SOURCES OF PCDDs AND PCDFs IN SEDIMENTS AND WETLAND SOILS FROM THE LOWER ROANOKE RIVER BASIN IN NORTH CAROLINA, USA: PART II

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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 pulp 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 DENR, the US EPA, and Weyerhaeuser collected sediment and wetland soil samples from the Roanoke River, Welch Creek, and Conaby Creek, 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 (PCA) and determined that (a) the sawmill was not a source of PCDDs and PCDFs to the Roanoke River; (b) the pulp mill and chloralkali plant are sources of PCDDs and PCDFs to Welch Creek; and (c) publicly-owned treatment works (POTW) in the area were potential sources of PCDDs and PCDFs.[1] Later, US EPA analyzed these data and similarly concluded that the sawmill was not a source of PCDDs and PCDFs to the river.[2] US EPA identified the pulp mill as the likely source of PCDDs and PCDFs in the Lower Roanoke River.

In this study, we collected 64 sediment, wetland soil, and POTW sludge and effluent samples from the Roanoke River Basin and analyzed them for PCDDs and PCDFs.

Materials and Methods

Samples and sampling

In January 2001, we collected 45 sediment samples from 41 locations in the Lower Roanoke River Basin. Sediment samples were grab samples (n=40) collected from the top 15 cm and cores (n=5) from sediment surface to 2.4 m below sediment surface. Samples were collected from the Roanoke River (n=24), Devils Gut (n=2), Warren Neck (n=1), Middle River (n=2), Welch Creek (n=6), Eastmost River (n=2), Conaby Creek (n=2), and Cashie River (n=6). We also collected nine wetland soil samples from eight locations in this area. All wetland soil samples were cores from the surface to 2.1 m below the surface. In August 2001, we and US EPA jointly collected effluent and sludge samples from the POTWs in Williamston, Jamesville, Plymouth, and Windsor, North Carolina. Each effluent sample was a 24-hour composite.

Analysis

The sediment, wetland soil, and sludge samples were dried and homogenized. Seventeen internal standards then were added to each sample. Next, each sample was extracted for approx. 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 then were 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 AX21/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.

Data evaluation

PCA[3] can identify differences and similarities in profiles among environmental samples.[4] In this study, the PCA was based on the concentrations of 2,3,7,8-substituted congeners and the total of each homologue for all 64 samples. All data were log-transformed and one-half the detection limit was used for values below the detection limit. The Roanoke River samples are designated (a) "SR1" for those upriver from Jamesville; (b) "SR2" for those downriver from Jamesville and upriver from Welch Creek; and (c) "SR3" for those downriver from Welch Creek. Samples collected from Welch Creek are designated "SW". Samples collected from other tributaries are designated "SR". The wetland soil samples are designated "WS". The POTW sludge and effluent samples are designated "PS" and "PE", respectively. *See* Table 1.

Table 1. Designations, types and sampling locations

Designation	Type	Location	n
SR1 (SE100-SE107)	Sediments	Roanoke River upriver Jamesville	8
SR2 (SE108-SE115)	Sediments	Roanoke River between Jamesville and Welch Creek	8
SR3 (SE116-SE123A)	Sediments	Roanoke River downriver Welch Creek	8
SW (SE800-SE805)	Sediments	Welch Creek	6
SR (SE200-SE701)	Sediments	Devils Gut, Warren Neck, Middle River, Welch Creek, Eastmost River, Conaby Creek, and Cashie River	15
WS (WS1-WS9)	Wetland Soils	Representative locations	9
PS	Sludge	POTWs	5
PE	Effluent	POTWs	5
		Total samples	64

Results

The PCA generated a 4-dimensional model that explained 90% of the variation in the data. *See* Figure 1. Principal components 1 and 2 explain 70 % and 9 % of the variation in the data, respectively. Six clusters were identified based on the major differences and similarities among these data. Cluster I includes three sediment samples from the Roanoke River upriver from Jamesville. Cluster II includes 5 of the 6 sediment samples from Welch Creek. 2,3,7,8-TCDD and 2,3,7,8-TCDF were prevalent in these Welch Creek samples, indicating a pulp mill influence.[5] Cluster III includes all but one of the remaining sediment samples. The samples in the left part of Cluster III are similar in PCDD/PCDF composition to those in Cluster I. Similarly, the samples in the right part of Cluster III are similar in PCDD/PCDF composition to those in Cluster II. Cluster IV includes only the sample collected at Albemarle Sound and exhibits a composition not found in any other sample. Cluster V includes the POTW effluents. These samples differ in PCDD/PCDF composition from all other samples, indicating a minimal

influence from the four POTWs. Cluster VI includes most wetland soil samples. These Cluster VI samples are similar in some respects to the other wetland soil samples in the upper left part of Cluster III. As noted above, some of these samples in Cluster III are similar to the Roanoke River samples upriver from Jamesville in Cluster I. Thus, the wetland soils likely impact the Roanoke River.

