

State of Wisconsin \ DEPARTMENT OF NATURAL RESOURCES

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October 30, 2006

Ms. Jane Patarcity
Beazer East, Inc.
One Oxford Centre, Suite 3000
Pittsburgh, PA 15219-6401

Subject: Supplemental Groundwater Investigation Scope of Work
Koppers Inc., Superior, Wisconsin Facility
BRRTs: 02-16-000484

Dear Ms. Patarcity:

This letter is to provide the Department's comments on the March 31, 2006 document titled, "Approach to Ecological Risk Assessment". For ease of reading we have put references, summaries of the referenced Department documents, and the schematic of the EPA Eight Step Process as attachments to this letter.

Comments on Potential Ecological Receptors

Rationales need to be provided as to why amphibians were not considered as receptors in the ERA approach. Frogs are considered bioindicators of environmental health. Frogs have a complex life-cycle and developmental phases that are particularly sensitive from exposures to contaminants. For example, different species of amphibians show variation in sensitivity to PAHs. PAHs can be extremely toxic to amphibians when the PAHs bioaccumulated in amphibians are simultaneously exposed to the UV component in sunlight.

The frog and toad species that occur in and are considered ecologically significant components of the Lake Superior Watershed are in the following list. The list is taken from "A Review of the Amphibians and Reptiles of the Lake Superior Watershed, Technical Report provided to the Terrestrial Wildlife Community Committee, for the Lake Superior Lakewide Management Plan," submitted by G. Casper, 2002. (<http://www.mpm.edu/collect/vertzo/herp/Casper/casper.html>). The Lake Superior Lake-wide Management Plan (LaMP 2000) has identified reptiles and amphibians as a critical group to be monitored, since they are sensitive to both anthropogenic perturbations and to chemical contaminants.

Anura: Frogs and Toads

Family Bufonidae: True Toads

Eastern American Toad - *Bufo americanus americanus*

Family Hylidae: Treefrogs and Relatives

Western Chorus Frog - *Pseudacris triseriata*

Northern Spring Peeper - *Pseudacris maculata*

Eastern Gray Tree frog - *Pseudacris crucifer crucifer*

Cope's Gray Treefrog - *Hyla versicolor*

Hyla chrysoscelis

Family Ranidae: Typical Frogs

American Bullfrog - *Rana catesbeiana*

Mink Frog - *Rana clamitans melanota*

Wood Frog - *Rana septentrionalis*

Northern Leopard Frog - *Rana sylvatica*

Rana pipiens

Rana palustris

Comments on Assessment and Measurement Endpoints

Page 3 of 6 of AMEC Approach.

Assessment Endpoint 1 – Potential Effects on Benthic Macroinvertebrate Populations

Measurement Endpoint 1 – Use of SQGs for comparison purposes.

The use of U.S. EPA's (2003) Equilibrium Sediment Partitioning Benchmarks (ESBs) approach should also be considered. Also, while it is indicated the Sediment Quality Guidelines (SQGs) will be used as sediment screening benchmarks, based on Attachment 1 below, WDNR uses SQGs both in the screening level step of the ERA and the risk characterization step as lines of evidence to be integrated with the other measurement endpoints (see the Janisch memorandum of December 9, 2004).

Measurement Endpoint 2 – Use of previously conducted site-specific benthic community analysis.

The Department disagrees with the interpretation of the data and metrics applied to the benthic community based on our preliminary assessment and the data interpretation as done by the consultant provided in the report titled, *Off-Property Investigation Data Summary Report for Koppers Inc. Facility* (see Attachment 2 below). For additional information, see the Janisch memorandums of Nov. 2, 2000 Memos (# 1 and 2) and summarized in March 20 2006 comments on the February 2006 *Off-Property Investigation Data Summary Report for Koppers Inc.*

Assessment Endpoint 2 – Potential Effects on Fish Populations from Exposure to COPCs in Surface Water and Sediment.

Measurement Endpoint 1 – Comparisons of surface water concentrations with screening benchmarks such as AWQC.

