



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

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October 8, 1993

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MEMORANDUM

SUBJECT: Technical Review of Bioremediation Treatability Testing Program Summary - Review, Standard Chlorine Site (93-RO3-001)

FROM: Mary E. Randolph, Microbiologist *ME*
Applications and Assistance Branch

TO: Katherine Lose, RPM, (3HW42)
DE/MD Section
EPA, Region 3

Per your technical support request dated September 20, 1993, the document entitled, "Bioremediation Treatability Testing Program Summary- Review," has been reviewed for technical merit and appropriateness by Dominic DiGiulio, Scott Huling, Hugh Russell, John Matthews, and me. If you have any questions or the Technology Support Center can be of further assistance, please contact me at 405-436-8616.

General Comments:

Overall, we feel that the treatability data is inconclusive and non-supportive with respect to the role of the biological fate of the compounds studied. This comment is supported by the following: (1) variability of the concentration of total chlorobenzenes (Tot-CB) observed in the flasks and the associated lack of confidence in the data, (2) the potential for volatile losses from the reactor flasks, (3) inconclusive stoichiometric release of chlorides, (4) no nutrient consumption, and (5) lack of microbial data. While it is widely accepted that dichlorobenzene is biodegradable and is possible that biodegradation may have occurred in these tests, the data presented is inconclusive in support of such degradation. It should be noted that while the results from these tests are inconclusive and unsupportive with respect to the role of biological processes, it is entirely possible that some form of bioremediation can be effectively used at this site.

The study included an anaerobic set of flasks to evaluate the fate of Tot-CB under anoxic conditions. The anaerobic process involving reductive dechlorination is a technology that is problematic with respect to in-situ field implementation. Presently, the ability to design, construct and implement a system involving successful application of this process has not been demonstrated. However, it is reasonable to expect that slurry

AR308544

phase treatment in a reactor vessel would be less problematic and may be feasible. To the best of our knowledge, this process has not been successfully demonstrated.

It is reasonable to expect that in aerobic biological systems, the greater the degree of chlorination, the slower the rate of biodegradation. Correspondingly, the accumulation of lower chlorinated compounds is unlikely. An exception to this trend would be if the lower chlorinated compounds were inhibitory to microbial processes. In such cases, these compound might accumulate. Under anaerobic conditions, the more oxidized (chlorinated) compounds (hexa, penta, tetra, tri) are more easily dechlorinated via reductive dechlorination processes, i.e. the compound acts as an electron acceptor; and the less chlorinated compounds (mono, di) are less amenable to the reductive dechlorination process. It follows that reductive dechlorination would be more effective on compounds that are highly substituted than the mono- and dihalogenated compounds.

This overall perspective should be considered when scoping the remediation feasibility options. For example, the primary form of contaminants at the site appear to be the mono- and dihalogenated compounds (i.e. Memo dated 8/26/93 transmitting the descriptive statistics for chemicals of concern in subsurface media). Based on the relatively low amount of the 3, 4, 5, and 6 chlorinated compounds, the costs associated with reductive dechlorination remediation may reduce the overall feasibility of this remediation approach. Further evaluation of this point is recommended.

In general, it appears that the scoping of the feasibility study should be re-evaluated. Information contained in this report indicates that the treatability study may have been implemented prior to identifying specific objectives of the study or scoping/screening of the overall remediation approach. For example, while the report is entitled, "Bioremediation Treatability Testing Program - Summary of Findings", it is unclear whether bioslurry, land treatment, in-situ, bioventing, etc., remediation technologies are targeted for this site. The potential target technology should be narrowed down so a screening test could be designed to address the feasibility of each target technology with respect to more focused, site specific issues.

Specific comments concerning the document are as follows:

Section 4.0 Sample Characterization Results

1. The initial concentration of total chlorobenzenes (Tot-CB) in the soil and aquifer material, and the initial concentration (Day 0) of Tot-CB in the flask reactors (i.e. Figures 2-7) are summarized in Table 1.

