Contaminated Aquatic Sediments

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ABSTRACT: A review of the literature published in 2014 relating to the assessment, evaluation and remediation of contaminated aquatic sediments is presented. The review is divided into the following sections: policy and guidance, methodology, distribution, fate and transport, bioavailability, bioaccumulation, risk, toxicity and remediation.

KEYWORDS: Activated carbon, biodegradation capping, dioxins, dredging, fate, furans, immobilization, metals, organics, PAHs, PCBs, toxicity, transport, treatment.

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Policy and Guidance

The Interstate Technology & Regulatory Council (ITRC) published guidance intended to assist decision makers in identifying which contaminated sediment remedial technology is most favorable for a given site (ITRC, 2014). Based upon an evaluation of site-specific physical, sediment, contaminant, and land and waterway use characteristics, a six-step remedy selection framework is provided. The United States Environmental Protection Agency (USEPA) published a technical resource document on monitored natural recovery (MNR) that was intended to complement prior USEPA guidance on MNR (USEPA, 2014). It provides detailed information on field-scale methodologies and approaches that can reportedly be used to measure and/or predict natural processes that contribute towards risk reduction at sediment sites. The United States Army Corps of Engineers published technical guidelines for performing sediment erosion and deposition assessments at Superfund Sites (Hayter et al., 2014). It outlines processes influencing sediment transport and describes methods that may be used in the assessments.

Methodology

Pore concentration and partition coefficients of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) were determined in sediments collected from five distinct contaminated sites in France (marine harbor, rivers, canals and highway sedimentation tank) (Charrasse et al., 2014). Using different empirical and mechanistic models it was observed that triple domain sorption (a total organic carbon, black carbon and oil phase model) could model PCB data successfully whereas the best fit for PAH partitioning was obtained by a Raoult's Law model. Apell et al. (2014) sought to validate the use of performance reference

compounds in passive samplers to assess pore water concentrations in sediment beds. Pore water concentrations were compared with the traditional equilibrium partitioning models which showed that considering sorption to only organic carbon substantially overestimated pore water concentrations but predictions improved greatly if sorption to black carbon was also considered. Solid phase microextraction (SPME) fibers inside perforated steel tubes were used by Stringer et al. (2014) as in situ passive samplers to measure PAH concentrations in sediment before and after treatment with activated carbon (AC). No treatment was observed 5 cm away from single injections, while at 2.5 cm, >90 % decrease of PAH pore water concentration was observed; multiple injections resulted in >90 % PAH pore water level reductions throughout the test vessel.

A selective pressurized liquid extraction technique was developed for the simultaneous extraction of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs) from contaminated sediments (Aguilar et al., 2014). Mean analyte recoveries of PCDD/Fs and dl-PCBs were 84±5.8% and 70±8.4%, respectively while mean surrogate recoveries for all PCDD/Fs using this method were reported to be greatly improved compared with USEPA methods 1613 (~25-155%) and 8290A (40-135%). Coleman et al. (2014) assessed the potential for membranes to be utilized as a mechanism to allow freely dissolved hydrophobic organic contaminants into a pathway isolation exposure chamber (PIC) while excluding all sediment particles and dissolved organic carbon (DOC). Seeking to assess the relevance of functional ecology in bioavailability of contaminated sediments at remediation sites, the polytetrafluoroethylene membrane was selected for use in the PIC, although exclusion of dissolved organic carbon was not achieved. Hou et al. (2014) proposed a new Life cycle assessment (LCA) method that seeks to offer several advantages including an expanded system boundary that reduces truncation errors, incorporating consequential benefits (i.e. tertiary impact) of remediation and covering social, economic and environmental impacts. Using this method to examine a sediment remediation project at the London Olympic Park Site, LCA was found to capture an additional 32% and 8% of secondary impact in soil washing and landfilling, respectively.

Distribution

Contaminants of Emerging Concern. Nilsen et al. (2014) investigated occurrence, transport pathways, and effects of polybrominated diphenyl ether (PBDE) flame retardants and other endocrine disrupting chemicals (EDCs) in aquatic media and the food web in the Lower Columbia River (USA). Frequently detected organochlorine (OC) compounds included hexachlorobenzene, penta-chloroanisole, dichlorodiphenyltrichloroethane (DDT) and its degradates, chlorpyrifos, and oxyfluorofen. Priac et al. (2014) presented an overview of the literature on methods for the elimination (removal and/or degradation) of trace organic contaminants of emerging concern with an emphasis on one class of endocrine disrupters, namely alkylphenols and their polyethoxylate derivatives, which are suspected to interfere with the hormonal system of

wildlife. Technologies proposed for alkylphenol treatment include membrane treatment using biological (membrane bioreactors) or physical processes (membrane filtration such as nanofiltration), biotechnological-based methods (biofilms, immobilized enzymes, etc.), adsorption-oriented processes using conventional (activated carbon) or nonconventional adsorbents (clays, cyclodextrin, etc.), and advanced oxidation processes (photocatalysis, photolysis, and sonochemistry). Sediments from two Korean industrial bays were fractionated into 5 sizes by using a gravitational split-flow thin fractionation technique and Dechlorane Plus (DP) distribution was investigated in different particle size fractions (Fang et al., 2014). Elevated DP levels in surface sediments were observed at locations closest to industrial sources and the highest concentrations of DP were detected in the finest grain-size.

