Chemosphere 91 (2013) 1648–1652

Contents lists available at SciVerse ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Technical Note

Evaluation of the gas stripping technique for calculation of Henry's law constants using the initial slope method for 1,2,4,5-tetrachlorobenzene, pentachlorobenzene, and hexachlorobenzene

Kerry N. McPhedran [a], Rajesh Seth [a,*], Ken G. Drouillard [b]

[a] Department of Civil and Environmental Engineering, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada N9B 3P4
[b] Great Lakes Institute for Environmental Research, University of Windsor, 401 Sunset Avenue, Windsor, Ontario, Canada N9B 3P4

HIGHLIGHTS

- Henry's law constant (HLC) reference uncertainty is high.
- HLCs assessed for 3 chlorobenzenes via gas stripping.
- Volatilization rates decreased over time according to three slope regions.
- Use of entire stripping data set leads to biased HLCs.
- Chlorobenzene HLCs differed from wide reference ranges.

ARTICLE INFO

Article history:
Received 7 March 2012
Received in revised form 29 November 2012
Accepted 1 December 2012
Available online 23 January 2013

Keywords:
Chlorobenzenes
Henry's law constant
Gas stripping
Glass adsorption

ABSTRACT

Henry's law constant (HLC) is an important factor used in environmental risk assessment and fate and transport models to describe mass transfer of chemical between water and air. HLCs and structure–property relationships were assessed for 1,2,4,5-tetrachlorobenzene (TeCB), pentachlorobenzene (PeCB), and hexachlorobenzene (HCB). HLCs were determined using the volatilization rate (k_v) of sparged chemical at 25 °C. Despite the assumption that k_v should be constant throughout the stripping duration, results indicated that k_v decreased over time according to three separate slope regions. Results of ANCOVA indicate that k_v is statistically different in the third slope region, which leads to the conclusion that use of the entire stripping data set would lead to biased HLCs. This decrease in k_v may be attributed to desorption from sparger surfaces, which has not been considered widely in the literature. Statistical analysis was possible because of the robustness of the current experimental procedure which included numerous replications (15 total spargers) and extensive data points available to discern key slope changes. HLCs determined using the gas stripping technique were 57, 33, and 30 Pa m^3 mol^{-1} for 1,2,4,5-TeCB, PeCB, and HCB, respectively. In comparison to literature values, current TeCB and HCB HLCs were within wide reference ranges spanning approximately an order of magnitude for each chemical. PeCB HLC of the current study was two times lower than the lowest reference data.

1. Introduction

Henry's law constant (HLC) is used to describe mass transfer of chemical between water and air. HLC is an important factor used in environmental risk assessment and fate and transport models (ten Hulscher et al., 2006). Additionally, HLC may also be used in fugacity models with standard partition coefficients to calculate fugacity capacity (Mackay and Paterson, 1981). Despite the need for accurate determination of HLC, the quality and uncertainty of HLC has recently been questioned (Goss et al., 2004; Brachet et al., 2005; Jantunen and Bidleman, 2006; ten Hulscher et al., 2006; Qian et al., 2011).

Measuring HLC directly by several experimental methods has been assessed and discussed previously (Mackay and Paterson, 1981; Fendinger and Glotfelty, 1988; Lau et al., 2006). In the absence of measured data, vapor pressure (V_p) and aqueous solubility (S) may be used to estimate HLC (HLC = P/S). The current gas stripping method has been used for calculation of HLC for sparingly soluble and semivolatile compounds (Oliver, 1985; Yin and Hassett, 1986; Warner et al., 1987; Dunnivant et al., 1988; ten Hulscher et al., 1992; Drouillard et al., 1998; Jantunen and Bidleman, 2006; ten Hulscher et al., 2006). Determination of HLCs for hydrophobic organic compounds (HOCs), such as chlorobenzenes, may

* Corresponding author. Tel.: +1 519 253 3000; fax: +1 519 971 3686.
E-mail address: rseth@uwindsor.ca (R. Seth).

0045-6535/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.chemosphere.2012.12.017

Table 1
Physicochemical properties of the chemicals at 25 °C (Suntio et al., 1988).

Chemical	MW	CAS#	V_p (Pa)	S (g m^{-3})	log K_{ow}	
					Selected	Range
1,2,4,5-TeCB	215.9	95-94-3	9.86	1.27	4.5	4.46–5.05
PeCB	250.3	608-93-5	0.88	0.65	5	4.88–5.79
HCB	284.8	118-74-1	0.245	0.005	5.5	4.13–6.53

be difficult due to low solubilities (ten Hulscher et al., 2006). Additionally, experimental artifacts related to adsorption of chemical to glass surfaces is a known issue for HOCs. (Brachet et al., 2005; ten Hulscher et al., 2006; Qian et al., 2011).

Chlorobenzenes (CBs) are a suite of varying physicochemical properties (Table 1). Three compounds (1,2,4,5-tetrachlorobenzene – TeCB, pentachlorobenzene – PeCB, hexachlorobenzene – HCB) were chosen for the current study. Each of these chlorobenzenes, especially HCB, have numerous literature HLCs available (Table 2). The goal of the current study is to establish HLCs for the three chlorobenzenes using the gas stripping technique. Given the wide range of literature HLCs, determination of accurate HLCs are valuable in future use of gas stripping in subsequent studies.

