Arsenic Concentrations in Water Resources of the Choke Canyon/Lake Corpus Christi Reservoir System: Surface and Ground Waters

Project funded in part by the TWRI for the period of Feb. 2001 to January 2002

The above-mentioned project focused on understanding the cycling and fate of heavy metals in Nueces River Watershed including both its surface and ground waters. The objectives of the project were to perform temporal and spatial monitoring of trace element concentrations, focusing on arsenic, in 1) waters of Lake Corpus Christi, Choke Canyon, and points along the tributary rivers: Nueces, Atascosa and Frio, as well as 2) selected ground water wells in this region. Surface water samples have been collected throughout the year 2001during three seasons (winter, spring and summer), and flood events represented by high water discharges into the reservoir system. Ground waters were sampled throughout a wide "grid" covering an extended area around Lake Corpus Christi. For each of the water samples, the total and dissolved fractions have been analyzed by Inductively Coupled Plasma Mass Spectrometry (ICPMS) for arsenic and a suite of other trace metals of interest. The results were interpreted in terms of temporal and spatial changes for surface waters and in terms of spatial variability for ground waters. Our data yielded a substantial suite of findings that are presented in the Abstract and project report below. The abstract represents the completed thesis work of Jill Brandenberger, whereas the project report encompasses only the chapter in the thesis focusing on freshwater resources in the lower Nueces River basin. A copy of the thesis manuscript will be delivered to TWRI upon binding. The research detailed in this thesis manuscript is funded in part by the TWRI project funds and have led to several presentations (see below) and will lead to further planned submissions of manuscripts to peer-reviewed journals (see below)

Presentations.

Brandenberger, J. M., Patrick Louchouarn, Bruce Herbert, Philippe Tissot, Patrick Michaud, Ron Parker, Martha Williams, Jim Bonner, and Mark Beaman. 2001. Behavior of Trace Metal Concentrations in Water Profiles from Lake Corpus Christi Subsequent to an Overturn Event. NOAA – Expanding Opportunities in Oceanic and Atmospheric Sciences. April 1-3, 2001, Jackson, MS.

Parker, Ronald, Bruce Herbert, Jill Brandenberger, and Patrick Louchouarn. 2001. Ground Water Discharge From Mid-Tertiary Rhyolitic Ash-Rich Sediments as the Source of Elevated Arsenic in South Texas Surface Waters. GSA Abstracts with Programs, Volume 33, Number 6, p. A 53.

Publications in Preparation

Brandenberger J., Louchouarn P., Herbert B., Tissot P., Michaud P., Parker R., and Beaman M. (2002 – In preparation). Geochemical behavior of trace metals in a sub-tropical fresh-water lake subsequent to an overturn event. **Chemical Geology**.

Brandenberger J., Louchouarn P., Herbert B., Tissot P., Michaud P., Parker R. (2002 – In preparation). A historical reconstruction of heavy metal non-point source inputs to the Nueces River/Lake Corpus Christi System, Texas. **Applied Geochemistry.**

ABSTRACT

GEOCHEMICAL CHARACTERIZATION OF TRACE METAL CYCLING IN THE
WATERS AND SEDIMENTS OF THE LOWER NUECES RIVER BASIN, TX

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Thesis for a M.Sc. in Environmental Sciences, Texas A&M University Corpus Christi
Co-Chairpersons of Advisory Committee: Dr. Patrick Louchouarn and Dr. Bruce Herbert

During the last several decades, human-related activities and populations have increased markedly along the Texas Gulf Coast, intensifying pressures on the water resources and ecosystems of this area. The Lake Corpus Christi/Choke Canyon reservoir system mitigates issues of water quantity while perturbing the quality of available fresh water resources. A driving force in the degradation of water quality is the potential loading and deposition of colloidal particles with a high affinity for trace metals and their incorporation into bedded sediments of the system. This "sequestration" may not be permanent, as redox sensitive metals (Mn, Fe, U, As and Mo) are susceptible to diagenetic remobilization due to oscillations in the hydrodynamic regime. This process may in turn result in a positive flux of metals to the water column adding a substantial stress to the aquatic environment and decreasing the quality of our freshwater supply.

This research thus assessed the water quality of Lake Corpus Christi as a function of 1) tributaries and ground waters within the Nueces River basin, 2) present geochemical cycling of trace metals during temporal, spatial, and event driven oscillations of dissolved oxygen, and 3) sedimentary reservoirs in diverse sections of the lake (historic water quality as inferred from sediment cores).

Water column profiles for trace metals assessed seasonal variations (summer vs. winter), an inflow event (episodic floods) and spatial distributions (oxygenated vs. stratified water column). The hypolimnetic cycling of Mn, Fe, Pb, Cr, V, Co and Ni resulted in higher enrichment factors in summer vs. winter and at the deeper station (stratified water column). The strong correlation of Pb and Mn cycling suggests diagenetic remobilization of Pb. However, the mildly reducing conditions did not entrain the cycling of As, Mo and U. Moreover, whereas Mo and U concentrations remain constant at background levels within surface waters of the whole system of study, dissolved As values in the Lower Nueces River basin (8-12 μg/L), are enriched by two orders of magnitude with respect to background levels measured in the upper basin (0.5 μg/L). The conservative behavior of As results in seasonally cycling with dilution during periods of higher inflow (winter and spring) and evapoconcentration in the summer. This contributes to the degradation of water quality and results in seasonal concentrations above the recently adopted standard for arsenic in drinking water (10 μg/L).

Sediment cores encompassed the three reservoir zones: riverine, transition, and lacustrine, each with unique depositional environments. Average metal concentrations in surface sediments are below the threshold effect level (TEL) with the exception of Ni, but discrete depths indicate layers of enriched metal content. Normalized sediment profiles give further evidence of periods of enrichment and depletion of As, Co, Cu, Pb, Ni and Mn suggesting historic fluctuations in metal accumulation throughout the sediment profiles. Historical changes in material inputs to the sedimentary environments of the lake are further supported by significant changes in total organic matter and its isotopic signatures ($\delta^{13}C$ and $\delta^{15}N$). Temporal trends, provided by the pre-reservoir conditions show decreasing values of Hg and Pb due to changes in atmospheric cycling and basin-wide collection/redistribution processes. The uniform distribution of U and Mo around average sediment values suggests that the transport of these metals from upstream uranium mines has not impacted the sediments of Lake Corpus Christi. However, sedimentary peaks in As may support the selective transport and sequestration of this heavy metal due to uranium mining activities in Live Oak County.

The extreme heterogeneity of As, Mo and U in ground waters suggests a mechanism for sequestration, such as sulfidization upon contact with water discharging along faults in Live Oak County enriched in H_2S. The concentrations of these metals in selected ground waters are elevated well above the drinking water standards. An emphasis was placed on As because elevated levels are seen in the surface waters as well as ground waters (~10 and ~20 μg/L, respectively) . However, the ground water samples provide the first indication of enrichment in U (47 μg/L) in the Nueces River basin well above drinking water standard (30 μg/L). Sources for these selective enrichments can include both anthropogenic activities such as past mining processes and agricultural pesticide used in the drainage/aquifer basin, and natural geological inputs to ground water reservoirs.

GEOCHEMICAL CHARACTERIZATION OF TRACE METAL CYCLING IN THE LOWER NUECES RIVER BASIN, TX

Jill M. Brandenberger
Thesis chapter for a M.Sc. in Environmental Sciences, Texas A&M University Corpus Christi

In the semi-arid climate of the south Texas Gulf Coast region, the availability of freshwater resources is a critical issue stressing the stability of communities. An additional stress on the naturally limited freshwater resources is the marked growth in population over the last several decades (Kufus, 2000). In an attempt to mitigate growing water demands, the City of Corpus Christi constructed, in 1982 and 1958, the Choke Canyon / Lake Corpus Christi reservoir system in the lower Nueces River basin (Figure 1). The reservoirs provide water to over 300,000 people in Corpus Christi and surrounding communities. The irony of reservoirs is that they mitigate water quantity concerns, while generating issues on water quality (Thornton et al., 1990).
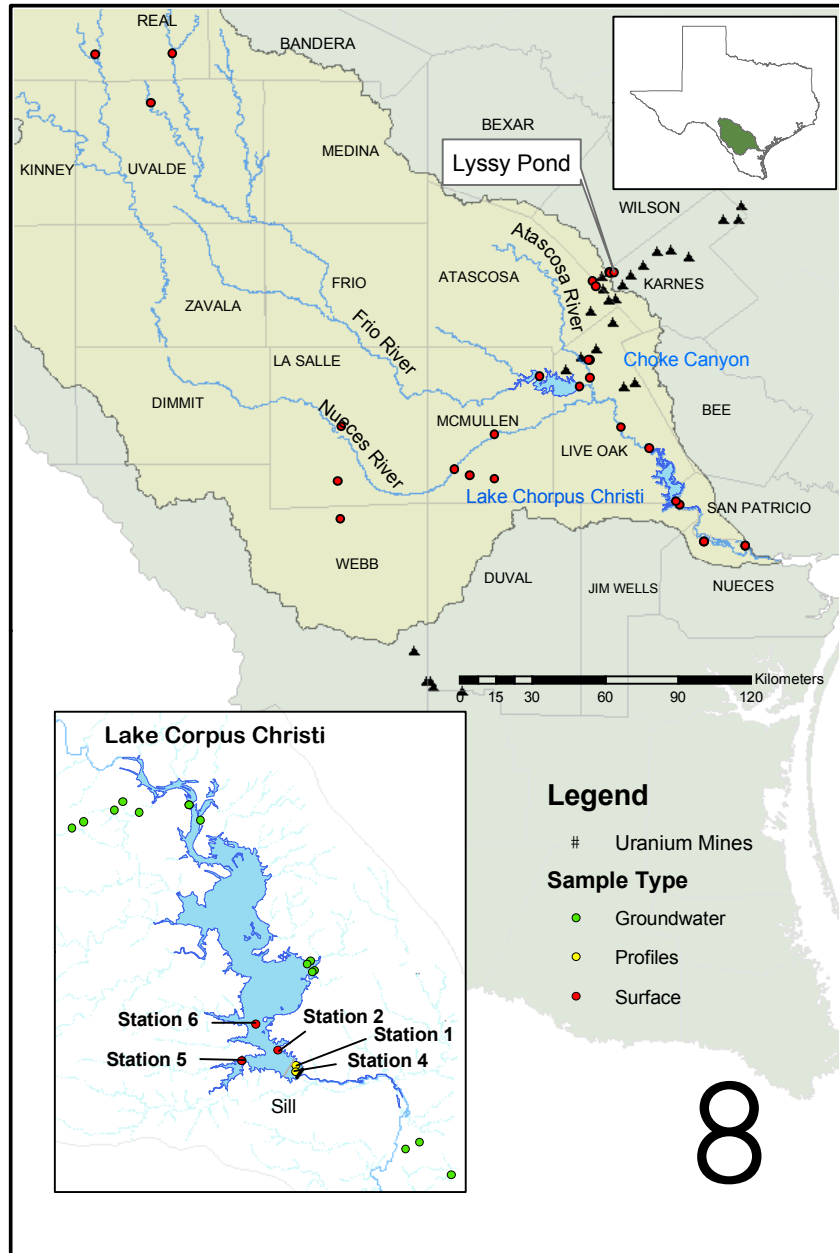
Figure 1. Sampling locations in the Nueces River basin, Lyssy Pond, and the inset of Lake Corpus Christi marking station and ground water sample locations.

