

## Effects of cold-climate environmental factors temperature and salinity on benzotriazole adsorption and desorption in bioretention cells



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### ABSTRACT

Benzotriazole, a common anti-corrosion additive in vehicle antifreeze products, is a polar contaminant frequently detected in urban runoff, particularly in cold seasons. Urban low impact development systems such as bioretention cells have shown promise to mitigate traditional stormwater contaminants. However, to date, their efficiency to reduce pollution by polar trace organic chemicals is unclear. In this study, the adsorption and desorption potential of benzotriazole to bioretention soil and hardwood mulch was investigated at varying temperature and salinity levels. The lower organic matter quality of bioretention mulch than soil, likely due to the dominance of lignin in the former and proteins in the latter, resulted in a higher affinity of benzotriazole on soil than mulch. The adsorption capacity increased with decreasing temperature. The low enthalpy changes of  $-5.6$  (soil) and  $-14$  kJ/mol (mulch) suggested adsorption via van der Waals forces and dipole-dipole interactions, respectively. Conversely, changes in salinity showed little effect on the adsorption of benzotriazole. Desorption was observed for both bioretention substrates, but was lowest at low benzotriazole concentrations. Altogether, despite low to moderate adsorption coefficients, these results showed that bioretention cells are able to retain benzotriazole particularly in cold climate conditions.

### 1. Introduction

Benzotriazole is a corrosion inhibitor commonly used in engine coolants and antifreeze liquids, aircraft de-icing and anti-icing fluids, and dishwashing detergents for silverware protection (Giger et al., 2006; Gruden et al., 2001; Vetter and Lorenz, 2013; Voutsas et al., 2006; Weiss et al., 2006). It is a nitrogen-heterocyclic compound that is polar and highly soluble in water (Table 1) (Hart et al., 2004; Richardson and Ternes, 2018). Benzotriazole is frequently detected in surface waters around the world in concentrations varying from ng/L to µg/L (Giger et al., 2006; Heeb et al., 2012; Kiss and Fries, 2009; Loos et al., 2009; Molins-Delgado et al., 2017; Nödler et al., 2014; Parajulee et al., 2017; Voutsas et al., 2006). It has been detected in tap water samples up to 227 ng/L (Janna et al., 2011; Wang et al., 2016) and in groundwater up to 1032 ng/L (Loos et al., 2010). It is often detected more frequently and at higher concentrations than its methylated derivative, tolyltriazole (Giger et al., 2006; Janna et al., 2011; Loos et al., 2010, 2009; Voutsas et al., 2006; Wang et al., 2016). The toxicity of benzotriazole has been evaluated through various bioassay analyses (Cancilla et al., 1997; Novak et al., 2000; Pillard et al., 2001), and it has been found to have anti-estrogenic effects (Harris et al., 2007). It is also a suspected human

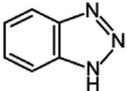
carcinogen (Richardson and Ternes, 2018). To date, no guidelines exist to regulate the release of benzotriazole to the environment; however, a drinking water guideline of 7 ng/L was established in Australia for tolyltriazole (Richardson and Ternes, 2018).

Benzotriazole is highly persistent in the aquatic environment due to its resistance to degradation and limited removal in wastewater treatment plants (Asimakopoulos et al., 2013; Giger et al., 2006; Molins-Delgado et al., 2017; Reemtsma et al., 2010, 2006; Voutsas et al., 2006; Weiss et al., 2006). Environmental concentrations tend to increase in colder months, likely due to an increase in use of de-icing and antifreeze products (Kiss and Fries, 2012), and peaks have been detected in the early spring due to high concentrations of benzotriazole in snowmelt (Alvey et al., 2016; Parajulee et al., 2017). Parajulee et al. (2017) found that the sources of benzotriazole and its transport in the aquatic environment are linked to those of road salts used for de-icing activities in winter months. While benzotriazole is toxic to aquatic plants and invertebrates at higher concentrations than what is currently observed, increased use of benzotriazole-containing products and its continued persistence in the environment may create conditions for more severe health impacts (Seeland et al., 2012).

Benzotriazole enters the environment through wastewater

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**Table 1**  
Physical and chemical properties of benzotriazole.

Structure	
	
CAS number	95-14-7
Chemical name	1H-benzotriazole
Molecular formula	C <sub>6</sub> H <sub>5</sub> N <sub>3</sub>
Molecular weight (g/mol)	119.13
Water solubility (g/L)	19.8
Log K <sub>ow</sub>	1.44
Vapour pressure (Pa)	3.28·10 <sup>-3</sup>
pK <sub>a</sub> <sup>a</sup>	8.37
Henry's Law constant (atm·m <sup>3</sup> /mol)	1.47·10 <sup>-7</sup>

Data obtained from SRC Inc. (Syracuse Research Corporation): <http://esc.syrres.com/fatepointer/search.asp>.

<sup>a</sup> pK<sub>a</sub> is reported for 20 °C; all other values are reported for 25 °C.

treatment plant effluents and runoff from urban roads and airports (Giger et al., 2006; Heeb et al., 2012; Janna et al., 2011; Parajulee et al., 2017; Voutsas et al., 2006). Due to its presence in urban stormwater runoff, bioretention cells collecting benzotriazole-containing runoff might be able to act as a sink for benzotriazole contamination. Bioretention cells are low impact development practices designed to manage peak flooding caused by urbanization while simultaneously improving water quality via physical, biological, and chemical processes (Davis, 2007; Davis and McCuen, 2005; Hsieh and Davis, 2005). Bioretention cells typically include vegetation, an engineered sandy-soil media, and a layer of hardwood mulch to allow evapotranspiration and infiltration of urban stormwater runoff. Bioretention cells have proven effective at reducing metal, nitrogen, phosphorus, and hydrocarbon contamination (Davis et al., 2006, 2003, 2001; Hong et al., 2006); however, little research has been conducted to date on the removal of polar trace organic compounds or the effects of cold-climate temperatures and salinity levels on pollutant removal (Kratky et al., 2017; LeFevre et al., 2015b).

