Chapter 20

Issues Regarding the Application of a Mass-Balance Equation to an Urban Creek

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Uniroyal Chemical Ltd. (Uniroyal) operates a chemical manufacturing facility in Elmira, Ontario (hereinafter referred to as "the site"). Contaminated groundwater from beneath some areas of the site discharges to Canagagigue Creek, which flows through the site. As part of a proposal to contain a portion of this groundwater, the Ontario Ministry of Environment and Energy (MOEE) required Uniroyal to prepare a contaminant loading model that would estimate the improvement in surface water quality following implementation of the groundwater containment system. This chapter describes the preparation of this model, which was developed by Conestoga-Rovers & Associates (CRA) on behalf of Uniroyal.

20.1 Background

Uniroyal operates a chemical manufacturing facility at the site as shown on Figure 20.1. Operations at the site began circa 1897, with the production of footwear products, and continued, in summary, as follows:

- 1897-1917 - footwear products;
- 1917-1929 - tennis shoe manufacturing;
- 1929-1941 - closed;

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Figure 20.1 Site layout - Uniroyal Chemical Ltd. Elmira, Ontario.

- 1941-late 1940s - aniline and diphenylamine production; and
- late 1940s-present - organic chemical products and intermediates for agricultural, plastics and rubber industries.

Historic waste disposal and manufacturing practices have contaminated the underlying soil and groundwater. The site is underlain by a complex geologic and hydrogeologic environment comprising glacial and fluvial deposits. Canagagigue Creek (Creek), a tributary of the Grand River, flows through the site.

The principal aquifer units beneath the site of interest (in order of depth from the ground surface) are:

- the Upper Aquifer (UA) comprising three subunits UA₁, UA₂, UA₃;
- the Upper Aquitard (UAT);
- the Municipal Aquifer (MA); and
- the Municipal Aquitard (MAT).

Figure 20.2 depicts a typical cross-section of these units and their relationship to the Creek.

Figure 20.2 Typical hydrogeologic cross-section. Uniroyal Chemical Ltd., Elmira, Ontario.

Following the discovery of n-nitrosodimethylamine (NDMA) in the Elmira water supply system in 1989, the MOEE issued a Control Order (an administrative order, similar to a U.S. EPA Unilateral Administrative Order) to Uniroyal which required Uniroyal to, among other environmental controls, contain contaminated groundwater under the site. Initial groundwater containment efforts were directed at the MA utilizing a network of groundwater extraction wells. The MA contaminant and treatment system, known as the on-site contaminant and treatment systems (OSCTS) was commissioned in 1992 with two extraction wells and supplemented with a third extraction well in 1993.

Surface water quality sampling conducted immediately downstream of the site indicated that contaminated UA_1 groundwater was discharging to the Creek. Water quality concerns with the results of Canagagigue Creek surface water monitoring led to the preparation of the Upper Aquifer Feasibility Study (UAFS) (CRA, 1994a). This report evaluated alternatives for UA groundwater containment that would improve surface water quality in the Creek. The UAFS concluded that containment of groundwater in the southwest portion of the site would result in a 95.5% reduction in the mass loading of contaminants to the Creek, and improvement in surface water quality such that Ontario surface water quality criteria would be met downstream of the site under low flow conditions.

Uniroyal submitted an application to the MOEE to amend its approved treatment system permit (Certificate of Approval or C of A) in a formal application accompanied by a support document (CRA, 1994b). The application requested approval to install and operate the Upper Aquifer containment and treatment system (UACS). The UACS would contain UA_1 groundwater in the southwest portion of the site via a network of eleven extraction wells.

The support document included the hydraulic design for the groundwater containment system, the treatment system design, and an assimilation model. The assimilation model was utilized to predict the impact to the Creek and the associated improvement in surface water quality that would result from the operation of the UACS.

Although the hydraulic design and the treatment system design were significant engineering and technical efforts, the assimilation model was the subject of intense technical review, evaluation and controversy.

The following sections describe how the model was constructed, manipulated and utilized to predict water quality conditions in the Creek.

20.2 Elements of Canagagigue Creek Model

There are several sources of water that discharge into Canagagigue Creek as it passes through the site. In order to create a model of the Creek, it was necessary to first enumerate these sources of water and determine how they

would be treated as elements of the model. Each of the elements is discussed below in Sections 20.2.1 to 20.2.6, and illustrated schematically in Figure 20.3.

Figure 20.3 Elements of the Canagagigue Creek model, Uniroyal Chemical Ltd. Elmira, Ontario.

20.2.1 Canagagigue Creek Background Flow

The first element of the model is the background flow of the Creek as it enters the site. The MOEE required that the model reflect low flow conditions, so that the model would estimate contaminant levels in the Creek under those infrequent conditions which would result in the maximum contaminant concentrations in the stream. The water in the Creek is not free of contaminants when it enters the site. A former municipal waste landfill is located immediately upstream of the site on the banks of the Creek.

20.2.2 UA₁ Groundwater Discharge

The Uniroyal site is underlain by a complex series of glacial and fluvial units, ranging in composition from coarse gravel to clay till. Much of the understanding of the hydrogeology underlying the Uniroyal site, and the surrounding Elmira area, is derived from the work of CRA's Uniroyal project hydrogeologist, Alan Deal.

