

## **Technical Comments on the U.S. Environmental Protection Agency's Inclusion of 1,3-Butadiene in the Draft Third Contaminant Candidate List under the Safe Drinking Water Act**

The U.S. Environmental Protection Agency (EPA) has published a draft list of chemicals that are known or anticipated to be public water system contaminants that may require regulation under the Safe Drinking Water Act (SDWA) (Federal Register, 2008). When issued in final, the list will become the third Contaminant Candidate List (CCL 3) issued since EPA published the SDWA Amendments in 1996. EPA has asked for comments on the draft CCL 3, which includes 1,3-butadiene (BD).

The SDWA Amendments list three criteria used to identify chemicals requiring regulation:

- The contaminant may have an adverse effect on the health of persons;
- The contaminant is known to occur or there is a substantial likelihood that the contaminant will occur in public water systems with a frequency and at levels of public health concern; and
- In the sole judgment of the Administrator, regulation of such contaminant presents a meaningful opportunity for health risk reduction for persons served by public water systems.

Data presented in this document show that BD is very unlikely to be present in public water systems because of its physical properties and because manufacturing controls mitigate against its release into the environment. With regard to chemical fate, as measured by environmental models, the atmosphere is the primary modeling compartment to receive BD from its manufacture. In the air, specific fate processes result in BD's physical degradation. BD is rapidly degraded in air and has a calculated half-life that ranges from two to six hours. BD is not expected to be present in public drinking water based on physical processes that remove volatile substances used in water treatment facilities and on the outcome of modeling that considered these processes together with BD's physico-chemical properties.

### **1,3-Butadiene Emissions from Manufacturing**

Total yearly emissions of BD are reported by industry to the EPA pursuant to the Emergency Planning and Community Right-to-Know Act. These data are made available to the public through the Toxics Release Inventory (TRI). The most recent data are from 2006, as reported in 2007, and listed in Table 1 (EPA, 2008). These data are used in the following sections to estimate the partitioning behavior of BD in the environment and its potential partitioning to drinking water.

The TRI data indicate that industrial emissions of BD declined by 69% during the years between 1988 and 2006 (the most recent reporting year), or from approximately 7.7 million pounds to 2.4 million pounds per year (EPA, 2008). Although the total emission of BD from the 2006 TRI was reported as 2.4 million pounds per year, only 1.6 million pounds was actually released to the environment and was reported within the following compartments (Table 1): point source and fugitive losses to air (1.498 million pounds), underground injection (0.102 million pounds), soil landfill both on- and off-site (685 pounds), and loss to surface water (113 pounds). The remaining 0.8 million pounds are classified as "storage" and not considered as an environmental emission.

**Table 1.** 2006 TRI data (pounds) for 1,3-butadiene reported to EPA and normalized to a yearly emission rate (kg/hr/yr).

Soil Emissions (lbs)			Air Emissions (lbs)		Water Emissions (lbs)	Other Emissions (lbs)
RCRA Subtitle C Landfill	Other On-Site Landfill	Other Land	Fugitive	Point Source	Surface Water	Underground Injection
78	292	315	545,228	952,503	113	102,406
Total (soil): 685 lbs (311 kg)			Total (air): 1,497,731 lbs (679,359 kg)		Total (water): 113 lbs (51 kg)	Total (other): 102,406 lbs (46,451 kg)
Emission rate used in modeling: 0.036 kg/hr/yr			Emission rate used in modeling: 77.6 kg/hr/yr		Emission rate used in modeling: 0.006 kg/hr/yr	Emission rate used in modeling: 5.3 kg/hr/yr

### **1,3-Butadiene Atmospheric Fate**

The atmosphere is the main environmental compartment of interest when considering fate processes that impact potential exposure to BD. BD is a gas and will partition to the air upon entering the environment even at reduced temperatures. Its behavior in the environment is largely explained by its vapor pressure, which has been reported as 856 mm Hg (1141 hPa) at -1.5 °C (Boublik *et al.*, 1984) and 2110 mm Hg (2813 hPa) at 25 °C (EPA, 2000). Although BD's water solubility has been reported as 735 mg/L at 25 °C (McAuliffe, 1966), suggesting that it has a degree of solubility, its Henry's Law constant (HLC), a measure of a chemical's volatilization rate from water, shows that BD will preferentially partition to air from solution. The HLC for BD is calculated as 20,699 Pa·m<sup>3</sup>/mole using the water solubility and vapor pressure data for 25 °C. The dissolution of BD from water as facilitated in a drinking water treatment plant is discussed below.

