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OF IRON MOUNTAIN

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Principals:
James R. Foley
John R. Garske
James J. Strigel
Michael L. DesRosier

May 10, 1996

Mr. Scott Watson
Wisconsin Dept. of Natural Resources
North Central District
107 Sutcliff
P.O. Box 818
Rhinelander, WI 54501

Re: C M Christiansen Co., Phelps, WI
Phase II Site Investigation

Dear Scott:

The purpose of this letter is to identify the proposed Phase II Site Investigation efforts for the above referenced project. The tasks outlined within this letter are based upon work conducted to date which was summarized in our January 18, 1996 correspondence. It is also based on the laboratory results of the second round of groundwater monitoring which were forwarded to the Department on March 5, 1996. The Phase II work is proposed to help further define the degree and extent of site conditions. The feasibility of biodegradation will also be evaluated through a bench scale box study, and through additional screening of on-site "in-situ" conditions.

In the January 18, 1996 and March 5, 1996 correspondence, the initial soil and groundwater laboratory data was presented. As a means of showing existing soil conditions we have enclosed a site drawing which displays the soil sample results in a color coded format. The drawing is intended to display, by boring, the relative concentration of certain analytes in soil. The color coded drawing does not apply to groundwater. However, groundwater quality has been evaluated by comparing the laboratory results to the Wisconsin Administrative Code, Chapter NR 140 Standards.

The Phase II work will be comprised of: eleven (11) soil borings; four (4) new groundwater monitoring wells; two (2) new piezometers; and ten (10) hand auger borings. The color coded map also shows the proposed locations for these borings and wells. As with any field effort, this estimate may be adjusted if conditions warrant. The Department will be kept apprised of the starting date of work activities, the progress of work and will be notified of any significant changes. Field activities will be conducted by the same methods and procedures outlined in the DNR approved Site Investigation Work Plan.

635 Industrial Park Drive - P.O. Box 607
Iron Mountain, Michigan 49801
(906) 774-3440
FAX: (906) 774-7776

Office Also Located At:
205 N. Harrison Street
Ironwood, Michigan 49938
(906) 932-5048
FAX: (906) 932-3213

Soil samples collected at each location will be laboratory analyzed for pentachlorophenol (PCP), Polynuclear Aromatic Hydrocarbons (PAH), Arsenic, Barium, Chromium, Copper and Lead. As already agreed, volatile organic compound (VOC) analysis has been discontinued. Also, it is requested that the metals regime be reduced to only those identified during the initial site investigation (Arsenic, Barium, Chromium, Copper and Lead).

Quarterly groundwater samples will be laboratory analyzed for PCP, PAH, Arsenic, Barium, Chromium, Copper and Lead. It is proposed to discontinue VOC analysis because the first two rounds of monitoring only reported Napthalene as exceeding current state standards and Napthalene is reported in the PAH analysis. It is also requested to reduce the metal regime to include only those metals that have been reported above existing state groundwater standards and those that have been identified for soil.

In addition, further "in-situ" site conditions will be evaluated in an attempt to assist with understanding the potential for natural attenuation/biodegradation at this site. This will be done through laboratory analyses of six (6) to eight (8) soil samples for pH, TOC, total nitrogen, ammonia nitrogen, nitrate + nitrite nitrogen, total phosphorous, cation exchange capacity, permeability, porosity, water holding capacity, bulk density, and soil classification. Four of the above samples will undergo plate counting for total bacteria and PCP biodegrading microorganisms. With regard to groundwater, three (3) samples will be collected from site wells and analyzed for pH, alkalinity, COD, iron, magnesium, manganese. Plate counts for total bacteria and PCP biodegrading microorganisms will also be performed.

The bioremediation bench scale box study that is being proposed is designed to determine if site conditions are suitable for biodegradation. The box study is designed to look at what conditions might be limiting factors (i.e., moisture, nutrients, PCP concentration, etc.). The box study will be conducted in accordance with the attached conceptual work plan. It should be noted that site conditions may suggest the need to modify the approach. If significant modification becomes necessary, the Department will be notified as soon as appropriate.

As you are aware, current weather conditions are not conducive to site access. Work activities will begin as soon as weight restrictions are lifted and site conditions are suitable for investigation efforts. The uncertainty of this start date will affect the schedule for any subsequent summer activity as sufficient data analysis results may not be available to undertake appropriate decisions. We will make every reasonable attempt to complete work in a timely manner.

As already discussed, the Department has offered to review and approve the next proposed Phase II Site Investigation efforts and approach prior to implementation. The C M Christiansen Co. and project team would like to thank you for your cooperation with regard to this project and appreciate the efforts you have made to streamline activities. We will continue to apprise the Department of the progress and outcome of work efforts as well as involve the Department in the decision making process.

