# MICHIGAN DEPARTMENT OF ENVIRONMENTAL QUALITY WATER BUREAU NOVEMBER 2004

# STAFF REPORT

# AN INVESTIGATION OF THE CEMENT KILN DUST SEEP DISCHARGE INTO LITTLE TRAVERSE BAY AT BAY HARBOR SEPTEMBER 7-8, 2004 EMMET COUNTY

During a routine inspection at the Petoskey Wastewater Treatment Plant (WWTP) on August 17, 2004 by Cadillac District (Gaylord Office) staff, it was determined that seep water from what is referred to as the Western CKD (cement kiln dust) pile at Bay Harbor had not been collected and discharged to the Petoskey WWTP since January 3, 2004. It is suspected that the CKD seepage water then migrated laterally, discharging to Little Traverse Bay, Lake Michigan. Cadillac District (Gaylord Office) staff made two site visits, the first on August 17, 2004 and the second on August 26, 2004, to investigate the seep discharge into Lake Michigan. During that investigation, pH measurements in exceedance of Michigan water quality standards were found as far as 90 feet off shore. A copy of the full report on that investigation is included as Attachment A. Follow-up by Surface Water Assessment Section (SWAS) staff was recommended to evaluate the chemical composition and possible aquatic toxicity of the seep discharge. SWAS staff performed a follow-up investigation on September 7-8, 2004 and collected an additional sample for toxicity testing on September 15, 2004, and the results are summarized below.

#### Site Description

The area of beach and shoreline affected by the seep discharge is located on Bay Harbor Company property along Coastal Drive adjacent to the golf course in Resort Township, Emmet County. The site is characterized by two vacant, adjacent lots on the lakeshore side of Coastal Drive, with an occupied house to the west and another to the east. The shoreline in this area is composed primarily of limestone rock and cobblestone of various sizes.

SWAS staff visited the site accompanied by Cadillac District (Gaylord Office) staff on September 7, 2004. Also present were Bill Byberg representing Bay Harbor Company, David Rivers and Dan Colwater of Conestoga-Rovers & Associates, and Scott Kendzierski of the Northwest Michigan Community Health Agency. During this visit to the site, the underside of many of the rocks and cobblestones were observed to have been stained black by the seep discharge. Also observed were shallow shoreline pools filled with nearly black water. These phenomena were not observed in areas unimpacted by the seep discharge.

# **Objectives**

The objectives of this investigation were to determine: 1) the chemical characteristics and aquatic toxicity of the seep discharge, 2) whether Michigan water quality standards are being met in the seep discharge, 3) whether the seep discharge has the potential to be injurious to the public health, wildlife and/or aquatic life, and 4) to compare the chemical characteristics of the

seep discharge to those of an unimpacted, nearshore area of Little Traverse Bay, Lake Michigan.

# Sampling Locations and Data Collection

A shallow Lake Michigan shoreline pool filled with nearly black water was designated the seep discharge sampling location, and a site approximately 2.5 miles west of this and approximately 7 feet off shore was selected to represent the normal chemical characteristics of unimpacted water within Lake Michigan.

To accomplish the stated objectives, on-site measurements of pH and specific conductance were taken in the shoreline pool and at the unimpacted site, samples were collected from the shoreline pool for chemical and aquatic toxicity testing, and samples were collected at the unimpacted site for chemical testing. An on-site measurement of pH was also taken in a nearshore area impacted by the seep discharge, approximately 7 offshore of the shoreline pool.

On-site measurements of pH and specific conductance were made using a YSI Model 600XL multiparameter sonde calibrated in accordance with the manufacturer's guidelines.

Water chemistry samples and the *Daphnia magna* aquatic toxicity test sample were collected at the seep discharge sampling location on September 7, 2004 by SWAS staff. The fathead minnow aquatic toxicity test sample was collected at the seep discharge sampling location on September 15, 2004 by Cadillac District (Gaylord Office) staff. Water chemistry samples were collected at the Little Traverse Bay, Lake Michigan location on September 8, 2004 by SWAS staff. Complete chain-of-custody procedures were followed for all samples.

At the seep discharge sampling location, sample collection took place after winds had calmed and the selected shoreline pool was no longer being directly influenced by the surf. A replicate and field blank were obtained for all water chemistry analytes sampled at the shoreline pool.

Low-level Hg samples were collected and handled in accordance with U.S. Environmental Protection Agency (USEPA) Method 1669. All other samples, including aquatic toxicity test samples, were collected and handled in accordance with Michigan Department of Environmental Quality (MDEQ)-approved procedures. All samples were collected via grab method.

# Summary of Water Chemistry Evaluation

Water chemistry samples were analyzed by the MDEQ, Environmental Science and Services, Laboratory Section. Total mercury was analyzed in accordance with USEPA Method 1631. All analyses were completed within applicable hold times.

For those contaminants for which Michigan water quality standards have been developed, sample results were compared against all available standards. If a human health standard was available, the drinking water standard was used. Drinking water standards were used based on R 323.1100(8) of the Part 4 Water Quality Standards, which protects Michigan waters of the Great Lakes as a public water supply source. No venting groundwater mixing zone has been granted by the MDEQ for this seep discharge.