The degradation of water quality is often associated to the high loading of particulate and colloidal materials (Thornton et al., 1990), such as clay and silt, which tend to sequester trace metals (Louchouarn and Lucotte, 1998; Santschi et al., 1999; Balogh et al., 1999; Sharma et al., 1999a; Forstner and Wittmann, 1979; Louchouarn et al., 1993; Martin et

al., 1995; Menounou and Presley, 1996; Wen et al., 1999; Baskaran and Santschi, 1993). The adsorption processes enhances the riparian transport of trace metals, as suspended particulates, through a watershed (Manahan, 2000), allowing the deposition of colloidal material in the relatively quiescent waters of reservoirs. Subsequently, incorporating sequester contaminants into the sedimentary record (Hemond and Fechner-Levy, 2000). However, the sedimentary record may not be permanent, as some metals, particularly redox sensitive metals (Mn, Fe, U, As and Mo) are susceptible to diagenetic remobilization due to oscillations in the hydrodynamic regime. Physiochemical alteration in the aquatic ecosystem may effectively reverse the role of sediments from a sink to a source for metals in the hypolimnion, degrading water quality by increasing metal bioavailability (Manahan, 2000; Salbu and Steinnes, 1995).

The dynamic hydrologic cycle typical in south Texas emphaizes the need to characterize contaminant sources, identify depositional environments and understand processes (i.e. temporal cycling) affecting remobilization and sequestration of trace metals. Managing water quality in reservoirs such as Lake Corpus Christi in the Nueces River basin (Roulet et al., 2000; Salbu and Steinnes, 1995; U. S. Environmental Protection Agency, 1999a) requires a holistic basin-wide scale. Initiatives such as the National Water-Quality Assessment (NAWQA) program identified potential contaminant sources and assessed the water quality in the Nueces River basin from 1996-1998 (Bush et al., 2000). The study focused specifically on the upper basin because it is the recharge zone for the Edwards aquifer, but failed to address water quality in the lower basin containing the reservoir system. Other initiatives assessed the susceptibility and loading of contaminants in the Nueces River basin to both freshwater resources -Safe Drinking Water Act Amendments of 1996 (Focazio et al., 2000), Clean Water Act (U. S. Environmental Protection Agency, 1999b) and Texas Clean Rivers (Fisher, 1996; Nueces River Authority, 2001) and the estuarine ecosystem (National Estuaries Program; Baird, et al., 1996). A common theme in all these programs is the lack of data on trace metal concentrations in Lake Corpus Christi reservoir. Compounding this lack of data is the failure to address the previously extensive uranium mining in South Texas as a potential source of trace metals. This could be a significant omission since the transport of mine tailings are widely recognized as substantial anthropogenic contributors of trace metals

and radionuclides to aquatic systems and their sediments (Langedal, 1997; Macdonald et al., 1991; Odhiambo et al., 1996; Ruttenber et al., 1984; U. S. Department of Energy, 1996; Van Metre et al., 1997c).

A zone of uranium mineralization extends across Texas from east central to the southern tip and into Mexico (Nugent et al., 1994). The zone contains clusters of uranium deposits enriched with a minimum of 500 tons of uranium oxide (U_3O_8) each (Finch, 1996). The uranium clusters resulted from the oxidation of volcanic ash by meteoric waters effectively mobilizing uranium along with other redox-sensitive metals (As, Mo V and Se), until remineralization in reducing environments (Eargle et al., 1971; Galloway, 1977; Galloway et al., 1982; Galloway and Kaiser, 1980; Henry et al., 1982; Henry and Kapadia, 1980; Ledger, 1981). By the 1970's, over 40 mines were located in Karnes, Atascosa, Gonzales, and Live Oak counties (Figure 1), ranking Texas third in uranium ore reserves with an estimated 6.6 million tons (Eargle et al., 1971). The pervasive uranium mining activities in Karnes County resulted in the transport of trace metals and radionuclides to both ground water (Blount et al., 1992; U. S. Department of Energy, 1995) and surface waters ecosystems (Batson et al., 1996; Blount et al., 1992; Bryson et al., 1988; Harrington et al., 1998; Parker et al., 1999; U. S. Department of Energy, 1991). Consequently, uranium mining is a major contributor to the degradation of water quality on a local level. The high geochemical mobility of trace metals associated with uranium mining highlights the need to assess their impacts on the Nueces River watershed since tributaries to Lake Corpus Christi drain areas of previous mining activities in Live Oak County.

The identification of Lake Corpus Christi reservoir as a potential recipient of trace metals associated to uranium mining activities emphasizes the need to better understand water quality as a function of the distribution and temporal cycling of trace metals in this aquatic system. Oscillations in dissolved oxygen due to seasonal stratification or episodic mixing events drives the cycling of trace metals (Salbu and Steinnes, 1995). Many studies characterized the cycling of trace metals in response to changes in redox state in seasonal or permanently anoxic hypolimnetic waters (Achterberg et al., 1997; Balistrieri et al., 1992a; Balistrieri et al., 1992b; Elbaz-Poulichet et al., 1997; Harrington et al., 1998; Kneebone and Hering, 2000; Morfett et al., 1988; Murray, 1987; Sigg et al.,

1987; Taillefert et al., 2000; Viollier et al., 1995; Viollier et al., 1997). These studies developed models for the biogeochemical cycling of trace elements across the oxic-anoxic interface in the water column (redox-cline) (Elbaz-Poulichet et al., 1997). Applying a stratified basin model to Lake Corpus Christi provides information on the potential cycling of redox sensitive trace elements as changes in heat balance, wind stress, and lake level affect the efficiency of mixing and depth of oxygen penetration in the water column. Therefore, it is paramount to consider these cycles when addressing water quality concerns, as redox-driven phase transformation of trace metals from particulate to dissolved phase deteriorates water quality by increasing metal bioavailability by orders of magnitude (Neff, 1984; Salbu and Steinnes, 1995). The substantial presence of trace metals in Lake Corpus Christi or its tributaries could substantiate a public health concern since the reservoir is a primary source of water for Corpus Christi and the only source for smaller surrounding communities.

This research evaluates impacts on water quality related to the distribution of trace elements in the lower Nueces River basin and Lake Corpus Christi reservoir. Seasonal and event driven depth profiles in Lake Corpus Christi provided information on the geochemical cycling of trace metals while surface and ground waters collected throughout the lower Nueces River basin provide information on the basin wide distribution of trace metals. The initial assessment of ground waters serves as the cornerstone for the modeling of trace metals in ground waters of Live Oak County.

STUDY AREA

The use of a reference site (Figure 1 - Lyssy Pond) in this study provided information on the geochemical cycling of trace metals in a system- 1) demonstrating elevated levels of trace metals and radionuclides directly attributed to uranium mining activities (Parker et al., 1999) and 2) undergoes strong seasonal stratification with installation of anoxia in the hypolimnion. Lyssy Pond is a stock pond located in Karnes County near the federally funded Uranium Mill Tailings Remedial Action (UMTRA) Project. For a detailed characterization of Lyssy Pond, see (Parker et al., 1999).

The Nueces River Basin covers approximately 44,000 km^2, encompassing all or part of 23 counties (Figure1). Presently, the major land use is farming and ranching with no major metropolitan areas in the immediate drainage basin, only larger communities

including Uvalde, Pleasanton, George West, and Three Rivers (Nueces River Authority, 2001). However, from 1967 until the early 1980's several uranium mines (Figure 1) operated in Live Oak County extracting ore from the Oakville Formation, which also hosts a major aquifer providing water for municipal, domestic and agricultural uses (Galloway et al., 1982).

The Choke Canyon/Lake Corpus Christi Reservoir system provides water to the City of Corpus Christi, as well as, South Texas Water Authority, Alice, Beeville, Port Aransas, Rockport, Mathis, Three Rivers, San Patricio Authority and Lamar Peninsula (Fisher, 1996). Lake Corpus Christi reservoir is the focus of this research and is located in Live Oak County (Figure 1). The major tributaries to the reservoir are the Frio (from Choke Canyon reservoir releases), Atascosa, and Nueces Rivers. The Nueces River flows into Lake Corpus Christi downstream of the confluence of the three rivers (Figure 1). The reservoir was impounded in 1958 with the completion of the Wesley Seale Dam located ~ 305 m downstream of the pre-existing reservoir's dam (La Fruta reservoir) (Cunningham, 1998). The remnants of the earthen La Fruta Dam remain and act as a sill (as denoted in Figure 1), restricting flow and altering the deposition regime near the new dam.

Summer conditions in Lake Corpus Christi have the potential to allow stratified conditions to develop in the water column as a result of minimal inflows and substantial evaporative losses potentially reaching 152 cm a year (Cunningham, 1998). Winter conditions are a marked contrast, as strong winds associated with cold fronts efficiently homogenize the water column. During this time, the winds are primarily out of the north, producing significant wave action, as the long axis of the lake is oriented to the north, enhancing the fetch along the lake. Consequently, geochemical cycles of trace metals may be dominated by wind-driven mixing in the winter (fully oxidized), periodic flood events (mixing), and large-scale evaporative losses in the summer.

SAMPLING AND ANALYTICAL TECHNIQUES

Water Column Profiles

Water column profiles for trace elements include three sampling events from Lake Corpus Christi (July, August and January) and one profile from Lyssy Pond (April 2001).

