Assessing an anthropogenic impact on Etobicoke Creek: the separated flow approach

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Abstract

This paper covers an attempt to apply the separated flow approach to water quality assessment. Separation of flow implies adequate allocation of the polluting sources in time and space. Hydrological requirements to the water quality samples and the conformance of available data with these requirements are considered as well. The SimpleBase model was used for river flow delineation into three generic components: baseflow, inter flow and surface flow. The separated flow approach was applied to Etobicoke Creek to assess the natural background and the anthropogenic impact of heavy metals in the river flow. The anthropogenic impact on the Etobicoke Creek flow in terms of additional burden of heavy metals to the natural background is amounted to 30, 80, 92, 95, 84 and 62% of the total yearly volume of arsenic, cadmium, and chromium, copper, lead, and mercury, respectively.

Introduction

The objective of this investigation and assessment is to assess daily concentrations and loadings of heavy metals in the creek flow using separated flow approach and assess the anthropogenic impact of these metals.

Heavy metals, being the top-priority pollutants are monitored in all environs: air, water, ground and biota. The watershed or hydrological approach to the environmental assessment provides the needed plentitude and system in measurements to identify the pollutants pathways and presence in a river flow. The approach implies that watershed (i.e. drainage basin of a river) is the source of all substances in the river outflow. In other words, the chemical content of water transported from drainage area for any time period is conditional to all bio-chemical and hydrophysical processes occurring within the area and stream itself during the specified time period. The yearly hydrograph of a river flow, the quantitative representation of the hydrological cycle of the particular watershed, is a result of weather (climate) cycle. Therefore, it is also a schedule for bio-chemical cycles occurring within the watershed and stream eco-system. Adequate delineation of the hydrograph allows allocating sources of water quantity and quality into permanent groundwater discharge, temporary surface and interflow: the discharge from the perched groundwater, from the zone of weathering adjoined to a river valley, and its alluvial deposits. Although the water quality monitoring in Canada does not refer to hydrological cycle and river regime, an interpretation of available data in terms of their pertaining to the particular water cycle event might be very informative and useful.

The plan of this paper is the following:

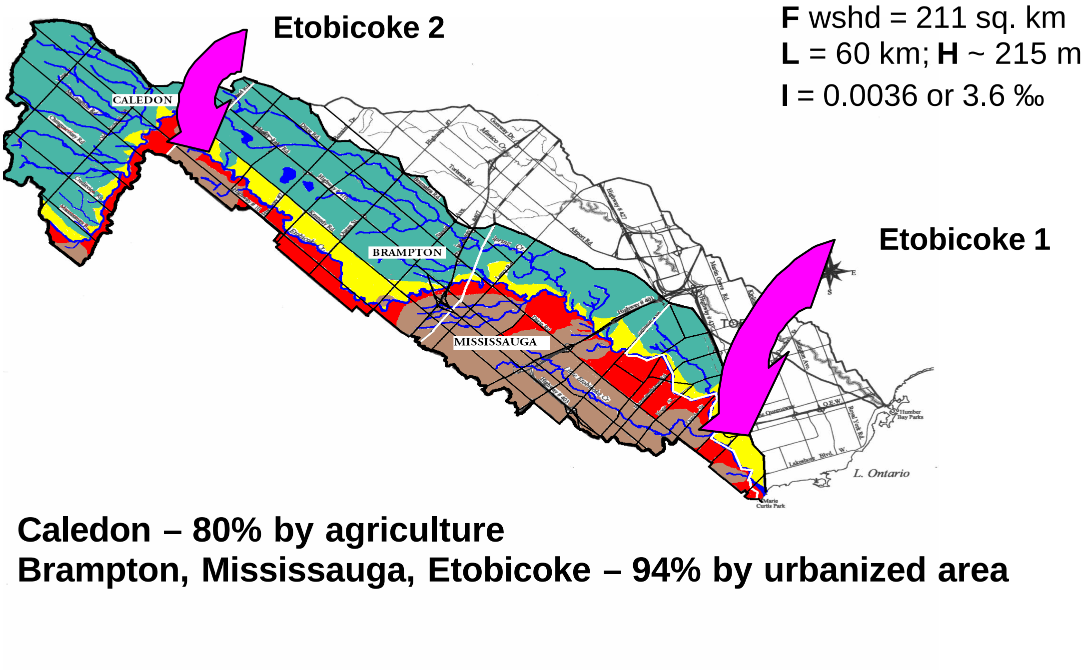
1. Description and quantitative estimation of the anthropogenic stress at the Etobicoke watershed
2. The examined elements (list of chosen heavy metals)
3. Dataset required for Etobicoke Creek to conduct the assessment in accordance to the standard watershed approach (based on the Russian standard*)
4. Gap analysis (based on the Russian standard*)
5. Separated flow approach as the assessment solution
6. Findings (Result of assessment)
7. Reliability of the result and ways of its improvement
8. Natural background and anthropogenic impact assessment, evaluation of aquatic habitat condition in Etobicoke Creek
9. Conclusions

** - Russian standard requirements and gap analysis based on these might be interesting for the engineers and scientists dealing with different methods of environmental assessment, water quality monitoring services, etc.*

1. Etobicoke Creek watershed: description of the anthropogenic stress

Etobicoke watershed is located within the Greater Toronto Area, which in turn is a part of a larger Great Lakes Basin (State of the watershed report, 1998). The creek watershed drains a total area of 211 km^2 and flows 60 kilometers before discharging into Lake Ontario (fig.1).

Fig.1 Etobicoke Creek watershed



There are four administrative (governing) territories on Etobicoke watershed (from the river head to the mouth): City of Caledon – 26%, City of Brampton – 34%, City of Mississauga – 33% (31% of which are occupied by Lester B. Pearson International Airport), and City of Toronto – 7%. The area of the City of Caledon almost coincides with upper subwatershed, 80% of which is an agricultural area. Brampton, Mississauga and Toronto represent a heavily urbanized area, 94% of which has an alternative drainage system through the storm sewage. The Table 1 (all tables are presented in the Appendix) presents distribution of population, land use and road parameters (anthropogenic burden) for both areas obtained from the tourist maps of Caledon, Brampton, Mississauga and Toronto (M: 1:25 000). Population info is accepted from the State of the Watershed report. The earth-roads were not taken into account in the Table 1. Lawns area is included in residential, industrial, business and government areas. For rough assessment of this area the following coefficients were used: 0.5 for the residential areas, and 0.1 for the others. There are five golf courses in the creek valley and 8 waste disposal locations situated within urbanized area.

The surficial geology of the watershed is primarily till moraine. There is an esker sized as 6 x 1.3 km in upper part of the lower, urbanized subwatershed. Both subwatersheds are similar in natural geo-morphological conditions, therefore, the principal difference in elements regime can be mainly associated with different land uses in these two regions.

2. The examined elements

Heavy metals, such as lead, zinc, iron, copper, nickel, cadmium and mercury, are listed as the pollutants for the Etobicoke Creek along with particulates, organic matter, pesticides, chlorides, nitrogen and phosphorus (State of the watershed report, 1998).