Analytical results are presented in Tables 1-4. The results of the comparison with Michigan water quality standards are presented in Table 5. Major findings are summarized below.

- 1. The pH of the seep discharge as measured on-site was 12.52 standard units (s.u.). This greatly exceeds the Michigan water quality standard range of 6.5 9.0 s.u. for pH. In fact, it represents a basicity over 1,000x greater than that allowed by the Michigan water quality standard, and over 10,000x greater than that of the unimpacted site (pH = 8.06 s.u.).
- 2. The specific conductance of the seep discharge as measured on-site was 37,439 umhos/cm. By comparison, the specific conductance measured at the unimpacted site was 285 umhos/cm.
- 3. The pH of the impacted, nearshore site as measured on-site was 10.15 s.u. This greatly exceeds the Michigan water quality standard range of 6.5 9.0 s.u. for pH. In fact, it represents a basicity over 10x greater than that allowed by the Michigan water quality standard, and over 100x greater than that of the unimpacted site (pH = 8.06 s.u.).
- 4. The concentration of total mercury in the seep discharge was 0.3 ug/L. This concentration exceeds the Human Noncancer Value (HNV = 0.0018 ug/L) and the Wildlife Value (WV = 0.0013 ug/L) for Hg by over 160x and 230x, respectively. (See Table 5 for definitions of these terms).
- 5. Seep discharge concentrations of copper (28 ug/L), nickel (220 ug/L), selenium (110 ug/L), vanadium (190 ug/L) and zinc (38 ug/L) exceed the Final Chronic Value (FCV) and Aquatic Maximum Value (AMV) applicable to these metals (see Table 5 for the metal-specific standards and for definitions of these terms).
- 6. The concentration of molybdenum in the seep discharge was 500 ug/L. This concentration exceeds the HNV of 120 ug/L for molybdenum.
- 7. The concentration of arsenic in the seep discharge was 220 ug/L. This concentration exceeds the FCV of 150 ug/L and the HNV of 50 ug/L for arsenic.
- 8. Concentrations of aluminum (17000 ug/L), titanium (46 ug/L), alkalinity (4000 mg CaCO3/L), chloride (1700 mg/L); sulfate (10800 mg/L), potassium (12900 mg/L), sodium (820 mg/L) and total dissolved solids (30000 mg/L) were 100-10,000x higher in the seep discharge (Table 1) than at the unimpacted site (Table 4).
- 9. Concentrations of all contaminants in the field blank were reported as Not Detected (ND) by the MDEQ Laboratory (Table 3). Results obtained for the replicate (Table 2) were consistent with those obtained for the sample. These facts indicate adherence to Quality Assurance/Quality Control measures during sample collection, handling and analysis.

## Summary of Aquatic Toxicity Evaluation

Staff of the SWAS Aquatic Toxicology Laboratory (ATL) performed *Daphnia magna* and fathead minnow acute toxicity tests on samples of the seep discharge from September 8-10, 2004 (*D. magna* test) and September 16-20, 2004 (fathead minnow test).

Toxicity testing was performed according to SWAS procedures #24 (*D. magna* test) and #42 (fathead minnow test), except that no modifications were made to sample pH before testing because the objective of the tests was to predict the direct impact of the seep discharge on aquatic life. Sample holding time was less than 36 hours before initiation of both tests.

*D. magna* used for the test were <24 hours old at test initiation. Fathead minnows used for the test were 12 days old at test initiation. Test water quality parameters met test acceptability criteria (Tables 6 and 7). Test results are summarized below:

- 1. The September 7, 2004 sample was highly acutely toxic to *Daphnia magna* ( $LC_{50}$ =3.2% sample; 31 TUa; Table 8).
- 2. The September 15, 2004 sample was highly acutely toxic to fathead minnows (LC<sub>50</sub>=3.2% sample; 31 TUa; Table 9).
- 3. Toxic effects to both *D. magna* and fathead minnows were extremely rapid in test concentrations as low as 10% sample. All individuals of both species died immediately upon contact with the 100% samples, and a 60% dilution of the samples. Time to complete mortality of *D. magna* exposed to other concentrations as low as 10% sample ranged from seconds to minutes. Time to complete mortality of fathead minnows exposed to other concentrations as low as 10% sample ranged from minutes to 24 hours.
- 4. The bodies of dead *D. magna* and fathead minnows exposed to high concentrations of the sample were unusually well-preserved during the test, indicating that microbial activity was suppressed by the toxicity of the sample.
- 5. Color was a good indicator of sample toxicity. Test solutions in test chambers of all concentrations of sample exhibiting a toxic effect (10%-100% sample) were visibly colored (photographs available upon request). In contrast, test chambers of concentrations exhibiting no toxic effect (0% 1% sample) were not visibly colored.
- 6. The toxicity of the samples was likely caused by pH and potassium. The pH levels of the samples (12.52 s.u., *D. magna* test; 11.99 s.u., fathead minnow test) greatly exceeded the allowable level for protection of aquatic life (9.0 s.u.). The concentrations of potassium in the samples (12,300 12,900 mg/L) exceeded expected acutely toxic levels (330 mg/L, *D. magna*; 380 mg/L, fathead minnows) by nearly 2 orders of magnitude. The concentration of copper in the sample used for the *D. magna* test (28 ug/L) also exceeded an expected acutely toxic level for *D. magna* (8.4 ug/L).
- 7. The results of the tests indicate that the seep discharge likely had a dramatic toxic effect on aquatic life in the seep discharge area. The high level of toxicity to *D*. magna and fathead minnows, combined with a lack of decomposition, indicates that little or no aquatic life would be expected to survive at concentrations of the seep discharge as low as 10%. Less dramatic impacts are expected at concentrations as low as 3.2% seep discharge, the level of sample predicted to cause a 50% kill of test organisms. In addition, the rapid impact of the toxicity indicates that avoidance of high concentrations of the toxic seep discharge by most aquatic life would be unlikely.
- 8. Because visible color was a good indicator of toxicity during the toxicity test, it is likely that areas of Lake Michigan visibly colored by the seep water discharge were subjected to acutely toxic effects caused by the seep discharge.