The surficial aquifer beneath most of the site is referred to as the Upper Aquifer - Top Beds, or UA₁. UA₁ is an unconfined sand and gravel formation which is approximately 5 m thick, the bottom 1 m to 2 m of which is saturated. UA₁ groundwater generally flows towards, and discharges to, Canagagigue Creek.

Groundwater beneath the Uniroyal site is contaminated due to Uniroyal's past waste management practices. Waste was buried on-site at several locations, however, the most significant source of groundwater contamination was the former unlined wastewater lagoons in the southwestern portion of the site. Due to the significant difference in groundwater quality in different portions of the site, the UA₁ groundwater that discharges to the Creek was divided into the following three components for the model:

- West Side-North;
- West Side-South (WSS); and
- East Side.

20.2.3 MISA Discharges

There are three Municipal-Industrial Strategy for Abatement (MISA) discharge points (MISA 0200, MISA 0400, and MISA 0800) to the Creek at the site, which discharge stormwater and non-contact cooling water to the Creek. Although non-contact cooling water discharges at two (MISA 0200 and MISA 0800) of the three MISA discharge points, it was treated as one discharge in the model. This simplification was appropriate because the same water quality (municipal potable water) discharges at both points, and because the purpose of

the model was to predict Creek water quality at a point downstream of both the MISA non-contact cooling water discharge points. Stormwater discharges from the MISA outlets were not considered in the model because the assimilation assessment was completed for low flow (drought) conditions, and therefore no stormwater would be present.

20.2.4 Municipal Aquifer Treated Groundwater Effluent

The treated groundwater from the MA treatment system (see Section 20.1) is discharged to the Creek at MISA 0800.

20.2.5 Shirt Factory Creek

Shirt Factory Creek is a small tributary which feeds into Canagagigue Creek on site. Shirt Factory Creek passes beneath the site inside a 200 m long corrugated steel culvert. This culvert discharges to Canagagigue Creek at MISA 0800.

20.2.6 UA₁ Treated Groundwater Effluent

The UACS will contain UA₁ groundwater in the southwestern portion of the site by extracting UA₁ groundwater via a network of eleven extraction wells. The UA₁ groundwater will be treated by granular activated carbon, followed by biological treatment. The UA₁ groundwater will then be mixed with MA groundwater and treated by ultraviolet oxidation followed by granular activated carbon. The treated UA₁ groundwater will then be discharged to the Creek at MISA 0800.

20.2.7 Parameter Selection

CRA developed a list of parameters to be included in the model using the following general steps:

1. An initial list of 204 parameters was created. This list included all parameters that had been analyzed for in 1993 in surface water samples, WSS groundwater, and the influent and effluent of the existing MA treatment system.
2. Parameters that had not been detected in any of these streams were eliminated from further consideration.
3. Parameters that had maximum detections below their respective surface water quality standards (Provincial Water Quality Objectives or PWQOs) were eliminated from further consideration.

4. Parameters that had no PWQOs, but had Ontario Drinking Water Quality Objectives (ODWOs), were eliminated from further consideration if there were no exceedences of the relevant ODWOs.
5. Inorganic parameters that were not indicative of contamination at the Uniroyal site were eliminated from further consideration.

The finalized parameter list for the model is provided in Table 20.1.

Table 20.1 Final parameter list.

General Chemistry		
Ammonia as N	Chloride	Cyanide
Formaldehyde	Sulfate	
Metals		
Cadmium	Iron	Lead
Sodium	Strontium	
Volatile Organic Compounds		
Benzene	Chlorobenzene	Ethylbenzene
m,p- Xylenes	o- Xylene	Toluene
Trichloroethylene		
Base/Neutral/Acid Extractables		
2,3,4-Trichlorophenol		2,4,5-Trichlorophenol
2,4,6-Trichlorophenol		2,4-Dichlorophenol
2,6-Dichlorophenol		2-Chlorophenol
2-Mercaptobenzothiazole		3/4-Methylphenol (m,p-Cresols)
4-Chloro-3-methylphenol (p-Chloro-m-cresol)		Aniline
Benzothiazole		bis(@-Ethylhexyl) phthalate
N-Nitrosodi-N-Butylamine (NBDA)		N-Nitrosodimethylamine (NDMA)
N-Nitrosodiphenylamine/Diphenylamine (NDPA/DPA)		
N-Nitrosomorpholine (NMOR)		Oxathiin (Carboxin)
o-Cresol		Phenol
Herbicides/Pesticides		
2,4-Dichlorophenoxyacetic Acid		Lindane
Dioxins/Furans		
2, 3, 7, 8-Tetrachlorodibenzo-p-dioxin (2, 3, 7, 8-Tetra CDD)		
2, 3, 7, 8-Tetrachlorodibenzofuran (2, 3, 7, 8-Tetra CDF)		

20.2.8 Structure of the Model

The purpose of the model was to estimate parameter concentrations in Canagagigue Creek at SS2, a compliance monitoring point immediately downstream of the site. Parameter concentrations at SS2 were calculated using the mass balance equation:

$$C_{SS2} = \frac{Q_{BACK}C_{BACK} + Q_{MISA}C_{MISA} + Q_{UT}C_{UT} + Q_{MT}C_{MT} + Q_{SFC}C_{SFC} + Q_{UA}C_{UA}}{Q_{TOTAL}}$$

where:

