

DATE: March 20, 2006

FILE REF:

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***General Comments**

In Table 1 below, I list most of the memos I have put together in the past that reviewed the past investigation reports and issues that are involved in the present data compilation. I may be missing some of my earlier memos to Cynde English when she was the project manager in the mid-1990's. These memos generally involved on-site groundwater well monitoring and dioxin/furan results and did not involve off-site data.

Specific comments**Risk-Based Cleanup Levels for 2,3,7,8 –Substituted Dioxins and Furans In Sediments and Floodplain Soils**

I note in several places in the Data Summary Report (e.g., page iii Executive Summary and on pages 3-7, 3-9, and 4-3), where dioxin/furan results are being discussed, BB&L enters into the discussion for comparison purposes the USEPA (1998) "allowable" residential soil concentrations for 2,3,7,8-TCDD of 1 ug/kg (assumed to be 1,000 pg TCDD-EQ/ g). Your January 22, 2004 letter to Beazer East, Inc. that was copied to BB&L clearly explained the process that is to be followed for deriving risk-based cleanup goals for dioxins in soils based on NR 720. Your letter also discussed the derivation of the EPA 1 ug/kg value and its inapplicability to the Koppers site. I discussed the issue in a November 21, 2003 comment memo to you. The cancer risk levels and associated soil concentrations in pg TCDD-EQ / kg are shown below from those comments. The soil concentration of 0.4 pg TCDD-EQ / g at a cancer risk level 1.0×10^{-7} would result using Wisconsin default assumptions in NR 720. The cancer oral slope factor of 156,000 mg/kg-day was used in the calculations. Revision of the slope factor (USEPA, 2000) to 100,000 mg/kg-day would lower the soil concentrations associated with the risk levels below.

Generic Cleanup Levels for Residential Soils Based On a Range of Cancer Risk Levels	
Lifetime Cancer Risks	pg TCDD-EQ / kg
2.5 x E-04	1,000 ^{1.}
1.0 x E-04	400
2.5 x E-05	100
1.0 x E-05	40
2.5 x E-06	10
1.0 x E-06	4
1.0 x E-07	0.4 ^{2.}

1. EPA's indicates that the cleanup level in residential soils of 1,000 pg TCDD-EQ / g is based on presently available information and using standard default assumptions for reasonable maximum exposure scenarios and is associated with a cancer risk level of 2.5 x E-04. Concentrations associated with lower cancer risk levels derived from this concentration/risk level relationship are shown in the above table.

2. Calculated by R. Pelayo, RR/3 using NR 720 default assumptions for human ingestion pathway in residential setting for Residual Contaminant Level (RCL). Target Cancer Risk Level of 1.0 x E-07; S_{Fo} = 150,000 mg/kg-d (Heast, 1995).

Given the practical application of any target risk levels to the specific residential and recreational uses on a site specific basis, some thoughts on appropriate target risk levels and associated TCDD-EQ concentrations related to human health risks are in the following table from my Nov. 21, 2003 memo. Addressing ecological risks as it applies to mammals and birds may result in lower concentrations than some of the human site-use related cleanup goals discussed below to be more protective of ecological endpoints.

Target Risk Level	Cleanup Goal pg TCDD-EQ/g	Recommended Appropriate Application of Target Cleanup Goals and Target Risk Levels for Human Exposure to Floodplain Soils
1.0 x E-07	0.4	Has more intensive use by humans especially children in areas like playgrounds. Would not be applicable to any creek or ditch contaminated area on the site.
1.0 x E-06	4	May have occasional seasonal use by humans especially children during normal outdoor play activities. Would be applicable to that section of the drainage ditch behind the homes on Hammond Avenue.
2.5 x E-05	100	May have some or limited use by humans during seasonal times of the year. Would apply to contaminated ditch channel and flat floodplain areas and all areas of the creek between the juncture with the ditch and downstream to the Creek's juncture with the Nemadji River.

My November 21, 2003 memo also discusses other possible toxicity benchmarks for TCDD-EQ for ecological receptors in different matrixes that could be used as screening values and as for lines of evidence to be integrated higher in the risk assessment process for characterizing risks to the selected site receptors of concern. This includes the WDNR CBSQGs and sediment and fish benchmark toxicity values from EPA. However, the selected site receptors, assessment and measurement endpoints, and toxicity benchmark and threshold value are something to be more thoroughly discussed in the first steps of the screening level ecorisk assessment with our input at the appropriate scientific management decision points. For the data review, it is questionable to be using an inappropriate EPA benchmark residential soil number for comparison purposes. Given your January 22, 2004 letter mentioned above, I don't know why the value is being used.

To put the 1,000 pg TCDD-EQ/g residential soil value into perspective, Wisconsin's landspreading program for paper mill sludge sets the following limitations based on land uses and concerns for bioaccumulation in the food chain: Silviculture – 10 pg TCDD-EQ/g; Agriculture – 1.2 pg TCDD-EQ/g; and Agriculture with grazing – 0.5 pg TCDD-EQ/g. The threshold and probable effect concentrations for 2,3,7,8-TCDD-EQ in the WDNR CBSQGs are 0.85 and 21.5, respectively.

Crawford Creek Pond Area Characterization

None of the map figures in the 2005 Data Summary Report contain an outline denoting the Crawford Creek Pond area allocation as a distinct body of water connected to the Creek except the Figure 1 topographic map appears to show the Pond outline. Maps in earlier reports had the Crawford Creek Pond area located and named. In my visits to the site in the 1990's, the Pond was always present with standing open water present. In one of my last visits to the site in 1999, it appeared downstream obstructions to flow may have been removed and water was confined to the Crawford Creek channel in the areas above the railroad grade. This resulted in the Pond area having the water table just at or below the ground surface. Under these conditions, the entire pond area could be walked and as such in 1999, I did some augering and dug shovel pits in a number of locations across the pond bottom. Under more freely flowing conditions in the main channel, standing water of any depth in the Pond area probably occurs only under heavy precipitation and runoff events.

Table 2 below summarizes the observations and sampling results that have been made by various entities over time involving the Crawford Creek Pond area. I've always wondered if the whole pond and floodplain area in the lower portion and along the north side of the Creek, 800 to 1,000 ft. upstream of the railroad grade have been adequately characterized. What always prompted my curiosity especially of the Pond area were the results of the 1992 LaValley sediment samples, which I'm assuming were surface samples, that had TPAH results of 5,338 and 11,336 mg/kg. The Fluor Daniel results of a sample in the middle of the Pond (SD-12) had TPAHs of 54 mg/kg in the surface and 5,800 mg/kg in the subsurface, with the results being minimal values due to very high reported detection levels for a number of PAHs (see my April 21, 1997 memo). It can be surmised that in the past when heavy creosote product loadings were being released from the site and transported down the Creek, with flows being backed up at the railroad grade, the non-aqueous phase creosote spread out/overflowed over the adjacent floodplain or backed up the channel from the Creek into the Pond area and was deposited. Similar overflows and creosote depositions likely occurred over the drainage ditch floodplain at and upstream of the ditch juncture with the Creek. The floodplain test pit observations in 2003 had one transect that went across some of the Pond bottom (CCTP-N3-1 to N3-4). Test pits N3-2 and N3-3 had a black stained layer at shallow depths (0.5 to 1.5 ft.) and isolated seams of creosote at lower depths and in cases, 12 ft. below the ground surface.

