FINAL REPORT

Survey of Organochlorine Pesticides and PCBs in McGrath Lake

University of California, Riverside
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EXECUTIVE SUMMARY

McGrath Lake is on the Clean Water Act Section 303(d) list for impairments due to PCBs, DDT, chlordane, dieldrin and toxicity in the lake sediments. The contamination is due to historical and current loading of contaminants from the agricultural lands and other sources in the McGrath Lake subwatershed. Samples collected in the late 1990s document some of the highest sediment concentrations of PCBs and organochlorine (OC) pesticides in the State of California. As a result, in 1999, McGrath Lake was identified under the Statewide Bay Protection and Toxic Cleanup Program (BPTCP) as a high priority toxic "hot spot". On October 1, 2009, the Los Angeles Regional Water Quality Control Board adopted the McGrath Lake OC Pesticides and PCBs total maximum daily load (TMDL). The TMDL assigns load allocations to the lake sediments for the TMDL constituents that will attain water quality objectives and protect beneficial uses. There are historical data on the levels of OC pesticides and PCBs in the lake sediments, but more current and extensive data are needed to determine potential remediation activities to attain the TMDL load allocations.

Sampling, laboratory analysis, and investigation of the extent of OC pesticide and PCB contamination in the lake sediments was conducted in 2010-11. A multifrequency hydroacoustic survey was conducted to characterize sediment properties, distribution, and thickness; this data was then used to guide sediment sampling and provide volumetric estimates of contaminated sediments. Sediment core samples were collected from 15 sites down the long axis of the lake, sectioned into 20 cm intervals and returned to the laboratory for sediment characterization and organochlorine and pesticide contaminant analyses.

Very high concentrations of total DDT and total chlordane were found in the sediments, with mean values of 919 and 34.9 ng g^{-1}, respectively. Levels in all sediments exceeded the ERL (Effects Range Low) value for total DDT (1.58 ng g^{-1}) and nearly all sediments exceeded the ERL for total chlordane (0.5 ng g^{-1}), generally by very large margins. Concentrations of organochlorine pesticides were h ighest at 60-80 cm depth at the north end of the lake. Total PCB concentrations were much lower and all samples were below the ERL of 22.7 ng g^{-1}. Over 30,000 m^3 of DDT- and chlordane-contaminated sediment (*i.e.*, above ERL) is estimated to be present in the lake.

1.0 INTRODUCTION

McGrath Lake is on the Clean Water Act Section 303(d) list for impairments due to PCBs, DDT, chlordane, dieldrin and toxicity in the lake sediments. The contamination is due to historical and current loading of contaminants from the agricultural lands and other sources in the McGrath Lake subwatershed. Samples collected in the late 1990s document some of the highest sediment concentrations of PCBs and organochlorine (OC) pesticides in the State of California. As a result, in 1999, McGrath Lake was identified under the Statewide Bay Protection and Toxic Cleanup Program (BPTCP) as a high priority toxic "hot spot".

On October 1, 2009, the Los Angeles Regional Water Quality Control Board adopted the McGrath Lake OC Pesticides and PCBs total maximum daily load (TMDL). The TMDL assigns load allocations to the lake sediments for the TMDL constituents that will attain water quality objectives and protect beneficial uses. There are historical data on the levels of OC pesticides and PCBs in the lake sediments, but more current and extensive data are needed to determine potential remediation activities to attain the TMDL load allocations.

A three-phase approach was adopted in this study. The initial phase involved georeferenced hydroacoustic measurements that allow determination of the bathymetry and sediment distribution in the lake. At the time of the hydroacoustic survey, surface sediment grab samples were collected with an Ekman dredge at a small number of sites for basic physical and chemical characterization (e.g., particle size distribution, organic C and total N contents).

Following analysis of the hydroacoustic data and development of maps of bathymetry and sediment distribution/thickness to guide sampling, a preliminary sampling campaign collected 6 cores that were sectioned, homogenized and analyzed for physical and chemical properties and concentrations of organochlorine pesticides and PCBs.

Based upon results from the first 2 phases, a final sampling campaign collected an additional 9 cores, which were analyzed in a similar fashion as the first 6. The distribution of organochlorine pesticides and PCBs measured from the sediment core measurements were combined with hydroacoustic measurements of sediment thickness to develop spatial representations of contaminant distributions within the lake, and used to estimate volume of contaminated sediments to aid in remediation design.

2.0 APPROACH

2.1 Sampling schedule

A hydroacoustic survey was conducted on December 8, 2010 to characterize bathymetry and sediment distribution in the lake, while preliminary sediment core sampling was conducted at 6 locations on the lake on February 16, 2011 (Table 2.1). The final phase 3 sampling campaign was conducted on October 2, 2011.

Table 2.1. Sampling schedule

Activity	**Date**	**Sites Sampled**
Phase 1 hydroacoustic survey	December 8, 2010	na
Phase 2 preliminary core sampling	February 16, 2011	Sites 1-6
Phase 3 final core sampling	October 2, 2011	Sites 7-15

2.2 Sampling procedures

Intact sediment cores for basic physical characterization (water content, organic C content) and organic contaminant analyses were collected from the lake, returned to shore, and sectioned into 20-cm sections or until the bottom of the core is reached. Samples were homogenized and subsampled into individual 500-mL wide-mouth glass jars with Teflon-lined lid, and stored on ice in a cooler and returned to UCR. Travel blanks were used in which reagent-grade sand was packed in new sample jars and analyzed as samples. Sediment core sample tubes are reused after cleaning on site with lake water to remove any retained sediment and ensuring no carryover of contaminated sediments between sites. Upon return to the laboratory, sediment was re-homogenized and subsampled for basic sediment characterization and PCB and organochlorine pesticide analysis.

2.3 Sampling equipment

Sampling at McGrath Lake was conducted from a 12' Sea Eagle inflatable catamaran with a 2.5 HP 4-stroke outboard motor (Table 2.2). Hydroacoustic measurements were conducted with a BioSonics echosounder, water column properties (temperature and conductivity) were measured using a YSI CTD, and sediment cores were collected with an Aquatic Instruments universal corer (Table 2.2).

Table 2.2. Sampling equipment.

Sampling Activity	**Equipment**
Navigation	12' Sea Eagle inflatable catamaran 2.5 HP 4-stroke Mercury outboard
Hydroacoustic survey	BioSonics DTX echosounder - 38-kHz single-beam transducer - 201-kHz split-beam transducer - 430-kHz single-beam transducer JRC 212W DGPS Dell ATX laptop
Surface Grabs	Ekman dredge
Sediment Cores	Aquatic Instruments universal percussion corer - four 2.4-m aluminum extension rods plus T-handle - 0.5, 1 and 2 m long plastic core tubes (2.5" ID, 1/16" wall) - sediment core extrusion piston and mount
Water column measurements	YSI CastAway CTD - thermister - conductivity cell - pressure transducer - built-in WAAS-enabled GPS

2.4 Hydroacoustic survey

As the initial phase of this study, a hydroacoustic survey of bottom sediment properties was conducted on December 8, 2011. Measurements were made from a 12' Sea Eagle inflatable catamaran with a 2.5 HP 4-stroke outboard using a BioSonics DTX echosounder along a series of transects with position recorded using a JRC 212W real-time differential GPS. Measurements were made with BioSonics 430-kHz and 38-kHz single beam transducers with integrated pitch-roll sensors multiplexed with a 201-kHz split beam transducer at 5 pings per second. Echograms were analyzed using Sonar5 Pro (Balk and Lindem, 2010) and BioSonics Visual Bottom Typer software (BioSonics, 2008). Surface sediment grab samples were collected using an Ekman dredge at 5 sites on the lake. Surface grab samples were homogenized and subsampled into individual 500-mL wide-mouth glass jars with Teflon-lined lid. Samples were stored on ice in a cooler and returned to the laboratory.

2.5 Analytical methodology

2.5.1 Basic sediment characterization

Water content was determined on subsamples that were heated overnight at 105 °C. Total C and N were measured by dry-combustion methods using a Thermo Flash EA NC soil analyzer (Nelson and Sommers, 1982). Inorganic C and $CaCO_3$ were determined manometrically following Loeppert and Suarez (1996), with organic C taken as the difference between total C and inorganic C. Duplicate analyses were conducted at a rate of at least one every 10 samples within an analytical batch.

2.5.2 Organochlorine pesticide and PCB extraction and measurement

Organic contaminants were extracted from sediment samples that were homogenized, freeze-dried and ground using a mortar and pestle. All samples were extracted using a Dionex (Sunnyvale, CA) ASE 350 accelerated solvent extraction (ASE) system. Pre-combusted Ottawa sand (0.5 g, Fisher Scientific) was placed in the bottom of each extraction cell, followed by five grams of a freeze dried sediment sample, which was capped with more sand to fill the remaining headspace. Prior to capping the cell with sand, surrogates (PCB 65 and PCB 209) were added to each sample. Samples are then extracted over 3 cycles at 100 ^{o}C and 1500 psi for 5 min with methylene chloride. The extracts were then dried using nitrogen gas and immediately 1 mL of hexane was added along with 2 g of activated copper to remove sulfur contamination. Samples were allowed to set for 10 min with copper prior to cleanup to ensure sufficient sulfur removal.

Sample cleanup was performed using Florisil solid phase extraction (SPE) cartridges (Fisher Scientific). Florisil cartridges were first conditioned for 5 minutes using 5 mL of hexane. Samples were transferred to the cartridge and the eluent was captured in a 15 mL collection vial. The target compounds were eluted from the cartridge using 3 mL of hexane: acetone (9:1) followed by 7 mL of hexane. The eluent was evaporated to dryness under a stream of nitrogen gas and immediately reconstituted with 0.5 mL of hexane and vortexed for 3, 10 second intervals before being transferred to a GC vial. Internal standards (PCB 30, PCB 205 and ^{13}C cis-permethrin) are then added to each vial and the final volume was brought to 1 mL before sealing the vial.

Extracts were analyzed using a Varian CP-3800 GC coupled with a 1200 Quadrupole MS/MS. The column oven temperature ramp was as follows: initial temperature of 80 ^{o}C, held

for 1 min, then increased to 200 ºC at a rate of 10 ^{o}C min^{-1} before increasing to 300 ^{o}C at a rate of 5 ^{o}C min^{-1} and then finally held for 5 minutes. The total run time was 38 minutes. A standard curve was run prior to and after analysis for PCBs (6 points) and OCPs (9 points). OCPs required a broader standard curve range than PCBs due to higher concentrations. Duplicates, matrix spikes and matrix spike duplicates were extracted, cleaned and analyzed at a frequency of 1 per 10 samples.

In addition to measurements of total concentrations of organochlorine pesticides and PCBs in the sediments, measurements of freely-dissolved concentrations (C_{free}) in sediment porewater were made using solid-phase microextraction (SPME) (Bondarenko et al., 2007). The emphasis of C_{free} measurement was on DDT and derivatives due to their dominant importance in the bulk chemical concentration profiles as shown in the preliminary core sampling. Many studies have shown that parameters such as C_{free}, rather than the bulk chemical concentrations derived from exhaustive solvent extraction, are more indicative of the bioavailability of hydrophobic contaminants in sediments. Therefore, SPME measured C_{free} predicts potential sediment toxicity from contamination by hydrophobic organic contaminants such as DDT and derivatives (Hawthorne et al., 2006). A method similar to that described in Bondarenko et al. (2007) was used. Briefly, sediment samples were saturated with water, equilibrated, and then centrifuged to obtain porewater. Aliquots (18 mL) of the derived sediment porewater were transferred to 20-mL autosampler vials. An automated SPME sampler, with polydimethylsiloxane (PDMS)-coated fiber from Supelco, was used for the sampling. The operational conditions, including fiber equilibration time in the sample, were similar to those used in recent studies (Bondarenko et al., 2007; Bondarenko and Gan, 2009; Delgado-Moreno et al., 2010; Wang et al., 2010). The organic contaminants enriched on the fiber were thermally desorbed after introduction into the GC inlet and swept through the analytical column to the MS/MS for detection and quantification. External calibration standards prepared in deionized water were analyzed simultaneously using SPME fibers under the same conditions (Bondarenko et al. 2007). After SPME sampling, the same sediment porewater samples were extracted with solvent (methylene chloride) and analyzed on GC-MS/MS to obtain the total concentration (C_w).

Due to the presence of dissolved organic matter (DOM) and other colloidal particles, C_{free} should be smaller than C_w. The differences between C_w and C_{free} will be indicative of the bioavailable fraction of DDT and derivatives in the sediments. It is expected that bioavailability of DDT and its derivatives may vary as a function of sediment depth (reflecting different

deposition or burial time and thus different lengths of aging) as well as spatial distribution due to changes in sediment organic carbon contents and properties. Please refer to the Standard Operating Procedures (Appendix A of the QAPP) previously submitted for additional details concerning laboratory procedures.

3.0 RESULTS

3.1 Hydroacoustic Survey

A 3-frequency hydroacoustic survey was conducted on December 8, 2010 to develop detailed maps of the bathymetry and acoustically-inferred thickness of sediments within McGrath Lake. This effort extended the measurements of water depth collected by Jacobi et al. (1999) at 51 sites on the lake by determining water depth and sediment thickness at 39,892 sites based upon acoustic response (Fig. 1a). The penetration of the lowest frequency (38-kHz) soundwave into organic sediments and reflection off of the contact with the hard dunal sand basin allowed estimation of the acoustical thickness of the organic sediments where hydrophobic organic contaminants would be concentrated.

3.1.1 Bathymetry

Depth was measured across the lake based upon transducer depth, known speed of sound and the time delay between the transmitted soundwave and the bottom echo return. Sediment depths were extracted from echograms using the bottom-detection algorithm in Sonar5 Pro. A bathymetric map of the lake was then developed from depth measurements, made at almost 40,000 points on the lake (Fig. 3.1a), using Surfer (Golden Software, Inc.) (Fig. 3.1b). McGrath Lake is a very shallow lake, with a maximum depth of only 2.6 m at the date of sampling.

Depth was found to increase from north to south, with depths <0.8 m in the northernmost part of the lake, to the maximum value (about 2.6 m) in a small deeper hole at the very southern end (Fig. 3.1b). Total surface area of the lake is estimated at 49,070 m^2 or 12.1 acres.

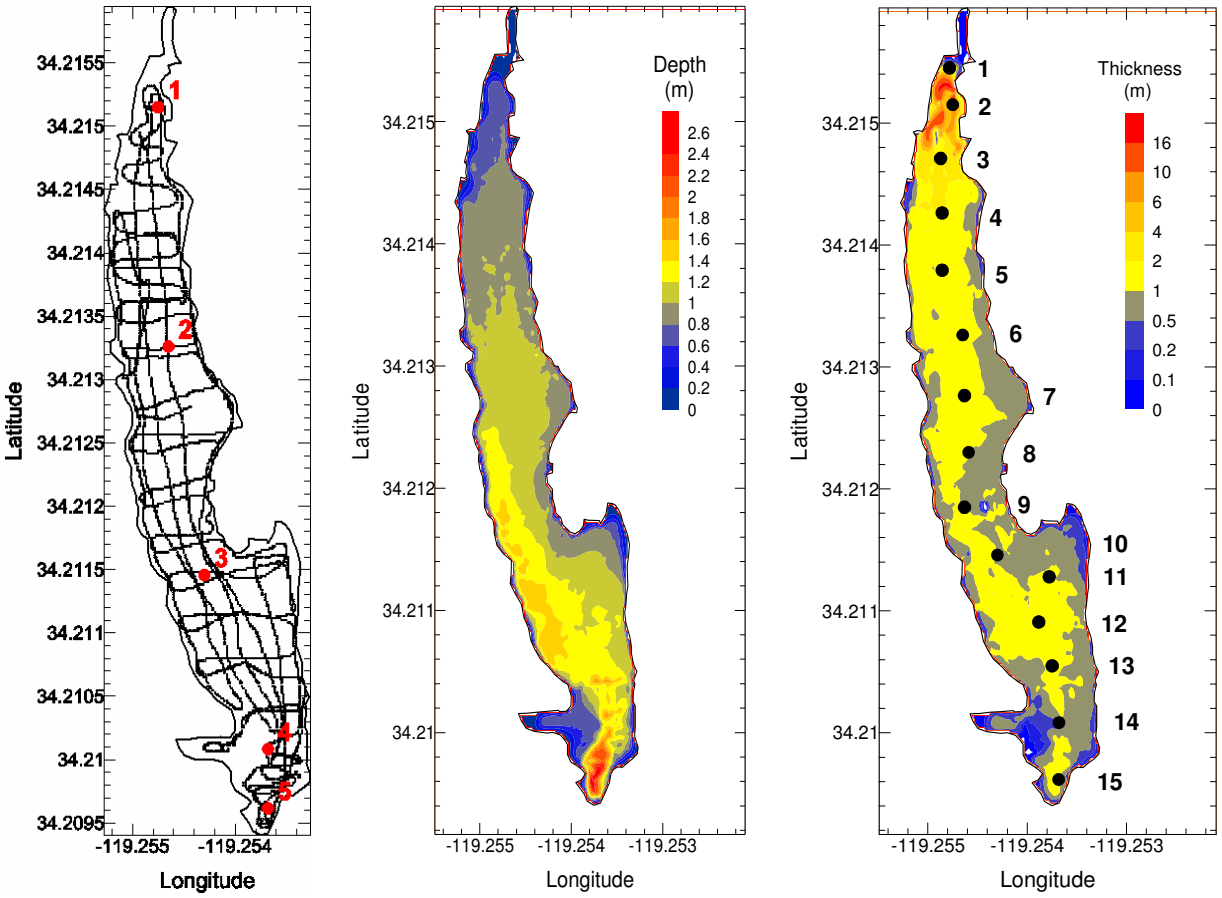

Fig. 3.1. Results from hydroacoustic survey: a) transects and preliminary sampling points; b) water column depth, and c) sediment thickness and final sediment core sampling sites.

