

Screening of Groundwater Contaminants Discharging to Urban Streams



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ABSTRACT

In urban and industrialized areas, groundwater-quality impacts to surface-water ecosystems have been generally detected as a consequence of land-based investigations of groundwater contamination. Beyond the local scale, there have been few studies that have examined the nature and extent of contaminant loading to aquatic ecosystems from groundwater discharge. In this preliminary study, we report on an approach to screening urban streams at the reach-scale for a range of contaminants in discharging groundwater. Both known and previously-unknown groundwater contaminant plumes were detected and roughly delineated in each of the three streams tested, using this screening methodology. These preliminary findings suggest that this approach may be useful for assessing cumulative effects of contaminated groundwater discharging to surface water ecosystems.

RÉSUMÉ

Dans les régions urbaines et industrialisées, les impacts de la qualité de l'eau souterraine sur les écosystèmes d'eau de surface ont été, de façon générale, constatés à la suite d'enquêtes sur le terrain menées consécutivement à une contamination de l'eau souterraine. Abstraction faite de celles effectuées à l'échelle locale, peu d'études ont été entreprises pour examiner la nature et l'étendue de la charge des contaminants provenant des vidanges de nappe souterraine dans les écosystèmes aquatiques. Dans la présente étude préliminaire, nous nous appuyons sur une approche qui consiste à examiner les ruisseaux en milieu urbain à l'échelle du secteur pour une variété de contaminants se trouvant dans des vidanges de nappe souterraine. À partir de la présente méthodologie d'évaluation, les panaches de contamination de l'eau souterraine, dont certains étaient connus et d'autres étaient jusqu'ici inconnus, ont été détectés et schématiquement délimités dans chacun des ruisseaux. Ces constatations préliminaires suggèrent que cette approche pourrait s'avérer utile pour évaluer les impacts cumulatifs des vidanges d'eau souterraine contaminée dans les écosystèmes d'eau de surface.

1 INTRODUCTION

Urban settings accommodate a host of activities and sites commonly associated with groundwater contamination (e.g. manufacturing, dry-cleaning, sewage transport, road salting, gas stations, landfills, etc.). Groundwater contaminants from such activities are known to discharge to surface water bodies (e.g. Vroblesky et al., 1991; Lorah and Olsen, 1999; Conant et al., 2004; Chapman et al., 2007), where they may adversely affect aquatic ecosystems. Microbial activity resulting from the presence of contaminants may also cause changes (e.g. pH, dissolved oxygen, iron and concentrations of other metals) to ambient groundwater conditions (e.g. Wiedemeier et al., 1999; Chapelle, 2001) and may compound the adverse effects of the discharging groundwater contaminants. The loading of contaminants to surface waters is a concern for protecting both organisms that reside within the open water column (e.g. fish, many invertebrates, algae) and benthic communities. However, consideration of the effects of discharging contaminated groundwater are likely more critical in the hyporheic zone (e.g. Harvey and Wagner, 2000) which is found below and around the surface water body; where groundwater and surface water interact. In this zone many organisms, particularly benthic invertebrates, live all

or part of their lives (Hancock et al., 2005). The majority of burrowing aquatic life resides within the first metre of the streambed surface (Williams and Hynes, 1974; Hynes, 1983). Many fish species (e.g. salmonids) also deposit their eggs in the upper portion of this zone (i.e. near the sediment-water interface). In the hyporheic zone, concentrations of contaminants are commonly higher than the overlying surface water where rapid dilution (Greenberg et al., 2002; Conant et al., 2004), entrapment in sediments (Smith and Lerner, 2008) or volatilization to the atmosphere (Chapman et al., 2007) provide mechanisms to maintain surface water contaminant concentrations at significantly lower levels than the corresponding groundwater discharge.