Cadmium, mercury, lead and arsenic have a cumulative effect as they move through the biological chain (Guseva et al, 2000). Excess of chromium, copper, lead and mercury points at industrial and medical waste, landfills, road traffic and dump sites (Banat and Howari, 2003; Karlén et al., 2002; Kishe and Machiwa, 2003; Lozano et al., 2003; and Muohi et al., 2003). Leaching of cadmium and mercury from rocks and suspends, dumps and landfills is sensitive to acidic condition (Prokop et al., 2003; Guseva et al, 2000). Leaching of arsenic, on the contrary, happens under the basic condition, when pH >8.3 (Anawar et al., 2003). Cadmium, chromium and copper react with chlorides, abundance of which (comparing with the natural background) in streams of Southern Ontario is caused by use of road salts for de-icing, snow melting and dust suppressing purposes (Road Salt, 2000). A lawn watering in summer using the municipal sources of water adds chlorides to the creek drainage system as well. The question that arises then is: can the excessive amount of chlorides in Etobicoke Creek cause additional leaching of the elements? Cadmium creates introverting relations like $2CdCl$? $Cd[CdCl_4]$. Copper creates dissolved ions of $CuCl^{2-}$, $CuCl^{3-}$ and $CuCl^{4-}$ under abundance of Cl^- in the water. Can the condition of the Etobicoke Creek outflow: 26 000 tons of chlorides per year (Vedom, 2002) be considered as abundance of chlorides? Chromium generates chloride/carbonate complexes absorbed by clay particles, for which till moraine is the excellent permanent source. Lead has preference to neither acidic nor basic condition: its transformation from suspended to ionized form depends on combination of chemicals and pH of the flow. However, its concentration in chloride thermal water can reach several milligrams per liter (Guseva et al, 2000). Thus, a metalloid - arsenic, and five heavy metals, cadmium, chromium, copper, lead, and mercury were chosen to assess daily presence in the creek flow: Established national Canadian limits for the element concentrations are the criteria for the environmental assessment.

3. Dataset required (based on Russian standard)

The standard dataset needed for daily assessment depends on the category of monitoring station, which is determined by the conservation and sustainability of fish and its habitat of the Etobicoke Creek and the level of anthropogenic stress on its watershed.

The lower station (Etobicoke 1, F = 204 km^2) is located in the mouth of the creek within the area with a population of more than 1 million and water that is highly contaminated (see List 1 in Appendix). The creek was a traditional place for spawning and breading of several roundfish species, which are the Lake Ontario habitants. Therefore, Etobicoke 1 can be identified as the station of the first category (Table 2). The first category station provides dataset from four programs: the mandatory full program and three short programs. Sampling frequency for each element depends on its position in the priority list of contaminants for each particular station, which should be established after the first year reconnoitering measurements and observations (we will consider the list mentioned in the beginning of previous paragraph as the priority list for Etobicoke 1). As a part of the mandatory program (Table 3) heavy metals should be measured at any station seven times a year covering main phases of the river regime: spring flood (on increase, at peak and on decrease), summer lowest flow and any storm flood, autumn pre-ice cover period, and the lowest winter flow (Appendix, Fig. 1, left section).

Natural weather-water-bio-chemical cycles are tightly interrelated. A spring flood, generally, indicates the beginning of vegetative and breading periods. Rain floods, depending on water temperature are always the time- or way-marks for biota. That is why major turning points of the natural water cycle should be measured and recorded. A pollution process is not caused by any natural cycle. That is why the polluting element should be measured monthly (12 samples a year) in addition to the mandatory program in frame of the third short program together with all other pollutants (pollution priority list), water discharge, velocity, temperature, pH, concentration of suspended substances, dissolved oxygen, BOD_5, and visual observation. All of our elements except arsenic are pollutants for the Etobicoke 1 (line “Avg” in the Table 4 clearly indicates this: average daily concentrations excess the Aquatic Life limits). As one of 23 main contaminants for the examined station, the element should be measured every decade (36-37 times per year) in frame of the second short program along with water discharge, temperature, pH, electrical conductivity, concentration of suspended substances, COD and BOD_5, and visual observation. It is difficult to say without the quantitatively established priority list which one, if any, of the examined elements is the main contaminant for this station. Lead seems to be one of the candidates. Regardless, whether it is the main contaminant or not, the corresponding flow condition measured every decade with main pollutants provides transition to decadal concentrations of the elements measured monthly and in frame of the mandatory program. The first short program provides measured condition of the flow, or daily program for the first category station, includes water discharge, temperature, dissolved oxygen, electrical conductivity, and visual observation. This provides transition of sample concentrations measured per phase, monthly and decadal to the daily water conditions for the first category station.

The upper station (Etobicoke 2, F = 63.4 km^2, represents the Caledon area) can be associated with the station of second category (in areas of moderately contaminated water used by fish for spawning and breading) or even third one (it is located around the city with population < 0.5 million people and low polluted water). In order to be more specific about the level of contamination, it is necessary to estimate the integrated index of hydrochemical contamination (IHC).

$$IHC = \sum_{i=1}^{n} \frac{Ci/MAC}{n}$$

where

Ci – concentration of i-element

MAC - Maximal Allowed Concentration of i-element

n - number of elements (usually 6-7 elements, mandatory ones from which are dissolved oxygen, pH, and BOD_5).

There are no BOD or COD measurements at Etobicoke 2 as there are no chlorides which are the main pollutants for any station in southern Ontario due to the regular use of road salt. Measured values of dissolved oxygen, pH, ammonium, phosphorus, phenols and lead averaged for the period (1990-93) were taken for that calculation. Obtained IHC (1.11) indicates the moderate level of contamination. The highest value of the index, 8.9, during the examined period was observed on May 27, 1992. This is a clear indication of the second category for the station. The second category station has the mandatory (7 times per year) and two short programs: the monthly third one for all pollutants and corresponding parameters of the flow mentioned above, and the first short program (flow condition) measured decadal. All of the elements mentioned in the pollutants list should be measured monthly (12 times/ year) plus decadal measurements of water conditions should be performed (36-37 per year), which provide a transition of measured monthly concentrations to a decadal condition. A transition from decadal to daily conditions for a station of second category is provided by a daily water discharge, temperature and a visual observation.

There are only two parameters estimated daily within any program besides visual observations. These are water discharge and water temperature. They provide a transition from sampling to daily parameters for slightly contaminated and pristine watersheds (stations of third and forth categories).

All parameters, elements or visual observations mentioned above are associated with particular time of sampling or measurements. The corresponding discharge is either measured during the time of sampling (monthly, decadal or during main phases of a river regime) or it is estimated for the particular time of measurements.

Requirements mentioned above were related to the frequency and plentitude of samplings. Now we are going to the next group of requirements – requirements to the samples themselves in terms of their conformity to general requirements and ones for the watershed approach.

According to the standard requirements for water samples, they should be:

1. measured precisely and accurate (general)
2. measured at the representative for the total flow place through the river cross-section , and
3. associated with the total discharge at the moment of sampling.

Let us check the conformance of the available data to these requirements.

For arsenic, cadmium, lead and mercury the enumerated results of measurements represent threshold of the tool's sensitivity, not actual concentrations, with notes in database "no measurable response" or "a measurable trace amount" at both stations. Chromium and copper at Etobicoke 1 are represented by ~ 50 and 100% of actual concentrations, respectively. At Etobicoke 2 these elements are represented mostly as trace amounts. Sensitivity threshold of cadmium measurements in both cases much lower than the maximal acceptable level of this element for aquatic life (Table 4). This is about accuracy required and actually performed.

