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COMPUTER MODEL FOR PREDICTION OF PCB DECHLORINATION AND BIODEGRADATION ENDPOINTS

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DISCLAIMER

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ABSTRACT: Mathematical modeling of polychlorinated biphenyl (PCB) transformation served as a means of predicting possible endpoints of bioremediation, thus allowing evaluation of several of the most common transformation patterns. Correlation between laboratory-observed and predicted endpoint data was, in some cases, as good as 0.98 (perfect correlation = 1.0).

INTRODUCTION

Although PCBs are relatively inert, biological degradation by anaerobic dechlorination and aerobic oxidation is possible (Abramowicz, 1990). The enzymes involved in the aerobic ring cleavage have been studied and reviewed extensively (Abramowicz, 1990; Furukawa, 1982); however, details are not known about the enzymes responsible for anaerobic dechlorination, primarily due to the difficulty in isolating the microorganisms responsible (Bedard and Quensen, 1995). The anaerobic dechlorination follows distinct dechlorination patterns, which refer to the type of chlorines removed, and is dependent on environmental conditions. As the knowledge of microbial dechlorination and degradation increases, it may soon be possible to control these bioremediation processes for optimal results.

METHODOLOGY

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 (Bedard and Quensen, 1995; Bedard et al., 1986; Williams, 1994). The model was developed for use on a personal computer using Microsoft Excel (Microsoft Corporation, Redmond, WA); and in order to utilize the various built-in functions offered in Excel, the construction of a new nomenclature for PCBs was incorporated. The nomenclature name was 11 characters wide, and both the position and the numeric value of a character in the name mark the chlorine substitution type.

The susceptibility of individual congeners to undergo anaerobic transformation has been postulated and demonstrated by Williams (1994), who found that the chlorine position on the PCB carbon backbone determined sensitivity to attack. These dechlorination systems were adapted, modified, and used in the computer model; the susceptibility for attack is based on simple rules related to the structure of the PCB congeners.

As previously mentioned, dechlorination processes do not result in destruction of PCBs — only alteration. The most common pathway of biological destruction is through aerobic cometabolism. There are two known enzymatic

oxidative processes, one that oxygenates the C-C bond in the 2,3- and 5,6-positions (Furukawa, 1982) and another that oxygenates the bond in the 3,4- and 4,5-positions (Bedard et al., 1986).

Rules for dechlorination systems and degradation systems used in predictions may be expressed as the Excel formulas shown in Figure 1. The structure of the congener under attack is found in column A, and the end-product structure in cells is found in column C. In this manner, any PCB congener can be evaluated for susceptibility, and the resulting end product can be determined.

	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))
8	20406-20050	=IF(OR(MID(A8,1,2)="00",MID(A8,4,2)="00"), "",A8)	=IF(OR(MID(B8,7,2)="00",MID(B8,10,2)="00"), "",B8)
9	20400-00400	=IF(OR(MID(A9,2,2)="00",MID(A9,3,2)="00"), "",A9)	=IF(OR(MID(B9,8,2)="00",MID(B9,9,2)="00"), "",B9)

FIGURE 1. Excel spreadsheet with underlying functions corresponding to dechlorination systems and oxidative degradation. Column A contains examples of congeners. The formulas describe doubly flanked meta chlorine (DFM), doubly flanked para chlorine (DFP), singly flanked para chlorine (SFP), singly flanked meta chlorine (SFM), unflanked meta chlorine on di- or tri-substituted ring (UFM), unflanked para chlorine on di- or tri-substituted ring (UFP), lone para chlorine on ring opposite substituted ring (LP), 2,3-dioxygenase attack, and 3,4-dioxygenase attack.

The dechlorination systems described above and by Williams (1995) 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 by letters such as C, H, H′, M, N, P, Q, etc. (Bedard and Quensen, 1995). 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 (Bedard and Quensen, 1995; Quensen et al., 1990).

RESULTS

Figure 2 shows the predicted dechlorination of Aroclor 1242 through process C. The individual charts were constructed by entering published values for Aroclor 1242 congener composition (Schulz et al., 1989) and evaluating each congener's susceptibility to dechlorination in a sequence of dechlorination systems:

1. doubly flanked *meta* (DFM), followed by
2. singly flanked *meta* (SFM), followed by
3. unflanked *meta* on di- or tri-substituted ring (UFM), followed by
4. unflanked *para* on di- or tri-substituted ring (UFP), and followed by
5. lone *para* on ring opposite substituted ring (LP).

