Predicting the Time Course of Radionuclides in Aquatic Food Webs Following Pulse Releases

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Abstract

Releases of radionuclides from nuclear facilities are frequently episodic and may lead to non-steady state concentrations of radionuclides in water. The transfer factor or concentration factor approach generally used to estimate radionuclide concentrations in biota is inappropriate under these conditions. A kinetic, mechanistic food web model was developed and tested for the Ottawa River at Chalk River Laboratories (CRL). The model predicts a range of ^{137}Cs concentrations that encompasses observed concentrations in Ottawa River pygmy smelt (*Osmerus spectrum*) and walleye (*Sander vitreus*), describes temporal variation due to pulse releases and handles the complexity of a partially mixed source term. This approach is readily adaptable for other sites and for other radionuclides and contaminants.

1. Introduction

Routine releases of radionuclides from nuclear facilities to freshwater and marine systems are often episodic or pulse in nature due to variations in operations and waste management [1-3]. Pulse releases can lead to rapidly changing concentrations in receiving waters and disequilibrium between water concentrations and concentrations in biota [1, 4, 5]. The concentration factor approach routinely used to estimate concentrations in biota from concentrations in water is only appropriate under equilibrium or steady state conditions. Estimating concentrations of radionuclides in aquatic biota under non-steady state conditions requires kinetic models.

Single compartment, first-order kinetic, mass balance models have been used to predict concentrations or burdens of organics [6-8], metals [9-10] and radionuclides [11-12] in aquatic food webs. These models share a basic structure that accounts for important uptake and elimination processes through first order rate constants. Central to the single compartment model is the assumption that contaminant uptake and elimination occurs to and from one compartment, i.e. tissues of the whole organism, even though the contaminant may preferentially reside in one or more tissue types. As long as elimination can be modeled as a first order process affecting the entire burden, then this approach is valid.

1.1 Model structure

1.1.1 Equilibrium or kinetic models?

Two types of models are used to describe chemical reactions in aquatic environments, thermodynamic (equilibrium) or kinetic. Equilibrium models are appropriate only for closed systems, i.e. those that do not exchange material with their surroundings, under fixed conditions (e.g. temperature and pressure) and where equilibrium has been reached. Kinetic models must be used both to describe the time course to equilibrium in closed systems and the time course to steady state in open systems [13]. For reactions that occur slowly, kinetic models are necessary to describe the nature of the stationary state that will be eventually achieved.

Open systems include those usually considered in aquatic biogeochemistry and ecotoxicology (whether in the lake, the ocean or the gut of a living organism), and require kinetic models with rate constants describing their approach to steady state [13]. When considering the processes of bioaccumulation of ^{137}Cs in aquatic food webs, biological half-lives of weeks to months can be expected. Thus, for modelling ^{137}Cs in aquatic food webs, where equilibrium is not relevant and steady state is often only approached, kinetic models are required.

1.1.2 General models of contaminant burden

The most general kinetic model for contaminant burden treats the organism as a single compartment in terms of contaminant uptake, elimination and distribution in tissue [14]. Contaminants can only be eliminated after they are assimilated. Although the contaminant burden is solely contained within the single compartment, the model allows for multiple inputs and outputs from the compartment (Figure 1).

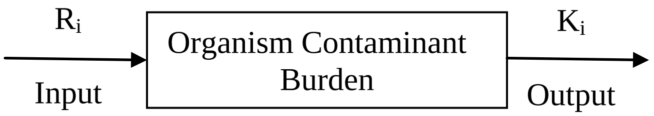

Figure 1. Schematic of a single compartment contaminant mass balance model with multiple inputs and outputs from the single compartment.

