



City of Gainesville and Alachua County

Comments and Recommendations

On

USEPA Superfund Proposed Plan Cabot Carbon/Koppers Superfund Site, Gainesville, Alachua County, Florida (July 2010)

Final

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Local Intergovernmental Team

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	R. Thomson, August 24, 2010

- Attachment BComments on ISBS Pilot Scale Study Report, Neil R.
Thomson, September 7, 2010
- Attachment C Thomson et al., 2008, *Rebound of a Coal Tar Creosote Plume Following Partial Source Zone Treatment with Permanganate. Journal of Contaminant Hydrology, v.* 102, p. 154-171.
- Attachment D CD of Documents Requested by City and County for Inclusion in Administrative Record

1.0 GROUNDWATER & SUBSURFACE REMEDY

INTRODUCTION

The nature and extent of contamination and the geology of the Koppers site will make successful remediation of the site challenging. Creosote Dense Non-Aqueous Phase Liquid (DNAPL) has been recovered from wells in the Surficial Aquifer (SA) and Upper Hawthorn Group (UHG) and, based on multiple lines of evidence, has penetrated the Lower Hawthorn Group (LHG) and the Upper Floridan Aquifer (UFA). Given the high polynuclear aromatic hydrocarbon (PAH) concentrations in groundwater offsite to the east in the UHG it appears that DNAPL has migrated laterally to the east of the Koppers property. Much of this DNAPL likely continues to be mobile, and unless removed or immobilized, will continue slowly migrating vertically and horizontally, ultimately causing increased groundwater contamination in the UFA. Of particular concern is that further contamination of the UFA will pose a material threat to the Murphree wellfield.

Dissolved-phase plumes of PAHs exist in the Surficial, UHG and LHG strata and in the UFA, and likely extend off-site in all formations. Beazer has constructed a relatively extensive UFA monitoring network at the site, although the extent of the UFA plumes has not yet been fully delineated. Most of the UFA monitoring wells indicate PAH concentrations below cleanup standards. However, there are regions in the interior of the site (i.e., identified by FW-6, FW20B, FW-12B, FW-21B and recently FW-27B, see Figure 1) where PAH concentrations are well above cleanup standards. These plumes will likely continue to expand without appropriate treatment. Of particular concern are the plume(s) in the interior of the site where contamination extends to an as-yet undefined depth (as indicated by wells FW-12B and FW-27B), and two locations (FW-22B and FW-16B) at the periphery of the site. The fact that PAH contamination in the UFA has reached these boundary wells is a clear indication that off-site migration of contaminants is occurring in the UFA – and in the case of FW-16B - has been occurring for some time. Hydraulic containment has been initiated as an interim action in the area of FW-22B (pumping approximately 28 gpm). However, actions have not yet been undertaken at the eastern site boundary (i.e. FW-16B), or in the interior of the site, other than the low rate pumping test (i.e. 2 gpm or less) at FW-6 and The southern part of the site remains without any LHG or UFA FW-21B. monitoring at all despite the large amounts of mobile DNAPL recovered from PW-1.

Treatment or removal of contaminants to reduce downward migration of DNAPL and mass loading of dissolved contamination are important in reducing the amount of contamination reaching the UFA. However, it will not be possible to treat all of the DNAPL, particularly within the LHG. Therefore, <u>hydraulic</u> <u>containment in the UFA is essential</u> in order to protect the Floridan Aquifer and community's water supply. Although Remedial Action Objectives are described generally in the USEPA Proposed Plan (p. 12), we strongly believe that specific priority goals (related to groundwater) can, and should, be stated in the remedial plan in the upcoming ROD (Record of Decision) and should include the following:

- A. Contain the contamination in the UFA on-site using hydraulic containment
 - (1) Reduce interior contaminant plumes by groundwater extraction within the UFA at rates sufficient to contain them (our preliminary estimates based on simulations using the GeoTrans model of the site indicate extraction rates of at least 100 gpm will be required to do this); and
 - (2) Prevent off-site migration of contaminants at all locations including FW-22B and FW-16B.
- B. Remove or immobilize creosote to the fullest extent possible in the UHG, LHG and Surficial Aquifer in order to:
 - (1) reduce vertical and horizontal migration of creosote DNAPL, and
 - (2) reduce dissolution and mass loading of contaminants into LHG and UFA groundwaters.
- C. Contain SA and UHG contamination by using hydraulic containment and slurry walls to minimize migration of contaminants; and
- D. Provide long-term monitoring (in the SA, UHG, LHG and UFA) to allow assessment of the performance of the remedy, verify compliance with cleanup criteria and assure no off-site migration of contaminants in the Floridan Aquifer.

COMMENTS AND RECOMMENDATIONS

The Proposed Plan does include, generally, elements intended to address each of the priority goals summarized above. We request that the upcoming ROD explicitly include these elements in relation to the Koppers site. We have the following comments and recommendations regarding the groundwater related elements of the Proposed Plan:

1. Hydraulic containment in the Floridan Aquifer must be more robust and extensive than is currently underway. The ROD must include hydraulic containment with the goal of capturing the plume in the interior of the site. Additionally, the ROD should contain specific criteria or principles (triggers) to determine when and where additional remedial actions will be required in the Floridan Aquifer.

The plan appropriately requires hydraulic containment in areas where contaminants exceed federal MCLs and Florida GCTLs outside of source areas. It also requires construction of additional extraction wells as necessary. The plan includes on-going monitoring in areas where constituents do not exceed cleanup goals. We support these provisions.

As we understand it, based on these provisions, hydraulic containment should be initiated to address UFA contamination in the interior of the site (as indicated by FW-12B and now FW-27B), as well as at the eastern site boundary (as indicated by FW-16B). The goal of the interior pumping should be to capture and contain the interior plume(s). EPA should not wait for the plume(s) to reach the property boundary before these actions are taken. The low rate pumping described in the Proposed Plan and currently implemented at FW-6 and FW-21B is not adequate to achieve this goal. Additional pumping at much higher rates in the interior of the site will be required to achieve this goal.

In addition to these provisions, we request that the ROD require a contingency plan that will be implemented if there is a definable increasing trend in constituents of concern (COCs) at a well indicating that contamination is spreading, even if cleanup goals have not yet been exceeded.

The installation of extraction well FW-31BE is an essential element in containing the Floridan contamination because migration off site in this area has been (and may still be) occurring. This extraction well is intended to address contamination leaving the site in the northwest region of the site near well FW-22B. However, additional monitoring wells are needed off-site to characterize the extent of off-site contamination at that location, and to ensure FW-31BE is adequately containing it.

Additional hydraulic containment will also be necessary to address Floridan Aquifer contamination at other locations on the site. This conclusion is based on:

- A. The results of the low rate pumping Interim Remedial Measure (IRM) at FW-6 and FW-21B (received August 3, 2010) indicate no significant improvement from the low rate pumping since it began in October 2009, and no evidence has been generated to support Beazer's claim that annular casing seepage is actually the cause of UFA contamination at these locations;
- B. Very high concentrations of naphthalene persist at several interior wells. Of particular concern is FW-12B and FW-27B which show high concentrations at an as-yet undefined depth in the UFA; and
- C. Concentrations persist above GCTLs at boundary well FW-16B.

The future analytical results from the most recently installed on-site Floridan monitoring wells (FW-27B, FW-28B and FW-30B) should provide further information on the extent of contamination in the UFA.

2. The Groundwater Contamination section of the Proposed Plan misstates the degree of contamination in the Floridan Aquifer. The ROD should accurately describe known site conditions.

The most important objective of the groundwater/subsurface remedy is to contain and clean up contamination in the UFA. However, the Groundwater Contamination section of the Proposed Plan makes several incorrect statements, and vastly understates the magnitude and extent of contamination in the UFA. For example, it makes no mention of the off-site contamination identified by monitoring locations FW-22B and FW-16B at the site boundary. The Conceptual Site Model (Figure 3, p. 9) shows no contamination in the UFA or contaminant migration pathways through the LHG.

The Proposed Plan (p. 11) refers to a single monitoring well near the former north lagoon which exceeded GCTLs but in which naphthalene concentrations "have decreased substantially since July 2004". This is incorrect; the statement can only refer to FW-6 because only that well existed near the former north lagoon in the UFA on the July 2004 date mentioned. Naphthalene concentrations in the well (FW-6) did decline between July 2004 and January 2008. However, since that time concentrations have fluctuated dramatically. August 2009 data were the highest yet measured (i.e., 2600 ppb naphthalene). More recent data, collected after initiation of the pumping at FW-6, have reported naphthalene concentrations between 580 and 1,100 ppb. At a minimum, the Conceptual Site Model and Groundwater Contamination descriptions in the ROD should acknowledge:

- A. Likely off-site migration of COCs to the east in the SA;
- B. Apparent off-site migration of DNAPL to the east in the UHG;
- C. Naphthalene concentrations in the LHG, which exceed 1,000 ppb across the width of the site, that result in continuing contamination of the UFA;
- D. PAH concentrations at FW-6 have fluctuated, but not shown a decreasing trend in FW-6 since its installation in 2004;
- E. PAH Concentrations in other interior wells (i.e. FW-21B & FW-12B) in excess of GCTLs, with FW-12B showing increasing PAH levels with depth;
- F. PAH concentrations exceeding GCTLs at boundary wells FW-22B and FW-16B; and

G. COC's have been detected at levels below COCs at several other boundary wells (FW-2, FW-3, FW-11B and FW-24B).

EPA's statement in the Proposed Plan gives the impression that contamination in the UFA at the former north lagoon is of minimal concern, and that minimal or no action is needed to contain it. We request that EPA review this section of the Proposed Plan closely and ensure that the description of the Groundwater Contamination contained in the ROD better reflect actual known site conditions. Also, we are submitting comments to Beazer's draft report on the Floridan IRM that EPA should consider when evaluating contamination in the UFA.

3. Financial assurance should be provided for the final remedy selected, including on-going operation of Floridan Aquifer containment.

The site will likely require containment of the Floridan Aquifer plumes via pump and treat for an extended period of time (i.e. decades). Beazer should be required to provide a form of financial assurance (such as a bond) to ensure that sufficient funds will be dedicated to completion of the final remedy, including the continued operation of the Floridan Aquifer Containment system and monitoring of the UFA.

4. The ROD should stipulate expansion of the Floridan Aquifer monitoring network to fully delineate the horizontal and vertical extent of off-site and on-site plumes.

Beazer has installed a relatively extensive UFA monitoring well network at the Koppers site. However, additional wells are needed at the following locations:

- A. off-site adjacent to FW-22B (and FW-31BE) to ensure that FW-31BE is indeed capturing the plume that had been leaving the site in the northwest (at FW-22B);
- B. off-site adjacent to FW-16B to delineate the off-site extent of this plume and to verify that future hydraulic containment efforts are successful in stopping this off-site migration;
- C. interior of the site to fully delineate the horizontal and vertical extent of the on-site plume or plumes being detected by FW-6, FW-12B, FW-21B and FW-27B;
- D. on the western property boundary at 26th Ave (the need for this is based on historical elevated COC levels in an offsite private UFA well (Geiersbach well) in this area, and on detections of COCs in FW-3); and
- E. Beneath (or immediately adjacent to) the former process area and south lagoon (both of these areas lack LHG wells so the depth of contamination is not known; the process area is of particular concern due to the mobile DNAPL being collected in the UHG, and the fact that the existing UFA well (FW-18B) is roughly 200 ft north of the process area).

The interior plume(s) are of great concern because of their high concentration and depth, which is as-yet undefined. Analytical results from FW-27B indicate that creosote contamination extends to at least the deepest sample-port in that well, 289 ft below ground surface. It is critical that Beazer install additional wells to <u>fully delineate the horizontal and vertical extent of this plume</u>, and to assure that it is not expanding and does not migrate off-site undetected.

- 5. The City and County request excavation and off-site disposal of the SA source areas. This remedy would provide the highest degree of confidence from the community, and provide the highest level of permanence for the site remediation.
- 6. We do not support In Situ Bio Geo Chemical Stabilization (ISBS) in the SA or UHG source areas. To the extent excavation cannot be applied in the SA, In-Situ Solidification/Stabilization (ISS/S) should be used. We do support the use of ISS/S for UHG source areas.

The need to remove or immobilize DNAPL to the fullest extent possible in the UHG and LHG (in addition to the surficial aquifer) is a primary concern to the City and County, and was emphasized in our responses to the August 2009 Draft Feasibility Study. The goal of this treatment is to reduce vertical and horizontal mass loading of DNAPL and dissolved phase constituents, with vertical mass loading being the most critical component. The proposed plan includes treatment of source areas using ISS/S in the UHG, and ISBS (alternatively referred to as In Situ Geo Chemical Stabilization (ISGS)) in the SA. As we understand it Beazer has proposed an approach utilizing ISBS in the UHG in combination with ISS/S or ISBS in the SA.

We believe that EPA's proposal to use ISS/S for the UHG is appropriate. ISS/S is a comparatively well-proven technology, although the depths and the clay layers present in the UHG at the site are likely to make implementation of any technology challenging. ISS/S provides the best technical approach for effectively treating the UHG source areas.

For the SA source areas, our first preference would be to remove and dispose off-site all of the DNAPL impacted sediments from the SA, with ISS/S in the UHG. If EPA does not select excavation as the remedy for DNAPL impacted sediments from the SA, it is the opinion of our technical team that the use of ISS/S in the SA, concurrently with ISS/S in the UHG, would provide the most appropriate remedy to achieve an acceptable level of groundwater protection.

We do not support the use of ISBS to treat SA or UHG source areas. In our previous correspondence (*GRU & ACEPD Proposed Performance Metrics for ISGS, May 10, 2010*) we expressed concern about the effectiveness of ISBS.

Upon further review we feel that ISBS is not appropriate for application in the SA or UHG source areas at the Koppers Gainesville site for the following reasons:

A. ISBS is not a proven technology (in contrast to ISS/S which is well-proven). There is very little information in the peer-reviewed literature to indicate that ISBS has been successfully applied at any site, and certainly not on the scale proposed at the Koppers Site. The application of ISBS technology reported for the Denver Koppers site used soil boring data to make conclusive statements about the treatability of a heterogeneous NAPL impacted zone. Results from these data were mixed and no attempt was made to quantify changes in mass loading. Comments from Dr. Neil Thomson on the Denver ISBS Treatment report are attached in Attachment A.

The pilot test of ISBS at the Koppers Gainesville site was similarly inconclusive in that the sweep of injected fluid in the SA was very uneven, leading to untreated zones close to the injection wells. The high injection pressures resulted in surface discharges ("day lighting") of the permanganate solution, apparently through inadequately sealed borings that are likely to also exist elsewhere on site with similar consequences. Comments from Dr. Neil Thomson on the ISBS pilot study at Koppers Gainesville are in Attachment B. Furthermore, using a similar technology, Thomson et al., (2008) reported a material decrease in mass discharge and/or total plume mass during monitoring performed 1 and 2 years post-treatment; however, 4 years after treatment, mass discharge and total plume mass for all monitored compounds rebounded to pre-treatment values (Thomson et al., 2008, Rebound of a coal tar creosote plume following partial source zone treatment with permanganate. Journal of Contaminant Hydrology, v. 102, p. 154-171). This article is in Attachment C

- B. Delivery of the ISBS reagent to contaminants under the conditions at the Koppers Gainesville site will be very uncertain. Delivery of the ISBS reagent to the surface of the creosote mass is critical. Beazer's hypothesis is that the ISBS will follow the same high conductivity features as the creosote DNAPL did. However, this phenomenon is likely to be limited by factors including:
 - (1) DNAPL itself is likely blocking at least some of the pathways through which the DNAPL migrated (ISBS solution will not displace creosote DNAPL);
 - (2) ISBS will preferentially flow to highest conductivity pathways that are not blocked by DNAPL, and will have limited contact with creosote that has migrated into more moderate conductivity pathways or pathways which are blocked or partially blocked by

DNAPL. Creosote DNAPL likely has migrated into moderate conductivity as well as high conductivity features because it has had 50 or more years under varying hydrologic conditions to do so. The ISBS pilot test showed clearly that the dense ISBS solution sank to the bottom of the SA causing poor sweep of the aquifer; and

(3) Much of the DNAPL mass is likely interconnected, which provides the mechanism by which DNAPL can continue to migrate. Even if the ISBS reagent is successful in contacting the outside surface of the DNAPL mass, this may not prevent DNAPL from continuing to migrate within the interior of the interconnected DNAPL mass. As you are aware, we disagree with Beazer's conclusion that DNAPL within the UHG and LHG exists primarily as disconnected ganglia.

Adequate distribution of the ISBS reagent was not obtained in the field pilot study at the Koppers Gainesville site.

- C. At this time there is no reliable way to determine if treatment goals are being achieved with ISBS. The treatment goals are to reduce the vertical and horizontal mass loading of DNAPL and dissolved phase constituents. Determination of the effectiveness of ISBS treatment in meeting these goals will require comparison of preand post-treatment contaminant mass loading measurements. It will <u>also</u> require measurement of the reduction in DNAPL vertical mobility. Methods which have been discussed for doing this include:
 - (1) Use of Core Data. The ability of core data to assess performance of ISBS is limited because cores represent a limited snapshot of subsurface conditions, which are likely to vary substantially over very short distances due to heterogeneities in the geology, DNAPL architecture and ISBS solution distribution.
 - (2) Measurement of Dissolved-Phase Mass Loading Using Flux Monitoring Devices. Technologies exist to measure <u>horizontal</u> dissolved phase mass flux. However, to date no method has been proposed to measure <u>vertical</u> mass flux, which is the most critical parameter for this site, as protection of the UFA is the ultimate objective of the treatment system. Horizontal mass flux is not an adequate indicator of vertical mass flux since the transport pathways are different.
 - (3) Use of UFA Extraction System Data to Measure Dissolved-Phase Mass Loading. In order to use UFA extraction system data to estimate mass load, it will be necessary to expand the UFA extraction system so that it captures the entire UFA plume(s). This will require installing pumping wells in the vicinity of the source

areas and expanding the treatment plant capacity to process the *additional* extracted groundwater, i.e., >100 gpm. (FW-31BE is capturing a portion of one plume as it is leaving the site. It is not capturing the entirety of the interior plume(s) such that a mass loading of contamination into the UFA could be assessed). Before the mass load reduction resulting from ISBS treatment could be assessed, data from this capture system would have to be collected and evaluated for a minimum of 1-2 years prior to ISBS treatment and several years (likely 5-10 years or more) post-treatment. The likely long lag time between treatment and UFA response makes this method impractical for determining the success of ISBS treatment in a timely manner. It would be unlikely that EPA could assess the ISBS success in the first 5-year review cycle.

(4) Measurement of Reduction in DNAPL Vertical Mobility. One method which has been proposed to assess the impacts of ISBS on DNAPL mobility is to observe changes in the volume of DNAPL collected in UHG monitoring wells. Five out of 6 of the monitoring wells installed in the UHG consistently yield DNAPL, but there are only 1 or 2 such wells within the footprint of each SA source area. Cessation of DNAPL collection in one of these wells immediately after treatment by ISBS may indicate that lateral DNAPL mobility was reduced in the vicinity of that well. However, this conclusion could not be applied across the entire source area. More UHG wells could be installed prior to ISBS treatment in an attempt to provide a better assessment across the source area. However, an apparent reduction in DNAPL recovery in a well that was recently installed prior to ISBS treatment does not conclusively indicate that the ISBS treatment was successful. An apparent reduction of DNAPL recovery in a recently installed monitoring well could be due to natural variation in DNAPL recovery rates (as observed in existing UHG monitor wells), or alternatively it could be because there was not enough DNAPL volume at that location to maintain a consistent collection rate. Several years of monitoring would be required to demonstrate consistent DNAPL recovery rates at the new wells, in order to conclude with any certainty that reductions in recovery after ISBS were, in fact, due to ISBS treatment. Additionally, even if a reduction in lateral mobility could be demonstrated, this may, or may not, reflect a reduction in vertical mobility.

We do not believe that any of the above proposed metrics will be effective at measuring ISBS performance at the site. There are inherent difficulties with each suggested method, which are described in detail above.

In contrast to ISBS, ISS/S is not plagued with such issues. ISS/S is a wellproven technology which has been used at multiple sites. Since it involves mechanical mixing of soils, distribution of the solidification agents is much less of an issue. To confirm treatment, soil cores of the solidified material can be collected to confirm the spatial extent of treatment. Changes to hydraulic conductivity, compression strength, and leachability in these cores can be easily measured using standardized methods to establish the degree of success of the treatment. Implementation of ISS/S in the SA and UHG will not require the otherwise difficult measurements of mass loadings described above for ISBS in order to assess the effectiveness of the selected remedy.