For small rivers with uniform, well mixed stream, a grab sample (the only type of samples used at Etobicoke Creek) taken at the centroid of the flow (Appendix, Fig.1, central section) is usually representative for the total flow at the moment of sampling (WMO No 168, 680). The Etobicoke Creek is identified as a small one with a uniform, well mixed stream. Let accept the second requirement as a satisfied one.

In the Canadian hydrometrical database only daily average discharges are available, not the ones obtained at the moment of sampling. What difference does it make for the assessment?

Figure 2 in Appendix illustrates the variety of different daily extremal and average discharges depending on watershed size and weather conditions (two different years).

These results were obtained based on data from standard hydrometeorological network of Estonia, where extremal discharges according to standard requirements are selected among instantaneous ones, not daily averages. Daily averages were obtained for the same date, as the extremal discharges were observed. It is necessary to clarify, that higher discrepancies for minimal total discharges do not indicate higher variability of baseflow than surface flow. This observation is typical on a pre-flooding day, when seasonal baseflow reaches its lowest discharge after a long dry or cold period and meets with surface and inter flow appearing, when heavy rain or snow melting occurs. These days or days before them are exactly moments for sampling at the lowest winter and summer flow. Year maximal discharges characterize the highest flood peaks and can be completely associated with daily variation of the surface component. This should be kept in mind when date of available sample coincides with the date of the beginning of a flood, because on such a day the highest possible discrepancy between instant and average discharges occurs. Separation of flow normalizes available water quality data allocating the highest variations to the temporary events: inter and surface components of the total flow. After examining both charts, it becomes evident that discrepancies between daily average and extreme discharges for streams with drainage area larger than 2000 km^2 can be neglected, since they do not exceed 10% of the actual discharge. For both subwatersheds of Etobicoke Creek discrepancies can be very essential. The third requirement can be satisfied by estimation of proper corresponding discharges.

4. Gap analysis (based on Russian standard)

Parallel daily flow data for both Etobicoke stations was available for the periods from January 1990 to September 1993. There are no daily water temperature measurements or visual observation at both stations. Parallel water quality data for arsenic, cadmium, chromium, copper and lead (total, unfiltered, grab samples, ~ 1 sample a month) was available for the 1990 – 97 periods. Flow condition parameters such as pH, conductivity, turbidity, alkalinity, and water temperature, BOD_5 or COD were measured at the sampling time. There is no information about flow conditions between samplings as well as there was no mercury sampling at the upper station during the periods mentioned above. The period between January 1990 and August 1993 was chosen for the assessment, since its initial data was more complete than during other periods.

Number of sampling, their frequency for examined six elements is not an issue of lack of data (excluding lead at Etobicoke 1, which can be one of the main contaminant for this station and therefore should have had 40-44 samples per year). Absence of the flow condition parameters between samples and in turning points of the river hydrograph is a problem, because they provide possibility for daily assessment of heavy metals (in our case). Among those parameters are: redox potential (pE), which determines possibility of metal migration from alluvial deposits, suspends and colloids into water and back along with pH, dissolved oxygen and water temperature, BOD_5 and COD, total chemical composition and biological condition of water. There are two biological monitoring programs at stations of first and second category: the short one conducted monthly and the full one conducted quarterly (Guseva et al, 2000). For those four elements, which are accumulated through biological chain (arsenic, cadmium, lead and mercury) it is very important to know the dynamic of biomass and its structure.

There is only one parameter that can provide transition from monthly sampling to daily concentrations for Etobicoke Creek. This is daily water discharge.

The shown up non-conformances is the base for qualifying of obtained results as approximate or even rough ones. This gives "permission" not to follow the standard procedure, but use the simplified one for the assessment due to result anyway will be approximate. Separation of flow is separation of different sources of contamination or nutrition. Surface or storm flow bio-chemical composition is based on air-born and surface-deposited pollutants. Inter flow, its physical and bio-chemical features for natural streams, is the result of delayed discharge into the stream from flood plains, vegetated river banks, alluvial deposits and the perched groundwater, the zone of weathering adjoined to the river. Permanent groundwater discharge, its quantity and quality parameters are presented as a baseflow. Separation of flow declines effect of the inconformity discussed above, because each component of flow is characterized by certain condition within the amplitude of its discharge fluctuation during the specified phase, but does not eliminate it. This is adequacy issue of flow separation, which is not standardized procedure yet, but performed as a very determine one in terms of flow chemical composition (Salmon and Walter, 2001; Ladouche et al, 2001).

5. The separated flow approach as the assessment solution

The idea of the separated flow approach derives from the statement that the concentration of each contaminant transported by the flow component is determined by its pathway. The total flow concentration (sampled one) is the proportional combination of flow components depending on their presence at the moment of sampling. Detail description of the method applied here and based on the idea is given below. This has six steps:

1. **Separation (delineation) of total flow into base, inter and storm components was performed using the SimpleBase model.** The SimpleBase spreadsheet model provides delineation of the total flow into three genetic components and is based on classical theory of the river flow formation, which states that total flow is the combination of permanent ground flow discharge into the river as a baseflow, and temporary ground- and surface flow caused by precipitation or snow melting events as inter- and surface flow, respectively. Upper boarder of baseflow and lower border of surface flow within any flood event outline the interflow – local increase of water table and groundwater discharge from adjoined friable deposits due to current recharge event (rainfall or melted water release) or delay of surface flow within hydrographical network (size of watershed area, vegetation and morphology of the watershed). Either baseflow or surface flow borders within a flood event were assessed using the same linear function, but different parameters and criteria for each flow component:

   $$Q_{b,s} = Q_o + t*dQ_{b,s}$$

   Where Q_o is the initial discharge prior to the flood event (the last day when baseflow is minimal and equal to total flow, and ideally should be sampled), $dQ_{b,s}$ – daily increase of the examined flow (base- or inter-), t – duration of each component of the flood event (days), $Q_{b,s}$ – examined base or surface flow within the flood event. The criterion of baseflow separation is the highest amount of separated peaks as an indication of permanency of the groundwater discharge into the creek. The separating line between surface and ground flow flood components is determined by daily increase roughly equal to 10 baseflow ones ($dQ_s = 10dQ_b$). It is very important that examined period would be hydrologically homogeneous. Homogeneous period accepted here is a period with the same set of water management practices within examined watershed (SWM manual, 2003).

Separation of flow allows allocating flow components as well as assessing their limits for daily variation obtained as dQ (daily linear, in our case, increase of base and interflow components) for both flow components. For Etobicoke 2 daily variations of base and interflow during selected periods of 1990-93 are limited by 0.012 – 0.106 and 0.12 – 1.06 m^3/s per day, respectively. For Etobicoke 1 these are 0.126 – 0.259 and 1.26 - 2.59 m^3/s. Values of the limits (dQ_b and dQ_s) depend on topographic, geomorphologic, and hydrogeology conditions of watershed: its surface slope and roughness, type of underlying deposits, the geomorphological structure of watershed, water table ratio between average for watershed and in the examined reach, and vicinity of the drainage base (Lake Ontario in our case).

Results of flow separation for Etobicoke 1 and 2 during the period 1990-93 are presented in Table 5.

