PCDDs AND PCDFs IN EFFLUENT AND SLUDGE FROM POTWs IN NORTH CAROLINA, USA

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Introduction

Last year, we used Principal Component Analysis to evaluate PCDD/PCDF data from sediment, wetland, and soil samples from the Lower Roanoke River Basin in North Carolina collected by the North Carolina Department of Environment, Health and Natural Resources (NC DENR), the United States Environmental Protection Agency (US EPA), and Weyerhaeuser.[1] Our evaluation indicated that (a) a former sawmill was not a source of PCDDs and PCDFs to the Roanoke River; (b) a pulp mill and former chloralkali plant are sources of PCDDs and PCDFs to Welch Creek, a tributary to the Roanoke River; and (c) four POTWs that discharge into the Roanoke River or its tributaries may be sources of PCDDs and PCDFs. As a result of the last conclusion, we collected effluent and sludge samples from the four POTWs and analyzed them for PCDDs and PCDFs.

Materials and Methods

Samples and sampling

In August 2001, we and US EPA jointly collected effluent and sludge samples from the POTWs in Williamston, Jamesville, Plymouth, and Windsor, North Carolina. A duplicate sample was collected from Plymouth. Figure 1 shows the POTW locations. Each effluent sample was a 24-hour composite. The sludge samples from Williamston and Plymouth were composites from sludge drying beds. The sludge samples from Windsor and Jamesville were liquid sludge from the secondary clarifier underflows.

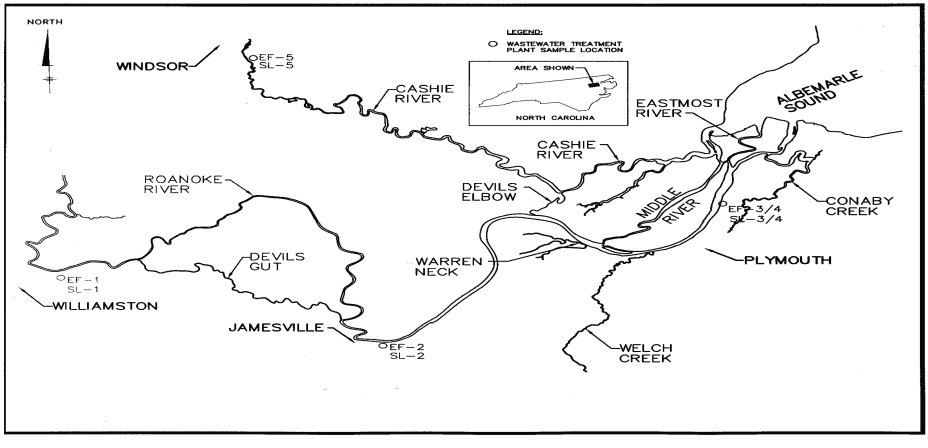

Figure 1. Map of the Lower Roanoke River Basin and POTW locations

LEVELS IN ABIOTIC COMPARTMENTS

Analysis

Each sludge sample was dried and homogenized. Seventeen internal standards then were added to each sludge 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. Seventeen internal standards were added to each effluent sample, which were then extracted with 240 mL of methylene chloride (3 x 80 mL). All 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 and Discussion

Table 1 includes the concentrations of 2,3,7,8-substituted congeners, the sum of each homologue group, the WHO-TEQ, the sum of PCDD and PCDF concentrations, and the D/F ratios for the effluent and sludge samples. All sludge samples contained detectable levels of all 2,3,7,8-substituted PCDDs. The sludge from Williamston, Plymouth, and Windsor contained similar concentrations of most congeners. The Jamesville sludge, however, was significantly lower for all congeners. 2,3,7,8-TCDD concentrations ranged from 0.32 (Jamesville) to 2.3 pg/g (Plymouth 2). OCDD was the dominant congener in all samples, ranging from 1,300 (Jamesville) to 16,000 pg/g (Williamston). The Jamesville sludge had the lowest WHO-TEQ, *viz.*, 3.6 pg TEQ/g. The remaining sludges had similar WHO-TEQs, ranging from 19 to 26 pg TEQ/g. Most PCDFs were detected in all samples, although 1,2,3,7,8,9-HxCDF was not detected in any sample.

