

## **Environmental Chemistry and Kinetics of Biotransformation of Chlorinated Organic Compounds in Ground Water**

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### **Introduction**

Responsible management of the risk associated with chlorinated solvents in ground water involves a realistic assessment of the natural attenuation of these compounds in the subsurface before they are captured by ground water production wells, or before they discharge to sensitive ecological receptors. The reduction in risk is largely controlled by the rate of the biotransformation of the chlorinated solvents and their metabolic daughter products. These rates of biotransformation are sensitive parameters in mathematical models describing the transport of these compounds to environmental receptors.

### **Environmental Chemistry of Biodegradation of Chlorinated Solvents**

Please skip to the next section if you are familiar with environmental chemistry. This section is designed specifically for engineers and mathematical modelers that have no chemistry background.

The initial metabolism of chlorinated solvents such as tetrachloroethylene, trichloroethylene, and carbon tetrachloride in ground water usually involves a biochemical process described as a sequential reductive dechlorination. This process only occurs in the absence of oxygen, and the chlorinated solvent actually substitutes for oxygen in the physiology of the microorganisms carrying out the process.

The chemical term "reduction" was originally derived from the chemistry of smelting ores of metals. Ores are chemical compounds of metal atoms coupled with other materials. As the

ores are smelted to the pure element, the weight of the pure metal was reduced compared to the weight of the ore. Chemically, the positively charged metal ions received electrons to become the electrically neutral pure metal. Chemists generalized the term "reduction" to any chemical reaction that added electrons to an element. In a similar manner, chemical reaction of pure metals with oxygen results in the removal of electrons from the neutral metal to produce an oxide. Chemists have generalized the term "oxidation" to refer to any chemical reaction that removes electrons from a material. For a material to be reduced, some other material must be oxidized.

The electrons required for microbial reduction of chlorinated solvents in ground water are extracted from native organic matter, from other contaminants such as the BTEX compounds released from fuel spills, or from volatile fatty acids in landfill leachate, or from hydrogen produced by the fermentation of these materials. The electrons pass through a complex series of biochemical reactions that support the growth and function of the microorganisms that carry out the process.

In order to function the microorganisms must pass the electrons used in their metabolism over to some ultimate electron acceptor. This ultimate electron acceptor can be dissolved oxygen, dissolved nitrate, oxidized minerals in the aquifer, dissolved sulfate, a dissolved chlorinated solvent, or carbon dioxide. Important oxidized minerals used as electron acceptors include iron and manganese. Oxygen is reduced to water, nitrate to nitrogen gas or ammonia, Iron (III) or ferric iron to Iron (II) or ferrous iron, Manganese (IV) to Manganese (II), sulfate to sulfide ion, chlorinated solvents to a compound with one less chlorine atom, and carbon dioxide to methane. These processes are referred to as aerobic respiration, nitrate reduction, iron and manganese reduction, sulfate reduction, reductive dechlorination, and methanogenesis.

The energy gained by the microorganisms follows the sequence listed above: oxygen and nitrate reduction provide a good deal of energy, iron and manganese reduction somewhat less energy, sulfate reduction and dechlorination a good deal less energy, and methanogenesis a marginal amount of energy. The organisms carrying out the more energetic reactions have a competitive advantage; as a result they proliferate and exhaust the ultimate electron acceptors in a sequence. Oxygen and then nitrate are removed first. When their supply is exhausted, then other

organism are able to proliferate, and manganese and iron reduction begins. If electron donor supply is adequate, then sulfate reduction begins, usually with concomitant iron reduction, followed ultimately by methanogenesis. Ground water where oxygen and nitrate are being consumed are usually referred to as oxidized environments. Water where sulfate is being consumed and methane is being produced are generally referred to as reduced environments.

Reductive dechlorination usually occurs under sulfate reducing and methanogenic conditions. Two electrons are transferred to the chlorinated compound being reduced. A chlorine atom bonded with a carbon receives one of the electrons to become a negatively charged chloride ion. The second electron combines with a proton (hydrogen ion) to become a hydrogen atom that replaces the chlorine atom in the daughter compound. One chlorine is replaced with hydrogen at a time; as a result, each transfer occurs in sequence. As an example, tetrachloroethylene is reduced to trichloroethylene, then any of the three dichloroethylenes, then to monochloroethylene (commonly called vinyl chloride), then to the chlorine-free carbon skeleton ethylene, then finally to ethane.

## **Kinetics of Transformation in Ground Water**

Table I lists rate constants for biotransformation of tetrachloroethylene (P.E.), trichloroethylene (TCE), cis-dichloroethylene (cis-DCE) and vinyl chloride that were extrapolated from field scale investigations. In some cases a mathematical model was used to extract a rate constant from field data. However, many of the rate constants were calculated from the published raw data of others by John Wilson. In several cases the primary authors did not choose to calculate a rate constant, or felt that their data could not distinguish degradation from dilution or dispersion.

