest that these metals are associated with a stable particulate phase (probably allochthonous alumino-silicates) enriched in unreactive Fe. This observation is supported by a parallel relationship in sediments collected across a broad range of sediment depositional processes (and histories) in the basin. Arsenic, though selectively enriched in the pond's water column, was dominated by dissolved species throughout the depth of the profile and showed no sign of geochemical cycling or interaction with Fe-rich particles. Arsenic (and other oxyanions) in the water columns of Lake Corpus Christi and Lyssy pond were not affected by the abundant presence of Fe-rich particles but instead behaved conservatively. No evidence was found of anthropogenic impacts of U mines beyond the purely local scale. Arsenic's presence within the Nueces drainage basin is related to interactions between surface and groundwaters with U- and As-rich geological formations rather than large-scale transport of contaminants downstream of the U mine pits and tailings. A quantitative mass balance model, constructed using monthly hydrological data for the reservoir, provides quantitative evidence of seasonal evaporative concentration of As in surface waters demonstrating the predominance of hydrodynamic over geochemical constraints, on the cycling of this element.

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## 1. Introduction

In semi-arid climates, such as the Southwestern United States, the continued growth in anthropogenic activities increases the demand for freshwater while further magnifying the natural stress on riparian and aquatic ecosystems (i.e., Sophocleous, 2000; Blomquist et al., 2001; Cohen, 2002). No other US region has experienced more the impact of water needs, fueled by a marked demographic expansion, its associated land development, and recurrent cycles of long-term droughts (Diaz and Anderson, 1995; Mace et al., 2000; Dunne, 2000). Similar to many other regions of the world with strong population growth, the building of large-scale water infrastructures (e.g., hydroelectric and freshwater drinking reservoirs) in the Southwest have sharply increased in the 20th century to remediate water scarcity and address increased water and energy demands from industrial, agricultural, and municipal activities (Gleick, 2000). It is now well recognized, however, that these reservoirs generate hydrological alterations with ramifications extending into large-scale disruptions of water flow and impaired water quality (Rosenberg et al., 2000). Selected examples of such environmental impacts induced by artificial lakes (reservoirs) include eutrophication (Elbaz-Poulichet et al., 1997; Rosenberg et al., 1997; Paerl et al., 2001), reduced downstream biodiversity (Rosenberg et al., 1997, 2000), increased cycling of heavy metals (Louchouart et al., 1993; Lucotte et al., 1999; Canavan et al., 2000; Montgomery et al., 2000), and increased releases of greenhouse gases to the atmosphere (Duchemin et al., 1995; St. Louis et al., 2000). Of critical concern for reservoirs, which sole use is for freshwater delivery and recreational/fishing activities, is the lack of information on temporal changes in water quality parameters, such as trace metal loading and cycling (see Van Metre and Callender, 1997; Canavan et al., 2000; Kneebone and Hering, 2000). This lack of information is significant because these reservoirs typically act as depositional environments for suspended particulate and colloidal materials (Thornton et al., 1990; Elbaz-Poulichet et al., 1997; Van Metre and Callender, 1997; Houel, 2003), which exhibit high sorption affinity for trace metals and radionuclides, and persistent organic pollutants (Baskaran and Santschi, 1993; Villholth, 1999; Wen et al., 1999).

Deposited sediments, however, do not necessarily become permanent sinks for contaminants that are susceptible to physical or diagenetic remobilization. Following short-term oscillations in physicochemical conditions in the water column, sediments may periodically act as sources of trace metals and radionuclides in a lake/reservoir hypolimnion through dissolution of redox sensitive minerals (i.e., hydroxides and sulfides; Carignan and Lean, 1991; Boudreau, 1999), ion exchange mechanisms at clay mineral surfaces and/or in-

terlayer sites (Evans et al., 1983), and biodegradation mechanisms of organic matter and concomitant release of sorbed metals (Warren and Haack, 2001). Such processes may thus lead to temporal degradation of water quality by increasing metal bioavailability by orders of magnitude (Salbu and Steinnes, 1995).

Although environmental exposure and determination of metal bioavailability are still difficult tasks to perform at the ecosystem level (cf. Plant et al., 2001), water management practices increasingly need to take into consideration the presence and phase distribution of metals on both spatial and temporal scales to evaluate the overall quality of water resources. Such practices are particularly important for watersheds that harbor large-scale non-point sources of such contaminants (cf. Nagorski et al., 2003), particularly since reservoirs imperfectly mediate upstream historical anthropogenic activities that have led to compromised environmental stream quality within watersheds (Marcus et al., 2001).

The present investigation evaluated water quality of the South Texas Lower Nueces River basin and Lake Corpus Christi reservoir (Fig. 1) as a function of trace element loading and cycling on such temporal and spatial scales. The major sources of metals and As to this system are the legacy of historical metal releases to the basin from extensive U mining of the Gulf Coast Uranium Province, current leaching from the large number of surface U mine pits and tailings, and natural geogenic weathering of the ore body through geologic time (Blount et al., 1992; Nugent et al., 1994; Parker and Herbert, 2000). This work was thus undertaken to quantify (a) the potential impact of past mining activities on water quality and in a small, upstream pond and a large downstream reservoir that provides drinking water to a population of close to half a million people and (b) the importance of seasonal redox fluctuations and event-based sediment resuspension processes on As and metal cycling within these 2 water bodies. This approach allowed us to generate a quantitative mass balance of As in the reservoir showing that hydrodynamic processes, rather than geochemical ones, control seasonal fluctuations of As concentrations throughout the lake.

## 2. Study area and uranium mining in the South Texas coastal plain

The southern Texas Coastal Plain is composed of a thick sequence of southeasterly dipping Tertiary and Quaternary basin-fill sediments (Eargle et al., 1975). These sediments, which collectively comprise the Texas Gulf Coastal Plain, are dominated by interstratified clastic sandstones and clays deposited in a series of fluvial, deltaic, estuarine, and marine marginal paleoenvironments that progressively decrease in age toward the

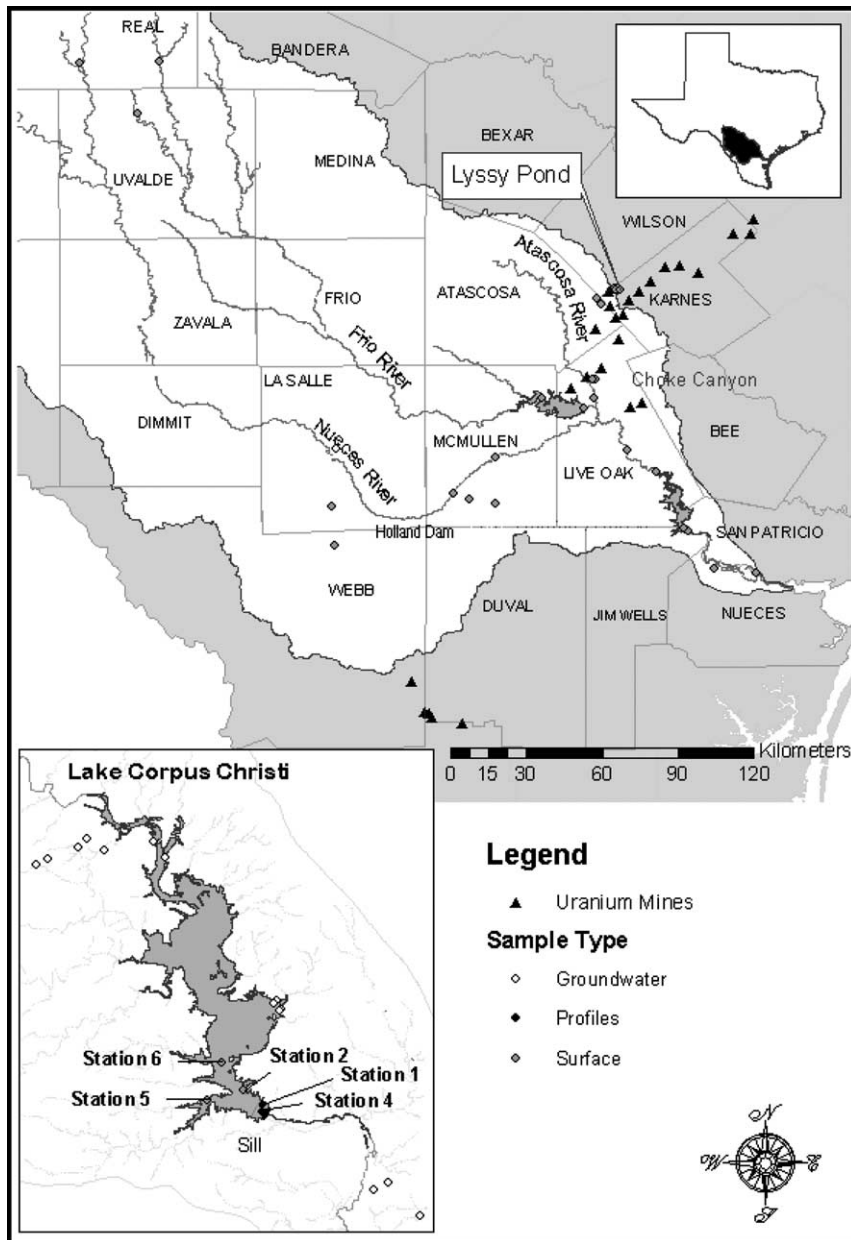


Fig. 1. Map of the Nueces River Basin, sampling stations, and old U mines. Lower left insert shows Lake Corpus Christi with sites of collected water profiles at the southern tip of the reservoir. ▲, sites of old U mines; ○, groundwater samples; ●, Lake Corpus Christi's vertical profiles; ◐, surface water samples (rivers and lakes).

modern coast (Table 1). Migration of the depocenter toward the south over time, combined with increased subsidence, has resulted in tilting of the post-Cretaceous strata at an average dip of 1–4° to the SE. The post-depositional tilting resulted in the generation of numerous strike parallel down-to-the-SE normal faults. Tilting and faulting enhanced the capacity of the granular sediments to act as fluid conduits and traps for groundwater.

The sedimentary sequence is punctuated by large volumes of interstratified volcanoclastic debris thought to have originated as airfall tuffs from extrusive volcanism in the Sierra Madre Occidental of Mexico and the Trans-Pecos region of West Texas. Much of this volcanogenic material is found in Oligocene and Miocene age strata and is thought to have been the original source of U and Mo mineralization (Galloway, 1977; Galloway et al., 1982; Galloway and Kaiser, 1980). Roll-front U

Table 1  
Stratigraphy of South Texas Uranium Province (modified from Galloway et al., 1979)

System	Series	Geologic unit	Description	
Quaternary	Holocene	Floodplain alluvium	Sand, gravel, silt, clay	
	Pleistocene	Pleistocene Beumont clay, Deweyville formation, Montgomery formation, Bentley formation, and Pliocene Willis sand	Sand, gravel, silt, clay	
Tertiary	Pliocene	Goliad sand <sup>a</sup>	Fine to coarse sand and conglomerate; calcareous clay; basal medium to coarse sandstone. Strongly calichified	
		Miocene	Fleming (Logarto) formation Oakville sandstone <sup>a</sup>	Calcareous clay and sand Calcareous, crossbedded, coarse sand
	Oligocene	Catahoula formation	Chusa tuff	Calcareous tuff; bentonitic clay; some gravel and varicolored sand near base.
			Soledad conglomerate <sup>a</sup>	Soledad grades into sand lenses in northern Duval and adjacent counties
			Fant tuff <sup>a</sup>	Light gray to green clay; local sand filled channels
	Eocene	Frio clay <sup>a</sup> (Southwest of Karnes County) Whitsett formation (Jackson group)	Fashing clay	Chiefly clay; some lignite, sand, <i>Corbicula</i> , oysters
			Tordilla sandstone, Calliham sandstone <sup>a</sup>	Very fine sand
			Dubose	Silt, sand, clay, lignite
			Deweesville sandstone <sup>a</sup>	Mostly fine sand; some carbonaceous silt and clay
			Conquista clay Dilworth Sandstone <sup>a</sup>	Carbonaceous clay Fine sand, abundant <i>Ophiomorpha</i>

<sup>a</sup>Indicates geologic units that were a source of U.

deposits resulted from the weathering of the volcanic ash by meteoric waters and transport in oxidizing ground waters through semi-confined aquifers until mineralization in fossil reduced freshwater aquifers (Goldhaber et al., 1978; Reynolds and Goldhaber, 1978). Uranium, As, Mo, Se, and V undergo reduction at differing values of Eh, which results in As, Mo, Se, and V zonation in the vicinity of the U ore (Galloway et al., 1982). Zonation, likened to chromatographic separation, creates Se enrichment updip, and Mo enrichment downdip of the U.