- C_{SS2} = concentration in Canagagigue downstream of Uniroyal.
- Q_{BACK} = background stream flow (Canagagigue Creek)
- C_{BACK} = background stream concentration
- Q_{MISA} = flow rate from MISA 0200 and MISA 0800 cooling water
- C_{MISA} = concentration in MISA 0200 and MISA 0800 cooling water
- Q_{UT} = effluent flowrate of on-site treatment plant for UA groundwater
- C_{UT} = concentration in treated UA groundwater effluent
- Q_{MT} = effluent flowrate of on-site treatment plant from MA groundwater extracted from PW1, PW3 and PW4
- C_{MT} = concentration in treated MA groundwater effluent
- Q_{SFC} = flow rate from Shirt Factory Creek
- C_{SFC} = concentration in Shirt Factory Creek
- Q_{UA} = discharge flowrate of UA groundwater (varies according to scenario of containment/no containment)
- C_{UA} = discharge concentration of UA groundwater
- $Q_{TOTAL} = Q_{BACK} + Q_{MISA} + Q_{UT} + Q_{MT} + Q_{SFC} + Q_{UA}$

The model did not attempt to account for losses of contaminants via mechanisms such as volatilization, photo-oxidation, or biological uptake/degradation. The model was calibrated with real Creek monitoring data (see Section 20.5) to verify that losses from such mechanisms were not significant.

The model was run as an Excel 4.0 spreadsheet. Each element of the model was represented by a column, and each parameter by a row.

20.3 Determination of Flow Values

The initial step in quantifying flows in the model was the determination of an appropriate background Creek flow that represented drought flow conditions. Typically in assimilation assessments, the published $7Q_{20}$ value is used, which represents the minimum consecutive 7-day average flow that has a probability of occurrence of once every 20 years. These values are published for numerous rivers and creeks in Ontario (Inland Waters Directorate, 1992). In the case of Canagagigue Creek, the published $7Q_{20}$ value was based on almost 30 years of creek flow measurements.

Two significant problems were associated with the published $7Q_{20}$. The first was that the $7Q_{20}$ was based on flow records both prior to, and after construction of the Woolwich Reservoir, a dam on Canagagigue Creek upstream from the site. The purpose of the reservoir is to maintain base flows in the Creek, and particularly to provide a minimum base flow for the Elmira sewage treatment plant (STP), located immediately downstream of Uniroyal.

The published $7Q_{20}$ was an unrealistically low value which did not reflect the significance of flow regulation following construction of the Woolwich Reservoir. CRA undertook an extensive effort to re-evaluate the Creek flow records for the period following construction of the reservoir to determine an appropriate $7Q_{20}$ for use in the assimilation assessment. This re-evaluation has been the subject of intense controversy with the MOEE.

Another difficulty with determining a suitable background Creek flow upstream of Uniroyal was that the Creek flow records used for $7Q_{20}$ calculations were obtained from an Environment Canada monitoring station which is located several kilometres downstream of Uniroyal. However, because of the extensive historical database available, it was possible to quantify flows from the various sources (such as the Elmira STP and flow from a tributary to the Creek) between the downstream gauging location and Uniroyal's site to determine a suitable upstream low flow value. Once this value was determined, assimilation calculations were performed with this background flow rate.

The background flow rate was determined as follows:

$$Q_{Back} = Q_{Total} - Q_{Other}$$

where:

$$\begin{aligned} Q_{Back} &= \text{background low flow upstream of Uniroyal} \\ Q_{Total} &= \text{minimum observed 7-day average flow at downstream station; 290 L/s (the minimum observed 7-day average flow occurred in 1987 and was 3\% less than the } 7Q_{20} \text{ of 298 L/s calculated by CRA).} \\ Q_{Other} &= \text{flows from other sources that flow into the Creek between the downstream station and Uniroyal (approximately 120 L/s)} \end{aligned}$$

Therefore:

$$Q_{Back} = 290 \text{ L/s} - 120 \text{ L/s} = 170 \text{ L/s}$$

Again, this approach was the subject of much debate between the MOEE, Uniroyal, CRA and other interested parties. It is interesting to note that if the published $7Q_{20}$ was used in the above equation, the resultant upstream flow would have resulted in a negative number. This fact supports CRA's approach.

Most sources that discharge to the Creek on Uniroyal's property are point-source discharges from outfalls, and these flows were quantified in the model by determining average flow values from historical databases.

An exception to the point source discharges noted above is the non-point source discharge from UA₁, which discharges to the Creek along its banks. These discharges were quantified using Darcy's Law:

$$Q = KiA = KibL$$

where:

Q = flow (m³/s)

K = hydraulic conductivity (m/s)

i = horizontal hydraulic gradient (dimensionless)

A = cross-section area (m²)

b = saturated thickness (m)

L = cross-section length (m)

Detailed calculations of the groundwater flux from UA₁ to the Creek were presented in the UAFS. Extensive hydrogeologic data were available from numerous groundwater monitoring sampling rounds, pumping tests, and single-well response tests performed using the on-site monitoring wells. Figure 20.3 presents a schematic representation of UA₁ discharges to the Creek.