The concentration in the flask reactors is generally lower than the site sample initial concentration reported in section 4.2. Since each reactor essentially consisted of approximately 20 g. of

AR308545

media and 80 ml of water (i.e. sections 6.2.1, 6.2.2), then the lower values can be partially attributed to the partitioning of Tot-CB to the water phase. Since 1,2- and 1,4-Dichlorobenzene (volatile compounds with Henrys Constants of 1.88×10^{-3} and 1.58×10^{-3} (atm-m³/mole)) compose the largest fraction of the contaminants, volatile losses occurring during sample transfer may have occurred as well. Variability in the fraction remaining may represent the heterogeneous nature of the sample material, sample transfer, or analyses. It is worth noting that the initial slurry phase Tot-CB concentrations do not reflect field concentrations, and that the initial slurry phase concentration is variable which may affect its fate in the reactor. Assuming the variability is due to analytical constraints, data confidence should be considered when evaluating the test results.

The high fraction remaining in the sediment sample indicates that the initial concentration estimate may have been incorrect. Correspondingly, the variability of the sediment sample results (Figures 6 and 7) may also reflect this observation.

Table 1 - Summary of Initial Total Chlorobenzenes in Site Samples and in the Flask Reactors.

Media	Site sample [Tot-CB]i (mg/Kg)	Flask reactors [Tot-CB]i (mg/Kg)	
		Aerobic	Anaerobic
Surface soil	5370	3700 (69%) ⁽¹⁾	3400 (63%)
		2400 (45%)	2600 (48%)
		1400 (26%)	2600 (48%)
Subsurface soil	1080	480 (44%)	450 (42%)
		420 (39%)	300 (28%)
		200 (19%)	250 (23%)
Sediment	190	430 (226%)	300 (158%)
		410 (216%)	250 (132%)
		290 (153%)	125 (66%)

(1) fraction remaining relative to the initial site sample concentration

Section 5.0 Experimental Design:

1. The anaerobic bioremediation scenario was conducted over 60 days, a timeframe that may not allow sufficient biodegradation by an unacclimated microbial population.

2. Triplicate flasks were used, but the data presented in Attachment 10 does not indicate whether the samples obtained were analyzed in triplicates. It is recommended that this data be clearly reported.

AR308546

Section 6.2 Aerobic Flask Tests:

1. The aerobic flasks were covered with loosely fitted plastic caps to minimize evaporative losses. This experimental design does not minimize volatile losses from the flasks. Therefore, volatilization must also be considered one of the fate mechanisms in the treatability study data analysis.

2. The abiotic control in the aerobic and anaerobic flasks were amended with a 37 percent formaldehyde solution. The volume of formaldehyde solution was not specified. It may be possible that formaldehyde, if present in low concentration, may have been used by microbes as substrate.

Section 6.3 Anaerobic Flask Tests:

1. It is not clear whether the control flask was amended with the digester sludge inoculum. Since the results from the amended flasks are compared to the control, it is prudent to amend the control flask with the digester sludge.

2. Since the flasks were opened at least three times during the experiment, volatilization from the anaerobic reactors cannot be ruled out as a loss mechanism from the reactors. This is particularly true when considering the volatility of the compounds.

Section 8.0 Findings

1. Section 8.4.1 indicates that the nutrients (N and P) were constant throughout the test period for all test scenarios. Although the data is not presented to evaluate more thoroughly, this indicates that no measurable utilization of nutrients occurred, which infers that biological processes may have been insignificant in these tests.

Section 9 Conclusions:

1. It is concluded in section 9.1 that presumptive evidence of biodegradation of Tot-CB is seen in the chlorinated benzene decline in conjunction with an increase in the chloride concentration for the anaerobic surface soil scenario. While it is true that the overall chloride concentration increases relative to the control, there were two anomalous trends. In the first 10 days, when the Tot-CB decreases significantly, there was not an increase in chlorides. Second, from days 10-30, there was an increase in the Tot-CB concentration, and an increase in the chloride concentration. These two observations are contradictory with respect to biological reductive dechlorination processes. It was not until days 30-60 when the decrease in Tot-CB occurred simultaneously with an increase in chlorides. Additionally, the abiotic control flask indicated essentially the same Tot-CB trends as the biotic treatment flasks. A strict interpretation would indicate abiotic processes dominated the fate of Tot-CB, rather than biotic.

