

Enhanced solubility of priority contaminants in high-biomass systems and associated impacts on biofilter operation

John W. Barton, Sandie A. Jones, Chris D. Vodraska, Brian H. Davison

Life Sciences Division, Oak Ridge National Laboratory, PO Box 2008
Oak Ridge, Tennessee 37831-6226 USA bartonjw@ornl.gov, davisonbh@ornl.gov

Summary

We report measurements of solubility limits and Henry's law constant partitioning values for benzene, toluene, TCE, and chloromethane in closed vessels that contain varying levels of biomass. The air/liquid partition constant for benzene decreased from $2.9 \times 10^{-3} \text{ atm m}^3 \text{ mol}^{-1}$ to as low as $0.1 \times 10^{-3} \text{ atm m}^3 \text{ mol}^{-1}$ and the solubility limit increased from 20 to 48 mM when biomass (in the form of yeast) was added to aqueous batch systems containing this pollutant. The Henry's law constant for toluene decreased from 6.4×10^{-3} to $0.17 \times 10^{-3} \text{ atm m}^3 \text{ mol}^{-1}$, while the solubility limit increased from 4.9 to greater than 20 mM. For TCE, the air/liquid partition constant decreased from $0.013 \text{ atm m}^3 \text{ mol}^{-1}$ to less than $0.00013 \text{ atm m}^3 \text{ mol}^{-1}$, and the solubility increased from 8 mM to more than 1000 mM. Experimentally measured partition values were also used to calculate intrinsic 'pure biomass' partitioning constants, which can be used to predict partitioning behavior. Solubility and partitioning values for TCE were most heavily impacted by biomass levels, changing by two orders of magnitude. These results should be directly applicable to predictive biofiltration models for a variety of sparingly soluble organic contaminants.

Introduction

Partitioning in biotreatment strategies. Post and present production of organic and chloroorganic compounds (TCE, BTEX, PAHs, PCBs, etc.) has left a need to deal with legacy environmental contamination as well as more effective end-of-pipe treatments. Accurate partition data on contaminants under actual conditions should be important. We have previously reported higher solubility limits for sparingly soluble alkanes (e.g., propane) in biofilter systems that result when high levels of biomass/organic matter are present (Davison et al., 2000), which may explain why typical variation between biofiltration removal rates of high- and low-solubility vapors is only about 1 order of magnitude—much less than the three orders of magnitude expected by sole consideration of pure-water solubility.

Transport and subsequent biodegradation of poorly soluble organics are impacted by how those chemicals partition from one phase into another. Sparingly soluble organic vapors typically partition between water and air according to Henry's law. Henry's law constants and other partitioning values for organics in pure water can be found for an extensive number of environmentally important compounds in studies reported by Mackay and Shiu (1981) and others (Hine and Mookerjee, 1975; Wilhelm et al., 1977; Lide and Frederikse, 1995). These 'pure water' values are used in almost all reported transport models, even those describing bioremediation processes where water may have high organic and/or salts content (Deviny et al., 1999; Barton, et al, 1998; Peng and Wan, 1998). We have previously published evidence (Davison et al., 2000) that using pure-water values can yield large errors in estimating actual transport.

Effective Henry's law constants. Active biofilm (or suspended biomass) can be envisioned as a "two-phase" mixture: a theoretical 'pure' biomass phase (membranes, lipids, proteins, etc.) and an aqueous biomass phase (water both inside and outside the cells). By treating water-saturated biomass as a single phase, an "effective" Henry's constant for water containing biomass can be measured. It is worthy to note that Henry's law is strictly true only for dilute solutions. In these studies, some concentrations can increase by up to two orders of magnitude (e.g. solubility increases from 8 to ~1000 mM for TCE for certain conditions); we assume that Henry's law will still apply to these solutions, which are still < 10% solute by mass.