We request that NR 105, Wis. Admin Code acute and chronic toxicity criteria for the protection of aquatic life that be used in any comparisons. NR 105 does not contain any numerical water quality criteria either for PAHs or dioxins-furans for the protection of aquatic life or wildlife.

Measurement Endpoint 2 – Evaluation of previously conducted site-specific fish community analysis.

As with the macroinvertebrate data collected for the site in 1999, there are differences in interpretation of the fish data collected for the site. See the Janisch Memorandum of November 2, 2000 Memo (#3) and summarized in his March 20 2006 comments on the February 2006 *Off-Property Investigation Data Summary Report for Koppers Inc. Facility* (see Attachment 3 below), there is disagreement on the interpretation of the data and metrics applied to the fish community based on our preliminary assessment and the data interpretation as done by the consultant.

Measurement Endpoint 3 - A 3rd Measurement Endpoint not included in the AMEC approach related to the potential effects to fish from TCDD-EQ bioaccumulated in their tissues that can be added is based on a comparison of the amount of bioaccumulated TCDD-EQ to fish tissue Toxicity Reference Values (TRVs) associated with effects. See the preliminary comparison in Attachment 4 below taken from Janisch's March 20, 2006 comments on the Off Property Investigation Data Report.

Page 4 of 6 of AMEC Approach

Assessment Endpoint 5 - Potential Effects on Aerial Insectivorous Avian Populations (e.g., tree swallow) .Resulting From Consumption of COPC Contaminated Prey (adult flying insects).

Additional information is necessary to evaluate the sensitivity of tree swallows to TCDD-EQ, one of the identified contaminants of concern for the site. Receptors differ in their relative sensitivities to dioxins and furans. Some such as the wood duck are apparently very sensitive (i.e., relatively low TRVs) while others such as tree swallows appear not to be (MDEQ, 2004). The tree swallow may not meet one of the criteria for selecting receptors for use in ecological risk assessments and that is sensitivity to the contaminant of concern. If not sensitive, it cannot be used as a receptor to assess site effects to avian species whose primary route of exposure is from ingesting aquatic insects with body burdens of TCDD-EQs.

The greater degree of tolerance to TCDD-EQ exposure may make the tree swallow useful in monitoring the uptake of environmental contaminants by birds. This may be relevant where contaminants are high enough to prevent breeding or be lethal to sensitive species leaving only the least contaminated individuals to sample. This in turn would lead to an underestimation of the level of contamination and the amount of contaminants being transferred from the aquatic to the terrestrial environment. Use of a more tolerant species such as tree swallows should provide a more representative range of contamination levels present (McCarty and Secord, 1999).

Comments on Figure 1 - Conceptual Site Model for Off-Property Ecological Exposures in Attachment A.