2. **Association of each available sample of a contaminant with the total flow as the certain combination of components.** This step initiates creation of the further model dataset (Vedom, 2002). Order of samples within the group (base, inter or surface) should be strictly chronological, especially for series of several years and longer, because of different types of trends that may misconduct the relations between concentration and a flow component: an ecological situation of different locations in last two decades has changed significantly. Besides, the climate trend for hydrological approach is particularly essential due to any changes in climate results in consequent alternation in quantitative water provision of bio-chemical cycles. To avoid any trend influence it is necessary to consider each year separately.

3. **Association of each sample with the season (winter, summer).**

This step is actually attempt to substitute the absent data of daily water temperature that brings under regulation all bio-chemical processes. Due to incompleteness of flow condition information per year (10-14 samples), only two seasons were used in the assessment. Presence of elements in the flow is a result of chemical and biological processes occurred along the water pathways as well as physical capacity of flow to transport them. Water, soil and air temperature, being a seasonal variation, is the main condition for the beginning and continuation of the processes. The same process may be different under different temperatures of water, air and ground (SWM manual, 2003). To estimate "switching" conditions between winter and summer "scenarios" of processes, ten-day average **air** temperature was used (the only one available daily). Air temperature supposes to be representative for the examined subwatershed or watershed. The only place of daily air temperature measurements at the watershed is Lester B. Pearson Airport, which is representative for 30% of lower subwatershed specific area. Switching condition for this particular watershed was found to be equal to 1°C in model calibration process. This is similar to climatologic or agronomical standardized procedures for estimation of season turn-over date (WMO No 100, 134). Switching of seasons were accepted the same for all elements due to scarce information of which heavy metal participate in which particular process driven by which temperature condition.

4. **Creation of relationships between discharge and a heavy metal concentration** for each flow component was considered for two-three-year periods to avoid influence of mentioned above trends. The real problem at this point is absence of samples and flow conditions at turning points of hydrograph (phases of hydrological regime) and necessity to extrapolate relationships to the maximal and minimal discharges. According to the standard, the extrapolation to the maximal discharge should not exceed 10% of the total discharge seasonal amplitude (Appendix, Fig.1, right section). For the minimal parameter this is equal to 15%. Accuracy of available samples is vital for this step. Discrepancy between daily instantaneous and average discharges comes out at this step as well.

5. **Creation of the model for daily assessment of the contaminant** for each flow component based on obtained relationships was performed using Excel spreadsheets. An example for chlorides was presented among The Sustainable City II papers (Vedom, 2002). It is necessary to say that elements naturally occurred in flow have totally different set of parameters than those invected by human as chlorides, for example. The

Water Quality Monitor Model includes several interrelated modules, some of which are changing simultaneously with the changes happening during the calibration process; some of them, such as season scenario switching and flow separation that change initial identification of dataset, are separated because of the complicity of their implementation into entire model.

6. Estimation of daily volumes of heavy metals and their conversion into specific discharges (µg/s per km^2) for upper and lower subwatersheds, monthly and yearly sums and averages. For inter and surface or storm water, obtained monthly averages of specific discharges are given per event as well (Table 6). They are very different from regular monthly averages due to variation in average duration of flood events per month for inter flow is 11 and 13 days for Etobicoke 1 and 2, respectively, and these are 5 and 2 days for surface or storm flow.

Monthly averages of an element concentration of inter and surface/storm flow (Table 6) were estimated taking into account only days when these events occurred. To get specific discharge for lower subwatershed, upper part volume for considered period (day, month or year) was subtracted from volume drained from total watershed and then divided by amount of seconds in the period and area of lower subwatershed.

6. Results

As a result of this assessment, daily concentration (Table 4), volume and specific discharge of each examined metal for two outlets of Etobicoke Creek were obtained, and then summarized into monthly (Tables 5 and 6) and yearly averages and sums (Table 7). Different units in each Table demonstrate variable use of results: concentrations can be compared with the environmental restrictions for water quality (assessment criteria); specific discharge of element is the most useful for transmission for another watershed or site assessment within the watershed or subwatershed; a load can be used for bioavailability and mass balance estimation. Comparing the results with the natural background (see Tables 4 and 7), it is possible to say that 80 million cubic meters of Etobicoke Creek's flow from 204 km^2 of its drainage area brings into Lake Ontario yearly around 87 kg of arsenic, 59 kg of cadmium, 336 kg of chromium, 1230 kg of copper, 1640 kg of lead and 3.2 kg of mercury, from which 80% of arsenic, 20% of cadmium, 11% of chromium, 9% of copper, 22% of lead and 38% of mercury are presented naturally in the creek flow (Table 8). It is necessary to remember that these numbers generally indicate "leftovers" from bio consumption of the elements by aquatic inhabitants.

7. How reliable this result is?

Quantitative evaluation of reliability (Table 7) of the obtained results was made using two parameters: a correlation coefficient (R) between observed and calculated concentrations (R^2 required to be = 0.8), and their average ratio (Cc/Co), which should be equal to 0.97-1.02. The second control parameter ensures that there are no differences in interpretation of initial data for each element or they are minimal. Both of these parameters are not estimated in routine standard procedures, because complete conformance with the standard provides very high reliability of the results (10-15%). Correlation in this case is higher than 0.97. How these should be interpreted for our elements? For copper and lead (r^2 = 0.8), all results are reliable from daily to yearly levels in spite of their obvious roughness. Daily assessments can have errors up to 50 - 75%: mostly extremal. For entire watershed (read for lower subwatershed as well) the copper element may be underestimated (Cc/Co < 0.97). For other elements, monthly and yearly results are more reliable than daily: correlation in the 0.8 - 0.9 intervals may lead to the errors of daily assessment up to 150-250% (extrapolation to unknown). Chromium and mercury results are overestimated for 4-5% in average (sounds funny after the previous sentence).

What are possible reasons for unsatisfactory reliability, some of which were mentioned above? Any non-conformance with the standard requirement or gap of a needed data may be a reason for reliability decreasing. The list of possible reasons is given below:

1. Samples are not representative for the total flow (especially grab samples)
2. Accuracy of data: procedure of measurements and accuracy of data presentation
3. Discrepancy between daily average and corresponding discharges

4. Lack of samples and flow condition measurements according to the program requirements
5. Possible temporal trend of contaminations and flow in case of using several years to create "flow – concentration" relationship
6. Adequacy of flow separation (accepted here *apriory*, due to non-standard nature of the approach)

The first reason formally can be eliminated in our case due to the grab sample for small rivers with well mixed flow is representative one. The second reason, which applicable for all examined elements at Etobicoke 2 and for arsenic, cadmium, lead and mercury at Etobicoke 1, is not improvable but is notified. Third one (applicable to all samples) can be evaluated and improved by estimation of the proper corresponding discharge for existing samples. Lack of samples and decadal and daily measurements of flow condition can be partially compensated by flow separation method. Establishing of self-recorders of water temperature, pH, electrical conductivity and dissolved oxygen can improved this in the future. Temporal trend (not applicable to our case) can be avoided using one-year set of data.

Finally, to improve the reliability of this particular assessment it is necessary to specify the corresponding discharge for every sample, using water level gauge records and rating curve specified for each period, and to repeat the assessment.

8. Natural background and anthropogenic impact assessment, evaluation of aquatic habitat condition in Etobicoke Creek

There are daily concentrations of examined elements broken into the flow components in comparison with Canadian water quality guideline limits and Russian summaries for pristine rivers in Table 4.