AR308547

Based on the variability of the Tot-CB concentration as observed during days 0, 10 and 30 (i.e. decreasing, increasing concentrations) there is questionable confidence that the concentration observed during day 60 represents a significant loss.

2. Section 9.5 indicates that nutrient addition in the wetland areas may promote natural degradation of contaminants, as seen in the anaerobic surface soil (Fig. 3) and aerobic subsurface soil (Fig. 4) tests. This conclusion is not supported by the data presented. There is no clear evidence, that the data from the anaerobic surface soil nor the aerobic subsurface soil can be attributed to biological processes. The amendment of a wetlands area with nutrients, based on the results of this study, has no technical merit. Additionally, nutrient amendment to wetlands is much more complex than simulated in this study and has major ecological implications. Careful evaluation is highly recommended.

The following specifically addresses the comment mentioned in the previous memo dated January 22, 1993 that all of the compounds are both volatile and amendable to aerobic biodegradation and could be good candidates for bioventing and/or soil vacuum extraction technologies. There is always the concern that some contaminant concentrations in some locations may be high enough to potentially inhibit microorganisms. Several figures have been prepared and attached to illustrate mass in the air phase versus the fraction of organic carbon content in soils. The equation describing this relationship is also included. It is apparent from inspection of these figures that chlorobenzene can be readily removed from soil using soil venting while dichlorobenzenes may or may not be effectively removed depending on the fraction of organic carbon content in soils at the facility. Tri, tetra, penta, and hexachlorobenzenes can not be effectively removed from soils by venting. In situ removal of these compounds may be possible through bioremediation of which bioventing is an option. Oxygen in the form of air can be introduced via air extraction and/or air injection wells. Oxygen consumption rates can be easily measured using vapor probes.

One factor limiting the effectiveness of venting/bioventing would be reduced permeability in highly contaminated areas, especially if higher chlorinated benzenes have precipitated out of solution or are present as polymers in soils. The compounds 1,4 dichlorobenzene, 1,2,3-trichlorobenzene, 1,3,5-trichlorobenzene, and all tetra, penta, and hexachlorobenzenes exist as solids at room temperature when present in pure chemical form. The Standard Chlorine Facility is known to have been subject to several gross spill episodes so the possibility of separate phase chlorobenzenes in soils exists.

It is recommended that: (1) site characterization data are re-evaluated with respect to phase distribution of the contaminants, (2) clean-up goals are identified, and (3) a list of the specific technologies applicable, given these criteria, are identified. A literature review focused on the fate, transport, and remediation

AR308548

options associated with site- specific compounds would yield useful information to design specific tests to evaluate the appropriate technologies.

cc: Rich Steimle, 5102W
Kathy Davies, Region 3
Phil Rotstein, Region 3
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AR308549

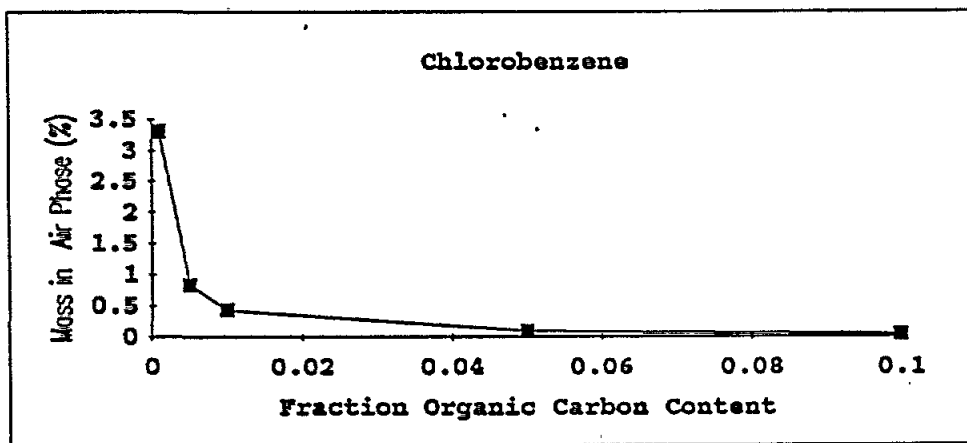
Volatility of Chlorobenzenes: Determination of Mass Fraction in Air Phase

