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Environmental release of dioxins from reservoir sources during beach nourishment programs ☆

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Dedicated to the memory of Thomas Hadley Rose (1942–2011); the environmental profession benefited from his immense knowledge, resourcefulness, and leadership

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ABSTRACT

In late 1990s, USEPA/FDA made an important connection regarding the presence of elevated levels of dioxins (e.g., 1500 ng kg^{-1} TEQ) in ball clays mined in Mississippi (USA) from a geological deposit dated to ∼40 million years (Mississippi Embayment) that stretches over several states (northern part of Mississippi to Kentucky) and levels of dioxins in selected animal food sources. Following a recent beach nourishment program along the mid-Atlantic coast of the US, a number of dark gray, blue tinted nuggets of varying sizes were found on beach strands and near the shoreline. Using the presence of these balls of clay (shape, color, and knowledge regarding their use in pottery) on the beach, together with our direct experience analyzing ball clays for dioxins, we made a possible association between these clays and elevated dioxins. Concerns regarding the potential of nourishment programs to cause severe damage to our beaches drove us to test the dioxin content of nourishment exposed clays. A number of the nuggets, along with freshly dredged and deposited sand (collected the morning after nourishment) with the same coloration, and others (sun-bleached), collected approximately 2 weeks after the completion of the nourishment efforts, were analyzed for the presence of PCDD/Fs, PCBs, and selected semi-volatile chlorinated organics. The clay PCDD/F WHO2005-TEQs (dry weight; ND = DL; EMPC = EMPC) ranged from 0.41 to 5.78 ng kg^{-1} with an average of 2.64 ng kg^{-1}, whereas the sand sample's TEQs ranged from 0.18 to 0.31 ng kg^{-1} PCDD/F WHO-2005, with an average of 0.22 ng kg^{-1}. The average total tetra- through octa-chlorinated dibenzo-*p*-dioxin concentration was 2700 ng kg^{-1} (with a maximum of 5800 ng kg^{-1}) for the clays and 8.5 ng kg^{-1} (with a maximum of 16.8 ng kg^{-1}) for the sand samples. The congener 2,3,7,8-TCDD (TEF = 1) was detected in half of the clay samples (0.11–0.77 ng kg^{-1}). All of the clay and sand samples displayed an unambiguous and dominating 1,4,6,9-chlorination pattern across homolog groups. No other chlorinated aromatics were detected above background levels. The observations, along with the absence or an extremely low level of polychlorinated dibenzofurans, together with the mineralogical analysis, supports the conclusion that off-shore dredging activities are reaching reservoir sources containing dioxin-tainted, smectic/kaolinite clay minerals. Subsequent beach erosion provides additional environmental releases over time, as buried balls of clay from previous nourishment efforts become exposed.

1. Introduction

Beach nourishment provides a mechanism for controlling erosion along the beaches of the United States. Since the enactment of legislation such as the Coastal Zone Management Act (1972), the Coastal Barrier Resources Act (1982), and the Coastal Zone Protection Act (1996), the US Government has maintained the geological integrity of coastal areas of the US through expenditures that are overseen by the Civil Works Branch of the US Army Corps of Engineers (USACE). The samples collected for this study were obtained from the USACE designated area named "Carolina Beach and Vicinity" during a beach nourishment phase in 2010. Specifically, they were collected within 100 m from both sides of one of the dredging discharge points in Kure Beach, NC, USA. Ocean floor sediments (known to contain the minerals kaolinite, illite, montmorillonite, and chlorite) were deposited on the beach during the dredging process (using equipment capable of dredging to ∼9 m). In studies conducted since the early 1990s (Hashimoto et al., 1990, 1995; Ferrario et al., 2000), deep sediments in Japanese coastal areas (>8000 years old) and from the Pacific Ocean floor (e.g., ∼1–10 million years old; 10 WHO1998-TEQ ng kg^{-1} in 10 m sediments at 6000 m in water depth), and later ball clays (e.g., 1500 WHO1998-TEQ ng kg^{-1} PCDD/F; continental US) have been shown to contain polychlorinated dibenzo-*p*-dioxins (PCDD) but little, if any, polychlorinated dibenzofurans (PCDF). Not only do

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Table 1
Summary results for beach-recovered clay samples (TEF congeners and WHO-2005 TEQ; on a dry weight (d.w.) basis). Non-detected congeners are reported with the corresponding estimated detection limit shown between parentheses. Square brackets are used to report target analytes whose ion-abundance ratio was found to lie outside of the ±15% window. The estimated maximum possible concentration [EMPC] derives from use of the theoretical ratio. On average, the samples' ITEQs were 30% higher than the listed WHO-2005 TEQs.

