TOXICITY REGULATION OF RADIOACTIVE LIQUID WASTE EFFLUENT FROM CANDU STATIONS – LESSONS FROM ONTARIO'S MISA PROGRAM.

D.W. Rodgers
Kinectrics
800 Kipling Ave.
Toronto M8Z 6C4.

Abstract

Toxicity testing became an issue for Ontario's CANDU stations, when it was required under Ontario's MISA regulations for the Electricity Generation Sector. In initial tests, radioactive liquid waste (RLW) effluent was intermittently toxic to both rainbow trout and Daphnia. Significant differences in RLW toxicity were apparent among stations and contributing streams. Specific treatment systems were designed for three stations, with the fourth electing to use existing treatment systems. Stations now use a combination of chemical analysis and treatment to regulate RLW toxicity. Studies of Ontario CANDU stations provide a basis for minimizing costs and environmental effects of new nuclear stations.

1. Introduction

CANDU pressurised heavy water power reactors (PHWR) differ from the pressurised light water reactors (PWR) prevalent elsewhere in a number of features which are relevant to discharge water quality. In general, the activity of fission product in CANDU systems is lower than in PWR designs, because the capacity for on-power fuelling facilitates prompt removal of failed fuel elements. However, tritium (^3H), which is formed by neutron activation of the deuterium oxide (^2H_2O) moderator and coolant, is a particular problem for CANDU reactors and is frequently the limiting radionuclide with respect to station emissions.

In Ontario, there are presently four Nuclear Stations, operated by Ontario Power Generation or Bruce Power, which are referred to within this paper as Station's A, B, C, and D. At present, the Stations include 18 CANDU reactors, each rated at more than 500 MW/Unit, and produce greater than 50 % of Ontario's electricity.

The radioactive liquid waste (RLW) system in Ontario's CANDU nuclear generating reactors collects, segregates, monitors, processes (as necessary) and discharges the water from numerous drains within the radioactive zones of the station. Details of the RLW systems at Ontario's CANDU nuclear stations vary, but the systems typically consist of multiple (5 to 12) large volume tanks, segregated for collection of low (<37 kBq/L) and high (>37 kBq/L) activity water. Individual tank volumes are about 120 m^3 with the total collection capacity ranging from 600 to 1700 m^3 per station. Grab samples of the individual tanks are also analysed for radioactivity prior to any pump-outs. The RLW effluent is monitored for on-line activity then discharged through the combined station condenser cooling water outfall, to the ambient lake. The combined condenser cooling water flows at CANDU multi-unit stations range from 120-170 m^3s^{-1} yielding dilution factors of at least 10^4 during RLW tank discharges.

Historically, restrictions on RLW discharge were solely based on radionuclide limits established by the Atomic Energy Control Board of Canada and its successor the Canadian Nuclear Safety Commission (CNSC). Derived Emission Limits (DEL's) for Station emissions of radionuclides are established through pathway analysis (air, water, direct irradiation) for exposure of identified critical groups of the public, such that these members of the public do not received radiation doses in excess of those recommended by the International Commission on Radiological Protection. The derived emission limits are site-specific and range from 4 – 36 x 10^4 TBq per month for ^3H (as tritiated water) and from 4 - 60 x 10^2 GBq per month of gross βγ activity discharged via aqueous pathways. Ontario CANDU Stations use a much more restrictive administrative limit, requiring that nuclear station radionuclide emissions not exceed 1% of the DEL. Actual radioactivity emissions via the RLW system are typically <0.1% of the DEL for both tritium and gross βγ activity.