Benzotriazole reduction from water through urban green infrastructure has been previously studied in soil filters and constructed wetlands (Felis et al., 2016; Matamoros et al., 2017, 2016, 2010; Stachel et al., 2010). To our knowledge, this is the first study to evaluate a potentially major removal mechanism of benzotriazole in bioretention cells, adsorption, and its counter mechanisms, desorption. The objectives of this research were (i) to quantify the adsorption and desorption potentials of benzotriazole to bioretention cell soil and mulch, and (ii) to investigate the effects of environmental factors temperature and salinity on benzotriazole adsorption and desorption.

## 2. Materials and methods

### 2.1. Site description

The bioretention cell site is located at the Kortright Centre for Conservation in Vaughan, Ontario, Canada (43° 49' 50.0304" N 79° 35' 24.09" W) and was installed in 2012. The inlet of the bioretention cell consists of a layer of river stones (2 m<sup>2</sup>, 0.2 m deep) above a layer of geotextile material (Terrafix® 270R). A drainage area of 265 m<sup>2</sup> consisting of non-permeable composite brick pavers of recycled tire-

derived rubber (Eco-flex® Churchill) discharges runoff through the inlet and into the 30-m<sup>2</sup> infiltration area of the bioretention cell. The bioretention cell includes 7.5 cm of hardwood mulch layered above 40 cm of bioretention soil. These are placed above a 15-cm clear stone gravel (20 mm) water reservoir wrapped with geotextile. The bioretention cell has no liner. Perforated drainage pipes (10 cm diameter) with anti-seepage collars are located above the geotextile. Effluent from the bioretention cell drains into a monitoring hut to be collected for water quality testing.

### 2.2. Substrates

Two substrates were used in the experiments: bioretention soil and hardwood mulch. Composite samples of both substrates were made by combining samples from multiple locations in the bioretention cell collected in December 2016 (4 locations), October 2017 (6 locations), and May 2018 (10 locations). Analysis was conducted for each new composite sample to ensure they were comparable (Appendix A). The hardwood mulch was removed from the top layer of the bioretention cell, and the soil was collected from the top 10 cm of the cell beneath the mulch. The hardwood mulch was air-dried, ground in a blender, and sieved to 2 mm. The mulch samples were stored at ambient temperature (22 ± 2 °C) until use. The soil (99% sand, 1% silt and clay) was wet-sieved to 2 mm, stored at 4 °C, and air-dried at ambient temperature prior to the adsorption and desorption experiments. Following OECD Guideline 106, storage did not exceed three months (OECD, 2000).

The bioretention soil and the hardwood mulch were analyzed by the University of Guelph Laboratory Services. Analysis of total carbon (TC), total inorganic carbon (TIC), total organic carbon (TOC), and total nitrogen (TN) was completed on both substrates using a vario MACRO cube (Elementar, Langensfeld, Germany). The samples were baked to ash at 475 °C for 3 h and then catalytically combusted at 950 °C. Desired compounds were isolated through gas separation and analyzed using thermal conductivity detection. The TOC was calculated as the difference between TC and TIC (Nelson and Sommers, 1982). To calculate the cation exchange capacity (CEC), the exchange sites of each sample were saturated with the barium cation (Ba<sup>2+</sup>) and then with the ammonium cation (NH<sub>4</sub><sup>+</sup>) to measure the amount of Ba<sup>2+</sup> displaced from the substrate (Rhoades, 1982). The organic matter content was measured through loss of ignition following ASTM D2974-14 (ASTM, 2014). Finally, the pH was measured in 0.01 M CaCl<sub>2</sub> following ISO Standard 10390 (ISO, 2005). The physical chemical properties of the substrates are summarized in Table 2.

### 2.3. Chemicals

Benzotriazole (C<sub>6</sub>H<sub>5</sub>N<sub>3</sub>, purity ≥ 98.0%) and calcium chloride dihydrate (CaCl<sub>2</sub>·2H<sub>2</sub>O, ≥ 99.0%) were purchased from Sigma-Aldrich (Milwaukee, USA). Biotechnology grade sodium chloride (NaCl, ≥ 99.5%) was purchased from BioShop (Burlington, Canada). Methanol (CH<sub>3</sub>OH, ≥ 99.9%), HPLC grade, was obtained from Fisher Scientific (Whitby, Canada). Milli-Q water (resistivity of 18.2 MΩcm) was obtained using a Millipore ultra-pure water system with a QPAK 1 Purification Cartridge (Etobicoke, Canada).