2. Theory

Gas spargers are spiked with HOCs and allowed to reach equilibrium with sparger surfaces overnight. Nitrogen gas (N2) is bubbled through the column, allowing equilibrium between gas and water. HLC can be determined via (Drouillard et al., 1998):

$$\mathrm{HLC} = k_v \frac{VRT}{F} \tag{1}$$

where V is the sparged water volume (L), R is the gas constant, T is temperature (K), F is the gas flow rate (L h^{-1}), and k_v is the first-order volatilization rate constant (h^{-1}). The volatilization rate constant (k_v) can be found via (Dunnivant et al., 1988):

$$\ln(m_{w(o)} - m_{\mathrm{N2}}) = -k_v t \tag{2}$$

where $m_{w(o)}$ is the initial mass of chemical spiked into the sparger and m_{N2} is the cumulative mass captured at the sparger outlet. A plot of $\ln(m_{w(o)} - m_{\mathrm{N2}})$ versus t allows the k_v term to be found via the slope. Two assumptions must be valid for these equations to hold (Hassett and Milicic, 1985): (1) the sparged gas must reach equilibrium with the water; and (2) k_v must be constant over the stripping duration (HLC is constant at a specified temperature).

3. Materials and methods

3.1. Chemicals and reagents

1,2,4,5-Tetrachlorobenzene (98% pure), pentachlorobenzene (98% pure), hexachlorobenzene (99% pure), 1,3,5-tribromobenzene (TBB; 98% pure) and Amberlite XAD2 (20–60 mesh) were purchased from Sigma–Aldrich (Canada). Stock solutions of 10 mg L^{-1} TBB (internal standard) and a mixture TeCB, PeCB and HCB (30, 10, and 10 mg L^{-1}, respectively) were prepared in hexane and methanol, respectively, and stored at 4 °C.

3.2. XAD2 resin trap preparation and extraction

XAD2 resins were cleaned prior to use using a flow-through column and distilled water, methanol, and hexane (ca. 20 times bed volume each at 1 mL min^{-1}) successively. XAD2 resins were dried using a nitrogen stream. Resin traps consisted of pasteur pipettes (7 mm ID) packed with ca. 3 cm of dried XAD2 and the adsorbent was contained using glass wool (cleaned with distilled water, methanol and hexane, successively) plugs at each end (see inset Fig. 1). Teflon tubing was heated and pressure fit onto the pipette on each end. A luer fitting was added to the downstream end of the pipette for connection of an electronic flow gauge during experimentation and a vacuum manifold for extractions. XAD2 resin traps were stored at 4 °C and reused for each experiment once verified clean via hexane extraction and gas-chromatography (see below). XAD2 resin traps were spiked with TBB (10 μL) prior to experimental use as an internal standard to verify extraction efficiency. Following sampling, each sampler was extracted using three 10 mL aliquots of hexane at ca. 0.5–1 mL min^{-1}. The first two aliquots were brought to 20 mL using hexane and placed into 30 mL storage vials without further processing and stored at 4 °C prior to analysis by GC–ECD. The third aliquot was used only for verification of full extraction and XAD2 resin cleaning via GC–ECD.

3.3. Multi-sparger system

A multi-sparger system (max. 6 simultaneous) was used for all experiments (Fig. 1). The apparatus consists of a high-purity nitrogen gas stream pre-wetted via a pre-sparger delivered to a 6-port manifold (individually valved). Each port delivers ca. 50 mL min^{-1} nitrogen to a 1 L sparger (flow rate measured using an electronic flow controller). Spargers were kept at 25 °C (±0.5 °C) via a circulating water bath.

Duplicate or triplicate 1 L samples of MilliQ water were spiked with 50 μL of the chlorobenzene mixture, mixed via hand-shaking and allowed to equilibrate ca. 18–24 h in the water bath prior to commencing experiments (allowing the MilliQ water to reach 25 °C and the CBs to reach equilibrium with glass surfaces). Prior to initializing experiments, XAD2 resin traps were spiked with the TBB internal standard (10 μL) and placed at the outlet of each sparger. Flow rates were corrected to 45–55 mL min^{-1} after changing each adsorbent (1 h intervals to 12 h, 4 h intervals to 24 h, and 12 h intervals to 48 h) to allow for variability in flow characteristics given the shared manifold. The overall sampling duration was reduced after initial experiments indicated a non-linear volatilization rate (see Section 4) to 12 h with increased sampling accordingly (0.5 h intervals to 6 h, 1 h intervals to 12 h). XAD2 resin traps were removed and replaced at the above sampling intervals. Following removal, the resin trap was capped using polyfilm and placed in sealed bags at 4 °C until extracted as described above.

3.4. Analytical methods

Analysis of all samples was carried out on a Varian 3600 GC equipped with split/splitless injector, a 30 m × 0.32 mm fused silica DB-5 column with a 0.25 μm film thickness (J&W Scientific) and an ECD detector. The injector was maintained at 250 °C with a flow rate of 2 mL min^{-1} He. A 1 μL injection was made into a 253 μm liner and the column was held at 140 °C for 2 min. Subsequently, the column was raised to 192 °C with a 6.5 °C min^{-1} ramp. The makeup gas flow rate was 29 mL min^{-1} N_2 and detector temperature at 250 °C. The limit of detection (LOD) is defined as the