Limited mobility of dioxins near San Jacinto super fund site (waste pit) in the Houston Ship Channel, Texas due to strong sediment sorption[☆]

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ABSTRACT

Sediments from a waste pit in Houston Ship Channel (HSC) were characterized using a number of molecular markers of natural organic matter fractions (e.g., pyrogenic carbon residues, PAHs, lignins), in addition to dioxins, in order to test the hypothesis that the dispersal and mobility of dioxins from the waste pit in the San Jacinto River is minimal. Station SG-6, sampled at the site of the submerged waste pit, had the highest dioxin/furan concentrations reported for the Houston Ship Channel/Galveston Bay (HSC/GB) system (10,000–46,000 pg/g), which translated into some of the highest reported World Health Organization Toxic Equivalents (TEQs: 2000–11,000 pg/g) in HSC sediments. Using a multi-tracer approach, this study confirmed our hypothesis that sludges from chlorinated pulps are a very likely source of dioxins/furans to this pit. However, this material also contained large quantities of additional hydrophobic organic contaminants (PAHs) and pyrogenic markers (soot-BC, levoglucosan), pointing to the co-occurrence of petroleum hydrocarbons and combustion byproducts. Comparison of dioxin/furan signatures in the waste pit with those from sediments of the HSC and a control site suggests that the remobilization of contaminated particles did not occur beyond the close vicinity of the pit itself. The dioxins/furans in sediments outside the waste pit within the HSC are rather from other diffuse inputs, entering the sedimentary environment through the air and water, and which are comprised of a mixture of industrial and municipal sources. Fingerprinting of waste pit dioxins indicates that their composition is typical of pulp and paper sources. Measured pore water concentrations were 1 order of magnitude lower than estimated values, calculated from a multiphase sorption model, indicating low mobility of dioxins within the waste pit. This is likely accomplished by co-occurring and strong sorbing pyrogenic and petrogenic residues in the waste pit, which tend to keep dioxins strongly sorbed to particles.

1. Introduction

The 50 mile long Houston Ship Channel (HSC) connects the San Jacinto River Basin to Galveston Bay (GB) and the Gulf of Mexico. The HSC is the busiest waterway in the U.S., involving annual vessel calls of more than 8300 large ships and 231,000 smaller commercial craft, including barges, carrying more than 230 million tons of cargo. The Port of Houston is the sixth largest seaport in the world and handles more foreign water-borne tonnage than any other U.S. port. The HSC is also host to the largest petrochemical complex in the U.S., and the 2nd largest in the world). Because of its industrial/urban watershed, the HSC is highly polluted with hydrocarbons and persistent organic contaminants such as dioxins from industrial and waste water effluents as well as runoff and atmospheric wet and dry deposition. Due to continuous erosion and deposition processes, the HSC needs to be continually dredged. The dredged sediment material is, in turn, typically used for the

development of dredge spoil islands and wetlands.

Primary sources of dioxins to the environment include the production of herbicides (Stellman et al., 2003), bleaching processes in pulp and paper mills, metal smelting, and the incineration of municipal and industrial waste (Fiedler, 1996; Hagenmaier et al., 1992; Sonnenberg and Nichols, 1995; Wilken et al., 1992). Automobile exhaust and combustion of landfill gases represent some non-industrial sources of dioxins (Hagenmaier et al., 1992). In the 1980s, pulp and paper mills were found to be important sources of dioxins to the environment (Macdonald et al., 1998). Dioxins are toxic and have a tendency to bioaccumulate in fish and benthic invertebrates (Wenning et al., 1992). These compounds are persistent in the environment due to their very long half-life and increasing number of sources (Wenning et al., 1992). Therefore, the mobility and bioavailability of these compounds has been a subject of considerable concern (Louchouarn and Brinkmeyer, 2009).

Until end of the 1980's, the pulp and paper mills around the HSC released their wastes directly as effluents into water bodies. The collapse of the pulp industry in early 1996, caused the pulp and paper mill in Pasadena to close its doors in January 1999 (Jensen et al., 1999). Even with the paper mill no longer in use and no longer producing contaminants, the environment was already damaged from many years of solid waste being released into the surrounding area of the HSC during its operation.

In 1990, an investigation of the HSC detected dioxins in fish and crab tissue (Crocker and Young, 1990). As a consequence, the Texas Department of Health issued a seafood consumption advisory for catfish and blue crabs throughout the HSC and upper GB. This advisory has remained in effect to the time of writing. The HSC was subsequently placed on the list of impaired water bodies as required by §303 (d) of the 1977 Clean Water Act (as amended, 1996). A total maximum daily loads (TMDL) study was then initiated by the Texas Commission on Environmental Quality (TCEQ). This study determined that dioxin concentrations exceeded the Texas Surface Water Quality Standard at the time (0.0933 pg/L) in more than 80% of all samples (Rifai et al., 2003; Louchouarn and Brinkmeyer, 2009). Despite regulatory efforts aimed at reducing dioxins during the past decade, Toxic Equivalents (TEQ) for dioxin were exceeded in 76% of sediment, 97% of fish, and 95% of crab samples analyzed. 2,3,7,8 Tetrachlorodibenzo-*p*-Dioxin (TCDD), the most toxic congener, was the major contributor to total TEQs in all samples (Rifai et al., 2003). In late 2005, the Texas Parks and Wildlife Department and the TCEQ identified a waste pit from a paper mill ('Champion Mill') on the San Jacinto River located in the upper HSC. During the 1960–1970's, unofficial reports suggest of 'mishaps' regarding waste disposal from the mill including the sinking of a paper mill barge and dumping of several tons of sludge directly into the HSC. Since the closing of the paper mill, the site of the sludge pits has slowly subsided and the earthen berms, meant to isolate the pit from the river, have eroded (See Chronosequence in Fig. 1 of SI; Koenig, pers. comm. 2009). In 2008, the pit was placed in the EPA's Superfund program for cleanup. In 2011, a reinforced concrete cap was installed to protect the river and adjacent landowners from leaks. However, major storm and flood events, such as the one experienced during hurricane Harvey in August 2017, may weaken and/or erode the protective cap potentially creating a situation in which dioxin contaminated sludge and sediments could be released into the HSC and GB.

Sediments sampled in the waste pit, prior to its capping, contain total dioxin concentrations as high as 46,000 pg/g dry weight (Hieke et al., 2016). There are no quality standards for dioxins in sediments, however, a conversion of sediment weight to volume indicates that dioxin TEQs are 9 orders of magnitude greater than the current surface water quality standard (0.078 pg/L; TCEQ, 2014). The San Jacinto waste pit has since been officially listed as a federal superfund site. High dioxin contamination in sediments extends from the upper HSC to the Port of Galveston and Bolivar Roads where ships enter the HSC from the Gulf of Mexico. Because of this, the Texas Department of State Health Services issued a new seafood consumption advisory for spotted sea trout and catfish in all of GB In July 2008. Several additional monitoring studies of dioxin levels in shrimp, crabs, and other finfish species in GB have been initiated by the TCEQ (e.g. Howell et al., 2011).

Widespread occurrence of known dioxin-degrading bacterial groups in the system of study were confirmed by Hieke et al. (2016), who found *Dehalococcoides* spp. bacteria in sediments throughout the HSC and GB. These authors determined half-lives of dioxins by anaerobic co-metabolic processes in organic carbon amended microcosms to be of the order of several years, in agreement with estimates by Adriaens and Grbic-Galic (1994). Anaerobic, sulfate reducing conditions, necessary for enhanced microbial dioxin degradation (Fu et al., 2001), were found to start from below a few cm in all sediments sampled. However bulk organic carbon ($\leq$1%), also essential for dioxin degradation, was found to be surprisingly low ($\leq$1%), in many of these sediments, except those from the waste pit.

Undisturbed aquatic sediments are considered to be a major sink for dioxins (U.S. EPA, 2000). Because of their high hydrophobicity, free dioxins occurring in water rapidly partition to organic carbon fractions (e.g., bulk organic and black carbon) in suspended solids and are transferred to sediments (Broman et al., 1992; Muir et al., 1992; Servos et al., 1992; Cornelissen et al., 2008a), like other chlorinated hydrocarbons (Cornelissen et al., 2004, 2006). Presence of black carbon, the most aromatic and condensed form of pyrogenic residues, has been shown to greatly increase sediment binding and thus, potentially decrease bioavailability of planar aromatic molecules (e.g., Gustafsson et al., 2001; Cornelissen et al., 2004, 2006; Lohmann et al., 2005) as well as lower their desorption rates. Other amorphous pyrogenic residues, like coal tar, can have a similar effect as black carbon (Arp et al., 2009).