**Table 2**  
Substrate characterization.

Substrate	pH	Total carbon (%)	Total inorganic carbon (%)	Total organic carbon (%)	Total nitrogen (%)	Cation exchange capacity (cmol/kg)	Organic matter content (%)
Bioretention soil	7.2 ± 0.1	11	1.9	9.1	0.6	38	13 ± 1
Hardwood mulch	5.7 ± 0.2	46	0.1	46	0.3	9.7	92 ± 4

#### 2.4. Batch adsorption and desorption experiments

Batch adsorption and desorption isotherm experiments were conducted in triplicate as per OECD Guideline 106 (OECD, 2000). In polypropylene centrifuge tubes, 2 g (dry weight) of soil or mulch were placed in contact with 9 mL or 36 mL of 0.01 M CaCl<sub>2</sub>, respectively. The tubes were pre-equilibrated for 16 h by shaking on a wrist-action shaker. Triplicate tubes were then spiked with a benzotriazole solution in 0.01 M CaCl<sub>2</sub> to reach initial concentrations of 2.5, 5, 10, 25, or 50 mg/L. This concentration range was selected based on the instrument limit of detection of 10 µg/L and to ensure that all samples remained above the limit of quantification of 100 µg/L throughout all experimental steps. Benzotriazole concentrations in urban runoff from non-point sources are typically lower than this range of concentrations (Heeb et al., 2012; Parajulee et al., 2017). However, peak concentrations in the low mg/L range have been observed particularly in airport facilities (Breedveld et al., 2003; Cancilla et al., 2003, 1998) whose effluents are subject to strict regulations and are often treated with green infrastructures (Castro et al., 2005; Murphy et al., 2015; Revitt et al., 2001). Therefore, the selected concentration range is appropriate to investigate the fate of benzotriazole in bioretention cells when present in high concentrations in the field, and it enables the extrapolation of the results obtained, with caution, to lower concentration levels as discussed below. The solid:liquid ratios for the soil and the mulch were 1:5 and 1:20 (g:mL), respectively (Appendix B). These different ratios were selected to ensure that the substrate's organic carbon (OC) content to solution volume ratio was similar for both substrates, at 0.018 g/mL for the soil and 0.023 g/mL for the mulch. After spiking, the tubes were shaken for 24 h to reach adsorption equilibrium, as confirmed through preliminary kinetic experiments (Appendix C). At adsorption equilibrium, the tubes were centrifuged at 5000 rpm; soil samples were centrifuged for 5 min, and mulch samples for 10 min. After centrifugation, the supernatant was decanted, filtered through a 0.22-µm nylon filter, and analyzed by high performance liquid chromatography with diode array detection (HPLC/DAD).

Three consecutive desorption steps were conducted following adsorption equilibrium. These experiments consisted of adding benzotriazole-free 0.01 M CaCl<sub>2</sub> solution to the samples and shaking for 24 h. The samples were then centrifuged, decanted, and analyzed by HPLC/DAD to determine the amount of benzotriazole desorbed from the substrate. All tubes were covered in aluminum foil for the duration of the experiments to minimize photolysis. Blanks with no benzotriazole and controls with no substrate were conducted in triplicate to verify the absence of benzotriazole contamination or loss during the experiments (Appendix D).

The adsorption and desorption isotherm experiments were conducted at 4, 10, 22, and 32 °C. Adsorption and desorption isotherms were also obtained with the addition of sodium chloride (NaCl) at both 4 and 10 °C. The salt concentrations selected were 0.8 and 3 g/L. The 0.8 g/L NaCl concentration was selected by estimating an average stormwater runoff salt concentration based on a typical parking lot road salt application rate in Ontario of 2 kg/100 m<sup>2</sup> and an average runoff event size of 2.54 cm (see details in Appendix E). The highest salt concentration, at 3 g/L, was taken as approximately four times the estimated average value to simulate a salt concentration peak in urban stormwater runoff. These values are within the range of those measured in the field (Environment Canada, 2001).

In all experiments, the pH of the supernatant solution was measured at each adsorption and desorption equilibrium step. All samples varied in pH between 5.1 and 7.7; in this range, more than 90% of benzotriazole in solution is expected to be in the neutral form (Bi et al., 2006; Jia et al., 2007; Wu et al., 2009). Therefore, pH was not expected to have a large effect on benzotriazole adsorption and desorption.

The adsorption isotherms were modeled using the linear and Freundlich models as described by Eqs. (1) and (2), respectively:

$$Q_{e,ads} = K_d C_e; \quad (1)$$

where  $Q_{e,ads}$  is the equilibrium concentration of benzotriazole adsorbed on the substrate (mg/g),  $K_d$  is the linear adsorption coefficient (mL/g), and  $C_e$  is the concentration of benzotriazole in the supernatant at equilibrium (mg/mL).

$$Q_{e,ads} = K_{f,ads} C_e^{n_{f,ads}}; \quad (2)$$

where  $K_{f,ads}$  and  $n_{f,ads}$  are the Freundlich adsorption coefficient (mL<sup>n<sub>f,ads</sub></sup>mg<sup>1-n<sub>f,ads</sub></sup>/g) and the adsorption regression constant, respectively. The isotherms can be considered linear when the value of  $n_{f,ads}$  falls between 0.95 and 1.05 (Calvet et al., 2005).

Normalized adsorption coefficients were determined by dividing the linear or Freundlich adsorption coefficients by the fraction of organic carbon in the substrate ( $f_{OC}$ , g/g).

$$K_{OC} = \frac{K_d}{f_{OC}} \quad (3)$$

$$K_{f,OC} = \frac{K_{f,ads}}{f_{OC}} \quad (4)$$

Desorption isotherms were described by the amount of variation from the adsorption isotherm. This is referred to as desorption hysteresis. Hysteresis may be due to some amount of the contaminant that is resistant to desorption, or to slow diffusion through constricted pore networks (Fu et al., 1994; Hunter et al., 1996). Desorption hysteresis is defined by the hysteresis coefficient ( $H$ , %), which is calculated by dividing the desorption regression constant ( $n_{f,des}$ ) by the adsorption regression constant as follows:

$$H = \frac{n_{f,des}}{n_{f,ads}} \times 100 \quad (5)$$

Larger values of  $H$  refer to larger percentages of desorption. When  $H$  approaches 100%, adsorption is fully reversible, and there is no apparent hysteresis.

