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The Environmental Significance of Sediment Surface Area as a Controlling Factor in the Preservation of Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans (PCDD/PCDF) in Sediments Adjacent to Woodfibre Pulp Mill, Howe Sound, British Columbia

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Abstract: A sediment core was retrieved from an area adjacent to a Pulp and Paper Mill in Howe Sound, British Columbia, in order to examine the accumulation dioxins (PCDDs) and furans (PCDFs). Downcore distribution of TOC in the bulk samples is relatively uniform (0.5–1.7 wt. %). Bulk PCDD/F concentration shows selective enrichment and depletion at specific sediment horizons, and a low to moderate correlation with surface area (r^2 = 0.23–0.54). TOC in size fractionated sediments ranges from 0.3–11 wt. % and shows a moderate correlation with surface area (r^2 = 0.51). The relationship between PCDD/Fs and surface area is congener specific, ranging from no significant correlation (TCDD; r^2 = 0.05), to a good correlation (i.e., OCDF; r^2 = 0.74). Results indicate that both dioxin and furan concentrations are related to organic matter concentration, molecular chlorination and sediment surface area.

Keywords: woodfibre pulp mill; organic matter; dioxins; furans; surface area; preservation

1. Introduction:

Polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) are serious threats to the environment due to their ubiquitous nature, toxicity and strong resistance to biodegradation [1–3]. It is known that these compounds have a strong affinity for sediment particles, particularly ab/adsorption onto high surface area sediments like organic rich particulates [4,5], making coastal sediments an ideal repository. PCDD/Fs occur in the sediments of most industrialized waterways in the United States, Europe and Asia [6–9]. The relationship between inorganic particle surface area and organic matter concentration has been established in uncontaminated sediments [10–15]. It also considered probable that surface area adsorption may be responsible for the preservation and distribution of organochlorine compounds in marine sediments [16]. This research has investigated the distribution of organochlorine compounds in organic rich marine sediment in Howe Sound, British Columbia, Canada to understand how the characteristics on the sediment influence the preservation of these toxins.

There are 75 PCDD congeners and 135 PCDF congeners, each with a different arrangement/quantity of chlorine atoms in the chemical structure. 2,3,7,8-terachlorodibenzo- p-dioxin (2378-TCDD) has received wide attention due to its carcinogenic nature, and has been shown to kill 50% of laboratory guinea pigs when administered at a dosage of 0.6 µg/kg of body mass [17,18], although such high

fatality rates are not observed in all species. Data show that the toxicity of individual congeners is related to the positioning of chlorine atoms in the chemical structure, and that congeners with chlorine atoms at the 2,3,7 and 8 positions are the most toxic [19]. PCDD/F toxicity in marine and fresh water sediments is measured against national guidelines set out by the Canadian Council of Ministries of the Environment (CCME). Values for PCDD/F of 0.85 ng/kg TEQ (Toxic Equivalency; ISQG-Interim Sediment Quality Guidelines) [20] and 21.5 ng/kg TEQ (PEL—Probable Effect Level) were chosen, based upon the degree of adverse biological effects resulting from exposure to contaminated sediments. TEQ is calculated by multiplying the measured sediment concentration in ng/kg by a TEF value (Toxic Equivalency Factor); 2,3,7,8-TCDD is known to be the most toxic and, therefore, has a TEF of 1.0. Since the more chlorine atoms present in the molecular structure, the lower the TEF value, OCDD (Octachlorodibenzodioxin) has a TEF of 0.0001. Sources of PCDD/Fs in the environment are numerous, although they usually originate as unwanted trace contaminants in industrial processes, and not from direct manufacture [21]. Atmospheric sources include combustion of wood and waste from incinerator plants [21,22], and coal fired power stations [23]. Effluent wastes from industrial processes, most notably from solid waste incineration [24] and from the pulp and paper industry, also contain PCDDs and PCDFs [25]. Chlorinated pesticides, dry cleaning distillation residues, automobile exhaust emission and combustion of landfill gases are also known sources of PCDD/Fs [21]. There are a number of distinct sources of PCDD/Fs, which contribute to the total contamination from pulp and paper mills. Prior to 1992, wood chips treated with tetra- and penta-chlorinated phenols to prevent fungal growth were supplied to pulp mills [26]. The tetra- and penta-chlorinated phenols were subsequently transformed into PCDD/Fs during the bleaching process and then carried through into mill effluent [25].

The use of polychlorinated phenol-treated chips was banned in Canada by the Canadian Environmental Protection Act (CEPA) in 1992 [26,27]. The bleaching process is the main source of PCDD/Fs in pulp mills, although since the ban on the use of elemental chlorine during bleaching by the CEPA, levels have fallen sharply [25]. Also banned under the CEPA was the use of defoamers, which contained PCCD/F precursor chemicals.

The strong chemical resistance of PCDD/Fs to biodegradation and their relatively low solubility in water (PCCD/Fs 10^{-6}–10^{-12} mol/L) [28,29] means that both chemical families have long residence times in the marine environment, and the potential to accumulate in sediments [30]. The organochlorine record in sediments from around the world is well documented in the literature [25,31–38], and generally exhibits a steady increase since the "industrial revolution" (approx. 1880–1910), rising to a maximum in the 1950's and 1960's when unchecked industrial emissions reached a peak [33,39]. The most likely pathway by which these organochlorine chemicals reach the sediments is via adsorption onto higher surface area, finer grained minerals and organic matter particulates which settle to the sediment interface [16]. As a result, grain size and total organic carbon (TOC) concentration, which are strongly related, are anticipated to correlate with PCDD/F concentrations. As with TOC, highest concentrations of PCDD/Fs should be found in fine silt and clay sized sediment fractions, where surface areas are large (≈15–40 m^2/g). Previous studies have also shown coarse grained sediments to have high TOC concentrations [40]. However, TOC in coarse silt and sand sized sediment fractions is considered to be independent of surface area, because it is mainly found as discrete macroscopic particles. Adsorption of PCDD/Fs may occur in the effluent itself, which can have a high inorganic content and often contains fine-grained particulate material that does not settle out in sludge ponds. Adsorption may also occur after effluent discharge in the receiving waters, or in the sediments themselves.

The aim of this project is to examine the partitioning of PCDD/Fs in sediments adjacent to the Woodfibre Pulp and Paper Mill, in a core retrieved from an area exposed to effluent discharge by the mill. The relationship between grain size and TOC, PCDD/F concentrations are assessed to ascertain if sediment surface area is a significant, contributing factor in the preservation of organochlorine compounds in marine sediments.

2. Methods:

2.1. Sample Preparations and PCDD/Fs Analyses

A sediment core was taken using a Kasten box corer (gravity corer) from the Canadian Coast Guard vessel CCGS Vector and sampling was conducted adjacent to the Woodfibre Pulp and Paper Mill (Figure 1) in Howe Sound, BC. The core was subsampled on deck at 1 cm intervals to a depth of 10 and 2 cm thereafter (core length, 52 cm). Samples were frozen onboard in pre-cleaned glass jars with Teflon lined lids by a 6 h soak in Extran 300 ^{TM}, triple rinsed in distilled water and baked overnight at 300 °C. Samples were kept frozen until subsampling.

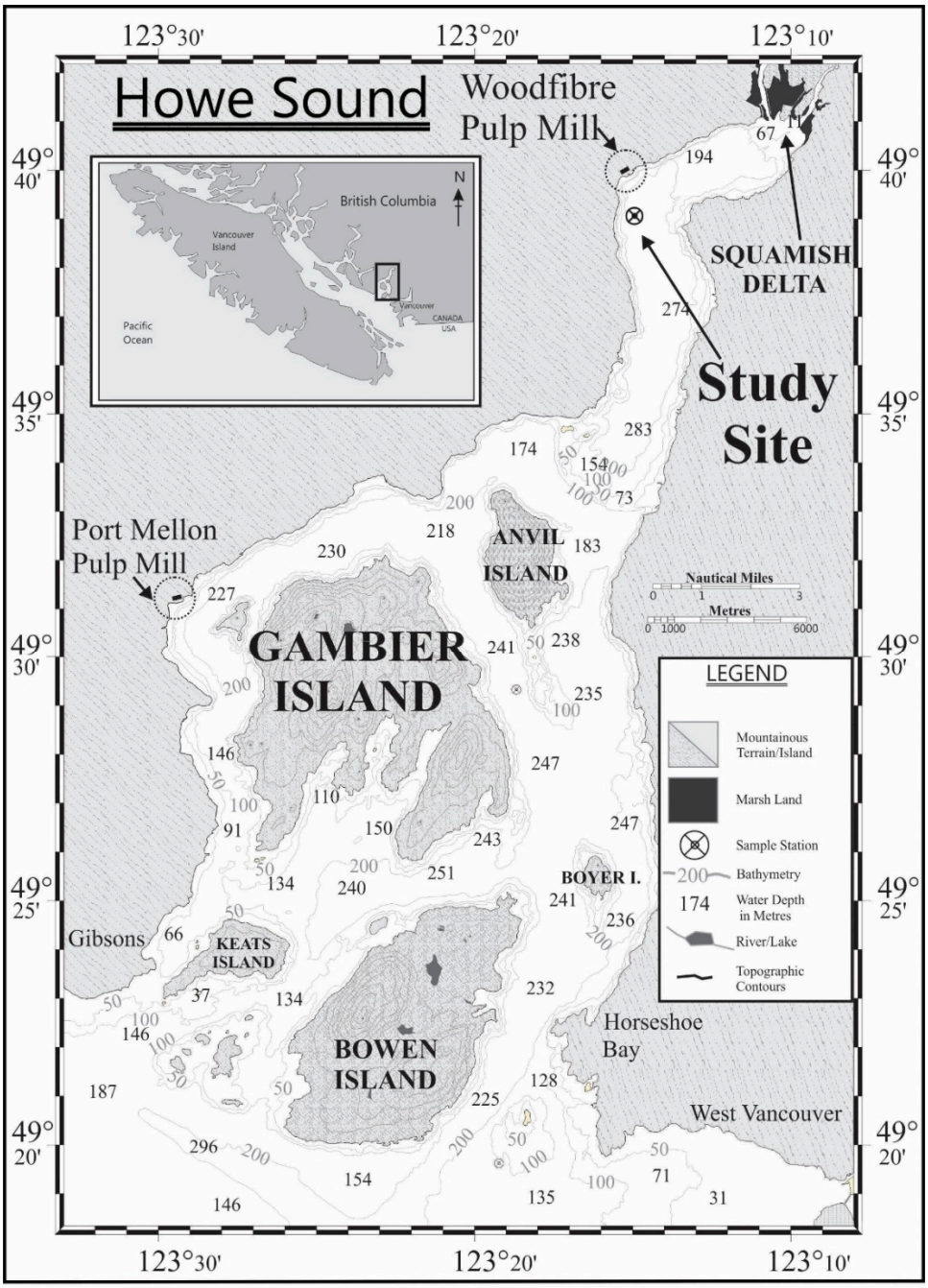


Figure 1. Map showing the location of the sample site in Howe Sound, BC, Canada.

Sample preparations were carried out in the regional dioxin laboratory at the Institute of Ocean Sciences (IOS), Sidney, BC, Canada. in order to reduce any potential sample contamination prior to organochlorine analysis. Bulk sediment samples were firstly analyzed to determine the PCDD/PCDF concentrations. Bulk sediment samples were homogenized unfrozen and 2 g aliquots were removed for moisture determinations. Analytical samples, approximately 10 g wet weight (w.w.), were dried with 125 g Na_2SO_4 in a mortar and transferred into the glass thimble of the Soxhlet where they were spiked with a mixture of $^{13}C_{12}$-labeled PCDD/Fs, a surrogate internal standard supplied by Cambridge Isotope Laboratories (Andover, MA, USA). The composition of the surrogate internal standard mixture and the concentrations are given in Table 1. The spiked samples were Soxhlet extracted for 16 h with 350 mL of toluene/acetone (80:20); washed with 40 mL of KOH, 80 mL of high performance liquid chromatography (HPLC) grade water and subsequently with 10 mL of H_2S0_4. The solvents were finally removed by rotary evaporation and the samples were reconstituted in 10 mL of DCM/hexane (1:1). This analytical procedure was repeated for size fractionated sediment samples.

Table 1. Composition of internal standard surrogate mixtures used to spike all samples analysed.

PCDD/PCDF Surrogates Spike Volume (pg)	PCDD/PCDF Surrogates Spike Volume (pg)
$^{13}C_{12}$-2,3,7,8-TCDD	1000
$^{13}C_{12}$-1,2,3,7,8-PeCDD	1000
$^{13}C_{12}$-1,2,3,6 7 8-HxCDD	1000
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	1000
$^{13}C_{12}$-OCDD	2000
$^{13}C_{12}$-2,3,7,8-TCDF	1000
$^{13}C_{12}$-1,2,3 7 8-PeCDF	1000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	1000
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	1000

Sample clean-up took place in four stages. In the first step, aliquots were passed through a multilayer silica column packed with successive layers of silica gel (basic, neutral, acidic, neutral) and eluted with DCM/hexane (1:1). Sulphur was removed from the samples during the second step by passing the silica extract through a column filled with copper fillings and eluted with 25 mL of hexane. This column was also packed with 25 g of Na_2SO_4 to remove any residual water. The third clean-up step was via a neutral alumina-activated column capped with anhydrous Na_2SO_4. The column was first washed with hexane to remove interfering compounds. Further elution with 1:1 DCM/hexane recovered the analytes of interest. Fractionation of the latter mixture was accomplished with an automated HPLC system utilizing a carbon fiber column packed with a 1:12 mixture of activated carbon/filter paper homogenate. With this arrangement the PCDD/Fs are separated from PCBs and other potentially interfering compounds and thus the detection limits of the method are enhanced significantly. The fractionation was performed successively with: (A) 20 mL of 5% DCM/hexane; (B) 44 mL of 50% DCM/hexane; (C) 50 mL of 50% ethyl acetate/benzene; and (D) back flushed with 60 mL of toluene. All three fractions collected from the carbon fibre system were concentrated to less than 10 µI and spiked with the corresponding $^{13}C_{12}$-labeled method performance standards prior to gas chromatography/high-resolution mass spectrometry analysis (GC/HRMS). The performance standards added to PCDD/F fraction were: $^{13}C_{12}$-l,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. For this study, only the PCDD/F fraction was analyzed by GC/HRMS and the PCBs fractions were collected for future studies.