For Etobicoke 2, the total flow parameters do not exceed the baseflow ones, except for chromium and copper. This is normal proportion at a pristine, undisturbed watershed for major chemical parameters (Ladouche et al., 2001; Salmon and Walter, 2001), so it is obvious to guess that for heavy metals it works the same way.

The grey background in Table 4 indicates non-compliance of the case with the guidelines for Aquatic Life, and bolded underlined numbers indicate exceeding of the MAC. Concentration of arsenic in both outlets does not exceed either any of established limits or natural background. Higher baseflow concentrations at Etobicoke 2 can be caused by higher fluxes of basic conditions (pH = 7.4-8.9) than at Etobicoke 1 (pH = 5.5-8.7). Average concentrations of the other elements (except cadmium) do not exceed established limits and natural intervals. Cadmium and lead are those elements that both point at some excessive conditions of the upper subwatershed flow. Lead concentrations overcome the natural interval, but keep natural proportions between the components: the highest concentrations in the baseflow and the lowest one in the surface flow component. The cadmium limit for aquatic life is permanently overcome at both subwatersheds. At the same time, Cd concentrations for the upper watershed do not exceed the edge of natural conditions. There is no mining, lead -zinc ore dressing or sulphur acid industry, which are the main anthropogenic sources of cadmium. It could have been interpreted as the indicator of the acidic condition of entire watershed (it is neutral-basic, actually), but concentration of mercury and chromium in this case should be at list close to the upper boarder of natural conditions as well. However, average chromium concentration occurs very close to the lower boarder of natural conditions, and mercury concentrations are far beyond the average natural interval (see the entire watershed, E1). Acidic condition of soils, grounds and water is natural in coniferous forest, swamps and bogs even in areas with limestone as an underlying rock, what is supposed to neutralize the acid. For example, pH of the bog water within the Tooma Bog Conservation Area (Estonia), which is located on the south slope of limestone Pandivere Hill, fluctuated from 4.0 to 6.5 during 1984-90 periods. Precipitation's pH on the same area during the same period was in the interval of 5.3 – 7.4 (Tooma Bog Station Yearbooks, 1984-90). This clearly indicates that acidic condition of the area is not the result of either acid rains (anthropogenic impact) or underlying rocks. This is the result of the combination of bio-chemical cycle of the coniferous forest with poor drainage condition of the area. For Etobicoke Creek, there is no such evidence of natural acidification. Besides, proportional composition of copper and chromium in the flow of upper subwatershed indicate their excessive content in the inter flow. Leaching of examined elements can be caused by excessive presence of chlorides in the creek flow. There are no chloride samplings in upper stream, but lower station data analysis indicates 42% of total chloride volume (26 000 ton/year) is presented in interflow, base- and storm flow have 29% each. The cadmium case, actually, represents inconformity between measurement accuracy, the aquatic life limit, and interval of natural concentration of cadmium: sensitivity threshold of measurement tool for cadmium more than ten times exceeds the AL limit without exceeding of natural background. Why it is abnormal? Such a situation in nature can be only in case of strong acidification of the examined drainage area (pH <5) caused by normal conditions of particular watershed (coniferous forest and swamp), under which the excessive leaching of cadmium may happened. Etobicoke Creek has neutral and basic condition, under which excessive content of cadmium within entire watershed is the only result of possible non-compliance of the Canadian AL limit and Russian norms for pristine rivers.

Maximal daily concentrations of different elements as usual occur at the same day with extremal water discharges, minimal or maximal depending on availability of the element for transportation and capacity of flow to carry it. Due to these discharges characterize the turning points of weather-water-bio-chemical cycles, it is necessary to assess maximal concentrations of some elements, for example lead, on regular basis: the toxic effect of lead compound can be enhanced in the presence of other metals (Otitoloju, 2003). And this is why samples should be done at lowest and highest points of river hydrograph: these are turning points of the watershed life cycles and they have to be measured.

Monthly specific discharges of flow, its components and examined elements are given in Tables 5 and 6. These units, L/s km^2 and µg/s km^2, are practical interpretation of watershed approach: they indicate netted amount of the element incoming to the stream from each square kilometer of its drainage area per second. This is transportation capacity of water participating in the water cycle within water basin of a stream, and “speed of readiness” of an element to be transported further. It is not difficult to see (Table 6) that monthly pattern of elements generally repeat the flow pattern, clear indicating their seasonal character and specific of land use. The upper, unpaved subwatershed indicates much lower summer baseflow than winter one (Table 5) due to regular loss of water for evapotranspiration. Lower subwatershed does not have such a pronounced difference between summer and winter due to high percentage of the paved area and watering of unpaved areas (Table 1) in summer period and redistribution of snow in winter period. Watering of lawns causes baseflow increase in June, July and August. Increase of paved area causes redistribution in inter and storm flow (Table 5) decreasing the duration and specific discharge of the inter flow and increasing duration and discharge of storm flow. Storm sewage system increases the transportation capacity of surface water dramatically, because this capacity depends on kinetic energy of water flow, which is determined by squared speed of flow (Vedom, 1995). It is necessary to emphasize, that transportation of suspended substances as well as ionized elements is equally determined by flow discharge (Nagano et al., 2003).

Yearly transport of the elements through Etobicoke 2 and 1 reaches is presented in Table 7. Comparison with the naturally presented volumes gives pretty definite information about sources of heavy metals. For Etobicoke 2, upper subwatershed, chromium and copper loads from interflow have very noticeable increase, which can be related with excessive presence of chlorides especially in the inter flow. Excessive content of lead in all flow components of the upper outlet can be also caused by chloride presence due to its content in chloride thermal waters is usually very high, up to several milligrams per liter (Guseva et al, 2000). The principal current uses of lead are battery and pigment manufacturing (together account for about 76% of the world production of lead). Rolled metal, cable sheathing and gas additives account together 14.4% (http://www.cws-scf.ec.gc.ca/publications/papers/88/tabl1_e.cfm). This information is totally supported by our result for Etobicoke 1: highest amount of lead occurs in surface water, which in urbanized area is presented mostly by roads and paved area out flash. All elements have unmistakably increased surface components in lower subwatershed. And this is a very distinctive indicator of urbanized area: presence of industry, traffic, and high percentage of the paved area (Banat and Howari, 2003; Karlén et al., 2002; Kishe and Machiwa, 2003; Lozano et al., 2003; and Muohi et al., 2003). Storm flow component characterizes water from paved part of watershed. 65% of Etobicoke watershed is covered by storm water sewage, which is almost 100% of the lower subwatershed. Baseflow characterizes unpaved areas, which are mostly lawns and parks, landfills and dumpsites. Inter flow reflects quality of water in flow-delayed structures like ponds, artificial wetlands and storm water management system in the urbanized lower subwatershed. It is interesting that positive correlation between copper (Cu) and lead (Pb), and negative one between cadmium (Cd) and Cu obtained in a lab (Muohi et al. 2003) is clearly seen for base and interflow of lower subwatershed (Table 7).

Surface flow of total watershed is characterized by excessive concentration of mercury, but its total volume is far beyond of natural conditions for Russia. It may be in-conformance between Russian and Canadian natural background for mercury as well as for cadmium.