# Conclusion

Results of the water chemistry evaluation indicate that the seep discharge greatly exceeds Michigan water quality standards for pH, arsenic, copper, mercury, molybdenum, nickel, selenium, vanadium, and zinc. Measurements of pH taken in nearshore waters of Lake

Michigan establish that the seep discharge is the causal factor in the high pH found at the impacted site. Results of the *D. magna* and fathead minnow aquatic toxicity tests indicate that the seep discharge is highly acutely toxic to aquatic life and likely had a dramatic toxic effect on aquatic life in the seep discharge area. These findings establish that exposure to the seep discharge will have an injurious effect on the public health, wildlife and aquatic life.

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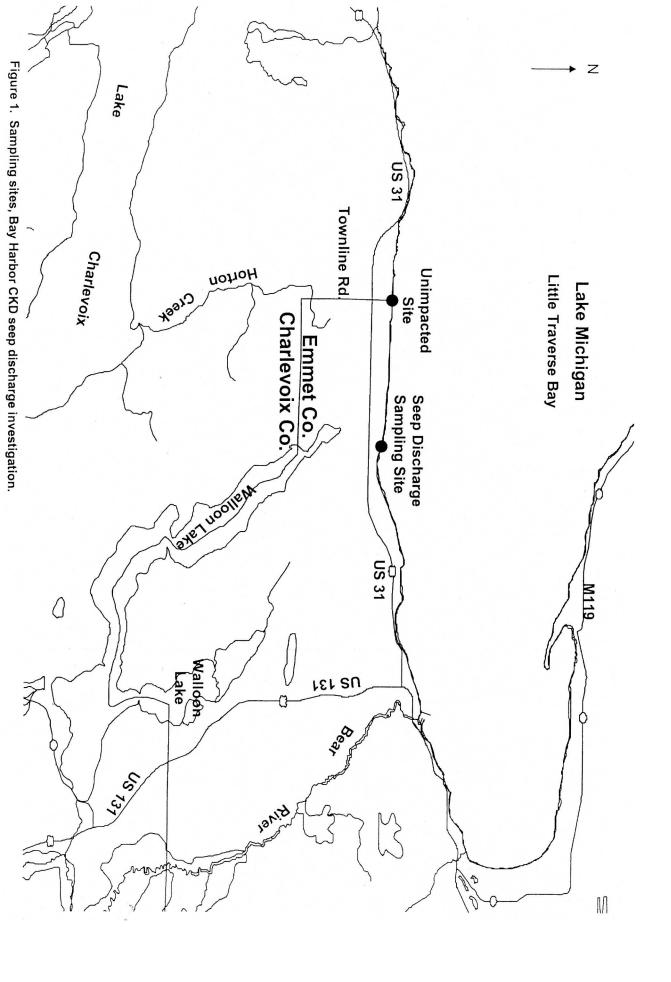


Table 1. Chemical characteristics of Bay Harbor CKD seep discharge sample.