The 1st order linear ordinary differential equation (ODE) that describes this model is:

$$\frac{dQ}{dt} = R - kQ \tag{1}$$

where Q is the contaminant burden (g or Bq), t is time (d), R is the uptake rate (g d^{-1}) and k is the specific elimination rate (d^{-1}). R can include terms for water and/or food uptake and k can include terms for elimination through different processes. Integrating Equation 1 using the integrating factor method [15] yields:

$$Q_t = \frac{R}{k}\left(1 - e^{-kt}\right) + Q_0 e^{-kt} \tag{2}$$

where Q_t is the burden at some time t, and Q_0 is the initial burden of the modeled time period. If there is no uptake from food or water (R=0) then:

$$Q_t = Q_0 e^{-kt} \quad \text{or} \quad \frac{Q_t}{Q_0} = e^{-kt} \tag{3}$$

Thus, from first principles, contaminant elimination rates should have units of g contaminant· g contaminant^{-1}·d^{-1} and describe the fraction of burden lost per unit time. Mechanisms for contaminant elimination that can be expressed this way include elimination through respiratory tissues, elimination from tissues through excretion and egestion, and metabolic transformation. The combination of the differential equations for the mass balances of growth and contaminant burden (or concentration) results in the specific growth rate (d^{-1}) appearing with these other elimination terms, but growth differs in that it does not reflect changes in the burden, only in concentration [16].

Contaminant elimination rates are often estimated from time series data using Equation 3 (see e.g. [17]). In practice, first order elimination may involve several pools that may be estimated through non-linear regression as:

$$\frac{Q_t}{Q_0} = f_1 e^{-k_1 t} + f_2 e^{-k_2 t} + f_3 e^{-k_3 t} + \dots\dots\dots \qquad (4)$$

where f_i is the fraction of contaminant associated with k_i, and $\sum f = 1$.

If data is not available for two or more times, Equation 2 can be simplified by assuming steady state ($Q_t = Q_0$):

$$Q = \frac{R}{k} \qquad (5)$$

Relationships describing contaminant concentration can also be derived separately or can be obtained by dividing Equation 2 by organism weight at time t.

1.2 Application of the kinetic approach to pulse releases

In this paper, I re-examine a data set from 1994 and present a novel approach using stable cesium (^{133}Cs) under steady state conditions to predict the time course of radiocesium (^{137}Cs) under pulse conditions through an aquatic food web. First, I parameterize Equation 1 using ^{133}Cs and solve for the only unknown (food consumption rate). Then I use non-steady state concentrations of ^{137}Cs in water to predict concentrations of ^{137}Cs in zooplankton, smelt that feed on zooplankton and walleye that feed on smelt and compare these predictions to measured concentrations. Finally, I discuss the potential for the use of kinetic approaches to modelling the bioaccumulation of radionuclides in aquatic food webs at nuclear facilities.

2. Methods

Walleye (*Sander vitreus*), pygmy smelt (*Osmerus spectrum*) and zooplankton (*cladocerans* and *copepods*) were collected from the Ottawa River bi-weekly during the ice-free period from May to December 1994. Walleye and pygmy smelt were collected downstream from CRL at Point au Baptệme using experimental gill nets. Impinged pygmy smelt were also collected from the pumphouse at CRL. Zooplankton were collected in the vicinity of Point au Baptệme using as plankton net with a mesh size of 150 µm to exclude phytoplankton. Temperature profiles were taken on sampling days.

Walleye growth structures (otiliths and scales) were removed prior to processing the fish for ^{133}Cs and ^{137}Cs analysis. Individual walleye were dried and ashed, age-class composites of pygmy smelt were dried and ashed and zooplankton were dried. Sub-samples were digested in nitric acid for ^{133}Cs analysis by ICPMS, with the remaining sample analyzed for ^{137}Cs by gamma spectroscopy. Gut content analysis indicated that walleye consumed pygmy smelt, with few exceptions, and pygmy smelt primarily consumed zooplankton. Growth rates of walleye and pygmy smelt were estimated by logistic regression of body size as a function of time. ^{133}Cs and ^{137}Cs burdens of walleye and pygmy smelt were estimated by logistic regression of body size as a function of time. Assimilation efficiencies for zooplankton and pygmy smelt prey were estimated from published values [12] and elimination rates were estimated from a general model with body size and temperature as inputs [17]. Concentrations of ^{133}Cs in water were determined by ICPMS [18]. Concentrations of ^{137}Cs were calculated from weekly discharges from CRL and weekly Ottawa River flow [19].