Inorganics. Ghanbarpour et al. (2014) assessed the spatial distribution of heavy metal concentrations (Al, As, Cd, Co, Cr, Cs, Fe, Ni, Sn and Zn) in the sediments of the Tajan River Watershed, an inflow to the Caspian Sea in Northern Iran. Comparison of four interpolation techniques (ordinary kriging, simple kriging, inverse distance weighted and local polynomial interpolation) via cross validation suggested that kriging was the most accurate spatial analysis technique for the majority of the elements. Concentrations of inorganic tin (Sninorg), tributyltin (TBT) and its degradation products dibutyltin (DBT) and monobutyltin (MBT) were measured in surface sediments and in two cores from Toulon Bay, France (Pougnet et al., 2014). Tin and butyl-Sn concentrations in the bay varied by orders of magnitude, with maximum values near the shipyards at concentrations of total Sn (1.3-112 μg/g), TBT (<0.5-2,700 ng/g), DBT (<0.5-1,800 ng/g) and MBT (0.5-1,000 ng/g) that generally decreased towards the open sea. Sediment contamination in Balanagar industrial area was investigated to determine extent and distribution of heavy metals (Cu, Cr, Ni, Pb, Zn, As) and to also delineate the source (Machender, et al., 2014). The concentration ranges of different heavy metals were Cr, 96.2-439.6 mg/kg; Cu, 95.7-810 mg/kg; Ni, 32.3-13,068.2 mg/kg; Pb, 59.2-512 mg/kg; Zn, 157.1-4,630.5 mg/kg; Co, 1.8-48.3 mg/kg; and V, 35.2-308.5 mg/kg. Soils, river sediments and waters samples from former As-Sb mining sites in FYR Macedonia were analyzed for As and Sb to assess their impact on the local environment (Alderton et al., 2014). Soils and river sediments were found to contain very high concentrations of As and Sb (medians 117 and 37 mg/kg), but were heterogeneously distributed. As part of a project to develop an integrated assessment for the St. Thomas East End Reserves (STEER) in the US Virgin Islands, 185 chemical contaminants were analyzed in sediments from 24 sites (Pait et al., 2014). The concentrations of PCBs, dichlorodiphenyltrichloroethane (DDT), Zn, Cu, Pb, and Hg were above a NOAA Effects Range-Low (ERL) sediment quality guideline at one or more sites.

Organics. Organochlorine pesticides and PCBs were analyzed for in sediments from the east coast of Thailand (Potipat and Cheevaporn, 2014). Organochlorine pesticides were detected in sediments at concentrations in the range of 1.06-3.71 ng/g and PCBs in the range of 0.04-3.03 ng/g. Mwanamoki et al. (2014) reported on the occurrence and spatial distribution of metals and persistent

organic pollutants (POPs) including organochlorine pesticides, PCBs, PBDEs, and PAHs in sediments from thirteen sites of the Congo River Basin and Lake Ma Vallée, both situated in the vicinity of the capital city Kinshasa (Congo Democratic Republic). The POPs and PAHs levels in all sediment samples were low, but in the area with maximum concentrations organochlorine pesticides ranged from 0.02 to 2.50, PCBs ranged from 0.07 to 0.99 and PAHs ranged from 0.12 to 9.39 μg/kg. PCBs were determined in sediments and two fish species collected from the Murchison Bay in Lake Victoria (Uganda, Africa), (Ssebugere et al., 2014). Total PCB concentrations varied widely with mean values ranging from 777 to 4325 pg/g dry weight (dw) for sediments and 80 to 779 pg/g wet weight (ww) for fish. Recent biodegradation studies in Africa have revealed the existence of exotic bacterial strains exhibiting unique and unusual PCB metabolic capability in terms of array of congeners that can serve as carbon source and diversity of congeners attacked (Gioia et al., 2014). These observations marks progress in the development of effective bioremediation strategies for PCB-contaminated matrices such as sediments and soils in tropical regions.

Deep sediments from the southern Cretan margin (Mediterranean Sea) were analyzed to establish baseline levels for various types of organic pollutants before an anticipated intensification of anthropogenic activities (Mandalakis et al., 2014). The total concentration of aliphatic hydrocarbons was similar to those reported for deep sediments of the western Mediterranean Sea, while lower levels were measured for PAHs. The levels of dl-PCBs in the surface sediments collected at 15 different sampling sites from the Tibetan Plateau to the Yellow River Estuary along the Yellow River were measured (Li, Jin et al., 2014). The concentrations of ∑dl-PCBs ranged from 2.3 to 14.8 pg/g and the TEQs of dl-PCBs were between 0.0014 and 0.0231 pg/g, with an average of 0.0073 pg/g. Sobek et al. (2014) measured the freely dissolved concentrations of PCDD/Fs and PCBs in sediment pore water and bottom water in eight areas along the Swedish coast of the Gulf of Bothnia, by using state-of-the-art passive samplers. Chemical activity ratios (calculated from freely dissolved concentrations in pore water and bottom water based on chemical activity ratios) for PCDD/Fs were higher than 1 at all stations suggesting that the sediments have a potential to act as a source of dissolved PCDD/Fs to the water column.

Mahmood et al. (2014) performed a study to investigate the PCB concentration level, spatial distribution pattern, and ecological risk assessment of water and sediment samples from two tributaries (Nullah Aik and Palkhu) of the River Chenab, Punjab Province, Pakistan. A total of 32 PCB congeners were analyzed, and PCB concentration in sediment and water samples ranged between 0.80 and 60 ng/g and 0.20 and 28 ng/L, respectively, where tetra-CBs and tri-CBs dominated over other studied PCB homologs. Mourier et al. (2014) presented historical records of PCB concentrations in sediment cores from eight sites on the RhÔne River, from Lake Geneva to the Mediterranean Sea. Maximum PCB concentrations (sum of seven indicator PCBs) increased downstream, from 11.50 μg/kg at the most upstream site to

417.1μg/kg at the most downstream site and at some sites peak concentrations occurred in sediment deposited as recently as the 2000s. Concentrations and profiles of 2,3,7,8-substituted PCDD/Fs and dl-PCBs were investigated in sediment and plants collected from a salt marsh in the Tejo estuary, Portugal (Nunes et al., 2014a). The highest PCDD/F and dl-PCB concentrations were detected in uncolonized sediments, averaging 325.25 pg/g and 8,146.33 pg/g, respectively and the plants *Sarcocornia perennis* and *Halimione portulacoides* growing in PCDD/F and dl-PCB contaminated sediments accumulated contaminants in roots, stems, and leaves.

