SOURCES OF PCDDS AND PCDFS IN SEDIMENT, WETLANDS, AND SOIL FROM THE LOWER ROANOKE RIVER IN NORTH CAROLINA, USA

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Introduction

The lower part of the Roanoke River flows east from Williamston, North Carolina, past Plymouth, North Carolina and discharges into the Albermarle Sound. This part of the river is surrounded by wetlands and swamps. Weyerhaeuser Corporation operates a pulp and paper mill and previously operated a chloralkali plant in Plymouth. Weyerhaeuser discharges its effluent into Welch Creek, which flows into the Roanoke River. Prior to 1981, Georgia-Pacific Corporation operated a hardwood sawmill approximately 1 km downriver of the Weyerhaeuser mill.

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 above and below Weyerhaeuser's pulp mill, Welch Creek, and Conaby Creek, another tributary to the Roanoke River near Albermarle Sound, and analyzed them for PCDDs and PCDFs. NC DENR also collected and analyzed soil samples from Georgia-Pacific's former sawmill. In this study, we used Principal Component Analyses (PCA) to identify potential sources of these compounds to the lower Roanoke River and its tributaries. To our knowledge, the PCDD and PCDF profiles have not previously been evaluated using PCA or any other method of source identification.

Methods and data evaluated

PCA has been used in environmental studies to illustrate the differences and similarities in profiles among different samples (1). The principal component scores are plotted and samples with similar PCDD and PCDF compositions will cluster (2). In this paper, PCA is based on the amount of 2,3,7,8-substituted congeners and the total of each homologue group. In performing the PCA, one-half the detection limit was used for non-detected values. All data were log-transformed prior to the PCA calculations.

We conducted two PCA calculations. First, we evaluated the 130 sediment, wetland, and soil samples collected and analyzed by NC DENR, US EPA, and Weyerhaeuser. These samples are summarized in Table 1; the underlying data are publicly available (3-5). The Roanoke River samples collected upriver of the confluence with Welch Creek are designated with a "U"; samples collected downriver of the confluence are designated with an "L". Samples collected in Welch Creek are designated with a "W". Samples designated with "C" were collected from Conaby Creek. Samples designated with "G" were collected from the former Georgia-Pacific sawmill and one sample from adjacent property. *See* Table 1.

Second, based on the existing data and potential sources in the lower Roanoke River, we evaluated the 130 samples and relevant PCDD and PCDF data from known sources of these compounds. Specifically, in addition to the 130 samples, the second PCA calculation included soil samples from municipal waste incinerators, which are designated with an "I" (6, 7); soil samples from chloralkali plants, which are designated with an "A" (6); pentachlorophenol and pentachlorophenate (PCP) data, which are designated with a "P" (8); sludge data from three publicly-owned treatment works (POTW) in North Carolina, which are designated with an "S" (9); and, sediment samples from the Leaf-Pascagoula River System in Mississippi, which are designated with an "M" (10). *See* Table 1. Because data from the pulp mill effluent were not available, we were not able to include it in our analysis.

Table 1. Types and Sources of Dioxin Data

Designation	Description	Matrix(es)	n	Ref.
U	Roanoke River upriver of Welch Creek	Sediment and Wetland	19	3, 4
L	Roanoke River downriver of Welch Creek	Sediment and Wetland	64	3, 4
W	Welch Creek	Sediment and Wetland	36	2, 3
C	Conaby Creek	Sediment and Wetland	4	2
G	Former Georgia-Pacific Sawmill	Soil	7	4
I	Municipal Waste Incineration	Soil	14	5, 6
A	Chloralkali Plant	Soil and Sediment	10	6
P	Pentachlorophenol and Pentachlorophenate	Chemical	4	7
S	Publicly-Owned Treatment Works	Sludge	3	8
M	Leaf-Pascagoula River in Mississippi	Sediment	65	9

Results

The first PCA included data from the 130 sediment, wetland, and soil samples from the lower Roanoke River and generated a four-dimensional model that explained 94% of the variation in the data. *See* Figure 1. This figure shows the major differences and similarities among these samples; three general clusters were identified. Clusters indicate a similar PCDD and PCDF congener pattern. The first cluster (I) includes samples from the Roanoke River upriver and downriver of the confluence with Welch Creek (U and L), Conaby Creek (C), and the upper part and some samples from the lower part of Welch Creek (W). The second cluster (II) includes only the soil samples from the sawmill and was dominated by octaCDD, heptaCDDs, and hexaCDDs, indicating the influence of PCP. This is consistent with the seasonal use of PCP at that facility. The third cluster (III) includes 14 samples from the lower part of Welch Creek (W) and was dominated by 2,3,7,8-tetraCDD and 2,3,7,8-tetraCDF. This is a strong indication of a pulp mill influence (11).

The second PCA included PCDD and PCDF data from known sources and also generated a four-dimensional model that explained 94% of the variation in the data. *See* Figure 2. Generally, four clusters were identified. The first cluster (I) includes the PCP samples (P) and the soil samples from the former sawmill (G). The second cluster (II) includes the chloralkali samples (A). The third cluster (III) includes incineration samples (I), POTW samples (S), the Welch Creek samples (W), the Conaby Creek samples (C), and the Roanoke River samples, both upriver (U) and downriver (L) of Welch Creek. We identified four POTWs that discharge into the lower Roanoke River and these are potential sources of PCDDs and PCDFs in the river. Also, certain

Welch Creek samples in the third cluster, appear close to cluster II, indicating multiple sources to this area. The fourth cluster (IV) includes the Leaf-Pascagoula River sediment (M). The Mississippi sediments did not cluster with any other samples.