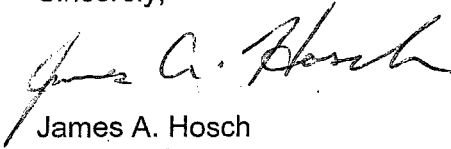
1. The Conceptual Site Model (CSM) is a visual representation of the predicted relationships between ecological entities and the site source -related chemical stressors of concern to which they may be exposed. Under the Primary Source column in Figure 1, there is a box titled "Historical Releases on-Site". The question an outside reviewer or stakeholder would ask is "Historical releases of what?" The box should read "Historical Releases of Wood Treatment Chemicals *" with the specifics given next to the asterisk placed immediately under the Primary Source and Secondary Source flow diagram with an identification of the wood treatment chemicals used, namely a) Pentachlorophenol with its manufactured dioxin/furan by-products, and b) creosote with a fuel oil carrier which contained PAHs. Useful information to be placed on the CSM along with the treatment products used would be the span of years each was used at the facility. We request that this further elaboration on the identification of the contaminants of potential concern be added.
2. It would seem a foot note is needed under the Secondary Source column in the CSM figure that indicates once the contaminant forms enter Drainage Ditch and Crawford Creek from the various Secondary Sources, they migrate or are transported in the system in various forms that may include dissolved, associated with sediment particles, as NAPLs (free product that is immiscible), as various mixtures of residual oils in various stages of weathering and sediments, and/or as sheens on the water surface. The fate and transport of the contaminants will need to be further elaborated on in the risk assessment.
3. It is recognized that as stated in Attachment A that remediation activities are anticipated for the portion of the ditch such that potential ecological risks that may exist under current conditions will be addressed by planned remediation activities. The ditch and its floodplain soils should be portrayed in the CSM figure as if remediation activities have not occurred. As with Crawford Creek, the Outfall 001 Drainage Ditch floodplain should be included under the Exposure Points column in the CSM diagram. It remains to be determined if the Primary Receptors and Secondary Receptors that apply to the Crawford Creek Floodplain Soils also apply to the 001 ditch floodplain soils. While the foot note on the CSM figure indicates the drainage ditch (floodplain not mentioned) was not quantitatively assessed as an aquatic habitat (with the assumption that remediation activities are planned), it would appear all of this needs to be discussed in the problem formulation process for the ERA. Even though it looks like the drainage ditch sediments, bank soils and floodplain soils will be remediated, the anticipated remediation has to be put into some context as to the type of habitats being remediated, what assessment endpoints will drive the remediation, the extent of the ditch bottom, banks, and floodplain soils that will be remediated, and what will be the cleanup goals of the remediation. Will the cleanup goals be performance-based standards or numerical cleanup goals based on certain site-related contaminants of concern? The drainage ditch and its associated floodplains have to be carried through the ERA process to answer these questions.
4. In the Figure 1 of the CSM, one of the Exposure Points is the Crawford Creek Floodplain Soils with one of the Primary Receptors being Adult Flying Insects and the Secondary Receptors being the aerial insectivores. The Exposure Point missing from the Figure 1 is that which involves the Crawford Creek and Drainage Ditch sediments and the Primary Receptor Group of the adult flying forms of insects that spend the early portions

of their life cycles in bottom sediments of surface waters, such as the larvae of midge flies. The Secondary Receptors for this group of emerged adult flying insects would also be aerial insectivorous birds and mammals.

5. We are more familiar with the sediment-related source of flying insects such as tree swallows consuming a predominantly aquatic-based diet than a floodplain soil source. We are not aware of an ERA that has used the latter source as a Primary Receptor group in a CSM. More elaboration will need to be provided on ERAs where floodplain source adult flying insects have been used in a risk assessment, the species of insects involved, the life cycle form that is contact and exposed to COPCs in the soils, and the seasonal timing of hatches and emergence of the insects involved. See Janisch's March 20, 2006 comments on the February 2006 Off-Property Investigation Data Summary Report for Koppers Inc. Facility (see extracted comments below in Attachment 1).

Thank you for opportunity to review the Supplemental Groundwater Investigation Scope of Work. If you have any further questions, please feel free to call me at (715)-392-0802.

Sincerely,



James A. Hosch
Hydrogeologist

cc:

John Robinson – Rhinelander
Mark Gordon – RR/3
Jeff Holden- BBL
Henry Nehls-Lowe - DHFS
Bob Egan - EPA Region 5

References in Letter

David, L. 2003. Development of a Herptile Monitoring Program for the Lake Superior Basin Results of a workshop held in Association with the 17th Annual Meeting of the Society for Conservation Biology. Duluth, Minnesota. June 30, 2003. Compiled by Lisa David October 2003.

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MDEQ (Michigan Dept. of Environ. Quality) Letter to Dow Chemical Co. Midland, MI. Feb. 4, 2004. Attachment A. Review Comments of Dr. Hector Galbraith of Galbraith Environmental Sciences on comments Dow Chemical Company submitted on December 19, 2003, relative to the Tittabawassee River Aquatic Ecological Risk Assessment contracted by the MDEQ. <http://www.deq.state.mi.us/documents/deq-whm-hwrp-further2.pdf>.