The ongoing dredging and local 'disposal' of dredged spoils in the HSC and its GB transect, exposes and transfers dioxin deeply buried in sediments to the surface environments and biota. In a supplemental study of the impacts of dredging on the resuspension of dioxins in the HSC, funded by the Texas General Land Office/ Coastal Management Program (TGLO/CMP) and the TCEQ, no statistically significant reduction of dioxin concentrations in sediments from actively dredged sites versus non-dredged sites were found (Yeager et al., 2007), indicating that removal of these sediments will do little to alleviate the contamination.

The main objectives of the present research where a) to characterize the sources of dioxin/furan inputs to the San Jacinto River waste pit through congener fingerprinting and multi-tracer approaches, b) evaluate the potential remobilization of dioxins from the waste pit to the HSC, c) estimate the sorption capacity of sediments for dioxins/furans within the San Jacinto waste pit by comparing measured porewater concentrations to those estimated with a multiphase sorption model using organic and black carbon concentrations measured in the sediments of study; and d) evaluate the role of co-occurring hydrophobic contaminants on sorption models.

2. Methodology

2.1. Field program

A total of seven coring stations (SG-1, 3, 4, 5, 6, 7, 8) were identified, and samples were collected from each over two field expeditions (Fig. 1), one in September 2006 and the second in April 2007. All cores were collected by divers. Sediment cores were
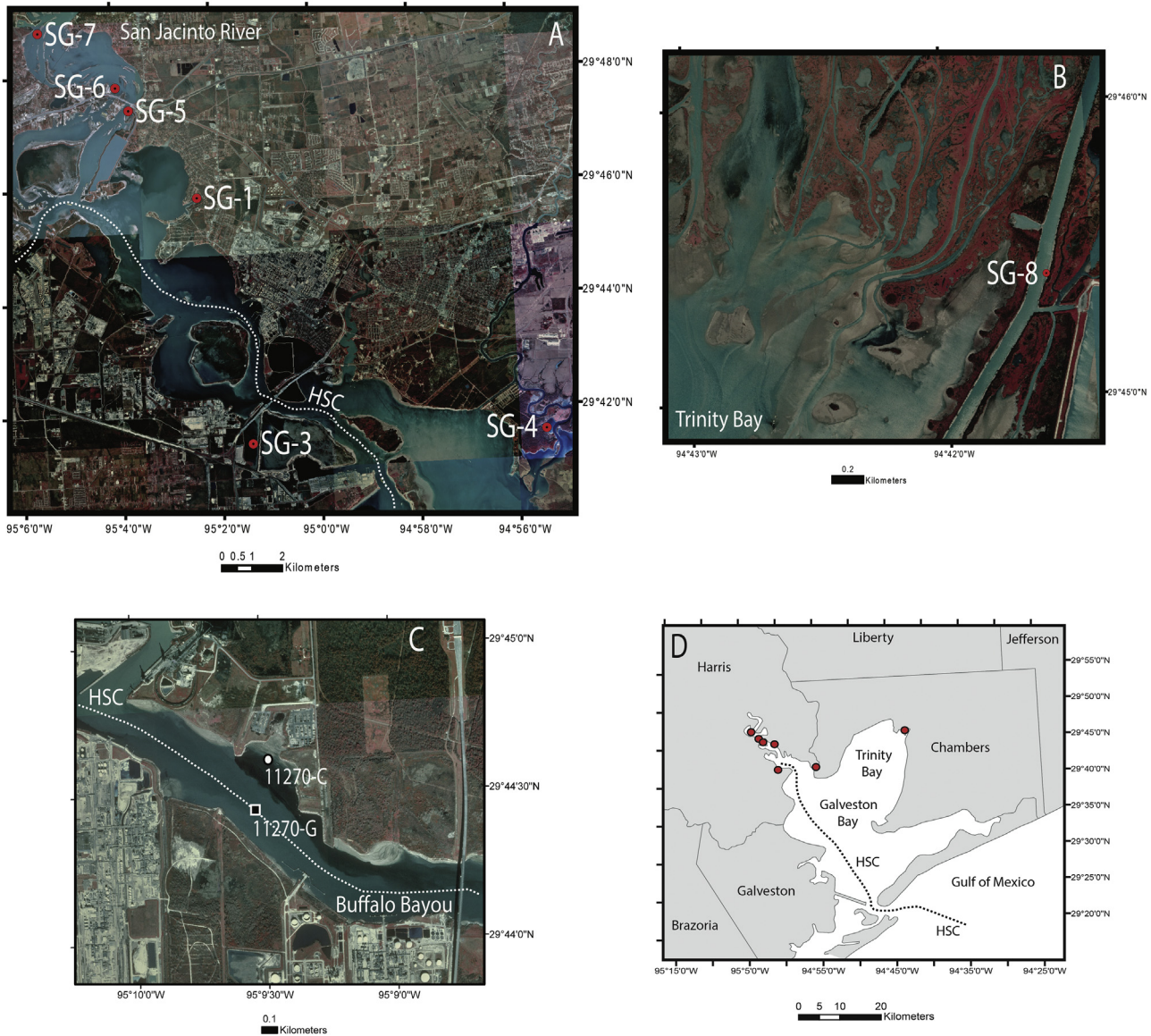
Fig. 1. Map showing all station locations, including stations located in NW Galveston Bay, the Houston Ship Channel, and lower San Jacinto River. Station SG-6 is at the paper mill sludge waste pit.

collected using PVC sleeves, physically driven to refusal (3–5 ft). Two sets of shorter cores were also collected to facilitate sediment pore water sampling (~60 cm) and RNA analysis (~30 cm). No discernible core shortening was observed for any cores. Each core was sub-sampled at centimeter intervals for the upper 50 cm and at 2 cm intervals thereafter. These subsamples were freeze-dried, ground in a mortar and pestle, homogenized, labeled, and stored for later analyses.

A total of 55 sediment cores were previously collected in 2004 from northwest Galveston Bay, the Houston Ship Channel, the lower San Jacinto River, and the lower Trinity River floodplain, Texas (Yeager et al., 2007). Three of these, two subaqueous cores collected by divers using PVC sleeves (11,270 and 11,193) and one terrestrial core collected from the wetlands adjacent to the Trinity River in an aluminum sleeve (FW1), were used for BC, lignin phenols and PAH analyses (shown in Fig. 1). Finally, a series of sediment grab samples were collected in 2004 (Fig. 1) and analyzed by a research group at the University of Houston for dioxins (Rifai et al.,

2005).

A chronosequence of the waste pit site, based on a geocoded series of aerial photographs, was provided by Larry Koenig (TCEQ; see Fig. 1 of the Supplementary Information - SI). This series of geocoded aerial photographs shows the evolution of the San Jacinto wetland north of I-10 after transformation into the waste pit illustrating periodic wash over and subsidence of the waste pit after emplacement.

2.2. Sedimentology and radiochemistry

Sediments were analyzed for grain size, ^{7}Be, ^{137}Cs, ^{210}Pb^{xs} according to Santschi et al. (1999, 2009) and Yeager et al. (2004, 2007).

Samples from the other HSC cores were already analyzed for physical properties (grain size and porosity) and radionuclides (^{7}Be, ^{137}Cs, and ^{210}Pb) and results were presented in Yeager et al. (2007).

2.3. Organic matter

The sediment core in the San Jacinto waste pit (SG-6; Fig. 1) was analyzed for organic and black carbon (OC and BC, respectively) as well as polycyclic aromatic hydrocarbons (PAHs) and terrigenous and biomass combustion biomarkers (lignin-derived oxidation by-products − LOPs, and levoglucosan, respectively). Determination of Soot-BC, via Chemothermal Oxidation method at 375 °C in air (CTO-375 method), as well as OC were described in detail by Louchouarn et al. (2007). PAH extraction and quantification methods followed the methods described by Kuo (2009) and Louchouarn et al. (2012). Combustion sources of PAHs (pyrogenic PAH) produce mixtures comprised primarily of non-alkylated PAH containing typically 4−6 condensed ringsÇ (Barrick and Prahl, 1987; Lima et al., 2003). Terrigenous biomarker analyses were performed using the CuO oxidation method according to Louchouarn et al. (2010), whereas levoglucosan extraction and analysis was performed according to Louchouarn and Brinkmeyer (2009). For each parameter, replicate analyses of sediments and standard reference materials (SRMs) were performed showing accuracies close to 100% and variability values of <5−10% for OC, BC-CTO, LOPs, and levoglucosan, and 10−20% for PAHs.

2.4. Dibenzo-p-dioxins and dibenzofurans

Some dioxin values were already determined for these samples from a previous study using EPA Method 1613B (Yeager et al., 2007), while the rest of the dioxin samples (core SG-6) were analyzed by Dr. Jermiah Shen (National Taiwan University) using the same method. The dioxin fingerprints of the grab samples are also presented as a comparison to the core samples analyzed in the present study.