Not adequately characterizing degree and extent of creosote-related contamination along the lower floodplain portions of the creek, especially in and around the Pond area, could result in an underestimation of the soil and sediment volumes that are contaminated. This could have implications for any removal planning and outcomes should the risk and remediation management decisions result in the selection of removal as an alternative. One question that will need to be addressed in addressing the risk management questions for the site is what to do if large areas of shallow substrata contain creosote residuals that are capped by clean clay deposits.

Association of Creosote-Contaminated Floodplain Soils and Channel Sediments

The *Off-Property Investigation Data Summary Report* describes the creosote-related contamination in the surface and subsurface of the soils and sediments separately but does not link the two. As I note in my Nov. 2, 2000 memo where I discuss my observations at the site during 8/18/99, there likely is a connection between the two for the lower reaches of Crawford Creek above the railroad grade (see Table 2 below for some of my 8/18/99 observations at the juncture of the channel from Crawford Creek

Pond to Crawford Creek. While not observed, it is possible the same connection between the creosote observed in the substrata of the floodplain soils of the drainage ditch and those observed in the ditch banks/sediments is similar. During the 8/18/99 visit, water levels in the Creek were low enough to allow the observation. I rod probed, augered and dug shovel pits in the sediments and floodplain soils along a stretch of Creek from the BB&L 1999 Transect 31 downstream to just above Transect 34 or a distance of approximately 800 ft. along the Creek. I observed at some distance above the water level in the Creek (varied from approximately 2 to 6 in.) in the vertical bank face, black creosote related materials in a distinct strata. Above these materials for various thickness (6 to 10 in.) in surface strata were what appeared to be uncontaminated clays that were deposited after the creosote loading to the Creek had ceased years earlier. I did not determine how far the thickness of the black creosote-related strata extended below the water line.

Shovel pits dug in the floodplain soils at various distances from the bank water line showed the creosote-related substrata to be present. This indicates there is likely a direct connection between the creosote-related strata visible in the vertical bank face and the creosote contaminated substrata in the floodplain soils that extends back from the Creek at varying distances. Disturbance of the creosote substrata in the bank face at and below the water line resulted in heavy sheening on the water surface of the Creek. The creosote-substrata in the bank face was most noticeable on the north side of the channel. The above situation was especially noticeable in the Creek channel at its juncture with the channel coming from the Crawford Creek Pond. I have pictures taken during the 8/18/99 survey. It would have been interesting if they would have also collected soil samples from segments below 6 inches for analysis at the time they were collecting their surface composites along the floodplain in 2005 (e.g., Soil-T6) to determine if the buried creosote residuals were present and in how many of the 22 areas sampled this occurred. It probably could be assumed in most cases that there would be a connection to creosotes buried in the floodplains near the river and the same layer of buried creosote being present along the Creek bank.

Degree and Extent of Creosote-Related Contamination In Crawford Creek Sediments Downstream of Railroad Embankment

The conclusions in *Off-Property Investigation Data Summary Report* states that 1) creosote-like product has not been observed in Crawford Creek sediments downstream of the railroad embankment, and 2) odor, staining, and or sheens were observed intermittently in Crawford Creek sediment downstream of the railroad embankment. Generally, point number 1 appears to be correct, as I have not observed non-aqueous phase liquid creosote product in sediments below the railroad embankment. From Figures 7 and 4-3C in the Report, it would appear the creosote contamination in the form of odor/stains/sheens is not intermittent for first the 800 ft. of the approximately 1,500 ft. of Creek involved but more continuous based on the information available. In the probing and shovel coring I did in this lower reach on 8/18/99 (see the Nov. 2, 200 memo) and 9/94 (see the 6/25/96 memo), creosote stained sediments were encountered in the lower 600 ft. of the Creek above its juncture with the Nemadji River. This includes probing upstream of the mouth between 1999 Transects 50 and 51 which we reached by boat in 1999. As noted in 1994, in the lower portion of the Creek, the creosote residuals seemed to be more integrated into the more consolidated bottom clay substrates than they were into the more unconsolidated surface clays. Given the information available, I would have a tendency to describe the creosote-related contamination in the lower portion of the Creek above its juncture with the Nemadji River as also being somewhat continuous.

Visual Observations / Descriptions

In Section 3.3.1 Visual Observations in the 2006 BB&L Report, the visual observations for 1996, 1999, 2003, and 2005 for sediment conditions were placed into three categories:

- 1) oily, creosote-like product observed in sediment matrix;
- 2) odor, staining, and/or oil sheen (but no creosote-like product was observed); or

3) no odor, staining, oil sheen, or creosote-like compound was observed.

In 1999, it appears for category 1 above, the visual observation used was "oily nonaqueous phase liquid (NAPL) was observed". The descriptions between the two reports appear different. The 2006 description appears to be describing an unweathered to somewhat weathered creosote mixed in various degrees with sedimentary material, whereas the 1999 description appears to be describing a largely unweathered creosote oil product present as NAPL with no or little sediment mixed in. Are the descriptions used between 1999 and 2006 different or are they intended to describe the same material? This is important because in 1999 the visual characterization of sediments as NAPL was used as an indicator of total PAH concentrations. The visual characterization of sediment and floodplain soils was found to be a relatively reliable indicator of total PAH concentrations (Section 4.6, 2000 BB&L Report). Does the visual and concentration relationships still hold if the 2006 category descriptor is used?

For the category 2 description above which is "odor, staining, and/or oil sheen (but no creosote-like product observed)", it seems more appropriate to say rather than no creosote-like product observed, to state "various amounts of creosote residual observed" to recognize that the staining that could vary from black to grayish black to gray due to the weathering state of the creosote and admixture with various portions of sedimentary material.

For the above category 1 descriptor above of "creosote-like product", isn't it assumed that creosote product is involved? Why the "creosote-like" descriptor? It is noted that a #6 fuel oil carrier for the creosote was used apparently since the facility began operation in 1928 and a petroleum carrier was used in the period of 1955 to 1979 when the wood was treated with penta. Wouldn't the descriptor "odor, staining, and or oil sheen (various amounts of creosote and petroleum oil residuals" be more appropriate for this descriptor category? Some of the earlier study DRO readings may have indicated the relatively high contributions of petroleum oil residuals to some of the sediment samples. I don't know what DRO results would be if only creosote residuals alone were present.

