Sorption kinetic coefficients for Tetrabromobisphenol A (TBBPA) in a wastewater sludge matrix from the Guelph municipal wastewater treatment system

Mohammad Showkatul Islam*, Hongde Zhou and Richard G. Zytner

School of Engineering, University of Guelph, Guelph, Ontario, N1G 2W1, Canada
*Email: mshowkat@uoguelph.ca

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Abstract
Tetrabromobisphenol A (TBBPA) is a fire retardant with endocrine disruption properties and unfortunately has been detected in trace amounts in various environmental samples. Studies have shown that TBBPA enters the aquatic environment, sediments, soils and biota predominantly through the wastewater treatment process. The dominant contributor to the fate and transport of TBBPA in wastewater treatment plants is sorption by the wastewater sludge matrix. Accordingly, the objective of this paper is to determine the sorption kinetics of TBBPA to MLSS from both conventional activated sludge and MBR systems. Additional research is also being completed on the degradation of TBBPA by these two biological processes. Currently an analytical method has been established for the nano-level determination of aqueous phase TBBPA concentration using gas chromatography-negative ion chemical ionization-mass spectrometry (GC-NCI-MS) in select ion monitoring (SIM) mode. One of the challenges in working with TBBPA is the adsorption to the glass vessel. As such, a series of experiments were conducted to determine the wall loss partition coefficient, \( K_W \). The sorption kinetic model reported is on the basis of the partitioning of TBBPA to the solid-liquid phases, \( \log K_P \) (4.53), sludge matrix organic carbon, \( \log K_{OC} \) (6.05) and glass wall, \( K_W \) (0.053).

Introduction
The environmental fate and transport of TBBPA has a strong inter-relation to the partitioning of TBBPA in aqueous phase and wastewater sludge matrix. TBBPA is introduced to the aquatic environment and ultimately to other environmental compartments through wastewater (Lee and Peart, 2002; Covaci et al., 2009; Labadie et al., 2010; McPhedran et al., 2014). Everyday use of plastic commodities containing TBBPA as a fire retardant component is the major cause of its increasing abundance either in the wastewater or in the landfills. TBBPA has been found in biota, blood serum, human milk and adipose tissues (Frederiksen et al., 2007; Thomsen et al., 2002; Cariou et al., 2005).

Partitioning coefficients are important for transport modeling of organic pollutants. Transport models help to understand the behaviour, trend or the relationship of partitioning in different environmental systems. Sometimes partition coefficients of pollutants are estimated by using an empirical equation, quantitative structure-activity
relationship (QSAR) or molecular connectivity index (MCI) where reliable experimental measurements are not possible (Schnoor, 1996). Unfortunately, experimental values of $K_{OC}$, $K_P$ and $K_W$ for TBBPA are seldom found in the literature. Accordingly, studies have been completed to experimentally estimate all these coefficients for TBBPA in municipal wastewater. Organic carbon content may be the dominant constituent for the adsorption of TBBPA in the activated sludge. As such, the sludge-water partitioning and the fate of the analyte TBBPA was investigated in this study from experimentally determined pertinent physical parameters.

Materials and Methods
All chemicals and reagents were purchased from Sigma-Aldrich Canada unless otherwise specified. Most chemicals were ACS grades and all solvents used were HPLC grades. Whatman GF/B filters, Whatman GF/F, Whatman 0.2 nylon membrane and nucleopore polycarbonate filters (Cat. No 0930069) were purchased from Fisher Scientific. Helium (99.9999%) and methane (99.9999%) were supplied by BOC Canada (Guelph, Ontario). Milli-Q water was produced from a Milli-pore Ultrapure Water System.

The analysis was performed by an Agilent 6890N GC equipped with an autosampler injector. The signal detector for quantification was an Agilent 5975 MSD. Helium was used as the carrier gas, under a constant pressure of 80 kPa. Methane was used as the reagent gas for the negative ion source and was maintained at 40% of flow. The interface, inlet and quadrupole temperatures were maintained at 250 °C, 250 °C and 150 °C respectively. Select ion monitoring mode was used. The ions monitored were 79 and 81 m/z for TBBPA, 71 and 74 m/z for DDT.