A detailed history of U mining in South Texas is given in Parker and Herbert (2000). In summary, mining of roll-front type U ores began in 1959 and peaked in 1970 with over 40 mines located in Karnes, Atascosa, Gonzales, and Live Oak counties (Fig. 1). With an estimated  $6.6 \times 10^6$  tons of ore reserves, the "Gulf Coast Uranium Province" of South Texas (Finch, 1996) ranked third nationally in uranium oxide production, in the late 1970s to early 1980s (Eargle et al., 1971). Environmental impact assessments of these mining activities confirmed the enrichment of trace metals and radionuclides near mining sites in both groundwater (Blount et al., 1992; US Department of Energy, 1995) and surface water ecosystems (Goldhaber et al., 1978; US Department of Energy, 1991; Blount et al., 1992; Batson et al., 1996). Uranium pit lakes showed particularly high levels of selectively monitored oxyanions

with concentrations ranging 1–4500, 5–33, and 10–650  $\mu\text{g/L}$  for U, As, and Mo, respectively (Brandt et al., 1994). Such high concentrations and the high geochemical mobility of U ore oxyanions under oxic slightly alkaline conditions (Plant et al., 2001; Smedley and Kinniburgh, 2002), thus highlight the need to assess As and trace metal loading and cycling downstream from South Texas mining sources including Lake Corpus Christi. Although prior initiatives have identified potential contaminant sources and assessed the water quality in the Nueces River basin (Fisher, 1996; Bush et al., 2000; Nueces River Authority, 2001), these efforts have limited their focus to the upper basin and coastal ecosystems and provide no data on trace metal concentrations in Lake Corpus Christi reservoir. Compounding this lack of data is the failure to address the potential impacts from extensive U mining activities in the upstream section of the basin.

The Nueces River Basin covers approximately 44,000  $\text{km}^2$ , encompassing all or part of 23 counties (Fig. 1). The reservoir was first impounded in 1930 with an earthen dam (La Fruta reservoir) but its level was raised in 1958 with the construction of Wesley Seale Dam to increase the volume by an order of magnitude to  $\sim 0.4 \text{ km}^3$  (Cunningham, 1998; Brown and Dodson, 1998). The volume capacity of Lake Corpus Christi has now been reduced by  $\sim 25\%$ , through sedimentation, to

reach a present volume of  $\sim 0.3 \text{ km}^3$  at maximum elevation (Nueces River Authority, 2001). The bathymetry of the lake is typical of many flood-plain reservoirs consisting of a shallow basin with a deep river channel, which in Lake Corpus Christi occurs along the eastern shore following the old Nueces River. Its deepest region is found in the southern section between the La Fruta and Wesley Seal dams and reaches 16–17 m at full capacity. During the year-long period of study, the reservoir's depth in the deepest section oscillated between 8 and 14 m ( $\sim 25\text{--}50\%$  capacity) and the mean water residence time, calculated as month-end storage divided by total monthly outputs (Kneebone and Hering, 2000), averaged  $169 \pm 66$  days.

The water budget for Lake Corpus Christi is controlled largely by substantial seasonal fluctuations with sudden inflow events and intense evaporative losses affecting reservoir level and water column conditions. The inflow budget for Lake Corpus Christi typically increases an order of magnitude from  $\sim 2 \times 10^6 \text{ m}^3/\text{month}$  during the summer to  $>55 \times 10^6 \text{ m}^3/\text{month}$  in the winter, whereas the evaporative losses decrease by the same magnitude during that period from up to  $\sim 15 \times 10^6 \text{ m}^3/\text{month}$  in the height of the warm period to  $\sim 2.5 \times 10^6 \text{ m}^3/\text{month}$  during the winter (Fig. 2). Water withdrawals are driven mostly by Corpus Christi's industrial and municipal activities, as well as by the needs of several communities around the lake. Total water outflows ( $12.3 \pm 4.9 \times 10^6 \text{ m}^3/\text{month}$ ; Fig. 2), are comprised of water withdrawals added to pass-through requirements, which are mandated to answer freshwater ecosystem

needs from receiving estuaries (TNRCC, 2001). The dynamic and seasonally variable hydrology in the lower Nueces River basin thus results in substantial changes in overall volume over short periods of time (Fig. 2), which may lead to significant shifts in water column physiochemical conditions. Consequently, geochemical cycles of trace metals may be dominated by fluctuating geochemical conditions and sediment resuspension events produced by wind-driven mixing in the winter to spring seasons (fully oxidized), episodic flood events in the spring and fall (mixed), and reduced  $\text{O}_2$  concentrations within the deep layers of the reservoir in the summer (stratified).

### 3. Experimental

#### 3.1. Water column profiles

Lyssy Pond, a livestock pond (Fig. 1), has been chosen both to assess the potential inputs of mine-derived trace metals to downstream freshwater reservoirs of the region and illustrate the role of geochemical cycling on the distribution of these metals during seasonal water-column stratification. Lyssy Pond is a prime site for the comparative study because (a) it has been subjected to localized environmental impacts attributed to U mining activities (Smith et al., 2002) and (b) strong seasonal fluctuations in redox conditions within its water column allowed the evaluation of the importance of geochemical processes on the cycling of mine-derived

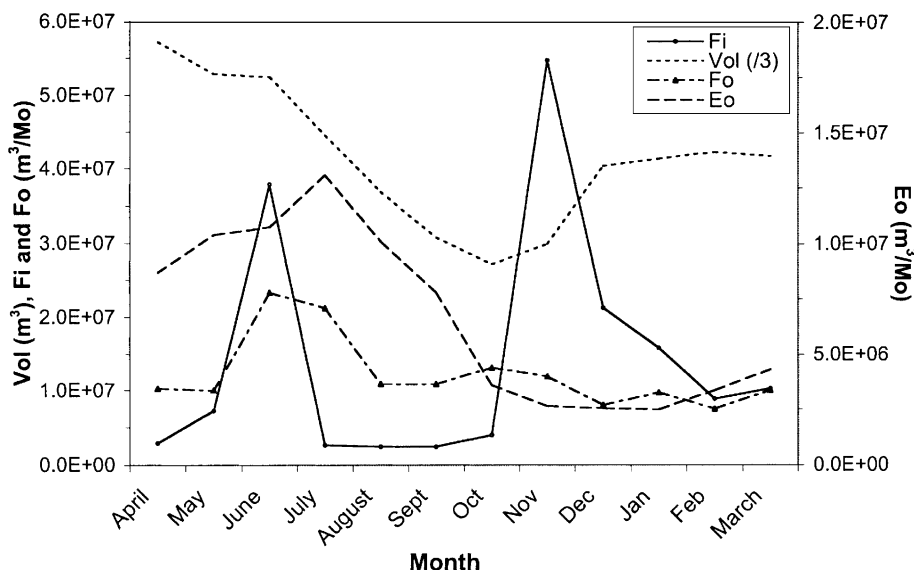


Fig. 2. Lake Corpus Christi water balance (from April 2001 to March 2002). Eo, evaporative flux ( $\text{m}^3/\text{month}$ ); Fi, river inflow ( $\text{m}^3/\text{month}$ ); Fo, river outflow ( $\text{m}^3/\text{month}$ ; combination of water withdrawals and passthroughs); Vol, lake volume ( $\text{m}^3$ ), divided by 3 to be on a comparative scale with Fo and Fi.

oxyanions in aquatic systems of the basin. The pond is located adjacent to the only open pit U mine in Texas that underwent remediation under the federally funded Uranium Mill Tailings Remedial Action Project (UMTRA; US Department of Energy, 1991; Parker and Herbert, 2000). Although initially included in the clean up plans, the sediments from the pond were never remediated and have been shown to retain a historical record of substantial radionuclide inputs from the mine (Smith et al., 2002).

Water profiles were sampled in the deepest parts of both Lyssy Pond (April 2002) and Lake Corpus Christi (July and August 2000, and January 2001). Water profiles from Lake Corpus Christi were collected at 2 stations (1 and 4; Fig. 1) during each sampling event. These are located less than a kilometer apart near the dam and represent slightly stratified (station 1) vs. well-mixed conditions (station 4) in the lake. The July 2000 profiles provide information on the conditions in the lake following a large surface inflow and subsequent mixing event (Fig. 2). The August and January sampling events represent, respectively, more typical seasonal conditions with low inflow and high evaporative losses in the summer and a mixed water column and increased positive water balance in the winter. Physiochemical parameters (pH, dissolved O<sub>2</sub>, temperature, and depth) were collected using a Hydrolab<sup>®</sup> probe operated from a small vessel. The pH probe was calibrated using pH 4 and 7 National Institute of Standards and Technology (NIST) buffers, and the O<sub>2</sub> sensor against water equilibrated with atmospheric O<sub>2</sub>.

All sampling equipments were acid-cleaned with 10% ultrapure HNO<sub>3</sub> and trace metal-clean techniques (Method 1669; USEPA, 1996c) were strictly followed throughout water sample collection and analysis. Water profiles were obtained using a customized sampling device designed to permit collection of filtered and unfiltered water samples from a boat at specified depths while preserving in situ redox conditions. This device, which consists of a large balasted PVC pipe attached to a graduated line, simultaneously collects 2 samples in distinct 50 ml acid-cleaned polypropylene syringes providing dissolved and particulate fractions and minimizing perturbation of the water column. Upon recovery, both syringes were immediately capped, double bagged and stored at 4 °C to reduce reaction kinetics. One of the 2 samples was filtered through acid-clean 0.45- $\mu$ m nylon syringe filters, either in the field using a portable glove box as a clean environment or in the lab under a Class 100 clean bench. This filtered portion is used to represent the “dissolved” metal fraction. Water samples collected from depth with dissolved O<sub>2</sub> (DO) < 3.0 mg/L were filtered under an ultra-high purity N<sub>2</sub> atmosphere in the portable glove box to prevent alteration of metal speciation due to oxidizing conditions or metal scavenging by Fe and Mn oxy-hydroxides. The dissolved and

unfiltered fractions (particulate by subtraction) were acidified with 0.2% Optima<sup>®</sup> HNO<sub>3</sub> to pH <2.0.