3. Results

3.1 Application to the Ottawa River food web

Application of the approach outlined above to the Ottawa River food web involves combining the mass balance of Cs (Equation 1) with the mass balance of body size:

$$w_t = w_0 e^{Gt} \tag{6}$$

where w_t is fish mass (g) at time t, w_0 is fish mass (g) at the beginning of the time period and G is the specific growth rate (d^{-1}). For freshwater fish, direct uptake of Cs from water is negligible and only uptake from food is considered:

$$\frac{dQ}{dt} = \alpha\left[Cs_{food}\right]Cw_0 e^{Gt} - (E+D)Q \tag{7}$$

where α is the assimilation efficiency from food (fraction), Cs_{food} is the concentration of Cs in the diet during the modeled period, C is the specific consumption rate (d^{-1}), E is the specific elimination rate (d^{-1}) and D is radioactive decay (if required, d^{-1}). Integrating Equation 7 using the integrating factor method [15] yields:

$$Q_t = \frac{\alpha\left[Cs_{food}\right]Cw_t\left(1-e^{-(G+E+D)t}\right)}{G+E+D} + Q_0 e^{-(E+D)t} \tag{8}$$

Q_t, Q_0, Cs_{food}, w_t and G are measured, D is known, α and E are estimated from published values and models [12, 17]. The only unknown in the equation is the specific consumption rate which is solved for:

$$C = \frac{\left(Q_t - Q_0 e^{-(E+D)t}\right)(G+E+D)}{\alpha\left[Cs_{food}\right]w_t\left(1-e^{-(G+E+D)t}\right)} \tag{9}$$

This equation is solved initially using stable cesium, ^{133}Cs, for walleye (*Sander vitreus*) and their prey, pygmy smelt (*Osmerus spectrum*), and their prey, zooplankton (Figure 2).

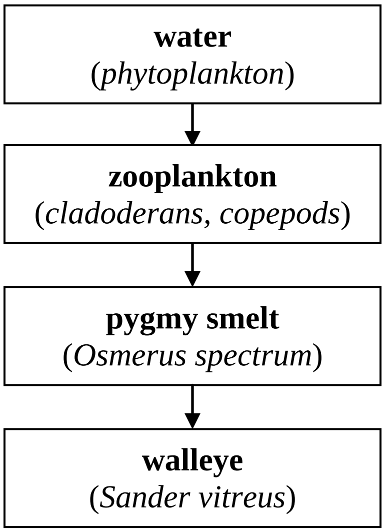

Figure 2. Simplified Ottawa River food web modeled for this study. Pygmy smelt primarily consume zooplankton and walleye primarily consume pygmy smelt. Zooplankton and their prey (phytoplankton) are assumed to be in steady state with water concentrations.

Once consumption is estimated from ^{133}Cs, Equation 8 can be divided by fish weight and then used to predict ^{137}Cs concentrations in fish exposed to pulse releases.

3.2 Source Term

A comparison of measured and calculated concentrations of ^{137}Cs in Ottawa River water downstream of CRL, during 1994, shows excellent agreement on most sampling dates (Figure 3). Calculated concentrations (Bq m^{-3}) were made from measured weekly releases of ^{137}Cs from CRL (Bq s^{-1}) and measured average weekly flow rates in the Ottawa River (m^{3} s^{-1}). The release of ^{137}Cs from CRL was not constant, but rather exhibited pulses prior to the start of this study (days 34, 69 and 120), with smaller pulses during the study, around day 210 and beyond day 320. These concentrations are indicative of non-steady state conditions and demonstrate that assumptions of equilibrium or steady state are not valid during this time period for the Ottawa River downstream from CRL.

