PCDDs AND PCDFs IN WETLAND SOILS IN NORTH CAROLINA, USA

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Introduction

The part of the Lower Roanoke River we studied flows east from Williamston, North Carolina, past Plymouth and discharges into the Albemarle Sound. This part of the river flows through wetlands. Weyerhaeuser operates a pulp and paper mill and previously operated a chloralkali plant in Plymouth. From 1937 to present, the mill discharged its wastewater into the Roanoke River and Welch Creek, which flows into the Roanoke River. Prior to 1981, Georgia-Pacific Corp. operated a hardwood sawmill approximately 1 km downriver of Welch Creek.

Previously, the North Carolina Department of Environment, Health and Natural Resources (NC DENR), the United States Environmental Protection Agency (US EPA), and Weyerhaeuser collected sediment and wetland samples from the Roanoke River, Welch Creek, and Conaby Creek, another tributary to the Roanoke River, and analyzed them for PCDDs and PCDFs. NC DENR also collected and analyzed soil samples from the sawmill. We evaluated these data using Principal Component Analysis and determined that (a) the sawmill was not a source of PCDDs and PCDFs to the Roanoke River; (b) the pulp mill was the primary source of PCDDs and PCDFs to Welch Creek; and (c) publicly-owned treatment works in the area were potential sources of PCDDs/PCDFs.[1]

In this study, we analyzed wetland soil samples from the Lower Roanoke River Basin to determine (a) the impact, if any, of possible herbicide spraying in this area; and (b) whether naturally-formed PCDDs exist in this area as they do in similar wetland or marine environments; and (c) the impact, if any, of flooding.

Materials and Methods

Samples and sampling

In January 2001, we collected nine wetland soil core samples from the Lower Roanoke River Basin. *See* Figure 1.Three of the nine cores contained two strata. All cores were collected from the surface to 2.1 m below the surface.

Analysis

Each sample was dried and homogenized. Seventeen internal standards then were added to each sample. Next, each sample was extracted for approximately 15 h with 150 mL of toluene in a Soxhlet extractor equipped with a Dean Stark collector. The extracts were purified in a multistep silica column, followed by a basic alumina column. The final step in the clean-up was made on a Carbon AX 21/ Celite column. The final extracts were evaporated in 30 µL tetradecane. HRGC/HRMS analysis was performed on each sample with a 60 m JW DB-5 GC column attached to a VG 70S instrument.

Results

Table 1 includes the concentrations of 2,3,7,8-substituted congeners, the sum of each homologue, the WHO-TEQ, the sum of PCDD and PCDF concentrations, and the D/F ratios for all wetland soil

