LIFE CYCLE OF CARBON-14 FROM NUCLEAR REACTOR PRODUCTION: GLOBAL AND NORTH AMERICAN ESTIMATES

By:

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Abstract

Carbon-14 is a byproduct originating from the operation of power nuclear reactors. There are currently approximately 435 operating power reactors world-wide, and it has been recently estimated that the cumulative production from all these reactors amounted to 21.1 PBq* (as reported in *Prog. Nucl. Energy*, 48: 2-36, 2006 – this paper will update this value including the 2004 figures). Approximately ~45% of is available for gaseous or liquid release, of which only a small portion has been released to the environment. At the end of year 2004, 122 reactors were operating in North America, with a cumulative production of 10.4 PBq. It is interesting to note that from this value, 6.9 PBq is available for release (this represents ~33% of the total worldwide cumulative production). Most of this inventory currently sits in Canada. Environmental releases of this inventory are small. However as inventories continue to increase, waste management will need to take this in consideration.

*(1 PBq = 10^{15} Bq)

1. Introduction

The naturally occurring isotopes of Carbon are of atomic masses of 12 (^{12}C), 13 (^{13}C) and 14 (^{14}C). The isotopes ^{12}C and ^{13}C are stable (i.e., non-radioactive), whereas ^{14}C is radioactive. The latter is produced in the upper atmosphere by the ^{14}N(n, p)^{14}C reaction by exposure of the precursor nitrogen gas to cosmic rays. This imparts a natural radioactivity to all the carbon present in the atmosphere, the biosphere, the recent carbon deposits in land areas (e.g., litter, peat, etc.), and oceanic carbon (mostly as bicarbonate). Because the main origin of ^{14}C is in the atmosphere, one expects a strong degree of mixing with the other naturally occurring carbon isotopes. On an atom basis, there is approximately 1 atom of ^{14}C to ~7×10^{11} atoms of stable carbon, or ~1.5×10^{-10} % of all carbon present. Using radioactive units, this gives a quasi-uniform value of 250 Bq(kgC)$^{-1}$ for the modern atmospheric carbon [Kotzer and Kramer, 1999].

Artificial or man-made ^{14}C originate mostly from former atmospheric weapon tests and from nuclear power reactors. Carbon-14 is an ubiquitous impurity produced in all reactors, and relatively small amounts are released to the environment through normal gaseous and liquid effluent release, and the disposal of solid radioactive waste. Because of its long half-life (5730 years) and its high mobility in the environment, ^{14}C is well mixed with inert carbon, and it enters the food chain to give a radioactive dose to biota and humans alike, as carbon is the fabric of life.

Global atmospheric mixing is fast (the half-life of Carbon in the atmosphere is ~3-12 years), hence any atmospheric emissions from artificial sources are readily mixed and recent plant material will reflect these levels [McNeely, 1994].

At present, nuclear reactors constitute the only major source of anthropogenic ^{14}C, because atmospheric nuclear weapons tests have been banned. Reactor-produced ^{14}C is not all bioavailable: a portion of it is trapped in fuel and in irradiated reactor components [Van Konynenberg et al., 1994; Yim and Caron, 2006], and engineered structures are in place to minimize releases to the environment. The irradiated components and fuel are non-reactive forms of ^{14}C, whereas substantial portions in engineered structures are primarily as dissolved bicarbonate ($H^{14}CO_3^-$) and its associated forms on ion exchange resins, and this form is available for gaseous release as $^{14}CO_2$. Although high containment levels are achieved, the overall inventory of this radioisotope continues to grow as the need for power production increases, and eventually, long-term options are needed to manage this radiocontaminant.

The main objective of this paper is to update global estimates of carbon-14 production from reactors, with specific emphasis on the situation in North America and Canada. It is recognized that Heavy Water Reactors (HWRs of the type CANDU) produce significant amounts of ^{14}C, compared to other reactor types [Liepins and Thomas, 1988; ACRP, 1995; Yim and Caron, 2006]. Hence, the North American focus is warranted because most of these reactor types are in Canada.