Superficial sediments collected by Nunes et al. (2014b) from seven estuarine systems located along the Portuguese coast were analyzed for 7 polychlorinated dibenzo-p-dioxins (PCDDs), 10 polychlorinated dibenzofurans (PCDFs), and 12 dl-PCBs. Total PCDD/F concentrations ranged from 4.6 to 464 pg/g, while that of dl-PCBs varied from 26.6 to 8,693 pg/g; PCDD/F revealed a predominance of octachlorodibenzodioxin (OCDD) to total PCDD/Fs, while PCB 118 was the major contributor to total dl-PCBs. Čonka et al. (2014) collected 34 river bottom sediment samples in 2006-2007 at five areas across Slovakia with industrial sources of persistent organic pollutants (Košice, Krompachy, Nemecká, Šala, Nováky) and one background area (Starina) and analyzed for seven 2,3,7,8-substituted PCDDs and 10 PCDFs, 12 dioxin-like and 6 indicator PCBs, hexachlorobenzene (HCB) and 1,1,1,-trichloro-2,2-bis(p-chlorophenyl)ethane (p,p'-DDT) with 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (p,p'-DDE). The most abundant congeners in all sediment samples among dioxins, furans and PCBs were OCDD, 1,2,3,4,6,7,8-HpCDF, PCB-118 and PCB-153. Malarvannan et al. (2014) reviewed data from pooled yellow European eel (*Anguilla anguilla*) samples from 60 locations in Flanders (Belgium) which were analyzed for persistent contaminants, such as PBDEs, hexabromocyclododecanes (HBCDs), PCBs and dichlorodiphenyltrichloroethane and its metabolites (DDTs). The data showed an on-going exposure of Flemish eels to PBDEs, HBCDs, PCBs and DDTs through indirect release from contaminated sediments or direct releases from various industries. Sampling was performed according to land use (agricultural, urban, and industrial) at two stations: Laguna del Plata and Campo Mare to evaluate the dynamic of Persistent Organic Pollutants (POPs) in different biotic and abiotic matrixes of the RAMSAR site (wetlands with international importance) at Mar Chiquita Lake, Argentina (Ballesteros et al., 2014). Hexachlorocyclohexanes (HCHs), Endosulfans, DDTs, PCBs and PBDEs were found in all matrixes at both stations.

Anezaki and Nagahora et al. (2014) determined the distribution of PCBs, pentachlorobenzene (PeCBz), hexachlorobenzene (HxCBz), and PCDD/Fs in surface sediments at 21 sites inside and outside Muroran Port, Japan. The concentration ranges and geometric means of PCBs, PeCBz, HxCBz, and PCDD/Fs and toxicity equivalence quantity (total TEQ) of dioxins inside Muroran Port were 1,100-65,000 pg/g, 37-220 pg/g, 31-810 pg/g, 69-410 pg/g, and 0.51-6.2 pg TEQ/g, respectively. PCBs and PAHs were analyzed in surface sediments from areas

receiving industrial (nine sites), river (one site), and urban (two sites) effluents in Hormozgan Province, Iran, on the Northern Persian Gulf (Nozar et al., 2014). The overall levels of PCBs ranged from 2.5 to 462 ng/g with CB153 congener dominating with a resemblance to Aroclor 1260 and 1254, while a wide range of 55.3 to 1231.6 ng/g was detected for PAHs that reflected both petrogenic and pyrogenic origins. Historical trends of the accumulation of PBDEs and PCBs in a typical tropical Asian environment were investigated using radio-dated sediment cores from Manila Bay, the Philippines and from the upper Gulf of Thailand (Kwan et al., 2014). Vertical profiles indicated earlier usage of PCBs than of PBDEs (which coincided with their industrial production) and possible evidence of anaerobic debromination of BDE-209 in the sediment cores. The spatial distribution of various organochlorinated compounds, e.g. PCBs, DDTs, HCB and HCHs, were investigated in sediments of the Gulf of Batabanó, Cuba (Alonso-Hernandez et al., 2014). Among the target organochlorine compounds measured, DDT isomers were the predominant contaminant with concentrations ranging from 0.019 to 1.27 ng/g, lindane was present in the range not detected to 0.05 ng/g, while PCBs and other organochlorine pesticide residues, such as HCB, Heptaclor, Aldrin and Mirex were lower than detection limits.

Fate and Transport

A mass balance model of contaminant fate-transport was applied to 11 organic compounds in the Bay of Quinte and its foodweb (Gandhi et al., 2014). Model results suggested that atmospheric deposition was the main source of lower molecular weight PCBs, TCDD/F and DDT, tributaries for higher molecular weight PCBs and Lake Ontario for mirex, atrazine and dieldrin loadings while the the main source of B[a]P was thought to be urban runoff. The Quantitative Water Air Sediment Interaction (QWASI) model for evaluating chemical fate and input parameter sensitivities in aquatic systems was updated (Mackay et al., 2014). The new QWASI water quality model can reportedly be of value for both evaluative and simulation purposes as a tool for obtaining an improved understanding of chemical mass balances in lakes.

Concentrations of PCBs and PBDEs in surface sediment samples collected from the East Lake, China in winter 2012 and summer 2013 were determined (Yun et al., 2014). Concentrations of PCBs in the sediment samples collected in summer were higher than those in winter, while the concentrations of PBDEs did not show much seasonal variations. Source analysis showed that the PCBs probably originated from urban runoff, industrial pollution and atmospheric deposition, and the PBDEs probably originated from historical usage of penta-BDE mixtures. Gong et al. (2014) summarized what is generally understood to date about the interactions between oil, oil dispersants and sediments, their roles in developing oil spill countermeasures, and how these interactions may change in deepwater environments. Effects of controlling parameters, such as sediment particle size and concentration, organic matter content, oil properties, and salinity on oil-sediment interactions are described in detail with special attention being placed on the application and effects of oil dispersants on the rate and extent of the interactions

between oil and sediment or suspended particulate materials. During 2011 and 2012, fifteen sites in on-site and off-site streams were sampled at the surface (<10 cm) and subsurface (20-30 cm) to characterize the extent of PCB contamination, to identify weathering and migration of PCB contamination and to explore potential PCDD and PCDF contamination (Kruse et al., 2014). It was noted that flow regimen, organic carbon and clay content play a very important role in the fate of PCBs in the environment at the surface as well as in downward migration. Fifteen stormwater ponds in the Minneapolis-St. Paul, MN, metropolitan area were studied to determine sources of PAHs to bed sediments through the application of several environmental forensic techniques, including a contaminant mass balance receptor model (Crane, 2014). The model results were reportedly quite robust and indicated that coal tar-based, sealant particulate washoff and dust sources were the most important sources of PAHs (67.1%), followed by vehicle-related sources (29.5%), and pine wood combustion particles (3.4%). Liu et al. (2014) evaluated As mobility in the As-contaminated Yangzonghai Lake in China. During summer, water temperature stratification reduced the dissolved oxygen (DO) at the sediment surface and increased the concentration of As in the water column with increasing depth while during winter, the concentration of As was quite similar at all depths of the lake because the water temperature was uniform during this period.

