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SPECIAL ISSUE: RADIATION IN OUR ENVIRONMENT

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Frosted trees along the Ottawa River bordering AECL's Chalk River Laboratories. Photo © Atomic Energy of Canada Ltd.

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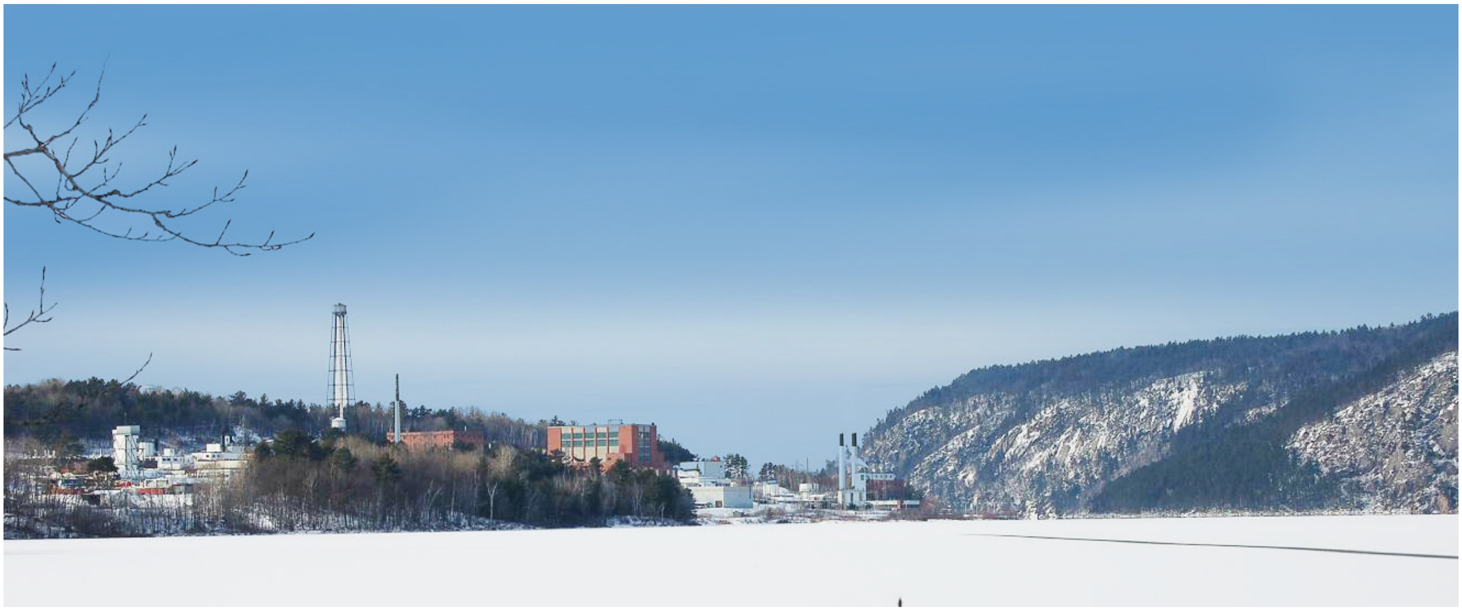
ERRATUM

EDITORIAL

INFORMING THE DISCUSSION

B. Sur, C. Butler, R. Didsbury, A. McIvor and G. Strati
***AECL Nuclear Review* Editorial Board**



Concern for the environment, along with public health, security, and safety is a ubiquitous feature of today's social consciousness. Radiation, as a sometimes feared and often misunderstood harbinger of both the beneficial and harmful consequences of nuclear science and technology, occupies a special niche in that consciousness. On the one hand, high-tech, clean nuclear energy provides the means for sustaining our lifestyles while avoiding millions of tons of greenhouse gas emissions and mitigating the environmental consequences of climate change and extreme weather events. On the other hand, the operation of nuclear facilities and storage of the radioactive nuclear fuel waste raises legitimate concerns around the spread of radioactivity in the environment and the perceived detrimental and sometimes multi-generational consequences on people and on the ecosystem. This equation, balancing benefits for people against real or perceived harm to the environment, applies to nearly all nuclear activities, including radiation therapy, nuclear medicine and the production and use of medical and industrial isotopes. The purpose of this special issue of the *AECL Nuclear Review* is to highlight some of the science that informs the discussion of radiation, the environment and health.

Radiation and radioactivity in our environment occurs both naturally and as a result of human activity. Disentangling the effects of natural radiation from man-made radiation in our environment, and the effects of the low-levels of environmental radiation from other effects such as chemical environmental contamination, is not easy; this makes the study of radiation in our environment a difficult multi-disciplinary effort and a sometimes controversial subject.

AECL sites have been involved in the scientific study of environmental radiation and radioactivity from the earliest days of the nuclear age. Legacy contamination from uranium refining operations at Port Hope, Ontario, from the 1930's to 1970's, is being remediated by the Port Hope Area Initiative. The Underground Research Laboratory, one of the earliest and most extensive scientific studies in the world of a deep underground geological repository for spent nuclear fuel, operated from the 1980's to early 2000's at AECL's Whiteshell Laboratories in Manitoba. Environmental research at Chalk River Laboratories in Chalk River, Ontario, has been carried out since its early operation in the 1940's. Environmental risk assessment and remediation efforts in the Chalk River Laboratories have been accelerated in recent years by the Canadian government's Nuclear Legacy Liabilities Program. The Chalk River site is thus one of the most extensively studied and comprehensively understood sites for environmental radioactivity in the world. Many of the articles and technical reports in this special issue are naturally based on work carried out at this site.

The ecological effects on the Ottawa River from 70 years of nuclear activity at the Chalk River Laboratories is of interest to a number of stakeholders: the project that is tasked with assessing and remediating these effects, the government that is funding the remediation efforts, and the public, including laboratory personnel, who value and enjoy this pristine, naturally beautiful stretch of water. This special issue of the *AECL Nuclear Review* is pleased to present a set of four articles with extensive new data and analysis that provide the sound scientific basis for a radiological risk assessment and an effective and efficient response to the issue.

Inadvertent leaks from the NRX reactor's irradiated fuel bays, shut down since 1992 and currently being decommissioned, have caused a well-documented ground water "plume" of radio-strontium and tritium that is decaying and at the same time, very slowly, migrating to the river. Olfert *et al*. ("Groundwater Monitoring and Plume Discharge Zone Characterization for the NRX Radiostrontium Plume at Chalk River Laboratories") highlight the best-in-class (as evaluated by the Canadian Nuclear Safety Commission) groundwater monitoring program at CRL and present new and extensive data that confirm the extent of the plume's interface with the river and the efficacy of current monitoring efforts.

Nuclear operations at Chalk River Laboratories, including the "once-through" river water cooling of the NRX reactor, the 1952 fuel failure accident, and other legacy activities have resulted in the previously documented deposition of particulate radioactivity in a localized area on the river bed. The article by Rowan *et al*. ("Biota-Sediment Accumulation Factors (BSAF) for Radionuclides and Sediment Associated Biota of the Ottawa River") provides extensive and groundbreaking evidence that the uptake of this radioactivity by sediment dwelling creatures such as pea clams, midges and mayfly larvae depends primarily on local radioactivity concentrations in the riverbed sediment and not on other factors such as the radioactivity concentration in the flowing river water.

The article by Bond *et al*. ("Drivers of Abundance and Community Composition of Benthic Macroinvertebrates in Ottawa River Sediment near Chalk River Laboratories") looks in turn at the diversity and abundance of the bottom dwelling creatures in the Ottawa riverbed, and again through extensive and first-of-a-kind data and scientific analysis demonstrates that the population is negligibly, if at all, affected by nuclear activities; rather it is affected more by water temperature, chemistry and other general environmental factors.

Finally, the article by Lee *et al*. ("Edibility of Sport Fishes in the Ottawa River near Chalk River Laboratories") presents for the first time statistically extensive data on game fish – walleye, northern pike, bass and the like – captured upstream and downstream of the laboratories, that show once again that radioactivity levels in the fish are negligibly affected, if at all, by current or legacy nuclear activities at the laboratories. Indeed to account for these somewhat surprising findings, Lee *et al*. speculate that the residual radioactivity levels in the game fish are the result of atmospheric bomb testing from the 1950's and early 60's!

Taken together, these four articles provide sound scientific evidence, not speculation, that while legacy activities have resulted in very localized low levels of radioactivity released into the Ottawa River, the effects of these activities on the river's ecosystem has been negligible. More importantly, the scientific effort has resulted in a deeper understanding of the extent and mechanism by which radiation affects this part of our environment, and this is leading to a mitigation of the harm and an enhancement of the benefits of the nuclear equation.

INVITED ARTICLE

Biota-sediment accumulation factors for radionuclides and sediment associated biota of the Ottawa River

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As Ottawa River contamination is historical and resides in sediment, ecological risk and trophic transfer depend on linkages between sediment and biota. One of the ways in which this linkage is quantified is through the use of the biota sediment accumulation factor (BSAF). In this study, we present the first field estimates of BSAF for a number of radionuclides. The strongest and most consistent BSAFs were those for ^{137}Cs in deposit feeding taxa, suggesting that sediment concentrations rather than dissolved concentrations drive uptake. For crayfish and unionid bivalves that do not feed on sediment, biota radionuclide concentrations were not related to sediment concentrations, but rather reflected concentrations in water. BSAFs would not be appropriate for these non-deposit feeding biota. BSAFs for ^{137}Cs were not significantly different among deposit feeding taxa, suggesting similar processes for ingestion, assimilation and elimination. These data also show that the concentration factor approach used for guidance would have led to spurious results in this study for deposit feeding benthic invertebrates. Concentrations of ^{137}Cs in Hexagenia downstream of the CRL process outfall range by about 2-orders of magnitude, in comparison to relatively uniform water concentrations. The concentration factor approach would have predicted a single value downstream of CRL, underestimating exposure to Hexagenia by almost 2-orders of magnitude at sites close to the CRL process outfall.

1. Introduction

The Ottawa River has received nuclear reactor effluent from Chalk River Laboratories (CRL) for more than 60 years, including releases from a partial fuel failure of the National Research eXperimental (NRX) reactor in 1952. In 1992, this “once through” research reactor was permanently shut down, significantly reducing the quantity of fission and activation products released to the river. Continuing releases from the National Research Universal (NRU) reactor are extremely low, approaching or exceeding analytical capabilities, and monitoring data now shows no increases in concentrations of ^{137}Cs and ^{90}Sr in Ottawa River water downstream of CRL. Recent interest in the potential impact of these historical releases and the possible need for remediation of a small region of sediment immediately downstream from the release point has led to comprehensive studies to assess risk to people and wildlife.

The CRL process outfall releases liquid effluent through a vertical diffuser located at a depth of approximately 22 m and contamination of river sediments by radionuclides declines exponentially for about 2 km downstream of the process outfall. This contamination has been well characterized by many studies conducted by Atomic Energy of Canada Ltd. (AECL) as part of the risk assessment process, see e.g. [1], and in this issue, Bond *et al*. present the results of a benthic community study of the CRL reach of the Ottawa River [2]. As the Ottawa River contamination is historical and resides in sediment, ecological risk and trophic transfer depend on linkages between sediment and biota. These linkages also include the transfer of sediment contaminants to insectivorous terrestrial wildlife (e.g., swallows and bats) by emergent aquatic insects, such as the burrowing mayfly (*Hexagenia*) [3], which is the most abundant profoundal benthic invertebrate in the Ottawa River [2]. One of the ways in which this linkage is quantified is through the use of biota sediment accumulation factors.

The biota sediment accumulation factor (BSAF), the ratio of contaminant concentrations in biota to those in sediment, was originally proposed to assess the potential bioaccumulation of hydrophobic organic contaminants by benthic invertebrates using equilibrium partitioning theory [4]. Equilibrium partitioning theory assumes that in biota, hydrophobic organic contaminants partition into lipid, and that for sediment, hydrophobic organic contaminants partition into carbon, or organic matter. This approach uses contaminant concentrations expressed on a lipid basis for biota and a carbon basis for sediment, and the ratio of concentrations in biota lipid to those in sediment carbon is defined as the biota-sediment accumulation factor [5]:

$$\boldsymbol{BSAF} = \frac{C_{biota}/f_{lipid}}{C_{sed}/f_{soc}} \tag{1}$$

where C_{biota} is the contaminant concentration in biota (μg kg^{-1} ww), f_{lipid} is the lipid fraction of the biota, C_{sed} is the contaminant concentration in sediment (μg kg^{-1} dw) and f_{soc} is the sediment organic carbon fraction (g organic carbon g^{-1} dw). The interest in sediment as a source of hydrophobic organic contaminants is due to the low solubility of these contaminants in water and the often historical nature of the contamination, e.g., PCB production was banned in North America in 1977.

The role of sediment in the bioaccumulation of metals by benthic invertebrates has been explored through several biokinetic models that consider sediment ingestion, partitioning between water and sediment, food ingestion and direct uptake from water [6, 7, 8]. Sediment was identified as the primary source of metals to deposit feeding invertebrates [7, 8] due to high sediment ingestion rates and metal assimilation efficiencies from sediment. These studies are usually interested in ongoing releases where concentrations in water may be expected to drive bioaccumulation and sediment-water partitioning. For both organics and metals, uptake from sediment is usually evaluated in the laboratory [9], often in conjunction with toxicity tests.

The use of the term BSAF was extended to include metals [10], due to the utility of the parameter in estimating concentrations of metals in benthic invertebrates from sediment concentrations for ecological risk assessments. Ecosystem specific BSAFs have also been determined as a component of ecological risk assessments in order to predict concentrations of metals and other contaminants in benthic invertebrates from sediment concentrations at other sites within the ecosystem [3]. Most of the existing metal BSAF data and studies on bioaccumulation of metals from sediment by benthic invertebrates are for a relatively small number of metals, particularly Ag, As, Cd, Cu, Cr, Ni, Pb, Se and Zn [6, 7, 8, 10, 11].

For radionuclides, virtually no data exists for benthic invertebrate BSAFs, with concentration factors (CF, biota/water) predominating both in studies and guidance [12, 13]. This, in part, reflects the regulatory bias towards ongoing releases that would be expected to drive concentrations both in water and sediment. A recent and comprehensive literature review by the IAEA EMRAS (Environmental Modelling for Radiation Safety) project [14] presented tables of BSAFs that indicated no data available for many common radionuclides, including ^{241}Am, ^{60}Co, ^{137}Cs, ^{210}Pb, ^{226}Ra and ^{90}Sr, although data was reported for stable Co, Pb and Sr [14]. The stable isotope data largely comes from Canadian uranium mine sites, and was excluded from the new IAEA handbook on radionuclide transfer to wildlife on the basis of uncertainty, site-specificity and lack of application in available assessment tools [15]. BSAF values available in the international wildlife transfer database [16] are limited to Am, Cm and Pu in insect larvae, molluscs and macrophytes from a single study [17], and a variety of stable element values for aquatic macrophytes from Canadian uranium mine sites. For radionuclides, the BSAF is calculated as [16]:

$$\mathbf{BSAF} = \frac{C_{biota}}{C_{sed}} \tag{2}$$

where C_{biota} is the activity concentration in biota (Bq kg^{-1} ww) and C_{sed} is the activity concentration in sediment (Bq g^{-1} dw). This definition will be used in this study.

A literature review for this study also found no field estimates of radionuclide BSAFs for benthic invertebrates. This is startling, as sediment is known to comprise ≥ 99% of particle reactive radionuclide (e.g., ^{241}Am and ^{137}Cs) inventories in contaminated aquatic ecosystems and even relatively soluble radionuclides, such as ^{90}Sr, can be largely associated with sediment (85%) [18]. In addition, benthic invertebrates are usually partially or totally immersed in sediment, receiving radiation dose from external exposure from these large inventories of sediment associated radionuclides and internal exposure from sediment in their digestive tracts and tissue concentrations. Benthivorous fish preying on these invertebrates are also known to have higher concentrations of ^{137}Cs than would be expected from their trophic level [19].

Aside from the regulatory bias towards water, it is possible that difficulties in sampling sufficient quantities of benthic invertebrates for radionuclide analysis discourages most from BSAF studies. For example, an earlier study on the bioavailability of ^{60}Co to benthic deposit feeders in the Ottawa River near the process outfall at Chalk River Laboratories (CRL) found invertebrate densities too low to determine ^{60}Co concentration despite high sediment concentrations, and conducted the study in the laboratory with Ottawa River sediment and commercially available cultures of *Tubifex sp.* [20]. Even in the highly contaminated Kiev reservoir system near Chernobyl, laboratory bioaccumulation studies were conducted due to difficulties in obtaining sufficient *in situ* benthic invertebrate biomass to detect radionuclide concentrations [21]. Another study on the CRL site on the fate of ^{60}Co in Perch Lake, presents a food web diagram that includes concentration factors for fish, turtles, amphibians, molluscs and aquatic plants, but with a "?" for insects [22]. With no literature on radionuclide BSAFs, a recent study on ^{134}Cs and ^{137}Cs in benthic invertebrates and sediment from Fukushima impacted streams did not calculate BSAFs from their data, even though it was possible [23]. Even for aquatic macrophytes, which are easy to sample in large quantities, and which have been shown to derive 75% or more of radionuclides in their tissues from sediment [24], concentration factors and not BSAFs are used in assessments [12, 13].

Where radionuclide contamination is largely historical, and water concentrations are not in steady state (or equilibrium) with buried radionuclides, BSAFs for sediment associated biota are much more relevant than CFs for assessing exposure and bioaccumulation [14]. As part of an ecological risk assessment of historical contamination from CRL nuclear operations on the Ottawa River, we conducted a large and comprehensive study of benthic invertebrate, macrophyte and sediment radionuclide concentrations upstream and downstream of the process outfall, and calculated BSAFs from these data.

In this paper, we present data for radionuclide concentrations in sediments and sediment associated biota for a variety of primordial (^{40}K, ^{210}Pb, ^{226}Ra and ^{228}Ra), cosmogenic (^{7}Be), and anthropogenic radionuclides (^{60}Co, ^{94}Nb, ^{137}Cs). Biota include macrophytes, crustaceans, bivalve molluscs, insect larvae and oligochaetes. Relationships between biota and sediment were then explored through regression analysis, with BSAFs calculated where appropriate. Finally, we identify biota and radionuclides for which BSAFs are appropriate, compare values with limited published data and discuss the utility of the BSAF approach in radiological assessments.

2. Method of Approach

Ottawa River sediment and biota were sampled along nineteen transects spaced either 0.5 or 1 km apart and covering 16 km this reach (Figure 1). Seven of these transects were located upstream of the CRL process outfall, with one located on the process outfall and the remaining eleven transects located downstream of CRL. Sampling locations were located on both sides of the river within 5 m depth intervals to 30 m, 30-50 m and maximum depth. At each site, five Ekman dredges were taken for benthos, along with one core for sediment. We were able to obtain sediment and benthic invertebrates from 214 sites. The more than 1000 Ekman dredge samples obtained for this study overcame the low abundance of benthic invertebrates that limited other studies. Sampling occurred during the ice-free period of 2009-2011.

The upper 5 cm of sediment from the cores were retained dried (60 °C), ground and packed for gamma spectroscopy analysis on low background High-Purity Germanium (HPGe) detectors. Ekman dredge samples were sieved through 250 µm mesh, deposit feeding benthic invertebrates were picked immediately in the laboratory, separated by species and allowed to clear their guts in Ottawa River for 24 hr at 4 °C. Samples were then treated the same as sediment in preparation for gamma spectroscopy. Sediment water content (fraction) was determined from dried samples and sediment organic content (fraction) was determined by ashing dried sediment at 450 °C.

Two species of unionid bivalves were collected: *Eliptio complanata* (31 sites) and *Lampsilis radiata* (8 sites). Only unionid bivalve flesh was analyzed. Insect larvae collected in sufficient quantity for detection of radionuclides include *Hexagenia sp.* (n = 28, 11 sites and 17 composites), *Limnodrilus hoffmeisteri* (n = 3, 1 site, 2 composites), *Pisidium sp.* (2 composites), *Tubifex tubifex* (1 composite), and chironomids (1 composite).

Macrophytes were collected on the same transects during 2011, with 60 samples representing 11 species. *Vallisneria americana* (n = 15) was the most commonly found species, followed by *Elodea canadensis* (n=10), *Potamogeton gramineus* (n = 8), *Potamogeton richardsonii* (n = 7), *Ceratophyllum demersum* (n = 5), *Myriophyllum sp.* (n = 4), *Potamogeton natans* (n = 3), *Nuphar variegatum* (n = 3), *Potamogeton robbinsii* (n = 2), *Potamogeton amplifolius* (n = 1), *Nymphaea sp*. (n = 1) and *Utricularia sp.* (n = 1). Dried sediment and biota were ground with a mortar and pestle to ensure homogeneity and packed into 50 ml Nalgene snap cap vials. Sample height in the container was measured to the nearest 0.5 mm, and with sample weight, was used to calculate the density of each sample. Efficiency was estimated for each sample using relationships between sample height, density and gamma energy. These relationships were determined using mixed radionuclide standards that included ^{241}Am and ^{210}Pb that were obtained from Eckert & Ziegler and spiking sediment and organic matter of varying density with known amounts of standard solutions. A series of sample heights were measured for each matrix. Multiple regressions of sample height (mm), density (g cm^{-3}) and energy (KeV) produced a general relationship used to calculate efficiencies for each sample. For radionuclides that were present in the standard solutions, single energy efficiencies were calculated based on sample height and density. Counting times for each sample were on the order of 24 hours, but some of the smaller benthos samples were counted for as long as a week. Sediment samples were measured on a

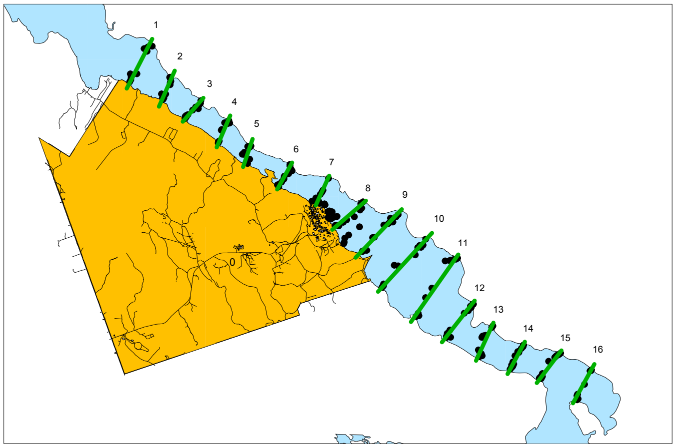

FIGURE 1: Ottawa River sediment and biota transects.

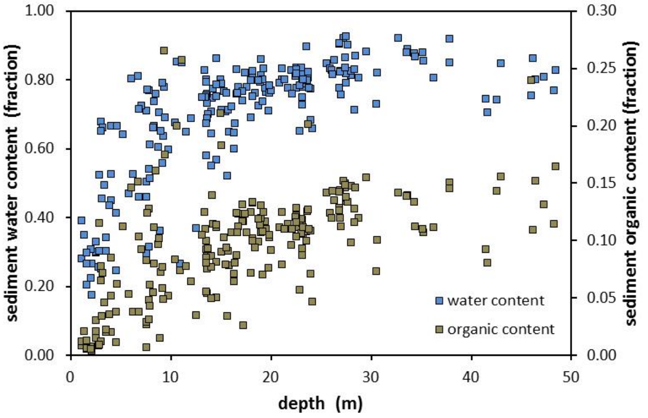

FIGURE 2: Sediment water content and organic content both increase rapidly with depth to about 13 m, and then increase much more slowly. Both parameters are highly variable at non-depositional (water content <0.6) and transitional sites, with much less variability at depositional sites (water content >0.6).

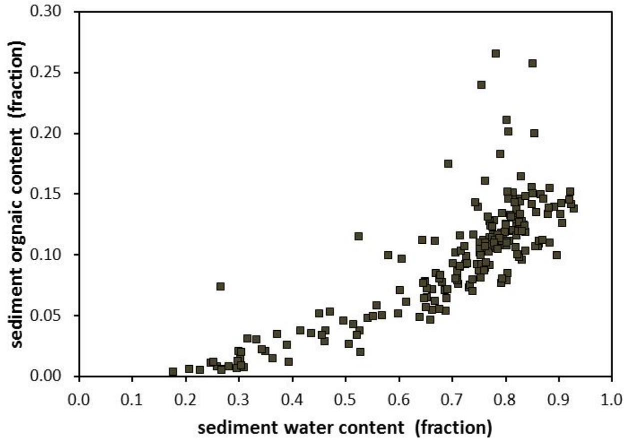

FIGURE 3: Sediment water content and organic content are highly correlated.

low background coaxial HPGe detector with biota samples measured on a low background planar HPGe detector with a carbon window. The latter detector was housed in a low background facility, constructed of materials low in U-Th series radionuclides and ^{40}K.

Above-ground macrophyte samples were rinsed thoroughly in river water immediately after collection, excess water was removed using a salad spinner and then samples were treated as above for analysis.

Crayfish were collected in 2012 on the same transects, with seven samples consisting primarily of *Orconectes rusticus* with some *Orconectes propinquis*. These samples will be referred to as *Orconectes sp.*in following sections and were prepared for analysis as above.

Activities of ^{7}Be, ^{60}Co, ^{94}Nb ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{210}Pb, ^{226}Ra, ^{228}Ra and ^{241}Am were directly determined by gamma spectroscopy. BSAFs were estimated from arithmetic and geometric means, and log-log and linear regressions from sediment and biota collected from the same site for macrophytes, unionid bivalves, *Orconectes sp.* and some *Hexagenia* sp., with sediment concentrations for the remaining *Hexagenia sp.* and benthic invertebrate composites estimated from weighted averages. All arithmetic means reported ± 2SE. All statistical analyses were performed using SYSTAT 13 software [25].

3. Results

3.1 Ottawa River sediment and biota

The Ottawa River near CRL is wide, deep and slow flowing, with lacustrine characteristics. Sediment was sampled from depths of 1 to 48 m and varied in texture from gravel to fine mud. Sediment water content and organic content both increase rapidly with depth to about 13 m, and then increase much more slowly with depth (Figure 2). Sediment water content <0.6 indicates sandy sediment and non-depositional environments, while water content >0.6 indicates mud and depositional environments. Both parameters were highly variable at shallow water and transitional sites, with much less variability at depositional sites. Sediment water content and organic content were highly correlated (Figure 3).

Macrophytes were collected from sites <3 m in depth, where sediment water content and organic content are 0.336±0.063 and 0.023±0.014, respectively. Crayfish were collected at depths of less than 1 m, typically among cobbles or under larger rocks, interspersed by coarse sand with water content and organic content of 0.291±0.043 and 0.010±0.004, respectively. *Hexagenia* were found at depths from 1 to 22 m. Mean site depth, water content and organic content were 13.5±1.4 m, 0.673±0.028 and

0.091±0.008, respectively. *Pisidium* were found in deeper water, (22.2±2.7m), with finer sediment (water content, 0.791±0.022) and higher organic content (0.118±0.010). *Limnodrilus, Tubifex* and chironomids were also found in deeper water (24.8±10.8 m, 25.2±2.6 m and 25.8±2.8 m, respectively), with fine sediment (water content 0.731±0.086, 0.780±0.016 and 0.790±0.022, respectively) and high organic content (0.096±0.014, 0.125±0.010 and 0.113±0.009).

Initial statistical analyses showed no significant differences in radionuclide concentrations among macrophyte or unionid bivalve species, and these data were pooled for subsequent statistical analyses and estimation of BSAFs. Inclusion of site depth, sediment water content and organic content in regressions of biota concentrations vs. sediment concentrations were never significant and will not be discussed in the following sections.

3.2 Primordial and cosmogenic radionuclides

Primordial and cosmogenic radionuclides were detected in biota of the Ottawa River. Primordial radionuclides include: ^{40}K ($t_{1/2}$ = 1.28x10^{9} y); two daughters of ^{238}U ($t_{1/2}$ = 4.4x10^{9} y), ^{226}Ra ($t_{1/2}$ = 1600 y) and ^{210}Pb ($t_{1/2}$ = 22.3 y); and one daughter of ^{232}Th ($t_{1/2}$ = 1.41x10^{10} y), ^{228}Ac ($t_{1/2}$ = 6.15 h). The decay of ^{232}Th leads to ^{228}Ra ($t_{1/2}$ = 5.75 y) followed by its very short-lived daughter, ^{228}Ac. Thus, the presence of ^{228}Ac in biota is indicative of its ^{228}Ra concentration at the time of sampling, and assuming secular equilibrium, ^{228}Ac activity measured in this study will be reported as ^{228}Ra. Similarly, other short-lived daughters of ^{238}U (^{214}Pb and ^{214}Bi) and ^{232}Th (^{208}Tl) that were detected will not be discussed, because these radionuclides were not present in biota at the time of sampling, and are not relevant from an uptake/retention perspective. The short-lived, cosmogenic radionuclide, ^{7}Be ($t_{1/2}$ = 53 d) was also detected in biota.

3.2.1 ^{40}K in Ottawa River biota and sediment

Potassium is an essential, regulated element in biota [9], and ^{40}K was detected in macrophytes, unionid bivalves, crayfish and sediment. Concentrations of naturally occurring ^{40}K in these biota and associated sediment showed no relationship to each other or to distance upstream or downstream of the CRL process outfall, as expected (Figure 4). Concentrations of ^{40}K were similar for macrophytes (44.6±7.1 Bq kg^{-1} ww) and crayfish (50.5±3.7 Bq kg^{-1} ww), with much lower concentrations in unionid bivalves (2.59±0.34 Bq kg^{-1} ww) (Table 1). In contrast with these littoral biota, ^{40}K was not detected in deposit feeding benthic invertebrates from deeper water, at least in part due to the smaller sample sizes of these organisms. Sediment concentrations of ^{40}K were much greater than those in biota, but are likely not the source of ^{40}K to sediment associated biota, as potassium enters aquatic foodwebs through direct uptake from water by primary producers (including macrophytes), with food the primary source for consumers [9].

3.2.2 Radium in Ottawa River biota and sediment

Radium behaves similarly to calcium in biota, present in tissues with high calcium content such as bone, mollusc shells and crustacean carapaces, and ^{226}Ra was detected in macrophytes, unionid bivalves, crayfish and sediment. As with ^{40}K, ^{226}Ra was not detected in deposit feeding benthic invertebrates from deeper water. ^{226}Ra is a daughter of ^{238}U, the primary component of fuels used in NRU and NRX, and significant releases of ^{238}U, could lead to increased ^{226}Ra through radioactive decay of two relatively long-lived daughters, ^{234}U ($t_{1/2}$ = 2.4x10^{5} y) and ^{230}Th ($t_{1/2}$ = 7.4x10^{4} y). Concentrations of ^{226}Ra in macrophytes, unionid bivalves and crayfish were not related to each other or to distance from the CRL process outfall, with no significant differences between upstream, adjacent and downstream sites (Figure 5), although the two highest macrophyte values were located in shallow water at the process outfall. Sediment ^{226}Ra at this site at the process outfall, however, was not elevated (Figure 5). Concentrations of ^{226}Ra were low and similar among biota (Table 1), with 3.44±0.48 Bq kg^{-1} ww in unionid bivalves, 2.59±0.64 in crayfish and 1.99±0.70 Bq kg^{-1} ww in macrophytes.

The distribution of ^{228}Ra (Figure 6) in biota and sediment was very similar to that of ^{226}Ra (Figure 5), with ^{228}Ra detected in macrophytes, unionid bivalves and crayfish, but not in deposit feeding biota. As with ^{226}Ra, concentrations in biota and sediment were unrelated to each other or to location relative to the CRL process outfall, although the two macrophyte samples highest in ^{226}Ra were also the highest in ^{228}Ra. This suggests a common mechanism of accumulation for the two radium isotopes, despite belonging to different decay schemes that are unrelated to CRL operations and releases. Concentrations of ^{228}Ra were low and similar among biota (Table 1), with 1.57±0.15 Bq kg^{-1} ww in unionid bivalves, 3.69±0.68 Bq kg^{-1} ww in crayfish and 2.01±0.92 Bq kg^{-1} ww in macrophytes.

For macrophytes, ^{228}Ra and ^{226}Ra were highly correlated (Figure 7):

$$\log(^{228}\text{Ra}) = 1.09\cdot\log(^{226}\text{Ra}) - 0.0028,\ r^2 = 0.86,$$
$$SE_{est} = 0.13,\ n = 26 \qquad (3)$$

The relationships between ^{228}Ra and ^{226}Ra for unionid bivalves and crayfish were not significant, and these biota show much less variability in radium isotopes relative to macrophytes (Figure 7). As calcium is an essential and regulated element, and radium enters aquatic foodwebs as a calcium analogue, uptake in aquatic foodwebs is dependent on the ratio of radium to calcium in water. The

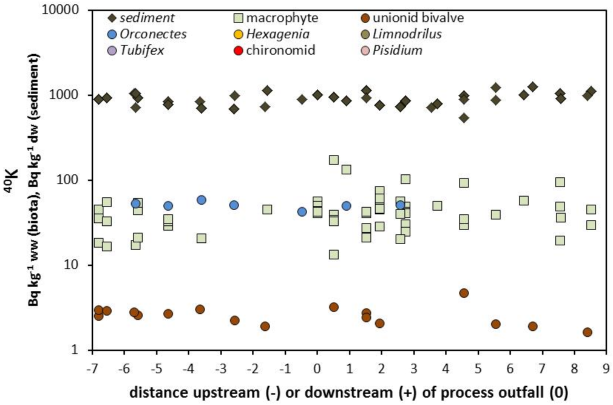

FIGURE 4: ^{40}K was only detected in macrophytes,unionid bivalves, crayfish (*Orconectes*) and sediment, with no significant correlations between biota and sediment. Concentrations in biota and sediment were unrelated to CRL operations and were consistent within taxa, as expected for an essential and regulated element.

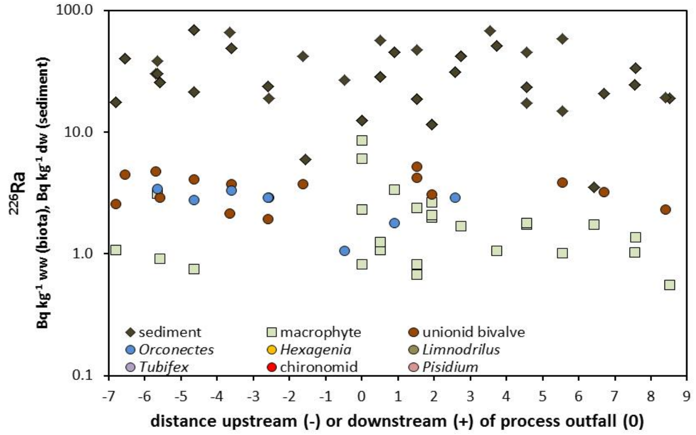

FIGURE 5: Concentrations of ^{226}Ra in macrophytes, unionid bivalves and crayfish were not related to sediment concentrations or distance from the CRL process outfall, with no significant differences between upstream, adjacent and downstream sites.

TABLE 1: Concentrations of Radionuclides in Ottawa River Sediment Associated Biota ± 2SE

radionuclides			macrophytes	mussels	crayfish	*Hexagenia*	*Limnodrillus*	*Tubifex*	chironomid	*Pysidium*
			(Bq kg^{-1} ww)	*(Bq kg^{-1} ww)*	*(Bq kg^{-1} ww)*	*(Bq kg^{-1} ww)*	*(Bq kg^{-1} ww)*	*(Bq kg^{-1} ww)*	*(Bq kg^{-1} ww)*	*(Bq kg^{-1} ww)*
primordial and cosmogenic radionuclides	all sites	^{7}Be	1.87±0.34							
		^{40}K	44.6±7.1	2.59±0.34	50.5±3.7					
		^{210}Pb	2.92±0.56	1.82±0.44						
		^{226}Ra	1.99±0.70	3.44±0.48	2.59±0.64					
		^{228}Ra	2.01±0.92	1.57±0.15	3.69±0.68					
anthropogenic radionuclides	upstream sites	^{60}Co								
		^{94}Nb								
		^{137}Cs	0.22±0.03	0.18±0.03	0.89±0.42	1.76±1.41	1.12	1.70		5.89
	adjacent sites (≤ 2km)	^{60}Co	2.29±2.20	1.02±0.43			22.7			
		^{94}Nb	0.39±0.22							
		^{137}Cs	0.88±0.62	0.30±0.07		25.8±17.2	92.7±179			
	down-stream sites	^{60}Co	0.14±0.06	0.49±0.19						
		^{94}Nb	0.37							
		^{137}Cs	0.64±0.24	0.35±0.10	1.54±0.52	4.25±1.63			5.08	1.01

patterns observed for unionid bivalves and crayfish were consistent with expectations. The much greater range and strong log-log relationship for macrophytes, suggests a common mechanism that is not related to uptake, but rather to adherence of sediment particles to macrophyte surfaces.

3.2.3 ^{210}Pb in Ottawa River biota and sediment

Lead is a non-essential element that is not readily incorporated into biota, and ^{210}Pb was only detected in macrophytes, unionid bivalves and sediment (Figure 8). ^{210}Pb is a daughter of ^{222}Rn that is deposited on land and water following the decay of outgassed ^{222}Rn ($t_{1/2}$ = 3.8 d). In aquatic ecosystems, ^{210}Pb is rapidly scavenged by particles, which subsequently settle and accumulate in depositional areas at depths where waves cannot entrain these fine-grained particles. Suspended particles also settle onto macrophyte surfaces to which they may adhere. Concentrations of ^{210}Pb in macrophytes, unionid bivalves and sediment were not correlated with each other or with location relative to the CRL process outfall (Figure 8). Concentrations of ^{210}Pb in macrophytes (2.92±0.56 Bq kg^{-1} ww) and unionid bivalves (1.82±0.44 Bq kg^{-1} ww) were low and similar (Table 1).

3.2.4 ^{7}Be in Ottawa River biota and sediment

^{7}Be is a short-lived, cosmogenic radionuclide, scavenged by precipitation and deposited on land and water surfaces, where it is rapidly scavenged by particles. ^{7}Be was detected in macrophyte samples, with none of the other biota or sediment samples analyzed soon enough after collection to detect the rapidly decaying ^{7}Be. The concentration of ^{7}Be for macrophytes averaged 1.87±0.34 Bq kg^{-1} ww (Table 1), and was not related to site location (Figure 9).

As both ^{210}Pb and ^{7}Be share common transport processes, it is not surprising that these radionuclides are highly correlated for macrophytes (Figure 10):

$$\log(^{210}\mathrm{Pb}) = 1.27 \cdot \log(^{7}\mathrm{Be}) + 0.56,\ r^2 = 0.77,$$
$$SE_{est} = 0.88,\ n = 32 \qquad (4)$$

Site specific variation in ^{210}Pb and ^{7}Be concentrations in water or on particles is not expected in the Ottawa River, and indeed, the most common sediment dating method assumes that the concentration of ^{210}Pb on settling particles remains constant. Thus, the strong correlation between the two isotopes for macrophytes is further evidence of the adherence of particles on macrophyte surfaces, with variation among samples due to the presence of more or less particulate matter.

3.3 Anthropogenic radionuclides

Anthropogenic radionuclides detected in Ottawa River sediment include ^{60}Co ($t_{1/2}$ = 5.3 y), ^{94}Nb ($t_{1/2}$ = 2.0x10^{4} y),

^{137}Cs ($t_{1/2}$ = 30 y), ^{152}Eu ($t_{1/2}$ = 13 y), ^{154}Eu ($t_{1/2}$ = 8.5 y), ^{155}Eu ($t_{1/2}$ = 4.7 y), and ^{241}Am ($t_{1/2}$ = 432 y). Atmospheric testing of nuclear weapons in the 1950's and 1960's resulted in deposition of a variety of radionuclides, including ^{137}Cs and ^{241}Am, which were detectable upstream and downstream of the CRL process outfall. The remaining radionuclides, ^{60}Co, ^{94}Nb, ^{152}Eu, ^{154}Eu and ^{155}Eu, were only detected in sediment downstream of the CRL process outfall and were released through CRL operations. Only ^{60}Co, ^{94}Nb and ^{137}Cs were detected in biota and will be discussed below.

3.3.1 ^{60}Co in Ottawa River biota and sediment

Cobalt is an essential trace element, and ^{60}Co, produced by neutron activation, was detected in macrophytes, unionid bivalves and *Limnodrilus* downstream of the CRL process outfall. Concentrations of ^{60}Co in sediment exceed 10^4 Bq kg^{-1} dw at the process outfall, declining rapidly with distance downstream, to less than 10 Bq kg^{-1} dw (Figure 11). Concentrations of ^{60}Co in *Limnodrilus* at the process outfall were 22.7 Bq kg^{-1} ww (Table 1). Macrophytes collected in shallower water adjacent to the process outfall had 1.5 to 12.3 Bq kg^{-1} ww ^{60}Co, with less than 0.5 Bq kg^{-1} ww at sites further downstream (Table 1). Small amounts of ^{60}Co were also detected in unionid bivalves downstream of the CRL process outfall, averaging 1.02±0.43 Bq kg^{-1} ww near the process outfall and 0.49±0.19 Bq kg^{-1} ww further downstream (Table 1).

In contrast with the primordial and cosmogenic radionuclides described above, ^{60}Co declines rapidly with distance downstream in both macrophytes and sediment. Concentrations of ^{60}Co in macrophytes (^{60}Co$_{mac}$) were correlated with concentrations of ^{60}Co in sediment (^{60}Co$_{sed}$) (Figure 12):

$$\log(^{60}\mathrm{Co}_{mac}) = 1.16 \cdot \log(^{60}\mathrm{Co}_{sed}) - 1.84,\ r^2 = 0.50,$$
$$SE_{est} = 0.47,\ n = 23 \qquad (5)$$

The slope of this regression is not significantly different than 1, suggesting sediment as a source of ^{60}Co for macrophytes.

Biota/sediment bioaccumulation factors (BSAF) were calculated for ^{60}Co in macrophytes on a wet weight (ww macrophytes/dw sediment) and dry weight (dw macrophytes/dw sediment) basis. The geometric and mean for ^{60}Co BSAFs were 0.0221 and 0.283, for macrophyte ww and dw, respectively (Table 2). ^{60}Co BSAFs for macrophytes were not significantly correlated with distance downstream from the process outfall, suggesting that sediment, and not ongoing emissions from the CRL process outfall were largely responsible for ^{60}Co in macrophytes. These results are in excellent agreement with a previous experimental field study on macrophyte uptake of radionuclides from Ottawa River sediment, which estimated a ^{60}Co BSAF of

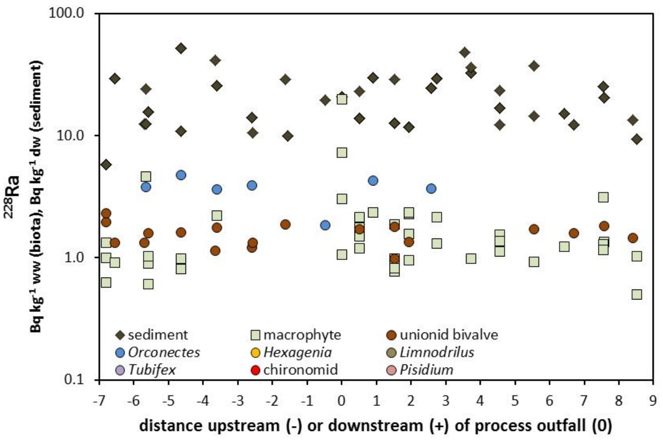

FIGURE 6: The distribution of ^{228}Ra in biota and sediment was very similar to that of ^{226}Ra, with ^{228}Ra detected in macrophytes, unionid bivalves and crayfish, but not in deposit feeding biota. Concentrations in biota and sediment were not correlated and were unrelated to location relative to the CRL process outfall.

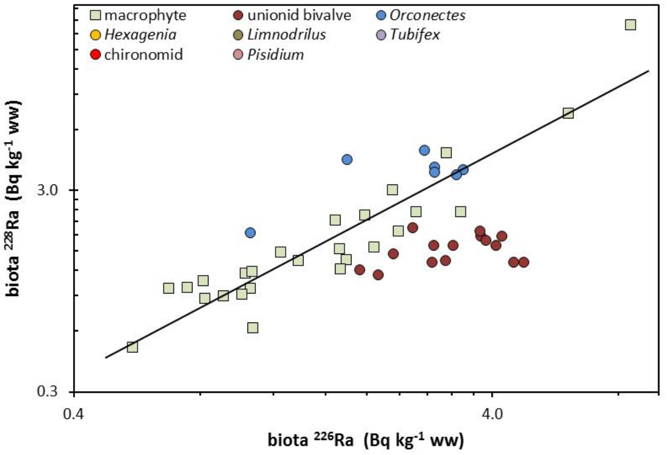

FIGURE 7: Relationship between ^{226}Ra and ^{228}Ra in Ottawa River biota. The line represents the strong correlation between macrophyte ^{226}Ra and ^{228}Ra (r^2=0.86). The relationships between ^{226}Ra and ^{228}Ra for unionid bivalves and crayfish were not significant, and these biota show much less variability in radium isotopes than macrophytes.