The proposed UACS will contain the UA₁ groundwater flux currently discharging to the Creek along the West Side South (WSS) portion of the property. Therefore, two conditions were modeled, first with the UA₁ WSS uncontained, and second with the UA₁ WSS contained. This was accomplished by setting the UA₁ WSS flux to zero for the contained scenario. In this way, the effects of the UACS on the Creek water quality could be modeled. With the UA₁ WSS contained, flow from the treated UA₁ groundwater was considered to be a source of discharge to the Creek in the model.

Current target flow rates were used to quantify flows from the three operating on-site MA extraction wells. The treated groundwater from these wells was included as a source of flow to the Creek.

Non-contact cooling water is obtained from the municipal water supply and is discharged through MISA 0200 and 0800. Average flow rates for the cooling water were obtained from MISA monitoring and municipal water usage records, and these were used to quantify this source in the model.

20.4 Determination of Water Quality Chemical Profiles

Water quality chemical profiles for the various sources considered in the model were developed using an extensive historical database which included:

1. the Uniroyal database which comprises all groundwater, surface water, and treatment system effluent analytical work conducted by Uniroyal from 1982 to the present;

2. Uniroyal MISA monitoring analytical results for cooling water discharges; and
3. the MOEE, Regional Municipality of Waterloo, and Ontario Clean Water Agency database for selected locations.

The manipulation of these data was not a trivial task. It involved compiling data from the several sources listed above, sorting through several thousand analytical results, and removing duplication.

Parameter levels for the Creek background water quality were calculated by combining historic data from several upstream Creek water sampling locations, including samples obtained by both Uniroyal and the MOEE.

Non-contact cooling water quality at the MISA outfalls was quantified by compiling Uniroyal's MISA analytical results.

Shirt Factory Creek (a tributary to Canagagigue Creek) water quality was determined by reviewing MOEE water quality data.

UA₁ contaminant concentrations were quantified by considering the most recent analysis of each parameter at each monitoring well screened in UA₁.

Treatment system discharges were handled differently than conventional assimilation assessments, where maximum allowable concentrations at maximum discharge rates are typically considered. The available database for the MA treatment system was used to determine representative effluent concentrations for this treatment system. The proposed UACS treatment system will utilize similar (and in some cases, better) treatment technology than the MA treatment system. Therefore, an effluent profile for the UACS was developed based on expected removal efficiencies determined from data obtained for the MA treatment system. This approach was taken because the intent of the assimilation assessment was to determine the impact of the expected discharge concentrations on the Creek, rather than to determine effluent criteria for the UACS. Effluent criteria for the UACS were ultimately determined by the MOEE from treatment technology limitations, not from the assimilative capacity.

A number of technical issues arise in determining a typical water quality profile for a body of water. The estimation of parameters is difficult because the data are frequently skewed (asymmetrical) and the data record usually contains numerous values reported as less than the detection level. CRA utilized two novel approaches to quantify representative concentrations for the various sources in the model. These were:

1. use of the geometric mean (as opposed to an arithmetic mean or 75th percentile); and
2. use of a sliding scale to quantify concentrations reported as being non-detect.

The rationale for these assumptions is discussed below.

CRA accounted for the skewed data by utilizing a log normal distribution to characterize the water quality data for the individual constituents. When data are skewed, the estimation of the arithmetic mean is strongly biased by a very small

subset (i.e. the outliers) of the entire data set. As a result, the arithmetic mean is not a very useful indicator of the central tendency of the data set. Consequently, CRA utilized the geometric mean as the indication of the central tendency. The geometric mean is also consistent with the log normal distribution indicated above.

To confirm the appropriateness of the log normal distribution assumption, CRA calculated the means and coefficient of variation (standard deviation divided by the mean) for both the arithmetic and geometric (log-transformed) data, for all inputs into the model. The coefficient of variation test indicated that the lognormal distribution better characterized the data than the normal distribution. Figure 20.4 illustrates the skewing effect of high analytical results on two relevant contaminants (toluene and chlorobenzene) in the UA₁ groundwater, and demonstrates that the geometric mean better represents the central tendency of the data.

An additional issue is how to characterize data reported as non-detect or less than the analytical detection limit. A number of different approaches have been published but the most relevant for this type of situation (for estimating the geometric mean) involve either:

1. assuming values of zero, one-half the detection level, or equal to the detection level, or
2. a sliding scale procedure where the replacement value is selected on the basis of three-quarters of the detection level if one-quarter of the data are less than, half the detection level if one half of the data are less than, and one-quarter of the detection level if three-quarters of the values are less than.

With respect to 1. above, the two end conditions (zero or equal to the detection limit) are extreme situations which do not reasonably reflect the real condition, and the middle condition (assuming one-half the detection level) is somewhat arbitrary.

CRA instead used a sliding scale procedure to quantify non-detects. When a sliding-scale calculation is performed, the percentage of the total number of samples that are non-detect values is determined. In the ensuing calculations, the sliding-scale factor associated with this percentage is multiplied by the detection limit of each non-detect to create a value to be used in calculation.

The sliding scale procedure adjusts the value for assignment of the non-detect data in accordance with the percentage of samples that are reported as non detects. If the number of samples that are reported as non-detects are a relatively large percentage of the total data set, then one expects that the actual concentration of the parameter in the non-detect samples must be close to zero. Alternatively, if the number of non-detect values is a relatively small percentage of the total data set, then one expects that the actual concentration of the parameter in the non-detect samples must be close to the detection limit.