USEPA. 2003. Procedures for the derivation of Equilibrium Partitioning Benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA-600-R-02-013.

| ECOLOGICAL RISK ASSESSMENT (ERA) PROCESS IN SUPERFUND and WDNR Schematic Diagram of the Superfund Eight-Step ERA Process | | |
|---|---|--|
| Compile Existing Information | Step 1: Screening Level Risk Assessment <ul style="list-style-type: none"> - Site Visit - Problem Formulation - Develop Conceptual Site Model - Toxicity Evaluation (Use of SQGs⁺) | Risk Manager; Risk Assessor' Stakeholder Agreement |
| | Step 2: Screening Level <ul style="list-style-type: none"> - Exposure Estimates (Use of SQGs⁺) - Preliminary Risk Calculation based on conservative plausible assumptions | SMDP * |
| Data Collection | Step 3: Baseline Risk Assessment <ul style="list-style-type: none"> - Problem Formulation – Refine Conceptual Site Model - Identify Receptors of Concern - Literature Search, Toxicity Evaluation - Identify Assessment Endpoints | SMDP |
| | Step 4: Study Design and DQO Process <ul style="list-style-type: none"> - Establish Measurement Endpoints to be used as Lines of Evidence (Use of SQGs⁺) - Study Designs, Sampling and Analysis Plan | SMDP |
| | Step 5: Field Verification of Sampling Design | SMDP |
| | Step 6: Site Investigation and Data Analysis <ul style="list-style-type: none"> - Analysis of Exposures and Effects | SMDP |
| | Step 7: Risk Characterization and Estimation <ul style="list-style-type: none"> - Integration of Measurement Endpoints as multiple lines of evidence (Includes SQGs⁺) to Characterize Risk and Establish Threshold Effect levels | SMDP |
| | Step 8: Risk Management <ul style="list-style-type: none"> - Risk Assessors Convey Results of Risk Characterization to Risk Managers and Stakeholders for Use In Making Sediment Management Decisions. Incorporated Into Feasibility Study to be considered with other factors to select remedial remedy | SMDP |
| | <ul style="list-style-type: none"> * SMDP - Scientific Management Decision Point + SQGs includes WDNR CBSQGs and EPA ESB <p style="text-align: center;"> Benchmark Values for PAH Mixtures </p> | |

ATTACHMENT 1

Extracted from the Following Correspondence/Memo:

DATE: March 20, 2006

TO: Jim Hosch – NOR/Superior

FROM: Tom Janisch – RR/3

SUBJECT: Review and Comments on the February 2006 *Off-Property Investigation Data Summary Report for Koppers Inc. Facility, Superior, Wisconsin*

Section 2.19. Page 2-10. 2005 Adult Flying Insect Sampling

Aquatic insects who have spent the larval, pupa, nymph, and immature portions of their life cycle in or near metal or organic chemical contaminated sediments and water may externally adsorb or internally assimilate the contaminants. With the exception of some portion of the contaminants shed with larval or pupal exuviae (external skin), body burdens of metals are retained following emergence to the adult flying stage from the immature form (Larsson, 1984). In this fashion, the contaminants may be passed on and be present in the emerged adult insect life form and as such, may serve as a link for the food chain transfer of the contaminants to organisms in higher trophic levels in the aquatic and nearby terrestrial ecosystems (Steingraber et al. 1995; Hare et al. 1991; Currie et al. 1997). For example, flying adults of the Dipteran (Chironomidae) family emerge from the sediments through the water column and become a significant portion of the diets of bats, swallows (Custer et al. 2004), redwing blackbirds, terns, and amphibians. Small mammals and some ducks and most ducklings also may ingest contaminated insects that have been associated with contaminated sediments. The diet of laying female dabbling ducks like mallards and blue-winged teal in the spring will consist primarily of insects and other invertebrates to satisfy protein demand related to egg production. The ducklings of all species consume a diet dominated by invertebrates during early stages of development. Many species of birds time their breeding cycles to take advantage of the seasonally abundant supply of emerging insects (Fairchild et al. 1992) with their protein content. Some omnivorous bottom-feeding forage fish feeding directly on contaminated invertebrates and in contact and consuming contaminated sediment particles as part of sifting and feeding, can have higher tissue concentrations than piscivorous fish (Hodson et al. 1984).