TABLE 2: Geometric Mean BSAFs for Ottawa River Biota

Radionuclide	macrophytes	*Hexagenia*	*Limnodrillus*	*Tubifex*	chironomid	*Pysidium*
	BSAF (ww dw^{-1})	*BSAF (ww dw^{-1})*	*BSAF (ww dw^{-1})*	*BSAF (ww dw^{-1})*	*BSAF (ww dw^{-1})*	*BSAF (ww dw^{-1})*
^{60}Co	0.0221		0.00139			
^{94}Nb	0.287					
^{137}Cs		0.0162	0.0104	0.0119	0.0200	0.00599

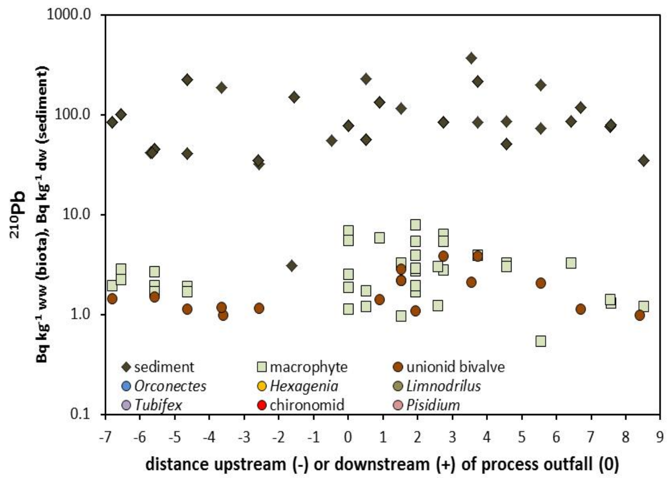

FIGURE 8: Concentrations of ^{210}Pb in macrophytes, unionid bivalves and sediment were not correlated with each other or with location relative to the CRL process outfall.

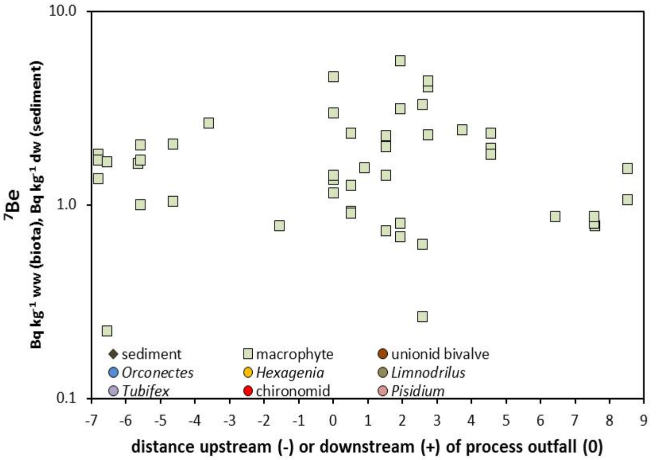

FIGURE 9: ^{7}Be was detected in macrophyte samples, with none of the other biota or sediment samples analyzed soon enough after collection to detect the rapidly decaying ^{7}Be. The concentration of ^{7}Be in macrophytes was not related to site location.

0.357±0.308 (dw/dw) for macrophytes grown in Ottawa River sediment, but in a lake not contaminated with ^{60}Co [14].

Unionid bivalve ^{60}Co, however, was not significantly correlated with sediment ^{60}Co (Figure 12). Incomplete mixing of process outfall water discharged to the Ottawa River could also produce the patterns observed for ^{60}Co in unionid bivalves. Unionid bivalves collected near the mouth of Perch Creek (1.5 km downstream of the process outfall), another source of ^{60}Co to the Ottawa River, had higher concentrations of ^{60}Co than those collected closer to the process outfall (Figure 11), suggesting that sediment is not the primary source of ^{60}Co to these biota. BSAFs were not calculated for unionid bivalves because unionid bivalve ^{60}Co was not significantly correlated with sediment ^{60}Co.

BSAFs for ^{60}Co were calculated for the deposit feeding *Limnodrilus* captured at the process outfall: 0.00139 and 0.00857, for *Limnodrilus* ww and dw, respectively (Table 2). This is more than an order of magnitude less than those observed for macrophytes.

3.3.2 ^{94}Nb in Ottawa River biota and sediment

Niobium is a non-essential, transition metal, and ^{94}Nb, produced by neutron activation, was present at very low concentrations in several sediment and macrophyte samples near the CRL process outfall (Figure 13). ^{94}Nb was not detected in any other biota. Concentrations of ^{94}Nb in macrophytes near the process outfall were 0.39±0.22 Bq kg^{-1} ww, with 0.37 measured in macrophytes collected across the river and downstream of CRL. ^{94}Nb was

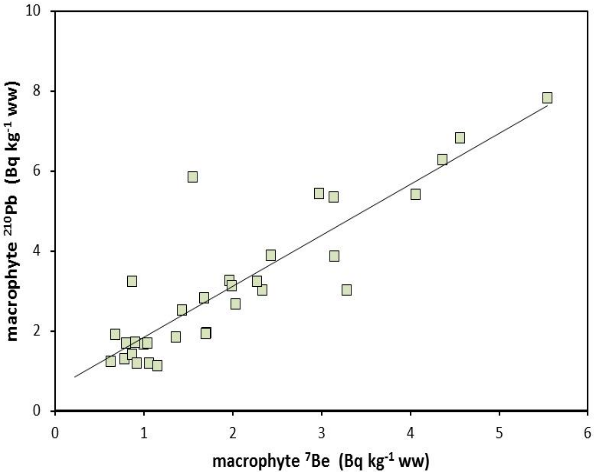

FIGURE 10: Strong correlation between ^{210}Pb and ^{7}Be in Ottawa River macrophytes (Equation 4, r^2 =0.77). The strong correlation is likely due to the adherence of particles on macrophyte surfaces, with variation among samples due to the presence of more or less particulate matter

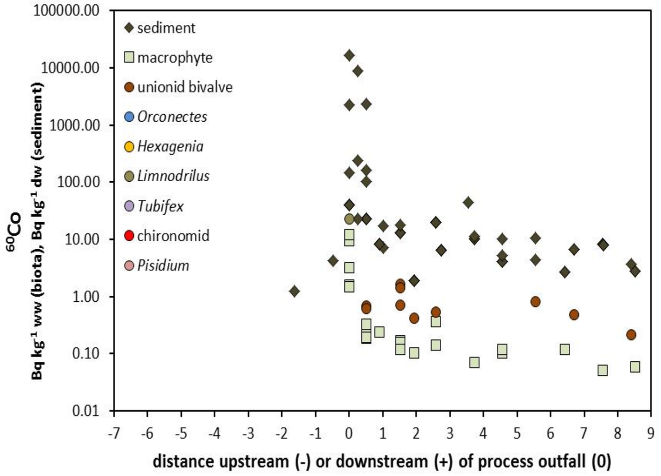

FIGURE 11: In contrast with the primordial and cosmogenic radionuclides, ^{60}Co declines rapidly with distance downstream in both macrophytes and sediment. Concentrations of ^{60}Co in unionid bivalves do not decline significantly with distance from the process outfall.

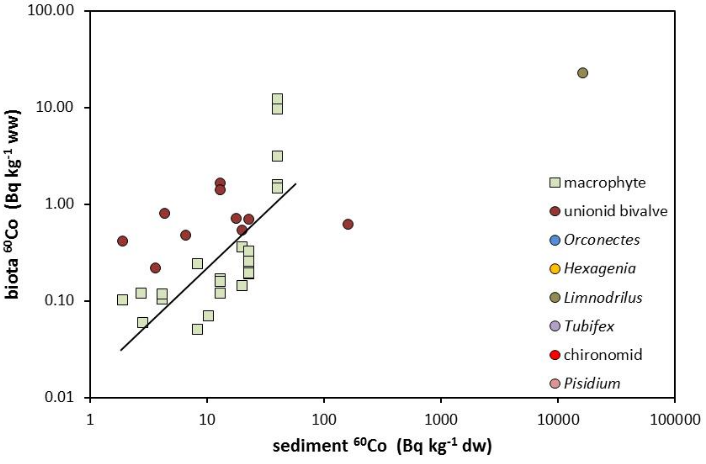

FIGURE 12: Relationship between ^{60}Co in Ottawa River macrophytes and sediment (Equation 5, r^2 =0.50, suggesting sediment as a source of ^{60}Co for these biota. Concentrations of ^{60}Co in unionid bivalves and sediment were not significantly correlated.

not detected in sediment at the two sites downstream of the process outfall where ^{94}Nb was detected in macrophytes. At the process outfall, ^{94}Nb was detected in both macrophytes and sediment, and geometric mean BSAFs were 0.259 and 2.69, for macrophyte ww and dw, respectively (Table 2).

3.3.3 ^{137}Cs in Ottawa River biota and sediment

Cesium is a non-essential element that enters aquatic foodwebs as an analogue of potassium [19]. ^{137}Cs is an abundant fission product that was dispersed globally through atmospheric testing of nuclear weapons during the 1950's and 1960's and ^{137}Cs is also released from the operation of nuclear reactors, including NRX and NRU at CRL. ^{137}Cs was the most common radionuclide detected in Ottawa River biota, found in macrophytes, unionid bivalves, *Orconectes*, and the deposit feeding benthic invertebrates *Hexagenia, Limnodrilus, Tubifex,* chironomid and *Pisidium* (Figure 14). Unlike the other anthropogenic radionuclides, ^{137}Cs was found in biota at sites upstream of the CRL process outfall (Figure 14). Historical releases from CRL led to about a 2-fold increase in ^{137}Cs concentrations in water [26], and concentrations in biota reflect this pattern (Table 1). Concentrations of ^{137}Cs in macrophytes and unionid bivalves collected at sites adjacent to the process outfall and from sites further downstream were significantly greater than those collected at upstream sites, but were not significantly different from each other. *Orconectes* have significantly greater concentrations of ^{137}Cs than either macrophytes or unionid bivalves, reflecting their omnivorous diet and higher trophic level [26, 27]. This suggests a step-like increase of about 2-fold downstream of the process outfall, which is a much less dramatic pattern than that observed for sediment (Figures 14, 15).

Neither macrophyte, unionid bivalve or *Orconectes* ^{137}Cs concentrations were significantly correlated with associated sediment ^{137}Cs concentrations (Figure 15). Thus, BSAFs were not estimated for these biota. These results are at odds with results from a field experiment on macrophyte uptake of ^{137}Cs from Ottawa River sediment collected at the process outfall, which showed significant accumulation of ^{137}Cs from sediment and a BASF of 0.332±0.265 (dw/dw) [24]. The sediments used in this field experiment, collected in relatively deep water at the process outfall, are silty mud rather than the coarse sands typical of the Ottawa River littoral zone where macrophytes were found.

Deposit feeding benthic invertebrate ^{137}Cs concentrations were significantly greater than those of macrophytes, unionid bivalves and *Orconectes* (Table 1) and appear to follow the pattern exhibited by sediment ^{137}Cs concentrations (Figure 14). A log-log regression of ^{137}Cs concentrations in *Hexagenia* ($^{137}Cs_{hex}$) and associated sediment ($^{137}Cs_{sed}$) was highly significant (Figure 16):

$$\log(^{137}Cs_{hex}) = 0.685 \cdot \log(^{137}Cs_{sed}) - 0.979,\ r^2 = 0.579,\ SE_{est} = 0.334,\ n = 28 \qquad (6)$$

A log-log regression of ^{137}Cs concentrations in the remaining deposit feeders, chironomids, *Pisidium*, *Limnodrilus* and *Tubifex* ($^{137}Cs_{dep}$) and associated sediment ($^{137}Cs_{sed}$) was also highly significant, and not significantly different than Equation 6 (Figure 16):

$$\log(^{137}Cs_{dep}) = 1.03 \cdot \log(^{137}Cs_{sed}) - 2.08,\ r^2 = 0.889,\ SE_{est} = 0.258,\ n = 7 \qquad (7)$$

All ^{137}Cs data for deposit feeding benthic invertebrates were combined, yielding a general relationship (Figure 16):

$$\log(^{137}Cs_{dep}) = 0.765 \cdot \log(^{137}Cs_{sed}) - 1.23,\ r^2 = 0.647,\ SE_{est} = 0.336,\ n = 35 \qquad (8)$$

In Figure 16, the solid line represents Equation 8. Log-log transformations are typically carried out to normalize variance across the range in data, but in this case, may have over-transformed the data. This is likely due to the greater analytical uncertainty in ^{137}Cs concentration in biota at low levels.

Linear regressions were also explored, and while exhibiting similar variance across the data range, led to clustering at low concentrations, with high leverage from three *Hexagenia* and one *Limnodrilus* samples collected adjacent to the process outfall. A linear regression of ^{137}Cs concentrations in *Hexagenia* ($^{137}Cs_{hex}$) and associated sediment ($^{137}Cs_{sed}$) was highly significant (Figure 17):

$$(^{137}Cs_{hex}) = 0.0127 \cdot (^{137}Cs_{sed}) + 0.982,\ r^2 = 0.939,\ SE_{est} = 5.45,\ n = 28 \qquad (9)$$

A linear regression of ^{137}Cs concentrations in the remaining deposit feeders ($^{137}Cs_{dep}$) and associated sediment ($^{137}Cs_{sed}$) was also highly significant, and not significantly different than Equation 9 (Figure 17):

$$(^{137}Cs_{dep}) = 0.0132 \cdot (^{137}Cs_{sed}) - 1.00,\ r^2 = 0.999,\ SE_{est} = 1.80,\ n = 7 \qquad (10)$$

All ^{137}Cs data for deposit feeding benthic invertebrates were combined, yielding a general relationship (Figure 17):

$$(^{137}Cs_{dep}) = 0.0130 \cdot (^{137}Cs_{sed}) + 0.441,\ r^2 = 0.980,\ SE_{est} = 4.96,\ n = 35 \qquad (11)$$

In Figure 17, the solid line represents Equation 10, and the slope of this line is the ^{137}Cs BSAF for these deposit feeding benthic invertebrates, 0.0130. ^{137}Cs BSAFs were also estimated as the ratio of concentrations in biota (Bq kg ww^{1}) to those in associated sediment (Bq kg dw^{-1})

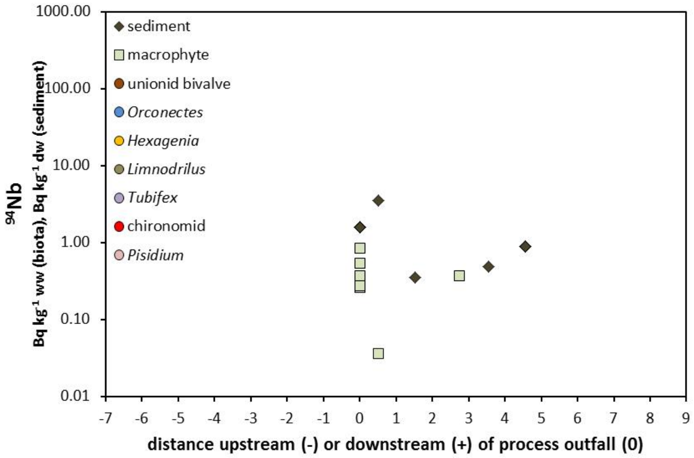

FIGURE 13: ^{94}Nb in Ottawa River macrophytes and sediment was detected only at a few sites downstream of the CRL process outfall

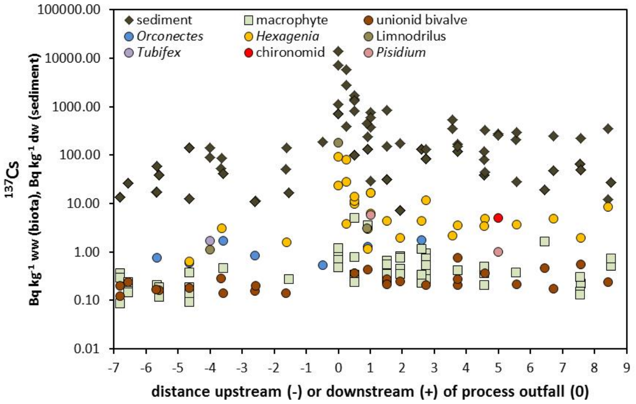

FIGURE 14: ^{137}Cs was the most common radionuclide detected in Ottawa River biota, found in macrophytes, unionid bivalves, *Orconectes*, and the deposit feeding benthic invertebrates, *Hexagenia, Limnodrilus, Tubifex,* chironomid and *Pisidium.* Macrophytes, unionid bivalves and *Orconectes* reflect concentrations in water, whereas deposit feeding benthic invertebrates reflect concentrations in sediment, which decline rapidly from the process outfall to about 2 km downstream of this point source.

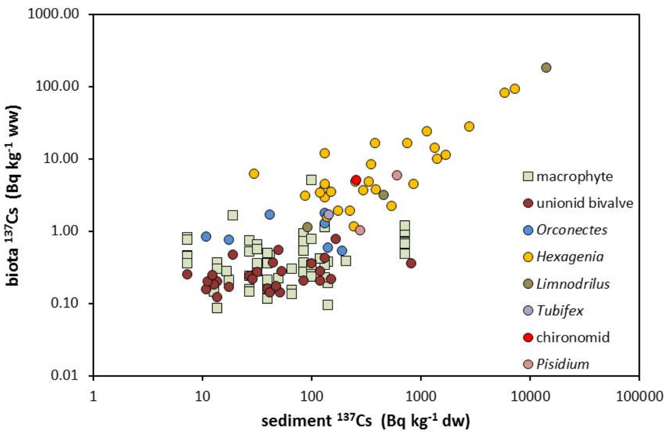

FIGURE 15: Concentrations of ^{137}Cs in Ottawa River Deposit feeding benthic invertebrates (*Hexagenia, Limnodrilus, Tubifex,* chironomid *and Pisidium*) were significantly correlated with sediment concentrations. Neither macrophyte, unionid bivalve or *Orconectes* ^{137}Cs concentrations were significantly correlated with associated sediment ^{137}Cs concentrations.

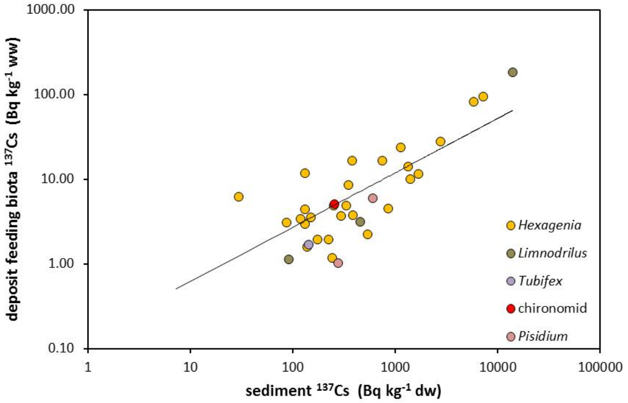

FIGURE 16: Log-log relationship between ^{137}Cs in deposit feeding biota and sediment (Equation 8, r^2 =0.65).

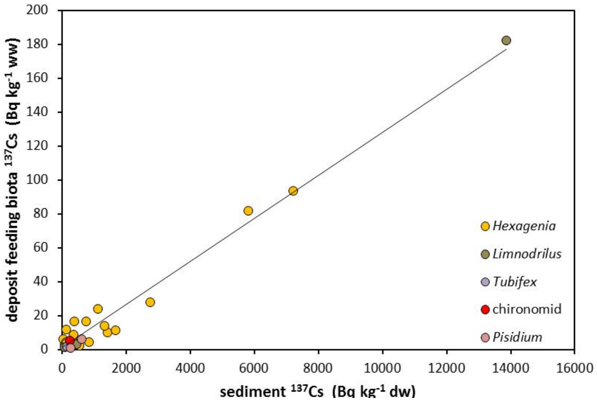

FIGURE 17: Linear relationship between ^{137}Cs in deposit feeding biota and sediment (Equation 11, r^2 =0.99).

and are summarized in Table 2. The geometric mean BASF for ^{137}Cs in deposit feeding biota, 0.0147 (n = 35, ww/dw), was very similar to the regression derived BSAF, 0.0130 (Table 2, Figure 17). On a dw/dw basis, the geometric mean BSAF for ^{137}Cs in deposit feeding biota was 0.111. These low BSAFs suggest that little of the ^{137}Cs in Ottawa River sediment is bioavailable.

4. Discussion

In this paper, we present data for radionuclide concentrations in sediments and sediment associated biota for a variety of primordial (^{40}K, ^{210}Pb ^{226}Ra and ^{228}Ra), cosmogenic (^{7}Be), and anthropogenic radionuclides (^{60}Co, ^{94}Nb, ^{137}Cs). Primordial and cosmogenic radionuclides were only detected in littoral zone biota: macrophytes, unionid bivalves and *Orconectes.* No primordial or cosmogenic radionuclides were detected in deposit feeding biota collected at greater depths. Concentrations of primordial and cosmogenic radionuclides in sediment and biota were consistent across the study area, with no upstream or downstream differences attributable to CRL releases, or significant correlations between biota and sediment. These results are consistent with the behaviour of essential elements (K), essential element analogues (Ra for Ca) and non-essential elements (Pb) with little potential for bioaccumulation. For macrophytes, strong correlations between the two radium isotopes, and between ^{210}Pb and ^{7}Be suggest that these radionuclides were associated with settling particles that adhered to macrophyte surfaces [14].

Anthropogenic radionuclides were detected in all biota, and concentrations of these radionuclides in sediment and biota were relative to location with respect to the CRL process outfall. Unlike the primordial and cosmogenic radionuclides described above, ^{60}Co in sediment declines rapidly with distance downstream of the CRL process outfall. ^{60}Co was detected in macrophytes, unionid bivalves and *Limnodrilus* downstream of the CRL process outfall. Concentrations of ^{60}Co in macrophytes were significantly correlated with sediment concentrations, whereas unionid bivalves were not correlated with sediment, but those collected near the mouth of Perch Creek (about 1.5 km downstream of the process outfall, had higher concentrations of ^{60}Co than those collected closer to the process outfall, suggesting that Perch Creek is a minor point source of this radionuclide. Sediment-biota accumulation factors (BSAF) estimated for macrophytes were in excellent agreement with a previous study, and more than an order of magnitude greater than those of *Limnodrilus.*

^{94}Nb was present at very low concentrations in several sediment and macrophyte samples near the CRL process outfall, but was not detected in any other biota. BSAFs (ww/dw) for ^{94}Nb in macrophytes were an order of magnitude greater than those of ^{60}Co.

^{137}Cs was the most common radionuclide detected in

Ottawa River biota, found in macrophytes, unionid bivalves, *Orconectes*, and the deposit feeding benthic invertebrates *Hexagenia, Limnodrilus, Tubifex,* chironomid and *Pisidium*. Due to nuclear weapon test fallout, ^{137}Cs was found in biota at sites upstream of the CRL process outfall. CRL nuclear operations increased ^{137}Cs concentrations in water and downstream sediment by about 2-fold, and concentrations in non-deposit feeding biota reflect this pattern. Neither macrophyte, unionid bivalve or *Orconectes* ^{137}Cs concentrations were significantly correlated with associated sediment ^{137}Cs concentrations, but rather exhibit about a 2-fold increase at all sites downstream of the CRL process outfall. Deposit feeding benthic invertebrate ^{137}Cs concentrations were significantly greater than those of littoral biota and were highly correlated with ^{137}Cs concentrations in associated sediment. Biota-sediment accumulation factors (ww/dw) for deposit feeding biota where similar and low whether estimated from linear regression (0.0132) or from the geometric mean of biota/sediment ratios (0.0147). These low BSAFs suggest that little of the ^{137}Cs in Ottawa River sediment is bioavailable. For example, bioamagnification factors (ratio of radionuclide concentrations in biota to their diet) are typically 4 for diets low in clay [27], or about 300-fold greater than observed in this study for benthic invertebrates feeding on sediment.

In this study, we cleared the guts of deposit feeding benthic invertebrates prior to analysis [28]. This was done so that we could assess the tissue concentration of radionuclides and estimate BSAFs without bias due to radionuclides in sediment present in guts. Sediment in benthic invertebrate guts has been shown to increase the measured metal concentration and increase the variability among invertebrate samples [29]. This effect tends to be greater for deposit feeders and for metals that are poorly assimilated [29]. Sediment in guts can also obscure relationships between tissue and sediment concentrations, with the effect increasing as the gut content of the organism increases, driving the relationship towards 1 [10]. For BASFs <1, such as those in this study, this leads to overestimation of the BSAF [10]. For many metals, the effect may be minimal, with < 22% of metal associated with gut contents [11], but these effects are typically observed for Cu and Zn which are essential elements with relatively high assimilation efficiencies and relatively low particle affinity. For many radionuclides (e.g., ^{137}Cs and ^{241}Am), particle affinity may be 1-3 orders of magnitude greater than those for most transition metals and assimilation efficiencies may also be very low. For example, fish that have a diet rich in clay (deposit feeding benthic invertebrates) have been shown to have very low assimilation efficiencies for ^{137}Cs (<10%) whereas fish that have a diet lacking sediment have ^{137}Cs assimilation efficiencies of 60-70% [30]. Lakes with high suspended sediment concentrations have also been shown to have fish with much lower ^{137}Cs bioaccumulation than fish from lakes with low suspended sediment concentrations [19]. For *Hexagenia*, where gut contents are about 12% of organism dry weight [11], and for sediment and BSAFs observed in this study, not clearing the guts prior to analysis would have resulted in overestimating the ^{137}Cs BSAF by about a factor of 2. For ^{60}Co in *Limnodrilus*, inclusion of gut contents in the BSAF would have resulted in overestimating the ^{60}Co BSAF by more than 10-fold.

5. Conclusion

In this study, we present the first field estimates of BSAF for a number of radionuclides. The strongest and most consistent BSAFs were those for ^{137}Cs in deposit feeding taxa, suggesting that sediment concentrations rather than dissolved concentrations drive uptake. These BSAFs were not significantly different among deposit feeding taxa, suggesting similar processes for ingestion, assimilation and elimination. These data also show that the concentration factor approach used for guidance would have led to spurious results in this study. Review of the limited literature on this topic, suggests that the paucity of radionuclide BSAFs is due to the sampling effort required to obtain sufficient benthic invertebrate mass for analysis. However, when considering historical releases to aquatic ecosystems, where the sediment inventories can comprise ≥99% of radionuclides, and where benthic invertebrates are immersed in sediment, receiving radiation dose from external and internal exposure, assessing bioaccumulation or dose using the concentration factor approach could lead to serious underestimates. For example, in this study, concentrations of ^{137}Cs in *Hexagenia* downstream of the CRL process outfall range about 2-orders of magnitude, in comparison to relatively uniform water concentrations. The concentration factor approach would have predicted a single value downstream of CRL, underestimating exposure to *Hexagenia* by almost 2-orders of magnitude at sites close to the CRL process outfall.

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Organically bound tritium (OBT) in soil at different depths around Chalk River Laboratories (CRL), Canada

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Atomic Energy of Canada Limited (AECL) Chalk River Laboratories (CRL) is a large nuclear research and test establishment with nuclear and non-nuclear facilities located in Chalk River, Ontario. The CRL Environmental Monitoring Program is designed to demonstrate that radiological exposure resulting from releases from the CRL site remain below the public dose limit specified in the regulations (1 mSv/year). This study was conducted to consolidate environmental effects following a continuous atmospheric tritium release observed at CRL.

Soil samples were collected at depths of up to 20 cm using soil probes at the CRL site and surrounding areas. The samples were sectioned at 5 cm intervals, and HTO and OBT concentrations were measured in the samples. Prevailing winds at CRL are from NW and SE, which was suggested to be in close relationship with tritium distribution in environmental samples such as soils and plant leaves. The HTO concentration was the highest in surface soil water and plant leaves at a given sampling point. This result suggests that the concentration of tritium in surface soil water and in plants tissue free water essentially reflects the surrounding atmospheric tritium concentration.

OBT concentrations in soil were measured at the historical HT release site, Plant Road, Mattawa Road and three background sites near CRL. The top layer of soil generally had the highest OBT concentration among collected soil samples. This result suggests that OBT concentrations are different from HTO concentrations at the same site and can be representative of previously released environmental tritium at the sampling point. The relationship between the OBT concentration in soil and the amount of tritium released into the environment will be useful for the evaluation of environmental tritium effects and the fate of tritium in the terrestrial ecosystem. The study points out that HTO shows shorter-term dynamic conditions, whereas OBT shows longer-term steady-state conditions.

1. Introduction

As a part of normal operations, nuclear facilities release controlled quantities of tritium into the atmosphere and bodies of water in a monitored manner [1]. These releases are regulated by the Canadian Nuclear Safety Commission (CNSC) to protect health, safety and the environment. The tritium results were well below limits for both gaseous and liquid effluent releases for nuclear facilities in Canada in 2010 [2].

The Chalk River Laboratories (CRL) site is a large nuclear research and test establishment with nuclear and non-nuclear facilities and activities [3]. Tritium releases from the CRL facility are below 1% of the derived release limit (DRL), which is an indirect estimation of release rate equivalent to the 1 mSv dose limit to members of the public.

CRL's Environmental Monitoring Program is designed to demonstrate that radiological exposures resulting from normal operation of the facilities remain below the public dose limit specified in regulations [3]. Therefore, radiological parameters are routinely measured on environmental samples from numerous locations at the site and in surrounding communities. These monitoring samples include ambient air, foodstuff, river water and other surface waters on and off site. The program also includes the monitoring of groundwater, beach sediment, surface water and meteorological conditions.

Clark *et al*. [4] reported that substantial year-to-year variations in organically bound tritium (OBT) in soils have been observed, which are greater than any potential trophic accumulation of OBT. It was concluded that temporal, seasonal variations in tritium distribution are more important than possible fractionation and trophic accumulation. In addition, OBT concentrations at the historical HT release site (HT release experiment was conducted in 1994) were considerably higher than HTO activity concentrations in the same soil samples. The results indicated that OBT activity concentrations can be reflective of historical tritium releases to the environment [5].

Tritium (HTO and OBT) measurements in soil are not part of regular monitoring programs at nuclear facilities around the world and limited information is available to study the environmental fate of OBT in soils

[6, 7, 8, 9]. Furthermore, Sheppard *et al*. [10] reported that no tritium data was found for Canadian soils. In this study, OBT activity concentrations were measured to investigate the distribution in different layers of soil and relationships with environmental factors around the CRL site. Due to relationship between plant and soil tritium, plant tritium monitoring data would be useful to soil-to-plant transfer parameters.

2. Materials and Methods

2.1 Experimental investigation site

CRL is located in Chalk River, Ontario on the south side of the Ottawa River, about 200 km northwest of Ottawa (Figure 1). CRL is located around 46° latitude, and on the border of the provinces of Ontario and Quebec.

Communities around CRL are the Village of Chalk River, 7 km west of the site, the Town of Deep River, 10 km upstream on the river, and the Town of Pembroke, 35 km downstream of CRL. Tritium is one of the main airborne contaminants of concern for humans and the environment resulting from CRL operations. The major sources of airborne radioactive effluents from CRL are the nuclear reactor stack that exhausts ventilation and cooling air from the National Research Universal (NRU) reactor, and roof vents at NRU. The release rate from NRU is comparable to that from the reactor stack. The historical atmospheric HT release site (HT experiment site) is located within CRL property, approximately 6 km away from the built-up portion of the site (Figure 1). The site is flat and consists of natural plant growth such as herbs [5]. Plant Road is the paved main entrance road and is located west of the stack. Mattawa Road is an unpaved, small emergency road located to the north along the Ottawa River.

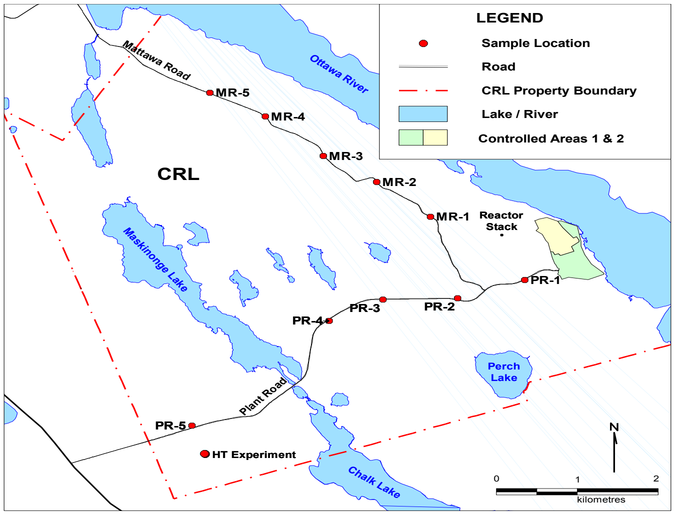

FIGURE 1: Sampling locations around the Chalk River Laboratories site.

2.2 Sampling of soils and plants

The soil samples were collected using a soil probe (AMS, USA) near the CRL site from June to August 2011. Soil core samples were sectioned at 5 cm intervals for most of the sampling points. For the historic HT release site, soil samples were collected up to 1 m deep and sectioned at 20 cm depth intervals to validate OBT movement into deeper soil depths. Collected soil samples were sealed in 250 mL Mason jars and frozen at -20 °C in the CRL background environmental laboratory until further analysis. Soil pore water and organic contents were measured and described by Kim *et al*. [5]. Table 1 summarizes information for the sampling points near CRL, which are Deep River, Pt. Alexander, Pembroke and Russell.

The plant sampling concept was to collect grass or plant leaves at the same site where soil samples were collected along both Plant and Mattawa Roads. All fresh samples were sealed in double polyethylene bags to minimize contact between the samples and ambient air, and frozen to minimize sample loss due to evaporation until analyzed.

2.3 Analytical methods

Tritium (HTO and OBT) analysis and QA were performed following CRL's procedures and the analytical uncertainties were 10% for HTO and 25% for OBT.

TABLE 1: Sampling Points near the CRL site (NAD 83). NAD 83 is North American Datum of 1983, which is a geodetic reference system.

Sampling point	Easting	Northing	Remarks
Deep River	306247.1	5106449.9	Wooded area
Pt Alexander	303546.2	5112377.3	Cottage on the Ottawa River
Pembroke	334180.0	5072267.4	Open field
Russell	471451.0	5010852.6	Urban residential area

2.3.1. HTO measurement

The water fraction of soil pore water was extracted from the frozen soil samples (approximately 150 g) using a laboratory-designed freeze-drying system. The soil pore water was extracted over 24 hours using a liquid nitrogen trap under vacuum. The dried soil sample was placed into a drying oven at 55 °C to ensure that the soil pore water was completely removed. Then, approximately 70 mL of tritium-free rinse water was applied to the dried soil to remove the exchangeable OBT or the residual soil pore water fraction [11]. The samples were re-frozen, the water was re-extracted and samples were dried again using the same process. All collected plant samples (Tissue free water tritium, TFWT) were treated the same as the soil samples (Soil pore water).

To determine the HTO activity concentrations, the collected water from the freeze-drying process (10 mL) was mixed with 10 mL Ultima Gold LLT (PerkinElmer, USA) in polyethylene vials. The HTO activity concentration was then measured using a liquid scintillation counter (Quantulus 1220) for six hours. The minimum detectable activity for 10 mL of water was approximately 2.0 Bq/L.

2.3.2. OBT measurement

For OBT activity concentration, the completely dried samples were combusted in two different systems depending on the organic contents [5, 12]. A tube furnace combustion system was used for soil samples, while a Parr (USA) combustion system was used for plant leaf samples. Approximately 120 – 150 g of the soil samples were combusted in the furnace at 700 °C to allow for complete combustion of the organic content using a dry-ice trap. The collected combustion water was distilled (no neutralization) to remove impurities and placed in a polyethylene vial, then made up to 10 mL with tritium-free water and mixed with 10 mL of Ultima Gold LLT (PerkinElmer, USA). Calculation of OBT activity concentration considered dilution due to the added tritium free water. The OBT activity concentration was expressed as the amount of OBT in the volume of combustion water in units of Bq/L. The minimum detectable activity for OBT in soil ranged from 10-15 Bq/L.

3. Results and Discussion

3.1 Tritium release and concentrations in plant leaves

CRL provides an overview of the tritium levels in various environmental media reflecting the potential effects of tritium release from the facilities [3]. Figure 2 shows both air and liquid tritium emissions from CRL in 2009.

CRL's tritium release was approximately 9.4 x 10^{14} Bq/year for air emissions and 1.1 x 10^{14} Bq/year for liquid emissions in 2009. The value (less than 1% of DRLs) is similar to every year and a previous study [13]. Boyer *et al*. reported that tritium released by Heavy Water Reactors (HWR), such as the Canadian CANDU reactors, has airborne effluent ranging from 0.1 to 1 PBq/year and liquid releases ranging from 0.1 to 0.5 PBq/year.

The measured ambient tritium-in-air concentration averaged 1.1 Bq/m^3 at the site boundary in 2009. The value was distinguishable from natural background levels of tritium-in-air in Ontario that were based on measurements by Health Canada, ranging from 0.09 to 0.26 Bq/m^3 [3]. The amount of air tritium emission was slightly higher than the liquid emission, and HTO concentrations in plant leaves or surface soil pore water will reflect in the air tritium emission.

Therefore, tissue-free water tritium and exchangeable OBT will reflect atmospheric tritium concentrations during periods when they are in steady-state with atmospheric moisture and soil humidity. However, non-exchangeable OBT is tightly bound to the organic matter and provides an integrated record of atmospheric tritium during the growing phase of the vegetation [14].

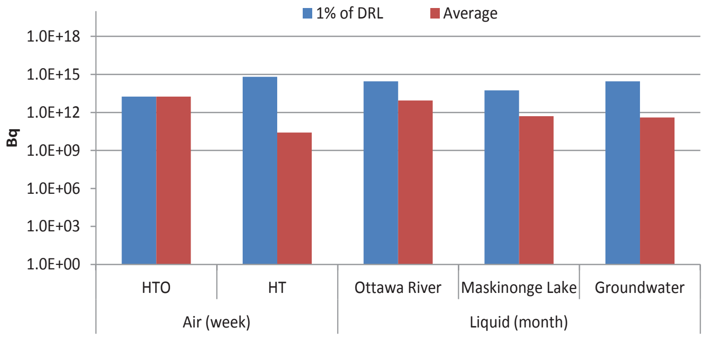

FIGURE 2: Average amount of tritium released from CRL in 2009.

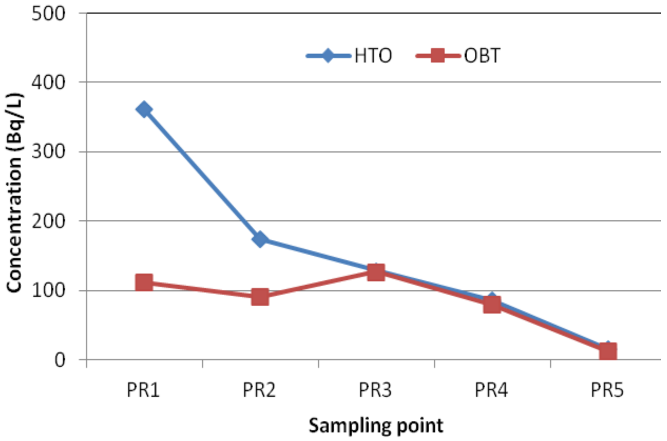

FIGURE 3: HTO and OBT concentrations in plant leaves collected along Plant Road.

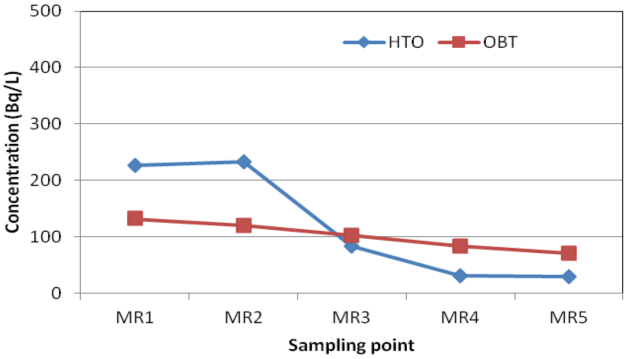

FIGURE 4: HTO and OBT concentrations in plant leaves collected along Mattawa Road.

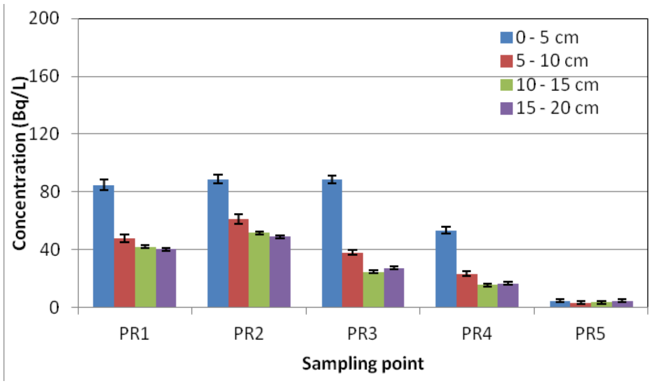

FIGURE 5: HTO activity concentrations of soil pore water with depths along Plant Road.

Figures 3 and 4 show HTO and OBT activity concentrations along two different sampling roads. Both HTO and OBT concentrations in plant leaves (Maple tree) showed a decreasing trend with distance from the CRL main stack.

The OBT concentration is the highest at PR3, but the concentration is very similar to the HTO concentration. The HTO concentration at PR1 is much higher than the OBT concentration at the same sampling point. The results suggest that the tritium plume was around PR1 under dynamic conditions and that there is no tritium effect at PR5 from CRL operations. The results support well-known tritium behaviour in the environment, and OBT in plant leaves reflect longer-term atmospheric tritium trends [13]. However, the HTO concentrations at MR1 and MR2 are higher than the other sampling points, except PR1, and the results suggest that the tritium plume was around the stack at the sampling time. The OBT concentration in plant leaves is a decreasing linear pattern with distance. Considering rates of OBT formation and loss, OBT concentrations are stable over shorter periods of time under semi-equilibrium conditions. Even though Mattawa Road is located under the main wind direction from CRL along the Ottawa River, the OBT concentration in plant leaves showed no significant difference with the prevailing wind direction and distance.

3.2 Tritium concentrations along Plant Road

CRL's main entrance is paved and soil samples were collected less than 10 m away from the roadside. Five sampling points were investigated along Plant Road (Figure 5). Soil samples were collected down to 20 cm; due to the presence of buried electrical lines, samples could not be collected deeper than this.

The HTO activity concentrations in surface soil pore water were similar at PR1, PR2 and PR3, which are closer to the main stack. The values are significantly lower than the values in plant leaves at the same sampling points. The results suggest that soil pore water reacted with ambient air slower than plant leaves did because there are different reaction mechanisms. Diffusion force and evaporation would be the major contributors between surface soil and ambient air moisture. There are differences between the different sampling points; however, for each point, the HTO activity concentrations at the layers deeper than 5 cm are the same. HTO by soil water tritium did not seem to be related to the external conditions, with the exception of precipitation. HTO by soil water tritium at PR5 were as low as background HTO concentrations in rain water less than 5 Bq/L.

OBT activity concentrations were approximately 1.5 times higher than HTO concentrations in soil pore water at the same sampling point. PR2 had the highest OBT activity concentrations in soil. The PR2 site had more forested area than the other sites and there were many fallen tree leaves. The tritium concentration was higher in the organic fraction

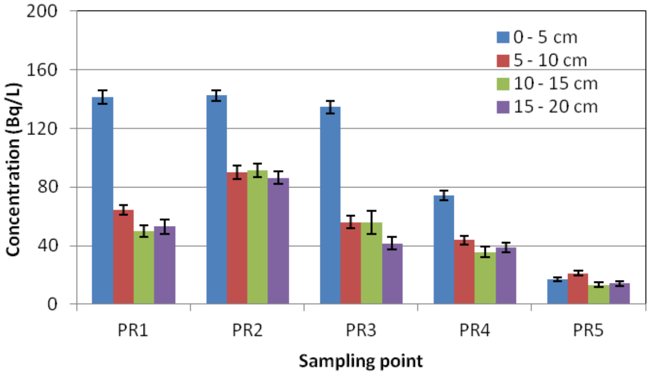

FIGURE 6: OBT activity concentrations of soil with depths along Plant Road.

of dead and degraded pine needles compared to soil samples because rain is responsible for water fractions in the samples [8]. Organic content and water content were not significantly related to OBT activity concentrations at all soil sampling points. In contrast, Sheppard *et al*. [10] reported that for soils in the field, much of the tritium may be in the soil pore water with less in the OBT related to the soil's organic matter. In this study, OBT activity concentrations were higher than HTO concentrations in soil pore water around the CRL site. Even with the lower HTO by soil water tritium at PR5, OBT values ranged from 13-20 Bq/L. The results suggested that OBT concentrations in background areas will be important to assess the effects of the long-term or historic tritium release into the environment.

3.3 Tritium concentrations along Mattawa Road

Mattawa Road is an unpaved emergency road that runs through a typical Canadian forest. The road is in the path of the prevailing winds transporting tritium from the CRL main site. Figure 7 shows HTO activity concentrations of soil pore water from sampling points along Mattawa Road.

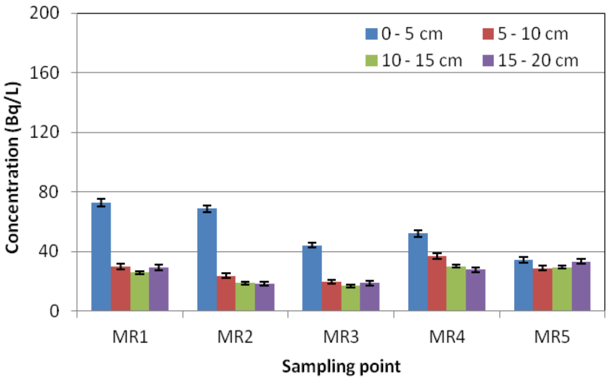

FIGURE 7: HTO activity concentrations of soil pore water with depth along Mattawa Road.

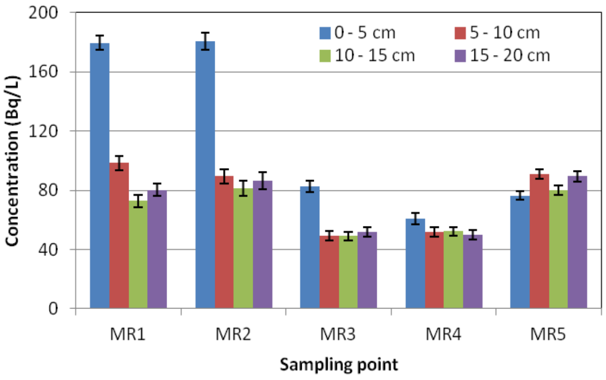

FIGURE 8: OBT activity concentrations of soil at depth along Mattawa Road. The bars represent the counting error.

