PREDICTION OF PCB DECHLORINATION AND DEGRADATION ENVIRONMENTAL ENDPOINTS

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PRESENTATION

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ABSTRACT

Several researchers have demonstrated the transformation of polychlorinated biphenyls (PCBs) by both aerobic and anaerobic bacteria. This transformation, or conversion, is characteristic and often dependent on PCB congener structure and, in addition, dictates the products or endpoints. Since transformation is linked to microbial activities, bioremediation has been hailed as a possible solution for PCB-contaminated soils and sediments, and several demonstration activities have verified laboratory results. This paper presents results from mathematical modeling of PCB transformation as a means of predicting possible endpoints of bioremediation. Since transformation can be influenced by both starting composition of the PCBs and microbial activity, this paper systematically evaluates several of the most common transformation patterns. The predicted data are also compared with experimental results. For example, the correlation between laboratory-observed and predicted endpoint data was, in some cases, as good as 0.96 (perfect correlation = 1.0). In addition to predicting chemical endpoints, the water solubility and the possible human effects of the PCBs are discussed through the use of documented dioxin-like toxicity and accumulation in humans before and after transformation.

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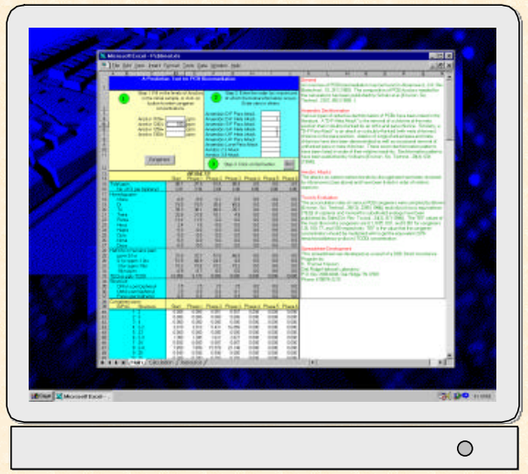
Abstract

This work presents the development of a predictive modeling tool to aid in evaluation of PCB degradation outcomes. This tool is a computer model based on the susceptibility of individual PCB compounds (congeners) to undergo bacterial transformation. The model has been tested and compared with experimental data taken from the dechlorination of complex PCB mixtures (Aroclors). The computer model also incorporates literature data to estimate the effects on humans and the water solubility.

Introduction

The dechlorination systems described in literature occur both in nature and in laboratory experiments in the form of combinations — not as isolated individual systems. The more complex of these systems are often referred to as dechlorination activities or processes, which are denoted with letters such as C, H, H´, M, N, P, Q, etc. For example, activity M is described as the removal of flanked and unflanked *meta* chlorines, and activity Q is described as the removal of flanked and unflanked *para* chlorines. Activity C can be described as a combination of activities M and Q. The significance is that dechlorination activities characterize the type of PCB structure susceptible for attack, and thus the products can be predicted via individual dechlorination systems.

Dechlorination processes do not result in destruction of PCBs — only alteration. The most common pathway of biological destruction is through aerobic cometabolism with biphenyl. It has been shown that the most common aerobic processes are carried out by enzymes that attack C-C bonds in the biphenyl structure when these carbons are not linked to chlorines. In general, this means that heavily chlorinated PCB congeners are less likely to be degraded, suggesting that a sequential anaerobic-aerobic bioremediation scheme is likely to yield the most complete destruction of PCBs. There are two known enzymatic oxidative processes, one that initially oxygenates the C-C bond in the 2,3-position, and another that oxygenates the bond in the 3,4-position.



Hypothesis

If knowledge exists about the starting concentration of each congener in a contaminated material, as well as information about the type of dechlorination/ degradation activity expected in a bioremediation effort (active or intrinsic), there is an opportunity to predict the endpoints (products) of microbial transformation.

The dechlorination process are made up from individual systems

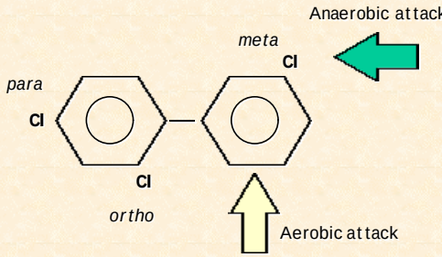
1. doubly flanked *meta* chlorine (DFM)
2. doubly flanked *para* chlorine (DFP)
3. singly flanked *para* chlorine (SFP)
4. singly flanked *meta* chlorine (SFM)
5. unflanked *meta* chlorine on di- or tri- substituted ring (UFM)
6. unflanked *para* chlorine on di- or tri- substituted ring (UFP)
7. lone *para* chlorine on ring opposite substituted ring (LP)

A degradation process is possible if either the

1. 2,3 or
2. 3,4 positions are chlorine-free.