Analyte	Lab method blank 1 (ng kg^{-1})	Clay 1 (ng kg^{-1})	Lab method blank 2 (ng kg^{-1})	Clay 2 (ng kg^{-1})	Clay 3 (ng kg^{-1})	Clay 4 (ng kg^{-1})	Clay 5 (ng kg^{-1})	Clay 6 (ng kg^{-1})	Clay 7 (ng kg^{-1})	Clay 9 (ng kg^{-1})	Clay 12 (ng kg^{-1})	Clay 13 (ng kg^{-1})
2,3,7,8-TCDD	(0.0570)	0.475	(0.0397)	[0.770]	(0.0895)	(0.0828)	(0.0663)	[0.108]	0.153	0.251	(0.145)	(0.0478)
1,2,3,7,8-PeCDD	(0.0881)	0.407	(0.0383)	0.309	(0.102)	(0.0727)	0.248	[0.197]	0.395	0.573	[0.175]	(0.052)
1,2,3,4,7,8-HxCDD	(0.102)	0.941	(0.0356)	0.449	0.429	(0.0826)	(0.0894)	0.137	0.755	1.08	0.175	0.411
1,2,3,6,7,8-HxCDD	(0.102)	9.16	(0.0347)	3.49	0.862	1.16	1.45	0.192	11.2	1.79	[0.218]	4.68
1,2,3,7,8,9-HxCDD	(0.123)	4.95	(0.0459)	5.51	2.44	1.35	2.16	0.293	12.8	4.75	0.389	10.2
1,2,3,4,6,7,8-HpCDD	(0.0983)	117	(0.0414)	135	71.6	44.9	46.6	1.22	221	85.2	1.59	197
OCDD	(0.216)	1050	(0.111)	2110	1550	1130	998	4.58	1760	1830	5.01	1830
2,3,7,8-TCDF	(0.0433)	0.120	(0.0254)	(0.0381)	(0.0462)	(0.0490)	0.0702	(0.0359)	[0.0258]	0.0929	(0.0905)	[0.0312]
1,2,3,7,8-PeCDF	(0.0474)	(0.0555)	(0.0229)	(0.0358)	(0.0489)	(0.0440)	(0.0374)	(0.0293)	(0.0242)	(0.0447)	(0.0845)	(0.0268)
2,3,4,7,8-PeCDF	(0.0468)	(0.0543)	(0.0205)	(0.0347)	(0.0452)	(0.0399)	(0.0373)	(0.0289)	(0.0233)	(0.0390)	(0.0864)	(0.0252)
1,2,3,4,7,8-HxCDF	(0.0638)	(0.0740)	(0.0250)	(0.0440)	(0.0531)	(0.0416)	(0.0404)	(0.0383)	(0.0291)	(0.0497)	(0.0710)	(0.0279)
1,2,3,6,7,8-HxCDF	(0.0538)	(0.0714)	(0.0223)	(0.0408)	(0.0515)	(0.0371)	(0.0384)	(0.0354)	(0.0289)	(0.0509)	(0.0651)	(0.0253)
2,3,4,6,7,8-HxCDF	(0.0568)	(0.0761)	(0.0245)	(0.0436)	(0.0500)	(0.0392)	(0.0435)	(0.0350)	(0.0299)	(0.0517)	(0.0646)	(0.0260)
1,2,3,7,8,9-HxCDF	(0.0884)	(0.0964)	(0.0329)	(0.0642)	(0.0747)	(0.0578)	(0.0603)	(0.0543)	(0.0421)	(0.0744)	(0.0947)	(0.0398)
1,2,3,4,6,7,8-HpCDF	(0.0747)	(0.0749)	(0.0230)	(0.0403)	(0.0623)	(0.0428)	(0.0389)	(0.0345)	(0.0274)	(0.0533)	(0.0646)	(0.0341)
1,2,3,4,7,8,9-HpCDF	(0.100)	(0.101)	(0.0340)	(0.0620)	(0.0853)	(0.0664)	(0.0582)	(0.0587)	(0.0422)	(0.0914)	(0.110)	(0.0535)
OCDF	(0.174)	(0.182)	(0.0759)	(0.0987)	(0.165)	(0.130)	(0.127)	(0.0896)	(0.0687)	(0.157)	(0.185)	(0.0876)
WHO-2005 TEQ (ND = 0; EMPC = 0)	**0.00**	**3.88**	**0.00**	**3.24**	**1.55**	**1.04**	**1.38**	**0.0758**	**5.75**	**2.99**	**0.0739**	**4.05**
WHO-2005 TEQ (ND = 0; EMPC = EMPC)	**0.00**	**3.88**	**0.00**	**4.01**	**1.55**	**1.04**	**1.38**	**0.380**	**5.76**	**2.99**	**0.271**	**4.05**
WHO-2005 TEQ (ND = DL/2; EMPC = 0)	**0.113**	**3.90**	**0.0553**	**3.29**	**1.67**	**1.14**	**1.43**	**0.154**	**5.76**	**3.01**	**0.241**	**4.11**
WHO-2005 TEQ (ND = DL/2; EMPC = EMPC)	**0.113**	**3.90**	**0.0553**	**4.03**	**1.67**	**1.14**	**1.43**	**0.395**	**5.77**	**3.01**	**0.378**	**4.11**
WHO-2005 TEQ (ND = DL; EMPC = EMPC)	**0.227**	**3.93**	**0.111**	**4.05**	**1.79**	**1.24**	**1.49**	**0.411**	**5.78**	**3.03**	**0.484**	**4.17**