Table 8 below summarizes the results of insect light trapping along floodplain areas of the Creek. TCDD-EQ concentrations ranged from 0.93 to 3.7 pg TCDD-EQ / g tissue and from 27.5 to 221.56 pg TCDD / g lipid from the study sites, and 0.75 and 40.9, respectively at the reference site. As a preliminary toxicity benchmark, Eisler (2000) indicates that the concentration of TCDD in an avian diet that is considered safe is 10 to 12 pg/g wet weight (assume this can be applied as TCDD-EQ). If 100% of a nestling or duckling diet was insects from the Crawford Creek areas would mean the TCDD-EQ concentrations in the insects at 0.93 to 3.7 are less than the 10 pg TCDD-EQ threshold value. This will need to be more thoroughly explored in the risk assessment.

A number of things need to be considered in using the Table 8 data in the risk assessment:

- The optimum time for the insect collections would have been in the May-June time period at the time of, for example, the midge hatch. Chironomidae larvae are the dominant invertebrate in the sediments of Crawford Creek. As indicated above, species of birds time their breeding cycles to take advantage of the seasonally abundant supply of emerging insects with their protein content. Mid-July is past the optimum breeding and nesting time for birds and most likely past the time of the peak emergence of midge flies from the larvae stage associated with the Creek bottom. BB&L indicate in their Feb. 10, 2005 letter responding to the WDNR comments on their sampling plan that they recognize the May/June timeframe should be ideal for sampling of adult flying insects but yet they sampled in Mid-July. By mid-July, the sensitive, early life nestling stages of most of the avian species will no longer be present.
- BB&L also indicates in their Feb. 10, 2005 response letter that they can separate aquatic from terrestrial insects during collection and weigh each group separately. This would have given an idea of the proportion of insects that were aquatic and emerging from the larvae in the sediments and those that were from terrestrial sources. The former would likely have higher bioaccumulated amounts of TCDD-EQ in their

tissues. However, the 2006 Report while it indicates the collected samples were dominated by terrestrial species (moths and beetles), with some aquatic insects (caddisflies and midges), there is no indication that the insects were separated and weighed separately to get an idea of the proportions that each type contributed. It is noted that BB&L identified that there were some caddisflies in the 2006 light traps. However, caddisfly larvae were only found in very minimal numbers in two replicate samples at one downstream location in the 1999 Hester-Dendy samples. What proportion of the aquatic insects in the 2006 light traps was caddisflies?

- Based on Figure 3 of the 2006 Report, it appears the light traps were located approximately 100 ft. from the Creek. FLY-4 next to the drainage ditch may have been closer than this. Assuming that 1) emerging aquatic insects would be carrying the highest body burdens of accumulated TCDDs because all species involved would have spent all of their early life stages in contact with and ingesting TCDD-contaminated sediments, and 2) nesting birds are timing their breeding cycles to take advantage of the aquatic insect emergence, the light traps should have been set up closer to the depositional areas of the Creek and placement timing during the period of maximum aquatic insect emergence in May-June. BB&L will need to elaborate on their rationales for light trap placement and mid-July timing of placement in their ecorisk assessment. They will need to elaborate through what routes the early life stages of terrestrial insects (beetles and moths) are being exposed to and accumulating TCDDs from matrices in the terrestrial floodplain habitats. Floodplain soil contaminant uptakes would normally be dealt by looking at uptake by earthworms and receptors that ingest earthworms (vermivorous receptors) as part of their diets (e.g., exposure to American robins). What was the difference between TCDD concentrations in the floodplain soils and Creek reaches in the areas of the light traps?