Alkalinity - Bicarbonate Alkalinity - Carbonate Alkalinity (as CaCO3) Aluminium - Total Antimony - Total Antimony - Total Arsenic - Total Beryllium - Total Aluminium - Total Antimony - Total An	Analyte	Result	Unit
Alkalinity - Carbonate     Alkalinity (as CaCO3)     Aluminium - Total     Antimony - Total     Arsenic - Total     Beryllium - Total     Cadmium - Total     Antimony - Total     Arsenic - Total     Barium - Total     Beryllium - Total     Cadmium - Total     Calcium - Total     Chloride     Chromium - Total     Choromium - Total     Cobalt - Total     Conductance     Copper - Total     Lead - Total     Low Level Mercury - Total     Monusple     Manganese - Total     Molupydenum - Total     Nonusple     Manganese - Total     Molupydenum - Total     Nonusple     Manganese - Total     Nonusple     Manganesium - Total     Nonusple     Manganesium - Total     Nonusple     Manganesium - Total     Nonusple     Manganese - Total     Nonusple     Ma			
Alkalinity (as CaCO3) Aluminium - Total Antimony - Total Antimony - Total Antimony - Total Arsenic - Total Beryllium - Total Beryllium - Total Cadmium - Total Calcium - Total Chloride Chromium - Total Cobalt - Total Copper - Total Copper - Total Copper - Total Cow Level Mercury - Total Manganese - Total Molybdenum - Total Nolybdenum -			
Aluminium - Total Antimony - Total Antimony - Total Arsenic - Total Barium - Total Beryllium - Total B		4000	
Antimony - Total         ND         μg/L           Arsenic - Total         220         μg/L           Barium - Total         13         μg/L           Beryllium - Total         ND         μg/L           Cadmium - Total         ND         μg/L           Calcium - Total         ND         μg/L           Chloride         1700         mg/L           Chloride         1700         mg/L           Chromium - Total         17         μg/L           Cobalt - Total         ND         μg/L           Conductance         37600         umhos/cm           Copper - Total         28         μg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         μg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         μg/L           Malgenium - Total         ND         μg/L           Molybdenum - Total         41         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         10		10.000 (0.000)	
Arsenic - Total Barium - Total Barium - Total Beryllium - Total Cadmium - Total Calcium - Total Calcium - Total Chloride Chromium - Total Cobalt - Total Copper - Total Chad - Total Copper - Total Chad - Total Copper - Total Cow Level Mercury - Total Molybdenum - Total Nolybdenum	Antimony - Total	ND	
Barium - Total         13         µg/L           Beryllium - Total         ND         µg/L           Cadmium - Total         ND         µg/L           Calcium - Total         8.0         mg/L           Chloride         1700         mg/L           Chromium - Total         17         µg/L           Cobalt - Total         ND         µg/L           Conductance         37600         umhos/cm           Copper - Total         28         µg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         µg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         µg/L           Manganese - Total         ND         µg/L           Molybdenum - Total         41         µg/L           Nickel - Total         220         µg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12         pg/L           Selenium - Total         10         µg/L           Solids - Suspended         12 </td <td>Arsenic - Total</td> <td>220</td> <td></td>	Arsenic - Total	220	
Beryllium - Total         ND         μg/L           Cadmium - Total         ND         μg/L           Calcium - Total         8.0         mg/L           Chloride         1700         mg/L           Chromium - Total         17         μg/L           Cobalt - Total         ND         μg/L           Conductance         37600         umhos/cm           Copper - Total         28         μg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         μg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         μg/L           Manganese - Total         ND         μg/L           Malgensium - Total         41         μg/L           Molybdenum - Total         500         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           Ph         12.6         pH           Potassium - Total         10	Barium - Total	13	
Cadmium - Total         ND         μg/L           Calcium - Total         8.0         mg/L           Chloride         1700         mg/L           Chromium - Total         17         μg/L           Cobalt - Total         ND         μg/L           Conductance         37600         umhos/cm           Copper - Total         28         μg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         μg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Magnesium - Total         ND         mg/L           Manganese - Total         ND         mg/L           Molybdenum - Total         500         μg/L           Nickel - Total         220         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           PH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         10         μg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved	Beryllium - Total	ND	. •
Calcium - Total         8.0         mg/L           Chloride         1700         mg/L           Chromium - Total         17         µg/L           Cobalt - Total         ND         µg/L           Conductance         37600         umhos/cm           Copper - Total         28         µg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         µg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Manganese - Total         41         µg/L           Molybdenum - Total         500         µg/L           Nickel - Total         220         µg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         10         µg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         ND         µg/L           Sulfate	Cadmium - Total	ND	
Chloride         1700         mg/L           Chromium - Total         17         µg/L           Cobalt - Total         ND         µg/L           Conductance         37600         umhos/cm           Copper - Total         28         µg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         µg/L           Lead - Total         ND         µg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Manganese - Total         41         µg/L           Molybdenum - Total         500         µg/L           Nickel - Total         220         µg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         µg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         10800         mg/L           Sulfate	Calcium - Total	8.0	
Chromium - Total         17         μg/L           Cobalt - Total         ND         μg/L           Conductance         37600         umhos/cm           Copper - Total         28         μg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         μg/L           Lead - Total         ND         μg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Magnesium - Total         41         μg/L           Molybdenum - Total         500         μg/L           Nickel - Total         220         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         μg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Solids - Total Dissolved         30000         mg/L           Sulfate         10800         mg/L           Thallium - T	Chloride	1700	-
Cobalt - Total         ND         µg/L           Conductance         37600         umhos/cm           Copper - Total         28         µg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         µg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Manganese - Total         41         µg/L           Molybdenum - Total         500         µg/L           Nickel - Total         220         µg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         10         µg/L           Solids - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Sulfate         10800         mg/L           Thallium - Total         ND         µg/L           Titanium - Total         46         µg/L           Vanadium - Total	Chromium - Total	17	-
Conductance         37600         umhos/cm           Copper - Total         28         µg/L           Hardness - Calculated         20         mg/L           Lead - Total         ND         µg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Manganese - Total         41         µg/L           Molybdenum - Total         500         µg/L           Nickel - Total         220         µg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         10         µg/L           Soliver -Total         ND         µg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Sulfate         10800         mg/L           Thallium - Total         ND         µg/L           Titanium - Total         46         µg/L           Turbidity         13         NTU           Vanadium - Total	Cobalt - Total	ND	