The mass spectrometer was operated at 10,000 resolution under positive EI conditions (35 eV electron energy) and data were acquired in the Single Ion Resolving Mode (SIR). Two or more ions, M^+ and M^{2+} in most cases, of known relative abundances, were monitored for each molecular ion cluster representing a group of isomers, and two for each of the $^{13}C_{12}$-labeled surrogate standards. Compounds were identified only when the GC/HRMS data satisfied all of the following criteria: (1) two isotopes of the specific congeners were detected by their exact masses with the mass spectrometer

operating at 10,000 resolving power or higher during the entire chromatographic run; (2) the retention time of the specific peaks was within three seconds to the predicted time obtained from analysis of authentic compounds in the calibration standards; (3) the peak maxima for both characteristic isotopic ions of a specific congener coincided within two seconds; (4) the observed isotope ratio of the two ions monitored per congener were within +15% of the theoretical isotope ratio; (5) the signal-to-noise ratio resulting from the peak response of two corresponding ions was greater or equal to three for proper quantification of the congener.

The concentrations of identified compounds and their minimum detection limits (MDLs) were calculated by the internal standard method using mean relative response factors determined from calibration standard runs made before and after each batch of samples were run. The specific compounds analyzed are listed in Table 2. The criteria for identification and quantification, and the quality assurance and quality control measures undertaken for the sample workup and the GC/HRMS analysis of all the analytes of interest were based on procedures described in the Environment Canada [41,42] protocols.

Table 2. Polychlorinated Dibenza-p-dioxins (PCDDs) and Polychlorinated Dibenza-p-furans (PCDFs) determined in each sediment sample analysed.

PCDD Congeners	PCDF Congeners
2,3,7,8-TCDD	2,3,7,8-TCDF
Total TCDD Homologue	Total TCDF Homologue
1,2,3,7,8-PeCDD	1,2,3,7,8-PeCDF
	2,3,4,7,8-PeCDF
Total PeCDD Homologue	Total PeCDF Homologue
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDF
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,7,8,9-HxCDD	2,3,4,6,7,8-HxCDF
	1,2,3,7,8,9-HxCDF
Total HxCDD Homologue	Total HxCDF Homologue
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDF
	1,2,3,4,7,8,9-HpCDF
Total HpCDD Homologue	Total HpCDF Homologue
OCDD	OCDF

Fractionation was carried out using a combination of wet sieving and settling techniques based on Stokes law [43]. Selected samples were chosen, based on highest bulk PCDD/PCDF concentration, for size fractionation into five size fractions (<2 µm, 2–10 µm, 10–20 µm, 20–63 µm and >63 µm). These selected samples for geochemical analyses are from the core depths of 14–16 cm, 20–22 cm, 34–36 cm and 46–48 cm. Three other sediment intervals, of similar depth to those used for organochlorine analysis, were separated using wet sieving techniques [43] in order to examine down core mass distribution, and to choose suitable size fractions that contained a mass sufficient for all the analyses. Samples were sieved at 63 µm, and the remainder was analysed using a Micromeritics® Sedigraph 5100 (Micromeritircs, GA, U.S.A) and results were combined to produce mass profiles for the four samples (Figure 2).

The sieve and spatulas used for sample fractionation were all stainless steel, and were triple solvent rinsed (Acetone 3 times, Toluene 3 times, Hexane 3 times) and baked at 150 °C for 1 h etween samples. All glassware used during the settling procedure was washed, triple solvent rinsed, baked overnight at 350 °C, and triple solvent rinsed again and dried inside a fume hood. All equipment used was covered/sealed in hexane rinsed aluminum foil immediately after cleaning. Narrow bore, flexible Teflon tubing (internal diameter of 2 mm), in conjunction with a disposable Pasteur pipette connected via rubber tubing to a water aspirator and was used to siphon off different size fractions during settling. The coarsest fraction, >63 µm, was sieved off, and the remaining solids, suspended

in distilled water, were transferred to 2 L glass beakers for settling. Once separated, sediment size fractions were stored in 250 mL solvent rinsed glass jars with Teflon lined lids, and frozen prior to analysis. To remove particles from suspension in the <2 μm fraction, the water was centrifuged at 3500 rpm using a Beckman 64R centrifuge (Beckman Coulter, Indianapolis, IN, U.S.A). Four, 1 liter polycarbonate centrifuge bottles were adapted by removing the neck of the bottle, so that they could be lined with hexane rinsed aluminum foil to prevent contamination (the polycarbonate centrifuge bottles could not be solvent cleaned in the same manner as glassware). Any leakage through the foil was discarded. The water was then stored in solvent rinsed 4 liter bottles and stored in the fridge at 4 °C.

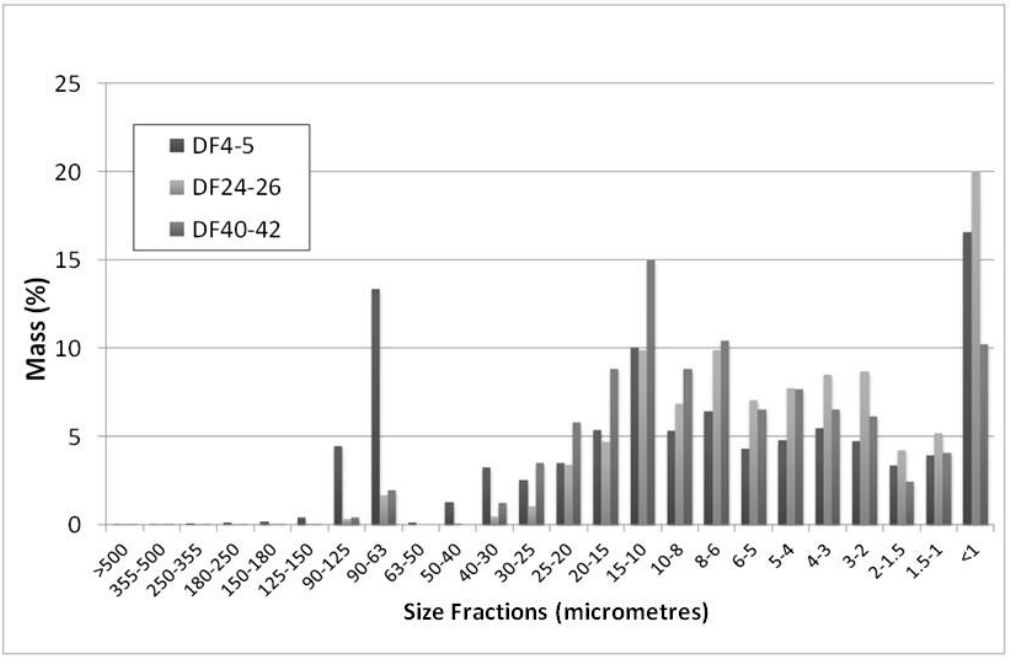


Figure 2. Mass distribution (%) of three samples (DF 4-5, DF 24-26, DF 40-42), used to select grain size classes (micrometres) for analyses on size fractionated sediments.

PCDDs, PCDFs were analyzed by GC/HRMS. The instrument was a VG Autospec high resolution mass spectrometer (Micromass, Manchester, UK) equipped with a Hewlett-Packard model 5890 Series II gas chromatograph and a CTC A200S autosampler (CTC Analytics, Zurich, Switzerland). The GC was operated in the splitless injection mode with a 60 m DB-5 fused silica capillary column (0.25 mm I.D. with 0.1 μm film thickness) from J&W Scientific (Folsom, CA, USA). The temperature program for the PCDD/PCDF analysis was as follows the initial column temperature was held at 100 °C for 2 min after injection and increased at 20 °C/min to 200 °C, then at 1 °C/minute to 215 °C, held for 7 min followed by a ramp of 4 °C/minute to 300 °C where it was held for 3 min.

2.2. Carbon and Nitrogen Analyses

Total carbon (TC; wt. %) and total nitrogen (TN; wt. %) of bulk and fractionated sediment samples was determined using a Carlo Erba NA-1500 CHN analyzer [44]. The standard error was +/− 1%. Macroscopic organic debris was removed prior to analysis under a binocular microscope. Total organic content (TOC) was determined by difference after the subtraction of inorganic carbon in carbonate form.

The amount of carbon in carbonate form in each sample was determined using a coulometric titration technique on a CO_2 coulometer (Coulometrics Incorporated, Model 5010, Chattanooga, TN, U.S.A.). The standard error was +/− 5%.

2.3. Surface Area

Samples were first oxidized using a combination of hydrogen peroxide (30%) and sodium pyrophosphate (0.1 M) [45] in order to remove organic matter from the samples. This process was carried out in a water bath (70–80 °C) for 48–96 hrs; aliquots of H_2O_2 were added twice daily until oxidation was complete as marked by the cessation of CO_2 evolution. Samples were then rinsed twice in distilled water to remove any residual inorganic salts and dried. Freeze drying, oven drying and oven drying under vacuum were tested as methods of sample drying prior to analysis; good agreement was found between all three methods.

A Micromeritics ASAP 2010 surface area analyzer was used to measure surface area by N_2 adsorption, using both single and multi-point BET (Brunauer, Emmett, Teller) methods [10,46]. Prior to analysis, samples were degassed at 350 °C for a minimum of 6 hrs. The standard error of the surface area ranged from 2–4%.

2.4. ^{210}Pb Dating

Dating of the sediment core was carried out using the ^{210}Pb method of [47] modified after [48]. One to two grams of sediment was weighed out into acid cleaned microwave digestion vessels and spiked with 208Po to allow for normalization of differences between samples during counting and plating [49]. The samples were then microwave digested using a combination of HNO_3, HCl and HF, to remove organic material, aluminosilicates and silica, and to liberate ^{210}Po from the sediment matrix [49]. The digested residue was dried overnight under heat lamps, resuspended in 10% HCl and digested again. The pH was then brought up to 6–9 using NH_4OH, forming an iron precipitate containing ^{210}Po, which was stored in 210 mL Nalgene bottles until plating (HDPE).

To plate the samples, the iron precipitate was redissolved in 10% HCI, centrifuged, and the supernatant decanted into acid cleaned 250 mL glass beakers. Sodium citrate (25%, 2 mL), $NH_2OH.HCl$ (20%, 5 mL) and $Bi(NO_3)_3$ (10%, 1 mL) were added to the supernatant and the pH was raised to 1.5–2.5 using NH_4OH. The solution was stirred and heated to a temperature range of 90–100 °C, and a polished silver disk in a Teflon holder was inserted into the solution. Plating of ^{210}Po onto the disks occurred for 4–5 hrs, after which the silver disks were cleaned with concentrated HCl to improve counting efficiency, washed in double distilled water and allowed to air dry. The disks were counted for at least 24 h in an Ortec 576A Multi-channel Analyser (Ortec, Oak Rdige, TN, U.S.A) and Alpha-counter.

The initial ^{210}Pb dating of the homogenized bulk samples taken from the study core failed to yield a linear chronology. The dating procedure was modified slightly, changing the ratio of sample to ^{208}Po spike, and repeated. Unfortunately, significant fluctuation in age was found with increasing core depth, which ultimately prevented meaningful temporal correlation with other data.

This dating technique has been successfully applied to other samples recovered from different areas in Howe Sound [33], and reasons for the apparent failure in this case are unclear, but are further discussed in later sections.

3. Results:

The result section has been subdivided based on analyses performed on bulk samples and size fractionated samples. Size fractions are <2 µm, 2–10 µm, 10–20 µm, 20–63 µm and >63 µm.

3.1. Bulk Analyses

3.1.1. Organic Carbon and Nitrogen Analyses

Total organic carbon (C_{org}) concentrations range from 0.5–1.7 wt. % and TN ranges between 0.04–0.1 wt. %. (Table 3). The highest concentrations of organic carbon occur at the base of the cored sediments (50 cm below the sediment-water interface) and C_{org} concentrations decline to the middle of the cored sediment at 30 cm depth (Figure 3A). The total nitrogen (TN) shows a similar trend of

decreasing concentration from 50 cm to 30 cm depth (Figure 3B). The C_{org} and TN concentrations both increase from 30 cm to 18 cm depth and no clear down-core trends exist between the depths of 0–18 cm.

Table 3. Organic Carbon (C_{org}), Total Nitrogen (TN), Carbon/Nitrogen Ratio (Cor/N) and Surface Area for bulk sediment samples from the core taken adjacent to Woodfibre Pulp Mill, Howe Sound, British Columbia, subsampled every centimeter for the first ten centimeters and every two centimetres thereafter.

Sediment Interval (cm)	C_{org} (wt. %)	TN (wt. %)	C_{org}/N	Surface Area (m^2/g)
DF0–1	1.00	0.08	12.88	4.21
DF1–2	1.38	0.10	13.78	6.13
DF2–3	0.93	0.07	13.43	4.90
DF3–4	0.57	0.05	11.99	2.43
DF4–5	0.71	0.05	14.04	3.17
DF5–6	0.49	0.04	12.61	2.88
DF6–7	1.09	0.08	13.34	8.47
DF7–8	0.96	0.06	15.25	3.32
DF8–9	1.17	0.08	15.43	3.34
DF9–10	1.11	0.09	12.41	5.80
DF10–12	1.21	0.08	15.15	2.49
DF12–14	0.82	0.05	16.03	2.53
DF14–16	1.52	0.09	17.42	5.86
DF16–18	1.24	0.09	13.11	10.94
DF18–20	1.18	0.08	14.66	9.33
DF20–22	0.91	0.06	14.08	6.74
DF22–24	0.95	0.06	16.08	5.94
DF24–26	0.51	0.04	11.83	4.05
DF26–28	0.79	0.06	12.55	3.65
DF28–30	0.73	0.06	13.16	5.44
DF30–32	0.68	0.05	12.52	4.60
DF32–34	0.75	0.05	14.99	3.92
DF34–36	0.92	0.06	16.08	4.20
DF36–38	1.32	0.08	17.43	5.67
DF38–40	1.56	0.08	19.07	5.45
DF40–42	0.80	0.05	16.67	3.36
DF42–44	1.16	0.07	16.39	5.67
DF44–46	1.33	0.08	17.24	7.63
DF46–48	1.65	0.09	18.10	7.14
DF48–50	1.71	0.07	23.86	11.96
DF50–52	1.40	0.07	20.37	N/A

C_{org}/N values range from 12–24, with a mean of 15 (Table 3). When plotted against depth (Figure 4), a similar increasing trend from 50 cm to 30 cm to that seen in Figure 3 is evident. There is no clear trend seen in C_{org}/N values from 0 to 30 cm depth. The spread of values for C_{org}/N is relatively narrow, and a slight overall increase in ratio can be seen with increasing depth (Figure 4). Figure 5 shows a moderate positive correlation (r^2 = 0.7) between TOC and TN. The positive y-intercept suggests the presence of inorganic nitrogen within the sediment profile.

