TREATMENT OF HEAVY METALS USING AN ORGANIC SULFATE REDUCING PRB

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ABSTRACT: A pilot-scale permeable reactive wall consisting of a leaf-rich compost-pea gravel mixture was installed at a site in the Vancouver area, Canada to evaluate its potential use for treatment of a large dissolved heavy metal plume. The compost based permeable reactive wall promotes microbially mediated sulfate reducing conditions such that dissolved metals are precipitated out as metal sulfides. The pilot-scale wall, measuring 10 m in length, 5.9 m in depth, and 2-2.5 m in width, has demonstrated good effectiveness in removing dissolved copper, cadmium, zinc, and nickel from ground water at the site over a 21-month period since installation. Performance has been particularly strong within the lower half of the wall where tidal influences are more limited and sulfate-reducing conditions are more easily maintained. Dissolved copper concentrations decrease from concentrations of over 4500 µg/L in the influent ground water to less than 10 µg/L within the lower half of the wall. Zinc, cadmium, and nickel concentrations decrease from average concentrations of over 2300 µg/L, 15 µg/L, and 115 µg/L, respectively to concentrations of less than 30 µg/L, 0.2 µg/L, and 10 µg/L, respectively within the lower half of the wall. The activity of sulfate reducing bacteria is evidenced by a significant increase in sulfide concentrations within the wall.
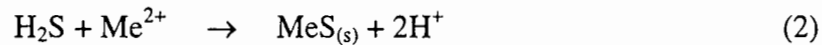
INTRODUCTION

As the number of successful permeable reactive barrier (PRB) installations at contaminated sites continues to increase, permeable reactive barrier technology is gradually being accepted as a viable alternative to conventional pump and treat. Much of the focus and field success to date has involved the use of zero valent iron-based permeable reactive barriers to treat chlorinated hydrocarbons such as the chlorinated ethenes. With the exception of chromium, limited work to date has focused on the use of permeable reactive barriers for treatment of heavy metals. This paper presents results from an organic-based sulfate reducing pilot-scale permeable reactive barrier installed at an industrial site in British Columbia to treat heavy metals associated with acid rock drainage.

The concept of using organic-based systems to treat acid rock drainage is not new. Engineered wetland systems have been used to treat acid rock drainage impacted surface water runoff at mining sites for many years. The use of organic-based permeable reactive barrier systems for treatment of acid rock drainage impacted ground water was first proposed in 1990 (Blowes, 1990). The first full-scale application of an organic-based sulfate-reducing permeable reactive barrier

for treatment of acid rock drainage was at the Nickel Rim site near Sudbury, Ontario in 1995 (Benner et al., 1997). Organic-based systems rely primarily on the microbially mediated conversion of sulfates to sulfides by sulfate-reducing bacteria residing in the organic media. The simplified reaction involving reduction of sulfate and oxidation of a typical organic substrate such as lactate is given below.

$$3SO_4^{2-} + 2CH_3CHOHCOO^- + 2H^+ \rightarrow 3H_2S + 6HCO_3^- \qquad (1)$$
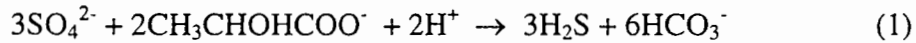
The reaction involves the production of both sulfide and bicarbonate. The bicarbonate produced plays an important role in regulating the pH environment of the sulfate-reducing bacteria. The sulfide produced is available to react with dissolved metals to form insoluble metal sulfides in accordance with the following reaction.

$$H_2S + Me^{2+} \rightarrow MeS_{(s)} + 2H^+ \qquad (2)$$

where Me^{2+} denotes a heavy metal such as Cd, Cu, Ni, Pb, Zn, etc. In order to ensure target metal removal from solution through the process of sulfate reduction, a sufficient quantity of sulfide must be produced to meet the demand of the heavy metal flux into the system. In a permeable reactive barrier application, under an ideal design scenario, the amount of sulfide produced would just equal the heavy metal flux into the wall. By avoiding excess production of sulfide, the organic media is not needlessly consumed and the lifetime of the wall is maximized.