Hardness - Calculated       20       mg/L         Lead - Total       ND       μg/L         Low Level Mercury - Total       300       ng/L         Magnesium - Total       ND       mg/L         Manganese - Total       41       μg/L         Molybdenum - Total       500       μg/L         Nickel - Total       220       μg/L         Nitrite       0.9       mg N/L         Ortho-phosphate       0.65       mg P/L         pH       12.6       pH         Potassium - Total       12900       mg/L         Selenium - Total       10       μg/L         Soliver -Total       ND       μg/L         Solids - Suspended       12       mg/L         Solids - Total Dissolved       30000       mg/L         Strontium - Total       38       μg/L         Sulfate       10800       mg/L         Thallium - Total       ND       μg/L         Titanium - Total       46       μg/L         Turbidity       13       NTU         Vanadium - Total       190       μg/L	Conductance	37600	
Hardness - Calculated         20         mg/L           Lead - Total         ND         μg/L           Low Level Mercury - Total         300         ng/L           Magnesium - Total         ND         mg/L           Manganese - Total         41         μg/L           Molybdenum - Total         500         μg/L           Nickel - Total         220         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         μg/L           Silver -Total         ND         μg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         μg/L           Sulfate         10800         mg/L           Thallium - Total         ND         μg/L           Titanium - Total         46         μg/L           Turbidity         13         NTU           Vanadium - Total         190         μg/L	Copper - Total	28	µg/L
Low Level Mercury - Total 300 ng/L Magnesium - Total ND mg/L Manganese - Total 41 µg/L Molybdenum - Total 500 µg/L Nickel - Total 220 µg/L Nitrite 0.9 mg N/L Ortho-phosphate 0.65 mg P/L pH 12.6 pH 12.6 pH Potassium - Total 12900 mg/L Selenium - Total 110 µg/L Silver - Total ND µg/L Sodium - Total 820 mg/L Solids - Suspended 12 mg/L Solids - Total Dissolved 30000 mg/L Strontium - Total 38 µg/L Sulfate 10800 mg/L Titanium - Total ND µg/L Titanium - Total 46 µg/L Titanium - Total 13 NTU Vanadium - Total 190 µg/L	Hardness - Calculated	20	
Magnesium - Total         ND         mg/L           Manganese - Total         41         μg/L           Molybdenum - Total         500         μg/L           Nickel - Total         220         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         μg/L           Silver -Total         ND         μg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Sulfate         10800         mg/L           Thallium - Total         ND         μg/L           Titanium - Total         46         μg/L           Turbidity         13         NTU           Vanadium - Total         190         μg/L	Lead - Total	ND	μg/L
Manganese - Total       41       μg/L         Molybdenum - Total       500       μg/L         Nickel - Total       220       μg/L         Nitrite       0.9       mg N/L         Ortho-phosphate       0.65       mg P/L         pH       12.6       pH         Potassium - Total       12900       mg/L         Selenium - Total       110       μg/L         Silver -Total       ND       μg/L         Sodium - Total       820       mg/L         Solids - Suspended       12       mg/L         Solids - Total Dissolved       30000       mg/L         Strontium - Total       38       μg/L         Sulfate       10800       mg/L         Thallium - Total       ND       μg/L         Titanium - Total       46       μg/L         Turbidity       13       NTU         Vanadium - Total       190       μg/L	Low Level Mercury - Total	300	ng/L
Molybdenum - Total         500         μg/L           Nickel - Total         220         μg/L           Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         μg/L           Silver -Total         ND         μg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         μg/L           Sulfate         10800         mg/L           Thallium - Total         ND         μg/L           Titanium - Total         46         μg/L           Turbidity         13         NTU           Vanadium - Total         190         μg/L	Magnesium - Total	ND	mg/L
Nickel - Total       220       μg/L         Nitrite       0.9       mg N/L         Ortho-phosphate       0.65       mg P/L         pH       12.6       pH         Potassium - Total       12900       mg/L         Selenium - Total       110       μg/L         Silver -Total       ND       μg/L         Sodium - Total       820       mg/L         Solids - Suspended       12       mg/L         Solids - Total Dissolved       30000       mg/L         Strontium - Total       38       μg/L         Sulfate       10800       mg/L         Thallium - Total       ND       μg/L         Titanium - Total       46       μg/L         Turbidity       13       NTU         Vanadium - Total       190       μg/L	Manganese - Total	41	μg/L
Nitrite         0.9         mg N/L           Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         µg/L           Silver -Total         ND         µg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         µg/L           Sulfate         10800         mg/L           Thallium - Total         ND         µg/L           Titanium - Total         46         µg/L           Turbidity         13         NTU           Vanadium - Total         190         µg/L		500	μg/L
Ortho-phosphate         0.65         mg P/L           pH         12.6         pH           Potassium - Total         12900         mg/L           Selenium - Total         110         µg/L           Silver -Total         ND         µg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         µg/L           Sulfate         10800         mg/L           Thallium - Total         ND         µg/L           Titanium - Total         46         µg/L           Turbidity         13         NTU           Vanadium - Total         190         µg/L	Nickel - Total	220	μg/L
pH       12.6       pH         Potassium - Total       12900       mg/L         Selenium - Total       110       μg/L         Silver -Total       ND       μg/L         Sodium - Total       820       mg/L         Solids - Suspended       12       mg/L         Solids - Total Dissolved       30000       mg/L         Strontium - Total       38       μg/L         Sulfate       10800       mg/L         Thallium - Total       ND       μg/L         Titanium - Total       46       μg/L         Turbidity       13       NTU         Vanadium - Total       190       μg/L	Nitrite	0.9	mg N/L
Potassium - Total         12900         mg/L           Selenium - Total         110         μg/L           Silver -Total         ND         μg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         μg/L           Sulfate         10800         mg/L           Thallium - Total         ND         μg/L           Titanium - Total         46         μg/L           Turbidity         13         NTU           Vanadium - Total         190         μg/L		0.65	mg P/L
Selenium - Total         110         μg/L           Silver -Total         ND         μg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         μg/L           Sulfate         10800         mg/L           Thallium - Total         ND         μg/L           Titanium - Total         46         μg/L           Turbidity         13         NTU           Vanadium - Total         190         μg/L	pH	12.6	pН
Silver -Total         ND         μg/L           Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         μg/L           Sulfate         10800         mg/L           Thallium - Total         ND         μg/L           Titanium - Total         46         μg/L           Turbidity         13         NTU           Vanadium - Total         190         μg/L	Potassium - Total	12900	mg/L
Sodium - Total         820         mg/L           Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         µg/L           Sulfate         10800         mg/L           Thallium - Total         ND         µg/L           Titanium - Total         46         µg/L           Turbidity         13         NTU           Vanadium - Total         190         µg/L		TOTAL OF STREET AL	μg/L
Solids - Suspended         12         mg/L           Solids - Total Dissolved         30000         mg/L           Strontium - Total         38         µg/L           Sulfate         10800         mg/L           Thallium - Total         ND         µg/L           Titanium - Total         46         µg/L           Turbidity         13         NTU           Vanadium - Total         190         µg/L			μg/L
Solids - Total Dissolved       30000       mg/L         Strontium - Total       38       µg/L         Sulfate       10800       mg/L         Thallium - Total       ND       µg/L         Titanium - Total       46       µg/L         Turbidity       13       NTU         Vanadium - Total       190       µg/L			mg/L
Strontium - Total       38       µg/L         Sulfate       10800       mg/L         Thallium - Total       ND       µg/L         Titanium - Total       46       µg/L         Turbidity       13       NTU         Vanadium - Total       190       µg/L		12	mg/L
Sulfate       10800       mg/L         Thallium - Total       ND       µg/L         Titanium - Total       46       µg/L         Turbidity       13       NTU         Vanadium - Total       190       µg/L			
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Strontium - Total		μg/L
Titanium - Total 46 µg/L Turbidity 13 NTU Vanadium - Total 190 µg/L		10800	mg/L
Turbidity 13 NTU Vanadium - Total 190 µg/L	A CONTRACT TO A CONTRACT OF THE CONTRACT OF TH		μg/L
Vanadium - Total 190 µg/L	- Control of the Cont		μg/L
F9-			
Zinc - Total 38 µg/L	A STAND STANDARD SALES OF THE STANDARD		
	Zinc - Total	38	μg/L