As we understand it EPA's basis for proposing ISBS in the SA in conjunction with ISS/S in the UHG is that the ISS/S in the UHG will provide a "floor", so that even if the ISBS in the SA is only partially successful, downward mass loading through the UHG will be limited. To be effective, the ISS/S floor will have to be implemented over an area extending well beyond the lateral boundaries of the UHG source zones to ensure that DNAPL from the SA does not migrate downward. In addition, the disturbance of the SA soils due to the augering during ISS/S will change the characteristics of the SA soils. Therefore, a pilot study would have to be carried out demonstrating the proposed ISS/S and ISBS treatment combination. Given the need for a minimum of 4 years (perhaps longer) to evaluate the performance of the ISBS portion of the pilot study, the final remedy for the site would be further delayed. Any further delay in the implementation of a remedy for this site is unacceptable to the City/County and local community.

Since ISS/S in the UHG will require auguring through the SA source area to reach the UHG, we believe it makes the most sense to apply ISS/S in the SA at the same time that it is applied in the UHG (per Alternative OnR-5F). Although EPA's cost estimate for the proposed plan (\$65 million) indicates a cost savings as compared to Alternative OnR-5F, in reality we feel there would be little if any cost advantage of the proposed remedy compared to use of ISS/S in both the SA & UHG (Alternative OnR-5F), particularly in light of the considerable risk that ISBS will not be successful, the likelihood of unforeseen complications with this remedy, and the delays that a combined ISS/S/ISBS pilot study would create. Given the length of time the community has waited for a final remedy for the site, it is important that the final remedy be as robust as possible, provide for the greatest opportunity for achieving the remedial objectives, and be implemented as quickly as possible.

Proposed ISBS Pilot Study

It is our understanding that EPA is considering a plan in which Beazer would implement a full-scale ISBS pilot study in the former process area. The study would be initiated immediately and would be conducted concurrently with remedial design and implementation of the other remedy components (i.e. the slurry wall and other components excluding DNAPL source zone treatment). The stated intention is that the study would not delay the overall remedy implementation, since it would be started immediately, would be conducted during remedial design, and be completed by the time DNAPL source area treatment would be initiated.

Our concerns with this pilot study approach are that: (1) the results of the study and success of the ISBS treatment will be uncertain and subject to much debate (for the reasons described above), and (2) the pilot test will result in a significant delay in remedy implementation. As described above, in research performed by Thomson et al (2008) at the Borden site, which was under much more controlled conditions with much more homogeneous and transmissive geology (in a sandy aquifer) than the Koppers Gainesville site, it took 4 years for the system to reestablish equilibrium after treatment. Given lower transmissivity and the more complex geology at Koppers Gainesville, it is likely to take even more time for the groundwater system to re-equilibrate post-treatment at this site. For these reasons we object to moving forward with the pilot study, and recommend selection and implementation of ISS/S and/or excavation as the remedy for treating SA and UHG source areas.

However, if EPA chooses to move forward with the ISBS pilot study, the study would need to be rigorously designed, implemented, and evaluated and the <u>burden of proving the success of the technology should be on Beazer</u>. The study would need to include the following at a minimum to provide defensible results:

- A. Development of metrics and criteria that can <u>adequately</u> <u>measure ISBS performance within the required timeframe</u> (i.e. the limitations of available performance metrics described above would have to be overcome);
- B. Characterization of DNAPL extent & architecture (the present characterization is not adequate for remedial or pilot study design or performance assessment);
- C. Concurrent pilot testing of ISS/S to provide side-by-side comparison of the technologies, and assist in providing performance criteria for comparison with ISBS;
- D. Pre-treatment monitoring (to establish baseline conditions); and
- E. Post-treatment monitoring, data analysis, and reporting.

Concurrent pilot testing of ISS/S at another source area would provide a side-byside comparison of the two technologies, and would help to provide an indication of the relative success of the ISBS. For example, assuming a methodology can be developed to measure downward mass loading, data from the ISS/S pilot would provide a relative reference point for comparison.

7. We support the Slurry Wall and cap components of the Proposed Remedy. We also support EPA's designation of all DNAPL as a principle threat waste. However, the ROD should also address UHG source areas east of the property boundary that are outside the slurry wall shown in the Feasibility Study.

Slurry walls are a well demonstrated technology for the purposes they are designed for. We believe the slurry wall will minimize lateral movement of contaminants within the SA and UHG. It will not (and is not intended to) affect vertical movement of contaminants in any aquifer unit, or lateral movement of contaminants in the LHG or UFA. Even with the most effective treatment of the DNAPL in the SA and UHG, there will continue to be a dissolved phase plume (or plumes) outside the source zones that will need to be contained. Therefore, the slurry wall will be an important component of any remedy.

We support EPA's designation of all DNAPL as a principle threat waste, and that "remedial actions proposed as a part of this Plan are intended to address DNAPL (i.e. principle threat waste) impacts, regardless of its location or source origination on the Koppers site."

There is evidence of DNAPL within the UHG to the east of the Koppers site which is outside of the footprint of the slurry wall as depicted in the Feasibility Study. Based on borings along the eastern boundary of the site and dissolved phase contamination in UHG wells, it is evident that DNAPL has migrated off-site within the UHG to the vicinity of the HG-26 well cluster on the Cabot Carbon Site. It is not clear from the Proposed Plan if or how these off-site source areas will be addressed. Treatment of DNAPL in these areas should be included in any final remedy since it is a principle threat waste and is an ongoing source of groundwater contamination. The fact that the area to the east of the Koppers site is not owned by Beazer does not preclude them from employing appropriate remedies in this area.

The CSX rail line on the eastern property boundary is unused to the south and terminates at 23rd Avenue. It is our understanding that to the north the closest user is Harwood Brick Distributors, Inc. (northeast of the Koppers site) at 3302 NE 2nd Street. It is important to consider the potential of this unused segment of railroad bed to be incorporated into the Koppers site and used to expand the area of the slurry wall to the east. Although this is a small area, it would provide additional area for containment of contamination in the surficial and UHG.

8. We support use of Chemox or ISBS in the LHG. However, existing LHG monitoring wells should either be retained or replaced.

Treatment of creosote DNAPL to reduce mobility and migration of contaminants into groundwater in the Hawthorn Group to the maximum extent possible is a high priority. We support the concept of injecting Chemox or ISBS into the LHG to immobilize DNAPL to the extent practicable. Although we have concerns about the performance of ISBS, the ability to deliver the reagent to adequately contact all the DNAPL, and the ability to measure the performance of ISBS (described above), we recognize that it is not possible to deploy ISS/S, excavation or other more robust remedies at the depth of the LHG with current technology. The depth, limited permeability and heterogeneity of the geological strata also make injection of Chemox, ISBS or other chemicals difficult. *Limitations of the ability to treat the LHG DNAPL make it all the more critical to employ effective monitoring and hydraulic containment in the UFA*.

The existing LHG monitoring wells are important for monitoring the status of the site and effectiveness of the site remedies. They will be particularly useful in long term monitoring of any remedies employed in the LHG. It would be preferable to retain the existing LHG wells, however, if they cannot be retained when ISS/S is implemented, they should be replaced after ISS/S is implemented. It is important to note that at the present time there are no LHG monitoring wells in the Process Area or South Lagoon – and we believe wells in the LHG are required at both of those source areas.

We do not object to injecting ISBS into a LHG well that must be removed before ISS/S treatment and replaced anyway, although their small diameter is likely to make them poorly suitable as injection wells. However, where possible, existing LHG wells should be retained and used, in conjunction with additional new LHG monitoring wells for long-term monitoring (ISBS or Chemox cannot be injected into wells that will be retained). ISBS or Chemox injection should be performed using new dedicated injection wells.

We propose that the ROD include a provision that Chemox or ISBS will be employed in the LHG using dedicated injection wells with existing, and new monitoring wells (as appropriate) being used to monitor the success of this action. We recommend that implementation of LHG remedies be staged to occur after implementation of the other site remedies to allow time for observing effects of remediation in the UHG and to permit installation of additional monitoring wells after the SA and UHG are stabilized. The exception to this would be that Chemox or ISBS will be deployed to the existing DNAPL impacted LHG monitoring wells that must be removed as part of the SA and UHG remedies.

9. Additional characterization is needed to delineate DNAPL source areas and dissolved phase plumes.

The Proposed Plan appropriately includes: "Expansion of surficial aquifer and HG monitoring network for: (1) establishment of sentinel locations; (2) demonstration of active natural attenuation processes; and (3) establishment of trigger locations

for contingency actions." We request a fourth objective be added to "further delineate DNAPL source areas to define the lateral limits of source zone treatment in the Surficial Aquifer and Hawthorn Group". Source areas should be defined on the basis of visual evidence of NAPL or staining in continuous soil cores or naphthalene concentrations in groundwater in excess of 1,000 ug/L (ppb). Note that the "source area" boundaries presented on plan view figures in the FS and other documents are based on estimated footprints of the lagoons and other areas that existed at the site at one time and the results of investigations of Surficial Aquifer contamination conducted in 2004; they likely underestimate the area over which DNAPL has spread in the SA and in the underlying UHG or LHG. The areas contaminated by residual and mobile DNAPL need to be fully characterized in all aquifers units as part of the remedial design so that remedies will be implemented as effectively as possible.

Additional HG well(s) are needed at the northern boundary to evaluate potential off-site migration in that area. Low levels of Koppers-related organics were detected in a private irrigation well in proximity to the northern boundary of the Koppers site.

The expansion of the surficial aquifer and Hawthorn Group monitoring network should include additional LHG wells near the source areas. At the present time there are no LHG monitoring wells in the Process Area or South Lagoon – we request that the ROD require specifically that such wells be installed.

Finally, the ROD should require characterization to locate potential, but as-yet unidentified, source areas. This includes investigations to determine if buried drums exist at the site, and to determine if there is contamination from other process or waste treatment areas that might have existed outside of the identified source areas.

10. The soil consolidation (if implemented) and cap, and any future development of the site should be configured so as not to significantly obstruct the ability to further treat source zones in the future.

Due to the uncertainties associated with the DNAPL treatments, particularly in the LHG, there may be a future need to further treat source areas and/or to add additional monitoring wells. In addition, there may be advances in technology which will allow more effective treatment. Therefore, the cap and soil consolidation, and any future development should be configured so as to not significantly obstruct the ability to access and treat source areas.

2.0 ON-SITE / OFF-SITE SURFACE SOILS REMEDY

COMMENTS AND RECOMMENDATIONS

- 11. The USEPA Proposed Plan remedy for the surface soils and the future land use assumptions made by USEPA have not been sufficiently coordinated with the City of Gainesville and local stakeholders. Additional coordination with the City of Gainesville and local stakeholders is needed regarding the future land use vision. The final remedy for the Koppers site must meet the following minimum criteria:
 - A. It should be based on an explicit redevelopment vision;
 - B. It should be compatible with a redevelopment scenario that includes a step down in land use types from east to west on the site;
 - C. Clean-up of soils to the west and north of proposed containment area to allow redevelopment with all residential land use categories;
 - D. Industrial re-use should not be considered appropriate land use for the site; and
 - E. Remedy should be compatible with eventual reuse of City of Gainesville Public Works property north of site.

The USEPA's efforts to solicit input from the City of Gainesville and the local community on the final site remedy and especially surface soil remediation and future land use issues has not been timely nor adequate and has not allowed sufficient time to solicit appropriate community input on impacts of the EPA proposed soil remedy. The reuse vision for the site discussed by USEPA's Reuse contractor, E², in presentations to the community has assumed a preselected remedy for soils that is not compatible with the City of Gainesville future redevelopment vision for the site. Insufficient time has been allowed to provide adequate and appropriate involvement from the City and local stakeholders in the remedy selection process.

The Code of Federal Regulation (CFR) Chapter 40, Section 300.430 prescribes clear requirements for EPA's obligations for community involvement prior to and during the RI/FS process and through ROD development. EPA has met few of these obligations. For example, the required Community Involvement Plan was ignored for over 20 years and was only recently updated. The 1989 Community Involvement Plan (CIP) was required to be updated every 3 years (7 times during the past 21 years) to solicit comment from the community throughout the multiple

RI, FS and RAO development process. Instead, the first CIP draft since 1989 was produced *after* EPA released its Proposed Plan. Additionally, the required local information repository at the Alachua County public library was not kept up to date for many years. These inactions on EPA's part denied local Gainesville residents the right to review key documents in the administrative record and provide crucial input to EPA throughout the RI, FS and remedy selection process. These inactions denied the community its rightful role in the selection of appropriate remedies for the site and in determining the types of future uses the site will accommodate following the remedial actions.

The City of Gainesville has previously provided input to EPA regarding its vision for future redevelopment of the site. It is not clear and it has not been communicated to the local community how the USEPA's proposed remediation scenario for the site will impact or limit future redevelopment of the site and how it may comply with the City's redevelopment vision. In particular, USEPA's proposal to meet FDEP commercial soil clean-up target levels (SCTLs) and not residential SCTLs for surface soils in the areas outside of the containment area as well as the construction of a large soil consolidation area will significantly impact future land use and adversely impact the financial health and vitality of surrounding properties and neighborhoods. Additional coordination with the City of Gainesville and local stakeholders is needed regarding the future land use vision. It is critically important to the local acceptance of any final remedy for the Koppers site that it meet the following minimum criteria described above.

The City Commission on June 23, 2008 adopted Resolution No. 071173 that authorized the City Manager to study the present and future land use of the Site including, but not limited to, those areas within the site with the highest levels of contamination, and to recommend any appropriate changes to the future land use and zoning maps that may include residential or mixed residential and commercial uses. The City Plan Board met on September 23, 2010, after receiving public comments and developed a land use policy recommendation for the Koppers site that recommends residential type development outside of the slurry wall area. Such a policy would also amend the City's Comprehensive Plan by adding a policy that will guide the future development of the Site for reuse that does not consider industrial use as an appropriate use for the Site. City staff presented the Plan Board general recommendation to the City Commission on September 27, 2010 and it was well received by the Community and the City Commission. The Comprehensive Plan amendment will be formally presented to the City Commission in the next few months and the amendments to the City's Comprehensive Plan are anticipated to be adopted by the end of summer 2011.

The City of Gainesville is currently developing reuse plans for the 10 acre City Public Works parcel north of the former Koppers Site. It is critical that the reuse plan for the Koppers site be coordinated with and be compatible with the reuse plans developed for the City's property. 11. Landfilling of contaminated on-site and off-site soils and sediments in a large on-site consolidation area is unacceptable to the community. USEPA did not evaluate off-site disposal of excavated surface soils and sediments despite statements in the FS that evaluation of offsite soil disposal would be completed.

The massive soil consolidation area should be eliminated as part of the final remedy and offsite disposal of excavated contaminated soils should be evaluated in an amended FS and considered as part of the final remedy.

USEPA should implement offsite disposal of excavated soils that originate from the area outside of the containment area as well as soils and sediments removed from adjacent residential and commercial properties, rights of way and creeks.

The City and County and the local community strongly object to the creation of a large, thirty-two acre soil consolidation area on top of the source area containment cap which could contain from 190,000 to 240,000 cu yds of soils contaminated with dioxins, arsenic, polynuclear aromatic compounds (PAHs) and other toxic soil contaminants. According to the presentation given to the local community on June 14, 2010 by E^2 , the land reuse consultant hired by USEPA, the height of this soil consolidation area may be as high as 8 to 10 feet above current land surface with a 3:1 slope on the sides. The community finds the magnitude of this soil consolidation area filled with toxic soils to be highly objectionable. The City and County request that this massive soil consolidation area be eliminated as part of the final remedy and that offsite disposal of excavated contaminated soils be evaluated in an amended FS and considered as part of the final remedy. Should soil cover be required as part of the low permeability cap over the source areas it should be constructed with the minimum height necessary for proper cover and drainage and the soils used should be uncontaminated clean soils.

The City and County believe that the creation of a significant soil consolidation area will significantly limit the types and amount of redevelopment possible for the property in the future. It will create a permanent mound of contaminated soils in the middle of the City of Gainesville that is incompatible with the adjacent urban residential and commercial areas.

In the Feasibility Study report, Section 2.6 presents "the technologies that will be carried forward in the evaluations based on the screening evaluations presented in Sections 2.4 and 2.5." (See page 2-44 of the FS report). Specifically included in Section 2.6.6 in the list of technologies to be evaluated in detail in the FS for untreated soils is "offsite landfill disposal". (See page 2-46 of the Koppers site FS report).

In spite of making a commitment in Section 2.6.6 to evaluate offsite soil disposal in detail, not a single remedial alternative in the FS report included an evaluation of offsite soil disposal, even for minimally contaminated soils. In fact the complete set of alternatives evaluated is consistent in that none of them considered the removal of any contamination from the site.

It appears that USEPA made a pre-determined decision during the FS to not evaluate any off-site disposal alternatives and to, in effect, turn the Koppers site into a permanent waste disposal facility for all on-site and off-site contamination. This decision was made without any effort to assess the benefits that removal of contaminated soil would have on the redevelopment potential of the site or other factors and with disregard to its statements in the FS report that offsite disposal would, in fact, be evaluated.

The City and County request that USEPA complete the evaluation of remedial alternatives that include offsite soil disposal as stated in the FS. The City and County request that USEPA implement offsite disposal of excavated soils that originate from the area outside of the containment area as well as soils and sediments removed from adjacent residential and commercial properties, rights of way and creeks.

The City's Wellfield Protection Code (section 30-200 through 30-204) would require a Wellfield Protection Special Use Permit for the landfilling of offsite hazardous waste materials on the Koppers site. Section 30-70 treats processes involving inorganic and organic chemicals as a specially regulated industry and is only allowed by special use permit. City staff is not likely to recommend the relocation of off-site soils and sediments because this area is within the wellfield protection zone. The City's own practice is to remove onsite contaminated soils and sediments, as performed on the Depot Park Site on South Main Street, and to transport such soils and sediments to a proper treatment facility.

12. The USEPA Proposed Plan remedy for surface soils for the area outside of the containment area is excessively vague about the specific actions that will be taken to meet FDEP SCTLs in this area. It is not clear if FDEP SCTLs will be met by covering contaminated soils or by removal of contamination followed by appropriate clean fill cover. There is also no detailed discussion of how FDEP Leaching Criteria will be met.

USEPA should provide more detail in an amended FS and commitment regarding specific actions to be taken to remediate soils in the western and northern areas outside of the proposed containment area.

Specific actions to be taken to remediate or address the elevated "hot spots" needs to be specified in the plan or ROD.

The proposed remedy for on-site non-source area surface soils is extremely vague regarding specific remedial actions to be implemented at specific areas of

surface soil at the site. According to the proposed plan, some surface soil could be excavated and consolidated under caps in the source zones (the Consolidation Area), some surface soil could be graded, and some surface soil could be graded and placed beneath a cap of unspecified composition outside of the source zones. The Feasibility Study (FS) report includes an even longer list of potential actions that might be implemented at any particular location for onsite surface soil, including:

- A. Excavation only
- B. Excavation with a 2 ft cover
- C. Placement of a two-foot soil cover without excavation
- D. Placement of a two-foot thick impermeable cover/cap
- E. Covering with a road and or paved parking area
- F. Covering with structures (e.g., buildings) that prevent soil exposure
- G. Placement of a lined treatment pond over exposed soil

The Proposed Plan does not specify at what locations any of these potential remedial actions will be applied. There are costs presented in the FS for excavation of 24 acres of surface soils, however it is not clear the source of this estimated amount of excavated soils and the locations from which it is to be excavated. This vagueness makes it impossible to understand what the site will look like after remediation, and most importantly, to understand the impacts of the remedial action on the potential for future site redevelopment.

The City and County object to this vagueness and believe that USEPA should be much more specific about remedial actions proposed for each area of surface soil at the site. The City and County are concerned that the potential surface soil remedies listed above will be applied in a hodgepodge manner that will seriously reduce the ease of and could in fact hinder redevelopment of the site. The City and County are also concerned that the remedial approach will be to simply cover contaminated soil with clean fill in an attempt to minimize the need to remove contaminated soils.

USEPA should especially provide more detail and commitment regarding specific actions to be taken to remediate soils in the western and northern areas outside of the proposed containment area. In particular, specific actions to be taken to remediate or address the elevated "hot spots" where contamination at levels significantly above FDEP SCTLs exists in the surface soils such as in the central western boundary of the site and in the northern wooded area (See Figures 3, 4 and 5) should be described in detail (that is, whether this area will be excavated, if so, to what depth, or whether two feet of clean soil will simply be dumped on it). Greater specificity will enable all parties to understand the degree to which the

selected remedial approach will facilitate or hinder future site development and provide details on how much contamination will remain on site.

13. Covering of contaminated soils outside of the containment area leaves permanent soil contamination and limits options for future redevelopment. Removal of contaminated soils in areas outside of the containment area should be prioritized before any soil covers are applied.