Input Parameters: bulk density = 1.7 g/cm³; volumetric moisture content = 0.2; porosity = 0.4

	Koc (cm ³ /g)	Kh
chlorobenzene	398	0.15
1,4-dichlorobenzene	2754	0.08
1,3,5-trichlorobenzene	14791	0.08
1,2,4,5-tetrachlorobenzene	39811	0.04
pentachlorobenzene	131826	0.03
hexachlorobenzene	257039	0.02

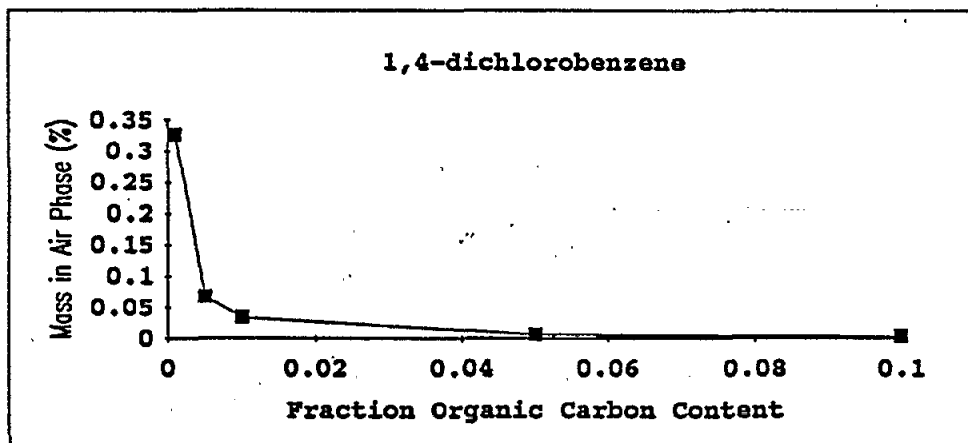
chlorobenzene

foc	air/soil K	Mass in Air (%)
0.001	6.04	3.309067
0.005	24.09	0.830335
0.01	46.64	0.428816
0.05	227.07	0.08808
0.1	452.60	0.044189



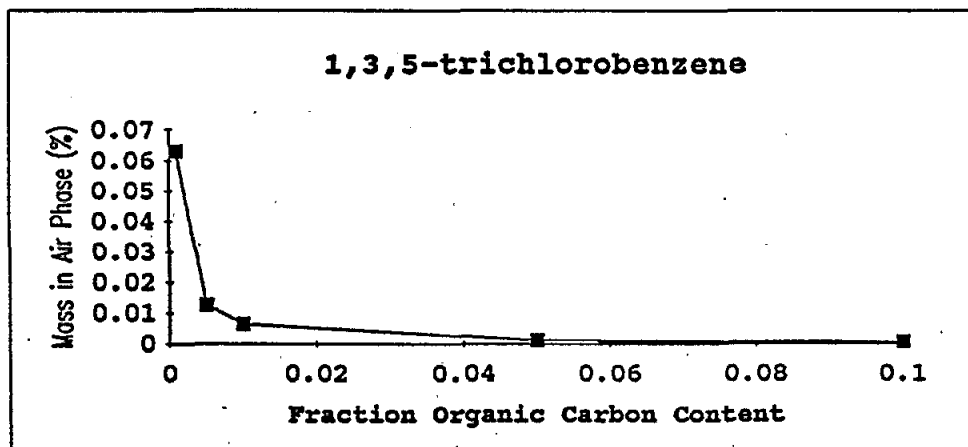
1,4-dichlorobenzene

foc	K	air/soil Mass in Air (%)
0.001	61.22	0.326677
0.005	295.31	0.067725
0.01	587.93	0.034018
0.05	2928.83	0.006829
0.1	5854.95	0.003416