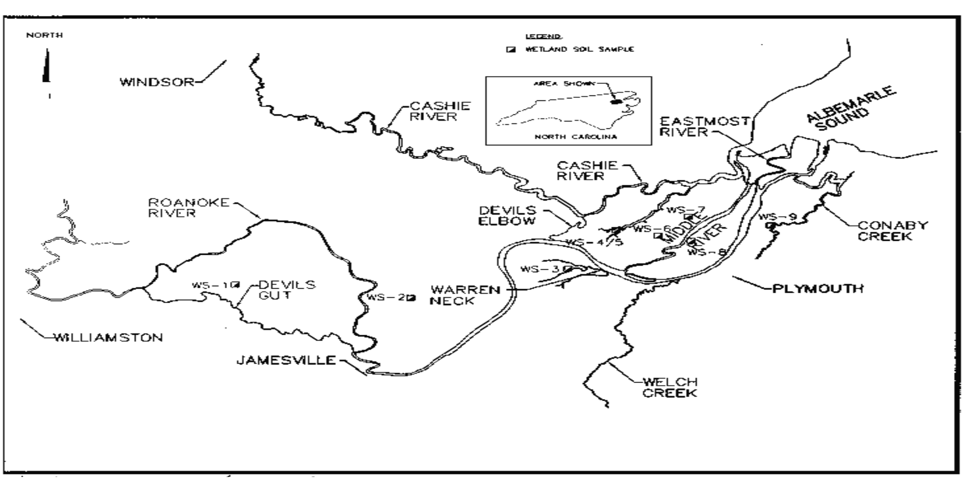

Figure 1. Map of the Lower Roanoke River Basin and sample locations

samples. In this paper, we only discuss the results for the surface strata of each core, *i.e.*, those designated with “A”. 2,3,7,8-TCDD was measured in six of the nine samples, ranging from 0.16 (WS-9) to 0.6 pg/g (WS-3A). 2,3,7,8-TCDF was measured in all nine samples, ranging from 0.5 (WS-4) to 5.2 pg/g (WS-8A). The WHO-TEQ ranged from 0.79 (WS-4) to 8.4 pg TEQ/g (WS-9).

All samples were dominated by OCDD and 1,2,3,4,6,7,8-HpCDD. OCDD ranged from 760 (WS-4) to 9,200 pg/g (WS-1); 1,2,3,4,6,7,8-HpCDD ranged from 23 (WS-4) to 670 pg/g (WS-9). Moreover, the HxCDD homologue in all samples was dominated by 1,2,3,7,8,9-HxCDD. The 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD ratios ranged from 1.67 (WS-3A) to 6.21 (WS-9). A 1,2,3,7,8,9-HxCDD/ 1,2,3,6,7,8-HxCDD ratio of approximately 1.5 or greater has been suggested as an indicator of naturally-formed dioxins.[2] Further, the D/F ratios ranged from 55.5 (WS-3A) to 517.5 (WS-9). This PCDD/PCDF profile is evidence of naturally-formed dioxin.[2, 3, 4, 5, 6, 7, 8]

In another part of our study, we reported that PCDDs and PCDFs in certain Roanoke River sediments have a similar PCDD/PCDF profile as the wetland soil samples.[9] This conclusion is supported by the data from the Roanoke River[10], where the sediments upriver from Jamesville are also dominated by OCDD and 1,2,3,4,7,8,9-HpCDD, and have 1,2,3,7,8,9-HxCDD/1,2,3,6,7,8-HxCDD ratios ranging from 1.67 to 2.14, with a mean ratio of 1.94. Therefore, the wetland soils in the Lower Roanoke River Basin likely contribute to the PCDDs and PCDFs in the Roanoke River. Conversely, the influence from the pulp mill can be seen in wetland soil samples in the vicinity of Welch Creek. Specifically, wetland soil samples WS-3A, WS-6, WS-7, and WS-8A exhibit a 2,3,7,8-TCDF and 2,3,7,8-TCDD profile indicating a pulp mill influence.[11]

Conclusions

1. OCDD and 1,2,3,4,6,7,8-HpCDD are the dominant congeners in all wetland soil samples. The low concentrations of 2,3,7,8-TCDD indicate that possible spraying of 2,4,5-T is not a significant source of PCDDs to the Lower Roanoke River Basin.
2. The HxCDD homologue in all wetland soil samples is dominated by 1,2,3,7,8,9-HxCDD. This HxCDD profile has been reported in other wetland or marine samples and has been identified as an indicator of naturally-formed dioxin.

3. The PCDD/PCDF profile, including the HxCDD pattern, for the wetland soils is similar to the profiles for some Roanoke River sediment samples, indicating that the wetland soils are a source of dioxin to the Roanoke River.

4. The 2,3,7,8-TCDF and 2,3,7,8-TCDD composition in wetland soils in the vicinity of Welch Creek indicate that the pulp mill is a source of these compounds to the wetlands.