After each sequence step, the concentration of each of the 209 possible PCB congeners was recalculated to account for the products created, and the individual congeners were combined into "peak concentrations" for comparison with experimental data (Quensen et al., 1990).

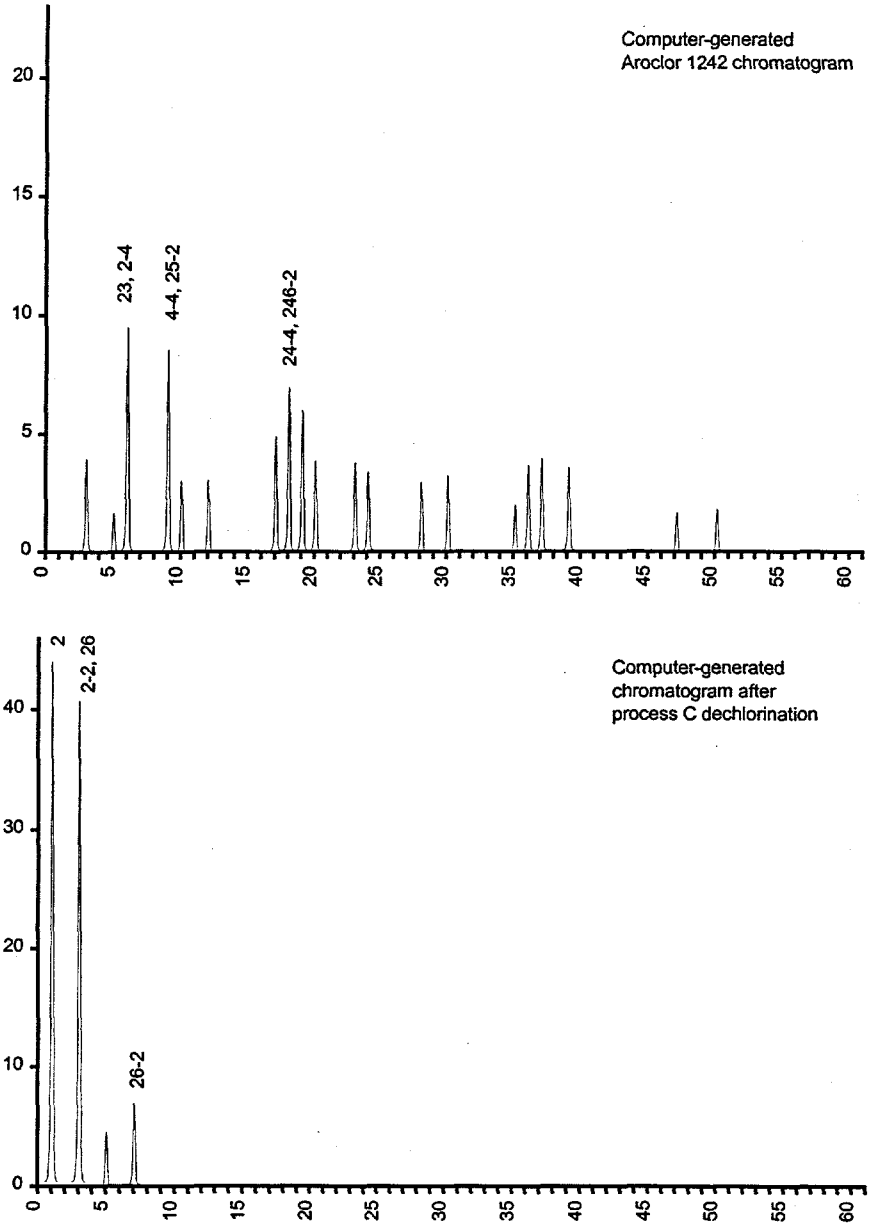

FIGURE 2. Dechlorination of Aroclor 1242 modeled via DFM+SFM+UFM+ UFP+LP. Values on the Y-axis refer to mole percent. The congeners in the three largest peaks have been identified.

The construction of the charts (displaying chromatograms) in Figure 2 was made by generating these congener-containing peaks. Quensen et al. (1990) obtained the laboratory data by combining Aroclor 1242 with Hudson River (NY) sediment organisms, inducing dechlorination activity. The correlation between starting values in the computer model and the sterile control in the experimental case was 0.95. The correlation of the final values in the predictive case and the experimental case was 0.98.

