Site: Chemplex Co II
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Break: 1.3
Other: EKI 10-5-92

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5 October 1992

Ms. Nancy J. Johnson, P.E.
Remedial Project Manager
Region VII
Environmental Protection Agency
726 Minnesota Avenue
Kansas City, KS 66101

Subject: Technical Data for PAH Biodegradation Rates:
Chemplex Site, Clinton, Iowa
(EKI 890052.11)

Dear Ms. Johnson:

On 6 July 1992, Erler & Kalinowski, Inc. ("EKI") prepared a memorandum which discusses the results of modeling the transport of polycyclic aromatic hydrocarbons ("PAHs") at the Chemplex site. This memorandum was transmitted to you in a letter from Kevin McAnaney of Dewey Ballantine on 31 March 1992.

The objective of the model effort was to determine the concentration of PAHs in soil that could be left in place such that Cleanup Standards in groundwater are met at the POC. Model runs focussed on the Previous Basin rather than the Landfill, the DAC Storage and Truck Loading Area, or Surface Impoundment C, because elevated concentrations of PAHs have been measured in the Previous Basin and there is a short travel path to the POC. Because of the short travel path, PAH compounds migrating to the POC will have undergone relatively little degradation or dispersion. For other source areas which are farther from the POC, greater degradation and dispersion would occur between the source area and the POC. Thus, for these other source areas, Cleanup Standards in groundwater could be met at the POC with higher levels of PAHs in the source soils. The Previous Basin analysis would result in the lowest levels of PAHs permissible in soil.

Model runs were performed for naphthalene, the most mobile and abundant of the non-carcinogenic PAHs, and for benzo(a)pyrene, a carcinogenic PAH which has been detected at the site. The groundwater Cleanup Standards for these two compounds are 20 ppb and 0.2 ppb, respectively. These two compounds are thought to be generally representative of the transport behavior of their respective chemical classes. Model runs were performed for both the non-carcinogenic and carcinogenic PAHs in order to determine which class would control the permissible levels of PAHs in soil at the site.

As discussed in the 6 July 1992 memorandum, the carcinogenic PAHs are extremely insoluble and adsorb strongly to soil so that transport of such compounds in groundwater is extremely slow. The results of the model indicate that transport via dissolution in groundwater is not a concern at the POC.

Model runs were also performed for naphthalene. As you recall, a biodegradation half-life of 258 days was employed in the model. Assuming this half-life, a naphthalene concentration of 6.5 ppb in groundwater is predicted at the POC which is less than the Cleanup Standard of 20 ppb. However, given the relative sensitivity of the transport model results to the half-life, EPA, during a meeting on 30 July 1992, expressed concern that the half-life may not be adequately conservative.

Since our meeting, EKI has worked with Dr. Colin Mayfield of the University of Waterloo and Waterloo Hydrogeology Advisors, Inc. ("WHA") to search the scientific literature for additional half-life data for naphthalene and to elucidate the various factors which affect in situ degradation rates. Attached is his report.

One of the principal conclusions of the report is that naphthalene degrades readily under aerobic conditions but degradation also occurs under denitrifying, sulfate-reducing, and methanogenic anaerobic conditions. In Table 1 of the report, WHA indicates that one measure of aerobic conditions is that dissolved oxygen in groundwater exceeds 1 mg/L.

At the Chemplex site, dissolved oxygen (DO) data have been measured in various groundwater monitoring wells downgradient of the Previous Basin, the DAC Storage and Truck Loading Area, and the Polishing Basin, where naphthalene transport might be a concern. As indicated in the attached Table A, DO exceeds 1 mg/L in all wells for which data are available. This suggests that the system as a whole is essentially aerobic. Under such conditions, the WHA report concludes that biodegradation half-lives would be on the order of 10 to 30 days. However, given the complexity of the subsurface environment at Chemplex, it is likely that there could be microenvironments where the system behaves anaerobically.