The HTO concentration of the surface soil was the highest at MR1 and lower than HTO concentrations in plant leaves at the same sampling point. The overall distribution of HTO concentrations partially corresponds to the distance to the source and partially follows the local topography, which can be associated with horizontal transport of HTO with surface runoff from MR2 to MR3 and from MR4 to MR5. As a result, little difference in HTO concentration with distance from the CRL site, except in the upper soil layer, is seen. At MR5, there is no difference in HTO by soil water tritium with soil depth; however, the reason for this is presently unknown. Also, the HTO by soil water tritium of deeper soil at MR4 and MR5 were higher than MR1, 2 and 3, which are closer to CRL's main site (Figure 7). Apart from the factor of topography, these results could be related to the enhanced mixing of HTO between soil layers at MR5 due to composition of soil supporting hydraulic conductivity and re-cycling of tritium in the root zone of vegetation.

OBT concentration in soil is not directly related to HTO by soil water tritium in soil because they have a different retention time and environmental behaviour. HTO of soil pore water was related closely to recent precipitation, but OBT in soil may be related to previously deposited organic compounds coming from plant leaves, microorganisms, etc. OBT concentrations in the top soil layer at MR1 and MR2 were higher than that at the other soil depths and sampling sites (Figure 8) and this is generally compatible with the factor of distance, there was no significant difference in OBT concentrations found between MR1 and MR5 except at the 0-5 cm depth. The same observation applies to the upper-soil layer at all sites. In this respect, the elevated concentration deeper under the surface at MR5 cannot be readily explained. However, OBT distribution and migration in soil is not well understood and requires further study.

However, Plant Road is characterized by the minor frequency of the wind occurrence, while Mattawa Road is under the prevailing winds, so tritium concentrations in environmental samples were expected to vary accordingly. It is known that the higher activity could be correlated with the higher wind occurrence frequency in that direction [14].

3.4 Tritium concentrations at the historic HT release site

Based on the previous study [5], OBT concentrations at CRL's historical HT release site were considerably higher than the HTO by soil water tritium, and most OBT existed in the top layer of the soil. In order to validate this pattern, the HTO and OBT profiles were investigated up to a depth of 1 m. It would have been preferable to collect much deeper soil samples, but it was impossible due to the existing hard rocks below 1 m depth.

HTO and OBT concentrations at the non-HT release site, which is only 100 m from the previous HT release point, are very similar to the regional background tritium concentrations (Table 2).

There is no trend with soil depth and the results were very consistent from the top layer to the deepest layer of HTO and OBT activity concentrations. The results suggest that the previous historic HT release experiments were not affected by releases from current operations in the surrounding area. The OBT/HTO ratios varied from 2.8 to 7, while the HTO concentration at the 0-20 cm depth was observed to be lower due to the recent precipitation (year 2011). For HTO in soil pore water, assuming average soil moisture content of 15% water per mass of moist soil, the geometric mean of 3.2 Bq/L water would be implied [10]. This value agreed well with measured HTO concentrations around surface soil pore water for the uncontaminated site (Pembroke and Deep River). Table 3 shows the HTO and OBT concentrations at the historical HT release site.

TABLE 2: HTO and OBT Concentrations at the Non-HT Release Site

Soil depth	HTO concentration (Bq/L)	OBT concentration (Bq/L)	OBT/HTO ratio
Grass	3.6 ± 1.9	13.2 ± 4.3	3.7
0-20 cm	2.2 ± 0.3	15.3 ± 3.5	7.0
20-40 cm	2.6 ± 0.2	13.8 ± 3.5	5.3
40-60 cm	4.4 ± 0.7	16.8 ± 7.6	3.8
60-80 cm	4.9 ± 0.9	13.6 ± 1.8	2.8
80-100 cm	5.4 ± 0.6	15.9 ± 2.1	2.9

TABLE 3: HTO and OBT Concentrations at the Historical HT Release Site

Soil depth	HTO concentration (Bq/L)	OBT concentration (Bq/L)	OBT/HTO ratio
Grass	3.1 ± 0.6	16.1 ± 4.5	5.2
0-20 cm	3.0 ± 0.9	380.1 ± 13.1	126.7
20-40 cm	2.7 ± 1.2	43.8 ± 2.0	16.2
40-60 cm	5.5 ± 1.5	39.3 ± 6.6	7.1
60-80 cm	7.3 ± 1.5	27.4 ± 3.5	3.8
80-100 cm	7.5 ± 3.2	40.7 ± 14.9	5.4

The HTO concentrations in grass and soil pore water up to 40 cm deep were very similar to 3.0 Bq/L, the value found in background areas in Ontario. HTO activity concentrations in deeper soil were higher than the surface soils. The results suggest that there has been no recent tritium input at the historical HT release site. It is still unknown whether there are contributions from OBT to HTO by soil water tritium by microbial decomposition or degradation over the years. The OBT in soil organic matter is less transient and remains in dry soil, but is rarely reported. Organic matter in soil is composed of materials of varying ages, sometimes up to centuries old. Thus, radioactive decay of tritium significantly affects the net OBT content of soils. Sheppard *et al.* [10] reported OBT concentrations were 0.03 Bq/kg of dry soil based on the organic content per dry soil. The measured values will be different due to the average age of the soil organic matter. However, OBT in soil has little biological relevance because organisms intake tritium largely from water ingestion. Figure 9 shows the vertical profile of OBT concentration with depth.

OBT concentrations in soil are difficult to measure and not well understood. The OBT concentrations in soil were higher than that in pine needles and litter at most of the sampling locations [7]. This suggested that historically high soil tritium concentration may be reflected in high OBT concentrations in soils at the present time. The 0-10 cm soil interval generally had the highest OBT concentrations in collected samples. In the historical HT release site, the majority of OBT activity is in the surface layer (0-20 cm), but some OBT activities exist at depths of up to 1 m. The result could be used to evaluate OBT migration in soil after accidental tritium release into the environment.

3.5 Environmental influence around the CRL site

Precipitation, wind direction and other environmental factors are important in understanding atmospheric

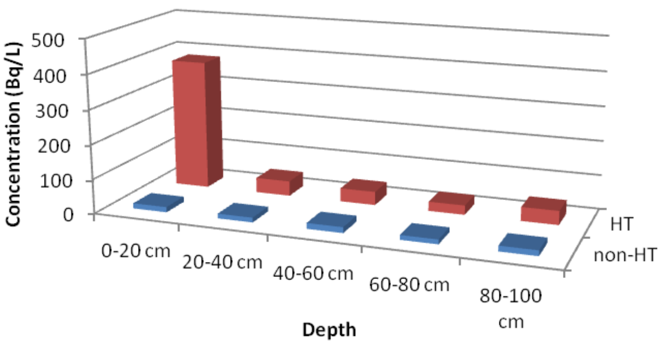

FIGURE 9: Vertical profile of OBT concentrations at the historical HT release site.

tritium behaviour in the environment [15]. CRL area has longer winters and shorter summers. Note that for almost six months of the year, precipitation at CRL occurs as snow. Table 4 shows precipitation amounts in 2011 at the CRL site.

In 2011, monthly average tritium concentrations ranged from 5 Bq/L to 48 Bq/L, which tended to be higher in the winter and lower in the summer. This can be attributed to seasonal differences in specific humidity. It is clear that washout could be a significant factor in environmental (including soil) tritium concentration in summer. Conversely, the frozen soil pore water in winter minimizes the movement of tritium under this condition. In addition to this seasonal variability there is significant variability in environmental tritium caused by site-specific weather. Figure 10 shows the frequency of wind occurrence at CRL.

Environmental tritium concentrations in the atmosphere are not sufficiently high to imply the variability in air deposition density effects since the tritium follows the air turbulence and is diluted by atmospheric dispersion. By following continuous tritium deposition on the ground, an exponential profile of tritium concentration could be formed in the exposed soils [13]. Then, most of the tritiated water in the soil can be re-emitted into the atmosphere. These results seem to confirm that the atmospheric pathway is dominant in these conditions. The physical and chemical properties of tritium are almost the same as hydrogen, especially as a constituent of water. Once tritium reaches the surface, tritiated water is easily incorporated into biological organisms as tissue free water tritium (TFWT) and OBT. In the humic layer, a small part of HTO is used to build organic matter during regular biomass production of soil microorganisms. OBT formed in soil was found to have a mean residence time of five years before being metabolized to HTO [16]. The soil organic materials come from dead plant leaves and will depend upon the climate in a region. Therefore, the majority of soil OBT may come from the surrounding plant leaves or biological materials. Following HTO released into the environment, plant leaves can occur OBT formation and incorporation with 0.03-0.05%/wk [17]. Once HTO is also deposited to soil, most will volatilize. Soils will become progressively enriched with tritium over time due to preferential volatilization of lighter isotopes. Therefore, soil tritium concentrations show the variability, which could be certain relation with volatilization rates, soil type and environmental conditions. Table 5 illustrates the OBT/HTO ratios at CRL site.

TABLE 4: Tritium Activity Concentrations in Precipitation at the CRL Site (2011)

Month	Snow (cm)	Rain (mm)	Concentration (Bq/L)
January	26.4	9.0	48 ± 2
February	34.2	3.8	31 ± 2
March	59.8	40.2	16 ± 1
April	28.0	57.1	13 ± 2
May	-	84.6	5 ± 1
June	-	116.3	16 ± 1
July	-	102.4	7 ± 1
August	-	78.6	5 ± 1
September	-	84.7	18 ± 1
October	2.8	73.6	10 ± 1
November	24.7	50.4	12 ± 1
December	43.7	17.5	32 ± 2
Total	219.2	718.2	-
Average	-	-	17.8 ± 12.9

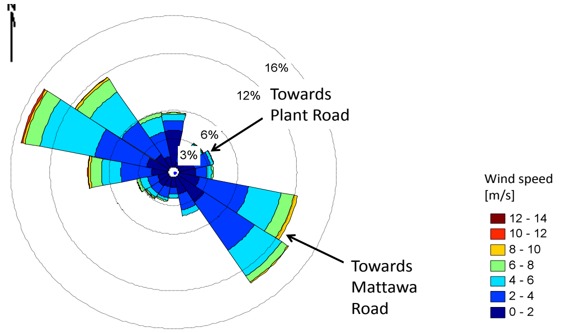

FIGURE 10: Averaged frequency of wind directions from the CRL main site from 2003-2010 measured at the 60 m high meteorological tower.

HTO and OBT have different residence times in soil and the ratios can reflect the historical tritium release or current steady-state conditions. The averaged OBT/HTO ratio varied from 1.1 to 4.4 for Plant Road and from 1.5 to 3.9 for Mattawa Road. Even though both sites are the same distance from the stack, the wind directions are different and this is reflected in different trends of ratios. Ratios for Plant Road and Mattawa Road are not significantly different. The variation could not be related to environmental parameters, such as soil substrate, volatilization rates and exposure to sun. etc.

Advection of HTO occurs due to the movement of water in roots and soil pore water. HTO also diffuses in soil. OBT is transported via photosynthetic allocation routes, and can be decomposed in the processes of autotrophic root respiration and heterotrophic respiration due to microbial decomposition of dead matter. Specific activity (SA) models are widely used for some radiologically important radionuclides that are long-lived, highly mobile in the environment and under homeostatic control in living organisms. ^{3}H, ^{14}C and ^{36}Cl have these characteristics and are modelled using specific activity concepts. According to the specific activity, the OBT/HTO ratio should be close to

TABLE 5: OBT/HTO Concentration Ratio at Various Soil Depths at CRL

Depth	PR1	PR2	PR3	PR4	PR5
0-5 cm	1.66	1.60	1.51	1.39	3.76
5-10 cm	1.35	1.47	1.47	1.88	6.87
10-15 cm	1.19	1.77	2.26	2.31	3.91
15-20 cm	1.32	1.77	1.53	2.37	3.13
Average	*1.4 ± 0.2*	*1.7 ± 0.1*	*1.7 ± 0.4*	*2.0 ± 0.5*	*4.4 ± 1.7*
Depth	**MR1**	**MR2**	**MR3**	**MR4**	**MR5**
0-5 cm	2.46	2.63	1.87	1.17	2.24
5-10 cm	3.30	3.80	2.53	1.42	3.16
10-15 cm	2.84	4.36	2.91	1.75	2.72
15-20 cm	2.76	4.75	2.79	1.82	2.70
Average	*2.8 ± 0.3*	*3.9 ± 0.9*	*2.5 ± 0.5*	*1.5 ± 0.3*	*2.7 ± 0.4*

unity (1.0) under equilibrium conditions [15]. Measured OBT/HTO ratios on Plant and Mattawa Roads were always greater than unity due to the different retention times of HTO and OBT in ecosystems.

There is no relationship between organic contents and OBT concentrations based on combustion water of soil samples (Figure 11). In most soil samples collected at CRL, the organic content is less than 5%. This is a reason for lack of relationship between OBT/HTO and organic content. Evaporative losses in soils could have lead to longer term enrichment of tritium in some soils over others as well as slow rate of accumulation in plants.

3.6 Tritium concentrations near CRL sites

HTO and OBT concentrations in soils were measured at four different sites to evaluate the effect of regionally different soil properties and environmental conditions on tritium distribution away from the CRL site. Deep River, Point Alexander and Pembroke are residential or cottage areas chosen for comparison with CRL in the Ottawa Valley. Russell is near the city of Ottawa and thus, no tritium influence from CRL operations is expected.

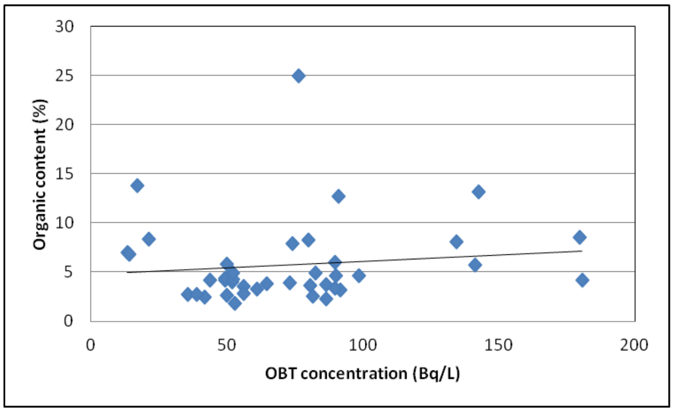

FIGURE 11: Relationship between organic content and OBT concentrations of soil samples collected on Plant Road and Mattawa Road.

Tritium in soil has often been used as a conservative tracer [18]. However, tritium may exhibit some retardation in soils due to isotopic exchange between tritium and hydroxyls in the crystal lattice of vermiculite and certain types of montmorillonite. Colloid mobilization decreases with clay content, while the mobility increases with the fraction of tritium in water. The distance from the tritium source leads to a dilution of atmospheric tritium with fraction of water vapour. The regional background observed at the CRL site is similar to that observed in Russell where there is no nuclear facility (Table 6). Choi *et al.* [19] found that most of the applied HTO had escaped to the air by evaporation and transpiration, and it showed rather slow downward movement.

The difference between HTO and OBT concentrations in soil near the CRL site is varied by a factor of 2-3 on a regional scale. HTO by soil water tritium and OBT concentrations in soil are not related to the distance from the tritium source term. It is a possibility that the effect of very small variation of tritium in soil, with distance from the source in the vicinity of CRL, is in fact related to OBT being close to steady-state post-nuclear tests background and, thus, being close to constant.

Soil characteristics are an important factor for tritium concentrations near nuclear facilities. Soil is made up of a

TABLE 6: HTO and OBT Concentrations in Soil Depths Near the CRL Site and Ottawa

Site	Depth (cm)	HTO (Bq/L)	OBT (Bq/L)	Water content (%)	Organic content (%)
Deep River	0-5	5.7	13.5	47.3	29.9
	5-10	4.7	11.4	33.1	10.4
	10-15	5.5	10.7	31.9	8.7
	15-20	5.1	12.9	31.3	8.1
	20-25	4.4	24.8	28.9	6.1
Point Alexander	0-5	17.4	33.1	18.6	8.5
	5-10	10.7	24.8	11.9	4.5
	10-15	13.1	22.7	9.4	3.1
	15-20	13.4	26.6	6.9	2.2
	20-25	15.1	25.5	5.3	1.5
Pembroke	0-5	<MDA	36.6	28.6	11.2
	5-10	<MDA	27.6	25.5	7.5
	10-15	3.1	23.9	21.7	5.8
	15-20	<MDA	25.1	19.8	4.6
	20-25	<MDA	31.9	18.9	3.5
Russell	0-5	<MDA	34.7	23.2	11.6
	5-10	<MDA	36.5	16.8	7.3
	10-15	<MDA	39.8	16.8	6.0
	15-20	<MDA	37.9	18.6	5.2
	20-25	<MDA	44.0	18.4	5.2

Minimum Detectable Activity (MDA) of HTO = 3.0 Bq/L mixture of decayed organic material, living organisms and minerals. Soil organic matter includes primary components (non-humic substances) that are inherited from plant and animal residues entering the soil and make up about 20-30% of total soil organics. On the other hand, secondary compounds (humic substances) are formed within the soil by the breakdown of organic structures or products of biochemical decomposition. However, humic substances make up to 60-80% of total soil organics.

OBT is higher than HTO in every sample and at every site. Also, there is no significant depth difference between HTO and OBT concentrations, while organic content and water content are different. Compared to the HTO by soil water tritium in soil depths, OBT concentrations are much higher. This suggests that, taking into account radioactive decay, current OBT levels in soil can reflect the high HTO levels in precipitation after the nuclear atmospheric tests in the 1960s. In addition, there might also be variability between areas with longer living plants with slower accumulation rates and shorter-term shrubs and grasses with faster accumulation rates, or in area with little organic material since plants accumulate OBT.

Overall, there is no consistent tendency for OBT concentrations in soil and the regional background of OBT in soil varied. Therefore, in order to evaluate the long-term environmental effects of tritium, background soil OBT concentrations around nuclear facilities should be quantified.

4. Conclusion

Soil is a conservative tritium tracer, that does not vary rapidly in the environment. This study demonstrated that HTO concentration in the top layer of soil at the CRL site decreased at PR4 and PR5 with distance from the tritium sources on Plant Road, but didn't decrease significantly on Mattawa Road, which is located in the main direction of the wind. OBT concentrations in soil showed a similar pattern to HTO by soil water tritium in soil on both roads. Higher organic content is not always related to high OBT concentrations, but sampling points with high OBT concentrations also had higher organic content. At the historical HT release site at CRL, the OBT concentration in soil can be measured to a depth of 1 m, but the major activity is in the top layer to about a 20 cm depth.

Variability of HTO by soil water tritium and OBT concentrations in soil samples near the CRL site was the same as the variability on the regional scale and there is no evidence that CRL operations have influenced environmental tritium concentration significantly. OBT is an important radionuclide for tritium and has longer residence time in the environment. OBT is likely a conservative tracer and can provide useful information regarding longer term atmospheric tritium releases around nuclear facilities. In contrast, HTO would be possible to use as a means to confirm effluent monitoring data and models.

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FULL ARTICLE

IN-VIVO NEUTRON ACTIVATION ANALYSIS FOR ALUMINUM IN BONE: SYSTEM UPGRADE AND IMPROVED DATA ANALYSIS

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An existing NaI(Tl) multidetector array at McMaster University used for in vivo *measurement of aluminum by means of neutron activation has been recently upgraded with an in-house built pulse processing system. The new system is capable of collecting spectra in coincidence and anticoincidence modes which allows for better discrimination between the 1.78 MeV ^{28}Al peak and the interfering ^{38}Cl peak. The system is interfaced with Matlab and controlled using a custom graphical user interface, which provides periodic spectral data storage during the acquisition. This feature makes it possible to validate the acquired data and the spectral fitting routines through half-life analysis of the radionuclides. A new set of calibration phantoms spanning a narrower range of aluminum concentrations than employed in the previous study, has also been developed. The combined effect of the new improvements resulted in the minimum detectable level of aluminum in aqueous solutions containing Na, Cl, and Ca in physiological levels, equal to approximately 3 μgAl/gCa.*

1. Introduction

In vivo neutron activation analysis of aluminum in bone is based on the ^{27}Al(n,γ)^{28}Al reaction. The first such systems were developed in the 1970s in response to the occurrence of dialysis encephalopathy [1]. At McMaster University, a system has been developed using a Tandetron accelerator as a neutron source, by means of the ^{7}Li(p,n)^{7}Be reaction. Work on this system has been reported previously [2, 3, 4], including estimates of bone aluminum made *in vivo* as a spin-off of a study to measure the accumulation of manganese in bone. Successive improvements to this system have also been reported elsewhere [5, 6, 7]. Three areas of improvement are reported here: the use of anti-coincidence counting, half-life analysis of the involved radionuclides, and development of new, lower aluminum concentration calibration standards.

2. Methods

The thermal neutron capture reaction on ^{27}Al has a cross-section of 231 mb. ^{28}Al is unstable with a half-life of 135 s and undergoes beta decay to a single excited state of ^{28}Si in 100% of all disintegrations. The ^{28}Si* nucleus de-excites by emission of a single 1.78 MeV gamma-ray with a branching ratio of 100%. Another reaction channel that leads to the production of ^{28}Al is the (n,α) reaction on ^{31}P, which has an effective threshold of approximately 3 MeV [8]. In practical applications, it is important to select a neutron source that will not activate this reaction channel, which would misrepresent the amount of aluminum present in the irradiated biological sample. In our system, we employed the accelerator-based neutron source (ABNS) using the ^{7}Li(p,n) reaction [9, 10, 11]. In the proton energy region of approximately 2.3 MeV, the maximum neutron energy produced is 0.55 MeV, so the contribution of the ^{31}P(n, α) can be safely neglected.

Isotopes of major elements that create delayed activity when subjected to neutron irradiation in biological systems are: ^{23}Na, ^{37}Cl, ^{26}Mg, and ^{48}Ca, creating the radionuclides shown in the gamma-ray spectrum in Figure 1. The aluminum gamma-ray at 1.78 MeV is close to, and usually dominated

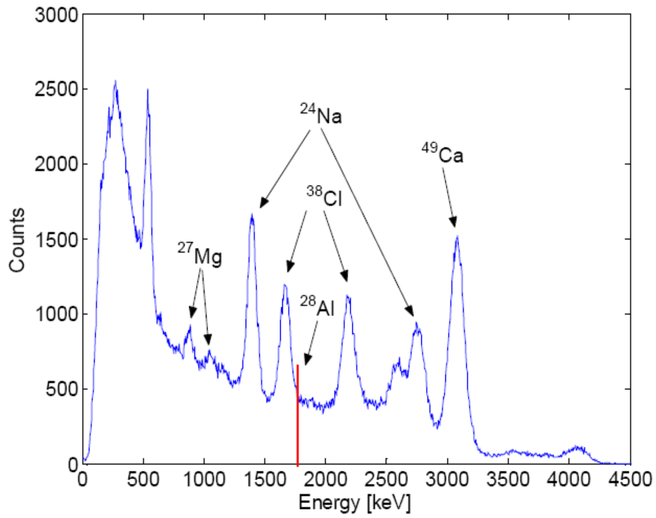

FIGURE 1: Major delayed gamma-rays detectable after neutron activation of a biological system. Red marker indicates position of the 1.78 MeV gamma-ray from aluminum.

by, the larger peak at 1.64 MeV from ^{38}Cl. However, using appropriate detection timing techniques the cascade emission of the gamma-rays following the decay of ^{38}Cl can be utilized to reduce the relative size of this peak in the spectrum. Beta decay of ^{38}Cl leads in 33.1% of all disintegrations to the 3.81 MeV excited level of ^{38}Ar which de-excites chiefly by cascade emission of two gamma-rays: 1.64 and 2.17 MeV. In 11.3% of disintegrations, the beta decay leaves the argon nucleus in the 2.17 MeV excited level, which assumes the ground state by the emission of a single gamma-ray, and in 55.6% of disintegrations, the beta decay leads directly to the ground state of the ^{38}Ar nucleus. Thus, the emission of 1.64 MeV gamma-ray is always accompanied by the emission of the 2.17 MeV gamma line. This observation, as well as the fact that the ^{28}Al nucleus following the neutron capture decays with the emission of a single gamma line, led us to consider an upgrade of our pulse processing system to detect anticoincidence events. Counting in anticoincidence discriminates against the 1.64 MeV peak and, therefore, in favor of the ^{28}Al peak. Another advantage of this counting mode is reduction of the continuum in the aluminum region of interest due to 1.37 and 2.75 MeV cascade peaks from the decay of ^{24}Na.

2.1 System upgrade

The previous configuration of the system was reported in references [5] and [6]. The physical detector arrangement remained unchanged and the upgraded components are the high-voltage-bias power supplies (HVPS) and the pulse processing system. The functional blocks of the new system are shown in Figure 2.

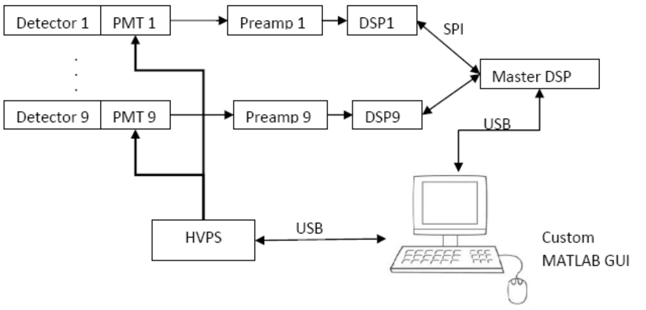

FIGURE 2: Functional blocks of the upgraded detection system.

The individual detectors receive bias voltage from a 9-unit modular HVPS (Surface Concept Gmbh, Germany) controlled through MATLAB [12] Graphical User Interface (GUI). The output signal from the photomultiplier tubes (PMT) is routed to preamplifiers and in-house built digital signal processing (DSP) units based on Freescale Semiconductor microcontroller model DSP56F807PY80. The sampling frequency of the integrated ADC is set to 40 megasamples per second, which is sufficient, considering the rise time of the input signal. The individual DSPs are interfaced through the serial peripheral interface (SPI) bus with the master DSP. The slave DSPs collect individual detector spectra (singles) while the master DSP resolves coincidences between slave DSP events in real time, and accumulates coincidence and anticoincidence spectra. The MATLAB GUI communicates with the master DSP via USB interface.

In order to determine pulse height from the incoming pulse, a running difference between two points of the digitized sample separated by a programmatically set interval is carried out on each slave DSP. It was observed that even such a simple implementation of the trapezoidal filter does not contribute significantly to the deterioration of energy resolution. Moreover, a filter with longer rise time than a single point was not implemented due to limited computing power of the microprocessor.

Gain stability of individual detectors in a multidetector array affects the energy resolution of the coincidence as well as anticoincidence spectra, and photomultipler tubes exhibit gain instabilities due to temperature variations and bias voltage drifts. Stabilizing a multidetector system poses considerable difficulty. Moreover, the NaI(Tl) detectors in our array are equipped with different models of PMTs, each characterized by a different temperature sensitivity. It is therefore important to monitor the long-term gain stability of the system. The HVPS provides a control protocol via the USB that allows reading and setting the HV bias for all nine detectors individually. The HVPS and the DSP are connected to the same PC and controlled by a custom GUI. This architecture allows the monitoring of gain stability of the system and the adjustment of the HV bias in the feedback loop.

2.2 Experimental

Evaluation of the pulse processing system for detection of aluminum in phantoms was made using phantoms containing varying amounts of aluminum. Composition of the phantoms and the irradiation setup was reported in reference [5].

Figure 3 shows a comparison of three detection modes: singles (off-line addition of events from all 9 DSPs), anticoincidences, and coincidences. As expected, the gamma-rays emitted in cascades, i.e., 1.37 and 2.75 MeV from ^{24}Na, as well as partial coincidence summation from the 1.64 and 2.17 MeV peaks from ^{38}Cl, were reduced in the anticoincidence spectrum, compared to the singles spectrum, by approximately a factor of four. The events not present in the anticoincidence spectra are visible in the coincidence spectra where new sum peaks have formed. Comparing the singles and anticoincidence spectra of the 3.08 MeV gamma-ray from ^{49}Ca, which is a single-gamma-ray emitter, it is evident that the net areas of the peaks remain unchanged. This indicates that the pulse processing algorithm correctly assigns coincidences and anticoincidences; therefore, the 1.78 MeV peak from ^{28}Al also remains unaffected.

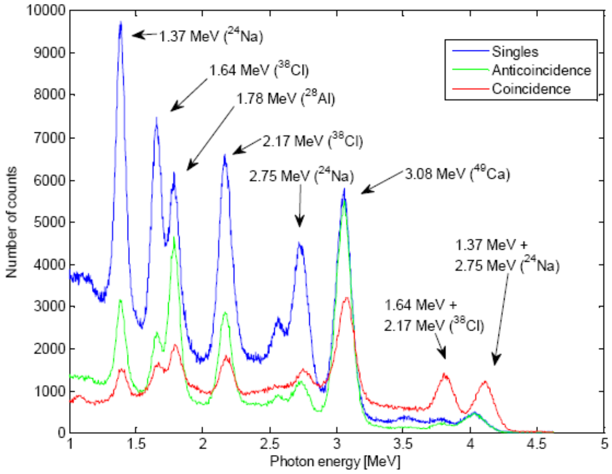

FIGURE 3: Comparison of data acquisition modes with the upgraded pulse processing system. A phantom containing 1335 μgAl/gCa was irradiated for 45 s with 400 μA proton current at 2.3 MeV proton energy. The spectrum was acquired for 10 minutes.

2.3 Data collection

Due to the low energy resolution of the NaI(Tl) detectors, the 1.78 MeV peak from ^{28}Al and the 1.64 MeV from ^{38}Cl partially overlap, which makes separating their contributions challenging. However, half-life differences (^{49}Ca has a half life of 8.72 min, ^{28}Al has a half life of 2.25 min, and the interfering ^{38}Cl has a half life of 37.2 min) can be utilized in the data analysis by noting that the resulting net peak areas from these three radionuclides in phantoms plotted as a function of time should follow the exponential decay law with their respective half-lives. In order to facilitate such analysis, the spectra should be saved every predefined time interval, and the individual spectra should be analyzed separately. In a biological system the removal rate of ^{38}Cl is increased by biological removal from the irradiated site but the well isolated 2.17 MeV peak from ^{38}Cl may be use to establish the effective removal rate. In order to allow sequential saving of the spectra, and to minimize the time needed for this operation, we used a semi-automatic approach with the help of MATLAB scripting language. The master DSP provides a communication interface over the serial bus that implements control commands. The MATLAB program sends the following sequence of control commands to the master DSP: stop acquisition, download spectra, reset buffer, and restart acquisition. The time needed by the master DSP to service this request was measured to be approximately 1.2 seconds. During this time, the master DSP is not available to accept new events from the slave DSPs. In our implementation, the spectra from the master DSP are recorded in MATLAB every 60-second interval. Considering the half-lives of the analyzed radionuclides, we concluded that 1.2 seconds needed for recording the data every 60 seconds will not have significant impact on the statistical quality of the data.

2.4 Data analysis

As mentioned earlier, the 1.78 MeV peak from ^{28}Al partially overlaps with the 1.64 MeV peak from ^{38}Cl. Even though the anticoincidence acquisition improves the ratio of the two in favor of the former, chlorine is an abundant element in biological systems, and the 1.64 MeV peak nearly always dominates. For this reason, we specified the region of interest, where we perform spectral fitting, as the section between 1.50 and 1.90 MeV which includes both peaks.

Reporting absolute aluminum content is subject to variations due to such confounding factors as: neutron field fluctuations, volume of the irradiated site, and position of the sample in the detector. It is more appropriate to report the results as the ratio of aluminum to calcium. Moreover, the assumption that aluminum is located uniformly in the bone makes this metric more consistent than quoting the absolute amount of aluminum. Because of this, both the aluminum peak area at 1.78 MeV and the calcium peak area

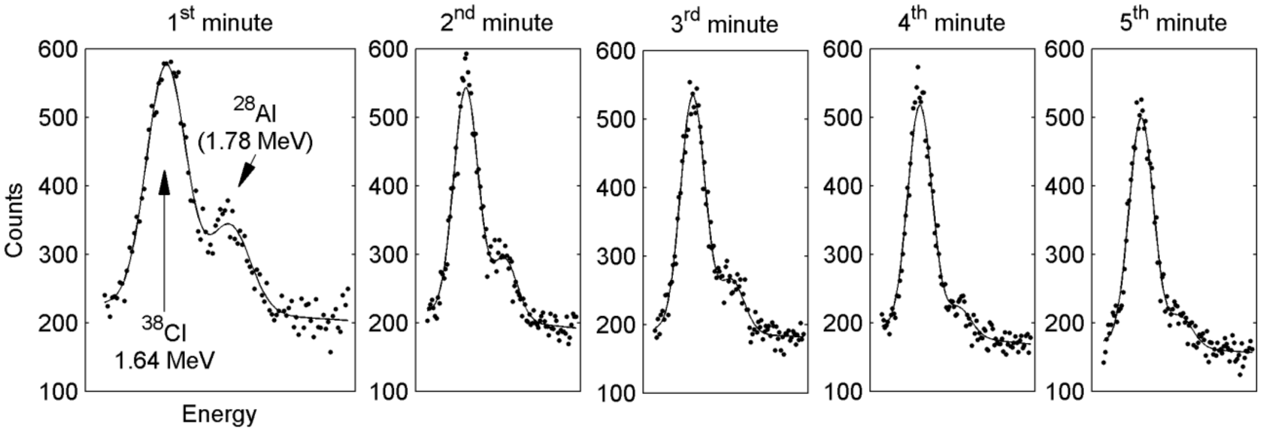

FIGURE 4: Spectra acquired with a phantom containing 16.6 μgAl/gCa in the region of interest around the ^{38}Cl and ^{28}Al peaks from consecutive one minute acquisitions (dots) and the fitted model (solid line).

at 3.08 MeV have to be established. Fortunately, the calcium peak is conveniently isolated and very well-defined so the analysis is rather straightforward, and a single Gaussian function is sufficient to find the net area reliably. The reported concentration of aluminum is quoted in units of μgAl/gCa.

In the first step of the analysis, the background has to be subtracted. However, rather than subtract the collected raw background data, we fit a model function to a long-count-rate background spectrum, and subtract count-time-adjusted background from the experimental data. The choice of subtraction of a model rather than raw data is dictated by the fact that background data collected over the same time interval as the *in vivo* data (usually 1 minute) suffer from poor statistical quality. The background in our region of interest consists of two double-escape peaks from ^{208}Tl and ^{214}Bi gamma-ray pair-production interactions located on a constant continuum due to Compton interactions of higher energy gamma-rays.

After background subtraction, the individual one-minute spectra are analyzed by fitting a model function (Figure 4). The fitting model consists of two Gaussians having their positions fixed relative to each other and their widths proportional to $E^{1/2}$, where E is the photon energy. Each one-minute spectrum contributes an intermediate estimate of aluminum contents in the sample, and the intermediate estimates are averaged with inverse variance weighting to produce the final value.

The net areas for the 1.78 MeV and 1.64 MeV peaks in phantoms should follow the exponential decay law when plotted as a function of time. However, the distinct exponential trend for ^{28}Al is visible only for aluminum

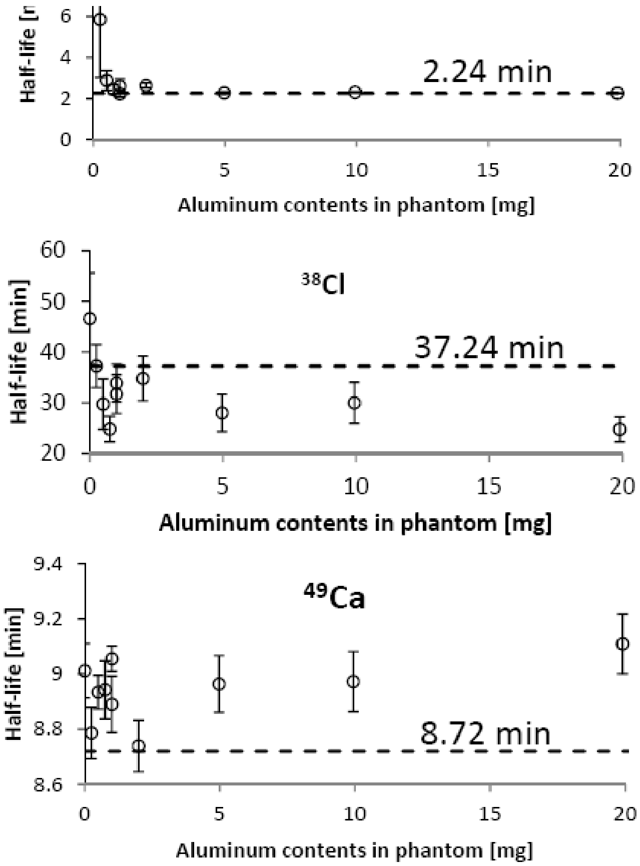

FIGURE 5: Half-life values of the three elements determined in the analysis as a function of amount of aluminum in phantom. The dashed horizontal line shows the library value.

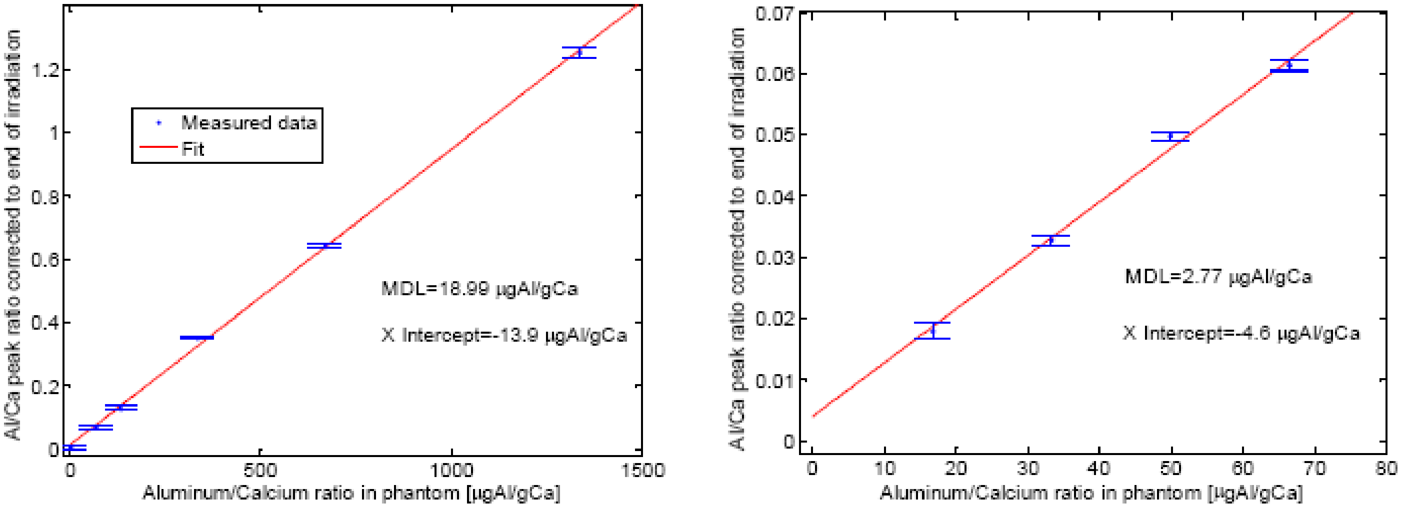

FIGURE 6: Calibration lines relating relative concentration of aluminum with relative sizes of 1.78 and 3.08 MeV peaks. The old (left) and the new (right) phantom sets.

concentrations well above physiological values (Figure 5). At lower aluminum concentrations the half-life values become higher, which indicates the influence of the neighboring longer half-life 1.64 MeV peak from ^{38}Cl. In addition, the 1.64 MeV peak shows consistently lower half-life values by approximately 20%, which indicates a deficiency in the fitting model. The calcium peak shows half-life values slightly higher than the library value. This may be due to the interference of a double escape peak from the sum ^{24}Na peak, which is located at 3.10 MeV, ^{24}Na having a much longer half-life.

2.5 System calibration

The calibration standards, by comparison with which the ratio of the 1.78 MeV and 3.08 MeV peak areas is converted to a ratio of aluminum to calcium in bone, were made as aqueous solutions of Cl and Na compounds in physiological concentrations with the addition of known amounts of Al, and contained in low density Nalgene 250-mL bottles. We found that the Nalgene plastic contains trace amounts of aluminum that varied from bottle to bottle; therefore we surveyed available cointainers but could not find a type with lower contents of aluminum. In order to mitigate the interference of aluminum in container material, we decided to alter our calibration protocol instead. Immediately after irradiation, the activated fluid is transferred to an unirradiated bottle in which it is counted in the detection system.

The original set of calibration standards reported in reference [5] had higher aluminum concentrations than observed in members of the general public. So new calibration standards have been made and the calibration of the whole system re-examined with background levels of aluminum as the target measurement. Figure 6 presents the calibration lines obtained with the upgraded system for the old and the new calibration standards. It is readily visible, that the minimum detectable level (MDL) of aluminum, as defined in our previous publication [5], is lower by almost an order of magnitude with the new standards. This is mostly attributed to limiting the calibration range from the old maximum of 1335 μgAl/gCa to the new maximum of 66.4 μgAl/gCa. In addition, the negative intercept is smaller for the new standards which indicates lower residual aluminum, e.g., present in the chemical compounds used to produce the phantoms.

3. Conclusions

Recent upgrades have been made to a system for detection of aluminum *in-vivo* using neutron activation analysis. Several factors have contributed to the improved detection limit of aluminum after the upgrade. First, anticoincidence acquisition mode efficiently discriminates against the 1.64 MeV peak from ^{38}Cl, thus improving the contrast between the 1.64 and 1.78 MeV peaks. Second, the data analysis method based on sequential one-minute acquisitions takes advantage of half-life differences between ^{28}Al and ^{38}Cl. This analysis method yields lower detection limits than the analysis of cumulative spectra. Optimization of the data storage interval, which is currently set at 60 s, is required and may potentially further decrease the MDL. Lastly, the MDL in phantoms was decreased also by the reduction in the calibration range based on previous *in-vivo* measurement results. Calibration standards will also be verified with chemical analysis of aluminum content.

The quality of the fitting model was evaluated by noting that the net areas of the analyzed peaks follow the exponential decay law. The fact that the 1.64 MeV peak in phantom results in a lower half-life than the library value, indicates a deficiency in the model that needs to be addressed. The effective half-lives in *in vivo* measurements are shorter due to biological removal of chlorine from the irradiated site. The half-lives may also serve as additional constraints in two dimensional (time-energy) surface fitting analysis.

Work is under way to implement the next generation of the custom digital pulse processing system based on a faster microcontroller and higher-capacity communication bus (USB 2.0). Among other features, the new architecture will be able to implement a more advanced pulse shaping filter as well as the LIST mode.

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FULL ARTICLE

Evaluation of Potential Mercury Releases from Medical Isotope Waste

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Mercuric (Hg) nitrate is used as a catalyst in the medical isotope production process at Atomic Energy of Canada Limited (AECL) Chalk River Laboratories (Chalk River, ON) to ensure consistent Mo-99 target dissolution. The subsequent high level radiological liquid waste is cemented into stainless-steel pails and shipped to a waste management area for long-term storage. Previous studies have confirmed that Hg tends to bind and precipitate I-131, thus minimizing its release to the environment. In order to assess the situation and evaluate the need for Hg monitoring, environmental media (vegetation, surface soil, groundwater, and air) surrounding this waste storage area were sampled and results were compared with applicable guidelines and/or background areas at AECL and other locations.

Mercury in groundwater, surface soil, and vegetation were found to be below applicable environmental guidelines and comparable to background locations. Atmospheric Hg near waste storage was found to be elevated above background, but well below applicable guidelines for continuous monitoring. Concentrations of Hg in air also dissipated quickly and were comparable to background within 60 to 80 m from source.

The atmospheric Hg monitor used in this study (TEKRAN 2537B) constitutes part of the custom-built portable TEAMS trailer that was designed to provide Chalk River Laboratories with the capability to measure, monitor and model Hg emissions, along with other radiological and non-radiological contaminants, for a wide range of situations. The trailer can also be easily re-configured to adapt to different monitoring needs.

1. Introduction

Mercury (Hg) released from natural and industrial sources can be transported long distances in the atmosphere. Significant anthropogenic sources typically include coal combustion (and other fossil fuels), the use of Hg-amalgamation in gold mining, municipal waste incineration, and waste from chlor-alkali production [1]. Volcanic activity, large-scale forest or grass fires, and dispersal into soils and sediments near cinnabar (HgS) deposits are typical natural sources of Hg in the environment [2, 3, 4, 5]. Once deposited, a portion converts to methylmercury (MeHg) and bioaccumulates in food webs to often unacceptable levels in fish and wildlife [6]. A considerable amount of research has been focused on the environmental fate and behaviour of Hg once released from these anthropogenic (e.g., Flin Flon smelter, Manitoba [7]) and natural sources. The dominant pathway for human exposure to Hg (as MeHg) is from consumption of significant amounts of contaminated fish [8, 9, 5].

Medical isotope (Mo-99) production at AECL involves the use of mercuric nitrate to enhance the dissolution of irradiated isotope targets prior to extraction of Mo-99 [10]. Once completed, the Mo-99 waste is cemented in 5-gallon stainless-steel cans and transferred to an outdoor waste-management facility for intermediate storage in concrete cylindrical tile holes. At current Mo-99 production rates, approximately 10 kg yr^{-1} of Hg in this cemented waste is placed in tile hole storage. Groundwater Hg monitoring downgradient of this outdoor waste management facility is currently the only method used to routinely assess environmental performance.