Profiles in Lake Corpus Christi are from two stations (1 & 4; Figure 1) in the lacustrine zone near the dam (Thornton et al., 1990). They are located less than a kilometer apart and selected to represent the deeper section with more restricted mixing (station 1) and a control station indicative of better-mixed shallower environments (station 4). The three sampling events encompass conditions in the water column subsequent to a mixing event and seasonal variations. The July 7, 2000 profiles provide information on the conditions in the lake following a large inflow and subsequent mixing event (Figure 2). Seasonal sampling events include summer (August 25, 2000) and winter (January 26, 2001).
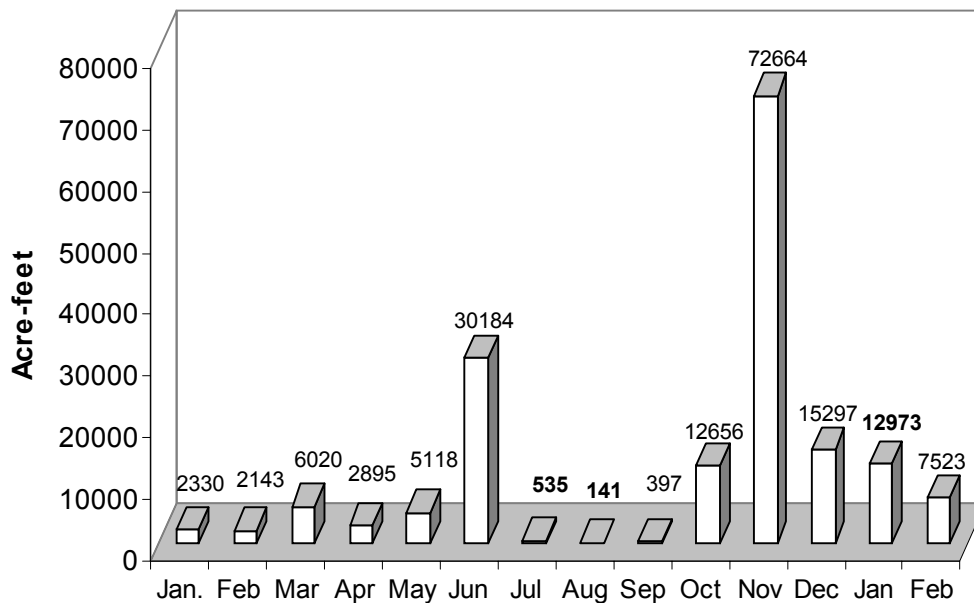
Figure 2. Inflow into Lake Corpus Christi from January 2000 to February 2001. Water column sampling occurred in July, August and January.

Figure 3. Multiple Underwater Syringe Sampling Tool (MUSST).

Physiochemical parameters (pH, DO, temperature, and depth) were collected using a Hydrolab®. Water column profiles were retrieved by *in-situ* sampling using a customized 4" polyvinyl chloride (PVC) sampling device (Multiple Underwater Syringe Sampling Tool – MUSST; Figure 3). The MUSST allows remote sample collection into two 50 ml acid-cleaned polypropylene syringes, minimizing perturbation of the water column while preserving *in-situ* water chemistry. The two-syringe design facilitated the simultaneous collection of samples for dissolved and particulate fractions eliminating the need to later split one sample for two fractions, potentially altering the *in-situ* chemistry.

All water samples were collected following EPA Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels (U. S. Environmental Protection Agency, 1996c). This method includes procedures specifically designed to reduce the possibility of contamination during collection and analysis of water samples. In accordance with this method, all equipment was acid cleaned and clean techniques were strictly followed throughout water sample collection and analysis.

Surface and Ground waters in the Nueces River Basin

The collection of surface water grabs encompassed three other stations (2, 5 and 6) in Lake Corpus Christi and 17 tributary samples of the three rivers in the Nueces River basin– three in the upper and 13 in the lower basin (Figure 1). Tributary samples taken along the Frio River progressed from points in the upper Nueces River basin to upstream and downstream of Choke Canyon Reservoir (Figure 1 –locations in red). The Atascosa River was sampled above the confluence of the three rivers. The Nueces River was progressively sampled in La Salle and McMullen counties.

Sixteen ground waters samples were collected from wells around Lake Corpus Christi (Figure 1- inset of Lake Corpus Christi) in acid clean low-density polyethylene (LDPE) bottles. Samples were retrieved from the well spigot, before any pre-treatment, by allowing water to flow for five minutes prior to collection.

Sample Processing

Upon collection, water samples were stored at 4°C to reduce reaction kinetics. A portion of each sample was filtered through acid-clean 0.45 μm nylon syringe filters, either in the field using a field-portable glove box as a clean environment or in a Class 100 clean bench. The filtered portion represents the "dissolved" metal fraction. Profile samples collected from waters with DO < 3.00 mg/L were filtered in an ultra-high purity nitrogen atmosphere in the field-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 (particulate by subtraction) fractions were acidified to 0.2% Optima® nitric acid or a pH <2.0.

Trace Elements Analysis

In accordance with EPA Method 1669, the dissolved fraction is operationally defined as passing through a 0.45 μm filter. However, many studies have shown that a significant percentage of trace metals are associated with the colloidal fractions between 1nm and 1 μm (Baskaran and Santschi, 1993; Benoit et al., 1994; Greenamoyer and Moran, 1997; Hoffman et al., 1981; Martin et al., 1995; Wen et al., 1999). Therefore, both the dissolved and total fractions were acid solubilized to destroy colloidal complexes, dissolving trace metals potentially adsorbed onto colloidal matter. EPA Method 1640

Section 12.2.7 - Total Recoverable Analytes (U. S. Environmental Protection Agency, 1996b) details the digestion method for water samples. Following pre-treatment, samples were analyzed on a Hewlett-Packard 4500 Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) following EPA Method 1638 (U. S. Environmental Protection Agency, 1996a) utilizing in-line addition of the internal standards Sc, Y, Ho, Tb. The ICP-MS was calibrated prior to analysis using a five-point calibration curve prepared with certified standards. The calibration curve for each metal showed a correlation coefficient of $r^2 > 0.999$. Table 1 shows the accuracy and precision of the instrument for each metal as assessed by the analysis of the NIST 1643d: Trace Elements in Drinking Water Standard. Table 1 also lists the method detection limits for each element (MDL) determined by the analysis of seven replicates of a 0.1 part-per-billion (ppb) standard. Other quality control measures included the analysis of continuing calibration verification (CCV) standards showing greater than 90% accuracy throughout the analysis, three types of blanks (sampling, method and reagent) which revealed no contamination of the samples and duplicates/triplicates indicating greater than 90% precision.

Table 1. Accuracy and precision of NIST 1643d and MDLs for trace metals in water.

Trace Metal	NIST 1643d Measure Value (9 samples)		NIST 1643d Certified Value		Average Accuracy	Percent Difference	
	Median	Range	Median	Range			MDL
As	55.9	± 1.7	56.0	± 0.73	100%	2.6%	0.0217
Cd	6.44	± 0.58	6.47	± 0.37	100%	6.9%	0.0458
Co	24.9	± 0.57	25.0	± 0.59	100%	1.6%	0.00922
Cr	19.6	± 2.3	18.5	± 0.20	106%	10%	0.114
Cu	22.8	± 0.48	20.5	± 3.8	111%	11%	0.0920
Fe	na	na	na	na	na	na	na
Mn	38.2	± 0.55	37.7	± 0.83	101%	1.7%	0.0683
Mo	113	± 3.2	113	± 1.7	100%	2.5%	0.0713
Ni	57.3	± 1.4	58.1	± 2.7	99%	2.3%	0.0284
Pb	17.9	± 0.54	18.2	± 0.64	98%	2.6%	0.0254
U	na	na	na	na	96%[1]	1.6%[2]	0.00945
V	35.3	± 1.02	35.1	± 1.4	100%	2.5%	0.0233

Concentrations determined by ICP-MS and reported in μg/L (ppb)
[1] Value determined by high purity standards
[2] Value determined by sample replicates

RESULTS

Lyssy Pond

The physiochemical conditions of Lyssy Pond (Figure 4) in April 2001 show partially stratified conditions in the water column with a slight redox-cline and thermocline around 250 cm. Because traces of DO were still measured in the hypolimnion, anoxic conditions existed only in the sedimentary layer. Despite the lack of anoxia in the hypolimnion, variations in vertical distributions of Mn, U and Pb suggest that the declining DO concentrations are enough to generate reducing conditions and entrain geochemical cycling of these metals between particulate and dissolved phase. This substantiates the use of Mn as a geochemical indicator of reduction in the oxidation potential (Eh) of the water column (Balistrieri et al., 1992b; Viollier et al., 1995). The distinct profile for Mn in Lyssy Pond, results from remineralization of organic matter and reductive dissolution of Mn oxy-hydroxides increasing dissolved Mn by nine orders of magnitude in the sub-oxic hypolimnion. The peak in particulate Mn at 325 cm suggests diffusive fluxes of reduced Mn^{2+} from the sediment-water interface into the water column where it is oxidized to the less soluble Mn^{4+} (Balistrieri et al., 1992a; Davison and Tipping, 1984; Mayer et al., 1982; Morfett et al., 1988; Mortimer, 1941; Viollier et al., 1995).