3.1.2 Sediment Thickness

The thickness of the sediments was determined from the difference between the return time of the leading edge and back edge of the bottom echo, after correction for speed of sound. The 38-kHz transducer was used to estimate sediment thickness due to its weak absorption by water and by organic-rich sediments, thus allowing penetration into and backscatter/reverberation from sediments until a relatively dense substrate with strong absorption was encountered (e.g., sand or rock substrate). An example echogram showing the upper and lower limits of strong acoustic backscatter is provided in Fig. 3.2. The x-axis represents the ping number, which has a corresponding GPS location, while the y-axis shows the depth (or range) from the transducer face (scale shown on far right side of echogram; here,

up to 5 m from transducer face). Thus we see how both depth and sediment thickness varied across this section of the lake; a small slightly deeper region (about 2 m) with a sediment thickness of about 1 m was found near pings 3800-3850, while much thinner sediments were found in nearby shallow water (e.g., ping 3990-4010; depth <0.4 m; thickness approximately 0.2 m) (Fig. 3.2).

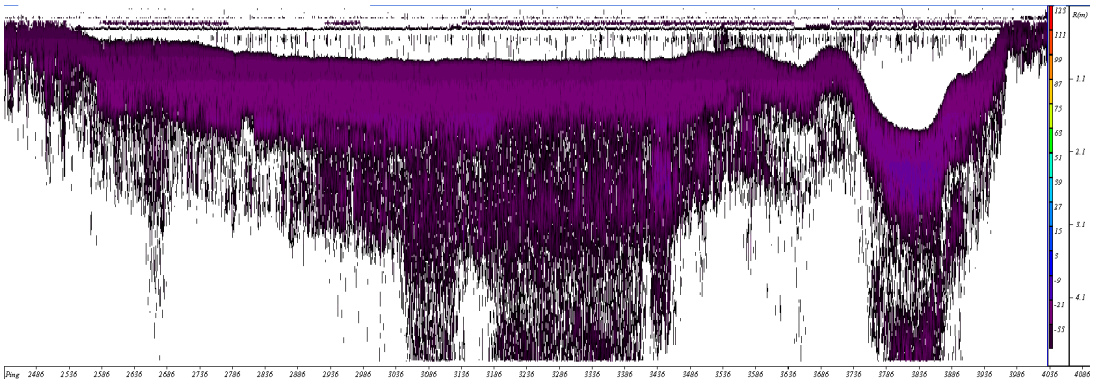

Fig. 3.2. Echogram measured at 38-kHz showing sediment backscatter and thickness.

Measurements made at known GPS coordinates across the lake were used to develop a contour map of acoustically-derived sediment thickness (Fig. 3.1c). Thickness varied across the lake, with very thin sediments near the lake margin and at a region in the southern part of the lake (shown in blue, Fig. 3.1c). Sediment thickness was generally 0.5 – 1 m over most of the lake area (shown in olive-yellow, Fig. 3.1c), while much thicker sediments (potentially 10-15 m thick) were found at the northernmost end (shown in red, Fig. 3.1c).

A more detailed view of sediment thickness down the transect is shown as a cross-section (site #1 is taken as the northernmost point) (Fig. 3.3). Very thick sediments at the north end of the lake were indicated from acoustic backscatter, although it was not possible to verify these substantial thicknesses using simple hand coring; as a result, these should be considered tentative thicknesses at this point in time. Within about 60 m or so, much thinner sediments (about 2 m) were present, and sediments generally remained <2 m down the remainder of the lake (Fig. 3.3).

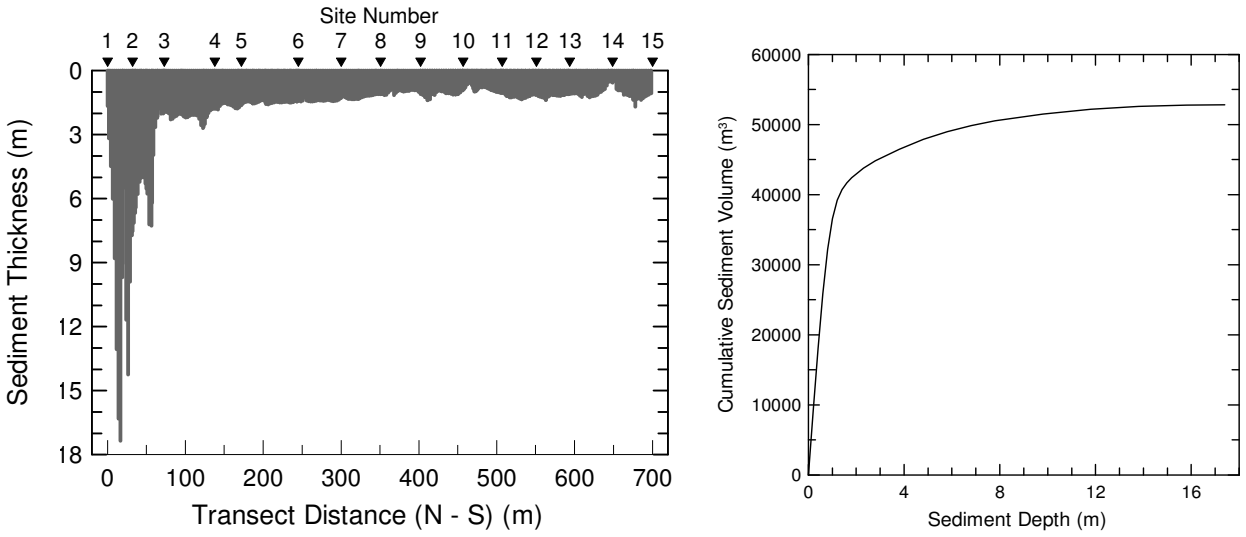

Fig. 3.3. Sediment measurements: a) thickness down center sampling transect of lake and b) cumulative distribution function showing sediment volume versus depth.

Using geospatial processing from data in Figs. 3.1c and 3.3, we estimated the lake surface area to be 49,070 m^2 (12.1 acres) and total sediment volume in the lake to be 52,815 m^3. Based upon these values, we estimate a mean sediment thickness over the whole basin of 1.1 m (Table 3.1). The majority of the sediment volume is located in the upper part of the sediment column (Fig. 3.3b). For example 39,204 m^3 (74.2%) of sediment is calculated to reside within the uppermost 1.2 m of the sediments.

Table 3.1. Basin morphometry for McGrath Lake.

Attribute	**Value**
Lake Surface Area	49,070 m^2
Sediment Volume	52,815 m^3
Mean Sediment Thickness	1.1 m

3.2 Sediment Properties and Contaminant Concentrations

Sediment cores were collected from 15 sites using a universal percussion corer (Fig. 3.1c). This sampling scheme provides essentially uniform sampling down the axis of the lake, provides greater spatial resolution, and will improve our understanding of contaminant distribution in the basin.

This level of spatial and vertical sampling, combined with corrected hydroacoustic measurements of sediment thickness, allowed for identification and volumetric estimates of "hot spots" based upon total pesticide concentrations and measurements of porewater concentrations and bioavailability as described in section 3.2.2.

3.2.1 Sediment Properties

Analysis of % organic C and water content varied with depth and across the different sites (Anderson et al., 2011b). The average sediment organic C content across all sites and depths was 2.14±0.86%, and there was a significant negative correlation with depth ($r = -0.339$, $P = 0.05$, $n = 53$, where r is the correlation coefficient, P is the alpha or significance level, and n is the number of samples). Water content of the sediments was also negatively correlated with increasing depth ($r = -0.411$, $P = 0.05$, $n = 53$) below the sediment surface, reflecting increased bulk density (positive correlations with depth; $r = 0.342$, $P = 0.05$, $n = 40$), consolidation and compaction in part due to overburden pressure. The percent organic matter and moisture were both inversely correlated with bulk density ($r = -0.894$, $P = 0.05$, $n= 40$; $r = -0.976$, $P = 0.05$, $n = 40$). The trends for percent moisture, bulk density and percent organic carbon with depth at each site can been seen in panels A, B and C of Figs. 3.4-3.18.

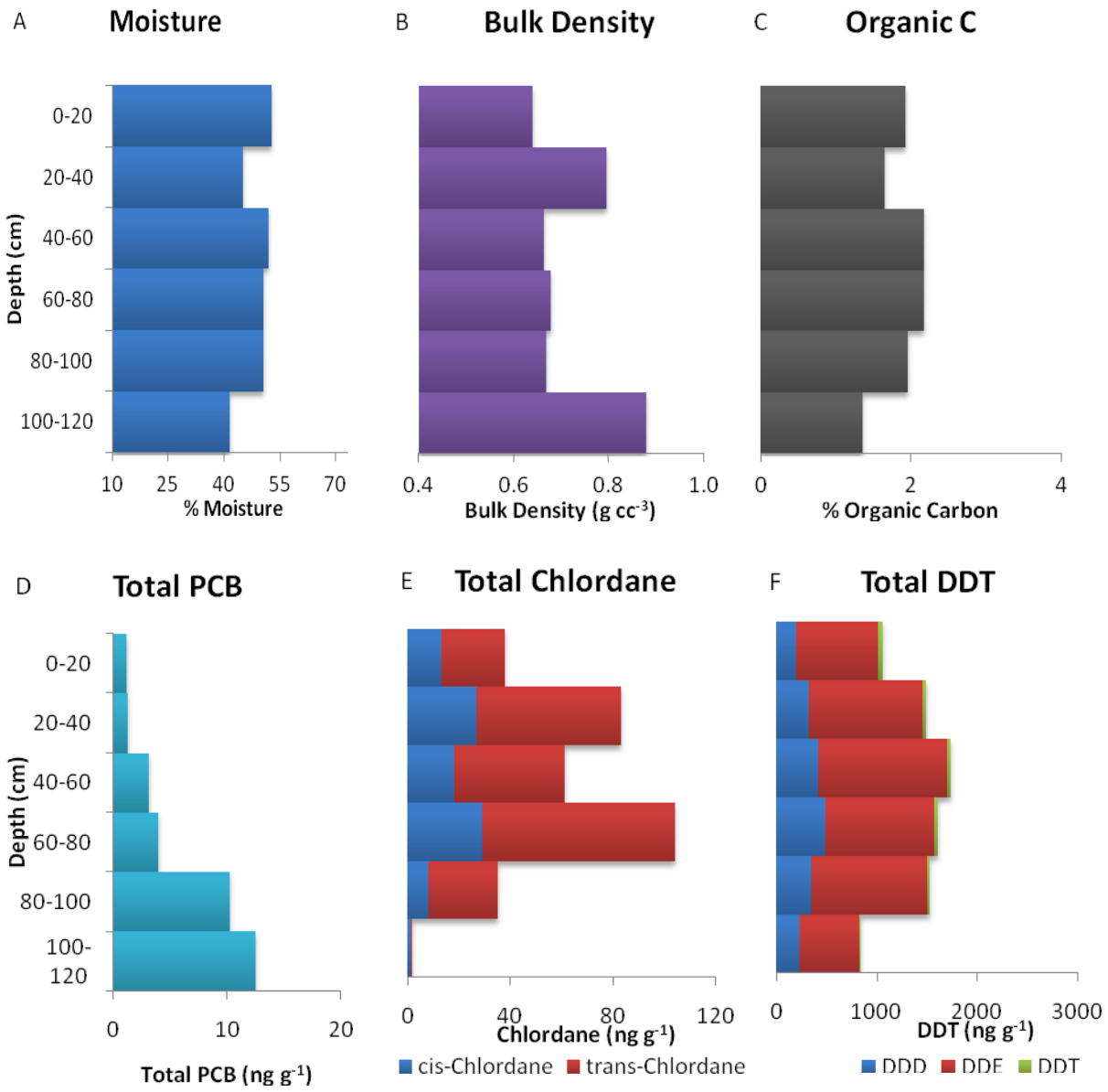

Figure 3.4. Soil properties and concentrations of the three target pollutant classes with depth at Site 1 along the sampling transect.

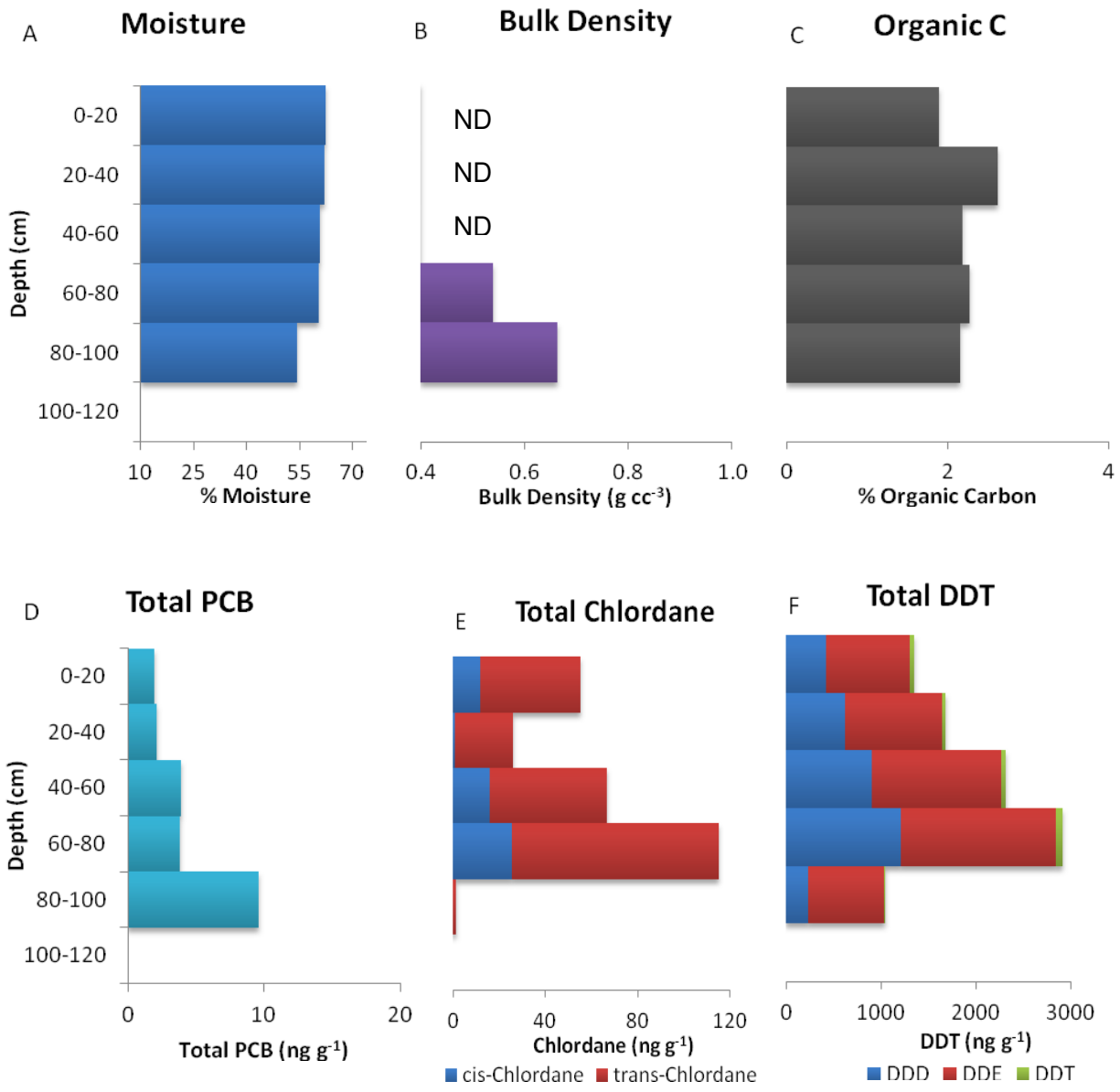

Figure 3.5. Soil properties and concentrations of the three target pollutant classes with depth at Site 2 along the sampling transect.