BD that enters the environment will primarily partition to the atmosphere, which is the major manufacturing route of loss. Results from an environmental distribution model, EQC Level III (Canadian Environmental Modelling Centre, 2004; Mackay, 2001; Mackay *et al.*, 1996), support this assessment. The EQC Level III model, which represents a steady state unit regional environment, is based on a number of default and user-selected parameters<sup>1</sup>. Using emission values from the 2006 IUR and physical-chemical and biological parameters from the EPI Suite™ package of programs (EPA, 2000) and the Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals (Mackay *et al.*, 2006), EQC predictions show the air compartment retaining 99.7% of the steady state mass of BD, with the

<sup>1</sup> EQC Level III fugacity model v2.02. Model input parameters from EPA (2000) for BD at 25 °C: molecular weight = 54.09; water solubility = 735 g/m<sup>3</sup>; vapor pressure = 281,300 Pa; log K<sub>ow</sub> = 1.99; melting point = -108.9 °C; air half-life (AOPWIN, v1.91) = 1.9 hours; water half-life (Mackay *et al.*, 2006) = 42 hours (within the range of suggested values); soil and sediment half-life (Mackay *et al.*, 2006) = 168 hours (within the range of suggested values and comparable to the Biowin 4 Primary Survey Model). Emission rates used in the model to soil, air, and water compartments are based on 2006 IUR data (Table 1).

remaining 0.3% residing in the water, soil, and sediment compartments. The mass balance calculation suggests that 97.32% of BD is reacted in the atmosphere. Another 2.67% is atmospherically advected from the defined unit environment (and will subsequently undergo atmospheric reaction outside the modelled system). Consequently, 99.99% of emitted BD is removed from the EQC model environment via atmospheric processes.

In spite of its water solubility, wet deposition of BD from the air is not likely to play a significant role in its atmospheric fate, once again because of repartitioning to the air, *i.e.*, net loss to the atmosphere. Additionally, partitioning to the air from aqueous solution for BD that may be entrained in process waters will also contribute to the net transfer to the atmosphere.

In the air, BD participates in a range of chemical reactions that leads to its degradation and the production of stable reaction products. These reactions are mediated by a variety of reactive species, but the predominant route of degradation is photooxidation via hydroxyl radicals (OH<sup>•</sup>) (Atkinson, 1985; Atkinson, 1989). The rate at which an organic compound reacts with OH<sup>•</sup> is a direct measure of its atmospheric persistence (Meylan and Howard, 1993). Atkinson (1985), in a review of reported kinetic data for BD, recommends the following rate constant:

$$k(\text{BD}) = 6.68 \text{ E-11 cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K (24.9 } ^\circ\text{C)}$$

Using an average concentration of  $5 \text{ E5 OH}^{\bullet} \text{ cm}^{-3}$ , the calculated atmospheric half-life for BD is 5.76 hours. Atkinson (1985) from a review of the literature reports that OH<sup>•</sup> concentrations in the lower troposphere have been estimated at less than or approximately equal to  $5 \text{ E6 molecules cm}^{-3}$ , and suggests the use of a daily average concentration of approximately  $5 \text{ E5 molecules cm}^{-3}$  for the northern hemisphere, as reported by Crutzen (1982).

EPA has developed a computer model that includes a calculation of the atmospheric oxidation potential (AOPWIN, v1.92, in EPA, 2000) as a result of OH<sup>•</sup> attack. AOPWIN estimates the rate constant for the atmospheric, gas-phase reaction between photochemically produced OH<sup>•</sup> and organic chemicals. The rate constants estimated by the program are then used to calculate atmospheric half-lives for organic compounds based upon an average atmospheric OH<sup>•</sup> concentration of  $1.5 \text{ E6 molecule cm}^{-3}$ . AOPWIN uses the following rate constant:

$$k(\text{BD}) = 6.66 \text{ E-11 cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 25 \text{ } ^\circ\text{C (298.15 K)}$$

Since the reactions necessary for this degradative process only take place in the presence of sunlight, the model normalizes atmospheric half-lives to a 12-hour day. BD is calculated by this model to have an atmospheric half-life of 0.16 day (1.9 hours) as a result of photolysis by OH<sup>•</sup> attack.