Site Description. The test site is located in the Vancouver area, British Columbia and has been impacted by acid rock drainage as a result of historical ore concentrate handling and transfer practices occurring on site. The oxidation of sulfide minerals on site has resulted in the underlying ground water being extensively contaminated with heavy metals including dissolved cadmium (Cd), copper (Cu), nickel (Ni), and zinc (Zn). Copper in ground water at the site has been measured at some locations at concentrations exceeding 200,000 µg/L. Impacted ground water at the site discharges into a nearby marine inlet thus posing a potential threat to the shoreline ecosystem.

The geology at the test site is comprised primarily of deltaic deposits consisting of sands and gravel with some cobbles. The shallow aquifer, which is unconfined, begins at approximately 1 m below ground level (bgl) and extends to at least 20 mbgl. Hydraulic conductivities in the upper 15 m of the aquifer are in the 10^{-2} to 10^{-3} cm/sec range based on bail tests conducted (McGregor et al., 1999). The average hydraulic gradient has been calculated at 0.001 based on 71-hour water level averages. Metal contamination within the ground water is confined to the upper 15 m of the aquifer with the majority of the contamination being present in the upper 6 m.

MATERIALS AND METHODS

Reactive Mixture. Selected batch tests were conducted with leaf-rich compost (obtained from the City of Vancouver municipal composting facility) prior to wall installation to ensure the compost would support sulfate reduction. The final reactive mixture utilized in the wall consisted of 15% (by volume) leaf-rich compost, 84% pea gravel, and 1% limestone and was based on the results of previous laboratory and field studies (Benner et al., 1997; Waybrant et al., 1998). The large percentage of pea gravel was required to achieve a minimum desired hydraulic conductivity of 10^{-1} cm/sec within the wall. The limestone was added to ensure suitable initial pH conditions for the establishment of a sulfate reducing bacteria population within the wall. The compost, pea gravel, and limestone were thoroughly mixed by tossing and turning the materials in batches with a backhoe bucket. The mixing process for each batch was conducted until a visually-based homogeneous mixture of the components was obtained.

Pilot Wall Construction. The pilot wall was installed using cut and fill excavation methods approximately 50 m inland from the shoreline of the site to avoid ongoing construction activities along the inlet shoreline. As a result, the wall was installed in a location of known up-gradient and down-gradient soil and ground water contamination. The wall was constructed using a Komatsu Model 310 excavator to a depth of approximately 5.9 m and a length of 10 m. The width of the wall is approximately 2.5 m at surface, narrowing to 2 m width at the final depth. Excavation initially involved benching down approximately one meter to a depth just above the water table. A guar gum based slurry was used during trenching to prevent trench collapse and allow emplacement of the reactive media. The reactive media was placed into the trench using a Manotowc 4500 clam shell unit and Komatsu Model 310 excavator bucket.

A total of 17 multi-level wells were installed in and around the wall following construction as shown in Figure 1. Each multi-level well consisted of seven lengths of 1.27-cm internal diameter (ID) high density polyethylene tubing with nytex screen affixed to a 1.9 cm (ID) PVC Schedule 40 center stalk at seven discrete depths. This allowed for sampling of up to 119 sampling points at seven depths within, up-gradient, and down-gradient of the wall.

