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DISCOVERY OF DIOXIN CONTAMINATION IN THE WOONASQUATUCKET RIVER. A PRELIMINARY STUDY OF THE CENTERDALE MANOR RESTORATION PROJECT SUPERFUND SITE, NORTH PROVIDENCE, RHODE ISLAND, USA

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Introduction

When high concentrations of heavy metals were found in fish from the Woonasquatucket River and Southeast Asian American (SEAA) fishermen were reportedly subsistence fishing in the river, EPA initiated an investigation. The results of that investigation of metals, pesticides, polychlorinated biphenyls (PCBs), dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in sunfish and eels (fillets and offal) showed unacceptable levels of PCDDs and PCBs. In particular, very high concentrations of the toxic PCDD congener, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), were detected. The discovery prompted an investigation of 2,3,7,8-TCDD in sediments behind seven dams along the river. This PCDD congener was subsequently found in high concentrations in the sediments behind all the dams, except one, the most northern dam. Highest concentrations were found in two impoundments near historic mill sites. An unknown peak later identified as 1,2,4,5,7,8-hexachloroxanthene (HCX) was also detected in the sediments of the river. The fact that 2,3,7,8-TCDD was found along with HCX was an indicator that the manufacture of the antibacterial pesticide hexachlorophene could be the source of the contamination. Behind the first river dam sampled, neither 2,3,7,8-TCDD and HCX were detected in the sediments. The sediments behind the second dam contained very high concentrations of both compounds and the levels then decreased with distance down the river. The discovery of 2,3,7,8-TCDD and HCX in sediment adjacent to a site originally used as a chemical manufacturing plant led to the discovery of high concentrations of PCDDs in soils and subsequently led to a full scale Comprehensive Environmental Response, Compensation and Liability act (CERCLA) investigation of the site, river and pond sediments and adjacent wetlands.

History

In May of 1994, Haley Wurzel, Vanessa Tomasic, and Kelley Park of Brown University collected sediment samples in the Woonasquatucket River RI at the Valley Street Dam and found high levels of heavy metals. In May of 1995, Siemay Lee of Brown University wrote "Are Turner Reservoir Fish safe to Eat? A risk Assessment of Rhode Island Southeast Asian American (SEAA) Fishers" and also found high levels of heavy metals in fish. Indira Balkinsoon of EPA Region 1 and RI DEP officials recognized this fact and as part of the EPA Urban Environmental Initiative and Rhode Island Greenway Project initiated a study of fish in the Woonasquatucket River. A sampling program was designed to investigate those areas where SEAA fishers were believed to catch fish for consumption. Further information about the SEAA fisherman indicated that the fish were prepared by frying the complete fish further causing possibly higher human health risk.

Initial investigation

Hook and line sampling resulted in the collection of sunfish (*Centrarchidae*) and American eels (*Anguilla rostrata*). Sampling was conducted on 1 June 1996. Sunfish were collected from the Valley Street impoundment and eels were collected near an old mill race way adjacent to Allendale Pond. Three sunfish muscle fillet and offal composites and two eel fillet and offal composites were analyzed. The fish were processed and analyzed at the EPA Narragansett laboratory (AED) facility. Samples were analyzed for mercury, cadmium, copper, nickel, chromium, lead and zinc as well as DDT, DDE, DDD, chlordane, transnonchlor, NOAA list PCBs, and PCDDs and PCDFs. The laboratory detected significant amounts of 2,3,7,8-TCDD and dioxin-like PCBs.

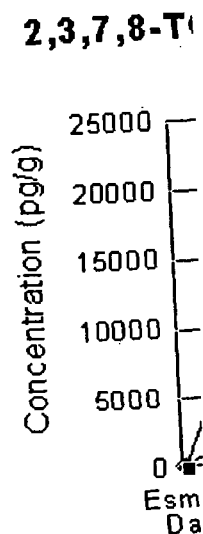
Concentrations ranging between 17 pg/g and 554 pg/g wet weight of 2,3,7,8-TCDD were measured in the fillet and offal samples. Region 1 EPA needed to confirm AED LRGC/MS results with Region 7 HRGC/HRMS data that could be used for risk assessment. The extracts from AED were sent for analysis and the data indicated that the results were comparable. In September 1996, the EPA Region 7 laboratory (R-7) confirmed the AED screening result with method 1613 results validated by Region 1. The comparisons are as follows: Sunfish TCDD-63.1 ppt (AED) vs 41.0 ppt (R-7); Eel TCDD - 91.7 ppt (AED) vs. 85.8 ppt (R-7). Using the above results, a risk screen was performed in September 1996 and the screen indicated that 95% of the risk was from 2,3,7,8 TCDD and 5% from PCB. This discovery prompted EPA to pursue further investigations in the impoundment sediments behind all the dams along the Woonasquatucket River.