Achieving FDEP Residential soil clean-up criteria for the entire area outside of the containment area but especially the areas near the western and northern boundary of the site should be targeted by the plan as the preferred alternative. This is a strong preference of the local community.

USEPA should amend the FS and provide separate cost calculations for the alternatives of removal of all contaminated surface soils outside of the containment area that are above FDEP residential or commercial SCTLs and leaching criteria.

The Koppers site is located in the heart of the City of Gainesville amidst an area of long established residential communities. The City of Gainesville has promoted "infill development," as opposed to urban sprawl, for many years. Maximizing the potential for redevelopment of the site is a crucial concern for the City and community.

For these reasons, the selected remedy should:

- A. Maximize <u>removal</u> and <u>not covering</u> of soils in areas outside the containment area and,
- B. Require removal of all contaminated surface soils outside of the containment area that exceed FDEP Residential SCTLs or FDEP Leachability SCTLs down to the water table.

USEPA should amend the FS and provide separate cost calculations for the alternatives of removal of contaminated surface soils outside of the containment area that are above FDEP residential <u>and</u> commercial SCTLs and Leaching criteria. By doing so, a decision can be made as to the feasibility of cleaning up these surface soils to meet commercial or the more stringent residential SCTLs by excavation. For example, review of the surface soil data from the site appears to indicate that removal of up to 2 feet of soils in several areas of the approximately 300 foot wide area near the western and northern boundary and in several additional locations in the areas outside of the consolidation area may allow reaching of FDEP residential SCTLs for dioxin and benzo-a-pyrene toxicity equivalents (TEQ) and potentially for arsenic impacts as well (See Figures 3, 4 and 5). Such a removal of surface soils along with a commitment to remove soils

from "hot spots" in this boundary area and in the northern area will provide more flexibility for future redevelopment of this property and minimize concerns about contamination from adjacent residential areas. This approach is a strong preference of the community. The City and County would like to see serious commitment to approaches that maximize removal of contamination in the area outside of the containment area.

14. Other unknown, potential source areas outside of the containment area may exist and may be covered or not identified in the soil remedy. These potential additional source areas need to identified and remediated in the final remedy.

Inspection of historic aerial photographs for the site indicates the potential presence of disposal trenches in the northern portion of the site. In addition, former site workers and local residents have indicated that some portions of the site may have been used for buried drum disposal or other waste disposal activities. Considering that the site was used as a heavy industrial facility for nearly 100 years, there is a significant possibility that areas of the site in addition to those currently being considered for remediation to have been used for waste disposal practices. USEPA should implement a site-wide screening and investigation to evaluate the presence of additional disposal or source areas at the site and conduct appropriate removal or treatment any additional source areas identified.

15. The off-site delineation of soil contamination is incomplete and must be expedited, in particular in the adjacent residential neighborhood in which residents continue to be exposed to Koppers contamination.

The City and County strongly support the proposed USEPA plan to complete the delineation of dioxin and other offsite contaminants to the State of Florida residential SCTLs for residential properties and FDEP commercial SCTLs for commercial properties. The City and County are against any effort to develop alternate clean-up standards for these offsite properties that will provide a lesser degree of protection of our citizens. State of Florida Residential SCTLs should also be met on all properties currently associated with residential uses.

Additional offsite soil sampling needs to be performed sufficiently beyond the point where the FDEP SCTLs are initially achieved to confirm that soil concentrations remain at or below the FDEP SCTL levels.

Additional offsite sampling should also be performed on and west of NW 6th Street west of the Koppers site to assure that commercial and residential areas on and west of NW 6th Street have not been impacted.

Additional offsite soil sampling should be performed on nearby school properties to confirm that these soils do not pose a risk to children's health.

Irrigation wells on nearby contamination impacted properties that are proposed for remediation in the offsite soil remedy should be identified by USEPA, sampled and tested for Koppers chemicals of concern and properly abandoned if determined to be contaminated or pose a threat to water quality.

The investigation into the extent of contamination at this site has been ongoing for several decades and is still incomplete. Based on recently obtained offsite soils data, it appears that residents adjacent to the site have been exposed to contamination from the Koppers site that has migrated onto their property. The City and County are concerned about the length of time it has taken USEPA to complete the offsite delineation of contaminated properties and reduce the exposure potential to offsite residents. The City and County urgently request that USEPA expedite the delineation and remediation of off-site contaminated areas.

The City and County are concerned that planned USEPA delineation of contamination on residential and commercial property in the neighborhood west of the Koppers site may cease when FDEP Residential SCTLs are reached on residential properties or FDEP commercial SCTLs are reached on commercial properties near the east side of NW 6th Street. Since commercial standards are higher than residential standards and the potential that windborne contaminants may have historically impacted a wider area, the achievement of commercial standards on the properties east of NW 6th Street may not provide assurance that either commercial or residential SCTLs are achieved on commercial and residential properties west of NW 6th Street. There are residential properties immediately west of NW 6th Street that should be investigated to assure residents that there are no impacts from Koppers contamination. The City and County are requesting that delineating the extent of soil contamination must include soil sampling on and west of NW 6th Street.

In addition, offsite sampling needs to be performed sufficiently beyond the point where the FDEP SCTLs are initially achieved to confirm that soil concentrations remain at or below the FDEP SCTL levels. In particular, the City and County and the local citizens are requesting that USEPA collect and analyze additional soil samples in the residential areas to the north of NW 33rd Ave north of the Koppers site. Although several soil samples along the southern right of way along NW 33rd Avenue were found not to contain contamination above the FDEP residential SCTL, considering the statistical variability and imprecision associated with sampling and testing for very low levels of dioxins in soils, the long term nature of historical discharges from the Koppers site, the shifting wind patterns, variable tree cover and stormwater flows which may have created pathways for the spread of contamination, it is important to confirm that areas north of the 33rd Ave and other such assumed limits of contamination are in fact free from impacts.

This is especially important due to the increased citizen concern and apprehension about impacts to their health and property values from being perceived to be close to a contaminated zone.

Due to the presence of offsite soil contamination in nearby neighborhood rightsof-ways, concern has been raised by the community about the impact of Koppers related contaminants on the soils at nearby public and private schools. USEPA is requested to sample and test the surface soils of school properties within a 2 mile radius of the Koppers site to determine whether the soil concentration of contaminants poses any risks to human health.

Irrigation wells are known to exist on offsite residential properties adjacent to the Koppers site. These wells may have been impacted by Koppers contamination. USEPA is requested to locate, sample and test these wells during any remediation of offsite properties and to require the proper abandonment of those wells that are contaminated or pose a threat to aquifer water quality.

16. The City and County and nearby residents are concerned about long term safety of USEPA proposed remedial plan for offsite contaminated soils which will allow property owners to select either excavation or engineering controls or institutional controls as the remedy for offsite properties. USEPA should restrict the use of engineering or institutional controls for offsite properties, especially those that will remain in separate individual resident ownership where it will be difficult to enforce institutional controls. USEPA should require that offsite residential properties are cleaned using removal and restoration as a preferred remedy rather than engineering or institutional controls.

Allowing engineering or institutional controls to be an option for offsite properties at the discretion of the property owner instead of requiring excavation of contamination and restoration raises significant concerns if the current property owner or future property owner does not abide by the engineering or institutional restrictions. This could cause the contamination in the soils to be exposed and cause a health risk to the new property owner and adjacent neighbors. This would be of particular concern with residential properties, although it is also a concern for commercial properties. The City and County want to avoid the possibility of creating a "hodgepodge" scattered pattern of cleaned and not cleaned properties in the neighborhood which will cause environmental concerns for future human exposure to toxic contaminants to remain in the neighborhood as well as impact property values. The City and County request that USEPA restrict the use of engineering or institutional controls on offsite properties that will remain in separate individual property ownership where engineering or institutional controls cannot be practically enforced or monitored.

3.0 OTHER OFFSITE IMPACTS

COMMENTS AND RECOMMENDATIONS

17. Neighboring residents to the Koppers site have expressed concern about the potential for indoor contamination of their homes. The Florida Department of Health has requested that USEPA require Beazer East investigate and clean-up nearby structures that have dust with site related contaminants that pose an unacceptable risk to human health. The City and County request that USEPA conduct appropriate investigations including sampling and take necessary remedial actions to address this issue.

Residents living west of the Koppers site have communicated to local government officials their concerns about potential indoor contamination of their residences based on independent testing using a USEPA screening analytical method for dioxin-like chemicals. The reliability of these test data have not been evaluated by the City, County or the local Health Department. However, because much of the migration of contamination from the Koppers site to offsite residential property likely occurred via air-borne transport of small particulates (i.e., contaminated dirt and dust) it is reasonable to expect that offsite properties with soil contamination may also have experienced deposition of these same particulates inside the homes.

The Florida Department of Health (FDOH) in a September 24, 2010 letter to Mr. Scott Miller of USEPA stated that "EPA should require the responsible party to investigate site related contaminants in the dust of nearby homes, schools, and businesses." The FDOH letter stated that "the 2009 AMEC Earth and Environmental, Inc. report is inadequate to assess this issue since it only addresses on site dust deposition under current conditions and does not address past off-site dust deposition. The report further states that the "EPA should require the responsible party to remediate nearby buildings found to have dust with site related contaminants at levels that pose an unacceptable health risk".

Because of the reasonable assumption that nearby homes and structures, structures may be contaminated, the recommendation of FDOH and the increasing anxiety of local residents concerning this issue, the City and County request that USEPA expeditiously take whatever actions are necessary to investigate and address this issue including sampling within nearby homes, businesses and schools (with the property owners consent) in the area to determine the degree to which the interiors of these structures may have been impacted by contamination from the Koppers site and take appropriate remedial actions.

18. The City and County recommend that USEPA identify and facilitate the mobilization of resources to address adverse health effects of individuals via a door-to-door health study in the neighborhood affected by the Koppers Superfund site contaminants, including but not limited to dioxins. To the extent that adverse health impacts are found to result from the Koppers offsite contamination, the USEPA is requested to enforce financial responsibility requirements on Beazer East.

Neighboring residents to the Koppers Superfund site have expressed to the local City and County officials and the Alachua County Health Department/Florida Department of Health their concern about what they believe to be adverse health impacts to residents in the neighborhood west of the Koppers site that they believe may be linked to Koppers site contaminants. The City and County believe it is important to investigate these concerns and request that USEPA identify and facilitate the mobilization of resources to address adverse health effects of individuals via a door-to-door health survey in the neighborhood affected by Koppers site contaminants, including but not limited to dioxins. To the extent that adverse health impacts are found to result from the Koppers offsite contamination, the USEPA is requested to enforce financial responsibility requirements on Beazer East.

19. USEPA should provide for permanent relocation assistance for residents near the Koppers site. Temporary relocation assistance should also be provided for residents if desired by the residents during offsite and on-site remediation activities.

The USEPA should also calculate the lost property value of homes impacted by contamination from the Koppers site and address the issue of providing compensation for property owners.

Relocation assistance for temporary and permanent relocation of residents adjacent to Superfund sites has been provided or required by USEPA at other Superfund site with similar contamination as the Koppers site and with similar proximity to residential property and receptors. Such relocation assistance is appropriate during remediation activities involving a large degree of soil disturbance such as is contemplated in the proposed plan. Such actions have a significant potential for creating further offsite impacts.

For these reasons, USEPA should provide for temporary relocation assistance to residents adjacent to or near the site during soil remediation activities. This relocation assistance is especially important for residents that are most vulnerable to potential health impacts, such as the elderly, very young or pregnant residents, or those with existing respiratory or related health problems. USEPA should also offer the option for permanent relocation of residents living

on properties that are within the delineated area impacted by contaminants from the site as a means to reduce their ongoing exposure.

Neighboring residents to the west of the Koppers site have reported to local government that their property values have been significantly negatively impacted by the recent discovery of contamination above FDEP SCTLs in the rights of ways in their neighborhood. Planned residential property sampling in the neighborhood may confirm that the contamination is widespread in the neighborhood. While USEPA's proposed plan calls for the clean-up of contaminated offsite soils, there is a contamination stigma now attached to these properties. The City and County request that USEPA address this situation by calculating the lost property value of the homes impacted by the contamination in the neighborhood and providing compensation to impacted property owners.

4.0 STORMWATER REMEDY

COMMENTS AND RECOMMENDATIONS

20. The Proposed Plan is overly brief in stormwater strategy and controls that are integral elements of the remedial action plan for the Site. The Plan does not include strategy, design criteria, essential site data and final cover landscaping descriptions. Additionally, the stormwater remedy should include the use of an underground pipe to replace the open stormwater ditch on the site.

The City and County requests that USEPA acknowledge these critical issues in the ROD and that USEPA commit to addressing them in the Remedial Design document.

The Proposed Plan does not include strategy, design criteria, essential site data and final cover landscaping descriptions. This information is essential to the City of Gainesville and the public to assess the quality of the plan in addressing pertinent stormwater issues and assessing the consistency of the associated redevelopment benefits/barriers of the Plan with the City's 'Vision' for this piece of Gainesville. Critical stormwater design and control issues that should be acknowledged and addressed in the ROD and Remedial Design documents include options for: 1) management of westerly neighborhood stormwater flows; 2) major ditch flows in conflict with the containment area; and 3) east side site stormwater flows where the containment area is very close to the property line. Conceptual level descriptions of these will aid in the review and understanding more fully the consequences of the choices posed in the proposed plan.

Control issues should include development of: 1) design criteria for stormwater; 2) soils data for the remaining former work area of the Site, and; 3) landscaping descriptions. The stormwater design criteria should include local industry standards as well as City of Gainesville requirements for the Hogtown Creek basin. These criteria should also include an analysis that determines the likely soil particle size to provide transport to site pollutants during storm flows. This analysis can then be used to determine the appropriate detention time for the basin(s) needed to capture the majority of those particles. Soil data is needed on the remainder of the former work area to determine thickness and extent of the compacted soil. This data will lead to an action plan to return the parent soil infiltration rate. Finally, outline work descriptions and specifications are needed for landscaping. This information is essential to evaluating elements of the stormwater design criteria and making judgments on how 'finished' the Site will be for future use.

The City and County request that Remedial Design and Proposed Plan include a commitment to implement a piped conveyance instead of an open stormwater

ditch for the stormwater leaving NW 23rd Avenue and crossing the site. This will minimize potential transport of contaminated sediments from the site.

5.0 CREEK SEDIMENT REMEDY

COMMENTS AND RECOMMENDATIONS

21. Cleanup of the sediments in Hogtown and Springstead Creeks is proposed only for those areas where contaminants exceed benthic Probable Effects Concentrations (PECs). However, FDEP has determined that exposed creek sediments potentially pose human health risks.

Contaminated sediments in both Hogtown and Springstead Creeks and the on-site and offsite stormwater ditches that lead to Springstead Creek must be excavated to the more stringent of the FDEP residential SCTL or the PEC for each chemical of concern. Excavated sediments should not be consolidated on-site.

In the Proposed Plan, USEPA has indicated that it plans to remediate creek sediments only where contamination exceeds the benthic Probable Effects Concentrations (PEC). This is inadequate.

FDEP has concluded that the exposed contaminated soils in the streambed and in other exposed sediments in these creeks pose a potential human health risk. Additionally, cleanup of the on-site and off-site stromwater ditches that lead to Springstead Creek is not addressed in the Proposed Plan.

For these reasons, contaminated sediments in both Hogtown and Springstead Creeks and the onsite and offsite ditches must be excavated to the more stringent of the FDEP residential SCTL or the PEC for each chemical of concern. Appropriate sediment confirmation sampling must be done after remediation to confirm that the excavation of these sediments is adequate.

The USEPA proposed plan states that contaminated sediments above FDEP criteria will be excavated from the creeks. Since the creek contamination may be linked to historical discharges from the former Cabot site as well as from the Koppers site, it is not clear which responsible party will be responsible for the remediation. The City and County understand that the Cabot Corporation has proposed a plan to remove tarry contamination from several locations in Springstead and Hogtown Creek. Review of this plan indicates that contaminated sediments will be disposed of off-site at an approved landfill. Therefore the USEPA proposal to move sediments on site is confusing and contradictory. USEPA should require that excavated, contaminated creek and ditch sediments be disposed of properly in an approve landfill and not stockpiled on site.

6.0 ADDITIONAL COMMENTS

22. The USEPA should make available in the local repository a complete Site file containing all project documents, correspondence and data related to the remedial investigation, risk assessment, feasibility study and remedial technology evaluation for the Koppers Superfund site.

Additionally, the City and County request that additional relevant documents be added to the Administrative Record File. The documents requested to be added to the Administrative Record file are contained in the attached electronic files (CD attached).

The City and County support and acknowledge that certain requests have been made to USEPA from the local community, including the group Protect Gainesville's Citizen's, Inc. (PGCI), seeking local access to the complete Site File documents and requesting that additional relevant documents be added to the Administrative Record. On June 1, 2010, the Mayor of Gainesville sent a letter to USEPA requesting that the information requested by PCGI be provide as soon as possible. A complete Site File has not been made readily available by USEPA to the community in the local repository. USEPA has provided a CD containing the Administrative Record to the local repository. However, there are many documents that we and/or local citizens believe are relevant to the site which are not part of the AR and are not in the local repository. Therefore, the City and County request the following:

- 1) The USEPA make available in the local repository a complete Site file containing all project documents, correspondence and data related to the remedial investigation, risk assessment, feasibility study and remedial technology evaluation for the Koppers Superfund site, and
- 2) Additional relevant documents identified by our citizens and City and County staff should be added to the Administrative Record File. The documents requested to be added to the Administrative Record file are provided as electronic files in the CD attached to this document and should be considered part of this document.

Figures

Well ID Mar. '09 May Aug. Nov.	FIAT20B FIAL29C FW-25B	Well ID Mar. '09 May Aug. Nov. FW-26B	
Well ID Mar. '09 May Aug. Nov.	FW-25C	FW-26C	
Well ID Zone May June Sept. Dec. Mar. June Sept. Dec. Feb. June Sept. Dec. Feb. May Aug.		Well ID Zone July '07 Sept. Dec. Feb. June Sept. D	ec. Feb. May Aug.
FW-23B 1 **1.3 2.5 J 3.5 B -		FW-23C 1 14 - </th <th></th>	
Well ID Zone June '07 Sept. Dec. Feb. June Sept. Dec. Feb. May Aug. FW-22C 1 1.6 J 1.1 J B -		Well ID Zone July '07 Sept. Dec. Mar. June Sept. Dec. F FW-4C 1 0.99 BJ - - - - 1 1	Teb. May Aug. .2 J -
	EW 22D	3 3.3 BJ 0.56 J	
Well ID Zone Sept. '06 Dec. Mar. June Sept. Dec. Feb. June Sept. Dec. Feb. May Aug.	FW-20B	Well ID Zone July Sept. Dec. Mar. June Sept.	Dec. Feb. June Sept. Dec. Feb. May Aug. Nov. Jan.
PVV-22B 1 - - - 0.63 - - - - - - - - - - - - - - - - - - - 13 17 5.3 J 6.6 21 58 - - - - 13 17 5.3 J 6.6 21 58 - - - 24 20 31 48 120 110 -	FW-22C	FW-20B 1 650 720 510 550 450 380 2 370 140 120 140 85 94 3 - 2.4 J 1.6 J - - - 5	210 450 260 310 420 730 1000 870 1200 690 99 49 100 58 73 96 150 170 83 63 5.8 B - - - - 5.9 J 1.6 J
	FW-31BE FW-4	4 0.89 J 2	2 J B 5.8 -
Well ID Zone July '07 Sept. Dec. Feb. June Sept. Dec. Feb. May Aug. FW-24B 1 - - - - - 4.7 J - 2 - 0.95 J - - - - - -	FW/24C EW/30B	FW-4C Well ID June Sept. Dec. Mar. July Sept. Dec. Feb FW-6 450 **535 380 **350 480 110 180 150	June Sept. Dec. Feb. May Aug. Nov. Jan.
3 1.3 BJ 0.95 J	FW-24B		
Well ID Zone July '07 Sept. Dec. Feb. June Sept. Dec. Feb. May Aug.	FW-27B	Well ID Zone Sept. '06 Dec. Mar. June Sept. De	c. Feb. June Sept. Dec. Feb. May Aug.
FW-24C 1 3 BJ -		FW-15B 1 - - - 4.8 2 - - - 0.46	
	FW-11BT FW-12B FW-13B WY-45	<u> </u>	5 - 4.3 J
Well ID Zone June Sept. Dec. Feb. June Sept. June June Sept. <th< th=""><th>FW-20B + EW-15B +</th><th>Well ID Zone June Sept. Dec. Mar. June Sept. FW-16B 1 9.9 15 16 16 28 29</th><th>Dec. Feb. June Sept. Dec. Feb. May Aug. Nov. Jan. 35 26 31 28 35 24 36 30 27 30</th></th<>	FW-20B + EW-15B +	Well ID Zone June Sept. Dec. Mar. June Sept. FW-16B 1 9.9 15 16 16 28 29	Dec. Feb. June Sept. Dec. Feb. May Aug. Nov. Jan. 35 26 31 28 35 24 36 30 27 30
2 - <th>FW-10B</th> <th></th> <th><u> IJI.5JB 4.11J -</u> <u> 1.1JB 1.9IJ -</u> 1.5JB 1.7JB0.9UJ - 5IJ -</th>	FW-10B		<u> IJI.5JB 4.11J -</u> <u> 1.1JB 1.9IJ -</u> 1.5JB 1.7JB0.9UJ - 5IJ -
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PVV-12B 1 45 40 43 40 47 47,75 11 46 53 40 63 83 83 91 17 2 15 12 17 15 16 21 21 B 6.1 4.5 J - - 1.2 J B - 1.2 J J 1.4 3 **455 370 410 540 780 830 550 760 870 770 280 750 950 970 680 7	4 I J 50 FW-16B-	2 **150 170 76 210 77 480 3 120 67 56 56 37 180 9	10 90 33 36 32 9.6 38 10 200 **170 5.7 - 28 - - 7.6 - NS NS
4 650 630 550 620 780 630 500 240 330 570 430 590 690 680 220 3	60 FW-21B	4 14 1.3 J 7.5 - 13 - 3	8 J - 27 NS NS
Well ID June Sept. Dec. Mar. July Sept. Dec. Feb. June Sept. Dec. Feb. May Aug. FW-3 - - - 0.86 J - **- - - 2 J - **0.93 UJ - **2.1 J	FW-5		Naphthalene Concentrations, Koppers Site, 2006 - 2010
			Koppers Site, 2000 - 2010
Approximate Screen Depths of 'B' Wells			DNAPL Source Area
Zone 1 156 to 166 ft bls			Extraction Well Single Screen Wells Multiport 'B' Wells
Zone 2 176 to 186 ft bls	FW-17B		New Single Screen Wells Multiport 'C' Wells
Zone 4 216 to 226 ft bls			NS = Not sampled
			Bold = Napthalene concentration is at or above GCTL (14 ug/L) "- " = Below laboratory detection limit
Approvimate Sampling			" ** " = Value represents average of primary and duplicate samples
Port Depths of 'C' Wells			"J" = Estimated value "UJ" = Estimated non-detect
Zone 1 315 ft bls			"B" = Indicates analyte was detected in the blank
Zone 2 342 ft bls		Figure 1	" I " = Indicates interference in blank 0 200 400
Zone 4 365 ft bls	FW-8		Feet 1:4,800 N