Should you have any questions or concerns, please feel free to contact the project team.

Sincerely,

COLEMAN ENGINEERING COMPANY
OR IRON MOUNTAIN

Mark A. Gregory
Environmental Scientist

MAG/al

cc: E. Christiansen - C M Christiansen Co.
R. Roder - Reinhart, Boerner, Van Deuren, Norris and Rieselbach
B. Premo - White Water Associates

Encl.

CEC Project #E-95042-A6

C.M. CHRISTIANSEN CO., PHELPS, WISCONSIN
-- Bioremediation Bench Scale Treatability Study for Pentachlorophenol and Polycyclic Aromatic Hydrocarbons Impacted Soil

I. INTRODUCTION

Biodegradation is believed to be the most important mechanism for degradation of organic compounds in soil systems and is utilized for transformation of organic compounds into innocuous products. Biodegradation of an organic compound is accomplished by a series of biochemical reactions in which the parent compound is gradually transformed into other organic compounds or mineralized into inorganic compounds.

In the original Penta formula used at the subject site, the wood treating solution consisted of approximately 5% pentachlorophenol (PCP) and 95% petroleum base product (diesel fuel range petroleum) which typically contains about 25 to 35% of aromatic organics such as alkylated benzenes, naphthalenes, and other polycyclic aromatic hydrocarbons (PAHs) (ASTM 1994). Based upon the original formula composition it is reasonable to state that the total concentrations of organic petroleum components were larger than the concentration of PCP when wood treating solution first moved into the soil phase during the wood treating operation years ago. However, the recent site investigation analyses of soil samples presented PCP and total PAHs concentration ratios of 259:1 (HA-7-2), 6:1(HA-7-1), 66:1 (HA-17), and concentration ratio of PCP and total VOCs and PAHs of 216:1 (B-4-1), respectively. In comparison with the original Penta formula these concentration ratios of soil samples suggest that the degradation extent of organic compounds such as VOCs and PAHs had been much greater than the degradation extent of PCP over the years through natural occurring processes. Even though some amount of PCP have probably been degraded over the years, the reverse proportion of PCP and fuel components strongly suggests PCP's persistence in the environment and its resistance to soil biological activities.

In review of the current site investigation findings, the primary concerns for soil treatment are PCP and PAHs. Since the requirements for biodegradation of PCP and PAHs in soil are similar and PCP concentrations determined from soil samples were much higher than PAH compounds, the following discussions on a bioremediation treatability study will primarily focus on PCP.

Biodegradation of PCP in soils has been extensively studied. PCP can be decomposed both aerobically and anaerobically (Sawhney and Brown 1989). Biodegradation of PCP involves dechlorination, which leads to a series of partially dechlorinated products. Partially dechlorinated compounds are major end products of anaerobic degradation and still arouse environmental concern due to their toxicity and increased water solubility. However, under aerobic conditions, these dechlorinated compounds undergo ring cleavage to form detoxified compounds, e.g., aliphatic acids, carbon dioxide (CO_2) and water (H_2O). Therefore aerobic degradation is preferred as a treatment process. The basic mechanism for biodegradation of PAHs is believed to involve hydroxylation, ring cleavage, a series of intermediate oxidative reactions and, finally, formation of aliphatic acids or CO_2 and H_2O (Chakrabarty 1982). Although PCP volatilizes to some extent, under neutral pH soil conditions (e.g., site soil pH value was determined to be 7.7), PCP molecules primarily exists in its ionized form, pentachlorophenate, which is not volatile (Crosby 1981). Even though the ultraviolet (UV) component of sunlight has the necessary energy to decompose PCP molecules, the photodegradation of PCP in contaminated soil is believed to be not significant due to light energy reduction in soil and the presence of a great number of soil constituents that are strong UV absorbents such as humic materials.

Inorganic and organic additives such as nitrogen and phosphorus salts and manure are commonly used in soil treatment to provide sufficient food, nutrients and/or trace elements in order to optimize the living environment and maintain a sufficient population of functional soil microorganisms (Mahaffey et al. 1991; Rasiah et al. 1991; Westlake et al. 1978). In a site treatability study, the biodegradation rates of PCP and PAHs were positively related to the level of manure added (McGinnis et al. 1991). However, Mahaffey et al. (1991) demonstrated that addition of manure alone did not significantly increase the biodegradation rates of PCP and PAHs at a wood treating site, while inorganic forms of nitrogen and phosphorus increased the rates threefold. These findings indicated that the success in applying additives to enhance treatment efficiency may vary with site conditions. Soil moisture and pH also play important roles in the PCP degradation process in soil.