A computer model prediction via DFM+SFM+UFM dechlorination of Aroclor 1242 compares well with experimental data (Quensen et al., 1990) for dechlorination of Aroclor 1242 with Silver Lake sediment organisms. The model accurately predicts major endpoint products, and the correlation between end values for the predictive case and the experimental case was 0.92. Algorithms proposed for the individual systems (Figure 1), when combined appropriately, accurately predict the same end products as those listed by Bedard and Quensen (1995), who summarized published dechlorination activities (processes). The computer simulation predicts that essentially all congeners remaining after a process C dechlorination of Aroclor 1242 would be biodegradable (Table 1), which perhaps overpredicts the effectiveness of a sequential anaerobic-aerobic bioremediation scheme. It is difficult to determine whether the model is too optimistic or whether the experimental conditions have not been ideal during reported experiments (Bedard et al., 1987).

The dioxin Toxic Equivalences (TEQs) of various PCB congeners have been reported by Safe (1994), and the accumulation extents of PCB congeners in organisms (including humans) have been reported by Brown (1994). To assess health-related issues, the endpoints for a potential sequential anaerobic-aerobic PCB degradation strategy were generated using the algorithms described earlier. All of the main dechlorination activities result in a substantial reduction of TEQ (Table 1). The activity of the 2,3-dioxygenase is predicted to be sufficient in reaching the lowest TEQ levels and does not have to be complemented with 3,4-dioxygenase activity. The most efficient anaerobic dechlorination processes preceding aerobic degradation are the ones that include DFM and SFM systems (activities M, C, H′, and N). Prediction shows that aerobic degradation of unaltered and altered Aroclors should be effective in reducing TEQs except in the case of unaltered Aroclor 1260 (not shown). The most effective activity in reducing the accumulation tendency in humans is dechlorination process C. This activity has not been observed with Aroclor 1260 (Bedard and Quensen, 1995); however, if it was or could be induced, the computer model predicts that all end products would have half-lives in humans of less than 0.1 year (data not shown).

The water solubility of PCB congeners was estimated as described by (Voice et al., 1983) using partition coefficients from Mackay (1982) and data from Holmes and Harrison (1993) at 1% dissolved solids with 4% organic carbon. It can be noted in Table 1 that all of the dechlorination activities result in increases of aqueous solubility of the altered PCBs, while the aerobic degradation decreases PCB solubility.

TABLE 1. Summary results of predicted anaerobic dechlorination[a] followed by aerobic degradation (via ring cleavage) by 2,3-dioxygenase, 3,4-dioxygenase, and a combination of both enzyme activities.

		Process for Aroclor 1242 (100 ppm)					
		None	M	Q	C	H'	H
Anaerobic only	Half-life in humans						
	ppm<0.1y	31.0	66.9	71.4	76.2	52.3	39.5
	0.1y<ppm<1.0y	51.5	4.8	12.6	0.0	30.1	45.4
	1.0y<ppm<10y	15.2	15.2	0.0	0.0	9.2	9.8
	10y<ppm	0.9	0.0	0.0	0.0	0.0	0.0
	TEQ as ppb TCDD	10.1	0.0	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	3.3	6.3	10.2	15.9	4.6	3.9
2,3-Attack	Half-life in humans						
	ppm<0.1y	0.7	0.1	3.8	0.1	3.8	0.7
	0.1y<ppm<1.0y	9.2	0.0	6.0	0.0	6.0	9.6
	1.0y<ppm<10y	0.0	0.0	0.0	0.0	0.0	0.0
	10y<ppm	0.7	0.0	0.0	0.0	0.0	0.0
	TEQ as ppb TCDD	0.0	0.0	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	0.1	0.0	0.1	0.0	0.1	0.1
3,4-Attack	Half-life in humans						
	ppm<0.1y	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
	1.0y<ppm<10y	15.2	15.2	0.0	0.0	9.2	9.8
	10y<ppm	0.9	0.0	0.0	0.0	0.0	0.0
	TEQ as ppb TCDD	10.1	0.0	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	0.4	0.6	0.0	0.0	0.4	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
	0.1y<ppm<1.0y	0.0	0.0	0.0	0.0	0.0	0.0
	1.0y<ppm<10y	0.0	0.0	0.0	0.0	0.0	0.0
	10y<ppm	0.7	0.0	0.0	0.0	0.0	0.0
	TEQ as ppb TCDD	0.0	0.0	0.0	0.0	0.0	0.0
	Aqueous solubility, ppb	0.0	0.0	0.0	0.0	0.0	0.0

[a]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; and activity H was modeled as DFP+DFM+SFP

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