2. Natural cycling of ^{14}C

A simplified natural cycle of Carbon is shown in Figure 1. Using the atmosphere as a central point, carbon is readily assimilated by biota through photosynthesis in both land and oceanic areas. Carbon is sequestered mostly in organic form in biota and non-living organic material in land areas, whereas most of this element is present as bicarbonate in oceans. From the Figure, it can be easily calculated that the average residence time (t_R) of Carbon in the atmosphere is ~3.6 years (obtained by dividing the inventory of a "box" by its influx or outflux). The organic biota has a slightly longer t_R, 7.5 years, whereas peat and litter have a t_R of ~31 years. When combined, the t_R of organic material in land areas has a mean t_R value of ~23 years. Carbon in shallow oceanic areas has a t_R of ~5.5 years, whereas it is ~900 years in deeper oceanic waters. Cycling of rocks is known for the geological scale [Berner et al., 1984], however this long-term cycling for inorganic sedimentary carbon is much slower (see Figure), hence it is no longer discussed.

It is recognized that this global cycling is an oversimplification, however it provides a useful guidance for the cycling of ^{14}C, because it follows the same pattern. For example, the ^{14}C from atmospheric nuclear weapons tests in the early 1960's is currently close to pre-bomb levels [Kotzer and Kramer, 1999], which is consistent with the fast atmospheric mixing mentioned above. Most of this influx (~230 PBq; see Yim and Caron, 2006 and references therein) was a one-time "pulse". Because of natural cycling, most of this artificial ^{14}C is approximately equally sequestered in land organic material and oceanic bicarbonate. The atmospheric ^{14}C content of

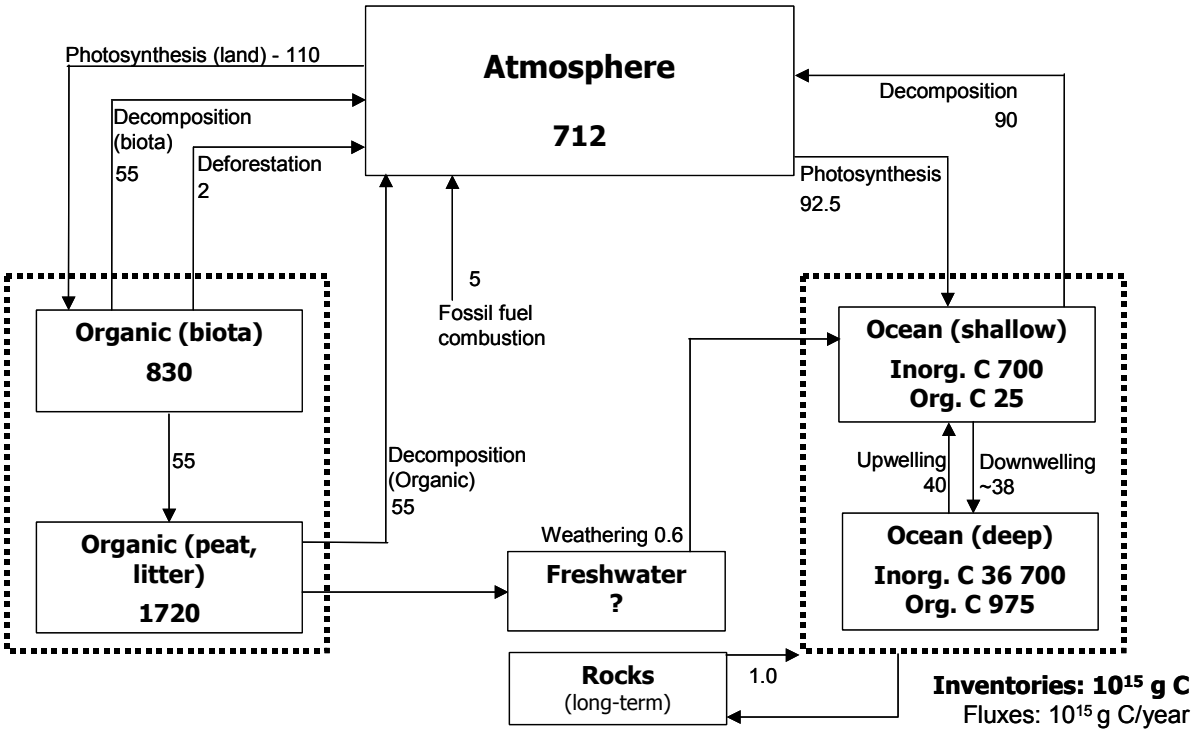

Figure 1: Global cycle of Carbon (modified from Morel and Herig, 1993).

