

# MASS BALANCE APPROACHES TO DIOXIN EXPOSURES IN A MICHIGAN RIVER, USA

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# BACKGROUND

- **Sediments contain a variety of toxic compounds**
- **Difficult to predict toxic potential using chemical analysis alone**
  - **Important compounds overlooked**
  - **Complex interactions**
- **Bioassays provide estimates of toxic potencies of complex mixtures**
  - **Compounds are not identified**

# OBJECTIVES

- **To determine the concentrations of PCDDs/DFs in surface sediments and flood plain soils collected along the Tittabawassee River, Michigan**
- **To subject sediment extracts containing target chemicals to gene expression *in vitro* bioassays for estimating total dioxin-like potencies**
- **To conduct mass balance for identifying specific compounds or class of compounds responsible for AhR mediated activity**

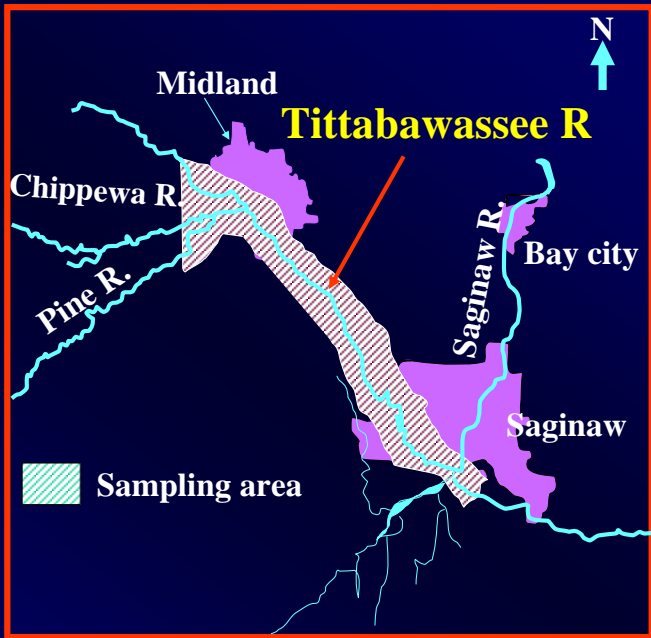
# Sample Collection



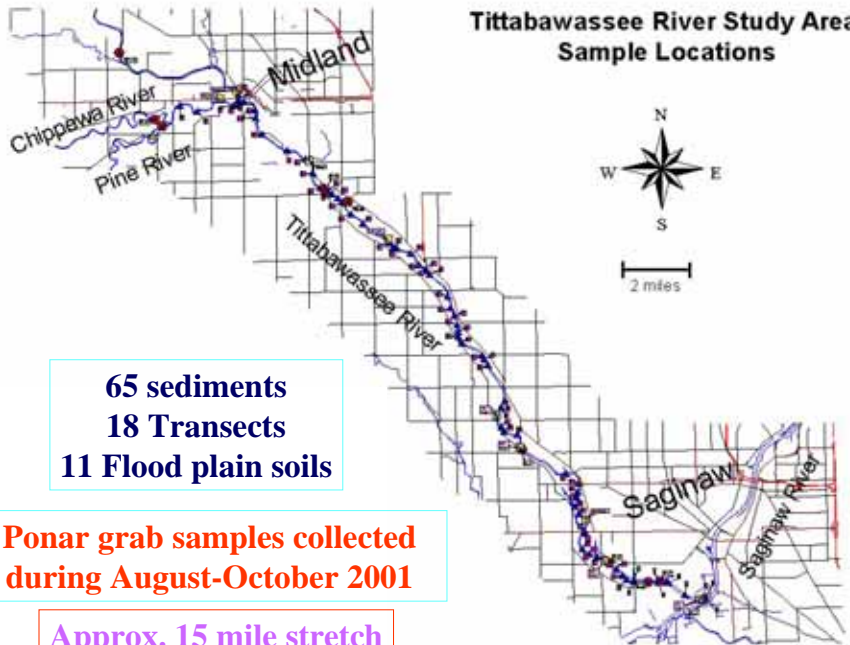
**K. Kannan**

**A. Taylor**

# Location of study area



## Tittabawasse River Study Area Sample Locations



**65 sediments**  
**18 Transects**  
**11 Flood plain soils**

**Ponar grab samples collected  
during August-October 2001**

**Approx. 15 mile stretch**

# Sample Collection



# Sample Collection

**Tittabawassee River, Michigan**

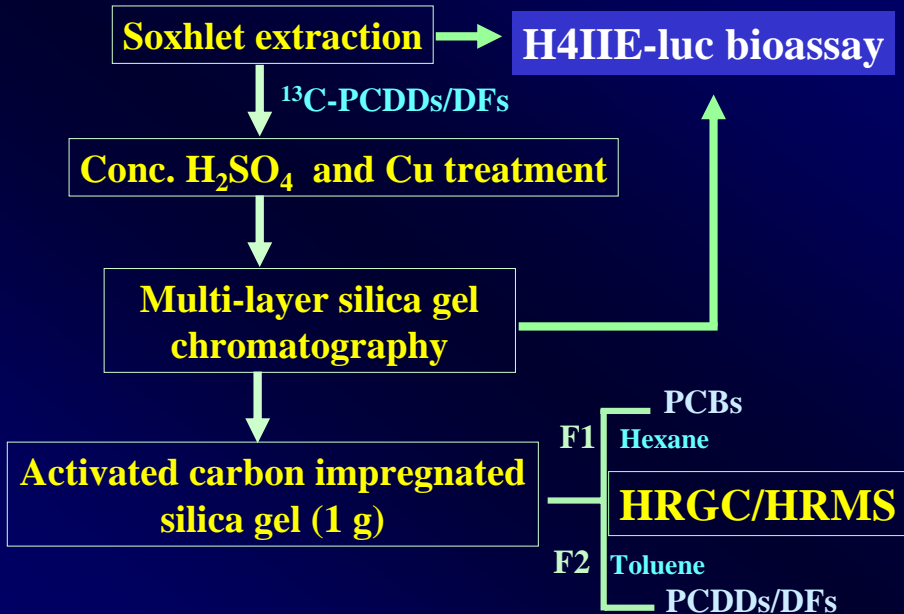


# Sample Collection

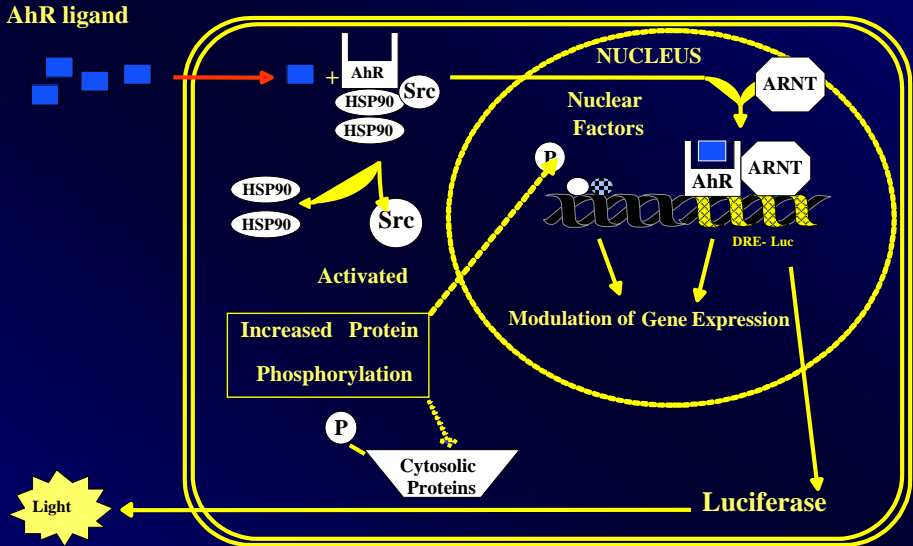
**Tittabawasse River, Michigan**



# Analysis



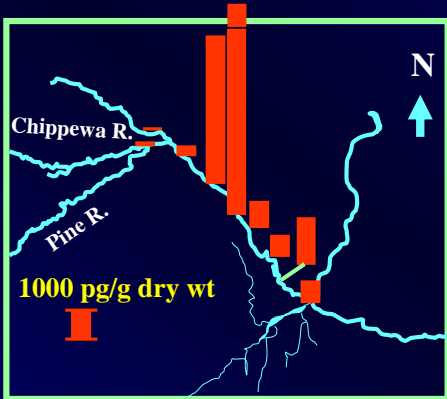
# H4IIE-luc cell bioassay for AhR-active compounds