Available studies of groundwater contamination discharging to surface water have generally focused on delineating individual groundwater plumes originating from particular sites (e.g. Vroblesky et al., 1991; Lorah and Olsen, 1999; Conant et al., 2004; Chapman et al., 2007). Only a few studies have reported on widespread loading of groundwater contaminants to streams in urban or highly industrialized settings. Kim and Hemond (1998) collected stream samples at a spacing of tens-to-hundreds of metres throughout an industrialized watershed in Massachusetts (US). Ellis and Rivett (2007) collected groundwater from sediments below the River

Tame, Birmingham (UK), using in-stream piezometers at a spacing of greater than 200 m along the stream. Both studies focused on estimating the contaminant loading of some common volatile organic contaminants (e.g. chlorinated solvents and petroleum aromatic compounds).

The extent to which benthic ecosystems in urban streams are affected by groundwater contamination is not well known. To assess this issue beyond the site-scale, a general understanding of the status of urban streams is required with respect to the extent and concentrations of various contaminants discharging from groundwater. The objective of this preliminary study was to develop and test a method for rapidly screening streams at the reach scale for a range of groundwater contaminants discharging to aquatic ecosystems. The emphasis of the screening was to determine the nature and approximate extent of contaminated groundwater discharge and not necessarily to characterize and delineate individual plumes in detail.

2 METHODOLOGY

Three urban streams were examined for the initial phase of this study. The streams were located in Angus, Ontario (see Conant et al., 2004); Amherst, Nova Scotia; and the Halifax Regional Municipality (HRM), Nova Scotia. The streams were primarily selected for opportunistic reasons; however, all three streams had a known area of groundwater discharge containing chlorinated solvents. These areas of known contaminated discharge allowed for the screening methodology to be tested for its ability to detect and approximate the extent of the known plumes. The sections of the three streams that were examined also varied in their physical characteristics. At the time of sampling the Angus stream was approximately 10 to 15 m wide and up to 1.5 m deep; the Amherst stream was approximately 1 to 2 m wide and less than 30 cm deep; and the HRM stream was approximately 10 m wide and up to 3 m deep.

Samples of discharging groundwater were obtained from stream-based positions using a drive-point technology to sample below the stream bed. Considering the project objectives, sampling below the streams provided several advantages over conventional land-based options for groundwater sampling. In particular, the sampling strategy allowed groundwater contaminants to be measured directly at the receptor and avoided land-access issues.

Groundwater from below the streambed was sampled using a mini-profiler system, which was driven into the sediment using a hand-held battery-operated hammer-drill (Figure 1). The mini-profiler was similar, but larger, to the one used by Conant et al. (2004). It consisted of one or more coupled hollow steel-rods (5/8" diameter) attached to a stainless drive-point with several rows of screened ports and a solid tip (Figure 1). The ports were internally connected to a 1/4" polyethylene tube that ran through the remainder of the rod to a peristaltic pump at the surface. Stream water was pumped down the tubing and out of the ports during emplacement to minimize clogging of the ports. Once the drive point reached the desired sampling depth, flow was reversed to

purge the lines and begin sampling. Subsurface water was then withdrawn with the pump at a low-flow setting to minimize losses of volatiles. Physicochemical properties (i.e. dissolved oxygen, pH, temperature, and electrical conductivity) were also monitored and measured using hand-held meters. If mixing of surface water with groundwater was suspected, the mini-profiler was advanced deeper and the pumped water re-examined. This monitoring of physicochemical properties also provided an indication of when the system was purged of surface water used while emplacing the mini-profiler.



Figure 1. Sampling drive-point (left) and installation below streambed from an inflatable boat (right)

The groundwater-surface water interface was targeted as the primary sampling location for this study. Following Triska et al. (1989), the groundwater-hyporheic interface, rather than the sediment-water interface, was used to demarcate the downstream boundary for groundwater (i.e. the groundwater discharge point). Under this definition, subsurface water in the hyporheic zone was not considered groundwater but rather transitional water between groundwater and surface water. Therefore, contaminant concentrations here could be diluted in comparison to the background groundwater. In addition, the hyporheic zone is characterized by considerable geochemical and biological activity (e.g. Jones and Mulholland, 2000) that may potentially attenuate or transform various contaminants. There is also evidence of greater sorption and degradation in the surface sediments of stream beds (Dahm et al., 1998; Conant et al., 2004; Smith and Lerner, 2008). Thus, sampling near the groundwater-hyporheic interface, and avoiding the hyporheic zone where possible, provided the best representation of the contaminant loading from groundwater discharge before any dilution or attenuation could occur in the hyporheic zone.