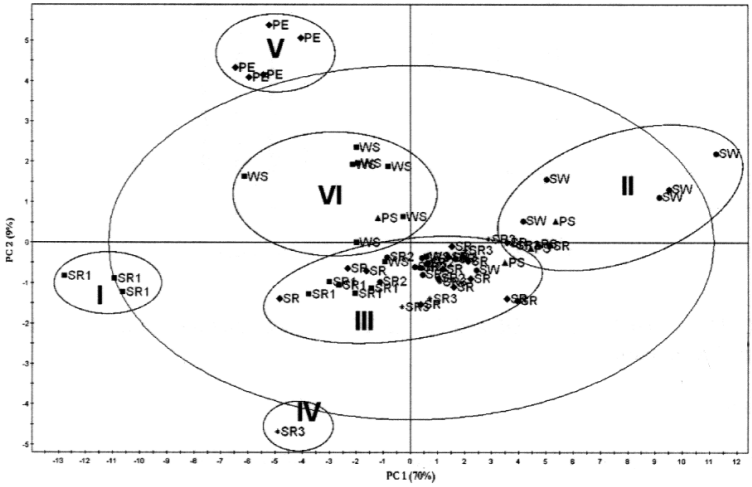

Figure 1. Score plot (PC1 vs. PC2) showing trends in PCDD/PCDF compositions

The PCDD/PCDF data from our study[6, 7] support our PCA results. Specifically, Clusters I, II, and III show changes in PCDD/PCDF composition in the sediments as the Roanoke River flows from Williamston to the Albemarle Sound. Figure 2, for example, shows the WHO-TEQs, and the 2,3,7,8-TCDF and 2,3,7,8-TCDD concentrations for the Roanoke River and Welch Creek samples. Essentially, the concentrations are constant, from 0.1 to 15 pg TEQ/g dm, upriver from Welch Creek. The TEQs increase by a factor of up to 5 below Welch Creek. Further, 2,3,7,8-TCDF contributes from 10 to 25 % to the total TEQ below Welch Creek. Thus, Welch Creek influences the Roanoke River and certain tributaries below Welch Creek. US EPA agrees with this finding.[2]

Conclusions

1. The Welch Creek sediments and the Roanoke River sediments below Welch Creek have similar PCDD/PCDF profiles, indicating the pulp mill is the primary source of certain PCDDs and PCDFs to the Roanoke River.
2. PCA indicates, and the data support, that the four POTWs are not a significant source of PCDDs and PCDFs to the Lower Roanoke River Basin.
3. PCA indicates, and the data support, that the wetland soil in the Lower Roanoke River Basin contribute PCDDs and PCDFs to the Roanoke River.

Acknowledgment

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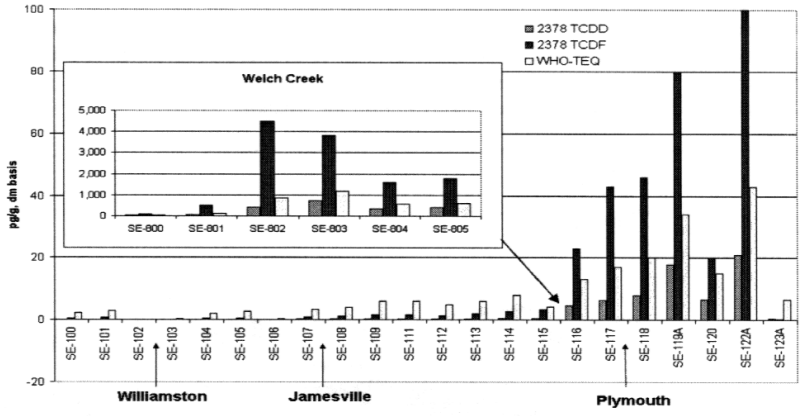

Figure 2. WHO-TEQs, and 2,3,7,8-TCDF and 2,3,7,8-TCDD concentrations for the Roanoke River and Welch Creek sediments

References

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