Related work. Octanol-air partition constants have been used as model systems to describe the partitioning of a compound from a gaseous phase into a "biomass" phase (Wania and Mackay, 1996). Several studies have been performed on a variety of systems, from terrestrial plants (Hiatt, 1998; Komp and McLachlan, 1997; Merk and Riederer 1997) to fish (de Wolf and Lieder, 1998), to test the validity of these models. Some of these studies, Hiatt (1998) and Komp and McLachlan (1997) in particular, have found that the partitioning of organic gases into varying biological systems can differ greatly from the partitioning predicted by an octanol-air model. Related work has also been conducted by Chawla et al. (2001), in which solubility of TCE was measured in water/alcohol mixtures. In that work, up to a ten-fold increase in solubility was reported for 50/50 mixtures. Others have also reported increased solubility effects for a variety of organics in the presence of soil, surfactants, and other types of phases which contain carbon (Field et al., 2000; Wang and Vipulanandan; Falta, 1998). Quantitative relationships, however, are rare. Since partitioning can vary from one biological system to another, and given the lack of reported data for partitioning of organic vapors into subsurface biomass, this study reports partition constants of priority contaminants for a well-characterized model biomass. These data are then used to calculate parameters which facilitate modeling of transport, uptake, mobilization, and sorption of organic contaminants such as benzene and TCE. The solubility data we present here are for relevant contaminants and should allow other researchers to estimate and extrapolate the influence of biomass on their own biotreatment process.

Materials and Methods

Microbiology and Biomaterials. The model biomass utilized was typical baker's yeast, *Saccharomyces cerevisiae* (Fleischmann's). The yeast was grown in a single batch using a 500-L stirred tank on a medium of 20 g L⁻¹ yeast extract, 10 g L⁻¹ peptone, 5 g L⁻¹ sodium chloride, and 40 g L⁻¹ glucose. Inoculum was grown in smaller batch vessels to reduce tank lag time. Yeast cells were collected and centrifuged (Sharples Equipment Division, Pennsalt Chemicals Corp., Model AS26NF) at 8000 rpm and stored at -5 °C prior to use. When needed, frozen yeast was thawed and then rinsed/resuspended three times in deionized water prior to use, followed by pasteurization at 70 °C for 1 hour to eliminate any residual carbon dioxide production. For the yeast slurries used in experiments, both wet and dry cell weight densities were determined on parallel representative samples by weighing known volumes of wet, salt/substrate-free slurry followed by drying.

Maximum Solubility. Henry's law constants were determined through equilibrium measurements between a headspace and a solvent phase in a sealed test tube. The test tubes were approximately 27 mL volume and 1.3 cm internal diameter. The exact volume of each test tube was determined gravimetrically; the tubes were then filled with ~23 mL of yeast slurry and deionized water. Benzene, toluene, or TCE were added quantitatively (2.0, 2.0, and 3.0 mL respectively) to each test tube, allowing for ~1 mL headspace. The exact amounts of organic and water/biomass were gravimetrically determined. Each tube was sealed with a PTFE-lined silicone rubber stopper (Kimble Glass) and aluminum crimp top. The test tubes were then shaken using a rotary shaker (Roto-Torque, Inc.) for at least 1 hr to allow for equilibration of the organic between the three phases—24-hour controls showed that equilibrium was reached within one hour. For any given contaminant, up to eight different yeast densities were used.

After equilibration, the maximum solubility of organic into the aqueous biomass phase was determined by either direct or indirect gas chromatography analysis: indirect extraction measurements (for TCE) were made by mixing 1 mL of the aqueous phase with 1 mL of acetone and 4 mL hexane in airtight extraction vials and shaking for 30 minutes to promote extraction of TCE into the hexane phase from the acetone/water phase. Sequential extractions of the water/acetone phase showed >99% removal of the organic contaminant. In some cases, aqueous yeast mixtures which contained an excess organic solvent phase formed a small rag layer (an emulsion phase) when shaken vigorously. This emulsion tended to break within minutes, but care was taken during experimentation to avoid sampling near the interface even when an emulsified rag layer was not apparent.

Deionized water controls were run with each set of experiments to check for unforeseen variables that may have impacted the results. Because Henry's law constants are known to be strongly temperature dependent, room temperature was measured for each experiment and vials were manipulated to avoid transfer of body heat into tubes and vials. Temperature variation between experiments was about 2 °C; data are presented with the actual operating temperature. Measured constants can be adjusted for temperature with van Hoft relationships.

Henry's law measurements. Henry's law constants were determined for the organic in each of the biomass test tubes used in the solubility experiments above. The exact volumes for a second set of test tubes were determined gravimetrically. Then 8 mL of the aqueous biomass layer from the previous set of tubes were added, and the tubes were sealed with a PTFE-lined silicone rubber stopper (Kimble Glass) and aluminum crimp top. The test tubes were then shaken using a Roto-Torque rotary shaker for at least 1 hr to allow for equilibration of the organic between the aqueous phase and the headspace.