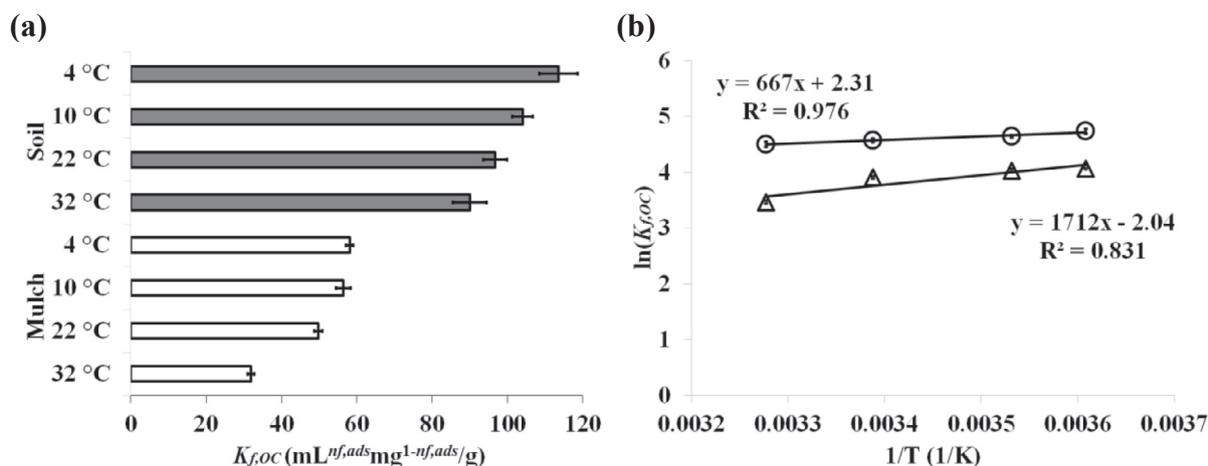
#### 2.5. HPLC/DAD analysis

All samples were analyzed using HPLC/DAD (Thermo Scientific UltiMate 3000). The HPLC was equipped with a pump (LPG-3400SD), autosampler (WPS-3000SL), oven (TCC-3000SD), and diode array detector (DAD-3000). The HPLC was fitted with an Accucore C18 column and guard column (100 × 2.1 mm, 2.6 µm packing). Benzotriazole was analyzed by isocratic elution with a mobile phase of Milli-Q water and methanol (70:30 v/v). The flow rate was 0.1 mL/min, and the oven was maintained at a constant temperature of 30 °C. Samples were injected in volumes of 50 µL, and benzotriazole was detected at a wavelength of 275 nm. The retention time was approximately 6 min. The limits of detection (LOD) and quantification (LOQ) for benzotriazole were 10 and 100 µg/L, respectively.

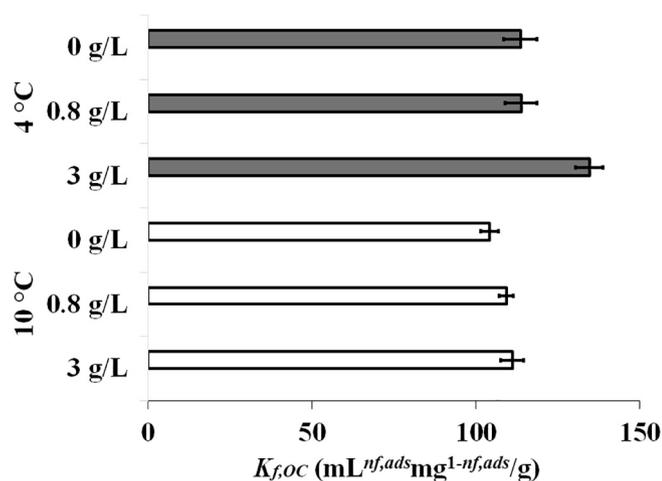
### 3. Results

#### 3.1. Temperature effects on benzotriazole adsorption to bioretention soil and hardwood mulch

Adsorption of benzotriazole to bioretention soil and hardwood mulch was well described using Freundlich adsorption isotherms. All adsorption data are presented in Fig. 1 and Appendix F. Both substrates showed nonlinear adsorption over the concentration range studied, with  $n_{f,ads}$  values ranging from 0.74 ± 0.02 to 0.78 ± 0.02 for soil and 0.84 ± 0.01 to 0.97 ± 0.01 for mulch with varying temperature. Because adsorption was nonlinear, the Freundlich adsorption coefficients normalized to the organic carbon fraction, i.e.  $K_{f,OC}$ , were compared. Note that the unit of  $K_{f,OC}$ , i.e. mL<sup>n<sub>f,ads</sub></sup>mg<sup>1-n<sub>f,ads</sub></sup>/g, depends on the value of  $n_{f,ads}$ . Comparison of  $K_{f,OC}$  values should therefore be done with



**Fig. 1.** (a) Freundlich adsorption coefficients normalized to the organic carbon fraction ( $K_{f,OC}$ , mL<sup>nf,ads</sup>mg<sup>1-nf,ads</sup>/g) at multiple temperatures for bioretention soil and hardwood mulch. The error bars represent the compounded uncertainty on  $K_{f,OC}$  (see Appendix F). (b) Enthalpies of reaction calculated from the slope of the linear regression for both the soil (open circles) and the mulch (open triangles) based on changes in the Freundlich adsorption coefficient ( $K_{f,OC}$ ) with temperature. The error bars represent the uncertainty on  $\ln(K_{f,OC})$  and are smaller than symbol size.