ND = Not detected.

Table 2. Chemical characteristics of Bay Harbor CKD seep discharge replicate.

Analyte	Result	Unit
Alkalinity - Bicarbonate	ND	mg/L
Alkalinity - Carbonate	3900	mg/L
Alkalinity (as CaCO3)	4900	mg/L
Aluminium - Total	16000	μg/L
Antimony - Total	ND	µg/L
Arsenic - Total	220	µg/L
Barium - Total	12	μg/L
Beryllium - Total	ND	μg/L
Cadmium - Total	ND	μg/L
Calcium - Total	7.3	mg/L
Chloride	1670	mg/L
Chromium - Total	18	µg/L
Cobalt - Total	ND	μg/L
Conductance	37000	umhos/cm
Copper - Total	28	μg/L
Hardness - Calculated	18	mg/L
Lead - Total	ND	µg/L
Low Level Mercury - Total	320	ng/L
Magnesium - Total	ND	mg/L
Manganese - Total	41	μg/L
Molybdenum - Total	500	µg/L
Nickel - Total	220	µg/L
Nitrite	0.9	mg N/L
Ortho-phosphate	0.51	mg P/L
рН	12.6	рН
Potassium - Total	12300	mg/L
Selenium - Total	110	μg/L
Silver -Total	ND	µg/L
Sodium - Total	793	mg/L
Solids - Suspended	17	mg/L
Solids - Total Dissolved	29000	mg/L
Strontium - Total	40	μg/L
Sulfate	10200	mg/L
Thallium - Total	ND	µg/L
Titanium - Total	53	µg/L
Turbidity	19	NTU
Vanadium - Total	190	µg/L
Zinc - Total	49	µg/L
ND = Not detected		

ND = Not detected.

Table 3. Chemical characteristics of Bay Harbor CKD seep discharge field blank.