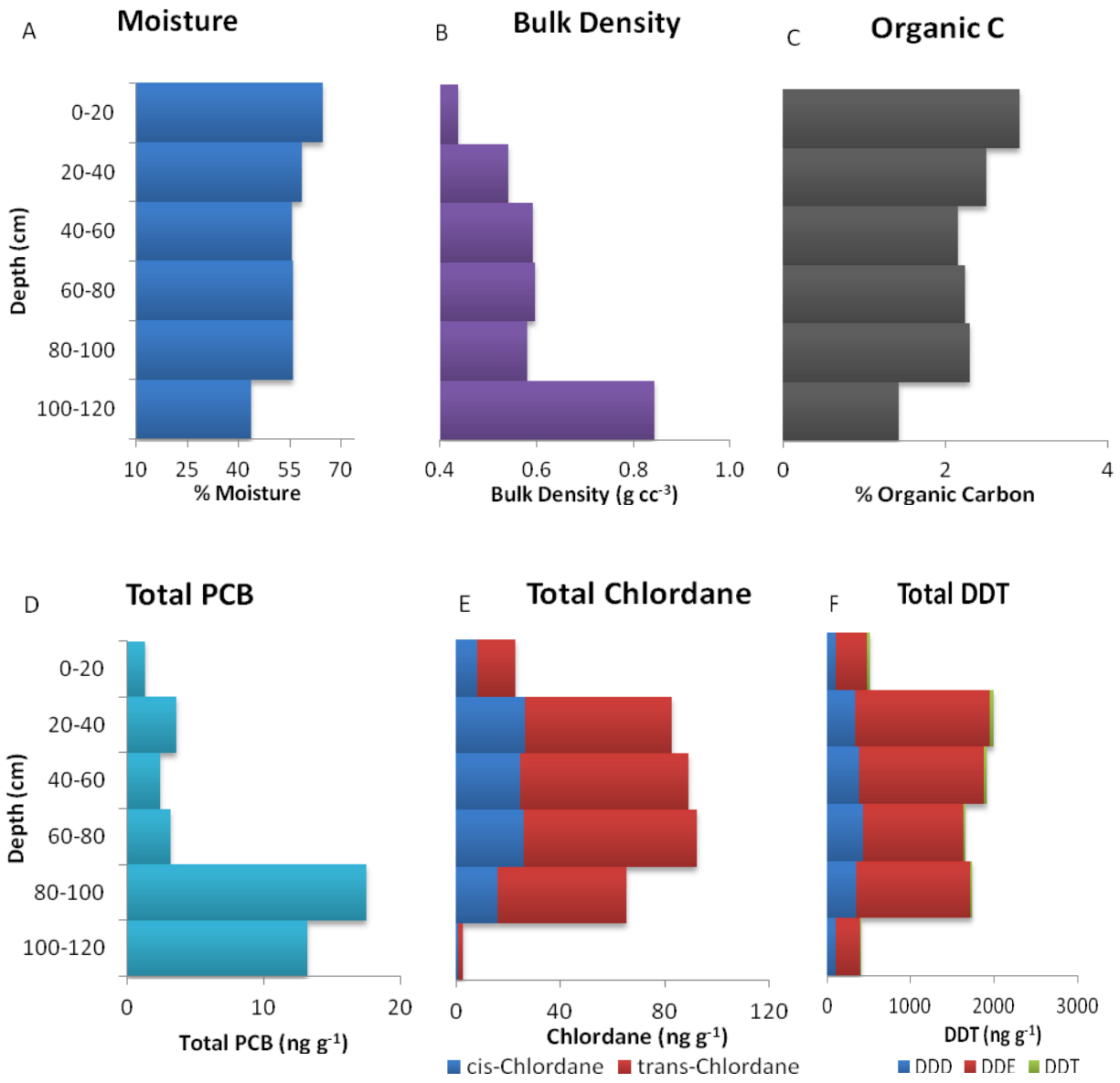

Figure 3.6. Soil properties and concentrations of the three target pollutant classes with depth at Site 3 along the sampling transect.

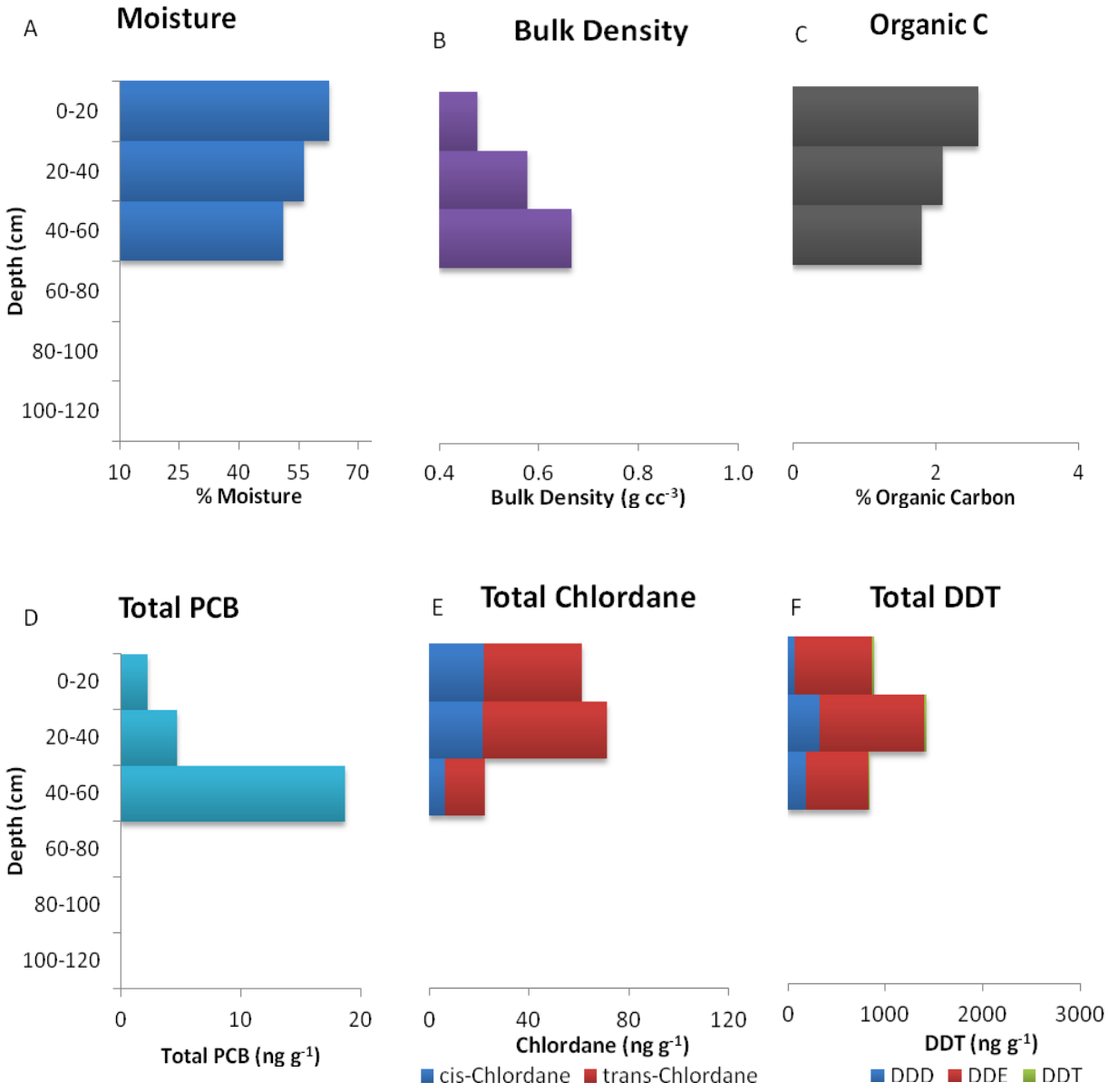

Figure 3.7. Soil properties and concentrations of the three target pollutant classes with depth at Site 4 along the sampling transect.

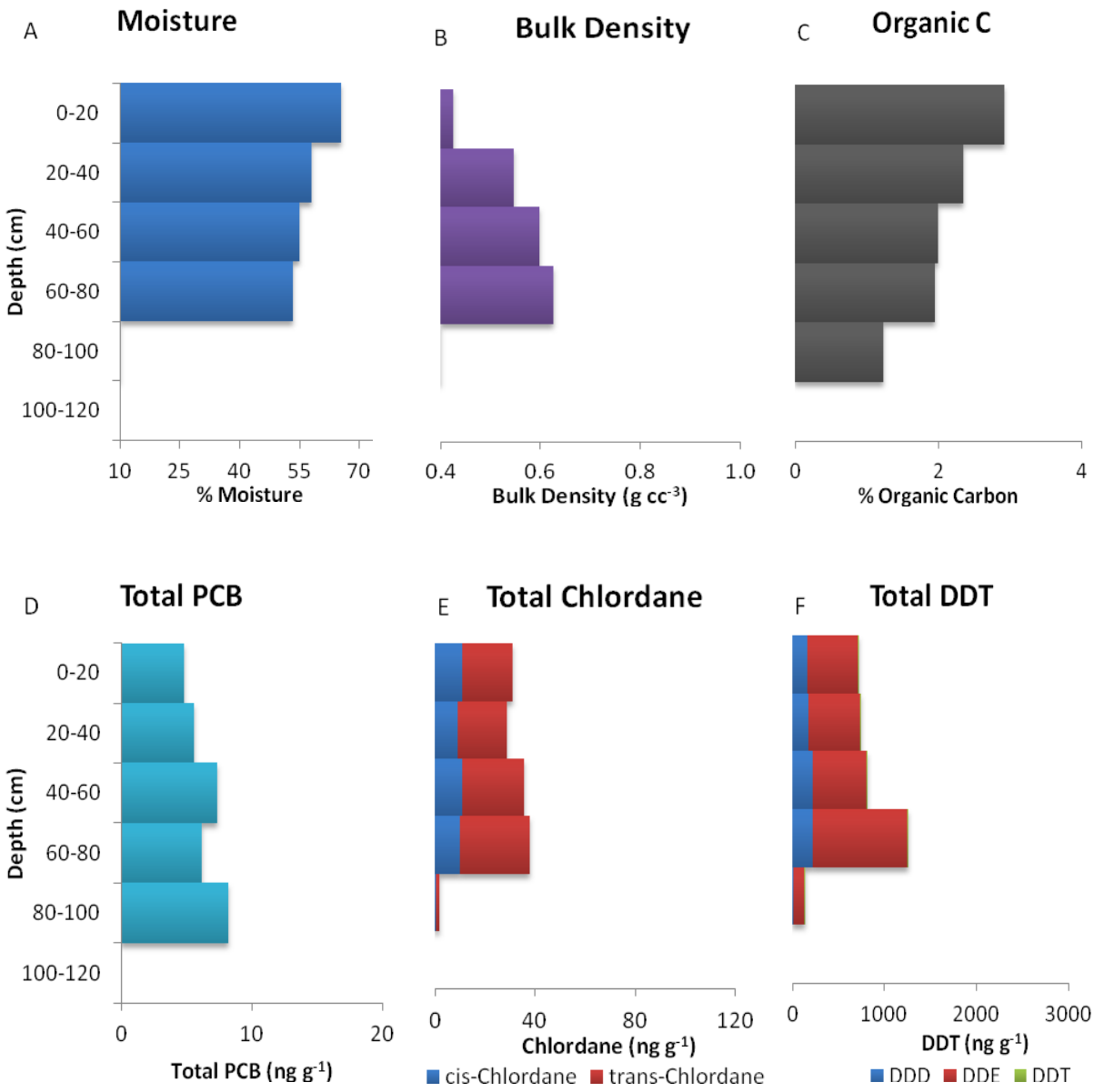

Figure 3.8. Soil properties and concentrations of the three target pollutant classes with depth at Site 5 along the sampling transect.

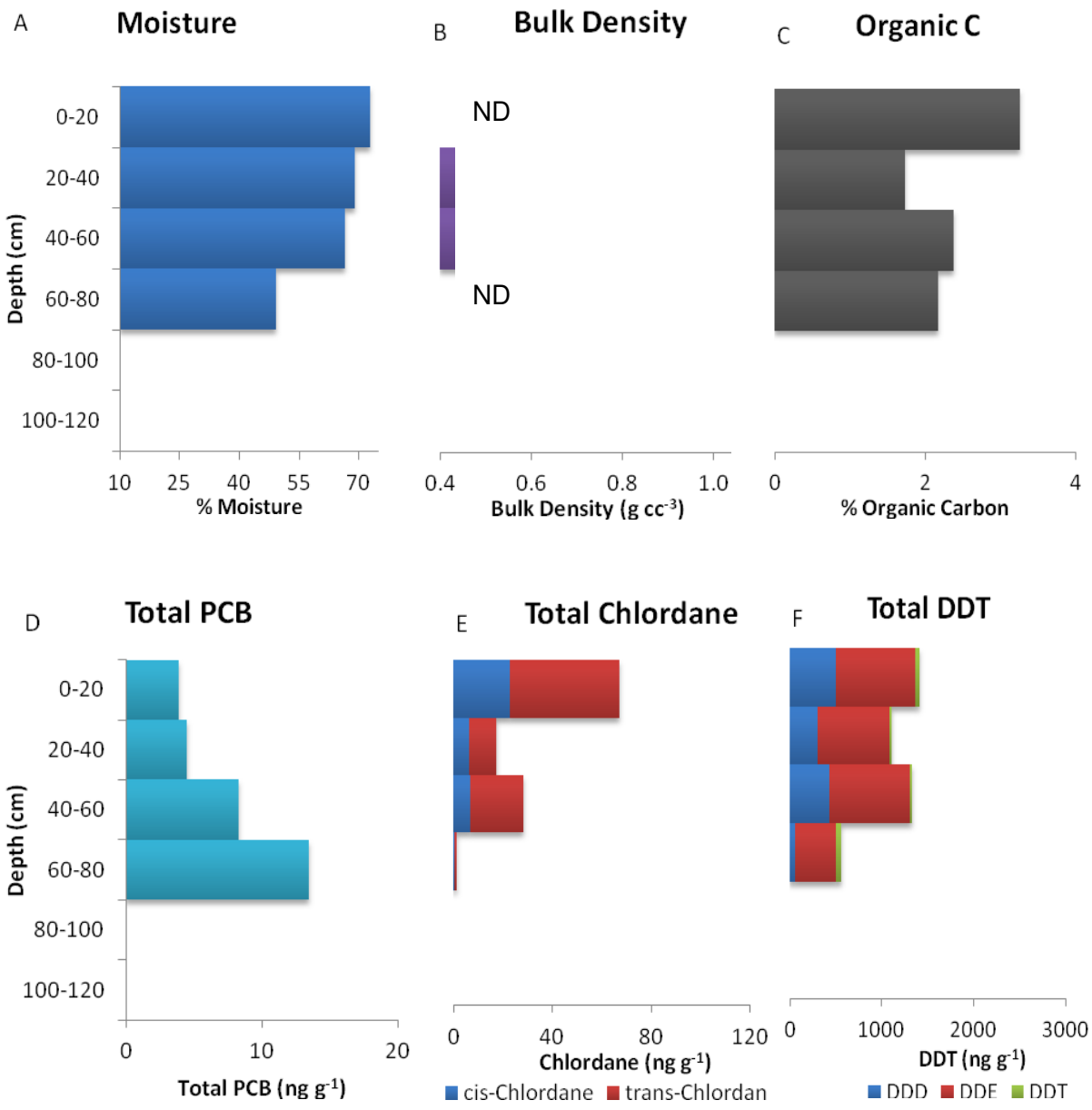

Figure 3.9. Soil properties and concentrations of the three target pollutant classes with depth at Site 6 along the sampling transect.