140-220 PBq, when divided by its mass content (Figure 1) gives a specific activity that is consistent with the modern carbon, 250 Bq/kg C. On the same basis, we have calculated an oceanic ^{14}C content of ~9500 PBq (including a small correction factor for the age of the deep see Carbon), which is close to an earlier estimate of 10^4 PBq [ACRP, 1995 – references therein]. Using the same specific activity approach, previous estimates of $8.4 – 11.5 \times 10^3$ PBq [Yim and Caron, 2006; references therein] appear high; we propose a ^{14}C inventory of 750 PBq for land areas (biota and all organic material), including the amount from the "bomb peak", which has re-distributed. Finally, the production in the upper atmosphere is 1–1.4 PBq/year. This value is generally well agreed upon [Yim and Caron, 2006; references therein].

3. Man-made production

Man-made production includes atmospheric nuclear weapons testing in the early 1960s, and nuclear power reactor production. Other production, such as research nuclear reactors and nuclear reactors in vessels (submarines, boats, etc.) is small and it is no longer discussed.

As mentioned above, the total production of Carbon-14 from testing contributed to ~230 PBq, which is approximately the same amount as the whole atmospheric inventory. Cycling has washed out most of it from the atmosphere. Conversely, the majority of ^{14}C produced in nuclear reactors is contained: trapped in fuel, in reactor structural materials, in waste holding structures, or in licensed waste management areas. Carbon-14 production takes place through irradiation of precursor atoms within and around the reactor core. The most common parent (stable) atoms are

Table 1: Carbon-14 production mechanisms and cross-sections.

Parent atom	Reaction	Capture cross-section (barns)	Isotopic abundance (%)
^{14}N	$^{14}N(n, p)^{14}C$	1.81	99.6349
^{13}C	$^{13}C(n, \gamma)^{14}C$	0.0009	1.103
^{17}O	$^{17}O(n, \alpha)^{14}C$	0.235	0.0383

^{14}N, ^{17}O and ^{13}C, which are ubiquitous in major components or impurities. The reactions involving these precursors to produce Carbon-14 are listed in Table 1. In 2004, there were 440 power reactors worldwide producing 16% of the world's electricity. The Carbon-14 production from all these reactors depend upon several factors:

1. The quantity or distribution of parent atoms;
2. The reactor design, which imparts a different distribution of parent atoms within structural or surrounding material;
3. The number of reactors of different designs, combined with their lifetime production.

3.1 Quantity or distribution of parent atoms

For the purpose of discussion, the parent atoms are divided into: (i) fuel, (ii) structural materials, and (iii) coolant.

(i) Fuel: formation of ^{14}C is primarily caused by nitrogen impurities contained in the fuel and the ^{17}O in UO_2 matrix. Production rates of ^{14}C are about four times higher for the $^{14}N(n, p)^{14}C$ reaction than for the $^{17}O(n, \alpha)^{14}C$ reaction.

(ii) Structural materials: production from structural materials is caused by the $^{14}N(n, p)^{14}C$ on ^{14}N impurities present in stainless steel and other alloys used as fuel and fuel support hardware [Van Konynenburg, 1994]. The graphite reactors (gas- or liquid-cooled) contain substantial amounts of ^{13}C precursors, hence both the $^{14}N(n, p)^{14}C$ and the $^{13}C(n, \gamma)^{14}C$ contribute to the ^{14}C inventory.

(iii) Coolant: for liquid-cooled reactors (light or heavy water), the oxygen atoms in the water molecules contribute to the ^{14}C load ($^{17}O(n,\alpha)^{14}C$ reaction), while the nitrogen dissolved in the water are the second most important mechanism ($^{14}N(n,p)^{14}C$ reaction). In gas-cooled reactors, the three reactions listed in Table 1 are expected if the coolant gas is CO_2, especially if nitrogen impurities are present. Part of this problem is circumvented with He-cooled reactors, in which only nitrogen impurities could contribute to the ^{14}C load.