Most 2,3,7,8-substituted PCDDs were not detected in most effluent samples. OCDD was the dominant congener in all effluent samples, ranging from 23 (Plymouth 1 and Windsor) to 130 pg/L (Williamston). 2,3,7,8-TCDD was not detected in any effluent sample, and 2,3,7,8-TCDF was detected only in one Plymouth sample at 0.64 pg/L. The WHO-TEQ for the effluent samples ranged from 0.95 (Plymouth 2) to 2.3 pg TEQ/L (Windsor).

In 1998, Rappe, *et al.*, reported PCDD/PCDF data for effluent samples from 17 POTWs in Mississippi.[2] We are not aware of any other studies reporting POTW effluent data. Generally, the PCDD and PCDF concentrations and congener profiles were similar to the data in this study.

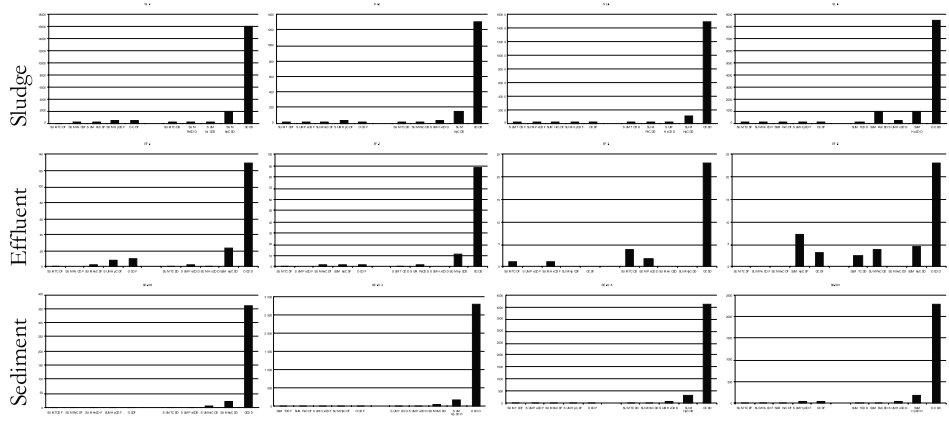

Figure 2. PCDD/Fs Profiles in POTW Sludge and Effluent and Sediment

Figure 2 shows the homologue profiles of the POTW sludge and effluent samples, and the sediment samples immediately downriver from the POTWs. The limited congeners detected in the effluents are not found in the sediment samples immediately downriver from the respective POTWs. Although OCDD was detected in all effluents and sediment samples, OCDD also was detected upriver of all POTWs. Thus, POTW effluents are not a significant source of PCDDs and PCDFs to the Lower Roanoke River Basin. US EPA's evaluation of the same POTW effluent samples reached a similar conclusion.[3]

Conclusions

1. The PCDD and PCDF concentrations of all effluent samples were similar.
2. The PCDD and PCDF concentrations of all sludge samples, except the sample from the Jamesville POTW, were similar.
3. OCDD was the dominant congener in all sludge and effluent samples.
4. The four POTWs are not significant sources of PCDDs and PCDFs to the Roanoke River Basin.

Acknowledgment

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References

1. Tysklind, M., Andersson, R., and Rappe, C. (2001). *Organohalogen Compds.* 51, 208-211.
2. Rappe, C., Andersson, R., Bonner, M., Cooper, K., Fiedler, H., and Howell, F. (1998). *Chemosphere* 36, 315-328.
3. Plumb, R. H., (March 22, 2002). Dioxin-Furan Fingerprinting of POTW Monitoring Data from the Lower Roanoke Basin (US EPA Report).

Table 1.