Figure 3 shows expected concentrations of ^{137}Cs after complete mixing of CRL effluent into the Ottawa River at Pembroke, but in the region of this study, incomplete mixing is more likely. A study of dilution of Chalk River effluent into the Ottawa River suggests that at the discharge point, the effluent immediately mixes into about 7% of the Ottawa River flow, and that during the ten hours it takes to reach Point au Baptême, 2 km downstream, effluent should be mixed into 34% to 75% of the Ottawa River flow [20]. Thus, the degree to which the steady state assumption is violated, increases as the process sewer outfall is approached. In subsequent figures (Figures 4, 5 and 6), ranges of concentrations are presented that represent the likely range that aquatic biota were exposed to.

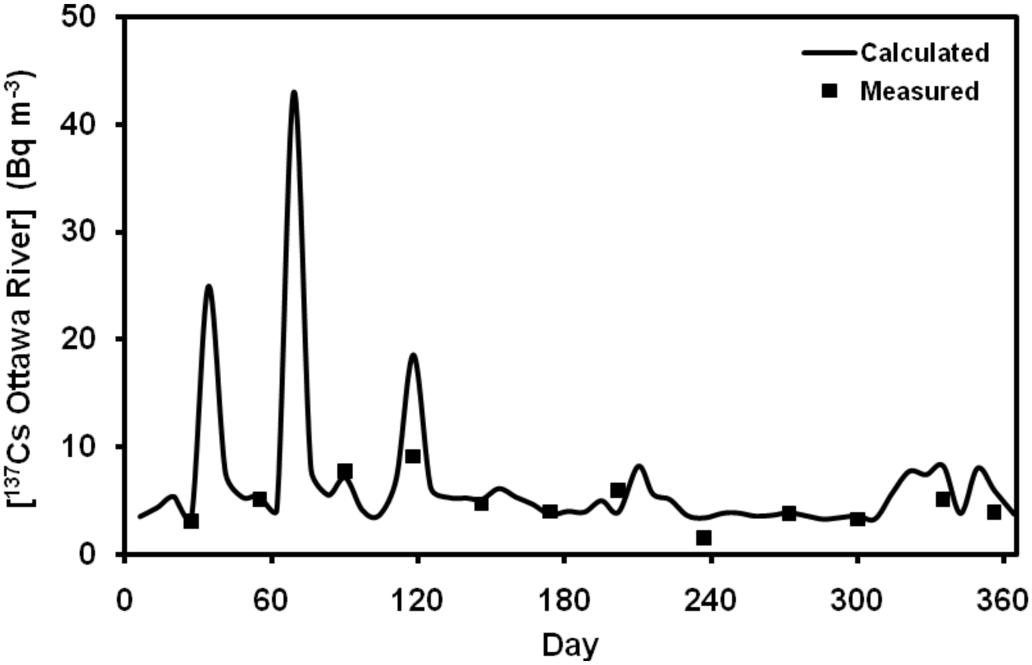

Figure 3 ^{137}Cs in the Ottawa River downstream from CRL during 1994 measured through routine monitoring and predicted from weekly concentrations in the process sewer and Ottawa River flow. Predictions are generally in excellent agreement with observations.

The lower limit is the upstream concentration of ^{137}Cs, attributable to atmospheric weapons tests during the 1950's and 1960's. It is possible that some fish move from upstream locations to locations downstream of CRL, and these fish would be expected to exhibit relatively low concentrations of ^{137}Cs. It is also possible that zooplankton could be carried from upstream to downstream locations by currents that are not influenced by CRL effluent. Fish could also move from downstream sites where CRL effluent is completely mixed into the Ottawa River. These fish would also be expected to have relatively low concentrations of ^{137}Cs, although slightly higher than upstream fish. The expected conditions at the sampling site (34% to 75% mixing) are also presented, along with a slightly less mixed condition (25%), representing a reasonable upper bound to CRL contributions to any local or regional food web.