Published research on cemented Mo-99 waste as an anthropogenic source of Hg is limited, but there are a number of unpublished studies at AECL that have evaluated the potential for leaching and longer-term stability of Hg in the cemented Mo-99 waste. Some of this previous work has been briefly discussed in this study, along with published studies, as they provide additional support for the conclusions drawn therein.

The purpose of this study was to evaluate potential Hg releases from the cemented Mo-99 waste stored in tile holes in an outdoor waste management facility at AECL and to determine whether these Hg emissions are above background and/or applicable guidelines.

2. Materials and Methods

2.1 Site description

The tile holes in the outdoor waste management facility where the cemented Mo-99 waste is stored (nine cans per tile hole) are located on a hill as part of a tile array in an area surrounded by sand and gravel fill material, with no vegetation (Figure 1A). Outside the waste management facility fenceline (~50 m from tile holes), a mixed forest dominates the landscape (e.g., pine, aspen, maple, birch). Tile holes are engineered concrete structures (extend 5 m below soil surface) surrounded by compacted soil and shielded with a concrete plug that have been used since the mid-1950's to store radioactive waste requiring high levels of shielding (Figure 2).

Cemented Mo-99 waste cans are transferred from the Mo-99 isotope production facility for storage in tile holes in the outdoor waste management facility with the use of a shielded waste transfer flask.

2.2 Sample collection and analyses

2.2.1 Soil

The sampling design assumes that the origin of the soil in the potentially contaminated area is from within the waste management facility, although the matrix is not necessarily representative of the native soil in the immediate area (i.e., fill material from elsewhere at AECL).

In November 2009, duplicate surface soil (5 cm) samples were collected throughout the waste-management facility in the area surrounding the tile holes and immediately outside the fenceline. Reference background soil fill material was collected from a sand pit near one of the AECL parking lots (Figure 1, near B outside CRL built-up area), along with fill used near a building located outside of waste management facility (Figure 1, B inside CRL built-up area).

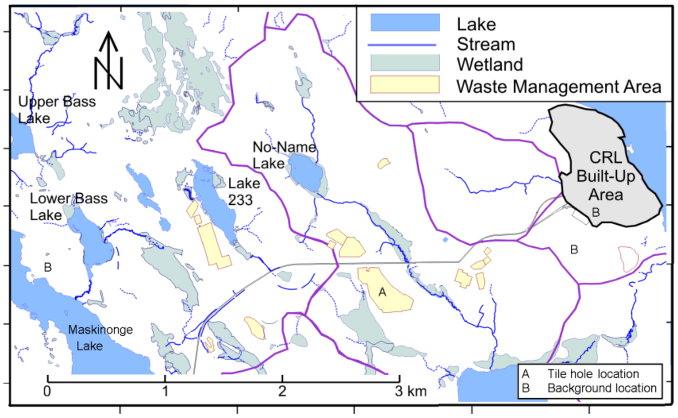


FIGURE 1: Sampling locations on the CRL property.

To provide further confirmation that soil Hg was not elevated near tile holes (4.72 m depth) with cemented Mo-99 waste, vertical soil sampling in the unsaturated zone was conducted in 2010 in the immediate vicinity (< 0.5 m) of selected older tile holes to evaluate potential for longer-term leakage from cemented waste using a rotary hammer drill rig equipped with hollow continuous flight stem augers for soil drilling and sampling. Vertical soil samples, including the deepest sample (last 15 cm) with the highest probability of soil contamination if tile holes had leaked, were collected with an AMS 5 cm diameter bucket auger and prepped for Hg analysis.

Soil samples were all shipped to an internal AECL lab and frozen. Soil samples were dried in ovens at 40 ^{o}C for 66 hrs. Soil weight remained the same (< 0.15% difference) for samples that were dried for an additional 66 hrs. A subset of samples (n = 23) and reference background soil material (n = 3) were then sieved through a 2 mm filter (to remove particulates in soil samples larger than sand) prior to shipment to University of Ottawa for total Hg analysis (surface soil). The University of Ottawa uses an SP-3D Hg analyzer with thermal decomposition, dual gold amalgamation to isolate and concentrate the liberated Hg, and cold vapor atomic absorption spectroscopy (CVAAS) for detection. The method detection limit (MDL) for this system is 0.01 ng Hg and can range up to 1000 ng Hg. Relative Standard Deviation (RSD, %) for MESS3 soil Standard Reference Material (SRM) was 2.61%.

Vertical soil samples were dried and shipped to Whiteshell Laboratories (Pinawa, MB) for Hg analysis using CVAAS. Uncertainties (95% CL) varied from 0.6 – 1.8 ng g^{-1}.

2.2.2 Groundwater

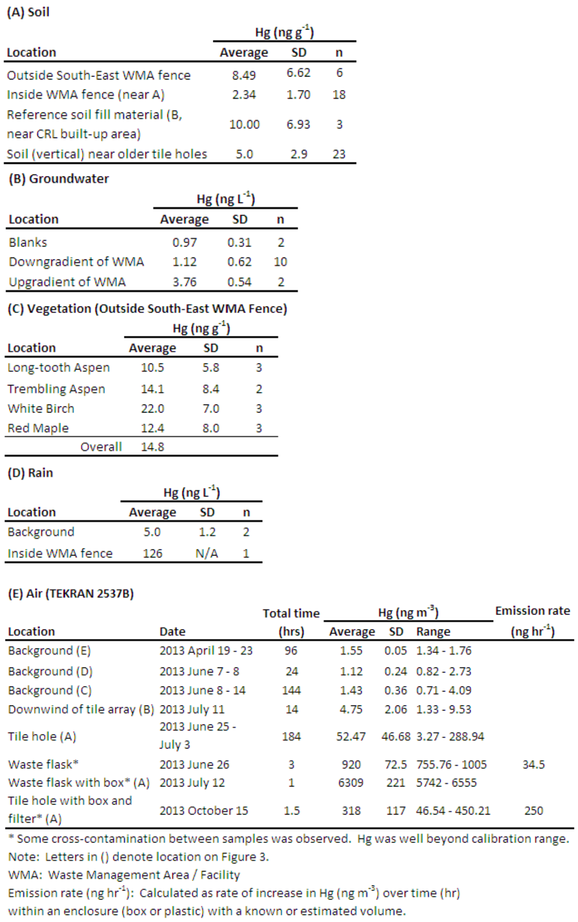
Filtered groundwater samples (180) are collected across AECL (30 sites) on a semi-annual basis during spring (April-May) and fall (September-October) as part of the groundwater monitoring sampling campaigns. These groundwater samples are analysed for the types of contaminants that are characteristic of the different source areas. Samples taken from monitoring wells (1.72 – 9.32 m depth to water) downgradient of the waste management facility tile hole arrays with cemented Mo-99 waste are analysed for physical, chemical and radiological parameters. Mercury analyses are performed following the methodology of EPA Method 245.1 (cold-vapor atomic fluorescence spectrometry) for which the MDL is 50 ng L^{-1}. There has been no evidence of sampling or analysis performance issues based upon Hg since the start of the groundwater monitoring program (*ca.* 1997).

Groundwater samples collected in Spring 2009 (all were

< 50 ng L^{-1}) were shipped to the University of Ottawa for analysis at a lower MDL (0.05 ng L^{-1}) in order to compare the groundwater Hg concentrations downgradient (general direction is from North-West to South-East) of the tile holes with cemented Mo-99 waste (Figure 3, groundwater was sampled from wells around North-East to South-East perimeter of waste management facility fence, < 100 m from tile holes) with concentrations at several reference (upgradient) locations (AECL groundwater typically has Hg < 50 ng L^{-1}). The University of Ottawa uses EPA Method 1631 for determination of Hg in filtered and unfiltered water samples by BrCl oxidation with NH_2OH reduction, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS: Tekran 2600). The RSD for serial dilution using 1000 ppm Fisher CSM114-100 Hg reference solution varied from 0.65 – 6.17% (standards: 0.88 – 6.94 ng L^{-1}). NIST SRM 1641c RSD was 8.66%.

Field blanks (Table 1B) were composed of distilled water. All samples, including blanks, were filtered through a 0.45 micron groundwater cartridge filter and preserved with 1 mL concentrated nitric acid in 125 mL high density polyethylene bottles.

TABLE 1: Concentration of Hg in Environmental Media



(A) Soil

Location	Hg (ng g^{-1}) Average	SD	n
Outside South-East WMA fence	8.49	6.62	6
Inside WMA fence (near A)	2.34	1.70	18
Reference soil fill material (B, near CRL built-up area)	10.00	6.93	3
Soil (vertical) near older tile holes	5.0	2.9	23

(B) Groundwater

Location	Hg (ng L^{-1}) Average	SD	n
Blanks	0.97	0.31	2
Downgradient of WMA	1.12	0.62	10
Upgradient of WMA	3.76	0.54	2

(C) Vegetation (Outside South-East WMA Fence)

Location	Hg (ng g^{-1}) Average	SD	n
Long-tooth Aspen	10.5	5.8	3
Trembling Aspen	14.1	8.4	2
White Birch	22.0	7.0	3
Red Maple	12.4	8.0	3
Overall	14.8		

(D) Rain

Location	Hg (ng L^{-1}) Average	SD	n
Background	5.0	1.2	2
Inside WMA fence	126	N/A	1

(E) Air (TEKRAN 2537B)

Location	Date	Total time (hrs)	Hg (ng m^{-3}) Average	SD	Range	Emission rate (ng hr^{-1})
Background (E)	2013 April 19 - 23	96	1.55	0.05	1.34 - 1.76	
Background (D)	2013 June 7 - 8	24	1.12	0.24	0.82 - 2.73	
Background (C)	2013 June 8 - 14	144	1.43	0.36	0.71 - 4.09	
Downwind of tile array (B)	2013 July 11	14	4.75	2.06	1.33 - 9.53	
Tile hole (A)	2013 June 25 - July 3	184	52.47	46.68	3.27 - 288.94	
Waste flask*	2013 June 26	3	920	72.5	755.76 - 1005	34.5
Waste flask with box* (A)	2013 July 12	1	6309	221	5742 - 6555	
Tile hole with box and filter* (A)	2013 October 15	1.5	318	117	46.54 - 450.21	250

* Some cross-contamination between samples was observed. Hg was well beyond calibration range.
Note: Letters in () denote location on Figure 3.
WMA: Waste Management Area / Facility
Emission rate (ng hr^{-1}): Calculated as rate of increase in Hg (ng m^{-3}) over time (hr) within an enclosure (box or plastic) with a known or estimated volume.

2.2.3 Vegetation

In August 2012, leaves were collected from Long-tooth Aspen, Red Maple, White Birch and Trembling Aspen trees in the predominant downwind direction (to South-East) outside of waste-management-facility fenceline (Figure 3). Leaves were dried and shipped to Whiteshell Laboratories (Pinawa, MB) for Hg analysis using CVAAS. Uncertainties (95% CL) varied from 0.6 – 4 ng g^{-1}.

2.2.4 Rain

In September 2010, five 5-gallon pails lined with plastic bags were placed next to a tile hole as it was in the process of being filled with cemented Mo-99 waste cans (1 week). Rain water collected in pails over this time period were combined and sent for radiological analyses. A rain sample (100 mL) was preserved with 1 mL of 5% $K_2Cr_2O_7$ solution, 1 mL of 70% HNO_3 and shipped to Whiteshell Laboratories (Pinawa, MB) for Hg analysis (CVAAS). Reference rain samples were also collected from unaffected (i.e., no known neighbouring surface or groundwater contamination sources) areas located on AECL property (Figure 1, B near Maskinonge Lake).

2.2.5 Air

In order to facilitate measurement and monitoring of Hg in air within the outdoor waste-management facility, a TEKRAN 2537B Continuous Hg Vapour Analyzer was incorporated into a custom-built portable trailer (TEAMS) in order to accommodate the argon gas cylinder, along with other associated equipment, in the field. The TEKRAN 2537B is used worldwide to measure ambient Hg levels in air (as Hg^0, detection limit is 0.01 ng m^{-3}). In 2012, air sampling consisted of measuring Hg (from two sampling lines sequentially) in background areas (Figure 3 C, D, E) (1 m height, 5 min sampling interval), adjacent to and downwind of tile hole array (at 0.5 m height above ground, 1 L min^{-1}, 2 x 5 min samples per line) (Figure 3B), near recently filled tile holes (for one week) with cemented Mo-99 waste (Figure 3A) where weather shield meets flask adapter pad (Figure 4A), a waste transfer flask with and without a 1 m^3 box encapsulating the flask (for one hour, Figure 4B), as well as from a tile hole with and without a 1 m^3 box encapsulating the tile hole (for one hour, one sampling line with box). The TEKRAN 2537B unit was operated for a minimum 72-hr period prior to doing an internal calibration check and initiating sample collection. Calibration was periodically verified with manual injections of 100 pg Hg^0 directly into the TEKRAN 2537B septum at start of sampling cycle. RSD for repeated manual injections was required to be within 95 – 105%.

FIGURE 2: Tile hole storage for cemented Mo-99 waste.

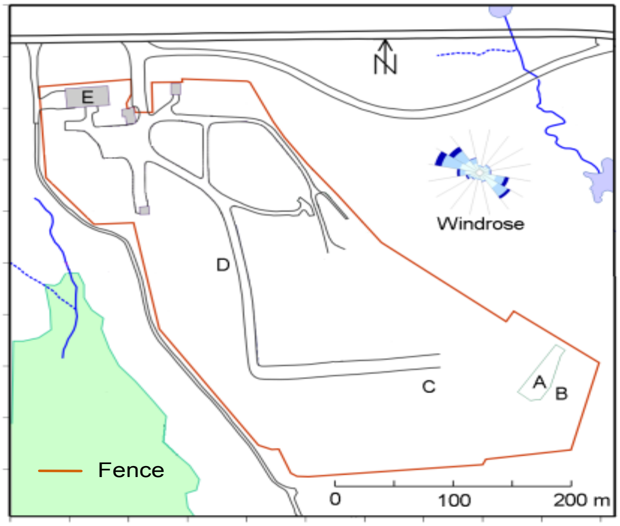


FIGURE 3: Sampling locations in Waste Management Facilities.

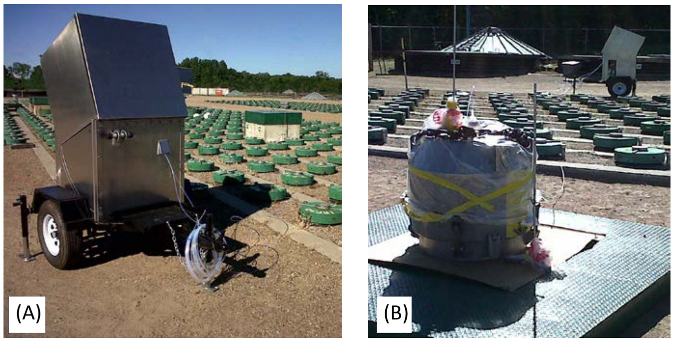


FIGURE 4: Portable TEAMS trailer (with TEKRAN 2537B) monitoring emissions from (A) a recently filled cemented Mo-99 waste tile hole and (B) a waste transfer flask.
Note: The weather shield is the green square lid sitting on the concrete flask adapter pad.

3. Results and Discussion

Mercury measured in environmental media near tile holes with cemented Mo-99 waste cans were evaluated against applicable guidelines and background reference samples. Reference samples were used to provide an indication of background environmental variability and to determine whether there are areas within the vicinity of this waste-management facility that naturally exceed these guidelines.

3.1 Soil

Surface soil Hg inside the waste management facility near the tile holes (Figure 3B, < 25 ng g^{-1}) was found to be below even the most conservative Canadian Soil Quality Guidelines (CSQG) (6600 ng g^{-1}), and within range for other reference soil-fill material at AECL (Table 1A, Figure 1B, inside and outside CRL built-up area) and typical Canadian and United States background surface soils. In Canada and the United States, the typical background concentration of Hg in surface soil is in the range 10 to 400 ng g^{-1}; except in areas of ore deposits, spills, landfills, and accidents at metal-processing plants [11,12].

Surface soil percent total organic carbon (TOC, %), which tends to co-vary with Hg content, explained most of the variability among sites (i.e., reference locations, inside and outside waste management facility) [6] (Figure 5). In a 2011 B.C. Hydro assessment report [13], organic carbon content explained 48% of the variability in total soil Hg. The report also stated that soils containing < 10% carbon are very unlikely to be elevated in Hg. Note that inside the waste-management facility, the soil-fill material surrounding the tile-hole storage has < 10% organic carbon.

Vertical soil Hg concentration in the immediate vicinity of selected older cemented Mo-99 waste tile holes was found to be 5.0 ng g^{-1} (1.2 to 11.6 ng g^{-1}), which was consistent with measured surface soil inside waste-management facility near tile array. The vertical soil organic carbon profile and Hg concentration (as long as waste was contained), were expected to be relatively constant since the tile-hole storage was constructed from fill material (top to bottom) and vegetation growth at soil surface is discouraged.

3.2 Groundwater

Groundwater Hg downgradient of the waste-management facility (located < 100 m from tile hole storage) was 1.122 ± 0.621 ng L^{-1}, which was not significantly different from blanks (0.97 ± 0.307 ng L^{-1}) and less than upgradient locations at AECL (Table 1B). Concentrations were also well below reported typical range for background (21 to 407 ng L^{-1}) [14] and the Ontario Ministry of the Environment's Background Site Condition Standard for groundwater (100 ng L^{-1}) [15]. Note that the AECL semi-

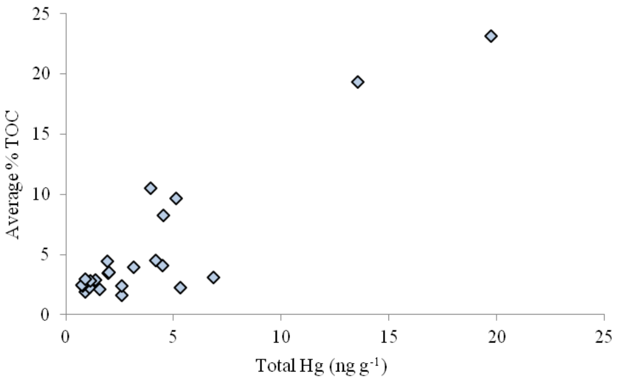


FIGURE 5: Surface soil Hg (ng g^{-1}) versus total organic carbon (TOC, %).

annual groundwater sampling campaign MDL (50 ng L^{-1}) is low enough to detect whether concentrations of Hg in groundwater are close to or above this standard. Annual inspection results of tile-hole interrogation tubes (Figure 2, pipe next to each tile hole) in the waste-management facility have also not found any indication that water has been released from cemented Mo-99 waste cans.

Previous research at AECL has shown that structural degradation of this particular cement product is expected to occur between 7 to 20 years after placement in a tile hole, resulting in increased surface area and higher leaching rates. In 1990, AECL tested seven-year-cooled cemented Mo-99 waste and found that 41% of theoretically available Hg is leached by water and a residual quantity (10%) remains in residue after leaching cement with acid (HNO_3). Poon *et al.* [16] added sodium silicate to cement and used acetic acid as a leachant instead of HNO_3, but initial results were similar and showed Hg decreasing with successive elutions.

3.3 Vegetation

Mercury measured in Red Maple, Long-tooth Aspen, Trembling Aspen and White Birch tree samples taken from the outer perimeter of the waste management facility (Figure 3, outside South-East fence) was lower than Hg concentrations found in the Experimental Lakes Area in northwestern Ontario, a background location [17]. The average Hg concentration in deciduous tree leaves was 29.3 ng g^{-1} in the Experimental Lakes Area and approximately 14.8 ng g^{-1} at AECL (Table 1C). Siwik [18] found leaf Hg concentrations to significantly vary among tree species located at the same site, which is consistent with the range observed amongst tree species located outside the waste-management facility at AECL (Table 1C).

In Ontario, the average background Hg concentration for maple-tree leaves ranges from 8.2 to 26.7 ng g^{-1}, increasing over the growing season with highest leaf Hg found in early autumn just before senescence. Higher leaf Hg concentrations were also found in tree leaves positioned deeper in the canopy [19]. This is comparable with the results found in the samples near the waste management facility at AECL, when the timing (August) and location (outer leaves) of sampling are taken into consideration. Mercury levels in vegetation can also be an indicator of soil Hg concentrations [20], which is consistent with the low Hg levels measured in vegetation and soil as part of this study.

3.4 Rain

Reported concentrations for total Hg in rain are 6.58 ng L^{-1} (0.81 – 21.29 ng L^{-1}) for St. Anicet, Quebec [21], 4.04 ng L^{-1} (0.95-9.31 ng L^{-1}) for Experimental Lakes Area in northwestern Ontario [22], 5.3 ng L^{-1} for a remote location in Nova Scotia (Big Dam West, Kejimkujik Park) [23], and 13.4 ng L^{-1} for Lake Michigan [24]. Range in values reported by other researchers varies from 5 ng L^{-1} at remote locations to 100 ng L^{-1} near industrial sites [22, 25].

Measured Hg (126 ng L^{-1}) in a single (n = 1) rain-water sample collected in 2010 near a tile hole in the process of being filled with cemented Mo-99 waste was above these values and ranges reported in the literature for background or industrial locations. The radiological activity was elevated in this sample, indicating atmospheric contamination from dissolved and/or particulate contamination (i.e., scavenged from air by rain or directly from flask during waste disposal). Background rain Hg, measured in AECL outer area, was 5 ng L^{-1} (n = 3) (Table 1D, Figure 1B, near Maskinonge Lake).

Subsequent radiological analyses on rain samples (2011 and 2012) indicated that atmospheric contamination had substantially decreased (often below MDL), so it was not deemed necessary to perform further Hg analyses on rain as an indirect indicator of atmospheric contamination. The TEKRAN 2537B had also arrived at AECL to directly measure Hg in air.

3.5 Air

Mercury was initially measured in air at various locations (Table 1E) in the waste-management facility to evaluate potential operational exposure, including (a) inside the main operational building (Figure 3E), (b) an area outside where there is no stored waste (Figure 3D), and (c) an area outside closer to location of tile holes (Figure 3C). This data was also used to establish what the background was at this location. This average background Hg in the waste-management facility varied from 1.24 (a), 1.12 (b), and 1.43 ng m^{-3} (c), which are comparable to the typical Ontario average background Hg (1.58 ± 0.23 ng m^{-3}, 1997 – 2000) [26].

Mercury measured in air adjacent to and directly downwind of this tile hole array (Table 1E) was found to be less

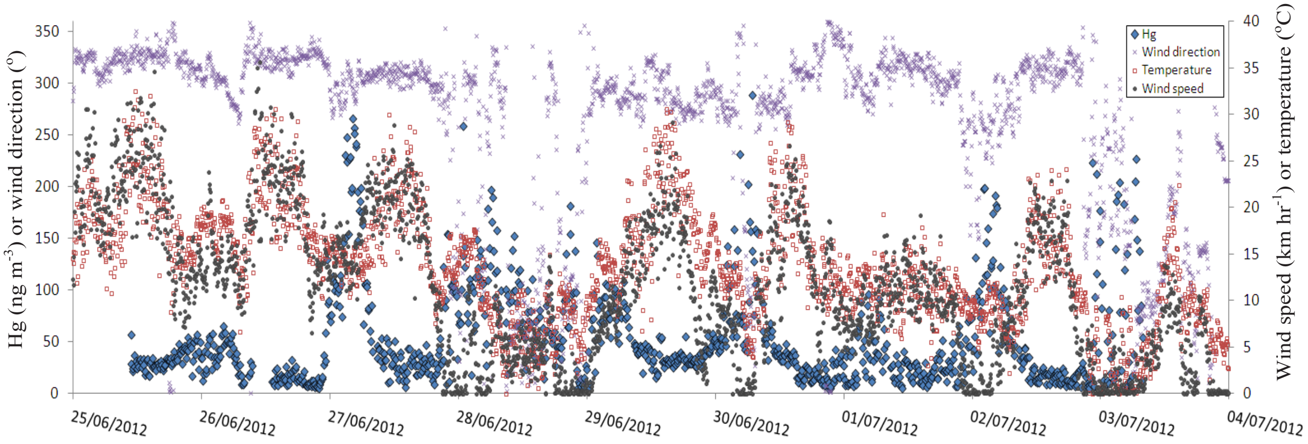


FIGURE 6: Mercury measured in air near a recently filled cemented Mo-99 waste tile hole plotted against wind speed, wind direction and temperature over time.

than 5 ng m^{-3} (Figure 3B), and dropped to background (< 1.6 ng m^{-3}) within 60 to 80 m (Figure 3C). This means that Hg concentration in air directly downwind, but outside the waste-management facility, should also be comparable to background.

Tile hole Hg air concentration (no box, measured over a week near source (see Figure 3A and 4A)) did not exceed 300 ng m^{-3} (Figure 6). Most of the variability in measured atmospheric Hg could be explained by changes in temperature and/or wind speed and direction. As wind speed and temperature increased during the day, atmospheric Hg concentration decreased. The highest atmospheric Hg levels were measured during cooler periods with calm winds at night. Changes in wind direction were also observed to influence the amount of atmospheric Hg measured (i.e., wind was moving air released from the tile hole storage towards or away from the sampling location). These diurnal patterns are consistent with those measured by O'Driscoll *et al*. [27] in Kejimkujik Park in Nova Scotia (a background location), which found that wind speed played an important role in Hg flux dynamics.

Mercury emission rate range from unmonitored landfills can vary from 57 to 11,415,525 ng hr^{-1} [28]. In our study, the emission rate from a lower activity cemented Mo-99 waste transfer flask (as measured from above hole in plastic surrounding waste flask (no box) in Figure 4B), was 34.5 ng hr^{-1} (assuming 0.5 m^3 of air in and around waste can contained in flask and plastic). Extrapolating this to a tile hole storing nine waste cans, emission rate would be approximately 310 ng hr^{-1}. If Hg had been measured on higher-activity waste (based on observed range in waste-emission characteristics, unpublished data), emission rate could be up to three times higher (tile hole: 930 ng hr^{-1}). Based on this conservative emission rate estimate, a tile-hole array could potentially release upwards of 4000 ng hr^{-1}, but this value is still well within the range for unmonitored landfills.

Mercury emission rate was also measured from a box encapsulating air above a recently filled tile hole (250 ng hr $^{-1}$), but this tile hole was equipped with an experimental I-131 charcoal-filter material that is suspected to have also considerably reduced Hg emissions (i.e., charcoal is well known for its ability to capture Hg) [29].

The Ontario Ministry of the Environment (MOE) continuous monitoring threshold is 2000 ng m^{-3} (24 hr average) [26]. The maximum Hg air concentration inside the cemented 5-gallon (0.02 m^3) waste can should be approximately 6600 ng m^{-3} based on Hg measured from inside a box encapsulating the waste flask. If no dilution is considered, tile hole (0.57 m^3) Hg concentration could potentially exceed monitoring threshold (9 cans, ~19000 ng m^{-3}). If dilution from source and/or mitigation (i.e., experimental filter) are considered, emissions measured from tile hole or extrapolated from waste-transfer flask are expected to be below the MOE continuous monitoring threshold (2000 ng m^{-3}). Note that this threshold assumes Hg emission is forced out through a stack, whereas tile-hole emissions are from the ground (no receptors nearby) with minimal flow (diffusion and wind driven emissions). There are currently no Canadian regulations in place that cover a ground-level Hg release from multiple source terms (tile holes) that are expected to decline over time with decreases in radiological decay heat.

4. Conclusions

Mercury in air was found to be elevated when in close proximity to the Mo-99 waste (waste flask and tile hole storage), but dropped to background within 60 to 80 m from this source (i.e., outside waste-management facility fence). Low levels of Hg in vegetation sampled in close proximity to waste-management-facility fence and surface soil provide longer-term evidence of lower Hg concentrations in air.

Results from this study (i.e., low Hg in soil at base of tile hole and in groundwater), along with other published and unpublished work, also indicate that short- and longer-term environmental degradation phenomena [30] should not leach significant amounts of Hg contamination into the environment.

Mercuric nitrate is an excellent iodine complexing agent, limiting its solubility by producing HgI_2 and $Hg(IO_3)_2$ [31,32]. Previous AECL inactive tests on mock cemented Mo-99 waste confirmed that Hg tends to bind and precipitate I-131, thus minimizing its release to the environment. Therefore, if Hg emissions from this waste remain below applicable guidelines, the presence of Hg in the waste should in this case be providing a net benefit by trapping the more hazardous radioiodines.

On the other hand, Wilmarth *et al*. [33] found elevated levels of dimethyl Hg in tanks containing high levels of Hg, spent nuclear fuel and nitric acid. Dimethyl Hg has not been studied as widely as other Hg species, but it is known to be extremely toxic. It is recommended that AECL evaluate methods to trap and measure dimethyl Hg from air, and/or confirm that the TEKRAN 2537B measures this species as a constituent of total Hg in air.

In response to concerns about Hg releases from the cemented medical isotope (Mo-99) waste produced and stored at AECL, environmental media in the area surrounding the tile holes where waste is stored was evaluated and found to be below applicable guidelines and/or comparable to background areas, which means that the tile holes do not require continuous monitoring. It is recommended that AECL continue to periodically return to the tile holes to monitor Hg and other contaminants in order to verify that conditions have not changed, taking into consideration the challenges with respect to dose risk and sampling method.

In addition to this, there are a multitude of interrelated environmental factors that can influence contaminant transport and fate in often difficult to access locations on the AECL Chalk River Laboratories site. The TEKRAN 2537B used in this study constitutes part of the custom-built portable TEAMS trailer that was designed to provide AECL with the capability to measure (with minimal dose risk), monitor and model (i.e., meteorological and contaminant data is used to generate a real-time plume model) Hg emissions, along with a number of other radiological and non-radiological contaminants, for a wide range of situations in these difficult to access locations. The TEAMS trailer was also designed to be easily re-configured to adapt to different or evolving monitoring needs.

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FULL ARTICLE

Drivers of Abundance and Community Composition of Benthic Macroinvertebrates in Ottawa River Sediment near Chalk River Laboratories

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The Ottawa River has received effluent from Chalk River Laboratories (CRL) for more than 60 years. Some radionuclides and contaminants released in effluents are bound rapidly to particles and deposited in bottom sediments where they may be biologically available to benthic invertebrates and other aquatic biota. As part of a larger ecological assessment, we assess the potential impact of contaminated sediments in the vicinity of CRL on local benthic community structure. Using bivariate and multivariate approaches, we demonstrate that CRL operations have had little impact on the local benthic community. Despite elevated anthropogenic radionuclide activity concentrations in sediment near CRL's process outfall, the benthic community is no less abundant or diverse than what is observed upstream at background levels. The Ottawa River benthic invertebrate community is structured predominantly by natural physical and biological conditions in the sediment, specifically sediment water content and organic content. These natural habitat conditions have a stronger influence on macroinvertebrate communities than sediment contamination.

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1. Introduction

The Ottawa River has received effluent from nuclear research reactors at Chalk River Laboratories (CRL) for more than 60 years. This liquid effluent is released from the process outfall (PO) through a vertical diffuser located at a depth of approximately 22 m. In 1992, a 'once-through' research reactor, National Research eXperimental (NRX), was permanently shut down, greatly reducing the quantity of fission and activation products released to the Ottawa River [1]. Recent environmental monitoring and stewardship initiatives conducted by Atomic Energy of Canada Limited (AECL) have identified an area with elevated activity concentrations of anthropogenic radionuclides and mercury in Ottawa River sediment, extending approximately 2 km downstream of the PO [1, 2]. Interest in the potential impact of this sediment footprint on human and ecological health has led to the initiation of comprehensive risk assessment studies. This paper focuses on the potential impacts of radiological contamination in sediment on benthic macroinvertebrate communities in the Ottawa River in a localized area referred to as the 'footprint' compared to upstream and downstream conditions.

Macroinvertebrate communities have been extensively used for biomonitoring of freshwater systems [3-6]. Benthic invertebrates in direct contact with and consuming contaminated sediments are often the biota highly exposed to sediment-associated contamination. Recent studies indicate that benthic community degradation may be occurring at much lower contaminant levels than those associated with critical effect levels (e.g., EC50–the concentration of a contaminant at which 50% of test organisms are affected using some end point) obtained in laboratory toxicity tests [7, 8]. Analysis of benthic community structure provides important information about the *in situ* effects of contaminants on resident biota, and is generally viewed as an effective method for environmental effects monitoring in freshwater ecosystems. By evaluating community structure (i.e., diversity, richness) and the abundances (i.e., density, biomass) of the benthic invertebrate taxa at a site, one can infer a measure of ecological integrity. Very few studies have examined the effects of elevated anthropogenic radionuclides on the abundance, spatial distribution, and community structure of benthic invertebrates. However, Hart *et al*. [3] studied benthic community structure in relation to sediment quality in the radionuclide and heavy metal-contaminated Port Hope Harbour, Lake Ontario, and reported that reduced benthic invertebrate densities were associated with highly contaminated sediment near a uranium refinery cooling water discharge.

The Ottawa River ecosystem at the CRL site has been studied previously, including assessment of ^{137}Cs bioaccumulation and biokinetics of invertebrates and fish [9-12] and bioavailability of radionuclides to aquatic macrophytes, epiphytes, and benthic deposit-feeders [13, 14]. However, there has not been a comprehensive study of the benthic community since the early 1950s [15]. One reason for this might be due to the extremely high spatial and temporal variability of benthic invertebrates in Ottawa River sediment [15], which can make sample collection, data analysis, and interpretation of results challenging.

The objective of this study is to assess the potential impact of radiologically contaminated sediments on the benthic community in the vicinity of CRL. More specifically, we seek to answer three questions: *(i)* what physical and chemical conditions determine benthic invertebrate structure in the Ottawa River near CRL; *(ii)* have historical operations at CRL, including releases of radionuclides to the sediment, affected the spatial distribution and community structure of benthic invertebrates in the Ottawa River; and *(iii)* given the observed spatial variability of benthic invertebrate distribution in Ottawa River sediments, what type of sampling programme is required to obtain a true measure of the benthic community?

In this paper, we present the results of a survey of the Ottawa River benthic community near CRL. We first discuss the relationships between various environmental parameters and benthic invertebrate abundance and community composition. We then compare benthic communities upstream from CRL, in the PO footprint, and downstream from CRL to determine whether CRL operations have altered the benthic community in the contaminated sediment footprint. Finally, we discuss the challenges associated with benthic sampling programmes in sediments where invertebrate densities are low, and sediment is spatially heterogeneous, such as those in the Ottawa River.

2. Methods

2.1 Study site

Ecologically, the Ottawa River reach at CRL is more lacustrine than fluvial, and is part of a natural 40 km long, deep section called Allumette Lake (Figure 1). With a width of 1.2 km, a mean depth of 14 m, and a maximum depth of 30 m in front of CRL, this cool-water temperate system thermally stratifies in the summer. The sediment is comprised of a cohesive combination of clay (42–57%), silt (40–54%), and sand (1–4%), and the sedimentation rate in this depositional habitat ranges from approximately 0.5 mm·yr^{-1} at 15 m to 1.3 mm·yr^{-1} at 25 m or deeper [16]. Near CRL, river flows range from 2,500 m^{3}·sec^{-1} during the spring freshet to 180 m^{3}·sec^{-1} during the fall (arithmetic mean annual flow = 800 m^{3}·sec^{-1}). Based on the substrate particle size, the current velocity near the bottom is likely less than 2 cm·sec^{-1} [17].

2.2 Sample collection and analyses

In November 2011, Ottawa River sediment was sampled along ten transects from 6.5 km upstream to 7.5 km downstream of the CRL site (Figure 1). Transects (and sites) 4, 7.5, 7.75, 8, 8.5, 9, 13, and 15 were named according to their distance downstream (km) from Transect 1. Upstream transects (reference sites) were spaced approximately 3 km apart, while transects near CRL's PO and downstream were spaced closer together and semi-arithmetically to capture rapidly changing sediment conditions near the PO [1]. In order to compare the shallow environment with the deep environment, half of the samples at each transect were taken at a depth of 15 m, while the other half were taken at a depth of 25 m. A total of 20 sites were sampled using a 3-inch Kajak-Brinkhurst (K-B) corer (Wildlife Supply Company, Yulee, FL, USA), which enclosed an area of 45.6 cm^{2} per core with five replicate samples per site, in accordance with Canadian metal mining and pulp and paper Environmental Effects Monitoring (EEM) guidelines [18, 19]. *A priori* power analysis indicated that five replicate samples per site should result in the capability to detect differences between sites of ±2 standard deviations with a probability of 0.90 ($\alpha = 0.10$). Immediately after collection, sediment core samples were sieved through a 150-μm mesh and picked for benthic invertebrates, which were preserved and later identified to Genus. In addition, the upper 5 cm from an additional core at each site was retained for quantification of sediment water content, organic matter content, and radionuclide determination. Sediment water content was determined by drying the whole sample in a drying oven at 60 °C (until a constant mass was achieved, generally 24–26 hours) and measuring loss of water mass. Organic matter content was determined by combusting a subsample of ground and homogenized dried sediment at 450 °C and determining weight loss on ignition (LOI). Radionuclide determination was conducted using gamma spectroscopy with a low-background high purity germanium gamma spectrometer (Canberra Industries, Meriden, CT, USA).

2.3 Data analyses

Benthic data were first summarized for each of the 100 cores collected (10 transects x 2 depths x 5 replicates). Due to the low densities of invertebrates, the five core sample replicates taken at each site were pooled into one mean value in order to increase the accuracy of abundance and benthic index estimates. Abundance data was converted to number of individuals or mass per m^{-2} using a conversion factor based on the surface area sampled per site. When required to meet assumptions of statistical tests, non-normal data were normalized using a log-transformation.

Benthic communities were described using a number of metrics, including biomass ($g{\cdot}m^{-2}$), density (number of individuals$\cdot m^{-2}$), taxa richness (number of taxa per site) and the Shannon diversity index *(H)* [20]. The Shannon diversity index, Equation (1), was chosen to quantify diversity because it takes into account the number of individuals, as well the number of taxa present, and the evenness of taxa in a community [21].

$$H = -\sum_i \left(\frac{ni}{n}\ln\frac{ni}{n}\right) \tag{1}$$

where, *n* is the total number of individuals encountered and *ni* is the number of individuals of taxon *i* encountered.

The Shannon index varies from zero for communities with only a single taxon to higher values for communities with many evenly represented taxa [20].

To examine the influence of various environmental variables (e.g., sediment water content, sediment organic content, depth, radionuclide activity concentrations) on invertebrate abundance (i.e., density, biomass) and community composition (i.e., diversity, richness), we assess multiple lines of evidence, using both bivariate and multivariate statistical approaches. Initial exploration of invertebrate–environmental data was conducted using Pearson product-moment correlation analysis. Canonical correspondence analysis (CCA) was then used to explore the relationships between the observed benthic macroinvertebrate assemblages and their environment [22, 23]. This multivariate method summarizes the maximum amount of variation in a biotic dataset, while constraining it to be associated with axes based on linear composites of the environmental data, allowing for a multivariate direct-gradient analysis of the local community and environment [22, 24].

Comparisons of macroinvertebrate abundance and community structure between sites located upstream, those in CRL's PO footprint, and downstream sites were conducted using a one-way Analysis of Variance (ANOVA). Upstream sites include (with distance from the PO in parentheses after site name): site 1 (-6.5 km), site 4 (-3.5 km), and site 7.5 (-0.1 km). Sites in the footprint include: site PO (0 km), site 7.75 (0.2 km), and site 8 (0.4 km). Downstream sites include site 8.5 (1 km), site 9 (1.5 km), site 13 (5.5 km), and site 15 (7.5 km) (Figure 1). In past studies (i.e., [1]), sites 8.5 and 9 have been shown to be slightly impacted by the PO; however, these two sites were classified as 'downstream' for

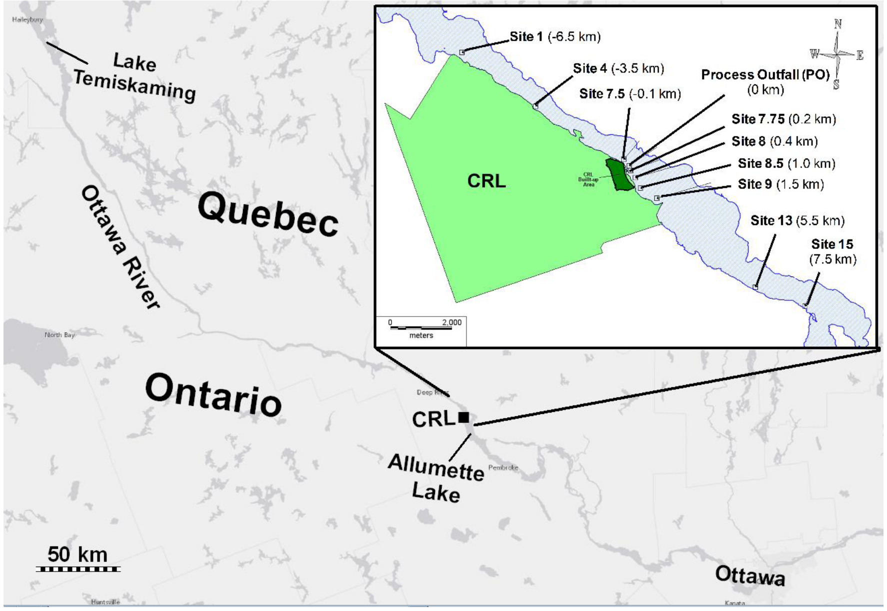

FIGURE 1: Map of study region of the Ottawa River, depicting sample locations (and distance from CRL's process outfall (PO) in parentheses) along transects upstream of, in CRL's PO footprint, and downstream of the PO footprint. At each transect, 5 cores were taken at 15 m depth and another 5 cores were taken at 25 m depth. The river flows from the northwest to the southeast.

this study to increase the sample size and statistical power. Downstream sites 8.5 and 9 are outside of the most heavily contaminated sediment footprint that extends up to 400 m downstream from the PO, and thus, including these sites in the 'downstream' grouping should not affect the results of our upstream *v.* PO footprint *v.* downstream comparisons. Visual examinations of CCA ordinations by site provided additional information regarding the spatial distributions of benthic invertebrates in relation to CRL. Because contaminant concentrations are known to co-vary with sediment grain size [25], analysis of covariance (ANCOVA) was used to statistically control for the effect of grain size, while comparing invertebrate abundance at locations upstream from the PO footprint, in the PO footprint, and downstream of the PO footprint.

A posteriori power analyses were conducted using benthic community metric (i.e., density, biomass, richness, Shannon diversity) data to determine required sample sizes to obtain statistical power of 0.8 for comparing the three groups (i.e., upstream, footprint, and downstream), using ANOVA at a significance level (α) of both 0.05 and 0.10. All statistical analyses were carried out using SigmaPlot (SYSTAT Software Inc., San Jose, CA) and PAST [26] software packages. Significance was judged at α = 0.05, unless otherwise stated.

TABLE 1: Summary of Ottawa River surficial sediment characteristics from sites upstream of CRL's process outfall (PO), in the PO footprint, and downstream of the PO footprint (15 m and 25 m samples combined).

Parameter	Units	Mean (and Range)		
		Upstream of PO (n = 6)	PO Footprint (n = 6)	Downstream of PO (n = 8)
Water content	fraction	0.73 (0.60–0.89)	0.77 (0.55–0.88)	0.76 (0.64–0.85)
Organic content	fraction	0.09 (0.07–0.11)	0.11 (0.05–0.15)	0.10 (0.06–0.14)
Bulk density	$g \cdot cm^{-3}$	1.33 (1.07–1.81)	1.15 (1.00–1.64)	1.35 (1.02–1.49)
Co-60	$Bq \cdot kg^{-1}$	1.78 (bdl–7.70)	1998.98 (69.1–2220.2)	32.00 (18.20–50.90)
Nb-94	$Bq \cdot kg^{-1}$	2.67 (bdl–16.0)	22.10 (4.40–76.2)	2.55 (bdl–10.90)
Cs-137	$Bq \cdot kg^{-1}$	101.87 (75.6–140.8)	3068.8 (597.7–7219.8)	603.65 (270.6–1566.7)
Eu-152	$Bq \cdot kg^{-1}$	0.55 (bdl–1.80)	185.42 (6.30–298.8)	10.67 (bdl–47.10)
Eu-154	$Bq \cdot kg^{-1}$	*bdl	573.90 (6.30–280.10)	3.05 (bdl–15.50)
Eu-155	$Bq \cdot kg^{-1}$	*bdl	19.78 (bdl–64.50)	*bdl
Am-241	$Bq \cdot kg^{-1}$	1.08 (bdl–2.30)	73.67 (5.60–162.20)	11.36 (bdl–30.40)

*bdl = below detection limit

TABLE 2: Pearson product-moment correlation matrix examining relationships between benthic invertebrate metrics and sediment characteristics, at 15 m depth (top) and 25 m depth (bottom), in Ottawa River sediments near CRL. P-values are displayed above the diagonals, while corresponding correlation coefficients (r) are displayed below the diagonals. All significant relationships (P < 0.05) are highlighted in bold. Significant relationships of ecological interest to this study are underlined.