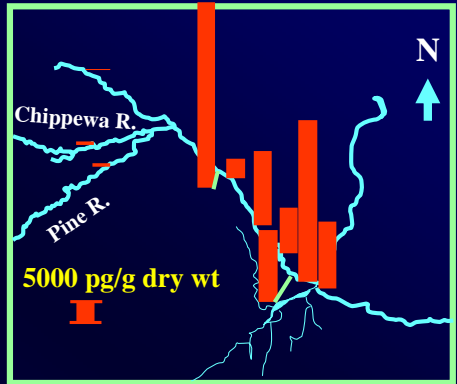
## Concentrations (pg/g, dry wt) of PCDDs and PCDFs in sediments, flood plain soils from the Tittabawassee River compared with those of the upstream locations

Sample (n)	PCDDs	PCDFs
Composite sediment (16)	2400 (560-7590)	3790 (1030-11400)
Transect sediment (18)	1480 (160-5710)	3140 (88-17700)
FP soil (7)	14800 (2730-38400)	10600 (2390-17200)
Ups. Comp sediment (3)	120 (92-140)	59 (27-120)
Ups. Transect sediment (4)	97 (35-200)	22 (9.2-47)
Ups. Soil (3)	320 (120-450)	46 (7.2-67)

## Transect sediment



## Floodplain soil



**Spatial trends in concentrations of total PCDD/DFs in surface sediment and floodplain soils collected along the Tittabawassee River**

## Concentrations (pg/g, dry wt) of PCDDs and PCDFs in Tittabawassee R sediments compared with those from other locations (Mean & Range)

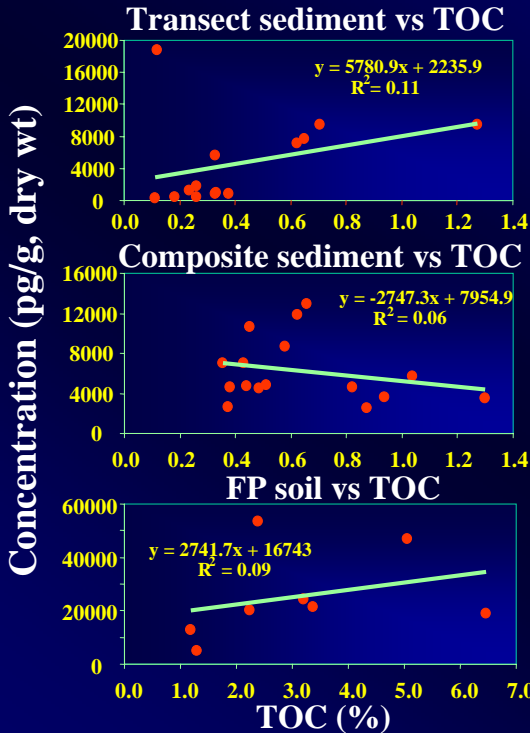
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Location	PCDD/DF (pg/g, dry wt)
Tittabawassee River	6630 (100-30500)*
Upper Detroit River	350 (110-1420)
Housatonic River	2060 (160-5400)**
Newark Bay	7020 (510-31700)
Thames River,UK	3000 (446-9310)

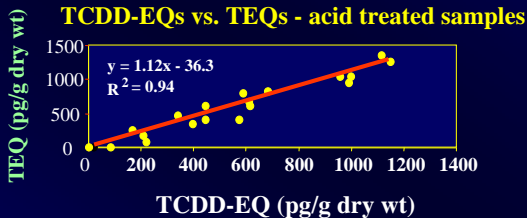
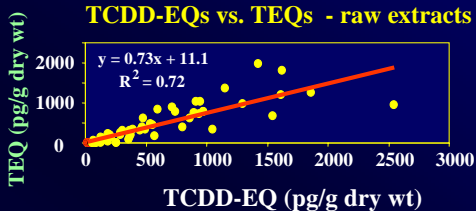
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\*soils not included