Analysta	l	
Analyte Biograph and the	Result	Unit
Alkalinity - Bicarbonate	ND	mg/L
Alkalinity - Carbonate	ND	mg/L
Alkalinity (as CaCO3)	ND	mg/L
Aluminium - Total	ND	μg/L
Antimony - Total	ND	µg/L
Arsenic - Total	ND	μg/L
Barium - Total	ND	μg/L
Beryllium - Total	ND	µg/L
Cadmium - Total	ND	µg/L
Calcium - Total	ND	mg/L
Chloride	ND	mg/L
Chromium - Total	ND	μg/L
Cobalt - Total	ND	µg/L
Conductance	7	umhos/cm
Copper - Total	ND	μg/L
Hardness - Calculated	ND	mg/L
Lead - Total	ND	µg/L
Low Level Mercury - Total	ND	ng/L
Magnesium - Total	ND	mg/L
Manganese - Total	ND	μg/L
Molybdenum - Total	ND	μg/L
Nickel - Total	ND	µg/L
Nitrite	ND	mg N/L
Ortho-phosphate	ND	mg P/L
PΗ	Interference	pН
Potassium - Total	ND	mg/L
Selenium - Total	ND	μg/L
Silver -Total	ND	µg/L
Sodium - Total	ND	mg/L
Solids - Suspended	ND	mg/L
Solids - Total Dissolved	ND	mg/L
Strontium - Total	ND	μg/L
Sulfate	ND	mg/L
Thallium - Total	ND	µg/L
Titanium - Total	ND	μg/L
Turbidity	ND	NTU
Vanadium - Total	ND	µg/L
Zinc - Total	ND	μg/L
ND = Not detected		

ND = Not detected.

Table 4. Chemical characteristics of unimpacted, nearshore Lake Michigan sample.

Analyte	Result	Unit
Alkalinity - Bicarbonate	94	mg/L
Alkalinity - Carbonate	ND	mg/L
Alkalinity (as CaCO3)	94	mg/L
Aluminium - Total	ND	μg/L
Antimony - Total	ND	µg/L
Arsenic - Total	ND	µg/L
Barium - Total	19	µg/L
Beryllium - Total	ND	μg/L
Cadmium - Total	ND	μg/L
Calcium - Total	34.8	mg/L
Chloride	11	mg/L
Chromium - Total	ND	μg/L
Cobalt - Total	ND	μg/L
Conductance	293	umhos/cm
Copper - Total	ND	µg/L
Hardness - Calculated	134	mg/L
Lead - Total	ND	μg/L
Low Level Mercury - Total	ND	ng/L
Magnesium - Total	11.5	mg/L
Manganese - Total	ND	μg/L
Molybdenum - Total	ND	μg/L
Nickel - Total	2.5	μg/L
Nitrite	ND	mg N/L
Ortho-phosphate	ND	mg P/L
pН	8.43	рH
Potassium - Total	1.3	mg/L
Selenium - Total	ND	μg/L
Silver -Total	ND	µg/L
Sodium - Total	6.2	mg/L
Solids - Suspended	6	mg/L
Solids - Total Dissolved	170	mg/L
Strontium - Total	120	µg/L
Sulfate	21	mg/L
Thallium - Total	ND	μg/L
Titanium - Total	ND	µg/L
Turbidity	ND	NTU
Vanadium - Total	ND	μg/L
Zinc - Total	ND	µg/L
ND = Not detected.		

Table 5.	
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Comparison of Bay Harbor CKD seep discharge metal concentrations with Michigan water quality standards. All values are in ug/L. Bold text indicates sample concentration exceeds the standard.

Analyte	Sample Concentration	FCV	HNV*	WV	AMV
Antimony	ND	240	1.7	NA	1100
Arsenic	220	150	50	NA	340
Barium	13	79	1900	NA	230
Beryllium	ND	0.041	160	NA	0.37
Cadmium	ND	0.68	2.5	NA	0.74
Chromium	17	20	120	NA	150
Cobalt	ND	100	ID	NA	370
Copper	28	2.3	790	NA	2.9
Lead	ND	1.7	14	NA	15
Manganese	41	470	3600	NA	1000
Mercury@	0.3	0.77	0.0018	0.0013	1.4
Molybdenum	500	800	120	NA	7200
Nickel	220	13	2600	NA	120
Selenium	110	5	120	NA	62
Silver	ND	0.06	130	NA	0.54
Strontium	38	8300	ID	NA	75000
Thallium	ND	10	1.2	NA	78
Vanadium	190	12	220	NA	110
Zinc	38	30	4500	NA	30

FCV =

HNV =

ID =

@= Bioaccumulative chemical of concern. AMV =

Aquatic maximum value = the highest concentration of a material in the ambient water column to which an

aquatic community can be exposed briefly without resulting in unacceptable effects.

Final chronic value = the level of a substance that does not allow injurious or debilitating effects in an aquatic organism

resulting from repeated long-term exposure to a substance relative to the organism's lifespan.

Human noncancer value = the maximum ambient water concentration of a substance at which adverse

noncancer effects are not likely to occur in the human population from lifetime exposure.

Insufficient data to derive value.

NA = Not applicable. ND =

Not detected. WV =

Wildlife value = the maximum ambient water concentration of a substance at which adverse effects are not likely

to result in population-level impacts to mammalian and avian wildlife populations from lifetime exposure.