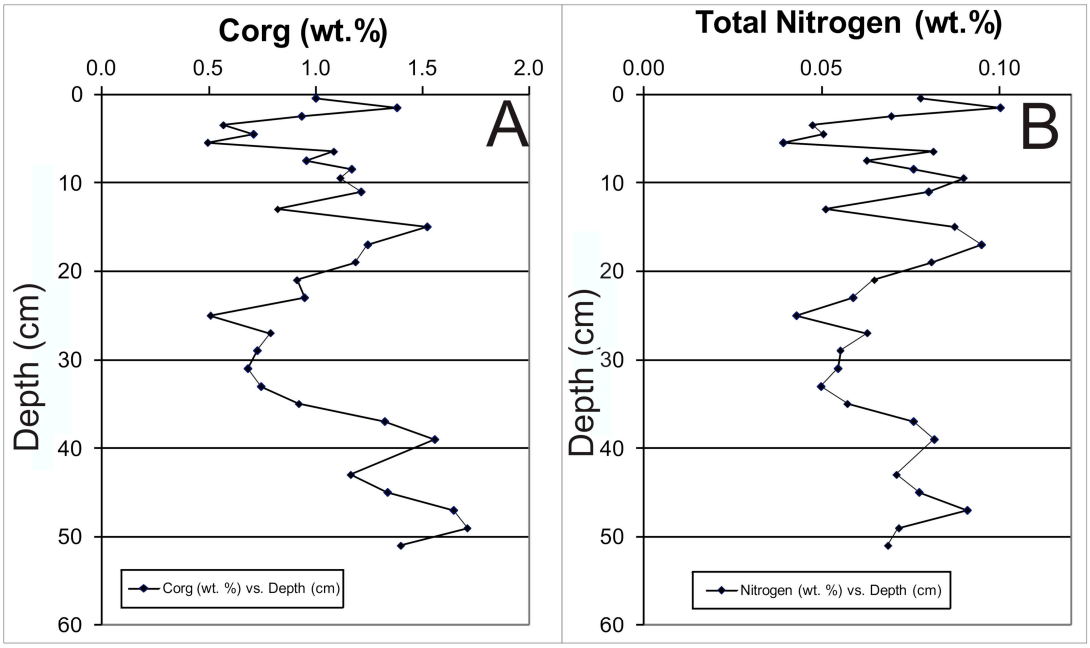


Figure 3. Downcore variations in Organic Carbon (C_{org}; **A**) and Total Nitrogen (**B**) for bulk sediment samples. Both Organic carbon and Total Nitrogen concentrations show similar trends with concentration highs at the base of the cored sediment (50 cm depth) which then decrease to approximately 30 cm core depth. Concentrations of C_{org} and TN both increase from 30 cm to 18 cm and then fluctuate towards the sediment-water interface (0 cm depth).

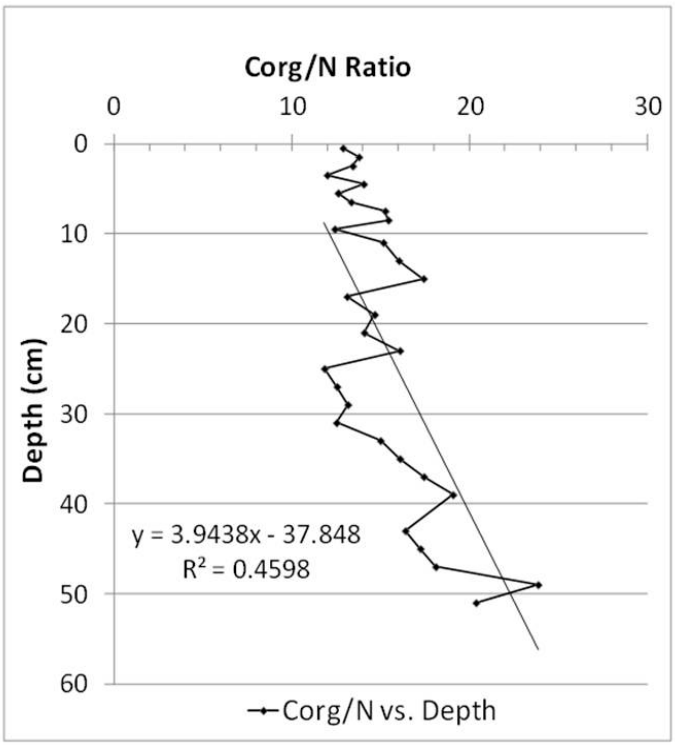


Figure 4. Downcore variation in Organic Carbon/Total Nitrogen ratio (C_{org}/N). The trend line depicts a gradual increase in C_{org}/N ration with increasing sediment depth.

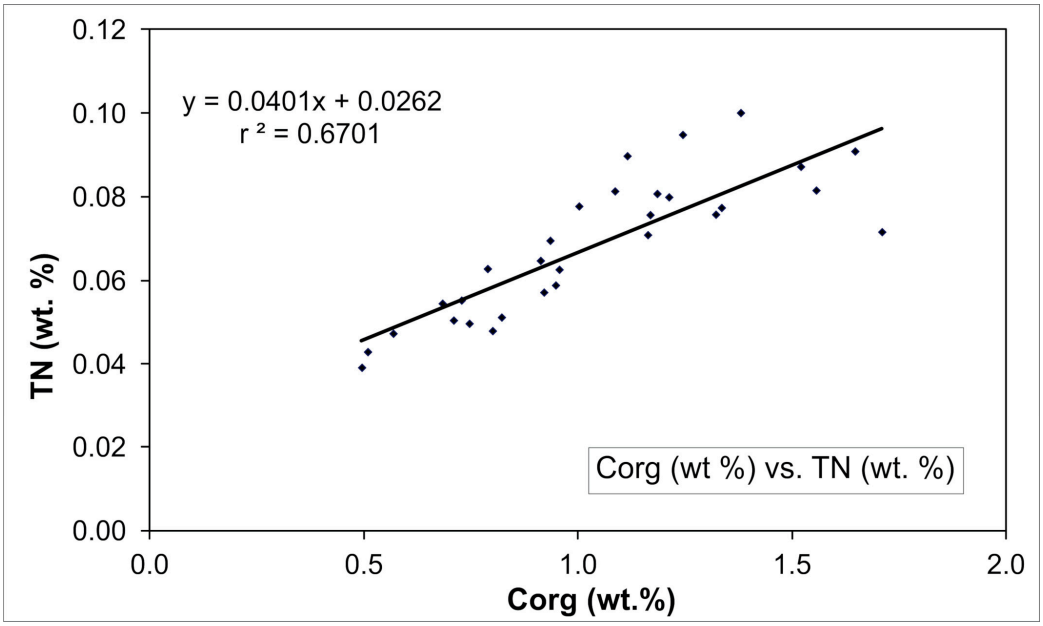


Figure 5. Plot of Organic Carbon (C_{org}) versus Total Nitrogen (TN) for bulk sediment samples. A positive correlation exists between the two parameters, modeled by a linear regression (r^2 = 0. 7).

3.1.2. Organochlorine Compounds

Total PCDD concentrations remains low and constant throughout the cored sediment (Figure 6a) with the exception of two concentration spikes at 14–16 cm (200 pg/g) and at 46–48 cm (700 pg/g) horizons (Table 4). TCDD (Tetra-), PeCDD (Penta-), HxCDD (Hexa-), HpCDD (Hepta-) and OCDD (Octa-) homologues all share the same concentration profile as total PCDD (Figure 7). HxCDD is present at significantly higher concentrations than the other dioxin homologues (Figure 7, Inset). If HxCDD is ignored, a positive relationship exists between increasing homologue concentration and the number of chlorine atoms present in the homologue molecular structure (Figure 7). Total PCDF (Figure 6) has an identical depth profile to TCDF (Figure 8 Inset). Overall concentrations of furan homologues are on the order of four times lower than their dioxin counterparts (Table 4). TCDF is the most concentrated furan homologue, present in concentrations approximately six times that of the next most concentrated homologue, HpCDF (Table 4). Unlike the dioxin homologues, furan homologues do not show the same relationship between relative concentration of a given homologue and its molecular chlorination (Figure 8). The downcore concentration profiles of individual PCDD/F (Figures 7 and 8) homologues as well as those for total PCDD/F (Figure 6) concentration are similar to that of TOC (Figure 3A), with corresponding peaks in concentration at 15, 35 and 45 cm.

3.1.3. Total Organic Carbon and Surface Area

Surface area values for bulk sediment samples range from 2.5–12 m^2/g (Table 3). Although peaks in surface area values do correlate with some increased TOC concentrations at certain depth intervals, a plot of TOC versus surface area (Figure 9) shows a moderate positive correlation (r^2 = 0.4) with surface area increasing with organic carbon concentration. Data scatter above and below the regression line, suggests the inorganic component (i.e., mineral grains) does influence the surface area characteristics of the sediments.

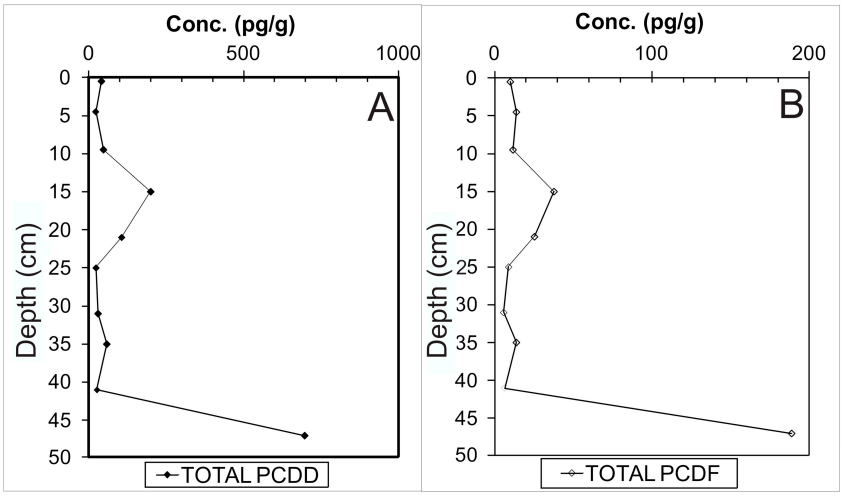


Figure 6. Downcore variation in Total Polychlorinated Dibenzo-p-dioxin (PCDD; **A**) and Total Polychlorinated Dibenzo-p-furan (PCDF; **B**) for bulk sediment samples.

Table 4. Homologue and total homologue (PCDD, PCDF) concentration (pg/g) for dioxins and furans in bulk sediment samples from selected depth intervals.

Sediment Interval (cm)	TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total PCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF	Total PCDF
DF0–1	3.13	3.84	15.78	7.29	11.76	41.8	3.72	1.48	1.44	2.32	1	9.96
DF4–5	0.45	0.91	7.51	5.13	8.69	22.69	1.04	0.74	2.57	4.93	1.5	13.78
DF9–10	1.47	2.52	17.68	9.58	16.39	47.64	3.56	1.37	1.85	3.3	1.55	11.63
DF14–16	16.86	24.05	108.35	24.68	26.34	200.28	23.5	5.51	3.23	3.95	1.55	37.74
DF20–22	1.52	3.89	66.75	14.11	19.52	105.79	14.19	2.46	2.42	4.45	1.78	25.3
DF24–26	0.4	0.87	10.96	4.4	7.46	24.09	3.74	0.73	0.91	2.23	1.27	8.88
DF30–32	0.13	1.47	14.06	6.32	8.23	30.21	2.27	0.89	0.98	1.26	0.46	5.86
DF34–36	0.64	2.27	32.4	9.56	13.45	58.32	6.69	1.74	1.88	2.44	1.1	13.85
DF40–42	0.13	0.45	14.58	4.54	7.31	27.01	3.42	0.4	0.65	1.44	0.49	6.4
DF46–48	6.88	22.3	517.76	62.71	87.95	697.6	129.25	13.75	13.8	23.33	8.58	188.71

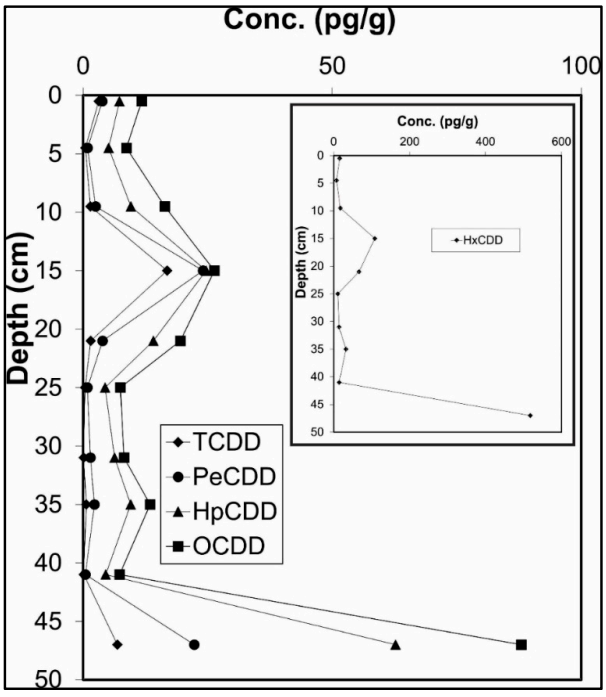


Figure 7. Downcore variation in dioxin homologue concentration for bulk sediment samples. Inset shows HxCDD, which is present at significantly higher concentrations than the other homologues.