As the oxidation potential of the hypolimnion changes, the profiles of redox sensitive metals such as U, As and Mo should also indicate alterations in speciation resulting in a shift between particulate and dissolved phases (Achterberg et al., 1997; Elbaz-Poulichet et al., 1997; Hamilton-Taylor and Davison, 1995; van der Weijden et al., 1990; Viollier et al., 1995; Viollier et al., 1997). However, in Lyssy Pond only the U profile shows near perfect mass balance with peaks in the particulate phase corresponding to declines in dissolved phase which results from the changing oxidation states between dissolved U^{6+} and reduced, more highly scavenged, U^{4+} (Figure 4). These observations suggest the oxidation potential in the water column may not be reducing enough to produce a phase transformation in As (Figure 4) and Mo species (not shown).
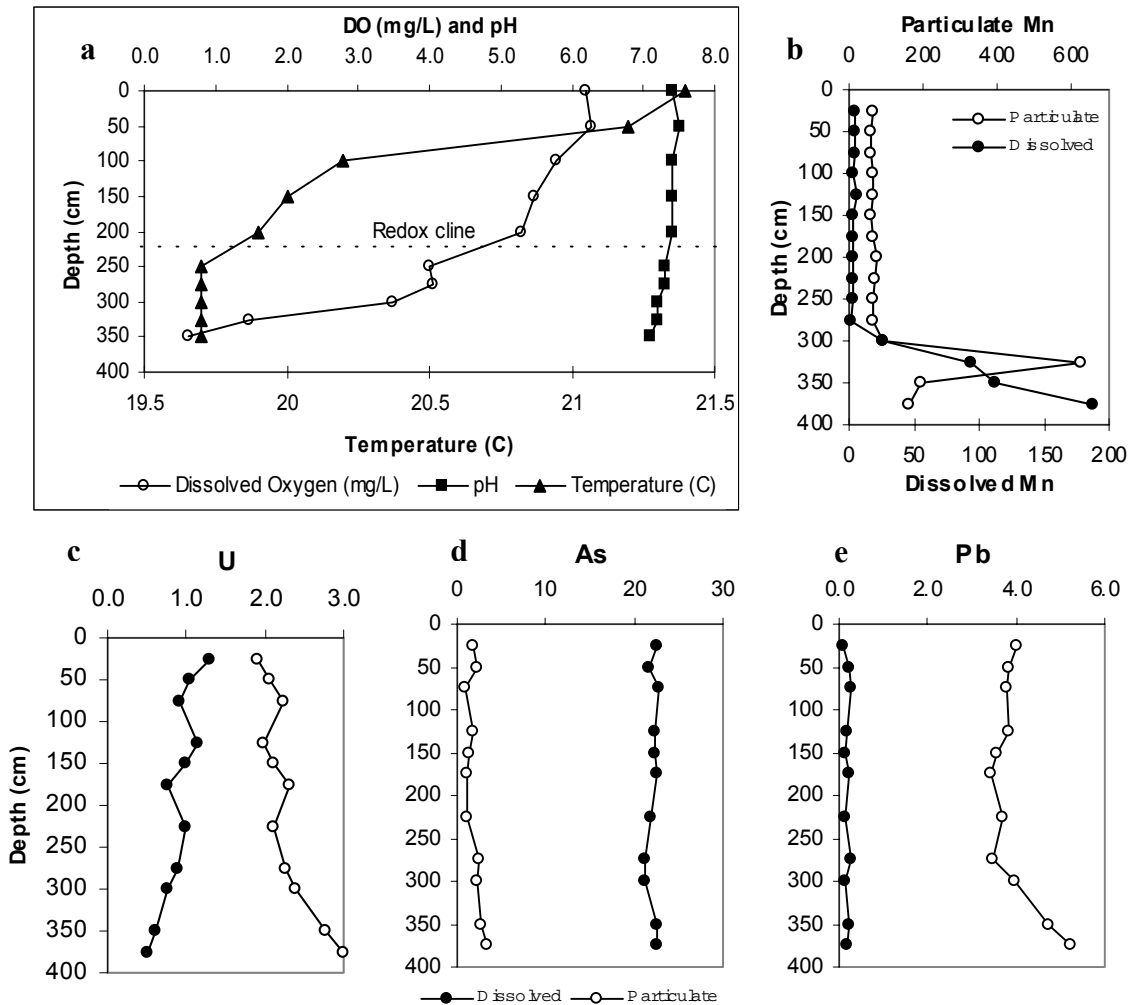
Figure 4. Lyssy Pond water profiles for (a) physical parameters, and the particulate and
dissolved fractions of (b) Mn, (c) U, (d) As and (e) Pb. (Values reported in
μg/L.)

Lake Corpus Christi Profiles

Physical Parameters

Figure 5 presents the water column profiles of DO, water temperature and pH in Lake
Corpus Christi produced by seasonal variations (August vs. January), an inflow event
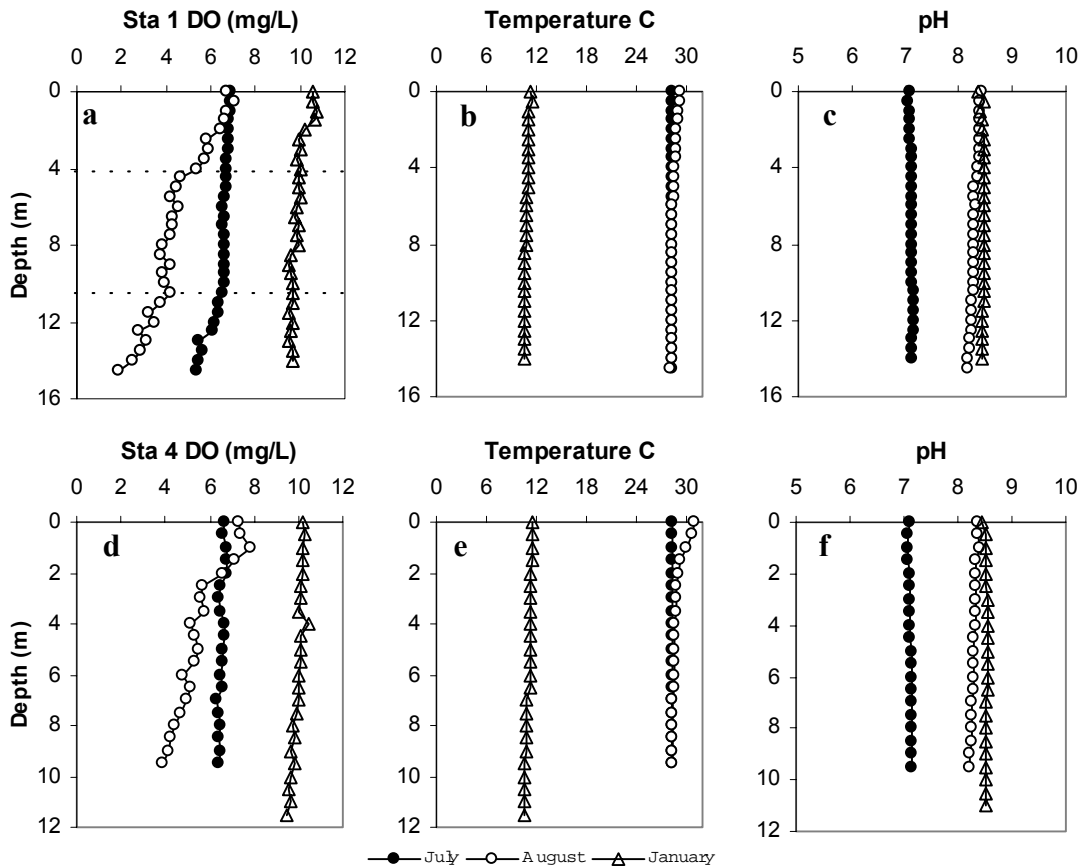(July 2000), and spatial distributions (stations 1 vs. 4). Dissolved oxygen is the only

Figure 5. Physiochemical conditions in Lake Corpus Christi for July, August and January. Depth profiles for station 1 (a) DO, (b) temperature and (c) pH and for station 4 (d) DO, (e) temperature and (f) pH.

parameter with a marked seasonal variation in vertical distribution, as seen by a virtually homogenous water column in January versus a partially stratified water column in August. The seasonal differences in DO may be typical, however, the generally shallow depths of the lake allow changing hydrologic conditions to rapidly alter seasonal physiochemical conditions. For example, substantial inflows to Lake Corpus Christi in June 2000 (Figure 2) lead to virtually homogenous conditions within the water column in July compared to the stratified conditions seen in August.

The collection of two profiles during each sampling event in Lake Corpus Christi provides data to assess any spatial variations in physiochemical conditions, and ultimately metal cycling within the lake. Spatial variation in the lake occurs as a function of depth, with seasonal and follow event driven mixing.

Trace Metal Profiles

Figure 6 presents the water column profiles of V, Cr, Mn, Co, Fe, Ni, Cu, As, Mo, Pb, and U as a function of seasonal variations in water chemistry, spatial variations between the two stations, and episodic mixing. The profiles consist of dissolved and particulate fractions for each metal during the three sampling periods (horizontally - July, August and January) for two stations (vertically – 1, 4).

The seasonal profiles illustrate the response of trace metals to partial stratification in August and a mixed water column in January. Comparing the characteristic profile of Mn obtained in Lyssy Pond to August profiles for Lake Corpus Christi, provides information on the oxidation potential of the water column. In Lake Corpus Christi, Fe values were used in conjunction with Mn to evaluate the oxidation potential of the water column since they have similar geochemical profiles offset slightly by differences in oxidation kinetics (Hites and Eisenreich, 1987; Salbu and Steinnes, 1995; Viollier et al., 1995). Station 1 profiles for both seasons show pronounced peaks in the hypolimnion of particulate Mn and Fe, while only August profiles for station 4 have peaks, although of smaller magnitude. The enrichment of particulate Mn and Fe at station 1 is, respectively, by factors of 7.3 and 10 in August and 6.6 and 2.8 in January. In comparison, enrichment factors for station 4 in August are notably lower enrichment factors (3.4 and 2.7, respectively). The profiles of both metals in August are mirror images of the DO profile with epilimnetic peaks in the metals corresponding to the decline in DO at 5.5 m. The peaks in particulate Mn and Fe suggest the oxidation potential is sufficiently reducing to alter the speciation of these metals. However, the oxidation potential favors only the reductive dissolution of Mn in station 1.