Prior to 1989, RLW effluent was not regulated by, or monitored for, conventional water quality parameters, except for pH. However, toxicity testing was among the parameters specified by the Ontario Ministry of Environment and Energy's the Municipal and Industrial Strategy for Abatement (MISA) program, which was promulgated under the Clean Water Act. MISA monitoring of Ontario Hydro discharges, including Ontario CANDU stations commenced in the initial fact finding year (June 1990 - June 1991)0, then resumed in 1995[1] and has continued to the present. Toxicity testing is integral to the MISA program, with stations required to tests both process effluent streams such as RLW, and non-process streams such as building effluent. Process streams were initially required to conduct monthly using acute lethality toxicity tests with *Daphnia magna*[2] and rainbow trout, *Oncorhynchus mykiss*[3]. After 12 consecutive months without failure of acute tests, the testing schedule for the effluent then progresses to quarterly acute toxicity tests and semi-annual chronic toxicity testing (fathead minnow, *Pimephales promenalis*, survival and growth test[4] and *Ceriodaphnia dubia*. survival and reproduction test[5]).

This paper summarizes the sequence from initial toxicity testing of RLW effluent, through identification of toxic components and installation of treatment processes, followed by continued monitoring to maintain RLW as a non-toxic effluent, once the actions and toxicity treatments were in place. Finally this paper suggests approaches to minimizing both treatment costs and environmental effects of potential RLW effluent toxicity for new stations.

2. Toxicity Testing, Identification and Elimination.

During the initial year of MISA monitoring, slightly more than 25% of the samples of radioactive liquid waste effluent were toxic to *D. magna* and/or rainbow trout[6]. These initial studies were followed by more detailed studies of RLW toxicity.[7] In all, more than 500 acute toxicity tests were conducted over more than four years, with extensive chemical analysis in parallel with toxicity testing. Throughout these tests, RLW effluent was intermittently toxic to *Daphnia,* trout or both in acute toxicity tests, with 20-40 % of samples toxic.

Results of these studies were analysed statistically using a variety of single and multiple variable parametric and non-parametric techniques. In all analyses, the levels of activity of the RLW effluent were not sufficient for radioactivity to be a factor in toxicity. Rather toxicity was the result from the actions and interactions of a range of conventional inorganic and organic pollutants. Although no single inorganic or organic compound or combinations thereof was consistently related to observed toxicity, elevated copper and zinc and low water hardness and conductivity were often important components in multivariate analysis of RLW toxicity data. Low hardness and conductivity are factors which are know to exacerbate the toxicity of metals and many other contaminants. Additional relationships could be discerned when effluents were examined on a source basis. In Stations with laundry waste streams, concentrations of Total Organic Carbon (TOC) provided a marker of the proportion of laundry waste in the effluent and Daphnia mortality increased at higher concentrations of TOC, with greater than 50% mortality observed in the majority of samples when TOC was greater than 12-15 ppm (Figure 1).

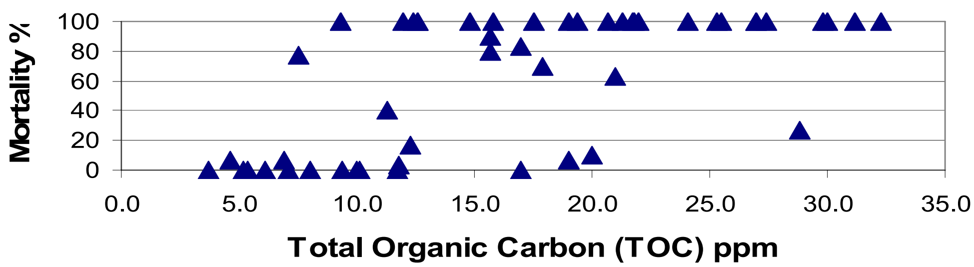

Figure 1: *Daphnia* Mortality versus Total Organic Carbon (Station B)

Hydrazine (N_2H_4) also emerged as a significant toxic component in RLW effluent from some stations. Hydrazine is used for oxygen and pH control in a number of components o f CANDU reactors. Because of its high reactivity, hydrazine was not on the original list of chemicals monitored in the first round of MISA but in subsequent tests, it was determined that

- N_2H_4 was reasonably persistent than anticipated in Great Lakes waters, with a half-life of days at 5 -20 ^oC
- N_2H_4 concentrations in toxic effluents were in the range of 0.2 - 0.5 mg/L
- The effluent was non-toxic after N_2H_4 removal but toxicity returned if 0.5 mg/L N_2H_4 added