9. Conclusions

1. Totally, anthropogenic impact on Etobicoke Creek flow in terms of additional presence of heavy metals in its mouse can be estimated as 30, 80, 92, 95, 84 and 62% of the total yearly load of arsenic, cadmium, chromium, copper, lead, and mercury, respectively.
2. Presence of heavy metals and metalloids such as arsenic, cadmium, chromium, copper, lead and mercury in the flow of upper subwatershed of Etobicoke Creek is determined mostly by natural conditions of drainage area. Excessive content of copper and chromium in the inter component of flow and lead in all components of flow can point the abundance of chlorides originated from the road salt within upper subwatershed.
3. Proportional composition of concentrations of flow components for heavy urbanized watershed it totally reversed to natural one: the highest concentration of any element is found in the surface/storm flow, and the lowest concentration belongs to baseflow.
4. Volume and specific discharge of each element obtained for lower subwatershed characterizes heavy urbanized area with altered hydrological cycle and excessive content of almost all examined elements in the surface and interflow components. Concentrations of copper and lead exceed the established limits for aquatic life in groundwater as well.

5. The main reason for possible low reliability of this result is absence of coordination between water quality and quantity monitoring. To improve the reliability of the results obtained by separated flow approach it is necessary to specify the corresponding discharges for available samples.
6. Separated flow approach is the perfect non-standard tool for assessment and investigation in case of initial data shortage and optimization of monitoring programs.

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Appendix

Table 1. Land development parameters of the Etobicoke Creek watershed

Type of road or land use	Caledon		Urbanized area		Total watershed	
	Area, km^2	%	Area, km^2	%	Area, km^2	%
Residential area	0.6	1.07	42.5	28.7	43.1	21.1
Industrial area	0	0	45.5	30.8	45.5	22.3
Government area	0.01	0.02	20	13.5	20.01	9.8
Business area	0.01	0.02	7	4.7	7.01	3.4
Green space	55.5	98.9	33	22.3	88.5	43.4
Total	56.1	100	148	100	204	100
Lawns area	0.3		28.5		28.8	
Population		4650		464350		469000
	length	density	length	density	length	density
	km	km/km^2	km	km/km^2	km	km/km^2
Expressway	0	0	45.1	0.30	45.1	0.22
Primary and secondary	8.3	0.15	16.2	0.11	24.5	0.12
County roads	10.6	0.19	74.1	0.50	84.7	0.42
Major roads	35.5	0.63	175.2	1.18	210.7	1.03
Runways	0	0	24.6	0.17	24.6	0.12
Local	7.7	0.14	502.1	3.39	509.8	2.50
Total	62.1	1.11	837.3	5.66	899.4	4.41

Table 2.* Programs and frequency of hydrochemical observation and measurements

Frequency of Measurements	Category of station			
	I	II	III	IV
Daily	Short program I	Visual Observations	None	None
Decadal	Short program II	Short program I	None	None
Monthly	Short program III			None
Main phases of river regime	Mandatory program			

* Accepted from Guseva, T.V., Molchanova, Y.P., Zaika, E.A., Vinichenko, V.N., Averochkin, E.M., 2000. Hydrochemical indicators of the environment, Reference book, Ecoline (Rus.)

Appendix

Table 3*. Content of the mandatory monitoring program

Parameter	**Units**	**Parameter**	**Units**
Water discharge (in streams)	M^3/s	Magnum **(Mg^{2+})**	Mg/dm^3
Velocity (in streams)	M/s	Sodium **(Na^{+})**	Mg/dm^3
Water level (reservoirs)	M	Potassium **($?^{+}$)**	Mg/dm^3
Visual observations	–	Ions total sum **($?_{?}$)**	Mg/dm^3
Temperature	??	Ammonium nitrate **(NH_4^{+})**	Mg/dm^3
Color	Degrees	Nitrite nitrogen **(NO_2^{-})**	Mg/dm^3
Transparency	Sm	Nitrate nitrogen **(NO_3^{-})**	Mg/dm^3
Smell	Marks	Mineral phosphorus **(PO_4^{3-})**	Mg/dm^3
Dissolved Oxygen	Mg/dm^3	Total iron **(Fe^{+})**	Mg/dm^3
Carbon dioxide	Mg/dm^3	Silicon **(Si^{+})**	Mg/dm^3
Suspended substances	Mg/dm^3	BOD_5	Mg $?_2$/dm^3
Hydrogen index (?H)	–	COD	Mg ?/dm^3
Redox potential (?h)	? ?	Petrochemicals	Mg/dm^3
Chlorides **(Cl^{-})**	Mg/dm^3	Surfactants	Mg/dm^3
Sulfates **(SO_4^{2-})**	Mg/dm^3	Phenols (volatilizable)	Mg/dm^3
Hydrocarbons **(HCO_3^{-})**	Mg/dm^3	Pesticides	Mg/dm^3
Calcium **(Ca^{2+})**	Mg/dm^3	Heavy metals	Mg/dm^3

* Accepted from Guseva, T.V., Molchanova, Y.P., Zaika, E.A., Vinichenko, V.N., Averochkin, E.M., 2000. Hydrochemical indicators of the environment, Reference book, Ecoline (Rus.)