Table 6. Daphnia magna toxicity test chambers (test dates September 8-10, 2004). Water quality characteristics of Bay Harbor CKD seep discharge sample

% Sample:	Control	trol	0.		1			10
Parameter	Day 0	Day 2	Day 0	Day 2	Day 0	Day 2	Day 0	Day 1 <sup>1</sup>
Temperature (°C)	25.0	25.4	24.5	25.2		25.2	25.4	25.2
Dissolved oxygen (mg/l)	7.4	7.9	7.4	7.9	74	7.8	73	76
pH (S.U.)	8.12	7 70	8 68	7 01	0 03	0 . 0	2 .	3 6
Conductivity (umhos/cm)	540	1	: 6	;			- - -	9.40
Alkalinity (mg/l)	48	1	1	1	1	1 1		1
Hardness (mg/l)	104	1	ł	ı	!		1 1	1
Water quality characteristic pheervations reported for day 1 honoring of complete	ione report	od for day 1	2000	family				
A COLOR OF THE PARTY OF THE PAR			00000	+			,	

Water quality characteristic observations reported for day 1 because of complete mortality of D. magna on day 0.

% Sample:	3(	U	99	0	100		
Parameter	Day 0	Day 1 <sup>1</sup>	Day 0	Day 1 <sup>1</sup>	Day 0	Day 1 <sup>1</sup>	
Temperature (°C)	25.3	25.2	25.5	25.1	25.2	25.1	
Dissolved oxygen (mg/l)	7.2	7.7	7.2	7.8	7.0	7.6	
рH (S.U.)	11.93	10.03	12.28	10.36	12.52	10.62	
Conductivity (umhos/cm)	1	1	1	1	27,890	;	
Alkalinity (mg/l)	1	ı	1	ŀ	4,680	1	
Hardness (mg/l)	1	.1	1	1	52	1	
Water quality characteristic observations reported for day 1 because of complete mortality of <i>D. magna</i> on day 0.	tions report	ed for day 1	l because o	f complete r	nortality of <i>D. n</i>	nagna on da	ıy 0.
							3

Table 7. Water quality characteristics of Bay Harbor CKD seep discharge sample fathead minnow toxicity test chambers (test dates September 16-20, 2004).

% Sample:	Cor	Control	,		10		30	
Parameter	Day 0	Day 4	Day 0	Day 4	Day 0	Day 1 <sup>1</sup>	Day 0	Day 1 <sup>2</sup>
Temperature (°C)	25.2	24.2	25.4	24.2	25 4	24.4	25.7	2/ /
Dissolved oxygen (mg/l)	8. 1	8.2	8	გ ა	α . Ο .	7 1	0 0	70
DH / N II /	771	1	)	· i				7.0
pπ (3.0.)	1.14	7.33	9.26	7.66	10.62	9.59	11.29	10.10
Conductivity (umhos/cm)	561	566	1	1	2.468	1	1	1
Alkalinity (mg/l)	44	46	•	1	1	!	l	
Hardness (mg/l)	104	98	1	ı	I	l	1	
Water quality characteristic observations and an actual beautiful.	tions and a	05 20.4 5						

Water quality characteristic observations ended on day 1 because of complete mortality of fish on day 1.

<sup>2</sup>Water quality characteristic observations ended on day 1 because of complete mortality of fish on day 0.

% Sample:	99	٥	10	0	
Parameter	Day 0	Day 1 <sup>2</sup>	Day 0	Day 1 <sup>2</sup>	
Temperature (°C)	25.2	24.4	24.2	24.2	
Dissolved oxygen (mg/l)	7.9	7.9	7.8	7.9	
рН (S.U.)	11.71	10.43	11.99	10.74	
Conductivity (umhos/cm)	ı	1	$37,300^3$	1	
Alkalinity (mg/l)	1	I	$4,450^3$	1	
Hardness (mg/l)	1	I	193	1	
2,					

<sup>2</sup>Water quality characteristic observations ended on day 1 because of complete mortality of fish on day 0.

<sup>3</sup>Analysis performed at separate analytical laboratory; value is arithmetic mean of analyses of 2 replicate samples.

Table 8. Percent mortality of *Daphnia magna* exposed to selected concentrations of Bay Harbor CKD seep discharge sample from September 8-10, 2004.

% Mortality after

			TO THIS I CAN	, 4,10,		
% sample	Contact	9 sec	2.5 min	24h	48h	Sum
0*	0	0	0	0	0	0
0.1	0	0	0	0	0	0
1.0	0	0	0	0	0	0
10	0	0	100			100
30	0	100				100
60	100					100
100	100					100

<sup>\*</sup>Control was aerated, activated carbon-filtered Lansing city water.

Table 9. Percent mortality of fathead minnows exposed to selected concentrations of Bay Harbor CKD seep discharge sample from September 16-20, 2004.

% Mortality after

% Sample	Contact	3.5 Min.	1h	24h	48h	72h	96h	Sum
0*	0	0	0	0	0	5	5	5
1.0	0	0	0	0	0	0	0	0
10	0	0	35	100				100
30	0	100						100
60	100							100
100	100							100

<sup>\*</sup>Control was aerated, activated carbon-filtered Lansing city water.