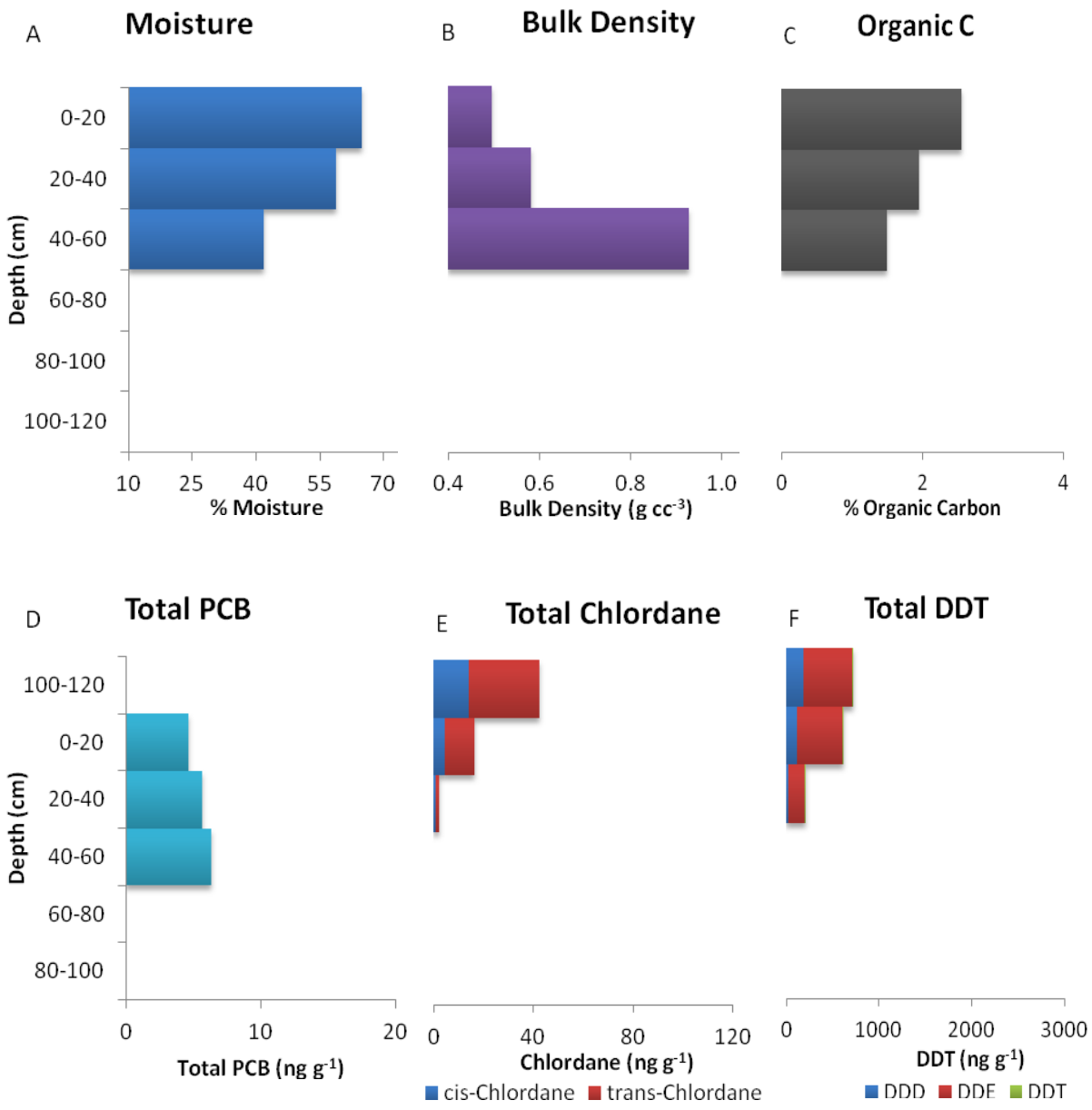

Figure 3.10. Soil properties and concentrations of the three target pollutant classes with depth at Site 7 along the sampling transect.

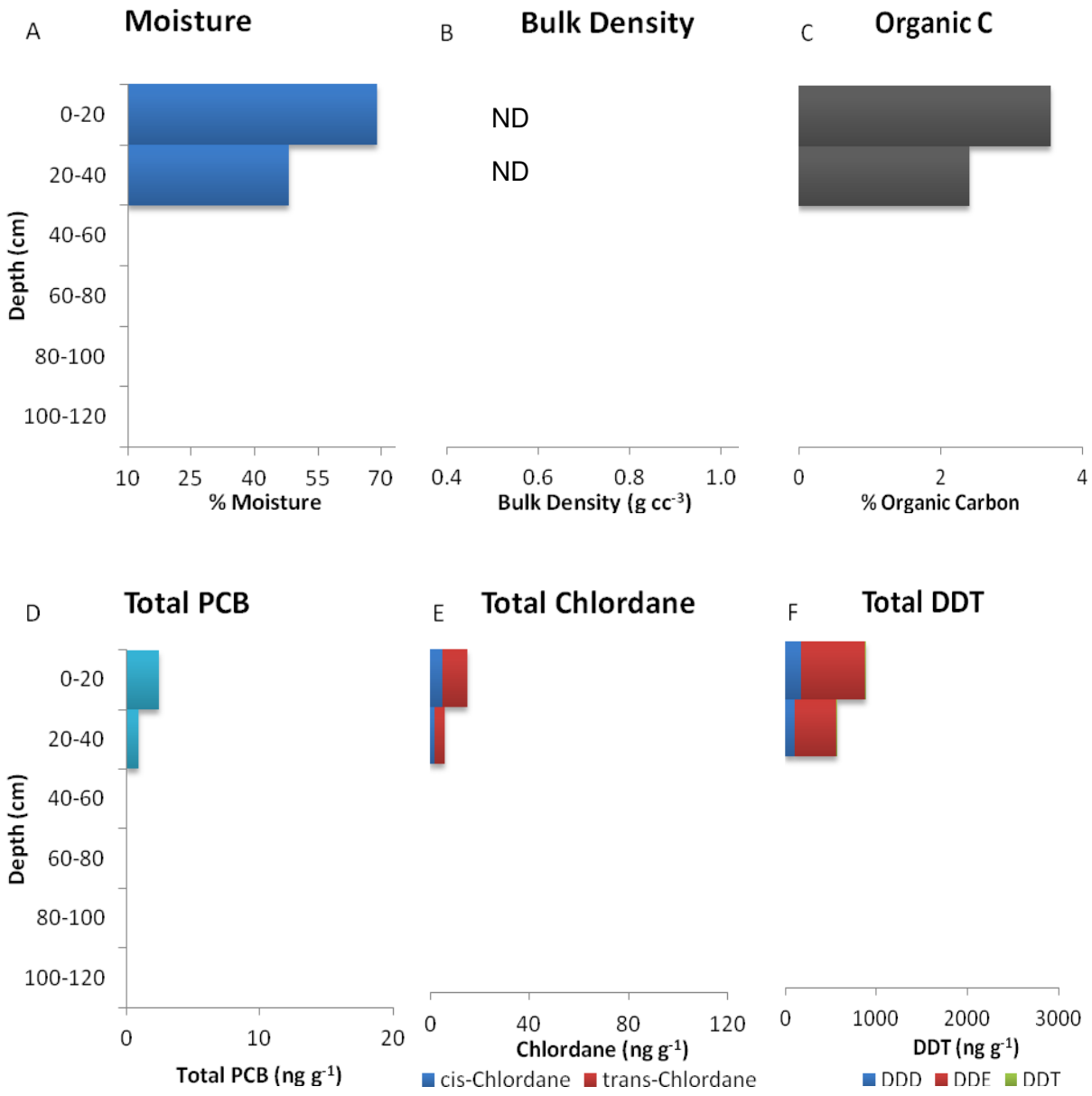

Figure 3.11. Soil properties and concentrations of the three target pollutant classes with depth at Site 8 along the sampling transect.

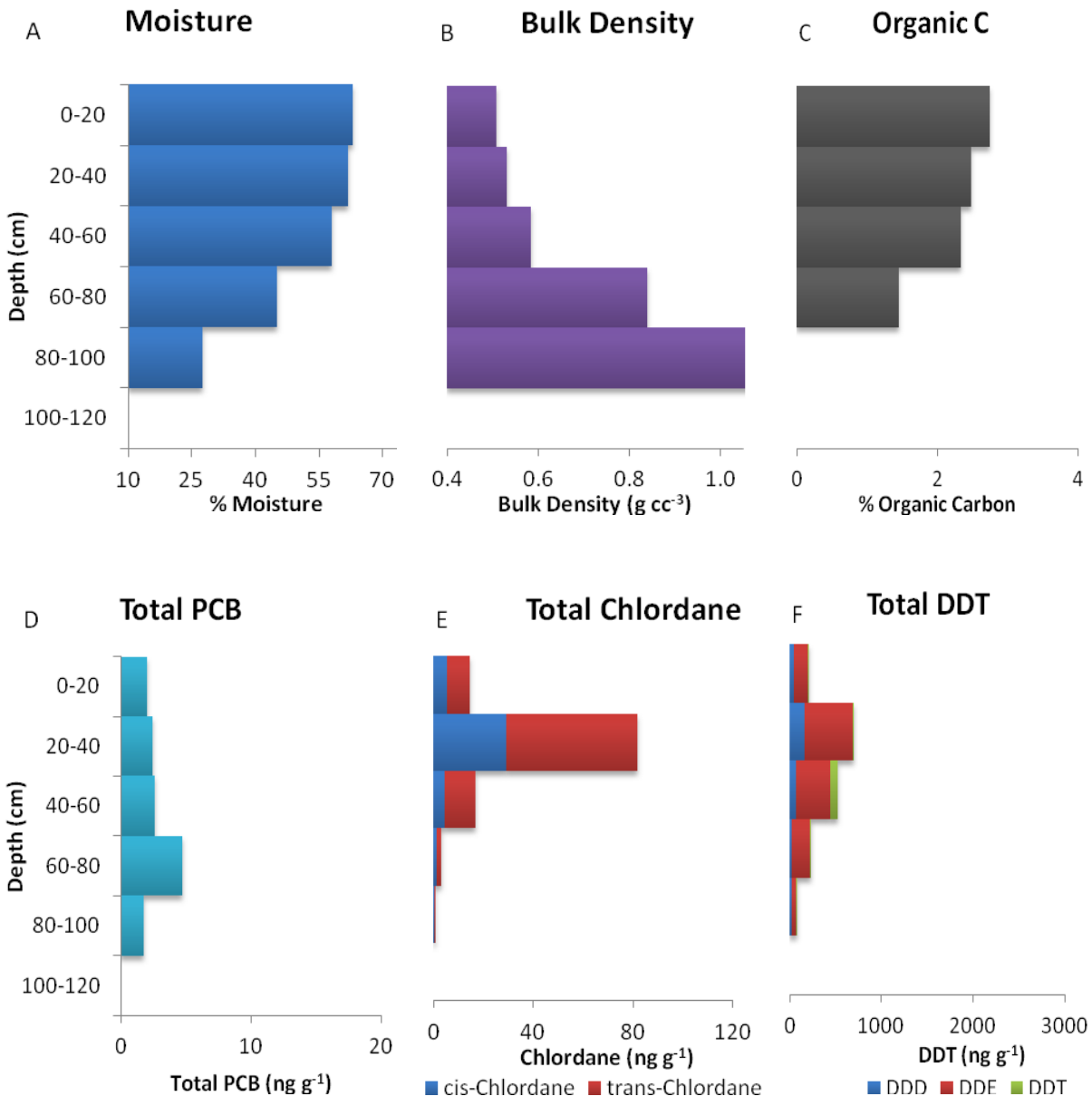

Figure 3.12. Soil properties and concentrations of the three target pollutant classes with depth at Site 9 along the sampling transect.

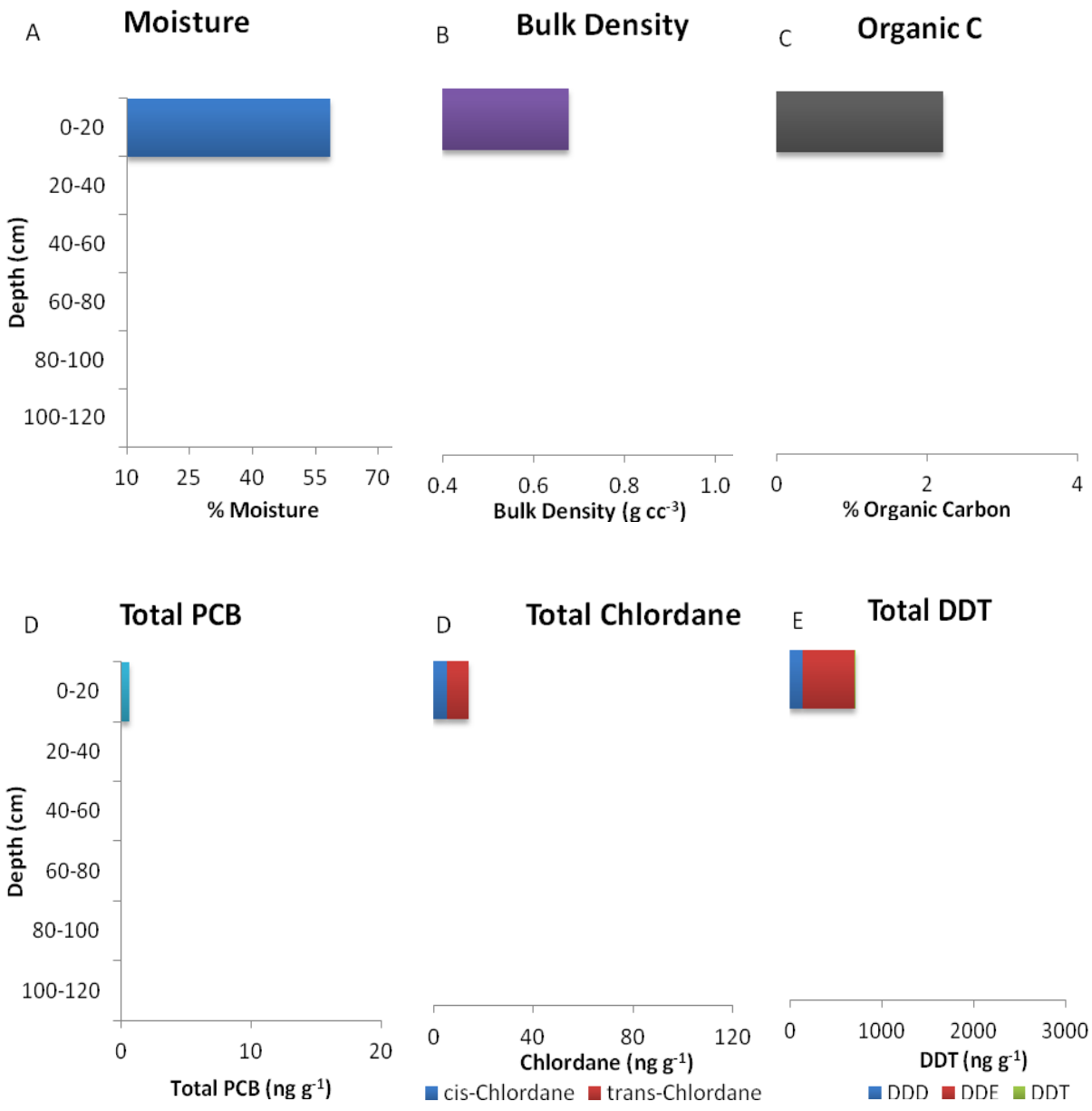

Figure 3.13. Soil properties and concentrations of the three target pollutant classes with depth at Site 10 along the sampling transect.

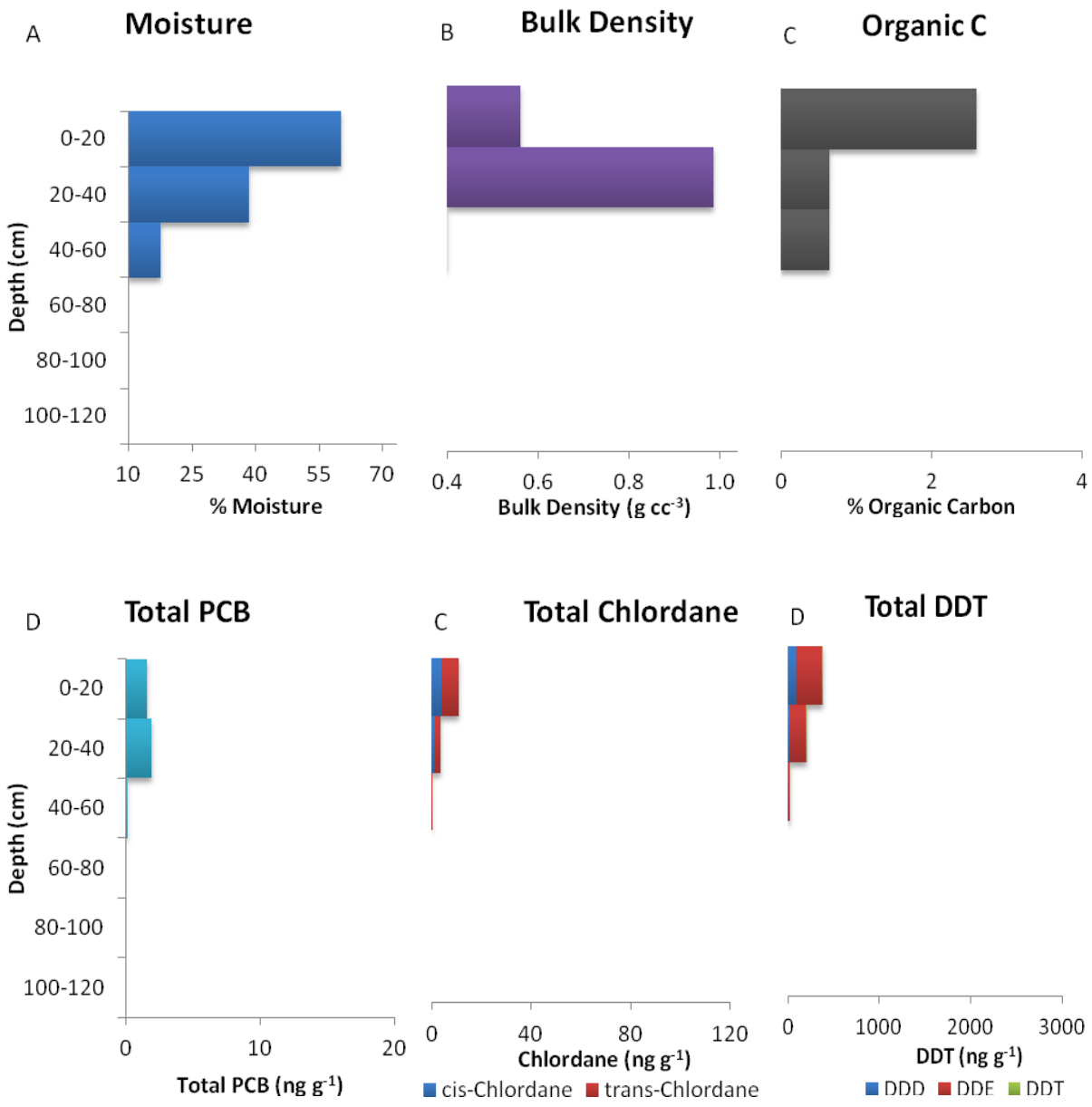

Figure 3.14. Soil properties and concentrations of the three target pollutant classes with depth at Site 11 along the sampling transect.