	Dens.	Biom.	Shann.	Rich.	% Wat	% Org	^{60}Co	^{94}Nb	^{137}Cs	^{152}Eu	^{154}Eu	^{155}Eu	^{241}Am
15 m													
Dens.		0.968	**0.038**	**0.009**	**0.005**	**0.003**	0.787	0.317	0.284	0.893	0.941	0.919	0.392
Biom.	-0.014		0.527	0.515	0.475	0.949	0.436	0.655	0.926	0.617	0.589	0.523	0.914
Shann.	**0.659**	0.228		**<0.001**	**0.029**	**<0.001**	0.185	0.486	0.773	0.268	0.252	0.280	0.571
Rich.	**0.773**	0.233	**0.976**		**0.014**	**<0.001**	0.334	0.783	0.909	0.482	0.454	0.484	0.875
% Wat	**-0.808**	0.257	**-0.684**	**-0.742**		**<0.001**	0.236	0.992	0.936	0.446	0.407	0.407	0.873
% Org	**-0.837**	-0.023	**-0.881**	**-0.910**	**0.905**		0.156	0.871	0.963	0.323	0.289	0.297	0.793
^{60}Co	-0.098	0.279	-0.456	-0.342	0.413	0.484		0.060	**0.016**	**<0.001**	**<0.001**	**<0.001**	**0.005**
^{94}Nb	0.353	-0.162	-0.250	-0.100	<0.001	0.059	0.612		**<0.001**	**0.011**	**0.015**	**0.022**	**<0.001**
^{137}Cs	0.376	0.034	-0.105	0.041	-0.029	-0.017	**0.732**	**0.937**		**0.001**	**0.002**	**0.003**	**<0.001**
^{152}Eu	0.049	0.181	-0.388	-0.252	0.273	0.349	**0.972**	**0.760**	**0.866**		**<0.001**	**<0.001**	**<0.001**
^{154}Eu	0.027	0.195	-0.399	-0.268	0.296	0.372	**0.981**	**0.738**	**0.846**	**0.999**		**<0.001**	**<0.001**
^{155}Eu	0.037	0.230	-0.379	-0.251	0.296	0.367	**0.986**	**0.708**	**0.825**	**0.993**	**0.997**		**<0.001**
^{241}Am	0.304	0.039	-0.204	-0.057	0.058	0.096	**0.805**	**0.936**	**0.990**	**0.915**	**0.900**	**0.884**	
25 m													
Dens.		**0.027**	0.324	0.069	0.054	0.060	0.974	0.943	0.312	0.542	0.879	0.857	0.179
Biom.	**0.692**		0.533	0.124	0.544	0.065	0.651	0.542	0.419	0.671	0.864	0.547	0.109
Shann.	0.348	0.225		**<0.001**	**0.003**	0.213	0.600	0.470	0.252	0.728	0.596	0.669	0.098
Rich.	0.594	0.519	**0.939**		**0.003**	0.063	0.718	0.640	0.174	0.621	0.662	0.834	0.058
% Wat	0.623	0.218	**0.835**	**0.835**		0.124	0.435	0.282	0.223	0.439	0.429	0.499	0.136
% Org	0.612	0.603	0.432	0.607	0.519		0.414	0.620	0.045	0.254	0.371	0.553	**0.031**
^{60}Co	0.012	-0.147	0.189	0.131	0.279	0.292		**<0.001**	**0.001**	**<0.001**	**<0.001**	**<0.001**	**0.025**
^{94}Nb	0.026	-0.220	0.259	0.169	0.378	0.179	**0.975**		**0.006**	**<0.001**	**<0.001**	**<0.001**	**0.045**
^{137}Cs	0.356	0.288	0.399	0.467	0.432	0.643	**0.867**	**0.798**		**<0.001**	**<0.001**	**0.003**	**0.005**
^{152}Eu	0.220	0.154	0.126	0.179	0.277	0.398	**0.936**	**0.894**	**0.894**		**<0.001**	**<0.001**	**0.014**
^{154}Eu	0.056	-0.063	0.192	0.158	0.286	0.318	**0.995**	**0.966**	**0.887**	**0.963**		**<0.001**	**0.014**
^{155}Eu	-0.066	-0.217	0.156	0.076	0.243	0.214	**0.995**	**0.976**	**0.819**	**0.918**	**0.987**		**0.044**
^{241}Am	0.461	0.538	0.552	0.592	0.506	**0.680**	**0.698**	**0.643**	**0.935**	**0.798**	**0.743**	**0.644**	

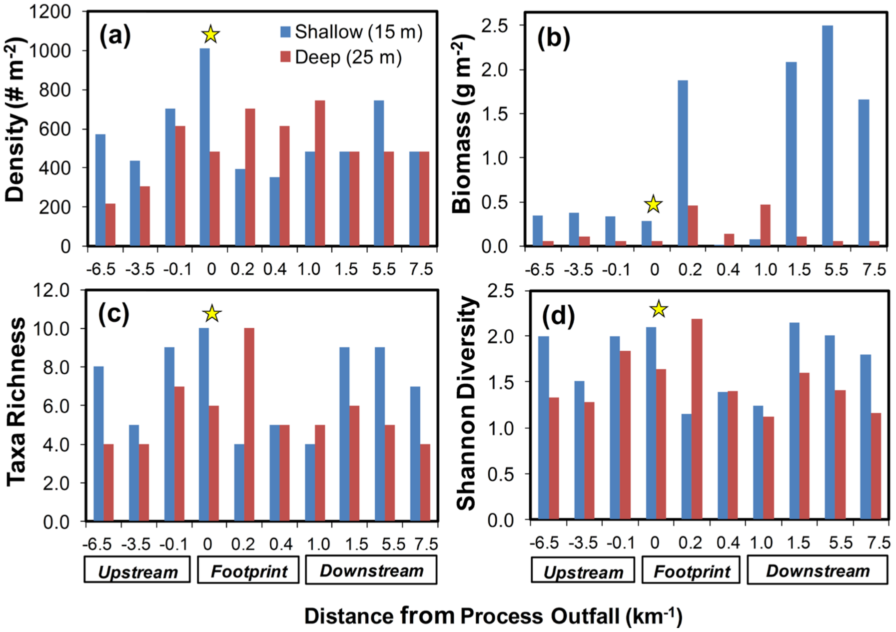

FIGURE 2: Benthic invertebrate (a) density, (b) biomass, (c) taxa richness, and (d) Shannon diversity index in relation to distance from the process outfall (PO) at CRL. Negative distances downstream represent upstream sites, distance zero (marked with yellow star) represents the PO, and positive distances represent downstream sites. Blue bars represent shallow (15 m) transects, while red bars represent deep (25 m) transects. High biomass values at several 15 m sites in panel (b) are due to the presence of *Hexagenia*.

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3. Results

3.1 Sediment properties

The sediments sampled near CRL are composed of gray silts and clays with a flocculent, brown oxidized layer in the upper 1–2 cm. Physical properties of the sediment, including water content (ANOVA, $F_{2,23} = 0.20$, $P = 0.82$) and organic content ($F_{2,23} = 0.65$, $P = 0.53$), were variable between individual sites, but did not vary at the larger spatial scale between upstream, footprint, and downstream (of CRL) locations (Table 1). Sediment bulk density varied between sites ($F_{2,23} = 4.42$, $P = 0.025$), with bulk density lower at the footprint sites than at upstream sites ($P = 0.031$) and downstream sites ($P = 0.033$), likely due to coarser sediments near the PO. Generally, sediment water content for the cores taken for this study ranged from 55% to 89%. The organic content of sediments ranged from 5% to 15%. Results of spatial radiochemical analysis of surficial (top 5 cm) Ottawa River sediments from this study are summarized in Table 1 and a comparable, but larger, sample set is discussed in greater detail in Rowan's [1] study of Ottawa River sediments near CRL. Anthropogenic radionuclide levels in sediments were highly variable. Concentrations are greatest in the PO footprint, rapidly dropping off within 2 km downstream [1]. In the PO footprint, sediment activity concentrations of ^{60}Co, ^{152}Eu, ^{154}Eu, ^{155}Eu, ^{94}Nb, ^{241}Am and ^{137}Cs are one-to-three orders of magnitude greater than upstream activity concentrations (Table 1). Different radionuclides were strongly correlated with each other (Table 2), due to the fact that sediments near the PO generally contained elevated activity concentrations of several radionuclides. Sediment organic content ($r = 0.77$, $P < 0.0001$) and sediment water content ($r = 0.74$, $P = 0.0002$) were both strongly positively correlated with depth, suggesting that with increasing depth, sediments become finer and contain more organic matter.

3.2 Macroinvertebrate community

Benthic invertebrate communities in Ottawa River sediment near CRL were typical of low-productivity, soft–bottom oligotrophic systems, with low density (< 1,000 individuals·m^{-2}) and low biomass (< 2.5 g m^{-2}) estimates. Of the 64 taxa collected from Ottawa River sediments, 3 taxa accounted for 76% of the total numerical standing stock, both at 15 m and 25 m depths. These included Oligochaetes (Tubificidae: *Spirosperma*; 48%), pea clams (Sphaeriidae: *pisidium*; 17%), and midges (Chironomidae spp.; 11%). Although not numerically abundant (4% of total community), burrowing mayflies (Ephemeroptera: Ephemeridae: *Hexagenia* spp.) contributed 64% of total biomass due to their large body size relative to other invertebrate taxa. *Hexagenia* were present at 15 m sites, but not at 25 m sites. The benthic communities sampled at 15 m were more diverse than those at 25 m, but numerical

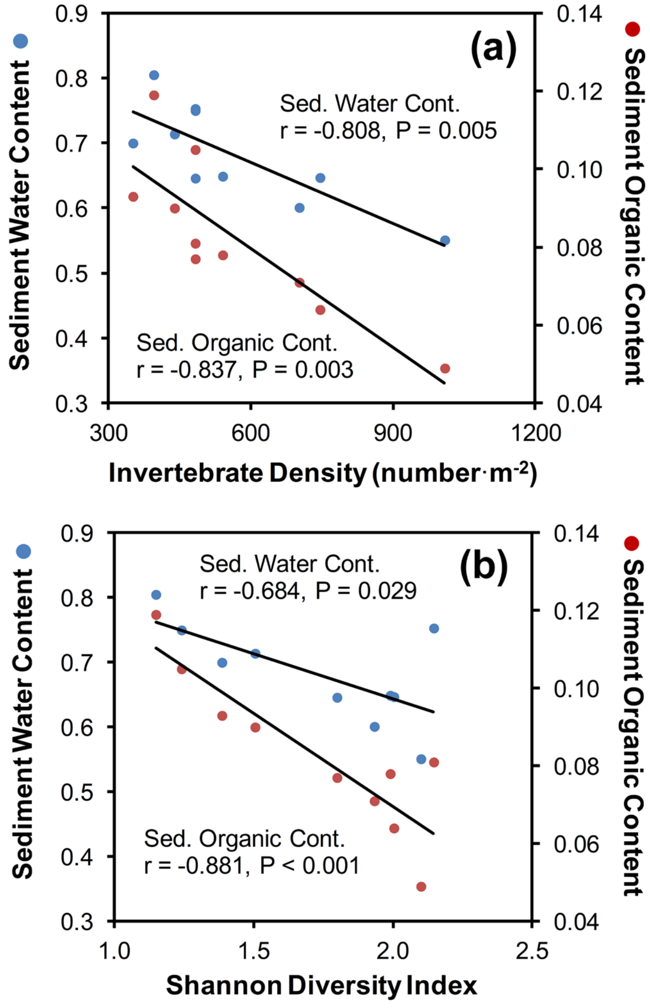

FIGURE 3: Significant relationships between sediment organic content (red markers), sediment water content (blue markers), and benthic macroinvertebrate density (a) and Shannon diversity index (b) in Ottawa River sediment (15 m depth) near CRL.

standing stocks were low at both, ranging from 438–1,008 individuals·m^{-2} at 15 m sampling stations and from 219–745: individuals m^{-2} at 25 m sampling stations (Figure 2).

3.3 Sediment characteristics and macroinvertebrates

Anthropogenic radionuclides, including ^{60}Co, ^{94}Nb, ^{137}Cs, ^{152}Eu, ^{154}Eu, ^{155}Eu and ^{241}Am, were not correlated with invertebrate biomass, density, richness, or Shannon diversity ($P > 0.19$ in all cases; Table 2). Sites with the highest anthropogenic radionuclide concentrations in sediment, located within 2 km downstream of CRL's PO (Table 1, [1]), were characterized by some of the highest values of biomass, density, and diversity observed in this study (Figure 2). However, these sites were also characterized

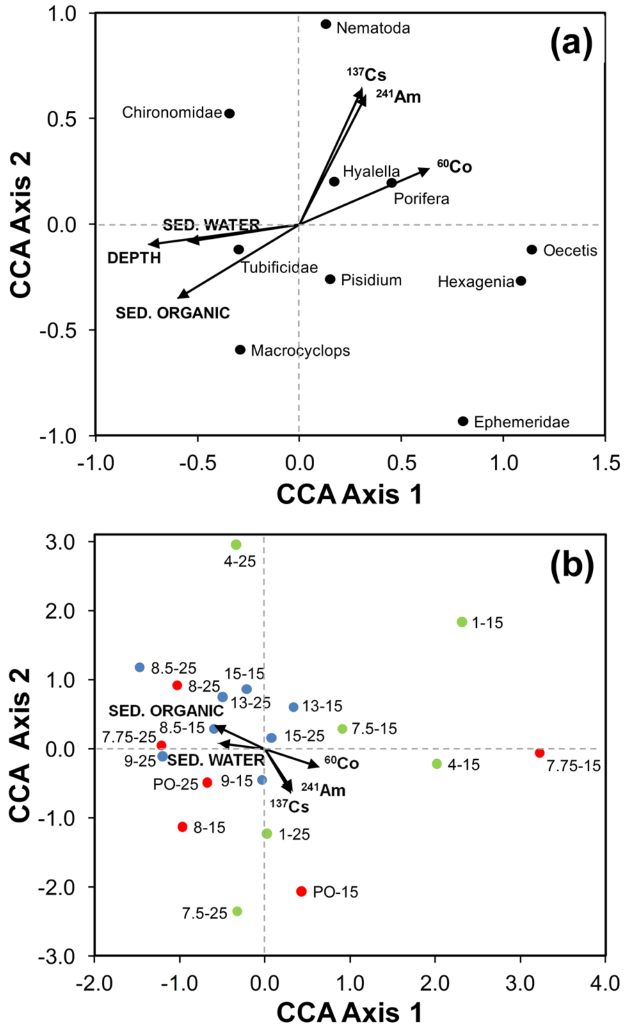

FIGURE 4: Canonical correspondence analysis (CCA) ordinations of benthic macroinvertebrate taxa in relation to environmental variables (black arrows) in Ottawa River sediment near CRL, (a) with and (b) without sample sites included. Sites upstream of the PO footprint (green), in the PO footprint (red) and downstream from the PO footprint (blue) are included. Axis 1 and Axis 2 accounted for 16.5% and 11.8% of the species by environment variance, respectively.

by low sediment organic content and low sediment water content relative to other sites, which is favorable physical habitat for many taxa (Figure 3).

Benthic invertebrate density, taxa richness, and Shannon diversity were all strongly negatively correlated with sediment water content and sediment organic content in samples taken at 15 m depth ($r > 0.68$, $P < 0.029$ in all cases; Table 2 and Figure 3). However, these strong associations between biotic measures and sediment organic and water

TABLE 3: One-way ANOVA test statistics comparing benthic invertebrate biomass, density, taxa density, and Shannon diversity index between sites upstream of CRL's process outfall (PO) footprint, in the PO footprint, and downstream of the PO footprint at shallow (15 m) and deep (25 m) transects (sites pooled). Specific values are shown in Figure 2. No significant differences between locations were detected (P > 0.10 in all cases).

Benthic Composition	*Shallow Sites (15 m)*			*Deep Sites (25 m)*		
Metric	F	d.f.	P-value	F	d.f.	P-value
Biomass (g·m^{-2})	2.005	2,9	0.367	1.791	2,9	0.408
Density (#·m^{-2})	0.389	2,9	0.823	2.509	2,9	0.285
Taxa Richness	0.696	2,9	0.706	1.224	2,9	0.542
Shannon Diversity	0.470	2,9	0.643	1.821	2,9	0.223

content were not prominent in samples from 25 m depth or for biomass at either depth (Table 2).

Sites characterized by predominantly silty sediment (50–60% water content) supported the most abundant and diverse invertebrate communities, while sites characterized by silty-clay (water content 60–90%) supported fewer and less diverse invertebrates (Figure 3). Likewise, sediments with low organic content (4–8%) supported the most abundant and diverse invertebrate communities, while sites with high sediment organic content (9–12%) were characterized by a less abundant and less diverse community (Figure 3).

Figure 4 shows CCA ordinations using invertebrate distributions and environmental variables. The top and bottom panels portray the same information; however, the bottom panel includes sampling sites for spatial comparisons. The CCA model indicated that axis 1 accounted for 16.5% of the species by environment variance, while axis 2 explained an additional 11.8% of the variance. Environmental variables combined explain up to 42.1% of the total variability in invertebrate community composition. The three factors with the highest loading values on axis 1 were depth (-0.745), ^{60}Co (0.638) and sediment organic content (-0.601), while the main loading factors on axis 2 were ^{137}Cs (0.647) and ^{241}Am (0.614). The CCA biplot showed that different taxa responded differently to the six environmental variables (Figure 4a). For some taxa, e.g., Tubificidae and *Macrocyclops*, abundance increased with depth and sediment organic content, while for others, e.g., *Hyalella* and Porifera, the reverse trend was observed. Likewise, Nematoda abundance increased with ^{137}Cs and ^{241}Am sediment concentrations. Chironomidae, *Pisidium, Oecetis, Hexagenia*, and Ephemeridae abundances were not explained by any of the environmental variables investigated in this study. Deeper (25 m) sites, identified by a 25 at the end of the site name (e.g., 8.5-25) in Figure 4b, generally cluster to the negative side of axis 1 and are associated with increased sediment organic and sediment water content (silty-clay), characterized by a benthic community consisting mostly of Tubificidae and *Macrocyclops*. Shallower (15 m) sites, identified by a 15 at the end of the site name (e.g., 8.5-15) in Figure 4b, show no pattern.

Two sites are of particular interest, as they separate out from the rest of the ordination cluster (Figure 4b). First, site 7.75-15, located approximately 150 m downstream from the PO at a depth of approximately 15 m, was characterized by sediment organic content (12%), sediment water content (80%), and ^{60}Co concentrations (8,675 Bq·kg^{-1}) greater than other sites near the PO. This site supported the freshwater sponge (Poriferia) and fingernail clams (*Pisidium*), and was one of the few study sites to support *Hexagenia*. Second, site 4-25, located 3.5 km upstream of the PO at a depth of approximately 25 m, was characterized by a relatively low Tubificid abundance (43 individuals·m^{-2}) for the relatively high sediment organic (12%) and sediment water (79%) content at this location (similar sediment conditions supported 219–570 Tubificids·m^{-2} at other nearby sites).

3.4 Spatial distribution of macroinvertebrates in relation to CRL

There was no significant difference in invertebrate biomass, density, taxa richness, or Shannon diversity index between pooled sites upstream from CRL, in the PO footprint, and downstream from CRL, at $\alpha = 0.10$ or 0.05 (Table 3). However, statistical power was lower than the desired 0.8 for comparisons of Shannon diversity between sites, as discussed later in this paper. Contaminant concentrations often co-vary with sediment grain size, as smaller sediments offer a greater surface area for sorption of both organic matter and chemical contaminants (due to a greater surface–volume ratio) [25, 27-28]. However, even when the effect of sediment water content (a proxy of grain size) on invertebrate abundance was statistically controlled for using ANCOVA, there was no difference between sites upstream of the PO footprint, in the PO footprint, and downstream of the PO footprint ($F_{2,6} = 0.25$, $P = 0.789$). In the CCA ordination (Figure 4b), sites upstream of the CRL process outfall are represented by green markers, sites in the PO footprint are represented by red markers, and sites downstream from the PO footprint are represented by blue markers. Visual examination failed to identify clustering of ecological groups or sites in response to spatial proximity to CRL's PO. In general, sites downstream of the PO footprint cluster more closely than upstream sites or sites in the PO footprint, and appear to be driven mainly by sediment organic content and sediment water content.

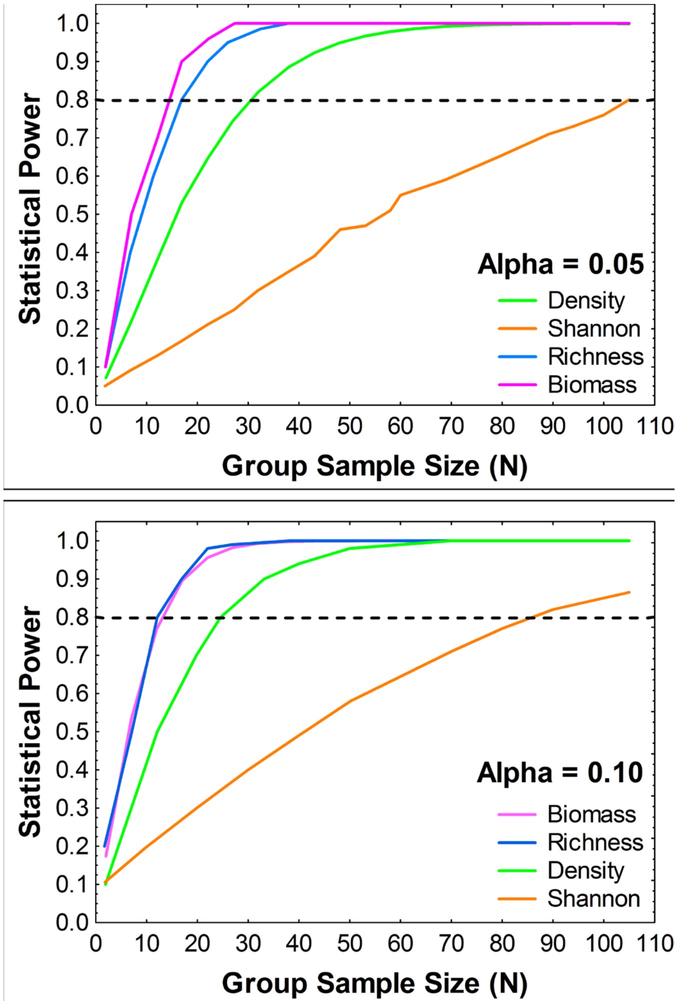

FIGURE 5: *A posteriori* power analysis plots demonstrating the required sample size necessary to conduct a 1-way ANOVA comparing various benthic community metrics at three locations (e.g., upstream vs. footprint vs. downstream of the CRL process outfall) using both alpha = 0.05 (top) and alpha = 0.10 (bottom) significance levels. The desired power (0.8) is identified by a horizontal broken black line.

3.5 Power analysis

Using an α-value of 0.05 and a desired power of 0.8, the number of replicate samples per site required to detect a significant difference between sites with 95% confidence using a 1-way ANOVA in biomass, taxa richness, density, and Shannon diversity are 14, 17, 30 and 105, respectively (Figure 5, top). When α is increased to 0.10 (as suggested by Environment Canada [18, 19]), the number of replicate samples per site required to detect a significant difference between sites with 90% confidence in biomass, taxa richness, density, and Shannon diversity decrease to 13, 12, 25 and 86, respectively (Figure 5, bottom). Our ANOVA tests comparing benthic community metrics between upstream sites, footprint sites and downstream sites were conducted at a statistical power ranging from 0.51–0.81 at an α of 0.05 (using 15–20 cores per location, pooled from 3–4 transects). When α is increased to 0.10, power increases to 0.64–0.91. Power for Shannon diversity comparisons is considerably lower, at 0.15–0.25 (Figure 5). In agreement with our *a posteriori* power analysis (Figure 5), estimates of density, biomass, and taxa richness generally asymptote (i.e., plateau) after 10–15 replicate core samples (Figure 6), which we met by pooling cores from sites into upstream, footprint, and downstream locations. As identified in the power analysis, Shannon diversity does not follow this trend, and even after 15–20 replicate core samples, the mean does not asymptote as it does for the other benthic indices (Figure 6).

4. Discussion

This study investigates drivers of benthic macroinvertebrate abundance and community structure in the Ottawa River near Chalk River Laboratories. In the following text, we discuss: *(i)* the relationships between physical and chemical sediment characteristics and benthic invertebrate abundance and community structure; *(ii)* spatial distributions of invertebrates in relation to CRL; and *(iii)* sources of error involved in this study and the challenges associated with sampling benthic invertebrates in a deep, oligotrophic, spatially heterogeneous environment, such as the Ottawa River.

4.1 Macroinvertebrate community in Ottawa River sediment

Benthic invertebrate distributions are strongly influenced by abiotic factors in the absence of contaminants [29, 30] and, in some cases, the effects of contaminants can be confounded by effects due to natural abiotic factors, such as sediment grain size or sediment organic content [31]. Thompson and Lowe [32] show how changes in benthic abundance and community composition are often linked to the interaction of fine sediments, sediment organic content and contaminants. The Ottawa River invertebrate community, in the study region, appears to be structured predominantly by natural physical and biological conditions in the sediment, specifically sediment water content and sediment organic content, as observed in many other aquatic systems (e.g., [5, 28, 33]). Our description of the physical sediment properties near CRL is similar to that of Evans *et al.* [13], who studied sediments near CRL's PO in the mid 1980's, suggesting that physical habitat conditions have not changed over the past 25 years.

Sediment water content provides an estimate of sediment substrate size–the higher the sediment water content, the finer the grain size. Sediments with fine silty-clay contained a high organic content, and supported the fewest and least

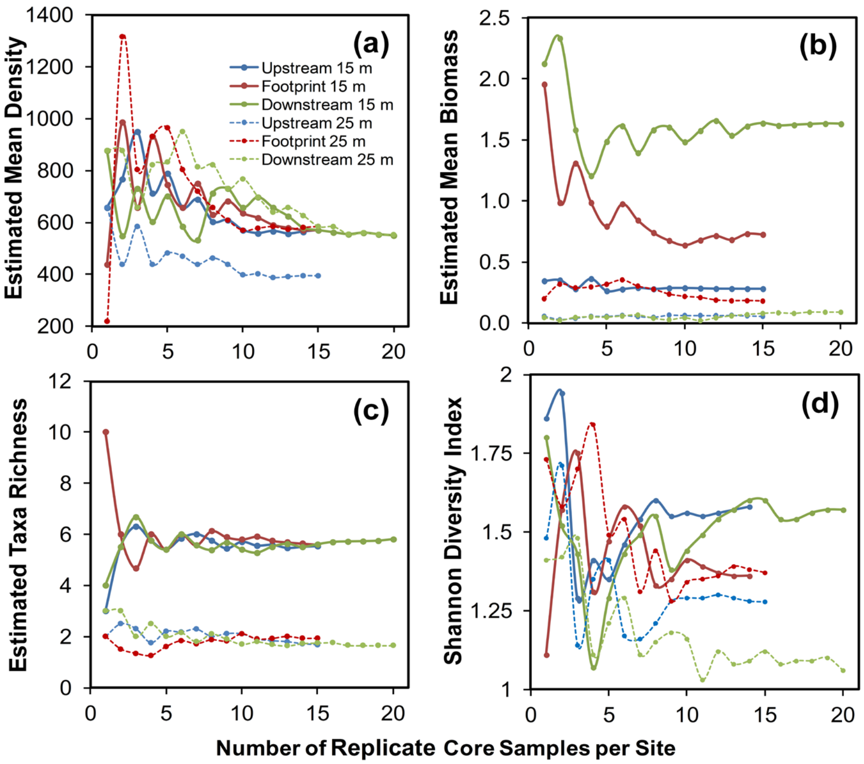

FIGURE 6: Estimates of (a) invertebrate density (number of individuals·m^{-2}), (b) biomass (g·m^{-2}), (c) taxa richness, and (d) Shannon diversity index as a function of the number of replicate core samples taken per location. Blue lines represent upstream of the PO footprint, red lines represent the PO footprint and green lines represent downstream of the PO footprint. Solid lines represent samples taken at 15 m depth, while broken lines represent samples taken at 25 m depth.

diverse benthic communities observed in this study (Figure 3). We found that both benthic invertebrate density and Shannon diversity were strongly negatively correlated with both sediment organic content and sediment water content ($r \geq 0.68$, $P \leq 0.029$ in both cases). The highest estimates of abundance and diversity in this study were at sites with silt–mud sediment (water content 55–65%), which had less than 7% organic content. Small-grain sediments (e.g., clay) are generally associated with high levels of organic matter, which support a large bacterial community [28, 32-34]. As bacteria feed on organic matter, oxygen levels are depleted and levels of sulfide and ammonia are elevated, causing natural toxicity to many benthic taxa [28, 34]. Furthermore, a sediment grain size that is either too small or too large can interfere with invertebrate's ability to burrow [31].

The relationship between macroinvertebrate community and sediment organic matter was investigated in ten soft-bottom oligotrophic lakes in France by Verneaux *et al.* [35]. In agreement with our results, a sediment organic matter preferrendum appeared at around 3% and once sediment organic content reached 10%, macroinvertebrate communities were adversely affected [35]. Hyland *et al.* [28] take a more conservative approach, suggesting organic impairment at 3.5% sediment organic content. Sediment organic content in Lake Temiskaming, 180 km upstream from CRL (Figure 1), ranged from 3–6% [36], lower than in the CRL section of the Ottawa River where it ranged from 5–15%. This is likely because the physical and hydrological properties of the CRL section of the Ottawa River create a depositional pool along the broader river network, in which particulate and organics settle out of the water column and accumulate on the bottom. Sediment organic content in the Ottawa River near the city of Ottawa, 190 km downstream from CRL, ranged from 0.4–11% [37].

The two most abundant taxa observed in Ottawa River sediment, pea clams (Sphaeriidae: *Pisidium*) and Oligochaetes (Tubificidae: *Spirosperma*), are indicative of an organically enriched environment, particularly in soft silty-clay sediments like those in the Ottawa River [38, 39]. *Pisidium* are filtering collectors and Tubificidae are gathering collectors, both with diets consisting of fine, organic detritus and bacteria [14, 40] that is present in the benthic zone of the depositional Allumette Lake segment of the Ottawa River (where CRL is located, Figure 1). Sediment organic matter has been found to strongly influence detritivore growth and abundance [39]. In shallow photic sediments (e.g., littoral zone), sediment organic matter is often determined by phytobenthos and algae (i.e., primary production) [41]. In the deeper profundal sediments investigated in this study, much of the sediment organic matter is in the form of woody debris.

Similar to the findings of this study, Rigler's [15] survey of the Ottawa River benthic community near CRL identified the most abundant invertebrates as Oligochaetes (by density) and *Hexagenia* (by biomass)–although spatial abundance estimates were not available for comparison. Sallenave and Barton [36] investigated the benthic invertebrate community in the Lake Temiskaming section of the Ottawa River and found that mean invertebrate abundance ranged from approximately 800–2,000 individuals·m^{-2} (at 10 m depth), compared to the estimates of 350-1,008 individuals·m^{-2} (at 15 m depth) observed in this study. In agreement with the results of this study, the most common invertebrate taxa observed in the upstream Lake Temiskaming benthic zone (at 10 m depth) included Chironomidae (*Procladius, Tanytarsus* and *Polypedilum*), Oligochaeta (*Tubifex tubifex)* and *Hexagenia* [36]. Our estimates of invertebrate biomass in Ottawa River sediment (0.1–2.5 g·m^{-2}) are considerably lower than those for the Lake Temiskaming reach of the Ottawa River (1.9–17.3 g·m^{-2}) [36], likely because we sampled the Ottawa River in November and Lake Temiskaming was sampled in May through August, when pre-emergence biomass is generally at its highest [42, 43].

Hexagenia are often used as an indicator of sediment degradation due to their high sensitivity to pollutants, including eutrophication [44], heavy metals [45], oil [46], acidic conditions [47], and organics [47, 48]. In the only previous study on the benthic invertebrate distribution in the Ottawa River near CRL, Rigler [15] found that *Hexagenia* was one of the most abundant benthic invertebrate taxa at depths from < 1–16 m, ranging from 10–20 individuals per m^2. *Hexagenia* are also an important component of the Lake Temiskaming benthic community, upstream from Chalk River, ranging from 25–103 individuals·m^{-2} [36]. In this study, we found *Hexagenia* densities to be similar, ranging from 0–131 individuals·m^{-2}. The highest *Hexagenia* density estimates are from sites at 15 m depth, particularly those with sediment water content ≤ 65% and organic content ≤ 7%. No *Hexagenia* were found at 25 m sites or at 15 m sites where sediment organic content was ≥ 9%. These habitat preferences are in general agreement with those described in the literature (e.g., [44]). A recent study by Carr and Rowan [49] reported *Hexagenia* densities of 19–30 individuals per m^2 in Ottawa River sediment (15–20 m depth) near CRL, considerably lower than the estimates obtained in this study. Carr and Rowan [49] sampled using a 9 x 9 inch Ekman dredge, which covers an area 12 times greater than the cores used in this study. Discrepancies in *Hexagenia* density might be due to over/under estimates when standardizing samples to 1 m^2 or temporal differences in abundance.

4.2 Spatial distribution of macroinvertebrates in relation to CRL

Where contaminant levels are sufficiently high in sediment, benthic community-level responses can often be observed. In cases of severe contamination, benthic invertebrates may be entirely absent or their abundance greatly reduced (e.g., [50]). Where contaminants do not entirely eliminate the benthic community, measures of benthic community (i.e., measures of taxa richness or abundance of contaminant-sensitive taxa) provide the most sensitive and reliable measure of community-level effects [51, 52]. Contaminated sediments may be characterized by a simplified benthic community consisting of a high abundance of tolerant taxa (e.g., Oligochaetae, Chironomidae) and low diversity [50]. For example, many mayfly taxa (e.g., *Hexagenia*) are extremely sensitive to contamination, as discussed above, and the presence or absence of this invertebrate is a strong indicator of sediment quality [50]. This study demonstrates that over 60 years of operations at CRL has had little impact on the local benthic macroinvertebrate community. Despite elevated anthropogenic radionuclide concentrations in CRL's PO sediment footprint [1], the benthic invertebrate community is no less abundant or diverse than what is observed upstream at background radionuclide levels. Analysis of benthic community structure in the Ottawa River near CRL revealed that taxa intolerant to contaminants, including the Tubificidea *Spirosperma* [53] and Ephemeridae *Hexagenia* [47] were present in the most contaminated sediments near CRL's PO (Figure 2). *Hexagenia* abundance is structured predominantly by natural physical habitat characteristics, such as sediment grain size [49], as the appropriate-sized substrate is required for burrowing.

Our results suggest that a threshold concentration of contamination exists, below which invertebrate abundance is more strongly controlled by other environmental factors (such as in this study), and above which the influence of the contaminant is more pronounced (e.g., [3]). Other studies have reported that habitat conditions can have a stronger influence on macroinvertebrate communities than sediment contamination [6, 54-56]. For example, in a comprehensive study of the factors that structure benthic invertebrate assemblages in the St. Lawrence River, Masson *et al*. [6] found that sediment contamination alone explained a very low percentage of the total variance of taxa (< 2%). However, environmental characteristics, such as sediment organic content and percent sand, explained between 13 and 15% of macroinvertebrate community structure.

Much of the published literature examining the effects of elevated anthropogenic radionuclide activity concentrations in sediment on benthic invertebrates comes from impact assessment studies at Canadian uranium mines and processing facilities (e.g., [57, 58]). Hart *et al.* [3] reported reduced benthic invertebrate abundance in Port Hope Harbour with radionuclide (^{238}U and ^{232}Th decay chains) activity concentrations as high as 739,000 Bq·kg^{-1} in sediment. Radionuclide levels in the tissues of *Limnodrilus hoffmeisteri* and *Tubifex tubifex* reached 25,000 Bq·kg^{-1} at the most contaminated locations. Tissue contamination levels showed the same spatial distribution as sediment contamination in the harbour [3]. The only anthropogenic radionuclide detectable in tissue from Ottawa River invertebrates near the PO footprint was ^{137}Cs, at activity concentrations ranging from 1-100 Bq·kg^{-1} [10, 59]. In agreement with the recent findings of Rowan *et al.* [59], Evans *et al.* [13] investigated ^{60}Co uptake by benthic invertebrates in sediment near CRL's PO and reported that ^{60}Co levels in tissue were below the detection limit. Spatially, tissue activity concentrations of ^{137}Cs followed Ottawa River sediment activity concentrations [13, 59].

4.3 Power analysis and sources of error

Power analysis should be used after any non-significant result is obtained in order to judge whether that result can be interpreted with confidence or the test was too weak to detect a significant result [60]. Statistical power depends on the chosen value of α, the sample size, the effect size to be detected and the variability inherent within the data [60]. The number of samples necessary for population estimation at a required precision (power) decreases with increasing population density (individuals·m^{-2}) and decreases with increasing sampler size (cm^2) [60]. There is an abundance of peer-reviewed discussion about how to best measure abundance and biodiversity in biologically diverse, high-density environments (e.g., [21, 29-30, 61]). However, there is a paucity of literature discussing how to do so in low-density, low-diversity environments, such as the Ottawa River benthic zone near CRL (but see [62-64]). The natural low abundance of invertebrates in the study section is likely due to the natural oligotrophic nature of the system and low habitat complexity of a large, deep river. The Canadian metal mining and pulp and paper EEM guidelines [18, 19] recommend five replicate core samples per site to obtain an accurate estimate and minimize sample error. However, these guidelines were likely developed with consideration to aquatic systems that are considerably more productive and easier to sample than the Ottawa River (e.g., wadeable streams, small rivers, littoral areas of lakes) [65].

To obtain sufficient statistical power, sites were pooled into three groups by location–upstream, PO footprint, and downstream–to increase sample size and decrease within-site variability. Using an α of 0.10, as suggested by the Canadian metal mining and pulp and paper EEM guidelines [18, 19], we found no difference in biomass, density, richness or Shannon diversity between upstream sites, the footprint, and downstream sites (Table 3). Power was appropriate for detecting differences between sites for richness and biomass metrics (power = 0.9); however, power was lower than desired for density and unacceptable for the Shannon diversity index (power = 0.64 and 0.25, respectively). To achieve a power of 0.8 for density and Shannon diversity indices, the number of sample replicates per site would have to be increased to 25 and 86, respectively (Figure 5, bottom). In agreement with our power analyses, Downing [66] suggests that at an observed invertebrate density of 100–1,000 individuals per m^2, using a sampler with an area of approximately 50 cm^2 (such as the cores used in this study), 5–11 replicate samples per site are necessary to obtain a standard error of replicate samples of 20% of the mean density. In an investigation of benthic invertebrate community in the upper Ottawa River, Sallenave and Barton [36] found that ten core replicates per site was appropriate for assessing the benthic community. Our results suggest that 15–20 replicates per location provided excellent statistical power for richness and biomass, moderate statistical power for density, and poor statistical power for Shannon diversity. Therefore, for three of the four benthic indices used in this study, additional replicates would not have changed our conclusions.

When using benthic indices for biological monitoring, it is important that a number of indices be employed in unison, as an impact may be detected by one metric but not another. For example, sediment contamination may cause a shift in species composition from a diverse and evenly represented benthic community to one dominated by one or two taxa tolerant to contaminants (e.g., [67, 68]). Detection of this impact would be highly probable if metrics involving community richness and evenness are employed, but may be low if only abundance and biomass are monitored. However, it is clear that some community metrics work better than others [69, 70], and no single sampling regime can adequately sample all components of a macroinvertebrate community [63].

Of the four benthic indices tested in this study, taxa richness and biomass provided the strongest statistical power and are best suited for testing for community differences in low-density environments, such as the Ottawa River (Figures 5 and 6). Density also works well; however, the high spatial variability associated with this measure results in increased within-sample variability and thus requires a larger sample size to reach an appropriate power (Figure 5). The Shannon diversity index is not well suited to detect an impact in the Ottawa River benthic zone. Using this index, which takes into account relative abundance, evenness, and taxa richness, would require approximately 86 replicate core samples per site to detect a difference, if one exists, between locations with a statistical power of 0.8 (Figure 5). The Shannon index constrains values (between zero and two in this study, as there were no sites that had a taxa richness >10), and is highly responsive to slight changes in richness and community evenness. Johnson [69] and Sandin and Johnson [70] compared benthic indices for their ability to detect change in Swedish rivers and lakes, and also found that taxa richness had the highest standardized effect size, as well as the highest statistical power (i.e., fewest sample required to detect change). Conversely, total density of individuals was the least informative metric, with the lowest effect size and highest spatial, temporal, and within-sample variability [70].

5. Conclusions

Despite elevated anthropogenic radionuclides in Ottawa River sediments near CRL's process outfall, benthic macroinvertebrate abundance and community structure does not appear to be different than upstream or downstream locations. Environmental variables, such as sediment organic content and sediment water content (a proxy for grain size), appear to be much more important than radionuclide activity concentrations in structuring the benthic community in the Ottawa River near CRL. Measuring more environmental variables describing habitat (e.g., dissolved oxygen, water temperature) would have likely improved the predictive power of the multivariate statistical models based on the Ottawa River invertebrates, and may have better explained habitat preference for a larger number of taxa. Although the Canadian metal mining and pulp and paper EEM guidelines [18, 19] are appropriate for assessing benthic community structure in many Canadian aquatic systems, they are not well suited for the Ottawa River due to low invertebrate densities and high spatial heterogeneity. Future research on the development of guidelines for sampling large, deep river ecosystems (e.g., 65, 71-72) would be useful and would improve EEM programmes for Canada's large river ecosystems.

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FULL ARTICLE

POST-CLOSURE PERFORMANCE ASSESSMENT OF A DEEP GEOLOGICAL REPOSITORY FOR ADVANCED HEAVY WATER REACTOR FUELS

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Many countries worldwide are investigating the use of advanced fuels and fuel cycles for purposes such as increasing the sustainability of the nuclear fuel cycle, or decreasing the radiological impact of used fuel. One common metric used to assess the radiological impact to humans of fuels placed in a repository is the total radiotoxicity of the fuel, but this approach does not take into account how engineered and natural (i.e., rock) barriers can remove many radiotoxic nuclides from ground water before they reach the surface. In this study, we evaluate the potential radiological dose consequences of advanced fuels in the context of a full system model simulation for release and transport from a repository, transport through the surrounding geosphere, release to the biosphere and dose consequences for the target critical group.

Heavy water moderated reactors, such as the CANDU® reactor, are well-suited to the use of advanced fuels, and the post-closure performance of a deep geological repository for spent natural uranium fuel from them has already been studied. For this study, two advanced fuels of current interest were chosen: a TRUMOX fuel designed to recycle plutonium and minor actinides and thereby reduce the amount of these materials going into disposal, and a plutonium thorium-based fuel whose main goal is to increase sustainability by reducing uranium consumption. The impact of filling a deep geological repository, of identical design to that for natural uranium, with used fuel from these fuel cycles was analyzed. It was found that the two advanced fuels analyzed had dose rates, to a hypothetical critical group of humans living above the repository, which remained a factor of 170 to 340 lower than the current acceptance limit for releases, while being 5.3 (for TRUMOX) and 2.6 (for thorium-plutonium) times higher than those of natural uranium. When the dose rates are normalized to total energy produced, the repository emissions are comparable. In this case, the maximum dose rates were found to be 6% lower for the TRUMOX fuel, and 16% higher for the plutonium thorium fuel, than for the used natural uranium fuel.

Definition of Terms

CANDU	The trademarked name of a type of HWR developed in Canada and used in Canada and around the world.
DGR	Deep Geological Repository
HWR	Heavy Water (moderated and cooled) Reactor
IRF	Instant Release Fraction. That portion of the fission product inventory which is soluble and, having migrated to the grain-sheath boundary, is potentially available for quick release from the fuel.
LWR	Light Water (moderated and cooled) Reactor
MOX	Mixed Oxide fuel. Generally, PuO_2 mixed with ThO_2 or UO_2.
NWMO	Nuclear Waste Management Organization. A Canadian organization which has assumed responsibility for the long term management of used nuclear fuel from Canadian reactors.
NU	Natural Uranium (uranium with ~0.71 wt.% U-235 in U-235+U-238)
TRU	Transuranic nuclides (see TRUMOX).
PuTh	Nuclear fuel with PuO_2 mixed into ThO_2.
Radiotoxicity	A measure of harm to humans focusing on the cancer causing potential due to the decay of an ingested, inhaled or injected radionuclide inside the body.
TRUMOX	MOX mixed with transuranic nuclides (Np, Pu, Am and Cm) separated from previously irradiated fuel.

1. Introduction

The impact of spent nuclear fuel on human health is commonly estimated by means of the spent fuel radiotoxicity, a measure of the harm caused to humans if the fuel is released and ingested or inhaled. Along with the benefits associated with advanced fuel cycles, one of the drawbacks will be the additional potential for human exposure to radionuclides due to the requirement for reprocessing LWR fuel to extract the plutonium. Such exposure, or exposure to spent fuel during transport to a deep geological

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repository (DGR), can be reasonably estimated using radiotoxicity calculations. However, once emplaced in a DGR, total fuel radiotoxicity is no longer an appropriate metric because it does not take into account how engineered and natural (i.e., rock) barriers will remove many radiotoxic nuclides from ground water before they reach the surface [1]. Detailed calculations have been performed here to estimate the impact of advanced fuels on the post closure performance of a DGR. A conceptual model was used in this study to estimate possible effects of the used fuel placed in a DGR on a critical group of humans (a farming community living above the repository). The model describes the release of contaminants from the repository and their transport through the geosphere to the biosphere, and computes the radiological consequences of releases to the environment. This calculation provides a clearer description of the radiological impact of changing to an advanced fuel cycle than does the traditional radiotoxicity calculation alone. In order to isolate the effects of the different spent fuel compositions, considerations such as potential canister or repository design changes for high burnup fuels have been ignored.

Advanced fuels and fuel cycles are under consideration by many countries to address issues surrounding management of used nuclear fuel and the sustainability of the fuel cycle. Heavy-water-moderated reactors (HWR), such as CANDU® reactors, are well-suited to provide solutions to both used fuel management issues and improved sustainability. Two potential advanced fuel cycles, which could be implemented in an HWR, will be discussed in the following sections. The first, labelled TRUMOX, is primarily oriented towards reducing the impact of used fuel by re-using transuranic actinides in new fuel, and the second, labelled PuTh, is primarily oriented towards increasing resource sustainability by reducing uranium consumption. Reactor physics calculations were first performed in order to determine the preliminary designs of the fuels, and to obtain the fresh and used fuel compositions. A radionuclide screening analysis was then applied to the used fuel compositions. The selected nuclides were then included in a model of a deep geological repository containing the advanced fuels and emissions to the surface over geologic time (10^7 years) were calculated.