3.2 The reactor design

Light-water reactors (LWRs) comprise two sub-categories, the boiling water reactors (BWRs) and pressurized water reactors (PWRs). In both cases, light water is used as primary coolant. The ^{14}C production in various components is reasonably well known [Yim and Caron, 2006; references therein]. An important feature is the control over nitrogen concentration in the liquid

and/or cover gas. In pressurized heavy water reactors (HWRs), which are mostly of CANDU-type, two heavy water loops go through the reactor core: the primary coolant, and the moderator. The latter surrounds the reactor core, and as such, a large quantity of the precursor atoms (^{17}O) is in close proximity to the neutron flux of the reactor. This allows potentially a large ^{14}C production, compared to other types of reactors. Finally, the gas-cooled reactors (Magnox, AGR, HTGR) are expected to produce only small amounts of ^{14}C in the gas phase, because in a large part of the low density of target atoms, compared to the liquid-cooled reactors. These types of reactors are expected to produce ^{14}C from the natural ^{13}C in the large mass of the graphite moderator.

The ^{14}C produced in the fuel and the structural material (including the graphite moderator) is expected to remain with the fuel. On the other hand, the coolant (liquid or gas), including the liquid moderator of HWRs, is expected to circulate in closed-loops. The heavy water moderator is cleaned with ion exchange resins, which are kept in reactor service buildings. The HWRs also have an annular gas system, which is released to the atmosphere. The ^{14}C released from this source is closely monitored and is at comparatively low levels.

The expected ^{14}C production for various reactor parts has been catalogued for the various types of reactors in Table 2. These estimates are normalized per electricity production.

Table 2: Carbon-14 production per type of reactor (modified from Yim and Caron, 2006).

Item	Carbon-14 Production (TBq/Gwe-a)				
	BWRs	**PWRs**	**HWRs**	**Magnox**	**AGR/ HTR**
Fuel*					
^{17}O in UO_2	0.15	0.14	0.96	0.4	0.12/0.06
^{14}N impurities – fuel	0.58	0.57	3.8	0.27	0.48/0.12
^{14}N impurities in fuel assemblies	0.51	0.38	N/A	1.3	1.2/ N/A
Coolant					
^{17}O in H_2O	0.54	0.22	0.38	N/A	N/A
Coolant (CO_2 or He)	N/A	N/A	N/A	0.31	0.30/0.0007
Dissolved N_2 in coolant	0.11 – 0.43	0.04 – 0.19	0.2	N/A	N/A
Other					
Moderator	N/A	N/A	27*	10.8**	3.5/3.2
Annular gas	N/A	N/A	0.038	N/A	N/A
Total	1.7 – 2.0	1.3 – 1.5	32.4	13.1	5.6/3.4

*Heavy water moderator; **Graphite moderator
N/A: Not available or not applicable.

3.3 Lifetime production from reactors and annual increase

The current distribution of reactor types, on a power output basis, is 65% for PWRs, 23% for BWRs, 5% for HWRs, and 7% for gas-cooled (Magnox, AGR, HTR) [Yim and Caron, 2006]. This distribution can be used along with the ^{14}C production rates for each reactor type, using the data from Table 2. Two conditions need to be met, however, to estimate the total ^{14}C produced since the beginning of the nuclear power production: (i) this distribution needs to be established with time; and (ii) the cumulative power production needs to be known, as ^{14}C production is function of the power output of reactors. Both are available, albeit simplifications need to be made to calculate a global production.

The relative distribution of power reactors types is given in Figure 2, while the cumulative power production is shown in Figure 3. It can be seen that, after ~1975, the relative distribution of the reactor types is relatively constant. For calculation purposes, the situation can be simplified by assuming the post-1975 relative distribution of reactors is constant. This simplification does not account for the higher relative proportion of graphite reactors (LWGR) before ~1975, but this is without major consequence, as the cumulative production up to that date (including pre-1970 estimates) amounts to less than 3% of the global production. The production estimates from Figure 3 gives a total value of 5.15×10^4 TWe-h from recorded history to 2004 (inclusive).