3.3 Water to zooplankton

Zooplankton and their food (phytoplankton) have been shown to reach steady state with water concentrations of cesium within a day or two of exposure. As the available release data consists of seven day averages [19], well within the time frame to expect steady state for zooplankton,

zooplankton were assumed to be in steady state with calculated water concentrations. Observed concentrations of ^{137}Cs in zooplankton are plotted along with predicted concentrations from release data and varying degrees of effluent mixing in Ottawa River flow (Figure 4). Zooplankton ^{137}Cs concentrations tend to reflect various degrees of mixing, with three points falling on or near the upstream prediction, three points falling between upstream and completely mixed conditions, three points falling on or near the 34% mixed condition and one near the 25% mixed condition. These results all lie within the expected range of concentrations predicted from steady-state ^{133}Cs analysis.

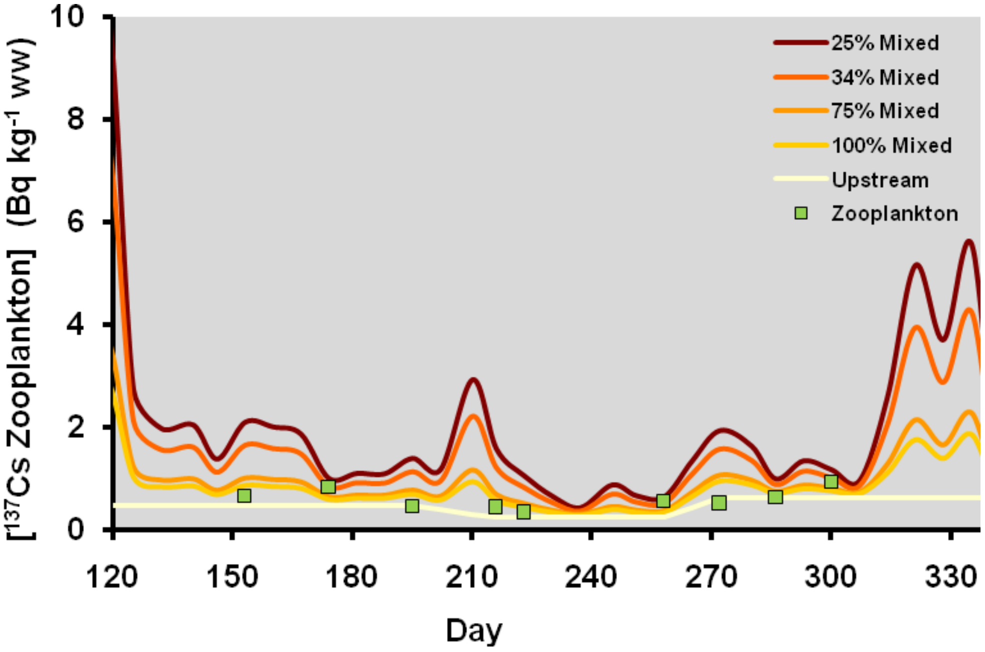

Figure 4. Observed and predicted concentrations of ^{137}Cs in Ottawa River zooplankton downstream from CRL. Observations tend to be on the low side of the expected range

3.4 Zooplankton to pygmy smelt

The transfer of ^{137}Cs from zooplankton to pygmy smelt occurs by consumption, and the predicted concentrations presented in Figure 4 serve as input food concentrations for pygmy smelt in Equation 8. Once again, predicted concentrations from expected mixing conditions of CRL effluent bracket the observed concentrations of ^{137}Cs in biota. Although three smelt samples suggest fish that moved from upstream or downstream to CRL, most fish have observed ^{137}Cs concentrations that suggest residence with the CRL effluent plume. Three points lie on or above the 25% mixed prediction, suggesting that concentrations in pygmy smelt food (zooplankton) were underestimated during the pulse releases that occurred just prior to their collection. Underestimation of peak concentrations in Ottawa River water and biota are probable because releases were measured from composite samples collected over seven days. Actual peak concentrations could have been much higher, rapidly assimilated by zooplankton and translated to pygmy smelt through ingestion. Even with these uncertainties in peak concentrations, predictions track observations very well and encompass the observed range of about 2-fold. It is interesting to note that with less rapid biokinetics due to greater body size, slower growth, consumption and elimination, the pulse release is damped out in pygmy smelt relative to water (Figure 3) or zooplankton (Figure 4).