The base of the hyporheic zone can be defined in various ways depending on the purpose (e.g. Harvey and Wagner, 2000). In this study the groundwater-hyporheic boundary was defined operationally in terms of the contrast in physicochemical properties (primarily dissolved oxygen concentration and electrical

conductivity) between the subsurface samples and the overlying surface water. For the three streams examined in this study, the groundwater-hyporheic interface was determined to commonly be between 25 and 50 cm below the stream bed and samples were generally obtained from these depths.

Sampling was focused near the shorelines of the wider streams and, depending on the stream depth, was obtained either from an inflatable boat (e.g. HRM, Nova Scotia) or from the shoreline or the stream by wading (e.g. Angus, Ontario). The stream in Amherst, Nova Scotia was small and shallow enough that sampling was performed along the midline of the stream by wading. Spacing between samples along the stream was approximately 10 m. This spacing was chosen somewhat arbitrarily based on an informal examination of the widths of documented plumes (e.g. Wiedemeier et al., 1999; Conant et al., 2004). For the purposes of this study, a 10 m spacing was deemed to provide an appropriate balance between plume detail and stream coverage. In general, sample spacing should be selected based on site conditions and objectives. The sampling locations in this study were georeferenced using a survey-grade GPS system (i.e. Magellan ProMark3).

Collected water samples were field preserved where appropriate and analyzed for a suite of common groundwater contaminants and basic geochemistry using standard analytical methods.

3 RESULTS & DISCUSSION

3.1 Assessing the Method

The known chlorinated-solvent plumes were detected and approximately delineated in each of the three streams. The widths of the plumes entering the streams appeared to range between 30 m and 60 m, indicating that contaminants were found in multiple samples. Previously unknown zones of contamination and/or unidentified contaminants were also identified in each of the three streams. In some cases the detection of unknown contaminants was not surprising based on known associations (e.g. 1,1,1, Trichloroethane or TCA and 1,4 dioxane). The maximum concentrations observed for a selection of contaminants are given for each site in Table 1. Because of the screening nature of this study, these maximum values should not be interpreted as maximum plume concentrations. Higher concentrations may exist at different locations or depths than those sampled. Further, the actual concentrations for groundwater discharging across the stream sediment interface may be lower due to various attenuation mechanisms potentially active in the hyporheic zone. It is also important to emphasize that no significant concentrations of contaminants were detected in corresponding samples of stream water in any of the three streams. Further information for each site is discussed in the following section and the HRM stream is discussed in greater detail.

It is anticipated that further experience and optimization of the field approach will improve productivity; however, for this initial developmental stage the average productivity (from an inflatable boat or

wading) was between 120 m and 150 m of stream length per day (or approximately 12 to 15 samples) with a 3-person crew. Actual daily productivity varied as each site presented its own particular set of challenges.

Table 1. Maximum observed concentrations of selected parameters ($\mu\text{g L}^{-1}$) measured in groundwater collected below the identified streams.