A locational description that is specific to bank and floodplain soils is the "isolated non-continuous seams of creosote-like product observed in isolated cracks/fractures of the clay soil matrix." This situation was apparently not found in the sediment substrates. Apparently the creosote and/or fuel oil as NAPL has migrated from the surface and through fractures into the subsurface to result in oil globules filling spaces or small cracks. Interestingly, based on Figure 1a of the 2006 Report at site NO3-4 associated with Crawford Creek Pond, the noncontinuous isolated seams of NAPL are found to a depth of 6 ft. below the surface and 245 ft. from the Creek channel. Did these materials move laterally through the soils from the Creek or were they deposited on top of the soils and migrated vertically? The inset photo on the right in Figure 4 of the 2006 Reports is titled "Representative of zones of non-continuous isolated seams of creosote-like product observed in discrete fracture of the clay matrix". The center of the photo does seem to show some creosote accumulated in an opening or fracture within the clay soils. At and below this fracture in the soil profile in the picture appear to be the seams of creosote residual in different layering as identified by the different coloring. Are these the non-continuous isolated seams that are being referenced above? There seems to be two properties involved that need to be distinguished. It appears they could be observed together or separately. One is the creosote product accumulated in openings/fractures/fractures in the clay soil matrix and the other is seams or layering of variously colored creosote residuals that were not continuous throughout the interval. The seams or layering were observed in discrete isolated locations. The question to me is whether these properties originated from surface depositions that were eventually covered by later depositions or by migration of NAPL through the clay soils. In some cases there might have been vertical migration after surface deposition of creosote product.

Possibly in the future, a descriptor system with definitions and use of the Munsell Soil Color Charts can be derived and used to provide more consistent information on what is being visibly observed in the field. Color photos of the soils/sediments associated with the different classifications would initially be

prepared for a reference when the soil/sediments are being sampled and observed. An example of a descriptor/classification system is in Table 3 below.

It would seem there is a need to establish what a baseline or reference soil profile for the floodplain areas looks like in the absence of any creosote or fuel oil inputs to any where in the profiles for comparison purposes. The soils in the floodplain are formed from the glacio-lacustrine clays of the Superior plain. Location-wise they will be classified as hydric or poorly drained soils. Characteristic of these soils are:

Properties of Hydric Soils Where the Profile is Dominated by a High Water Table or an Impervious Layer Impeding Percolation		
Feature	Characteristic	Observation
Drainage	Poor (Hydric Soils)	Wetland and Poned Areas
Position	Nearly Level to Depressional	
Duration of Saturation	Long Periods to Near-Surface to Poned at Times	
Surface layer	Some Profiles May Develop an Organic Horizon Above the Mineral Surface	Results in organic materials from deposited plant materials in wetlands
Surface Colors (Munsell Color Chart)		
Hue	5YR, 7.5YR, 10YR	Where the color falls among the primary spectral colors
Value	Neutral	The darkness or brightness of a color
Chroma	2 to 4; 0 to 2	Refers to the purity or strength of the color. Soils which remain under saturated conditions for long periods of time usually have low chromas
Reduction of red parent material (2.5YR) due to duration of saturation	Gleyed layer forms directly below surface layer. Hue – 10YR to 5Y; Value – 4 to 6; Chroma – 1 or 2 (grayish)	Gleying occurs through a process of chemical reduction, and usually occurs within 12" of the surface in hydric soils. Gray with a bluish gray or greenish tint (chroma of 1 or less). They occur under conditions of long term saturation where essentially all the iron and manganese are reduced. In a depleted matrix, the iron has been removed from the top of the profile, resulting in a pale or light gray matrix
Mottles	Common to many hydric soils. Yellow, red, brown	The mottles result from the reoxidation of iron and other minerals around zones in the soil that contain oxygen such as root channels or macropores

The important characteristic of the hydric soils is the gley horizon that may form. This subaqueous horizon is generally gray often with a bluish or greenish tinge. The horizon can often be black or bluish black. There could be a black organic surface horizon, underlain by a bluish- gray gleyed horizon (also could be black or bluish black), which in turn is underlain by the reddish clay parent material. It would seem that it would be important to distinguish the soils above due to natural features from those produced by the mixing in of various amounts of creosote product and residuals into the soils that would seem to result in similar colorations. Have any gleyed soils at the site been observed and distinguished from soils stained by creosote when observed in dug pits and core samples. None of the investigation reports discussed this.

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/fishseval.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.

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 were 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?
- BB&L has indicated they will use tree swallows as an upper trophic level insectivorous receptor in the risk assessment for the Site. At least as far as the TCDD-equivalencies of certain PCB congeners, the accumulations of PCBs in eggs and nestlings of tree swallows at concentrations high enough to cause much higher levels of adverse effects in more sensitive avian species suggests tree swallows may be more resistant to the effects of PCBs than many other species studied (McCarty and Secord, 1999). Whether this applies to the TCDD-equivalencies of 2,3,7,8-substituted forms of dioxin/furans is unknown. If swallows are not sensitive to exposures to dioxins, this may reduce the usefulness of the tree swallow as a receptor species in conducting ecological risk assessments at sites where TCDDs are the contaminant of concern and documenting the effects of contamination. 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 insects with body burdens of TCDDs. The greater degree of tolerance to TCDD 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 of sensitive species or kill sensitive individuals 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).

Section 2.9. Page 2-11. Sheen Sampling from 2006 Data Summary Report

Table 6 below summarizes the results of the sheen analysis from samples collected from the surface waters of the Creek derived from Table 10 of the 2006 Report. The proportions of LMW and HMW in the samples were calculated. While the GC/FID analytical method used is for identifying petroleum hydrocarbons and therefore various petroleum products, it is assumed no petroleum-related products were in the sheen samples such as fuel oil, which was used as a carrier at the site. However, this is not discussed in the 2006 Report. It is assumed the hydrocarbon groups and targeted analytes identified are representative of creosote products. Within the petroleum hydrocarbon fractions, the balance between aromatic and aliphatic constituents is assumed to be 20:80 (CCME, 2000). The ratios of these fractions in the Crawford Creek sheens were the reverse of this ratio. No GC/FID chromatograms were provided

in Attachment B of the 2006 Report. The chromatograms would show if there were a relatively high concentration of unresolved complex mixtures (UCM) in the samples. Creosote, even under weathered conditions, would have very little UCM compared to petroleum products. Paired ratios for some PAH isomers (e.g., Fluoranthene/Pyrene and Anthracene/Phenanthrene) are representative of creosote product (Stout et al. 2001). The LMW:HMW PAH ratio in manufactured creosote products is approximately 80:20. The range of the LMW:HMW ratios in the Crawford Creek sheen samples was generally 50:50 with the ratio in the Sheen-3 sample of 69:31. This would indicate that the creosote in the sheen samples has weathered to some degree with loss of the LMW PAHs and HMW PAHs being retained (higher K_{oc} values, lower solubilities and volatility, more recalcitrant to degradation). To put into perspective the range of TPAH concentrations in the sheen samples of 114, 000 to 215,000 mg/kg, the following considerations are made: 1) it is assumed the sheen eventually is deposited in a 0.5 cm layer on the Creek bottom or floodplain soil surface, 2) the background TPAH concentrations in the sediments/soils is 100 mg/kg, and 3) if a 15 cm core sample was taken, the weighted average TPAH concentration in the 15 cm core segment based on the above would range from 3,900 to 7,300 mg/kg based on the sheen sample TPAH range.