Manufacturing processes result in air being the primary compartment to which BD will migrate upon release. The results of the two calculations, using the recommended rate constants cited by Atkinson and AOPWIN, show that the half-life for BD in air is relatively short, ranging from approximately 2 to 6 hours, depending on OH<sup>•</sup> concentration. Because of its short air half-life, BD is not expected to be in air at sufficient concentrations to act as a potential source of contamination to drinking water. Additionally, concentrations of BD in surface water as a result of manufacturing processes will significantly dissipate to the air based on its relatively high HLC.

### **1,3-Butadiene Environmental Partitioning**

As mentioned above, BD has a relatively high water solubility. Consequently, there are two relevant drinking water sources that may result in BD exposure. These include: surface water, with loadings from atmospheric deposition, soil runoff and direct water discharges; and groundwater, with loadings mainly from underground injection.

Using the EQC Level III model, as described above with 2006 emissions taken from Table 1, the role of surface water in the environmental fate and exposure of BD was explored. Model results suggest that 0.15% of the overall steady state mass is found in surface water. Subsequently, based on these US emission rates applied over the EQC unit area of  $10^5 \text{ km}^2$  (10% of which is water surface area and the remaining 90% is soil area), the resultant surface water concentration is 0.0015 ng/L. Hence, based on these predictions, the amount of BD in surface water is negligible.

Underground injection represents 6.4% (102,000 pounds) of the total environmental emissions of BD. The main drinking water concern is dissolution into groundwater. Exposure of groundwater to the atmosphere will result in BD depletion similar to that described for surface water. In most cases, groundwater will also be treated before consumption. During this process, aeration or air stripping of the groundwater will be important to BD mitigation. EPA has indicated that air stripping is one of the best-available technologies for removing volatile organic compounds (VOCs) from groundwater (Dyksen, 2005). To simulate BD volatilization resulting from aeration, the STP model (Clark *et al.*, 1995) was used. This model is generally used to predict the fate of chemicals in sewage treatment facilities, consisting in part of an aeration tank. By defining the model system as a single aeration tank and using typical water treatment facility properties, this process can be examined.

Aeration basins of water treatment facilities are usually between 3-5 m deep, 3-9 m wide, with a width:depth ratio of  $\leq 2$  for optimal mixing, and the length is governed by the desired water detention time, usually between 10-30 minutes (Dyksen, 2005). The aeration rate for treatment is set between 0.0008-0.012  $\text{m}^3$  air/L of water. For a water flow rate of 226.8  $\text{m}^3/\text{h}$  (upper range of typical values), aeration rates equate to 181-2722  $\text{m}^3/\text{h}$ , and tank volumes of 37.8-113.4  $\text{m}^3$ , for detention times of 10-30 minutes, respectively. Assuming an aeration tank depth of 5 m, the subsequent tank area based on this water flow rate of 226.8  $\text{m}^3/\text{h}$  would be 7.56-22.68  $\text{m}^2$ . The mass transfer coefficients (MTC) used for this analysis were 23.46 m/h for air-side and 0.01 m/h for water-side (Mackay and Yeun, 1983), which represent relatively conservative values (*i.e.*, higher MTC values would result in greater volatilization). Based on these inputs, model results indicate that between 86.2-98.9% of BD would be removed by volatilization in the defined water treatment aeration tank.

During the water treatment process, other implemented mitigation technologies would further decrease the amount of BD in water. The use of dissolved air flotation (DAF) units in the water clarification process can be another significant removal pathway for VOCs due to the introduction of air to the treatment water. Oxidation is yet another potential loss mechanism, especially in both the aeration and DAF processes. There also are sorption technologies applied that may help remove residual levels of BD that are aqueous dissolved. Consequently, after treatment it is unlikely that BD would be present in drinking water.

### **Summary**

In summary, BD is unlikely to be present in drinking water. Emissions of BD from manufacturing facilities have decreased over the period 1988-2006. Modeling shows that the air is the primary environmental compartment to receive BD from manufacturing because of its physical properties. In air, atmospheric fate processes result in its rapid degradation, with an atmospheric half-life of two to six hours. Any BD released to surface or groundwater from manufacturing, or that enters surface or groundwater through run-off, will subsequently partition significantly to air based on its physical properties. In the unlikely event that any BD remains in water entering a drinking water treatment facility, standard water treatment processes will likely remove it. Since BD is unlikely to be present in drinking water, EPA should remove it from the draft CCL 3.

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