The particulate values of V, Cr, Co, Ni and Pb also increase in the hypolimnion, analogous to peaks in Mn and Fe. The August profiles at station 1 show greater hypolimnetic enrichments of the particulate metals by factors of 26, 11, 6.6, 16 and 6.4, respectively; relative to January; which had enrichments values of 3.9, 2.7, 4.0, 5.1 and 3.7, respectively. At station 1, only particulate Co and Pb increase by factors 2.2 and 2.9. Among the dissolved phase metals, only Pb shows significantly higher values in the hypolimnion at station 1 in January.
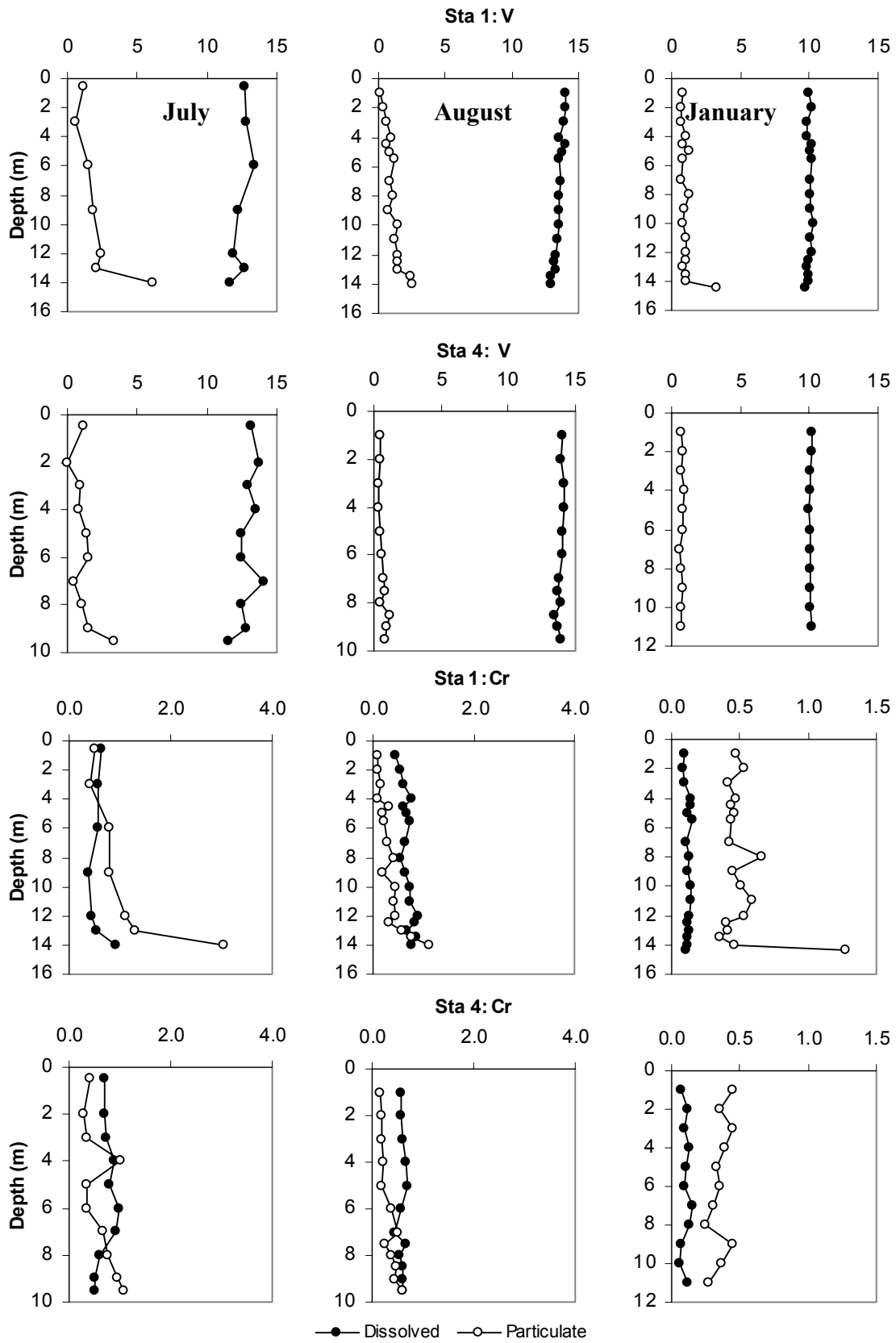
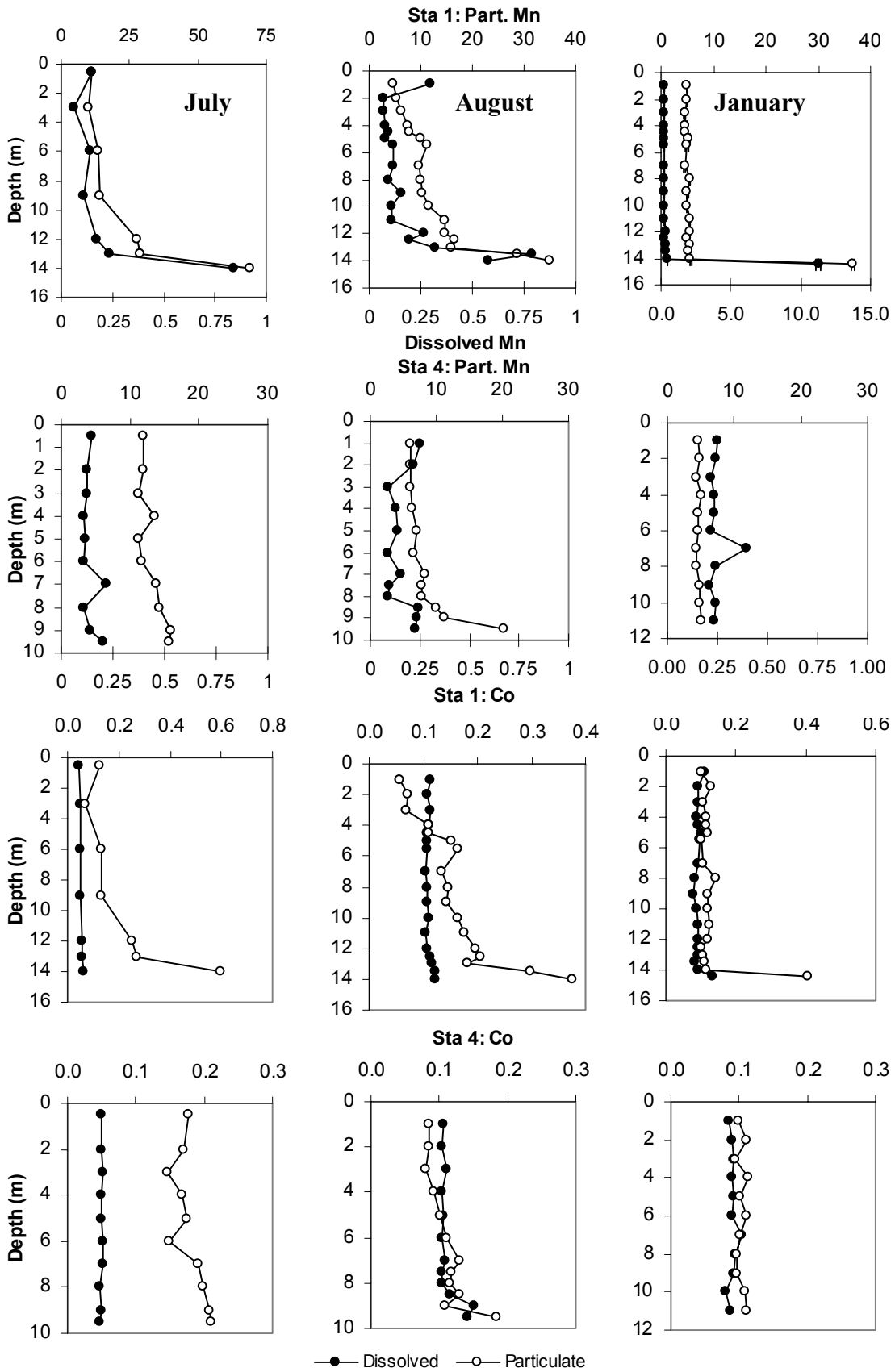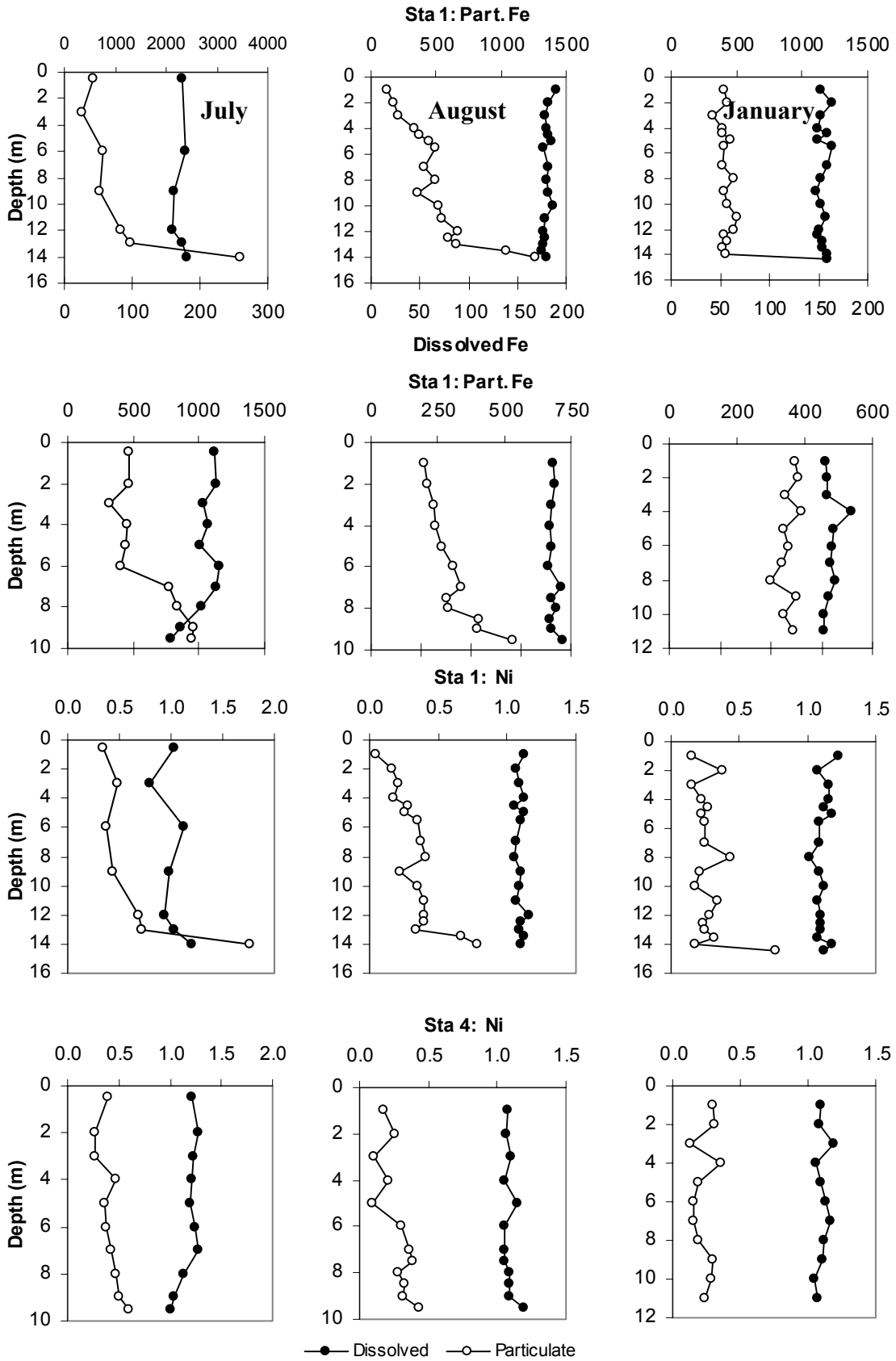Figure 6. Trace metal profiles for July, August and January at stations 1 and 4.