Attachment A Comments on ISBS Treatment at Koppers, Denver, Neil R. Thomson, August 24, 2010

Comments on ISBS Treatment at Koppers, Denver

Neil R. Thomson August 24, 2010

Phase 1 (2003)

Background

Treatment Target

- LNAPL in Zone A (alluvial deposits/cobbly sand)
- 8% saturation
- creosote/pentachlorophenol NAPLs (LNAPL in Zone A and DNAPL in Zone B)
- 2 foot thick saturated zone
- "Data indicate that most NAPL accumulations at the site are at or below residual saturation, and are therefore immobile" (pg 3)
- "results of laboratory analysis support in-situ pilot tests that demonstrate significant LNAPL and DNAPL recovery is technically impracticable at the site" (pg 3)
- pilot scale area 75 ft x 95 ft in off-site area
- 13 injection points (5 ft screen) installed to top of Zone B (bedrock)
- 1,850 gallons (7000 L) of 30 g/L KMnO₄ per well in 2 episodes at low pressure

Relevant Treatment Objectives

- "reduce the free-phase NAPL thickness and recovery volumes in wells within the defined test area" (pg 3)
- "evaluate the ability of the ISBS processes to stabilize creosote/penta NAPL residuals" (pg 4)

Performance Monitoring

- monitoring of 17 wells (field parameters only)
- water level and NAPL thickness
- soil borings (5 in treatment area and 2 (controls) in up-gradient on-site area) to top of Zone B
- samples from borings analysed for total PAHs/penta and leachable PAHs/penta

Results

- R1. "discernible" decrease in LNAPL thickness in wells in treatment area and no "discernible" LNAPL thickness in wells outside treatment area (pg 15)
- R2. following treatment NAPL recovery decreased by greater than 40% in 4 of 5 wells (pg 16)
- R3. comparisons between the treated and background soil boring samples
 - "indicate a 19% decrease in the total PAH residual mass" (pg 16)
 - "indicate a 76% decrease in the total PAH leachable from the treated soils" (pg 17)
 - indicate "a 53% reduction in the residual mass of total chlorinated phenols" (pg 17)
 - indicate "no differences in the amounts of leachable chlorinated phenols between the treated and un-treated soils" (pg 17)

Issues

- 1. If the NAPL was truly non-mobile then why was if being collected in wells? Seems like a site characterization problem and a flaw in the CSM.
- 2. It is well known that hydraulic fluctuations can alter LNAPL distribution and the observed thicknesses in wells. The injection of 91,000 L of 30 g/L permanganate solution into the treatment zone would have caused substantial changes in the hydraulic regime in this area clearly impacting the LNAPL distribution. The non-treatment area did not receive an equivalent hydraulic perturbation and hence this is not a fair comparison. Results R1 and R2, which are jointly connected, are not supported by the site data collected. Moreover, NAPL flow into wells can be a highly transient and sporadic process. Little pre-treatment NAPL thickness time series data were collected and no attempt at a trend analysis (aside from visual) was reported.
- 3. Use of soil boring data to make conclusive statements about the treatability of a heterogeneous NAPL impacted zone is plagued with numerous problems related to "representativeness". To have any confidence in the results an appropriate statistical sample population is required.

The statements listed under R3 are based on 2 background (control) samples and 4 treatment samples. Two samples are insufficient to calculate a sample variance. Data in Tables 4 to 7 indicate other sample data were available but excluded from the calculations with no justification.

The control samples are not really controls since they were not subjected to the same hydraulic conditions as the treatment samples – again an unfair comparison.

No statistical significance testing was preformed clearly ignoring the high degree of concentration variability in both the control and treatment samples. Table A (below) provides an example analysis for the total PAH soil residuals (data extracted from Table 4). The results indicate that the mean total PAH residual mass for the control and treatment cores are not statistically different (assuming that the standard assumptions hold for a *t*-test).

In conclusion this sparse and highly variable data set does not appear to support the statements listed under R3 (note a comprehensive analysis of the all data would need to be undertake before a definitive conclusion could be supported).

Statistic	Control	Treatment				
	13274	2515				
	5916	10402				
	11478	7207				
	3587	10961				
n	4	4				
mean	8564	7771				
variance	20819310	15013964				
STDEV	4563	3875				
t stat	0.265					
t crit	2.45	(5% LOS)				
accept null hypothesis / no						
difference between means						

Table A. Example statistical analysis.

Phase 2 (2004)

Background

Treatment Target

- NAPLs on Dewy Lake Property (off site)
- area of 22,667 ft²
- injection 350,000 L of 30 g/L KMnO₄ solution
- 44 injection points and 3 trenches (3 to 6 feet to top of bedrock)

Relevant Treatment Objectives

- Not provided

Performance Monitoring

- Not provided (some baseline soil samples were collected from 6 borings)

Results

- Not provided

Attachment B Comments on ISBS Pilot Scale Study Report, Neil R. Thomson, September 7, 2010

Comments on ISBS Pilot Scale Study Report

I have reviewed the following documents associated with the ISBS Pilot Scale Test:

ISBS Pilot Test Final Report (dated January, 2009)
Appendix A - Phase I Field Report (dated March 31, 2008)
Appendix E - Drilling and Well Installation (dated April 2, 2008)
GRU Comments to Phase1-ISBS-Field Pilot Study Report (undated)
GRU Comments on the ISBS Pilot Study Report (dated February 27, 2009)
Beazer Response to ACEPD Comments on ISBS Report (dated June 1, 1009)
Beazer Response to GRU Comments on ISBS Report (dated June 1, 2009)
Mueller et al., Battelle ppt Presentation (May, 2010)

I will not repeat many of the comments made by both the GRU Team and the ACEPD, but will identify them at the appropriate location. Also, I will restrict this review to ISBS and not provide comments on the groundwater variance sampling issue.

For appropriate background and context for this review, I prepared a summary of permanganate oxidation of creosote NAPLs (Appendix A) that contains relevant discussion of permanganate chemistry, oxidation induced weathering, enhanced mass removal, precipitate formation, and the *in situ* bio-chemical stabilization (ISBS) concept. I have also provided a summary of the limited information I have been able to gather on the Carus RemOx EC Stabilisation Reagent which was used in this pilot test.

Background Summary

As stated on pg 9 of the ISBS Pilot Test Final Report, the specific objectives of this pilot study were to:

- 1. "Validate the ability of the ISBS reagent to stabilize NAPL residuals (defined herein as phase separated but non-mobile hydrocarbons)";
- 2. "Confirm the effectiveness of the selected construction methods to properly introduce the ISBS reagents into the subsurface";
- 3. "Identify the composition of the developed "crusts", degree of encapsulation, and reduction in permeability produced by ISBS"; and
- 4. "Estimate the longevity of the stabilized matrix under in situ conditions."

The approach was to apply the stabilization reagent (SR) in the surficial aquifer (SA) at the former North Lagoon Area. Groundwater flow is to the northeast at ~21 ft/day. The water table was ~12 ft bgs and the top of the HG upper clay is at ~ 20 ft bgs. Two different SR delivery methods were used in two areas: temporary injection points (TIPs) and direct injection points

(DIPs). Only 2 TIP (TIP-3 and TIP-4) were installed (screened between 9 and 19 ft bgs) to the bottom of the SA), and 16 DIP (using GeoProbe tools) were used.

TIP-3 received ~540 gallons and TIP-4 received ~40 gallons of 100 g/L (10%; SG of 1.12) SR at a pressure of 200 psi. At each DIP location a bottom up approach was used (18-20, 14-16, 9-11 ft bgs) to delivery 525 gallons of 45 g/L (4.5%; SG of 1.05 to 1.10) SR at a pressure between 25-75 psi. Some shallow intervals were skipped due to day-lighting of the SR.

Performance Monitoring and Methods

Unfortunately, the only form of performance monitoring was soil cores. According to the ISBS Pilot Test Final Report "mobile NAPL does not exist in the monitoring area".

Pre-injection cores (various names; 3 in each area), SR verification cores (VB-1 to VB-7) and post-injection cores (DVB-1 to DVB-3, and TVB-1 to TVB-3) were collected.

Pre-injection cores were collected with Rotosonic drilling (does not yield intact cores). Each 2 ft long core was split into 3 sections. Each section was homogenized and sampled. A 200 g sample was leached (at 150 mL/day to generate 2 L over 14 days) and the leachate and leached soil were sampled.

SR verification cores were collected to estimate zone of influence and SR distribution.

Post-injection cores were collected 60 days after injection using a GeoProbe macro-core direct push sampler. Attempts were made to sample the same depth interval as the pre-injection cores. Only one homogenized sample over the 2 ft core length was available for use (sampled and leaching). The leachate generation procedure used for the pre-injection cores was not possible due to slow flow so an alternative method was used (soil sample added to jars for 1 week).

Comments

- 1. The test objectives seem reasonable; however, the methods used and data gathered do not provide sufficient evidence to satisfy <u>all</u> these objectives. For example the term stabilize has many meanings and in the context of this study a clear definition of the behaviour of the post stabilized system should be stated and then carefully addressed.
- 2. In the details provided in these documents there is no mention of design loading targets and pore volume sweep. These estimates are critical to this technology. What was the total oxidant demand estimate? How was this calculated? What was the expected consumption/interaction with the SA material (other reduced aquifer species)? What was the target objective for field application? How successful was this? What data were collected to demonstrate this? What lab-to-field scale-up relationships were used? The Battelle ppt slides indicate that some spatial coverage was expected for both the DIP and TIP injection areas, and details on application rate are provided. It is unclear how the specified oxidant loading (permanganate to soil mass) values were determined. It is surprising that the application rate for the DIP area was 10% of the pore volume and the application rate for the

TIP area was 4% of the pore volume. Given these low pore volume numbers and expected coverage areas I would have expected that the integrated system response would have been used as a performance metric rather that strategic soil cores. Slide 3 in the Battelle ppt presentation clearly recognizes that flux (mass load) reduction was expected, but yet this test was executed without collecting the information required to estimate this critical response.

- 3. The statement that the SR will "tend to migrate throughout the targeted treatment zone reacting preferentially with residual NAPL" is simply not correct. The SR will react with all reduced species present in a competitive manner.
- 4. High solution density will result in density induced flow and SR migration to at least the top of the Upper HG clay unit and deeper if possible. The data collected from the SR verification borings are not included nor is a comprehensive summary provided of the collected data— in my estimation there was not sufficient data collected in the critical areas (deep) to make a defendable conclusion.
- 5. The statements that the ISBS technology has an "inherent ability to "seek" vertical migration pathways and seal or entomb them in situ", and "preferential flow paths both vertical and horizontal should be treated and hydraulically sealed as a result of the ISBS precipitation reactions and COI encrustation" are not founded. NAPL presence will reduce the relative permeability and result in a bypassing of the SR around the zones most heavily impacted by DNAPL. The migration of the SR is controlled by the injection pressure and the formation permeability distribution (with the mobile and immobile NAPL in place). Once the injection phase is over, SR migration is controlled by ambient groundwater flow and in this study large density effects too.
- 6. The solution density difference between TIP and DIP, and limited data on SR distribution does not allow for comparison between injection methods; therefore, Objective 2 was not achieved. There is also limited data to support the stated radius of influence. Moreover these delivery approaches resulted in much of the SR sinking to the bottom of the SA. While complete contact with all the NAPL is not a requirement of this technology a more complete "sweep" will provide a higher probability of the important SR/NAPL contact that is required (*GRU Team Comment 4*). In addition, the high injection pressures used for both the TIP and DIP locations are excessive these pressures appear to exceed the total effective vertical stress and most likely resulted in liquefaction of the formation.
- 7. Appearance of the SR in the UH extraction well (UHG-EW-01) suggests that there exists a hydraulic connection between the SA and the Upper HG. Perhaps a well seal/construction problem or window/discontinuity in the Upper HG Clay.
- 8. Use of soil cores to make conclusive statements about the treatability of an impacted zone is problematic due to heterogeneities in both the NAPL distribution and lithology. Attempts at "core paring", while a step in the right direction, is plagued with the same issues. All conclusions based on the soil core data should be statistically based. This then calls for a sufficient number of representative samples for statistical analysis testing the number collected in this study is limited and insufficient for a statistical based comparison. (*ACEPD Comment 2*)
- 9. Difference in leachate generation methods does not allow for an unbiased comparison. Bias is introduced and there is not enough information to sort out which direction (*GRU Team Comment 5*, and *ACEPD Comment 1*). The connection between slow leachate flow rate for the post-injection soils and the precipitate presence was not established some concerns

related to differences in soil texture (*ACEPD Comment 8*). Again a problem comparing pre and post injection cores.

- 10. A mass balance should have been performed on the soil coil samples (soil concentration = leached concentration + remaining soil concentration). This would provide a check on the closure and quality of these data. Not enough data is provided to make these calculations independently. (*ACEPD Comments 3 and 4*)
- 11. The seven petrographic thin sections prepared from 5 individual core sections clearly support the local scale interaction between the SR and NAPL precipitate formation at the NAPL interface and reduction in porosity (*GRU Team Comment 6*, and *ACEPD Comment 7*).
- 12. The mineralogy of the precipitates as stated are "aluminum silicate hydroxides" where is the aluminum from and what happened to the mass of injected manganese? Perhaps some potential reactions could be provided to support this observation. Also more information related to the longevity of these fresh precipitates is warranted.
- 13. The translation of this local scale observation to a macro-scale phenomenon with an ensuing reduction in mass loading from the SA is not evident from this study (*GRU Team Comment* 8). No attempt was made to capture data to estimate this impact.

Summary Comments related to the Pilot Scale Study Objectives:

Since there are issues related to using soil cores and subsequent experimental methods there is insufficient evidence to show, at the scale of these injections, that the SR was able to stabilize NAPL residuals (Objective 1).

The concentration (which impacts the reactivity and density) of the injected SR at the TIP and DIP locations was different. As well some DIP locations received less SR volume. SR distribution data is limited. Hence little can be concluded on the two delivery methods used (Objective 2).

The petrographic thin sections provide conclusive evidence that precipitation occurred at the NAPL interface and reduced porosity was present at this observation scale. The connection to a permeability reduction is speculation, but at the scale of these observations can be justified (Objective 3). There is no indication on the spatial extent of these reductions.

There is no data in this study to support an estimate of the longevity of the stabilized matrix under *in situ* conditions (Objective 4). Speculation is provided based on the mineralogy of the observed precipitates.

Some Issues Related to the EPA Proposed Plan

The results from this pilot test do not demonstrate unequivocal success. Thus if ISBS (or ISGS) will be used to treat the vadose-zone and SA, and perhaps the Lower HG then additional pilot scale tests and treatability studies must be performed if this technology is to be employed at this site.

- 1. To optimize implementation, DNAPL impacts will need to be better characterized in all potential application areas and specifically in the Lower HG. Is the assumption that all the creosote NAPL is at or below residual saturation in the porous medium (immobile)?
- 2. Confirmation of SR delivery to target DNAPL zones will need to be developed. Note that the porous medium must be suitable for flushing SR (have sufficient K). The influence of heterogeneities on delivery performance will need to be established.
- 3. A high SR concentration is required to maximize the reaction a balance needs to be made with respect to density effects.
- 4. Delivery to the NAPL must occur for the required precipitate formation to occur at a reaction interface close to the water/NAPL interface.
- 5. The role of NOD (reaction with other reduced aquifer species) must be understood to optimize delivery by avoiding unproductive SR consumption.
- 6. Performance metrics related to a quantifiable reduction in mass loading need to be established and then demonstrated at the pilot scale. For the SA this relates to a vertical mass loading into the Upper HG, and for the Lower HG this relates to both horizontal and vertical mass loadings. These metrics will have to be established and demonstrated both short (months) and long term (years).
- 7. Additional support for the expected longevity of the fresh precipitates is required.
- 8. Metals mobilization? It remains a concern.
- 9. Creosote is a complex mixture of 100's of compounds including polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs; phenolic compounds including cresols; and nitrogen-, sulfur-, and oxygen-heterocyclics including dibenzofurans, and hence *in situ* by-product generation and fate must be established. Will stable toxic by-products be generated?
- 10. Has permanganate reactivity with all COCs been established? Here is what I know (to be completed):

COC	Permanganate Reactivity	Source
Naphthalene	yes	Forsey et al. (2010)
Acenaphthalene	?	
2-methylnaphthalene	yes	Forsey et al. (2010)
pentachlorophenol	?	
arsenic	-	
carbazole	yes	Forsey et al. (2010)
dibenzofuran	not reactive	Forsey et al. (2010)
1,1 biphenyl	not reactive	Forsey et al. (2010)
Phenol	?	
2-phenol	?	
2-methylphenol	?	
2,4-dimethylphenol	?	
3/4-methylphenol	?	
Acenaphthene	yes	Forsey et al. (2010)
benzo(a)anthracene	?	

benzo(a)pyrene	?	
benzo(b)fluoranthene	?	
benzo(k)fluoranthene	?	
chrysene	yes	Forsey et al. (2010)
bis(2-ethylhexyl) phthalate	?	
fluoranthene	yes	Forsey et al. (2010)
fluorine	yes	Forsey et al. (2010)
n-nitrosodiphenylamine	?	
phenanthrene	yes	Forsey et al. (2010)
benzene	no	Forsey et al. (2010)

APPENDIX A. Permanganate Oxidation of Creosote NAPLs

Working Document

N.R. Thomson

Relevant Permanganate Chemistry

Little research has been directed at the treatment of creosote contamination and specifically the oxidation of arenes (i.e., compounds based on benzene rings such as benzene and toluene) by permanganate. Rudakov and Lobachev (1994), and Rudakov et al. (1996) proposed two parallel oxidation mechanisms for the permanganate oxidation of an alkylbenzene: (1) attack at the carbon hydrogen bond in the alkyl substituent, and (2) attack at the benzene ring.