Calculation of Henry's Law Constant. Henry's law constants were determined using the standard form of Henry's law equation; headspace concentrations were determined through direct gas chromatography. Aqueous concentrations were determined by indirect gas chromatography of extracted samples. All H values are reported in $\text{atm m}^3 \text{mol}^{-1}$ (volume-based concentrations) or atm kg mol^{-1} (mass-based concentrations); the latter are used for theoretical, calculated values of the intrinsic, 'pure biomass' values for the Henry's law constant.

Gas Chromatography Analysis. All gas chromatography was performed on a Hewlett Packard 5890 series gas chromatograph, equipped with flame ionization detection and operating at a constant oven temperature of 45°C. The injection temperature and detector temperatures were both 200°C. The capillary column used was 30 m by 0.53 mm ID with 1.5 mm Phase DB-1 film thickness (J&W Scientific, Inc.).

Results and discussion

Controls. For each set of experiments and for each organic contaminant, the maximum solubility and Henry's law constant were determined for pure deionized water as a check on the procedures being used. These controls were run in parallel with all other experiments to confirm experimental technique and accuracy. Henry's constants are reported in either units of $\text{atm m}^3 \text{mol}^{-1}$ or atm kg mol^{-1} , which only differ by the solution density. The range of solution densities for experiments was approximately 0.99 g mL^{-1} to 1.10 g mL^{-1} .

Yeast. Saturation limits and Henry's law constant determinations were possible from 0 to about 350 g dry wt biomass L^{-1} using prepared yeast slurries. Some initial control experiments were performed with living cells; CO_2 generation was noted in those experiments. After pasteurization, the yeast used in these experiments did not show any signs of being metabolically active. Under a microscope, pasteurized cells appeared to have been caught in a wide range of metabolic states, including schmoos, buds, haploid cells, and cytosolic cellular material shrinking away from the ascus. The wide range of growth states suggest that pasteurization halted metabolic activity without greatly altering the gross biochemical makeup.

Determination of a fundamental alkane/biomass solubility. In Davison et al. (2000), we introduced a theoretical intrinsic Henry's law constant, H_{biomass} , for a "pure", water-free, biomass phase and described how the following mixing rule could be derived from standard definitions:

$$\frac{1}{H_{\text{mixture}}} = \frac{1}{H_{\text{biomass}}} \frac{m_{\text{biomass}}}{m_{\text{biomass}} + m_{\text{water}}} + \frac{1}{H_{\text{water}}} \frac{m_{\text{water}}}{m_{\text{biomass}} + m_{\text{water}}}$$

This general equation, which assumes no volume change on mixing, can be used to calculate Henry's law constants for "pure" biomass if the ratio of biomass and water (i.e., the biomass density) and Henry's

constant for the mixture are known or measured. Note that it is not necessary to know the mass of organic solute in each of the two solvent phases. An alternative derivation using concentrations based on volume of the solvent (mol L^{-1}) is possible, but the equation above is more useful for calculating pure-biomass values of the Henry's constant since it does not require specific knowledge of the pure-biomass volume. Note that Henry's constants used will have units based on the solution mass, but can be converted to a volumetric basis via the solution density, which is easily measured.

In this paper, experimentally measured values for water (H_{water}) and for yeast/water mixtures (as H_{mixture}) are used to determine pure-yeast Henry's law constants for priority subsurface contaminants. Although these values are artificial constructs, they can be used to predict the effective solubility of dilute organic in a water-biomass mixture over a wide range of solution densities if the solution density is known.

Maximum solubility measurements. Biomass/water mixtures with varying amounts of yeast were contacted with a pure organic phase to determine the maximum solubility of the organic in the mixture. Three organics were used: benzene, toluene, and trichloroethylene. In each case, either 2 or 3 mL of organic were added to sealed test tubes containing about 25 mL of a yeast/water mixture. The dry density of the aqueous yeast/water phase varied from 0 to about 350 g L^{-1} , and typically 5 to 8 densities were tested for each organic. The solutions were allowed to reach equilibrium over the course of 24 hours. With the exception of high biomass cases for yeast/TCE, a free organic phase was present over the entire range of densities tested after equilibrium was established. Note that chloromethane is a gas at room temperature and atmospheric pressure; thus, maximum solubility measurements do not apply to this substance under those conditions.