Following these initial studies, the focus shifted to individual stations and streams, using a multifaceted approach to reducing and eliminating RLW toxicity within each station. A key component was a critical review by the station personnel of the chemicals entering the RLW system. Where possible, toxic chemicals were replaced or usage reduced, and potentially toxic streams were isolated and treated separately. In parallel with the station review, we conducted a series of treatment based toxicity reduction tests with RLW from each station. In particular, there was a focus on utilizing the existing radioactivity control process (filtration and selective sorption) to reduce toxicity, rather than seeking new processes which could require extensive alterations. In addition, broadly based treatments were favoured to account for future unknown toxicants.

D. magna were usually more sensitive than rainbow trout to RLW during the initial acute toxicity tests[8] and a much smaller volume of effluent is required for the *D. magna* test. Accordingly, initial treatment-based tests were conducted using *D. magna*, followed by trout tests of the preferred treatment options.

In general, modifications of existing filtration and sorption-based treatment systems were able to reduce toxicity of non-laundry effluents. However, laundry waste required separate treatment. As sorption-based treatment systems would create additional solid radwaste, a secondary objective was to maximize sorbent efficiency.

The toxic components detected and treatment processes applied were specific to each station and are summarized below.

Station A

Status and toxic components

- No laundry waste
- Hydrazine (N_2H_4) was the principal toxic component

Treatment

- Hydrazine was removed by oxidation with sodium hypochlorite (NaOCl)

$$\mathbf{N_2H_4 + 2NaOCl \rightarrow N_2 + 2H_2O + NaCl}$$

- Excess NaOCl (120 – 150%) added on the basis of measured N_2H_4
- Final effluent was polished with activated charcoal to remove residual N_2H_4 or NaOCl

Stations B and C

Status and toxic components

- Laundry waste was a significant toxic stream
- Total Organic Carbon (TOC) up to > 200 mg/L
- Copper was a common toxic component of non-laundry effluent
- **Hydrazine was a sporadic factor in toxicity**

Treatment Station B

- Laundry diverted to common facility.
- Existing filtering and selective sorption treatments were used to treat remaining effluent (unable to use activated carbon as it was incompatible with treatment columns)
- Breakthrough remains a concern
- **Filters and spent resin may create significant solid waste problem**

Treatment Station C

- Laundry diverted to common facility.
- Back end treatment beds (activated carbon followed by IX resin and $CaCO_3$ filtering) used for remaining effluent
- Breakthrough remains a concern
- Spent activated carbon and resin may create significant solid waste problem

Station D

Status and toxic components

- Site of combined laundry for all stations.
- Laundry waste is a major toxic stream.
- Copper and other metals cause intermittent toxicity of non-laundry effluent
- Hydrazine a sporadic factor in toxicity

Treatment

- Reverse osmosis(RO)
- Pretreatment - coagulant added before RO to remove suspended solids
- As RO effluent was of low conductivity and pH (often below 6.0) a final polishing with $CaCO_3$ filter bed was added to normalize pH

Operational Experience

Following installation of treatment and control systems, unexpected problems were encountered in the initial phases of operations at some stations. In the first week of operation of treatment systems at Station C, waste from a long neglected sump overwhelmed the system resulting in a toxic effluent. At station D, the initial RO effluent was toxic of effluent to trout likely due to metabolic breakdown products of the laundry surfactant, nonylphenol ethoxylate (NPE), in holding tanks. The problem was resolved through removal of detergents containing NPE from the laundry stream, and a combination of increased cleaning and decreased retention time in holding tanks.