If nuclear fuel is reprocessed to remove actinides that are put into new fuel, then there will be forgone emissions from the previous fuel if it was intended for replacement in a repository. No attempt has been made to calculate this effect here.

2. Advanced Fuels Chosen for Analysis

2.1 Advanced fuel cycle for spent nuclear fuel management (TRUMOX)

In Canada, the adopted solution for used fuel management is Adaptive Phased Management [2], which involves the construction of a DGR for centralized containment and isolation of used fuel, with the option of retrievability of the fuel. Similar solutions are being adopted by other countries. Although many technical solutions regarding disposal of used fuel exist, their political and social implementation remains a challenge in many jurisdictions around the world. For this reason, many countries have research and development (R&D) programs with the objective of reducing the long term impacts of used fuel. These R&D programs involve partitioning and transmutation (P&T) of used fuel. Partitioning is chemical separation of used fuel into groups of constituent elements. The transmutation stage puts those elements back into a neutron flux, generally either a nuclear reactor or an accelerator driven system, with the goal of changing those isotopes into shorter-lived isotopes through a series of neutron captures and decays, and via fission.

The goal of P&T is to increase the capacity of long-term geological disposal sites. This happens in two ways:

- By recycling the fissile material in the used fuel, more energy is extracted. Thus, there is less fuel mass to be disposed of per unit energy that was produced.
- The amount of the various constituents of the fuel that have a significant impact on the repository over the long-term is reduced.

Several of the minor actinide isotopes, particularly Am-241 with a half life of 433 years, are the targets of P&T. Am-241 is a major contributor to the long-term decay heat, which can be a limiting factor on the capacity of a DGR. The primary contribution of Am-241 occurs between 100 and 1000 years after the fuel exits the reactor. Am-241 is produced in the reactor during irradiation, but most of the Am-241 in used nuclear fuel results from the decay of Pu-241 (half life of 14.3 years) after the fuel has been discharged from the reactor.

Typical advanced fuels for P&T contain recycled minor actinides (Am, Cm, and Np), with or without recycled plutonium in a fertile matrix such as uranium. The advanced fuel considered here contained plutonium, neptunium, americium and curium (together known as the transuranic nuclides, or TRU), mixed with natural uranium. The mixed fuel is called TRUMOX (for TRansUranic Mixed OXide).

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[1] For example, "Thorium", available online at http://www.world-nuclear.org/info/inf62.html, 2012 August.

2.2 Advanced fuel cycle to improve sustainability

Thorium is estimated to be three times more abundant in the Earth's crust than uranium. Many studies[1] predict that the world will run out of easily extracted uranium between 2040 and 2070. Some countries, such as India and China, which have large electricity generation expansions planned, have few national uranium resources, but have substantial thorium reserves. The greater abundance of thorium and the uneven distribution of uranium world-wide have lead to increased interest in thorium fuel cycles in recent years.

Thorium exists in nature in a single isotopic form, Th-232, and can be transmuted to the fissile isotope U-233. A neutron capture by Th-232 creates Th-233, which β decays into Pa-233, which in turn β decays into the fissile isotope U-233, an isotope with a very high fission to capture ratio.

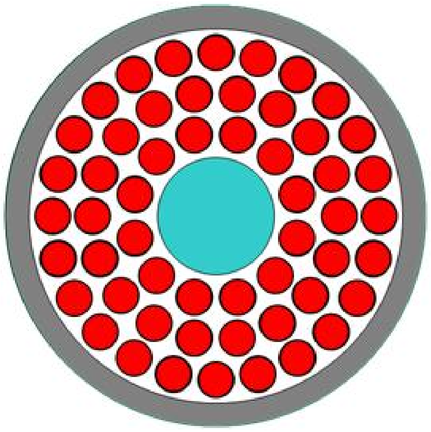

FIGURE 1: Fuel bundle designs for the TRUMOX bundle.

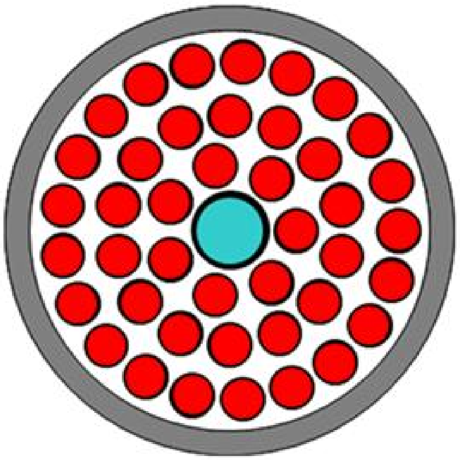

FIGURE 2: Fuel bundle designs for the PuTh bundle.

TABLE 1: Fresh Fuel Composition for the TRUMOX and PuTh Fuels (wt.%)

Nuclide	TRUMOX		PuTh	
	15-year Cooled	30-year Cooled	5-year Cooled	30-year Cooled
Np-237	5.35	5.59		
Pu-238	2.40	2.13	2.5	2.3
Pu-239	47.89	48.02	54.2	59.8
Pu-240	21.44	21.66	23.8	26.3
Pu-241	6.79	3.29	12.6	4.2
Pu-242	6.55	6.57	6.8	7.4
Am-241	7.58	10.91		
Am-242m	0.01	0.01		
Am-243	1.52	1.53		
Cm-244	0.39	0.22		
Cm-245	0.05	0.05		
Cm-246	0.01	0.01		
Vol.% TRU	6.8	8.3	3.75	4.18
Burnup (MWd/kg)	51.3	52.5	20.7	21.1

Since the initial material is not fissile, thorium requires some fissile nuclide, for example Pu-239, to be present initially. Plutonium can be recycled from spent uranium based fuels. A plutonium-driven thorium fuel (PuTh) was modeled in this study.

3. Calculation of the Used Fuel Compositions

The reactor physics calculations were performed using WOBI Version 3.1 [3], a code that links WIMS-AECL 3.1 [4, 5] and ORIGEN-S 5.1 [6]. WIMS-AECL performs the flux calculation, and ORIGEN-S performs the depletion calculations, as well as calculating other quantities such as decay heat and activity, which are not available through WIMS-AECL. ORIGEN-S has a large nuclide library, which enables WOBI calculations to produce the detailed and comprehensive used fuel compositions required for the DGR calculations.

The transuranic nuclide-bearing fuel bundle concept (TRUMOX) is shown in Figure 1. This bundle contains 54 fuel elements and a larger centre element that contains a mixture of 50 vol.% dysprosia (Dy_2O_3) in zirconia (ZrO_2), in order to reduce the coolant void reactivity. Two fuel compositions (Table 1) were used, corresponding to 15-year and 30-year cooled transuranic elements separated from light water reactor used fuel. The amount of TRU mixed in the natural UO_2 fuel matrix was adjusted to obtain a burnup of approximately 50 MWd/kg. This burnup required 6.8 vol.% and 8.3 vol.% TRU for the 15-year cooled and 30-year cooled cases, respectively. Detailed specifications can be found in [7]. The transuranic composition is that of the SF97-4 [8] fuel assembly, from the Japanese Takahama-3 PWR. It has an initial enrichment of 4.1 wt% U-235 and was taken to a burnup of ~47 MWd/kg.

The plutonium-driven thorium fuel bundle design (PuTh) is shown in Figure 2. The bundle design has 42 fuel elements and a centre element consisting of a tube of zirconia-filled hafnium [9]. This configuration serves to introduce a neutron poison to the center of the bundle in a way that is simple and easy when creating computer models. The composition of the center poison can be changed later when a particular bundle design is chosen for fuel cycle development. The amount of plutonium in the thoria fuel was adjusted to obtain a burnup of approximately 20 MWd/kg. Two cooling times, five years and 30 years, were applied to the light water reactor used fuel from which the plutonium was derived. The input plutonium content was 3.75 vol.% and 4.18 vol.% Pu for the five-year cooled and 30-year cooled fuels respectively. The input plutonium compositions are given in Table 1.

To obtain a used fuel composition for the repository analysis the average mass for each nuclide in the used fuel between the two decay times was taken for each fuel type. For the nuclides that are important to the repository performance there was little difference in the composition between the two decay times.

4. Radionuclide Screening Analysis

Used fuel contains hundreds of different radionuclides, among which the ability to cause harm to humans and the environment varies significantly. To determine the radionuclides that should be considered more carefully, and to screen out those that will not pose a significant threat, reducing the amount of work required for the full performance assessment, a screening analysis is performed using Radionuclide Screening Model (RSM, Version 1.1 [10]).

RSM is a performance assessment code developed under the SYVAC3 executive for the Canadian nuclear fuel waste management program. RSM closely resembles SYVAC3-CC409 (SYstems Variability Analysis Code, version 3.12, Canadian Concept, version 4.09 [11]), but RSM utilizes sufficient conservative assumptions such that estimates of dose rate impacts are overestimates. The code is capable of running up to 1000 radionuclides and ranking them for potential radiological impacts at the surface. The parents and progeny of the screened-in radionuclides are also included in the simulations to ensure that ingrowth of daughters is included. This analysis eliminates a large portion of nuclides that either have very small inventory, decay significantly before reaching the surface (biosphere), or have no significant consequence once they reach the surface.

The model was performed for an NWMO (Nuclear Waste Management Organization) multi-barrier design and post-closure safety of a DGR in a hypothetical crystalline Canadian Shield setting [12] with the same data as were employed in the screening analysis of used CANDU fuel [13].

The screening assessment of the advanced fuels ranked the radionuclides according to their dose rate. From these ranked lists, all radionuclides with a maximum estimated dose rate, within 10^6 years following disposal, exceeding $3x10^{-6}$ Sv/a, were selected for further study. $3x10^{-6}$ Sv/a is about 1% of the maximum dose rate recommended by the International Commission on Radiological Protection (ICRP) for disposal of long-lived radioactive waste, and equal to about 0.2% of the dose rate associated with natural radiological background in Canada. All other radionuclides were excluded from further detailed consideration.

The screening has been applied separately for each used advanced fuel with the result that a radionuclide might be eliminated for one waste stream, but included in another. The screening study has shown that, for the reference case scenario, many radionuclides would not produce a significant radiological impact and could be eliminated from detailed consideration. The study identified a much shorter list of radionuclides recommended for further study in post-closure assessments. These include four chains and 14 single radionuclides. The parents and progeny of the screened in radionuclides are included in the simulations to properly account for their ingrowth. The simplified chains are:

4n Chain:

Cm-248 → Pu-244 → Pu-240 → U-236 → Th-232 → Ra-228 → Th-228 → Ra-224

4n+1 Chain:

Am-241 → Np-237 → Pa-233 → U-233 → Th-229 → Ra-225 → Ac-225

4n+2 Chain:

Pu-242 → U-238 →Th-234 → U-234 → Th-230 → Ra-226 → Rn-222 → Pb-210 →
Bi-210 → Po-210

4n+3 Chain:

Cm-247 → Am-243 → Np-239 → Pu-239 → U-235 → Th-231 → Pa-231 →
Ac-227 → Th-227 → Ra-223

Important fission products and activation products were: Be-10, C-14, Cl-36, Cs-135, I-129, Kr-81, Pd-107, Rb-87, Se-79, Sn-126, Sb-126[2], Sm-147, Tc-98, and Tc-99.

5. The Deep Geological Repository Model

5.1 Assessment of post-closure safety of a deep geological repository

The SYVAC-CC409 [11] conceptual model was used to estimate possible effects of the used fuel placed in a DGR on a critical group that lives above the repository. This model describes the release of contaminants from the repository, their transport through a geosphere to biosphere, and

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[2] Sb-126, Sb-126m1 and Sb-126m2, all decay products in equilibrium with their parent – Sn-126, are included here.

computes the radiological consequences of releases to the environment. The post-closure safety assessment done by SYVAC-CC409 adopts scientifically informed, physically realistic assumptions for processes and data that are understood and can be justified on the basis of the results of research and/or future site investigation. Where there are high levels of uncertainty associated with processes and data, conservative assumptions are adopted and documented to allow the impacts of uncertainties to be bounded. Other conservative assumptions are built into the reference model source term, specifically the assumption of higher than expected burnup of the fuel, and the use of conservative values for Instant Release Fractions (IRF)[3].

SYVAC-CC409 consists of four main sub-models: spent-fuel containers, engineered barriers, the geosphere, and the biosphere. The spent-fuel container is a steel vessel enclosed in a copper outer shell. It was assumed that, due to manufacturing defects, three containers will each have a single pin-size defect through which water will access the fuel. After water ingress, the fuel sheaths are assumed to offer no protection and the instant release fractions (IRF) of each nuclide in the spent fuel are assumed to be immediately dissolved. These conservative assumptions are the same as that made for a natural uranium DGR [12]. These three containers were considered to be placed in the DGR location having the fastest pathway to the biosphere. When water comes into contact with the fuel, radionuclides within the fuel matrix are released by two mechanisms: instant release and congruent dissolution. A small fraction of the inventory of radionuclides that are very soluble, and that can be accessed by water right away (located in the fuel sheath gap or at grain boundary), is released instantly. Congruent release is a slower process, as a result of which radionuclides are released as the fuel matrix itself dissolves. The model also takes into account precipitation, radioactive decay and ingrowth. When released from a container, the diffusive and advective transport of the contaminants through the engineered barriers was calculated. The resulting flow is passed to the geosphere sub-model.

The geosphere sub-model used a simplified one-dimensional (1D) transport network comprised of representative groundwater flow pathways leading from the repository to discharge points at the surface. The representative groundwater flow pathways were selected based on a more detailed flow field computed using hydrogeological models such as FRAC3DVS-OPG [14]. Each selected pathway was represented as a combination of direct-path segments with uniform rock properties. The effects of the well drawdown on adjacent node heads are accounted for via an analytical well model within the aquifer, and by a site-specific well-effects model outside the aquifer. The contaminants that reach the geosphere-biosphere interface discharge directly to a well and a surface water body (for example a lake, river or peat bog).

The biosphere sub-model is based on characteristics of the Canadian Shield region. Biosphere processes modelled include: sediment contamination, uptake of contaminants by plants and animals, suspension and volatilization of contaminants from the surface water to the atmosphere as well as deposition of contaminants from the atmosphere onto surface soil, release of contamination into the air from fires, irrigation using well and/or surface water, and domestic use of water by humans (drinking, cooking, bathing, etc). The impact of contaminated water further downstream is not assessed in this model.

5.2 Reference model

The Reference Model is described in the Fourth Case Study (4CS) conducted by the NWMO for CANDU fuel [12]. For the advanced fuels considered in this study, the repository study parameters were assigned the same values as those in the 4CS case to allow a comparison. In the 4CS case, the reference waste form was a standard CANDU 37-element fuel bundle with a burnup[4] of 220 MWh/kgU (9.2 MWd/ kgU), and an average fuel bundle power during operation of 455 kW. The Reference Model for a repository contained 360 used NU fuel bundles (weighing 19.25 kg each) in each of the 12778 containers, for a total used fuel mass of 8.85×10^7 kg. A repository with this mass of used fuel will be referred to in this study as a 'standard' repository. The Reference Model is then a standard repository with used NU fuel. Assuming an average burnup of 7.5 MWd/kg, the amount of used fuel in the reference repository represents the production of 6.64×10^8 MWd (664 TWd) of energy.

In the current reference case design, the containers were made of steel with a copper shell. The majority of these containers are expected to be very durable (without significant degradation over the time period of this study), with only three containers failing due to undetected manufacturing defects. In this study, which was extended to 1×10^7 years in order to determine the approximate peak of the biosphere dose rate, the undefected containers[5] were assumed to remain intact. The release of nuclides was assumed to occur after the repository was closed and re-saturated with ground water, allowing the release of radionuclides from the fuel through the undetected defect in the containers. In this study, the time of saturation was set to 100 years.

It is likely that, for medium to high burnup fuels such as the

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[3] The Instant Release Fraction of a nuclide is defined as that fraction of inventory that is available for a rapid release from the fuel matrix at the time of a container failure.

[4] The average burnup for those bundles going into a repository is expected to be close to 7.5 MWd/kg. The higher burnup used in the reference case gives a conservative estimate of the radionuclide source term.

[5] Those containers other than the three assumed to have pinhole leaks due to manufacturing defects.

TABLE 2: Emplaced Inventory (per kg of Initial Heavy Elements in NU Fuel) of Nuclides in the TRUMOX and PuTh Fuels which Passed Initial Screening

Nuclide	Half Life (years)	Initial Inventory (mol)		Instant Release Fraction	
		PuTh	TRUMOX	Reference DGR	99% IRF
Ac-225	2.74E-02	1.70E-11	--	0[1]	0
Ac-227	2.18E+01	6.23E-08	--	0	0
Am-241	4.33E+02	8.98E-03	2.28E-02	0	0
Am-243	7.37E+03	2.39E-03	9.11E-03	0	0
Be-10	1.60E+06	6.92E-07	1.35E-06	0	0
C-14	5.70E+03	1.57E-07	3.77E-07	2.80E-02	6.37E-02
Cl-36	3.01E+05	9.86E-07	9.86E-07	6.00E-02	8.33E-02
Cm-247	1.56E+07	1.01E-08	2.19E-06	0	0
Cm-248	3.39E+05	4.18E-10	2.47E-07	0	0
Cs-135	2.30E+06	1.54E-03	3.60E-03	4.01E-02	6.33E-02
I-129	1.57E+07	1.12E-03	2.14E-03	4.01E-02	6.33E-02
Kr-81	2.10E+05	1.66E-10	3.39E-10	8.10E-02	1.04E-01
Np-237	2.14E+06	2.83E-04	1.25E-02	0	0
Np-239	6.45E-03	2.09E-09	7.97E-09	0	0
Pa-231	3.28E+04	1.50E-04	4.84E-10	0	0
Pa-233	7.39E-02	3.59E-12	4.31E-10	0	0
Pd-107	6.50E+06	2.69E-03	6.23E-03	9.91E-03	4.15E-02
Pu-239	2.41E+04	2.02E-02	5.33E-02	0	0
Pu-240	6.56E+03	4.05E-02	7.29E-02	0	0
Pu-242	3.74E+05	1.56E-02	3.06E-02	0	0
Pu-244	8.26E+07	2.14E-07	7.05E-07	0	0
Ra-223	3.13E-02	8.98E-11	--	2.50E-02	4.34E-02
Ra-224	1.00E-02	4.41E-09	--	2.50E-02	4.34E-02
Ra-225	4.08E-02	2.52E-11	--	2.50E-02	4.34E-02
Ra-226	1.60E+03	4.86E-10	1.87E-11	2.50E-02	4.34E-02
Ra-228	5.75E+00	1.63E-09	--	2.50E-02	4.34E-02
Rb-87	4.70E+10	1.40E-03	2.09E-03	8.10E-02	1.04E-01
Sb-126	3.38E-02	--	1.25E-11	6.01E-03	9.49E-03
Se-79	2.95E+05	4.95E-05	6.87E-05	6.01E-03	9.49E-03
Sm-147	1.06E+11	1.35E-03	2.65E-03	0	0
Sn-126	2.30E+05	1.57E-04	2.95E-04	5.00E-04	9.90E-04
Tc-98	4.20E+06	2.45E-09	7.15E-09	9.91E-03	4.15E-02
Tc-99	2.11E+05	5.13E-03	1.11E-02	9.91E-03	4.15E-02
Th-227	5.11E-02	1.45E-10	--	0	0
Th-228	1.91E+00	8.40E-07	1.63E-09	0	0
Th-229	7.34E+03	5.00E-06	3.56E-11	0	0
Th-230	7.54E+04	1.83E-06	1.98E-07	0	0
Th-232	1.41E+10	4.08E+00	2.89E-09	0	0
Th-234	6.60E-02	--	5.57E-11	0	0
U-233	1.59E+05	3.72E-02	1.26E-07	0	0
U-234	2.46E+05	2.78E-03	4.15E-03	0	0
U-235	7.04E+08	1.90E-04	9.90E-03	0	0
U-236	2.34E+07	1.46E-04	3.24E-03	0	0
U-238	4.47E+09	9.19E-07	3.78E+00	0	0

advanced fuels considered here, changes to the repository (such as the number of containers stored) or canister design (such as spent fuel mass per canister) are likely in order to accommodate various potential concerns like decay heat or transport safety. Indeed some work has been done on likely design changes required for high burnup fuel (different than the ones here) suggesting that the spent fuel mass per canister would have to be reduced [15]. Such possibilities are not considered here. In the case of a reduced mass canister and more canisters per repository, a constant manufacturing defect rate ensures the same conclusions as before. If the number of canisters per repository is limited, then our conclusions for advanced fuel types become conservative, but of course the number of repositories must increase in the same proportion.

5.3 Instant release fractions

The radionuclide Instant Release Fractions (IRF) are not well-known parameters and depend on material properties (such as granularity) as well as fuel operating parameters (such as burnup and linear power rating). Generally, fission product releases from NU CANDU fuel bundles are low and almost constant with burnup for fuel with less than ~40 MWd/kgU, and a linear increase of fission gas release is seen with respect to element linear power ratings [16]. However, beyond 40 MWd/kgU, and for thorium-based fuels generally, little experimental or theoretical work has been done, so the situation is uncertain for the advanced fuels being considered here.

Because linear power ratings for the fuel types considered here (PuTh and TRUMOX) are lower, peak and average, than natural uranium CANDU used fuel, the radionuclide IRF were set to the same values as for natural uranium CANDU used fuel [17]. All radionuclides of the same element are all assumed to have the same IRF. The IRF values, particularly for I and Cs, are considered to be conservative for natural uranium UO_2 fuel, as they are based on experimental work [18] that utilized fuels with generally higher burnups and (peak) linear power ratings compared to those expected for typical natural uranium CANDU fuel. The values for the reference DGR case and for 99% IRF are presented in Table 2.

Only a constant temperate climate is considered for this preliminary study, and no glaciation effects were taken into account. It is conservatively assumed that the members of the critical group are farmers, living in the local biosphere and obtaining all their food, water, fuel and building materials locally.

6. Deep Geological Repository Results

For the selected group of radionuclides (Table 2), the performance and safety assessment simulations were completed for the advanced fuels inventories for the

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[1] No instant release fraction for this waste form.

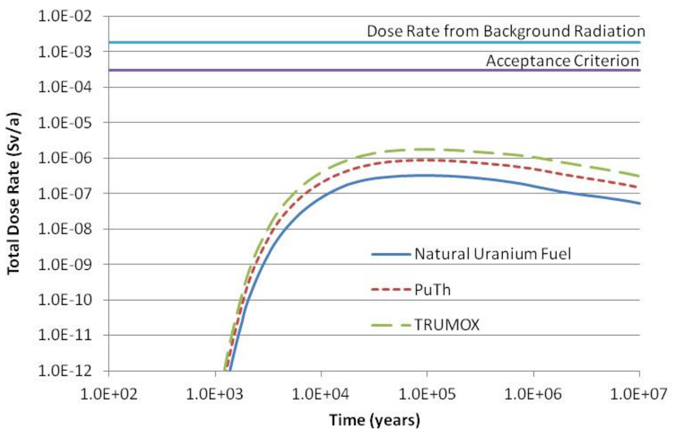

FIGURE 3: Total dose rate, calculated per standard repository, for the TRUMOX, PuTh NU fuel.

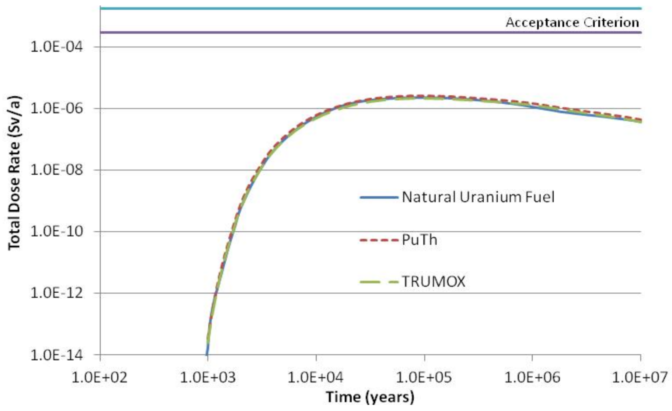

FIGURE 4: Total dose rate, calculated for a non-standard repository containing a quantity of used NU, PuTh or TRUMOX fuel corresponding to the lifetime electricity requirements for the current population of Canada.

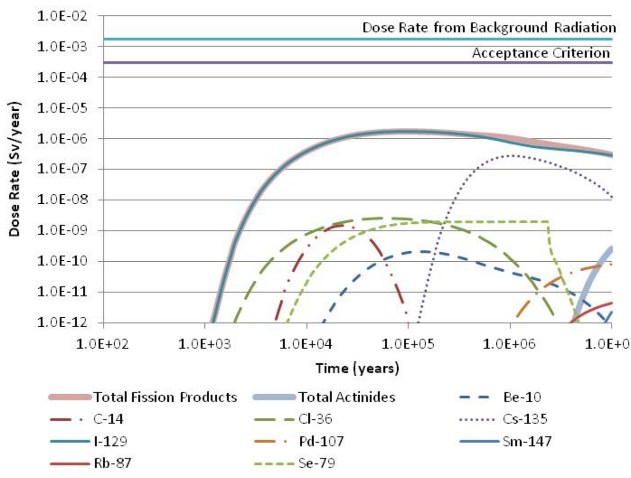

FIGURE 5: Dose rates, calculated per standard repository, for individual radionuclides in used TRUMOX fuel.

Reference DGR conditions. The DGR results for TRUMOX and ThPu are summarized in Table 3 and illustrated in Figures 3 to 6. Figure 3 shows estimated total dose rates versus time. According to the results, the estimated total dose rates produced by the waste generated by advanced fuel, are somewhat higher than the total dose rates estimated for the natural uranium used fuel. The dose rates are higher for TRUMOX fuel compared to PuTh fuel. The maximum dose rate is 5.3 times higher for TRUMOX fuel and 2.6 times higher for PuTh fuel than for the used NU fuel filled DGR. However, even in the higher advanced fuel cases, the total dose rates are well below the natural background level and the acceptance criterion, which is an annual individual effective dose rate of 0.3 mSv/a in accordance with [19] and [20]. It is significantly less than the average Canadian individual dose rate of 1.8 mSv/a received from background radiation [21]. One can therefore conclude that wastes from the advanced fuels, with no further conditioning, will yield acceptable dose rates in the Deep Geological Repository.

The amount of energy that is produced by the TRUMOX and PuTh fuels is 5.6 and 2.3 times greater than that of natural uranium fuel. However, in a Canadian context, the total amount of fuel going into repositories is likely to correspond to that required to produce a specific amount of energy, rather than to a specific fuel mass. This would reduce repository dose rates for the advanced fuels by amounts equal to the ratio of the natural uranium burnup (7.5 MWd/ kg) to the advanced fuel burnups (47 or 20 MWd.kg). Figure 4 shows the dose rate due to a repository containing fuel which has produced the electricity requirement of the whole current Canadian population over their lifespan. In this case, the various maximum dose rates become quite close, about 6% lower for the TRUMOX fuel and 16% higher for the PuTh fuel than for the used NU fuel. The calculated maximum dose rate from this repository remains more than a factor of 100 lower than the acceptance criterion.

Figure 5 and Figure 6 (normalized again by mass, rather than electricity production) show the individual contributions to the total dose rate from the most significant radionuclides for the TRUMOX and PuTh fuels, respectively. It can be seen that in both cases I-129 is the dominant dose rate contributor, followed by Cs-135. This is because I-129 has a sizeable initial inventory, a non-zero IRF, a very long half-life, is non-sorbing in the buffer, backfill and geosphere, and has a significant radiological impact on humans. Other fission products and actinides either decay away, or are released very slowly as the fuel dissolves and are thereafter sorbed in the engineered barriers and geosphere.

The particularly rapid drop-off of Se-79 after ~10^6 years deserves comment. Se-79 has a very low solubility and most of the element released from the fuel matrix remains in the container in an undissolved residue. After approximately 1 million years, the rate of addition to this residue of new Se-79 from the fuel is lower than the dissolution and removal rate

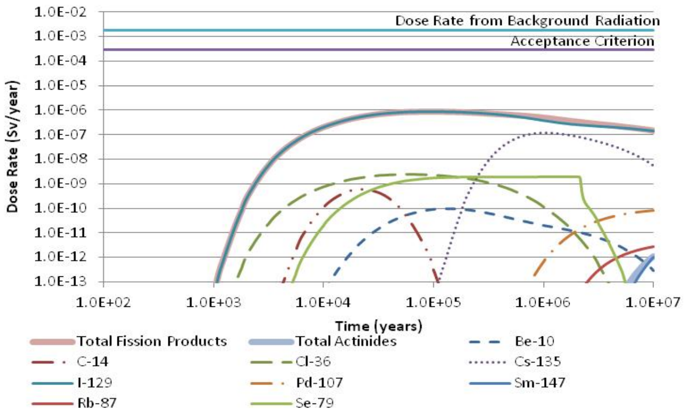

FIGURE 6: Dose rates, calculated per standard repository, for individual radionuclides in used PuTh fuel.

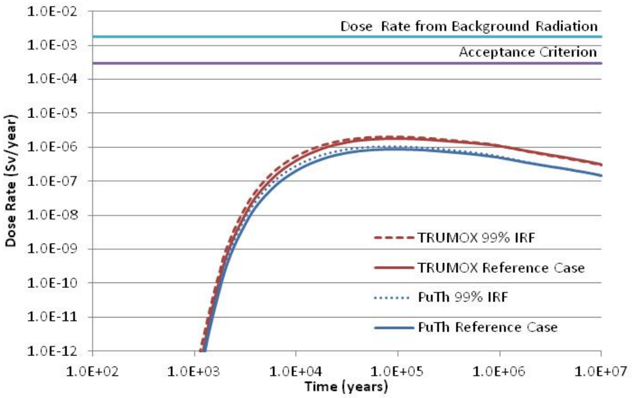

FIGURE 7: Sensitivity of the estimated total dose rates to the instant release fraction values for TRUMOX and PuTh fuels.

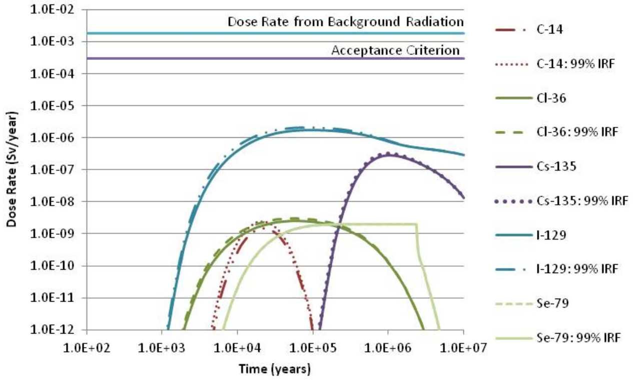

FIGURE 8: Dose rates for individual radionuclides calculated for TRUMOX fuel with the instant release fraction values set highest values at the 99th percentile.

from the container, and the residue starts to disappear. For several hundred thousand years thereafter the dissolution of the residue supports the continued outflow of Se-79 from the container at the earlier rate, but when the residue disappears completely the rate of Se-79 removal drops rapidly to a rate consistent with its removal from the fuel matrix. This effect, a sustained constant output followed by a rapid drop off, arises due to a particular combination of half-life, transport time to the surface and low solubility, and is most pronounced in Se-79 in this study. Over longer timescales, similar behaviour would be seen with some Pu and U nuclides as well. Figure 3 indicates that wastes from the advanced fuels, with no further conditioning, will yield acceptable dose rates in the DGR.

7. Sensitivity of the Results to Instant Release Fractions

A sensitivity study was performed to estimate the effects of varying the IRF on the total dose rate. For the sensitivity case, the IRF values were set to the 99th percentile of the Probability Distribution Function (PDF) for the corresponding radionuclides, while the rest of the case parameters remained the same as for the reference case. The values for the reference case and for the 99% IRF case are presented in Table 2.

The comparison of total dose rates calculated for the reference and the sensitivity cases are shown in Figure 7 for TRUMOX and PuTh fuels. It is clear that an increase in IRF values results in a slight increase in the total dose rates, mostly in earlier times, for both fuels. Nevertheless, even in the worst case, the peak dose rate from all scenarios stays well below the acceptance criterion. The contributions to the total dose rate from the most significant individual radionuclides for the TRUMOX and PuTh fuels are shown in Figure 8 and Figure 9, respectively. Obviously, only radionuclides with a changed IRF were affected. The results for actinides did not change as their IRF is always zero.

As discussed previously, IRF values for thorium-based fuels (such as the ThPu) or very high burnup fuels (such as the TRUMOX) are not available and may be outside the 99th percentile bounds placed upon them in this study.

8. Summary and Conclusions

An initial investigation of the potential impacts of advanced fuels on the post-closure performance of the current hypothetical Deep Geologic Repository for natural uranium CANDU used fuel location and design was conducted. Two fuels, PuTh and TRUMOX, have been considered in this study. The potential radiation dose rates were estimated using RSM110 (Radionuclide Screening Model Version 1.1) and SYVAC3-CC409 (SYstems Variability Analysis Code, version 3.12, Canadian Concept, version 4.09) models.

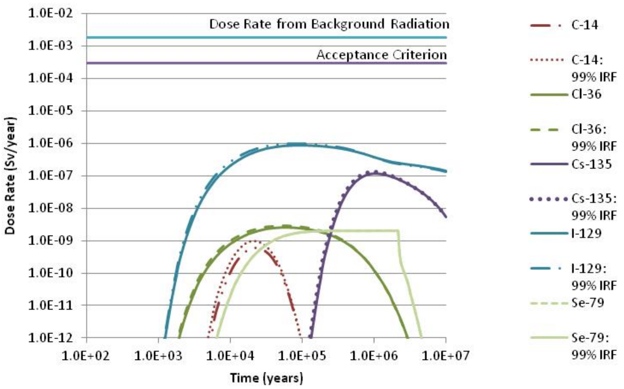

FIGURE 9: Dose rates for individual radionuclides calculated for PuTh fuel with the instant release fraction values set to the highest values at the 99th percentile.

TABLE 3: Maximum Dose Rates Calculated for the TRUMOX, PuTh and Natural Uranium Fuels

Maximum Dose Rate	NU	TRUMOX		PuTh	
	Sv/year	Sv/year	Fuel/NU-1	Sv/year	Fuel/NU-1
For one full DGR	3.32E-07	1.76E-06	+431.5%	8.73E-07	+163.1%
Acceptance Limit	3.00E-04				
Background Radiation	1.80E-03				

Per GWde produced by the used fuel[a]	1.56E-12	1.20E-12	-6%	1.47E-12	+16%%
Per energy production of all fuel stored in the NU repository[b]	3.32E-07	2.55E-07		3.13E-07	
Per entire lifetime electricity consumption for the current population of Canada[c]	2.75E-06	2.11E-06		2.59E-06	
Acceptance Limit		3.00E-04			
Background Radiation		1.80E-03			

[a] assumes a 0.32 electrical efficiency

[b] assumes the same container failure rate as the NU DGR

[c] per capital yearly electricity consumption for Canada is 15145 kWh (2012), [IEA 2012]; average life expectancy is 80.8 years [World Bank, 2013], assumes lifetime consumption at 2012 level; population of Canada is 34,482,779 [World Bank, 2013]; assumes lifetime electricity consumption is 100% nuclear.

The impacts of the advanced fuels were compared to those of NU CANDU fuel. It was found that the radiological dose rates to a critical group of humans living above the repository are larger for the advanced fuels, but still well lower than acceptable dose limits. When normalized to total energy produced (i.e. assuming that the used fuel in any repository corresponds to the same energy production as that in the reference NU repository) the advanced fuels produce comparable or lower total doses. However, this calculation entirely neglects the reduction in dose to future generations which would be achieved by the elimination of LWR fuel repositories in a combined LWR/HWR scenario. Thus the benefits of advanced fuels (such as sustainability) can be obtained and at the same time significantly decreasing repository-derived doses to humans.

IRF is not a well-known parameter for high burnup fuels, fuels with high TRU content, or thorium fuels and could potentially affect the repository design. A sensitivity study was performed to estimate of the effects on the total dose rate of varying the assumed IRF. For radionuclides with a non-zero IRF, these values were increased to the 99th percentile of their probability distribution (for low burnup uranium fuels) while all other parameters remained unchanged. It was found that the IRF values considered in this study have no significant impact on the estimated dose rates to the critical group.

Actinides (such as Th, U, Np, Pu, Am, Cm) are not released quickly from the fuel matrix and are not transported easily to the biosphere. No actinide species were found to be important to the dose rate experienced on the surface. This removes much of the difference between the different fuel types. Virtually the entire dose rate at the surface is due to long-lived fission products which build up in the fuel linearly with burnup. Of these fission products, I-129, which is released quickly if the fuel comes into contact with water, and is also highly soluble, contributes nearly all the dose rate seen on the surface.

9. Future Work

The current work highlights gaps in our knowledge of IRF in advanced fuels. A better understanding and estimation of the IRF for different elements from the advanced fuel wastes, including higher burnups and thorium fuels, would benefit the future performance assessment studies.

Decay heat, and its variation through the repository lifetime, is often a significant parameter affecting design. The effect of the higher decay heat of the advanced fuels has not been studied and it is not known whether this would necessitate a different container design or changes to the repository size or fuel spacing.

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FULL ARTICLE

Groundwater Monitoring and Plume Discharge Zone Characterization for the NRX Radiostrontium Plume at Chalk River Laboratories

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Groundwater is the principal pathway for the migration of most radiological and non-radiological compounds from past and present operating areas at Atomic Energy of Canada Limited's Chalk River Laboratories (CRL). The CRL Groundwater Monitoring Program (GWMP) was established to measure the groundwater quality around the perimeters of areas affected, or potentially affected, by groundwater plumes. One of these is the NRX Rod Bays plume, a legacy plume that originated from the fuel storage bays of the National Research Experimental (NRX) reactor. This plume contains primarily ^{90}Sr migrating along the groundwater flow system to the Ottawa River. A characterization study of the shoreline region was completed recently to map the plume discharge zone by collecting samples from mini-piezometers and groundwater seeps (springs) during a period of low river level. Analysis of discharging groundwaters determined that the ^{90}Sr concentrations were very similar to those sampled from nearby (upgradient) GWMP monitoring wells. With this favorable correlation, the high density of seep and mini-piezometer sampling along the shoreline allowed refinements to be made in defining the northerly and southerly boundaries of the radiostrontium plume. The seep and mini-piezometer sampling also provided evidence that the monitoring wells sampled routinely within the CRL GWMP are positioned appropriately for providing representative sampling of the plume. Shoreline seep and mini-piezometer sampling can lead to refinements in the conceptual site model for plumes with limited effort and cost. The supplemental characterization work can also potentially identify other targets for routine groundwater monitoring.

1. Introduction

Environmental monitoring programs are an integral part of nuclear sites. Due to the complexity of the sites, there are multiple contaminant pathways that need to be monitored. These include airborne and liquid effluents. Groundwater is the principal pathway for the migration of most radiological and non-radiological compounds from past operating areas at Atomic Energy of Canada Limited (AECL)'s Chalk River Laboratories (CRL). The CRL Groundwater Monitoring Program (GWMP) was established to assess and track groundwater quality around and downgradient of facilities that have released, or could release, contaminants to the environment. As part of the GWMP, roughly 180 wells located on land are sampled routinely, with a wide range of physical, inorganic, chemical and radiological parameters collected at each location. These wells are installed at 30 different monitoring sites at CRL: the CRL Waste Management Areas, old landfills and next to nuclear facilities with systems that could release contaminants to the subsurface without prompt in-facility detection. The CRL GWMP is extensive, but it is considered necessary for the size and complexity of the nuclear research site.

Another component of the GWMP at CRL is detailed characterization studies (plume updates) of the contaminant plumes on a set frequency. One of these is the NRX Rod Bays plume, a legacy plume that originated from the fuel storage bays of the National Research Experimental (NRX) reactor. Although a wide range of radionuclides were released from the leaking bays structure, tritium and ^{90}Sr are the only radionuclides that have migrated along the groundwater flow system to the Ottawa River. NRX is currently undergoing decommissioning and the source of the plume has been eliminated. Tritium is now absent, but ^{90}Sr continues to be present in the groundwater plume. Monitoring wells are located approximately 20 to 40 m from the Ottawa River in a transect across the NRX plume and are routinely monitored, but the plume discharge zone in the Ottawa River had not previously been mapped.

For the NRX Rod Bays groundwater plume, one of the monitoring objectives is to track the migration of ^{90}Sr along the groundwater flow system to ensure that radionuclide discharges to the Ottawa River remain at levels that do not pose a human or ecological risk. In order to provide better spatial resolution of discharges to the river, the objectives of this study were: a) to conduct a shoreline investigation using mini-piezometers and seep sampling to map the discharge zone of the NRX plume, and b) compare the results to those obtained by the GWMP from shoreline monitoring wells.

2. Site Location and Hydrogeology

CRL is located on the Ontario side of the Ottawa River, approximately 150 km northwest of Ottawa (Figure 1).

Within the large CRL research site (37 km^2), there is a small built-up region approximately 48 hectares in size on the southwest shore of the Ottawa River where most of the nuclear facilities and supporting infrastructure are located (Figure 2).

The majority of the shore of the Ottawa River in this area is a relatively steep, northeast-facing, bedrock-controlled slope, rising 50 to 70 m above the river. The built-up portion of the CRL site, however, is located in an area where a wedge of unconsolidated sediment about 600 m wide and 2 to 10 m thick has been deposited against the bedrock slope. These sediments are fluvial terraces from higher stages of the Ottawa River, of which there have been several in the last 10,000 years. Bedrock is moderately to highly fractured

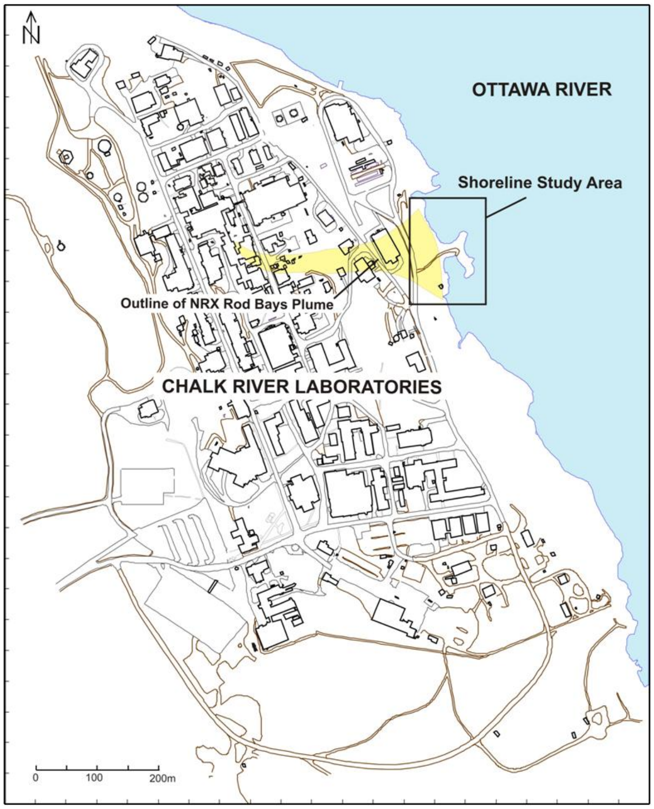

FIGURE 2: Location of NRX Rod Bays plume and shoreline study area.

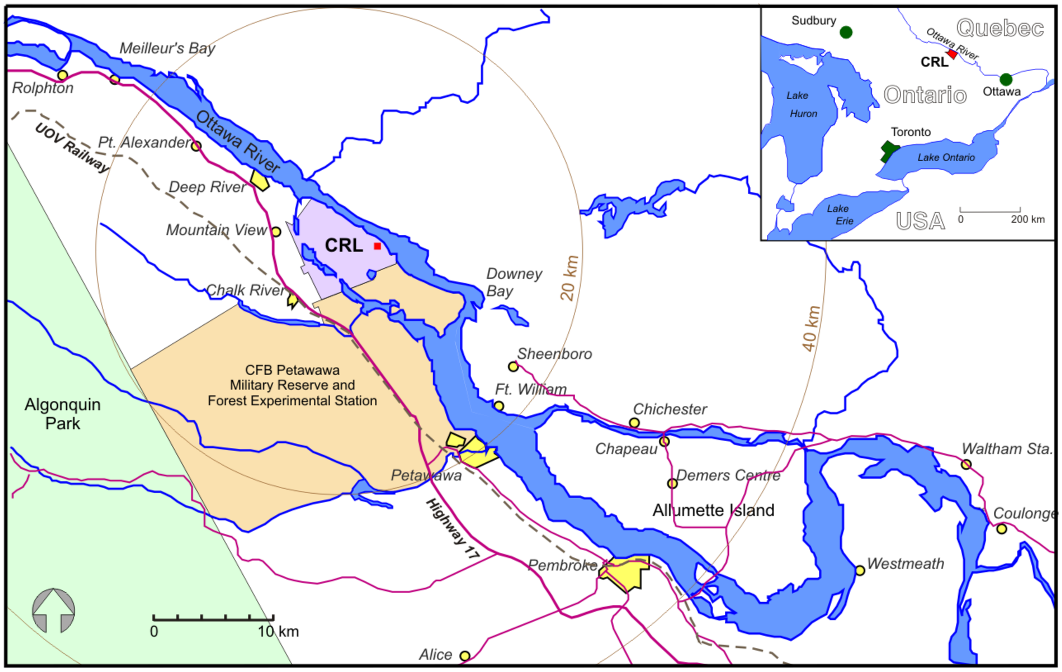

FIGURE 1: Location of Chalk River Laboratories.

crystalline granitic gneiss. Bouldery, sandy, glacial till locally overlies the bedrock and is in turn overlain by fluvial deposits that are predominantly fine sand, but which also feature lenses and strata of silty sand and silt. Development of the CRL site has resulted in the widespread presence of fill (predominantly sand, but locally including coarser granular material) overlying the fluvial deposits.