Parameter	Angus ON	Amherst NS	HRM NS
PCE	68	0.6	2500
TCE	7	207	1400
cis-DCE	157	106	2800
1,1-DCE	1	68	17
Trichloromethane	nd	nd	19
1,1,1-TCA	nd	90	nd
1,1-DCA	0.5	74	nd
1,4-dioxane	nd	45	nd
Benzene	0.2	0.4	410
Ethylbenzene	0.3	nd	2000
Naphthalene	0.6	nd	64
MTBE	20	nd	4
DIPE	0.2	nd	0.3
Nitrate	5000 ^c	4700	13 000
Phosphate	120	110	390
Chloride	167 000	126 000	3 600 000
Iron	33 000	17 000	146 000
Arsenic	Pending	Pending	154
Cadmium	Pending	Pending	2
Chromium	Pending	Pending	2
Cobalt	Pending	Pending	36
Copper	Pending	Pending	4
Lead	Pending	Pending	4
Molybdenum	Pending	Pending	6
Nickel	Pending	Pending	17
Selenium	Pending	Pending	4
Vanadium	Pending	Pending	18
Zinc	Pending	Pending	171

^cless than stream value

nd-concentrations below analytical detection

Quality assurance of the analytical results showed some evidence of minor carry-over of VOCs (volatile organic compounds) from locations with high contaminant concentrations to field blanks and potentially subsequent samples. The concentration in field blanks and samples with suspected carry-over were all below $1 \mu\text{g L}^{-1}$. A strict quality control and assurance protocol (e.g. new tubing for each location) would remedy this issue; however, it would considerably reduce the sampling rate. Given that sampling speed was one of the primary considerations in the development of this screening method, some low-level carry-over was deemed acceptable for the purposes of this study.

3.2 Assessing the Sites

Angus, Ontario

Groundwater sampling in Angus provided an opportunity to evaluate the screening methodology against a well characterized plume discharging to an urban river. Conant et al. (2004) mapped the lateral extent of the plume, originating from a former dry-cleaning facility, by collecting 80 groundwater samples from 30 cm below the stream bed using approximately a 2 m x 4 m grid pattern. Groundwater sampling from this current study identified a zone of approximately 50 m in length along the stream's east bank where tetrachloroethene (PCE) and its degradation products (e.g. trichloroethene, TCE and cis-dichloroethene, c-DCE) were detected. The area coincided with the plume detailed by Conant et al. (2004). Concentrations reported by Conant et al. (2004) for PCE and its degradation products were often greater than 1000 µg L⁻¹. The maximum concentrations observed from this study (Table 1) were at least an order of magnitude lower. However, the higher concentrations reported by Conant et al. (2004) tended to be offshore by several metres from where samples were collected for this study. The apparent discrepancy in concentrations may simply be the result of missing the high-concentration zones or may indicate a temporal or permanent decline in plume concentrations. No evidence of the plume was found from samples collected near the west bank, where Conant et al. (2004) reported contaminants only at very low concentrations.

In addition to the detection of chlorinated solvents, previously undocumented BTEX (benzene, toluene, ethylbenzene and xylene) and naphthalene were found at low concentrations in the plume area. An unidentified hydrocarbon source or mixed source with the PCE are possible explanations. Farther up-stream of the known plume, one sample location had detectable levels of MTBE (methyl tert-butyl ether) and DIPE (diisopropyl ether); both fuel oxygenates. There were no detectable levels of other volatile petroleum hydrocarbons detected in this area (e.g. BTEX, naphthalene, tri-methyl benzenes, etc.). The relative resistance of MTBE to biodegradation (e.g. Schirmer and Barker, 1998) and sorption (Squillace et al., 1997) compared to BTEX compounds suggest the detection of fuel oxygenates could represent the leading edge of a petroleum plume or represent the remnants of an historical plume. Additional sampling in this area would be needed to determine the exact nature of this contamination.

Dissolved oxygen was less than 0.7 mg L⁻¹ for all groundwater samples compared to 7 to 8 mg L⁻¹ for the stream water.

Amherst, Nova Scotia

The Amherst location provided an opportunity to test the performance of the screening methodology under slightly greater uncertainty than found at the Angus site. As is generally the situation, no direct information was available regarding the contaminant levels in the groundwater discharging to the stream. However, the stream section sampled (175 m in length) was found at the downstream boundary of a relatively well characterized contaminated site. Contamination at this site is associated with a former aerospace facility (until recently a registered federal contaminated site) where chlorinated solvents were

routinely used for degreasing and other industrial applications. The dominant chlorinated solvents detected in the groundwater below this small stream were TCE and 1,1,1-TCA (1,1,1-trichloroethane) and their degradation products. The detection of chlorinated solvents at various concentrations in all 15 samples collected was not unexpected. The compounds were consistent with the known usage at the adjacent site and previous site assessments had occasionally detected low concentrations of particular solvents in surface water samples.