**Fig. 2.** Freundlich adsorption coefficients normalized to the organic carbon fraction ( $K_{f,OC}$ , mL<sup>nf,ads</sup>mg<sup>1-nf,ads</sup>/g) for bioretention soil with varying levels of NaCl. The error bars represent the compounded uncertainty on  $K_{f,OC}$  (see Appendix F).

caution; however, as noted above, the  $n_{f,ads}$  values for each substrate showed little variation with temperature, particularly for the soil. As a result, the  $K_{f,OC}$  values can be reasonably compared within each substrate, whereas only the  $K_d$  and  $K_{OC}$  values obtained for a given initial concentration of benzotriazole can be used to compare the adsorption capacity of the soil to that of the mulch. Results from all experiments, including all adsorption coefficients and regression constants, were compiled from sample sizes of three; as a result, no meaningful statistical analysis could be done to evaluate these values beyond comparison of their error bars corresponding to one standard deviation.

Adsorption coefficients for both substrates increased with decreasing temperature (Fig. 1a). For a given initial concentration of benzotriazole, linear adsorption coefficients were compared. The  $K_d$  values of the mulch were much higher than those for the soil (Table F.2 in Appendix F) due to the higher TOC content of the mulch, at 46%, than of the soil, at 9.1% (Table 2). Conversely, the  $K_{OC}$  values for the mulch were lower than those for the soil, suggesting that the functional groups in the soil organic matter were more favourable for benzotriazole adsorption than those in the mulch organic matter. In all experiments, the linear adsorption coefficients were the highest at the lowest initial concentrations of benzotriazole (Table F.2 in Appendix F).

The enthalpies of reaction ( $\Delta H_r$ ) for the adsorption of benzotriazole to the soil and the mulch were calculated based on the Freundlich adsorption coefficients,  $K_{f,OC}$ , obtained across the range of temperatures studied (Appendix G and Fig. 1b). The enthalpies of reaction for the soil and the mulch were low, at  $-5.6$  and  $-14$  kJ/mol, respectively, suggesting that benzotriazole adsorption to bioretention soil was dominated by van der Waals forces, while adsorption to mulch was dominated by dipole-dipole interactions (von Oepen et al., 1991). Stronger bonding types would be expected to dominate when  $\Delta H_r$  values are more negative, i.e. when the absolute values of  $\Delta H_r$  are larger. In all experiments, adsorption of benzotriazole to both substrates was exothermic.

### 3.2. Salinity effects on benzotriazole adsorption to bioretention soil

Sodium chloride was used to simulate the effect of road salt on benzotriazole adsorption to bioretention soil, particularly at lower temperatures when road salt would be used for de-icing activities in colder climates. The addition of NaCl appeared to slightly alter the linearity of benzotriazole adsorption. The regression slope,  $n_{f,ads}$ , increased from  $0.74 \pm 0.02$  to  $0.79 \pm 0.02$  with the addition of salt at  $4$  °C and from  $0.77 \pm 0.01$  to  $0.82 \pm 0.02$  at  $10$  °C. Increased NaCl concentrations also slightly increased the values of  $K_{f,OC}$  from  $114 \pm 5$  mL<sup>0.74</sup>mg<sup>1-0.74</sup>/g to  $135 \pm 4$  mL<sup>0.78</sup>mg<sup>1-0.78</sup>/g at  $4$  °C, and  $104 \pm 3$  mL<sup>0.77</sup>mg<sup>1-0.77</sup>/g to  $111 \pm 4$  mL<sup>0.82</sup>mg<sup>1-0.82</sup>/g at  $10$  °C (Fig. 2).

### 3.3. Desorption hysteresis as a function of concentration, temperature, and salinity

The hysteresis coefficient,  $H$ , consistently increased with increasing benzotriazole concentration under all experimental conditions (Fig. 3 and Appendix F). The hysteresis coefficient also increased as temperature decreased, nearing completely reversible adsorption for soil at the highest initial concentration of  $50$  mg/L at  $4$  °C (Fig. 3a); however, the  $H$  values at the lowest concentration of benzotriazole were consistently below 50% for all temperatures studied. For the lowest concentrations of benzotriazole, the mulch showed higher  $H$  values than the soil.

The addition of NaCl resulted in a slight increase in hysteresis coefficient at the lowest initial concentration of benzotriazole, but a slight decrease at the highest concentration. For example, the  $H$  values for the  $2.5$  mg/L initial benzotriazole concentration were  $38 \pm 3\%$  ( $4$  °C) and  $34 \pm 2\%$  ( $10$  °C) for  $0$  g/L of NaCl and increased to