Figure 20.4 Geometric means vs. arithmetic means. Surface water modeling of Canagagigue Creek.

The sliding-scale factors used by CRA in the determination of all ground-water, surface water and effluent water quality profiles are:

Percent of Samples Which are Non-detect	Sliding-scale Factor (Fraction of Detection Limit)
≤ 37.5%	0.75
> 37.5% and ≤ 62.5%	0.5
> 62.5%	0.25

Both the use of the geometric mean, and the use of a sliding scale to quantify non-detects, were the subject of debate between the MOEE and CRA.

20.5 Simulation of Existing Conditions

After setting up the model, it was necessary to determine if the model would provide estimates of Creek water quality downstream of the site that were accurate. Surface water stations upstream and downstream of the site were monitored for water quality and flow during four monitoring rounds in 1993. For each sampling round, CRA input the observed upstream flow and upstream water quality into the model, and then used the model to estimate downstream water quality. Each modeled downstream parameter concentration was divided by the actual parameter concentration (as measured during the sampling round) to provide a comparative ratio. These comparative ratios were thus indicative of the validity of the model.

The MOEE fundamentally disagreed with CRA’s decision to calculate average UA₁ groundwater contaminant levels using geometric means. The MOEE felt that using geometric averages would inappropriately mitigate the impact of those monitoring well samples that contained high concentrations of contaminants. However, CRA believes that the use of geometric averages was appropriate, based on the lognormal distribution of the data. To address the MOEE’s concerns, comparative ratios were calculated for the model using both geometric means and arithmetic means to quantify UA₁ groundwater quality. These comparative ratios are summarized in Table 20.2

As shown by the comparative ratios in Table 20.2, the model using geometric means estimated downstream parameter concentrations that more closely matched the actual sampling data than the model using arithmetic averages. In fact, the version of the model using geometric means was remarkably accurate in modeling the downstream Creek water quality for the four 1993 surface water sampling events. The comparative ratios ranged from 0.022 to 6.148, and the overall average comparative ratio was 1.284. Given the complexity of the many different elements that were being modeled, the

Table 20.2 Summary of comparative ratios.

Parameter	Using Geometric Mean Values For UA ₁ Groundwater			Using Arithmetic Mean Values For UA ₁ Groundwater		
	Minimum Comparative Ratio	Maximum Comparative Ratio	Average Comparative Ratio	Minimum Comparative Ratio	Maximum Comparative Ratio	Average Comparative Ratio
General Chemistry						
Ammonia as N	0.431	1.461	0.940	0.887	2.032	1.473
<u>Volatile Organic Compounds</u>						
Benzene	0.345	1.457	0.975	1.491	6.619	3.539
Chlorobenzene	0.287	5.763	2.343	2.112	51.305	19.269
Ethylbenzene	0.670	1.890	1.267	3.413	10.027	5.620
m,p-Xylenes	1.248	1.925	1.672	1.130	12.105	7.029
o-Xylenes	1.185	1.689	1.500	3.207	9.229	6.975
Toluene	0.109	1.354	1.689	1.357	10.516	6.469
Trichloroethylene	0.022	1.053	1.697	1.050	2.512	1.323
<u>Base/Neutral/Acid Extractions</u>						
2,3,4-Trichlorophenol	0.978	0.994	0.986	1.066	1.246	1.159
2,4,5-Trichlorophenol	0.492	0.995	0.865	0.685	1.407	1.093
2,4,6-Trichlorophenol	0.982	0.998	0.993	1.198	1.673	1.402
2,4-Dichlorophenol	0.230	1.121	0.858	1.310	6.860	3.546
2,6-Dichlorophenol	0.967	1.020	0.998	1.344	2.315	1.932
2-Chlorophenol	1.002	1.006		4.109	12.596	8.522
2-Mercaptobenzothiazole	0.107	3.501	2.361	0.788	22.224	14.436
Aniline	0.693	6.148	2.710	3.747	31.057	13.260
Benzothiazole	0.264	2.900	1.025	3.858	15.607	7.386
Carboxin	0.348	1.494	1.107	2.655	10.212	6.029
m,p-Cresols	1.043	1.217	1.121	1.151	1.584	1.383
NDBA	2.328	3.064	2.696	3.972	5.619	4.796
NDEA	2.020	2.020	2.020	5.736	5.736	5.736
NDMA	0.227	1.840	0.894	3.690	20.972	10.094
NMOR	0.387	1.851	1.117	1.407	9.611	5.509
o-Cresol	0.684	1.010	0.925	0.908	1.503	1.189
p-Chloro-m-Cresol	0.984	0.996	0.990	1.022	1.081	1.053
Phenol	1.013	1.022	1.016	7.474	14.262	14.262
<u>Herbicides/Pesticides</u>						
2,4-D	0.907	1.107	1.012	2.235	5.021	3.165
Lindane	0.993	1.447	1.172	0.993	1.448	1.172
	Range of Comparative Ratios		0.022-6.148			0.050-51.305
	Range of Average Comparative Ratios		0.689-2.710			1.053-19.269
	Overall Average		1.284			5.555

Note: Comparative ratio is the modeled concentration at SS2 divided by the actual concentration at SS2.

simulation of the actual 1993 sampling events provided excellent correlation between the model and observed conditions.