Wall Sampling. Six discrete sampling events occurred over an initial 21-month span following installation of the wall. The initial two sampling events covered all 17 multi-level wells. Sampling events thereafter were limited to a center-transect through the wall consisting of wells ML2, ML6, ML10, ML13 and ML16, as initial results indicated this transect was adequate to monitor wall performance. Sampling events consisted of ground water level measurements, and collection and analysis of ground water samples. Ground water samples were collected using a low-flow peristaltic pump with Teflon tubing and filtered through 0.45 µm cellulose acetate filters. Field measurements included pH, E_H (corrected to standard hydrogen electrode), temperature, conductivity, alkalinity, sulfide, and ferrous iron. Field measurement techniques and equipment including
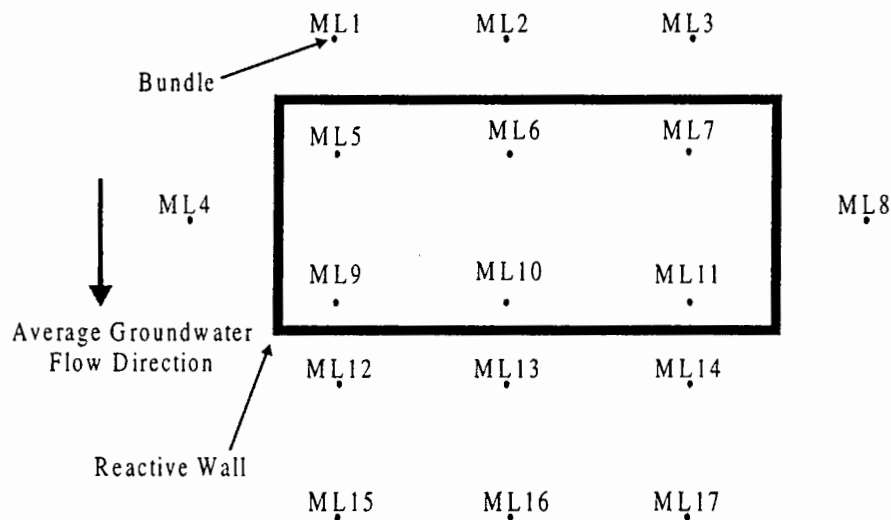
FIGURE 1. Location of monitoring bundles relative to the reactive wall (plan view).

QA/QC procedures employed are described in McGregor et al. (1999). Samples were analyzed for anions by ion chromatography and dissolved metals by ICP-OES and/or ICP-MS.

RESULTS AND DISCUSSION

Indicators of sulfate reduction within the pilot-scale wall 21 months after installation included an increase in dissolved sulfide concentrations, a decrease in the redox potential, and a decrease in metal concentrations relative to the influent ground water. Other indicators consistent with sulfate reduction included an increase in alkalinity and increase in pH although the dissolution of limestone within the reactive wall may have contributed significantly to these observed increases. Vertically averaged results for the center transect multi-level wells after a 21-month period are provided in Table 1. Metal concentration profiles through the center of the wall are shown in Figure 2. Figure 2 shows that treatment is generally greatest within the lower half of the wall where sulfate-reducing conditions are likely more easily maintained. The upper half of the wall shows poorer treatment presumably due to a greater susceptibility to influences from tidal fluctuations (i.e. wet/dry cycles and back flushing) and perhaps also oxygen intrusion from the surface. In addition, Figure 2 shows high concentrations of metals immediately down-gradient of the wall at shallow depths. This is attributed to the effects of recharge water from the surface that becomes laden with heavy metals as it infiltrates through the overlying sulfide impacted soils into the ground water on the down-gradient side of the wall.