Bioavailability

Jia and Gan (2014) used a matrix solid-phase microextraction (SPME) method to measure the freely dissolved concentration (Cfree) of PBDEs as a parameter of their potential bioavailability and evaluated the differences among biochar, charcoal, and activated carbon. At 1% amendment rate in sediment with low organic carbon content (0.12%), Cfree of six PBDEs was reduced by 47.5-78.0%, 47.3-77.5%, and 94.1-98.3% with biochar, charcoal, and activated carbon, respectively, while the sequestration was more limited in sediment with higher organic carbon content (0.87%). Mackenbach et al. (2014) tested a previously developed Tenax model by examining the impacts of remediation on surface sediment concentrations, Tenax extractable concentrations, and tissue concentrations of laboratory-exposed *Lumbriculus variegatus*. They noted that at nondredged sites, bioaccumulation was better predicted by the Tenax model, with 86% of the data falling within the 95% confidence intervals, than at dredged sites, for which only 64% of the data fit the Tenax model. In both pre- and post-dredge conditions, when the model failed, it was conservative, predicting higher PCB concentrations than observed in the oligochaetes, particularly for the post-dredge data. Parks et al. (2014) studied the capacity of single-walled carbon nanotubes (SWNTs), amended to PCB-contaminated New Bedford Harbor sediment, to reduce the toxicity and bioaccumulation of these HOCs to benthic organisms. Overall, SWNT amendments increased the survival of two benthic estuarine invertebrates, *Americamysis bahia* and *Ampelisca abdita*, and reduced PCB bioavailability and accumulation in the benthic polychaete, *Nereis virens*.

Bioaccumulation

Judd et al. (2014) explored field-based, benthic invertebrate biota-sediment chemical concentration relationships using data from the USEPA Mid-Continent Ecology Division biota-sediment accumulation factor (BSAF) database. They found that approximately two thirds of the 262 relationships investigated were very poor ($r^2 < 0.3$ or p-value ≥ 0.05); for some of the biota-sediment relationships that did have a significant nonzero slope (p-value < 0.05), lipid-normalized tissue concentrations tended to decrease as the colocated organic carbon-normalized sediment concentration increased. Bioaccumulation testing using the oligochaete, *L. variegatus*, and passive sampling (using SPME) were performed to study the bioaccumulation potential of highly hydrophobic organohalogen flame retardants (HHOFRs), including decabromodiphenyl ether (deca-BDE), decabromodiphenyl ethane (DBDPE), and dechlorane plus (DP), in laboratory-spiked and field-collected sediments (Li, Zhang et al., 2014). They noted that HHOFRs were bioavailable to *L. variegatus* even though their biota-sediment accumulation factors were low, hydrophobicity and stereoisomerism affected HHOFR bioavailability and HHOFR concentrations on the SPME fibers correlated with those in biota.

The transfer of HOCs including PAHs, PCBs, and PCDD/Fs to resident/migratory biota was investigated in 11 finfish species and blue crabs (*Callinectes sapidus*) in the Passaic River estuary (Khairy et al. (2014). Bioaccumulation factors and trophic magnification factors (TMFs) were >1 for most PCBs and tetra- and penta-CDD/DFs, indicating that they underwent biomagnification in the food web, while all PAHs, PCB 11, and other lower chlorinated PCBs and PCDD/Fs did not magnify. Jahnke et al. (2014) evaluated the thermodynamic potential for bioaccumulation of persistent organic pollutants from sediment. They noted that PCBs in duck mussels, roach, eel, pikeperch, perch and pike were mostly below the equilibrium partitioning level relative to the sediment, whereas hexachlorobenzene (HCB) was near equilibrium between biota and sediment.

Bluegill sunfish were caged in the Detroit River, Ontario, Canada, for 64 days to determine bioaccumulation rates of PCBs (McLeod et al., 2014). During summer, fish exhibited significant increases in body weight, lipid content (sediment associated cages only) and lipid normalized PCB concentrations, whereas in winter, these factors did not change. Similarly, James and Kleinow (2014) investigated the seasonal influences on PCB retention and biotransformation in fish. They observed that elimination of PCBs occurs much more slowly when fish is acclimated at low temperatures than at warmer temperatures suggesting that the body burden of PCBs in fish from a contaminated location is likely to vary with season. Figueiredo et al. (2014) evaluated the validity of two bioaccumulation models, BIOv1.22 and AQUAWEBv1.2, for application to a multispecies aquatic food web. They observed that site-specific concentrations in sediment pore water did not affect the modelling endpoints, but accurate site-specific measurements of freely dissolved concentrations in water turned out to be crucial for obtaining realistic model-predicted concentrations in biota. Blue mussels (*Mytilus edulis*) and sediments collected by

Subedi et al. (2014) from 1991 to 2005 from New Bedford Harbor (Massachusetts, USA), were analyzed for two polycyclic musks (HHCB or Galaxolide® and AHTN or Tonalide®), PBDEs, PAHs, PCBs, and organochlorine pesticides. Based on the temporal trends in the concentrations of HHCB, AHTN, ∑PAHs, and ∑PBDEs found in the mussels, it was estimated that between 5.5 and 12 years were required for the concentrations of these compounds to decrease by half (i.e., environmental halving time) of the levels found in 1991.