Benzene. Reported solubility limits for benzene in pure water typically fall between 20 and 25 mM (Lide et al., 1991; Budavari et al. 1989; Klotz, 1999). There appears to be much less scatter in literature values for this compound and toluene as compared with TCE. Our measured value for benzene fell within the reported range, and was found to increase rapidly with rising biomass density in an aqueous phase (see Figure 1). In general, solubility more than doubled over the range of dry densities examined; the increase in solubility was found to rise most rapidly at very low biomass densities. **Toluene.** Reported solubilities for toluene in water typically fall between 5 and 8 mM in pure water (Lide et al., 1991; Budavari et al. 1989). Our measured value for toluene in pure water fell within the reported range, and the value was found to increase with rising biomass density in an aqueous phase (see Figure 1). Solubility more than quadrupled over the range of dry densities examined (0 to 0.25 g mL^{-1}); data were best fit by a power law. **TCE.** Reported solubilities at room temperature for trichloroethylene in pure water vary significantly, but typically fall between 5 and 15 mM (McGovern, 1947; Banerjee et al. 1980; Mackay et al., 1993; Chiao et al., 1994). Our measured value for trichloroethylene in pure water fell within the reported ranges, and the values for yeast/water mixtures were found to increase rapidly with rising biomass density (see Figure 2). In general, solubility increased by one and a half orders of magnitude (from about 8 mM to more than 1000 mM) over a very short range of dry densities (0 to $0.14 \text{ dry g mL}^{-1}$). The increase in solubility was found to rise most rapidly at very low biomass densities. Data were best fit by power law. In experiments with yeast/water densities higher than 0.18 g mL^{-1} , all of the TCE added (about 2 mL) dissolved completely and only one phase was apparent (data not shown). Centrifugation of these solutions, both before and after sonication, could not separate TCE from the yeast solution, and TCE was not visible under the microscope as a separate phase or as part of an emulsion. Apparently, the maximum solubility was greater than could be achieved under these experimental conditions. The effective solubility of TCE was impacted much more strongly by the presence of biomass than either benzene or toluene. Also, the impact was larger than any effects that had been reported previously for propane or methane in yeast/water mixtures (Davison et al., 2000).

Effective Henry's law constant measurements. Partition constants between an aqueous/biomass and an air/headspace phase were measured for four compounds and are reported here in the form of Henry's law constants. For three of the compounds, the Henry's constant for the mixture changed substantially as biomass levels increased within the aqueous phase. We also calculate and report values for Henry's law

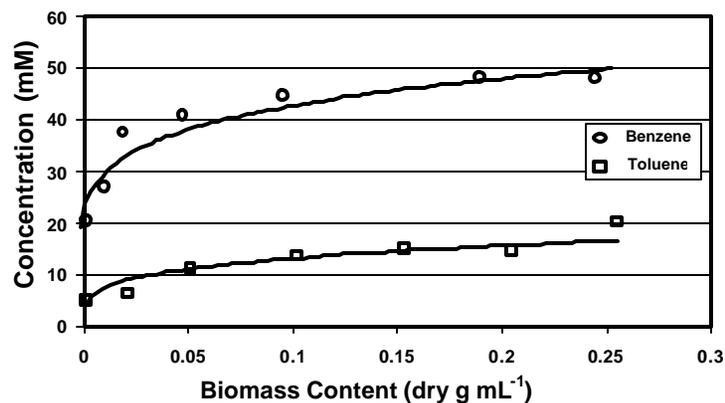


Figure 1. Measured solubility limits of toluene and benzene in water containing biomass, as a function of the dry-weight concentration of biomass. The limit increases over the range of biomass tested, and is more than double the limit in pure water for both chemicals at relatively low biomass concentration in water. The solid lines represent power law fits of collected data. The measurement temperature was 22.5 °C for benzene and 21.5 °C for toluene.