As shown in Table 1, field measurements of pH and E_H at well ML2 indicate ground water entering the wall exhibits a relatively high redox potential (E_H of +430 mV), a pH of 6.36, and an alkalinity of 89 mg/L as $CaCO_3$. The ground water entering the pilot-scale wall is also characterized by high concentrations of copper, nickel, and zinc. As ground water passes through
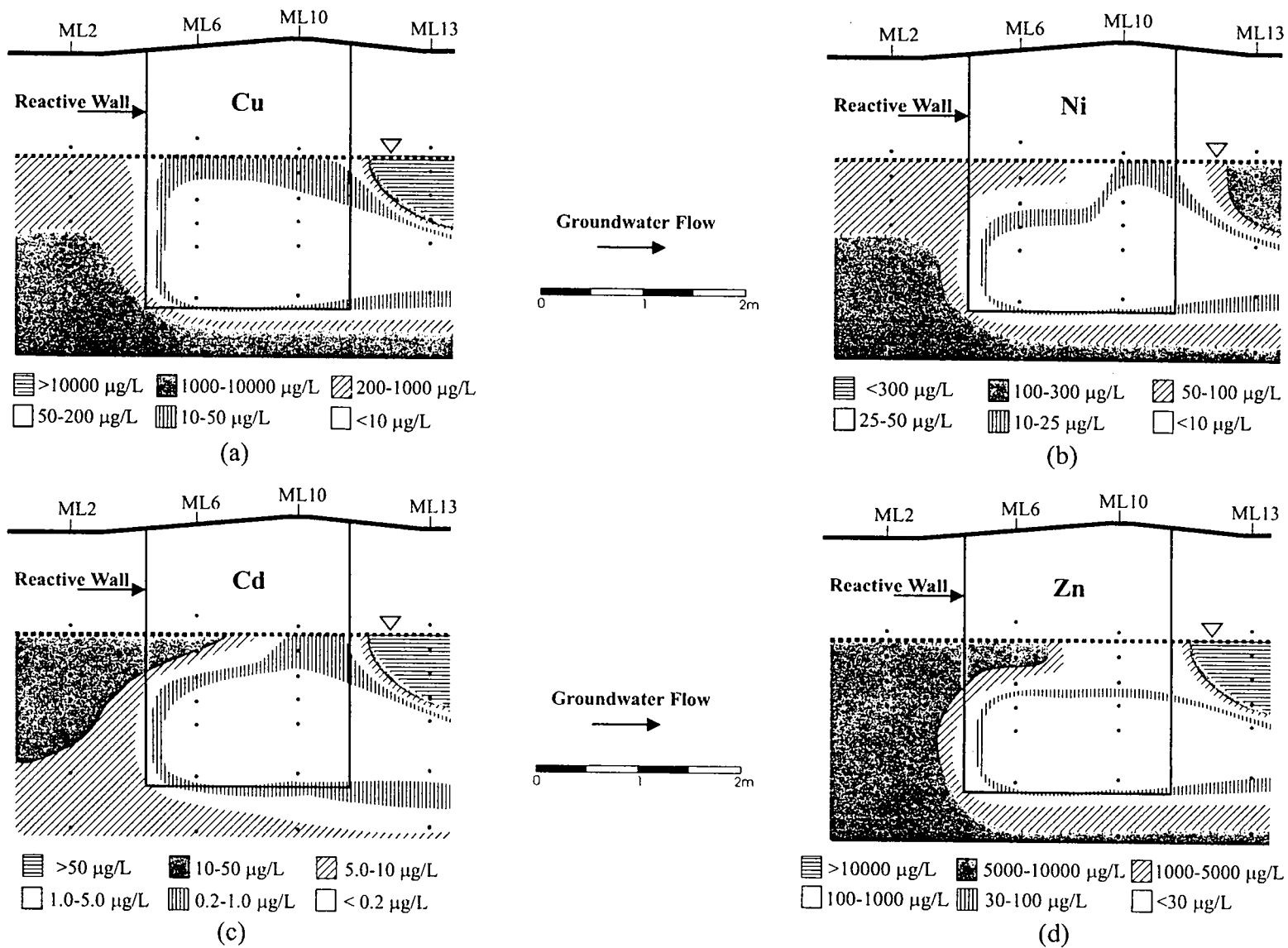
(a)

ML2 ML6 ML10 ML13

Reactive Wall Cu

▽

| ☰ >10000 µg/L | 1000-10000 µg/L | ⧄ 200-1000 µg/L |
| 50-200 µg/L | 10-50 µg/L | <10 µg/L |

(b)

ML2 ML6 ML10 ML13

Reactive Wall Ni

▽

| ☰ <300 µg/L | 100-300 µg/L | ⧄ 50-100 µg/L |
| 25-50 µg/L | 10-25 µg/L | <10 µg/L |

(c)