### 3.2. Surface and groundwaters in the Nueces river basin

The collection of surface water grabs included 3 other stations in Lake Corpus Christi (2, 5, and 6) and 16 tributary samples in the Nueces River basin – 3 in the upper and 13 in the lower basin (Fig. 1). Tributary samples taken along the Frio River progressed from points in the upper Nueces River basin to upstream and downstream sections of Choke Canyon Reservoir (Fig. 1). The Atascosa River was sampled above the confluence of the 3 rivers. Surface grabs were sampled by immersing closed acid clean low-density polyethylene (LDPE) bottles underwater with gloved hands, opening underwater to prevent sampling of the surface micro-layer, and capping underwater. Sixteen groundwater samples were collected from wells around Lake Corpus Christi (Fig. 1 inset of Lake Corpus Christi) in acid clean LDPE bottles. Untreated water samples were retrieved from the well spigot after 5 min of flushing the well-head prior to collection.

### 3.3. Trace element analysis

In accordance with EPA Method 1669, the dissolved fraction is operationally defined as that passing through a 0.45- $\mu$ m filter. However, many studies have shown that a significant percentage of trace metals are associated with the colloidal fractions between 1 nm and 1  $\mu$ m (Benoit et al., 1994; Martin et al., 1995; Greenamoyer and Moran, 1997; Wen et al., 1999). Therefore, both the dissolved and total fractions were acid solubilized according to EPA Method 1640 (USEPA, 1996b) in order to destroy colloidal complexes, dissolving trace metals potentially adsorbed onto sub-particulate matter. Following pre-treatment, samples were analyzed on a Hewlett-Packard 4500 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), using in-line addition of the internal standards Sc, Y, Ho, and Tb (USEPA, 1996a). The ICP-MS was calibrated prior to analysis using a 5-point calibration curve ( $r^2 > 0.999$ ) prepared with certified standards. Table 2 shows the accuracy and precision of the instrument for each metal and As as assessed by the analysis of the NIST 1643d: Trace Elements in Drinking Water Standard. Table 2 also lists the method detection limits for each element (MDL) determined by the analysis of 7 replicates of a 0.1  $\mu$ g/L standard. Other quality control measures included the analysis of continuing calibration verification (CCV) standards, showing greater than 90% accuracy throughout the analysis, 3 types of blanks (sampling, method, and reagent), which revealed no contamination of the samples, and duplicates/triplicates indicating greater than 90% precision.

Table 2

Accuracy and precision of NIST 1643d and method's detection limit (MDL) for trace metals in water

Trace metal	NIST 1643d measured value ( $n = 9$ )		NIST 1643d certified value		Average accuracy <sup>a</sup> (%)	Percent difference <sup>b</sup> (%)	MDL
	Median	Range	Median	Range			
As	55.9	±1.7	56.0	±0.7	100	2.6	0.022
Cd	6.4	±0.6	6.5	±0.4	100	6.9	0.046
Co	24.9	±0.6	25.0	±0.6	100	1.6	0.009
Cr	19.6	±2.3	18.5	±0.2	106	10.0	0.114
Cu	22.8	±0.5	20.5	±3.8	111	11.0	0.092
Mn	38.2	±0.6	37.7	±0.8 <sup>c</sup>	101	1.7	0.068
Mo	113.0	±3.2	113.0	±1.7	100	2.5	0.071
Ni	57.3	±1.4	58.1	±2.7	99	2.3	0.028
Pb	17.9	±0.5	18.2	±0.6	98	2.6	0.025
U	na	na	na	na	96	1.6	0.009
V	35.3	±1.0	35.1	±1.4	100	2.5	0.023

Concentrations are reported in  $\mu\text{g/L}$  (ppb).

<sup>a</sup> Values determined with high purity standards.

<sup>b</sup> Values determined by replicate sample analyses.

## 4. Results and discussion

### 4.1. Lyssy Pond

Despite the shallow depth of Lyssy Pond ( $\sim 3.5$ – $4.0$  m), physiochemical conditions of the water column show partially stratified conditions in the water column with an oxy-cline and thermocline around 2.5– $3.0$  m (Fig. 3). The slightly lower pH values in deeper layers of the pond with respect to surface waters suggest that the decreased DO concentrations are related to mineralization of organic matter, which is most probably fueled by eutrophic conditions in this livestock pond. Although truly anoxic conditions probably only existed in the sediments at the time of sampling, the suboxic conditions observed in the hy-

polimnion (DO  $\sim 0.6$  mg/L) should be sufficiently reducing to entrain geochemical cycling of redox sensitive metals (i.e., Mn and Fe) between particulate and dissolved phases. Manganese and Fe profiles, in permanently or seasonally stratified lakes, have successfully been used in the past as geochemical indicators of redox-clines in such systems and have been studied to illustrate phase transformations and mobility of oxyanions across redox boundaries (Balistrieri et al., 1994; Spliethoff et al., 1995; Viollier et al., 1995, 1997; Kneebone and Hering, 2000).

In Lyssy Pond, the distinct profiles of particulate and dissolved Mn (Fig. 4) suggest some redox cycling of this element whereby soluble  $\text{Mn}^{2+}$ , the predominant form under reducing conditions, is precipitated as insoluble  $\text{MnO}_x$  in oxic media. The enrichment of particulate Mn

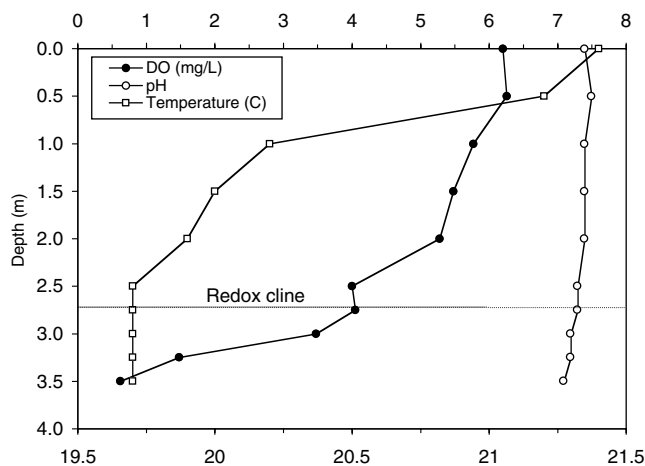


Fig. 3. Physical parameters (dissolved  $\text{O}_2$ , pH, and temperature) in Lyssy Pond water profile.

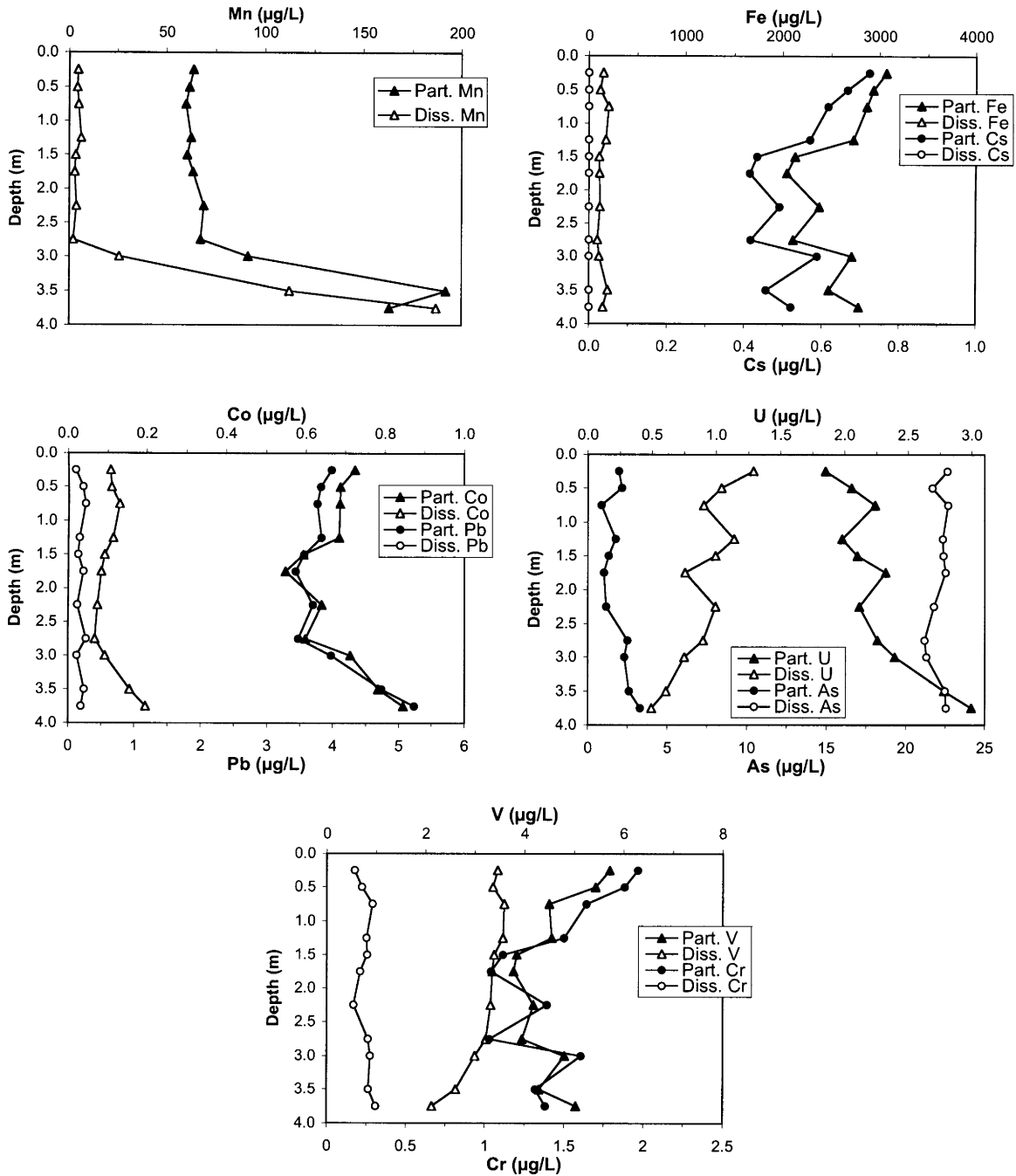


Fig. 4. Metal distribution in Lyssy Pond water profile.  $\circ$  and  $\triangle$ , dissolved concentrations ( $\mu\text{g/L}$ );  $\bullet$  and  $\blacktriangle$ , particulate concentrations ( $\mu\text{g/L}$ ).

below 3.0 m depth appears at  $\text{O}_2$  levels (1.0–1.5  $\text{mg/L}$ ) consistent with those reportedly responsible for precipitation of Mn oxides at the redox boundaries of stratified lakes (Viollier et al., 1995; Balistrieri et al., 1992b, 1994; Kneebone and Hering, 2000). Similarly, Co shows a

3-fold increase in its dissolved concentrations in the hypolimnion (Fig. 4) supporting previous observations that redox-driven cycling of Mn has a dramatic influence on Co distribution within reducing water columns (Balistrieri et al., 1992a,b, 1994; Viollier et al., 1995, 1997;



Achterberg et al., 1997). The concomitant increases in particulate Co and Mn concentrations in Lyssy Pond's hypolimnion suggest geochemical cycling of these 2 metals within this section of the water column probably leading to scavenging of Co by Mn oxy-hydroxides. The strong relationship between particulate Pb and Co ( $r^2 = 0.87$ ), however, suggests that resuspension of particles in the water column may also be an important process for metal phase distribution in Lyssy Pond's water column. Although it is often assumed that Pb is diagenetically immobile, recent studies have shown it to be impacted by hydroxide cycling (Gobeil and Silverberg, 1989) with selectively strong sorption to Mn oxy-hydroxide phases (Hettiarachchi et al., 2000). The increased values of particulate Pb and Co in the suboxic zone of the water column thus point to increased scavenging of these 2 metals by Mn oxy-hydroxides whereas, in surface oxic waters, fluctuations in these metals are decoupled from particulate Mn distribution and correspond more tightly to those of particulate Fe (Fig. 4). The covariation between particulate Fe and Cs ( $r^2 = 0.88$ ; Fig. 4) shows that, in this system and in contrast to Mn cycling, Fe seems to be driven by particle resuspension rather than geochemical phase transformation. Indeed, Cs is a diagenetically stable element that is usually conservatively sorbed to clay mineral interlayers (cf. Viollier et al., 1995, 1997) and which low solid-to-solute mobility is controlled by ion-exchange reactions rather than redox cycling (Evans et al., 1983; Facchinelli et al., 2001; Zachara et al., 2002). In Lyssy Pond, Cs occurs exclusively in the particulate form (Fig. 4) and shows decreasing concentrations from the surface to the hypolimnion independent of the changing redox conditions. Because reduction of Fe oxy-hydroxide occurs more slowly and at lower redox potentials than Mn oxides (Hamilton-Taylor and Davison, 1995; Kneebone et al., 2002), the suboxic waters of Lyssy

Pond may not be reducing enough to induce significant redox cycling of Fe. Moreover, detailed analysis of particulate and dissolved phases of Fe in Lake Corpus Christi (see discussion below) points to a strong association of Fe to alumino-silicates rather than reactive oxy-hydroxides in the drainage basin further supporting sediment resuspension processes as control mechanisms for the presence of particulate Fe in Lyssy Pond. These particles may thus carry a series of associated trace metals, some of which (Pb and Co) show remobilization and selective association with Mn oxides in the suboxic zone of the water column and some (Cs, V, and Cr) showing continuing association with the Fe-rich particles.