The compound 1,4-dioxane was also found in most of the samples. This compound is a common co-contaminant with 1,1,1-TCA, and TCE; however, it is not routinely analyzed for and has not been previously identified at the site. The 1,4-dioxane concentrations were positively correlated with both 1,1,1-TCA and TCE concentrations, as expected.



Figure 2. Schematic of HRM stream, surroundings and sampling locations (approximately 10 m apart measured along the stream axis). Numbers refer to sample stations.

Dissolved oxygen of the samples ranged from 0.25 to 7.8 mg L⁻¹, compared to 9.6 mg L⁻¹ in the stream water indicating some mixing with surface water (i.e. hyporheic exchange) in several samples.

Halifax Regional Municipality (HRM), Nova Scotia

The stream located in the HRM was the longest (i.e. approximately 650 m) of the three stream sections screened in this study. Figure 2 shows a schematic of the sampling locations and zoning in the area surrounding the HRM stream. The stream is salmon bearing and efforts continue to be made to restore fish stocks to historical levels. With the exception of one historical dry-cleaning operation with known groundwater contamination, no other groundwater contamination was known or suspected along the reach examined. These circumstances provided a setting to evaluate the screening method's ability to detect groundwater contamination without prior knowledge.

The concentrations for selected contaminants observed in groundwater below the stream are shown in Figure 3. Groundwater samples containing PCE and its degradation products were located primarily between stations 5 and 25. These locations were downstream of a former dry cleaning operation with known groundwater contamination. Although not shown, the plume width was wider based on c-DCE (e.g. ~ 50 m) concentrations than PCE or TCE (e.g. ~ 30 m), suggesting that dechlorination has been occurring within the subsurface. Coincident with the chlorinated solvent plume, a previously unknown (or undisclosed) petroleum plume was also detected from BTEX, TMB (trimethylbenzenes) and low concentrations of MTBE. The petroleum plume is likely associated with current and/or historical fuel storage in the area.

Another unknown petroleum-based plume was detected farther up-stream (~ stations 48 to 55). The characteristics of this plume differed from the previous petroleum plume in terms of the relative proportions of the BTEX compounds, TMBs and fuel oxygenates (i.e. MTBE and DIPE). This may reflect compositional differences in the petroleum source or may reflect other specifics related to the plume's release and evolution in the subsurface (e.g. release history, local geology, intrinsic biodegradation status, etc.). Regardless, the differences may assist in identifying and/or distinguishing the sources of the various petroleum plumes along the stream. Detectable levels of MTBE were also found in three samples (~ station 42 to 44) that showed no other petroleum compounds. The MTBE could indicate the leading edge of a plume (as discussed previously for the Angus site) or the remnants of an older plume where BTEX and other compounds have been degraded up-gradient. Low concentrations of chlorinated solvents were also detected in the vicinity of the second petroleum plume.

High chloride (e.g. greater than 230 mg L⁻¹) and corresponding sodium concentrations were detected in most groundwater samples collected below the stream (Figure 4). The proximity of a major road adjacent to the stream (i.e. left side of Figure 2) suggests that road salt is the likely source. Melting of salt-contaminated snow at the shoreline is not believed to be a viable explanation for concentrations detected in these samples, which were collected in late September. It is suspected that the chloride concentrations reflect long-term groundwater contamination in this area.