The world's estimate of ^{14}C global production is given by, for each reactor type:

$$^{14}C \ production = \sum Rate_i \times component_i$$

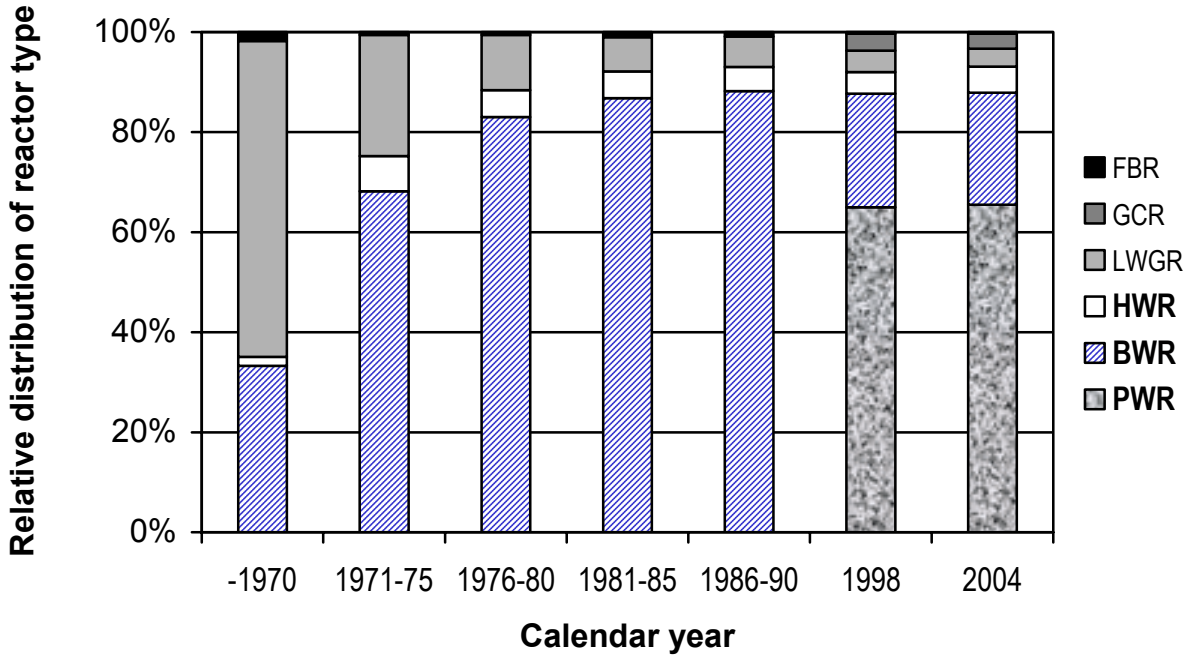

Figure 2: Relative distribution of reactor types ([Liepins, and Thomas, 1988], data prior to 1990; [AECL, 1999], data for 1998; [WNA, 2005], data for 2004.