Based on the preliminary nutrient analysis of site specific soil and groundwater samples, the nitrogen and phosphorus concentrations in soil appeared to be low compared to general optimum conditions for soil microbial activities. Presence of some natural organic matter often helps to facilitate biodegradation of persistent compounds like PCP. Because of the complexity of the soil system and the relative persistence of PCP in the environment, it is necessary to gain an understanding of the site specific soil conditions, and to investigate the soil biological treatability, limiting factors, and potential biological enhancement agents. Although studies have shown successful biodegradation of PCP in soils, the feasibility of this technique depends on various controlling factors, one of which is the treatment target PCP cleanup level. The biodegradation process of organic compounds with low water solubilities such as PCP and PAHs can become very slow and ineffective due to their extremely limited bioavailability, which could make low cleanup levels (often in parts per billion range) difficult to accomplish. One of the objectives of this study is to investigate the feasibility of this biological soil treatment method.

II. BENCH SCALE TREATABILITY STUDY DESIGN

2.1. Design Considerations

A. The subject site contains two types of soil, one is silty sand and the other is peat soil which appeared to be mostly saturated and anoxic. Since different types of soils usually result in different predominant microorganism species, these two types of soil are proposed to be investigated as separate study objects to provide an understanding of their roles in the biodegradation process. A mixure of these two types of soil is also proposed to be studied in order to evaluate the potential application in pilot or full scale remediation.

B. The site investigation data shows that the concentrations of PCP varied quite a bit among the sampled locations. The rates of biodegradation of organic compounds in soil are, in general, dependent upon the initial concentrations of these target organic compounds. Therefore, it is proposed to divide each study soil object into two PCP concentration groups, i.e. high PCP concentration group (higher than 100 mg/kg) and low PCP concentration group (less than 100 mg/kg).

C. The relatively high existing concentrations of PCP and some metal ions may be toxic to the naturally occurring microorganisms, which may be partially reflected by the relatively low observed bacteria counts from site soil samples. It is assumed that by introducing nutrients and/or commercially available functioning microorganisms the resident microbial population and its microbial activities would be stimulated or would be enhanced.

D. Control systems with no variable adjustment must be conducted simultaneously in order to perform a comparative evaluation among systems. It must be noted that a objective biological activity lag period at the beginning of the treatability study is anticipated to occur which allows the microbial population to acclimate with the study environment.

2.2. Methodology

The treatability of PCP (and PAHs) with bioremediation will be investigated through a box study. A series of boxes will be loaded with an equal amount of impacted soil from the subject site and engineered with treatment variables. The treatment variables will include soil type, initial concentration of PCP, inorganic nutrient level, organic nutrient level, and microbial population. In order to complete the treatability study or, at least, to obtain reasonable amount of information within a reasonably short time frame, the box study will be conducted indoor under relatively stable room temperature. Soil moisture adjustment and manual aeration will be performed on a weekly basis. Study boxes will be covered, but not sealed, to minimize volatilization of target compounds and soil moisture. The study boxes will be kept in the dark to minimize photodegradation of target compounds except when they are sampled or treated. It is assumed that the loss of target compounds through volatilization and photodegradation will be minimal and negligible under the box study conditions. Therefore, the concentration reduction of target compounds in each box could be considered as the loss due to biodegradation.

Soil samples will be collected from each box periodically over time. Upon the completion of this study the biodegradation rates may be calculated using mass balance of completely mixed batch reactor model. The degradation rates would then be used to assist in remediation design for pilot or full scale remediation if bioremediation is found to be feasible for the site specific soils.

2.2.1. Materials

Study Soil: The study soil batches will be collected from the subject site from desired depths with respect to types of soil and initial concentration ranges. Since the objective of this treatability study is to provide an understanding and design information for potential site remediation, the study will focus on the locations of most concern. The same types of soil with similar magnitude of PCP concentrations will be thoroughly mixed as one batch, be sampled for PCP, total organic carbon (TOC), total nitrogen and phosphorus, and be distributed into boxes in equal amounts. It is important for each box in the same group to begin the treatment process at the same soil conditions so that the parallel comparison of the treatment results can later be ensured.

Boxes: Study boxes can be stainless steel, or glass, or ceramic coated metal wares with lids or equivalent. (Ideally, the soil volume at time zero (Vo) will be similar to the soil volume upon study completion (Vf), where the soil volume taken out of the system as samples during the study could be assumed negligible.)

Inorganic Additives: Commercially available inorganic nutrients such as nitrogen and phosphorus.

Organic Additives: Chicken or cow manure.

Bulking Agent: As a bulky agent, it is recommended that a small percentage of woodchips be added into the peat soil to enhance oxygen diffusion.

