LCRA Study of Sediments in the Colorado River Basin

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Executive Summary

In 2005, LCRA conducted a study to determine the concentrations of metals, pesticides and PCBs in sediments in the Colorado River and its tributaries. The purpose of the study was to determine if any of the sediment contained concentrations of harmful constituents that were high enough to be an ecological concern. LCRA reported the study results to the Texas Commission on Environmental Quality (TCEQ) so that the data can be used in future assessments.

LCRA staff collected 47 sediment samples at 21 sites from upstream of Lake Buchanan to Caney Creek. The sites represent 18 TCEQ designated segments within the Colorado River and adjoining coastal basins. Segment 1402 was sampled at three sites because of its long length; all other segments were sampled at one site. Each site was sampled on two or more occasions.

The samples were analyzed for 20 pesticides, 13 metals, and 8 PCBs and lab results were compared with two state screening levels: the Probable Effects Level (PEL) and the state-wide 85th percentile. The PEL represents a concentration that, if exceeded, is likely to be toxic to aquatic organisms. The 85th percentile value serves as a warning that a particular constituent could be a concern.

One pesticide (DDE) was detected in the samples that were analyzed but it was below both screening levels. All eight of the PCBs were below any detectable concentration. Seventeen samples were found to have detectable concentrations of metals, with six metals exceeding the 85th percentile screening level. One sample exceeded the 85th percentile and the PEL for cadmium. This sample, collected June 13, 2005 at the Llano River at Llano site, exceeded TCEQ's cadmium PEL (0.55 mg/kg) with a concentration of 7.09 mg/kg.

Results from the study indicate that metals, pesticides and PCBs were not present in sediment at levels sufficient enough to cause a water quality concern. This project will be discussed at an upcoming Coordinated Monitoring Meeting to determine if continuation of sediment monitoring is warranted. The data from this sediment study will be used by the TCEQ for their 2006 water quality assessment report.

INTRODUCTION

In 2005, LCRA collected and analyzed 47 sediment samples. These samples were collected from 21 sites and represent 18 segments within the Colorado River basin. The purpose of the monitoring was to determine if any of the sediment from samples collected contained concentrations of constituents that were high enough to be of concern. The data were reported to the Texas Commission on Environmental Quality (TCEQ) and will be evaluated by TCEQ in future assessments.

Table 1 shows the stream segments that were sampled and number of samples that were collected from each segment. Segment 1402 because of its long length was sampled at three sites. In reservoirs LCRA collected samples nearest the dam as these sites can be representative of a reservoir's depositional zone. Six reservoir and 12 stream sites were sampled. Sediment was also sampled at two tidally influenced streams sites.

As of the writing of this report, TCEQ assessment methodology requires that 10 sediment samples per segment be collected within a five-year period for the sediment to be assessed. Table 1, besides containing summary of segments and sites collected in 2005, also contains the number of samples collected in 2004. Sediment samples were not collected by LCRA between 2000 and 2004. Table 1 is helpful in determining the number of samples collected by LCRA in each segment and the approximate resources that have been expended in sediment collection and analysis.

Table1. Segments and sites that LCRA monitored.

Segment	Site	LCRA 2005 samples/site	LCRA 2004 samples/site
1304	12148	2	1
1401	12281	2	1
1402	12249	2 (1402A)	1
	12284	2	1
	12290	1	0
1403	12294	3	1
1404	12302	2	1
1405	12319	3	1
1406	12324	2	1
1407	12336	3	1
1408	12344	3	1
1409	12355	2	1
1410	12358	2	1
1414	12372	3	1
1415	12386	3	1
1416	12392	2	1
1417	12394	2	1
1427	12436	2	1
1428	12466	2	1
1501	12515	2	1

A review of the Coordinated Monitoring Schedule shows that TCEQ region offices and City of Austin (COA) have also collect sediment samples. Table 2 shows the number of samples that are shown in the Coordinated Monitoring Schedule for TCEQ region offices and COA and sediment monitoring that has been performed by LCRA. Table 2 does not break down the samples into TCEQ assessment units. For example, Cummins Creek is segment of 1402A and is shown in Table 2 simply as 1402. Table 2 shows the number of sediment values that are available for TCEQ assessment.

Table 2. Segments monitored by LCRA, TCEQ and COA.