Groundwater generally flows in an easterly direction from the bedrock ridge that defines the southwestern boundary of the built-up area to the Ottawa River and is maintained by infiltration of precipitation through the permeable surficial sediments. Hydraulic gradients are relatively steep (averaging 0.08) below the built-up area, and the water table is frequently located just above or below the bedrock surface (i.e., most groundwater flow is in the bedrock's fracture network). Near the Ottawa River, where the water table flattens as the bedrock surface continues to fall, shallow groundwater flow is in the unconsolidated fluvial deposits. A groundwater transit time of four years has been defined by the movement of tritiated water along the 330 m flowpath from the facility of particular interest in this paper – the NRX Rod Bays – to the Ottawa River.

3. Groundwater Contamination

Groundwater contamination is present below portions of the built-up area of the CRL site. One example is a well-defined plume of radiological contamination arising from the NRX Rod Bays. The Rod Bays are a linked set of in-ground concrete trenches and tanks that, when the NRX reactor was in operation, were filled with water and used to handle, test and temporarily store irradiated fuel and material from the reactor. The leakage of contaminated water from the NRX Rod Bays was first detected in 1959 shortly after the bay system had been extensively modified. The leak was found at the connection between the original bays and an added section, and a number of efforts over the years were not successful in eliminating the water and contaminant loss. NRX shut down in 1992 and decommissioning activities associated with the reactor began. In 2006, the NRX Rod Bays were completely drained and have remained dry since then, thus eliminating the source of the leak.

Groundwater contamination arising from the NRX Rod Bay leak has been monitored since it began, with the first delineation of the plume completed in 1962 and periodic updates of the entire plume since then. The most recent mapping of the entire NRX Rod Bays plume was undertaken in 2009. In addition to the periodic evaluations of the entire NRX Rod Bays plume, AECL's Groundwater Monitoring Program samples a limited set of wells located near the source and along a transect across the plume near the Ottawa River on a twice-yearly schedule. Although water in the NRX Rod Bays contained a wide variety of radionuclides, only two have exhibited appreciable mobility in the local subsurface. Tritium, present as tritiated water, moves in the subsurface at the speed of the transporting groundwater and as noted above, the clearance of tritium from the flow system following its removal from the bay water in 2000 provides an excellent measure of groundwater velocity in the affected portion of the flow system.

The other radionuclide that is distributed through the flow system between the NRX Rod Bays and the Ottawa River is ^{90}Sr. Strontium interacts with the mineral grains that make up the unconsolidated sediments that the groundwater passes through and with the surfaces of the fractures that provide the flowpaths in the bedrock. There are extensive data on the behavior of ^{90}Sr in the fluvial sediments that are widespread on the CRL site (e.g.[1]), which show that much of the radionuclide moves in a fashion that can be reasonably simulated using the retardation equation, although solution/solid interactions also include kinetically-controlled reactions and some essentially permanent sorption. Radiostrontium movement in fractured bedrock, where solution/solid reactions are limited to the coatings on hydraulically-conductive fracture surfaces, is less well-characterized. Equilibrium exchange sorption, however, which again can be described by a simple retardation equation, does appear to be a major component of ^{90}Sr interactions in the bedrock. In the NRX Rod Bays plume, ^{90}Sr reached the Ottawa River within 10 years of the start of the leak. Although the source was entirely removed in 2006, ^{90}Sr will continue to be present in the flow system for many years into the future due to its long half-life of approximately 29 years and its relatively slow migration in groundwater. Routine monitoring of wells that transect the plume near the Ottawa River have found almost constant ^{90}Sr concentrations over the past 15 years and slow decreases are expected in the future.

In addition to the clearly defined plume arising from the NRX Rod Bays leak, groundwater sampling in other portions of CRL's built-up area has locally encountered very low levels of radiological contamination (frequently below drinking water limits) that are not readily linked to a specific source or easily defined as discrete entities in the groundwater flow system. This contamination, which is again mostly limited to tritium and ^{90}Sr, is attributed to small spills or temporary leaks that have occurred over the site's 70 year history. Various investigations at CRL have sometimes encountered this low-level contamination and the shoreline transect of wells that are routinely sampled provide ongoing tracking of groundwater flowing to the Ottawa River. The spacing of these wells (nominally 50 m) is adequate to provide delineation and temporal trend data for the NRX plume and they also broadly define the zone

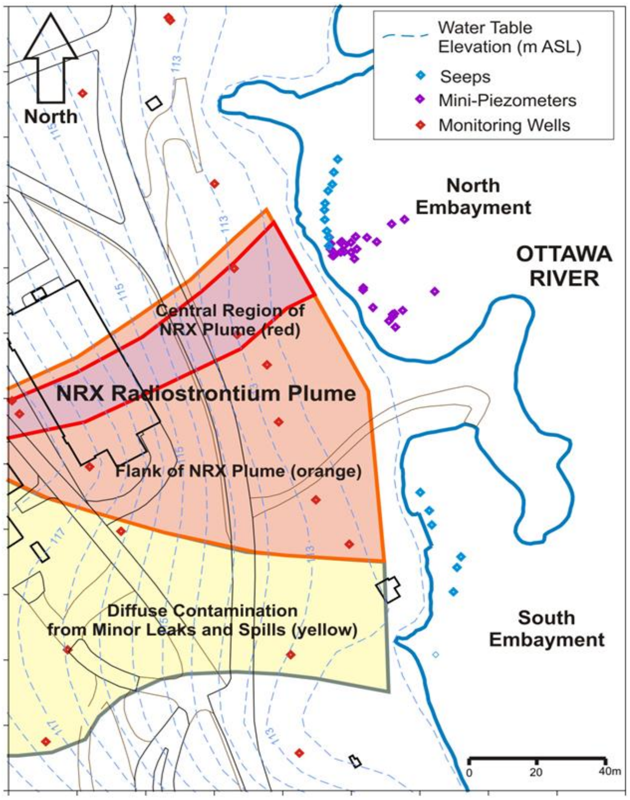

FIGURE 3: A map of sampling locations. The red diamonds show the GWMP sampling wells, the blue diamonds represent the seep sampling locations and the purple diamonds represent the mini-piezometers.

of diffuse, low-level groundwater contamination. More closely-spaced information on the quality of groundwater being discharged to the Ottawa River would, however, be a useful adjunct to the current monitoring program.

Past plume investigations have not directly mapped the discharge zone in the Ottawa River, allowing only a conceptual understanding of this aspect of contaminant migration. The study area is a 160 m length of shoreline of the Ottawa River where many seeps (springs) are present in low river water conditions. The projected discharge zone of the NRX Rod Bays plume exists over much of this region, but the southern section of the study site comprises the shoreline section where groundwater from the region of diffuse, low-level groundwater contamination reaches the Ottawa River.

4. Methods

Figure 3 shows the location of the GWMP wells, the shoreline seeps and the mini-piezometers discussed in this study.

4.1 Groundwater monitoring program sampling and analysis

Within the NRX Rod Bays plume, the contaminant of primary interest is ^{90}Sr. To determine the ^{90}Sr concentration, a volume of water equal to double the well volume was purged and 125 mL of water were collected from each well. The water samples were filtered through 0.45 μm cellulose-acetate filters and preserved with 1 mL of concentrated nitric acid. Up to 125 mL of the sample was evaporated onto a stainless steel planchette and counted for gross beta for 20 minutes per sample after storing the sample for sufficient time to ensure that ^{90}Y, the short-lived progeny of ^{90}Sr, was present in the sample at secular equilibrium. The gross beta analyses were done on a gas flow proportional counter (Oxford-Tennelec LB5100 α/β) calibrated with ^{90}Sr/^{90}Y. Other radiological analyses have confirmed that ^{90}Sr and its daughter product yttrium-90 (^{90}Y) are the dominant contributors to the gross beta measurement at this site and there are no major gamma-emitters detected. Thus, the ^{90}Sr concentration would be equal to half of the gross beta concentration [2]. The results presented in this paper are five-year averages representing 2008 to 2013.

4.2 Plume discharge zone characterization

Mini-piezometers were used to collect groundwater samples [3]. A mini-piezometer consists of a 2 m length of polyethylene tubing with holes approximately 0.3 cm in diameter punched in the bottom 10 cm. The holes are covered with a 0.2 mm nylon screen secured to the tube at either end of the screen with electrical tape. The screen-end of the tubing is plugged to force water to flow into the tube through the screen material. The piezometer is installed in the riverbed with the screen-end in first. A plastic bag is then attached to the other end to collect the discharging groundwater. Thirty-three mini-piezometers were installed in the riverbed throughout and surrounding the area where GWMP data projected the plume to discharge. As shown in Figure 3, the mini-piezometers were installed over an area of about 750 m^2, stretching about 30 m along the shoreline in the North Embayment.

Details on constructing and installing mini-piezometers can be found in Lee and Cherry (1978) [3]. Artesian flow typically resulted in groundwater discharging into the bag. During periods of low water, samples were obtained by pumping the mini-piezometers with a battery-powered peristaltic pump. A 1-L sample of the groundwater was then transferred into a sample bottle.

After sample collection, the groundwater was filtered through a 0.45 μm cellulose-acetate filter and acidified with nitric acid to a final concentration of 1%. Five hundred milliliters of each sample of groundwater were evaporated onto a stainless-steel planchette and fixed with collodion

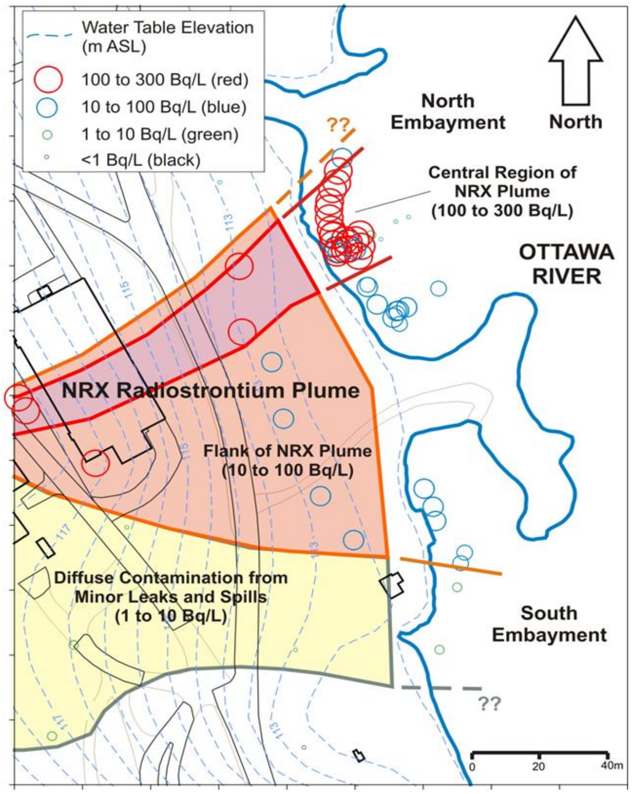

FIGURE 4: Measured and estimated ^{90}Sr concentrations in each sample type. The size of the circles is proportional to the concentration of ^{90}Sr.

(10% collodion, 90% acetone). The planchettes were then counted for gross beta on a Tennelec LB5100 α/β counter. The ^{90}Sr concentration was determined from the gross beta measurement in the same way as described in Section 2.1. The results presented in this paper are three-year averages representing 2010-2013.

During a period of very low river water level in 2012, a strip of shoreline that is normally covered by river water was exposed and seventeen small zones of groundwater seepage discharge were identified along two stretches of the shoreline. Ten seepages were located over a 30 m length of riverbed extending north from the region where the mini-piezometers were installed and a further seven seepages were located along a 50 m reach of riverbed in the South Embayment (Figure 3). At these locations, groundwater samples were collected by digging shallow depressions in the flowing seeps in the sandy shoreline sediment and collecting the water that filled the depression. This sampling was performed during a period of low precipitation to avoid rainfall diluting the discharging groundwater. The seventeen seepage samples were then analyzed for ^{90}Sr as described in Olfert *et al*. (2013) [4].

5. Results

Figure 4 displays the ^{90}Sr concentrations in the groundwater samples collected from the difference sources. The results in Figure 4 are displayed as concentration-proportional symbols, enabling easier examination of spatial trends between the different methods of sampling. Figure 5 shows the actual average concentrations at each sampling location. Both figures show the approximate location of the NRX Rod Bays radiostrontium plume. A summary of the sampling results is provided in Table 1.

5.1 Results of sampling groundwater monitoring wells

As noted, the NRX Rod Bays plume has been subject to detailed characterization studies. The last study was completed in 2009, with one finding being that the radiostrontium plume extending from the bays structure to the Ottawa River did not change appreciably from the previous study conducted in 1997. As documented in the CRL GWMP Annual Report [2], routine (twice-yearly) sampling of wells that transect the downgradient end of the plume near the shoreline show that generally, the concentrations of ^{90}Sr have been reasonably constant for the past 15 years. The plume studies have shown that the plume extends from the source 330 m to the Ottawa River, following a trajectory that is generally perpendicular to water table elevation contours, and is projected to discharge over a width of approximately 120 m (Figure 4, orange outline).

Although the plume appears to widen significantly towards the discharge zone, the highest ^{90}Sr concentrations remain limited to a relatively narrow band (10 to 20 m wide) along much of the flow path. Within this band, (Figure 4, red outline), ^{90}Sr concentrations in the groundwater range between 100 and 300 Bq/L. The presence of this band with higher concentrations suggests that there should be a small area of higher discharge downgradient of this location. Despite the elevated ^{90}Sr in the NRX plume, the annual flux to the Ottawa River is less than 0.005% of the site's release limit and results in no measurable increase in downstream radiostrontium concentrations [5]. South of the central portion of the NRX Rod Bays plume, ^{90}Sr concentrations have averaged between 10 and 100 Bq/L. Further south is a region with ^{90}Sr concentrations in the 1 to 10 Bq/L range. In part, this zone represents the margin of the NRX plume, but part of the contamination in this region arises from the small-scale and scattered releases from other nuclear facilities and buried drain lines that has been observed in up-gradient wells. As noted above, these scattered and episodic releases do not lend themselves to the formation of well-defined plumes, but the ^{90}Sr is slowly advected to the Ottawa River. The existing set of monitoring wells adjacent to the river have appeared to provide adequate data for tracking the

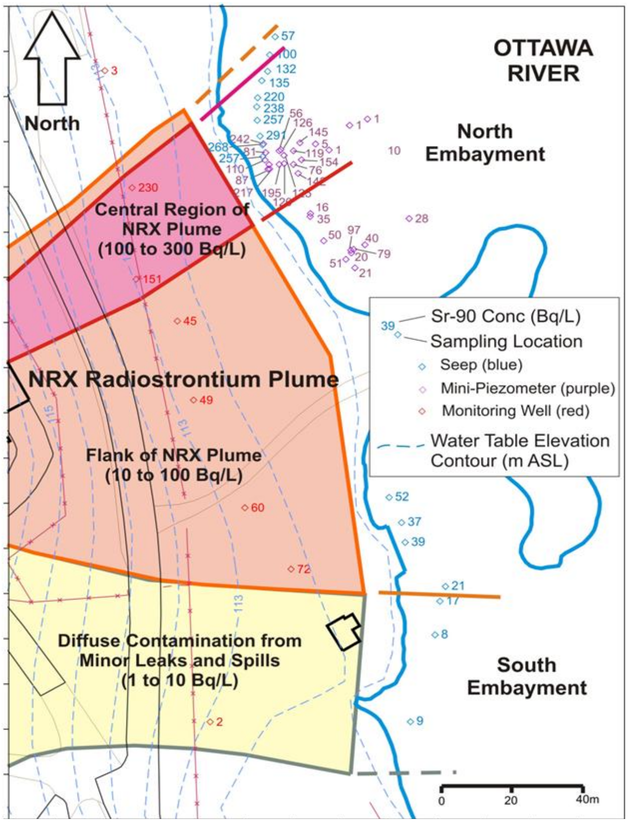

FIGURE 5: Measured and estimated ^{90}Sr concentrations in each sample type.

movement of this diffuse contamination, but higher-density data are always valuable in providing additional assurance that thin zones of appreciably higher contamination are not present. This paper demonstrates that sampling of seeps and mini-piezometers in the groundwater discharge area can be an inexpensive means of generating additional characterization data that can augment the groundwater monitoring conducted in that area. As shown in Table 1 and Figure 5, the data obtained for the NRX plume using mini-piezometer and seep sampling agreed very well with the data obtained from the GWMP, resulting in a larger data set and a better picture of the discharge zone in the Ottawa River.

5.2 Shoreline seep and mini-piezometer results

The gross beta concentrations in the groundwater samples collected from the mini-piezometers ranged from 1.5 Bq/L to 483 Bq/L, equating to ^{90}Sr concentrations of 0.8 Bq/L to 242 Bq/L. The highest concentrations were observed very close to the shoreline (Figure 5), with a marked decrease as the distance from shore increased. This was anticipated, since the hydraulic gradients driving groundwater discharge to a surface water body are highest at the shoreline. The mini-piezometer data show that most of the discharge of the NRX Rod Bays plume occurs within about 12 m of the shoreline, with groundwater ^{90}Sr concentrations beyond this distance dropping to background.

The measured ^{90}Sr concentrations in the seep samples ranged from 58 Bq/L to 291 Bq/L in the North Embayment, and 8 Bq/L to 52 Bq/L in the South Embayment (Figure 5). The highest concentrations in the North Embayment agree very well with those from the mini-piezometer samples in both concentration and location. As shown in Figure 5, seepage samples were also collected further north in the North Embayment, where subsurface conditions prevented the installation of mini-piezometers. Use of the two groundwater discharge sampling methods together enabled extended coverage of groundwater sampling, which was sufficient to fully define the width of the discharge zone of the NRX Rod Bays plume.

The seep sample and mini-piezometer data together indicate that the main portion of the discharge zone of the NRX Rod Bays plume spans approximately 24 m in width within the North Embayment (with ^{90}Sr concentrations ranging between 100 and 300 Bq/L). Mini-piezometer sampling results immediately south of this zone, as well as seep sampling results from the South Embayment, indicate the presence of modest impacts from ^{90}Sr migration (10 to 100 Bq/L typically). Another key observation from the shoreline monitoring is that there were consistent spatial trends in the data on either side of the main part of the radiostrontium plume. This would suggest that the impacts observed in the North Embayment are attributed to the NRX Rod Bays plume, as the plume width broadens towards the discharge zone. Within the seep data from the South Embayment, however, it was possible to identify the southern boundary of the NRX Rod Bays plume, where the

TABLE 1: Summary Comparison of ^{90}Sr Concentrations Among the Different Sampling Locations

Monitoring Region	Sr-90 Concentration (Bq/L)		
	Groundwater	Seeps	Mini-Piezometers
North of NRX Plume	1 to 3	n/a	n/a
Centre of NRX Plume	100 to 230	100 to 300	100 to 240
South Flank of NRX Plume	20 to 100	20 to 50	20 to 100
South of NRX Plume	1 to 10	<10	n/a
Further South of NRX Plume	<1	n/a	n/a

^{90}Sr concentration dropped from roughly 20 Bq/L to less than 10 Bq/L.

As indicated in Figure 3, seeps were not present further south along the shoreline, which would have been beneficial in identifying the southern boundary of the slight impact from leaks from buried services and other nuclear facilities. Other shoreline sampling would also be beneficial in confirming the absence of other radiological impacts along the shoreline, as is the finding of routine groundwater monitoring conducted along the shoreline monitoring wells. In observing the agreement between seep and mini-piezometer sampling, further study of groundwater impacts will be conducted using a systematic array of mini-piezometers installed in this southerly region.

Collectively, the data obtained in the shoreline investigation provided a clear (and independent) evaluation of the NRX Rod Bays Plume's discharge zone in the Ottawa River.

5.3 Comparison of GWMP data to shoreline data

As noted, Figures 4 and 5 display the ^{90}Sr concentrations in the groundwater samples collected from monitoring wells, seeps and mini-piezometers. In Figure 4, the results are displayed as concentration-proportional symbols, enabling easier examination of spatial trends between the different types of sampling. Figure 5 displays actual ^{90}Sr concentrations for a subset of the study area. Table 1 gives a comparison of the ^{90}Sr concentrations between the three sampling types in different regions of the shoreline study area.

As is evident from the comparison, ^{90}Sr concentrations agree well in all regions of the shoreline, particularly near the northern boundary of the NRX Road Bays plume where the highest concentrations are present. What is most evident in the data is the close agreement between the three sets of data both in the spatial trends in ^{90}Sr that they define and in the magnitudes of the concentrations measured. The strong correlations demonstrate the validity of using seeps and mini-piezometers as an additional form of environmental sampling to assist in characterizing the impacts of site operations on the quality of groundwater.

With respect to the spatial characteristics of the NRX Rod Bays radiostrontium plume, the data from the mini-piezometers and seep samples confirms the GWMP finding that there is a relatively narrow area of higher ^{90}Sr concentrations near the northern boundary of the plume. The data from the discharge zone sampling also confirm the GWMP delineations of the northern and southern boundaries of the NRX plume, and the asymmetry inferred from the monitoring well data. The agreement in concentration values also shows that the placement of the GWMP wells is suitable for providing representative samples for routine monitoring of the plume (i.e., refinements to the monitoring network are not required). Although not apparent in Figures 4 and 5, the seeps sampling in the northern and southern extremes of the shoreline study enabled slight refinements to the northern and southern boundaries of the NRX Rod Bays plume. This was the result of the close spacing between the shoreline sampling locations, i.e., a 1 to 3 m interval compared to an interval of 20 to 60 m for the monitoring wells located along the transect 20 to 40 m in from the shoreline. These refinements optimize the plume conceptualization developed from the previous groundwater studies of the plume.

Since seeps were not present north and south of the two embayments, and mini-piezometers have not been deployed in the South Embayment, it is not possible to confirm the groundwater impacts (i.e., the lack thereof) further south along the shoreline. However, the agreements between the results from sampling seeps and mini-piezometers in the North Embayment indicate that an array of mini-piezometers installed along the shoreline in this southerly region could be a low-cost method of providing additional characterization of impacts on groundwater quality.

6. Conclusions

The integration of the GWMP data and the discharge zone investigation data has provided a more complete characterization of the downgradient reach of the NRX Rod Bays radiostrontium plume. The seep and mini-piezometer sampling of the shoreline investigation was conducted in order to complement the plume monitoring provided within the CRL GWMP and address a data gap with respect to the discharge zone of the NRX Rod Bays plume. A comparison of the ^{90}Sr concentrations in groundwater collected from the GWMP wells, mini-piezometers and seep samples showed close agreement between the three sets of data, both in terms of ^{90}Sr concentrations and spatial trends. This not only validates the discharge zone projections made using the GWMP data (i.e., confirming the site conceptual model for the plume), but it provides the first empirical representation of the actual groundwater discharge zone in the Ottawa River. It also confirms that the existing GWMP wells are suitably located within the plume to provide representative routine monitoring of ongoing contaminant migration. This is an important finding from the shoreline investigation and it demonstrates the validity of sampling discharging groundwater in seeps and mini-piezometers as an additional form of environmental sampling to assist in characterizing the impacts of site operations on the quality of groundwater.

As a result of the favorable correlations observed, additional mini-piezometers will be installed along the CRL shoreline both north and south of the segment studied here. Although the data from this study did not define any notable ^{90}Sr discharges that were not identified in the monitoring well network, additional hydrogeologic investigations will be conducted should the extended discharge zone sampling reveal previously unidentified contaminant releases. Further investigation of the sensitivity of seepage zone sampling to short-term precipitation events will also be assessed.

ACKNOWLEDGEMENTS

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FULL ARTICLE

Edibility of Sport Fishes in the Ottawa River near Chalk River Laboratories

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To address the question of edibility of fish in the Ottawa River near Chalk River Laboratories (CRL), 123 game fish were collected for analysis from four locations: Mackey and Rolphton (45 km and 35 km upstream of Chalk River Laboratories (CRL), respectively), the Sandspit (Pointe au Baptême) and Cotnam Island (1.6 km and 45 km downstream of CRL, respectively). Twenty-six to thirty-six game fish were collected at each location in 2007 and samples of flesh or bone were analyzed. Trap nets were used to collect only the fish required, allowing release of management-sensitive species. The focus was on walleye (Sander vitreus) because they are abundant and popular among anglers. A few northern pike (Esox lucius) and a smaller number of smallmouth bass (Micropterus dolomieui) were also collected at three of the four sites. Samples of the fish were analyzed for cesium-137 (^{137}*Cs), strontium-90 (*^{90}*Sr), mercury (Hg), and selected organo-chlorine compounds. Concentrations of *^{137}*Cs in the flesh and *^{90}*Sr in the bones of sport fish were low and similar at all four locations and appear to reflect the global residuals from nuclear weapons testing (primarily in the 1960's) as opposed to releases from CRL. Possible explanations are: 1) Reductions in radionuclide releases from CRL in recent decades and 2) Relatively large foraging ranges of sport fish. Mercury concentrations were elevated in fishes in the Ottawa River and were significantly higher at the Sandspit and Rolphton than at Mackey and Cotnam Island (p<0.001). Mercury concentrations from the four sites are comparable to concentrations in other Ontario and Quebec lakes. It is advisable therefore, that consumers follow the fish consumption guidelines issued by provincial authorities when eating fish from the Ottawa River. Organo-chlorine compounds were not detected in walleye; however, they were detected in all eight of the pike collected at Cotnam Island. The highest organo-chlorine concentrations were measured in two of the three pike collected at Mackey. PCB values were less than the consumption guideline in all fish analyzed.*

1. Introduction

People value lakes and rivers if the water is clean, the fish are safe to eat, and the water is fit for swimming and can be readily disinfected for drinking. Significant historical and natural features exist along the Ottawa River [1] and the upper and middle reaches of the river appear, superficially, to be nearly pristine. Fish are commonly used as indicators of natural system health as they are high in the food web and are eaten by humans. Have activities on the property of Atomic Energy of Canada Ltd. (AECL) at Chalk River Laboratories (CRL) or at Garrison Petawawa influenced the quality of the water and therefore the fish? While analysis of fish is included in the annual environmental monitoring program at CRL, and the conclusion that the fish are safe to eat has been supported year after year [2], the numbers of fish and the collection points have been insufficient for tests of statistical differences in this section of the river.

The governments of Quebec and Ontario analyze few fish for mercury or organo-chlorine compounds in the Ottawa River, and there is a paucity of published data on water and fish quality, especially in the middle and upper reaches of the Ottawa River. Therefore, when questions arise, it is difficult for a member of the public or even a government agency to find data on this section of the Ottawa River. The primary businesses in the middle reach of the Ottawa River are focussed at CRL (nuclear research, isotope production, and decommissioning) and at Garrison Petawawa (military training and readiness). The quality of fish for human consumption bears directly on the food of sport fishers, which is important to local people and to the tourism industry. As AECL occasionally comes under intense scrutiny, it was important to collect larger samples of fish than are collected annually and to collect them at locations that could show changes in fish quality in the study reach.

Based on past analysis of ^{137}Cs concentrations in the flesh of fish collected from the Ottawa River, lower at Rolphton than below CRL (e.g. [2, 3]), we expected small, but statistically significant, increases in the ^{137}Cs concentration in fish flesh below CRL as compared with the flesh of fish upstream of CRL. In 1992, the NRX reactor was shut down and nuclear fuel was no longer in contact with water that re-entered the river. As a result, concentrations of ^{137}Cs in the river downstream of CRL decreased such that only by analyzing a substantial number of fish from upstream and downstream of CRL might it be possible to discern a downstream increase in game fishes.

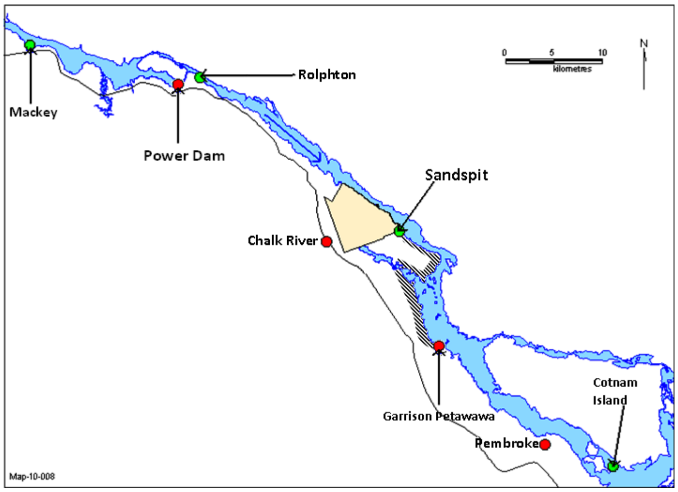

FIGURE 1: Map of the four fish collection sites upstream and downstream of Chalk River Laboratories (CRL) on the Ottawa River (green dots). The property of Atomic Energy of Canada Ltd. is shown in beige colour. Black shading denotes the river waterfront of Garrison Petawawa, downstream of CRL. Upper Allumette Lake is the part of the Ottawa River from the Power Dam to the upstream side of Cotnam Island.

Initially the scope was to analyze only ^{137}Cs and mercury in walleye (*Sander vitreus*) flesh and ^{90}Sr in walleye bone. Strontium-90 concentrates in bone and therefore the skeleton provided a concentrated sample in which lower levels of ^{90}Sr could be detected. Due to the scarcity of data on fish from the middle reaches of the Ottawa River, staff at the Ontario Ministry of the Environment (OMOE), Toronto, volunteered to analyze mercury and their standard suite of 23 chlorinated organic compounds (pesticides, pesticide derivatives, and polychlorinated biphenyl compounds) in the fish we collected to augment their database that forms the basis of the Ontario fish consumption guide [4].

This study was intended to test the hypothesis that human activities in the study reach of the Ottawa River cause measurable changes in contaminants that could affect the edibility of sport fishes. A secondary intention was to initiate collaborative work with provincial ministries and improve the understanding of river-water quality in the study area.

2. Methods

2.1 Rationale for fish collection sites

Approximately 30 fish were collected from each of two sites upstream and two sites downstream of CRL (Figure 1). Collection sites were selected to provide a geographical and statistically meaningful examination of fish quality that might be attributed to CRL operations. This work would also supplement routine sampling and analysis of fish [2]. If there were variations in the radionuclides, chlorinated organic compounds, and mercury in the river along the study length, the location where the fish were caught could indicate the source. For example, if fish contained significantly elevated levels immediately downstream of CRL, as compared with fish caught above the power dam at Rolphton (Rapides Des Joachims), then CRL would be identified as a source.

The upstream control was at Mackey, approximately 45 river kilometres above CRL and above the 40-m-high power dam, which acts as a barrier to fish migration. Two sampling locations below the power dam, Rolphton and the Sandspit, were located in Upper Allumette Lake. A fourth sampling location was located on the downstream side of Cotnam Island, which is just below Allumette rapids. All but the Mackey site were, from a fish's point of view, separated only by distance, and distance is only a partial barrier to fish movement. The Rolphton collection was netted just downstream of the tailrace of the power dam, a popular fishing area, 30 km upstream of CRL.

The Sandspit, 1.6 km downstream of CRL, on the Ontario side of the river, was selected as the most likely place to

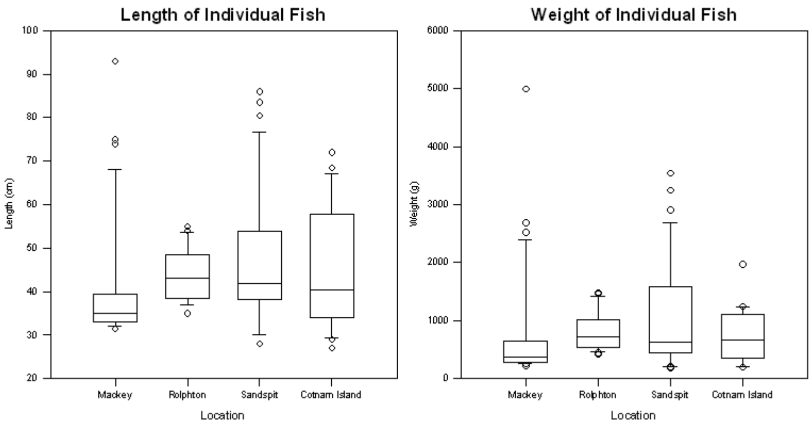

FIGURE 2: Box and whisker graphs showing the data on the lengths and weights of the fish collected in this study.

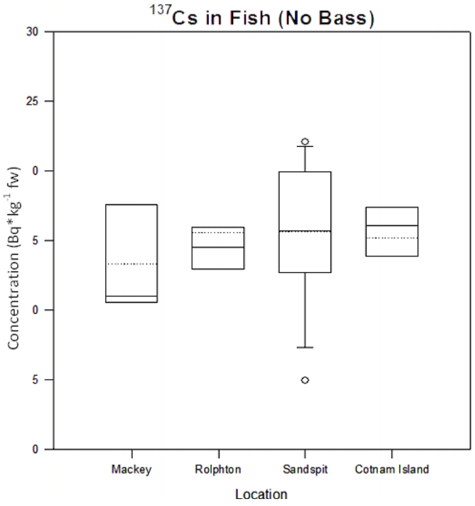

FIGURE 3: Box and whisker graph showing the concentration of ^{137}Cs in fish at the four sampling locations.

detect effects due to CRL. Although vertical mixing of CRL cooling water effluent is complete by the time the water reaches the Sandspit, transverse mixing (and dilution) is incomplete, and therefore any substances from CRL will be more concentrated near the Ontario shore, until the water leaves the 45-m-deep, 7-km-long basin between CRL and the narrows, 8 km downstream [5]. Perch Creek, which carries water from the majority of the CRL waste management areas, enters the river between the CRL cooling water discharge and the Sandspit. Therefore, CRL's releases are not diluted into the entire cross-section of the river until it is several kilometres downstream of the Sandspit. Sediments upstream of the Sandspit, in water 10 to 30 m deep, adjacent to the built-up area of CRL, contain above-background concentrations of radioactivity [6]. This area of sediment extends from the cooling-water discharge of CRL more than 400 m downstream toward the Sandspit. The principal isotopes in the sediment are ^{137}Cs and ^{90}Sr. The only liquid releases from CRL that would not be present in the river at the Sandspit are the relatively smaller amounts that enter the river via Sturgeon Lake approximately 13 km downstream of CRL.

Fish were also collected downstream of Cotnam Island in Lower Allumette Lake. Fish tagging and telemetry have shown limited downstream movement of walleye from Upper Allumette Lake through the Allumette Rapids to the downstream side of Cotnam Island [7, 8]. Walleye, in which a radio transmitter had been surgically implanted, were observed moving over 68 km in Upper Allumette Lake and its tributaries [7]. The tracking studies also showed that walleye have a strong tendency to travel upstream rather than downstream [7, 8]. Of the 12 walleye tracked in Upper Allumette Lake (May 1997 to January 2000), none were observed below the Allumette Rapids [7]. Of the 591 walleye tagged in Upper Allumette Lake, 84 were recaptured in Upper Allumette Lake and none were recaptured in Lower Allumette Lake [8]. While downstream migration of walleye through Allumette Rapids could occur, the tracking studies suggested that Cotnam Island walleye are somewhat separated from the walleye in Upper Allumette Lake, at the Rolphton and Sandspit collection sites.

2.2 Fish collection

Trap nets, as opposed to gill nets, were used so that only the fish that were needed were kept and all by-catch was released. It was especially important to release lake sturgeon (*Acipenser fulvescens*), as they are a protected species. At each of the four sites, the 6 ft by 6 ft trap-net box (Near-shore Community Index Nets, Superior Net & Twine Co.) was set offshore and fish were deflected to the box by a 150 ft. lead, which was anchored in shallower water near

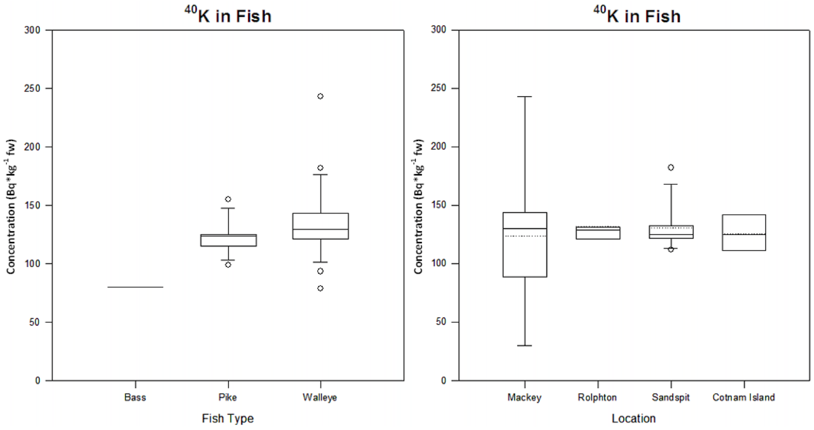

FIGURE 4: Box and whisker graphs of ^{40}K by fish species and by sampling location.

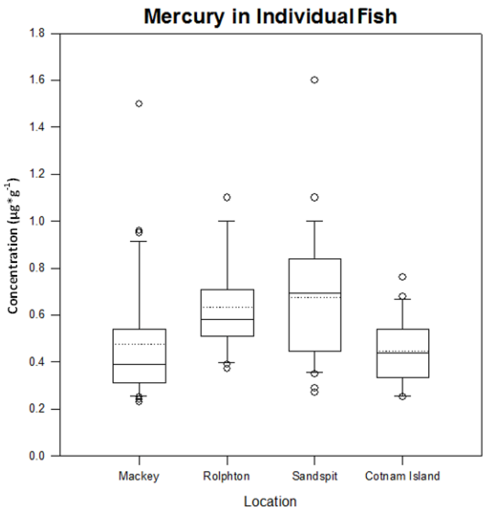

FIGURE 5: Mercury concentration in fish at the four sample locations.

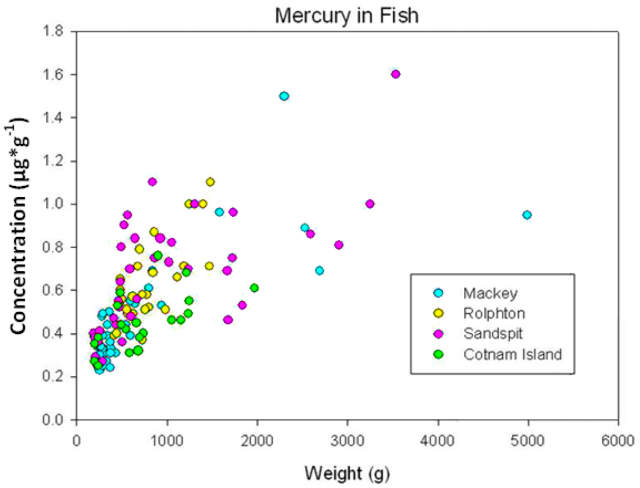

FIGURE 6: Mercury concentration versus weight in fish at the four sample locations.

the shore in accordance with a provincial fish collection permit. Fish were collected in 2007 over a two-month period, 28 August to 25 October.

2.3 Analytical methods for radionuclides, mercury, and organo-chlorine compounds

Skinless, boneless fillets of dorsal flesh from each fish were used for analysis of all contaminants except ^{90}Sr, which was analyzed using the bones of the walleye. Analyses were conducted on individual fish with few exceptions as described below. Gamma spectral analysis was completed on four grams of ashed fish flesh, using a high purity Germanium detector that had been calibrated for the detection of common environmental and anthropogenic nuclides. Throughout the process, sample weights were recorded such that the final results are expressed as Bq*kg^{-1}, fresh weight (fw), which is equivalent to wet weight (ww).

Entire vertebral columns of six walleye from each of the four sites were steamed and carefully cleaned of non-boney material with two hours of effort per fish. The bones were dried, weighed, and ashed at 450 °C. Two of the samples of ashed bone were tested at CRL, but the levels of ^{90}Sr were below the limit of detection. The remaining 22 samples of fish bone were shipped to Kinectrics, Inc. (Toronto, Ontario) for low-level ^{90}Sr analysis. At Kinectrics, the ashed bone was dissolved in strong acid and separated radio-chemically by chemical trapping using Sr-specific resin, followed by elution of Sr and in-growth of ^{90}Y, which was measured in a gas-flow proportional counter. Potassium-40 (^{40}K) was determined by gamma spectrometry.

The suite of persistent organic compounds that are part of the Ontario Sport Fish Monitoring Program of the OMOE include DDT (and metabolites), DDE (a primary metabolite), DDD, poly chlorinated biphenyls (PCBs), organo-chlorines (OCs), chloro-benzenes (CBs), and mercury (Hg). Analysis was performed in the Toronto Lab by staff of the Ontario Ministry of Environment, using cold vapour flameless atomic absorption spectroscopy for mercury analysis [9] and gas liquid chromatography-electron capture detection for determination of organo-chlorine compounds [10]. Four DDT compounds (o,p'-DDT; p,p'-DDD; p,p'-DDT; p,p'-DDE) have a detection limit of less than 2 ng*g^{-1}. The OMOE lab also measured total DDT and metabolites, which is the sum of the above organo-chlorine compounds [10].

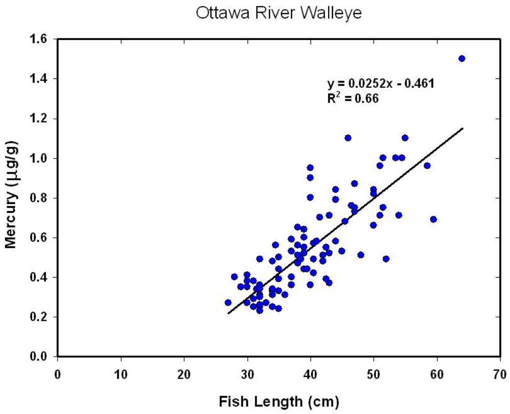

FIGURE 7: Mercury concentration versus length for walleye at all four sampling locations.

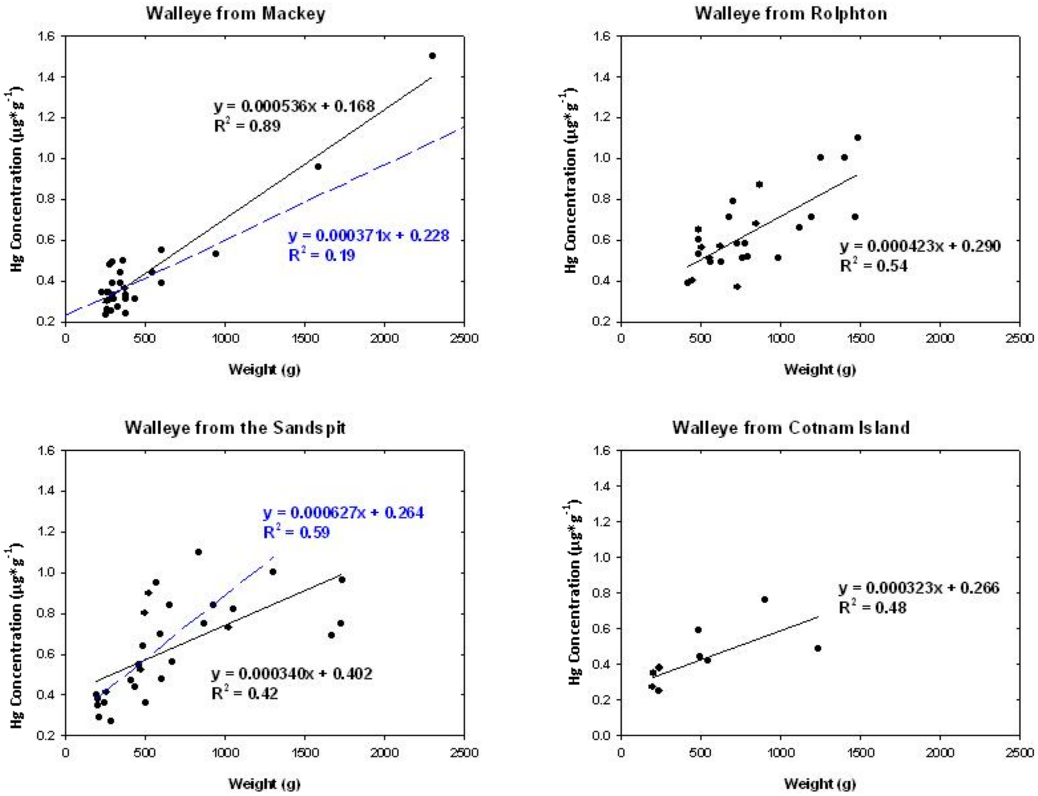

FIGURE 8: Mercury concentration versus weight for walleye at each of the four sample locations.

2.4 Statistical analysis

Statistical tests on the concentrations of substances in fish at the four locations were broken down into two steps. The first step determined if there was a difference in the concentrations of the substance within the three species collected. If there was no statistical difference, then concentrations from all fish species were used when looking for statistical differences of the substance at the four locations. If the concentrations of the substance in one species were found to be statistically different from the concentrations in the others, then values for that species were not used when doing the comparison at the four locations. As differences were being looked for in random samples from more than two groups that cannot be attributed to random sampling variations, Analysis of Variance (ANOVA) was used for comparisons. The sample data was examined using the Shapiro-Wilk test, to determine whether or not the underlying population distributions were likely to be normal, and the Levene Median test, to determine if the group variances were equal [11]. If the samples were drawn from normally distributed populations and the group variances were statistically equal, then the parametric One Way ANOVA test was used to compare the group means. Otherwise, the non-parametric Kruskal-Wallis ANOVA on Ranks (K-W ANOVA) test was used to compare the groups [12]. If the ANOVA test returned a probability (p-value) greater than 0.05, it was concluded that there was no statistically significant difference between the groups being compared. However, if the p-value was less than or equal to 0.05, then there was a statistically significant difference between the groups and a post hoc test was necessary to define that difference. For parametric data, the Holm-Sidak test [13] was used for all pairwise comparisons of the means. For non-parametric data, Dunn's test [12] was used for all pairwise comparisons of the ranks.

