

## Chemical reactivity as a tool for prediction of persistence

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### Introduction

A route for describing persistence of chemicals has recently been suggested based on its chemical reactivity and physico-chemical properties<sup>1</sup>. The term persistence has been used extensively in many different ways<sup>1-4</sup> which has made it difficult to reach a uniform understanding. With an unclear definition of persistence and a number of doubtful tests like ready biodegradability tests (RBT), substances may pass or fail on pure technicalities and not because of their chemical properties e.g. decabromodiphenyl ether is a very reactive compound in photochemical<sup>5,6</sup> and reductive reactions (unpublished results) but degrades slowly when using RBTs due to its poor water solubility.

The present work has focused on the development of a set of test reactions which are inexpensive, reproducible and easy to perform. This type of model reactions will, together with physico-chemical properties, provide a measure of the persistence of a substance, based solely on the chemical reactivity<sup>1</sup>. The reaction rates for oxidations-, photolysis<sup>5</sup>-, radical-, hse-<sup>7</sup> and reduction reactions will be determined.

Based on the reaction rates measured, a model will be constructed and used to simulate the different compartmental (air, water, soil and sediment) reactivity's. Mackay<sup>8</sup> has constructed a model with these four separate media but only dealing with one type of reaction for each compartment. This is vapor phase hydroxyl radical reactions in air, our model suggests that all reactions are possible in all compartments. This hopefully gives a wider representation of the environment. The type of degradation, abiotically or by microorganisms is not of importance since all reactions will be given a value  $x$ , designating their potential towards each type of degradation reaction. These reactions and rates can be combined in a matrix representing the inherent reactivity and reactive power as shown in Figure 1.

$$\begin{pmatrix} S_{ox} & S_{red} & S_{hse} & S_{hv} & S_{rad} \end{pmatrix} * \begin{pmatrix} \epsilon_{ox-air} & \epsilon_{ox-wat} & \epsilon_{ox-soil} & \epsilon_{ox-sed} \\ \epsilon_{red-air} & \epsilon_{red-wat} & \epsilon_{red-soil} & \epsilon_{red-sed} \\ \epsilon_{hse-air} & \epsilon_{hse-wat} & \epsilon_{hse-soil} & \epsilon_{hse-sed} \\ \epsilon_{hv-air} & \epsilon_{hv-wat} & \epsilon_{hv-soil} & \epsilon_{hv-sed} \\ \epsilon_{rad-air} & \epsilon_{rad-wat} & \epsilon_{rad-soil} & \epsilon_{rad-sed} \end{pmatrix} = \begin{pmatrix} k_{air} & k_{water} & k_{soil} & k_{sed} \end{pmatrix}$$

**Figure 1.** The reactive power of the environment expressed as a 4x5 matrix multiplied with the substance reactivity constants (derived from rate constants) gives a multimedia fate model which provides a measure of the chemical's persistence

### Material and Methods

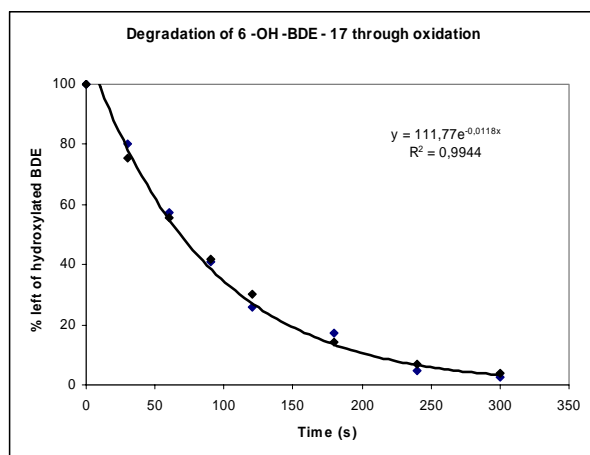
*Instruments:* The pH measurements were performed using pH-meter 718 Stat Titrimo from Metrohm (Herisau, Switzerland). High-performance liquid chromatography (HPLC) was performed on a Shimadzu (LC-9A and LC-10AD) (Kyoto, Japan) equipped with an UV detector (Spectra 100, Spectra-Physics) (USA) and a C<sub>4</sub> reversed phase column (Ace 5 C<sub>4</sub>, 250 x 4.6 mm, 5µm particles) from Advanced Chromatography Technologies (Aberdeen, Scotland). The detection wavelength was set at 245 nm and the mobile phase was varied between 0.1% trifluoroacetic acid in water: methanol (4:1) and pure methanol. Gas chromatography-mass spectrometry

(GC-MS) was performed on an ion trap GCQ instrument from Finnigan Mat. The gas chromatograph was equipped with a fused silica capillary column (DB-5, 30 m x 0.25 mm, 0.025 mm film thickness, J & W Scientific, Folsom, USA). The temperature program was 80°C for 2 min, raised at 10°C min<sup>-1</sup> to 280°C which was held for 15 min. The injections were made in split less mode using an injection temperature of 260°C. Helium was used as carrier gas. Mass spectra were recorded in electron ionization mode at an ion source temperature of 140°C and an electron energy of 70 eV. The spectrophotometer was a double beam instrument U3000 from Hitachi (Tokyo, Japan). The scanning rate was 0.5 nm s<sup>-1</sup> with a slit width of 1 nm. UV spectra were recorded in a phosphate buffer for determination of disappearance rate.