Segment	LCRA	TCEQ 2003-2006	COA 2003-2006	Total
1304	3	2		5
1401	3	3		6
1402	7	6		13
1403	4	4	7	15
1404	3	4		7
1405	4	4		8
1406	3	3		6
1407	4	4		8
1408	4	4		8
1409	3	3		6
1410	3	3		6
1414	4	4		8
1415	4	4		8
1416	3	4		7
1417	3	0		3
1427	3	4		7
1428	3	0	2	5
1501	3	0		3

METHODS AND DATA ANALYSIS

LCRA sediment samples were collected by using a petite ponar dredge and were analyzed for 20 organochlorine pesticides, eight polychlorinated biphenyls (PCBs) and 13 metals. Additionally, the sediment samples were analyzed for four sediment texture tests, percent moisture and total organic carbon. LCRA's Environmental Laboratory Services performed the analysis of the samples. Organic compounds are expressed in micrograms per kilogram (µg/kg) while metal results are expressed in milligrams per kilogram (mg/kg).The list of constituents analyzed in the sediment, analytical method, detection limit and parameter code used to report the data to TCEQ are shown in Table 3.

Table 3. List of constituents analyzed in sediment. Units are expressed as µg/kg unless noted otherwise.

Analyte	Analytical Method	Detection Limit	Parameter Code
Beta-BHC	SW 8081A	5	34257
delta-BHC	SW 8081A	5	34262
Endosulfan sulfate	SW 8081A	5	34354
Endrin aldehyde	SW 8081A	5	34369
alpha-Chlordane	SW 8081A	5	39064
gamma-Chlordane	SW 8081A	5	39067
alpha-BHC	SW 8081A	5	39076
4,4'-DDT	SW 8081A	5	39301
4,4'-DDE	SW 8081A	5	39311
4,4'-DDD	SW 8081A	5	39321
Aldrin	SW 8081A	5	39333
Dieldrin	SW 8081A	5	39383
Endrin	SW 8081A	5	39393
Toxaphene	SW 8081A	50	39403
Heptachlor	SW 8081A	5	39413
Heptachlor epoxide	SW 8081A	5	39423
Methoxychlor	SW 8081A	5	39481
gamma-BHC	SW 8081A	5	39783
trans-Nonachlor	SW 8081A	5	78657
cis-Nonachlor	SW 8081A	5	78924
alpha-BHC	SW 8081A	5	39076
Arochlor 1221	SW 8082	50	39491
Arochlor 1232	SW 8082	50	39495
Arochlor 1242	SW 8082	50	39499
Arochlor 1248	SW 8082	50	39503
Arochlor 1254	SW 8082	50	39507
Arochlor 1260	SW 8082	50	39511
Arochlor 1016	SW 8082	50	39514
PCB	SW 8082	50	39519
Arsenic	SW 6020	0.5 mg/kg	01003
Barium	SW 6010B	0.5 mg/kg	01008
Cadmium	SW 6020	0.05 mg/kg	01028
Chromium	SW 6010B	0.05 mg/kg	01029
Copper	SW 6010B	0.05 mg/kg	01043
Lead	SW 6010B	0.05 mg/kg	01052
Manganese	SW 6010B	0.05 mg/kg	01053
Nickel	SW 6010B	0.5 mg/kg	01068
Silver	SW 6010B	0.5 mg/kg	01078
Zinc	SW 6010B	2.5 mg/kg	01093
Aluminum	SW 6010B	2.5 mg/kg	01108
Selenium	SW 6020	0.25 mg/kg	01148
Mercury	SW 7471A	0.1 mg/kg	71921

Analyte	Analytical Method	Detection Limit	Parameter Code
% clay	Hydrometer	0 %	49900
% silt	Hydrometer	0 %	49925
% sand	Hydrometer	0 %	49906
% gravel	Hydrometer	0 %	80256
% moisture	MSA 9	0 %	81373
Total organic carbon	SM 5310B	1500 mg/kg	81951

The lab results are compared to two screening levels, Probable Effects Levels (PEL) and state-wide 85th percentile. Both screening levels were obtained from TCEQ's Guidance for Assessing Texas Surface and Finished Drinking Water Quality Data, 2004. The PEL is a concentration that if exceeded is likely to be toxic to organisms living in the water body. The National Oceanic & Atmospheric Administration (NOAA) developed the PELs. TCEQ uses the PELs as a screening tool for reservoir, streams and tidal water bodies. The 85th percentile value represents the concentration of the constituent when all available data is analyzed by TCEQ. The 85th percentile concentrations are lower than the PELs and serve as a warning that a particular constituent is reaching a concentration that may be of concern. The 85th percentile values are revised yearly by TCEQ from state-wide data that they evaluate.