Compounds comprising an alkyl substituent were found to be attacked predominately at the C-H bond in the alkyl group. For example the reaction of toluene with permanganate can be written as (Rudakov and Lobachev, 1994)

$$C_{6}H_{5}CH_{3} + OMnO_{3}^{-} \rightarrow \{C_{6}H_{5}H_{2}C\cdots H\cdots OMn(IV)O_{3}^{-}\}$$

$$\rightarrow C_{6}H_{5}H_{2}COMn(V)O_{2}(OH^{-}) \rightarrow C_{6}H_{5}H_{2}COH + Mn(V)O_{3}^{-}$$

$$(1)$$

where the final oxidation product is benzoic acid, and the manganese (V) is reduced to manganese dioxide ($Mn(IV)O_2$). The reactivity of the alkylbenzenes studied was determined to follow the energy required for homolysis of the C-H bond; that is the stronger the benzylic C-H bond the more resistant the compound was to oxidation. For example, in terms of benzylic C-H bond strength in the alkyl group

$$C_6H_5CH_3 > C_6H_5CH_2CH_3 > C_6H_5CH(CH_3)_2$$
 (2)

and therefore the relative reactivity order for these compounds is reversed. As bond strength decreases from a compound with a primary hydrogen (toluene) to the compound with a tertiary hydrogen (iso-propylbenzene), reactivity increases. Rudakov and Lobachev (1994) noted that this trend is similar to that exhibited by hydrogen atom abstraction by radicals and concluded that permanganate reacts in a similar fashion to an oxygen radical in the cleavage of the alkyl C-H bond despite the fact that permanganate itself has no radical character. If the reaction were a free radical reaction, the relative reactivity of the compounds could be inferred by examining the stability of the radical intermediate; however, the oxidation of these compounds by permanganate is not a free radical reaction but the relative reactivity trends are similar. By analogy, it is expected that intermediate compounds formed during permanganate oxidation exhibit similar stabilities. Therefore, compounds yielding reaction intermediates with high stability (low potential energy) will be less readily oxidized than those that yield intermediate compounds with lower stability (high potential energy).

The second mechanism proposed by Rudakov and Lobachev (1994) involves an attack by the permanganate anion on the aromatic ring and it proceeds via electrophilic aromatic substitution. In their examination of the relative contributions of the two oxidation pathways (i.e., C-H bond attack or electrophilic substitution), Rudakov and Lobachev (1994) suggested structural

properties that would determine the dominant pathway. While attack at the C-H bond in the alkyl group was determined to be preferential, the contribution of this attack decreased with deactivation of the C-H bond and activation of the benzene ring with methyl groups.

Creosote contains a wide variety of alkylbenzenes, and alkyl substituted and non-substituted polycyclic aromatic hydrocarbons that are susceptible to oxidation by the two mechanisms stated.

Forsey et al. (2010) determined the permanganate second-order rate coefficients for some creosote constituents including:

biphenyl, naphthalene, anthracene. phenanthrene, fluoranthene. chrysene, pyrene, darbazole dibenzofuran 1 -methylnaphthalene 2-methylnaphthalene fluorene acenaphthene benzene methylbenzene ethylbenzene Isopropylbenzene, tert-butylbenzene

The compounds investigated exhibit a wide range of reactivities that follow the two different suspected reaction mechanisms. Compounds such as pyrene that do not have benzylic hydrogens, but are observed to be reactive to permanganate, are likely oxidized by electrophilic aromatic substitution. Polycyclic aromatic hydrocarbons that have a benzylic hydrogen (e.g., 1-methylnapthalene) are susceptible to oxidation via an abstraction of a benzylic hydrogen and/or electrophilic aromatic substitution. For these compounds a strong correlation between the second-order rate coefficient and C-H bond dissociation energies implies that abstraction of the benzylic hydrogen is the dominant oxidation pathway. The susceptibility of a compound to electrophilic aromatic substitution generally increases with the number of arene rings, thus the reactivity increases in the series: naphthalene < phenanthrene < pyrene. The reactivity of PAHs can be predicted by considering likely intermediate compounds in the oxidation process. Aromatic compounds with intermediates that retain some degree of aromaticity are more thermodynamically likely to undergo oxidation than those whose intermediates lose their aromaticity.

Since not all of the creosote compounds are susceptible to permanganate oxidization some residual NAPL will remain following treatment.

Dissolution and NAPL Weathering

For oxidation to occur the compound must be in the aqueous phase; therefore mass transfer must occur from the NAPL to the aqueous phase. A typical mass transfer expression for this process is given by

$$\frac{dC_w^m}{dt} = k(C_{sat}^m - C_w^m) \tag{3}$$

where C_w^m is the aqueous phase concentration of compound *m*, C_{sat}^m is the aqueous solubility of compound *m*, and *k* is the bulk mass transfer coefficient. Essentially Eq (3) shows that mass transfer depends on a mass transfer coefficient, and driving force (i.e., the difference in concentrations). The mass transfer coefficient depends on a number of factors including the Reynold's number, NAPL saturation, interfacial area, and mean or median grain size. For creosote NAPL, the aqueous phase solubility of each NAPL constituent may be estimated from the solubility analog of Raoult's Law

$$C_{sat}^m = x^m C_{sat,m}^o \tag{4}$$

where x^m is the mole fraction of component *m* in the NAPL mixture, and $C^o_{sat,m}$ is the solubility of the pure compound. Eq (4) assumes an activity coefficient equal to unity and is usually valid for mixtures of lower alkane and aromatic hydrocarbons. For PAHs that exist as solids in their pure phase, the super-cooled liquid solubility is used for $C^o_{sat,m}$ and can be calculated according to

$$C_{sat,m}^{o} = C_{sat,m}^{solid} \exp[6.8T_m/(T-1)]$$
⁽⁵⁾

where $C^{solid}_{sat,m}$ is the solid phase solubility, T_m is the melting temperature, and T is the system temperature. Laboratory studies conducted by Lee et al. (1992) indicated that Raoult's Law provided a reasonable approximation between predicted and measured solubilities of PAHs.

If permanganate is able to be delivered in close proximity to the NAPL where the dissolved phase concentration of all the NAPL constituents is controlled by Eq (3), then a competitive oxidation process occurs with the most reactive (largest reaction rate coefficient) dissolved constituents being degraded first. This will result in an increase in the mass transfer of these constituents from the NAPL and an associated reduction in their mole fraction. Eventually, the aqueous phase concentration of the most reactive constituents will decrease according to Eq (4), and the aqueous phase concentration of the less soluble or less reactive constituents will increase. This preferential change the NAPL composition is known as *oxidation induced weathering* and may result in changes in the NAPL physical properties (increase in density and viscosity).

Enhanced NAPL mass removal (relative to an equivalent treatment with water) results from (1) direct oxidation of the most reactive compounds, and (2) an increased solubility of the remaining NAPL constituents. In an ideal system the degree of enhanced NAPL mass removal depends on constituent reactivity, solubility and mole faction.

Precipitate Formation

The half-cell reaction for the reduction of MnO₄⁻ between pH 3.5 and 12 is

$$MnO_4^- + 3e^- + 4H^+ \rightarrow MnO_{2(s)} + 2H_2O$$
(6)

According Eq (6) and manganese speciation, permanganate will be reduced to manganese dioxide under pH and Eh conditions commonly present during ISCO (i.e., low pH and high Eh).

Manganese dioxide is a dark brown, water-insoluble solid. It is highly polar and has a high tendency to coagulate by aggregation and form hydrated colloids with high water contents (Morgan and Stumm 1963; Perez-Benito and Arias, 1991). The degree to which the colloids will aggregate depends on the experimental conditions, and it is possible that the colloids can be stabilized for long periods. For example, the presence of phosphate ions can slow down the coagulation of MnO_2 because the colloidal particles obtain a negative electrostatic charge after phosphate ions are adsorbed onto their surface (Perez-Benito and Arias, 1991). Alternatively, the presence of polyvalent cations (e.g., Mg^{2+} , Ca^{2+}) can increase the rate of formation and aggregation of the colloids (Morgan and Stumm, 1963). MnO_2 production is visually confirmed by a dark brown to black area within the subsurface (Schroth et al., 2001; Conrad et al., 2002; MacKinnon and Thomson, 2002). Upon initial production, the MnO_2 solids are colloidal in size though they can agglomerate into larger size particles. MnO_2 solids produced during permanganate ISCO have been observed using scanning electron microscopy (SEM) demonstrating their colloidal nature.

The fact that MnO_2 aggregates into colloids is important with respect to its ability to form a barrier between the aqueous phase and the NAPL, and its ability to plug the pore spaces in the vicinity of the NAPL. The formation and subsequent accumulation near the NAPL is the required *precipitate formation and plugging* to facilitate ISGS. Although the volume occupied by the MnO₂ alone may be small, there is some evidence that bound water can account for 90% of the weight of a colloid (Siegrist et al., 2002). This dramatically increases the volume occupied by the MnO₂ colloids. This precipitate accumulation results in a reduction in permeability and a decrease in mass transfer (water/NAPL).

In many cases, the manganese dioxide present on the surface of the colloids is further reduced according to:

$$MnO_{2(s)} + 2H^{+} + 2e^{-} \rightarrow MnO_{(s)} + H_{2}O$$
⁽⁷⁾

The manganese oxide will then remain at the colloid surface, or under very acidic conditions, may be reduced even further to Mn^{2+} , which would dissolve into solution according to

$$MnO_{(s)} + 2H^+ \rightarrow Mn^{2+}_{(s)} + H_2O$$
(8)

The degree to which MnO_2 is further reduced depends on the experimental conditions (Perez-Benito and Arias, 1991), and is increasingly likely as the acidity of the system increases.

Stabilizing NAPL with Permanganate

The underlying mechanisms required for NAPL stabilization with permanganate (ISBS or ISGS) are:

- enhanced mass removal
- oxidation induced weathering
- precipitate formation and plugging

These three mechanisms in concert will give rise to a macro-scale reduction in mass loading from the treated system. However, for this to be effective, delivery of the permanganate solution to most of the hydraulically accessible NAPL is required. The resulting impact or system response depends on the NAPL architecture – not all systems will respond the same.

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Carus RemOx EC Stabilization Reagent (incomplete)

Information has been difficult to track down...

ISBS solutions contain NaMnO₄, and additives: concretizing agents (Ca^{+2} , Mg^{+2} , silicate oxides), and Fe to develop more structurally sound crusts), and buffers (perhaps carbonates to maintain an elevated pH). Carus manufactures the ISBS reagents but ADVENTUS owns the technology.

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Rebound of a coal tar creosote plume following partial source zone treatment with permanganate

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ABSTRACT

The long-term management of dissolved plumes originating from a coal tar creosote source is a technical challenge. For some sites stabilization of the source may be the best practical solution to decrease the contaminant mass loading to the plume and associated off-site migration. At the bench-scale, the deposition of manganese oxides, a permanganate reaction byproduct, has been shown to cause pore plugging and the formation of a manganese oxide layer adjacent to the non-aqueous phase liquid creosote which reduces post-treatment mass transfer and hence mass loading from the source. The objective of this study was to investigate the potential of partial permanganate treatment to reduce the ability of a coal tar creosote source zone to generate a multi-component plume at the pilot-scale over both the short-term (weeks to months) and the long-term (years) at a site where there is > 10 years of comprehensive synoptic plume baseline data available. A series of preliminary bench-scale experiments were conducted to support this pilot-scale investigation.

The results from the bench-scale experiments indicated that if sufficient mass removal of the reactive compounds is achieved then the effective solubility, aqueous concentration and rate of mass removal of the more abundant non-reactive coal tar creosote compounds such as biphenyl and dibenzofuran can be increased. Manganese oxide formation and deposition caused an order-of-magnitude decrease in hydraulic conductivity.

Approximately 125 kg of permanganate were delivered into the pilot-scale source zone over 35 days, and based on mass balance estimates < 10% of the initial reactive coal tar creosote mass in the source zone was oxidized. Mass discharge estimated at a down-gradient fence line indicated >35% reduction for all monitored compounds except for biphenyl, dibenzofuran and fluoranthene 150 days after treatment, which is consistent with the bench-scale experimental results. Pre- and post-treatment soil core data indicated a highly variable and random spatial distribution of mass within the source zone and provided no insight into the mass removed of any of the monitored species.

The down-gradient plume was monitored approximately 1, 2 and 4 years following treatment. The data collected at 1 and 2 years post-treatment showed a decrease in mass discharge (10 to 60%) and/or total plume mass (0 to 55%); however, by 4 years post-treatment there was a rebound in both mass discharge and total plume mass for all monitored compounds to pre-treatment values or higher. The variability of the data collected was too large to resolve subtle changes in plume morphology, particularly near the source zone, that would provide insight into the impact of the formation and deposition of manganese oxides that occurred during treatment on mass transfer and/or flow by-passing.

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Overall, the results from this pilot-scale investigation indicate that there was a significant but short-term (months) reduction of mass emanating from the source zone as a result of permanganate treatment but there was no long-term (years) impact on the ability of this coal tar creosote source zone to generate a multi-component plume.

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1. Introduction

Coal tar creosote that is produced from the fractional distillation of crude coal tars is a brownish-black/yellowish dark green non-aqueous phase liquid (NAPL) with a density between 1.01 and 1.20 g/cm³ (Wu et al., 2000). Creosote is a complex mixture and may contain more than several hundred different chemical compounds; however, the chemical composition is influenced by the origin of the coal and by the nature of the distilling process and thus creosote components are rarely consistent in their type and concentration. Mueller et al. (1989) reported that the approximate mass fractions are 85% aromatic hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs) and alkylated PAHs; 10% phenolic compounds including cresols; and 5% nitrogen-, sulfur-, and oxygen-heterocyclics including dibenzofurans. Groundwater and soil impacted by creosote-contaminated sites may potentially contain a number of these chemical compounds depending on the NAPL composition and the aqueous solubility, vapour pressure, and subsurface attenuation processes (e.g., dispersion, reactions, sorption) of the individual compounds (Priddle and MacQuarrie, 1994; King and Barker, 1999). Characteristic of NAPL contaminated sites where low solubility compounds are present, dissolution of the organic solutes is slow and hence the presence of coal tar creosote poses a long-term source of groundwater contamination. Due to the potential toxicity, carcinogenicity and mutagenicity of many of these compounds at low concentrations (IARC, 1998), these sites pose a threat to groundwater resources and other biosphere receptors.

Over the last 15 years, *in situ* chemical oxidation (ISCO) using permanganate has received considerable attention as a technique with the potential to destroy various chlorinated ethenes in the subsurface (Schnarr et al., 1998; Siegrist et al., 2001, Mackinnon and Thomson, 2002; ITRC, 2005; USEPA, 2006; Thomson et al., 2007). While field scale and laboratory studies have focused on the application of permanganate for the oxidation of chlorinated ethenes and certain PAH compounds (Gates-Anderson et al., 2001; Brown et al., 2003), little effort has been directed at treatment of coal tar creosote contamination and specifically the oxidation of arenes by permanganate.

Rudakov and Lobachev (1994), and Rudakov et al. (1996) proposed two parallel oxidation mechanisms for the permanganate oxidation of an alkylbenzene: (1) attack at the carbon hydrogen bond in the alkyl substituent and (2) an attack on the aromatic ring that proceeds via electrophilic aromatic substitution. In their examination of the relative contributions of the two oxidation pathways, Rudakov and Lobachev (1994) suggested structural properties that would determine the dominant pathway. Coal tar creosote contains a wide variety of alkylbenzenes, and alkyl substituted and nonsubstituted polycyclic aromatic hydrocarbons that are susceptible to oxidation by these two mechanisms. Forsey (2004) determined the permanganate second-order rate coefficients for some coal tar creosote constituents including pyrene, fluoranthene, phenanthrene, chyrsene, naphthalene, carbazole, fluorene, and biphenyl (Table 1). The compounds investigated exhibit a wide range of reactivities that follow the two different suspected reaction mechanisms. The second-order rate coefficients in Table 1 are similar in magnitude to those reported in the literature for chloroethenes, except for naphthalene which has a second-order rate coefficient similar to toluene (Waldemer and Tratnyek, 2006).

While the oxidation of some creosote compounds is likely to occur during ISCO treatment of a coal tar creosote source, not all of the compounds of concern will be susceptible to permanganate oxidization and hence a source will remain following treatment which will require long-term site management. For sites where contaminant mass removal is not the primary remedial goal, technologies that isolate or stabilize the NAPL source may be the best practical solution, since they can reduce the contaminant mass loading to the plume and associated off-site migration. An important product of the reduction of permanganate is manganese oxide, which forms at the point of reaction and is a water insoluble solid that is highly polar and tends to coagulate by aggregation to form hydrated colloids with high water contents (Perez-Benito and Arias, 1991). The degree to which the colloids will aggregate depends on the presence of other ions as well as the system Eh and pH (Morgan and Stumm, 1963). Laboratory research has demonstrated that the precipitation of manganese oxides and the formation of CO_2 , another reaction product, decreased the hydraulic conductivity between 50 and 90% (Schroth et al., 2001) in sand-packed columns, caused flow divergence around regions of higher NAPL saturations in a two-dimensional physical model (Li and Schwartz, 2004), and resulted in pore plugging and the formation of a distinct manganese oxide layer in the vicinity of the NAPL that reduced the post-treatment mass transfer (Mackinnon and Thomson, 2002; Conrad et al., 2002; Urynowicz and Siegrist, 2005). The longevity of the trapped CO₂ is temporary, but the manganese oxide deposition is believed to be stable as long as the geochemical conditions are conducive (e.g., pH>3; Appelo and Postma, 1999). As a result, it is hypothesized that treatment of a coal tar creosote source zone by permanganate will initially result in some degree of mass destruction until manganese oxide deposition has reached a level to impact hydraulic conductivity and mass transfer. When this point is reached either the manganese oxides will adversely affect the performance of the treatment system and/or the rate of mass destruction will decrease.

The objective of this study was to investigate the potential of partial permanganate treatment to reduce the ability of a

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156 Table 1

Second-order reaction rate coefficients and suspected oxidation mechanism of selected coal tar creosote compounds

Compound	Formula	Structure	Oxidation mechanism	Rate coefficient ^a [M ⁻¹ s ⁻¹]
Naphthalene	C ₁₀ H ₈	00	EAS ^b	$1.1 \times 10^{-2} \pm 2 \times 10^{-3}$
1-methylnaphthalene	$C_{11}H_{10}$	\sim	ABH ^c	$1.4 \times 10^{-2} \pm 2 \times 10^{-3}$
2-methylnaphthalene	$C_{11}H_{10}$	άř	ABH	$1.8 \times 10^{-2} \pm 3 \times 10^{-3}$
Biphenyl	C ₁₂ H ₁₀	\odot	-	NR ^d
Acenaphthene	C ₁₂ H ₁₀	\mathcal{Q}	ABH	$2.1 \times 10^{-1} \pm 3 \times 10^{-2}$
Fluorene	C ₁₃ H ₁₀	00	ABH	$4.3 \times 10^{-1} \pm 3 \times 10^{-2}$
Carbazole	$C_{12}H_9N$	α_{1}^{0}	ABH	$4.4 \times 10^{-1} \pm 8 \times 10^{-2}$
Dibenzofuran	C ₁₂ H ₈ O	00	-	NR
Anthracene	$C_{14}H_{10}$	$\tilde{\omega}$	EAS	>6.8 ^e
Phenanthrene	$C_{14}H_{10}$	00	EAS	$4.2 \times 10^{-1} \pm 3 \times 10^{-2}$
Fluoranthene ^f	$C_{16}H_{10}$	後 3 3 3 3 3 3 3 3 3 3 3 3 3	EAS	$9.0 \times 10^{-1} \pm 3 \times 10^{-1}$
Pyrene ^g	C ₁₆ H ₁₀	43>	EAS	$1.7 \times 10^{0} \pm 6 \times 10^{-1}$
Chrysene ^h	C ₁₈ H ₁₂	050	EAS	$1.2 \times 10^{-2} \pm 1 \times 10^{-2}$

Notes:

^a Second-order reaction rate coefficient and 95% confidence interval from Forsey (2004).

^b Oxidation by permanganate is suspected to be initiated by electrophilic aromatic substitution.

^c Oxidation by permanganate is suspected to be initiated by abstraction of a benzylic hydrogen.

^d No reaction observed over the 2 day reaction period.

^e Reaction rate was too fast to measure; estimate based on initial rate.

^f Rate coefficient based on initial data; reaction does not go to completion.

^g Rate coefficient based on pseudo first-order portion following initial decrease.

^h Rate coefficient tentatively assigned due to solubility issues.

coal tar creosote source zone to generate a multi-component plume at the pilot-scale over both the short-term (weeks to months) and the long-term (years). It was not our intent to deliver ample permanganate mass to the source zone to satisfy the stoichiometric requirements of all the reactive coal tar creosote compounds and the permanganate natural oxidant demand (NOD), but rather to provide enough permanganate mass so that sufficient manganese oxide deposition occurred to impact hydraulic conductivity and mass transfer. Hence, we have termed this approach partial permanganate treatment in contrast to a situation where the remedial goal would be to completely "clean-up" the source zone. The site used to explore this partial source zone treatment is located at the Canadian Forces Base (CFB) Borden near Alliston, Ontario, Canada and has ~10 years of synoptic plume data that was used to develop a comprehensive baseline of the plume morphology and trends. To support the pilot-scale experimentation, a series of preliminary bench-scale experiments were conducted to evaluate the potential for permanganate to oxidize a coal tar creosote residual NAPL source and to provide specific information on mass removal, changes in post-treatment effluent concentrations, hydraulic conductivity and manganese oxide deposition.