The data were collected or estimated to build a statistical picture of the distribution of rate constants, in support of a sensitivity analysis of a preliminary assessment using published rate constants. They serve as a point of reference for "reasonable" rates of attenuation. It is inappropriate to apply them to other sites without proper site specific validation.

The estimates of rates of attenuation tend to cluster within an order of magnitude. Figure 1 compares the rates of removal of TCE in those plumes where there was evidence of biodegradation. Most of the first order rates are very close to 1.0 per year, equivalent to a half life of 8 months. Table I also reveals that the rate of removal of P.E., TCE and cis-DCE and Vinyl Chloride are similar; they vary by little more than one order of magnitude.

Table II lists first-order and zero-order rate constants determined in laboratory microcosm studies. The rates of removal in the laboratory microcosm studies are similar to estimates of removal at field scale for TCE, cis-DCE, and Vinyl Chloride. Rates of removal of 1,1,1-trichloroethane (1,1,1-TCA) are similar to the rates of removal of the chlorinated alkenes.

### **Summary**

The rates of attenuation of chlorinated solvents and their less chlorinated daughter products in ground water are slow as humans experience time. If concentrations of chlorinated organic compounds near the source are in the range of 10,000 to 100,000 ug/liter, then a residence time in the plume on the order of a decade or more will be required to bring initial concentrations to current MCLs for drinking water. Biodegradation as a component of natural attenuation can be protective of ground water quality in those circumstances where the time of travel of a plume to a receptor is long. In many cases, it will be necessary to supplement the benefit of natural attenuation with some sort of source control or plume management.

## DISCLAIMER

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Table I. Apparent attenuation rate constants (Field Scale Estimates).

Location	Ref- erence	Distance from source	Time from source	Residence time	TCE	cis-DCE	Vinyl chloride
		(meters)	(years)	(years)	Apparent Loss Coefficient (1/year)		
St. Joseph, Michigan	15 16 19	130 to 390	3.2 to 9.7	6.5	0.38	0.50	0.18
		390 to 550	9.7 to 12.5	2.8	1.3	0.83	0.88
		550 to 855	12.5 to 17.9	5.4	0.93	3.1	2.2
Picatinny Arsenal, New Jersey	8 13	240 to 460	2.2 to 4.2	2.0	1.4	produced	produced
		320 to 460	2.9 to 4.2	1.3	1.2	produced	produced
		240 to 320	2.2 to 2.9	0.7		1.6	
		0 to 250	0.0 to 2.3			0.5	
Sacramento, California	4	70 to 300	0.5 to 2.3	1.8	1.1	0.86	3.1
Necco Park New York	12	0 to 570	0.0 to 1.6	1.6	0.7		
		0 to 660	0.0 to 1.8	1.8	0.7		
Plattsburgh AFB, New York	21	0 to 300	0.0 to 6.7	6.7	1.3	produced	produced
		300 to 380	6.7 to 8.6	1.9	0.23	0.6	1.16
		380 to 780	8.6 to 17.7	9.1	absent	0.07	0.47

Table I continued. Apparent attenuation rate constants (Field Scale Estimates).

Location	Ref- erence	Distance from source	Time from source	Residence time	P.E.	TCE	cis-DCE
		(meters)	(years)	(years)	Apparent Loss Coefficient (1/year)		
Tibbitt's Road, New Hampshire	20	0 to 24	0.0 to 2.4	2.4		0.21	produced
		0 to 40	0.0 to 6.4	6.4		0.42	0.68
		0 to 55	0.0 to 10	10		0.73	>0.73
San Francisco Bay Area, California	3				4.4	5.11	
Perth, Australia	2	0 to 600	0.0 to 14			0.32	
Eielson, AFB, Alaska	9					0.73 2.3	
Not Identified	6				0.8	0.8	0.8
Cecil Field NAS, Florida	22	0 to 140	0.0 to 1.2	1.2	3.3 to 7.3		3.3 to 7.3

Table II. Apparent attenuation rate constants from laboratory microcosm studies.