Another perspective on the hydrocarbon fraction concentrations in the sheens reported in Table 6 below can be derived with comparing the concentrations with the Canadian-Wide Standards for petroleum hydrocarbons (PHC CWS) in soil for the same general carbon ranges. The PHC CWS are:

- A 3-tiered remedial standard for soil and subsoil protective of human health and environmental health including both terrestrial invertebrates and plants and surface water aquatic life from PHC deposited on land and transported to nearby waterways.
- Four generic land uses are protected –agriculture, residential/parkland, commercial and industrial.
- Soil standards for four broad physico-chemical fractions were derived : 1) F1 – C_6 to $>C_{10}$; 2) F2 - C_{10} to C_{16} ; 3) F3 - C_{16} to C_{34} ; and 4) F4 - C_{34+}
- Chronic, subchronic, acute, and lethal responses of plants and invertebrates relevant to the sustainable functioning of soil under the four are used to derive Tier 1 levels.
- The Tier 1 levels in the PHC CWS present the lower of the values generated for human health and ecological protection such that both are protected when Tier 1 levels are applied.

Table 7 below compares the Canadian Tier 1 concentrations for the hydrocarbon fractions in soils to protect the soil receptors of invertebrates and plants and aquatic life in the case of PHC released on land and having the potential to move to nearby surface waters, to the concentrations for the same general fractions reported in the surface sheens sampled from Crawford Creek. The latter concentrations are orders of magnitude greater than the Tier 1 Standards. It is recognized that the PHC fractions were measured in surface sheens in the Creek water (as mg/kg solids) and the PHC CWS apply to soils. However, surface sheens may end up deposited on the Creek banks and/or bottom or under certain conditions of high flows may end up deposited on the floodplains. Assuming meiofauna and macrofauna associated with the creek bottom or water column are as sensitive to the hydrocarbon fractions as soil invertebrates, the soil standards can be tentatively applied to the bottom substrates of the Creek. As such, protective concentrations of PHC fractions in the Creek substrates would need to be less than 150 – 200 mg/kg. An assumption is made that the hydrocarbon compounds in fractions of creosote have similar toxicity as the hydrocarbon compounds in petroleum in making the above comparisons.

Section 3.2. Page 3-2. Surface water Analytical and Flow Data

The grab surface water samples collected from 7 locations (2 in drainage ditch) in 1996 and from 4 locations in 1999 are discussed. Samples collected in August 1999 were collected under low flow conditions. Samples in 1996 were collected just below the surface. In 1999, while additional water samples were collected over a range of flow conditions, they were only analyzed for TSS and not any of the contaminants of concern for the site. Detection levels for the 1999 samples at 5 ug/L were greater

than the detection levels for the 1996 samples (generally 0.02 to 0.06 ug/L). I discussed in my April 21, 1997 memo the derivation of water quality criteria for PAH compounds following the protocols described in USEPA's Water Quality Guidance for the Great Lakes System (EPA, 1995) for developing secondary values through a Tier II method. The following table was in my comments that shows toxicity values that were developed by the method in the EPA Report to protect aquatic life.

Water Quality Acute and Chronic Toxicity Values for PAH Compounds for Screening Purposes		
PAH Compound	Tier II or Secondary Values to Protect Aquatic Life (ug/L)	
	Acute Toxicity Value	Chronic Toxicity Value
Acenaphthene 1.	80	23
Acenaphthalene	124	9.9
Anthracene	0.024	0.0013
Benzo(a)Anthracene	0.49	0.027
Benzo(a)Anthracene	0.24	0.014
Benzo(a)Pyrene	0.24	0.014
Fluoranthene 1.	33.6	6.16
Naphthalene	353	23.4
1-Methylnaphthalene and 2-Methylnaphthalene	154	12
Phenanthrene	37.1	3.23

1. NAWQ Values (National Ambient Water Quality Criteria Values).

Some observations from the above:

- It needs to be determined if the above toxicity values above apply to the ditch and Creek surface water classifications.
- The concentrations of anthracene (0.16 ug/L) and benzo(a)pyrene (0.10 ug/L) from a 1996 ditch sample exceed the acute and/or chronic toxicity values in the above table.
- The detection limits achieved for the 1999 water samples of 5 ug/L is greater than many of the toxicity values in the above table (i.e., the PAH could be present above the table concentrations and not be detected). While the 2006 Report states that the PAH concentrations decrease in a downstream direction when both years of monitoring are combined, the difference in detection levels between the years and the minimal grab sampling makes this uncertain.
- I'm not sure much can be determined about surface water quality conditions at the site with a minimum of grab samples below the surface under low flow or base flow conditions under which they were collected. Ideally, flow weighed samples of longer duration and over various flow events, both baseline and storm events, and at various locations in the water column could have been obtained including TSS samples with analysis of the solids for contaminants. The 2006 sheen samples and the 1996 TCLP leaching tests would indicate the system has a large potential to release and transport site contaminants in the Creek system.

Section 3.4.2. Page 3-6. Sampling Data

On page 3-7 of the 2006 report, the bank and floodplain results for PAHs are discussed. It is noted that for calculating the Benzo(a)pyrene equivalent concentrations that BB&L references a 1993 USEPA document (also used for sediment samples). For the site soils, the 1997 WDNR guidance document would be more relevant in this regard. The EPA approach uses relative potency factors (toxic equivalency factors - TEQ) for 6 PAH compounds to benzo(a)pyrene, while the WDNR approach uses the TEQs for 17 PAH compounds to Benzo(a)pyrene. The TEQ values for the 6 compounds in the EPA approach are the same as the TEQs values in the WDNR approach. With the exception of Benzo[g,h,i]perylene and anthracene where TEQ = 0.01), the TEQ for the remaining 10 PAHs is equal to

0.001. Using the WDNR approach, the summed benzo(a)pyrene TEQ values would be somewhat greater than BB&L has calculated in their tables.

The generic residual cleanup levels for total PAHs and Benzo(a)pyrene equivalents in the WDNR guidance for perspective along with the average concentrations found in the Crawford Creek system are in the following table.