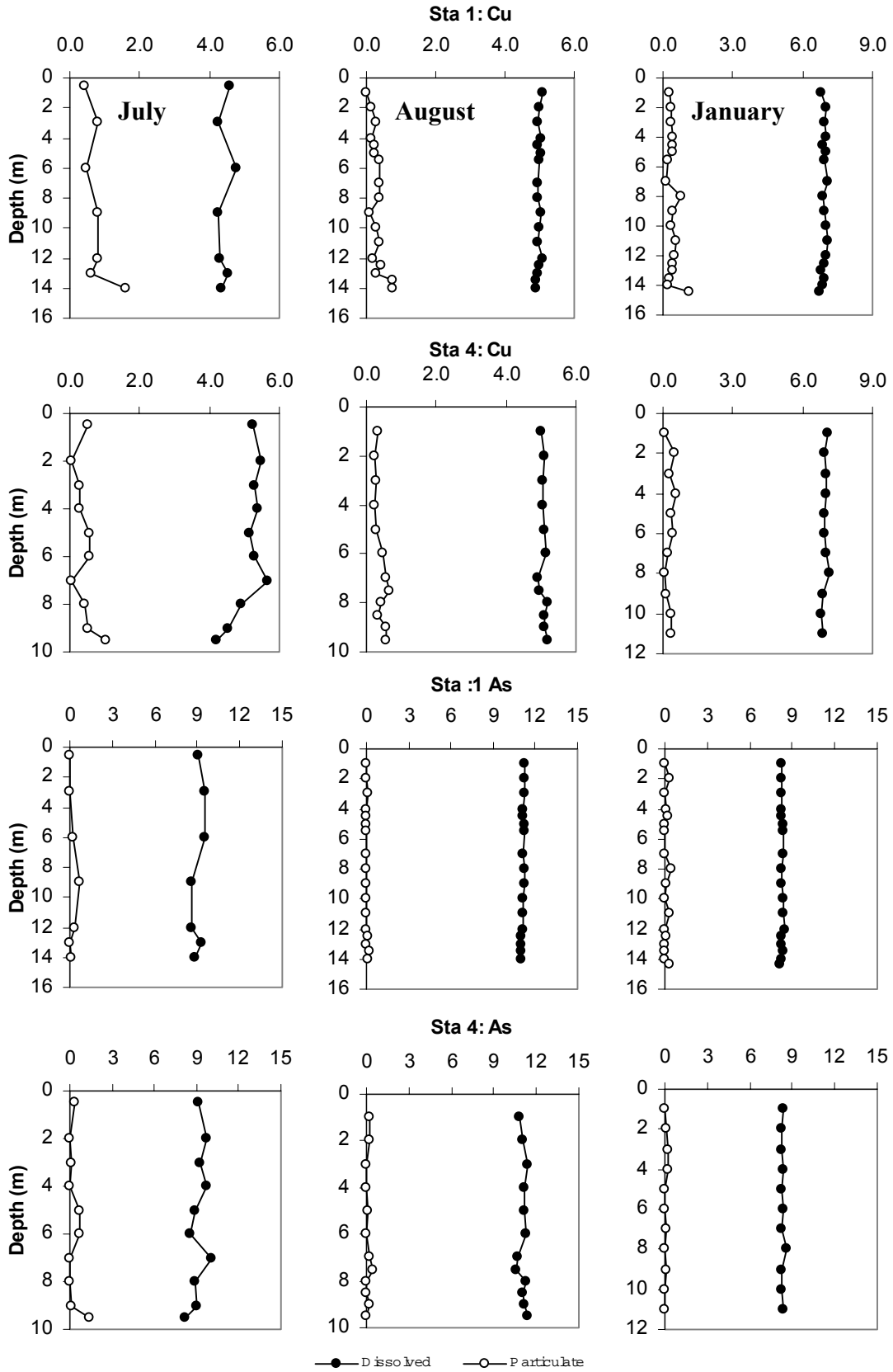Figure 6. Continued.

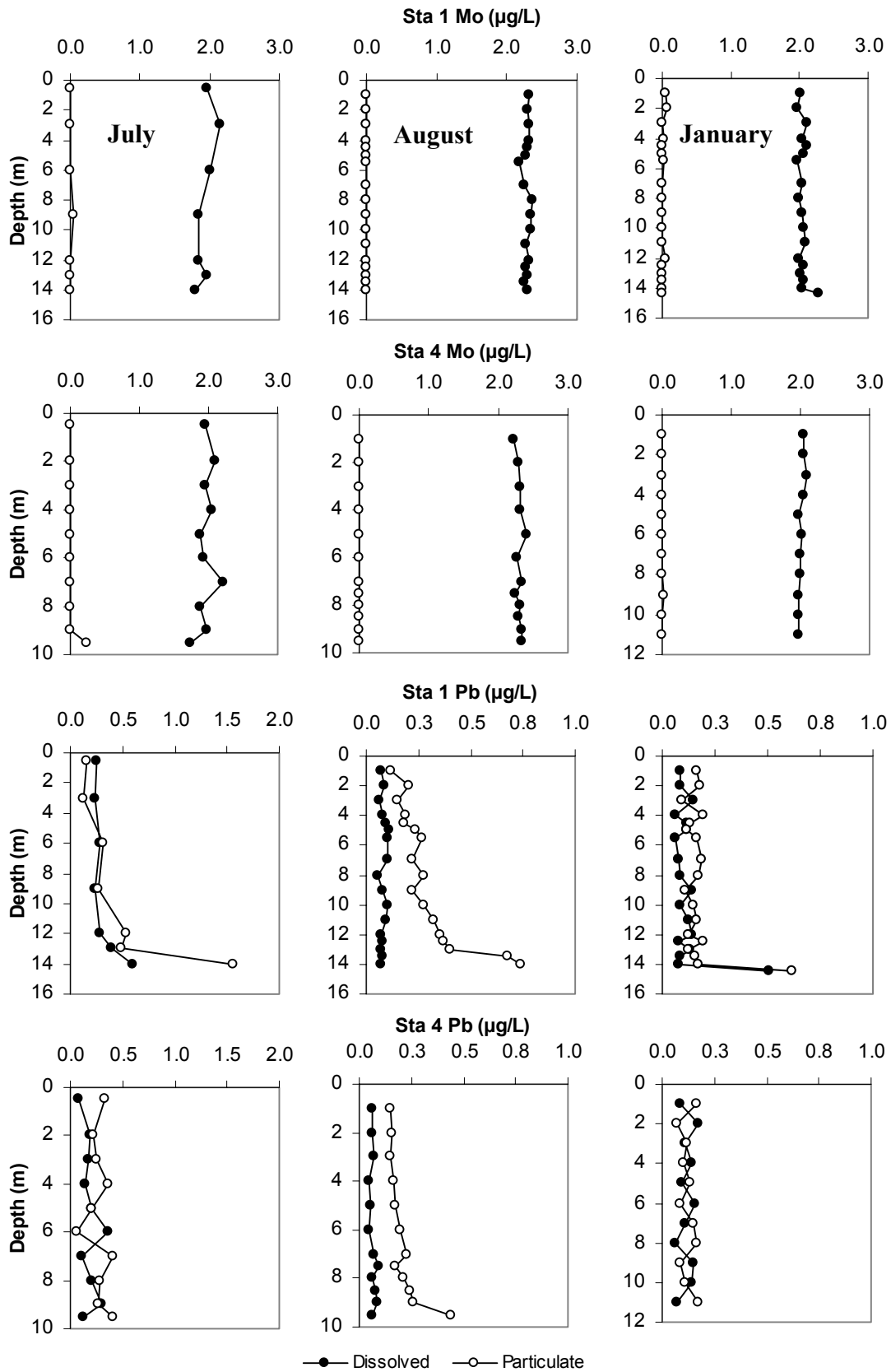Figure 6. Continued.

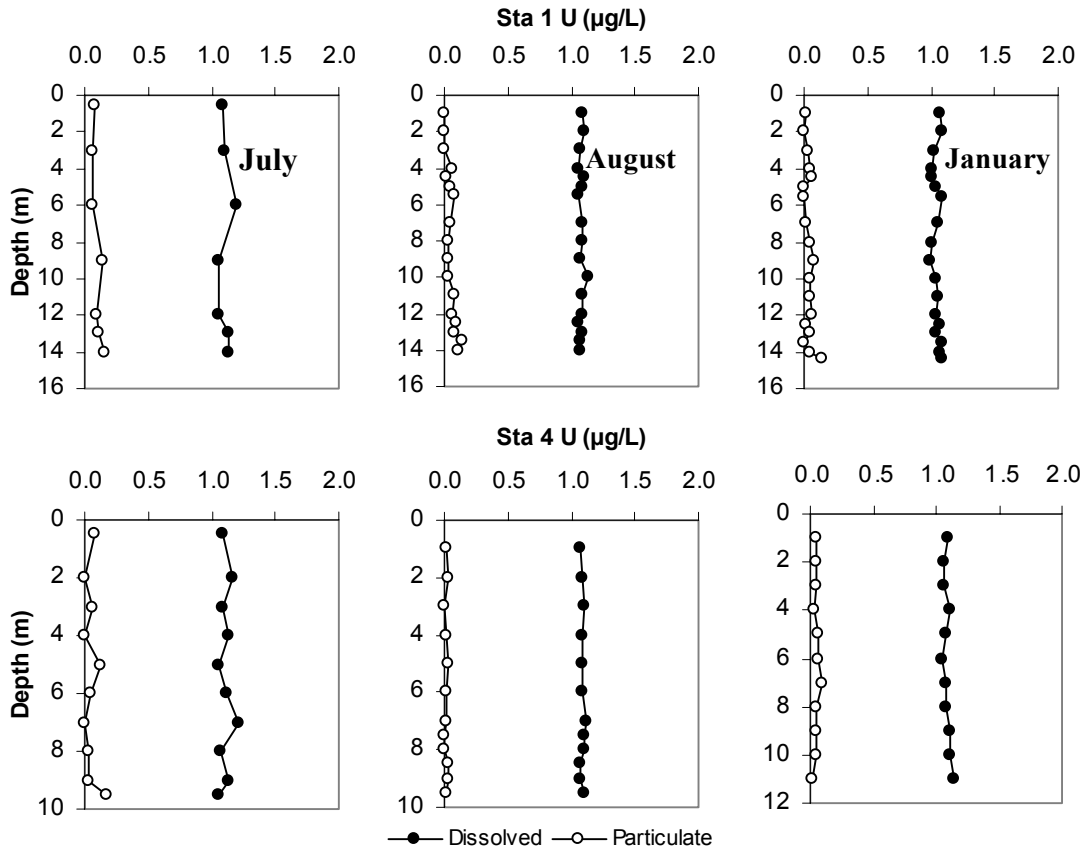Figure 6. Continued.

Figure 6. Continued.

Figure 6. Continued.

In Lake Corpus Christi, the oxidation potential of the water column during both seasons, as inferred from Mn and Fe profiles, does not appear to be sufficiently reducing to catalyze the phase transformation of redox sensitive metals such as U, Mo and As, since they all occur exclusively in the dissolved phase during all sampling periods.

The average epilimnetic metal values show little seasonal variations in concentrations with the exception of higher V and As in the summer and higher Cu in the winter. The summer values for V and As averaged 14 and 11 μg/L, respectively, vs. 10 and 8 μg/L, respectively, during the winter. Value for Cu increased from 5 to 7 μg/L from summer to winter. 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 ranging from 0.2 μg/L (Salbu and Steinnes, 1995) to 3.75 μg/L (Anderson and Bruland, 1991).

The two stations sampled in the lacustrine zone of Lake Corpus Christi provided

information on the spatial variations in trace metals as a function of depth. On average, the epilimnetic waters show very little spatial variation in metals. The heterogeneity in hypolimnetic DO consistently produced spatial variations of Mn, Fe, V, Cr, Co, Ni and Pb at station 1. In contrast, station 4 profiles show the vertical distribution of trace metals is relatively homogenous, except in August.