2.5. Pore water dioxins

Dioxins in the pore water were determined with passive samplers, according to Cornelissen et al. (2004). These passive samplers are composed of sheets of plastic that get into equilibrium with the pore water. Pre-calibrated sampler-water distribution ratios are then used to compute freely dissolved concentrations (Arp et al., 2015).

3. Results and discussion

3.1. Sedimentology and radiochemistry

The depth of short term (~1yr) sediment mixing was determined using the ^{7}Be profile for each core. Sediment mass accumulation rates (MAR) using ^{210}Pb$_{xs}$ were determined where appropriate using the constant flux-constant sedimentation (CF-CS) model (Robbins, 1978; Yeager et al., 2004), where sedimentation rates are calculated assuming steady-state conditions, little sediment mixing, and at relatively constant porosity, using eq. (1a), (b):

$$[A(z)] = [A(0)]\exp(-\alpha z) \tag{1a}$$

$$\alpha = (\lambda/S) \tag{1b}$$

where [A(z)] and [A(0)] are the ^{210}Pb$_{xs}$ activity concentration at depth z and at the sediment-water interface, respectively; S is the sediment MARs (g cm^{-2} yr^{-1}) and λ is the isotope decay constant (^{210}Pb = 0.031 yr^{-1}). Some ^{210}Pb$_{xs}$ profiles (Fig. 23 SI) confirm episodic deposition events over a longer time frame and as such are unsuitable for use in determining a sediment MAR. Sediment MARs

have also been determined where possible using ^{137}Cs by eq (2):

$$S = (A_{pk}/T) \tag{2}$$

where A_{pk} is the mass depth (g cm^{-2}) at which the ^{137}Cs maximum occurs (1963), or alternatively, the first time ^{137}Cs can be determined (1953), and T = time (yr) since 1963 or 1953. This model assumes limited vertical mobility of cesium in sediments (Wenning et al., 1992). Sediment chronology was determined, where appropriate, using the mean ^{210}Pb$_{xs}$ and ^{137}Cs derived sedimentation rates. Radionuclide inventories (Tables 1 and SI) indicate that substantially more ^{7}Be, ^{137}Cs and ^{210}Pb$_{xs}$ are present in these sediments than can be accounted for by atmospheric deposition in the Houston area (Santschi et al., 1999), indicating sediment focusing effects, i.e. the process of sediment redistribution within a basin by hydrological transport to a particular coring location (e.g. Chillrud et al., 1999).

Profiles of ^{7}Be, ^{137}Cs, and ^{210}Pb$_{xs}$ (difference between total and ^{226}Ra supported ^{210}Pb), along with grain size, are given in Figs. 2−30, SI. Tabular results are summarized in Tables 1−8, SI. Core SG-6 (N29.79,402°, W95.06218°), collected on April 14, 2007 at the site of a paper mill sludge waste pit located where the San Jacinto River and the upper HSC meet (Santschi et al., 2009), exhibited low surface mixing and bioturbation, as indicated by shallow penetration of ^{7}Be into the sediments (Fig. 22 SI), indicating limited vertical movement of sediment, with mixing confined to the near surface (3 cm or 2.67 g cm^{-2}). However, lateral transport of different types of sediment produced a layered sediment structure with abrupt changes in grain size and chemical characteristics. This is illustrated in Fig. 23 SI. While the upper and lower portions of the section are dominated by fine-grained sediments (silt and clay), the chaotic distribution and importance of the sand fraction in the middle portion of the section (~20−35 g cm^{-2}) indicates episodic deposition.

A minimum estimate of sediment MAR is possible using the ^{137}Cs profile (Fig. 24 SI). The maximum depth of measurable Cs indicates a minimum sediment MAR of 1.14 ± 0.02 g cm^{-2} yr^{-1} (Table 1 SI). The ^{137}Cs peak at 65 cm amounts to 44 years since 1963 (the peak bomb fallout year), and the first appearance of ^{137}Cs in sediments amounts to 54 years since 1953. This yields an average sedimentation rate of 1.5 cm/yr.

3.2. Organic matter fractions

In core SG-6, OC values fluctuated through depth with peak values at 10 cm (~2%) and between 31 and 37 cm depth (~4−8%, Fig. 2, Table 9 SI). Lignin concentrations (represented as the sum of eight phenol oxidation products: Σ8) followed this same trend, with values ranging from ~1 to 12 mg/g (Fig. 2; Tables 12 and SI). In particular, the very high lignin oxidation product (LOP) concentrations observed mid-depth (32 cm) for SG-6 (10−12 mg/g), match lignin levels in pure plant organic matter (OM); this has only been reported in the environment in sediments heavily impacted by pulp and paper mill effluents (Louchouarn et al., 1999). Low cinnamyl:vanillyl (C/V) and high syringyl:vanillyl (S/V) phenol ratios for these sediments identify the source of the lignin as woody material from angiosperm species (Goñi and Hedges, 1992). The strong relationships between lignin and OC (r^{2} = 0.91) and the high C/N values (15−60; Fig. 2) confirm the terrestrial nature of OM throughout this core. Similar combinations of elemental ratios and LOP concentrations have been reported in coastal sediments heavily impacted by the dumping of pulp mill wastes (Macdonald et al., 1992; Louchouarn et al., 1999).

Values for BC fluctuated throughout the SG-6 core (Fig. 3), with three large peaks at 10, 32 and 80 cm depth (0.2, 0.3 and 0.4%,
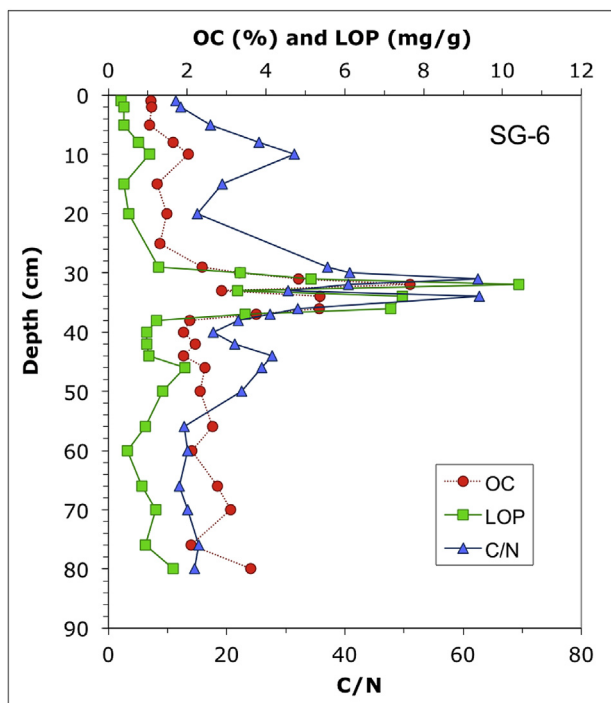
Fig. 2. Organic carbon concentrations (OC, percent weight), atomic carbon:nitrogen ratios (C/N), and lignin (Σ8, sum of eight lignin-derived phenols in mg/g) concentrations in sediment core SG-6 in the San Jacinto waste pit, which collectively indicate terrestrial sources. Lignin confirms the large inputs of pulp and paper waste products as well as flooded wetland vegetation.
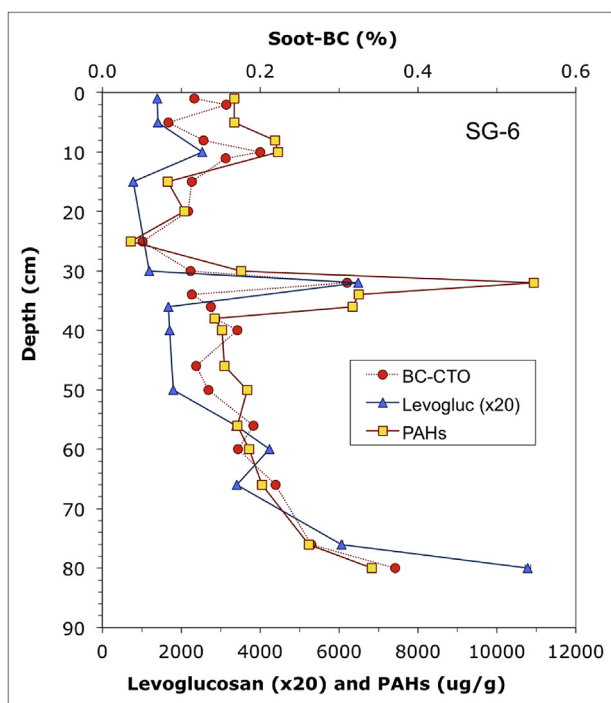
Fig. 3. Hydrophobic organic contaminants (PAHs), BC geosorbents (Chars and Soot), in Core SG-6. PAH confirm combustion by-products and large hydrocarbon dumping; BC (soot) confirms high-temperature combustion by-products (correlated to PAHs) and levoglucosan confirms biomass low-temperature combustion (correlated to BC and PAH). The trends in co-occurrence of all these markers are unique to this environment and are not seen elsewhere.

respectively; Fig. 3). BC comprised 2–14% of the OC, with an average value of 7%, close to the literature average for 90 sediments of 9% (Cornelissen et al., 2005, 6881). The concentrations of Levoglucosan, an unambiguous marker of biomass combustion (Kuo et al., 2008; Louchouarn and Brinkmeyer, 2009), also peak at these three depths suggesting the presence of a wide range of combustion byproducts from low temperature chars (characterized by levoglucosan but completely missed by BC-CTO) to high temperature, condensed pyrogenic carbon from fossil sources (characterized by BC-CTO).