	POTW Sludge (pg/g d.m.) [a]					POTW Effluent (pg/L) [a]				
Location	**Williamston**	**Jamesville**	**Plymouth 1**	**Plymouth 2**	**Windsor**	**Williamston**	**Jamesville**	**Plymouth 1**	**Plymouth 2**	**Windsor**
Analyzed amount	11.9 g	6.36 g	19.48 g	18.19 g	3.85 g	0.89 L	0.93 L	0.91 L	0.94 L	0.95 L
% LOI	35.81	50.39	34.98	36.20	51.90					
2378 TCDF	4.3	0.79	4.9	3.1	3.8	(0.29)	(0.34)	0.64	(0.31)	(0.80)
SUM TCDF	22	11	46	40	47	0.92	0.65	1.3	-	-
2378 TCDD	1.9	0.32	2.2	2.3	0.76	(0.48)	(0.50)	(0.68)	(0.49)	(1.3)
SUM TCDD	46	14	36	24	100	0.9	1.1	3.9	-	2.6
12378 PeCDF	1.3	0.19	0.86	(0.059)	1	(0.34)	(0.40)	(0.58)	(0.41)	(0.96)
23478 PeCDF	0.97	0.23	0.62	0.46	0.77	(0.35)	(0.42)	(0.58)	(0.42)	(0.99)
SUM PeCDF	39	5.2	29	46	28	-	-	-	-	-
12378 PeCDD	7.4	1.5	11	8.9	6.9	0.65	(0.65)	(0.92)	(0.63)	(1.6)
SUM PeCDD	140	17	160	78	940	2.4	2.1	1.8	2.3	4
123478 HxCDF	5.6	0.54	4	3	2.5	(0.48)	(0.55)	(0.81)	(0.58)	(1.2)
123678 HxCDF	2.1	0.47	2.3	2.7	2.5	(0.42)	(0.47)	(0.67)	(0.48)	(0.95)
234678 -HxCDF	2.9	0.76	3	2.7	3.3	0.7	(0.58)	(0.82)	(0.59)	(1.2)
123789 -HxCDF	(0.68)	(0.11)	(0.16)	(0.11)	(0.27)	1.4	1.3	1.5	(0.68)	(1.3)
SUM HxCDF	100	10	46	48	51	2.9	1.3	1.2	-	-
123478 HxCDD	3	0.61	3	3.2	3.6	(0.76)	(0.88)	(1.2)	(0.87)	(1.8)
123678 HxCDD	21	2	14	8.5	21	(0.61)	(0.71)	(1)	(0.72)	(1.4)
123789 HxCDD	11	3.1	13	12	16	(0.58)	(0.74)	(1.1)	(0.72)	(1.5)
SUM HxCDD	170	29	160	130	220	1.6				
1234678 HpCDF	110	15	83	67	53	5.2	1.8	(0.93)	(0.67)	4
1234789 HpCDF	5.8	0.42	2	1.7	2.1	(0.79)	(0.93)	(1.3)	(0.93)	(1.7)
SUM HpCDF	390	26	150	120	110	8.6	2.1	-	-	7.2
1234678 HpCDD	850	59	380	310	420	11	4.9	(1.4)	1.5	1.9
SUM HpCDD	1900	140	970	800	950	23	11	-	2.8	4.4
OCDF	330	19	140	130	99	10	2.3	(1.9)	2.6	3.2
OCDD	16000	1300	15000	12000	8500	130	89	23	26	23
WHO-TEQ	26	3.6	24	20	19	1.5	1.1	1.5	0.95	2.3
Sum PCDFs	881.00	71.20	411.00	384.00	335.00	22.42	6.35	0.60	2.60	10.40
Sum PCDDs	18256.00	1500.00	16326.00	13032.00	10710.00	157.90	103.20	28.70	31.10	34.00
D/F Ratio	20.722	21.067	39.723	33.938	31.970	7.043	16.252	47.833	11.962	3.269

[a] Limit of detection in parenthes es