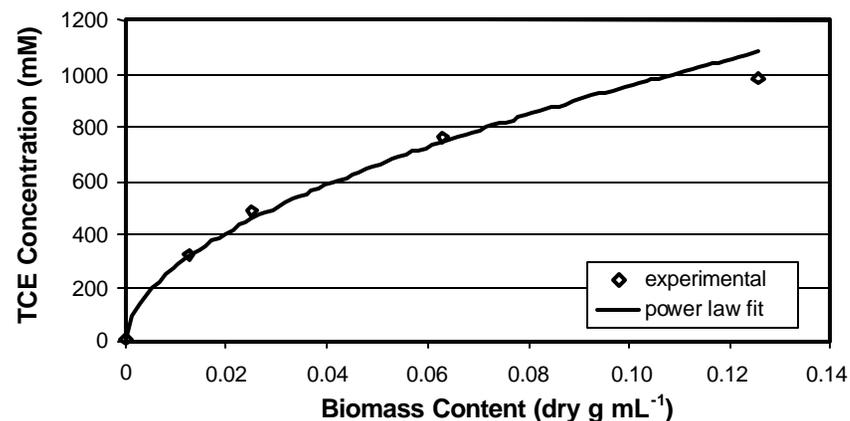


Figure 2. Measured solubility limits of TCE in water containing biomass, as a function of the dry-weight concentration of biomass. The limit increases over the range of biomass tested, and is more than two orders of magnitude higher than the value in pure water at the higher range of biomass concentrations tested. The solid line represents a power law fit of collected data. In pure water, the Henry's law constant in pure water is approximately 10 mM. The measurement temperature was 22.0 °C.

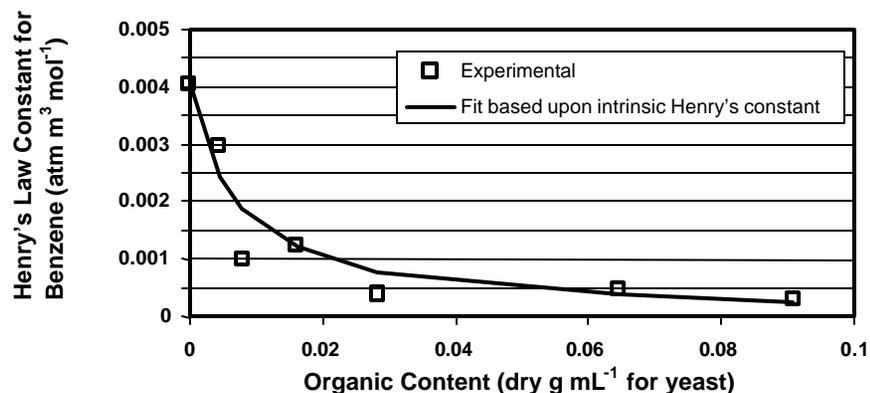


Figure 3. Henry's law constants for benzene in mixtures of yeast and water. As the biomass concentration increases (greater amount of yeast), benzene solubility increases and Henry's law constant decreases. Open squares represent experimentally collected points while the solid line represents a fit of the data based upon the intrinsic Henry's law constant for 'pure biomass'. The measurement temperature was 22.5 °C.

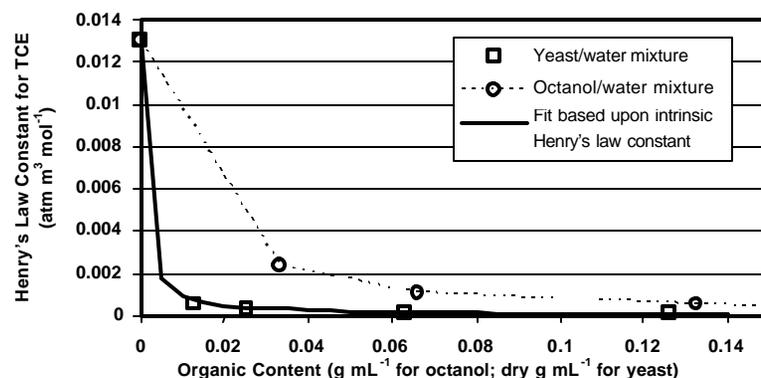


Figure 4. Henry's law constants for TCE in mixtures of yeast and water, as well as octanol and water. As the organic content increases (greater amount of yeast or octanol), TCE solubility increases and Henry's law constant decreases. Open squares and circles represent experimentally collected points while the solid line passing through squares represents a fit of the yeast/water data based upon the intrinsic Henry's law constant for 'pure biomass'. Note that TCE is much more soluble in mixtures of yeast/water than in octanol/water for similar organic contents. The measurement temperature was 22.0 °C.

constant for a 'pure biomass' phase, which is useful as a parameter in mixing rules that allow prediction of the solubility enhancement effect.