2. Preliminary bench-scale investigations

A series of column experiments was conducted to assess the reactivity of specific coal tar creosote compounds to permanganate, and to provide representative information on potential or expected reductions in mass discharge and hydraulic conductivity due to byproduct formation and deposition within a coal tar creosote residual source. Each

experimental series consisted of a control and a treatment column. Stop-flow column experiments with a creosote saturation of 8% were intermittently flushed with either Milli-Q water (control) or a permanganate solution (8 g KMnO₄/L) (treatment) for 172 days. This intermittent or pulsed flushing allows for a prolonged residence time to maximize the oxidation reaction and hence mass removed. The mass distribution of selected compounds and manganese oxide deposition following permanganate treatment were determined at 1 cm intervals. Flow-through column experiments with a creosote saturation of 3% were used to investigate hydraulic conductivity impacts, and the relationship between mass removal and associated changes in mass discharge. This series of experiments was flushed with Milli-Q water (control) and permanganate solution (15 g KMnO₄/L) at a flow rate of \sim 3.3 mL/h (velocity of \sim 2.0 cm/h) for \sim 7 days to mimic the physical and NAPL conditions of the pilot-scale site at CFB Borden. All column experiments were performed with the same sand and the raw coal tar creosote used to construct the CFB Borden source (King and Barker, 1999).

2.1. Methods

The stop-flow columns (diameter 5 cm, length 12 cm) were constructed of thick walled glass tubing fitted with stainless steel end plates. As required, a 50 mL syringe was used to inject either Milli-Q water or permanganate solution into the column from the bottom, and the effluent was allowed to exit freely from the top of the column into a 60 mL sample vial. Periodically a 13 mL aliquot from the sample vial was analyzed for selected compounds (Table 2) following the addition of 1 mL of a saturated bisulfite solution to quench any residual permanganate.

The continuous-flow columns were constructed of nominal 2.54-cm Schedule 40 PVC pipe (length 12.5 cm) modified to accommodate inlet and outlet tubing, and contained glass beads (0.59 to 0.84 mm diameter) to act as flow distributors at either end. The columns were operated under up-flow conditions where the inlet was maintained at a constant flow rate and the outlet was maintained at a constant hydraulic head. A piezometer was attached to the column influent tubing to monitor hydraulic head.

The chemical composition of the creosote (Carbochem Ltd. Mississauga ON) used in this experimentation is listed in Table 2. The selected compounds represent 56.5% of the total creosote mass assuming the molecular weight of the unknown fraction was 200 g/mol based on a qualitative comparison of the gas chromatograph (GC) retention times for identified and unidentified compounds. The mass spectrum of a sample of this creosote indicated that the unknown mass fraction was predominately made up of heavy molecular weight PAHs with a smaller percentage of unknown phenol and heterocyclic compounds. The density of the creosote was measured to be 1.10 g/mL at 21 °C.

To generate a homogeneous mixture of creosote and sand, 30 mL of Milli-Q water and 300 mL of sand were well-mixed and then the required volume of creosote was added to the wet sand and stirred thoroughly. Each column was packed with material from the middle of the mixture and gently packed in ~1 cm lifts. To estimate the initial mass of individual creosote compounds added to each column, a 20 g sample of the mixture was taken as each column was being packed and analyzed for the bulk soil concentration of selected creosote compounds. After packing, each column was flushed with CO_2 for 1 h and then slowly flushed with Milli-Q water from the bottom to minimize trapped air.

The bulk soil concentration of selected creosote compounds was determined by soxhlet extraction using a modified version of the EPA Method 3540C (extracting with a 200 mL mixture of CH_2Cl_2 and acetone (1:1) for 24 h). The analytical determination of the concentration of all creosote compounds reported in this paper was performed on a GC (HP5890A) equipped with a splitless injection port, a 0.25 mm×30 m glass DB5 capillary column with a film thickness of 0.25 µm and a flame ionization detector (FID). The oven temperature was held at 40 °C for

Table 2

Coal tar creosote chemical composition, variability of bulk soil concentration quantification, and the results from the stop-flow and continuous-flow column experiments

Compound	MW	Aqueous	Mass	MDL	Standard	Stop-flo	w experi	iments			Continuou	s-flow exper	iments
	[g/mol]	solubility ^a	fraction	[µg/L]	deviation ^b [g/kg]	b Initial [g/kg]	Control		Treatment		Control	Treatment	Percent
		[mg/L]	[%]				Final [g/kg]	Percent change	Final [g/kg]	Percent change	discharge [mg/day]	discharge [mg/day]	change
Phenol	94.1	82,000	0.07	32	_	13	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
<i>m</i> -xylene	106.2	196	0.01	5.8	-	2.4	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
o-cresol	108.1	25,920	0.04	8.7	-	7.2	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
p and m-cresol	108.1	24,000	0.12	8.7	-	21	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
2,6-dimethylphenol	122.2	6150	0.02	4.3	-	4.1	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
2,4 and 2,5-	122.2	-	0.05	4.3	-	7.9	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
dimethylphenol													
2,3-dimethylphenol	122.2	14,000	0.08	4.3	-	10	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
3,5-dimethylphenol	122.2	12,000	0.01	4.3	-	4.1	<mdl< td=""><td>-100</td><td><mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<></td></mdl<>	-100	<mdl< td=""><td>-100</td><td>-</td><td>-</td><td>-</td></mdl<>	-100	-	-	-
Naphthalene	128.2	31.7	8.1	4.3	±18	2400	2400	0	1000	-58	0.29	0.25	-14
Indole+2-	142.2	24.4	3.9	4.7	±13	480	420	0	260	-46	0.035	0.026	-26
Methylnaphthalene ^c													
1-methylnaphthalene	142.2	28.5	1.8	2.7	±6.2	610	610	0	600	-2	0.017	0.012	-29
Acenaphthylene	152.2	-	0.2	2.7	±0.81	42	40	0	35	-17	0.0086	0.0021	-76
Biphenyl	154.2	7.5	1.5	4.8	±7.5	280	240	-14	65	-77	0.013	0.025	92
Acenapthene	154.2	3.9	6.0	2.3	±94	1350	1350	0	370	-73	0.047	0.021	-55
Fluorene	166.2	2	4.7	2.7	±19	1100	1100	0	280	-75	0.028	0.0098	-65
Carbazole	167.2	1	0.87	4.7	±3.8	94	83	-12	27	-71	0.043	0.0013	-97
Dibenzofuran	168.2	10	4.0	2.7	±20	720	720	0	640	-11	0.032	0.046	44
Phenanthrene	178.2	1.3	10.4	6.5	±110	2900	2900	0	2400	-17	0.025	0.012	-52
Anthracene	178.2	0.07	1.1	3.6	±3.7	220	220	0	2.1	-99	0.0097	0.0039	-60
Fluoranthene	202.3	0.26	5.2	5.2	±22	2200	2200	0	2000	-9	0.0029	0.0041	41
Pyrene	202.3	0.14	4.0	4.3	±17	810	830	0	560	-31	0.0015	0.00029	-81
Benzo(a)anthracene	228.2	0.3	1.2	3.3	±4.6	250	250	0	170	-32	<mdl< td=""><td>< MDL</td><td>-</td></mdl<>	< MDL	-
Chrysene	228.2	0.002	1.1	6.3	±4.1	230	230	0	220	-4	<mdl< td=""><td>< MDL</td><td>_</td></mdl<>	< MDL	_
Benzo(b)fluoranthene	252.3	-	0.64	20	±1.7	140	140	0	170	21	<mdl< td=""><td>< MDL</td><td>-</td></mdl<>	< MDL	-
Benzo(k)fluoranthene	252.3	-	0.3	20	±1.4	37	39	5	19	-49	<mdl< td=""><td>< MDL</td><td>_</td></mdl<>	< MDL	_
Benzo(a)pyrene	252.3	0.003	0.44	24	±1.4	54	56	0	4	-93	<mdl< td=""><td>< MDL</td><td>-</td></mdl<>	< MDL	-
Benzo(g,h,i)perylene	276.3	0.084	0.14	<32	±0.28	11	12	0	<mdl< td=""><td><mdl< td=""><td><mdl< td=""><td>< MDL</td><td>_</td></mdl<></td></mdl<></td></mdl<>	<mdl< td=""><td><mdl< td=""><td>< MDL</td><td>_</td></mdl<></td></mdl<>	<mdl< td=""><td>< MDL</td><td>_</td></mdl<>	< MDL	_
Indeno(1,2,3,c,b) pyrene+	278.4	-	0.48	<62	±1.1	22	21	0	4	-82	<mdl< td=""><td>< MDL</td><td>-</td></mdl<>	< MDL	-
Dibenzo(a,h) Anthracene ^d													
Total:			56.0			14,100	13,900	-1	8830	-37	0.55	0.41	-25

Notes:

^a From Mueller et al. (1989), MacKay et al. (1992), and Forsey (2004).

^b Bulk soil concentration standard deviation as estimated from the extraction and analysis of 4 samples.

^c Since indole and 2-methylnaphthalene elute at the same time they are combined. The MW and solubility shown are for 2-methylnaphthalene.

^d Since indeno(1,2,3,c,b) pyrene and dibenzo(a,h)anthracene elute at the same time they are combined. The MW shown is for dibenzo(a,h)anthracene.

0.5 min and then ramped to 300 °C at 15 °C/min where it was held for 10 min. The FID was maintained at 325 °C and the helium carrier gas flow rate was 25 mL/min. Quantification was by external and internal standards. The method detection limit (MDL) for the monitored creosote compounds are provided in Table 2. To assess the degree of variability inherent in the soxhlet extraction procedure and subsequent analysis procedure, creosote, sand and water were mixed similar to the method used prior to packing the columns and four subsamples were removed and the bulk soil concentrations were estimated. The results of this assessment (Table 2) indicate that for some compounds there is considerable variability; for example the standard deviation of the dibenzofuran bulk soil concentration was estimated to be ± 20 g/kg.

For the stop-flow columns the permanganate solution or Milli-Q water was added, on average, every 2 days at room temperature (21 \pm 2 °C) at rate of ~ 13 mL/min using the syringe. The permanganate solution was added to the treatment column first and the injection episode was terminated when the permanganate concentration in the effluent was approximately the same as the injection concentration. An equivalent volume of Milli-Q water was injected into the control column. After 172 days the stop-flow column experiment was terminated and each column was sectioned into 1-cm thick increments and the bulk soil concentration of the monitored creosote compounds and manganese oxides was determined from ~30 g subsamples. Manganese oxides were removed with an acidified solution of hydroxylamine hydrochloride (Chao, 1972). To each sample 70 mL of hydroxylamine hydrochloride (0.025 M in 0.01 M HNO₃) and 10 mL of 6 M HNO₃ was added and mixed for 5 min. The concentration of manganese removed by the extraction was determined by atomic adsorption (Varian Model 1475 Atomic Absorption Spectrophotometer) with a MDL of 0.02 mg/L.

For the continuous-flow column experiments the treatment column was flushed with Milli-Q water for ~1 day before the influent was switched to the 15 g KMnO₄/L permanganate solution. After ~7 days of flushing, the influent on the treatment column was switched back to water and the treatment column was flushed for another day. The control column was flushed exclusively with Milli-Q water for ~7 days. Aqueous samples were collected from the effluent of the control and treatment columns during the pre and post-treatment water flushes.

Following the termination of the continuous-flow column experiment, the bulk soil concentration of the monitored creosote compounds and total manganese was determined for the material in both the control and treatment columns. From each column, three ~5 g samples were analyzed for bulk soil manganese concentration using inductively coupled plasma emission spectroscopy (Spectro Analytical, Fitchburg, MA). Soil samples were dried (85 °C), reweighed, and then digested using 2 mL of 50% HNO₃ and 10 mL of 50% HCl for 1 h at 100 °C (Method 3030F, APHA, 1998). In this method, all the manganese species present are converted to Mn^{+2} and the MDL was 0.07 mg/L Mn. The bulk soil concentration of selected creosote compounds for the remainder of the soil in the treatment and control columns were determined as described above for the stop-flow columns.

Permanganate solutions were made by dissolving solid KMnO₄ (BDH, Toronto, CA) into Milli-Q water. Permanganate

concentration was quantified on filtered samples (0.45-µm glass fibre, Pall Corporation) by spectrophotometry at 525 nm with a MDL of 1.3 mg/L. The spectrophotometer was calibrated prior to each sampling event using a standard stock solution (APHA, 1998).

2.2. Results and discussion

2.2.1. Stop-flow column experiments

A total of 96 injection episodes were performed over the 172 day duration of the stop-flow column experiments resulting in ~29 g of KMnO₄ injected into the treatment column. At the end of the first injection the characteristic dark purple colour rapidly faded as it was reduced to manganese oxides by easily oxidizable creosote compounds. As additional permanganate was added in subsequent injections the dark purple colour persisted and, through the glass column walls, preferential flow pathways were clearly distinguished by the dark purple permanganate solution, and diffusion into pore spaces that were initially bypassed were visible. After the injection of 16 pore volumes (PVs) the bottom screen in the treatment column became plugged, presumably due to manganese oxide deposition, and an 18 gauge needle was used to make small holes in the screen so additional permanganate solution could be added. Magnesium oxides deposition on the screen did not become a problem again until 41 PVs had been injected into the column and the experiment was terminated. The effluent sample from the treatment column frequently contained visibly flocculent brown particles, presumably mobile manganese oxides. No gas phase (e.g., CO₂) was observed in the treatment column during the stop-flow column experiment.

Effluent concentrations from both the control and treatment columns showed a rapid decrease in the aqueous concentrations for the more soluble compounds such as phenol, o-cresol and m-xylene (not shown). The less soluble compounds such as biphenyl, carbazole, dibenzofuran and anthracene were continually dissolved from NAPL as shown in Fig. 1. Interpretation of these effluent data is complicated by the stop-flow nature of this column experiment. After each injection episode the aqueous concentration of an individual compound would be significantly decreased in both the control and treatment columns and then gradually increase to reach its effective aqueous solubility; however, in the treatment column the rate of mass transfer is affected by the presence of permanganate. Specifically, in the treatment column the aqueous concentration of oxidizable compounds will remain depressed for a longer period of time resulting in increased dissolution of each oxidizable compound and hence the more readily oxidizable compounds will be removed to a greater extent than the less reactive or non-reactive compounds. Since the permanganate concentration was observed to decrease to approximately zero between injection episodes, the effective aqueous solubility in the treatment column was most likely reached before the next injection episode. If a sufficient mass of reactive compounds were removed, then the NAPL mole fraction would decrease along with the effective aqueous solubility consistent with the solubility analog of Raoult's Law (King and Barker, 1999). Studies examining mass transfer rates have shown that equilibrium concentrations can be reached quickly (minutes



Fig. 1. Effluent concentrations for (a) biphenyl, (b) carbazole, (c) dibenzofuran, and (d) anthracene from the stop-flow column experiments (open square—control column; filled square—treatment column).

to hours) for chlorinated organics (Anderson et al., 1992), but for slow-stirring batch experiments with diesel fuel and column experiments with creosote it took 40 to 60 h for all of the components to reach aqueous phase equilibrium (Priddle and MacQuarrie, 1994; Schluep et al., 2001). Since the residence time between injection episodes was ~48 h we believe that this was sufficient to allow the more abundant and soluble creosote components to reach equilibrium concentrations in both the control and treatment columns. For the nonreactive compounds (e.g., biphenyl, dibenzofuran) the effluent concentrations in both the control and treatment column remained relatively constant while more than 42 PVs of solution was flushed through each column. Considering the initial high mass fraction of these compounds in the NAPL this suggests that the effective solubility of at least these two compounds remained relatively unchanged. The differences in effluent concentration between the control and treatment columns were presumed to be due to slight variations in column packing and NAPL heterogeneity. For the reactive compounds such as carbazole and anthracene, the effluent concentration from the treatment column was substantially lower relative to the control column indicating that enhanced mass removal of these compounds occurred. Given the

residence time between injection episodes, there seems to be little difference between the carbazole and anthracene effluent concentrations despite the order-of-magnitude difference in their second-order reaction rate coefficient.

Table 2 lists the initial and final bulk soil concentration of each monitored compound in the control and treatment columns. The overall bulk soil concentration of the monitored creosote compounds in the treatment column was reduced by 37% compared to only 1% for the control column, clearly indicative that oxidation of selected compounds occurred in the treatment column. For compounds that are readily oxidized by permanganate (e.g., carbazole, fluorene, anthracene) the percent mass removed was much higher in the treatment column compared to the control column. Surprisingly, compounds that are resistant to permanganate, such as dibenzofuran and biphenyl, were also removed to a greater extent in the treatment column relative to the control column. presumably due to an increase in their NAPL mole fraction values. For example the data indicated that 77% of the biphenyl mass was removed from the treatment column compared to 14% from the control column despite the fact that biphenyl is resistant to permanganate oxidation.

For the soil samples evaluated in this investigation, it was assumed that the predominant manganese species was MnO_2 and hence the manganese results are reported in terms of MnO_2 per mass of dry soil. The average bulk soil manganese concentration precipitated in the treatment column after 172 days was 20.8 g MnO_2/kg , and varied from 14.5 g MnO_2/kg at the top of the column to 26.0 g MnO_2/kg at the bottom of the column. This variation is consistent with the orange/brown precipitate observed near the top of the column that gradually became blacker further down the column and at the very bottom a hard manganese oxide deposition was present. The average bulk soil manganese concentration of the sand used in these bench-scale experiments was ~0.4 g MnO_2/kg .

2.2.2. Continuous-flow column experiments

Approximately 8.5 g of KMnO₄ was injected into the treatment column over the 7 day treatment period or about 1/3 of the permanganate mass injected into the stop-flow treatment column. The mass discharge of the monitored creosote compounds, as estimated from the product of the measured aqueous concentration and flow rate, for the posttreatment water flush are listed in Table 2. With the exception of biphenyl, fluoranthene and dibenzofuran, the listed mass discharge estimates were lower for the treatment column by 14 to 97% relative to the control column. Based on the kinetic data in Table 1, it was expected that biphenyl and dibenzofuran, being resistant to permanganate oxidation, would increase in mole fraction in the NAPL and hence mass discharge. This increase results in a higher mass removal which is consistent with observations from the stop-flow experiments. Fluoranthene, while susceptible to oxidation by permanganate, displayed similar trends to biphenyl and dibenzofuran. The reason for the increase in the fluoranthene mass discharge is unclear but in kinetic studies it was observed that fluoranthene was not completely oxidized by permanganate and the reaction stopped within the first 3 min following the addition of permanganate (Forsey, 2004). Thus the rate coefficient given in Table 1 is for the initial reaction and not for the complete

oxidation of fluoranthene. This apparent increase in fluoranthene mass discharge may be due to either incomplete oxidation of fluoranthene or production of an oxidation byproduct with a gas chromatograph retention time similar to that of fluoranthene. Considering that the initial NAPL saturation in the continuous-flow experiments was considerably lower than in the stop-flow experiments (3% compared to 8%) it was not surprising that the percent mass removal of the monitored creosote compounds in the control column (not shown) was much higher (15 to 40%) than those observed in the stop-flow column experiments. However, the mass removal trends between the treatment and control column for the continuous-flow experiment are consistent with the observations from the stop-flow column experiment.

Following the introduction of permanganate to the treatment column, there was a marked increase in the hydraulic gradient across the column, resulting in a decrease in hydraulic conductivity from 1.3×10^{-3} to 1.6×10^{-4} cm/s over 1 day. The hydraulic gradient continued to increase and, at the completion of the permanganate flush, the hydraulic conductivity was estimated to be 9.3×10^{-5} cm/s. The hydraulic gradient across the control column was relatively constant compared to the treatment column. The evolution of the increased hydraulic gradient and corresponding decrease in hydraulic conductivity is a result of the formation and subsequent deposition of manganese solids within the treatment column presumably obstructing flow pathways. At the termination of the continuous-flow experiment the average bulk manganese concentration in the treatment column was 5.5 g MnO₂/kg which was significantly (α =5%) larger than the average bulk manganese concentration in the control column of 0.4 g MnO₂/kg, confirming that manganese oxides had been deposited within the treatment column. The bulk manganese concentrations reported for the stop-flow experiment were considerably larger than for the continuousflow experiment due to a higher permanganate dosing. While hydraulic conductivity reduction due to the production of CO₂ gas has been observed by others (e.g., Schroth et al., 2001), no CO₂ production was observed over the course of this continuous-flow experiment.