The extraction and analysis of aqueous samples require multiple steps of processing. Process flow for the analysis is provided below

![Figure 1 Analysis process flow diagram](image-url)
A Shimadzu TOC-V unit equipped with a solid sample module 5000A was used for TOC measurement. Calibration curves were updated every 2-3 months as specified in standard methods (APHA, 2012). Basic water quality parameters such as dissolved oxygen (DO), pH and temperature were recorded onsite using a pH/conductivity/DO meter (probe model sensION6, Hach, USA).

Adsorption losses on to the container wall for the determination of organic compounds have been reported (Kerr et al., 2000; Kokkola et al., 2014). Similar to other organic compounds, TBBPA has a tendency to be adsorbed on to the surface of the glass vessel indicating adsorptive losses (Covaci et al., 2009). Thus, care must be taken to compensate for adsorption losses. To account for TBBPA’s tendency to be adsorbed on to the surface of the glass vessel, the vessel-wall partition coefficient (K_W) was defined as the partition coefficient between glass wall and the aqueous phase (after Backhus and Gschwend, 1990):

\[
K_W \text{ mL cm}^{-2} = \frac{[TBBPA]_{\text{Wall}}}{[TBBPA]_{\text{aq}} \cdot \frac{SA}{V}} \quad (1)
\]

The wall loss coefficient was determined by spiking 100 µL of 100 µg/L TBBPA to 500 mL Milli-Q water in borosilicate glass Erlenmeyer flasks. The equilibration period was over 24 h to achieve complete equilibrium before extraction and analysis. The flasks were wrapped with aluminum foil and were placed in the dark chamber for 72 h in order to avoid photo-degradation losses. The initial concentration was estimated from instantaneous extraction and quantification of the spike solutions. According to the Equation 1, wall loss coefficient (K_W) was estimated from the geometry and equilibrium concentrations between aqueous phase and borosilicate glass surface. The details of the experiment are illustrated in the Table 1.

Organic carbon content in activated sludge was measured by a TOC analyzer while the spiked concentration of TBBPA was extracted and analyzed in parallel by GC-MS for the determination of K_OC. The organic carbon partition coefficient (K_OC) of activated sludge was estimated from Equation 2.

\[
\frac{[TBBPA]_{\text{Tot}}}{[TBBPA]_{\text{aq}}} = 1 + K_{OC} [OC] + K_W \left[ \frac{SA}{V} \right] \quad (2)
\]

Sorptive partitioning to activated sludge was estimated from the sludge-water partition coefficient (K_P). The solid-liquid partition coefficient is given by the following equation:

\[
K_P = \frac{[TBBPA]_{\text{Sorp}}}{[TBBPA]_{\text{aq}}} = \frac{[TBBPA]_{\text{Tot}} - [TBBPA]_{\text{aq}}}{[TBBPA]_{\text{aq}}} \quad (3)
\]
KP is a very useful parameter for predicting partitioning of organic compounds in biological treatment system. The distribution of TBBPA in activated sludge process was estimated from Equation 3. The sludge-water partition coefficient (KP) is directly related to the organic fraction of the sludge. The relationship can also be empirically expressed as:

\[ K_P = K_{OC} \times f_{OC} \] \hspace{1cm} (4)

Where, fOC is the organic fraction of the sludge. If the proportion of organic carbon increases, the propensity of sorptive partitioning to sludge increases.

There are many factors that may influence the normal distribution of pollutants in the sludge matrix. The fraction of organic matter in the sludge can be obtained from the measurement of VSS and TSS. The direct measurement of organic carbon concentration by TOC analyser may have some limitations in terms of organic fractions in the total solids. However, all these parameters are empirically related to each other for developing partitioning model. Experimentally measuring the octanol-water partition coefficient (KOW) is much easier than measuring KOC and KP from the sludge matrix. This then allows determination of KP from the following model for organic contaminant partitioning in the activated sludge (Schwarzenbach et al., 2003; Carballa et al., 2008):

\[ K_P = 0.74 \times K_{OW} + 0.15 \] \hspace{1cm} (6)

However, Karickhoff (1981) originally proposed a linear relationship for modeling KP from KOW as follows:

\[ K_P = f_{OC} \times 0.41 \times K_{OW} \] \hspace{1cm} (7)

The partition model in Equation 7 clearly necessitates the experimental determination of organic carbon in the sludge. To overcome the limitation of empirical modeling, we have experimentally determined partition coefficients for developing the fate model of TBBPA in activated sludge process.