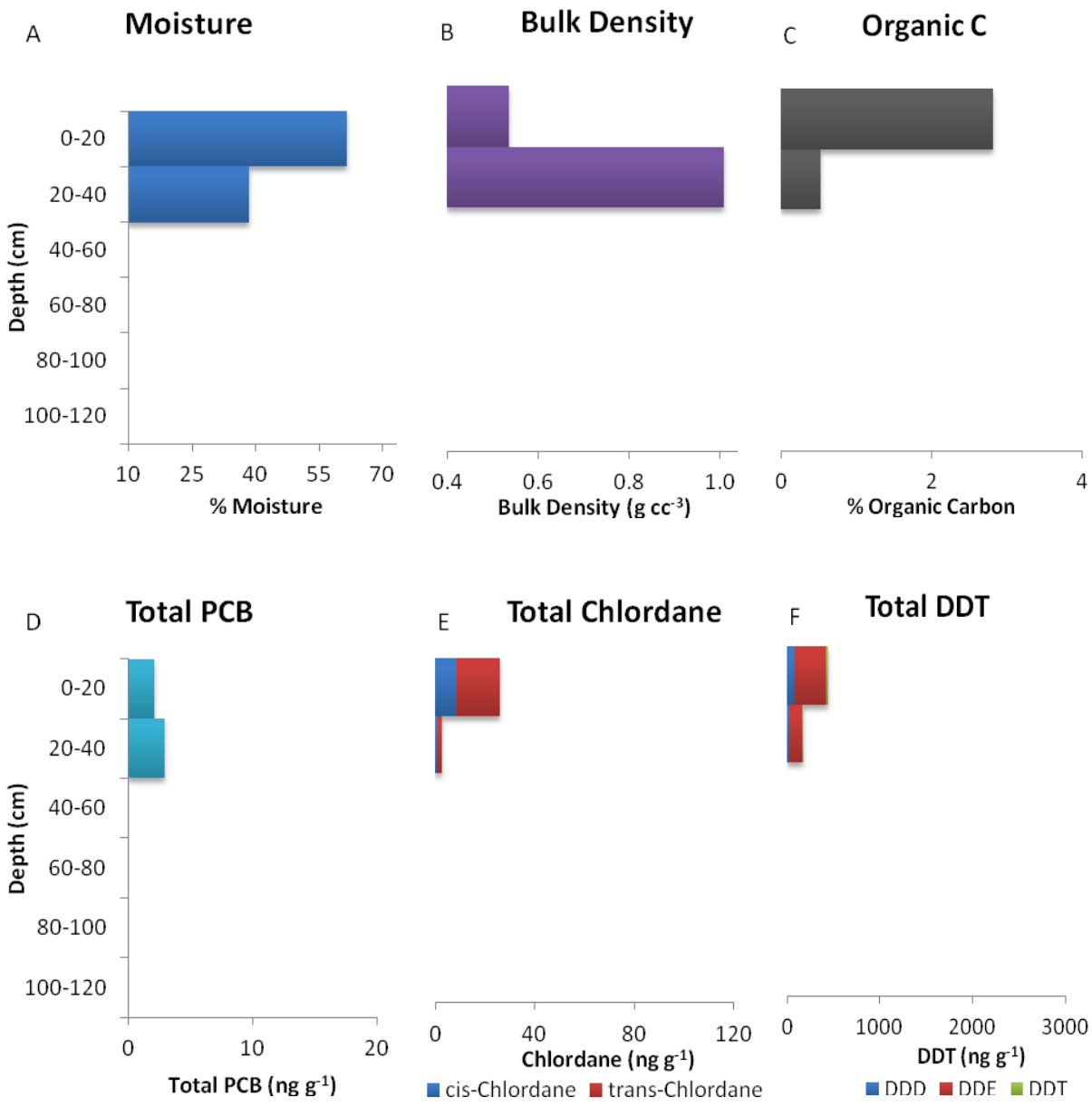

Figure 3.15. Soil properties and concentrations of the three target pollutant classes with depth at Site 12 along the sampling transect.

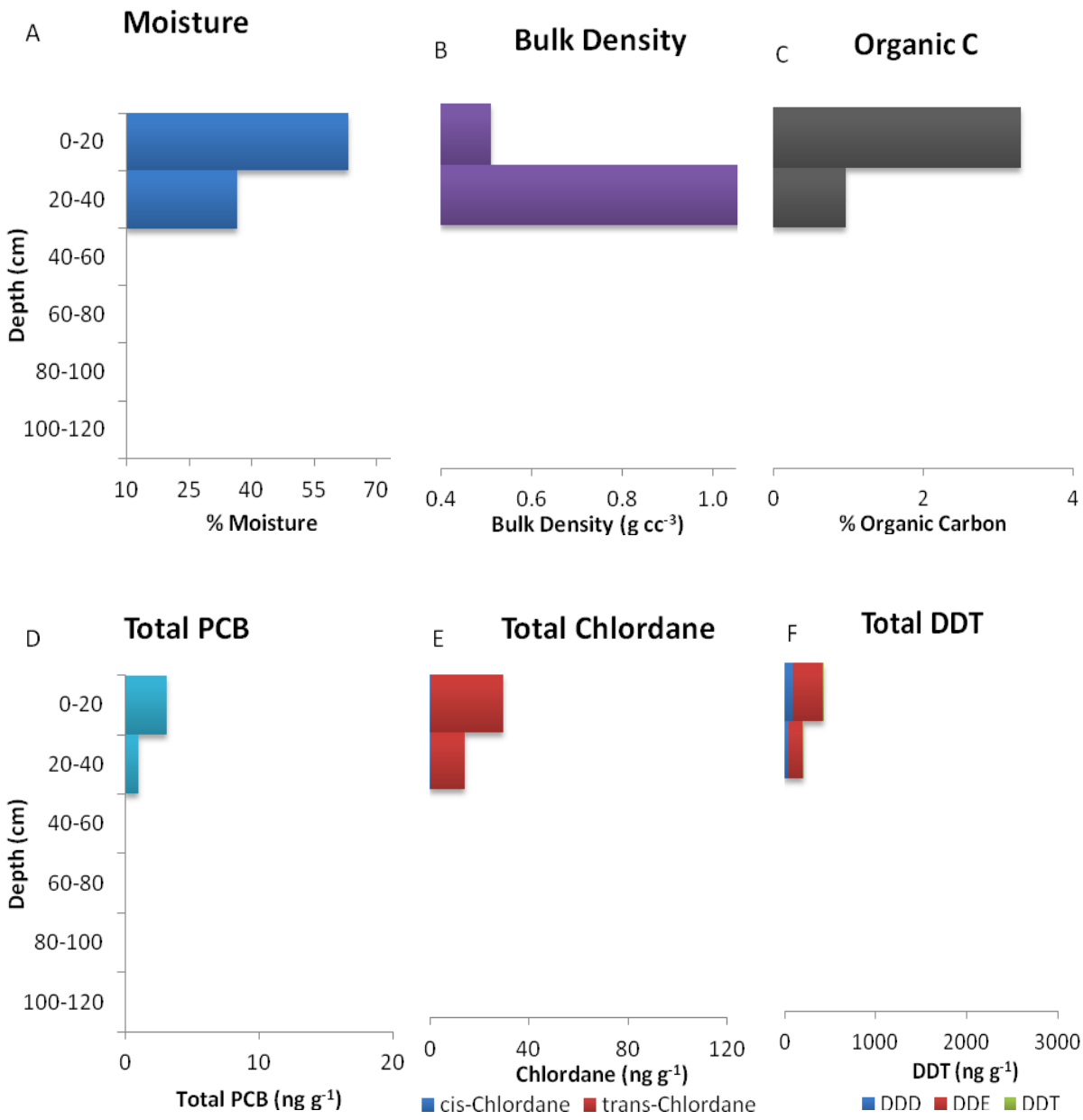

Figure 3.16. Soil properties and concentrations of the three target pollutant classes with depth at Site 13 along the sampling transect.

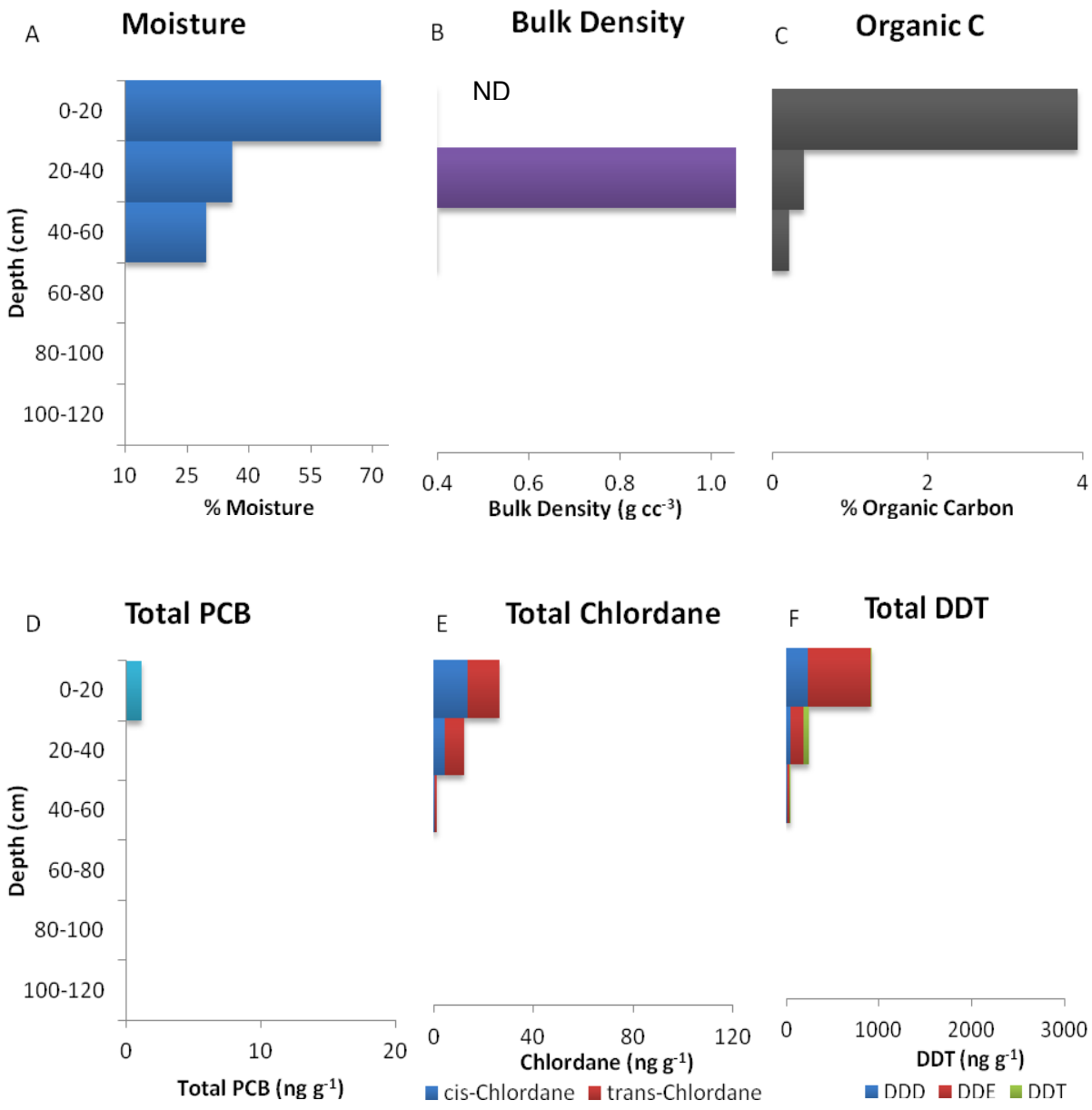

Figure 3.17. Soil properties and concentrations of the three target pollutant classes with depth at Site 14 along the sampling transect.

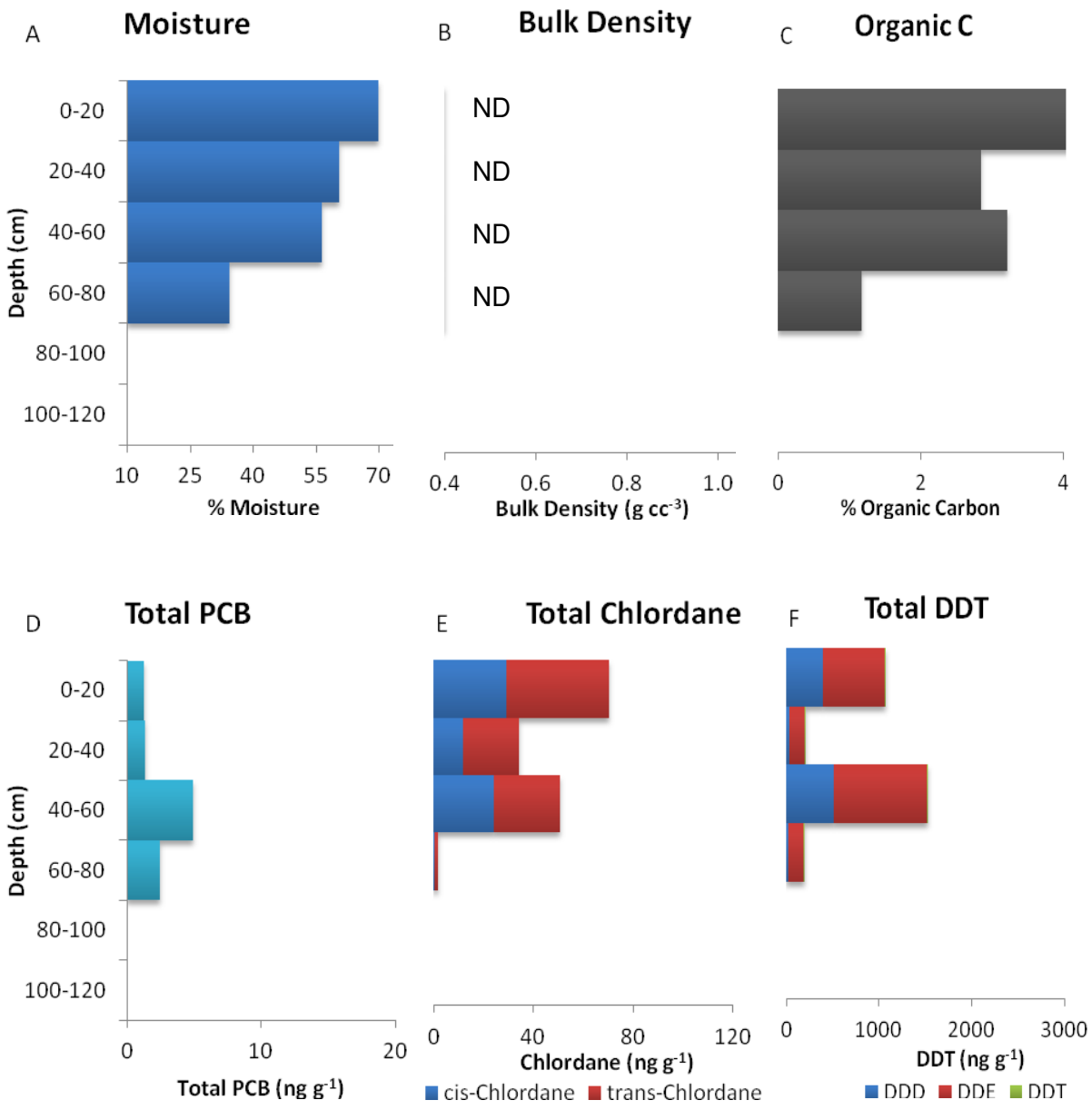

Figure 3.18. Soil properties and concentrations of the three target pollutant classes with depth at Site 15 along the sampling transect.