Once initial problems were resolved, the focus changed to maintaining the system and dealing with system irregularities. The problems encountered centred on the following issues:

- Saturation of treatment systems. When the exchange resin approaches saturation, there is a potential for toxicity breakthrough. Further at the end of their cycle, some resin systems may selectively absorb Ca, which would exacerbate metals toxicity.
- Treatment systems may not be sufficient for unknown toxicants - especially water soluble organics
- Irregular cleaning and excessive retention times in holding tanks may generate secondary toxicity issues

One of the best examples of problems caused by system irregularities is illustrated by a series of events at Station B in 2001 In March 2001, Station B RLW samples started to consistently fail the Daphnia IQ® screening test. The Daphnia IQ® is a toxicity screening test whose results correlated well with the results of the Daphnia acute test.[9] It was used by many of the Stations to evaluate the toxicity of RLW samples prior to discharge.

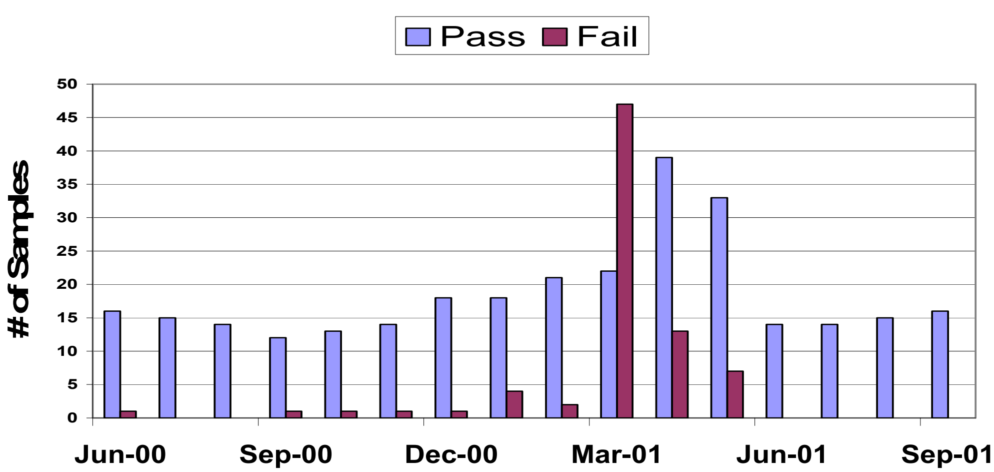

Figure 2: Station B - Daphnia IQ® Pass/Fail incidence of pre-discharge RLW samples