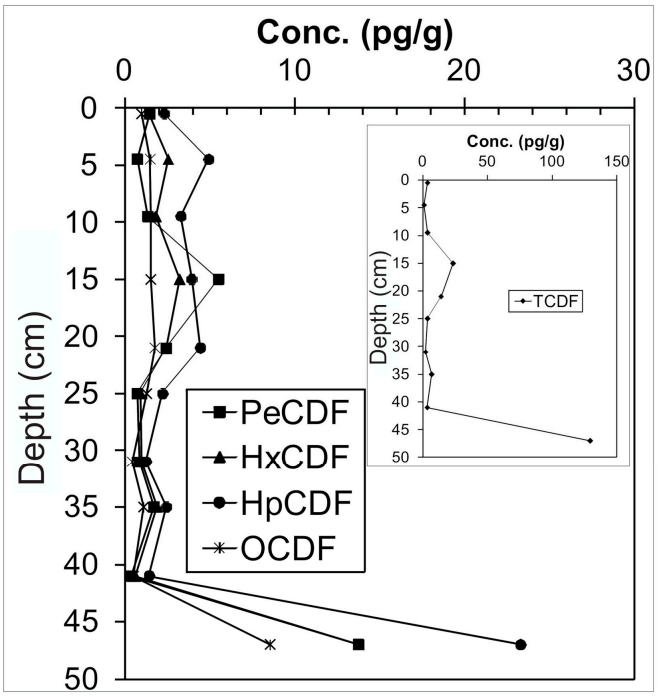


Figure 8. Downcore variation in furan homologue concentration for bulk sediment samples. Inset shows TCDF, which is present at significantly higher concentrations than the other homologues.

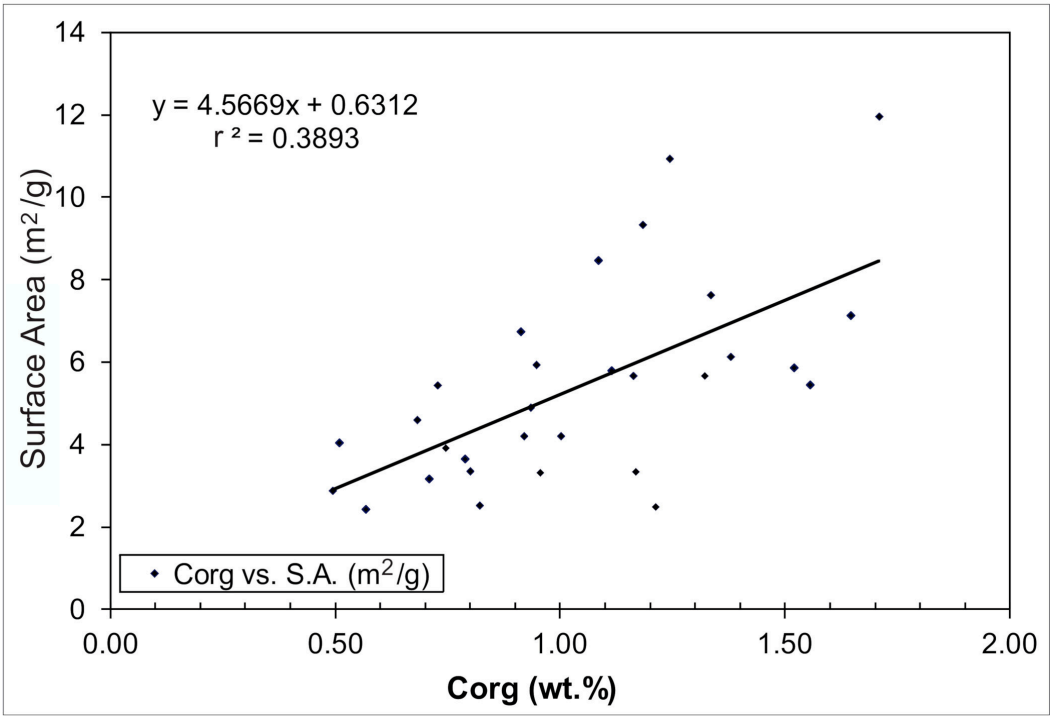


Figure 9. Plot of Surface Area (m^2/g) versus Organic Carbon (C_{org}) for bulk sediment samples, showing a moderate positive linear regression, $r^2 = 0.4$.

3.1.4. PCDD/Fs and Surface Area

When plotted against surface area, total PCDD, total PCDF and the five homologues analysed for each sample show a low to no correlation with r^2 varying from 0.23 to 0.54.

3.2. Size Fractionated Organic Analyses

3.2.1. Carbon and Nitrogen

TOC values for the four samples selected for size fractionation, ranged from 0.3–11 wt. % (Table 5). TN concentrations range from 0.03–0.2 wt.% (Table 5). For the four samples analyzed, the >63 μm fraction contains the highest concentration of both TOC (5–11 wt. %) and TN (0.15–0.2 wt. %; Figure 10a). The <2 μm fraction contains the second highest concentration of TOC and TN, ranging from 1–3 wt. % and 0.8–0.2 wt. % respectively (Table 5; Figure 10a,b).

Table 5. Organic Carbon (C_{org}), Total Nitrogen (TN), Carbon/Nitrogen Ratio (C_{org}/N) and Surface Area (SA) for sediment samples from selected depth intervals, size fractionated into five fractions: <2 μm, 2–10 μm, 10–20 μm, 20–63 μm and >63 μm.

Sediment Interval (cm)	Size Fraction (Micrometres)	C_{org} (wt. %)	TN (wt. %)	C_{org}/N	Surface Area (m^2/g)
DF 14–16	<2	1.51	0.11	13.43	16.68
	2–10	0.91	0.06	16.04	5.20
	10–20	0.88	0.05	19.10	2.72
	20–63	0.70	0.03	21.48	1.49
	>63	4.90	0.18	26.77	2.64
DF 20–22	<2	1.12	0.08	13.44	16.37
	2–10	0.28	0.02	14.41	3.92
	10–20	0.35	0.02	16.76	2.37
	20–63	0.78	0.04	20.27	1.78
	>63	5.45	0.15	35.78	5.60
DF 34–36	<2	1.59	0.10	15.29	21.80
	2–10	0.67	0.04	16.36	6.61
	10–20	0.42	0.03	17.01	3.55
	20–63	0.69	0.03	21.50	2.08
	>63	5.43	0.17	31.14	1.53
DF 46–48	<2	3.15	0.17	19.00	20.75
	2–10	1.68	0.07	23.55	8.62
	10–20	1.71	0.06	27.87	6.58
	20–63	1.36	0.03	41.21	2.34
	>63	10.94	0.21	52.99	9.17

C_{org}/N values for size fractionated samples range from 13–53, with a mean of 23, indicating a dominant terrestrial signature for the organic matter present in the samples. The C_{org}/N ratio increases with increasing grain size (Table 5). A significant increase in C_{org}/N values occurs between the 20–63 μm fraction and the >63 μm fraction. Figure 11 shows TOC plotted against TN with the >63 μm fraction grouped separately from the remaining size fractions. The separation of the >63 μm data from the other size fractions, which all fall on a single regression line (r^2 = 0.8; Figure 11), is the result of significantly higher organic carbon contents in that fraction due to particulate organic matter (OM).

The intermediate size fractions, 2–10 μm, 10–20 μm and 20–63 μm contain varying amounts of TOC and TN at lower concentrations to those observed in the <2 μm and >63 μm fractions (Table 5; Figure 10a,b). Both DF 14–16 and DF 46–48 have approximately equal amounts of TOC and TN in the 2–10 μm and 10–20 μm fractions and the lowest concentrations of TOC and TN in the 20–63 μm fraction. DF 20–22 shows the opposite, approximately equal amounts of TOC and TN in the 2–10 μm and 10–20 μm fractions, and higher concentrations in the 20–63 μm fraction, whilst DF 34–36 shows the lowest concentrations of TOC and TN in the 10–20 μm fraction and approximately equal amounts in the 2–10 μm and 20–63 μm fractions.

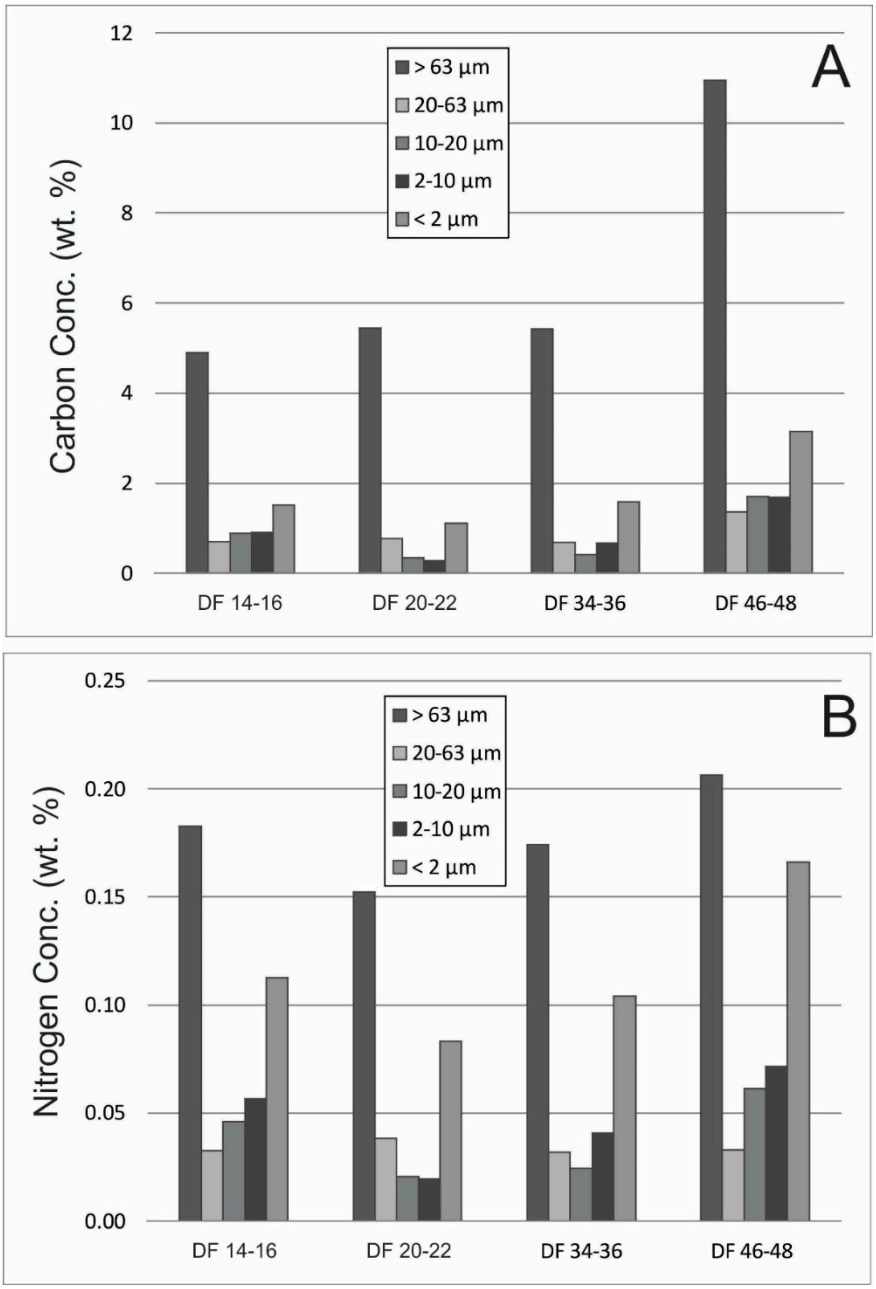


Figure 10. Distribution of Organic Carbon (**A**) and Total Nitrogen (**B**) for four selected samples, size fractionated into five fractions: <2 µm, 2–10 µm, 10–20 µm, 20–63 µm and >63 µm.

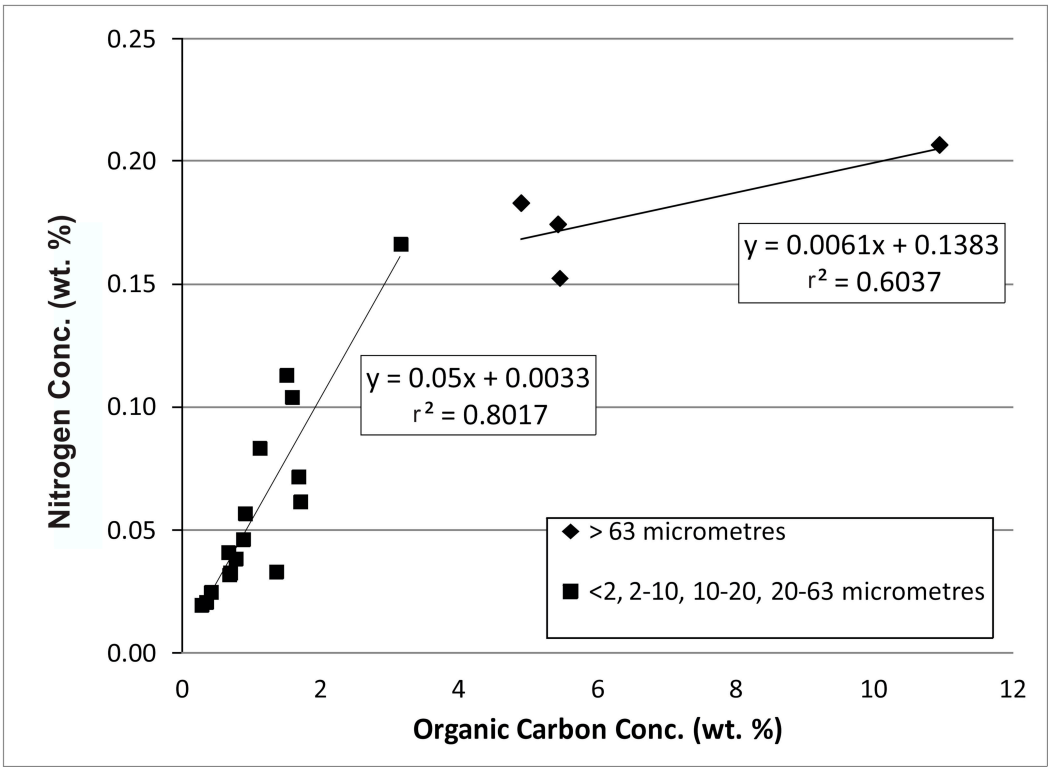


Figure 11. Plot of Organic Carbon (C_{org}) versus Total Nitrogen (TN) for size fractionated samples. Note, the 63 µm fraction falls on a separate regression (r^2 = 0.6) than the other four fractions (r^2 = 0.8).