DDT and Derivatives

High concentrations of total DDT (taken as the sum of o,p-DDD, o,p-DDE, p,p-DDD, o,p-DDT, p,p-DDE and p,p-DDT) were present in the sediments (Table 3.2). The concentration of total DDT varied with depth, with consistently lower levels present at the bottom of the cores (Figs. 3.4 – 3.18). The bottom of the cores at sites less than 100 cm in depth reflected the contact with the dunal sand that forms the lake basin there and is often associated with a marked reduction in % water content. Total DDT averaged 919 ng g^{-1} in the sediment samples, and exceeded the effects range low (ERL) guidelines compiled by the National Oceanographic and Atmospheric Administration (1.58 ng g^{-1}) in all samples analyzed (Table 3.2). The concentration gradient with depth can be seen for total DDT in panel F on Figs. 3.4-3.18.

p,p-DDE was the dominant form of DDT present in the sediments (Table 3.2), accounting for an average of 75% of the total DDT found. DDE is formed from dehydrochlorination of DDT under aerobic conditions and is the most common form in historically contaminated soils and waters. The mean concentration of total DDE (p,p-DDE and o,p-DDE) was 644 ng g^{-1} and exceeded its ERL value of 2.2 ng g^{-1} in all (100%) of the core samples by a wide margin (Table 3.2). The sum of the DDD species (o,p-DDD and p,p-DDD) averaged 224.4 ng g^{-1} in the core samples and exceeded the ERL for DDD (2 ng g^{-1}) in 100% of the samples analyzed as well (Table 3.2). p,p-DDT was found in much lower concentrations in the sediments (mean value of 21.5 ng g^{-1}) relative to most of the other species, but still exceeded its ERL value in 85% of samples (one should note that the ERL listed in Table 3.2 for DDT is based upon the sum of concentrations of both p,p'-DDT and o,p'-DDT, although it was not possible to fully resolve o,p'-DDT from p,p'-DDD under the chromatographic conditions used here, so mass recovered was assigned exclusively to the more dominant p,p'-DDD species).

Table 3.2. Concentrations of DDT and related compounds in core samples.

		Sediment Concentration (ng g^{-1})		
Compound	**ERL[a]**	**Mean (n=54)**	**Range**	**ERL Exceedance**
Total DDT	1.58	919.1	16.2 - 2914	54 (100%)
DDE	2.2	644.4	13.8 - 1637	54 (100%)
DDD	2	224.4	4.3 – 1212	54 (100%)
(pp) DDT	1	21.5	BD - 77.2	46 (85%)
Total PCB	22.7	4.5	BD - 18.7	0 (0%)
Total Chlordane	0.5	34.9	0.1 - 115.0	51 (94%)

[a]*Effects Range Low concentration compiled by NOAA (Buchman, 1999);*

Notwithstanding, it is clear that DDT and its daughter products that are more commonly found in contaminated sediments and waters are at levels that exceed, often by a wide margin, effects range low concentrations throughout much of the sediment in McGrath Lake. Moreover, the concentrations found here are broadly similar to values reported by Jacobi et al. (1999). In that study, they found total DDT concentrations in the surface (0-5 cm) sediments that ranged from 919 - 3488 ng g^{-1} (Jacobi et al., 1999). This can be compared with concentrations that ranged from 16 - 2914 ng g^{-1} (Table 3.2). Surface (0-20 cm) sediment concentrations (199 - 1416 ng g^{-1}) of DDT were somewhat lower than the levels found in 1998 however. This may be due to the greater thickness of the surface sediment sampled here, burial, or other mechanisms. The concentrations measured by Jacobi et al. (1999) at other sediment depths were sometimes slightly higher at the 35-65 cm depth interval than at the surface, especially near the northern half of the lake.

While it is difficult to conclude that the total DDT concentration has changed markedly in the past 12 years, it does appear that p,p'-DDT has decreased in concentration and the relative concentration of the metabolites have increased. This can be seen by noting that the concentration ratio of p,p'-DDT to p,p'-DDE has decreased from a range of 0.13-0.54 (mean of 0.21±0.11) in surface samples in 1998 (Jacobi et al., 1999) to 0.001-0.088 (mean of 0.039±0.023) in surface samples reported herein. These decreases may indicate microbial transformations over time.

In comparison to other contaminated sites within the region, the concentrations of DDT (and its degradation products) are found at higher concentrations in the sediments of McGrath Lake (Table 3.3). The values of DDT from other contaminated areas, such as the Salton Sea, San Francisco Bay, Colorado River Delta and the Sacramento River are their highest at 205 ng g^{-1} for total DDT, whereas the maximum sediment values for total DDT in McGrath Lake reach 2914 ng g^{-1}. The maximum values of DDT derivatives in McGrath Lake all exceed the maximum values reported in the Salton Sea and Sacramento River (Table 3.3).

Total Chlordane

Core samples were also analyzed for total chlordane concentrations (cis-chlordane and trans-chlordane). The surface concentrations of total chlordane averaged 36.47 ng g^{-1}, while lower concentrations were found at increasing depth within the sediments for most sties. Sites 1, 9, 11 and 12 all show an increasing concentration below the surface sediment with a

maximum concentration between 60 – 80 cm. Site 13 had an increase in concentration between 20 – 40 cm, but a sharp decline below this depth. The pattern of chlordane concentration at depth is nearly identical to the trend for total DDT concentration at each site. The mean cis-chlordane concentration was 34.9 ng g^{-1}, with 51 samples exceeding the ERL value of 0.5 ng g^{-1} (Table 3.2). The trends in cis-, trans- and total chlordane with depth at each site can be seen in panel E of Figs. 3.4-3.18.

The total chlordane concentrations found in McGrath Lake also exceed those generally found in the literature, although not to the extent of DDT. Total chlordane values in McGrath Lake were between 0.1 to 115 ng g^{-1}, while concentrations in the Colorado River did not exceed 3.03 ng g^{-1} (Table 3.3).

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Table 3.3. Concentrations of previously published literature and values obtained in this study for DDT (it's derivatives), chlordane and PCBs.

	Colorado River Delta[a]	**San Francisco Bay[b]**	**Salton Sea[c]**	**Sacramento River[d]**	**McGrath Lake**
	ng g^{-1}				
op-DDE				<0.5 - 2.14	0.7 - 99.4
pp-DDE			<0.15 - 30	0.84 - 33.9	13.1 - 1545
∑ DDE			<0.15 - 30		13.8 - 1637
op-DDD			<0.12 - 6.7	<0.84 - 25.1	0.5 - 335
pp-DDD			<0.16 - 2.8	<1.04 - 58.1	
∑ DDD			<0.16 - 6.7		4.3 - 1212
op-DDT			<0.12 - 4	<0.5- 21.1	
pp-DDT				<0.5 - 67.4	BD - 77.2
∑ DDT			<0.12 - 4	3.05 - 205	
Total DDT	BD - 46.9	<0.2 - 21	6.8 - 40.2		16.2 - 2914
trans-Chlordane					BD - 26.5
cis-Chlordane					0.1 - 89.4
Total Chlordane	BD - 3.03				0.1 - 115
∑PCB (LMW)	BD - 2.34		48 - 239		BD - 2.22
∑PCB (HMW)	0.02 - 2.90		22 -131		BD - 16.65
Total PCB	0.7 - 4.9	0.8 - 34	116 - 304		BD - 18.7

[a]Lugo-Ibarra et al. 2011; [b]Venkatesan et al. 1999; [c]Sapozhnikova et al. 2004; [d]Hwang et al. 2009

Total PCB

The total PCB concentrations were low in our sampling (Table 3.2). Concentrations of total

PCBs in the surface (0-20 cm) depth interval were between 0.4 – 4.8 ng g^{-1} (average 2.3 ng g^{-1}) a range much lower than that reported by Jacobi et al. (1999) (41.4 – 309.5 ng g^{-1}). The concentrations in all samples are below the ERL for total PCBs of 22.7 ng g^{-1}(Table 3.2). The vertical distribution of total PCBs was also different, with higher concentrations often at the lower depth intervals, while Jacobi et al. (1999) generally found reduced concentrations at depth. The change in concentration of total PCBs with depth can be seen in panel D of Figures 3.4-3.18. The basis for the apparent inconsistency in total PCB concentrations between the two sampling events is not clear, although different analytical methods were used. The tandem mass spectrometer allowed identification and quantitation of 41 different congeners (with PCB pairs 138/158 and 153/168 eluting from the GC column simultaneously and the total concentration of each pair being calculated), with reasonable recovery of PCB-65 and PCB-209 congeners in samples (101±14% and 91±14%, respectively) and low average relative percent error in duplicates (13%).

The reported values of total PCBs in Salton Sea sediment were 116 – 304 ng g^{-1}, while the values from the Colorado River Delta (0.7 – 4.9 ng g^{-1}) and San Francisco Bay (0.8 – 34 ng g^{-1}) were similar to concentrations in McGrath Lake (BD – 18.7 ng g^{-1}) (Table 3.3). The sediments of McGrath Lake also contained higher concentrations of high molecular weight (HMW; Congeners 87 to 206) PCBs compared to the Salton Sea. Low molecular weight (LMW; 18 to 81) PCBs are more volatile and water soluble than HMW PCBs. Therefore, the HMW PCBs were likely deposited in McGrath Lake by a nearby source, while the LMW PCBs could be from a nearby source or have been transported to McGrath Lake.

3.2.2 Geospatial analysis

Geospatial analysis was used to develop maps and derive volume estimates for the distribution of the contaminants in the lake. Maps of OC pesticides and PCB contamination were developed using measured sediment contaminant concentrations combined with (corrected) hydroacoustic measurements of sediment thickness.

For this analysis, it was assumed that the primary gradient in concentration is down the long-axis of the lake, and that concentrations do not vary substantially on the short transverse axis. The lateral distribution in contaminant concentration within each layer was mapped using Surfer software with the kriging gridding algorithm (Figs. 3.19-3.21). The outline of the lake shoreline is shown in all figures, with the reduced area of sediments reflected in the lower

spatial extent with depth. It was not possible to core beyond 1.2 m depth due to lignin and other woody or cellulosic material in the sediments at the north end of the lake, so no samples were collected from the deeper sediment there, although as can be seen in the Figs 3.4-3.18 and Figs. 3.19-3.21, maximum OC pesticide and PCB concentrations were found at intermediate depths (generally 40-80 cm sediment depth).

Total DDT concentrations were greatest at the north end of the lake and at 60-80 cm depth, frequently exceeding 2000 ng g^{-1} (Fig. 3.19). Generally much lower concentrations were found in the southern part of the lake, indicating greater deposition of contaminants at the north end, presumably associated with soil particles eroded from the watershed. The reduction in total DDT levels near the surface presumably reflects phasing out of use in more recent times. It is worth noting that total DDT concentrations were above the ERL of 1.58 ng g^{-1} for virtually all sites and depths.

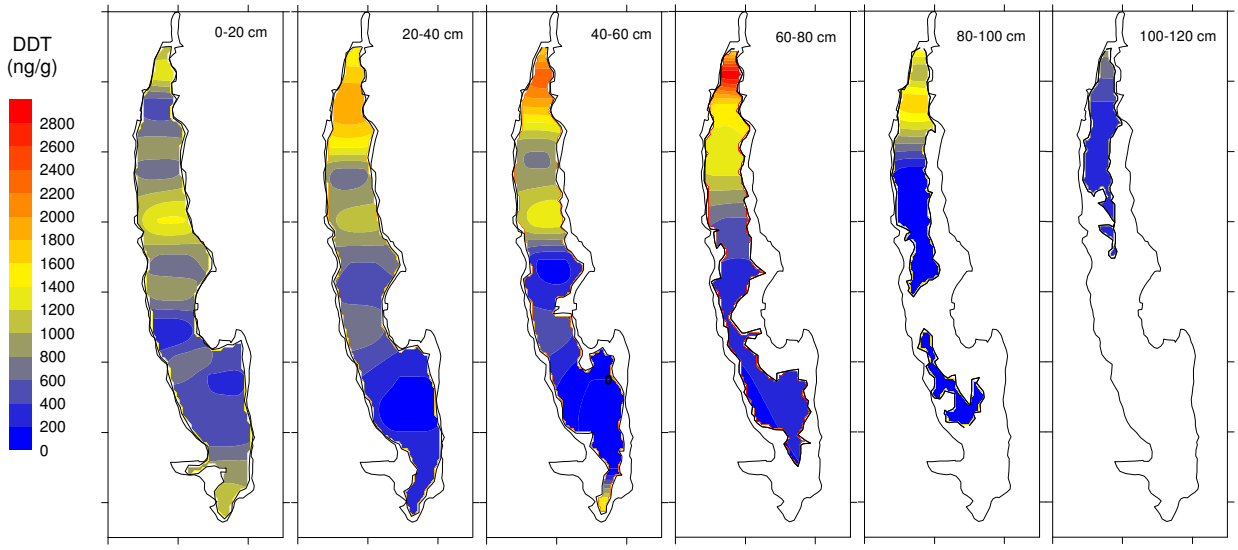

Fig. 3.19. Total DDT concentrations in McGrath Lake.

Total chlordane concentrations in the sediments exhibited broadly similar trends as DDT, with concentrations again higher in the north end of the lake, with maximum concentrations at 60-80 cm depth (Fig. 3.20). Both pesticides were widely used beginning in the 1950's and banned in the 1970's. Their similar vertical (and horizontal) distribution in the lake is consistent with their use and highly hydrophobic and recalcitrant chemical properties. As with DDT, total chlordane concentrations exceeded the ERL (0.5 ng g^{-1}) by a wide margin for almost every sample analyzed.

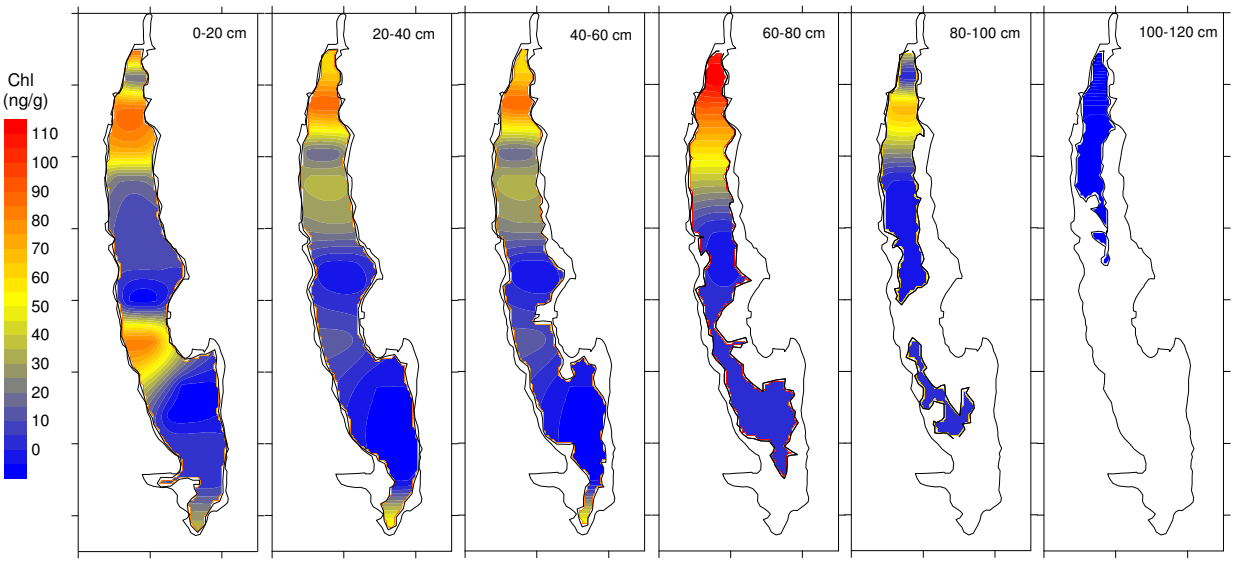

Fig. 3.20. Total chlordane concentrations in McGrath Lake.

The concentrations and distribution of total PCBs differed from that of total DDT and chlordane (Fig. 3.21). Most importantly perhaps, only relatively low concentrations were found in the sediments, with no samples exceeding the ERL of 22.7 ng g^{-1}. The distribution was also more variable, with only very low concentrations in the uppermost 20 cm of sediment; higher concentrations were found in the northern and central part of the lake at sediment depths >40 cm or so (Fig. 3.21).