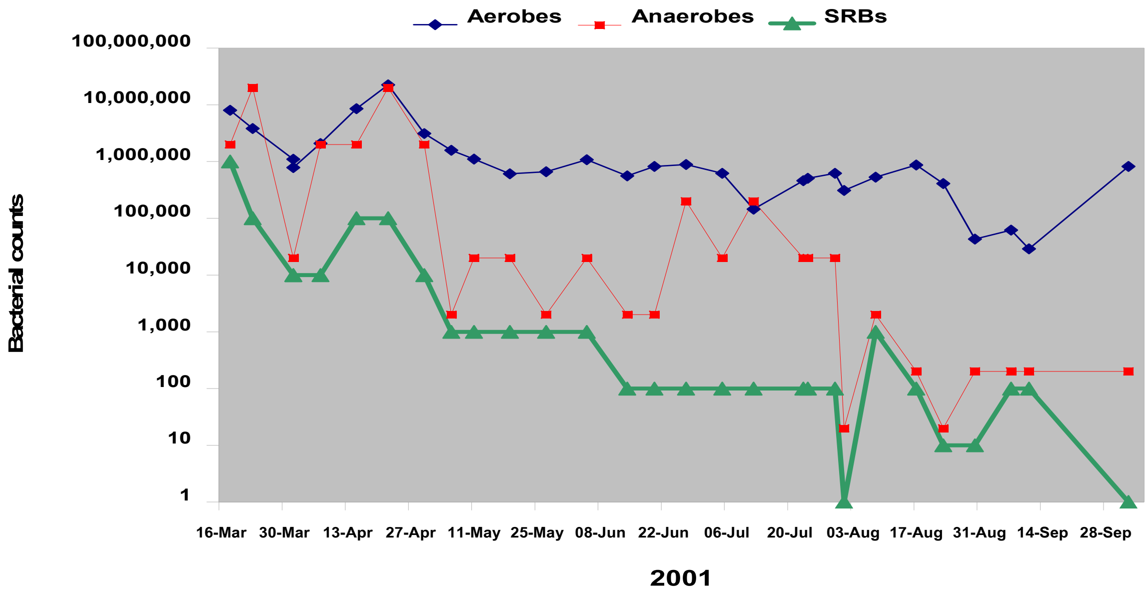

Figure 3: Bacterial counts in Station B, RLW holding tanks

The consistent failure of RLW samples in the Daphnia IQ® screening test stimulated extensive additional testing and analysis of the RLW system. In particular, bacteria sampling and characterization studies revealed very high numbers of anaerobic and sulfate reducing bacteria (SRB) in holding tanks within the RLW system (Figure 3); which then declined as the effluent toxicity decreased.

The high numbers of anaerobic and sulfate reducing bacteria were of particular concern because of the concomitant suite of changes in the chemical composition of RLW samples. These included the following.

1. Decrease in dissolved oxygen from > 6 to < 3 ppm

2. Decrease in pH from >6.5 to < 5.5

3. Increase in sulphide from >20 ppb to 1000 ppb

4. Increase in total metal concentrations
   • Cu up to 160 ppb; • Zn up to 320 ppb
   • Pb up to 75 ppb • Fe up to 1500 ppb
   .
5. Increase in concentrations of organic compounds
   • Total Organic Carbon (TOC) up to 400 ppm;
   • acetaldehyde up to 274 ppm
   • ethanol up to 120 ppm
   • methanol up to 20 ppm

In general, *Daphnia* IQ® test and acute toxicity failures were associated with elevated metal concentrations, although elevated concentrations of sulphide and organic compound may also have been factors. Consequently treatments which reduced metal concentrations (i.e. IX resin) were effective in reducing RLW toxicity

In detailed analysis of the RLW system following the *Daphnia* IQ failures, a significant leak of ethylene glycol from a refrigeration unit to the RLW was discovered. The elevated concentrations of TOC resulting from the leak stimulated bacterial growth within the system (Figure 3). In turn, the increased bacterial growth led to anaerobic conditions a drop in dissolved oxygen and pH. The decrease in pH, and increase in SRB activity appears to have mobilised metals within the RLW system, which were primarily responsible for the *Daphnia* IQ failure. The elevated concentrations of small organic compounds observed were derived from secondary fermentation of original bacterial growth in response to the ethylene glycol food source.

Operational changes at Station B following the Daphnia IQ® failures included

1. Reduction in the number of "routine operational" holding tanks to decrease tank retention time to less than 3d
2. Regular bacterial monitoring of RLW tanks; with a system review when anaerobes are greater than aerobes
3. Addition of aeration capabilities for RLW tanks

Following these changes, the frequency of Daphnia IQ failures has again decreased and the numbers of aerobic and anaerobic bacteria decreased (Figures 2 and 3). As a result of the toxicity screening system in place at the time, the station was able to avoid releasing a toxic effluent. Toxicity screening thus served as a "process control" which integrated all components of the RLW system and provided information not only about effluent toxicity but also about system performance.

Continuing Operations

With improvements to RLW treatment systems, many of which were worked out as a result of toxicity screening, Ontario CANDU stations are now confident that pre-discharge chemical analysis is sufficient to ensure effluent quality and toxicity screening. Rapid toxicity testing was critical to the development of effective RLW effluent treatment systems, but was eventually discontinued due to continuing economic pressures, the low frequency failure compounded by the occurrence of false positives, and the fact that the toxicity screening tests are outside of existing regulatory requirements.

3. RLW Toxicity in New Stations

As noted in the introduction, regulations for toxicity control of RLW were enacted for existing stations only after the stations were operational and toxicity controls had to be installed within the station “as built”. However, new stations in Ontario will be subject to these same regulations and should be able to avoid many of the difficulties encountered by existing stations by integrating planning for toxicity control with other design and construction activities. Toxicity related considerations should include the following.