PCP degrading bacterium: Commercially available PCP degrading *Flavobacterium* which can be purchased from the American Type Culture Collection (ATCC). The ATCC strain can be obtained in freeze-dried form and needs to be cultured in a ATCC recommended growth medium prior to use.

2.2.2. Analytical Regime

All the analyses associated with this treatability study, except biological testing, will be performed by White Water Associates, Inc. in Amasa, Michigan. The following is a list of analytical parameters for each study box and their sampling frequencies.

Parameters	*Sampling Frequency*
PCP	Every two weeks
PAHs	Beginning and end of study, and once during the study
Bacteria Enumeration	Every four weeks
Total Organic Carbon	Beginning of study
Total Phosphorus	Beginning of study
Total Nitrogen	Beginning of study
Nitrogen, ammonium	Beginning of study
Nitrogen, nitrate/nitrite	Beginning of study
PCP and Other Chlorophenols	Beginning and end of study

2.2.3. Box Design Matrix

The following table content represents the soil type and corresponding treatment materials for each box proposed for this bench scale treatability study.

Box ID	*Silty Sand*	*Peat Soil*	*Silty Sand& Peat*	*High PCP*	*Low PCP*	*Nutrients Inorganic*	*Manure Addition*	*Bacterium Addition*
Box 1	**Yes**	No	No	**Yes**	No	No	No	No
Box 2	**Yes**	No	No	**Yes**	No	**Yes**	No	No
Box 3	**Yes**	No	No	**Yes**	No	No	**Yes**	No
Box 4	**Yes**	No	No	**Yes**	No	No	No	**Yes**
Box 5	**Yes**	No	No	No	**Yes**	No	No	No
Box 6	No	**Yes**	No	**Yes**	No	No	No	No
Box 7	No	**Yes**	No	**Yes**	No	**Yes**	No	No
Box 8	No	**Yes**	No	**Yes**	No	No	No	**Yes**
Box 9	No	**Yes**	No	No	**Yes**	No	No	No
Box 10	No	No	**Yes**	**Yes**	No	No	No	No
Box 11	No	No	**Yes**	**Yes**	No	**Yes**	**Yes**	No
Box 12	No	No	**Yes**	No	**Yes**	No	No	No

Boxes 1, 5, 6, 9, 10 and 12 are control systems for each soil type without addition of treatment materials. Based upon the nutrient analysis of the soil, an inorganic nutrient solution will be mixed into the soils in Boxes 2, 7 and 11 to bring the soil nutrient levels to an approriate range. Manure (approximately 10% weight/weight) will be blended into the soils in Boxes 3 and 11. PCP degrading bacteria growth culture will be distributed within the soils in Boxes 4 and 8 to bring the bacteria population to approximately 10^6 cells per gram of soil. After the above preparation of the boxes are completed, soil samples will be collected immediately from each box for the analyses of PCP, PAHs, bacteria enumeration, organic nitrogen, inorganic nitrogen, total phosphorus, TOC and other chlorophenols. These analyses will establish the baseline information for all the treatment boxes and the results will be considered as values at time zero for the beginning of bioremediation process.

Step-by-step experimental set-up is as follows:

a. Collect soil from the site.
b. Mix six homogenous batches of soil -- 1) silty sand/high PCP; 2) silty sand/low PCP; 3) peat soil/high PCP; 4) peat soil/low PCP; 5) silty sand-peat soil/high PCP; and 6) silty sand-peat soil/low PCP.
c. Sample each of the above soil batch for PCP, total organic carbon, nitrogen, and phosphorus.
d. Distribute soil from each above mixed soil batch 1) into Boxes 1, 2, 3 and 4, soil batch 2) into Box 5, soil batch 3) into Boxes 6, 7 and 8, soil batch 4) into Box 9, soil batch 5) into Boxes 10 and 11, soil batch 6) into Box 12, respectively with equal quantity.
e. Label each box.
f. Add treatment materials into corresponding boxes based on the box matrix information and mix them with soil thoroughly.
g. Sample each box for all the listed parameters to establish the baseline information.
h. Place the box lids on the boxes and let them sit until next sampling interval or soil moisture adjustment/aeration interval.

III. DATA ANALYSIS

Concentrations profiles of PCP and PAHs over time in each box would be graphically presented. The comparative effectiveness of PCP biodegradation in box systems with respect to different treatment variables would be evaluated. Using the completely mixed batch reactor mass balance, biodegradation rates of each box system may be estimated. The system volume of each box will be assumed constant (the sample size is negligible in comparison with the soil volume in the box).

It should be noted that the detailed approaches such as number of boxes, sampling frequency and study duration are subjected to adjustment over the course of the study.

REFERENCES

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