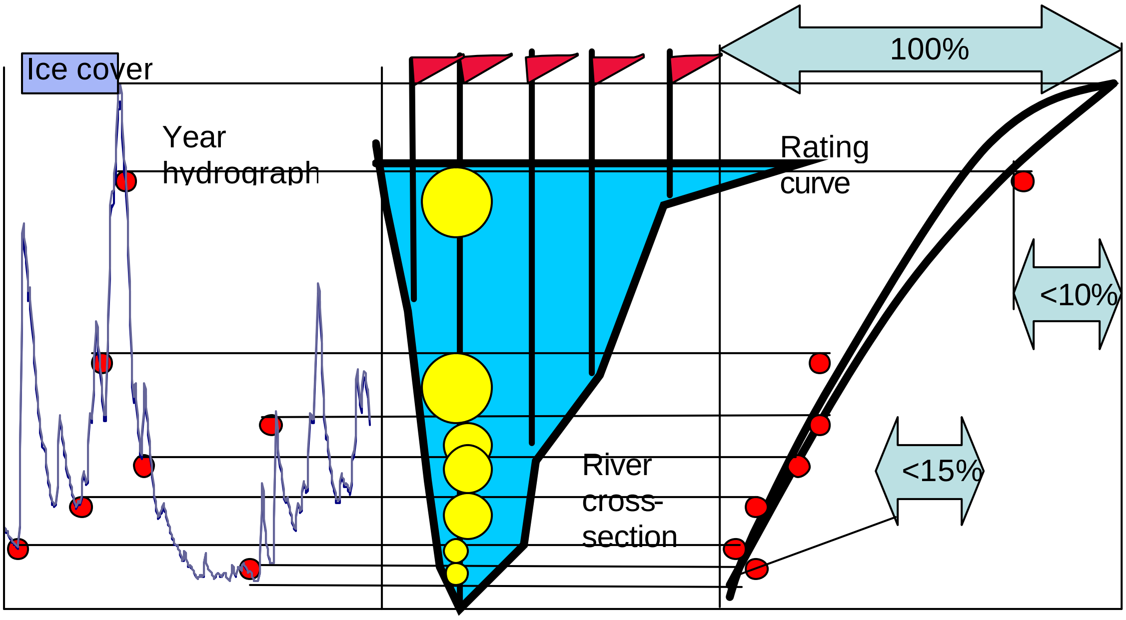

Fig.1. Representative time-space sampling matrix

Appendix

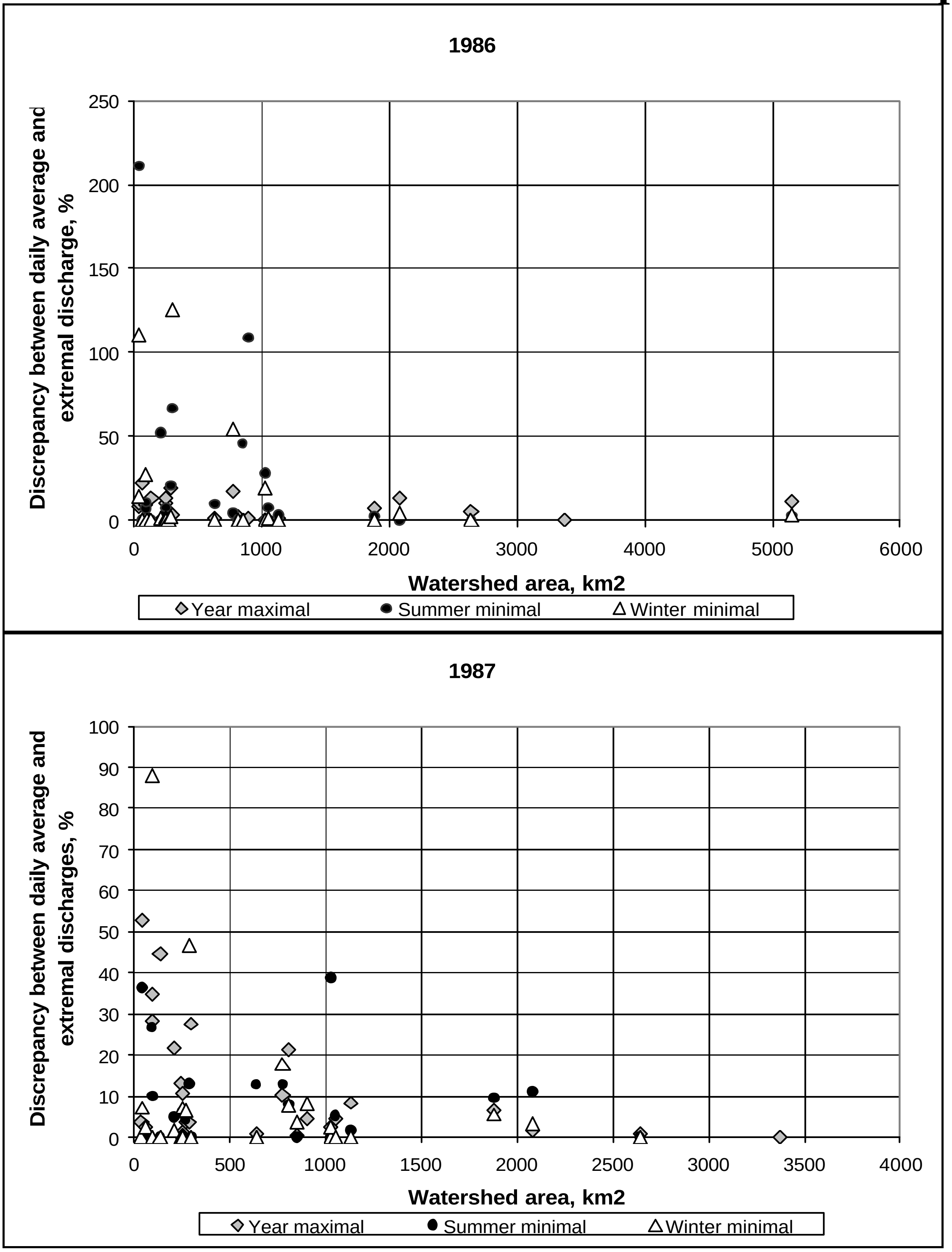

Fig. 2. Discrepancy between daily average and extremal discharge for winter and summer minimal flow, and year maximal as a function of watershed size for some Estonian rivers in 1986 and 1987.

Appendix

Table 4. Daily average and extremal concentrations of flow broken into the components comparing with established limits for Aquatic Life (AL) and Maximal Acceptable Concentrations (MAC), and pristine waters

Element	Type	Etobicoke 2 (63.4 km^2)				Etobicoke 1 (204 km^2)			
		Mg/L				Mg/L			
		Base	Inter	Surface	Total	Base	Inter	Surface	Total
Arsenic	Max	0.0017	0.0015	0.0010	0.0017	0.0010	0.0015	0.0026	0.0025
MAC (Canada) = 0.025 AL (Canada) = 0.005	Min	0.0009			0.0009	0.0010			0.0006
Natural (Rus): 0.001-0.005	Avg	0.0012	0.0009	0.0007	0.0011	0.0010	0.0009	0.0007	0.0010
Cadmium	Max	0.0002	0.0002	0.0002	0.0002	0.0006	**0.0051**	**0.0215**	0.0036
MAC (Canada) = 0.005 AL (Canada) = 0.000017	Min	0.0002			0.0002	0.0002			0.0001
Natural (Rus): 0.0001-0.0005	Avg	0.0002	0.0002	0.0001	0.0002	0.0002	0.0007	0.0008	0.0004
Chromium	Max	0.0012	0.0040	0.0003	0.0037	0.0030	**0.605**	**0.193**	0.0151
MAC (Canada) = 0.05 AL (Canada) = 0.01	Min	0.0005			0.0003	0.0020			0.0008
Natural (Rus): 0.0005-0.005	Avg	0.0007	0.0021	0.0002	0.001	0.0022	0.0212	0.011	0.0029
Copper	Max	0.0052	0.0141	0.0080	0.0125	0.0066	**1.0550**	0.175	0.0747
MAC (Canada) = 1.0 AL (Canada) = 0.004	Min	0.0011			0.0011	0.0033			0.0016
Natural (Rus): 0.002-0.030	Avg	0.0019	0.0037	0.0024	0.0024	0.0045	0.0116	0.0265	0.0067
Lead	Max	**0.0144**	0.0050	0.0050	**0.0135**	0.0065	**0.0634**	**0.1358**	**0.1244**
MAC (Canada) = 0.01 AL (Canada) = 0.007	Min	0.0050			0.0050	0.0043			0.0030
Natural (Rus): 0.0001-0.005	Avg	0.0053	0.005	0.0034	0.0052	0.0052	0.0046	**0.0268**	0.0075
Mercury* μg/L	Max					0.020*	0.078*	0.243*	0.225*
MAC (Canada) = 1.0 AL (Canada) = 0.1	Min					0.020*			
Natural (Rus): 0.01-0.5	Avg					0.020*	0.035*	0.025*	0.024*

Table 5. Averaged monthly flow structure for Etobicoke 1 and 2 (1990-93).