Residual Contaminant Levels (RCLs) For Soils Related to PAHs for Non-Industrial (Residential) Scenario (WDNR, 1997)				
	Total PAHs		Benzo(a)pyrene Equivalency (18 PAHs)	
Target Cancer Risk Level	1.8 x E-06	1 x E-05	7 x E-07	7 x E-06
mg/kg	0.16	0.9	0.061	0.61
1. The availability of suggested generic soil cleanup levels for PAHs should not be construed to preclude site-specific decision making. Higher levels could be calculated if supported by a site-specific evaluation under s. NR 720.19, Wis. Admin. Code.				
Bank and Floodplain Soil Samples From Crawford Creek System (7 PAHs)				
Surface Samples (n = 93) Ave.	546		77	
Subsurface samples (n = 32) Ave.	4,910		208	

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

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

Miscellaneous Comments

1. I note in comparing the 2,3,7,8-TCCD-EQ concentrations for sampling locations C1, C1A, C3, C3A, CB, T29-C, and T-34 in Table 13D (page 1 of 4) of the 2006 Report that they do not match the concentrations for the same sites in Table 4-8 of the 2000 Report (Vol. I of II). The only concentration that matches between the two tables is the one for site T-18C. What is the explanation for the differences and which table has the correct values in it?
2. The title boxes in Figures 8, 9, 10, 12, 13, and 14 of the 2006 Report appears to indicate the concentration results for the contaminants displayed on the figure are representative of the 0 – 1 ft. depth interval. In the case of many sample locations, the sample depth was only 4 inches and what the concentration of the contaminants in lower segments at these sites is not known because they were not sampled and analyzed.
3. Table 13C (pages 1 and 2 of 16) of the 2006 Report shows the sediment sampling data obtained for 11 sites in the drainage ditch and Crawford Creek in 1999. Both a surface segment (0 -0.5 ft.) and a subsurface segment (0.5 ft. – variable depths) were sampled and analyzed at each of the 11 sites.

However, Table 13C of the 2006 Report does not show the results for the subsurface segments at a number of the sites (e.g., SD-08, SD-09, SD-10, SD-11, SD-12, and SD-14). What is the reason the analytical results for the subsurface segments at these locations are not shown? As noted in my April 21, 1997 comments, the reported total PAH concentrations for these 1999 samples has to be considered minimal values because the reported detection limits for a number of PAHs in all the samples was unusually high (in cases up to 200 mg/kg). The concentrations given in the tables of the 1999 and 2006 Reports is the total only for those PAHs that were reported out as quantified concentrations. If more normal; detection limits would have been achieved, the total PAH concentrations would likely would have been two times or more than those being used.

4. I note in the 1996 Report, Fluor Daniel report the results from some TCLP testing from two of the sediment samples (shown in Table 9 below). The purpose of the TCLP test is to determine if a solid waste exhibits hazardous characteristics. The sediment material was leached with an acidic solution to simulate conditions that would be found in a landfill and is used to gauge the potential of the contaminants to contaminate groundwater. The total detectable PAH concentrations in the leachate from the sediment samples ranged from 183 to 1,500 ug/L. Naphthalene was the PAH with the highest concentrations in all the samples (94 to 1,100 ug/L). Based on Section 3.2, page 3-2 of the 2006 Report, PAHs were only found in minimal concentrations in the water column samples from the site. The leaching results may possibly have some applicability in the relationship between the sediments and sediment pore water, convective flows and in the near bottom area between the sediment and the immediate overlying surface waters.
5. Pages 3-4 and 3-9 of the 2006 Report state that only four surface sediment samples have historically been analyzed for DROs. However, in 1999, 11 surface sediment samples and corresponding subsurface segments were analyzed for DRO or a total of 22 samples. The results are discussed on pages 7 to 9 of my April 21, 1997 comment memo which includes a discussion of the effect levels we established for DRO concentrations on Hog Island Inlet/Newton Creek and a comparison with the DRO levels found in the Crawford Creek sediments.
6. The 3rd bullet on page 4-1 of the Conclusions of the 2006 Report mentions that tetrachlorophenol and acid extractable phenolics were not detected in any of the water samples. No mention is made of the detection of these compounds in the sediments. Based on the 1996 Report, some phenolic compounds were detected in the sediments at two of the eleven sediment sampling locations. It was also noted that the reported detection levels for most of the phenolic compounds were relatively high meaning a number of them may have been present but not detected at the high reporting levels achieved. Phenolic compounds were not analyzed for in the sediments after 1996. I did not agree with the conclusion in the 1996 Report that AEPs were limited in distribution. See my comments on this issue on pages 10 to 15 in my April 21, 1997 comment memo.
7. The 1st bullet on page 4-2 of the Conclusions of the 2006 Report states that: "*Low-level concentrations (less than 1 mg/kg) of penta were detected in 8 of the 14 sediment samples collected in 1996. Penta was not detected in any of the 186 sediment samples collected in 1999 and 2005.*"

Counting both segments from 11 sites, 22 sediment samples were collected for penta analysis in 1996 plus two bank samples along the drainage ditch. Penta concentrations in two bank samples (each composites of 0 – 2 ft.) along the drainage ditch were 87 and 100 mg/kg. Penta was detected in 11 of the 22 sediment samples at concentrations (mostly estimated concentrations) that ranged from 0.024 to 0.530 mg/kg. As discussed in my April 21, 1997 comment memo, some of the penta concentrations exceeded the SQGs for estimated effects to benthic organisms based on chronic toxicity.

It was noted that for the 1996 sediment samples, the reported detection limit for penta was typically low (e.g., 0.015 mg/kg). In 1999 and 2005, the reported detection limit for penta was typically 0.330

mg/kg or higher. This is the reason why no penta was detected in the 1999 and 2005 samples compared to the 1996 samples. As discussed in my April 21, 1997 memo, penta concentrations less than 0.330 mg/kg can be related to predicted effects to benthic organisms. Non-detection at the levels achieved does not mean that penta is not important as a contributor either alone or in conjunction with other COPC to possible toxicity to aquatic organisms.

8. The 6th bullet on page ii of the Executive Summary of the 2006 Report states:

“Low-level concentrations of polychlorinated dibenzi-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) were detected in sediment samples throughout the Outfall 001 drainage ditch and Crawford Creek. All samples of 2,3,7,8-tetrachlorodibenzo-p-dioxin toxic equivalents (2,3,7,8-TCDD TEQ) values less than 0.5 ug/kg.”