With changes in oxidation potential, the profiles of redox sensitive oxyanions such as U, V, and Mo should also indicate alterations in speciation resulting in less mobile particulate forms under reducing conditions (van der Weijden et al., 1990; Balistrieri et al., 1994; Viollier et al., 1995, 1997; Achterberg et al., 1997). Arsenic is somewhat distinctive in that it can remain relatively mobile under a broad range of redox potentials particularly at the neutral to slightly alkaline pH values typically found in surface and groundwaters (Smedley and Kinniburgh, 2002). Immobilization of As into solid phases occurs mostly, under oxic conditions and neutral to slightly acidic pH, by interaction with Fe and Mn oxides (through co-precipitation/adsorption processes) and, in highly sulfidic environments, through the precipitation of sulfide minerals containing co-precipitated As (Smedley and Kinniburgh, 2002; Ryu et al., 2002; Moldovan et al., 2003).

Uranium total concentrations in Lyssy Pond's water column remain constant throughout most of the profile ( $\sim 3.0$ – $3.5$   $\mu\text{g/L}$ ; Fig. 4). These low concentrations are consistent with background values observed in pristine aquatic systems (van der Weijden et al., 1990; Viollier

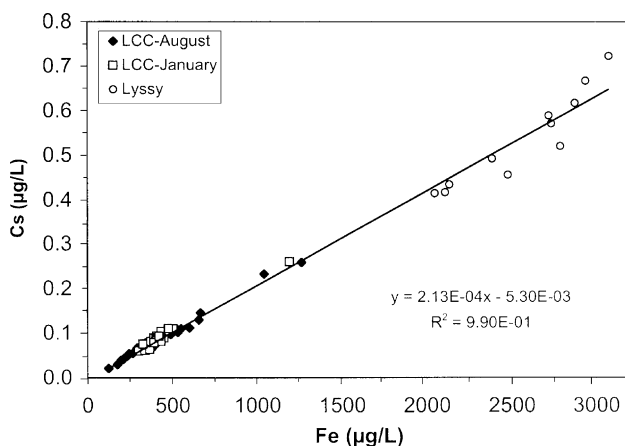


Fig. 5. Relationship between particulate Cs and Fe concentrations in Lyssy Pond's and Lake Corpus Christi's water columns.

et al., 1995; Langmuir, 1997), showing no measurable impact of the neighboring U mine pit and tailings on the aqueous concentrations of this metal in the pond. The particulate and dissolved U profiles (Fig. 4) show a near perfect mass balance with an increase in the particulate phase corresponding to a decline in the dissolved phase toward the hypolimnion. A slight increase in total U concentrations at depth suggests, however, that sedimentary sources of particulate U may contribute to the increased particulate concentrations at the bottom of the water column. In contrast to U distribution, total As concentrations in the pond ( $24 \pm 0.8 \mu\text{g/L}$ ) are enriched by an order of magnitude with respect to natural surface waters ( $0.5\text{--}2.0 \mu\text{g/L}$ ; Smedley and Kinniburgh, 2002). The distribution of As shows a predominance of dissolved phase (90%; Fig. 4) and nearly constant levels throughout most of the profile. The lack of correlation between As and Fe-rich particles further suggests that Fe is not very reactive in this system. Although the pH in Lyssy Pond waters (7.0–7.5) is in the lower  $\text{pH}_{\text{zpc}}$  range of most natural Fe oxy-hydroxide minerals ( $\sim 7.0\text{--}9.0$ ; Bowell, 1994; Warren and Haack, 2001), it should still favor some positive charge on oxide surfaces encouraging some sorption of oxyanions such as As (cf. Bowell, 1994). The absence of covariance between Fe particulates and As (given the large concentrations of both elements), thus point to an Fe form with low  $\text{pH}_{\text{zpc}}$  (i.e., goethite) and/or not linked exclusively to amorphous reactive oxides but more strongly bound to detrital aluminosilicates. These findings support a previous study (Kuhn and Sigg, 1993) showing that in lakes that receive large proportions of allochthonous and geochemically stable particulate fractions, Fe has little influence on As speciation and phase distribution and that only the cycling of reactive Mn oxides affected the redox speciation of inorganic As within the water column. The slight redox cycling of Mn in Lyssy Pond is probably not sufficient to affect substantially the speciation of As in the water column although the reoxidation of As(III) into As(V), if it occurred, would probably not affect the total mass balance distribution of this element resulting in the constant profiles observed.

Dissolved V concentrations decrease by  $\sim 30\%$  in the hypolimnion and are relatively balanced by the particulate phases yielding a somewhat constant profile for total concentrations in the deep section of the water column. The distribution of particulate V is, however, well correlated to that of particulate Fe and Cs ( $r^2 = 0.84$  and  $0.82$ , respectively) suggesting that V is associated with diagenetically stable minerals and clay particles and is not very mobile in this system. This interpretation is consistent with previous studies in a river-wetland-lake system (Elbaz-Poulichet et al., 1997) showing that V can be strongly associated to detrital aluminosilicate fractions and can remain stable in the particulate form despite strong redox fluctuations. Close

to perfect relationships between Fe and Al as well as between V and Fe–Al have been observed in sediment cores representing wide ranges (and histories) of sediment depositional processes within Lake Corpus Christi (Fig. 6; data from Brandenberger, 2002). The observed correlations across an order-of-magnitude range in metal concentrations and widely different depositional environments support the assertion that V can be associated with detrital aluminosilicate fractions and remain geochemically stable in certain aquatic systems (cf. Elbaz-Poulichet et al., 1997). A strong relationship has also been observed between particulate Cr and Fe–Cs ( $r^2 = 0.83$  and  $0.97$ , respectively) in Lyssy Pond's water column, and between Cr and Fe–Al ( $r^2 = 0.75$  and  $0.73$ , respectively). Data from Brandenberger, 2002) in all sediments of Lake Corpus Christi. Balistrieri et al. (1994) have reported a strong co-variance between oxyanion-forming Cr and V in a permanently stratified lake showing that these 2 metals tend to be preferentially associated with Fe phases. The similar behavior between Cr–V and Fe–Cs particulate phases in Lyssy Pond thus sustains a stable association of these oxyanions with Fe-rich particles and clay minerals, under geochemical conditions that do not favor strong redox cycling of Fe mineral phases. In contrast, the observed large increases in Pb and Co concentrations and more moderate ones in As, in Lyssy Pond's suboxic layer, point to a possible association of these elements with Mn-rich particles. Arsenic and Co have indeed been shown to be released from Mn phases in suboxic and anoxic zones of stratified lakes (Balistrieri et al., 1994; Viollier et al., 1995), supporting enhanced and selective cycling of these elements as a function of redox Mn phase distribution.

#### 4.2. Lake Corpus Christi

Fig. 7 presents the temporal and spatial distribution of physicochemical parameters (DO, temperature, and pH) in Lake Corpus Christi's water column as a result of seasonal variations (August vs. January) and inflow events (July). Dissolved  $\text{O}_2$  is the only parameter that shows a significant variation in vertical distribution within a specific season. While seasonal changes in DO concentrations are representative of temperature variations in the water column (higher saturation level and aeration in the winter), the vertical gradient observed in August at stations 1 and 4 ( $6.7\text{--}1.9$  and  $7.3\text{--}3.9 \text{ mg/L}$ , respectively) points to the installation of a slight chemical stratification at least in the deepest part of the lake. In contrast to Lyssy Pond, however, the DO levels barely reached anything more than hypoxic conditions in the deepest part of Lake Corpus Christi's water column. The small reduction in pH values, along the same gradient (from 8.4 to 8.2) in August, seems to confirm increased respiration rates and reducing conditions in

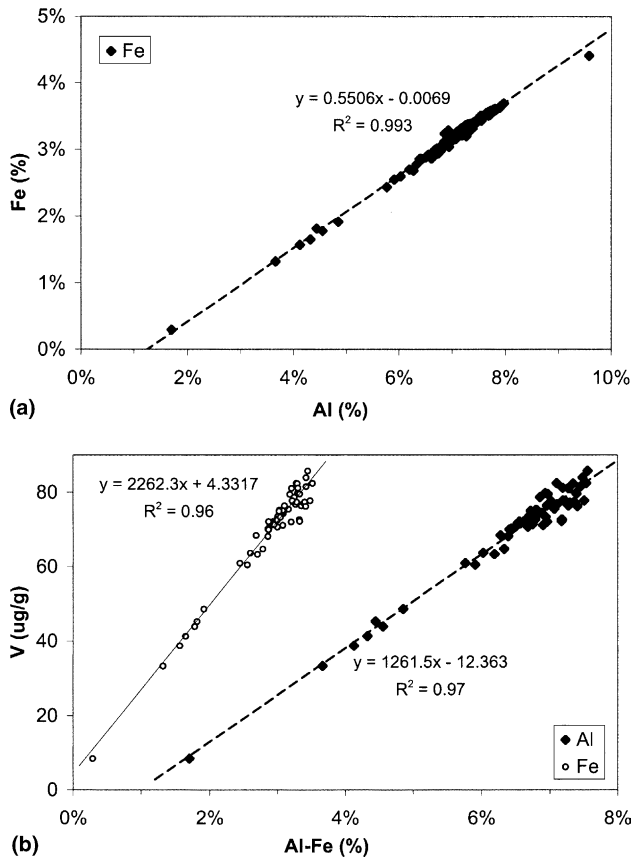


Fig. 6. Relationship between (a) particulate Fe and Al concentrations (top) and (b) particulate vanadium and iron–aluminum concentrations (bottom) in Lake Corpus Christi sediments.