BC values at the other studied sites were variable and low (0.04–0.37%). The values were not consistent on a regional scale, suggesting more localized inputs. Station UH11270 (Table 11 SI) had the highest proportions of BC as a fraction of OC (6–76%), showing the importance of combustion processes on inputs to these sediments. PAH concentrations were also variable, with the pit (SG-6; Table 12 SI) usually showing the highest values. Sources were found to be a mixture of pyrogenic and petrogenic inputs with the proportion changing dependent on location. This indicates that inputs of PAHs to the environment are not exclusively from combustion processes. Such a mix of sources is to be expected in the ship channel of a petrochemical complex since PAHs could also be added through oil spills.

3.3. Fingerprinting of PCDD/Fs - sources and fate of dibenzo-p-dioxins and dibenzofurans

Complete dioxin congener data are provided in the Supplementary Information (SI) Section (Tables 14 and 15 SI), including specific concentration data on the most toxic dibenzo-*p*-dioxin and dibenzofuran congeners (2,3,7,8 TCDD and 2,3,7,8 TCDF, respectively), toxicity-based concentrations (toxic equivalents: TEQ) for each interval, and the chronological data derived from the radionuclides where possible.

Throughout the HSC, dioxins showed large variations in concentrations that spanned 4–5 orders of magnitude (Fig. 4; Tables 14–15 SI). The present study confirmed the expectation that total PCDF would be higher in the pit site sediments (SG-6) than values for total PCDD. In contrast, at all other locations in the HSC, total PCDDs were higher than total PCDFs in the sediments, leading to a 2–3 orders of magnitude shift in the PCDD/PCDF ratio from the reference site (FW1: ~32) to the pit site (SG-6 and Sta15: 0.4–1.8). In addition, it has been shown that since dibenzodioxins (DBD) have a higher reactivity with respect to dechlorination than dibenzofurans (DBF), a small number of lower chlorinated PCDD are expected to be detectable due to pulp chlorination (Dimmel et al., 1993). This also be the case for the sludge pit samples.

As expected, the sludge waste pit (SG-6) showed the highest dioxin concentrations, confirming the high contamination of this area. The combined total PCDDs and PCDFs ranged from ~10,000 to ~46,000 pg/g (Fig. 5). In this core, approximately 50–70 percent of the total amount of dioxins present in each sediment depth interval were represented by 2,3,7,8-TeCDF, which is primarily associated with pulp mills by-products (Macdonald et al., 1992). 2,3,7,8-TeCDF was 2- to 6-fold higher than OCDD, the second most common congener in these sediments. 2,3,7,8-TeCDD was also substantial, but TeCDF was still approximately four to six times more prevalent. This distribution of congeners is expected for bleached pulp (Dimmel et al., 1993).

The shift in concentrations and congener ratios (TCDD/OCDF and TCDF/OCDF), and therefore source inputs, is clearly illustrated in Figs. 4–5. Both figures show the orders of magnitude difference in total dioxins, and specifically of tetra-chlorinated congeners,
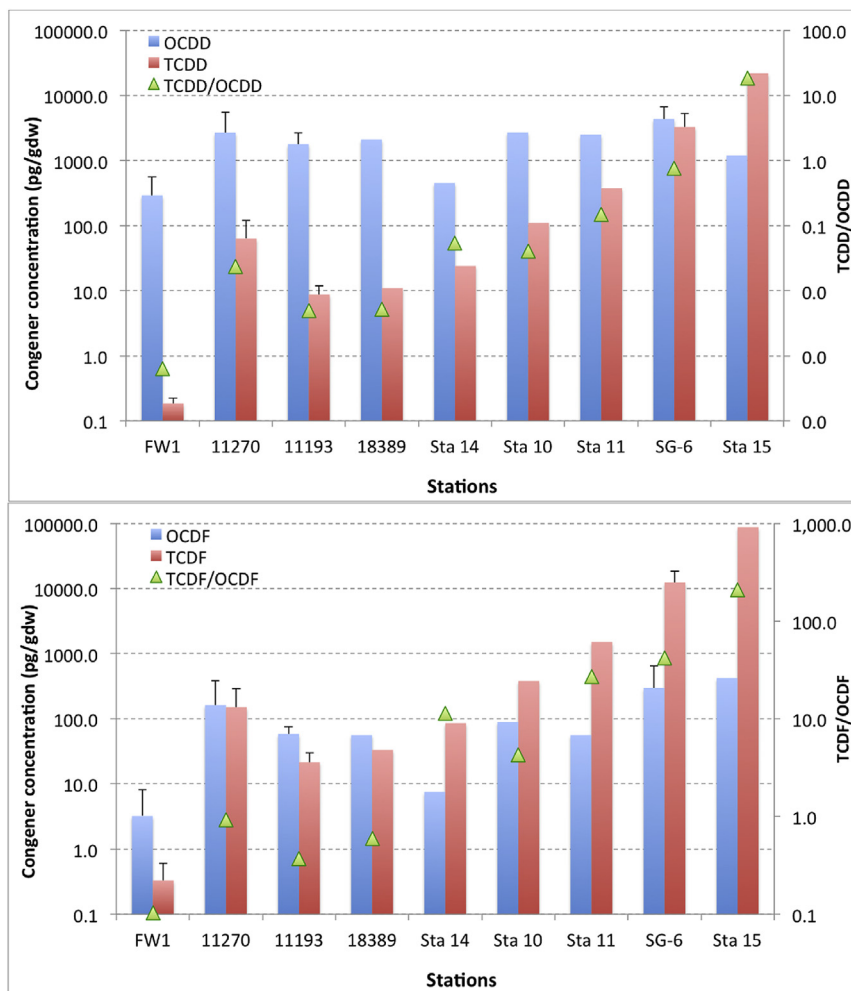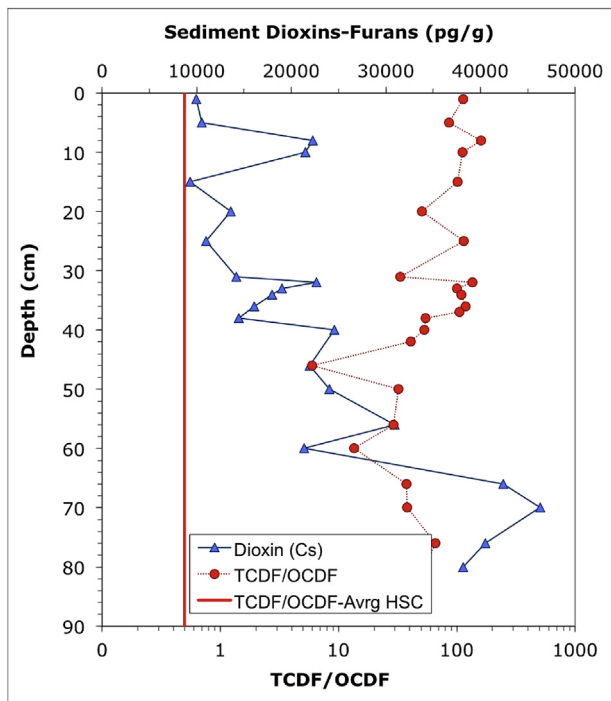
Fig. 4. Concentrations and tetra-to octa-chlorinated PCDD and PCDF in HSC stations. Error bars represent 1 std deviation around mean of the respective core.