For the purpose of running a conservative transport model, therefore, it was assumed that the system is anaerobic and accordingly a long half-life (258 days; Howard and others; 1991) was selected. The results of the literature search conducted by WHA indicates that anaerobic half-lives vary on the order to 100 to 250 days. Therefore, the half-life used in the model is conservative for anaerobic conditions. Given that the actual system is not completely anaerobic, actual half-lives for the subsurface at Chemplex must be considerably shorter.

Based on the available biodegradation half-life data for naphthalene in the recent scientific literature and the available dissolved oxygen data for groundwater at the Chemplex site, the 258 day degradation rate for naphthalene used in the transport model is considered to be extremely conservative. Given this half-life, the model predicts that naphthalene dissolved in groundwater will not exceed the Cleanup Standard at the Point of Compliance. Therefore, it can be concluded that groundwater transport of PAHs from potential source soils is not a vector of concern at the Chemplex site.

If you have any comments or questions regarding any of these materials, please don't hesitate to call.

Very truly yours,
ERLER & KALINOWSKI, INC.

Theodore G. Erler, P.E.
Project Manager

Carey E. Peabody, Ph.D, R.G.
Project Geochemist

Attachments

TABLE A

Dissolved Oxygen and Other Field Measurements for Groundwater
Chemplex Site
Clinton, Iowa

Well Number	Date Sampled	Temperature, C	pH	Dissolved Oxygen, PPM
3	12/8/91	10.9	7.45	NA
3A	12/8/91	8.5	6.92	6.5
DG-1	12/18/91	10.7	7.42	NA
DG-1	12/6/91	10	6.63	3.3
DG-2	12/18/91	7.5	7.92	0.2
DG-5	12/10/91	12.9	7.21	NA
DG-11	12/8/91	14.5	7.41	NA
DG-12	12/7/91	10.6	6.42	4.6
DG-13	12/20/91	10.9	7.55	NA
DG-18B	1/6/92	9	7.48	7.8
DG-18B	12/6/91	10.4	7.35	NA
DG-19B	12/8/91	10.8	7.31	NA
DG-22	12/17/91	10	7.64	1.7
DG-24	12/10/91	11.3	7.53	NA
DG-25	12/10/91	12.3	7.5	NA
H-2	12/11/91	8.9	7.38	20.2
J-4	12/7/91	11	6.8	NA
MW-1	12/19/91	11.7	NA	NA
MW-38	12/19/91	10.3	6.85	NA
MW-39A	12/13/91	10	7.21	0.4
MW40A	1/7/91	5.8	6.75	2.1
MW-41	12/6/91	11	7.53	5.5
MW-41	12/7/91	12.4	7.63	2
MW-48A	12/7/91	11.7	7.09	NA
MW-49A	12/18/91	7	6.86	NA
MW-50A	12/9/91	11.1	7.29	NA
MW-50A-1	12/19/91	9.2	6.89	3.8
MW-51A	12/8/91	12.2	7.63	2.1
MW-51A-1	12/7/91	8.9	7.35	2.3
MW-52A-1	12/11/91	8.2	7.56	18.5
MW-53-1	12/12/91	11	5.8	NA
MW-53A	12/12/91	11.8	7.31	6.6
MW-53A-1	12/12/91	NA	7.2	NA
MW-67A-1	12/17/91	11	7.16	12.1
MW-69A	1/5/92	10	7.24	NA
MW-69A	12/11/91	10.6	7.31	18.1
MW-86A	12/11/91	11.4	7.04	NA
MW-87A	12/17/91	11.1	7.3	NA
MW-91A	12/18/91	9.7	7.16	NA
MW-94A	1/5/92	9.1	7.81	NA
UG-1	12/17/91	10.2	7.5	NA
UG-2	12/19/91	12.1	7.02	8.9
UG-2B	12/21/91	11	7.08	3.2

NA indicates data not available

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Naphthalene Biodegradation

To: Erler and Kalinowski, Inc.