Based on the values reported in Table 4-8 of the 2003 Report, two sediment samples collected in the upper and middle reaches of the drainage ditch had 2,3,7,8- TCDD-EQ concentrations that exceeded 500 pg TCDD-EQ (0.5 ug TCDD-EQ) level used in the above statement. C-1A and C-3A had concentrations of 690 and 550 pg TCDD-EQ/g, respectively based on Table 4-8 of the 2000 Report. . The “A” designation in the samples appears to indicate samples taken in the same general location as the C-1 and C-3 samples but outside the area of any stained soils. That the 2,3,7,8-TCDD-EQ concentrations were higher in the non-stained soils would seem to indicate that soil staining is not an indicator of elevated 2,3,7,8-TCDD-EQ concentrations. This was borne out by the test pit sampling along the floodplains in 2003 where soils that oily product in them did not have significantly elevated TCDD-EQ concentrations. The oily product was likely creosote that would not be expected to have any significant TCDD-EQs in the manufactured product. In the period of time penta was used at the facility, I assume it was used in some type of petroleum solution as a carrier. That penta was released from the facility when it being used can be judged by the TCDD-EQ detects in the ditch, sediments and floodplain soils. Other than the one ditch bank soil sample that had a TCDD-EQ concentration of 5,500 pg/g, all the other levels are lower throughout the system. The Christiansen facility that used penta had much higher TCDD-EQ concentrations associated with the sediments in the associated Creek. Given that penta degrades relatively fast in the environment, the concentrations of penta detected are not a good indicator of how much TCDD-EQ can be expected. In the case of the Christiansen site, penta levels were relatively low and yet the TCDD-EQ levels were relatively high due to the persistence of these components in the manufactured penta product. Given that penta was used for a relatively short time at the Koppers facility compared to the creosote, less penta along with its petroleum carrier , if used, may have been released.

9. The 6th bullet on page iii of the Executive Summary states:

“Low-level concentrations of PCDDs/PCDFs were detected in bank/floodplain soil samples throughout the Outfall 001 drainage ditch and Crawford Creek areas. With the exception of one sample collected along the Outfall 001 drainage ditch (sample D-2, 3.29 ug/kg, calculated 2,3,7,8-TCDD TEQ values in soils were below the USEPA’s allowable residential soil concentration of 1 ug/kg.”

As to the USEPA residential soil value, see the first comment above on page 1. I note the above sample D-2A value of 3.29 ug TCDD-EQ/ kg is from Table 14E of the 2006 Report. It does not match the 5.5 ug TCDD-EQ/kg (5,500 pg TCDD-EQ/g) concentration for sample D-2A reported in Table 4-8 of the 2000 Report. I noted above some other differences reporting the TCDD-EQ concentrations between the two tables in the 2000 and 2006 BB&L Reports. Were the TCDD-EQ concentrations recalculated using different TEQ values or where non-detect values handled differently between the two reports to result in different values. No explanation is given.

10. I'm still trying to get an overall sense of the degree and extent of contamination in the sediments and floodplains on a spatial basis. It may have helped in displaying the sample results on the maps to have used a larger scale and put only parts of the drainage ditch and Crawford Creek on each map. For example, dividing the Creek into 1,000 foot lengths for display on each page with the concentrations of just one contaminant (i.e., total PAHs, B(a)P-TE, or penta) per page at each location with concentrations shown at depth as appropriate. Different years results could be put in different colors. One set maps could be for sediment-related results and one set could be for bank/floodplain results. Another approach is to list contaminant concentrations in tables in an upstream to downstream fashion with the distance the sample point is downstream from some reference point, for example, Hammond Avenue noted. For example, see Figures 4-5A – 4-5F of the 2000 Report.
11. In a large numbers of boring logs in Attachment A of the 2006 Report under Stratigraphic Description, a description of "No Recovery" is given for segments as long as 8 ft. What is involved in the "No Recovery" description?
12. It would be useful to have all the TOC data collected for the sediments for all sampling events compiled and put into one summary table denoting the sampling year and the sample site involved. TOC data will be needed in using the WDNR CBSQGs (2003) and the EPA (2003) ESBs for PAH mixtures as measurement endpoints in the risk assessment to gauge potential impacts to the benthic invertebrate communities in the Creek.
13. The last bullet on page 4-2 of the Conclusions states that of the 100 bank/soil floodplain samples in 1996 and 1999, only 9 had detects of penta and of the 25 samples collected from floodplain soils in 2005, none had detects of penta. It is noted that the detection level for penta in the 1996 and 1999 samples was generally 0.333 mg/kg with quantified concentrations generally less than 2 mg/kg with the exception of 2 ditch bank samples. The reporting limit for the 2005 samples generally was in the 2.5 – 3.0 mg/kg range. Therefore it is possible penta was present in the soil samples in 2005 but not detected.
14. The 3rd bullet on page 4-3 of the Conclusions provides rationales why it is not necessary to sample the floodplain soils downstream of the railroad embankment. One reason given is that the floodplains are disconnected because of the railroad embankment. The Creek channel in the culvert under the railroad embankment could have served as a conduit for transport of creosote NAPLs to downstream. Under conditions where high flows in the Nemadji River were causing backups in Crawford Creek, the NAPLs may have settled out over floodplain areas below the embankment. At some locations in the Creek channel, sediments along transects T/FP-37 and T/FP-39 have relatively high PAH concentrations at depth. Downstream transects such as T-36, T-37, T-39, T-42, T-46, and T-48 have staining, sheening, or odor observed with probing in the Creek banks generally at the waterline. One question is if this visible presence in the bank face is associated with and connected to buried creosote residual distributed over the floodplain away from the Creek. I believe on some of my earlier visits to the site, I observed beaver dams in the area of transect T/FP-37 just downstream of the embankment. The beaver dams may have been responsible for overflows onto the adjacent floodplains and settling out of any creosote product that the flow was carrying. The deposited creosote may have been covered over time by latter deposits of clay materials from the watershed.
15. It is noted that in the 2003 floodplain test pit observations that creosote residuals were present at many floodplain locations as a black-stained layer in a sandy-silt or silty-sand substratum that generally extended from 2 ft. to 3/4/5 ft. below the ground surface. In some cases the silty-sand substratum was closer to the surface. It was indicated that the black stained layer was continuous within the specified depth interval. There was no discussion in the reports for the

possible factors responsible for this spatial location of the creosote residuals. I'm assuming that the deeper silty sand substratum layers in the soil profile were laid down at the time of glacial stream deposits and then overlaid by lake clays. The silty-sand substratum layers are likely connected to the ditch and Creek channels at their sides or bottom. Creosote as NAPL being transported in the channels moved vertically from the channels into the silty-sand substratum at times of positive horizontal groundwater gradients where water in the ditch and creek was recharging the groundwater at certain times. Given that the variability of the groundwater gradients is expected, groundwater contaminated by creosote residuals in the sandy silt layers likely discharge to the ditch and creek channels under conditions of negative horizontal gradients.

I'm also assuming that a black stained layer closer to the surface (within 0.5 to 1.0 ft.) found in the floodplain soil profile is from the creosote residuals being deposited on top of the soil and later covered by clays eroded from soils of the watershed, transported in the flows, and deposited out over the floodplain areas. However, since in most cases, the creosote residual staining in these shallower layers is also associated with silty sand materials, it may also be a case of the creosote moving horizontally from the channel into this substrata rather than being carried in overflows and then deposited out and covered up later with clay deposits. Both horizontal movement and surface deposition of creosote residuals may be involved.