Benzene. Reported values for the Henry's law constant for benzene at room temperature in pure water typically fall between 0.004 and 0.010 atm m³ mol⁻¹ (Schwarzenbach et al., 1993; Yurteri et al., 1987; Ashworth et al., 1988). Experimentally, the value at 22.5 °C determined by repetitive experiments was $4.0 \pm 0.6 \times 10^{-3}$ atm m³ mol⁻¹, which falls within the reported range. The Henry's law constant for benzene decreases significantly (i.e., benzene becomes more soluble) in solutions of yeast ranging in dry density from 0 to 0.100 dry g mL⁻¹ (see Figure 3). At higher densities, the constant drops to less than 10 percent of its pure water value, and the trend is similar to that noted for propane and yeast (Davison et al., 2000). An intrinsic value of the Henry's law constant of benzene for 'pure biomass' was calculated to be 0.028 ± 0.003 atm kg mol⁻¹. **Toluene.** Reported values for the Henry's law constant for toluene at room temperature in pure water typically fall between 0.004 and 0.008 atm m³ mol⁻¹ (Schwarzenbach et al., 1993; Hartkopf and Karger, 1973; Hoff, Mackay, et al., 1993). We obtained an experimental value at 21.5 °C of 0.0064 ± 0.0009 atm m³ mol⁻¹, which falls within the reported range. The Henry's law constant for toluene decreased (i.e., toluene becomes more soluble) in solutions of yeast ranging in dry density from 0 to 0.100 dry g mL⁻¹ (data not shown). At higher densities, the constant drops to less than 10 percent of its pure water value, similar to benzene. An intrinsic value of the Henry's law constant of toluene for 'pure biomass' was calculated to be 0.048 ± 0.006 atm kg mol⁻¹. **TCE.** Reported values for the Henry's law constant for trichloroethylene at room temperature in pure water typically fall between 0.006 and 0.020 atm m³ mol⁻¹. (Chawla et al, 2001; ATSDR, 1995; Chiao et al., 1994; Tancrede and Yanagisawa, 1990; Ervin, Mangone, et al., 1980; Mackay and Shiu, 1981). We obtained an experimental value at 22 °C of 0.013 ± 0.002 atm m³ mol⁻¹, which falls within the reported range. The Henry's law constant for trichloroethylene decreased significantly in solutions of yeast biomass ranging in dry density from 0 to 0.300 dry g mL⁻¹ (see Figure 4). At higher densities, the constant drops by more than two orders of magnitude from its pure water value. The trend is similar to that noted for benzene and toluene, although neither the Henry's constant for benzene nor toluene drop by the same extent. An intrinsic value of the Henry's law constant for 'pure biomass' was calculated to be 0.019 ± 0.002 atm kg mol⁻¹. Note that for part of the range in Figure 4, TCE is more soluble in a yeast/water mixture than an octanol/water mixture at the same organic content. **Chloromethane.** Chloromethane, also known as methyl chloride, is a common environmental pollutant in landfills and waste sites due to its use in the production of silicones, butyl rubber, methyl cellulose and agricultural chemicals. Reported values for the Henry's law constant for chloromethane at room temperature in pure water typically fall between 0.006 and 0.010 atm m³ mol⁻¹ (Gossett, 1987; Glew and Moelwyn-Hughes, 1953; McConnell et al., 1975). Experimentally, the value at 24.0 °C determined by repetitive experiments was 0.0070 ± 0.0005 atm m³ mol⁻¹, which falls within the reported range. The Henry's law constant for chloromethane did not change significantly in solutions of yeast ranging in dry density from 0 to 0.150 dry g mL⁻¹. Although some of the constants appeared to drop by as much as 10% in some of the individual measurements, these values were statistically within the bounds of the measured value for pure water. No overall trend was apparent (data not shown). This result is very different from the measured Henry's law constants for propane (which is also a sparingly soluble gas) benzene, toluene, and TCE; we are uncertain as to why the impact is negligible.