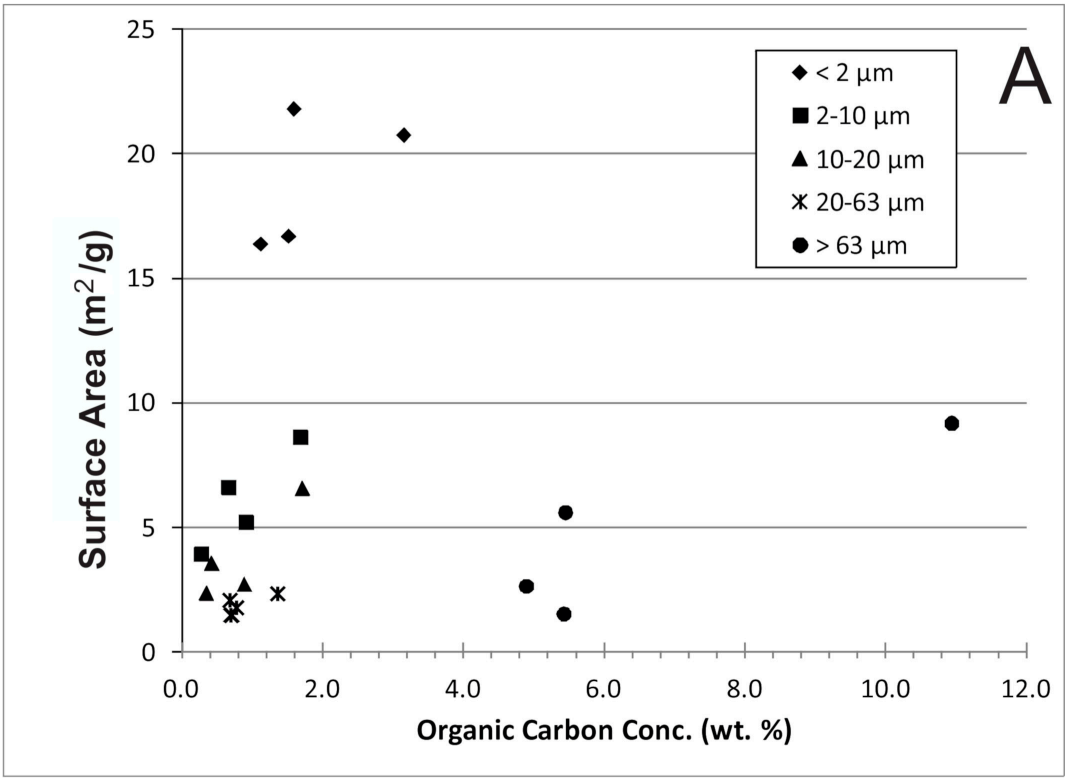
3.2.2. Surface Area of Size Fractionated Samples

Surface area values for size fractionated samples range from 1.5–22 m^2/g, with highest values found in the <2 µm fraction (16–22 m^2/g) and lowest values in the 20–63 µm fraction (1.5–2.4 m^2/g; Table 5).

The TOC concentrations for individual size fractions plotted against surface area show data clustering occurs amongst each size fraction (Figure 12a). Two end members exist, the <2 µm fraction which has high surface area values compared to TOC content (Table 5), and the >63 µm fraction which has high TOC content and low surface area values (Table 5). The remaining size fractions, 2–10 µm, 10–20 µm and 20–63 µm, cluster between the two end members. Figure 12a suggests that no relationship between surface area and TOC content exists (r^2 < 0.1), and that organic matter is not adsorbed to sediment particle surfaces. However, if data from the >63 µm fraction is considered as outliers (because organic matter in this fraction is probably detrital, occurring as discrete particles, and therefore independent of surface area), then the correlation between TOC content and surface area is significantly improved. Figure 12b shows the same data with the >63 µm fraction omitted, producing and r^2 value of 0.51 which suggests a relationship between surface area and TOC concentration via adsorption of organic matter.

3.2.3. Organochlorine Compounds

The majority of trends observed in individual dioxin and furan congeners with respect to grain size and concentration are represented by their parent homologues (Table 2). Thus, concentrations are discussed here with reference to homologues rather than to each individual congener. The concentrations of each homologue and total homologue (PCDD, PCDF) for both dioxins and furans are shown for a selection of sample depths (DF 14–16 cm; DF 20–22 cm; DF 34–36 cm and DF 46–48 cm) and their size fractionated samples (Table 6 and Figures 13–16).



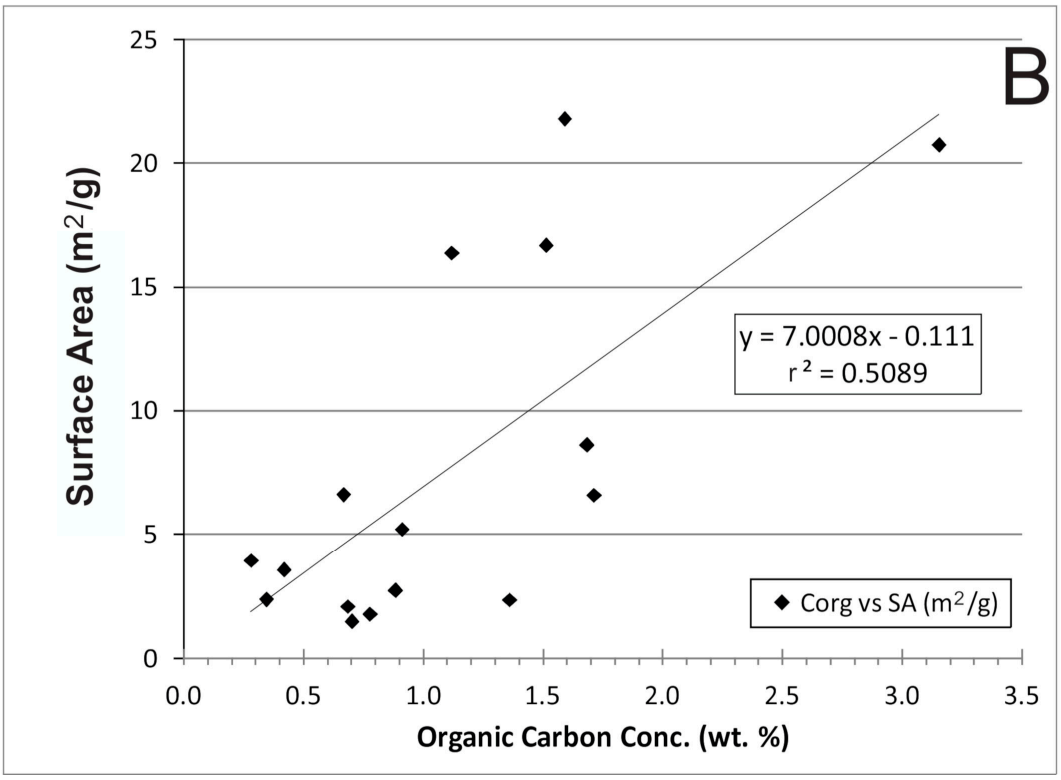


Figure 12. (**A**) Plot of surface area versus organic carbon (C_{org}) for size fractionated samples. The >63 µm fraction plots to the right of the graph due to its high C_{org} content and low surface area. (**B**) Plot of surface area and C_{org} for size fractionated samples with the >63 µm fraction removed. The plot has a moderate positive correlation, $r^2 = 0.5$.

Table 6. Homologue and total homologue (PCDD, PCDF) concentration (pg/g) for dioxins and furans, in selected size fractionated sediment samples.

Sediment Interval (cm)	Size Fraction (Micrometres)	TCDD	PeCDD	HxCDD	HpCDD	OCDD	TOTALPCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF	Total PCDF
DF 14–16	<2	2.75	8.06	82.87	23.08	33.77	150.5	9.11	3.99	3.72	5.56	1.91	24.27
	2–10	23.8	24.61	107.8	22.56	23.56	202.3	19.61	5.62	2.9	4.6	1.78	34.52
	10–20	51.51	52.19	133.8	26.27	20.9	284.4	26.59	6.5	3.05	3.05	0.98	40.17
	20–63	18.94	16.77	51.11	14.6	16.6	118.7	14.38	2.74	1.19	2.47	0.86	21.64
	>63	42.81	42.58	243.3	76.49	93.69	498.9	76.9	17.94	9.51	11.09	4.2	119.65
DF 20–22	<2	2.17	6.43	141.7	28.42	37.55	216.2	18.4	3.82	4.75	9.46	3.54	39.97
	2–10	1.82	3.88	65.4	10.56	13	94.66	12.28	2.11	2.1	5.11	2.15	23.81
	10–20	3.13	4.54	56.15	9.37	10.67	83.87	13.03	2.28	1.44	2.21	0.67	19.63
	20–63	4.53	6.79	76.55	17.53	23.77	129.2	19.74	3.7	2.79	4.6	1.74	32.57
	>63	19.87	22.81	240.1	122.0	133.6	538.4	84.81	11.86	8.02	12.79	5.4	122.9
DF 34–36	<2	0.64	3.25	50.01	15.06	19.72	88.74	6.15	2.07	2.65	3.7	1.24	15.8
	2–10	1.2	3.21	39.55	10.54	12.01	66.51	6.73	1.19	1.76	2.32	0.74	13.34
	10–20	1.45	3.37	32.44	8.73	9.97	55.96	7.14	1.73	1.46	2.01	0.61	12.97
	20–63	1.46	3.67	36.41	10.07	11.77	63.37	8.29	2.19	2.17	1.95	0.56	15.17
	>63	4.83	9.22	110.0	30.19	29.42	183.7	33.07	5.61	4.35	5.43	1.63	50.09
DF 46–48	<2	9.47	37.29	1257	159.9	214.1	1678	135.3	22.85	28.6	48.11	18.14	253.0
	2–10	6.63	23.59	654.8	62.9	74.81	822.8	103.4	12.52	12.95	22.84	6.67	158.3
	10–20	9.73	26.47	551.3	49.88	58.37	695.8	121.2	13.48	10.51	14.59	4.01	163.8
	20–63	11.05	25.34	515.7	42.99	52.77	647.8	119.3	12.72	6.92	13.98	5.28	158.2
	>63	45.23	99.19	1480	170.3	200.9	1996	476.7	57.23	38.41	44.36	13.97	630.6

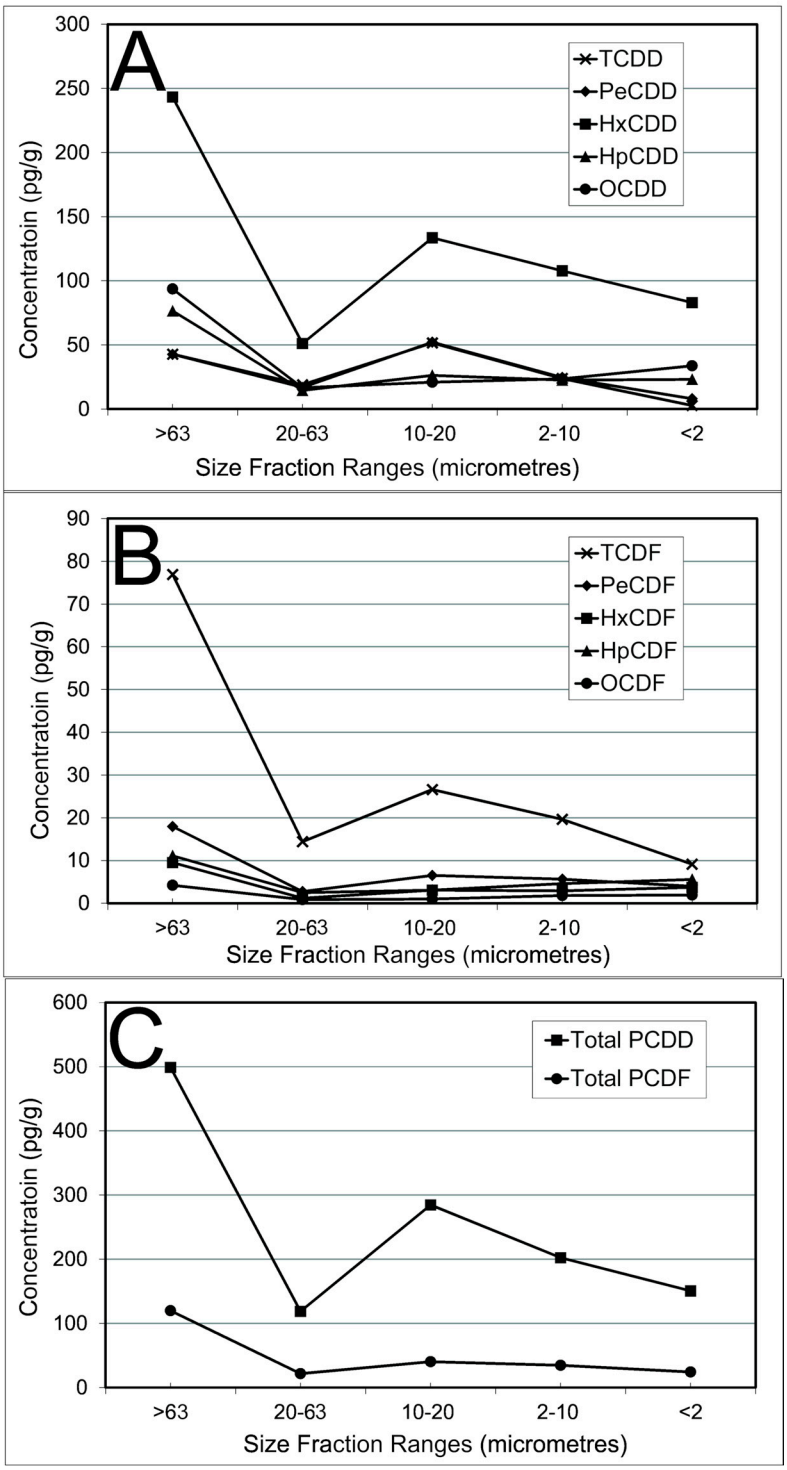


Figure 13. Plot showing the changes in concentration of dioxins (**A**), furans (**B**) and total homologues (**C**) between different size fractions at the 14–16 cm depth interval. The overall trend is of decreasing concentration with progressively finer grain size.