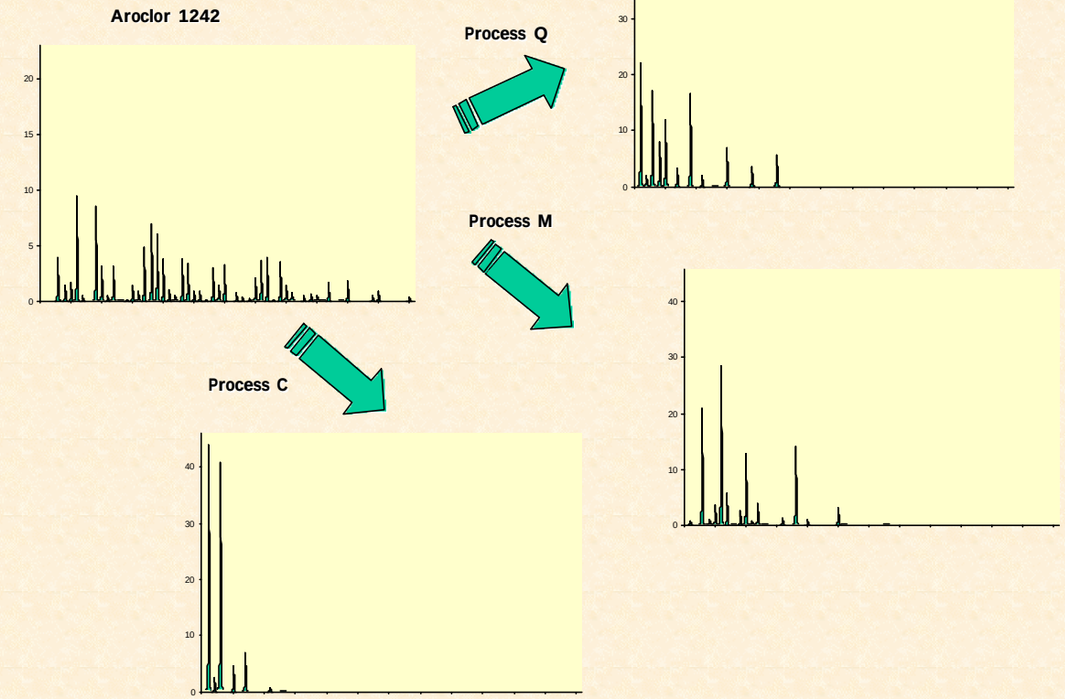
	A	B	C
1	23450-20450	=SUBSTITUTE(A1,"234","204")	=SUBSTITUTE(B1,"456","406")
2	23450-20450		=SUBSTITUTE(A2,"345","305")
3	23450-20450	=SUBSTITUTE(A3,"340","300")	=SUBSTITUTE(B3,"045","005")
4	23450-20450	=SUBSTITUTE(SUBSTITUTE(A4,"230","200"),"034","004")	=SUBSTITUTE(SUBSTITUTE(B4,"450","400"),"056","006")
5	20406-20050	=SUBSTITUTE(SUBSTITUTE(A5,"03056","23000"),"03006","20000")	=SUBSTITUTE(SUBSTITUTE(B5,"3050","3000"),"20050","20000")
6	20406-20050		=SUBSTITUTE(A6,"2040","2000")
7	20400-00400	=IF(LEFT(A7,5)="00000",A7,IF(MID(A7,8,3)="040",REPLACE(A7,8,3,"000"),A7))	=IF(RIGHT(B7,5)="00000",B7,IF(MID(B7,2,3)="040",REPLACE(B7,2,3,"000"),B7))

	A	B	C
1	20406-20050	=IF(OR(MID(A1,1,2)="00",MID(A1,4,2)="00"),"",A1)	=IF(OR(MID(B1,7,2)="00",MID(B1,10,2)="00"),"",B1)
2	20400-00400	=IF(OR(MID(A2,2,2)="00",MID(A2,3,2)="00"),"",A2)	=IF(OR(MID(B2,8,2)="00",MID(B2,9,2)="00"),"",B2)



Structure is Important

The literature is promoting structural dependence of anaerobic chlorine removal a as well as aerobic ring-cleavage. The computer programing takes advantage of this belief. If accurately measured individual congener susceptibility for microbial attack was available, it would complement the computers predictions.