From: Colin I. Mayfield and James F. Barker,
Waterloo Hydrogeology Advisors Inc.

Date: 28th Sept. 1992

Biodegradation of naphthalene.

Introduction

The objective of this report is to summarize the recent information available on the biodegradation of naphthalene and the factors that influence the rate and extent of such activity. Of particular relevance and concern is the role of oxygen status and anaerobic environments in such activities. Actual rates reported in the literature will be quoted and can be used as a comparison for the proposed 250 day half-life used in the Erler & Kalinowsky PAH modelling memorandum (6th July, 1992).

Naphthalene biodegradation will be considered in this report in the context of groundwater evolution, especially as it relates to low oxygen and anaerobic environments. Then the main factors affecting naphthalene biodegradation will be covered together with a summary of biodegradation rates actually obtained under the various environmental conditions.

Evolution of groundwater; effects on microbial activities including naphthalene biodegradation.

The reason for stating and briefly explaining the observed geochemical and microbial changes in a "typical" groundwater is to demonstrate the complexity of the processes involved and to show that it is impossible to get different biodegradation rates that would apply to each one of the many zones without a very detailed knowledge of the oxygen levels, nutrient levels and detailed geochemistry of the complete plume or flow regime. To complicate matters even further, small-scale differences in aquifer properties (of the order of 1 to 10 cm) and differences in microorganisms and their physiology lead to microenvironments of the same order of magnitude. It is therefore important to summarize the biodegradation rate in a conservative manner.

Depending on the nutrient status of the groundwater, in particular the concentration of organic carbon, there will always be changes in oxygen levels and redox potentials (Eh or pE) along the flow path. This is due to the activity of bacteria present in all aquifers. High levels of nutrients will lead to a decrease in dissolved oxygen due to bacterial aerobic respiration processes. This will be followed by anaerobic activity of various physiological groups of bacteria as the pE changes. The changes themselves are mediated by the activities of the bacteria and the geochemistry of the aquifer. Typically, aerobic activities lead to depletion of oxygen (below titration detection limits) and, subsequently, decreasing redox potentials lead to anaerobic heterotrophic activity (organic carbon is the electron acceptor for metabolic processes), denitrification (nitrate is the electron acceptor), sulfate reduction (sulfate is the electron acceptor and methanogenesis (carbon dioxide is the electron acceptor). The products of the microbial processes are organic materials, nitrogen, hydrogen sulfide and methane, respectively. They are all dependent upon the previous process in the sequence causing changes in geochemistry and pE such that the particular group of bacteria is able to grow and metabolize. Typically, the environment is not completely homogeneous; most aquifers show small-scale variation in porosity, geochemistry, nutrient status, etc. that permit microenvironments to occur. This means that the processes overlap somewhat so that denitrification and anaerobic heterotrophic activities can occur in the same general region of the aquifer due to the presence of these different microenvironments. Another factor causing variation is the very common observation that the processes (such as denitrification, sulfate reduction, etc.) can operate over a range of pE values; different bacteria, or even different strains of the same species of bacteria, have different tolerance levels and different nutrient and environmental requirements. It is important to note that the evolution of anaerobic conditions is sequential; high carbon levels are required to support microbial activity which then leads, in sequence, to denitrifying, sulfate-reducing and methanogenic conditions.

One way to examine potential microbial activities in an aquifer is to use the geochemistry of the groundwater to predict the stage of groundwater evolution. This is, in many cases, superior to actual measurements of Eh or pE since these measures are notoriously difficult to perform accurately in the aquifer environment.

Table 1. shows the typical criteria for redox parameters that are used to assign a groundwater to a particular redox group such as denitrification, sulfate reduction, etc.

Biodegradation of naphthalene under various environmental conditions.

a). Oxygen status.