ML2 ML6 ML10 ML13

Reactive Wall Cd

▽

| ☰ >50 µg/L | 10-50 µg/L | ⧄ 5.0-10 µg/L |
| 1.0-5.0 µg/L | 0.2-1.0 µg/L | < 0.2 µg/L |

(d)

ML2 ML6 ML10 ML13

Reactive Wall Zn

▽

| ☰ >10000 µg/L | 5000-10000 µg/L | ⧄ 1000-5000 µg/L |
| 100-1000 µg/L | 30-100 µg/L | <30 µg/L |

Groundwater Flow

0   1   2m

FIGURE 2. Vertical profile for metals through center transect of wall 21 months after installation.
(Vertical scale 1 cm = 1.2 m)

TABLE 1. Chemistry of the ground water entering, within, and exiting the reactive wall.

Sample Location*	pH	E_H	Alk.	Sulfide	Cd	Cu	Ni	Pb	Zn
ML-2 Influent	6.36	430	89	<1.0	15.9	4510	118	3.8	2396
ML-6 Wall front	6.76	177	155	1704	2.7	4.4	23.4	4.3	567
ML-10 Wall back	6.63	141	202	613	<0.1	10.5	5.4	1.9	82.2
ML-13 Effluent	6.57	175	180	130	<0.1	7.7	6.5	0.7	27.5

* Vertically averaged values for monitoring points. # E_H values corrected to standard hydrogen electrode. All units µg/L except pH, Eh (mV) and alkalinity (mg/L as $CaCO_3$).

the wall, alkalinity increases to an average of 155 mg/L (as $CaCO_3$) near the front end of the wall and an average of 202 mg/L near the back end of the wall. A slight increase in pH values is also noted, ranging from 6.76 near the front end of the wall to 6.63 near the back end of the wall. Dissolved sulfide concentrations within the wall increase to as high as 1704 µg/L and redox potential decreases to +141 mV.

As ground water flows through the pilot-scale wall, dissolved copper, nickel, cadmium, and zinc concentrations are significantly reduced. Copper is reduced from a vertically averaged concentration of 4510 µg/L in ground water entering the wall to averages of 4.4 µg/L and 10.5 µg/L, at the front and back ends of the wall, respectively. Figure 3 shows copper removal trends within the lower half of the wall for six sampling events spanning a 21-month period. As can
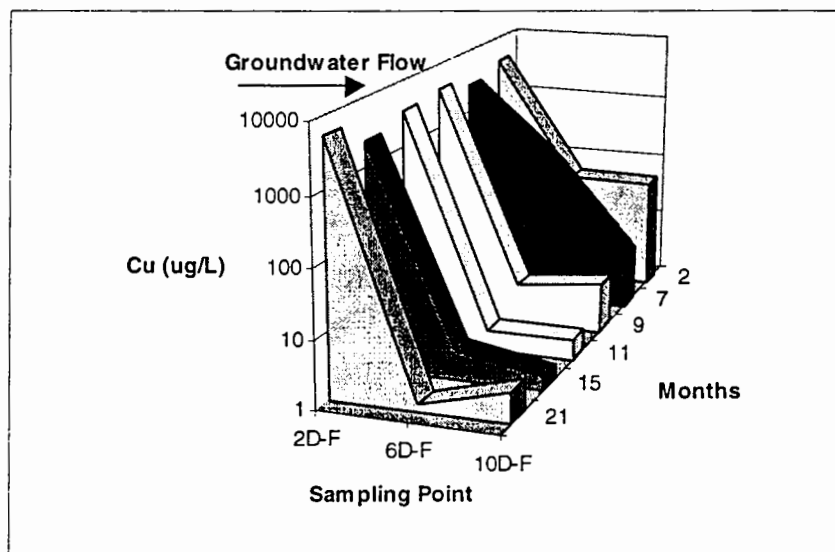

FIGURE 3. Copper concentration trends with time within lower half of reactive wall.

be observed, a lower removal efficiency occurs over the first seven months followed by a significantly higher removal efficiency thereafter. This is presumably linked to a lag in the establishment of strong sulfate-reducing conditions within the wall.