As discussed previously, the model did not attempt to account for losses of contaminants via mechanisms such as volatilization, photo-oxidation, or biological uptake/degradation. These mechanisms are likely part of the reason why the model computed contaminant concentrations that were an average of 1.284 times higher than the concentrations detected in observed sampling events.

20.6 Predicted Improvement in Creek Quality

Following the determination of all input parameters, and the calibration of the model, assimilation calculations were completed for the following conditions:

- UA₁ WSS groundwater uncontained, (i.e. current conditions); and
- UA₁ WSS groundwater contained.

Table 20.3 presents the results of the model for UA₁ WSS uncontained (current conditions).

The model computed that iron, toluene, aniline, and bis(2-ethylhexyl)phthalate would exceed their respective PWQO or guideline concentration at SS2. The predicted exceedences of iron and toluene are consistent with the parameters at SS2 which historically exceed their PWQO in sampling at SS2.

While computed aniline concentrations exceed the proposed PWQO, the actual mean aniline concentration at SS2 is less than the PWQO. The assimilation model overestimates aniline concentrations by a factor of 73. It is not known why the model significantly overestimates aniline concentrations, whereas the model accurately computes similar compounds such as benzothiazole and carboxin.

Likewise, while computed bis(2-ethylhexyl)phthalate concentrations exceed the PWQO, the observed mean concentration at SS2 is less than the PWQO. Bis(2-ethylhexyl)phthalate is a common analytical laboratory contaminant, and false detections are often reported by laboratories. The computed exceedence of bis(2-ethylhexyl)phthalate is due to the elevated level assumed in the calculations for the background Creek concentration, which has resulted from suspected false detections.

With the exception of aniline, the modeled SS2 values were very good predictors of observed Creek concentrations.

Table 20.4 presents the results of the assimilation calculations for UA₁ WSS contained. The assimilation calculations estimated that toluene and aniline would be reduced below their PWQO/G and would be reduced to non-detect concentration levels.

Table 20.3 Assimilation calculations. UA₁WSS uncontained.

	C Back	Modeled SS+855	PWQO [1]	Ratio Model PWQO
General Chemistry (mg/L)				
Ammonia as N [2]	--	--		--
Chloride	28.6	44.2		N/A
Cyanide	ND(0.005)	ND(0.005)	5	--
Formaldehyde	0.126	--	0.8	--
Sulfate	34.6	45.1		N/A
Metals (mg/L)				
Cadmium	ND(0.003)	ND(0.003)	0.0002	[3]
Iron	0.704	0.663	0.3	2.21
Lead	ND(0.025)	ND(0.025)	0.005	[3]
Sodium	13.7	26.2		N/A
Strontium	0.235	0.303		N/A
Volatile Organic Compounds (µg/L)				
Benzene	ND(0.5)	ND(0.5)	15	--
Chlorobenzene	ND(0.5)	2	8	0.13
Ethylbenzene	ND(0.5)	ND(0.5)	2	--
m,p-Xylenes	ND(0.5)	ND(0.5)	40	--
o-Xylenes	ND(0.5)	ND(0.5)	0.8	--
Toluene	ND(0.5)	9.8	20	12.24
Trichloroethylene	ND(1)	ND(1)		--
Base/Neutral/Acid Extractables (µg/L)				
2,3,4- Trichlorophenol	ND(2)	ND(2)	18	--
2,4,5- Trichlorophenol	ND(2)	ND(2)	18	--
2,4,6- Trichlorophenol	ND(1.2)	ND(1.2)	18	--
2,4- Dichlorophenol	ND(1.2)	ND(1.2)	0.2	[3]
2,6- Dichlorophenol	ND(1.2)	ND(1.2)	180.2	[3]
2- Chlorophenol	ND(2)	ND(2)		--
2- Mercaptobenzothiazole	ND(10)	73.7		N/A
Aniline	ND(2)	40.9		20.43
Benzothiazole	ND(2)	4.1		N/A
Bis(2-Ethylhexyl) phthalate	2.8	2.7	0.6	4.53
Carboxin	ND(2)	15.1		N/A
m,p- Cresols	ND(2)	ND(2)	1	[3]
NDBA	ND(10)	ND(10)		N/A
NDEA	0.017	0.103		N/A
NDMA	ND(0.01)	0.115		N/A
NDPA/DPA	ND(5)	--	7	N/A
NMOR	ND(10)	ND(10)		N/A
o-Cresol	ND(2)	ND(2)	1	[3]
p-Chloro-m-Cresol	ND(2)	ND(2)		N/A
Phenol	ND(1.1)	ND(1.1)	5	--
Herbicides/Pesticides (µg/L)				
2,4- D	0.067	0.106	4	0.03
Lindane	ND(0.003)	0.004	0.01	0.43
Dioxins/Furans (ηg/L)				
2,3,7,8- Tetra CDD	0.0003	0.0003 [4]		N/A
2,3,7,8- Tetra CDF	0.0002	0.0002 [4]		N/A
Total TEQ	0.0013	0.0012 [4]		N/A

Notes:

- [1] PWQO - Provincial Water Quality Objective or Interim Provincial Water Quality Objective
- [2] See Table 20.5 for ammonia assimilation calculations.
- [3] The PWQO for this compound is less than the detection limits.
- [4] No standard detection limits available for dioxins and furans.
Detection limits not stable due to the very low levels of detection involved.
- Data not available
- N/A No applicable PWQO
- ND Concentration deemed non-detect because it is lower than the standard detection limits shown in parenthesis.
- Indicates concentration exceeds the PWQO.