between waste pit and the reference site (FW1). The TCDD/OCDD vs. TCDF/OCDF in sediments of the waste pit (SG-6 core and 15-G), when graphed on a property-property plot (Fig. 6), fall along or even above the pulp and paper end member signatures, confirming the origin of the pit waste sludge. Only two other stations (11 and 14) show values that seem substantially impacted by pulp sludge materials (within 10% of the pulp and paper signatures). Very rapidly, the signatures of the HSC cores drop towards values that are more typical of other industrial processes and atmospheric particulate fallout, all enriched in octa-chlorinated PCDD/Fs (Wenning et al., 1992; Baker and Hites, 2000). The strong shift in signatures observed just south of Interstate-10 (stations 11,193-G and 11,193-core) further suggests that contaminated sediment particles from the pit had not been remobilized substantially and redistributed throughout the entire HSC system at the time of sampling. Deviating from this trend, several core intervals in station 11,270 plot closer to the pulp and paper endmember signature than the closer station 11,193. Station 11,270 is in the second "hottest" area of HSC sediment and water concentrations. It was selected because it lies near or downstream from a former paper mill wastewater discharge points (Abitibi-Consolidated paper Mill at Sheldon, Texas outfall within sight of 11,270). The increase in TCDD/OCDD and TCDF/OCDF ratios in these sediments seems to support the idea that pulp and paper effluents inputs have contributed substantially to the PCDD/F load at that location. Station 11,270 is

also near discharges by other types of potential dioxin sources: a herbicide plant, a plastics plant, a chlor-alkali plant (now closed), a steel mill, and petrochemical plants. Inputs of PCDD/Fs in the rest of the HSC are thus probably due to sources other than the pit sludge materials and may include a combination of industrial point-sources, incineration of municipal and industrial waste, and secondary by-products of atmospheric photochemical reactions of chlorinated compounds (i.e. pentachlorophenol). The predominance of OCDD/Fs in the reference (control area) at the FW1 core strongly indicates atmospheric inputs as the primary source in this area (Baker and Hites, 2000; Yeager et al., 2007).

Different industrial processes produce PCDD and PCDF in different proportions. Therefore, as shown in Fig. 6, congener ratios can be used as first-hand indicators of source fingerprints of dioxins in sedimentary systems. At the locations in the HSC away from the pulp mill, PCDD values on average exceeded those of PCDF by a factor of 26. On the other hand, at the pulp mill site, the majority of dioxins present were PCDFs. The difference in the isomeric distributions found between these samples and those of the pulp waste site suggest different sources, with pulp mill acting as a point source to the SG-6 site, but with little to no influence on areas away from the mill indicating limited PCDD/F transport away from the waste pit site. A caveat to this interpretation is that the sampling for the present study was performed before to Hurricane Ike (which itself occurred prior to the capping of the waste pit). So, a more

Fig. 5. Total concentrations of dioxins and furans (PCDD and PCDF, respectively) in Core SG-6. The ratio of tetra-chlorinated to octa-chlorinated furans along core depth is also plotted in comparison to the average value observed in other HSC cores (red line) and showing 2–3 orders of magnitude higher values in support of pulp and paper mill source inputs. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

accurate evaluation of the potential redistribution of contaminated sediments post-flooding events needs to be performed before a conclusion on efficient sequestration in the pit can be reached. Similarly, the uniqueness of the dioxin fingerprints and the high concentrations in the waste pit offer an ideal opportunity to assess potential stability of the contaminated sediments under the capping protection following extraordinary flooding conditions such as were experienced during Hurricane Harvey.

3.4. Relationships of dioxins to other organic matter compounds

Lignin concentrations show a relationship to polychlorinated dibenzodioxins and furans (PCDD/Fs; Fig. 7) in the top and bottom sediments of core SG-6 ($r^2 = 0.61$), suggesting that the inputs of these HOCs are tightly linked to some inputs of pulp and paper waste products. This finding is consistent with earlier findings showing that chlorination of pulps was a strong source of PCDD/Fs to the aquatic environment until environmental regulations and/or changes in industrial processes have curbed such point-source emissions (e.g., Jonsson et al., 1993). However, a strong discrepancy exists in this relationship for the middle of the core (30–45 cm depth), which is characterized with extreme lignin concentrations for sediments (Louchouarn et al., 1999) but moderate PCDD/F concentrations relative to top and bottom values. The organic matter in the mid-section of the core may represent pulp waste highly enriched in lignin following mechanical separation from cellulose (rather than chemical, which is responsible for PCDD/F formation). More importantly, the substantial relationship between lignin and PAHs ($r^2 = 0.92$ in the 30–45 cm interval and 0.68 along the entire core) further suggests that the pulp waste products regardeless of production, were heavily contaminated with a suite of HOCs. On average, about a quarter ($24 \pm 7\%$) of all PAHs were derived from combustion (pyrogenic), whereas the rest tended to be mostly from petrogenic sources. The relationship existing between soot-BC and pyrogenic PAHs ($r^2 = 0.63$) and levoglucosan ($r^2 = 0.89$), further confirms the abundance of a mixture of combustion by-products in the waste sludge deposited in the pit. To our knowledge, this is the first and only study that reports co-occurrence in sediments of pyrogenic products from the entire combustion continuum. All prior studies have reported decoupling of high-temperature vs. low-to mid-temperature pyrogenic byproducts (Louchouarn et al., 2007; Kuo et al., 2011; Hanke et al., 2017), highlighting differences in the long-range atmospheric vs more local to regional hydrologic transport mechanisms for transfer of soot vs charred pyrogenic materials to sediments (Hanke et al., 2017). The high concentrations of all pyrogenic byproduct classes and their strong co-occurrence in core SG-6 suggest that the waste material was either burned prior to dumping, or burned on site prior to the site's subsidence and subsequent capping.
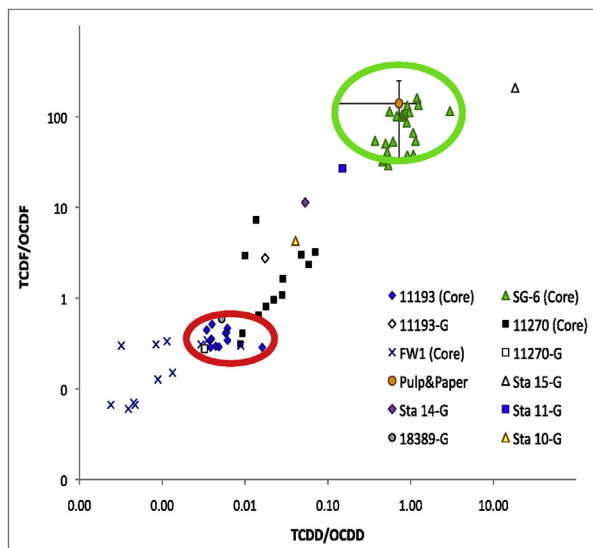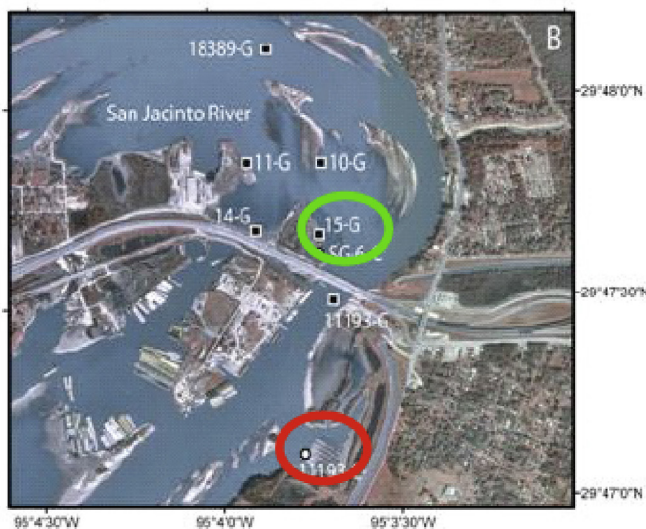
Fig. 6. Graph of TCDD/OCDD vs. TCDF/OCDF ratios, indicating that SG-6 data plot within close range of the pulp and paper end member signatures, which strongly indicates the origin of the pit waste sludges is pulp and paper. Literature values for pulp and paper endmember are from Rappe et al. (1987) and Macdonald et al. (1998).
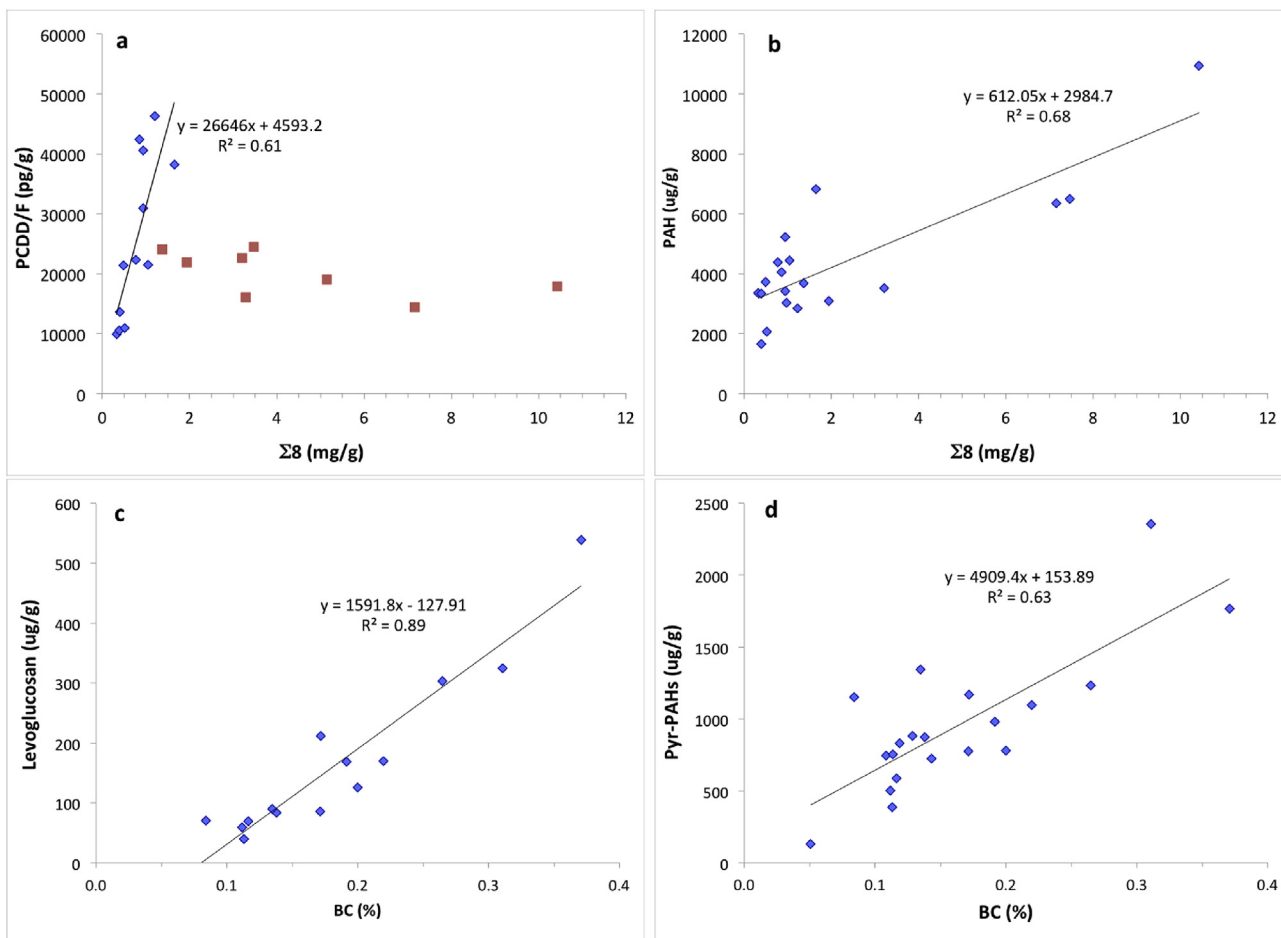
Fig. 7. a: Correlation between dioxins and lignin phenols found in the San Jacinto waste pit (SG-6). b: Correlation between PAHs and lignin phenols. c: Correlation between levoglucosan (marker of low temperature biomass combustion products) and BC (marker of high temperature combustion byproducts). d: Correlation between pyrogenic PAHs and BC.