A comparative analysis of bioaccumulation behavior of dl-PCBs and PBDEs was conducted involving simultaneous measurements in settling particles and a detritivorous fish (Sabalo, *Prochilodus linneatus*) collected in the sewage impacted Buenos Aires coastal area (Cappelletti et al., 2014). It was observed that lipid/organic carbon-based BSAFs that ranged between 5 and 20, a lower bioavailability of more planar non-ortho-PCB versus mono-ortho-PCB, BSAFs of PBDEs differed markedly among bromine homolog groups and the log BSAFs-log K_{OW} relationship of dl-PCBs and PBDEs presented a parabolic pattern maximizing at log K_{OW} 6–7. After evaluating the brown mussel *Perna perna* as a sentinel organism for environmental concentrations of organochlorine pesticides and PCBs, Galvao et al. (2014) reported original data on the relationship between the concentrations of these chemicals in bottom surface sediments, suspended solids (SS) and concentrations bioaccumulated by this bivalve. Variations in the organochlorine pesticides and PCB concentrations bioaccumulated by the bivalves tended to be similar to those observed in the sediment, but differed from those found in SS. Sezmis et al. (2014) investigated factors that govern species-specific accumulation patterns of PCDDs, PCDFs and dl-PCBs in a food web from Sydney Estuary (Australia). The results indicated that physiological characteristics, (lipid %, distance from a point source) and life history characteristics of the organisms, such as diet and home range, influence PCDD/F and dl-PCB tissue concentrations to varying degrees. PCBs, DDT, and chlordanes were measured in juvenile and adult male and female stingrays from areas in Southern California (USA), and a nearby offshore island, Santa Catalina (Lyons et al., 2014). Both mainland juvenile male and female stingrays showed a significant dilution effect but after maturity, summed contaminant concentrations significantly increased with size for adult males (median 11.1 μg/g lipid wt) and females (5.2 μg/g lipid wt); however, the rate of bioaccumulation was substantially greater in male stingrays than in females, likely a result of the females' ability to offload contaminants to offspring during pregnancy.

Brent and Berberich (2014) investigated the relative importance of waterborne versus sediment-borne Hg in controlling biological uptake of Hg into the aquatic food web. They noted that Hg in the water column is much more important in controlling biological uptake than Hg in near-field sediments and as a result, future remediation efforts need to focus on strategies that either remove Hg from the water column or decrease flux to the water column. In a lake naturally separated into three basins, the thermocline and oxycline of an experimental basin were deepened by 4 and 3 m, respectively, to study the effect on

methylmercury (MeHg) accumulation (Perron et al., 2014). This action decreased hypolimnetic MeHg concentration by approximately 90%, zooplankton concentrations by 30 to 50% and in some fish by 45%, thereby providing a potential remediation method for small lakes with MeHg accumulation. Hodson et al. (2014) performed a spatial survey of Hg concentrations in sediments, amphipods, and yellow perch (*Perca flavescens*) in Lake Saint Francis, a fluvial lake on the Saint Lawrence River near Cornwall, Ontario (Canada). Concentrations of total or MeHg in sediments and pore water were found to be unrelated to concentrations in amphipods and yellow perch, suggesting that 'legacy' Hg in surficial sediments is not bioavailable to aquatic biota tributaries and atmospheric deposition are possible sources of bioavailable Hg.

Risk

The contamination history and recovery of a watercourse heavily loaded by the chemical wood industry were studied by analyzing PCDDs, PCDFs and PCBs from vertical sediment samples and by measuring hepatic EROD activity from rainbow trout intraperitoneally dosed with the sediment extracts (Ratia and Oikari, 2014). No PCDDs or PCDFs were found; only small amounts of PCB congeners 101, 138, 153, and 180 were present and no increased EROD activity was observed in fish (indicating the absence of any AhR-activating compounds) leading to the conclusion that organochlorines and other AhR-ligands no longer posed a threat to the previously heavily polluted watercourse.

Toxicity

A sediment toxicity identification evaluation (TIE) was conducted to examine how targets established for Cu, Cd, Pb, Zn, chlordane, DDTs, PCBs, and PAHs, in Ballona Creek Estuary (California, USA) sediment corresponded to toxicity observed with the estuarine amphipod *Eohaustorius estuarius* (Greenstein et al., 2014). Concentrations of the target chemicals were found to often exceed target values but were not observed at concentrations likely to cause toxicity. The authors concluded that pyrethroid pesticides were more likely the cause of the observed toxicity than any of the other contaminants targeted for cleanup. Gomes et al. (2014) assessed the toxicity of Barcelona Harbor sediments to the polychaete *Capitella teleta* by assessing and linking individual-level responses such as body weight (growth) and egestion rate (feeding) with subcellular-level responses including antioxidant (catalase and superoxide dismutase) and neurotransmission related (acetyl cholinesterase) enzyme activities. Behavior responses were better correlated to chemical contamination than those of biomarkers and the sediments produced neurotoxicity, promoted oxidative stress and reduced egestion and growth rates in exposed worms suggesting that *C. teleta* worm can be used to assess chemical effects. Morales-Mora et al. (2014) employed the USEtox™ model to evaluate environmental fate, exposure, and effect of nine organic compounds (including PAHs and PCBs), a heavy metal (lead), and the effect of the industrial wastewater emitted into the Coatzacoalcos River (Veracruz State, Mexico). According to the authors, the model estimated that 96 %

(3,247 kg/day) of organic compounds is transferred from the water into air, whereas only 4 % (151 kg/day) remained in the water and that the main human exposure to PCBs (congeners 28 and 153) was by eating contaminated fish.

Remediation

Biodegradation. Passatore et al. (2014) summarized the bioremediation and phytoremediation technologies proposed so far to detoxify PCB-contaminated sites. The review elaborates on the environmental variables affecting contaminant degradation rates, summarizes the amendments recommended to enhance PCB degradation and addresses issues connected with PCB toxicology, actual field remediation strategies and economical evaluation. The impact of GAC on anaerobic dechlorination by putative organohalide respiring bacteria indigenous to sediment from Baltimore Harbor (USA) was examined (Kjellerupet al., 2014). GAC caused a substantial shift in the congener distribution whereby a smaller fraction of highly chlorinated congeners was more extensively dechlorinated to mono- through tri-chlorinated congeners compared to the formation of tri- through penta-chlorinated congeners in unamended sediment.