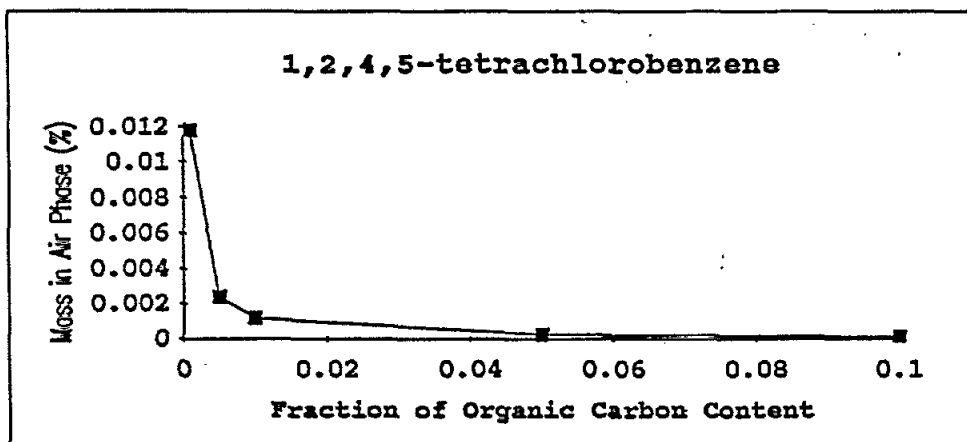


1,3,5-trichlorobenzene

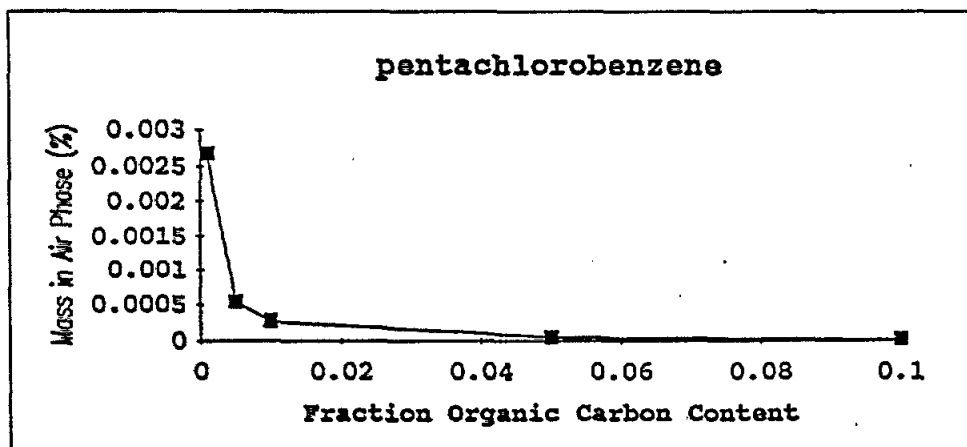
foc	K	Air (%)
0.001	317.01	0.06309
0.005	1574.24	0.012705
0.01	3145.79	0.006358
0.05	15718.14	0.001272
0.1	31433.58	0.000636



1,2,4,5-tetrachlorobenzene		
foc	K	Air (%)
0.001	1.70E+03	0.011784
0.005	8.47E+03	0.002363
0.01	1.69E+04	0.001182
0.05	8.46E+04	0.000236
0.1	1.69E+05	0.000118



pentachlorobenzene		
foc	K	Air (%)
0.001	7.48E+03	0.002675
0.005	3.74E+04	0.000535
0.01	7.47E+04	0.000268
0.05	3.74E+05	5.35E-05
0.1	7.47E+05	2.68E-05



Estimation of Total Soil Concentration from Vapor Concentration

$$C_t = C_g \left[\frac{\rho_g K_p}{K_h} + \frac{\theta}{K_h} + \phi \right]$$

Where: C_t = total volatile organic concentration (mg/cm³ soil)

C_g = vapor concentration (mg/cm³ air)

ρ_g = bulk density of soil (g/cm³ soil)

K_p = soil-water partition coefficient (cm³/g)

K_h = Henry's Law Constant (dimensionless)

θ = volumetric moisture content (dimensionless)

ϕ = volumetric air content (dimensionless)