3.5. Dioxin mobility

To evaluate the capacity for these sediments to release dioxins to the water column (through equilibrium with pore water), the theoretical sorption and free porewater concentrations (C_{PW}) ($ng.L^{-1}$) of dioxins were estimated based on a three-phase model which incorporates both amorphous OC and soot-derived BC as sorbents (eq. (3)):

$$C_S = f_{AOC}K_{AOC}C_W + f_{BC}K_{BC}C_{PW}^{\eta F,BC} \qquad (3)$$

C_s is the sediment dioxin concentration (ng/kg); f_{AOC} and f_{BC} are, respectively, the sediment mass fractions of amorphous OC and BC; K_{AOC} is the AOC-water distribution ratio (L/kg); C_{pw} is the freely dissolved dioxin equilibrium concentration in porewaters (pg/L); K_{BC} is the concentration-independent Freundlich BC-water distribution coefficient ((pg/kg BC)/(pg/L)); and $\eta_{F,BC}$ is the Freundlich exponent of BC sorption. No literature values are available for $\eta_{F,BC}$ for dioxins. Therefore, the empirical value for phenanthrene (0.61) was used in this model to calculate the sorption to BC (Cornelissen et al., 2008a).

In the K_{AOC-BC} model, theoretical values of C_W were modeled based on known solid-phase dioxin, amorphous organic carbon (AOC), and BC concentrations in the sediments of study and empirical K_{AOC} ($L.kg^{-1}$) and K_{BC} ($ng.kg^{-1}$ BC)/($ng.L^{-1}$) values. K_{AOC}

and K_{BC} were obtained from extensive studies in comparable environments (Cornelissen et al., 2008a, 2008b). The results of the models allowed for the calculation of the potential saturation of the sorbents or, on the other hand, the preservation of hydrophobic contaminants in the solid phase. These calculations can help discern if dioxins are either being released into the water column or taken out of the water column with a subsequent decrease in their potential bioavailability through sorption.

The results of these calculations show that pore water TEQ concentrations of dioxins measured directly with passive samplers were one order of magnitude lower than estimated values from the multiphase sorption models using K_{OC}, K_{BC} values, indicating limited dissolution of dioxins in SG-6 sediments (Fig. 8). This observation also suggests that sediments in the HSC have enough sorption capacity, which exceeds that predicted from the empirical models and accounting for the presence of pyrogenic geosorbents. This excess sorptive capacity may be due to the unique nature of the combusted pulp and paper sludge material, which keeps the freely dissolved fraction of HOCs to a level ~0.1–0.2 pg/L. Arp et al. (2009) discussed how non-BC pyrogenic and petrogenic residues can contribute to strong sorption, such as observed here. Further, much of the dioxins present could be essentially trapped in areas in the sediment that have small pores or are otherwise inaccessible to porewater.
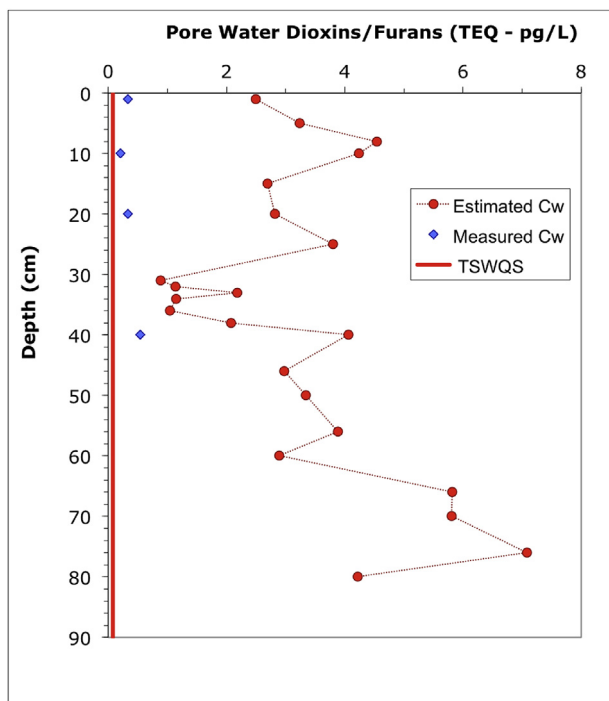
Fig. 8. Predicted and measured pore water dioxins/furans toxicity-weighted concentrations. (toxic equivalents or TEQs) at SG-6, showing an order of magnitude difference (lower) between prediction and measurement, which is within "error" of models (less than ± factor 30 for K_{OC}; Arp et al., 2009). Measured porewater concentrations (1.1—2.6 pg/L) were obtained using passive samplers (Cornelissen et al. 2008a,b) on a few depths, with sediment concentrations ranging 9000—46,000 pg/g (~70%of TEQ contributed by TCDD). Estimated porewater TEQs (total concentrations of 12—30 pg/L) were also calculated using an empirical sorption model (Cornelissen et al. 2008a,b) and measured geosorbent concentrations (OC and BC). The red line marks the most recent Texas Surface Water Quality Standard for dioxins (expressed as TEQ). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.6. Environmental implications and relevance

The unique and diverse environmental forensics approach presented in this paper, which used organic biomarkers to distinguish possible contamination sources, could be used in other contaminated sites, including super fund sites, to identify the sources and mobility of PCDD/F or similar contaminants. Our finding of the immobile behavior of PCDD/F within pulp and paper residue waste pit may indicate that PCDD/Fs are immobile in other such waste pits. However, remobilization can also occur through migration of colloidally bound dioxins, which might still be bioavailable. Haye et al. (2006) clearly showed that colloidally bound trace elements were still bioavailable to oysters, though that bioavailability depended on co-factors such as the presence of alginates, and likely, on kinetics. On the other hand, studies of Karlsson et al. (2009) and Sobek et al. (2014) indicate only a small chance that aged dioxins in the colloidal size fraction would be bioavailable. Furthermore, confirming our results of limited mobility of waste pit dioxins, PCDD/Fs results from tissue analyses of catfish and crabs that were carried out decades ago (Suarez et al., 2005) indicate significant differences from those of the waste pit sediments shown here (e.g., Fig. 6). This would strongly suggest that bioavailability of waste pit dioxins is limited, and other, more diffuse, sources, are responsible for bio-uptake in the HSC.