RESULTS AND DISCUSSION

In this section LCRA's sediment results are discussed. A description of the analyte and its impact in the environment is included.

Only one organochlorine pesticide was detected in sediment samples that were analyzed in 2005. That sample was collected at Lake Austin near Tom Miller Dam (site 12294) and it contained 4,4'-DDE (dichlorodiphenyldichloroethylene). The 9.59 µg/kg concentration measured at this site was below the state-wide 85th percentile. NOAA has not developed a PEL concentration for 4,4'-DDE.

Before 1973 when it was banned, DDT entered the air, water, and soil during its production and use as an insecticide. Most DDT in the environment is a result of past use. DDE is only found in the environment as a result of contamination or breakdown of DDT. DDT, DDE, and DDD persist in the soil for a very long time, potentially for hundreds of years. Most DDT breaks down slowly into DDE and DDD, generally by the action of microorganisms. In surface water, DDT will bind to particles in the water, settle, and be deposited in the sediment. DDT is taken up by small organisms and fish in the water. It can accumulate to high levels in fish and marine mammals (such as seals and whales), reaching levels many thousands of times higher than in water. In these animals, the highest levels of DDT are found in their adipose tissue.

Interestingly, in 2005 DDE was detected in 12 fish collected downstream of Austin at Webberville, site 12466. None of the fish tissue concentrations of DDE were high enough

to be of concern, according to Texas Department of State Health Services health-based assessment comparison value.

All eight of the PCB analytes were below the detectable concentration. The non-detection of PCBs or arochlors in the sediment samples indicates that these do not pose a concern at the time and location that sediment was sampled. PCBs are synthetic chlorinated organic compounds with biphenyl as the basic structural unit. They are a family of 209 chemicals with varying numbers of chlorine atoms attached in varying positions to two connected benzene rings. There are 209 possible PCB isomers and congeners theoretically that can exist, but it is improbable that all are present in nature. Most PCB mixtures contain only about 130 isomers or congeners.

Monsanto Corporation, who produced half of the world's PCB's and all of North America's PCB's, designated them as Arochlors with a 4 digit number where the first two digits for a PCB mixture is "12" and the third and fourth digits represent the weight percentage of chlorine**.**

Nine metals that were analyzed had concentrations less than TCEQ's 85th percentile screening level. Results of the four sediment metals analysis that exceeded the 85th percentile screening values are shown in Table 4. The 85th percentile screening values are exceeded seven times for cadmium, three times for both copper and lead and twice for nickel. Onion Creek had two cadmium values exceed the 85th screening level. Inks Lake near dam had two copper concentrations that were greater than the 85th level. The Colorado River east of San Saba had two lead values greater than the 85th screening level.

One 7.09 mg/kg cadmium value collected at the Llano River at Llano (site 12386), exceeded both the 85th percentile and the PEL, 3.53 mg/kg. The sample result that exceeded the PEL for cadmium level is bolded in Table 4. The Llano River was sampled three times in 2005 and two times the cadmium concentration was below detection, while once the concentration was higher than the PEL. Sphaelorite, a naturally occurring mineral in the Llano uplift area, may be a possible source of cadmium in Llano County. No known industrial or agricultural source of cadmium is known to exist in the Llano River watershed upstream of the monitored site.

Table 4. Results of metals sediment analysis, results are expressed in mg/kg.

Analyte	**Site #**	**Site**	**Result**	**85th Percentile**
Cadmium	12358	Colorado River at Winchell	0.61	0.55
Cadmium	12372	Pedernales River near Johnson City	0.70	0.55
Cadmium	12148	Caney Creek at Chambliss Road	1.25	0.75
Cadmium	12436	Onion Creek at US 183	1.28	0.55
Cadmium	12436	Onion Creek at US 183	1.29	0.55
Cadmium	12294	Lake Austin near Tom Miller Dam	1.62	0.73
Cadmium	12386	Llano River at Llano	**7.09**	0.55
Copper	12466	Colorado River at Webberville County Park	16.0	14.5
Copper	12336	Inks Lake near Inks Dam	28.5	26.8
Copper	12336	Inks Lake near Inks Dam	29.8	26.8
Lead	12466	Colorado River at Webberville County Park	29.7	20
Lead	12355	Colorado River east of San Saba	31.8	20
Lead	12355	Colorado River east of San Saba	55.1	20
Nickel	12436	Onion Creek at US 183	18.4	15.5
Nickel	12436	Onion Creek at US 183	28.4	15.5