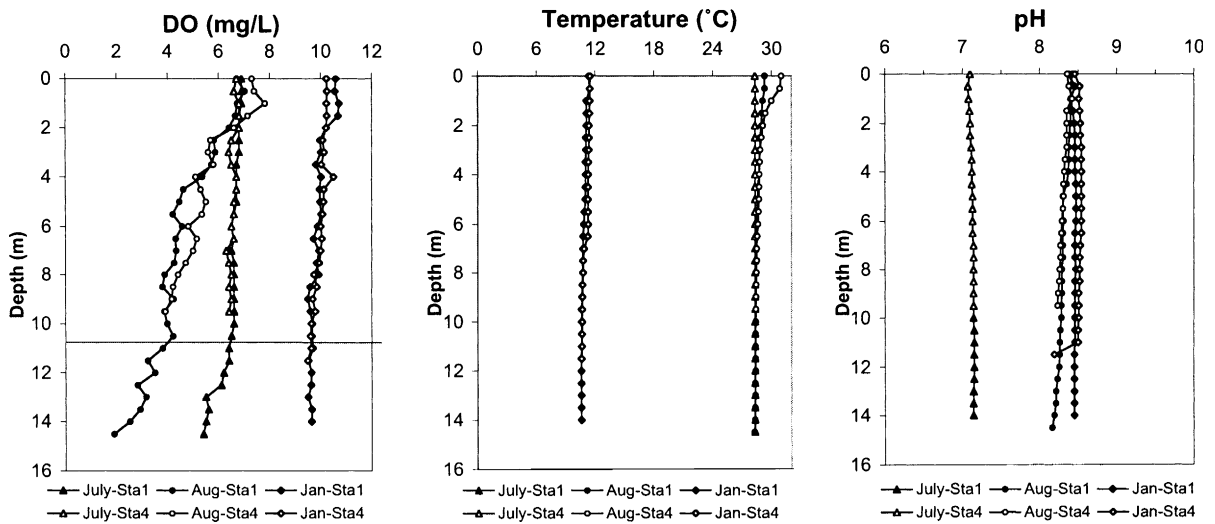


Fig. 7. Temporal and spatial distribution of physical parameters (dissolved O<sub>2</sub>, temperature, and pH) in Lake Corpus Christi water profiles.

deep water layers. The generally shallow depth of the lake, however, allows for rapid alterations of physiochemical conditions through changing hydrologic conditions that generate extensive mixing of the water column. This is observed subsequent to a large inflow event in June (Fig. 2) that led to virtually homogenous conditions within the water column in July compared to the stratified conditions seen in the midst of the summer season. After such an inflow, a small depletion in hypolimnion DO is only observed in the deepest site (Station 1: 6.9–5.4 mg/L). Another remarkable effect of the inflow event is the decrease in pH by an order of magnitude relative to summer and winter values of around  $8.4 \pm 0.1$ . The relatively high pH values in lakes like this one are typical of evaporative effects observed in arid climates on alkalinity and pH (Langmuir, 1997; Faure, 1998), while lower July values seem to be a product of a rapid dilution driven by a substantial inflow of meteoric waters through the Nueces River in June (Fig. 2).

Dissolved and particulate concentrations of Mn were a factor of 5–10 lower in Lake Corpus Christi than those measured in Lyssy Pond’s water column (Figs. 4 and 8), with a total pool almost entirely comprised of particu-

late species (98% of the total concentrations). This is in contrast to the distribution observed in the pond where dissolved phases contributed 10 to 50% of the total Mn in oxic and suboxic layers, respectively. The slightly reducing conditions in Lake Corpus Christi’s deepest layers during the summer months are attended by 4- to 5-fold increases in dissolved Mn levels in what looks like redox-induced cycling of this metal (cf. August; Figs. 7 and 8). However, these values are several orders of magnitude lower than those usually observed in suboxic/anoxic lacustrine systems where dissolution of sedimentary and settling particulate  $MnO_x$  lead to a high flux of  $Mn^{2+}$  into the water column below the redox interface (Balistrieri et al., 1992a, 1994; Viollier et al., 1995, 1997). In light of the relatively large particulate Mn concentrations, the increases in dissolved Mn observed here could be explained either by minimal reductive dissolution of oxides or desorption of exchangeable metals from high particle loads in the water column. One would expect to see this latter process increased in waters with high particle content even under well-oxygenated conditions. The immediate and higher increase in both particulate and dissolved Mn levels in the deepest section of the January profile

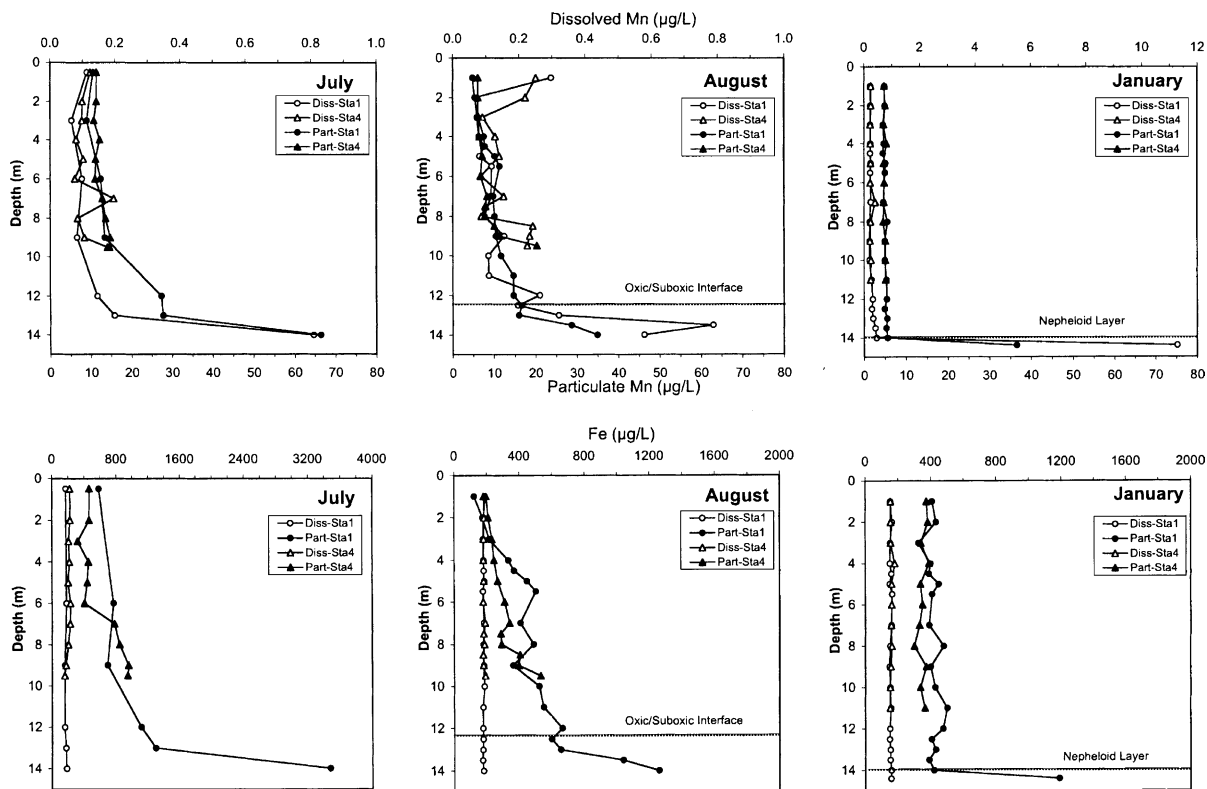


Fig. 8. Metal distribution in Lake Corpus Christi water profiles. ○ and ●, dissolved and particulate concentrations (µg/L), respectively, for Station 1; △ and ▲, dissolved and particulate concentrations (µg/L), respectively, for Station 4.

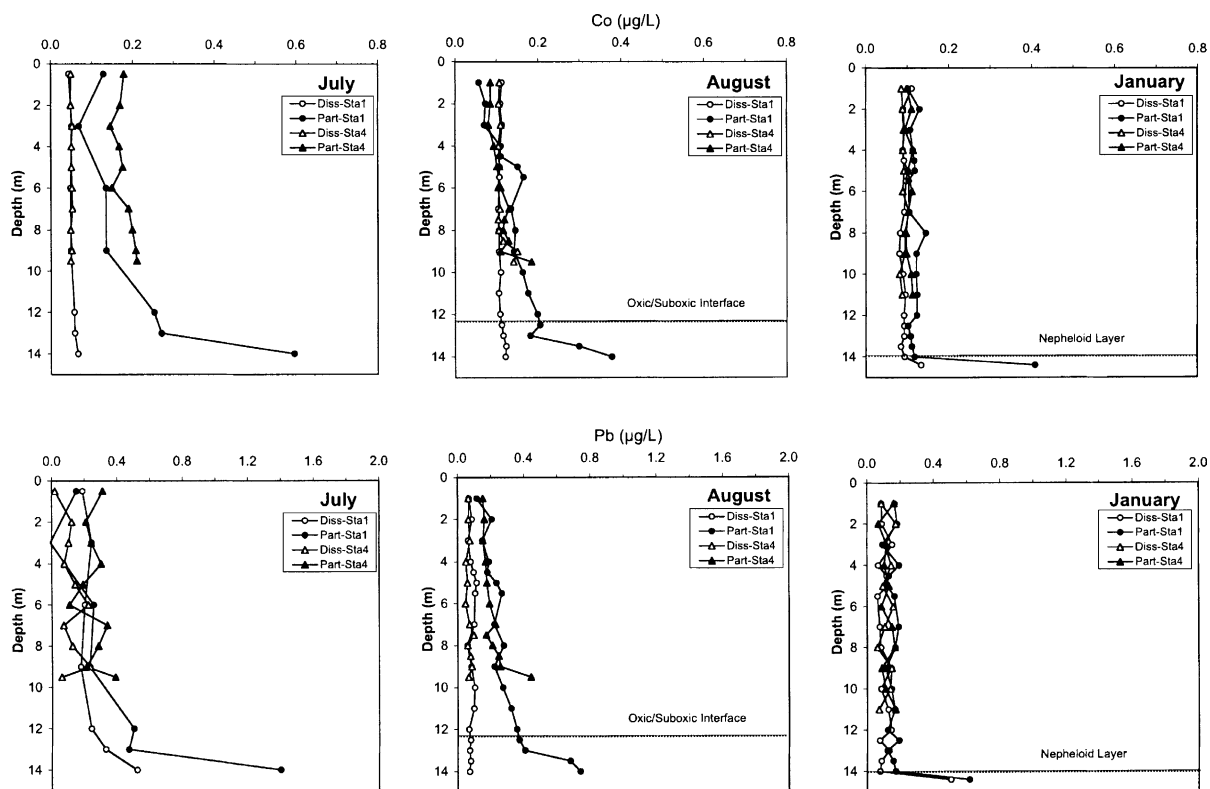


Fig. 8 (continued)

(Fig. 8) seems to support this conclusion. Indeed, the syringes brought from this depth presented visual evidence of large amounts of particles in suspension confirming the sampling of a particulate-rich layer at or close to the sediment/water interface (nepheloid layer) with a higher Mn dissolved/particulate distribution (25:75). Consistent with earlier studies (Balistrieri et al., 1992b, 1994; Viollier et al., 1995, 1997) and with Lyssy Pond data, the concomitant increases in dissolved concentrations of Mn, Pb, and Co in the nepheloid layer in the January profile suggest that a slight dissolution or desorption of Mn particulate forms is responsible for the release of elements such as Pb and Co. Similarly, in July an increase in dissolved Mn at the bottom of the well-mixed profile parallels the increase in particulate Mn in the deep layers ( $r^2 = 0.94$ ) suggesting that the distribution of Mn in Lake Corpus Christi's water column is controlled more by sorption/desorption than by redox-cycling processes (cf. Balistrieri et al., 1994).