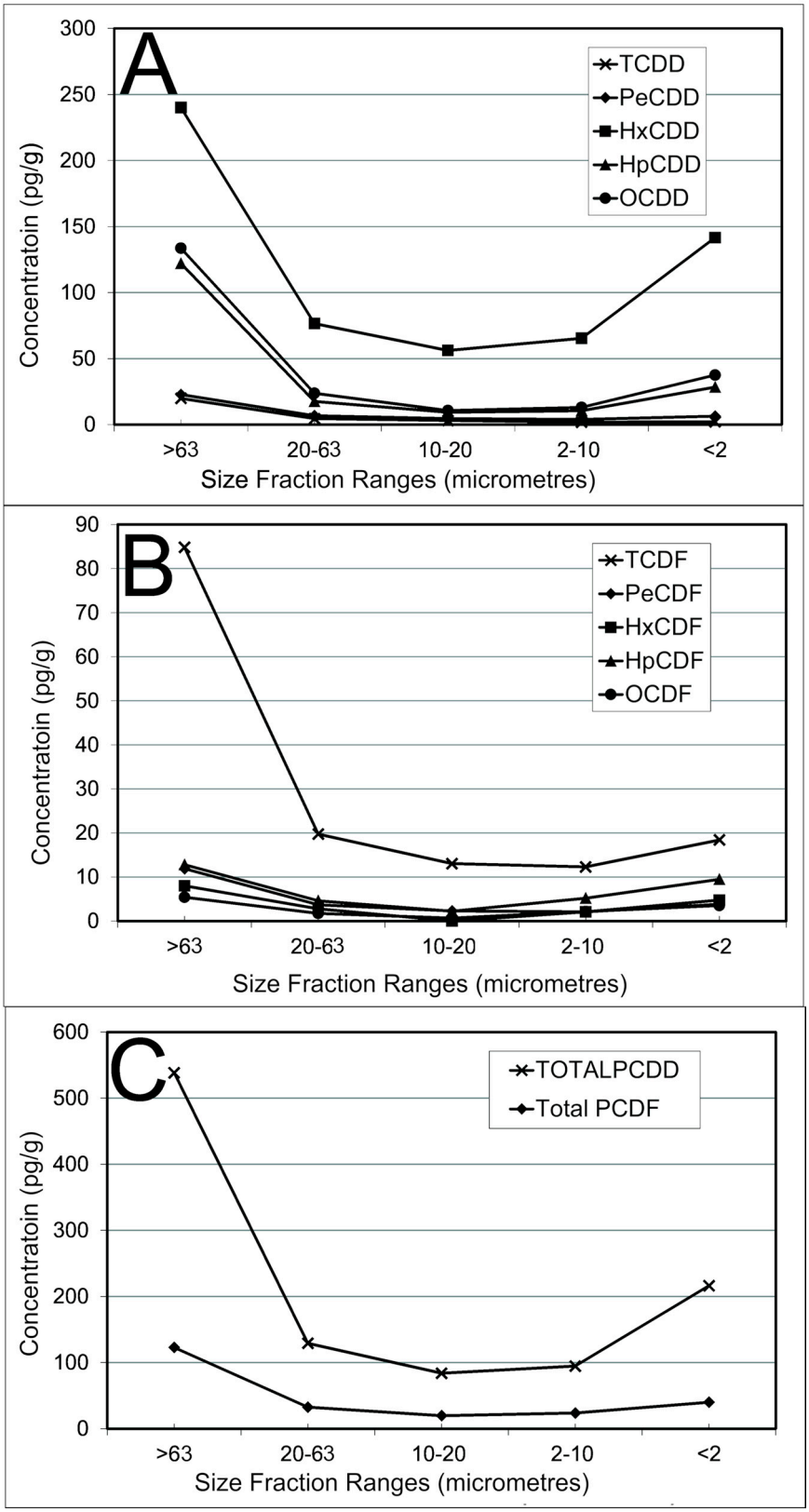


Figure 14. Plot showing the changes in concentration of dioxins (**A**), furans (**B**) and total homologues (**C**) between different size fractions at the 20–22 cm depth interval. Peak concentrations occur in the coarsest fraction. Dioxin concentration increases in the finest two size fractions, whilst furan concentration remains relatively constant throughout.

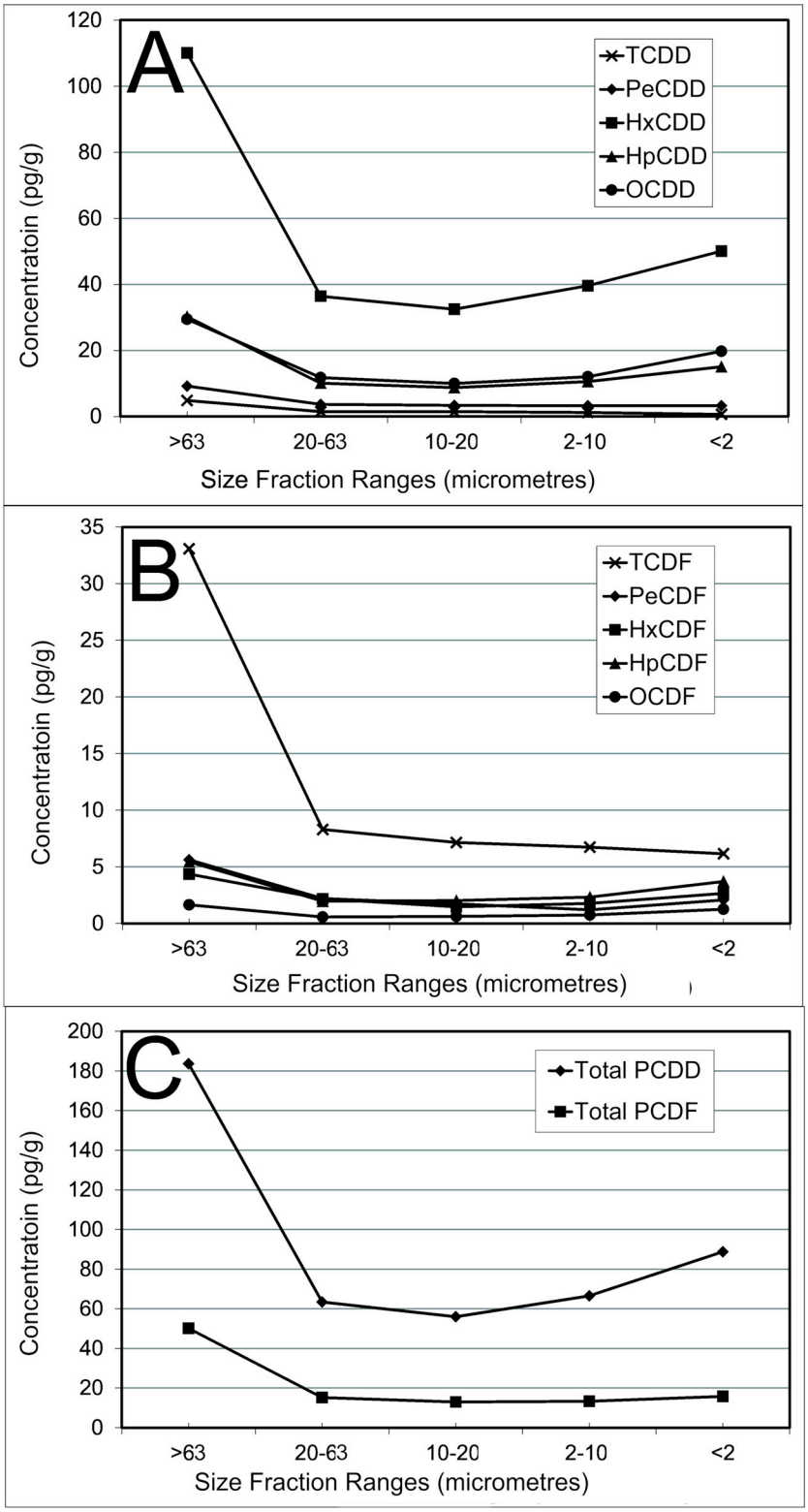


Figure 15. Plot showing the changes in concentration of dioxins (**A**), furans (**B**) and total homologues (**C**) between different size fractions at the 34–36 cm depth interval. Peak concentrations occur in the coarsest fraction. Some dioxin and furan homologues increase in concentration in the finest two size fractions, whilst other homologues show steady decrease in concentration.

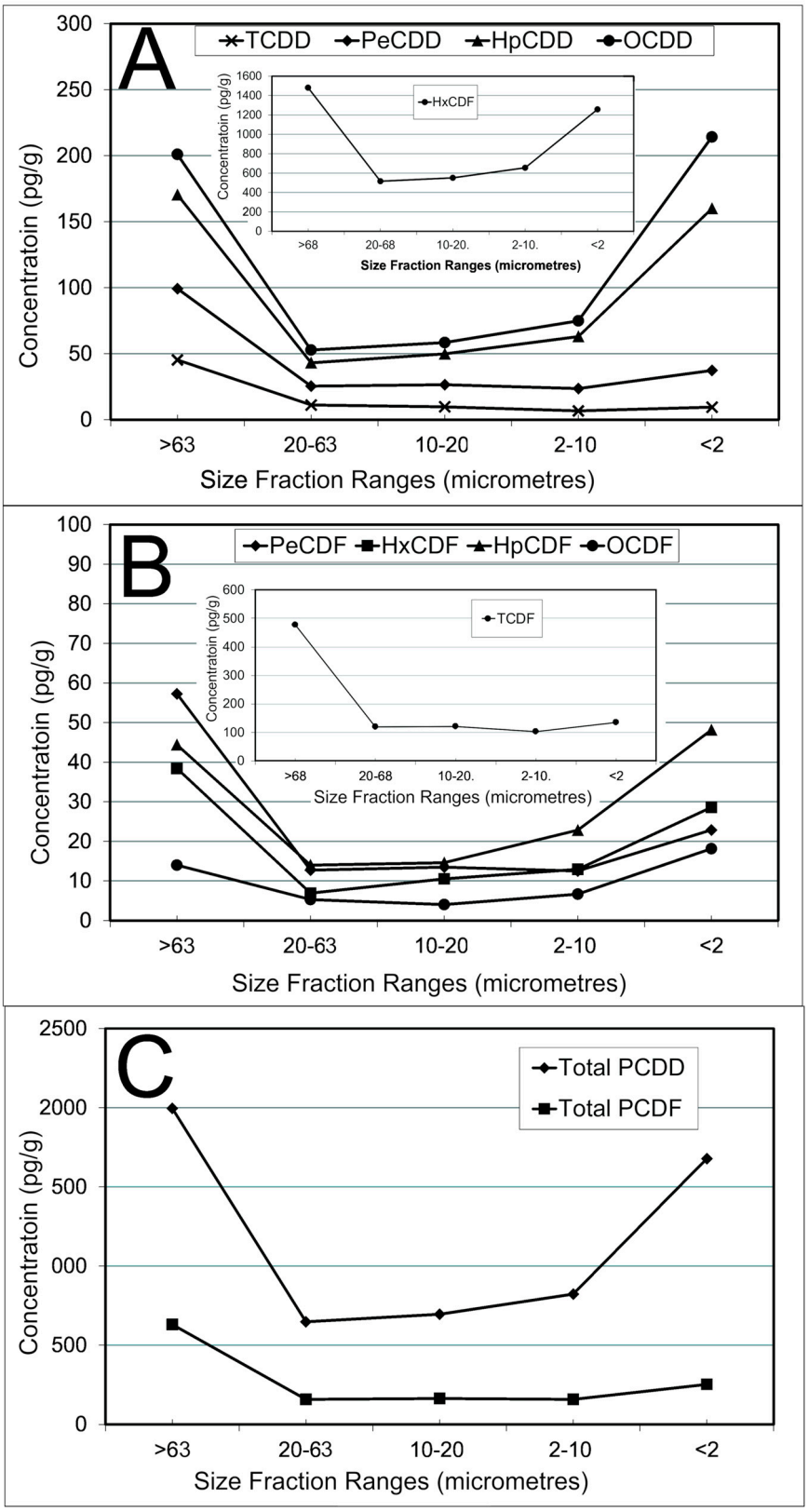


Figure 16. Plot showing the changes in concentration of dioxins (**A**), furans (**B**) and total homologues (**C**) between different size fractions at the 46–48 cm depth interval. The majority of dioxin and furan homologues show significant increase in concentration in the finest three fractions. Insets show homologues, HxCDF and TCDF, present at concentrations significantly higher than other homologues.