16. I note components of the ecological risk assessment other than those in the 2006 Report were in the 2000 Report (e.g., Section 3.4.1 and Section 6. I assume this information will be used in the ERA for characterizing habitat types and developing the conceptual site model (CSM).

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Table 1. Listing of Correspondence/Memo in Files that Related to Koppers Site Issues and Document Reviews		
Date	To	Subject
4/19/2005	John Robinson	Review of BB&L Feb. 10, 2005 Response to WDNR Comments Dated Jan. 21, 2005. BBL Project # 388.75. Koppers, Inc. Superior, WI Facility
12/9/2004	Jim Hosch	Comments on Nov. 17, 2004 BBL Work Plan for Outfall 001 Drainage Ditch and Crawford Creek Investigation Activities – Koppers Inc. Wood Treating Facility, Superior
11/17/03	Jim Hosch	Review and Comments on BB&L June 26, 2003 Report on Crawford Creek Floodplain Investigation Results Related to Koppers Inc.
11/25/2003	Henry Nehls-Lowe	Response to Your 11-24-03 e-mail re Fraction OC-Sediment and Fraction Lipid Values Used in BB&L/AMEC Calculations to Estimate Dioxin Fish Uptake in Crawford Creek.
11/21/2003	Jim Hosch	After Thoughts from 11-21-03 Meeting About Koppers Issues – Dioxin Exposure Risk Levels
8/13/2003	Jim Hosch	Comments On AMEC Letter pf July 10, 2002 that Addressed WDNR Concerns of Dioxin/Furan and PAH Bioaccumulation in Fish From Crawford Creek Due to Past Releases from Koppers Industries, Inc.
8/20/2001	Tom Kendzierski	Review of the July 25, 2001 BB&L Scope of Work (SOW) for Additional RFI Activities at Koppers – Superior (WID 006 179 493)
11/2/00	Tom Kendzierski	Memo #1 Koppers Meeting of Nov. 2, 2000
11/2/2000	Tom Kendzierski	Memo #2 Bureau of Watershed Management Comments on the July 2000 Supplemental Surface Water and Streambed Sediment Investigation Report for the Drainage Ditch and Crawford Creek Associated with the Koppers Site, Superior
11/2/2000	Tom Kendzierski	Memo #3 Comments on the Fish Survey Conducted on Crawford Creek by BB&L
8/12/1998	Tom Kendzierski	Bureau of Watershed Management Comments on the May 1998 <i>Supplemental Investigation Work Plan, Surface Water and Streambed Sediment for Koppers Industries, Inc. Site Superior as Prepared by BB&L</i>
4/21/1997	Jim Hosch	Bureau of Watershed Management Comments on the March 1997 <i>Preliminary Characterization Report, Surface Water and Streambed Sediment, Koppers Industries, Inc., Superior, WI. WID 006-179-493. Prepared by Fluor Daniel GTI for Beazer East, Inc.</i>
6/25/1996	Lee Liebenstein	Summary of Status and Site Observations at the Koppers Wood Treatment Facility in Superior Township Related to Potential Impacts to Off-Site Surface Waters

Year	Investigator	Observations / Results												
7-18-85	WDNR – Liebenstein, Sullivan, Pratt	Sediment sample from Crawford Creek Pond Area. "Creosote product was found beneath 5 in. layer of clay"												
8-11-92	WDNR-LaValley	Sediment samples at upstream reference and impacted areas. Assume surface grab samples. Total PAH mg/kg K06 Drainage ditch S. Hammond Ave. 459 K02 North Edge of Crawford Creek Pond 5,338 K03 Middle of Crawford Creek Pond 11,336 K04 Creek Channel Upstream of RR 15,272												
6-12-96	Fluor Daniel GTI	Sediment sample from Center Crawford Creek Pond. Figure 3-9 in 1997 report indicates pond 150 ft. wide. Blackish-brown layer 5-12 inches, staining and odor, highest PID reading of all samples; reddish brown clay in layers below and above 5 – 12 with no odor or staining. Appendix A photographs in 1997 report show SD-12 in pond area with core picture showing brown clay in upper 6 in. and black creosote-related in 6-12 with brown clay below 12 in. Samples by core out of boat. Minimum TPAH values due to high reported MDLs for a number of PAHs. <table border="1"> <thead> <tr> <th>Core Length (in.)</th> <th>mg/kg TPAH</th> <th>% DRO</th> <th>% TOC</th> </tr> </thead> <tbody> <tr> <td>SD-12A 0 – 5</td> <td>53.7</td> <td>1,000</td> <td>16</td> </tr> <tr> <td>SD-12B 5 – 14</td> <td>5,782</td> <td>18,000</td> <td>16</td> </tr> </tbody> </table>	Core Length (in.)	mg/kg TPAH	% DRO	% TOC	SD-12A 0 – 5	53.7	1,000	16	SD-12B 5 – 14	5,782	18,000	16
Core Length (in.)	mg/kg TPAH	% DRO	% TOC											
SD-12A 0 – 5	53.7	1,000	16											
SD-12B 5 – 14	5,782	18,000	16											
8-18-99	WDNR-Janisch	Observations in drainage channel from Crawford Creek Pond at juncture with creek and augering and shovel pits along channel and throughout Crawford Creek Bottom. Black staining and odor from creosote layer beneath cleaner clays exposed along channel bank face. Pits and augering throughout Pond bottom commonly found ~ 6 in. of clean clay over black and grayish black stained substrata that was creosote related.												
1999	BB&L	Transect T/FP-33 with samples C-8-A, -B, and -C taken in creek channel at depth along transect. FP samples taken within 15 and 30 ft. of channel. Highest TPAHs in FP samples were 5 – 10 mg/kg at depth (1.0 – 1.5 ft). Sediment samples generally had highest TPAH concentrations of all CC sediment samples. TPAHs in 0 – 0.5 ft. of C8-C of 33,000 and 54,000 mg/kg with odor/staining/sheen observed in surface segments and oily, non-aqueous phase liquids observed in lower segments												
2003	BB&L	2003 Floodplain Test Pit Cross Sections. Along Transect 3 across Crawford Creek Pond area, isolated creosote seams down to 12 ft. and 245 feet from creek channel (e.g., NO3-4). Widest observed of all transects across Creek. Near-surface staining and odor observed in 2 of 4 N. side pits.												
2005	BB&L	Floodplain soil samples T5 and T6 on north side of Creek in area of CC Pond. Each a composite of 5 grabs over 150 ft. TPAHs in T5 and T6 were 0.12 and 1.65 mg/kg, respectively.												