Table 20.4 Assimilation calculations. UA₁WSS contained.

	C Back	Modeled SS+855	PWQO [1]	Ratio Model PWQO
General Chemistry (mg/L)				
Ammonia as N [2]	--	--		--
Chloride	28.6	47.0		N/A
Cyanide	ND(0.005)	ND(0.005)	5	--
Formaldehyde	0.126	--	0.8	--
Sulfate	34.6	47.0		N/A
Metals (mg/L)				
Cadmium	ND(0.003)	ND(0.003)	0.0002	[3]
Iron	0.704	0.654	0.3	2.21
Lead	ND(0.025)	ND(0.025)	0.005	[3]
Sodium	13.7	29.0		N/A
Strontium	0.235	0.308		N/A
Volatile Organic Compounds (µg/L)				
Benzene	ND(0.5)	ND(0.5)	15	--
Chlorobenzene	ND(0.5)	ND(0.5)	8	0.13
Ethylbenzene	ND(0.5)	ND(0.5)	2	--
m,p-Xylenes	ND(0.5)	ND(0.5)	40	--
o-Xylenes	ND(0.5)	ND(0.5)	0.8	--
Toluene	ND(0.5)	ND(0.5)	20	--
Trichloroethylene	ND(1)	ND(1)		--
Base/Neutral/Acid Extractables (µg/L)				
2,3,4- Trichlorophenol	ND(2)	ND(2)	18	--
2,4,5- Trichlorophenol	ND(2)	ND(2)	18	--
2,4,6- Trichlorophenol	ND(1.2)	ND(1.2)	18	--
2,4- Dichlorophenol	ND(1.2)	ND(1.2)	0.2	[3]
2,6- Dichlorophenol	ND(1.2)	ND(1.2)	0.2	[3]
2- Chlorophenol	ND(2)	ND(2)		--
2- Mercaptobenzothiazole	ND(10)	ND(10)		N/A
Aniline	ND(2)	ND(2)		20.43
Benzothiazole	ND(2)	ND(2)		N/A
Bis(2-Ethylhexyl) phthalate	2.8	2.7	0.6	4.53
Carboxin	ND(2)	15.1		N/A
m,p- Cresols	ND(2)	ND(2)	1	[3]
NDBA	ND(10)	ND(10)		N/A
NDEA	0.017	0.100		N/A
NDMA	ND(0.01)	0.112		N/A
NDPA/DPA	ND(5)	--	7	N/A
NMOR	ND(10)	ND(10)		N/A
o-Cresol	ND(2)	ND(2)	1	[3]
p-Chloro-m-Cresol	ND(2)	ND(2)		N/A
Phenol	ND(1.1)	ND(1.1)	5	--
Herbicides/Pesticides (µg/L)				
2,4- D	0.067	0.096	4	0.03
Lindane	ND(0.003)	0.004	0.01	0.43
Dioxins/Furans (ng/L)				
2,3,7,8- Tetra CDD	0.0003	0.0003 [4]		N/A
2,3,7,8- Tetra CDF	0.0002	0.0002 [4]		N/A
Total TEQ	0.0013	0.0012 [4]		N/A

Notes:

[1] PWQO - Provincial Water Quality Objective or Interim Provincial Water Quality Objective

[2] See Table 20.5 for ammonia assimilation calculations.

[3] The PWQO for this compound is less than the detection limits.

[4] No standard detection limits available for dioxins and furans.

Detection limits not stable due to the very low levels of detection involved.

-- Data not available

N/A No applicable PWQO

ND Concentration deemed non-detect because it is lower than the standard detection limits shown in parenthesis.

Indicates concentration exceeds the PWQO.

Iron concentrations (a natural constituent of Canagagigue Creek surface water) would be relatively unaltered and were computed to still exceed the PWQO. Bis(2-ethylhexyl)phthalate concentrations were computed to also be unaltered and also exceed its PWQO. However, the calculated exceedence of bis(2-ethylhexyl)phthalate is solely a function of the elevated background concentration. These calculations are significantly biased by the detection limits available for this compound and by the preponderance of evidence which has established that this compound is a common laboratory contaminant and should be regarded as a sampling artifact (see the USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, (USEPA, 1993)).

Some parameters such as cadmium, lead, 2,4- and 2,6-dichlorophenol, and m,p- and o-cresols were modeled to be non-detect, however, current detection limits for these compounds are above their respective PWQOs.

Computed ammonia concentrations are calculated differently than other parameters because:

1. ammonia is typically reported as total ammonia (ammonia plus ammonium); and
2. the PWQO for ammonia relates only to the un-ionized fraction of the total ammonia.

The percentage of un-ionized ammonia in an aqueous ammonia solution can be calculated if the pH and temperature of the liquid is known. Therefore, when determining in-stream compliance with the PWQO, the pH and temperature of the receiving stream (in this case Canagagigue Creek) must be known.

The MOEE provided CRA with total ammonia, pH, and temperature records for sampling Station CC1-A (located in Canagagigue Creek upstream of Uniroyal). The data record for this station extends back to 1975, however, field pH measurements were not routinely obtained until 1987. Since the pH can vary significantly between field values and laboratory values, only the data from 1987 to date were considered in the assimilation assessment.