Complex Activities vs. Individual Systems

Activity M was modeled as DFM+SFM+UFM,
activity Q was modeled as DFP+SFP+SFM+UFP+LP,
activity C was modeled as DFM+SFM+UFM+UFP+LP,
activity H´ was modeled as DFP+DFM+SFP+SFM,
activity H was modeled as DFP+DFM+SFP,
activity P was modeled as DFP+SFP, and
activity N was modeled as DFM+SFM.

Correlation with literature data was 0.98 and 0.92 for process C and M dechlorination of Aroclor 1242.

Results

		Process for Aroclor 1242 (100 ppm)						Process for Aroclor 1254 (100 ppm)								Process for Aroclor 1260 (100 pm)				
		None	M	Q	C	H'	H	None	M	Q	C	H'	H	P	N	None	H'	H	P	N
Anaerobic only	Half-life in humans																			
	ppm<0.1y	31.0	66.9	71.4	76.2	52.3	39.5	2.3	50.5	48.7	66.3	30.1	3.7	7.0	30.4	2.2	38.8	2.4	3.5	36.4
	0.1y<ppm<1.0y	51.5[1]	4.8	12.6	0.0	30.1	45.4[2]	59.8	14.8	29.9	0.0	51.8	79.5	78.2	40.2	45.0	42.2	76.6	80.9	43.6
	1.0y<ppm<10y	15.2	15.2	0.0	0.0	9.2	9.8	25.3	11.9	0.0	0.0	0.7	3.7	1.8	11.9	17.2	0.2	5.9	0.7	1.7
	10y<ppm	0.9	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	0.0	0.0	1.4	1.4	0.0	39.0	0.2	6.8	6.6	0.0
	TEQ as ppb TCDD	10.1	0.0	0.0	0.0	0.0	0.0	5.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	3.3	6.3	10.2	15.9	4.6	3.9	0.5	3.1	2.9	9.4	1.7	1.2	1.2	1.7	0.2	1.1	0.6	0.6	1.0
2,3-Attack	Half-life in humans																			
	ppm<0.1y	0.7	0.1	3.8	0.1	3.8	0.7	1.3	1.9	13.0	1.8	12.9	1.3	1.6	10.6	2.2	29.4	2.2	3.2	14.4
	0.1y<ppm<1.0y	9.2	0.0	6.0	0.0	6.0	9.6[2]	27.6	0.0	19.1	0.0	19.3	31.5	31.9	6.6	35.1	27.3	54.2	55.3	2.5
	1.0y<ppm<10y	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.7	0.0	0.0	2.6	0.1	1.8	0.0	0.2
	10y<ppm	0.7	0.0	0.0	0.0	0.0	0.0	8.1	0.0	0.0	0.0	0.0	1.4	1.4	0.0	32.5	0.2	6.8	6.6	0.0
	TEQ as ppb TCDD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	0.1	0.0	0.1	0.0	0.1	0.1	0.2	0.0	0.4	0.0	0.4	0.3	0.3	0.2	0.2	0.6	0.3	0.3	0.2
3,4-Attack	Half-life in humans																			
	ppm<0.1y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.1y<ppm<1.0y	4.9	3.5	0.0	0.0	1.6	1.6	3.2	14.8	0.0	0.0	4.6	4.8	1.0	14.8	1.5	2.9	5.5	0.1	31.4
	1.0y<ppm<10y	15.2	15.2	0.0	0.0	9.2	9.8	25.3	11.9	0.0	0.0	0.7	3.7	1.8	11.9	16.7	0.2	5.9	0.7	1.7
	10y<ppm	0.9	0.0	0.0	0.0	0.0	0.0	10.3	0.0	0.0	0.0	0.0	1.4	1.4	0.0	39.0	0.2	6.8	6.6	0.0
	TEQ as ppb TCDD	10.1	0.0	0.0	0.0	0.0	0.0	5.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.0	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	0.4	0.6	0.0	0.0	0.4	0.4	0.2	0.5	0.0	0.0	0.1	0.1	0.0	0.5	0.1	0.0	0.1	0.0	0.4
2,3- & 3,4-Attack	Half-life in humans																			
	ppm<0.1y	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	0.1y<ppm<1.0y	0.0	0.0	0.0	0.0	0.0	0.0[2]	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.3	0.0	0.0	0.0	0.0
	1.0y<ppm<10y	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.7	0.0	0.0	2.1	0.1	1.8	0.0	0.2
	10y<ppm	0.7	0.0	0.0	0.0	0.0	0.0	8.1	0.0	0.0	0.0	0.0	1.4	1.4	0.0	32.5	0.2	6.8	6.6	0.0
	TEQ as ppb TCDD	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0

TEQ = toxic equivalence concentration of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)

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