Iron shows a strong increase in concentration towards the deep section of the lake, though this is only true for particulate phases (Fig. 8). Since the reduction rate of Fe hydroxides is slower than that of Mn oxides, one would not expect to see a significant input of dissolved Fe to Lake Corpus Christi's water column

from reductive dissolution of oxidized Fe species. The constant concentrations of dissolved Fe throughout the water column, further suggest that desorption of exchangeable Fe is not a significant process affecting Fe cycling in this system. The high concentrations in particulate Fe and Mn observed during the high inflow event in July may thus be due to important inputs of clay-rich particulate matter into this system and/or resuspension of bottom sediments rather than to changes in redox conditions. The strong relationship observed between particulate Cs and Fe in the lake and the pond ( $r^2 = 0.99$ ; Fig. 5) is matched by those of particulate V–Cr and Fe ( $r^2 = 0.95$  and  $0.92$ , respectively; Fig. 9). Although correlations between elements do not validate a particular mechanism of association, the tight relationships between Fe, Cs, V, Cr, and Al in basin-wide suspended particles and sediments point to stable detrital clay minerals, rather than reactive oxo-hydroxides, as the predominant Fe-rich phases in this system. Hence, despite periodic inputs of Fe-rich particles into the Lake Corpus Christi water column, the increased abundance of these particles bears no impact on the distribution of reactive trace metals through either scavenging or dissolution/desorption reactions.

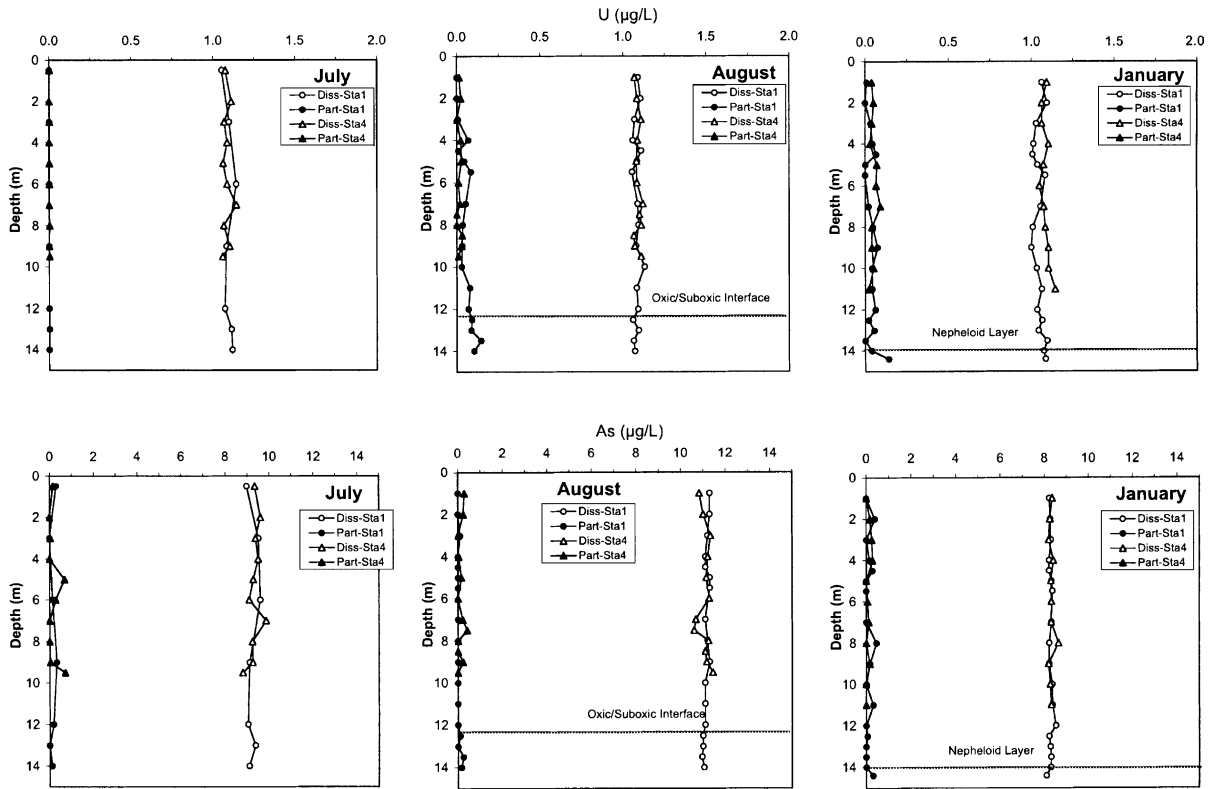


Fig. 8 (continued)

Further supporting the lack of reactivity of Fe in the lake, As and U remained stable throughout the entire water profiles across the different seasons (Fig. 8). Dis-

solved As levels decreased by half with respect to those observed in Lyssy Pond ( $22.1 \pm 0.5 \mu\text{g/L}$ ) and showed a significant seasonal change in concentrations with low

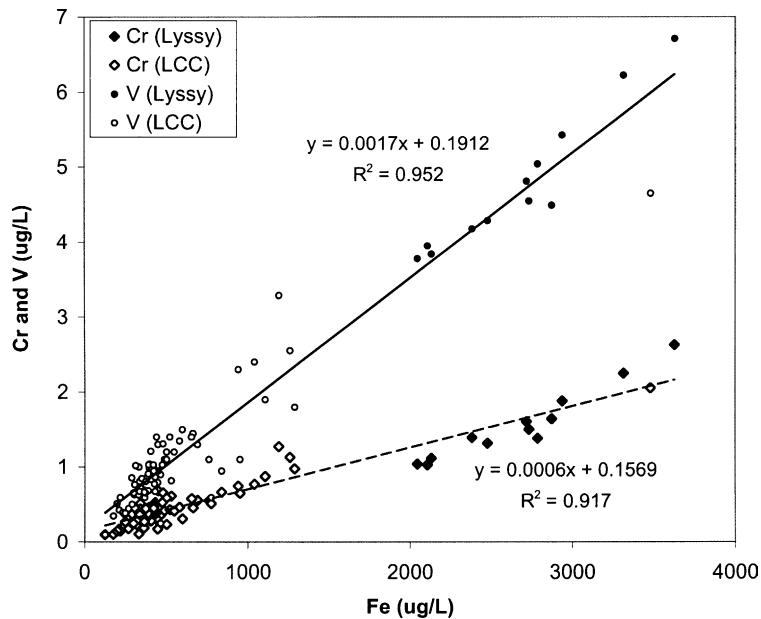


Fig. 9. Relationship between particulate Cr–V and Fe concentrations in Lyssy Pond’s and Lake Corpus Christi’s water columns.

levels in the winter ( $8.3 \pm 0.2 \mu\text{g/L}$ ), highest values observed in the height of the summer ( $11.1 \pm 0.2 \mu\text{g/L}$ ), and intermediate concentrations following the spring inflow event ( $9.0 \pm 0.3 \mu\text{g/L}$ ). Such seasonal changes are concomitant with variations in dissolved V concentrations that range from  $10.1 \pm 0.2 \mu\text{g/L}$  in the winter to  $13.8 \pm 0.4 \mu\text{g/L}$  in the summer. This parallel variation leads to a constant As/V ratio throughout the whole lake ( $0.80 \pm 0.04$ ; temporal and spatial data combined) suggesting a similar behavior for the dissolved phases of these 2 oxyanions. A strong relationship between As and V has previously been reported for groundwaters (Smedley et al., 2002; Lee and Herbert, 2002), and seems to be the product of similar geogenic sources of these metals in the studied aquifers. Principal component analysis of large groundwater data sets (Lee and Herbert, 2002) has further demonstrated that the very similar redox behavior of these 2 elements explains most of their covariance and abundance in Texas aquifers. To the authors' knowledge, however, this is the first time such a relationship has been observed in surface waters.

The noted seasonal cycling of As in Lake Corpus Christi is of particular importance since the levels in the lake are an order of magnitude above reported background levels in uncontaminated lakes ( $0\text{--}2 \mu\text{g/L}$ ; Smedley and Kinniburgh, 2002). Although As concentrations diminished with respect to those of the pond, the dissolved proportion of As increased to  $\sim 100\%$  in Lake Corpus Christi (Fig. 8), indicating that all of the As in the lake is now in the dissolved phase and not influenced by sorption to the abundant particulate Fe or Mn present in suspension. In the lake, pH values in summer and winter ( $8.0\text{--}8.3$ ) are high enough to favor neutral to negative charges on oxide surfaces (cf. Bowell, 1994; Warren and Haack, 2001) leading to substantial reductions in the potential sorption of oxyanions such as As and U. Even in the nepheloid layer, sampled in January, particulate As concentrations did not increase substantially with respect to water column values despite increases in all other particulate metal concentrations. Low inputs of particulate As from resuspended sediments are supported by low As levels in sediments collected underneath station 1 ( $5.7 \pm 0.6 \mu\text{g/g}$ ; Brandenberger, 2002) and metal to As ratios (i.e., Fe, Pb, Co, V, and U) in suspended particulate matter that correspond tightly with those measured in surficial sediments from this core ( $0\text{--}10 \text{ cm}$ ; Brandenberger, 2002). These observations further demonstrate that little exchange exists between the dissolved and particulate phases in Lake Corpus Christi's water column and that underlying sediments do not act as a substantial source or sink of As in the system.

Uranium values showed a marked change in distribution with respect to the profile from Lyssy Pond. Although dissolved values remained in the same background range measured in the small pond ( $1.0\text{--}1.2 \mu\text{g/L}$ ),

particulate values dropped from representing 60–80% of the total distribution in Lyssy Pond to become negligible (less than 1% of the total distribution) in Lake Corpus Christi (Figs. 3 and 7). Similarly to with As concentrations, U showed no sign of interaction with particle load in the water column. This behavior was also observed for Mo (data not shown), which confirms that oxyanion-forming elements in this oxic and slightly alkaline lake do not interact strongly with particles probably due to the lack or reduced amount of reactive sites in particles present in the water column.

#### 4.3. Surface and groundwaters in the Nueces river basin

The tributary and groundwater samples were collected to enhance the understanding of the distribution of As in the Nueces River basin. Fig. 10(a) illustrates the distribution of As in the upper Nueces River basin to the lower basin including Lake Corpus Christi and a series of tap water samples in the city of Corpus Christi. The distribution of As in the Nueces River shows a gradient of increasing values toward Lake Corpus Christi from  $0.6 \pm 0.1 \mu\text{g/L}$  in the upper basin, to  $2.5 \mu\text{g/L}$  at Holland Dam in La Salle County, and reaching  $6.8 \pm 1.7 \mu\text{g/L}$  at the entrance of the lake. The notable increase in As concentrations downstream of Holland Dam suggests that the sources for As are spatially influenced within the basin itself. Compiling As concentrations from National Uranium Resource Evaluation (NURE), Texas Water Development Board (TWDB) and National Water Information System (NWIS) into a GIS database provides an unambiguous indication that the dominant sources for As in the Nueces River basin are the geologic formations enriched in U ore, such as the Catahoula and the Oakville Formations (Parker et al., 2001; Clark, 2002; Lee and Herbert, 2002). Therefore, the significant increase in As concentrations in the Nueces River downstream of Holland Dam probably results from the meander of the river along these formations and an increased influence of baseflow from groundwaters in contact with them. The values in the Nueces River basin are in direct contrast with the neighboring San Antonio basin, which is characterized by a higher density of U mines than the Nueces basin, particularly within Karnes County and hosts the only UMTRA project in Texas. Arsenic levels in the San Antonio and San Marcos Rivers average  $3.0 \pm 0.9 \mu\text{g/L}$  (Bush et al., 2000; Parker, *pers. comm.*), demonstrating that the abundance of old U mines does not necessarily give rise to high levels of As in surface waters. Indeed, the San Antonio and San Marcos Rivers run perpendicular to the Catahoula formation minimizing contact with, and thus potential impact by, the formation. Conversely, the Nueces River flows for miles along this formation optimizing exchanges between groundwaters and the surface system.