**Results and Discussions**

The vessel-wall partition coefficient was determined through triplicate measurements and the experimental value obtained was 0.053 mL cm⁻². This value serves as the correction coefficient for a unit volume of TBBPA solution per unit surface area of borosilicate glass. The correction coefficient compensates for the adsorptive losses on to the vessel wall for the determination of TBBPA. See Table 1 for all the experimental values.
The organic carbon partition coefficients ($K_{OC}$) and sludge-water partition coefficients ($K_P$) were determined experimentally. The details of the experimental are given in Table 2. The resulting $K_{OC}$ value is 6.05, with $K_P$ equal to 4.53. The sludge-water partition ($K_P$) coefficient follows the similar trend with $K_{OC}$. However, the organic carbon partition coefficient is more of an intrinsic parameter like $K_{OW}$ than $K_P$. $K_P$ is a phase equilibrium constant which approaches the Freundlich constant ($K_F$) if the exponent of sorbate intensity (1/n) becomes unity. $K_{OC}$ is specific to the type of organic matter present in the biological process. The value of $K_{OC} > 3$ provides high potential for sorption to the sludge (Birkett and Lester, 2003). The higher sorption potential for TBBPA in MBR and activated sludge was reported by the authors from sorption kinetic study (Islam et al., 2014).

The values obtained in this study were within the expected range as well as similar to the estimated literature values. Table 3 provides a comparison of our experimental results with that of the model estimated literature values.
### Table 3 Comparison of coefficients with Literature values

<table>
<thead>
<tr>
<th>Partitioning coefficients</th>
<th>Measured values</th>
<th>Literature values</th>
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<tbody>
<tr>
<td></td>
<td>Experimental</td>
<td>Estimated</td>
</tr>
<tr>
<td>logK$_{OC}$</td>
<td>6.05</td>
<td>5.43$^a$ (KOCWIN, V. 2.0, MCI)</td>
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<tr>
<td></td>
<td></td>
<td>6.80$^a$ (QSAR using logK$_{OW}$)</td>
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<tr>
<td></td>
<td></td>
<td>4.52$^a$ (Derived from logK$_{OW}$)</td>
</tr>
<tr>
<td>logK$_P$</td>
<td>4.53</td>
<td>6.49$^b$ (EPIWIN, V. 3.04; BFRIP Report)</td>
</tr>
<tr>
<td>K$_W$</td>
<td>0.053</td>
<td>-----------------</td>
</tr>
</tbody>
</table>

$^a$ Environment Canada: Physical and Chemical Properties of TBBPA
$^b$ BFRIP: Data Summary and Test Plan for TBBPA

It was observed that the organic carbon partition coefficient for TBBPA is linearly influenced by the organic carbon content in the activated sludge. The fate and partitioning correlation models for TBBPA in the activated sludge process are shown in Figure 1. The K$_{OC}$ for TBBPA increases linearly ($r^2=0.91$) with the organic carbon content exhibiting similar correlation with the solid-water partition coefficient K$_P$ ($r^2=0.82$) in the activated sludge. Xia et al. (2005) have found linear relationship of logK$_P$ with logK$_{OW}$ for selected compounds similar to our experimental result.

![Figure 1 Correlation of LogK$_{OC}$ with organic carbon and K$_P$](image)

**Summary**

The partitioning coefficients presented in this paper were successfully measured by the experimental method. The developed correlation models for partition coefficients will be useful to determine the fate of TBBPA in wastewater treatment process. The partitioning and transport model of TBBPA in this study was obtained from the experimentally determined kinetic coefficients.
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References