| Table 8. Results of the 2005 Analysis of Adult Flying Insect Samples ¹ from Crawford Creek Floodplain Areas for 2,3,7,8-TCDD-EQ | | | | |
|--|-------|-------|--------|-------|
| pg TCDD-EQ / g Insect Biomass | | | | |
| FLY-REFERENCE | FLY-4 | FLY-3 | FLY-2 | FLY-1 |
| 0.75 | 1.3 | 1.1 | 3.7 | 0.93 |
| % Lipids | | | | |
| 1.83 | 1.02 | 0.89 | 1.67 | 3.38 |
| Lipid Normalized pg TCDD-EQ / g Lipid in Insect Biomass | | | | |
| 40.9 | 127.5 | 123.3 | 221.56 | 27.5 |
| 1. Flying insects captured by light traps in Mid-July 2005 from floodplain locations approximately 100 ft. from Creek | | | | |

References

Custer, C.M., T.W. Custer, C.J. Rosiu, M.J. Melancon, J.W. Bickham, and C.W. Matson. 2004. Exposure and effects of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in tree swallows (*Tachycineta bicolor*) nesting along the Woonasquatucket River, Rhode Island, USA. *Environ. Toxic. Chem.* 24:93-109.

Currie, R.S., W.L. Fairchild, and D.C.G. Muir. 1997. Remobilization and export of cadmium from lake sediments by emerging insects. *Environ. Toxicol. Chem.* 16:2333-2338.

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ATTACHMENT 2

Extracted from the Following Correspondence/Memo:

DATE: March 20, 2006

TO: Jim Hosch – NOR/Superior

FROM: Tom Janisch – RR/3

SUBJECT: Review and Comments on the February 2006 *Off-Property Investigation Data Summary Report for Koppers Inc. Facility, Superior, Wisconsin*

Section 3.5.1. Page 3-9. 1999 Benthic Macroinvertebrate Survey.

The macroinvertebrate study conducted in Crawford Creek as part of the BB&L 1999 investigations is discussed in the 2006 Report. Macroinvertebrates were collected from three locations in the Creek and an upstream reference site. It is stated in the Report that:

“The benthic metrics for the dredge samples and sweepnet samples are different among upstream (reference) survey locations and downstream locations; however, the differences in the macroinvertebrate community are not considered significant and are likely related to differences in habitat. The differences in the communities do not parallel the sediment PAH concentrations and are not believed to be a result of Site-related impacts.”

I reviewed and commented on the 1999 macroinvertebrate study in two Nov. 2, 2000 memos (Memo #1 and Memo #2). Opposed to the above statements, my review and interpretation of the macroinvertebrate data showed that the benthic communities at downstream sites 1 and 2 were severely impacted and the community at site 3 was moderately to severely impacted. Site 3 was below the railroad embankment. The benthic community at the reference site was judged to be nonimpaired using standard bioassessment protocols. The 1999 benthic data needs to be revisited and reviewed as to the metrics used in the evaluation.

As to the point in the statement above that the differences in the communities do not parallel the sediment PAH concentrations, there is no basis for this statement. Sediment samples for chemical analysis were not taken at the same locations as the macroinvertebrate samples during the 1999 investigation. Based on the discussion in my Nov. 2, 2000 Memo # 1, sediment samples for chemical analysis were taken from 80 to 100 ft. upstream and 150 to 690 ft. downstream from the benthic macroinvertebrate sample locations. On this basis, no associations can be made between the benthic community metrics and the chemical concentrations in sediments. See my Nov. 2, 2000 memos for more discussion of the issues. A summary of the Crawford Creek benthic community data evaluated using the EPA Rapid Bioassessment method for biological condition scoring and impairment condition identification is in the table below.

| Analyzing the 1999 Crawford Creek Benthic Community Data Using EPA Rapid Bioassessment Method | | | | |
|---|----------------|------------|------------|--------------------|
| Based on 10 Metrics | Reference Site | Location 1 | Location 2 | Location 3 |
| Total Score | 48 | 6 | 10 | 14 |
| Biological Condition | Nonimpaired | Severe | Severe | Moderate to Severe |

ATTACHMENT 3

Extracted from the Following Correspondence/Memo:

DATE: March 20, 2006

TO: Jim Hosch – NOR/Superior

FROM: Tom Janisch – RR/3

SUBJECT: Review and Comments on the February 2006 *Off-Property Investigation Data Summary Report for Koppers Inc. Facility, Superior, Wisconsin*

Section 3.5.2. Page 3-10. 1999 Fish Survey

Fish surveys by electrofishing along 100 ft. sections of the Creek at two upstream and three downstream locations were conducted in 1999. While not stated in the 2006 Report, the 1999 BB&L Report states that the differences in the fish communities between the reference locations and the downstream study locations are not significant, and are likely attributable to differences in habitat and not as a result of site-related impacts.