Naphthalene biodegradation rates have been measured under various oxygen levels and redox potentials. Each observation and rate is only an average of the rates in differing microenvironments. It is well established that the aerobic degradation of naphthalene is rapid; typical values for half-lives range from 10 to 60 days depending upon the environment, nutrient status, oxygen levels, pH, and prior exposure of the bacteria to naphthalene (or sometimes related PAHs). In the 1988 EPA document "Treatment Potential for 56 EPA-listed Hazardous Chemicals in Soil" (Number PB 88-174 446/AS), the half life of naphthalene under aerobic conditions in a sand loam is 2.1 days. The naphthalene was used as a sole carbon source for growth by the microorganisms (as was phenanthrene and anthracene), while the higher ring number PAH compounds (four, five and six rings) were more recalcitrant (half-life of +200 days) and were considered to be degraded by co-metabolic processes. They were also more recalcitrant when present as pure compounds instead of part of a complex mixture of waste materials (again suggesting com-metabolic processes). The rate of transformation of naphthalene in various environments can be summarized as follows;

$$T_{\text{transformation}} = \frac{\text{incubation time}}{\text{\% of naphthalene transformed}}$$

By this definition, used to summarize the results from different conditions and periods of incubation, the observed aerobic rates are closely similar from many different experiments and test environments, including pure culture studies, mixed cultures, water, sediments and landfarming operations. Anaerobic rates (e.g. Mihelcic and Luthy, 1988) were slower.

Reference	Microorganism/conditions	$T_{\text{transformation}}$
Walker and Colwell 1975	Indigenous/sediment*	41
Walker et al 1975	Indigenous/water*	41
Herbes & Schwall 1978	Indigenous/sediment*	1.6
De Kreuk 1986	Indigenous/landfarming*	40
Mihelcic & Luthey 1988	Indigenous/sediment (aerobic)	10
Mihelcic & Luthy 1988	Indigenous/sediment (denitrifying)	63
Shiaris 1989	Indigenous/sediment*	13
Srivastava et al 1990	Mixed culture/sediment	60

* represents the presence of naphthalene in the system prior to testing, i.e. acclimation could have taken place.

Walker and Colwell. 1975. *Some effects of petroleum on estuarine and marine microorganisms.* **Can. J. Microbiol. 21, 305-313.**

Walker, Colwell and Petrakis. 1975. *Evaluation of petroleum-degrading potential of bacteria from sediment and water.* **Appld. Microbiol 30, 1036-1039.**

Herbes and Schwall. 1978. *Microbial transformation of polycyclic aromatic hydrocarbons in pristine and petroleum-contaminated sediments.* **Appld. Environ. Microbiol. 35, 306-316.**

De Kreuk 1986. *Microbiological decontamination of excavated soil. In*: First International Conf. on Contaminated Soil, Utrecht, The Netherlands. pp. 669-678. Ed. by Assink and Brink.

Mihelcic & Luthy 1988 - see below.

Shiaris 1989. *Seasonal biotransformation of naphthalene, phenanthrene and benzo[a]pyrene in surficial sediments.* **Appld. Environ. Microbiol. 55, 1391-1399.**

Srivastava, Kilbane, Kelley, Gauger, Akin, Hayes and Linz. 1990. *Bioremediation of former gas plant sites. In*: **Proc. 44th Industrial Waste Conf.** Purdue, Lewis Publishers. pp. 49-60.

In **Howard, Boethling, Jarvis, Meylan and Michalenko.** 1991. *Handbook of Environmental Degradation Rates.* **Lewis Publishers Inc., Chelsea, Michigan,** the slowest biodegradation rate listed was that under anaerobic conditions where naphthalene had a half-life of 258 days (50% degradation in 258 days).