\*\*outlier removed



**Relationship  
between  
concentrations  
of PCDDs/DF  
and TOC in  
sediments**

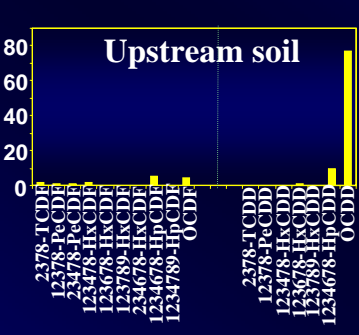
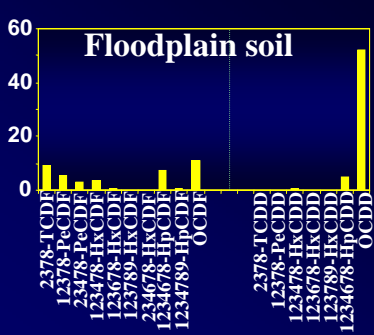
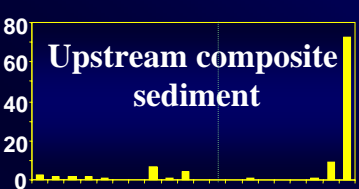
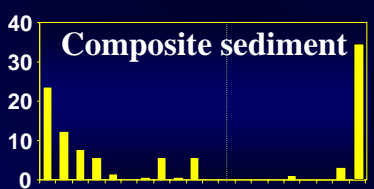
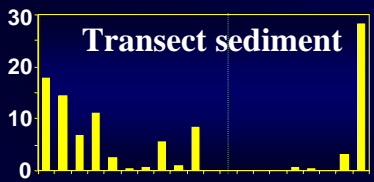


**Relationship between PCDD/DF - TEQs and  
bioassay derived TCDD-Eqs in soil/sediments  
from the Tittabawassee River basin**

**Concentrations (pg/g, dry wt) of TEQs and TCDD-Eqs  
in sediments/soils from the Tittabawassee River  
(Mean & Range)**

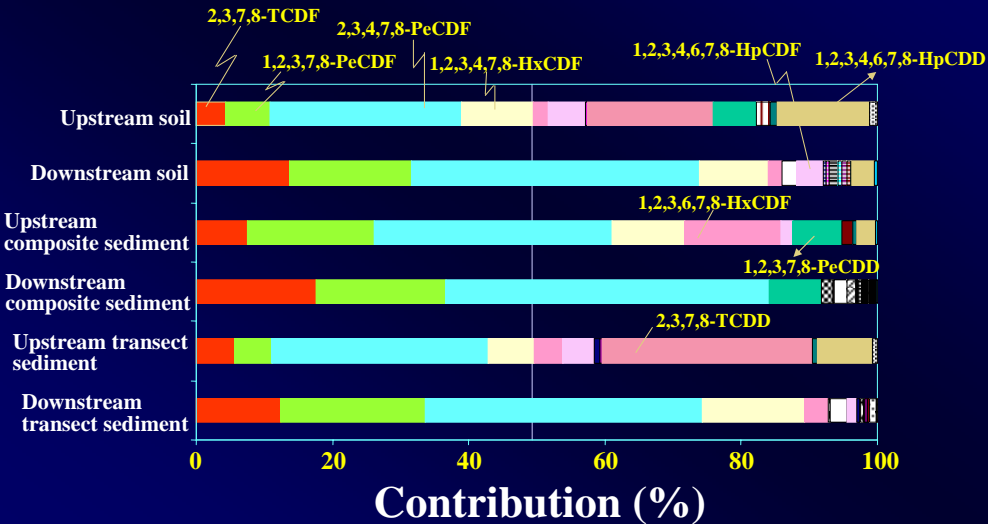
<b>Sample (n)</b>	<b>TEQs</b>	<b>TCDD-Eqs</b>
<b>Composite sediment (16)</b>	<b>550</b> <b>(41-1810)</b>	<b>370</b> <b>(34-2430)</b>
<b>Transect sediment (18)</b>	<b>440</b> <b>(6.3-2770)</b>	<b>300</b> <b>(8.6-1450)</b>
<b>FP soil (7)</b>	<b>1150</b> <b>(350-1890)</b>	<b>1100</b> <b>(290-2450)</b>
<b>Ups. Comp sediment (3)</b>	<b>8.2</b> <b>(2.5-19)</b>	<b>4.3</b> <b>(0.8-9.8)</b>
<b>Ups. Transect sediment (4)</b>	<b>2.3</b> <b>(0.56-5.5)</b>	<b>7.6</b> <b>(0.4-25)</b>
<b>Ups. Soil (3)</b>	<b>6.2</b> <b>(2.1-10)</b>	<b>165</b> <b>(20-240)</b>