The selected sediment intervals presented in Table 6 show similar trends in homologue concentrations for both PCDDs and PCDFs. Majority of samples show the highest concentration of dioxins and furans in sediment size fractions of >63 µm. The majority of samples show the second highest concentration of all homologues in the <2 µm size fraction with the exception of the size fractionated samples of DF 14–16 cm that show higher concentrations of homologues in the 10–20 µm size fraction compared to <2 µm size fraction. There are a few other exceptions where the 20–63 µm size fraction has the second highest concentration of TCDD, PeCDD, TCDF or PeCDF in DF 20–22, DF 34–36 and DF 46–48 samples.

3.2.4. Organochlorine Compounds and Surface Area

Relationships between surface area and homologue concentration in size fractionated samples are highly variable with majority of size fractionated samples and homologues showing no correlation to surface area (Table 7). Only sample DF 46-48, shows a (positive) correlation between OCDF, HpCDF, OCDD and HpCDD with surface area (Figure 17), however the remaining homologues or total dioxin/furan concentrations do not show any correlation with surface area at this depth. DF 46–48 does have the highest concentration of homologues in the sample suite and this be a factor in showing a relationship with surface area. The lack of correlation within the entire sample suite illustrates that surface area of mineral matter does not appear to be a significant factor in the accumulation of dioxins or furans in this sediment.

Table 7. Regression co-efficient (r^2) values for dioxin/furan/total homologue concentration (pg/g) versus surface area (m^2/g). Negative values indicate a negative correlation between the two parameters. The number of size fractions indicates how many data points were used to generate the regression coefficient; r^2 values using four size fractions exclude the >63 µm fraction from the calculation, r^2 values using five size fractions include all the fractions.

Sediment Interval (cm)	TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total PCDD	TCDF	PeCDF	HxCDF	HpCDF	OCDF	Total PCDF
DF 14–16	−0.52	−0.39	−0.08	−0.05	−0.007	−0.13	−0.18	−0.09	−0.004	0.002	0.00005	−0.11
DF 20–22	−0.01	0.0004	0.15	0.01	0.02	0.05	0.01	0.004	0.15	0.29	0.21	0.01
DF 34–36	−0.03	−0.16	−0.03	−0.01	0.008	0.02	−0.18	−0.12	−0.004	0.01	0.06	−0.11
DF 46–48	−0.002	0.02	0.41	0.52	0.62	0.4	0.0003	0.03	0.35	0.66	0.74	0.03

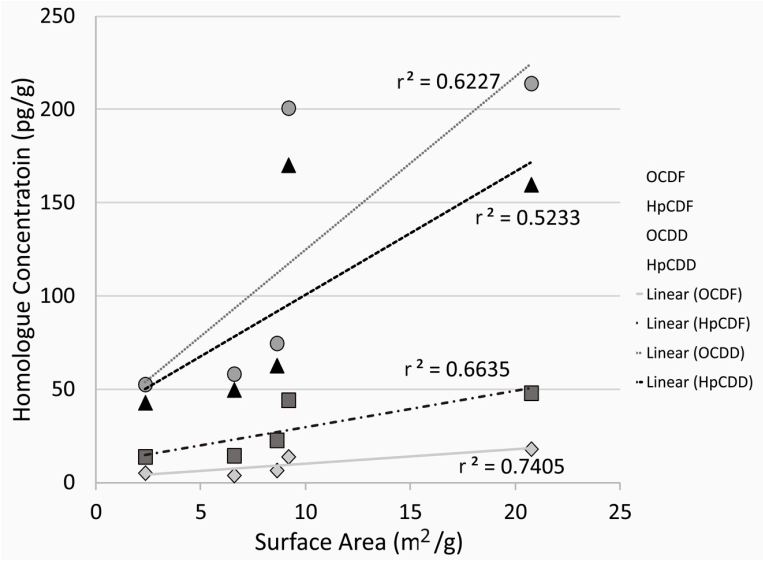


Figure 17. Positive relationship between the concentration of four homologues and mineral surface area in sample DF 46–48. This is the only homologues that show a correlation between homologue concentration and surface area from the fractionated size samples.

3.2.5. PCDD/Fs and Organic Matter

A good correlation exists between PCDD/F and total organic carbon (C_{org}) concentration in both bulk and size fractionated sediments. Figure 18 shows TCDD through OCDD plotted against C_{org} concentration for size fractionated samples. TCDD has the weakest correlation, r^2 = 0.28, whilst HpCDD has the strongest correlation, r^2 = 0.63. Figure 19 depicts the same relationship, without the >63 µm fraction, which was omitted based on previous data that suggested that unlike finer fractions, it is not related to mineral surface area. Regression co-efficient (r^2) values are higher for HxCDD through OCDD (r^2 = 0.8; Figure 19), whilst the strength of the relationship decreased for TCDD and PeCDD.

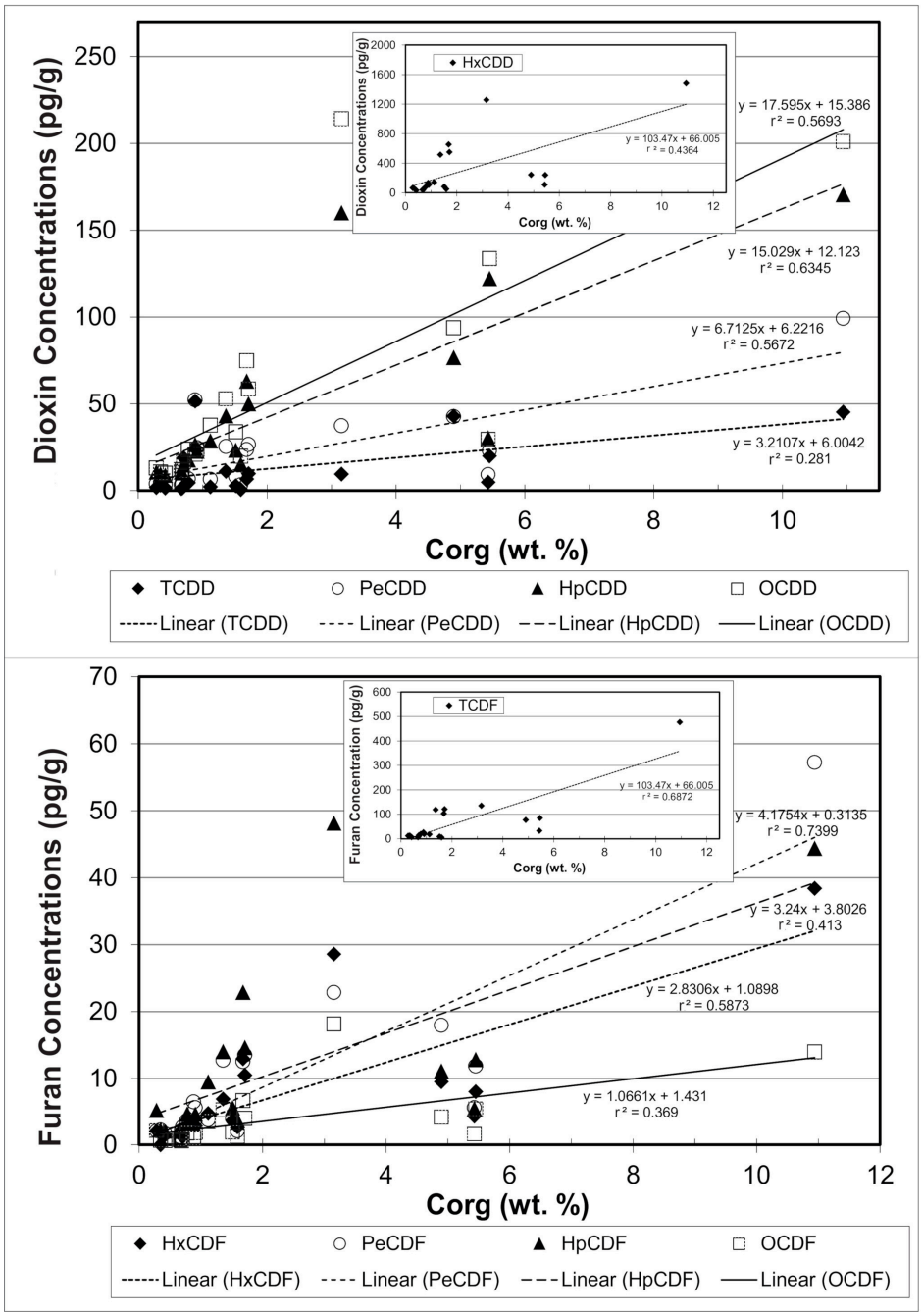


Figure 18. Plot showing the correlation between dioxin and furan concentration and organic matter concentrations in size fractionated sediments. Inset plots are those congeners, the HxCDD and TCDF, with concentrations that are significantly higher than other congeners.

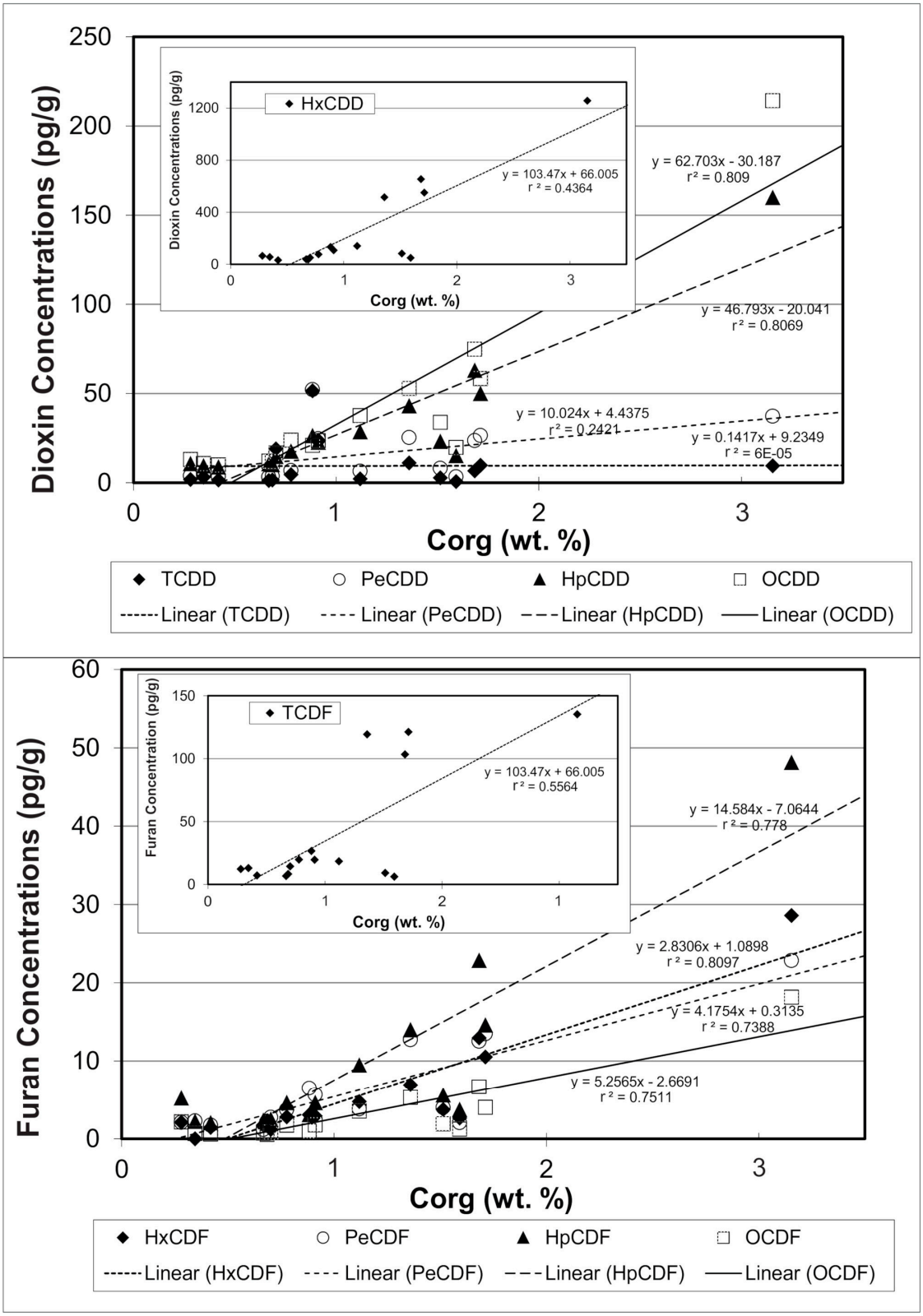


Figure 19. Plot of dioxin and Furan concentration versus organic matter concentration with the >63 μm fraction removed. Note the increase in r^2 value for HxCDD through OCDD dioxin and the decrease in r^2 value for TCDD and PeCDD.

4. Discussion

4.1. Organic Matter, Total Nitrogen and Surface Area

The concentration of TOC and TN (0.5–1.7 wt. % TOC; 0.04–0.1 wt. % TN; Table 3) in the bulk sediment samples is typical for a paralic environment such as Howe Sound, and is similar to TOC and TN concentrations found to the north in the Squamish Delta sediments [40]. However, the range of TOC concentrations is smaller than values obtained in other cores of comparable length taken further south along Howe Sound [33]. Unlike the cores taken by [33], the core sample taken in this study does not show a progressive decrease of TOC to a background concentration with increasing sediment depth (Figure 3A), as is often the case [11]. Reasons for this are unclear. Upon visual inspection, the core did not seem to be significantly affected by bioturbation, and this was confirmed during subsampling. The location of the core, chosen based upon its proximity to the Woodfibre Pulp Mill, could also be a contributing factor to the observed TOC profile. The area receives not only sediments from the north, supplied from the distal reaches of the Squamish Delta, but also from the south. A return gyre affects this area, supplying sediments from other areas in the Sound [50]. The proximity of the core to the Woodfibre Pulp Mill might result in a TOC signature that is directly linked to temporal changes in the discharge and composition of mill effluent. As a result, it is likely that a combination of these factors may be the cause of the irregular downcore changes in TOC concentration. This may also explain the ambiguity that arose from ^{210}Pb dating, where multiple sediment sources could have disrupted the steady accumulation and decay of ^{210}Pb from a single sediment source [47].