Conclusions

Yeast biomass can have a substantial effect on the Henry's law constant and maximum solubility of contaminants (TCE, benzene, toluene) tested in the biomass slurries; however, the exception of chloromethane indicates that the effect is not universal. At 100 g biomass L⁻¹ the Henry's value for TCE was about 2% of that in pure water and the solubility limit was > 1000 mM. However, even at relatively low biomass levels such as 10 g L⁻¹, the partitioning constant was less than 10% of that in pure water. Overall, with the exception of chloromethane, Henry's law data for yeast biomass could be fit by a power law correlations; mixing rules were also able to fit the data accurately, with calculation of an intrinsic 'pure biomass' Henry's constant. By comparison of the yeast and octanol/water partition data for chloromethane and TCE, it is clear that octanol/water partitioning is not a reliable predictor of the effect of biomass on chloroorganic solubility. The fundamental 'intrinsic' Henry's law constants, H_{biomass} , for

benzene, toluene, and TCE in biomass were calculated and were found to be 0.028 ± 0.003 , 0.048 ± 0.006 , and 0.010 ± 0.0009 atm kg mol⁻¹ respectively. These solubility data will allow other researchers to estimate and extrapolate the possible influence on a variety of systems which contain significant amounts of biomass, including subsurface matrices and above-ground bioreactors.

Acknowledgments

This research was supported by the U.S. Dept. of Energy - Environmental Management Science Program.

References

- Ashworth RA, Howe GB, Mullins ME, Rogers TN. 1988. Air-water partitioning coefficients of organics in dilute aqueous solutions. *J. Haz. Mater.* 18:25-36.
- ATSDR (Agency for Toxic Substances and Disease Registry), 1995. Toxicological profile for trichloroethylene. US Department of Health and Human Services.
- Barton, JW, Davison BH, Klasson KT, Gable CC III. 1999. Estimation of mass transfer and kinetics in operating trickle-bed bioreactors for removal of VOCs. *Environ Prog* 18:1-5.
- Barton, JW, Hartz S, Klasson KT, and Davison BH. 1998. Microbial removal of alkanes from dilute gaseous waste streams: Mathematical modeling of advanced bioreactor systems. *J Chem Technol Biotechnol* 72:93-98.
- Barton JW, Klasson KT, Koran LJ Jr., Davison BH. 1997. Microbial removal of alkanes from dilute gaseous waste streams: Kinetics and mass transfer considerations. *Biotech Prog* 13:814-321.
- Budavari S, O'Neil MJ, Smith A, Heckelman PE. 1989. *The Merck Index, Eleventh Edition.* Merck & Co., Inc: Rahway, NJ.
- Chawla RC, Doura KF, McKay D. 2001. Effect of alcohol cosolvents on the aqueous solubility of trichloroethylene. *Proceedings of the 2001 Conference on Environmental Research, Kansas State University, Manhattan, Kansas*, 52-66.
- Chiao FF, Currie RC, McKone TE. 1994. Intermedia transfer factors for contaminants found at hazardous waste sites. Office of Scientific Affairs, Dept. Toxic Substances Control & the California Environmental Protection Agency, Sacramento, CA.
- Davison BH, Barton JW, Klasson KT, Francisco AB. 2000. Influence of high biomass concentrations on alkane solubilities. *Biotech. Bioeng.* 68:279-284.
- Davison BH, Thompson JE. 1993. Sustained degradation of n-Pentane and isobutane in a gas-phase bioreactor. *Biotech Lett* 15:633-636.
- Davison BH, Thompson JE. 1994. The removal of alkanes in a liquid-continuous gas-phase bioreactor: preliminary considerations. *Appl Biochem Biotechnol* 45/46:17-923.
- Devinny, JS, Deshusses MA, and Webster TS. 1999. *Biofiltration for air pollution control.* Lewis Publishers: CRC Press. 299 p.
- Ervin AL, Mangone MA, Singley JE. Trace organics removal by air stripping in *Proceedings of the Annual Conference of the American Water Works Association.* 1980. 507-530.
- Falta RW. 1998. Using phase diagrams to predict the performance of cosolvent floods for NAPL remediation. *Ground Water Monitoring & Remediation* 18:94-102.
- Field JA, Sawyer TE, Schroth MH, Humphrey MD, Istok JD. 2000. Effect of cation exchange on surfactant enhanced solubilization of trichloroethene. *J. Contaminant Hydrology* 46:131-149.
- Glew, D.N., and Moelwyn-Hughes, E.A., 1953, Chemical statics of the methyl halides in water: *Discussions of the Faraday Society*, no. 15, p. 150-161.
- Gossett, J.M., 1987, Measurement of Henry's law constants for C1 and C2 chlorinated hydrocarbons: *Environmental Science and Technology*, v. 21, no. 2, p. 202-208.
- Hartkopf A, Karger BL. Study of the interfacial properties of water by gas chromatography. *Acc. Chem. Res.* 1973. 6:209-216.
- Hekmat D, Linn A, Stephan M, Vortmeyer D. 1997. Biodegradation dynamics of aromatic compounds from waste air in a trickle-bed reactor. *Appl Microbiol Biotechnol* 48:129-134.
- Hiatt MH. 1998. Bioconcentration factors for volatile organic compounds in vegetation. *Anal Chem* 70:851-856.