2.3. Conclusions

The results from these preliminary column experiments indicate that sufficient mass removal of reactive compounds can be achieved during permanganate treatment so that an increase in the NAPL mole fraction of nonreactive compounds is realized. This increase in mole fraction results in an increased effective solubility and aqueous concentration for the more abundant non-reactive compounds. Consequently, the rate of mass removal of these compounds also increased. For the continuous-flow column experiments the 25% decrease in the mass discharge was associated with a 33% decrease in compound mass; however, there was no relationship between the percent mass of reactive compounds removed and the corresponding percent reduction in discharge for individual compounds. Both column experiments demonstrated the physical impact of manganese oxide formation and deposition; continual clogging of the inlet screen in the stop-flow experiment giving rise to injection problems, and an order-of-magnitude decrease in the hydraulic conductivity of the continuous-flow column. The manganese concentration in the treatment column is within the range (2 to 24 g MnO_2/kg) reported in the literature (Mackinnon and Thomson, 2002; Siegrist et al., 2002; Li and Schwartz, 2004) and suggests that mass transfer impacts may have occurred.

3. Pilot-scale field investigation

3.1. Site description and history

The pilot-scale field investigation component of this study was conducted on a creosote source zone installed on August 28, 1991 in the ~ 10 m thick unconfined aquifer at the CFB Borden (Fig. 2). The detailed monitoring network depicted in Fig. 2(a) was originally installed by Mackay et al. (1986) as part of a previous plume study. The timeline used to monitor events associated with this source zone are denoted by the number of days since source zone installation which is Day 0.

The creosote used to construct this source zone comprised ~70 kg of raw creosote (Carbochem Ltd. Mississauga ON) augmented with 0.45 kg carbazole, 0.50 kg *p*-cresol, 1 kg phenol and 3 kg *m*-xylene. This modified creosote was mixed with ~5800 kg of sand with a hydraulic conductivity of 3.6×10^{-4} m/s to reach a NAPL saturation of 7% (v/v). The hydraulic conductivity of this sand is approximately a factor of four higher than the native Borden aquifer material (8.5×10^{-5} m/s) and was used to ensure that groundwater flow though the source zone would not be inhibited by the NAPL presence. The creosote and sand mixture was then installed in two adjacent zones (denoted as the east and west source areas. For additional details on the source zone emplacement see Malcolmson (1992), and King and Barker (1999).

Prior to permanganate treatment, a detailed plume monitoring program was undertaken on Day 278, 626, 1357 and 3619 (King and Barker 1999; King et al., 1999). This monitoring program involved sampling of 63 to 179 multilevel wells and required the analysis of 717 to 2415 samples for each sampling episode. Mass entering the plume from the source was estimated at an up-gradient boundary coincident with the row of multilevel samplers located \sim 2.7 m from the source (denoted here as the 3-m fence line shown on Fig. 2). King and Barker (1999) developed a model based on the solubility analog of Raoult's Law to simulate the dissolution of compounds from the source zone using a constant groundwater flux of 0.03 m/day and a crosssectional flow area of 6 m². Results from this model were within a factor of 2 of observed dissolved concentrations in the source. Using this model, it was estimated that there was ~350 mol of creosote compounds remaining in the source zone at the start of permanganate treatment (Day 3675) and that ~150 mol are associated with the known reactive compounds listed in Table 1.

3.2. Source zone treatment

3.2.1. Methods

Based on the findings from the column experiments, and to meet the objective of this pilot-scale field investigation, a N.R. Thomson et al. / Journal of Contaminant Hydrology 102 (2008) 154-171



Fig. 2. Creosote source zone and plume monitoring network: (a) plan view of source zone and plume monitoring network (each plume monitoring location represents a multilevel sampler); (b) plan view of the source zone with permanganate injection/extraction wells, piezometers, core locations, and 0.3-m sampling fence line shown.

semi-passive pulse injection system was employed to deliver permanganate to the source zone using the 4 up-gradient injection wells shown on Fig. 2(b). A delivery system of this type is possible in this investigation due to the hydraulic conductivity of the source zone which, by design, is equal to or greater than the native aquifer material. Injection wells were constructed from 5 cm diameter PVC stock well material and installed by a direct push technique to a nominal depth of 3.5 m below ground surface (bgs) and screened (10-slot) over the 2.2 m depth of the source zone. A pulse injection system can sustain permanganate concentrations in the source zone to maximize the oxidation reaction rates and diffusion related concentration gradients (e.g., Schnarr et al., 1998; Lowe et al., 2002; Thomson et al., 2007). Each injection episode was designed to deliver a total of 3200 L of permanganate solution (800 L/well) up-gradient of the source zone. To generate a uniform permanganate treatment to each source area, injection into one well up-gradient of each source area was followed by injection into the other well, thus creating overlapping injection zones. With the aid of results from groundwater flow simulations using MODFLOW-2000 (Harbaugh et al., 2000) an injection rate of 5 L/min was selected for delivery of the design volume in ~ 10 h, resulting in minimal disturbance to the ambient flow field. Based on an estimated average linear groundwater velocity of 10 cm/day, the tail of each permanganate pulse was expected to migrate sufficiently down-gradient of the injection wells in ~7 days to necessitate another injection episode to maintain the presence of permanganate within the source zone. To limit density effects and maximize permanganate concentration, a design concentration of 15 g KMnO₄/L was selected which has a specific gravity of 1.01 at 20 °C (Carus Corporation, 2007). Prior to each injection episode, the required permanganate solution was mixed on site by adding a sufficient mass of solid KMnO₄ (CAIROX® Technical Grade Potassium Permanganate, Carus Chemical) to uncontaminated groundwater to achieve the target concentration. The permanganate solution was filtered (<5 µm) and then injected using a centrifugal pump with a throttled outlet to control the flow rate.

The permanganate NOD represents the consumption of permanganate by the naturally occurring reduced species (organic carbon, and reduced minerals containing Fe(II), Mn (II, III) and S(-I, -II)) associated with the aquifer material (Siegrist et al., 2001; Mumford et al., 2005; Honning et al., 2007), and for native Borden aquifer material has been estimated to range from 0.4 to 3.5 g-KMnO₄/kg (Thomson et al. 2007). This permanganate NOD is consistent with the low TOC and mineralogy of the Borden aquifer material (calcite, quartz, plagioclase, and feldspar minerals with surface coatings of iron and manganese oxyhydroxides) (Ball et al., 1990). The NOD of the sand material used to construct the source area is not known but it is expected to be less than the Borden aquifer material NOD. Permanganate consumption by groundwater was expected to be minimal.

One week after each permanganate injection episode, permanganate breakthrough was monitored at a sampling fence line located ~0.3 m down-gradient from the source (identified here as the 0.3-m fence line). The 0.3-m fence line comprised 7 multilevel bundles with 13, 3 mm inside diameter stainless steel points per bundle. Samples were collected into 40 mL sample vials using a single-tube vacuum system (King and Barker, 1999). Quantification of permanganate concentration was completed at the University of Waterloo following the procedure described in Section 2.1.

To monitor hydraulic conditions during permanganate treatment, 9 multilevel piezometers were installed using a direct push technique around the source zone (Fig. 2(b)). Each piezometer was constructed from 1.25 cm diameter high

density polyethylene tubing notched, screened with Nitex®, and arranged in bundles of 4 tubes extending to nominal depths of 1, 2, 3 and 4 m bgs.

Sixty days prior to initiating permanganate treatment and 150 days after the termination of treatment, a performance assessment comprised of ambient mass discharge (King et al., 1999; Einarson and MacKay, 2001; ITRC, 2004) and forced mass discharge measurements was performed. Under ambient gradient conditions a round of samples (~80) from the 0.3-m fence line were collected and analyzed for representative coal tar creosote compounds. Samples were collected into 40 mL sample vials using a single-tube vacuum system (King and Barker, 1999). At least 40 mL of groundwater was pumped through the system prior to sample collection. Samples were preserved with 0.4 mL of 10% sodium azide solution, placed in coolers and transported to the University of Waterloo for analysis. These data were used to establish an estimate of the mass loading from the source zone to the plume under ambient gradient conditions. This mass loading or dissolution rate (i.e., the rate at which the mass of a specific coal tar creosote compound crosses the plane defined by the 0.3-m fence line) was calculated by integrating the spatial distribution of the aqueous mass flux over the 0.3-m fence line (King et al., 1999; Einarson and MacKay, 2001; ITRC, 2004; Kubert and Finkel, 2006).

In contrast to the ambient mass discharge estimate which is subject to variable hydraulic conditions and spatial integration errors, the forced mass discharge estimate allows for a large degree of control between assessment measurements since a similar pumping and hence flow field can be established through the source zone. The forced mass discharge measurement is similar to the integral pumping test used to quantify mass fluxes (Bockelmann et al., 2001; Béland-Pelletier et al., submitted for publication). Four extraction wells located ~0.5 m down-gradient of the source zone were installed, identical to the permanganate injection wells described above, to facilitate the forced mass discharge estimate. During the forced mass discharge assessment, uncontaminated site groundwater water was injected into the 4 injection wells, while groundwater was pumped from the 4 extraction wells. Extracted groundwater was blended prior to a groundwater sample collection port and then passed through a carbon filter (Calgon Corporation, model F300) and released to the ground surface >50 m downgradient. Periodic groundwater samples were collected in 40 mL vials with no head space, preserved with 0.4 mL of 10% sodium azide solution, placed in coolers and transported to the University of Waterloo for analysis. The forced mass discharge estimate to the extraction wells from the source zone was calculated as the product of the total extraction flow rate times the concentration of coal tar creosote compound (Ptak and Teutsch, 2000; Bockelmann et al., 2001; ITRC, 2004).

Two intact soil cores were extracted from the source zone 110 days prior to permanganate treatment using a piston core barrel technique similar to that described in Starr and Ingleton (1992). The core tube consisted of 5-cm ID aluminum pipe and brass core catcher, and was driven to depth with a jackhammer. Each core tube was capped and placed in a cooler for transport to the University of Waterloo where they were stored in a walk-in refrigerator prior to opening. In order to develop an understanding of the bulk soil concentration vertical distribution for a number of compounds, the entire length of one core was sub-sampled in 1 or 2 cm lengths (see Fig. 2(b) for location). Sample extraction and analysis were as described in Section 2.1.

Approximately 180 days following permanganate treatment 3 intact soil cores were collected from in and upgradient of the source zone. One core was taken immediately



Fig. 3. Spatial distribution of permanganate (g KMnO₄/L) at the 0.3-m fence line (a) 7 days after the first injection episode, (b) 7 days after the 3rd injection episode (c) 7 days after the 5th injection episode, and (d) 35 days after the 6th injection episode. The east and west source area is on the left and right respectively.

down-gradient of an injection well but outside the source zone, and the other 2 cores were taken from the up-gradient and down-gradient edges of the east source area (see Fig. 2 (b) for locations). Each of the post-treatment soil cores were sub-sampled (1 mL) using a pre-cleaned micro-sampling tool on a 1 cm grid and mixed to produce 3 composite samples for each core. A sub-sample from each composite was analyzed for the bulk soil creosote compound concentrations identical to the pre-treatment analysis. A second sub-sample was analyzed for total manganese by ASTM method D 3974-81.

3.2.2. Results and discussion

3.2.2.1. Permanganate delivery system. A total of 6 pulsing episodes were preformed with an average permanganate concentration of ~13 g KMnO₄/L for a total of ~125 kg of KMnO₄. The injections were completed up-gradient of the source zone from Day 3675 to Day 3710. The volume of permanganate solution injected during each pulsing episode varied from 1700 to 2300 L; well short of the design injection volume of 3200 L. The design injection rate of 1 L/min was not able to be sustained during any of the pulsing episodes. Even though the permanganate solution was filtered prior to injection, the injection rate had to be reduced on each successive injection episode in response to a presumed decrease in the surrounding hydraulic conductivity since there was no evidence of screen clogging and no solid precipitate was observed in any of the injection wells. The difficulty in delivering the permanganate was attributed to the formation and deposition of manganese oxides and a subsequent reduction in hydraulic conductivity in the source zone which affected the ability of the injection wells to function as expected. Given the proximity of the injection wells to the source zone, this observation is similar to the continuousflow column experiments where a continual reduction in hydraulic conductivity was observed during permanganate treatment. The apparent reduction in hydraulic conductivity manifested itself in the localized mounding of the groundwater table.

Permanganate concentration contours at the 0.3-m fence line 7 days after the 1st, 3rd and 5th pulsed injection episodes, and 35 days after the 6th pulsed injection episode are presented in Fig. 3. The spatial distribution of permanganate at the 0.3-m fence line 7 days after the 1st delivery episode indicates that much of the injected permanganate mass had been consumed between the injection wells and the fence line due to oxidation of selected creosote compounds and satisfaction of the NOD. The permanganate spatial distribution at the 0.3-m fence line 7 days after the 3rd and 5th pulsed injection episodes are consistent with the other distributions (not shown) and illustrates the heterogeneity of the permanganate distribution down-gradient of the source zone. It appears that the delivered permanganate was able to migrate through much of the source zone; however, there were areas where lower down-gradient permanganate concentrations were observed (e.g., the right edge of the east source area, and the upper portion of the west source area). The maximum permanganate concentration observed in the 0.3-m fence line was typically located coincident to the bottom of the west source area and, for some sampling rounds, was close to the average injected concentration of ~13 g KMnO₄/L indicative of little permanganate consumption. These data suggest that the pulsed injection system was able to deliver permanganate to the source zone as designed. Permanganate was detected at the 0.3-m fence line at a concentration of ~ 6 g KMnO₄/L 35 days following the final injection episode (Fig. 3(d)) presumably due to the slow depletion of permanganate mass trapped in lower hydraulic conductivity regions in the source zone. Monitoring conducted ~5 months following the final injection episode indicated that no detectable permanganate was present in any of the samples collected from the 0.3-m fence line.

Table 3

Pre- and post-treatment ambient and forced gradient discharge estimates for selected coal tar creosote compounds

Compound	Ambient	Ambient gradient discharge					Forced gradient discharge				
	Pre-treatr	nent	Post-treat	Post-treatment		Pre-treatr	nent	Post-treat	ment	Percent	
	$[\mu g/L]^{a}$	[mg/day]	$[\mu g/L]^{a}$	[mg/day]	change	[µg/L] ^b	[mg/day]	[µg/L] ^b	[mg/day]	change	
Naphthalene	12,000	750	12,600	310	-59	910	2900	470	2200	-24	
1-methylnaphthalene	850	200	780	120	-40	250	810	150	710	-12	
Acenaphthylene	60	15	80	6	-58	19	60	8	35	-42	
Biphenyl	300	84	380	71	- 15	110	360	83	400	11	
Acenaphthene	1500	430	1500	200	-53	600	1900	280	1200	-37	
Fluorene	430	110	340	51	-54	190	630	85	400	-37	
Carbazole	270	61	200	18	-70	130	400	35	170	-58	
Dibenzofuran	860	250	1100	210	- 16	260	1200	250	1200	0	
Phenanthrene	300	96	280	60	-37	160	520	110	520	0	
Anthracene	150	31	170	14	-55	41	130	24	110	-15	
Fluoranthene	60	13	77	11	- 11	19	61	18	86	41	
Pyrene	46	9	27	3	-63	14	45	7	35	-22	
Benz(a)anthracene	<mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<></td></mdl<></td></mdl<>	-	<mdl< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<></td></mdl<>	-	-	<mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<>	-	<mdl< td=""><td>-</td><td>-</td></mdl<>	-	-	
Chrysene	<mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<></td></mdl<></td></mdl<>	-	<mdl< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<></td></mdl<>	-	-	<mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<>	-	<mdl< td=""><td>-</td><td>-</td></mdl<>	-	-	
Benzo(a)pyrene	<mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<></td></mdl<></td></mdl<>	-	<mdl< td=""><td>-</td><td>-</td><td><mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<></td></mdl<>	-	-	<mdl< td=""><td>-</td><td><mdl< td=""><td>-</td><td>-</td></mdl<></td></mdl<>	-	<mdl< td=""><td>-</td><td>-</td></mdl<>	-	-	
Total		2048		1075	-47		9016		7066	-22	

Notes:

^a Peak concentration in the 0.3-m fence line.

^b Average concentration in blended effluent.

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3.2.2.2. Ambient mass discharge. Pre- and post-treatment ambient mass discharge estimates were determined by spatial integration of the 0.3-m fence line data. The spatial area associated with each individual concentration measurement was determined by the Theissen polygon method (Thiessen, 1911). Since the monitoring network used was of insufficient spatial extent to capture the entire plume, no attempt was undertaken to extrapolate beyond the spatial extents of the monitoring fence line. A uniform Darcy flux of 5.4 and 4.4 cm/day were estimated for the pre- and posttreatment spatial distribution, respectively, based on observed hydraulic gradients estimated from the surrounding piezometers on the day of sampling, and an assumed constant hydraulic conductivity of 8.5×10^{-5} m/s (Mackay et al., 1986). Both laboratory and field evidence strongly suggests that permanganate application to the source zone results in a decrease in hydraulic conductivity, but no in situ measurements of hydraulic conductivity were obtained. However, given that the hydraulic conductivity of the source zone following permanganate application was expected to be lower, the assumption of an unchanged hydraulic conductivity value will result in a conservative estimate of the mass discharge. Table 3 presents the results of the ambient discharge calculations based on data obtained pre- and post-treatment.

The results of the ambient discharge calculations indicate that the mass discharge for all the compounds examined decreased between pre- and post-treatment. The total load decreased from 2048 to 1075 mg/day. All compounds indicated a >35% reduction in mass discharge except for biphenyl, dibenzofuran and fluoranthene which is consistent with the findings from the continuous-flow column experiments. There was a general trend toward higher reductions in compound concentrations at the 0.3-m fence line in areas associated with observed higher permanganate concentration during treatment. Fig. 4 presents the pre- and posttreatment carbazole concentration spatial distribution at the 0.3-m fence line. The general trends are consistent with the ambient mass discharge calculations and clearly show that the extent of detectable concentrations of carbazole was substantially decreased following permanganate treatment. In particular, the pre-treatment distribution for the east source area indicates two distinct zones of relatively high carbazole concentration, while the post-treatment distribution indicates that both zones remain but with decreased peak concentrations.

3.2.2.3. Forced gradient discharge. About 100 days prior to permanganate treatment a quasi-steady state flow field was established across the source zone by injecting uncontaminated site groundwater into the 4 injection wells at a cumulative rate of ~4 L/min while simultaneously extracting groundwater from the 4 extraction wells at a cumulative rate of 2.2 L/min. The combined effluent from the 4 wells was blended and sampled daily for ~9 days. It was not possible to re-create the identical hydraulic conditions ~215 days following permanganate treatment due to the well efficiency issues discussed above and thus only the 4 extraction wells were used but were operated at a slightly higher cumulative flow rate of ~3.3 L/min. During the pre-treatment assessment the hydraulic gradient across the source zone between corre-



Fig. 4. (a) Pre-treatment and (b) post-treatment carbazole concentration contours (μ g/L) at the 0.3-m fence line. The east and west source area is on the left and right respectively.

sponding pairs of injection/extraction wells was relatively uniform at ~0.35 m/m, while during the post-treatment assessment the hydraulic gradient across the source zone varied from ~0.25 m/m for the outermost pairs of injection/ extraction wells to ~0.10 m/m for the innermost pairs of injection/extraction wells. In spite of this difference in hydraulic gradient, the spatial extent of the capture zone for each assessment is comparable, suggesting that extracted groundwater was drawn from similar areas. The hydraulic head contours for the post-treatment assessment indicate a deflection between the two source areas, suggestive of a lower conductivity in the source zone relative to the native aquifer material.

The time series concentration data for the various monitored coal tar creosote species in the blended effluent during both the pre- and post-treatment assessment showed some initial variability (a coefficient of variation of <0.1 for the pretreatment assessment and <0.3 for the post-treatment assessment) over the initial 2 to 5 days of extraction and then stabilized. The higher variability observed for the post-treatment assessment was assumed to be a result of the reduced control over the flow field compared to the pre-treatment assessment. The average concentration of the last 2 days of the time series data were used to estimate the mass discharge for each species under forced gradient conditions (Table 3). The results indicate that the mass discharge for all compounds, except biphenyl, dibenzofuran, phenanathrene and fluoranthene, decreased following permanganate treatment. There was essentially no change in the mass discharge of dibenzofuran and phenanathrene, and the increase in post-treatment mass discharge for biphenyl and fluoranthene is consistent with the finding from the preliminary bench-scale experiments.