Lombard et al. (2014) developed a method to measure rate of dechlorination in the aqueous phase at very low PCB concentrations that utilized a polymer functioning concurrently as a passive dosing system for maintaining a steady-state PCB substrate concentration in the water phase and as a passive equilibrium sampler to monitor the dechlorination products. They observed that using passive samplers to measure the concentration of dissolved PCBs in the porewater combined with knowledge of congener-specific rates for organohalide respirer(s), it would be possible to project the in situ rate and final concentration of PCBs for a specific site after treatment by bioaugmentation. Cruz et al. (2014) investigated the ability and the role of *Aeromonas molluscorum* Av27 bacterium on TBT degradation in an estuarine system, using a microcosm approach in order to mimic environmental conditions. Results revealed that TBT degradation was significantly enhanced by the presence of Av27a with maximum TBT degradation rate of 28% accompanied by the detection of the degradation products over time. Hosseinkhani et al. (2014) developed a biogenic nanopalladium-based remediation method for reducing chlorinated hydrocarbons from marine environments by employing indigenous marine bacteria. These biogenic catalysts were used to dechlorinate trichloroethylene (TCE) in simulated marine environments where complete dehalogenation of 20 mg L^{-1} TCE was achieved within 1 h using 50 mg L^{-1} biogenic nanopalladium. Gupta et al. (2014) highlighted the physicochemical properties, bioremediation treatment and its mechanism for waste containing PAH that end up in sediment. They also highlighted the molecular approaches which are helpful in revealing functional, structural and communal information about microbial diversity for exploring the routes of degradation pathway of bioremediation process and future scope to bioremediation of PAHs. A total of 35 halophilic bacterial strains belonging to different genera such as *Alcaligenes, Vibrio, Kurthia, Staphylococcus* and members of the family Enterobacteriaceae were isolated from 21 Vembanad Lake

(India) sediment samples (Sowmya et al., 2014). Heavy metal removal efficiency of selected isolates showed a maximum reduction of 37 and 99% of Cd and Pb, respectively.

Immobilization. Tomašević et al. (2014) investigated the use of supported nanoscale zero-valent iron with bentonite and kaolinite for immobilization of As, Pb and Zn in contaminated sediment from the Nadela River Basin (Serbia). The authors report that their test results indicated that the treated sediment was safe for disposal. Hwang et al. (2014) developed a novel mixed binder of MgO (magnesia) and supplementary cementitious materials that can reportedly solidify sediments contaminated with heavy metals as well as store CO_2 through mineral carbonation reactions. The binder exhibited a compressive strength of 11.9 MPa, which was similar to that of Portland cement (PC) and sequential extraction of treated sediments showed that the stabilization capacity of the MgO-based binder for heavy metals (Cu, Cd, Ni, Pb, and Zn) was two times higher than that of PC. Two types of modified zeolites, including aluminum-modified zeolites (AlMZs) and zirconium-modified zeolites (ZrMZs) were prepared and used as sediment amendments to control the release of phosphorus (P) from Taihu Lake sediments (Yang, Lin et al., 2014). Observations indicated that AlMZs and ZrMZs are promising amendments for controlling phosphate-P release from Taihu Lake sediments, and ZrMZs are more suitably used as sediment amendments to control phosphate-P release than AlMZs.

Treatment. Brosillon et al. (2014) assessed the treatment of sediments contaminated by organotin compounds using heterogeneous photocatalysis. In the sediment, TBT degradation yield ranged from 32% to 37% after only 2 h of irradiation (TiO2-UV) and the by-products: dibutyltin (DBT) and monobutyltin (MBT) were degraded very rapidly in comparison with TBT.

Yang, Sheu et al. (2014) developed a three-stage system to cleanup total petroleum hydrocarbons (TPH)-contaminated sediments from the Kaohsiung Harbor in Taiwan (TPH concentration of 8,105 mg/kg), which included a river water (RW) washing stage followed by a surfactant (Triton X-100) washing and then a Fenton-like oxidation stage. Results showed that approximately 6% of TPH was removed after the RW washing stage, up to 71% of TPH was removed by surfactant washing and approximately 8% of TPH was removed through the Fenton-like oxidation with a total of 86% of TPH being removed after the three-stage process. Removal of deca-bromo diphenyl ether (BDE-209) from contaminated sediments by UV/H_2O_2 treatment was investigated under different reaction conditions including different UV irradiance and H_2O_2 concentrations (Feo et al., 2014). After 10 h of UV/H_2O_2 treatment, 90% of BDE-209 was removed with a half-life time ($t^{1/2}$) of 3.5 h and a kinetic constant (k) of 0.22 h^{-1}.

The oxidation of 16 PAHs in sediments by sodium persulfate ($Na_2S_2O_8$) activated by temperature and nZVI as the source of catalytic ferrous iron was investigated (Chen, Binh et al., 2014). Results indicated that increasing temperature or the addition of nZVI into a persulfate-slurry system could enhance the persulfate

oxidation process and the best removal efficiency (86.3%) was attained after 24 hr while adding nZVI (0.5 g/L) to persulfate (170 g/L) at a temperature of 25 ºC.

Hadnagy et al. (2014) evaluated the subaqueous amendment delivery and mixing efficiency of a pilot-scale in situ sediment remediation system consisting of a hydraulically operated steel casing that provided contained conditions for amendment delivery and mixing to occur and the mixing tool consisting of a hollow vertical shaft with horizontal mixing blades housed in the casing. The in situ remediation system showed potential in terms of successful amendment delivery and mixing into subaqueous sediments.

Extraction. Lasheen and Ammar (2014) examined the influences of contact time and EDTA to sequentially extract metals from contaminated dredged sediments from Helwan area (H) in Egypt with mainly Pb (685 mg/kg), and from Talkha area (T) with significant Cd (236 mg/kg), Cu (229 mg/kg), and Zn (2,888 mg/kg). For sediment (H), the maximum lead removal was 72.54% while for sediment (T), the maximum cadmium removal was 53.58%. Comparisons of cell and stack designs for the electrodialytic removal of heavy metals from two harbor sediments, were made (Pedersen, 2014). The highest percentages removed for the cell designs were 82% Cu, 81% Pb and 92% Zn while for the stack experiments the highest clean-up levels were 21% Cu, 42% Pb and 73% Zn. The efficiency of three organic and inorganic salts (ammonium acetate, ammonium nitrate, and sodium potassium tartrate) to salt out heavy metals was evaluated in sediment washing waters containing nonionic surfactants (Álvarez et al., 2014). The proposed process was applied to model aqueous solutions containing two representative heavy metals (zinc and copper) which resulted in removal values higher than 80% for copper and 90% for zinc.