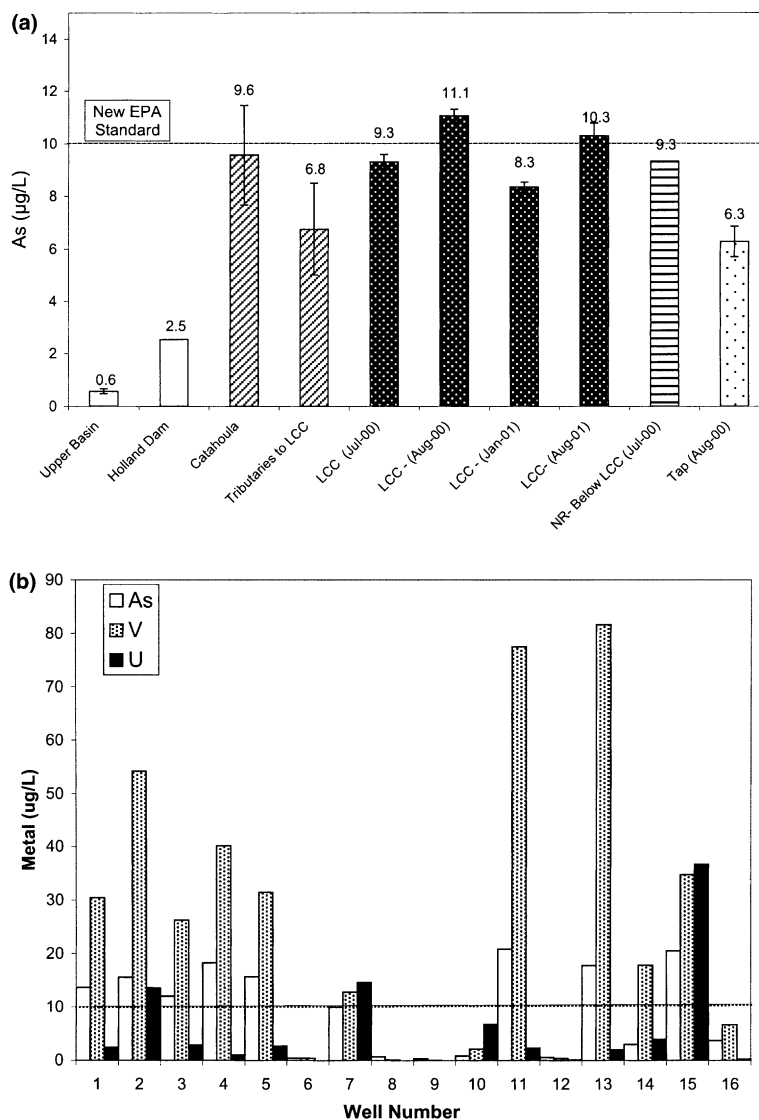


Fig. 10. (a) Arsenic concentrations ( $\mu\text{g/L}$ ) in surface waters of the Nueces River Basin, including tap water from the city of Corpus Christi. (b) Arsenic, U, and V concentrations ( $\mu\text{g/L}$ ) in groundwaters around Lake Corpus Christi.

Fig. 10(b) illustrates the distribution of As, U, and V in the 16 groundwaters sampled around the lake with concentrations ranging 0.1–37, 0.5–21, and 0–82  $\mu\text{g/L}$  for U, As, and V, respectively. More than 50% of all wells show As levels above the new EPA As drinking water standard of 10  $\mu\text{g/L}$ . One well showed a U concentration (37  $\mu\text{g/L}$ ) above the US drinking water standard of 30  $\mu\text{g/L}$  whereas more than 60% had values that exceeded the revised WHO (1998) guideline value for drinking water of 2  $\mu\text{g/L}$ . Although the following discussion emphasizes As cycling in the basin, the groundwater samples provide the first, if only limited, indication of enrichment in U in some parts of the

Nueces River basin studied. The occurrence of this radiogenic element is significant as a health concern, and may also suggest the potential for elevated levels of U daughter products, such as Ra and Rn.

Evaluating the basin data using ratios of As and U to V, all enriched in U ore deposits, may indicate areas of selective enrichment of As through the recognition of unique signatures that mark increased inputs of this element to certain sites of the basin. Comparisons of element/compound concentrations or ratios in property–property plots is a common practice in geochemical studies and can help identify input source(s) and/or mixing processes between several components having



different chemical and/or isotopic compositions (Hedges and Prahl, 1993; Faure, 1998). Fig. 11 illustrates the signatures of different waters from all sampling events in Lake Corpus Christi, the Nueces River basin, U mine drainages, groundwaters around Lake Corpus Christi, as well as a series of tap water samples from the city. The relationship between As and V throughout most of the system (Fig. 11(a)) is very consistent with data from aquifers in Texas and Argentina (Lee and Herbert, 2002; Smedley et al., 2002), which show that these 2 elements have very close redox behaviors and co-occur significantly in groundwaters in a way that approximates a lognormal distribution. In both cases As and V are likely to derive mostly from similar mineral sources in the aquifers under high pH conditions that favor their desorption.

Two sites, Lyssy pond and a small creek draining a U mine, show important departure from the apparent lognormal distribution suggesting selective inputs of As and/or enrichment processes over time in these water systems (Fig. 11(a)). Previous work on Lyssy pond has shown that this system has received large and sustained inputs of radionuclides from the early 1960s to the late

1970s during the period of most intense mining activities (Smith et al., 2002). However, after peaking during the mid 1970s, radionuclide activities in the pond's sediments receded to levels close to the pre-mining era, indicating that substantial export of radiogenic material from the mine to aquatic systems was likely limited to the mining period. Contrastingly, the particularly high mobility of As in neutral to slightly alkaline waters and over a wide range of redox conditions (Smedley and Kinniburgh, 2002; Smedley et al., 2002) may result in a selective mobilization of As from the proximate U mine spoil piles and lead to the observed enrichment in the pond's water column. Metal ratio analysis (Fig. 11(b)) further confirms that large anomalies in As concentrations are limited to Lyssy pond whereas waters from mine pits and surface water drainages near U mines indicate selective enrichment of U relative to V, subsequently altering their ratio signatures. Despite these specific cases of geographically restricted U and As enrichment, the constant ratio signatures from the upper basin to the lower Nueces River confirm the relative lack of large-scale impact from U mine tailings and spoil piles on the Nueces River basin. In the following section the

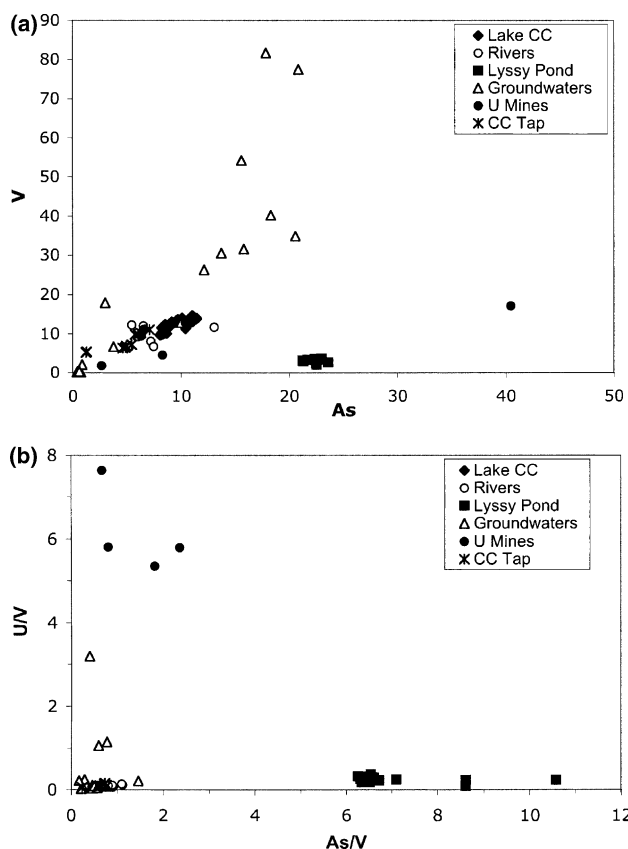


Fig. 11. (a) Relationship between V and As in surface and groundwaters of the Nueces River watershed. (b) Property–property plots of metal ratios (U/V vs. As/V) in surface and groundwaters of the Nueces River watershed.

authors contend that the moderately elevated levels of As in Lake Corpus Christi are due to cycles of evaporative concentration of groundwater baseflow into the system rather than long distance transport of metals from U mines in the basin.

#### 4.4. Temporal arsenic cycling in the Nueces River basin

Temporal variations in As concentrations within Lake Corpus Christi were assessed quantitatively for the period of study using a simple box modeling approach and treating As as a conservative element. The basic assumption of such models is that any portion or the entirety of a lake is so well stirred that it is homogeneous in composition and can be treated as a uniform “box” (Berner and Berner, 1997). The concentration of the selected substance in such a box is then controlled by the relative magnitude of inputs and outputs and, in its simplest form, the modeling considers the whole lake as a single box. The rate of change of mass of the substance of interest in the lake with time,  $\Delta M/\Delta t$ , thus becomes:

$$\Delta M/\Delta t = C_i Q_i - C Q_o + R_d - R_p, \quad (1)$$

where  $C_i$  is concentration of the dissolved substance in stream water;  $Q_i$  is the rate of stream water inflow (rainwater and groundwater inputs are considered negligible);  $C$  is the concentration in the lake;  $Q_o$  is the rate of outflow through the lake outlet;  $R_d$  is the rate of addition via dissolution of solids in suspension in the water column or from the sediment/water interface; and  $R_p$  is the rate of removal via precipitation/sorption processes and sedimentation. Such a mass balance approach has been applied successfully in the past to demonstrate the lack of accumulation of As in an intermittently stratified reservoir in California receiving large inputs of As from geothermal sources (Kneebone and Hering, 2000). Although a certain amount of seasonal variations was observed in the phase distribution of this element, this was attributed to internal cycling within the water column rather than to releases of As from sediments. This single box model approach is applicable to Lake Corpus Christi since the temporal and spatial observations suggest that geochemical conditions in the water column and the lack of abundant reactive sites in suspended particles produce conditions that favor conservative behavior of As. Furthermore, the homogeneous concentrations of As throughout the entire water column suggest fast and thorough stirring of the lake which makes this element a useful conservative tracer for water motion illustrating variations in any non-steady state water balance. Hence, the terms for  $R_d$  and  $R_p$  can be neglected in Eq. (1) leading to a simplified formula:

$$As_L(t) = As_L(t-1) + ([As]_i Q_i) - ([As] Q_o), \quad (2)$$

where  $As_L$  is the total As load (mass) in Lake Corpus Christi at time  $t$  or  $(t-1)$ ;  $[As]_i$  is the concentration of dissolved As in the Nueces River;  $Q_i$  and  $Q_o$  are the monthly rates of water inflow and outflow, respectively, into and out of the lake ( $Q_o$  is the sum of withdrawals and pass-throughs); and  $[As]$  is the As concentration in Lake Corpus Christi. The average As concentration in the lake at time  $(t)$  can then be calculated with the following equation:

$$[As](t) = As_L(t)/Vol(t), \quad (3)$$

where  $As_L(t)$  and  $Vol(t)$  are the total As load (mass) and volume of water, respectively, in Lake Corpus Christi at time  $t$ .