1. Identify chemicals and process to be used in the Station.

    - Inventory known toxic substances and replace where possible.
    - Isolate and treat known toxic substances which cannot be avoided (i.e. collect and treat high hydrazine lay-up water before it reaches the common RLW system)

2. Alter process and holding tank design to avoid toxicity.

    - Minimize retention time and schedule regular cleaning
    - include aeration capability
    - Incorporate the capability to include new methods in treatment processes (i.e. metal specific resins in preference to general IX).

.

3. Laundry waste remains problematical. Both reverse osmosis and evaporation are expensive options. Alternatives include the following.

    - Use of less toxic laundry chemicals – avoid NPE and related compounds.
    - Segregation and separate treatment of aqueous laundry waste – biological based systems
    - Use of non-aqueous laundry methods (may lead to other chemical concerns)
    - Disposable suits (may add to solid waste disposal)

4. Despite the above, there may well be toxic events with RLW effluent, particularly during commissioning phases. Rapid toxicity tests can be very effective during start-up in screening potential treatments on a real time basis.

4. Acknowledgements

This paper summarizes several studies conducted over many years. Much of this work was conducted in collaboration with Dave Evans (Kinectrics/OPG) and we were ably assisted by a large supporting cast including L.Vereecken-Sheehan, L. Bremner, J. Schroeder, I. Cord, C. Donovan, D. Illic, H. Kowalyk, and C. Rose-Taylor.

This work was supported and samples provided by Ontario Hydro and its successors, OPG-N and Bruce Power. Numerous individuals at both companies have contributed to these studies and I acknowledge and thank R. Al-Samadi, J. Borremeo, M. Brett, T. Dobson, Ian Hartford, R. Hester, S. Khalid, P. Skelton, P. Wiancko and F. Wigley of OPG and S. Andrews, R. Bonner, W. Catton, L. Peerla Proulx, J. Roberts, B. Stepaniak, and C. Tripati of Bruce Power for their help and support.

5. References

[1] Effluent Monitoring and Effluent Limits - Electric Power Generation Sector, Ontario Regulation 215/95 made under the Environmental Protection Act, filed April 13, 1995.

[2] Environment Canada, Biological test method: Reference method for determining acute lethality of effluents to *Daphnia magna*, Environmental Protection Publications, Conservation and Protection, Reference Method EPS 1/RM/14 Second Edition 2000.

[3] Environment Canada, Biological test method: Reference method for determining acute lethality of effluents Rainbow Trout. Environmental Protection Publications, Conservation and Protection, Reference Method EPS 1/RM/13 Second Edition.2000.

[4] Environment Canada, Biological Test Method: Test of Larval Growth and Survival Using Fathead Minnows. Environmental Protection Publications, Conservation and Protection, Reference Method EPS 1/RM/22.1992.

[5] Environment Canada, Biological Test Method: Test of Reproduction and Survival Using the Cladoceran, Ceriodaphnia dubia. Environmental Protection Publications, Conservation and Protection, Reference Method EPS 1/RM/21. 1992.

[6] R.W. Maruska, A review of Ontario Hydro's MISA monitoring results. Toronto, ON, Canada: Ontario Hydro, June 1992, NOCS-IR-07291-OUO/TISD-07291-0001.1992.

[7] D.W. Rodgers. Toxicology studies in support of Program Approval for Ontario Hydro Nuclear Compliance to the Effluent Monitoring and Effluent Limits – Electric Power Generation Sector Regulations. Ontario Hydro Technologies Report 6704-001-1998-RA-0001-R00 1998. .

[8] Rodgers, D.W., J. Schröder and L. Vereecken-Sheehan, Comparison of Daphnia magna, rainbow trout and bacterial-based toxicity tests of Ontario Hydro aquatic effluents. Water, Air Soil Pollution 90, 1996. pp 105-112.

[9] Rodgers D.W. The rise and fall of short-term toxicity testing for Ontario CANDU stations. Society of Environmental Toxicology and Chemistry (SETAC) North America 27th. Annual Meeting. 6–9 November 2006**,** Montréal, Quebec.