MEMORANDUM

TO: Allan Brouillet, Brenda Brouillet, and Sue Kaelber-Matlock (Michigan DEQ)
FROM: Hector Galbraith (GES)
DATE: February 28, 2005
SUBJECT: Contamination of Tittabawassee River Watershed by dioxins and furans

1. Introduction

As requested, I have completed three work tasks aimed at: 1) summarizing our understanding of the extent to which ecosystem components in the Tittabawassee River are contaminated with polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs); 2) quantifying differences in contamination levels among ecosystem components upriver and downriver of the City of Midland; and 3) Comparing levels of PCDDs, PCDFs and/or TCDD-Equivalent (TCDD-EQ) contamination in the Tittabawassee Watershed with those from contaminated sites elsewhere. Lastly, this memorandum addresses two further issues: the identification of ecosystem components for which contamination data are sparse or non-existent, and additional steps that could be taken to further clarify the implications of the existing data set.

2. The extent to which PCDDs/PCDFs have become incorporated into aquatic and terrestrial ecological communities.

The objective of this task is to summarize the extent to which PCDDs and/or PCDFs in sediments and soils have penetrated and contaminated aquatic and terrestrial ecosystems in the Tittabawassee River and its floodplain. The existing data sets that were used in this analysis include recent Michigan State University biota data, MDEQ sediment, soils, and fish data, DOW Wild Game Study data, and U.S. FWS waterfowl data.

Figure 1 summarizes the available PCDD/PCDF data from the aquatic ecosystem of the Tittabawassee River, downriver of the City of Midland. The data on which Figure 1 is based unambiguously confirm that a number of important ecosystem components are contaminated with PCDD/PCDFs. These include riverbed sediments, and forage, benthivorous, and predatory fish species. Although sample sizes are smaller, the existing data also confirm PCDD/PCDF contamination in surface water, aquatic plants, benthic invertebrates, the emergent forms of the benthic invertebrates, and at least two species of predatory and/or omnivorous birds: hooded merganser and the wood duck. Furthermore, the data also show that all of the major trophic levels of the river system (primary producers, detrivores, herbivores, and predators), have become pervasively contaminated.

The only aquatic ecosystem components that have not been shown to be contaminated are those for which data have not yet been collected (insectivorous birds feeding on emergent insects, piscivorous mammals, and plankton). In contrast, all ecosystem components that have been...
sampled and analyzed have been contaminated with PCDDs/PCDFs. In summary, PCDD/PCDF contamination is not limited to only a minority of elements of the aquatic ecosystem, but is pervasive throughout the system.

Figure 2 summarizes the data that are available from the terrestrial ecosystems on the floodplain of the Tittabawassee River downriver of the City of Midland. These data provide conclusive support for the finding that several important geophysical and ecosystem components have become contaminated with PCDD/PCDFs. These include floodplain soils, herbivorous mammals (deer mice, white-tailed deer, fox squirrels and eastern chipmunks) and birds (wild turkey), and insectivorous mammals (shrews and deer mice). Although sample sizes are smaller, the data in Figure 2 also confirm PCDD/PCDF contamination in terrestrial vegetation, invertebrates, earthworms, and the eggs of domestic fowl penned on the floodplain. The data presented in Figure 2 also confirm that most of the major trophic levels of the floodplain (primary producers, detrivores, herbivores, and insectivores) have become pervasively contaminated.

The only floodplain ecosystem components that have not been shown to be contaminated are those for which data have not yet been collected (predatory and insectivorous birds and mammals). In contrast, all floodplain ecosystem components that have been sampled and analyzed have been contaminated by PCDDs/PCDFs. In summary, PCDD/PCDF contamination is not limited to only a minority of elements of the floodplain ecosystems, but is pervasive throughout the system.
Figure 1. Extent of contamination by PCDDs/PCDFs of aquatic ecosystem in Tittabawassee River downriver of the City of Midland. Green indicates adequate data sets on which to base conclusions regarding levels of contamination; blue indicates that data sets are smaller and that additional samples would be valuable (though the existing data are adequate enough to form conclusions about the presence or absence of contamination); pink indicates that no data as yet exist.
Figure 2. Extent of contamination by PCDDs/PCDFs of terrestrial ecosystems on floodplain of the Tittabawassee River downriver of the City of Midland. Green indicates adequate data sets on which to base conclusions regarding levels of contamination; blue indicates that data sets are smaller and that additional samples would be valuable (though the existing data are adequate enough to form conclusions about the presence or absence of contamination); pink indicates that no data as yet exist.
3. Comparison of PCDD/PCDF contamination levels among ecosystem components upriver and downriver of the City of Midland

In this task, the data sets were examined to determine the extent to which PCDD/PCDF concentrations (converted to TCDD-EQ using WHO avian toxicity equivalence factors [Van den Berg et al., 1998]) in soils, sediment and biota from the Tittabawassee River and its floodplain downriver of Midland compare with the same matrices and taxa from above Midland.