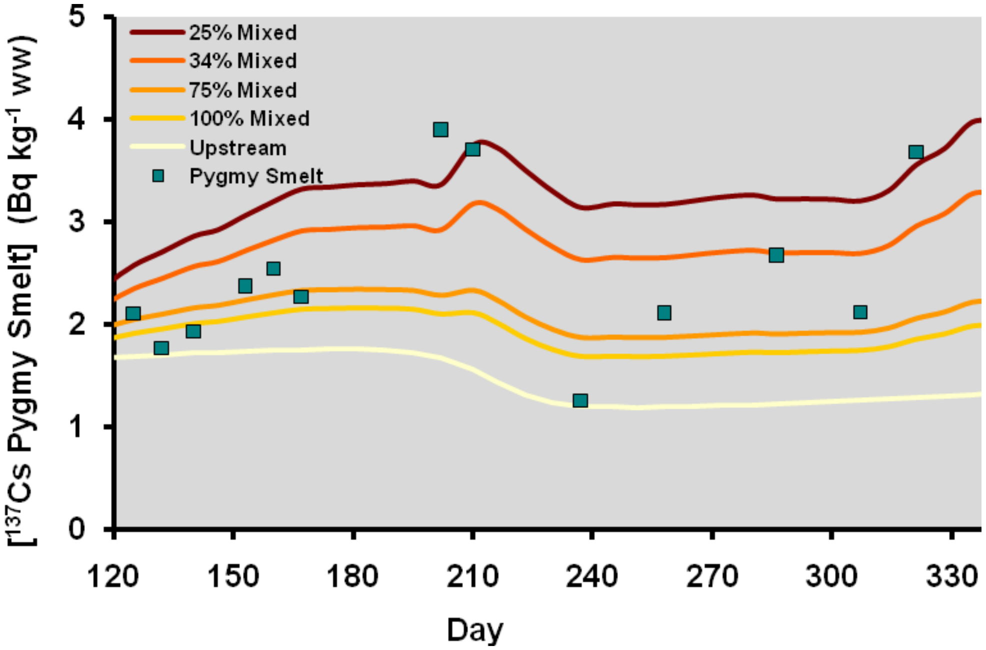

Figure 5 Observed and predicted concentrations of ^{137}Cs in Ottawa River pygmy smelt downstream from CRL. Predictions match the observed trend and most fish fall within the expected range of values.

3.5 Pygmy smelt to walleye

Walleye in the Ottawa River near CRL consume smelt almost exclusively, and the predicted concentrations of ^{137}Cs in smelt shown in Figure 5 were using as input to Equation 8 to calculate ^{137}Cs concentrations in walleye (Figure 6). Most observed ^{137}Cs concentrations fall within the predicted upper and lower bounds, and there is remarkable agreement of predictions with the decreasing trend observed during the study period. ^{137}Cs in walleye dropped by almost two-fold during the open water period of 1994 from about 20-25 Bq kg^{-1} ww to 10-15 Bq kg^{-1} ww. The trend in walleye ^{137}Cs concentrations does not reflect short term changes in water concentrations due to pulse releases, but rather shows an overall decrease from higher concentrations that may be related to the relatively greater pulse releases prior to the start of this study. The decrease in concentration also likely reflects growth dilution due to rapid growth from days 210 to 270. The decrease is also driven by concentration of ^{137}Cs in walleye prey (pygmy smelt) that are insufficient to maintain the relatively high starting concentrations observed in May 1994. ^{137}Cs in walleye collected at Point au Batême reflects the expected range for fish that are resident at the site for substantial periods of time. Walleye are known to migrate during spawning, but these walleye are immature and unlikely to move with mature fish to spawning grounds upstream of CRL at rapids below Des Joachims Dam. It is more likely that these fish would move downstream as they disperse from their spawning areas. This is supported by the observation that young of the year walleye were not observed near CRL until early fall 1994.