4. Conclusions

Sediments of a waste pit in the San Jacinto River (Station SG-6) are characterized by the highest dioxin/furan concentrations reported for the HSC/GB system (10,000—46,000 pg/g), which translated into extremely high World Health Organization Toxic Equivalents (TEQs: 2000—11,000 pg/g). Using a series of different markers, including lignin and dioxin congener signatures, this study confirmed our early assumption that sludges from chlorinated pulps are very likely sources of dioxins/furans to this pit. However, this material also contained large quantities of additional hydrophobic organic contaminants (PAHs) and pyrogenic markers (soot-BC, levoglucosan), suggesting the presence of a complex mixture of petroleum hydrocarbons and combustion byproducts. The very high levels of combustion-derived contaminants (low and high temperature pyrogenic byproducts), suggest that the sludge wastes were either pre-combusted before dumping, or combusted onsite prior to burial.

Comparison of dioxin/furan signatures in the waste pit with those from sediments of the HSC and the control site suggest that the remobilization of contaminated particles had not occurred beyond the close vicinity of the pit itself. The sediments of the HSC thus receive more diffuse inputs, entering the sedimentary environment through the air and water, which are comprised of a mixture of industrial and municipal sources.

Using an empirically-derived multiphase sorption model and concentrations of geosorbents and dioxins present in sediments, the estimated porewater concentrations (C_{PW}) in the pulp mill waste pit were an order of magnitude higher than pore water concentrations measured directly with passive samples, indicating limited dissolution of dioxins in SG-6 sediments. This further suggests that diffusive transport of dioxins is very unlikely from these sediments and that the only potentially significant export mechanism from the waste pit is advective transport of particulate- or colloid-sorbed dioxins. The very unique fingerprint signatures of these compounds in the waste pit makes it easy to track their potential release following major erosional events, such as may have happened during the recent catastrophic flooding resulting from hurricane Harvey.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2018.02.003.

References

Adriaens, P., Grbic-Galic, D., 1994. Reductive dechlorination of PCDD/F by anaerobic cultures and sediments. Chemosphere 29, 2253—2259.

Arp, H.P.H., Breedveld, G.D., Cornelissen, G., 2009. Estimating the in situ sediment—porewater distribution of PAHs and chlorinated aromatic hydrocarbons in anthropogenic impacted sediments. Environ. Sci. Technol. 43 (15), 5576—5585.

Arp, H.P.H., Hale, S.E., Elmquist Kruså, M., Cornelissen, G., Grabanski, C.B., Miller, D.J., Hawthorne, S.B., 2015. Review of polyoxymethylene passive sampling methods

for quantifying freely dissolved porewater concentrations of hydrophobic organic contaminants. Environ. Toxicol. Chem. 34 (4), 710–720.

Baker, J.I., Hites, R.A., 2000. Is combustion the major source of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans to the environment? A mass balance investigation. Environ. Sci. Technol. 34, 2879–2886.

Barrick, R.C., Prahl, F.G., 1987. Hydrocarbon geochemistry of the Puget Sound Region III. Polycyclic aromatic hydrocarbons in sediments. Estuar. Coast Shelf Sci. 25, 175–191.

Broman, D., Naf, C., Zebühr, Y., 1992. Occurrence and dynamics of polychlorinated-p-dioxins and dibenzofurans and other combustion related organic pollutants in the aquatic environment of the Baltic. Chemosphere 25, 125–128.

Chillrud, S.N., Bopp, R.F., Simpson, H.J., Ross, J.M., Shuster, E.L., Chaky, D.A., Walsh, D.C., Choy, C.C., Tolley, L.R., Yarme, A., 1999. Twentieth century atmospheric metal fluxes into central park lake, New York city. Environ. Sci. Technol. 33, 657–662.

Cornelissen, G., Kukulska, Z., Kalaitzidis, S., Christanis, K., Gustafsson, Ö., 2004. Relations between environmental black carbon sorption and geochemical sorbent characteristics. Environ. Sci. Technol. 38 (13), 3632–3640.

Cornelissen, G., Haftka, J., Parsons, J., Gustafsson, O., 2005. Sorption to black carbon of organic compounds with varying polarity and planarity. Environ. Sci. & Technol. 39, 3688–3694.

Cornelissen, G., Breedveld, G.D., Kalaitzidis, S., Christanis, K., Kibsgaard, A., Oen, A.M.P., 2006. Strong sorption of native PAHs to pyrogenic and unburned carbonaceous geosorbents in sediments. Environ. Sci. Technol. 40 (4), 1197–1203.

Cornelissen, G., Cousins, I.T., Wiberg, K., Tysklind, M., Holmström, H., Broman, D., 2008a. Black carbon-dominated PCDD/Fs sorption to soils at a former wood impregnation site. Chemosphere 72, 1455–1461.

Cornelissen, G., Wiberg, K., Broman, D., Arp, H.P.H., Persson, Y., Sundqvist, K., Jonsson, P., 2008b. Freely dissolved concentrations and sediment-water activity ratios of PCDD/Fs and PCBs in the open Baltic Sea. Environ. Sci. Technol. 42, 8733–8739.

Crocker, P.A., Young, C., 1990. Tetrachlorodibenzo-p-dioxins and dibenzofurans in edible fish tissue at selected sites in Arkansas, Louisiana, and Texas. U.S. EPA, Region 6: Dallas, TX. Unpublished report.

Dimmel, D.R., Riggs, K.B., Pitts, G., White, J., Lucas, S., 1993. Formation mechanisms of polychlorinated dibenzo-p-dioxins and dibenzofurans during pulp chlorination. Environ. Sci. Technol. 27, 2553–2558.

Fiedler, H., 1996. Sources of PCDD/PCDF and impact on the environment. Chemosphere 32, 55–64.

Fu, Q.S., Barkovskii, A.L., Adriaens, P., 2001. Dioxin cycling in aquatic sediments: The Passaic River estuary. Chemosphere 43, 643–648.

Goñi, M.A., Hedges, J.I., 1992. Lignin dimers: structures, distribution, and potential geochemical applications. Geochem. Cosmochim. Acta 56, 4025–4043.

Gustafsson, O., et al., 2001. Evaluation of a protocol for the quantification of black carbon in sediments. Global Biogeochem. Cycles 15 (4), 881–890.

Hagenmaier, H., She, J., Benz, T., Dawidowsky, N., Düsterhöft, L., Lindig, C., 1992. Analysis of sewage sludge for polyhalogenated dibenzo-p-dioxins, dibenzofurans, and diphenylethers. Chemosphere 25, 7–10.

Hanke, U.M., Reddy, C.M., Braun, A.L.L., Coppola, A.I., Haghipour, N., McIntyre, C.P., Wacker, L., Xu, L., McNichol, A.P., Abiven, S., Schmidt, M.W.I., Eglinton, T.I., 2017. What on Earth have we been burning? Deciphering sedimentary records of pyrogenic carbon. Environ. Sci. Technol. 51 (21), 12972–12980.

Haye, J.M., Santschi, P.H., Roberts, K.A., Ray, S., 2006. Protective role of alginic acid for metal uptake by American Oysters (*Crassostrea virginica*). Environ. Chem. 3, 172–183.

Hieke, A.-S.C., Brinkmeyer, R., Yeager, K.M., Schindler, K.J., Zhang, S., Xu, C., Louchouarn, P., Santschi, P.H., 2016. Widespread distribution of Dehalococcoides spp. in the Houston Ship Channel and Galveston Bay, Texas, sediments and the potential for reductive dechlorinaton of PCDD/F in an estuarine environment. Mar. Biotechnol. 18 (6), 630–644.

Howell, N.L., Rifai, H.S., Koenig, L., 2011. Comparative distribution, sourcing, and chemical behavior of PCDD/F and PCB in an estuary environment. Chemosphere 83 (6), 873–881.