The ammonia data were summarized by month and these data were used as C_{BACK} for ammonia. It is noteworthy that exceedences of the PWQO have occurred at least once at CC-1A in all months except January and December.

Ammonia assimilation calculations performed for the UA₁ WSS contained are presented in Table 20.5

The ammonia assimilation calculations performed for the UACS showed that with the UACS operating and low flow conditions in the Creek, un-ionized ammonia was predicted to exceed the PWQO in the warmer months of the year, specifically June, July, and September. The calculations showed that the PWQO would be exceeded by a maximum factor of 1.40 at SS2; however, during the month of June, the mean upstream Creek water quality at CC-1A already exceeds the PWQO due to natural background water quality or upstream human-induced conditions.

Table 20.5 Ammonia assimilation calculations. UA₁ WSS contained.

Ammonia Concentrations (mg/L)	C Back Total Ammonia (1)	Average Conversion Factor (1)	C Back Un-ionized Ammonia	Modelled SS2 Concentration (Un-ionized Ammonia)	Actual SS2 (2) (Un-ionized Ammonia)	Ratio Model Actual	Ratio Model PWQO
January	0.416	1.09 %	0.005	0.006		--	0.286
February	0.592	1.85 %	0.011	0.012		--	0.623
March	0.891	1.02 %	0.009	0.009	0.001	9.42	0.471
April	0.475	3.47 %	0.016	0.020		--	1.00
May	0.173	5.17 %	0.009	0.017	0.011	1.51	0.832
June	0.384	5.43 %	0.021	0.027	0.012	2.26	1.35
July	0.277	6.87 %	0.019	0.028	0.102	0.28	1.40
August	0.187	4.42 %	0.008	0.015	0.047	0.31	0.737
September	0.227	7.55 %	0.017	0.028	0.010	2.77	1.39
October	0.194	5.14 %	0.010	0.017	0.002	8.72	0.872
November	0.216	2.47 %	0.005	0.009	0.010	0.88	0.442
December	0.107	2.20 %	0.002	0.006	0.001	5.86	0.293

Note:

- (1) Based on MOEE data from Canagagigue Creek Sampling Station CC-1A.
 (2) Actual SS2 concentrations based on quarterly Creek sampling conducted by Uniroyal.

Indicated concentration exceeds the PWQO of 0.02 mg/L.

The C of A for the UACS provides Creek water quality compliance requirements that are closely tied to the assimilation model results. For most parameters considered in the assimilation model, the in-stream compliance concentration at SS2 is set well below the PWQO. Should the predicted improvements of Creek water quality not occur after operation of the UACS, Uniroyal could potentially be in violation of a condition of the C of A.

Assimilation assessment calculations were also performed downstream of the point of compliance for Uniroyal. Other downstream sources of flow to the Creek were considered for these analyses, such as sewage treatment plant discharges and flows from tributaries to the Creek. These assimilation calculations were also presented in the C of A support document for the UACS.

20.7 Conclusions

The Uniroyal Creek model formed the basis for CRA's conclusion that the proposed UACS would improve water quality in the Creek to provincial water quality standards under low flow conditions, except where background water quality would not permit sufficient improvements. The model then gave rise to a series of recommended contingency measures which would be implemented if the water quality standards were not met. These contingency measures included:

- a hydraulic containment contingency plan; and
- a surface water quality contingency plan.

The MOEE concurred that contingency plans were required and a considerable effort was expended by both Uniroyal and the MOEE to ultimately agree on the scope of the contingency plans.

However, the MOEE and CRA were not able to reach agreement on the predictions made by the Creek model. The MOEE's criticisms centered on three central issues, as follows:

- the assumed value of the Creek Low Flow (7Q20);
- the handling of non-detects; and
- the calculations of representative parameter concentrations using geometric means from the various sources of input to the Creek.

The basis for CRA's determination of the 7Q20 for the Creek and the development of input parameters was described above. The MOEE believed that the appropriate value of the 7Q20 was 30 to 70 L/s, versus the 170 L/s evaluated by CRA. The MOEE also believed that arithmetic means of contaminant concentrations should be used in the assimilation calculations, despite the excellent calibration results obtained by using geometric means as discussed above.

In the end, the MOEE chose to disagree with our modeling effort in general, but to approve the implementation of the UACS on the basis that water quality

would be improved and further groundwater containment measures would be implemented if they were shown to be necessary. The criteria selected to determine whether or not downstream surface water was significantly impacted by the uncontained discharges from the UA were based principally upon the output of the model. Other factors were taken into account, such as analytical quantitation limits and analytical variability. However, the model was utilized in the new C of A as the principal measuring stick for the performance of the UACS.

Construction of the UACS treatment system is expected to begin in April 1996, pending weather conditions and receipt of a final C of A for one component of the treatment system. The extraction wells have already (February 1996) been installed. Operation of the UACS is scheduled to begin in the fall of 1996.

The reliability of the model will be tested by in-stream measurements of surface water quality shortly after start-up and over the life of the operation of the system. By the time we can fully validate the model, we will know more about the relationship between the UA and the Creek than this model could have ever predicted.

References

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- USEPA 1993, USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review, United States Environmental Protection Agency, Publication 9240.1-05, February 1993, p82.