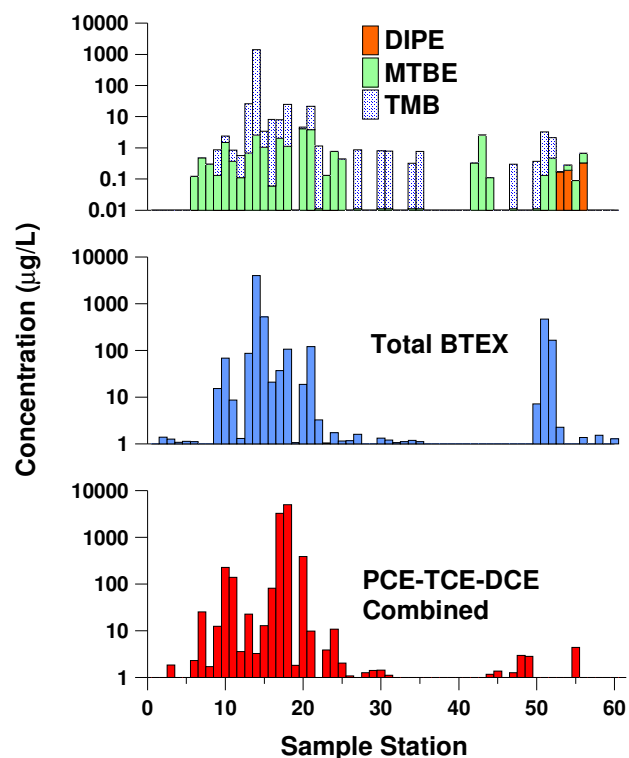


Figure 3. Observed concentrations for select contaminants in groundwater collected below the HRM stream. See Figure 2 for station locations.

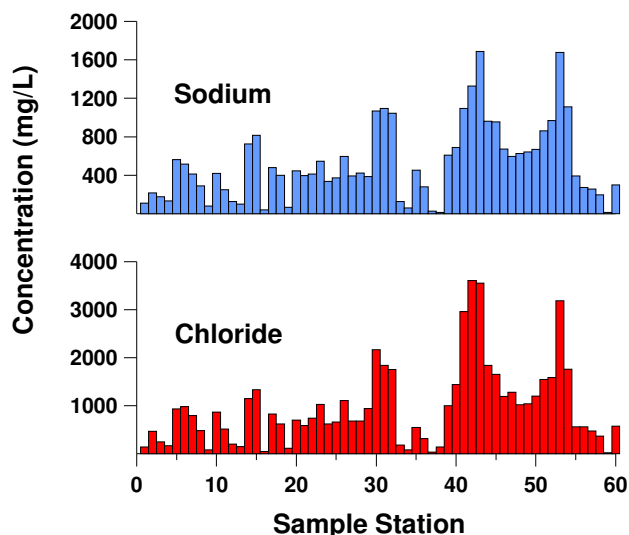


Figure 4. Observed concentrations of sodium and chloride in groundwater collected below the HRM stream.

Elevated nitrate concentrations were detected in several locations (Figure 5) although a clearly identified source was not determined. Lawn-care products and leaking sewage infrastructure are two possible sources suggested when nitrate is interpreted in combination with

other analyses such as silver, cadmium and chloroform (not shown). Cadmium has been identified in both fertilizers and sewage (Lymburner, 1974), silver in fungicides and water treatment devices as an antimicrobial (Health Canada, 1986), and chloroform in fumigants and insecticides (Fetter, 1999). Chloroform detected down-stream (e.g. between station 5 to 25) is likely a degradation product of carbon tetrachloride (e.g. Wiedemeier et al., 1999) associated with the historical dry-cleaning operation previously discussed. Additional sampling for nitrogen isotopes or other compounds (e.g. pesticides and/or pharmaceuticals) could help resolve the nitrate source.