Sediment Investigation

In October 1997, seven surface sediment samples were collected directly behind each of the seven impoundment dams on the Woonasquatucket River from Centerdale to North Providence. Figure 1 depicts the sampling locations and concentrations (pg/g=ppt) of 2,3,7,8-TCDD and 1,2,4,5,7,8-hexachloro-(9H)xanthene (HCX). The levels of 2,3,7,8-TCDD detected were considered very high compared to the 1.0 ppb TCDD nominal Superfund clean-up level (2).

Initially chemists at AED using full scan low resolution gas chromatography discovered a non dioxin peak and tentatively identified the peak as HCX. The presence of this compound was later confirmed by EPA Region 7. This discovery led to speculation that the presence of 2,3,7,8-TCDD along with HCX was a result of the manufacture of hexachlorophene from 2,4,5-trichlorophenol (4). Similar discoveries were documented by EPA Region 7 chemists during the investigation of the Times Beach Superfund sites in Missouri. The origin of the Missouri contamination was found to be the manufacture of 2,4,5-trichlorophenol, 2,4,5-TP Silvex, and hexachlorophene (1).

Figure 1. Concentration of 2,3,7,8-TCDD in the Woonasquatucket River sediments. Based on the sediment concentrations.



from a chemical mill. The little 2,3,7,8 TCDD concentrations were property along the original mill was a apartment/condo include the analysis closed for the pro

In September 1997, results of those samples from the river bank (3).

Soil investigation
Due to the discovery of investigations on the Centerdale Woonasquatucket bordered Allendale

These results prompted and later non-timber erosion of contaminated

dae) and American eels were collected from the way adjacent to Allendale and offal composites were at laboratory (AED) chromium, lead and zinc as and PCDDs and PCDFs. n-like PCBs. 3,7,8-TCDD were measured. RGC/MS results with e extracts from AED were. In September 1996, the h method 1613 results 63.1 ppt (AED) vs 41.0 ove results, a risk screen the risk was from 2,3,7,8 er investigations in the t River.

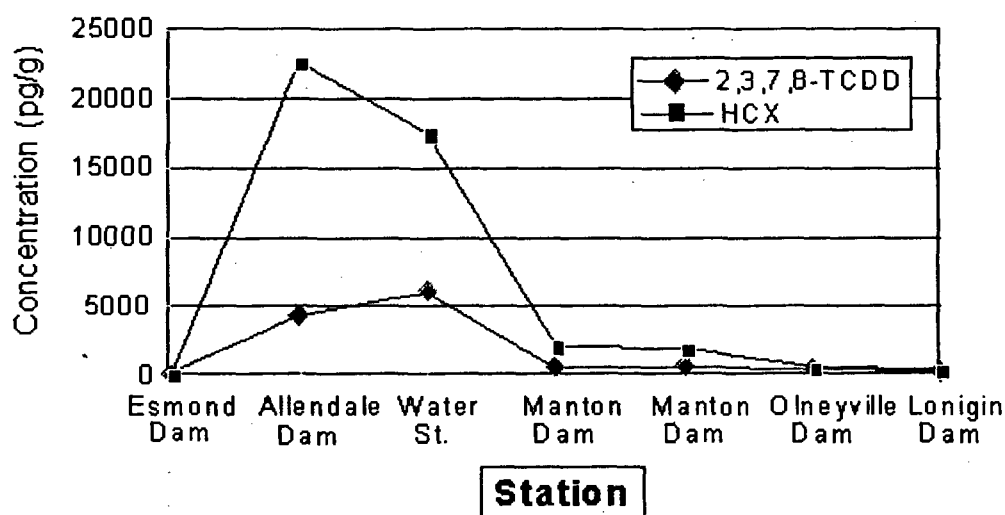
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Figure 1. Concentrations of 2,3,7,8-TCDD and 1,2,4,5,7,8-hexachloroxanthene in sediments from the Woonasquatucket River.