3.2.2.4. Soil cores. The bulk soil concentration data for the pre-treatment soil core for 4 compounds are presented in Fig. 5. These data are typical of the other monitored compounds and illustrate that the bulk soil concentration is guite variable throughout the depth of the source zone. Based on a geostatistical analysis, these spatial distributions where determined to be highly variable and randomly distributed. This randomly distributed bulk soil concentration distribution highlights the inherent difficulty with the extrapolation of a point bulk soil concentration measurement to a larger volume even for this carefully emplaced source zone. As a result of this highly variable and random spatial distribution of mass within the source zone, no statistically significant change (α =5%) in mass for any of the monitored species was evident between the pre-treatment soil core and either of the post-treatment soil cores extracted from the source zone. Furthermore, there is no statistical difference in the mean bulk soil concentrations for the core taken from the up-gradient edge of the source zone and the core taken from the down-gradient edge of the source zone.

The analysis of pre- and post-treatment core material also included an evaluation of total manganese. While the precise composition of the manganese solid that forms during permanganate oxidation of various creosote species is unknown, it is expected to be of the form MnO_x . The average bulk soil manganese concentration in the post-treatment source zone cores (~ 6.0 g MnO₂/kg) was statistically higher than the average bulk soil manganese concentration in the pre-treatment soil core (~0.8 g MnO₂/kg). There is no statistically significant difference in the mean bulk soil manganese concentrations between the post-treatment soil core taken from the up-gradient edge and down-gradient edge of the source zone. The elevated manganese concentration in the post-treatment source cores was similar to the manganese concentration in the continuous-flow treatment column. Given that the hydraulic conductivity reduction observed in the treatment column was attributed to the formation of manganese oxide deposition it is possible that a similar hydraulic conductivity reduction occurred within the source zone.

3.2.2.5. Permanganate mass balance. Monitoring data indicated that permanganate was consistently detected at the 0.3-m fence line. These data were used to estimate the total mass of permanganate that crossed this fence line using the same approach as employed to determine the ambient mass discharge, and assuming a linear temporal variation in discharge between monitoring episodes. The results from these calculations indicate that ~90 kg or ~570 mol of permanganate migrated across the 0.3-m fence line. Since ~790 mol of permanganate were delivered up-gradient of the source zone during the 35 day treatment period, ~200 mol of permanganate were assumed to be consumed through oxidation of coal tar creosote compounds within source zone, if the NOD of the source zone material is assumed to be insignificant. If the average stoichiometric mole ratio between permanganate and selected coal tar creosote compounds is 18 to 1, assuming complete mineralization of the selected coal tar creosote compounds, then $\sim\!11$ mol of the 150 mol or $\sim\!7\%$ of reactive coal tar creosote compounds that were estimated to be present in the source zone at the start of treatment were oxidized by permanganate.

3.3. Long-term post-treatment plume monitoring

Long-term post-treatment monitoring focused only on the down-gradient plume which was comprehensively sampled on Day 4315 and Day 5140, or approximately 2 and 4 years following treatment. On Day 4065 only the 3-m fence line was sampled. Fig. 6 shows dissolved concentration contours created using the maximum observed concentration of each compound at each multilevel sampler for two pre-treatment (Day 1357 and Day 3619) and the two post-treatment (Day 4315 and Day 5140) sampling episodes. For comparison purposes 4 plume metrics were used: mass discharge crossing the 3-m sampling fence line (see Fig. 2(a) for location), total plume mass, the down-gradient plume mass profile, and the plume spatial extent. The mass discharge (mg/day) of each compound (Table 4 and Fig. 7) crossing the 3-m fence line was estimated as described for the 0.3-m fence line in Section



Fig. 5. Bulk soil concentrations from a pre-treatment source zone soil core for (a) naphthalene, (b) biphenyl, (c) dibenzofuran, and (d) chrysene.



(0.03 m/day) was used. The initial sampling fence line used on Day 278, Day 626 and Day 1357 consisted of 8 multilevels with 14 vertical sampling points and was expanded to 15 multilevels with 14 vertical sampling points for the remaining sampling episodes. The 3-m fence line instead of the 0.3-m fence line was used in this long-term plume monitoring to be consistent with the previous historical data collected (King and Barker, 1999). In general the mass discharge crossing the 0.3-m fence line is \sim 2.5 times larger than the mass discharge crossing the 3-m fence line due to the significant level of biotransformation that occurs between these two fence lines (King et al., 1999). The uncertainty in the reported mass discharge estimates was determined by considering analytical error associated with the quantification of the concentration of each compound, variation of groundwater velocity, and data density (Béland-Pelletier et al., submitted for publication). The error bars in Fig. 7 represent ±1 standard deviation as estimated from a coefficient of variation of 0.28 for Day 278, Day 626 and Day 1357, and 0.12 for the remaining sampling days. For each sampling episode the total plume mass for each compound (Table 4 and Fig. 8) was estimated as the sum of the mass in the dissolved and sorbed phases using $R M_d$ where M_d is the dissolved mass estimated using a threedimensional integration of the multilevel sampler concentrations (King et al., 1999), and $R = (1 + \rho_b K_d / \theta)$ is the compound specific retardation factor. Retardation values (Table 4) were calculated using a porosity (θ) of 0.33, a bulk density ($\rho_{\rm b}$) of 1810 kg/m³ (Mackay et al., 1986), and distribution coefficients (K_d) from laboratory data (King et al., 1999) or estimated from literature correlations (Karickhoff et al., 1979) and octonalwater partition data. The uncertainty in the total plume mass estimate was determined by considering the mass balance errors reported from previous natural gradient conservative tracer experiments conducted within the same densely monitored area of the Borden aquifer (Freyberg, 1986; Mackay et al. 1986; Hubbard, 1992) and the uncertainty associated with the estimate of sorbed mass. Thus, the uncertainty estimates vary between compounds; however, in Fig. 8 a coefficient of variation of 0.36 was used for all compounds to capture the highest uncertainty. To provide an indication of the down-gradient dissolved plume mass profile the threedimensional integration of the sampling network was used to assign plume mass into ~1 m intervals or slices (Fig. 9) for Day 3619, Day 4315 and Day 5140. Note that the mass in a pseudosteady state plume typically decreases with increasing distance from the source due to biotransformation processes (King et al., 1999).

3.2.2; however, a constant and uniform groundwater flux

3.3.1. Discussion

Naphthalene and *m*-xylene were undergoing significant attenuation at the time of treatment and it was not possible to separate the effects of the source zone treatment from that of the ongoing plume shrinkage. Following treatment all of the remaining monitored compounds, except for anthracene, followed a similar trend that was characterized by an initial decrease in mass discharge on Day 4065 and/or total plume

Fig. 6. Dissolved plume concentration contours of (a) biphenyl, (b) carbazole, (c) dibenzofuran, and (d) anthracene. Permanganate treatment occurred between Day 3675 to Day 3710 (dashed line).

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Table 4

Estimated mass discharge (J_D) at the 3-m fence line, and to	otal plume mass	$(M_{\rm T})$ at the given	n sampling day
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Compound	Retardation value ^a		Sample day								
			278	626	1357	3619	4065	4315	5140		
<i>m</i> -xylene	2.2 ^b	J _D (mg/day)	3000	1000	280	4.0	3.3	0	0		
		$M_{\rm T}(g)$	580	230	92	4.4	-	0.86	0		
Naphthalene	2.2 ^c	J _D (mg/day)	2800	2200	1100	340	220	230	160		
		$M_{\rm T}(g)$	410	750	1300	220	-	110	110		
1-methyl naphthalene	2.3 ^c	J _D (mg/day)	93	130	99	82	49	80	68		
		$M_{\rm T}(g)$	11	22	42	75	-	45	57		
Biphenyl	7.5 ^b	J _D (mg/day)	25	63	17	34	24	39	38		
		$M_{\rm T}(g)$	3.5	13	14	37	-	29	50		
Acenaphthene	6.6 ^b	J _D (mg/day)	130	220	190	170	75	140	140		
		$M_{\rm T}(g)$	18	31	64	170	-	130	180		
Fluorene	11.2 ^b	J _D (mg/day)	19	58	-	43	21	33	39		
		$M_{\rm T}({\rm g})$	2.4	7.1	-	40	-	31	59		
Carbazole	5.6 ^c	J _D (mg/day)	24	43	16	22	9.7	14	25		
		$M_{\rm T}(g)$	4.5	11	18	48	-	21	41		
Dibenzofuran	4.7 ^c	J _D (mg/day)	66	79	78	95	78	110	120		
		$M_{\rm T}(g)$	14	28	24	88	-	73	180		
Phenanthrene	10.9 ^c	J _D (mg/day)	0.70	3	21	31	28	28	41		
		$M_{\rm T}(g)$	0.31	1.1	8.0	35	-	40	81		
Anthracene	20.1 ^b	J _D (mg/day)	2.0	9	10	11	9.2	8	7.0		
		$M_{\rm T}(g)$	0.5	2.4	3.5	14	-	14	8.8		

The dashed vertical line represents the permanganate treatment interval (Day 3675 to 3710). Notes:

^aAssociated estimates of *R* according to $R = 1 + (\rho_b/\theta)K_d$.

^bvalue of K_d from literature values of log K_{ow} using log K_{oc} = 1.00 log K_{ow} - 0.21 and K_d = $f_{oc}K_{oc}$.

^cvalue of K_d determined from laboratory batch testing by King et al. (1999).

mass on Day 4315, and then a rebound in both mass discharge and total plume mass to pre-treatment values or higher by Day 5140 (see Table 4). Mass discharge on Day 4065 was 10 to 60% lower relative to Day 3619 values, and total plume mass on Day 4315 was 0 to 55% lower relative to Day 3619 values. This overall trend was observed for both reactive and non-reactive compounds.

Pre-treatment plume trends of reactive compounds (e.g., carbazole) indicate an increasing plume size (Fig. 6(b)) and total plume mass (Fig. 8 (b)). The pre-treatment mass discharge of carbazole peaked on Day 626 and then remained relatively constant. Following treatment the maximum concentrations within the carbazole plume, total plume mass and mass discharge decreased on Day 4315; however, the plume spatial extent remained the same. By Day 5140 the dissolved plume concentrations, total plume mass and mass discharge values had returned to pre-treatment values. The approximate location of compounds that emanated from the source zone during the 35 day treatment period was calculated considering only advective transport, estimated from retarded velocity values using a groundwater velocity of 9 cm/day and retardation factors (Table 4) assuming that there was no change to the organic content of the aquifer solids due to exposure to permanganate. On Day 4315 carbazole would have traveled \sim 10 m post-treatment (Fig. 9(b)) and while the mass within this region of the carbazole plume is at its greatest, just up-gradient (<10 m) there is a distinct decrease in mass. By Day 5140 the portion of the carbazole plume that emanated from the source zone during treatment was estimated to be at ~23 m, which is

near the leading edge of the carbazole plume where concentrations significantly decrease and become <MDL by ~28 m. All reactive compounds showed some degree of decrease in mass discharge on Day 4065 since the location of the treated region of each plume was within ± 2 m of the 3-m monitoring fence line.

Prior to treatment, compounds that were non-reactive to permanganate (e.g., biphenyl and dibenzofuran) showed increasing plume size and total plume mass. Biphenyl mass discharge at the 3-m fence line peaked on Day 626 then remained relatively constant while the dibenzofuran mass discharge continued to increase. Following treatment on Day 4315 there appears to be a general concentration depression within the core of the biphenyl and dibenzofuran plumes (Fig. 6(a) and (c))) which is captured by the total plume mass estimate (Fig. 8(a) and (c)); however, this decrease in total plume mass is within the data uncertainty and therefore is not statistically significant. Mass discharge estimated on Day 4065 shows a decline for both biphenyl and dibenzofuran, but by Day 5140 the mass discharge and the total plume mass had rebounded to pre-treatment estimates. By Day 4315 biphenyl and dibenzofuran that emanated from the source zone during treatment would have migrated ~7.5 m and ~11 m downgradient. The biphenyl location is coincident with a depression in the dissolved mass profile (Fig. 9(a)), while the dibenzofuran location corresponds to a mass peak within the plume with the depression in dissolved plume mass located <11 m suggesting that the assumed dibenzofuran retardation factor was too low. By Day 5140 dibenzofuran that emanated





Fig. 7. Estimated mass discharge at the 3-m fence line for (a) biphenyl, (b) carbazole, (c) dibenzofuran, and (d) anthracene. Squares represent pretreatment and triangles represent post-treatment data. The error bars represent ±1 standard deviation as estimated from a coefficient of variation of 0.28 for Day 278, Day 626 and Day 1357, and 0.12 for the remaining sampling days.

from the source zone during treatment would have migrated ~ 28 m which is beyond the extent of the detected dibenzofuran plume. The temporary decrease in mass discharge and plume mass for the non-reactive compounds was not expected; however, it is clearly associated with the source zone treatment.

Anthracene was the only compound that showed a continued decrease in plume spatial extent, total plume mass and mass discharge following treatment. The trend in the anthracene plume prior to treatment was an increasing plume size (Fig. 6(d)), total plume mass (Fig. 8(d)), and mass discharge (Fig. 7(d)). Anthracene is strongly sorbed (Table 4) and thus the region of the anthracene plume that emanated from the source zone during treatment was just beginning to enter the monitoring network (~3.0 m from the source) by Day 4315, and was \sim 6.5 m down-gradient of the source by Day 5140 which is within the network. Unlike the other monitored compounds, this slowly migrating treated region of the anthracene plume was captured in all post-treatment sampling episodes giving rise to decreased plume metrics. It is hypothesized that, in future sampling episodes, the treated region of the anthracene plume will have migrated sufficiently down-gradient that the anthracene total plume mass and mass discharge will have rebounded to post-treatment levels.

Based on the findings from the laboratory experiments it was expected that if the NAPL was significantly impacted by permanganate treatment that the biphenyl and dibenzofuran plume mass would increase, due to enhanced dissolution of reactive compounds, which would increase their mole



Fig. 8. Estimated total plume mass (dissolved and sorbed) for (a) biphenyl, (b) carbazole, (c) dibenzofuran, and (d) anthracene. Squares represent pretreatment and triangles represent post-treatment data. The error bars represent ± 1 standard deviation as estimated from a coefficient of variation of 0.36 which captures the greatest uncertainty.


Fig. 9. Dissolved plume mass profile for (a) biphenyl, (b) carbazole, (c) dibenzofuran, and (d) anthracene for pre-treatment Day 3619, and post-treatment Day 4315 and Day 5140. The vertical line represents the estimated advective distance each compound migrated based on retarded velocity values for Day 4315 (solid line) and Day 5140 (dashed line).

fractions. Both biphenyl and dibenzofuran show an increase in plume mass on Day 5140 compared to Day 4315. While the increase in the biphenyl total plume mass is perhaps consistent with the pre-treatment trends, the increase in dibenzofuran total plume mass of more than 100% is suggestive of some NAPL impact.

The ~90 kg of residual permanganate that was not utilized in the source zone may have migrated through the monitoring network prior to the first post-oxidation sampling event (Day 4315). This migrating permanganate plume, if not depleted by NOD, would cause a reduction in sorbed mass and therefore affect the plume shape or mass of reactive compounds. There is no evidence of extensive oxidation of sorbed compounds such as anthracene or fluorene in the plume. Selected groundwater samples collected up-gradient of the source zone (background), from within the source zone, from the 3-m fence line and from within the plume on Day 5140 were analyzed for dissolved manganese. These data indicate that manganese concentrations at the 3-m fence line (1.1 mg/L) was about twice the background and source zone concentration (0.5 mg/L) and slightly higher than the manganese concentrations in the plume. This suggests that there is slightly elevated manganese concentrations emanating from the source zone presumably associated with the presence of manganese oxides deposited in the source during permanganate treatment.

It was surprising that both reactive and non-reactive compounds showed similar post-treatment plume metric trends. On Day 5140 it appears that the decrease in mass between 5 to 10 m down-gradient of the source persists after rebound of the plume metrics has occurred. We believe that the entire plume has been encapsulated by the monitoring network and so essentially all chemical mass discharge was likely considered, although the sample density (4 to 8 points/ m^2) suggests a relative mass estimate uncertainty of <10% (Béland-Pelletier et al., submitted for publication). This long-term change in the plume mass profiles near the source zone may be related to a decrease in the hydraulic conductivity and mass transfer rate within the source zone due to manganese oxide deposition. These alterations to the source zone may have caused a shift in the plume behavior just down-gradient of the source zone that manifests as a marked depression in the dissolved mass profiles but does not affect the mass discharge estimate at the 3-m fence line.

4. Summary

Remediation techniques that are limited by NAPL/groundwater mass transfer (e.g., pump-and-treat) are often deemed unpractical for the long-term management of the multicomponent plume generated from coal tar creosote-contaminated sites. One possible solution is to stabilize the source zone by creating a rind of manganese oxide precipitates in close proximity to the NAPL by flushing the source zone with a concentrated permanganate solution. Previous laboratory observations have indicated that the formation and deposition of manganese oxides can give rise to flow by-passing and decrease NAPL/groundwater mass transfer following treatment. The focus of this study was to investigate the impact of partial permanganate treatment of a coal tar creosote source zone to reduce its ability to generate a multi-component plume at the pilot-scale.

The results from the series of preliminary column experiments, using the same raw coal tar creosote and sand material as the pilot-scale investigation, indicated that a mass removal of 33% resulted in a 25% decrease in mass discharge or loading of the monitored compounds relative to the control column. Sufficient mass reduction of the reactive compounds was achieved to cause the effective solubility, aqueous concentration and therefore rate of mass removal of the more abundant non-reactive coal tar creosote compounds such as biphenyl and dibenzofuran to increase. Manganese oxide formation and deposition was visually observed and resulted in an order-ofmagnitude decrease in hydraulic conductivity.

Approximately 125 kg of permanganate was delivered into the pilot-scale source zone over 35 days using a pulsed well delivery system. As the injection episodes progressed, the injection rate had to be reduced in response to a presumed decrease in the source zone hydraulic conductivity. Monitoring data indicated that permanganate was able to migrate through

the source zone with $\sim 70\%$ of the injected 125 kg of permanganate estimated to cross the 0.3-m sampling fence line. Based on a permanganate mass balance estimate, and using an average stoichiometric mole ratio between permanganate and selected coal tar creosote compounds, <10% of the initial reactive coal tar creosote mass in the source zone was oxidized. In spite of this, mass discharge estimated at the 0.3-m fence line indicated a >35% reduction for all monitored compounds 150 days after treatment, except for biphenyl, dibenzofuran and fluoranthene, which is consistent with the bench-scale experimental results. This decrease was supported by forced gradient discharge measurements which, although not showing the same magnitude of decrease, displayed similar trends for each compound. Pre- and post-treatment soil core data indicated a highly variable and random spatial distribution of mass within the source zone and hence provided no insight into the mass removed of any of the monitored species. Finally, bulk soil manganese concentration data obtained from subsampling source zone cores indicated elevated levels consistent with the preliminary bench-scale experiments. Although no direct source zone hydraulic conductivity measurements were performed, a localized mounding of the water table around the source zone suggested a reduction in hydraulic conductivity had occurred following treatment.

The down-gradient plume was monitored approximately 1, 2 and 4 years following treatment to assess the long-term impact of this partial permanganate treatment. The data collected at 1 and 2 years post-treatment showed a decrease in mass discharge and/or total plume mass; however, by 4 years post-treatment there was a rebound in both mass discharge and total plume mass for all monitored compounds to pre-treatment values or higher. This overall trend was observed for both reactive and non-reactive compounds. The observed decrease in mass discharge and total plume mass at 1 to 2 years post-treatment was attributed to the presence of the portion of the plume for each compound that emanated from the source zone during treatment in the monitoring network. Rebound occurred once this treated portion of the plume passed through the monitoring network.

The long-term data indicate that the observed decrease in mass discharge at the 0.3-m fence line 150 days following treatment was temporary, and, once the system had recovered from treatment, rebound to pre-treatment behavior occurred. For highly sorbing compounds, like anthracene, the time required for this plume monitoring system to show rebound was >4 years following treatment. The timeframe associated with this rebound is especially important for the development of post-remediation monitoring strategies. Due to the rather large variability of the plume metrics used in this investigation, we are unable to resolve subtle changes in plume morphology, particularly near the source zone, that would provide insight into the impact of the formation and deposition of manganese oxides that occurred during treatment on mass transfer and/or flow by-passing. Nevertheless, for this pilot-scale study ~ 10% of the coal tar creosote mass in the source zone was oxidized and increases in bulk manganese soil concentrations were observed but no significant long-term effect on the dissolved plumes emanating from the source resulted. We acknowledge that perhaps additional permanganate treatment may have produced different results and support this method as a potentially viable approach to stabilize NAPL source zones.

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Attachment D CD of Documents Requested by City and County for Inclusion in Administrative Record

Note: CD of Documents is not included with electronic copies of this report. CD is included with paper copies of this report, or can be provided separately upon request.