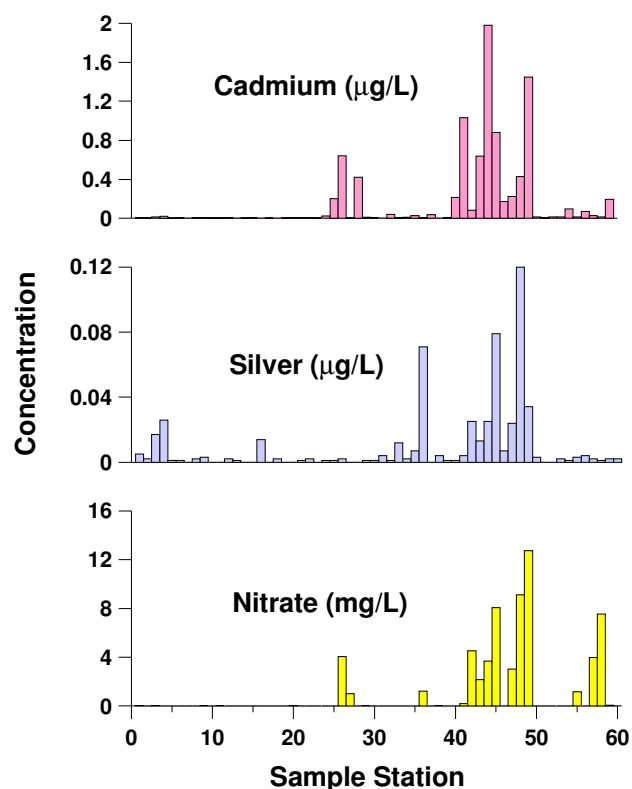


Figure 5. Observed concentrations of cadmium, silver and nitrate in groundwater collected below the HRM stream.

Two areas with elevated phosphate (i.e. greater than 0.1 mg L^{-1} ; the detection limit available in this study) were also detected between stations 1 and 10 and between 25 and 40 (Figure 6). Leaking sanitary sewers are suggested as a possible source of this phosphate. In general the water chemistry in these two areas appears distinctly different than other sections of the stream. Sodium, chloride (Figure 4) and strontium (not shown) were generally lower in areas of elevated phosphate. Approximately coincident with the elevated phosphate were relatively elevated concentrations of lead (not shown), zinc (not shown), and copper; a relationship consistent with water associated with municipal distribution systems (e.g. Méranger, 1981; Health Canada, 1979, 1992a, 1992b). The detection of elevated

boron (not shown), used extensively in cleaning products (Health Canada, 1990), provides additional support for a waste water source.

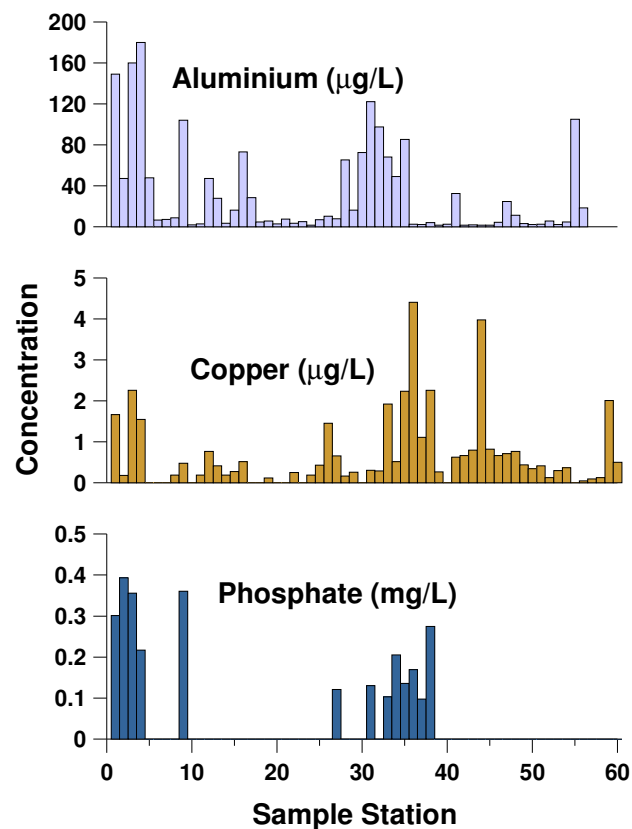


Figure 6. Observed concentrations of aluminium, copper and phosphate in groundwater collected below the HRM stream.