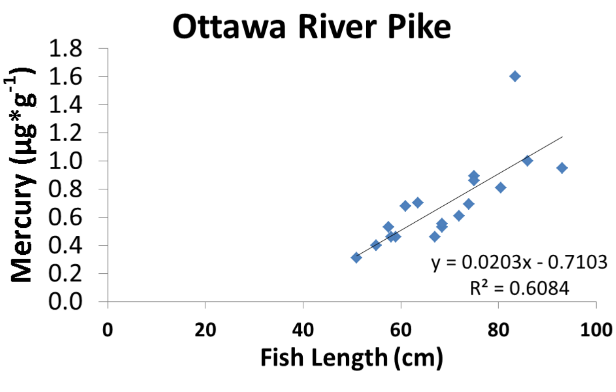

FIGURE 9: Mercury concentration versus length of pike.

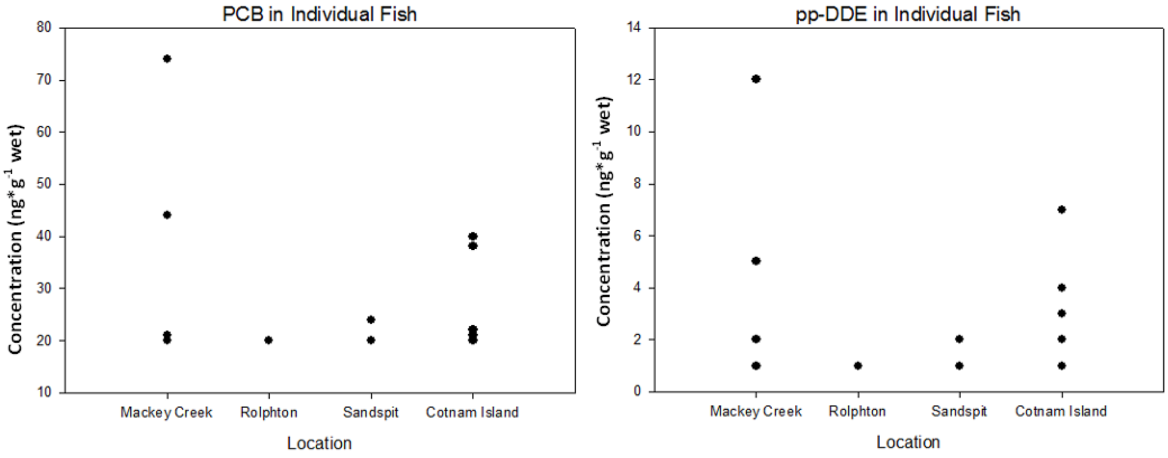

FIGURE 10: PCB and p, p'-DDE concentrations in individual fish at the four sample locations.

"Box and whisker" plots were used to show the results graphically. The lower boundary of the box indicates the 25th percentile and the upper boundary represents the 75th percentile. A solid line within the box shows the median and a dotted line marks the mean. At least nine data points are required to show the error bars (whiskers) above and below the box, which indicate the calculation of 90th and 10th percentiles, respectively. Points outside the 10th and 90th percentiles are shown as circles.

If a substantial change in fish quality occurred in the series of sampling locations, then a box and whisker diagram could illustrate the change. For example, if a substance, entering the river at CRL, were detected in the fish at higher concentrations at the Sandspit but not at Mackey and at intermediate concentrations at Rolphton and with some dilution of concentration in the fish at Cotnam Island (45 km downstream of CRL, Figure 1), this could be clearly illustrated by a box and whisker diagram of the data.

3. Results

3.1 Fish collection

A total of 98 walleye were collected at each of the four study locations (Table 1). Walleye length varied from 27 to 64 cm and weight varied from 190 to 2300 g. A total of eighteen northern pike were caught at Mackey, the Sandspit, and Cotnam Island; however, no pike were caught at Rolphton. The pike varied from 51 to 93 cm in length and from 452 to 4993 g in weight. A total of seven smallmouth bass were caught at Mackey and Cotnam Island. These fish varied from 33 to 40 cm in length and from 482 to 840 g in weight (Table 1). Figure 2 shows the variety of lengths and weights of fish collected. These sizes of fishes are typical of the fish caught and consumed by people in this reach of the Ottawa River. It should be noted that Rolphton was the only study location in which the fish collected were of similar size.

TABLE 1: Summary of Numbers, Lengths, and Weights of Fish from each Sampling Location

Location	Parameter	Species			Total Number
		Northern Pike	Smallmouth Bass	Walleye	
Mackey	Number	3	4	28	35
	Length (cm)	74 - 93	33 - 39.5	31.5 - 64	
	Weight (g)	2527 - 4993	482 - 840	230 - 2300	
Rolphton	Number			26	26
	Length (cm)			35 - 55	
	Weight (g)			416 - 1480	
Sandspit	Number	7		29	36
	Length (cm)	63.5 - 86		28 - 59.5	
	Weight (g)	1238 - 3538		190 - 1735	
Cotnam Island	Number	8	3	15	26
	Length (cm)	51 - 72	36 - 39	27 - 52	
	Weight (g)	452 - 1971	662 - 702	196 - 1237	
Overall	Number	18	7	98	123
	Length (cm)	51 - 93	33 - 39.5	27 - 64	
	Weight (g)	452 - 4993	482 - 840	190 - 2300	

TABLE 2: Summary of ^{137}Cs Concentrations ($Bq*kg^{-1}$ fw) in Fish Flesh

Location	Parameter	Species			Total Number
		Northern Pike	Smallmouth Bass	Walleye	
Mackey	Number	3	1	5	9
	Length (cm)	74 - 93	36.75	32.6 - 64	
	Weight (g)	2527 - 4993	691	276 - 2300	
	^{137}Cs ($Bq*kg^{-1}$ fw)	10.5 - 11.1	1.69	10.5 - 18.4	
Rolphton	Number			8	8
	Length (cm)			37.56 - 54	
	Weight (g)			492 - 1468	
	^{137}Cs ($Bq*kg^{-1}$ fw)			12.3 - 25.6	
Sandspit	Number	5		8	13
	Length (cm)	66.3 - 86		30.7 - 59.5	
	Weight (g)	1586 - 3538		282 - 1735	
	^{137}Cs ($Bq*kg^{-1}$ fw)	11.3 - 22.1		4.97 - 21.3	
Cotnam Island	Number	4	1	3	8
	Length (cm)	54.5 - 72	37.3	33.6 - 49.25	
	Weight (g)	590 - 1971	682	321 - 1069	
	^{137}Cs ($Bq*kg^{-1}$ fw)	13.9 - 19.2	9.28	9.28 - 17.4	

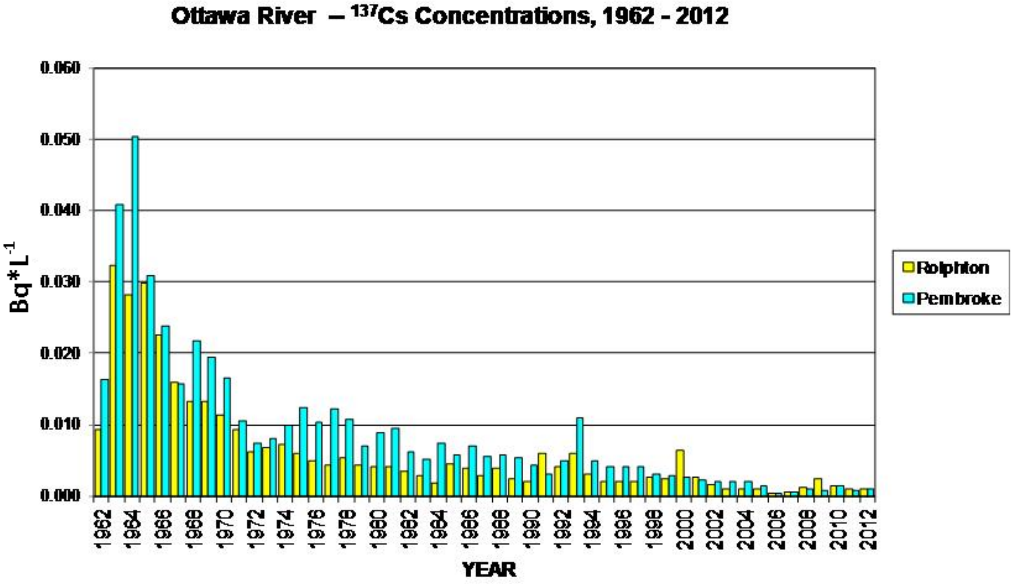

FIGURE 11: Annual average concentration of ^{137}Cs in the water of the Ottawa River upstream (Rolphton) and downstream (Pembroke) of CRL from 1962 – 2012.

3.2 ^{137}Cs in fish flesh

Flesh of the smaller fish had to be combined to provide enough mass for low-level radionuclide analysis. Table 2 shows the groups analyzed for each species at each location and the range of ^{137}Cs values. Based on parametric One Way ANOVA, the concentration of ^{137}Cs was significantly lower in bass (p=0.013) than the concentration of ^{137}Cs in either pike or walleye. No significant difference was found in the concentration of ^{137}Cs in walleye compared to the amount in pike.

Figure 3 shows the box and whisker plots for ^{137}Cs in fish flesh of pike and walleye at the four sites. Although there were wider variations at the Sandspit data as compared with the other sites, there was no significant difference (One-Way ANOVA p=0.621) in the concentration of ^{137}Cs in fish from these four locations.

3.3 ^{40}K in fish flesh

Potassium-40 (^{40}K) is the dominant natural radionuclide in most aquatic systems and its biological behaviour is similar to that of cesium, especially in soft waters such as the Ottawa River [3]. Concentrations of ^{40}K (Table 3) were approximately 25 times greater than the concentrations of ^{137}Cs in Ottawa River fish (cf. Figures 3 and 4). The non-parametric ANOVA on Ranks test found no significant difference in the amount of ^{40}K in the fish flesh of the three fish species, and differences in the concentration of ^{40}K at the four locations were not significant (p=0.924) (Figure 4). There was a wider range of ^{40}K concentration in fish collected at Mackey as compared to the other sites (Table 3, Figure 4).

3.4 ^{90}Sr in walleye bone

The vertebrae of 22 walleye were analyzed for ^{90}Sr in the hope that this nuclide could be used to identify specific fish that foraged longer than other fish, near the Sandspit. However, the results revealed low concentrations at all four sites (Table 4). Although the average value at the upstream location (Mackey) was somewhat elevated, the statistical analysis showed no difference (p=0.26) in the ^{90}Sr values between the four locations. As the upstream values of ^{90}Sr at Mackey were equal to or greater than the other sites, it appears that most, if not all, of the ^{90}Sr measured in fish bone has come from global thermonuclear weapons testing rather than a specific source of ^{90}Sr in this section of the Ottawa River. As the ^{90}Sr concentrations were low and not different among the sites, analysis of ^{90}Sr in fish flesh was not performed.

3.5 Mercury

A total of 118 mercury measurements were made. As the ten small walleye from Cotnam Island, which were available for mercury analysis, did not contain enough mass for individual mercury analysis, they were paired to make five composite samples. The average mercury concentration in the flesh of game fish in this study, across all sizes and species, was 0.571 μg*g^{-1}. This is comparable to the average mercury values in game fish across the Province of Ontario, which, in 2007, amounted to 0.613 μg*g^{-1}. The provincial average for walleye in 2007 fell from 0.613 to 0.609 μg*g^{-1}, when the 118 values from this study were added to the provincial dataset. The consumption guideline for sport fish in Ontario [4] gives values of <0.61 μg*g^{-1} and

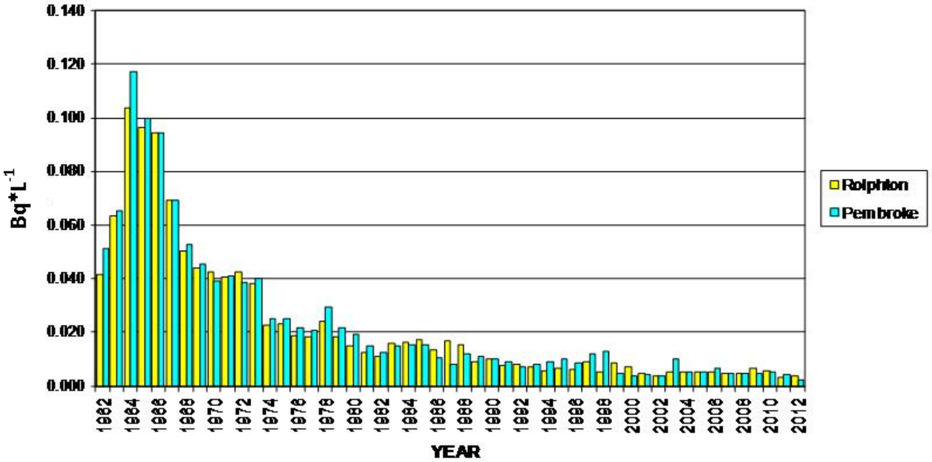

FIGURE 12: Annual average concentration of ^{90}Sr in the water of the Ottawa River upstream (Rolphton) and downstream (Pembroke) of CRL from 1962 – 2012.

<0.26 μg*g^{-1} of mercury for unrestricted consumption of fish by the general and sensitive populations, respectively and >1.84 μg*g^{-1} and >0.52 μg*g^{-1} of mercury for the "do not eat" criteria for consumption of sport fish. Most of the mercury values for Ottawa River fish fell in the range 0.3 to 1.0 μg*g^{-1}, and this is consistent with the levels found in Ontario and Quebec fish [14 - 19].

Average values of mercury do not explain the situation properly because the concentration of mercury in a fish depends upon fish size [4], age, food and surface-water concentrations. The action of anaerobic microbes in the sediment and bioaccumulation in the food chain caused the concentration of mercury in 70-cm pike to increase by a factor of 3 to 7 within a decade after soils within hydroelectric reservoirs were flooded in Quebec [19].

TABLE 3: Summary of ^{40}K Concentrations (Bq*kg^{-1} fw) in Fish Flesh

Location	Parameter	Species			Total Number
		Northern Pike	Smallmouth Bass	Walleye	
Cotnam Island	Number	4	1	3	8
	Length (cm)	54.5 - 72	37.3	33.6 - 49.25	
	Weight (g)	590 - 1971	682	321 - 1069	
	^{40}K (Bq/kg fw)	119 -155	131	93.6 - 145	
Mackey	Number	3	1	5	9
	Length (cm)	74 - 93	36.75	32.6 - 64	
	Weight (g)	2527 - 4993	691	276 - 2300	
	^{40}K (Bq/kg fw)	99.1 - 130	29.9	78.7 - 243	
Rolphton	Number			8	8
	Length (cm)			37.56 - 54	
	Weight (g)			492 - 1468	
	^{40}K (Bq/kg fw)			115 - 171	
Sandspit	Number	5		8	13
	Length (cm)	66.3 - 86		30.7 - 59.5	
	Weight (g)	1586 - 3538		282 - 1735	
	^{40}K (Bq/kg fw)	112 - 125		120 - 182	

Mercury analysis showed large differences between minimum and maximum values for all three species (Table 5). The non-parametric K-W ANOVA test was used to compare the mercury concentrations in the three fish species and no significant difference (p=0.072) was found.

Figure 5 shows the box and whisker plots for mercury in the flesh of all game fishes collected at the four sites. This figure combines the data for the majority of fishes that are consumed by people in this reach of the Ottawa River. The non-parametric K-W ANOVA test was used to compare the mercury concentrations from all species of fish collected at the four locations. A significant difference (p<0.001) was found. Mercury concentrations in fish collected at Mackey and Cotnam Island were similar to each other and were significantly lower than the mercury concentrations in fish collected at Rolphton and the Sandspit, which were also similar to each other (Dunn's Test). This result may indicate a source of mercury in the Rolphton/Sandspit section of the river in Upper Allumette Lake that causes the small, but statistically significant, elevation in the levels of mercury in the fish of this reach of the Ottawa River. CRL, Garrison Petawawa, or a municipality could be a contributor.

TABLE 4: Summary of ^{90}Sr Concentrations (Bq*g^{-1} Dry Weight) in Walleye Bone

Location	N	Minimum (Bq/g dw)	Maximum (Bq/g dw)	Average (Bq/g dry dw)
Mackey	6	0.072	0.110	0.092
Rolphton	6	0.061	0.102	0.073
Sandspit	5	0.022	0.095	0.072
Cotnam Island	5	0.051	0.093	0.072

Figure 6 shows the increase in mercury concentration of fish is related to increasing weight. This is the reason that the fish consumption guideline [4] recommends people eat fewer larger fish or, for sensitive groups of people and for some water bodies, no large fish in many water bodies.

3.5.1 Walleye

The mercury concentration in walleye varied from 0.23-1.5 µg*g^{-1} (Figure 7). As has been noted previously, e.g. [16, 20], a linear relationship exists between log (length of fish) and log (Hg concentration). In this study, the logarithmic relationship was found to be log (Hg) = 0.56*log (length) - 1.83 with R^2=0.73, and the linear relationship, as nearly as good, (Figure 7): Hg = 0.0252*length - 0.461, with R^2 = 0.66. As expected, there was also a linear relationship between log (weight of fish) and log (Hg concentration). Mercury concentration versus length of walleye at each of the four locations combined (Figure 7) shows that 49-cm-long walleye in this section of the Ottawa River had a Hg concentration of approximately 0.77 µg*g^{-1} ww. This is consistent with a mean value of 0.759 µg*g^{-1} ww for 49.4 cm walleye in northeastern North America [15].

Figure 8 has solid lines showing the regressions on all the available walleye data. The R^2 values are low due to the large variation in the data. The forms of the regression equations for all four sites were statistically significant (Mackey, Rolphton, and the Sandspit p<0.001; Cotnam Island p= .026). Solid lines on the Mackey and Sandspit graphs show the regression for all data at those sites. Dashed lines on the Mackey and Sandspit graphs show the regression lines with the three largest fish removed from each of the two data sets.

The y-intercept for Mackey (0.168 µg*g^{-1}) was lower than that for the other sites; conversely, the y-intercept for the Sandspit (0.402 µg*g^{-1}), was marginally higher than the other sites (Figure 8). These two sites happened to have three fish larger than 1.5 kg, whereas the other two sites did not. The dashed lines shown on the Sandspit and Mackey plots are regressions on the data *without* the three heaviest fish. Without the three largest fish, the intercepts of these regressions became quite similar to what was found in fish collected at Rolphton and Cotnam Island. This shows how a few unusually large fish and the small size of the collection can influence an interpretation. The p values for the intercepts were still <0.001. The new regression equations were statistically significant (Mackey p=0.029; the Sandspit p<0.001).

Note the scatter in the Hg concentration in fish of a given weight (Figure 8). Because the fish in this study were not aged, we were unable to relate age differences to contaminant concentration, as had been done previously [21]. Where there were a number of fish in the same weight range, the regression equation was likely accurate. However, at larger weights, there were fewer fish and therefore there is more uncertainty in the average Hg concentration in the larger fish. Being at the end of the x-axis range, the larger weights shifted the regression line, thus having a large effect upon the values of the slope and intercept. While the sample sizes were far too small to reach robust conclusions, the results of this study were consistent with the fact that larger fish have higher mercury content. Analysis of more fish in a narrower size range at each site could yield a more detailed examination of slope and intercept for the mercury versus fish size regressions at each site.

TABLE 5: Summary of Mercury Concentrations (µg*g-1 ww) in Fish Flesh

	All Species	Northern Pike	Smallmouth Bass	Walleye
Number	118	18	7	93
Average	0.57	0.69	0.49	0.55
Standard Deviation	0.25	0.30	0.13	0.24
95% UCLM	0.61	0.83	0.59	0.60
90th Percentile	0.92	0.97	0.64	0.89
Minimum	0.23	0.31	0.32	0.23
Maximum	1.60	1.60	0.69	1.50

TABLE 6: Summary of Chlorinated Organic Compounds (µg*g^{-1} ww) in Fish Flesh

Location	Parameter	Species			Total Number
		Northern Pike	Smallmouth Bass	Walleye	
Mackey	Number	3	4		7
	Length (cm)	74 - 93	33 - 39.5		
	Weight (g)	2527 - 4993	482 - 840		
	DDT & Metabolites (ng*g^{-1} ww)	<2 – 12 (1)	<2 – 5 (1)		
	p,p'-DDE (ng*g^{-1} ww)	<1 – 12 (2)	<1 – 5 (1)		
	PCBs (ng*g^{-1} ww)	<20 – 74 (2)	<20 – 44 (1)		
Rolphton	Number			5	5
	Length (cm)			51 - 55	
	Weight (g)			1191 - 1480	
	DDT & Metabolites (ng*g^{-1} ww)			<2 (0)	
	p,p'-DDE (ng*g^{-1} ww)			<1 (0)	
	PCBs (ng*g^{-1} ww)			<20 (0)	
Sandspit	Number	7			7
	Length (cm)	63.5 - 86			
	Weight (g)	1238 - 3538			
	DDT & Metabolites (ng*g^{-1} ww)	<2 (0)			
	p,p'-DDE (ng*g^{-1} ww)	<1 – 2 (3)			
	PCBs (ng*g^{-1} ww)	<20 – 24 (1)			
Cotnam Island	Number	8	3		11
	Length (cm)	51 - 72	36 - 39		
	Weight (g)	452 - 1971	662 - 702		
	DDT & Metabolites (ng*g^{-1} ww)	<2 – 7 (4)	<2 – 3 (1)		
	p,p'-DDE (ng*g^{-1} ww)	2 – 7 (8)	<1 – 3 (2)		
	PCBs (ng*g^{-1} ww)	<20 – 40 (5)	<20 (0)		
Overall	Number	18	7	5	30
	Length (cm)	51 - 93	33 – 39.5	51 - 55	
	Weight (g)	452 - 4993	482 - 840	1191 - 1480	
	DDT & Metabolites (ng*g^{-1} ww)	<2 – 12 (5)	<2 – 5 (2)	<2 (0)	
	p,p'-DDE (ng*g^{-1} ww)	<1 – 12 (13)	<1 – 5 (3)	<1 (0)	
	PCBs (ng*g^{-1} ww)	<20 – 74 (8)	<20 - 44 (1)	<20 (0)	

3.5.2 Northern pike

Mercury concentration in the flesh of the pike ranged from 0.31-1.6 µg*g^{-1}. The relationship between log (length of fish) and log (Hg concentration) was log (Hg) = -3.89 + 2.02*log (length) with R^2 = 0.66. As expected, there was also a linear relationship with R^2 = 0.61. A graph showing mercury variation due to pike size is shown in Figure 9, which illustrates that pike in the 70 cm range had mercury concentrations of 0.5 to 0.9 µg*g^{-1}. This is a typical value for 70-cm-long pike in small pristine lakes in northern Quebec [17], and it is likely a typical value for small pristine lakes in northern Ontario.

3.5.3 Smallmouth bass

The mercury concentration in bass flesh varied from 0.32-0.69 µg*g^{-1}, but there were not enough data points for this species to establish any relationships or make general observations.

3.6 Organo-chlorine compounds

The OMOE analyzed 30 of the 123 fish from this study for chlorinated organic compounds. The analysis included five walleye and all of the northern pike and smallmouth bass caught at the Mackey, Sandspit, and Cotnam Island locations. Five walleye from the Rolphton location were analyzed for organics. No pike or bass were caught at Rolphton. The number and range of length and weight and the organics detected are shown in Table 6. Of the 23 chlorinated organic compounds for which the OMOE analyzed, only DDT metabolites, p,p'-DDE, and PCBs were detected. Table 6 shows values in brackets to indicate the numbers of fish in which the compound was detected.

Figure 10 shows the PCB and p,p'-DDE data for the individual fish at the four sample locations. The detection limit for the PCB data, shown on the left in Figure 10, was 20 ng*g^{-1} and the detection limit for the pp-DDE data, on the right, was 1 ng*g^{-1}. The highest concentration of PCB (74 ng*g^{-1}) was observed in one of the three pike caught at Mackey. A second pike caught at Mackey contained 21 ng*g^{1}, which is close to the detection limit for PCBs, and one of the seven pike from the Sandspit contained 24 ng*g^{-1}. The consumption guideline for sport fish in Ontario, [4], gives values of <105 ng*g^{-1} of PCBs for unrestricted consumption of fish and >844 ng*g^{-1} and >211 ng*g^{-1} of PCBs for the "do not eat" criteria for consumption of sport fish. As few fish were analyzed, it was not possible to evaluate the effect of size on the observed concentrations.

No pesticides were detected in the Rolphton collection, but this could be because pesticides were found only in pike and bass, which were not collected at this location.

Only one of the seven smallmouth bass had detectable concentrations of PCBs. One of the four bass at Mackey contained 44 ng*g^{-1} of PCBs; none of the three bass at Cotnam Island had detectable amounts of PCBs. The same smallmouth bass at Mackey had detectable amounts of DDT and metabolites and p,p'-DDE (5 ng*g^{-1} in both cases). Of the three smallmouth bass at Cotnam Island, one had detectable amounts of DDT & metabolites and p,p'-DDE (3 ng*g^{-1} in both cases) and one other bass had detectable amounts of p,p'-DDE (2 ng*g^{-1}).

PCBs were detected in two of the three pike from Mackey in amounts of 12 ng*g^{-1} and 74 ng*g^{-1} and in one of the seven fish from the Sandspit (24 ng*g^{-1}). Of the eight pike collected at Cotnam Island, five contained PCBs in amounts of 21 to 40 ng*g^{-1} of PCB. Of the two pike with detectable PCBs, one fish at Mackey had detectable amounts of DDT and metabolites and p,p'-DDE (12 ng*g^{-1} in both cases) and the other had detectable amounts of pp-DDE (2 ng*g^{-1}). Three of the seven pike collected at the Sandspit, including the fish with detectable PCBs, had detectable amounts of p,p'-DDE (2 ng*g^{-1}). Cotnam Island was unique among the locations sampled in that all eight of the pike collected contained detectable amounts of p,p'-DDE. Four of these pike also had elevated levels of DDT and metabolites. The data did not suggest a source of PCBs or p,p' DDE organics in the Rolphton/Sandspit section of the Ottawa River. Unfortunately, the data on organo-chlorine compounds were insufficient for statistical analysis.

4. Discussion

4.1 Radionuclides

One could ask, "Why were ^{90}Sr and ^{137}Cs not elevated in fishes immediately downstream of the CRL site, which has been a potential source of these fission products to the river since the 1950's?" Rowan [21], using data collected in 1994, 2.5 years after the shut-down of the NRX reactor, found that the ^{137}Cs content in fish was elevated by approximately a factor of 2 in walleye collected about 2 km downstream of CRL as compared with walleye collected upstream, above the Rolphton power dam. However, no such trend was found in this study. The lack of site-to-site differences in ^{137}Cs in fish flesh and the ^{90}Sr in fish bone may be due to the following:

1. Improvements in environmental stewardship at CRL and 15 years between the shutdown of NRX reactor operation and the collection of fish reported in this study.
2. Variability of concentrations among individual fish over the range of sizes collected in this study.
3. Lack of statistical analysis and the small number of fish collected annually for routine monitoring [2].

There have been temporal decreases in the concentrations of ^{137}Cs and ^{90}Sr in the water of the Ottawa River as illustrated in Figures 11 and 12. In these figures, a gold bar shows an annual average concentration value for Rolphton (30 km upstream of CRL, Figure 1) while a blue bar shows an annual average concentration at Pembroke (40 km downstream of CRL, Figure 1). Although the analytical detection limits for ^{90}Sr and ^{137}Cs have improved with time, the methods of analysis for these nuclides have remained the same, thus the data spanning the past 50 years are comparable (Figures 11 and 12). Five observations were based on the record of ^{90}Sr and ^{137}Cs concentrations upstream and downstream of CRL:

1. Global nuclear weapons testing added anthropogenic isotopes to the Ottawa River.
2. During the period of record, additional quantities of these isotopes entered the Ottawa River between Rolphton and Pembroke, and those additions were almost certainly attributable to nuclear operations at CRL.
3. Concentrations did not rise above 2.5% of the limit on ^{90}Sr for consumption of drinking water and never above 0.5% of the limit on ^{137}Cs for consumption of drinking water.
4. Concentrations of these isotopes in the Ottawa River show the values during the 1960's corresponding to atmospheric testing of nuclear weapons. This is consistent with radionuclide deposition and progressively lower concentrations as atmospheric concentrations dropped, as runoff of ^{137}Cs- and ^{90}Sr-labelled soils fell and as the radionuclides decayed.
5. Low concentrations in the river from the late 1990's onward are consistent with the ^{137}Cs and ^{90}Sr concentrations measured in fish in this study. So low were the concentrations in the river in recent years that some of the average annual concentration values were higher upstream than downstream (Figures 11 and 12). Upstream and downstream concentrations in fish would naturally reflect the concentrations in water, particularly because walleye, the principal fish in this study, can travel considerable distances [7, 8, 18].

Although future analysis of more fish of more uniform size and similar species, including aging of the fish, might reveal a statistically significant increase in ^{137}Cs in fish downstream of CRL, this may cause an unwarranted sacrifice of ecologically important, edible fish. Of the two nuclides we looked for, ^{90}Sr could be the most important from an edibility perspective because it has a long biological half-life. However our analysis of bone, in which Sr would be highly concentrated relative to flesh, failed to show elevated concentrations downstream of CRL as compared with the Mackey control. Thus, neither ^{137}Cs nor ^{90}Sr pose edibility issues and, therefore, the sampling of additional fish would seem unwarranted.

4.2 Mercury

The consumption restriction guideline for mercury, for the most sensitive human population group, is 0.26 μg^*g^{-1} ww [4]. Therefore, regular consumption of the smallest fish in this set of data would be of low risk for children under 15 years of age and women of childbearing age. Clearly, this section of the Ottawa River is similar to many Ontario lakes such that fish consumption guidelines promulgated by the OMOE [4] should be consulted before eating a substantial amount of freshwater fishes.

There appear to be no satisfactory explanations for the significantly higher concentrations of mercury in fish collected at the Rolphton and Sandspit sites as compared with the fish collected above the power dam and at Cotnam Island. However, it is known that the sediments of the Ottawa River contain As, Cr, Cu, Pb, Hg, Ni and Zn at higher concentrations in, and upstream of, Upper Allumette Lake than downstream [22]. Concentration profiles of Cu, Zn, Pb and Hg of the sediment 2.5 km upstream of CRL and 8 km downstream of CRL contain abrupt increases in metal concentrations, which, based on ^{210}Pb dating, correspond to the early 1900s, when mining began in the upper parts of the Ottawa River basin [6]. Thus, mining and other anthropogenic disturbances of the land may be related to elevated Hg in the sediments of Allumette Lake. However, this does not explain the decreased concentrations below Allumette Lake, as observed previously [22].

4.3 Organo-chlorine compounds

DDT (dichlorodiphenyltrichloroethane) and related compounds degrade slowly in nature, are soluble in fatty tissue, and therefore, like methyl mercury, bioaccumulate in aquatic food webs. Organo-chlorine compounds have been applied to agricultural and forested lands in North America, and, like mercury, they can be carried far from source areas by the atmosphere. DDT and its primary metabolite, DDE, have been associated with increased health risks for top predators, including humans, especially for women of childbearing age and children less than 15 years of age.

While fish consumption could be a concern when eating larger predatory fishes due to the higher levels of PCBs that may be present in larger fish, the consumption restriction guideline for the most sensitive population group is 105 ng^*g^{-1} ww for total PCBs [4]. This is higher than the highest PCB value measured in this study, 74 ng^*g^{-1} ww, and most of the fish did not have detectable PCBs (Table 3). Therefore, PCBs do not appear to be an issue for fish consumption in this section of the Ottawa River.

5. Conclusions

Analysis of over 26 game fish at each of four locations from 45 km upstream to 45 km downstream of the Chalk River Laboratories did not show a statistically significant increase in the ^{137}Cs concentration of fish flesh. It is noteworthy that levels of ^{137}Cs and ^{90}Sr in this central reach of the Ottawa River have declined markedly in the last few decades. This was attributed to the cessation of atmospheric nuclear weapons testing in the 1970's, atmospheric washout, radioactive decay, and the shutdown of the NRX reactor at CRL in 1992. The lack of a statistically significant increase in the concentrations of ^{137}Cs or ^{90}Sr in downstream fish is consistent with the water-quality record.

Mercury concentrations of Ottawa River game fish were comparable to values for similarly sized fish in the freshwater bodies of northeastern North America. The average concentration of mercury in the flesh of the fish analyzed in this study was 0.57 $\mu g{*}g^{-1}$ wet weight, which was marginally less than the Ontario provincial average. As has been observed in many other studies, mercury concentrations increase with fish size.

The mercury concentration of fish collected at Rolphton (upstream) and at the Sandspit (1.6 km downstream) was elevated slightly as compared to levels in fish collected near Mackey and Cotnam Island. Thus, it is possible that human activities have added Hg to this section of river.

Anthropogenic chlorinated organics (DDT and related metabolites, p,p'-DDE, and PCBs) were detected in the flesh of 30 fish. However, the concentrations appeared to be of lesser importance than mercury for people consuming fish.

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TECHNICAL NOTE

REACTIVE SANDPACKS FOR IN-SITU TREATMENT OF CONSTRUCTION DEWATERING EFFLUENT

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Dealing with contaminated effluent can be problematic when dewatering is required in the course of removing buried tanks, excavating contaminated soils or constructing groundwater remediation systems. An engineering solution put forward in this paper is the emplacement of a sandpack, around the dewatering well(s), that reacts with and sequesters groundwater contaminants of concern. If an appropriate granular reactive material is available, placing that material around the dewatering well screen can achieve a degree of contaminant treatment in-situ that may considerably reduce the costs of storing, securing and treating the water before it is released. In the preferred situation, the contaminants remain underground and the extracted water is suitable for surface release as it is pumped from the ground. We used laboratory columns of granular reactive material (clinoptilolite) and a radiostrontium tracer to evaluate the usefulness of this approach in a hypothetical situation where the water table needed to be lowered 2 m in order to install a permeable reactive barrier. Results were consistent with the concept of reducing the environmental liabilities of construction dewatering in areas of groundwater contamination.

1. Introduction

Temporary lowering of the groundwater table by pumping is often required during the construction of drains, footings and subsurface remediation systems [1]. If the groundwater contains a contaminant, treatment of the dewatered effluent to environmental standards may be necessary prior to discharging it to land or to surface waters. To meet legislative requirements [e.g., 2, 3] effluent typically has to be stored, tested and decontaminated before it can be released.

In this technical note, we introduce the reactive sandpack method for dewatering when groundwater contamination exists within the capture zone of the dewatering well. A reactive sandpack or filter pack would be designed to address both the geochemical and the hydraulic conditions at the site as well as the specific contaminant. The purpose of this method is to achieve an appreciable degree of decontamination *in situ*, during pumping. This novel method may also find application as a pre-treatment for above-ground pump-and-treat systems. This note also provides guidance on how reactive materials may be evaluated.

Several reactive granular materials have been proven effective in a permeable reactive barrier (PRB) where the groundwater moves through the material under natural gradients and is treated [4]. If contaminant reaction rates are sufficient under the faster flow conditions that would occur within a sandpack, then PRB materials may be candidates for reactive sandpacks of dewatering wells. In this note, clinoptilolite was used as a material example to illustrate the method of evaluation of materials for reactive sandpacks. Clinoptilolite is a naturally occurring zeolite with a high affinity for strontium [5, 6, 7]. A critical issue with reactive sandpacks is the ability of the reactive media to attenuate contamination at the high velocities, and under the short residence times, that would occur near the intake screen of a dewatering well. Although the attenuation capacity of clinoptilolite has been demonstrated in column tracer studies [6, 7] and in a PRB [8], those studies were performed at natural-gradient flow rates, which are far lower than that which would occur near a dewatering well. The literature, while encouraging, has not considered kinetic effects that could become important in limiting contaminant removal by a reactive sandpack. To evaluate the influence of fast flow on contaminant attenuation, a laboratory study was conducted to evaluate 14 x 50 mesh clinoptilolite using a radiostrontium tracer at velocities that would occur in a sandpack.

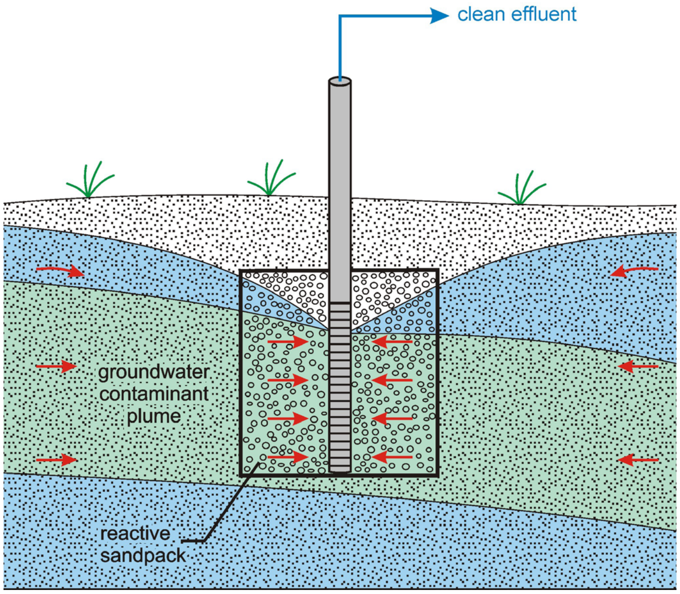

FIGURE 1: A schematic showing the reactive sandpack method.

2. Methodology

Tracer velocities were selected using a simulated dewatering well, which was designed for the hydrogeological conditions of a water table aquifer at Atomic Energy of Canada Ltd., Chalk River, Ontario [8]. The physical properties of the clinoptilolite batch used in the columns were taken from other work that used the same batch of materials [9]. The Thiem solution for steady state radial flow in an unconfined aquifer was used to select linear groundwater velocities of 30, 60 and 100 m/day. These flow rates would occur in a 1.5 m radius reactive sandpack around a well designed and pumped to lower the water table by 2 m [10, 11]. To examine sorption of $^{90}Sr^{+2}$, six 40 cm long by 4.8 cm diameter aluminum columns were packed with 14 X 50 mesh clinoptilolite [11]. Aquifer characteristics [8], well development and filter-pack properties were considered in designing the reactive sandpack tested in this study.

The selection of 14 x 50 mesh clinoptilolite for the filter pack was based on the guidance for construction of gravel and sandpacks [12]. This took into account the grain size distribution of the aquifer [8] so that, in an actual application, the sandpack would enhance and preserve the hydraulic connection between the sandpack and the aquifer. Column length was eight times the column diameter to reduce the probability of channeling, based on the recommendation of Relyea [13]. Sampling ports were installed at 10 cm intervals along the columns to facilitate the collection of tracer samples every 4 to 8 hours while pumping. The tracer solution consisted of strontium-85 ($^{85}Sr^{+2}$) in deionised water with several salts added to simulate empirically the ambient hydrochemistry of the water table aquifer at Chalk River. Ambient hydrochemistry was necessary in order to evaluate the possibility of competing cations affecting attenuation. Prior to running the radiostrontium tracer test, a chloride tracer was run through each column to estimate column dispersivity, hydraulic conductivity and effective porosity as well as to test for channelling. At the end of the $^{85}Sr^{+2}$ tracer test, the columns were cut into three sections and the reactive material carefully extruded in 0.5 cm intervals at the tracer inflow end, where fine resolution was required, and in 2 cm long intervals at the column outflow end. Both dried effluent and solid phase samples were analyzed with a Canberra Gamma Analyst Integrated Gamma Spectroscopy Instrument (Gamma Analyst), model S590 and with Canberra Genie 2000 data processing and reporting software [11].

3. Results and Discussion

Chloride tracer tests, conducted at each of the three selected velocities, provided estimates of dispersivity (0.52 to 4.24 cm) and effective porosity (0.38 to 0.47). The chloride breakthrough curves showed that flow was laminar and channelling did not occur at the three velocities [11].

During the tracer tests, the ^{85}Sr tracer penetrated only 3 cm to 7 cm into the columns. Each column pair showed relatively good agreement regarding position of the ^{85}Sr sorption front. In Column 6, the sorption front advanced only 5.25 cm after 200 L (4500 pore volumes) of tracer solution had moved through the column at a linear flow rate of 100 m/day. This shows clinoptilolite has significant potential as a reactive sandpack material. The mass balances between total influent activity and total sorbed activity ranged from 89% to 120% with one outlier of 145% for Column 5. These results indicated, with the exception of Column 5 data, which were excluded from modeling, that there were no gross errors in activity measurement of the solid phase and that the results were suitable for numerical analysis. As tracer breakthrough did not occur during the tests, aqueous phase radiostrontium concentrations were estimated from the analytically-determined concentrations in the clinoptilolite, using the Parker and van Genuchten

TABLE 1: Summary Column Study Results. K_d is the distribution coefficient [11].

Column ID	Velocity (m/day)	K_d estimate (mL/g)
C2	31	10 000
C4	29	30 000
C1	66	10 000
C3	55	5 400
C6	100	32 000

solution for advective-dispersive transport with a third type boundary condition [14, 15]. Dispersion coefficients were estimated by fitting the 1D solute transport model CXTFIT [16] to the chloride breakthrough profiles, resulting in excellent correlation between the observed and fitted data achieved.

The attenuation capacity of the clinoptilolite was evaluated using a single solute equilibrium (distribution coefficient (K_d)) approach. The K_d values estimated in this study (Table 1) fell on the high side of the range of values (300 ml/g to 32,000 ml/g) for clinoptilolite reported in the literature [6, 7, and 9]. Although an equilibrium approach is an over-simplification, where kinetically controlled processes are occurring, reasonable agreement between measured and model-fitted data from many past studies using K_d has perpetuated the use of this method [7]. For this study, where column velocities were significantly greater than those that occur under natural groundwater flow conditions, a K_d-based modeling approach was selected with the understanding that kinetic influence on attenuation should result in K_d values decreasing with increasing velocity. However, the K_d values, calculated based on the experimental data, did not follow a progressive decrease with increasing velocity (Table 1).

Variability in the experimental results points to the need for additional work and perhaps greater attention to column packing, which may have caused the variations. Regardless, the short penetration depth of the radiostrontium tracer in all of the experimental columns demonstrated that the reactive sandpack concept has good potential for in-situ treatment of groundwater during construction dewatering.

Future experiments that continue until tracer breakthrough is confirmed would support the use of a more robust multi-solute transport model for estimating attenuation capacity. Field-scale application of the reactive sandpack concept will require careful attention to placement of reactive material and well development to maximize contaminant removal and well efficiency.

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ERRATUM

ERRATUM FOR "THE EFFECT OF IRRADIATION ON NI-CONTAINING COMPONENTS IN CANDU® REACTOR CORES: A REVIEW"

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1.0 Introduction

In the June 2013 edition of the AECL Nuclear Review, Volume 2, Number 1, the last sentence in paragraph three of the Introduction of the article "The Effect of Irradiation on Ni-containing Components in CANDU ® Reactor Cores: A Review" was incomplete and should be:

Just as Zr is unusual in having a very low neutron absorption cross-section (the reasons why it is the most commonly used core material), Ni also has certain unusual properties in a radiation environment compared with other metals used in structural alloys for nuclear reactor cores, although the effect of irradiation is less benign in this case [5-7].

Figure 10 used the correct spectrum but with a neutron flux that was ~ 2x lower than what might be reasonably expected (power and burn-up varies depending on time and location). The power condition was not defined. The figure and caption are revised to make it more exact.

The scale marker for Figure 13 should have been 5 mm and not 1 mm.

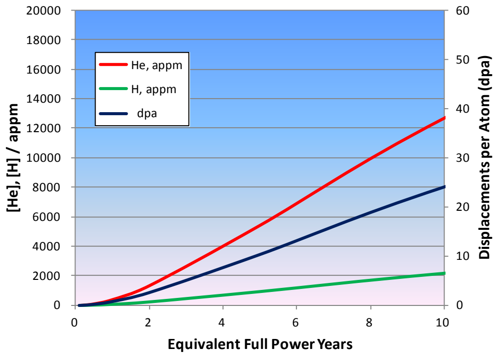

FIGURE 10: Helium, hydrogen and displacements per atom for Inconel 600 flux detector components in the core of a CANDU reactor for an average power condition at zero burn-up [10].

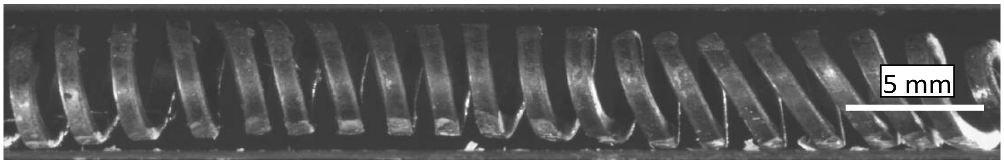

FIGURE 13: Comparison of (a) unpinched and (b) pinched sections of irradiated spacers removed after about 14 EFPY of service and after mechanical testing at ambient temperature (about 25 °C). The unpinched sample exhibited brittle intergranular failure while the pinched sample deformed without failure when subjected to the same load [33].

AECL NUCLEAR REVIEW SPECIAL ISSUE: "THE FUTURE OF NUCLEAR" (DECEMBER 2014)

This is a call for papers for the December 2014 Special Issue of the AECL Nuclear Review highlighting science and technology related to the future of nuclear. This issue will discuss topics such as (but will not be limited to):

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