Month	Etobicoke 2								Etobicoke 1							
	Monthly averages				Event averages				Monthly averages				Event averages			
	Specific discharge, L/s km2				Duration, days		L/s km2		Specific discharge, L/s km2				Duration, days		L/sk m2	
	Base	Inter	Storm	Total	Inter	Storm	Inter	Storm	Base	Inter	Storm	Total	Inter	Storm	Inter	Storm
Jan	4.15	5.25	4.29	13.69	14	3	13.1	32.3	4.87	1.99	4.17	11.02	11	4	6.90	24.8
Feb	4.12	5.25	1.71	11.08	12	2	13.8	103.3	4.84	2.50	3.22	10.55	10	4	8.29	42.1
Mar	5.72	10.78	10.85	27.34	20	4	9.3	52.2	7.07	5.34	8.64	21.05	16	8	7.07	18.3
Apr	7.19	7.32	6.11	20.62	17	4	12.7	39.2	8.39	3.34	10.03	21.76	15	7	6.55	26.5
May	3.05	2.00	1.87	6.92	10	1	15.9	107.2	4.30	1.37	4.32	9.99	10	5	9.16	40.6
Jun	1.85	1.40	0.05	3.31	11	0	7.4	34.6	3.10	1.69	2.33	7.12	10	5	6.36	15.6
Jul	1.80	2.11	0.32	4.24	13	2	13.3	45.0	3.21	1.61	4.76	9.58	12	5	6.76	28.1
Aug	1.58	2.43	0.60	4.60	11	1	14.5	68.1	3.20	2.09	5.36	10.65	11	5	8.55	34.6
Sep	1.85	2.01	0.30	4.16	9	1	8.1	46.2	3.06	1.52	3.83	8.41	8	5	6.63	16.8
Oct	2.63	2.55	0.29	5.47	12	1	12.1	28.5	4.04	2.16	2.63	8.84	12	5	6.90	19.4
Nov	4.26	5.94	6.19	16.39	13	3	15.0	94.1	5.16	2.86	7.42	15.44	12	6	8.53	46.8
Dec	4.74	6.25	4.00	14.99	15	3	8.5	46.2	6.06	3.40	6.47	15.93	15	7	7.14	17.0
Year	3.58	4.44	3.05	11.07	156	25	12.0	58.1	4.77	2.49	5.26	12.53	141	67	7.41	27.5

Appendix

Table 6. Monthly total flow and elements characteristic for E2 (63.4 km^2) and E1-2 (141 km^2)

Month	Flow L/s km2		Arsenic µg/s km2		Cadmium µg/s km2		Chromium µg/s km2		Copper µg/s km2		Lead µg/s km2	
	E2	E1-2	E2	E1-2	E2	E1-2	E2	E1-2	E2	E1-2	E2	E1-2
January	13.7	9.97	6.27	9.98	1.25	4.70	10.2	64.2	37.7	275	31.3	423
February	11.1	9.45	4.60	9.56	0.923	4.31	9.87	53.4	32.6	215	23.1	312
March	27.3	18.5	12.9	23.0	2.50	25.3	16.1	127	65.0	417	62.6	500
April	20.6	21.9	8.97	28.7	1.83	30.5	7.48	125	16.6	490	45.7	661
May	6.92	11.6	3.28	14.0	0.634	12.7	2.52	68.5	5.58	268	18.5	391
June	3.31	8.69	1.58	8.19	0.293	5.77	1.52	26.5	2.36	73.5	7.53	58.6
July	4.24	12.2	2.01	12.9	0.388	10.1	2.05	59.6	3.16	224	10.8	313
August	4.60	13.6	2.19	16.5	0.421	16.2	2.20	60.4	3.48	231	11.4	316
September	4.16	10.2	1.91	9.42	0.369	6.69	1.93	42.4	3.02	146	11.0	194
October	5.47	10.5	2.57	8.97	0.501	6.13	2.61	35.3	4.15	96.9	14.6	89.2
November	16.4	14.7	7.32	17.4	1.45	18.1	5.65	73.1	13.2	273	36.3	298
December	15.0	16.6	6.85	16.4	1.37	7.49	11.8	95.8	43.5	390	34.3	545

Table 7. Yearly average volume of water and heavy metals of Etobicoke 1 (E1) and Etobicoke 2 (E2) broken into the flow components, 1990-93

Element	Total volume, kg/year		Flow components, kg/year			Flow components, %			Reliability	
	Estimated	Natural	Base	Inter	Storm	Base	Inter	Storm	R	Cc/Co
Flow, M.c.m,(E2)	22.1	22.1	7.15	8.88	6.10	32.3	40.1	27.6		
Flow, M.c.m, (E1)	80.6	80.6	30.7	16.0	33.9	38.1	19.9	42.0		
Arsenic, (E2)	22.4	22-100	7.63	8.66	6.12	34.1	38.6	27.3	0.50	1.00
Arsenic, (E1)	87.3	75-400	30.7	15.7	40.9	35.2	17.9	46.9	0.86	0.99
Cadmium, (E2)	4.4	2 – 10	1.43	1.78	1.22	32.3	40.1	27.6	0.86	1.00
Cadmium, (E1)	59.3	7.5 – 40	6.87	17.6	34.9	11.6	29.7	58.8	0.84	1.00
Chromium, (E2)	27.4	10-100	5.47	20.5	1.46	20.0	74.7	5.30	0.73	1.01
Chromium, (E1)	336	40-400	67.1	43.1	226	20.0	12.8	67.2	0.81	1.06
Copper, (E2)	85.4	40-650	15.4	43.6	26.5	18.0	51.0	31.0	0.90	0.99
Copper, (E1)	1234	150-2400	142	77.0	1015	11.5	6.2	82.2	0.92	0.96
Lead, (E2)	114	2 – 100	38.9	44.4	30.6	34.1	39.0	26.9	0.90	1.00
Lead, (E1)	1635	7.5-400	164	68.2	1403	10.0	4.2	85.8	0.94	0.99
Mercury (E2)		0.25-12.5				19.0	22.3	58.7	0.83	1.07
Mercury (E1)	3.24	0.75-40	0.614	0.723	1.90					

Appendix

Table 8. Natural fractions of the elements in the Etobicoke Creek flow, %

Element	Etobicoke 1				Etobicoke 2			
	Baseflow	Interflow	Surface	Total	Baseflow	Interflow	Surface	Total
Arsenic	100	88	40	70	94	89	65	84
Cadmium	89	16	9	20	100	86	65	85
Chromium	23	16	4	9	65	19	82	34
Copper	24	20	2	5	51	19	17	24
Lead	81	87	5	16	79	74	56	71
Mercury	100	38	17	38				

List 1

Criteria for monitoring station category assessment

First category station located at the medium and large rivers:
- Vicinity of the city with population 1million and up
- Breading, spawning and winter quartering places of the top priority fish species and aquatic organisms
- Places of repeatedly emergency released contaminants
- Waste water outlets resulting in **high level contamination**

Second category station located at any size rivers:
- Vicinity of the city with population 0.5-1 mln.
- Breading, spawning and winter quartering places of the high priority fish species and aquatic organisms
- Near-dam area of reservoirs
- Storm water sewage outlets
- Place of river crossing the state boarder
- Places of **moderate level contamination**

Third category station:
- Vicinity of the city with population lower than 0.5 mln.
- Large and Medium river’s mouth
- Mouth of the contaminated tributary of a large river or lake (reservoir)
- Waste water outlets resulting in **low level contamination**

Forth category station:
- Pristine rivers and lakes (reservoirs)
- Rivers and lakes located within conservation areas