The observed concentration of aluminum provides further insight into the phosphate source discharging to the HRM stream. The drinking water supply in the HRM is from surface water which presumably would be reflected in the chemical composition of the water from leaking supply mains and sanitary sewers. Miller et al. (1984) reported that only 9% of groundwater drinking supplies (pre-treatment) sampled had aluminum greater than $14 \text{ } \mu\text{g L}^{-1}$ compared to 78% of surface water supplies. The use of alum in water treatment systems may further contribute to the aluminum concentrations in finished water (e.g. Health Canada, 1998). It is suggested that the elevated aluminum found in the vicinity of high phosphate concentrations originated from leaking sanitary sewers. An examination of the locations of local sewer infrastructure combined with additional sampling would be required to confirm the phosphate source.

Elevated levels of other metal species, particularly iron, manganese (not shown) and arsenic, were detected in a number of locations (Figure 7) below the HRM stream. Most of these coincide with the

locations of petroleum and chlorinated solvent plumes (Figure 3) discussed previously. Occurrences of high background concentrations of arsenic are known in the area (e.g. Grantham and Jones, 1977); however, it is suggested that the elevated arsenic observed in this study results from the release of natural arsenic by reductive dissolution of hydrous ferric oxides (HFO). In this process arsenic is mobilized as HFOs dissolve in response to the development of reducing conditions from the degradation of organic contaminants in the aquifer. A correlation between iron and arsenic consequently is observed. This mechanism has been well documented in the context of landfill leachate plumes (e.g. Stollenwerk and Coleman, 2004) but limited information appears readily available related to petroleum or chlorinated solvents plumes. This aspect will be explored further as the study progresses.

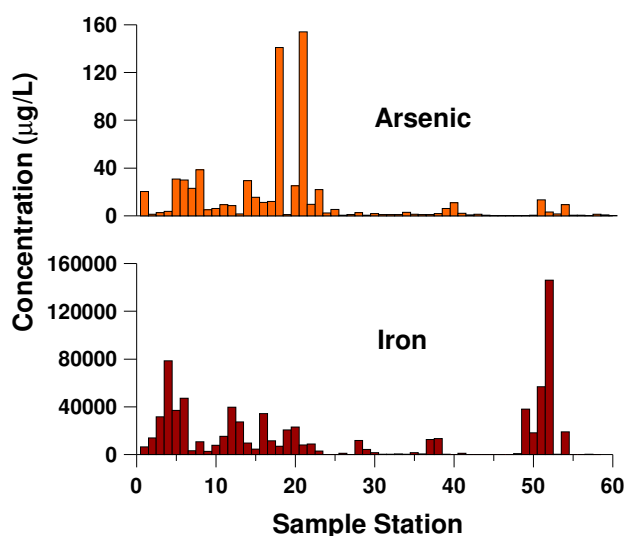


Figure 7. Observed concentrations of arsenic and iron in groundwater collected below the HRM stream.

When groundwater contaminants are considered collectively for the HRM stream, it is found that virtually the entire stream section examined has one or more parameters that would exceed protection-of-aquatic-life guidelines used in Canadian jurisdictions (see Figure 2).

4 SUMMARY

In the three streams examined, known groundwater plumes were detected and roughly delineated using the screening method developed for this study. In addition, unknown contaminants and/or previously unknown groundwater plumes were detected under each of the streams examined. In the case of the HRM, the results demonstrated the utility of the screening approach as a tool for assessing the cumulative effects of groundwater discharging to the stream. This study is continuing by expanding the network of streams examined and engaging the benthic ecology community to assess

impacts of groundwater discharge on benthic communities. The overall goal of these endeavours is to develop some national perspectives on the effects that groundwater quality has on Canadian urban streams and their associated aquatic ecosystems.

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