Nickel concentrations are reduced from an average of 118 µg/L to averages of 23.4 µg/L and 5.4 µg/L at the front and back ends of the wall,

respectively. Within the lower half of the wall, nickel concentrations are reduced to less than 10 µg/L (Figure 2b). Cadmium concentrations are reduced from an average of 15.9 µg/L to 2.7 µg/L and <1.0 µg/L, respectively at the front and back ends of the wall. Within the lower half of the wall, cadmium is reduced to concentrations of less than 0.2 µg/L (Figure 2c). Zinc concentrations are reduced from an average of 2396 µg/L to averages of 567 µg/L and 82.2 µg/L at the front and back ends of the wall. Within the lower half of the wall, zinc concentrations are reduced to less than 30 µg/L (Figure 2d).

Since the sulfate reduction process involves replacement of less dense organic substrate (specific gravity 1 to 2) with more dense metal sulfide precipitate (specific gravity 3 to 5), a decrease in permeability associated with metal sulfide precipitation within the pilot-scale wall would theoretically not be expected over time. Clearly, however, other precipitation reactions (e.g. hydroxides) may occur within the wall depending on the site-specific conditions in effect and these may ultimately impact the hydraulic conductivity of the wall.

The utility of an organic-based sulfate-reducing permeable reactive barrier system will depend on site-specific needs. For larger plumes where large barrier systems may be required, the low cost of using an organic substrate may be attractive. Organic-based sulfate-reducing permeable reactive barrier systems can also have the added ecological benefit of helping to restore down-gradient ecosystems by removing ferrous iron acidity from ground water and simultaneously generating a carbonate alkalinity plume. Removal of ferrous iron from the ground water prior to discharge into a surface water body prevents iron oxidation and the precipitation of ferric iron hydroxides, and production of acid that would otherwise occur in accordance with the following reaction.

$$4Fe^{3+} + O_2 + 10H_2O \;\rightarrow\; 4Fe(OH)_3 + 8H^+ \qquad (3)$$
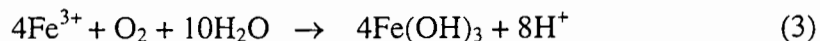
The production of a carbonate alkalinity plume associated with the sulfate reduction process has been observed at the Nickel Rim site (Benner et al, 1997). There, influent ground water was converted from a net acid producing potential of 7.8 to 46 meq/L to a net acid consuming potential of 16 to 45 meq/L following passage through the organic substrate based reactive wall.

Wall longevity will be dependent on the reactive material maintaining its permeability and reactivity properties. Benner et al (1997) calculated that the organic-based reactive wall at the Nickel Rim Site consisting of 50% organic substrate (by volume) could be effective for a minimum of 15 years based on column study results. Metal sulfides precipitated out within the wall can be expected to remain stable provided they are not subjected to oxidizing conditions. As long as the metal sulfides remain below the water table, the oxidizing potential is likely to be limited.

Two additional monitoring events have occurred on the pilot-scale wall since the 21-month sampling event. Both of these sampling events continue to demonstrate sulfate reduction and metals removal within the wall. The chemistry from these sampling events is currently being validated and interpreted to determine recent wall performance. It is intended that the pilot-scale wall will

continue to be monitored to determine the long-term performance of the wall and serve as an "early warning system" for "break-through" for full-scale installation.

CONCLUSIONS

The monitoring of geochemical ground water parameters of a compost-based pilot-scale wall over a 21-month period has indicated that the leaf-rich compost is providing a suitable organic carbon source for microbially mediated sulfate-reduction and that dissolved metals (Cd, Cu, Ni, and Zn) are being effectively attenuated by reactions within the pilot-scale wall. Continued monitoring is planned to evaluate the long-term performance of the wall.

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DISCLAIMER

The views expressed in this paper are those of the individual authors and do not necessarily reflect the views and policies of Environment Canada or the U.S. Environmental Protection Agency.

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16. ABSTRACT

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