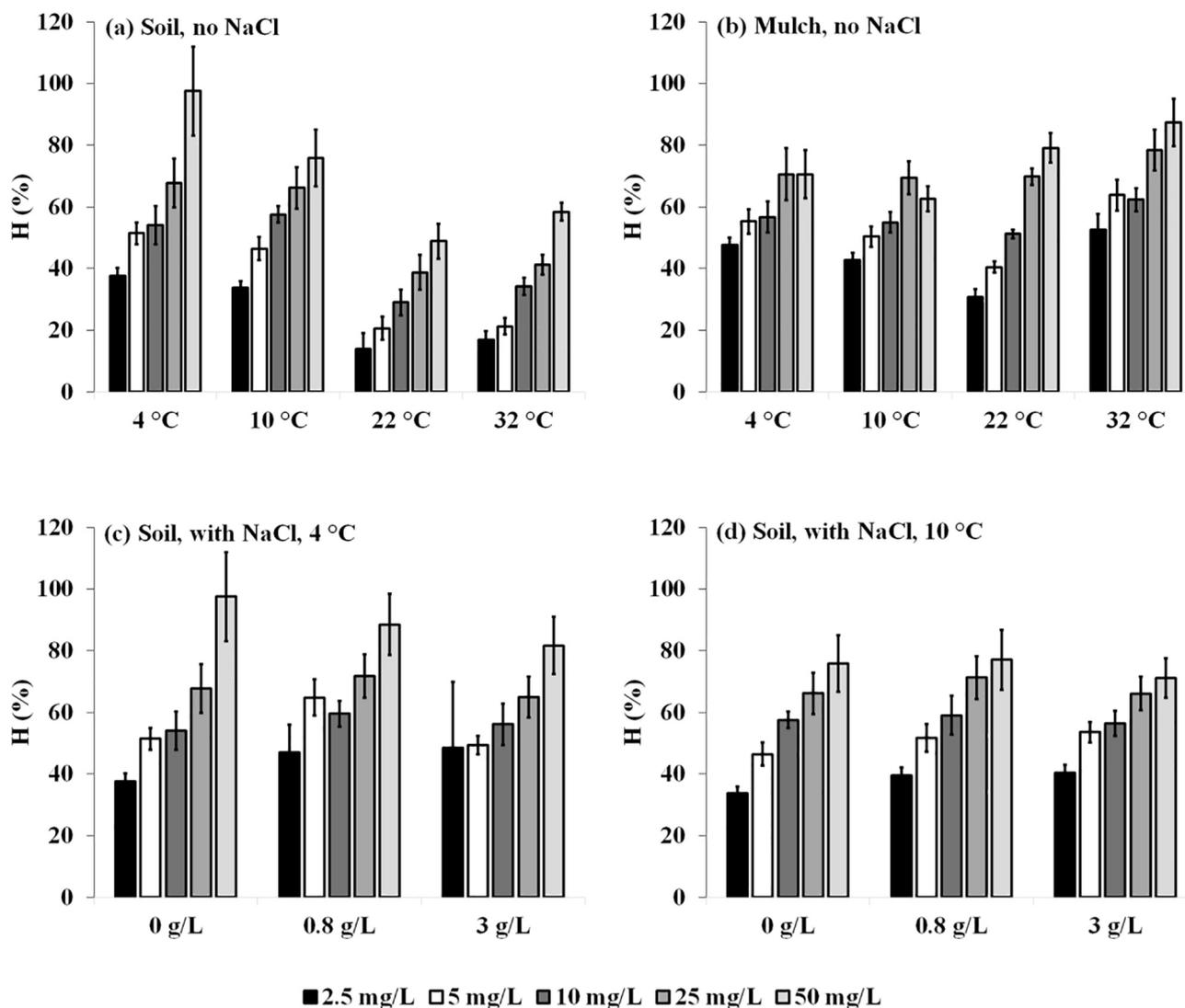


Fig. 3. Hysteresis coefficients for all benzotriazole concentrations in each desorption experiment: (a) soil desorption with temperature, (b) mulch desorption with temperature, (c) soil desorption with NaCl at 4 °C, and (d) soil desorption with NaCl at 10 °C. The error bars represent the compounded uncertainty on  $H$  (see Appendix F).

$49 \pm 21\%$  (4 °C) and  $41 \pm 3\%$  (10 °C) for 3 g/L of NaCl. Conversely, the  $H$  values for the 50 mg/L initial benzotriazole concentration were  $98 \pm 14\%$  (4 °C) and  $76 \pm 9\%$  (10 °C) for 0 g/L of NaCl and decreased to  $82\% \pm 9$  (4 °C) and  $71 \pm 6\%$  (10 °C) for 3 g/L of NaCl. The  $H$  values remained within error between 0.8 and 3 g/L NaCl concentrations.

## 4. Discussion

### 4.1. Adsorption of benzotriazole to bioretention cell substrates

Differences in  $K_d$  and  $K_{OC}$  between the two substrates at given initial concentrations of benzotriazole can be attributed to the amount and composition of the organic matter in the soil and the mulch. The  $K_d$  values were consistently higher for the mulch than the soil, which was due to the higher OC content of the mulch than the soil (Table 2). This is consistent with the literature, as organic matter is known to have a high affinity for many organic pollutants. For benzotriazole in particular, the highest  $K_d$  adsorption coefficients,  $> 6.0$  mL/g, have been found for soils with high OC contents,  $> 11\%$  (Hart et al., 2004; Yu et al., 2009). Indeed, the higher  $K_d$  values for the mulch than the soil were expected as mulch is known to provide a large amount of organic matter in bioretention cells (Hsieh and Davis, 2005). However, the

normalized  $K_{OC}$  values were consistently higher for the soil than the mulch, which suggests that benzotriazole adsorbs to organic matter components that are more abundant in the soil than in the mulch.