Conclusions

Based on our evaluation of the available data, we conclude:

1. The former sawmill is not a source of PCDDs and PCDFs to the Roanoke River.
2. The pulp mill and former chloralkali plant are sources of PCDDs and PCDFs to Welch Creek but not to the Roanoke River.
3. The PCDD/PCDF patterns in the lower Roanoke River and tributaries are consistent with patterns from POTWs in other areas, suggesting that POTWs in this area are a potential source of these compounds.

Because of the limited design of this sample collection and certain quality issues respecting the data, we are conducting a comprehensive study of the sediments and wetlands in the lower Roanoke River and its tributaries. We have collected sediment and wetland soil samples from more than 50 locations in this area and are seeking access to the four POTWs to sample their effluent and sludge.

Acknowledgment

This research project was sponsored by Georgia-Pacific Corporation, Atlanta, Georgia, USA.

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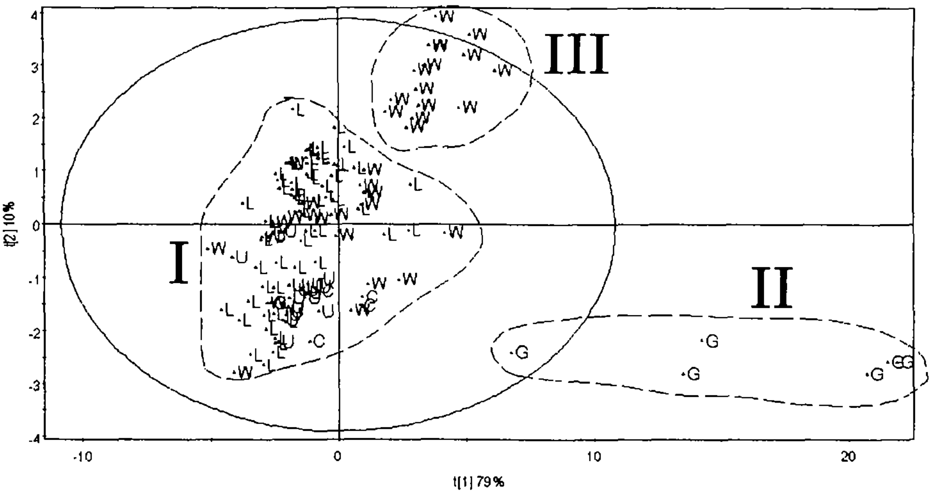

Figure 1. The score plot (t1 vs. t2) showing the dominating trends in the composition of PCDDs and PCDFs in the Lower Roanoke River. U=Roanoke River upriver of Welch Creek; L= Roanoke River downriver of Welch Creek; W=Welch Creek; G=former sawmill; C= Conaby Creek.

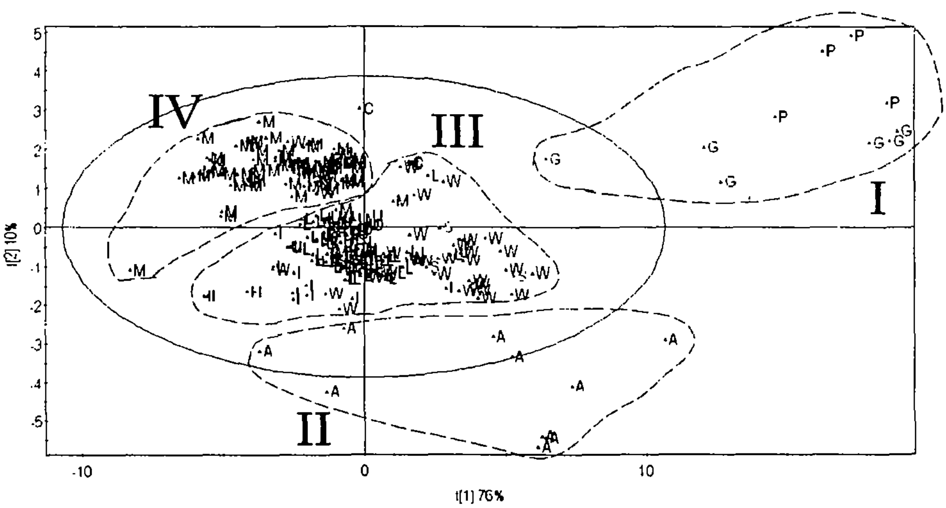

Figure 2. The score plot (t1 vs. t2) showing the dominating trends in the composition of PCDDs and PCDFs in the Lower Roanoke River and known PCDD and PCDF sources. U=Roanoke River upriver of Welch Creek; L= Roanoke River downriver of Welch Creek; W=Welch Creek; G=former sawmill; C= Conaby Creek; I= Municipal Waste Incinerators; A= Chloralkali plants; P=Pentachlorophenol and Pentachlorophenate; S=Sludge from POTW; M=Leaf River and Pascagoula River sediments.