In three publications (**Mihelcic and Luthy. 1988.** *Degradation of polycyclic aromatic hydrocarbon compounds under various redox conditions in soil-water systems* **Appld. Environ. Microbiol. 54, 1182-1187; Mihelcic and Luthy. 1988.** *Microbial degradation of acenaphthalene and naphthalene under denitrification conditions in soil-water systems.* **Appld. Environ. Microbiol. 54, 1188-1198; Mihelcic and Luthy. 1991.** *Sorption and microbial degradation of naphthalene in soil-water suspensions under denitrification conditions.* **Environ. Sci. Technol. 25, 169-177.**), the authors showed that naphthalene could be degraded under denitrifying conditions (pE, presence of nitrate and suitable other nutrients). An initial concentration of 7 mg/L was degraded to non-detectable levels in 45 days. Degradation was slow or absent under anaerobic conditions. Other workers (**Grbic-Galic. 1989.** *Microbial degradation of homocyclic and heterocyclic aromatic hydrocarbons under anaerobic conditions.* **Dev. Industr. Microbiol. 30, 237-253.** and **Al-Bashir, Cseh, Leduc and Samson 1990.** *Effect of soil/contaminant interactions on the biodegradation of naphthalene in flooded soil under denitrifying conditions.* **Appld. Microbiol Biotechnol. 34, 414-419**). have shown biodegradation under methanogenic and denitrifying conditions, respectively.

Denitrification (one of the processes shown to facilitate naphthalene degradation) can occur at significant (but low) oxygen concentrations. If the denitrifying bacteria, nitrate and a metabolizable organic substrate are present, then nitrogen gas and nitrous oxide are produced (nitrate is used as the electron acceptor) even with measurable oxygen present. Most of this data comes from soil studies. The bacteria involved in denitrification are facultative anaerobes; they use oxygen more efficiently as a terminal electron acceptor (it has a higher energy yield), but can switch to using nitrate when oxygen becomes limiting.

A recent presentation (**Thierrin, Davis, Barber, Patterson, Pibac, Power and Lambert.** 1992. *Natural biodegradation rates of BTEX compounds and naphthalene in a sulphate reducing groundwater environment.* **Proceedings of the In-Situ Bioremediation Symposium, Edited by S. Lesage. Niagara-on-the-Lake, Canada, Sept. 20th, 1992**) demonstrated that naphthalene biodegradation occurred in sulphate reducing anaerobic conditions in a field injection test using deuterium-labelled naphthalene. The half-life of naphthalene in the tracer test was 33 ± 6 days and in the groundwater plume was 160 ± 20 days (calculated from input function and measured remaining concentrations).

b). Other environmental factors.

Many different commonly occurring genera of bacteria can degrade naphthalene; they include the genera *Alcaligenes, Aeromonas, Achromobacter, Beijerinckia, Flavobacterium, Nocardia, Moraxella, Pseudomonas* and

Rhodococcus. The ability to degrade naphthalene is so widespread that it is unlikely that absence of suitable organisms is a factor in whether or not the compound is degraded.

Acclimation of the microorganisms to the presence of the PAH has been observed; Mihelcic and Luthey (above) observed a 2-week acclimation period for naphthalene under denitrifying conditions.

Temperature does not appear to be a limitation to naphthalene biodegradation. In groundwater, temperatures tend to be more stable than in surface soils and to be approximately 10C as shown by average temperature in wells from data supplied by FAX (31/08/92). This temperature range is typical of sites in the northern states and Canada. In a fresh water lake subject to continual PAH input, biodegradation was rapid and occurred at temperatures as low as 0C (**Cooney, Silver and Beck. 1985.** *Factors influencing hydrocarbon degradation in three freshwater lakes.* **Microb. Ecol. 11, 127-137.**

The absence of nutrients could conceivably be a limiting factor in naphthalene biodegradation. In most studies using radiolabelled substrate, naphthalene was used as an energy source and a carbon source for growth of the organisms. Thus, carbon will be supplied by the naphthalene itself. If carbon is supplied, the limiting nutrients in aquifers tend to be either nitrogen or phosphorus in most studies where limitations have been found. The ratio of carbon:nitrogen:phosphorus usually approximates 100:15:1 (the ratio found in microbial cells).