A novel extraction/washing technique utilizing chelating agent and elevated pressure in consecutive cycles of compression and decompression was developed for heavy-metal-contaminated sediment washing in the presence of chelating agent (Lin, Hong et al., 2014). Results from a study of the technique showed that up to 70% of Cu can be removed from the sediments when 10 atm of pressure was applied for washing and up to 55% when the pressure dropped to 6 atm. A laboratory-scale physical separation process using froth flotation, Wilfley table (WT), and physical separation column (PSC) as the key unit operations was studied using Sandy Beach sediments (Gaspé, Canada) contaminated with metals (mainly Cu) and PAHs (Veetil et al., 2014). Overall, the treatment process resulted in a cleaned sediment recovery of 74-75% (w/w) with the following pollutants removed: 71-80% PAHs, 61-65% Cu, 27-33% Zn, and 36-40% Pb. Hahladakis et al. (2014) investigated the sequential application of a chelating agent (citric acid) followed by a surfactant in the simultaneous electroremediation of actual contaminated sediments from toxic metals and PAHs using two innovative non-ionic surfactants, commercially known as Poloxamer 407 and Nonidet P40. The results indicated a removal efficacy of approximately 43% and 48% for the summation of PAHs (∑PAHs), respectively for the two surfactants, which was much better than obtained from the use of Tween 80 (nearly 21%).

Activated Carbon. Three commercial granular activated carbons (GACs) were studied at laboratory scale with a view to the combined adsorption and biodegradation of PCBs in aquatic sediment (Mercier, 2014). Results suggested that PCB bio-transformation by the bacterial community attached to the GAC is influenced by GAC's physico-chemical characteristics so a properly selected GAC could effectively be used to sequestrate and concentrate PCBs from contaminated aquatic sediment and act as a support for efficient PCB degradation by an autochthonous bacterial biofilm. Field experiments were performed to evaluate the effect of granulated coal ash (GCA) on remediation of coastal sediments through removal of phosphates and hydrogen sulfide (Kim, Hibino et al., 2014). The authors concluded that GCA is an effective material for remediating organically enriched coastal sediment. Jia et al. (2014) proposed a method that used activated carbon fiber felt (ACFF) to remediate persistent organic pollutants in contaminated sediments. It was found that ACFF could efficiently remove DDTs released from the sediments and the removal efficiency of DDTs using ACFF was influenced by the initial spiking concentrations, hydrophobicity of DDTs, aging times of the contaminated sediments, and organic carbon contents of the sediments.

Chen, Chen et al. (2014) studied the base-promoted dehydrochlorination kinetics of low-level (~1.25 mg/g) 1,1,2,2-tetrachloroethane (TeCA) adsorbed to 17 different ACs varying in origin and physicochemical properties. Activated carbon-bound TeCA exhibited significant reactivity - at a given pH the apparent reaction kinetic constants of AC-bound TeCA were 13-70% of the respective kinetic constants of dissolved TeCA suggesting that carbonaceous materials not only sequester contaminants, but also allow contaminants to be slowly degraded in situ. Rakowska, Kupryianchyk, Smit et al. (2014) derived kinetic parameters for extraction of PAHs from sediment by GAC, using a first-order multi-compartment kinetic model. PAH uptake rate constants (kGAC) by GAC ranged from 0.44 to 0.0005 d^{-1}, whereas GAC sorption coefficients (KGAC) ranged from 105.57 to 108.57 Lkg^{-1} and show that ex situ extraction with GAC is sufficiently fast and effective to reduce the risks of the most available PAHs. Rakowska, Kupryianchyk, Koelmans et al. (2014) presented pseudo-equilibrium as well as kinetic parameters for sorption of a series of PAHs and PCBs to powdered and GAC after three different sediment treatments: sediment mixed with powdered AC (PAC), sediment mixed with granular AC (GAC), and addition of GAC followed by 2 d mixing and subsequent removal (sediment stripping). Remediation efficiency was assessed by quantifying fluxes of PAHs towards SPME passive samplers inserted in the sediment top layer, which showed that the efficiency decreased in the order of PAC > GAC stripping > GAC addition.

Two years of column experiments were conducted to simulate field conditions with two study sediments contaminated with petroleum and PCBs and variations in AC-sediment contact times, initial AC mixing regimes and distribution, AC particle sizes, and pore-water flow (Choi, Cho and Luthy, 2014). After two years of stagnant contact, the contaminant uptake in polyethylene

passive samplers embedded in the columns was reduced by 95-99% for PAHs and 93-97% for PCBs with 5 and 4 wt % AC dose, respectively, when AC was initially applied by mechanical mixing. The validity of a hydrophobic organic contaminant mass transfer model to predict the effectiveness of this in situ activated carbon (AC) treatment under stagnant sediment-AC contact was studied for different contaminants and sediments (Choi, Cho, Werner and Luthy, 2014). The model successfully reproduced the relative effects of AC-sediment contact time, contaminant properties, AC particle size, AC mixing regime, AC distribution, and hydraulic conditions observed in the prior sediment column experiments. Activated carbons were applied to evaluate the effects of surface oxidation on bioavailability and bioaccumulation of Cd and Cu in freshwater sediment along with *Eisenia fetida* biomass change (Kim, Min et al., 2014). Inhibited growth of *E. fetida* due to AC could be responsible for the reduced bioaccumulation of Cd and Cu in the earthworms as AC inhibited the movement of earthworms, leading to less bioturbation and decreased consumption of nutrients. Jonker and Mourik (2014) investigated the sorption of 2 known infochemicals, hypoxanthine-3-N-oxide (H3NO) and pyridine-N-oxide (PNO), to 5 different powdered ACs. Sorption isotherms of these low-molecular-weight, polar fish kairomone substances appeared highly nonlinear, with logarithmic Freundlich sorption coefficients of up to 7.6.