I reviewed and commented on the 1999 fish survey in two Nov. 2, 2000 memos (Memo #2 and Memo #3). As opposed to the above statement, my review and interpretation of the of the fish survey data showed that the great loss of species, numbers, and lower IBI (Index of Biological Integrity) scores downstream sites points conclusively that they are impacted. The IBI is a standard assessment tool used by Fish and Habitat Management to measure environmental quality in warmwater streams. A summary of the use of the IBI tool on the 1999 Crawford Creek samples is in the following table (see Nov. 2, 1999 Memo #3 for more details).

| Application of the Index of Biological Integrity (IBI) to the 1999 Crawford Creek Fish Survey Data | | | | |
|--|--|--|---|---|
| | Fish Survey Locations | | | |
| | Reference Site # 2 500 ft. Upstream of Outfall Ditch 001 Drainage Ditch | Location # 1 200 ft. Downstream of 001 Ditch | Location # 2 Vicinity of Crawford Creek Pond | Location # 3 300 ft. Downstream of Railroad Embankment |
| IBI Rating | 52 | 44 | 17 | 20 |
| Biotic Integrity Rating | Good | Fair | Very Poor | Poor |

ATTACHMENT 4

Extracted from the Following Correspondence/Memo:

DATE: March 20, 2006

TO: Jim Hosch – NOR/Superior

FROM: Tom Janisch – RR/3

SUBJECT: Review and Comments on the February 2006 *Off-Property Investigation Data Summary Report for Koppers Inc. Facility, Superior, Wisconsin*

Section 2.7. Page 2-9. 2005 Sampling and Analysis of Fish Tissue for 2,3,7,8-TCDD Equivalents

In July 2005, BB&L collected forage fish from 6 impacted locations along Crawford Creek and an upstream reference site location. Whole body composites of the fish from each location were analyzed for dioxins/furans and PAHs. For a preliminary look, the dioxin/furan results are summarized in Table 4 below based on Table 8 in the 2006 Report. The concentrations in Table 4 are expressed on a pg TCDD-EQ / g whole body basis and on a lipid normalized basis. The lipid normalized concentrations from the impacted reaches of the Creek ranged from 35.9 to 93.2 pg TCDD-EQ / g lipid compared to 5.5 at the reference site. The upstream concentrations of TCDD-EQ in the fish from the upstream reaches of the Creek were somewhat greater than those on the downstream reaches (76.8 vs. 61.7).

To get a preliminary idea of the significance of the tissue levels of TCDD-EQ in the Crawford Creek fish, Table 5 below presents some tissue residue-based toxicity benchmarks that have been derived from the results of individual studies selected from the literature (Steevens et al. 2005). The benchmarks are established as distributions rather than single point estimates. Benchmark distributions allow the selection of a tissue concentration that is associated with the protection of a specific percentage of organisms, rather than linked to a specific receptor. The endpoint used to develop the toxicity benchmarks in Table 5 was egg and embryo development. Maternal TCDD uptake and transfer to eggs was deemed the most ecologically relevant exposure pathway. The effect residues of TCDD and dioxin-like compounds in fish eggs can be readily related to maternal tissue concentrations after lipid normalization. For nonpolar organic compounds, the ratio of chemical on a lipid-normalized basis is found to be approximately 1:1 egg to adult fish (Steevens et al. 2005). In other words, the same lipid normalized TCDD concentrations found in adult female fish will be passed on to their eggs and embryos. This allows the lipid-normalized TCDD concentrations in the Crawford Creek fish to be compared with the toxicity benchmarks in Table 5 in order to gauge what the toxicity will be to their eggs and embryos.