The TOC and TN trends observed in the size fractionated sediments are identical (Figure 10a, b), with the >63 μm fraction containing 55–70% of the TOC and 40–50% of the TN in each sample. The <2 μm fraction contains 15–20% of the TOC and 25–30% of the TN in each sample, with the remainder being distributed between the three intermediate size fractions. The enrichment of TOC in the >63 μm fraction is attributed to the presence of particulate rather than adsorbed OM on the surfaces of mineral grains, and is therefore independent of surface area [40]. However, the OM in the <2 μm fraction, which probably represents approximately one fifth of the OM present in the sample, is most likely adsorbed to mineral surfaces [40] and represents the recalcitrant portion of the sample that is no longer susceptible to remineralization [11].

The C_{org}/N ratio trend for the bulk sediment samples shares a similar downcore profile as TOC (Figure 3A). C_{org}/N values change from 13 to 23 over the length of the core (Figure 4), which suggests a dominant terrestrial source for the organic matter [51]. However, minor scatter around the regression line in Figure 5 suggests the presence of either an additional type of OM, or a secondary source. C_{org} versus TN relationship for the size fractionated sediments is also variable (Figure 11), particularly in the >63 μm fraction, which appears to have consistently higher TOC than TN concentrations, as shown by the >63 μm regression. This is similar to results from sediment samples collected from the Squamish Delta [40], where the >106 μm fraction falls on a more "carbon rich" regression line. This is attributed to the dominance of particulate or "detrital" OM over adsorbed OM in the coarsest fraction [40]. However, in this study, the >63 μm fraction probably contains both detrital OM and some adsorbed OM due to the larger variation in grain size within this fraction.

Linear regression of surface area and TOC for bulk sediment samples (Figure 9) explains 40% of the variance. Many studies have found significantly better correlation between these parameters, especially with samples collected from continental shelves [11,52]. Larger degrees of variation between surface area and TOC content is not uncommon in paralic settings [40], and is attributed to variable proportions of detrital OM, and a much larger range of grain sizes in the bulk samples. The relationship between surface area and TOC in size fractionated samples highlights the effects of detrital OM and grain size on the correlation (Figure 12a,b). There is little relationship between surface area and TOC when all size fractions are considered, primarily due to the four samples from the >63 μm, which have higher than expected TOC contents for their surface areas (Figure 12a). These samples also have high surface area values (Table 5) when compared to intermediate size fractions, which may be the result of

macroscopic mica flakes (probably muscovite) that are more common in this fraction. The remaining size fractions show a stronger relationship between surface area and TOC (r^2 = 0.51; Figure 12b). However, three of the four <2 μm fraction samples have lower than expected TOC contents than the regression predicts, a phenomenon not uncommon in paralic settings where TOC loadings are often lower than sediments of similar grain size from continental shelf regions [11,53]. Excluding these outliers from Figure 12b further improves the regression, but is probably not representative of the actual relationship between TOC and surface area in the samples.

4.2. Controls on Organochlorine Concentrations

As this study is focussed on a single cored interval within the Howe Sound, the discussion on spatial distribution is limited to stratigraphic distribution and will not discuss lateral distribution of the pollutants within the sediments.

Downcore concentration trends in polychlorinated organic pollutants show selective enrichment at specific horizons rather than gradual enrichment or depletion with increasing depth, as is usual with organic-rich sediments [11,54,55]. Thus, concentrations of total PCDD and PCDF are relatively constant except for the 10–25 cm interval and below 42 cm, where large increases in concentration occur (Figure 6a,b). Unfortunately, problems with ^{210}Pb dating prevented derivation of a chronology for the core. Previously published data [33] from other parts of Howe Sound shows peak concentrations of 8 pg/g, 65 pg/g, and 30 pg/g (TCDF) and 660 pg/g, 480 pg/g and 340 pg/g circa 1970, 1982 and 1989 respectively, but without more accurate information on sedimentation and accumulation rates, and potential surface mixing within the sediments, it is impossible to correlate these dates with peak concentrations in the core. Bioturbation was observed in a similar core retrieved from the eastern arm of Howe Sound [33], suggesting that the sediments in the study core may have been mixed, but visual inspection upon retrieval and subsampling did not reveal evidence of bioturbation. It is also possible that any mixing that may have occurred resulted from the coring procedure and subsequent subsampling, although every effort was made to minimize disturbance during retrieval and processing. However, the complex sedimentary environment that was the likely cause of the disrupted ^{210}Pb results may also be the reason for the unusual response observed in the organochlorine compounds. This is likely, especially if the organochlorine compounds are related to surface area in the same manner as TOC. Without accurate temporal data it is not possible to relate current concentration levels of dioxins and furans with the initial concentrations in either effluent discharged from the Woodfibre Pulp Mill or atmospheric inputs from other sources. Thus, any change in concentration from the time of initial input cannot be taken into account when assessing preservation of dioxins and furans and their relationship with surface area.

Downcore trends in individual homologues (Figures 7 and 15) are very similar to those of PCDD and PCDF. In both the dioxin and furan families, hexachlorinated homologues are present in much higher concentrations than other homologues. When HxCDD is considered separately, a correlation between chlorination and increasing concentration is observed (Figure 7), suggesting that preservation potential may also be a function of the number of chlorine atoms present in the molecule. This phenomenon is not observed in furans (Figure 15), where the abundances of TCDF and OCDF are reversed, OCDF being the least concentrated of the five homologues, and TCDF being the most concentrated. The lipid content of the TOC may also be a factor in the concentration of homologues as increasing chlorination of PCDD and PCDF increases their lipophilicity [5]. Higher polychlorinated organic compounds may be preferentially concentrated in the sediments due to higher lipid content of the organic matter in the sediment. More research is needed on the composition of the organic matter to determine if this is the case.

There is evidence in the size fractionated sediment data to suggest that organochlorine compounds are selectively adsorbed to inorganic particle surfaces, and that their concentration in the <2 μm fraction increases with depth. A commonality that exists in all four of the size fractionated samples is the high abundance of organochlorine compounds in the >63 μm fraction (Figures 13–16). This is

attributed to the presence of particulate OM that is not adsorbed to particle surfaces. DF 14–16 shows depletion of both total and individual homologues in both dioxins and furans with progressively finer grain size, which strongly suggests that surface area adsorption is not the mechanism by which OM and organochlorine compounds are associated at this sediment depth (Figure 13). However, other homologues from sample DF 14-16 show an opposite trend, with increasing concentrations in finer size fractions. OCDD, HxCDF, HpCDF and OCDF all show minor enrichment in the <2 μm fraction versus the 2–10 μm fraction (Figure 13a,b). Samples DF 20–22 and DF 34–36 show progressive enrichment from the 10–20 μm through to the <2 μm fraction in total PCDD and PCDF, and in a number of individual homologues as well (Figures 14 and 15). This suggests an increasing association of organochlorine compounds with finer sediment fractions and thus increasing importance of surface area as the mechanism by which these compounds are preserved. This trend is more pronounced in sample DF 46–48, which shows increasing concentrations of total PCDD, HxCDD, HpCDD, OCDD, and all of the furan homologues except for TCDF, from the 20–68 μm fraction to the <2 μm fraction (Figure 16). The increase between the 2–10 μm and <2 μm fractions is significantly greater than increases between coarser fractions, which highlights the significant increase in surface area in the <2 μm fraction compared to coarser fractions. DF 46–48 has the largest concentration of organic carbon, compare the other samples and this organic matter would contain large internal surface area which would adsorb organochlorine compounds.

It is evident from Table 4 (Figures 6–8) that neither a downcore enrichment nor depletion trend exists for homologue or total homologue concentration in dioxins of furans. However, when concentrations are compared to surface areas, the highest concentrations, which are found in the 14–16 cm, 20–22 cm, 34–36 cm and 46–48 cm intervals, do correspond to the highest observed surface area values in three of the four intervals, which suggests some link between surface area and concentration. Correspondingly, depth intervals 4–5 cm, 24–26 cm and 40–42 cm which contain the lowest measured concentrations for the majority of the compounds analysed also have the lowest surface area values. Regression analyses of the concentration of organochlorine compounds and surface area are poor and mineral surface area is not the only controlling factor in concentration of these pollutants.

The relationship between organochlorine compound concentrations and surface area are poor in all samples. The relationship does improve for sample DF 46–48 which may be due to the higher dioxin and furan concentrations. The majority of the homologues from the 46–48 cm interval have a moderate positive correlation with surface area (Table 7; Figure 17). There are strong positive correlations that exist between the TOC (Corg) content and dioxin and furan concentrations (Figure 18) with some homologues preferentially absorbing in this fraction (Tetra-Pentachlorinated PCDD/F). The r^2 values also increase for hexa- through octachlorinated dioxin/furan when the >63 μm was removed (0.4/0.6 to 0.8 dioxins, 0.4/0.7 to 0.8, furans; Figure 19). Correspondingly, r^2 values decreased in tetra- and pentachlorinated dioxin/furan when the >63 μm was removed (0.6/0.3 to <0.2, Dioxins, 0.7 to 0.6, Furans; Figure 19). This suggests an intrinsic relationship between tetra- and pentachlorinated dioxin/furan and the >63 μm fraction, whilst other homologues appear to be directly related to finer fractions. The improvement of the relationship between OM and homologue concentration in sediments <63 μm (Figure 19), as well as the strength of the relationship ($r^2 \approx 0.8$, PCDD/F) suggests a strong link between OM and homologue concentrations. Similarities in downcore concentration profiles of dioxins and furans to that of TOC (Figures 3A, 7 and 8) also support this conclusion. When placed in the context of surface area, which is a significant factor in controlling homologue preservation in sediments (Table 7; Figure 17), it appears likely that the relationship is somewhat symbiotic. The organochlorine compounds adsorb to the OM, which can be adsorbed to inorganic particle surfaces or as discrete particles within the sediment.

Although sediment toxicity was not the focus of this study, it is interesting to note that the toxicity of bulk sediment samples ranges from 0.4 ng/kg TEQ to 20.6 ng/kg TEQ, with only four of the bulk samples analysed exceeding the ISQG value of 0.85 ng/kg TEQ. These four samples were those selected for size fractionation: 14–16 cm, 20–22 cm, 34–36 cm and 46–48 cm. None of the TEQ values for these

four samples exceeded the PEL value of 21.5 ng/kg TEQ. TEQ values for size fractionated samples fell above the ISQG value, but were usually less than the PEL value. However, several size fractions did exceed the PEL value, most notably in the 46–48 cm depth interval, where the >63 μm fraction and <2 μm fraction had TEQ values of 67 and 40 respectively, suggesting significant contamination.

5. Conclusions

Analysis of bulk sediment samples taken from a core in Howe Sound, adjacent to the Woodfibre Pulp and Paper Mill, showed organic matter concentrations typical for a paralic environment. The average C_{org}/N ratio of 15 suggests that the dominant source of sedimentary organic matter is terrestrial. Further analyses revealed the presence of tetra- through octachlorinated dioxins and furans, which were likely sourced directly from Woodfibre Pulp Mill via effluent discharge into Howe Sound.

The primary source of organic and inorganic sediments for the Woodfibre area is the Squamish River, which discharges into the north end of Howe Sound via the Squamish Delta. However, complex currents in this area often rework sediments, and can also transport sediments from secondary sources further south in Howe Sound. Other sources of organic and inorganic sediments include the Woodfibre Mill effluent, the barges that deliver unprocessed woodchips to the mill and material directly from the steep terrestrial slopes surrounding Howe Sound. This complex sedimentary setting is the main causal factor in the unusual down core trends seen in TOC and TN concentration, C_{org}/N ratio, chlorinated organic compound concentration, and the failure of ^{210}Pb dating in producing a reliable chronology for the core.

Surface area values for bulk sediments were typical of a paralic environment, show moderate correlation with organic carbon and organochlorine pollutants, suggesting in turn that sediment surface area is a factor in the retention of both naturally occurring organic material and man-made organic pollutants in the sedimentary record.

Results from the analysis of selected size fractionated samples showed significant enrichment of both TOC and industrial pollutants in the coarsest and finest sediment fractions. Organic matter and associated pollutants present in coarse grained sediments is likely particulate in nature and not adsorbed to particle surfaces. A strong relationship between OM and dioxin/furan concentrations also occurs which supports the theory that pollutants absorb onto organic matter surfaces and remain as discrete particles of both the pollutant and OM adsorption on to mineral surfaces. Some homologues (tetra- and pentachlorinated) are directly related to the coarsest sediment fraction (> 63 μm), whilst other homologues (hexa- through octachlorinated) are concentrated in the finer sediment fractions (<63 μm).

The strength of the relationship between surface area and dioxin and furan concentration is governed by organic matter concentration and relative chlorination. Increasing organic matter concentration increases the concentration of pollutants; while dioxin and furan compounds with higher numbers of chlorine atoms in their molecular structure e.g., hex-octachlorinated PCCD/F, appear to be better preserved through adsorption to particle surfaces. The lack of variation observed in the geochemical composition and mineralogy of sediments in the upper reaches of Howe Sound [40] indicates that the composition of the inorganic sediment fraction is not a factor in the adsorption of organic matter or pollutants on to particle surfaces. This observation was also found by other workers [56,57].

The fate of industrial pollutants in inland waterways and paralic environments has been the focus of intense scrutiny over the past four decades. The relationship between sediment surface area and pollutant concentration demonstrated in this study is intrinsically related to the relationship between OM and surface area which is also observed by other workers [11,13]. It is unlikely that this relationship is confined only to dioxins and furans, but is probably ubiquitous throughout many other industrial chemical classes such as PCBs, polychlorinated insecticides et cetera, as well as other types of pollutants such as heavy metals from the mining industry. It is not clear, however, as to the extent of surface area preservation within other chemical classes, or whether there is any potential for

desorption and release of pollutants back into the environment following changes in sedimentological or redox conditions within the sediments.

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