**Chemicals:** 3,3',5,5'-Tetrabromobisphenol A (TBBPA), 3,3',5,5'-tetrachlorobisphenol A (TCBPA), bisphenol A (BPA), 2-bromophenol, 2,4,6-tribromophenol, 2,4-dibromophenol, 2,6-dibromophenol, 2,3,4,6-tetrabromophenol and barium phosphate were purchased from Aldrich Chemical Company, Inc (Gillingham, UK). Methanol, acetic acid, hexane, dichloromethane, sodium dihydrogen phosphate and potassium permanganate were from Merck (Darmstadt, Germany). Trifluoroacetic acid was purchased from Supelco (Bellefonte, USA). All solvents were of pro analysis grade. The water was deionised prior to use.

**Rate dependence on phosphate buffer and barium phosphate:** Studies on compound degradation related to phosphate buffer, and barium phosphate were done by measurements performed by the UV spectrophotometer, scanning from 220 nm to 320 nm. A solution was prepared with phenol (1 µM); barium hydrogenphosphate (2 mM) and phosphate buffer (0.3 mM) in 0.1 l degassed water. A UV spectrum was recorded and the solution was left in the dark for 96 hours when a new spectrum was recorded. pH was measured before each scan and found to be the same. When comparing the two, no degradation was shown to have occurred, which is in accordance to Freeman and Kappos<sup>9</sup>.

**Permanganate oxidation experiments:** Stock solutions of phenol (usually 1.9 x 10<sup>-4</sup> M), phosphate buffer (5.6 x 10<sup>-4</sup> M) and potassium permanganate (10<sup>-2</sup> M) in water were prepared by weighing. The phenol solution contained a small amount of sodium hydroxide to assure all phenols were dissolved. A stock solution was also prepared of sodium bisulphite (4.8 x 10<sup>-2</sup> M) in 70% methanol and 30% water. An aliquot of the phenol solution (0.5 ml) was added to a flask containing barium hydrogenphosphate (50 mmol). The volume was adjusted to 100 ml. Into the phenol solution was added 0.5 ml of the oxidant solution. The progress of the reaction was monitored by taking out samples of 0.5 ml, by a HPLC-syringe, and quenching them in 0.5 ml of the bisulphite solution. These samples were then analysed by HPLC and the loss of starting material was monitored and the results are shown in Figure 2.



**Figure 2.** Degradation of 6-OH-BDE-17 by use of permanganate ion (50 times excess) as oxidising agent in a phosphate buffer. The reaction was performed at 50 degrees Celsius.

**Results and discussion**

Initially, oxidation reactions were performed on a test set of substances including brominated phenols and bisphenol A derivatives. The resulting half-life times and reaction rate constants are given in Table 1. Secondly, brominated diphenylethers and their hydroxylated metabolites were oxidized with the developed method and the results are given in Table 2. Each reaction was performed at least twice for each compound to assure reproducibility.

**Table 1.** Second order rate constants for the oxidation of parent compound with 50 times excess of oxidizing agent, potassium permanganate.

Substance	Temp ( $^{\circ}\text{C}$ )	$2^{\text{nd}}$ K ( $\text{mol}^{-1} \text{S}^{-1}$ )	$T_{1/2}$ (s)
2-bromophenol	0.5 – 1	7.1	2 050
2,4-dibromophenol	0.5 – 1	9.0	1 500
2,6-dibromophenol	0	21	660
2,4,6-tribromophenol	0	4.0	3 500
	17 – 21	14	1 000
2,3,4,6-tetrabromophenol	54 – 55	6.7	2 000
Bisphenol A	0 – 1	39	350
Tetrabromobisphenol A	0 – 1	110	120
Tetrachlorobisphenol A	0 – 1	170	86

**Table 2.** Second order rate constants for the oxidation of BDE or OH-BDE with 50, 700 or 1000 times excess of oxidizing agent.

Substance	Temp ( $^{\circ}\text{C}$ )	$2^{\text{nd}}$ K ( $\text{mol}^{-1} \text{S}^{-1}$ )	$T_{1/2}$ (s)
BDE – 47 <sup>b</sup>	48.8	0.04	17 600
BDE-49 <sup>c</sup>	48.8	0.04	18 900
6 – OH – BDE – 17 <sup>a</sup>	50	210	64
p – OH – BDE – 17 <sup>a</sup>	50	960	14
6 – OH – BDE – 47 <sup>a</sup>	50	21	640
o – OH – BDE – 49 <sup>a</sup>	48.8 – 50	46	300
o – OH – BDE – 66 <sup>a</sup>	48.8 – 50	960	15
o – OH – BDE – 85 <sup>a</sup>	48.8 – 50	4.3	3 200
o – OH – BDE – 90 <sup>a</sup>	48.8 – 50	6.1	2 300
o – OH – BDE – 137 <sup>a</sup>	50	2.0	6 700

Table 1 and Table 2 indicate a relationship between number of halogen and half-life of halogenated phenols. For oxidation reactions the half-life is increased with increasing number of halogens, probably due to electronic interactions. For photolysis reactions the order is reversed and increasing halogen substitution gives shorter half-lives and smaller substance reactivity constants. Regarding bisphenol A and its derivatives, results indicate similar trends except for TCBPA and TBBPA where the higher electronegativity of chlorine probably affects the reaction rate.

Table 2 presents the differences in rate of oxidation for some selected bromodiphenyl ethers (BDEs) and their primary metabolites, hydroxylated brominated diphenyl ethers. When adding a hydroxyl group to a BDE it becomes much more susceptible to oxidation. Half-lives also become much longer when increasing the halogen content in the primary diphenyl ether.

**Table 3.** Half-life's for the decomposition of selected compounds through photolysis.

Substance	T <sub>1/2</sub> (s)
Bisphenol A	41 400
Tetrabromobisphenol A	960
Tetrachlorobisphenol A	2 760
2-bromophenol	6 900
2,6-dibromophenol	5 220
2,4,6-tribromophenol	900
BDE-47	1 044 000

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