- Hine, J, and Mookerjee PK. 1975. The intrinsic hydrophilic character of organic compounds. correlations in terms of structural contributions. *J Org Chem* 40:292-298.
- Hoff JT, Mackay D, Gillham R, Shiu WY. Partitioning of organic chemicals at the air-water interface in environmental system. *Environ. Sci. Technol.* 1993. 27:2174-2180.
- Klotz M, Parallel change with temperature of water structure and protein behavior, *J. Phys. Chem. B*, 103 (1999) 5910-5916.
- Knox, R. C., Sabatini, D. A., and L. W. Canter, *Subsurface Transport and Fate Processes*. Lewis Publishers, Boca Raton, Florida, 1993.
- Komp P, McLachlan MS. 1997. Interspecies variability of the plant/air partitioning of polychlorinated biphenyls. *Environ Sci Technol* 31:2944-2948.
- Leson G, Winer AM. 1991. Biofiltration: An innovative air pollution control technology for VOC emissions. *J Air Waste Mgmt Assoc* 41:1045-1054.
- Lide, DR, Frederikse HPR. *CRC Handbook of Chemistry and Physics*, 76th Edition. Boca Raton, FL: CRC Press, Inc.
- Mackay D, Shiu WY. 1981. A critical review of Henry's law constants for chemicals of environmental interest. *J Phys Chem Ref Data* 10:1175-1199.
- McConnell, G., Ferguson, D.M., and Pearson, C.R., 1975, Chlorinated hydrocarbons and the environment: Endeavour, v. 34, p. 13-18.
- Merk S, Markus R. 1997. Sorption of volatile C1 to C6 alkanols in plant cuticles. *J Exper Bot* 48:1095-1104.
- Palumbo, AV, Eng W, Strandberg GW. 1991. In *Organic Substances and Sediments*, ed. R. Baker. Lewis Publishers, Chelsea, MI, pp 225-38.
- Peng, J, A Wan. 1998. Effect of ionic strength on Henry's constants of volatile organic compounds. *Chemosphere* 36:2731-2740.
- Rihn MJ, Zhu X, Suidan MT, Kim BJ, Kim BR. 1997. The effect of nitrate on VOC removal In trickle-bed biofilters. *Water Res* 31:2997-3008.
- Schwarzenbach RP, Gschwend PM, Imboden DM. 1993. *Environmental Organic Chemistry*. Wiley-Interscience.
- Sorial GA, Smith FL, Suidan MT, Pandit A, Biswas P, Brenner RC. 1997. Evaluation of trickle-bed air biofilter performance for BTEX removal. *J Environ Eng* 123:530-537.
- Stewart, PS. 1998. A review of experimental measurements of effective diffusive permeabilities and effective diffusion coefficients in biofilms. *Biotechnol Bioeng* 59:261-272.
- Tancrède MV; Yanagisawa Y. An analytical method to determine Henry's law constant for selected volatile organic compounds at concentrations and temperatures corresponding to tap water use. *J. Air. Waste Manage. Assoc.* 1990. 40:1658-1663.
- Wang S-Y, Vipulanandan C. 2000. Enhancing TCE solubility by biosurfactant produced from used vegetable oil. Poster presentation, CIGMAT 2000 Conference, Houston, Texas.
- Wania F, Mackay D. 1996. Tracking the distribution of persistent organic pollutants. *Environ Sci Technol.* 30:390-396.
- Wilhelm, E., Battino R, and Wilcock RJ. Low-pressure solubility of gases in liquid water. *Chem Rev* 77:219-262.
- de Wolf W, Lieder P. 1998. A novel method to determine uptake and elimination kinetics of volatile chemicals in fish. *Chemosphere* 36:1713-1724.
- Yurteri C, Ryan DF, Callow JJ, Gurol JJ. 1987. The effect of chemical composition of water on Henry's law constant. *J. Water Pollut. Control Fed.* 59:950-956.