Trace metal profiles were also evaluated for responses to an episodic mixing event driven by a substantial inflow of meteoric waters from the Nueces River in June. The DO profiles indicate the near complete oxygenation of the water column. This resulted in the oxidation of Fe and Mn oxy-hydroxides, marked by higher particulate values for these metals in the July sampling. In July, particulate Mn at station 1 ranged between 11.0 - 69.4 µg/L, showing an overall enrichment factor of 1.9 relative to August (4.77 – 34.9 µg/L). Particulate Fe shows a slightly greater enrichment in July (583 – 3476 µg/L) by a factor of 2.3 relative to August (123 – 1260 µg/L). However, the cycling of As is marked by dilution following the inflow event with dissolved values of 9.1 ± 0.94 µg/L compared to August (11.1 ± 0.34 µg/L).

Surface and Ground waters in the Nueces River Basin

The tributaries and ground water samples enhanced the understanding of the distribution of As in the Nueces River basin, since Lake Corpus Christi values are elevated above background. Figure 7 illustrates the distribution of As from the ambient levels in the upper Nueces River basin to the tap water in Corpus Christi. The low concentrations of As in the Frio and Nueces Rivers (upper Nueces River basin), averaging 0.56 µg/L, are characteristic of background surface values. This is in marked contrast to the average 6.0 µg/L measured in the Frio River near Choke Canyon and 6.4 µg/L in the Atascosa River. The distribution of As in the Nueces River also shows a gradient of increasing values toward Lake Corpus Christi ranging from 2.5 µg/L at Holland Dam in La Salle County to 6.17 µg/L at the entrance to the lake.
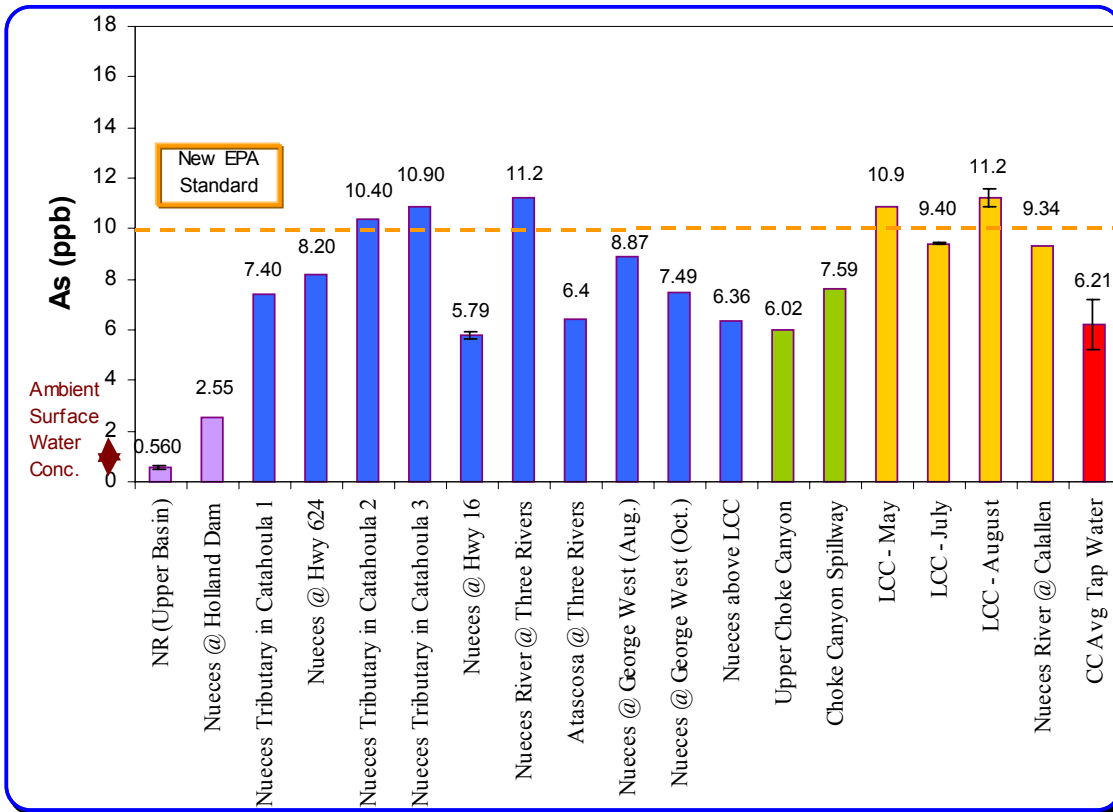
Figure 7. The distribution of arsenic in the Nueces River (NR) basin, including Lake Corpus Christi (LCC). Samples grade from the upper basin (left) to the tap water of the City of Corpus Christi. The dashed line represents the new EPA standard for arsenic in drinking water.

Figure 8 illustrates the distribution of As, U and Mo in the 16 ground waters sampled. The values illustrate the typical heterogeneity of complex ground water systems. Concentrations range from 0.34 – 47 µg/L for U and 0 – 16 µg/L for Mo. The values for As range from ambient levels of around 0.6 µg/L to 24 µg/L, which is more than twice the new EPA arsenic drinking water standard of 10 µg/L (Todd Whitman, 2001).
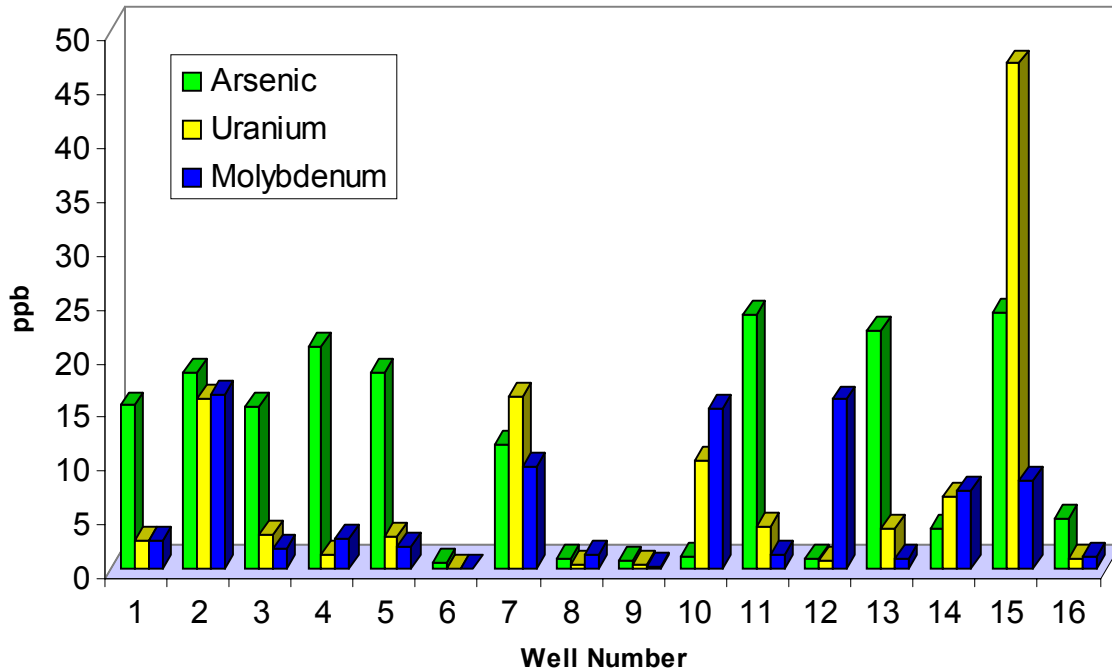

Figure 8. Concentrations of arsenic, uranium and molybdenum in ground water samples.

DISCUSSION

The enrichment and cycling of trace metals in the water column of Lake Corpus Christi due to alterations in redox conditions may have a tremendous influence on water quality. In Lake Corpus Christi, redox driven cycles of trace metals seems to be controlled by variations in dissolved oxygen both temporally and spatially. These oscillations in dissolved oxygen entrain changes in the speciation of Mn and Fe characterized by increasing particulates just above the redox cline and increasing dissolved Mn in the more reducing hypolimnion. These characteristic depth profiles indicate the redox boundary migrates within the water column in the summer creating

partially stratified conditions in the summer and well-mixed conditions in winter and following hydrological mixing events, January and July. As in Kneebone and Hering (2000), the hypolimnetic increases in dissolved Mn at station 1, regardless of hydrologic conditions, suggesting that even during well-mixed conditions the sediments remained reduced. This implies the sediments remain a constant source of reduced Mn (dissolved) diffusing across the sediment-water interface into the hypolimnion. The seasonal and event driven mixing of the water column at station 4, however, suggests the sediments may reverse from a sink to a source for metals in the hypolimnion, degrading water quality as the cycling of Mn and Fe oxy-hydroxides results in the scavenging of trace metals in oxic regimes and the release of associated trace metals in reducing regimes (Balistrieri et al., 1992b; Viollier et al., 1995; Viollier et al., 1997).

Metals enriched in the hypolimnion with Mn and Fe are particulate Cr, V, Co, Ni and Pb. Two processes appear to control the cycling of hypolimnetic metals. The distribution of metals such as Cr may be attributed to changes in speciation driven by redox reactions (Achterberg et al., 1997). While, the enrichment of metals such as V, Co, Ni and Pb may be attributed to scavenging by Mn and Fe oxy-hydroxides (Achterberg et al., 1997; Balistrieri and Murray, 1986; Balistrieri et al., 1992b; Hamilton-Taylor and Davison, 1995; Pohl and Hennings, 1999; Taillefert et al., 2000; Viollier et al., 1995; Viollier et al., 1997). Previous studies have proposed the adsorption of V and Pb are intrinsically linked to the cycling of Fe (Hamilton-Taylor and Davison, 1995; Viollier et al., 1995), whereas Co is linked to Mn (Balistrieri and Murray, 1986; Balistrieri et al., 1992b; Taillefert et al., 2000; Viollier et al., 1995). However, in both Lake Corpus Christi and Lyssy Pond linear regression analysis indicates a much stronger correlation between Pb and Mn (Figure 9) than between Pb and Fe ($r^2 = 0.33$ in Lyssy Pond and 0.865 in Lake Corpus Christi). This is in agreement with (Pohl and Hennings, 1999) who suggest the phase distribution of Pb in the water column is specifically controlled by the cycling of Mn. Many studies document the diagenetic remobilization of Mn (Balistrieri et al., 1992a; Davison and Tipping, 1984; Mayer et al., 1982; Mortimer, 1941; Viollier et al., 1995; Viollier et al., 1997), which inferring from the correlation above, may led to the remobilization of Pb. This directly contradicts the assumption that the high affinity of Pb to particulate matter limits the aquatic residence time of Pb by favoring sedimentation
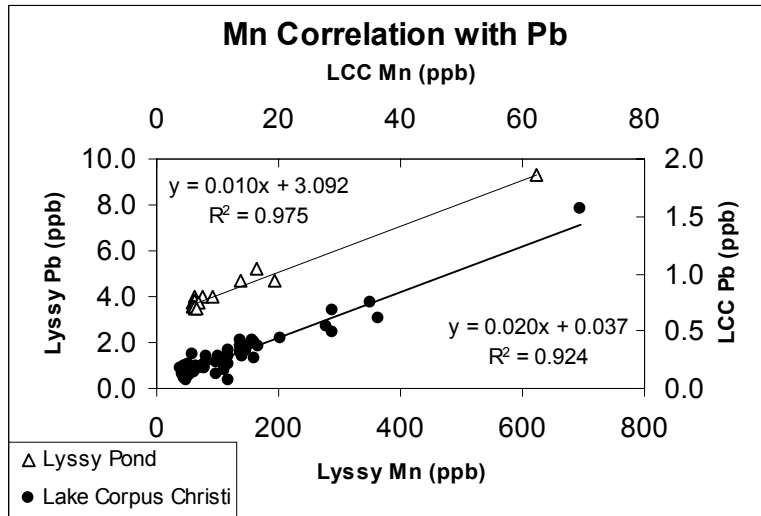
Mn Correlation with Pb