Capping. Ebrahimi et al. (2014) presented a method that was developed to evaluate the geotechnical stability of an in situ cap placed on soft sediments. The technical approach involved estimating the design lift thickness of the cap and the waiting period between lifts. He et al. (2014) investigated the highest bottom shear stress, induced by wind in an area of Hamilton Harbour, Ontario (Canada) known as Randle Reef in support of a component of a contaminated sediment remediation plan utilizing a thin layer of sand to manage contaminated sediments. The results showed that the modeled and measured flow velocity components agreed reasonably well at most of the water depths with the correlation coefficients being greater than 0.6; however, agreements between the modeled and measured bottom flow speeds were worse than expected due to the error contributions from both the modeled velocity components. Dorjee et al. (2014) investigated sorption properties of inorganic antimony species Sb(III) and Sb(V) by humic acid-coated and non-coated nano-zero valent iron (nZVI). The IC-ICP-MS chemical speciation analysis demonstrated that nZVI has a strong potential to reduce Sb(V) to Sb(III).

A bio-reactive capping barrier composed of polysulfone/granular activated carbon (PS/GAC) hybrid membranes immobilized with microorganism was developed for the remediation of nitrobenzene in sediments (Wang, Li et al., 2014). The authors observed that nitrobenzene can be effectively removed from contaminated sediments by microbial degradation in the bio-reactive capping system. The effect of a thin sand capping layer (7.5 cm) on the bioavailability of hydrophobic organic compounds (PCBs and naphthalene) was studied using oligochaete worms, and the results compared to previously obtained bioavailability tests with a reactive core mat (RCM) cap (Meric et al., 2014). Results

indicated that the thin sand cap alone reduced the average bioavailability of PCBs by a factor of 100 compared to direct exposure, but had no effect on the bioavailability of naphthalene.

The effects of bioturbation on the performance of attenuation by sediment deposition and activated carbon to reduce risks from DDT-contaminated sediment were assessed for DDT sediment-water flux, biouptake, and passive sampler (PE) uptake in microcosm experiments with a freshwater worm, *L. variegatus* (Lin, Cho et al. (2014). A mass transfer model together with a biodynamic model were developed to simulate DDT flux and biouptake, respectively. Both experimental measurements and modeling predictions implied that thin-layer activated carbon placement on sediment is effective in reducing the risks from contaminated sediments in the presence of bioturbation, while natural attenuation process by clean sediment deposition may be delayed by bioturbation. A numeric simulation indicated that a capping layer of 40 cm with hay, straw, tree bark or shrimp waste is sufficient to reduce groundwater vinyl chloride (VC) concentration below a threshold level of 5 μg/l before discharging into the Zenne River, Belgium (Atashgahi et al., 2014). Of several materials tested, the persistent colonization of tree bark by *D. mccartyi* combined with the lowest stimulation of methanogenesis, singled out tree bark as a long-term electron donor for organohalide respiration of cis-dichloroethene (cDCE) and VC in bioreactive caps.

Removal. Laboratory studies mimicking sediment resuspension during dredging operations in western Lake Erie were conducted to determine whether suspended sediments affect walleye eggs and fingerlings (Suedel, Clark, Lutz et al., 2014). Data indicated no significant effects of suspended sediment on egg hatch success or fingerling survival after three days of exposure. Cabrita (2014) studied changes in suspended particulate matter, turbidity, dissolved Cr, Ni, Cu, Cd, Hg and Pb concentrations, and phytoplankton biomass and composition during a 5-month period dredging operation, in a trace element contaminated area of the Tagus Estuary (Portugal). It was observed that significant rise in sediment resuspension and trace element mobilization caused by dredging influenced the community structure but not the overall biomass. Also, Cabrita et al. (2014) studied changes in Cr, Cu, Zn, Cd, Hg and Pb concentrations in the dissolved fraction, suspended particulate matter and immobilized *Phaeodactylum tricornutum* Bohlin (Bacillariophyceae), as well as of microalgae specific growth rates, during the 5-month dredging operation noted above for the Tagus Estuary. Immobilized cells exposed to dredging environmental conditions showed significantly higher concentrations of Cr, Cu, Zn, Cd, Hg and Pb than under no dredging conditions and specific cell growth was significantly lower suggesting that elements released with dredging affect the microalgae physiology.

Sediment containing five selected heavy metals (Cd, Cu, Cr, Hg and As) were used to simulate the release of heavy metals in sediment from Baihua Lake during dredging (Wang, Huang et al., 2014). It was observed that the release potential of the heavy metals varied with dredging depth and the elapsed time after dredging. Suedel, Clarke, Wilkens et al. (2014) performed a

laboratory study mimicking sediment resuspension during annual dredging operations in the James River to assess the impacts of dredging on the eastern oyster (*Crassostrea virginica* Gmelin). Data indicated no significant effects of suspended sediment on survival, percent of time open, total number of shell movements, weight change and condition index after 7 days of exposure. Wang, Zhou et al. (2014) evaluated the influence of sediment dredging on sedimentary As release for the Inner Lake, a typical tide-influenced waterfront body in the middle to lower reaches of the Yangtze River in Zhengjiang, China. The results showed that the amounts of sedimentary As release during the tidal cycles in the flood season and the dry season after dredging were reduced by 14.6 and 28.1%, respectively, compared with before dredging. Birch et al. (2014) studied the effectiveness of remediation of a former Pb-contaminated industrial site in Homebush Bay on Sydney Estuary (Australia) through sampling of inter-tidal sediments and mangrove (*Avicennia marina*) tissue (fine nutritive roots, pneumatophores, and leaves). Results indicated that since remediation 6 years previously, Pb and other metals (Cu, Ni and Zn) in surficial sediment had increased to concentrations that approached pre-remediation levels and that were considerably higher than pre-settlement levels (3–30 times), as well as relative to the reference site.

Di Palma et al. (2014) compared the effectiveness of thylene-diaminetetraacetic acid (EDTA) and rhamnolipid in Cu removal from an artificially contaminated sediment in terms of metal extraction yield and mobilization. Results showed that, under acidic conditions established during washing, EDTA ensured higher extraction efficiencies of Cu (up to 95 %) than rhamnolipid, although there was less mobilization into bioavailable forms with the use of rhamnolipid. Sediment traps and passive samplers were deployed to measure particulate and dissolved PAHs and PCBs in the water column prior to, and following, removal of a small, low-head dam in the Pawtuxet River, an urbanized river located in Rhode Island, USA (Cantwell et al., 2014). Overall, it was concluded that dam removal did not cause measurable sediment disturbance or increase the concentration or fluxes of dissolved or particulate PAHs and PCBs.

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