Conclusions

1. All extant aerobic biodegradation rates for naphthalene are faster than anaerobic rates. The median half-life in aerobic environments is approximately 10 to 30 days whereas the half-life in anaerobic environments tends towards 100 to 250 days.

2. Naphthalene is degraded anaerobically under denitrifying, sulfate-reducing and methanogenic anaerobic conditions. The rates of degradation vary under these different conditions, but tend to be longer under the more anaerobic conditions.

3. There will be small-scale variations in dissolved oxygen, other physical and chemical factors, biodegradable organic substrates, nutrients, bacterial distribution, and naphthalene concentration causing differences in biodegradation rate. It is therefore reasonable to assess a conservative rate based on the slowest anaerobic biodegradation rate in the literature.

4. If any dissolved oxygen is present (approx. 1 mg/L), there will probably be aerobic biodegradative activities. In studies with toluene, the presence of even trace quantities of oxygen led to aerobic degradation and removal in a sandy aquifer (**Patrick, Barker, Gillham, Mayfield and Major**. 1986 *The behaviour of soluble petroleum product derived hydrocarbons in groundwater. Phase II.* Petroleum Association for Conservation of the Canadian Environment, Report Number 86-1 and **Berry-Spark, Barker, MacQuarrie, Major, Mayfield, and Sudicky**. 1988. *The behaviour of soluble petroleum product derived hydrocarbons in groundwater. Phase III.* Petroleum Association for Conservation of the Canadian Environment. Report Number 88-2.).

For comparison purposes, toluene has an octanol-water partition coefficient (K_{ow}) of 380 and an aqueous solubility of 554 mg/L whereas naphthalene has a K_{ow} of 2594 and a solubility of 32 mg/L (solubility values from **Kebe, Brookman, Atkins, and Unites**. 1984. *An evaluation of the natural fate of aqueous gasoline components and treatment alternatives. Task 1A - Literature Survey: hydrocarbon solubilities and attenuation mechanisms.* **Report to the American Petroleum Institute** and K_{ow} values averaged from data in **Hansch and Leo**, 1979. *Substituent constants for correlation analysis in chemistry and biology.* **John Wiley & Sons Inc. New York. N.Y.**).

5. The extent of any co-metabolic and secondary substrate utilization is unknown but could increase any single substrate biodegradation rate derived from single substrate studies. Naphthalene is so readily degraded aerobically that it is unlikely that these processes would contribute significantly to the observed degradation rates.

Table 1. Criteria for redox parameters used for assigning redox status to groundwater samples. Values are in mg/L

Parameter	Aerobic	Nitrate-reducing	Mn-reducing	Fe-reducing	Sulfate-reducing	Methano-genesis
Oxygen	>1.0	<1.0	<1.0	<1.0	<1.0	<1.0
Nitrate	-	-	<0.2	<0.2	<0.2	<0.2
Nitrite	<0.1	-	<0.1	<0.1	<0.1	<0.1
Ammonium	<1.0	<1.0	-	-	-	-
Mn(II)	<0.2	<0.2	>0.2	-	-	-
Fe(II)	<1.5	<1.5	<1.5	>1.5	-	-
Sulfate	-	-	-	-	-	<40
Sulfide	<0.1	<0.1	<0.1	<0.1	>0.2	-
Methane	<1.0	<1.0	<1.0	<1.0	<1.0	>1.0

From: J. Lyngkilde, T.H Christensen, B. Skov, and A. Foverskov. 1991. Redox zones downgradient of a landfill and implications for biodegradation of organic compounds. *In: In situ* Bioreclamation; Applications and Investigations for Hydrocarbon and Contaminated Site Remediation. (Ed. by Hinchee, R.E. and Olfenbuttel, R.F.). Pages 363-376. Butterworth-Heinemann, Boston, USA.