Jensen, K., DeKing, N., Routson, J., Keaton, D., Rudder, G., McIntosh, N., 1999. Unprecedented Restructuring via Mergers and Mill Closures Is Lowering Costs as the Industry Tries to Regroup after Lackluster Year. North American Status Report. Pulp & Paper Magazine.

Jonsson, P., Rappe, C., Kjeller, L.-O., Kierkegaard, A., Hakanson, L., Jonsson, B., 1993. Pulp-mill related polychlorinated organic compounds in Baltic Sea sediments. Ambio 22, 37–43.

Karlsson, O.M., Malmaeus, J.M., Wiberg, K., Cornelissen, G., Josefsson, S., 2009. Organohalogen Compd. 71, 793–797.

Kuo, Li-Jung, 2009. Multiproxy Approach on Black Carbon Characterization and Combustion Products Source Discrimination in Environmental Media. PhD Dissertation. Texas A&M University.

Kuo, L.-J., Herbert, B.E., Louchouarn, P., 2008. Can levoglucosan be used to characterize and quantify char/charcoal black carbon in environmental media? Org. Geochem. 39, 1466–1478.

Kuo, L.-J., Louchouarn, P., Herbert, B., Brandenberger, J., Wade, T., Crecelius, E., 2011. Combustion-derived substances in deep basins of the Puget Sound: historical inputs from fossil fuel and biomass combustion. Environ. Pol. 159, 983–990.

Lima, A.L., Eglinton, T.I., Reddy, C.M., 2003. High-resolution record of pyrogenic polycyclic aromatic hydrocarbon deposition during the 20th century. Environ. Sci. Technol. 37, 53–61.

Lohmann, R., Macfarlane, J.K., Gschwend, P.M., 2005. Importance of black carbon to sorption of native PAHs, PCBs, and PCDDs in Boston and New York Harbor sediments. Environ. Sci. Technol. 39, 141–148.

Louchouarn, P., Brinkmeyer, R., 2009. Fate of Dioxin in the Houston Ship Channel and Evaluation of Natural Remediation Processes. Texas Commission on Environmental Quality. Work order No. 582-5-O72502. Work Plan 13.

Louchouarn, P., Lucotte, M., Farella, N., 1999. Historical and geographical variations of sources and transport of terrigenous organic matter within a large-scale coastal environment. Org. Geochem. 30, 675–699.

Louchouarn, P., Chillrud, S.N., Houel, S., Yan, B., Chaky, D.A., Rumpel, C., Largeau, C., Bardoux, G., Walsh, D.C., Bopp, R.F., 2007. Elemental and molecular evidence of soot- and char-derived black carbon inputs to New York City's atmosphere during the 20th Century. Environ. Sci. Technol. 41, 82–87.

Louchouarn, P., Amon, R., Duan, S., Pondell, C., Seward, S.M., White, N., 2010. Analysis of lignin-derived phenols in standard reference materials and ocean dissolved organic matter by gas chromatography/tandem mass spectrometry. Mar. Chem. 118, 85–97.

Louchouarn, P., Kuo, L.-J., Brandenberger, J., Marcantonio, F., Garland, C., Gill, G., Cullinan, V., 2012. Pyrogenic inputs of anthropogenic Pb and Hg to sediments of the Hood Canal, Washington, in the 20th century: source evidence from elemental ratios, stable Pb isotopes, and PAH signatures. Environ. Sci. Technol. 46 (11), 5772–5781.

Macdonald, R.W., Cretney, W.J., Crewe, N., Paton, D., 1992. A history of octachlorodibenzo-*p*-dioxin, 2,3,7,8-tetrachlorodibenzofuran, and 3,3',4,4'-tetrachlorobiphenyl contamination in howe sound, british columbia. Environ. Sci. Technol. 26, 1544–1550.

Macdonald, R.W., Ikonomou, M.G., Paton, D.W., 1998. Historical inputs of PCDDs, PCDFs, and PCBs to a British Columbia interior lake: the effect of environmental controls on pulp mill emissions. Environ. Sci. Technol. 32, 331–337.

Muir, D.C.G., Lawrence, S., Holoka, M., Fairchild, W.L., Segstro, M.D., Webster, G.R.B., Servos, M.R., 1992. Partitioning of polychlorinated dioxins and furans between water, sediments and biota in lake mesocosms. Chemosphere 25, 199–224.

Rappe, C., Andersson, R., Bergqvist, P.A., Brohede, C., Hansson, M., Kjeller, L.O., Lindström, G., Marklund, S., Nygren, M., Swanson, S.E., Tysklind, M., 1987. Overview on environmental fate of chlorinated dioxins and dibenzofurans. Sources, levels and isomeric pattern in various matrices. Chemosphere 16, 1603–1618.

Rifai, H., Palachek, R., Jensen, P., 2003. Total Maximum Daily Loads for Dioxins in the Houston Ship Channel. unpublished report prepared for Total Maximum Daily Load Program. Texas Commission on Environmental Quality, Austin, TX.

Rifai, H., Palachek, R., Jensen, P., 2005. Total Maximum Daily Loads for Dioxins in the Houston Ship Channel. Report prepared for Total Maximum Daily Load Program. Texas Commission on Environmental Quality, Austin, TX.

Robbins, J.A., 1978. Geochemical and geophysical applications of radioactive lead. In: Nriagu, J.O. (Ed.), Biogeochemistry of Lead in the Environment. Elsevier Scientific, Amsterdam, pp. 285–393.

Santschi, P.H., Allison, M., Asbill, S., Perlet, A.B., Cappellino, S., Dobbs, C., McShea, L., 1999. Sediment transport and Hg recovery in Lavaca Bay, as evaluated from radionuclide and Hg distributions. Environ. Sci. Technol. 33, 378–391.

Santschi, P.H., Yeager, K.M., Brinkmeyer, R., Louchouarn, P., Hieke, A.-S.C., Zhang, S., Xu, C., Schindler, K., 2009. Factors Regulating Microbial Degradation of Dioxins in Estuarine Sediments: Houston Ship Channel and Galveston Bay, TX (Report prepared for Texas Sea Grant Program).

Servos, M.R., Muir, D.C.G., Webster, G.R.B., 1992. Environmental fate of polychlorinated dibenzo-p-dioxins in lake enclosures. Can. J. Fish. Aquat. Sci. 49, 722–734.

Sobek, A., Wiberg, K., Sundqvist, K.L., Haglund, P., Jonsson, P., Cornelissen, G., 2014. Coastal sediments in the Gulf of Bothnia as a source of dissolved PCDD/Fs and PCBs to water and fish. Sci. Total Environ. 487, 463–470.

Sonnenberg, L.B., Nichols, K.M., 1995. Emissions of hydrochloric acid, PCDD and PCDF from the combustion of chlorine-containing kraft pulp mill bleach plant waste. Chemosphere 31, 4207–4223.

Stellman, J., Stellman, S., Christians, R., Weber, T., Tomasallo, C., 2003. The extent and patterns of usage of Agent Orange and other herbicides in Vietnam. Nature 422, 681–687.

Suarez, M.P., Rifai, H.S., Palachek, R., Dean, K., Koenig, L., 2005. Polychlorinated dibenzo-p-dioxins and dibenzofurans in Houston ship channel tissue and sediment. Environ. Eng. Sci. 2 (6), 891–906.

Texas Commission on Environmental Quality, 2014. Chapter 307. Texas Surface Water Quality Standards, 2014. Texas Administrative Code, Title 30: Environmental Quality.

U.S. Environmental Protection Agency, 2000. Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-P-Dioxin (Tcdd) and Related Compounds.

Wenning, R.J., Harris, M.A., Ungs, M.J., Paustenbach, D.J., Bedbury, H., 1992. Chemometric comparisons of polychlorinated bibenzo-*p*-dioxin and dibenzofuran residues in surficial sediments from Newark Bay, New Jersey and other industrialized waterways. Arch. Environ. Contam. Toxicol. 22, 397–413.

Wilken, M., Neugebauer, F., Fabarius, G., Zeschmar-Lahl, B., Jager, J., 1992. PCDD/

PCDF contamination of different pesticides produced in former GDR. Chemosphere 25, 1,525—1,531.

Yeager, K.M., Santschi, P.H., owe, G.T., 2004. Sediment accumulation and radionuclide inventories (^{239,240}Pu, ^{210}Pb and ^{234}Th) in the northern Gulf of Mexico, as influenced by organic matter and macrofaunal density. Mar. Chem. 91 (1—4), 1—14.

Yeager, K.M., Santschi, P.H., Rifai, H.S., Suarez, M.P., Brinkmeyer, R., Hung, C., Schindler, K.J., Andres, M.J., Weaver, E.A., 2007. Dioxin chronology and fluxes in sediments of the Houston Ship Channel, Texas: influences of non-steady state sediment transport and total organic carbon. Environ. Sci. Technol. 41, 5291—5298.