Table 3. Example System for Describing Visual Characteristics of Creosote Contaminated Sediments and Soils

Visual Observation Categories	Munsell Soil Color Chart Reading	Identify as Appropriate in Sample													
		Creosote/Fuel Oil Odor				Sheening									
		Hue	Value	Chroma	Heavy	Mod.	Light	None	Heavy	Mod.	Light	None			
Oily Nonaqueous Phase Liquid (NAPL) Creosote Product Present	Staining Black to Grayish-Black to Grayish ↓														
Heavy ¹ Creosote Residual in Soil/Sediment Matrix															
Moderate Creosote Residual in Soil/Sediment Matrix															
Low Creosote Residual in Soil/Sediment Matrix															
No Visible Creosote Residual in Soil/Sediment Matrix															
Isolated Non-continuous Seams of Creosote Residuals Observed in Subsoils (Describe Layering)															
Isolated Creosote Product/ Residual in Cracks/Fractures/Openings of the Clay Soil Matrix															
Natural Gley Soil Horizons Present Grayish to Bluish Gray to Black															

1. The descriptor terms Heavy, Moderate, and Low are an estimate of the relative proportion and weathered state of the creosote in the soil/sediment matrix based on the stain color; e.g., Heavy would be associated with black staining throughout the sample.
2. Other characteristics to be recorded would be thickness and depth of segment with the described characteristics in the profile, the characteristics of the materials above and below the impacted segment, presence of any natural organic materials, and mineral particle size proportions present (i.e., estimate of the amount sand, silts, and clays. Pictures should be taken of all samples.

pg TCDD-EQ / g Fish Tissue						
Reference	Upstream of Railroad Embankment			Downstream of Railroad Embankment		
	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	

Species Protection Level	Benchmark Value pg TCDD-EQ / g Lipid in Fish Eggs and Embryos		
	Lower Confidence Level	Mean	Upper Confidence level
Geometric Mean of No Observable Effects Residue (NOER) and Lowest Observable Effects Residue (LOER)			
99 %	15	57	201
97.5 %	40	151	510
95 %	88	321	1,050
90 %	199	699	2,220
Geometric Mean of Median Lethal Residue (LR50)			
99 %	0.3	58	382
97.5 %	2.5	169	802
95 %	11.7	386	1,430
90 %	58.3	909	2,640

Parameter	mg/kg			
	SHEEN - 1	SHEEN - 2	SHEEN - 3	SHEEN - 4
Extractable Petroleum Hydrocarbons (EPH) by GC/FID				
C9 – C18 Aliphatics	18,000	16,000	28,000	18,000
C19 – C36 Aliphatics	59,000	46,000	71,000	42,000
C-11 – C22 Aromatics ¹	300,000	359,000	310,000	210,000
Total PAHs (SVOCs by 8270 SIM)	215,320	193,760	199,850	114,110
Total EPHs (sum of above)	592,320	614,760	608,850	384,110
Unadjusted C11 – C22 Aromatics ²	560,000	630,000	640,000	310,000
% LMW PAHs	48.9	52.1	68.7	46.9
% HMW PAHs	51.1	47.9	31.3	53.1

1. C11 – C22 Aromatic Hydrocarbons exclude the concentration of Target PAH Analytes.
2. Not included in Table 1o of the 2006 Data Summary Report but in Attachment B.

Table 7. Summary of Generic PHC Soil Quality Guidelines (mg/kg soil) Recommended for Surface Soils in Canada and Comparison With the Hydrocarbon Fractions Found in the Sheens From Crawford Creek.

Receptor		Petroleum Hydrocarbon Compound Fraction ¹ Canada-Wide Standards mg/kg			
		Fraction 1 C ₆ – C ₁₀	Fraction 2 > C ₁₀ – C ₁₆	Fraction 3 > C ₁₆ – C ₃₄	Fraction 4 > C ₃₄
Soil Invertebrates and Plants					
Agricultural and Residential/Parkland	Coarse Soils	130	450	400	2,800
	Fine Soils	280	900	800	5,600
Commercial and Industrial	Coarse Soils	330	760	1,700	3,300
	Fine Soils	660	1,500	2,500	6,600
Aquatic Life					
All Land Use Categories		230	150	NA	NA
Fraction Composed Of					
Aromatics		C _{>7} – C ₈ C _{>8} – C ₁₀	C _{>10} – C ₁₂ C _{>12} – C ₁₆	C _{>16} – C ₂₁ C _{>21} – C ₃₄	C _{>34}
Aliphatics		C ₆ – C ₈ C _{>8} – C ₁₀	C _{>10} – C ₁₂ C _{>12} – C ₁₆	C _{>16} – C ₂₁ C _{>21} – C ₃₄	C _{>34}
Results of 2005 Surface Water Sheen Sampling² From Crawford Creek					
Sheen 1		mg/kg			
C ₉ – C ₁₈ Aliphatic			18,000		
C ₁₉ – C ₃₆ Aliphatic				59,000	
C ₁₁ – C ₂₂ Aromatic + PAHs			515,320		
Sheen 2					
C ₉ – C ₁₈ Aliphatic			16,000		
C ₁₉ – C ₃₆ Aliphatic				46,000	
C ₁₁ – C ₂₂ Aromatic + PAHs			552,760		
Sheen 3					
C ₉ – C ₁₈ Aliphatic			28,000		
C ₁₉ – C ₃₆ Aliphatic				71,000	
C ₁₁ – C ₂₂ Aromatic + PAHs			509,850		
Sheen 4					
C ₉ – C ₁₈ Aliphatic			18,000		
C ₁₉ – C ₃₆ Aliphatic				42,000	
C ₁₁ – C ₂₂ Aromatic + PAHs			324,110		
<ol style="list-style-type: none"> 1. Soils type (coarse grained vs. fine grained) needs to be considered in Standard derivation. 2. The Creek bottom and/or banks were agitated by a metal rod at sampling locations to induce sufficient sheen quantities for sample collection. 					

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

Table 9. Results of TCLP Testing for Two 1999 Sediment Samples Along With Contaminant Concentrations in the Sediments.

PAHs	SD-06 Drainage Ditch		SD-10 Crawford Creek	
	0 – 0.5 ft.	0.5 – 1.0 ft.	0 – 0.5 ft.	0.5 – 1.4 ft.
	Results of TCLP Testing (ug/L) ¹			
Benzo(a)pyrene	< 2.0	8.6	< 0.50	8.9
Benzo(a)anthracene	< 2.0	8.9	< 0.50	8.6
Phenanthrene	87	190	36	67
Fluorene	78	110	27	42
Naphthalene	300	1,100	94	580
Anthracene	16	< 25	4.8	23
Pyrene	< 20	75	6.8	41
Benzo(b)fluoranthene	4.3	12	14	64
Benzo(k)fluoranthene	< 2.0	< 5.0	< 0.50	5.0
Total Detectable Leached PAHs (ug/L)	485.3	1,504.5	182.6	839.5
Parameters in Sediment				
Leachable pH	6.6	6.0	6.4	6.3
Diesel Range Organics (mg/kg)	690	25,000	490	560
Total PAHs (mg/kg) ²	221.3	145.1	66.9	35.4

1. Shows only results for where a PAH was detected in at least one of the leached samples.
2. As discussed in the comments, are minimal values given the high reported detection concentrations for a number of PAHs.