Lignin is one of the main components of hardwood mulch, often forming 23–30% of the wood mass (Boyer et al., 2018; Thompson, 1996), while soil has a larger proportion of protein (Boyer et al., 2018). Hong et al. (2006) found that lignin in the mulch layer of bioretention cells was a good trap for hydrocarbons due to its high adsorption affinity for non-ionic organic compounds; however, results of the current study suggest that adsorption of polar compounds such as benzotriazole to lignin is not strong. The bioretention soil had a larger cation exchange capacity (CEC) than the mulch (Table 2) which implies that the organic matter in the soil contained more polar functional groups such as carboxy-, phenoxy-, and hydroxyl-groups known for contributing to CEC (Broadbent and Bradford, 1952; Schwarzenbach et al., 2003); whereas, lignin is known to lack these carboxy-groups (Garbarini and Lion, 1986). The results of this study are similar to those of Breedveld et al. (2003) who found that adsorption coefficients of benzotriazole were the highest for substrates with the largest OC values. The results of these authors also showed that the adsorption coefficients normalized to the OC content were the highest for substrates with the largest CEC values (Breedveld et al., 2003). As mentioned, however, benzotriazole

is predominantly in its neutral form in these experiments, therefore bonds between benzotriazole and charged functional groups are expected to be weak, as confirmed by the low enthalpies of reaction calculated (Jia et al., 2007).

Previous work by Bi et al. (2007, 2006) suggested cation bridging with  $\text{Ca}^{2+}$  in solution as a possible adsorption mechanism for neutral benzotriazole. They postulated that benzotriazole could form complexes with both surface-bound  $\text{Ca}^{2+}$  cations as well as  $\text{Ca}^{2+}$  in solution to form cationic complexes capable of binding with anionic adsorption sites on the solid surface (Bi et al., 2007). These interactions are thought to occur between the cation and the pi-electron system of the nitrogen-heterocyclic group in benzotriazole (Bi et al., 2006). In this case, these complexes could then bind to the anionic carboxy- and phenoxy-groups dominant in the soil structure. Cation-pi interactions are noncovalent bonds that are expected to be stronger than hydrogen bonds (Chatterjee et al., 2001), therefore it is expected that this type of bonding would yield more negative values of  $\Delta H_r$  than those calculated in this study. Such strong bonds would also be inconsistent with the amount of desorption observed in these experiments. Furthermore, Chatterjee et al. (2001) found that nitrogen-heterocyclic compounds with localized lone-pairs of electrons, similar in structure to benzotriazole, are more likely to form hydrogen bonds than cation-pi interactions. Therefore, it is unlikely that cation bridging played a significant role in the adsorption of benzotriazole in these experiments.

#### 4.2. Adsorption of benzotriazole in cold climate conditions

The  $K_{f,OC}$  values increased with decreasing temperature, which is consistent with results from past studies for several compounds including benzotriazole (Bi et al., 2007), polycyclic aromatic hydrocarbons (Tremblay et al., 2005), and metals (Paus et al., 2014; Søbberg et al., 2014). This increase in adsorption with decreasing temperature is due to a decrease in solubility with temperature, causing more benzotriazole to adsorb to the substrates (Schwarzenbach et al., 2003). Decrease in solubility with temperature is often small between 0 and 80 °C (Schwarzenbach et al., 2003), which explains why the changes in adsorption were small. Results of kinetics experiments at 4 and 22 °C confirmed that changes in temperature had no effect on adsorption equilibrium (Appendix C).

Similar to the effect of temperature on adsorption, the slight increase in  $K_{f,OC}$  values with the addition of NaCl is due to a change in compound solubility (Schwarzenbach et al., 2003). This effect is also consistent with past studies on both organic and inorganic compounds (Bi et al., 2007; Søbberg et al., 2014; Tremblay et al., 2005). The presence of dissolved salts causes a decrease in solubility of nonpolar or weakly polar organic compounds known as the salting-out effect (Schwarzenbach et al., 2003). The salting-out effect is expected to increase exponentially as salt concentration increases (Schwarzenbach et al., 2003); however, this was not observed in this study over the range of NaCl concentrations studied as changes in adsorption with NaCl were quite small. Benzotriazole is a polar molecule, polarized by 3 lone-pairs of electrons in the nitrogen-heterocyclic ring (Hart et al., 2004). This high polarity likely hindered the expression of a large salting-out effect on benzotriazole adsorption.

#### 4.3. Mobility of benzotriazole in the environment

The enthalpy of reaction of  $-5.6$  kJ/mol for the soil suggests that benzotriazole adsorption was dominated by van der Waals forces, which occur when the enthalpy changes between  $-4$  and  $-8$  kJ/mol (von Oepen et al., 1991). Comparatively, the enthalpy of reaction for mulch, at  $-14$  kJ/mol, falls within the range of dipole-dipole interactions, which dominate when  $\Delta H_r$  is between  $-2$  and  $-29$  kJ/mol (von Oepen et al., 1991). While there is overlap in the  $\Delta H_r$  ranges for van der Waals forces and dipole-dipole interactions, the results suggest that benzotriazole adsorbs to both substrates through weak bonds, which is

consistent with the large desorption hysteresis coefficients observed. More negative values of  $\Delta H_r$  would have suggested non-reversible adsorption, e.g., chemisorption, which dominates when  $\Delta H_r$  is between  $-60$  and  $-80$  kJ/mol (von Oepen et al., 1991).