Figure 3 shows that for each of the two matrices and five biological taxa for which comparable data are available, the TCDD-EQ concentrations from downriver of the City of Midland exceed those from upriver by factors of between 56 (insects and sediments) to 277 (forage fish). One-sided two-sample Wilcoxon rank sum statistical tests were performed on these data to determine whether the differences between the upriver and downriver samples were statistically significant. The results are shown in Table 1.

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<th>Table 1. Statistical comparisons of mean TCDD-EQ concentrations (ppt) in biota from above and below the City of Midland.</th>
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<td>Mean TCDD-EQ above Midland</td>
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<tr>
<td>Floodplain Soil</td>
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<td>Sediment</td>
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<td>Forage fish</td>
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<td>Terrestrial insects</td>
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<td>Small mammals</td>
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The p values in Table 1 show that the measured differences between means are highly significant for each of the matrices and taxa. Thus, the mean concentrations in soils, sediments, forage fish, benthos, earthworms, terrestrial insects, and small mammals collected downriver of the City of Midland are significantly higher than those collected upriver of the City of Midland. This has been confirmed to be the case for riverbed sediments in a previous study (Hilscherova et al., 2003). No medium has yet been analyzed for which this result was not the case.
Figure 3. Mean TCDD-EQ concentrations (WHO\textsubscript{avian} tef) in soils, sediments, and biota upriver and downriver of the City of Midland. Note the logarithmic scale on the y axis.
4. Comparison of PCDD/PCDF concentrations in bird eggs from the Tittabawassee River and its floodplain with those from other contaminated sites.

Figure 4. Ranges of TCDD-EQ measured in bird eggs from sites contaminated with PCBs, PCDDs, and/or PCDFs. The leftmost bar in each case is the minimum concentration and the rightmost is the maximum. All TCDD-EQs calculated using WHO $\text{avian}$ tefs. NC=neotropical cormorant; BCNH=black-crowned night-heron; GE=great egret; TS=tree swallow; WD=wood duck; AK=American kestrel; HM=hooded merganser.

Figure 4 shows ranges of TCDD-EQs measured in bird eggs at a number of PCDD/PCDF/PCB contaminated sites in the US and Canada, compared with wood duck and hooded merganser egg concentrations from the Tittabawassee River. These data are not intended to be a thorough review and analysis of all of the bird egg data that are reported in the scientific and/or grey literature, since that would require a considerable effort to obtain and convert the original data (especially older data sets) to TCDD-EQ using WHO $\text{avian}$ tefs. Rather, they are intended to preliminarily express the concentrations measured in wood duck and hooded merganser eggs on the Tittabawassee River in a wider context of contaminated sites.

The data in Figure 4 show that the TCDD-EQ concentrations in wood duck and hooded merganser eggs from the Tittabawassee River are typically higher than concentrations reported in bird eggs from PCDD/PCDF/PCB contaminated sites elsewhere. This is particularly the case for hooded merganser eggs in which the concentration range is generally elevated in comparison to all other species and sites, except for tree swallows breeding at a highly contaminated site (Woonasquatucket River) in Rhode Island. It should also be noted that the sample sizes for the Tittabawassee River wood ducks and hooded mergansers are small (5 and 3, respectively). Consequently, they almost certainly underestimate the actual maxima at the site, and the comparisons shown in Figure 4 under-represent the comparatively high degree of contamination among Tittabawassee River wood ducks and hooded mergansers.
5. Additional data

The existing data sets are more than adequate to show the broad extent of contamination throughout the aquatic and terrestrial ecosystems (Figures 1 and 2), and the resulting risks to wildlife. However, there are gaps in the data set that it would be advantageous (though not essential from the perspective of evaluating risk) to fill. This is particularly the case in the terrestrial ecosystems where it would be helpful to have data on organochlorine concentrations in the eggs of predatory and insectivorous birds nesting on the floodplain.

For the aquatic ecosystems, it would be useful to increase the hooded merganser and wood duck egg sample sizes and to collect egg data from insectivorous birds that depredate emergent aquatic insects (e.g., tree swallows), and piscivorous mammals such as mink.

6. References