Location of material	Reference	Distance from source	Time from source	Incubation time	TCE	cis-DCE	Vinyl Chloride	1,1,1-TCA
		(meters)	(years)	(years)	Apparent First Order Loss (1/year) Apparent Zero Order Loss (ug/L*day)			
Laboratory Microcosm Studies done on material from field scale plumes								
Picatinny Arsenal, NJ	7	240	2.2	0.5	0.64	0.52		
	17	320	2.9	0.5	0.42	9.4		
		460	4.2	0.5	0.21	3.1		
St. Joseph, MI	10			0.12, 0.077	1.8, 1.2			
Traverse City, MI	18	300		1.8	1.8			
Tibbitts Road, NH	14	At Source			4.8			
Laboratory Microcosm Studies done on material not previously exposed to the chlorinated organic compound								
Norman Landfill, OK	5	Aerobic Material					4.2 <u>10</u>	
	11	Sulfate Reducing						1.28 <u>1.62 1.75</u>
		Methanogenic						1.20 <u>1.65 1.42</u>
Florida	14	Reducing						3.6
	1	Reducing					0.012	



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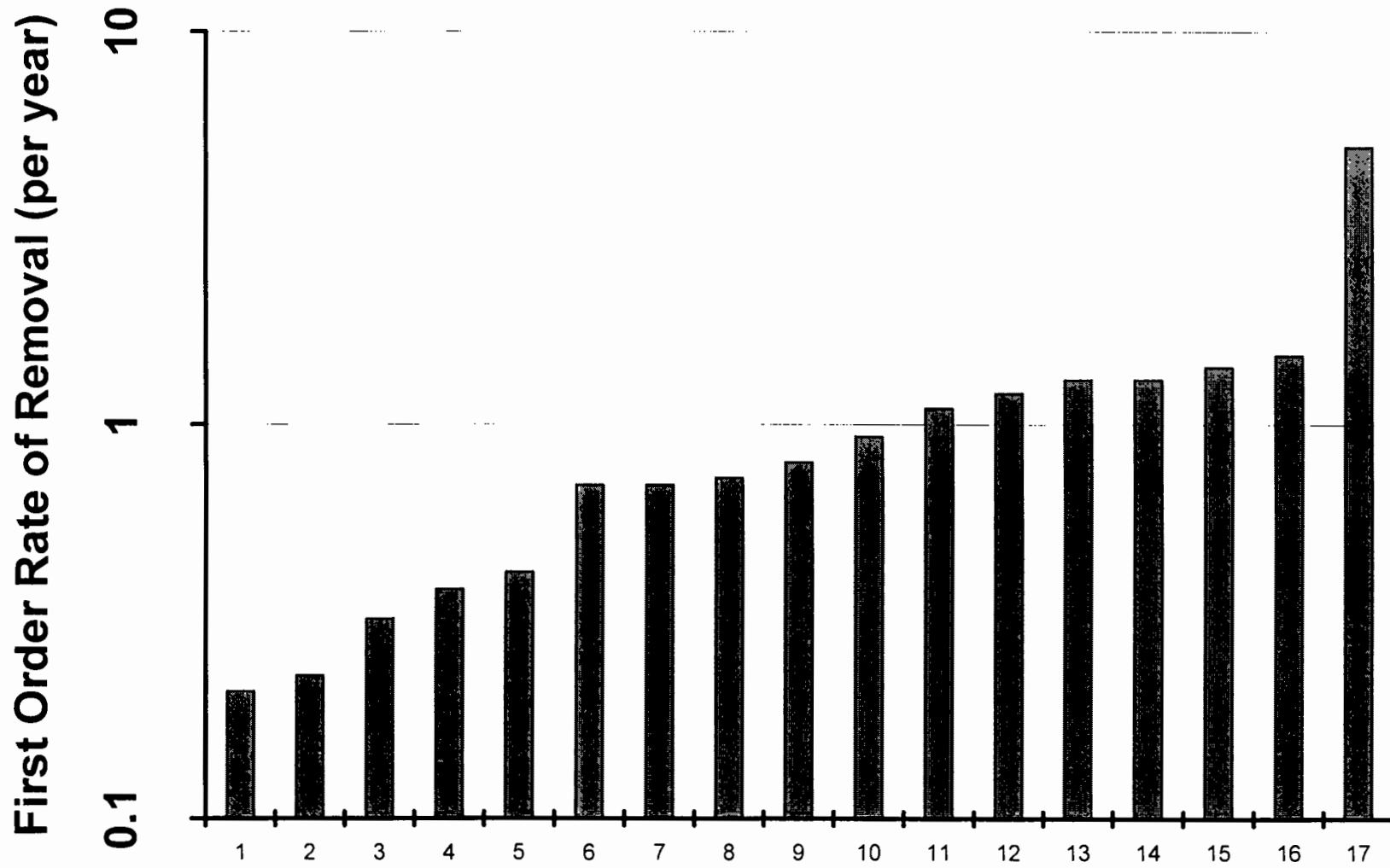
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Figure 1. The first order rate constant for biotransformation of TCE in a variety of plumes of contamination in ground water.

# TCE Removal in Field



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