The largest desorption observed for the highest benzotriazole concentrations suggests that the bioretention substrates had limited ability to permanently retain benzotriazole. In addition, the  $n_{f,ads}$  values for all experiments were less than 1, indicating that adsorption decreased with increasing concentration (Schwarzenbach et al., 2003). These adsorption and desorption results are two separate lines of evidence that benzotriazole bound to the surface with increasingly weaker free energies as its concentration increased. Lower desorption was observed for lower initial concentrations of benzotriazole as energetically-favoured adsorption sites were filled first (Bi et al., 2007; Kan et al., 1998; Schwarzenbach et al., 2003). As the initial concentration of benzotriazole increased, less energetically-favoured adsorption sites began to fill. Adsorption to these sites occurred with weaker free energies, thus favouring desorption.

Temperature and salinity were not expected to have a considerable effect on desorption, as limited desorption would be expected due to decreases in compound solubility. In order to evaluate these potential impacts, the percent of benzotriazole desorbed for a given set of conditions was compared for each of the three desorption steps (Appendix F). For the highest concentrations of benzotriazole, the percent desorbed in the three desorption steps was constant, yet this value decreased for lower concentrations of benzotriazole. In most cases, the percent desorbed in the third desorption step for the 2.5 mg/L samples was half of the percent desorbed in the first step. For example, the experiment on soil at 4 °C showed a change in percent desorbed from  $21 \pm 1\%$  (desorption step 1) to  $11 \pm 2\%$  (desorption step 3) for the 2.5 mg/L sample. Conversely, the 50 mg/L sample showed no change from  $40 \pm 1\%$  (desorption step 1) to  $40 \pm 2\%$  (desorption step 3). These results suggest that more than three desorption steps were needed for the desorption percent to stabilize and to obtain more accurate estimates of the amount of benzotriazole that irreversibly adsorbed to the bioretention substrates.

## 5. Conclusions

The physical and chemical properties of soil and mulch may vary from one bioretention site to another. However, it is important to note that bioretention cell soils must meet regional requirements in grain size distribution and organic matter content before being approved for installation. As a result, despite caution should be exerted to avoid over-generalizing the results of this study, they are appropriate indicators for the general adsorption and desorption behavior of benzotriazole in bioretention cells. These findings are important for understanding the fate of polar trace organic contaminants in bioretention cells in cold climates. The results of this study showed that the effects of cold-climate conditions, i.e. lower temperatures and use of de-icing road salts, did not negatively impact bioretention cell retention for benzotriazole. Indeed, benzotriazole adsorption increased under these conditions, suggesting that bioretention cells are able to manage the increased environmental concentrations of benzotriazole in cold seasons. While the results of these batch experiments enable characterization of the fundamental mechanisms governing benzotriazole adsorption and desorption on bioretention soil, further research is needed to evaluate the adsorption and desorption behavior of benzotriazole under intermittent flow conditions, e.g., using column experiments. The generally low to moderate  $K_{f,OC}$  values determined in this study showed that benzotriazole is expected to be mobile to moderately mobile in bioretention cells. These results are specific to the concentration range studied which is at the higher end of typical field concentrations of benzotriazole. However, linear adsorption coefficients were the highest for the lowest initial concentrations of benzotriazole, and extrapolation of these results to lower field-relevant concentrations, which should be

done with caution, suggests that benzotriazole can moderately adsorb on bioretention soil and mulch at low temperature and high salinity levels characteristics of cold climate conditions. Further study is needed to estimate benzotriazole adsorption and desorption coefficients at lower concentrations and evaluate the full potential for its desorption, e.g., during spring and summer conditions.

As done for enhanced phosphorus removal with aluminium-based water treatment residuals (Lucas and Greenway, 2011; O'Neill and Davis, 2012; Yan et al., 2016), red mud (Lucas and Greenway, 2011), and fly ash (Zhang et al., 2008), additives could be incorporated into bioretention soil media to support stronger retention of benzotriazole. For example, Jia et al. (2007) found that zerovalent iron and ferrihydrite had high adsorption affinities for benzotriazole, suggesting that these could be added to bioretention soil to enhance benzotriazole retention. Alternative additives include biochar, which Ulrich et al. (2015) found could retain benzotriazole in biochar-amended sand columns. Biochar amendments to vegetated columns of bioretention media also showed excellent removal (> 99%) of 5-methyl-1H-benzotriazole, an isomer of tolyltriazole (Ulrich et al., 2017a); however, specific removal mechanisms were not identified. In an additional study, Ulrich et al. (2017b) found that added dissolved organic carbon from straw or compost increased biodegradation of benzotriazole in aqueous microcosms, indicating that the addition of organic material to bioretention soils could accelerate its microbial degradation. Other removal mechanisms have also proved effective for benzotriazole at low concentrations (Castro et al., 2005, 2004, 2003; LeFevre et al., 2015a). For example, LeFevre et al. (2015a) observed that more than 99% of benzotriazole was irreversibly taken up by *Arabidopsis* plants in hydroponic systems. Similarly, Castro et al. (2004) found that increasing the temperature and aeration of a hydroponic solution yielded higher rates of benzotriazole plant uptake. Further research on benzotriazole remediation in bioretention cells should investigate the relative contribution of these transfer and transformation mechanisms using typical bioretention cell plants and soil amendments.

Benzotriazole has been shown to degrade under photolysis at pH between 5 and 9 (Borowska et al., 2016; Janssen et al., 2015), the same range as that observed in the current study. Photolysis is not relevant in properly functioning bioretention cells; however, other urban green infrastructures, e.g. constructed wetlands, may prove more effective at supporting benzotriazole photolysis, which should be investigated further.

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## Supplementary data

Supplementary data to this article containing Appendices A to G can be found online at <https://doi.org/10.1016/j.ecoleng.2018.11.016>.

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