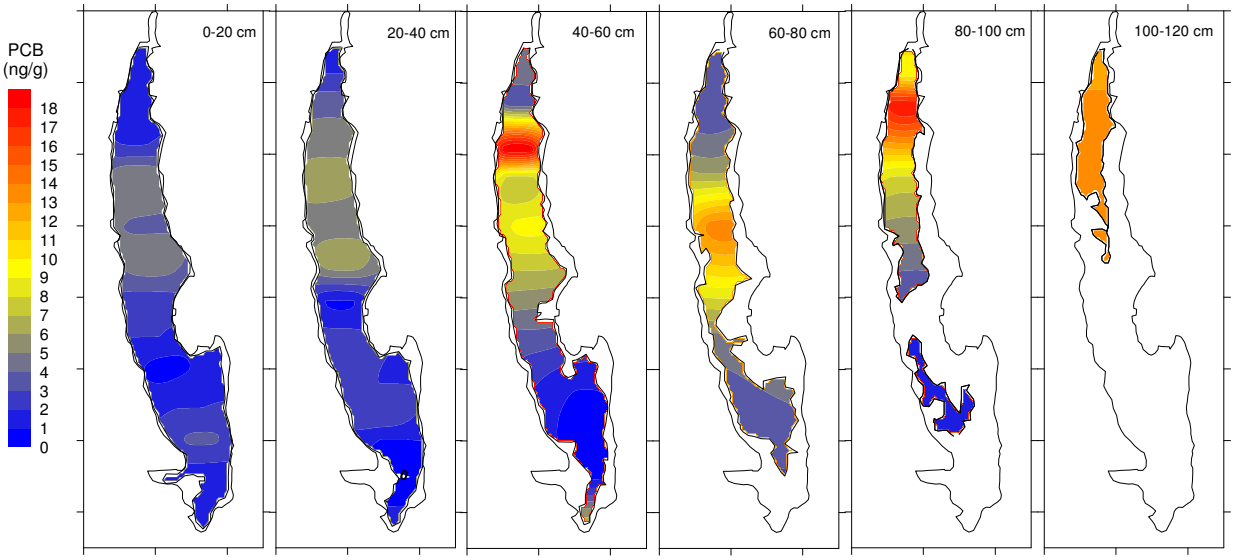

Fig. 3.21. Total PCB concentrations in McGrath Lake.

The lateral distributions of these contaminants in each of the depth intervals were used to determine the areas and volumes corresponding to given contaminant concentrations and develop sediment volume-concentration curves (Fig. 3.22). Thus, we see that virtually all of the sediment volume in the upper 1.2 m of sediments exceeds the ERLs for total DDT and total chlordane (almost 30,000 m^3). In contrast, no sediment volume exceeded the ERL for total PCBs, and about half of the sediment volume in the lake had total PCB levels below detection. The plots provide, then, a first estimate of the volume of sediment that would need to be removed to remediate the largest concentrations of DDT or chlordane. Since the average bulk density of the sediment in the upper 1 m of sediment is about 600 kg m^{-3}, one can also estimate the dry-weight mass of sediment.

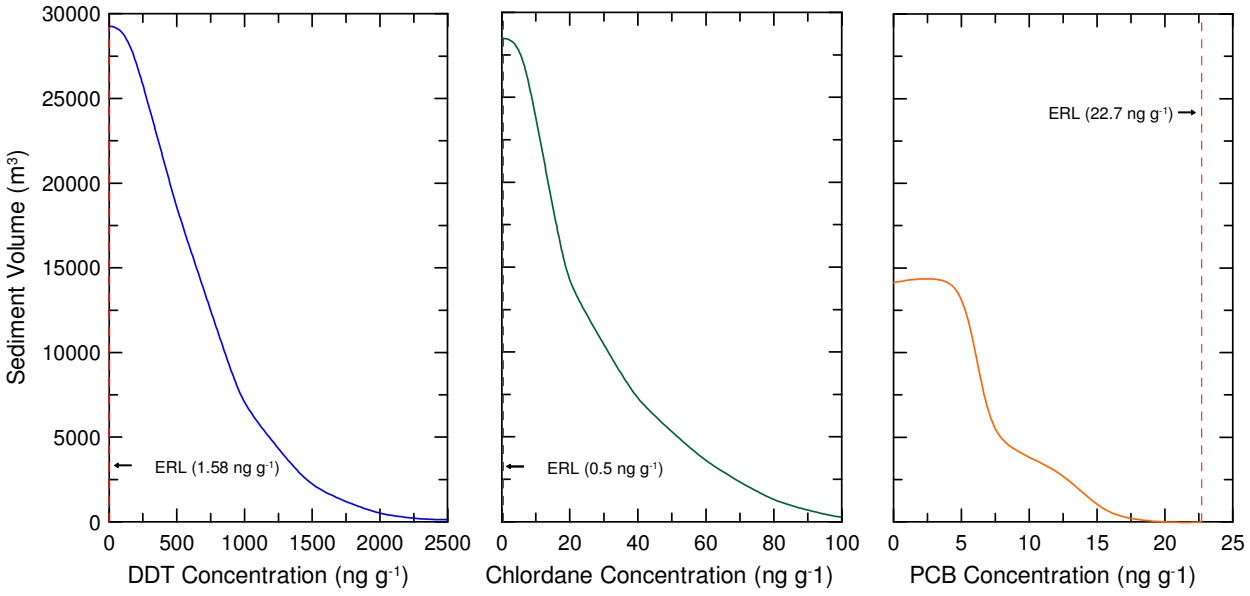

Fig. 3.22. Sediment volume vs. contaminant concentration: a) total DDT, b) total chlordane and c) total PCB.

3.2.3 Solid Phase Microextraction

Solid phase microextraction (SPME) was performed on all sites of at least 80 cm in depth to assess the freely dissolved concentrations of the OC pesticides. PCB analysis was not performed using SPME due to the low concentrations observed in the sediment. The freely dissolved concentrations of the OC pesticides represent the bioavailablity of the compounds of

interest and may provide further information about the nature of contamination in the lake. DDE was detected in all samples while DDD (29) and chlordane (29) were detected in most of 31 samples analyzed. DDT was only detected in 8 samples (Table 3.4). The free concentrations of OC pesticides did not exceed ERL for any sample but did exceed water column numeric targets for most samples.

Porewater samples were also extracted to determine the concentrations of each compound that was bound to dissolved organic matter (DOM). Instrument sensitivities are not as low for this extraction procedure (compared to SPME), therefore only (pp) DDE was regularly detected. There were only a handful of detections for the other compounds among all samples. The DOC, total DDT, total Chlordane and total dissolved pp-DDE concentrations are shown in Figs. 3.23-3.29. The range of freely dissolved concentrations in the McGrath Lake sediments are much higher than those found in two South China estuaries for DDT (DDE: BD – 0.146; DDD: 0.81 – 3.02; DDT: BD – 0.15 ng L^{-1}), although the total DDT sediment concentrations were less than 200 ng g^{-1} (Xing et al., 2009). Therefore the difference in freely dissolved concentrations of DDT may be due to the variation in sediment concentrations.

Table 3.4. Results from solid-phase microextraction analyses (concentration of freely dissolved and readily bioavailable contaminants).

Contaminant	Detections (n=31 samples)	Mean Conc (ng L^{-1})	Range Conc (ng L^{-1})
Total DDE	31	29.7	7.8 – 166.4
Total DDD	29	10.9	BD – 53.3
Total DDT	8	1.3	BD – 5.2
Total Chlordane	29	10.6	BD – 110.5

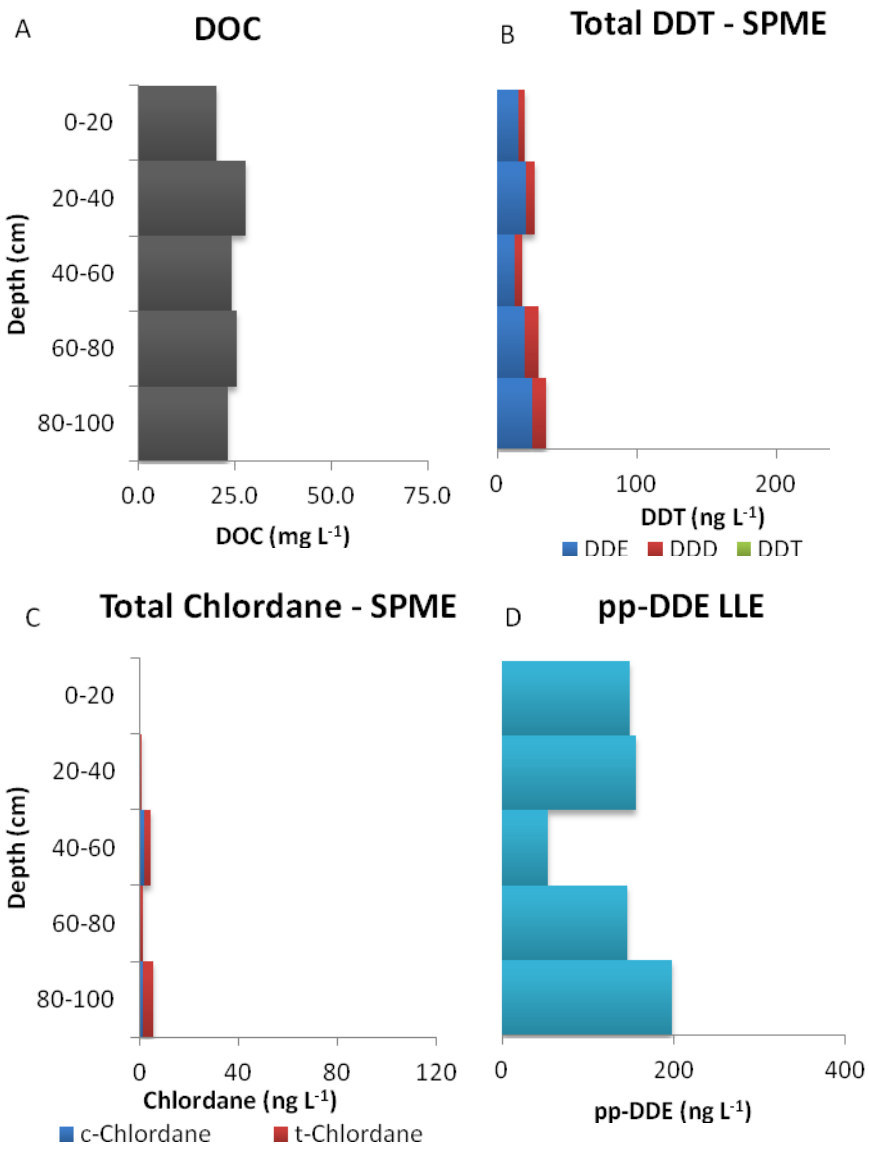

Fig. 3.23. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 1 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

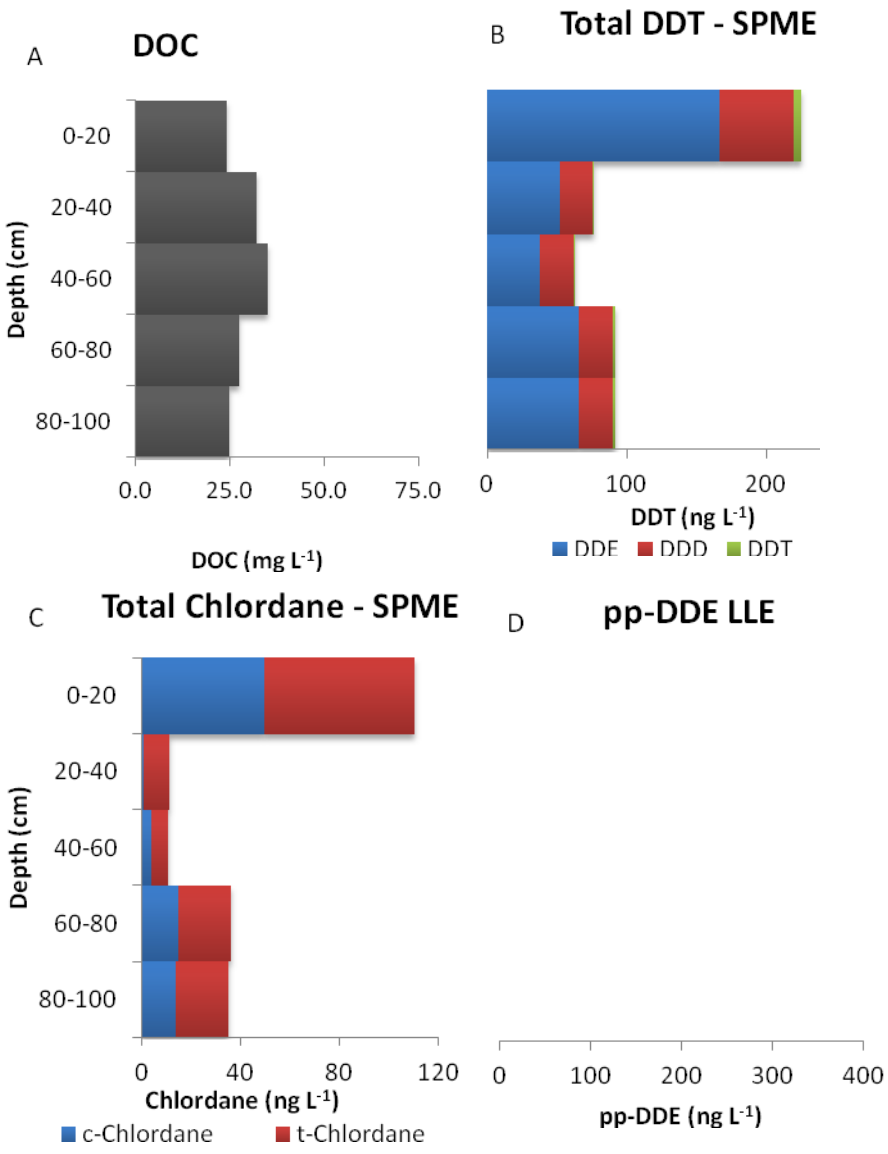

Fig. 3.24. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 2 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

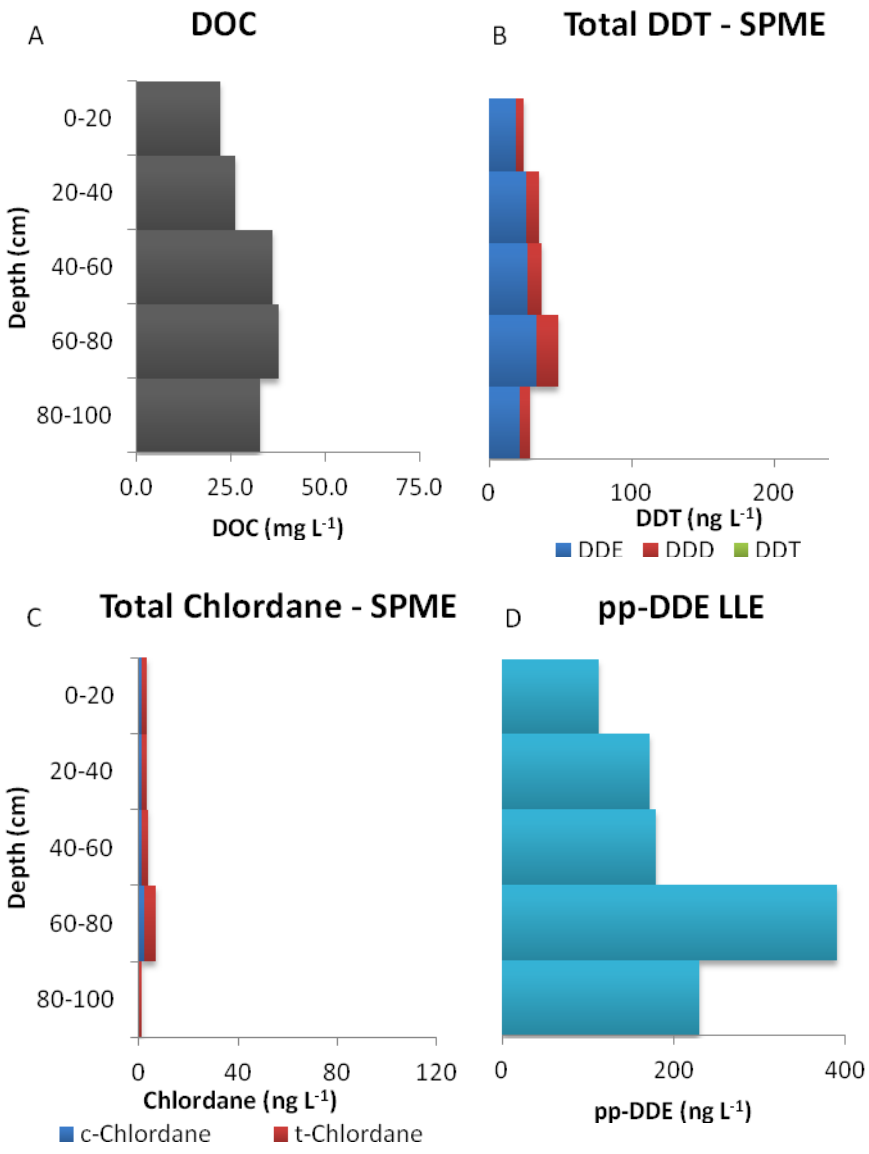

Fig. 3.25. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 3 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