The Agency for Toxic Substances and Disease Registry estimates that 25,000 to 30,000 tons of cadmium are released to the environment each year. About half of this total comes from the weathering of rocks into river water and then to the oceans. Cadmium in nature is rarely found as a pure metal. It is often combined with other elements such as oxygen, chlorine or sulfur. Cadmium is most often present as complex oxides, sulfides and carbonates in zinc, lead and copper ores. The metal can change forms and can bioaccumulate in aquatic organisms. In humans, cadmium may cause kidney, lung and intestinal damage. According to the U.S. Department of Health and Human Services, cadmium compounds may reasonably be anticipated to be carcinogens.

One sample had values greater than the 85th percentile for more than one analyte. Cadmium and nickel exceeded the 85th percentile on the samples collected February 14 and July 12, 2005 at site 12436, Onion Creek at U.S. Highway 183.

Table 5 shows the “hits” on organic constituents. The “hits” are actual detectable concentrations of an organic analyte. All other analytes were below a detectable concentration. None of the detectable concentrations of organic constituents, collected during three collection efforts, was at a concentration that exceeded the applicable PEL.

Table 5. Organic "hit" comparison through various collection efforts.

Organic	**1994-1997**	**2004**	**2005**
4,4'- DDD	2	0	0
4,4'- DDE	2	0	1
4,4'- DDT	4	0	0
Endrin Aldehyde	2	0	0
Heptachlor	4	0	0
PCB	1	0	0
Beta- BHC	0	1	0

Table 6 shows a comparison of values that exceeded the 2004 85th percentile values. In 1994 through 1997, LCRA was sampling Town Reservoir. One lead value, collected from Town Reservoir in the 1994-1997 time frame exceeded the PEL value shown in TCEQ's 2004 assessment methodology. LCRA did not monitor Town Reservoir in either 2004 or 2005.

Table 6. Metals exceeding TCEQ's 2004 85th percentile through various collection efforts.

Metal	**1994-1997**	**2004**	**2005**
Cadmium	31	2	7
Copper	3	2	3
Lead	2	0	3
Nickel	3	1	2
Silver	2	0	0
Selenium	4	0	0

SUMMARY AND RECOMMENDATION

LCRA's 2005 sediment monitoring showed that of organic constituents only 4,4- DDE was found at a detectable concentration. The 4,4- DDE concentrations was less than TCEQ's 85th percentile screening level. In 2005, one cadmium concentration was found to be greater than TCEQ's 2004 PEL concentration. The Llano River at Llano site, collected June 13, 2005 exceeded TCEQ's cadmium PEL, 0.55 mg/kg. The cadmium concentration measured was 7.09 mg/kg. In LCRA's 2005 sediment collection, the cadmium value that exceeded the PEL screening concentration was bracketed in time by values that were less than detectable, 0.05 mg/kg. This variability in results points to the "patchiness" of sediment sample results. Often, samples collected next to one another can have widely variable results.

A comparison of organic and metals results from LCRA's three collection efforts going back to 1994 does not show an evident decrease in sediment quality. In the three collection efforts only two values exceeded the PEL. Town Reservoir sediment collected December 22, 1994 exceeded the lead PEL, 34.8 mg/kg. The lead concentration at the site was 117 mg/kg. The Llano River site cadmium value collected in 2005, containing a concentration of 7.09 mg/kg, also exceeded the PEL.

A recommendation is proposed here to collect sufficient samples for an assessment to be performed by TCEQ in the next assessment period. The responsibility of collecting the samples and data can be shared by TCEQ region offices, City of Austin and LCRA. Sediment samples should be discussed and collection efforts coordinated at the 2006 TCEQ Clean Rivers Program Coordinated Monitoring meetings. TCEQ assessment staff should be asked to bring information such as the number of sediment samples needed to complete the upcoming assessment for each segment or assessment unit to the Coordinated Monitoring meetings.

REFERENCES

Agency for Toxic Substances and Disease Registry:
http://www.atsdr.cdc.gov/tfacts5.html, http://www.atsdr.cdc.gov/toxprofiles/phs35.html

Texas Commission on Environmental Quality, "Guidance for Assessing Texas Surface and Finished Drinking Water Quality Data 2004," August 15, 2003.

University of Waterloo Environmental Microbiology:
http://wvlc.uwaterloo.ca/biology447/modules/module5/pcbdegradation.htm