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Table 1. PCDD and PCDF concentrations in wetland soil (pg/g d.m.)[a]

Sample Id	WS-1	WS-2A	WS-2B	WS-3A	WS-3B	WS-4	WS-5	WS-6	WS-7	WS-8A	WS-8B	WS-9
% LOI	7.70	19.30	45.38	57.36	92.98	92.53	75.52	43.60	57.23	67.50	50.86	68.20
Anal. amount.	12.43 g	6.87 g	2.68 g	2.98 g	6.64 g	7.86 g	2.63 g	3.24 g	2.91 g	2.67 g	5.3 g	4.7 g
2378 TCDF	1.7	1.2	0.76	3.3	1.6	0.5	1.8	3.1	3.3	5.2	5.1	0.92
SUM TCDF	13	12	10	31	39	4.4	15	21	26	23	79	6.6
2378 TCDD	0.21	0.21	(0.16)	0.6	(0.071)	(0.051)	(0.13)	0.57	0.2	(0.17)	0.13	0.16
SUM TCDD	5.3	14	18	17	14	3.3	12	31	13	14	39	17
12378 PeCDF	0.32	0.19	(0.12)	1.1	0.18	(0.042)	(0.11)	0.45	0.3	(0.89)	1.7	0.1
23478 PeCDF	0.59	0.22	(0.12)	0.56	(0.048)	0.35	1.1	0.63	1.2	(1.1)	0.44	0.23
SUM PeCDF	9.7	7	1.8	13	3.4	4	5.3	2.5	2.4	21	21	4.5
12378 PeCDD	1.1	0.67	0.37	(0.23)	0.12	(0.21)	0.91	1.1	0.45	0.79	(0.11)	(0.14)
SUM PeCDD	16	27	16	12	4.1	7.2	2.9	34	20	2.6	9.1	23
123478 HxCDF	1.5	0.8	(0.16)	1.4	(0.065)	0.25	0.65	1.2	1	0.81	0.24	0.62
123678 HxCDF	0.64	0.45	(0.13)	0.66	(0.058)	0.073	0.18	0.57	0.37	0.3	0.17	0.32
234678-HxCDF	0.78	0.42	0.23	0.8	0.078	0.11	0.44	0.58	0.64	0.36	0.26	(0.23)
123789-HxCDF	0.22	0.21	0.42	0.4	0.18	0.11	0.8	0.47	0.79	0.39	1	0.33
SUM HxCDF	19	6.4	1.2	8.6	0.24	0.95	6.8	5.1	7	5	8.4	2.5
123478 HxCDD	2	1.3	0.4	0.8	0.11	(0.12)	0.56	1.3	0.54	0.42	0.47	(0.33)
123678 HxCDD	5.4	2.8	1.4	1.5	0.36	0.19	0.44	3.3	0.63	0.62	0.57	0.74
123789 HxCDD	10	6	5	2.5	0.49	0.47	1.3	6.4	1.5	1.1	1.7	4.6
SUM HxCDD	92	75	60	39	7.2	12	43	47	48	25	13	73
1234678 HpCDF	11	3.7	0.69	4.1	(0.081)	(0.26)	(0.84)	4.9	(0.51)	(0.85)	(0.18)	(0.96)
1234789 HpCDF	0.51	(0.18)	(0.23)	(0.35)	(0.095)	(0.3)	(0.95)	0.41	(0.57)	(0.96)	(0.3)	(1.6)
SUM HpCDF	26	6.8	0.74	5.9	-	-	-	9.5	0.85	-	-	-
1234678 HpCDD	240	160	120	73	10	23	110	200	97	73	49	670
SUM HpCDD	570	370	260	150	19	48	240	470	240	130	120	1000
OCDF	14	6.4	0.97	8.5	(0.12)	2.2	3.5	(0.36)	2.3	2.2	(0.55)	(1.4)
OCDD	9200	7100	4700	3500	190	760	2700	5200	2000	2700	980	5200
WHO-TEQ	7.3	4.7	3	3.3	0.59	0.79	3.5	6.2	3.3	3.1	2	8.4
Sum PCDFs	81.70	38.60	14.71	67.00	42.64	11.55	30.60	38.10	38.55	51.20	107.85	12.20
Sum PCDDs	9883.30	7586.00	5054.00	3718.00	234.30	830.50	2997.90	5782.00	2321.00	2871.60	1161.10	6313.00
D/F Ratio	120.971	196.528	343.576	55.493	5.495	71.905	97.971	151.759	60.208	56.202	10.766	517.459

[a] Limit of detection in parentheses