To test this approach, Eqs. (2) and (3) were used to predict the changes in As load between July to August 2000 using lake-wide concentrations of As averaged from all profiles and surface samples for each period ( $9.0 \pm 0.3$  and  $11.1 \pm 0.2$   $\mu\text{g/L}$ , respectively), as well as the average As concentration measured in tributaries just upstream of the lake ( $[As]_i$ :  $6.7 \mu\text{g/L}$ ; Fig. 9(a)). All monthly values of water inflow ( $Q_i$ ) and outflow ( $Q_o$ ), precipitation ( $P_i$ ), and evaporation ( $E_o$ ), were obtained from the Nueces River Authority's archives. Over this period, As outputs ( $3.2 \times 10^5$  g) were an order of magnitude higher than inputs ( $3.5 \times 10^4$  g) due to much larger water withdrawals from the reservoir ( $32.1 \times 10^6$  m<sup>3</sup>) than river inflows into it ( $5.2 \times 10^6$  m<sup>3</sup>) and yielded a  $\sim 20\%$  reduction in the lake's total As load illustrating the non-steady state nature of the water balance in Lake Corpus Christi (Fig. 2). In addition to the flow-through deficit, the lake lost almost the same amount of water ( $23.1 \times 10^6$  m<sup>3</sup>) through evaporation further reducing its volume and leading to an increase in As concentration in the lake from a theoretical value of  $8.9$   $\mu\text{g/L}$  (calculated without taking into consideration evaporation) to a calculated value of  $11.2$   $\mu\text{g/L}$ . The perfect agreement between this estimate and the measured lake concentrations in August ( $11.1 \pm 0.2$   $\mu\text{g/L}$ ) suggests that As does indeed behave conservatively in this system and that its levels in the summer months are controlled by water mass balances, with substantial influence from evaporative concentration processes. The role of such processes on As concentrations has previously been documented in shallow groundwater systems (Welch and Lico, 1998; Levy et al., 1999; Ryu et al., 2002; Smedley et al., 2002), but these studies were based on linear correlations with stable elements (i.e., Cl and Li) rather than quantitative mass balance calculations. Strong evidence in favor of conservative evaporative concentration of As comes from a recent study of shallow groundwaters in a relict and now desiccated lake in the high desert of southeastern California (Ryu et al., 2002). In this system, As concentrations increase consistently with brine formation and are paralleled by en-

richments in stable isotope signatures ( $\delta D$  and  $\delta^{18}O$ ) ascribed to evaporation of meteoric waters. The strong correlations between  $\delta D$ , electrical conductivity, and As concentrations point to the important role of evaporative concentration and event-based dilutions on regulating the concentration of this element in aquatic systems under arid to semi-arid conditions (see also, Smedley and Kinniburgh, 2002). Furthermore, despite a high potential for solute-solid interactions in the Owens Lake groundwater system, Ryu et al. (2002) found no evidence of solid controls on As distribution. Rather, As distribution was entirely dominated by dissolved phases further supporting the author’s observations that hydrodynamic processes can act as major factors controlling As concentrations in some aquatic systems.

The mass balance approach has been applied to the full period of study (April 2000–March 2001) once again based on all monthly water mass balance parameters for Lake Corpus Christi (inflow, outflow, evaporation, and precipitation) and using the average As concentration measured in tributaries just upstream of the lake ( $6.8 \pm 1.7 \mu\text{g/L}$ ; Fig. 9(a)). The results of the model are presented in Fig. 12 and plot an envelope of estimates using minimal and maximal values of  $[As]_i$ . Measured As concentrations obtained from several profiles and surface samples during each of the 3 sampling events are also plotted, as well as the lake’s water budget curve for the period of study. One notable feature of the model is its tendency to generate overestimated predictions when the upper limit of  $[As]_i$  ( $8.5 \mu\text{g/L}$ ) is used in the calculations. This results from an estimated buildup of the As load in the lake following calculated peak in As flux derived from the large inflows during October–November. It is doubtful that As con-

centrations in the tributaries of the lake remain high year round. Most probably, these are substantially diluted during high flow events such as those observed in the fall of 2000 in the Nueces River Basin (Fig. 2). During peak hydrological events, groundwater baseflow would be expected to make up a reduced proportion of the incoming surface water sources to the head of the lake with resulting lower stream As concentrations than during low flood conditions. Rapid changes in water fluxes have been reported to drastically change stream metal loadings over short periods leading in some instances to substantial diluting effects (Nagorski et al., 2003). Similarly, an inverse relationship between As concentrations and stream flow has been observed in the Patuxent River (Chesapeake Bay watershed; Riedel et al., 2000) and has been ascribed to the dilution of a fixed source such as groundwaters, or a point source whose output of As is independent of flow. Since groundwaters in the region of lake Corpus Christi do show substantially larger values than surface waters ( $\sim 20 \mu\text{g/L}$  vs.  $6.0 \pm 1.7 \mu\text{g/L}$ , respectively), and surface flow rates can vary by as much as an order of magnitude in just a few days (Fig. 2), such a process is feasible in the Nueces River Basin. To account for a dilution effect, the authors have thus run the model using the average  $[As]_i$  value of  $6.8 \mu\text{g/L}$  for most regular flow months, and using the minimal value of  $5.1 \mu\text{g/L}$  for periods of high flow (June, and October–December). The results (Fig. 12; full line) show a remarkable match between the predicted and measured values and suggest that, overall, the As concentrations in tributaries to Lake Corpus Christi remain well under the new EPA standard for drinking water of  $10 \mu\text{g/L}$ . The Lake, in contrast, shows higher average concentrations with seasonal fluctuations above the  $10 \mu\text{g/L}$

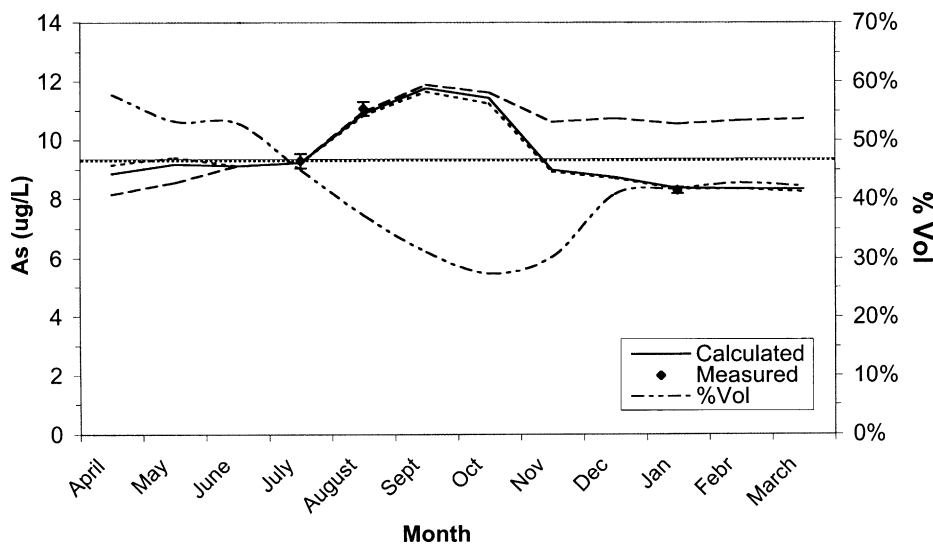


Fig. 12. Mass balance model of As concentrations in Lake Corpus Christi over the period of study. Full line, calculated values using fall dilution effect (see text for details of estimates). Dotted lines, envelope using minimum and maximum ranges ( $\pm 1$  SD). Dashed line, lake’s percent of total volume capacity.

mark during the warmest and driest part of the year (August–October). The observed inverse trend between As concentrations and the lake's water budget further confirms that the seasonal hydrodynamic regime, rather than geochemical reactions, controls As concentrations in Lake Corpus Christi. The lack of interaction between As and Fe in this system, and the hydrological constraints on As cycling, point to a need for alternative scenarios of As cycling in surface waters besides the well-recognized interactions between this metal and Fe–Mn hydroxides in aquatic systems (cf. Smedley and Kinniburgh, 2002).

## 5. Conclusions

Changes in geochemical conditions have been recognized as important factors in determining the phase distribution and speciation of certain trace elements within the water column and sediment pore waters of most freshwater lakes. Other mechanisms impacting phase distribution of metals in lake waters include sorption/desorption to/from reactive Fe oxyhydroxides and uptake by phytoplankton. In contrast, in the present study few elements are affected substantially by any of these mechanisms as redox conditions changed only to a limited extent within the lakes' water columns, and suspended particles seem to be predominantly detrital in origin and carry only a limited fraction of reactive Fe.

In Lyssy pond, geochemical cycling of metals was limited to Co and Pb, which seemed to be mostly associated with redox cycling of Mn mineral phases, and U, which suggested reductive precipitation in the pond's hypolimnion. The strong relationships observed between particulate Cr, Cs, V, and Fe suggest that these metals are associated with a stable particulate phase (probably allochthonous aluminosilicates) enriched in unreactive Fe. This observation is supported by a parallel relationship in sediments collected across a broad range of sediment depositional processes (and histories) in the basin. Arsenic, though selectively enriched in the pond's water column, remained stable and mostly in solution throughout the depth of the water column and showed no sign of interaction with Fe-rich particles. Similarly, As (and other oxyanions) in Lake Corpus Christi's water column are not affected by the abundant presence of Fe-rich particles but instead behaved conservatively throughout the entire period of study. This behavior is an apparent departure from commonly accepted models of As cycling in surface waters that cite sorption to Fe hydroxides as a predominant mechanism of As scavenging from water columns into sediments. The resolution of that paradox probably lies in the lack of reactivity of particulate Fe in this system.

In this study, the authors found no evidence of anthropogenic impacts of U mines beyond the purely local scale. Arsenic does decrease in concentration downstream

from U mining sites but its presence within the Nueces drainage basin is related to interactions between surface and groundwaters with U-rich geological formations rather than long-scale transport of contaminants downstream of the U mine pits and tailings. The occurrence of U above the WHO standard in many of the groundwaters of the Lake Corpus Christi area is significant as a health concern and may also suggest the potential for elevated levels of U daughter products, such as Ra and Rn. Such findings warrant further studies in a region where most rural drinking water derives from shallow groundwater.

To the authors' knowledge, the mass balance model for Lake Corpus Christi provides the first quantitative evidence of seasonal evaporative concentration of As in surface waters demonstrating the predominant role of hydrodynamic constraints on the cycling of this element in selected aquatic systems. Since Lake Corpus Christi is used primarily as a source of drinking water for a large community in South Texas, temporal monitoring of As levels in the lake must be performed by water management utilities to avoid periods of high As concentrations in waters supplied to the public. Although the levels of As in Lake Corpus Christi are only moderately elevated, the increases in concentrations during the summer months do reach levels above the recently accepted federal standard for drinking water (10 µg/L). This could generate a water quality issue for selected populations of the region since some water utilities do not have access to "dilution" options as is the case with the City of Corpus Christi's Water Department. Indeed, tap water for the City of Corpus Christi in August averaged  $6.3 \pm 0.6$  µg/L (Fig. 9(a)), which is about 60% of the lake values at the time. This decrease corresponds to a similar proportion in the blend ratio between Lake Corpus Christi and Lake Texana waters and may suggest a simple dilution ratio between these 2 sources of water. A small study on household filters showed that reverse osmosis was the only system that showed substantial decreases of As in tap waters (Brandenberger, 2002) and that dissolved As in these waters may escape conventional filtration pretreatment prior to incorporation into the public water supply system. The impact of hydrological fluctuations on As concentrations in the studied freshwater reservoir thus shows the importance of adaptive management strategies of natural resources which consider temporal variations on the quality of such resources.

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