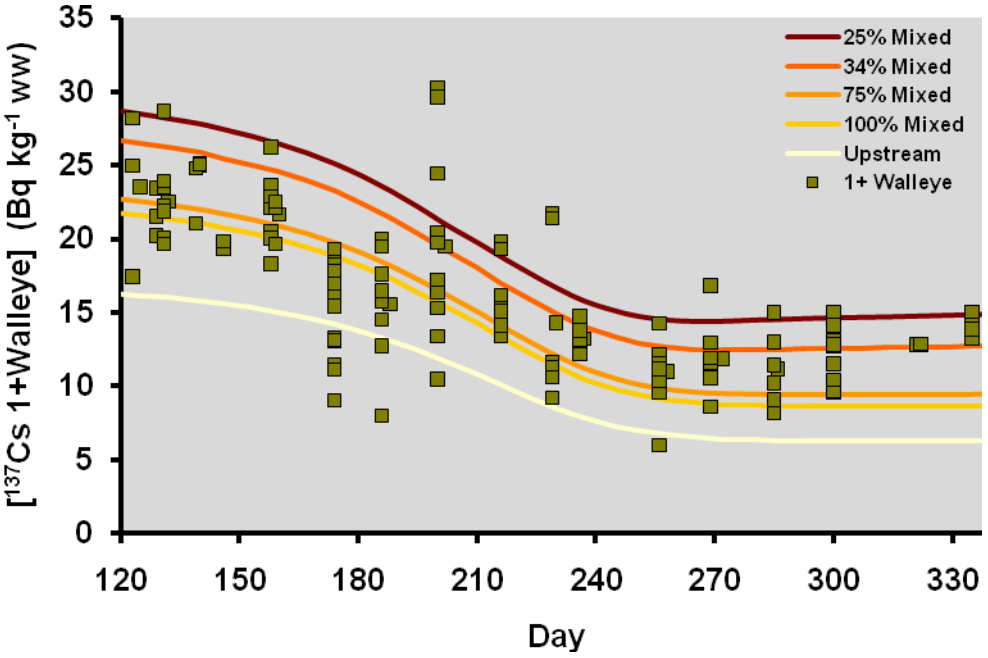

Figure 6. Observed and predicted concentrations of ^{137}Cs in Ottawa River walleye downstream from CRL. Predictions match the observed decreasing trend and most fish fall within the expected range of values.

4. Conclusion

Releases of ^{137}Cs from the CRL process sewer to the Ottawa River during 1994 were not constant, but rather were pulse in nature. These pulse releases to the Ottawa River resulted in variable concentrations of ^{137}Cs in water and made the use of equilibrium or steady state modelling approaches typically used at nuclear facilities inappropriate. The use of kinetic or biokinetic models coupled with a well characterized source term yielded predicted concentrations in zooplankton and fish that bracket the two-fold variation in observed concentrations. These predictions also described the temporal variation observed in pygmy smelt and walleye due to pulse releases, fish biokinetics and fish bioenergetics.

This cesium isotope approach also handled the complexity of a partially mixed source term due to incomplete mixing of CRL effluent in the Ottawa River flow at the study site and the possibility of fish movements upstream and downstream of CRL. By using realistic ranges in mixing and upstream concentrations, maximum and minimum limits on fish ^{137}Cs concentrations were both accurate and precise.

This approach is readily adaptable to other sites, other radionuclides and other contaminants with site specific parameters that can be obtained from a single sampling season, and estimates of elimination rates and assimilation efficiencies. As most nuclear facilities release radionuclides in pulses, only approaches that can account for non-steady state conditions are valid for assessing the bioaccumulation of radionuclides in aquatic food webs at these sites. Unlike equilibrium and steady state models and approaches that are unable to make predictions about the fate of accidental releases, this mechanistic, biokinetic approach provides models that can predict the time course of radionuclides in aquatic food webs from routine or accidental releases.

5. References

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