Composition (%)



Profiles of PCDD/DF congeners in soil and sediments

# Contribution of PCDDs/DF Congeners to TEQs



# Source characteristics of PCDDs/DFs

**PCBs:** only PCDFs [TCDF > PeCDF > HxCDF > HpCDF]

**Chlorophenols and products:** 2,4,5-T, 2,4-D, PCP

TeCDF, PeCDF, HxCDF, HxCDD, HpCDD, **OCDD**

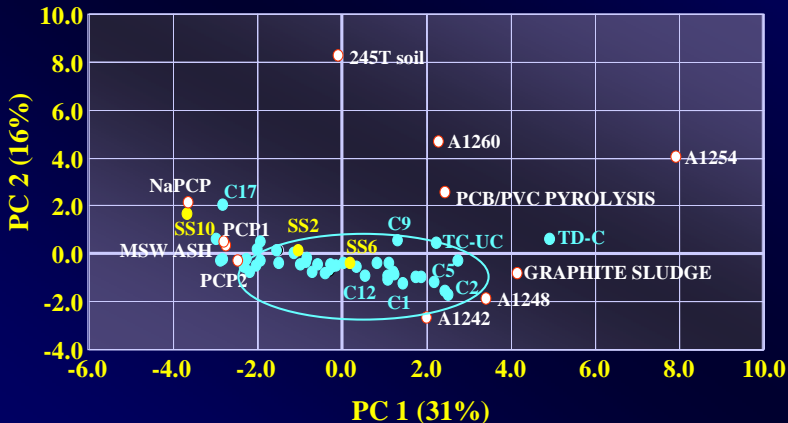
**Chloralkali production:**

OCDF > HpCDF > HxCDF > OCDD > HpCDD

**Pulp mill:** **TCDF**

**OCDD** and **TCDF** were the predominant congeners, which suggests a unique pattern of mixed sources of PCDDs/DFs in the sediments.

# Principal Component Analysis of PCDD/DF Congener Profiles in Sediments, Soils and Representative Sources



# Conclusions 1

Relatively great concentrations of PCDD/DF were found in sediments and flood plain soils collected downstream of an industrial complex in Midland, Michigan. Concentrations in floodplain soils were 10-fold greater than those in sediments.

OCDD and TCDF were the predominant congeners, which suggests a unique pattern of PCDDs/DFs in sediments, which is probably from multiple sources.

Concentrations of PCDD/DF were not related to sediment TOC and no spatial gradient in concentrations could be discerned. Hydrological characteristics seem to influence the spatial distribution in concentrations.

## **Conclusions 2**

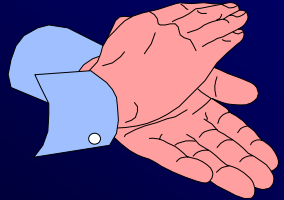
**Bioassay derived TCDD-Eqs were similar to those of instrumentally derived TEQs. A significant correlation existed between bioassay derived TCDD-Eqs and TEQs suggesting the utility of bioassays to detect dioxin-like compounds in environmental matrices and for detailed mapping and monitoring.**

**PCDDs/DFs were the compounds responsible for dioxin-like activity. Contributions by other compounds such as PAHs or PCBs to dioxin-like activity was negligible.**

## **Conclusions 3**

**Based on a principal components analysis (PCA) the pattern of PCDD/PCDF observed in the Tittabawassee River sediments and floodplain soils were not exactly the same as any of the patterns to which they were compared, but rather were intermediate suggesting several sources, including PCP and other chlorinated compounds such as PCBs**

# Thank You



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