Based on the sediment data (Figure 1) it was presumed that the TCDD/ HCX may have originated

2,3,7,8-TCDD and 1,2,4,5,7,8-Hexachloroxanthene



from a chemical manufacturing facility near or on the river below the Esmond dam, where very little 2,3,7,8 TCDD was found, and the Allendale and Lymonsville Dams, where high concentrations were measured. Historical records indicated a mill located on Centerdale Manor property along the shore of the Woonasquatucket River and adjacent to Allendale Pond. The original mill was destroyed in the Mid 70's by fire and was replaced in the Mid 80's by two apartment/condominium buildings. The initial site investigation results for the property did not include the analysis of PCDDs/PCDFs. Further investigation also indicated that when the mill closed for the production of cloth it was converted into a chemical manufacturing facility.

In September 1998, EPA collected 45 soils and sediment samples at the Centerdale property. The results of those samples indicated 4 parts per billion TCDD in Centerdale soils and 14 ppb along the river bank.⁽³⁾

Soil investigations

Due to the discovery of the high levels of predominately 2,3,7,8-TCDD, EPA initiated further investigations on the Centerdale property and the adjacent wetlands and residences. Concentrations on the Centerdale Manor property were found as high as 140 ppb. Shore line sediments along the Woonasquatucket River were found up to 8 ppb 2,3,7,8-TCDD near homes and athletic fields that bordered Allendale and Lymonsville Ponds.

These results prompted EPA to perform several time critical investigations on affected properties and later non-time critical stabilization of the shoreline and wetlands sections to prevent further erosion of contaminated soils.

Chemical contamination origins

Further investigation of the chemical manufacturing practices at the site indicated that the chemical company started to produce hexachlorophene by the reaction of 2,4,5-trichlorophenol with formaldehyde during the 1960's. By-products of this process include HCX and 2,3,7,8-TCDD. The ratio of TCDD and HCX from soil samples collected in 1998-99 at the site was approximately 1, 2,3,7,8-TCDD, to 20 HCX. This ratio is indicative of the manufacture of hexachlorophene from 2,4,5-trichlorophenol and not the manufacture of 2,4,5-trichlorophenol as the initial reactant. Several other sites in the US are contaminated with 2,3,7,8-TCDD and other PCDD congeners due to the manufacture of 2,4,5-trichlorophenol from tetrachlorobenzene (4). It is well known that between 1960 and 1970 the production of 2,4,5-trichlorophenol without 2,3,7,8-TCDD contamination was very difficult. Many clean-up steps need to be employed to produce a colorless, dioxin free 2,4,5-trichlorophenol.

The toxicity of 2,3,7,8-TCDD is well known, but the toxicity of HCX is not well characterized at this time but has been estimated in later EPA work that will be discussed in future papers.

Discussion:

Thus, from a small sampling of fish from the Woonasquatucket River to study risks to SEAA fishers, indications of significant environmental contamination were discovered. The discovery of 2,3,7,8-TCDD and HCX and the use of 2,3,7,8-TCDD/HCX ratios proved an important indicator of site specific dioxin contamination. This helped to pin down where the chemicals were manufactured, by whom, and for what purposes. Previous information from the Region 7 2,3,7,8-TCDD/HCX research was critical in helping to determine the contamination source.

Disclaimer: Although the information in this document has been funded wholly by the USEPA, it does not necessarily reflect the views of the agency and is no official endorsement should be inferred.

References:

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CONTAMINATED OFFICE OF FISH AND WILDLIFE CENTREDALE

1 U.S. Environmental Protection Agency
2 Battelle Memorial Institute

Introduction

As part of the Renwick
Manor Restoration
Environmental Project
(USACE), a Baseline
Assessment (BER)
Investigation are to

- evaluate exposure Woonasquatucket river basin
- develop

A BHHRA would assess and risk
hazard identification
assessment and risk

The hazard identification
dioxin (specifically
TCDD); 1,2,4,5,7,8-
the site in soil, sediment
were found at elevated
compounds (VOCs)
analyzed for same
methods, data suggest
PCBs) in sediment
Manton and Dye
correlation between

The exposure assessment
potentially exposed
Contaminated water
high levels of dioxin