A comparison of the lipid-normalized TCDD concentrations in Crawford Creek fish of 35.9 to 93.2 pg TCDD-EQ / g lipid with the mean toxicity benchmark concentrations in Table 5 indicates the levels are associated with protection of 97.5 – 99% of the forage fish species. If lower confidence level benchmark values are used, protection would be at or slightly lower than 90% for the LR50 values. One assumption in doing the comparison is that the toxicity benchmarks in Table 5 derived largely from larger game fish species are applicable to the smaller forage fish species sampled in Crawford Creek.

As expected the LMW PAHs were found in the highest proportions accumulated in the fish tissues compared to the HMW PAHs, with approximately 78% of the total being contributed from LMW PAHs at the two sites with the greatest accumulations (9.97 and 25.56 mg/kg). The BaP-TE concentrations in the study site forage fish ranged from 0.10 to 0.26 mg/kg. Mixtures of the seven polynuclear aromatic hydrocarbons (PAHs) that are classed as probable human carcinogens can be preliminarily assessed based on a screening value concentration of 0.015 mg/kg calculated as a sum potency equivalency concentration (PEC) using methods described in EPA's Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories, Vol. 1, (EPA 823-R-95-007) and Vol. 2 (EPA 823 B-00-008 (<http://www.deq.state.va.us/fishtissue/documents/fishsedeval.pdf>)). Humans will not be consuming forage fish from the Creek so the 0.015 mg BaP-TE/kg is not immediately applicable to these fish. It would be applicable to the higher trophic level game fish that consume the forage fish. The question that needs to be addressed in the HHRA is what part of the diet of game fish in the Nemadji River consists of forage fish from the

Creek, what portion of the fishers diet is made up of these game fish, and importantly, how much of the BaP-TE concentration in the forage fish is transferred to the game fish?

Other assessment endpoints that need to be looked at in the ecological risk assessment is biomagnifications of the TCDDs up the food chain through consumption by higher trophic level fish species in the Nemadji River (forage fish leaving the Creek and moving into the River), and by avian and mammalian receptors consuming the forage fish from the Creek.

It appears the goal of the fish sampling was to obtain an adequate amount of tissue mass (40 to 70 fish / location) at each of the 7 locations for analysis purposes. It doesn't appear the number and type of each fish species were recorded. If so, additional information would have been available to assess possible impacts from contamination in the Creek to the fish populations in each sampling reach as was done in 1999. See comment below in regard to interpreting the 1999 fish sampling results. However, the sampling designs may have needed to be different from those used in 2005.

References

Steevens, J.A., M.B. Reiss, and A. V. Pawlisz. 2005. A methodology for deriving tissue residue benchmarks for aquatic biota: A case study for fish exposed to 2,3,7,8-tetrachlorodibenzo-p-dioxin and equivalents. *Integrated Environmental Assessment and Management*. 1(2):142-151.

| Table 4. Results of Analysis of 2005 Fish Sampling in Crawford Creek for 2,3,7,8-TCDD-EQ | | | | | | |
|---|--|--------------|--------------|--|--------------|--------------|
| pg TCDD-EQ / g Fish Tissue | | | | | | |
| | Upstream of Railroad Embankment | | | Downstream of Railroad Embankment | | |
| Reference | FS-R6 | FS-R5 | FS-R4 | FS-R3 | FS-R2 | FS-R1 |
| 0.34 | 2.0 | 1.5 | 1.3 | 0.89 | 0.48 | 0.56 |
| % Lipids | | | | | | |
| 6.16 | 3.14 | 1.61 | 1.77 | 1.16 | 1.38 | 1.56 |
| Lipid Normalized pg TCDD-EQ / g Lipid in Fish | | | | | | |
| 5.52 | 63.7 | 93.2 | 73.5 | 76.7 | 72.5 | 35.9 |
| | Mean | 76.8 | | Mean | 61.7 | |
| | Std. Dev. | 15.0 | | Std. Dev. | 22.4 | |