Figure 9. Correlation between Mn and Pb in Lyssy Pond and Lake Corpus Christi.

with minimal diagenetic remobilization (Hites and Eisenreich, 1987).

The profiles show the enrichment of Mn, Fe and Cr and their associated metals (Pb, V, Co and Ni) are inversely proportional to the oxidation potential of the water column. This relationship produces seasonal variations as metals have higher enrichment factors in summer when oxidation potentials are lower. In fact, the enrichment factors measured in August may be underestimates of summer conditions as the water column was completely oxygenated just prior to sampling. The relatively high values for particulate Mn and Fe in July substantiate enrichment of the hypolimnion with respect to these metals prior to the inflow event. This relationship also provides an explanation for the spatial variations between the hypolimnion of the two stations, as the sediments at station 1 remain reducing resulting in greater hypolimnetic enrichment of metals.

Although both stations were in the lacustrine zone near the dam, dissolved oxygen measurements indicate only slightly reducing conditions corroborated by the phase distribution of Mn and Fe. The relatively shallow depths and large fetch of the lake may drive episodic and seasonal hypolimnetic mixing (Thornton et al., 1990). Although true equilibrium in trace metal cycling is rarely achieved in reservoirs, the dynamic nature of Lake Corpus Christi may even prevent the achievement of steady state (Manahan, 2000). This might explain why U, Mo and As occur entirely in the dissolved phase and only U values in Lyssy Pond, under suboxic conditions, indicate phase transformation.

Arsenic

The occurrence of As in the waters of Lake Corpus Christi is elevated above ambient levels (0.5- 1 µg/L (National Academy of Sciences, 1997) by almost an order of magnitude and occurs entirely in the dissolved phase both seasonally and even under mildly reducing conditions. This stability may be attributed to the lack of strongly reducing conditions since profiles of Lyssy Pond similarly reported no As cycling. Additionally, the high pH values, of ~ 8.5, in the lake further contributes to the redox stability of the more soluble As (V) even under moderately reducing conditions, while decreasing adsorption affinity to mineral surfaces (Levy et al., 1999). Furthermore, the relative depletion of Fe in this system (Brandenberger et al., in preparation) suggests a strong lack of preferential adsorption of As onto Fe oxy-hydroxides (Aurillo et al., 1994; Belzile and Tessier, 1990; Crecelius, 1975).

This conservative behavior of As allows for dilution during periods of higher inflow resulting from events (July) or seasonal variations marked by higher inflows into Lake Corpus Christi. Additionally, the substantial evaporative losses and minimal inflows to the lake lead to evapoconcentration of As in the summer (La Force et al., 2000; Levy et al., 1999; McLaren and Kim, 1995; Michel et al., 1999; Riedel et al., 2000; Welch and Lico, 1998). The conservative behavior resulting in temporal enrichment of As up to 12 µg/L contributes to the degradation of water quality in Lake Corpus Christi reservoir and ultimately the drinking water it provides, as only a small percentage of As is removed during standard water treatment. This data is particularly timely, as the USEPA finally adopted the new arsenic in drinking water standard of 10 µg/L (Todd Whitman, 2001). The new standard is in agreement with World Health Organization standards and was guided by studies (National Academy of Sciences, 1999) indicating the old standard of 50 µg/L was not sufficiently low enough to protect human health. According to USEPA, arsenic is the only known substance for which there is adequate evidence of carcinogenic risk by both inhalation and ingestion routes of exposure (U. S. Environmental Protection Agency, 1998) and for which exposure through drinking water has been clearly demonstrated to cause skin, bladder, lung and prostate cancer in humans (Christen, 1999; Morales et al., 2000; National Academy of Sciences, 1999). Tap water for the City of Corpus Christi in August averaged 6.2 µg/L, which is below the standard. The dilution

relative to the lake values in August, averaging 12 µg/L, may be attributed to the blending of Lake Corpus Christi waters with Lake Texana waters from the Mary Rhodes Pipeline prior to incorporation into the public water supply system. However, this is not an option for several small communities using Lake Corpus Christi as the sole source for freshwater and may result in arsenic concentrations above the new drinking water standard.

Arsenic – Basin Review

The distribution of As in the Nueces River basin provides information on potential sources. Values for As in the basin range from the ambient levels reported in the upper basin (0.5 µg/L) to values in Nueces Bay of > 10 µg/L (Fisher, 1996). Even the urbanized areas around San Antonio, subject to anthropogenic contamination, only reported values around 2 µg/L As (Bush et al., 2000). In addition, values along the Nueces River increase considerably downstream of Holland Dam. This suggests the sources for As occurs within the basin itself. Compiling arsenic 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 assumption that the dominant sources for As in the Nueces River basin are the formations enriched in uranium ore, such as the Catahoula and the Oakville Formations (Parker et al., 2001). Therefore, the significant increase in As in the Nueces River downstream of Holland Dam results from the meander of the river across these formations. The values in the Nueces River basin are in direct contrast with the neighboring San Antonio basin, similarly impacted by uranium mining and potentially to a greater extent, as Karnes County is the origin of uranium mining and now hosts the UMTRA project. Arsenic levels in the San Antonio and San Marcos Rivers average 2.98 ± 0.9 µg/L.

Evaluating the basin data using ratios of As to Mo and U, all enriched in uranium ore deposits, identifies areas of selective enrichment of As by creating unique signatures for identifying potential sources of waters. Figure 10 illustrates the signatures of different water sources such as the three sampling events in Lake Corpus Christi, the upper basin, uranium mine drainages, and ground waters. The ratio signatures identify the selective
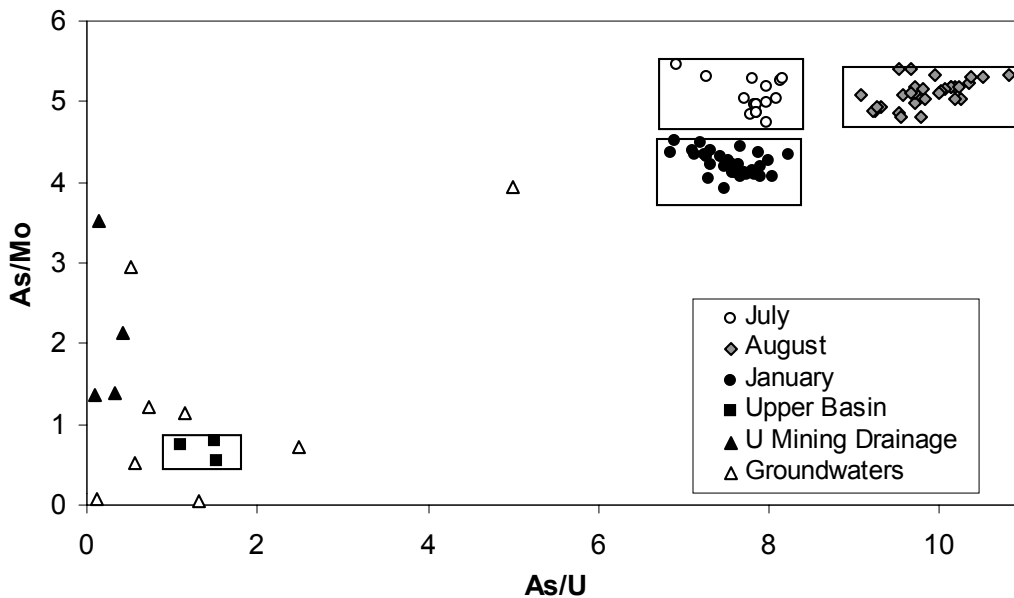
Figure 10. Ratios of As to U and Mo showing signatures of the three sampling events in Lake Corpus Christi, the upper Nueces River basin, uranium mining and ground waters.

enrichment of As during periods of evaporative concentration in August relative to January and the selective dilution of As in July. In comparison, the ratio signatures in the upper basin confirm its relative isolation from uranium mining, and provide the signatures expected in systems un-impacted by uranium deposits. However, surface water drainages near uranium mines indicate selective enrichment of U relative to As and As relative to Mo, subsequently altering the ratio signatures. In comparison, ratios for the Lyssy Pond profile are not shown as they overlap Lake Corpus Christi water profiles, but the signatures within the depth profile are distributed between July and January signatures as a function of the distribution of Mo in the water column.

Ground Waters

The extreme heterogeneity of As, Mo and U in ground waters suggests a mechanism for sequestration, such as sulfidization upon contact with water discharging along faults in Live Oak County enriched in H_2S (Henry et al., 1982). The concentrations of selected ground waters are elevated above the new drinking water standard. An emphasis was placed on As because elevated levels are seen in the surface waters as well as ground

waters. However, the ground water samples provide the first indication of enrichment in U and Mo in the Nueces River basin. The occurrence of U (48 μg/L) above the drinking water standard of 30 μg/L is significant, not only as a health concern for U, but also suggest the potential for elevated levels of the U daughter products, radium and radon. The ratios of As, U and Mo in ground waters reveal a scattering of signatures suggesting As is not selectively enriched. This results from the non-conservative behavior of these redox sensitive trace metals in ground waters produced by the removal of evapoconcentration and dilution as factors potentially influencing the selective enrichment of arsenic. Therefore, significant investigations are required to further understand the distribution of As, U and Mo in the ground waters of the lower Nueces River basin.

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