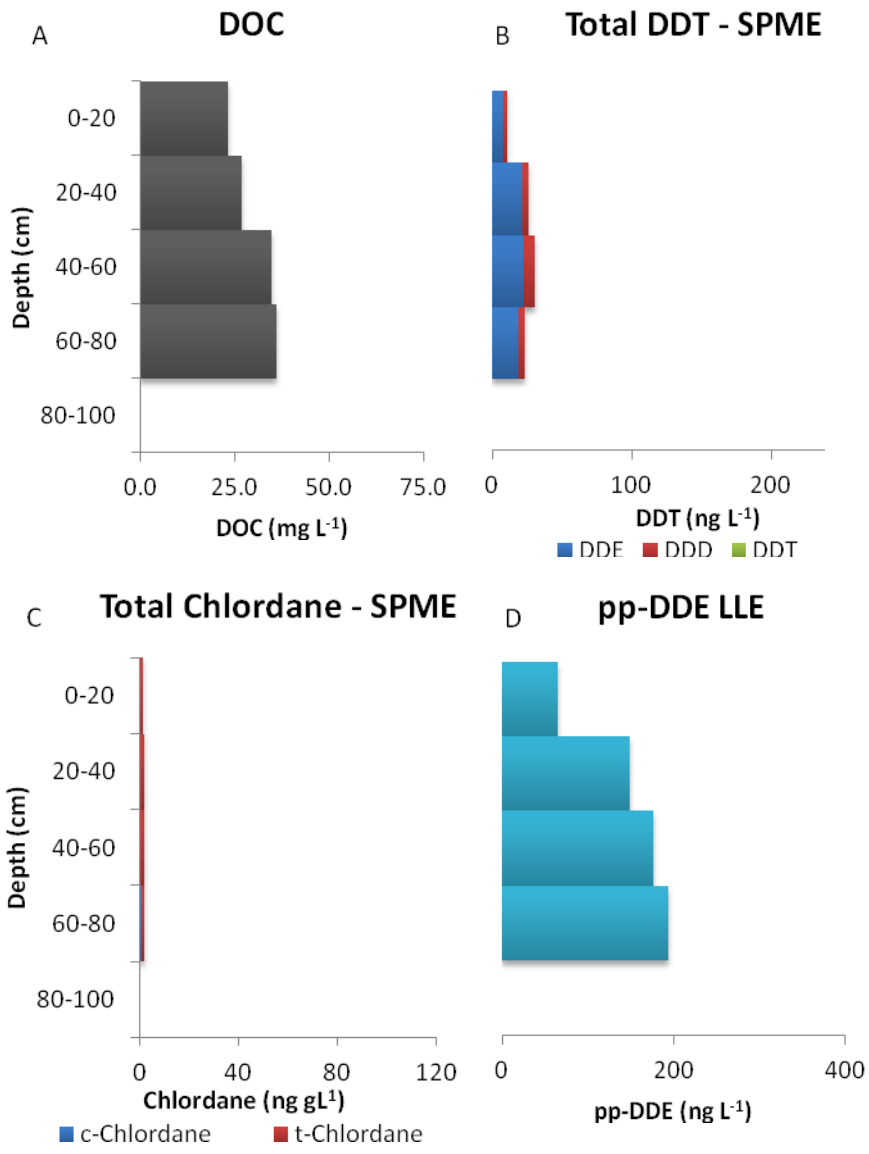

Fig. 3.26. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 5 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

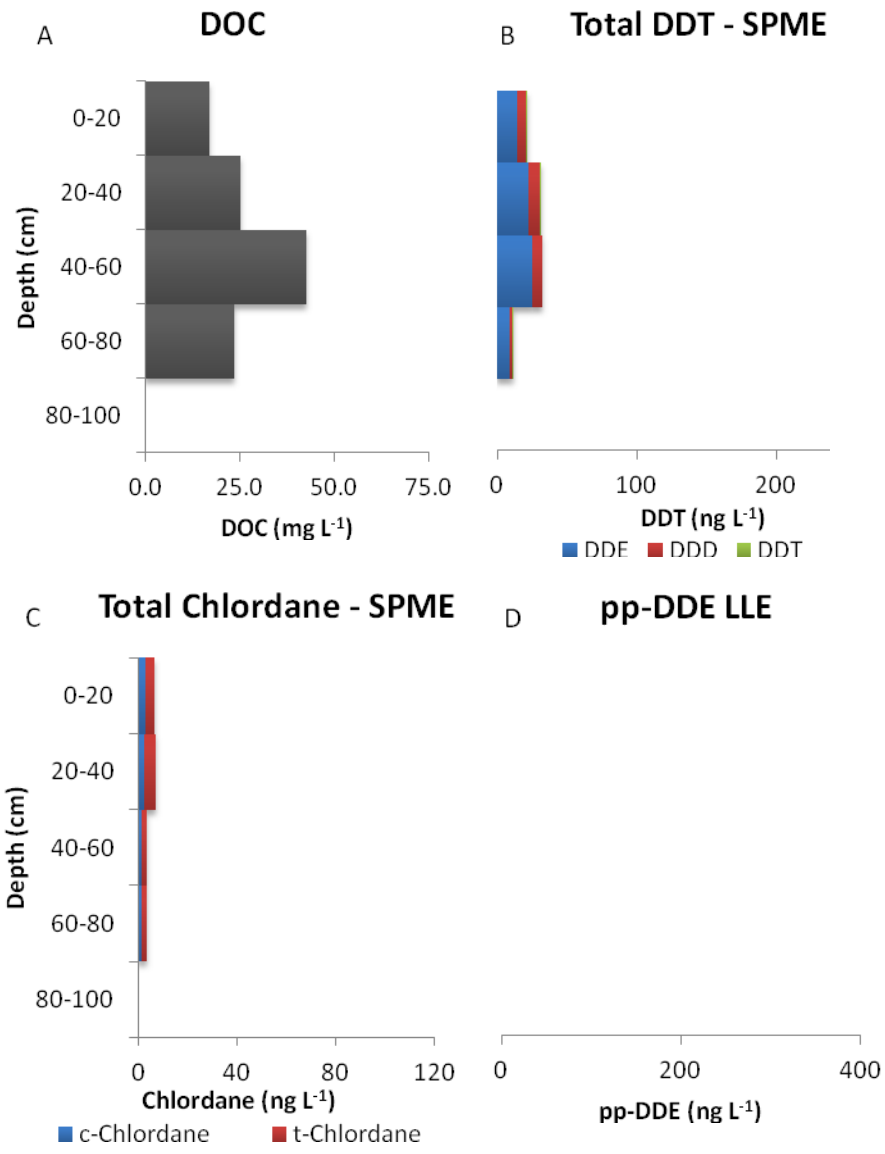

Fig. 3.27. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 6 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

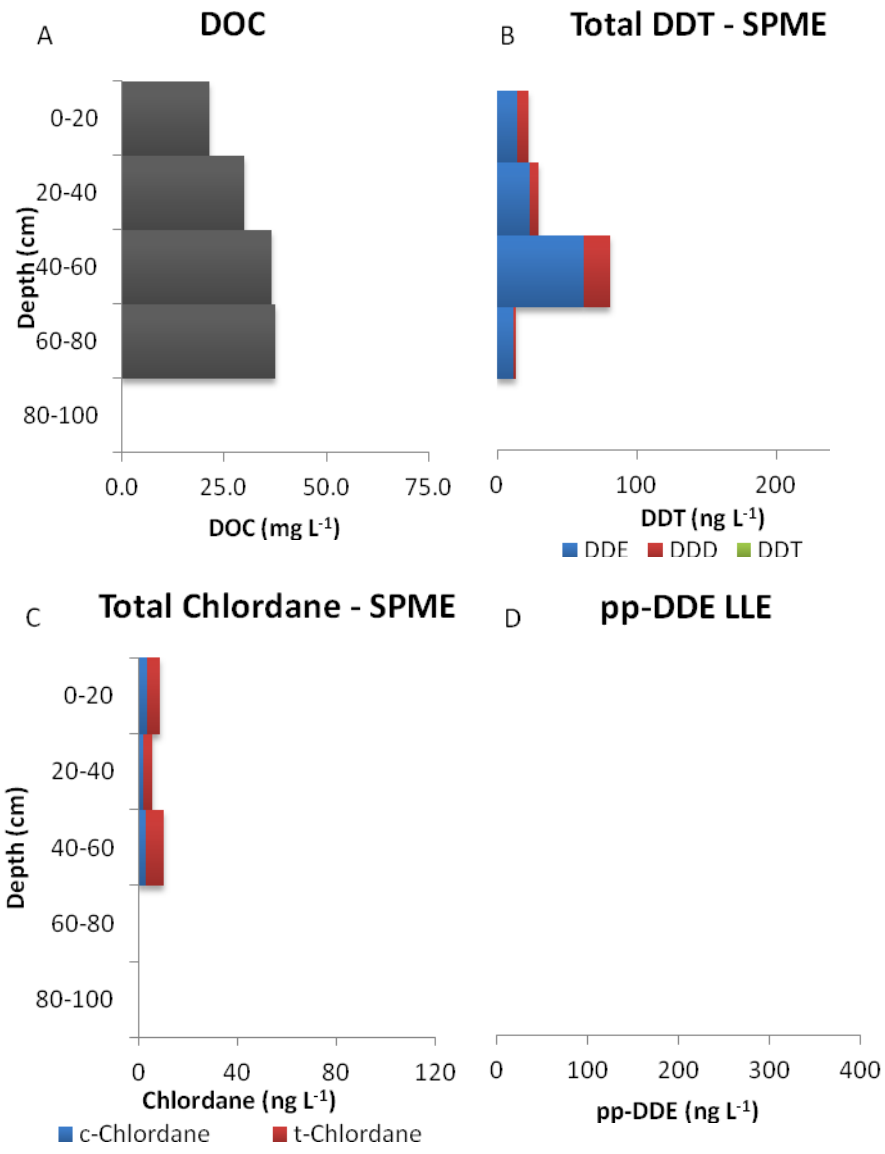

Fig. 3.28. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 9 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

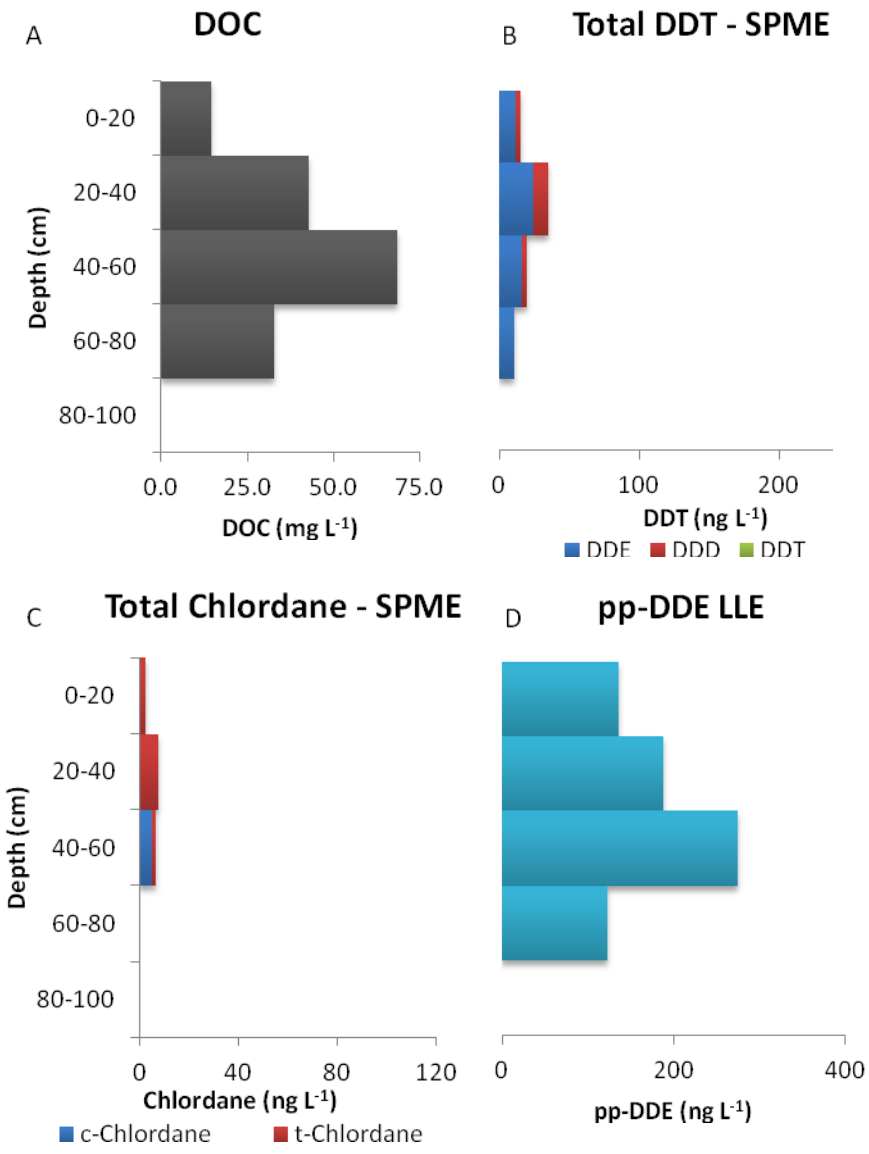

Figure 3.29. Concentrations of dissolved organic carbon (DOC) and the freely dissolved total concentrations of DDT and chlordane calculated using SPME at Site 15 along the sampling transect. Additionally, the concentration of the total concentration of pp-DDE in dissolved in the aqueous phase (freely dissolved and sorbed to DOC).

3.2.4 Results from prior study at the lake (Jacobi et al., 1999)

Jacobi et al. (1999) conducted a detailed study of chemical and biological measures of sediment quality in McGrath Lake. The study included measurements of total organic C and grain size of bottom sediments, concentrations of nutrients in sediment porewater, analyses of trace metals, PCBs, DDT and other chlorinated pesticides in sediments and water, and toxicity testing using 10-d amphipod (*Eohaustorius estuarius*) and 96-h mysid (*Neomysis mercedis*) tests (Jacobi et al., 1999). An initial reconnaissance survey of the lake involved measurements of water depth, total organic C content and grain size on surface sediment samples at 50 sites on the lake that most heavily sampled the lower half of the lake (35/50 sites). Following that initial characterization, 11 cores were taken and analyses for chemical contaminants were conducted on 0-5 cm, 5-35 cm, 35-65 cm and >65 cm depth intervals on the cores.

Jacobi et al. (1999) reported surface concentrations (0-5 cm) of total DDT broadly similar across the lake, while total PCBs varied somewhat more, although concentrations were lower at the northernmost and southernmost sites. Concentrations of total DDT were generally lower in the deeper part of the sediments within the southern part of the lake, while relatively high concentrations were present down to 65 cm in the northern half of the lake. This was observed to a lesser extent also for total PCBs. Although a smaller number of cores were collected in the northern half of the lake, the results of Jacobi et al. (1999) suggested that volumetrically a larger fraction of contaminated sediments is located there. The results from this sampling and analysis confirm that the highest levels of contamination by DDT and chlordane are found at the northern end of the lake.

3.2.5 Comparison with select samples analyzed by Babcock Labs

Two samples (site 7: 20 to 40 cm and site 3: 100-120 cm) which were representative of the contaminant concentrations we observed throughout McGrath Lake were provided to Babcock Labs for analysis. They examined samples for p,p-DDD, p,p-DDE, p,p-DDT as well as 7 sets of PCB congeners (noted as Aroclors in the lab report). The Babcock report is provided as a separate appendix and reports all concentrations as sediment wet weight (i.e., as collected and received). Therefore, these values were converted to dry weight before comparison to our results. Babcock Labs detected both p,p-DDD and p,p-DDE in each sample (Table 3.5). They did not however find p,p-DDT or any of their target PCB analytes. The percent difference between the Babcock analytical results and those present in this study range from 10 to 37% for

individual compounds and 8 to 14% for total DDT. With regards to PCB contamination, the Babcock detection limits for each of their 7 target congeners were 900 ng g^{-1}, which is much higher than the concentrations we observed for total PCBs in the sediments of McGrath Lake. Therefore, due to the high detection limits utilized by Babcock labs, we cannot resonably compare our PCB results with theirs.

Table 3.5. Comparison between contaminant concentrations (ng g^{-1}) reported by Babcock Labs and UCR. Total DDT is taken as the sum of p,p-DDD and p,p-DDT.

	Compound	Babcock	UCR	% Difference
Site 7	p,p-DDD	116.8	80.6	37%
	p,p-DDE	510.9	464.5	10%
	Total DDT	627.7	545.1	14%
Site 3	p,p-DDD	104.6	80.8	26%
	p,p-DDE	212.8	263.9	21%
	Total DDT	317.4	344.7	8%

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