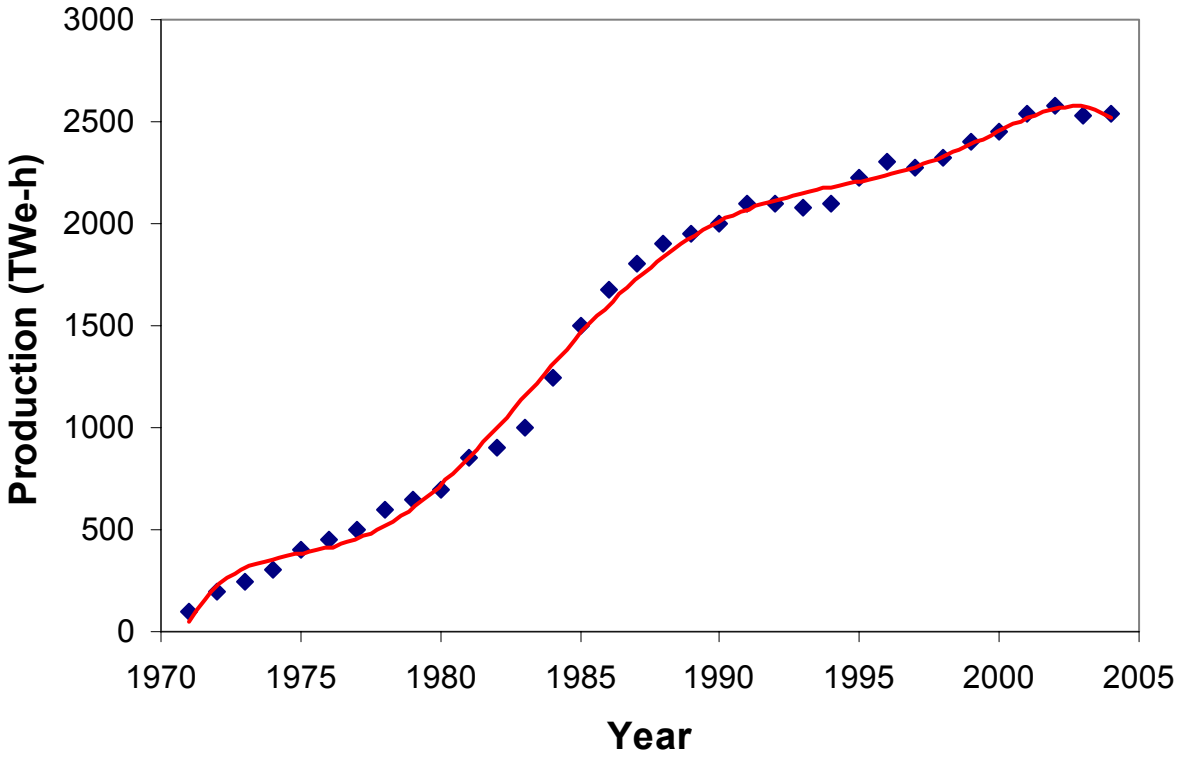

Figure 3: Total electricity production from the world's reactors up to year 2004 [WNA, 2005].

The reactors have been categorized into 4 types, for calculation purposes (Table 3), along with their relative percentages, normalized for the historical proportions from Figure 2. This calculation indicates that 22.0 PBq of ^{14}C have been produced by all power reactors, worldwide. This estimate does not include fast breeders, research reactors, reactors in submarines and vessels, and shutdown or decommissioned reactors [Yim and Caron, 2006], because of their anticipated small contributions.

Using the same approach and the total production of 2538 TWe-h for 2004, one can calculate the annual increase to be 1.09 PBq for 2005, should the power production remain the same. This production term is very similar to the natural production of 1–1.4 PBq/a in the upper atmosphere.

3.4 Forms available for release

The vast majority of ^{14}C, upon its generation in reactors, is contained in or near its original location: it can remain in the structural/fuel materials, in the coolant and the moderator (HWRs), on ion exchange resins used in purification. Only a small portion of it is released via gaseous or liquid effluents, typically less than 5%. The dominant released form is gaseous $^{14}CO_2$, with small amounts of organic ^{14}C, the latter coming from primary coolant [Yim and Caron, 2006; references therein]. These emissions are well below regulatory limits. The dissolved ^{14}C in the coolant or the heavy water moderator is mostly as dissolved bicarbonate (and its associated

Table 3: Global estimate of Carbon-14 production, by reactor type (modified from [Yim and Caron, 2006]).

Reactor type	Component	Production rate TBq/GWe-y	% of world capacity	Calculated ^{14}C production PBq
PWR	Fuel	0.72	65%	2.8
	Coolant	0.30		1.1
	Zircaloy + hardware	0.38		1.5
BWR	Fuel	0.73	23%	1.0
	Coolant	0.59		0.8
	Zircaloy + hardware	0.51		0.7
PHWR	Fuel	3.76	5%	1.1
	Coolant	0.38		0.11
	Moderator	27.0		7.9
Gas-cooled (Magnox/AGR/HTR)	Fuel	6.1/1.8/0.17	7%	1.1*
	Coolant	0.31/0.3/~0		0.06*
	Moderator (GR)	10.8/3.4/3.1		4.0*
Total – all reactors				**22.1**

*Total for all gas-cooled reactors.

inorganic carbon species). Resins used for purification or for chemical controls will pick up some or most of the bicarbonate, hence these will also be available for release. At present, spent resins are contained in dedicated storage tanks within reactor stations.

The chemical form of the ^{14}C in the fuel is mostly carbide, oxycarbide or elemental C, while the species in irradiated components are not well defined. The forms in fuels and irradiated components are considered to be unavailable for environmental release.

The values given in Table 3 are divided into fuel/zircaloy (structural component), and coolant/ moderator (HWRs). The latter are available for release, while the former are not. It can be readily calculated from the Table that ~10 PBq of the world's production is available for release, which is approximately 45% of the total production.

4. The North American and Canadian perspectives

At the end of 2004, 122 reactors were operational in North America; the distribution by type is shown in Table 4. From this, 2 reactors were in Mexico, 17 in Canada and the rest (103) was in the U.S. These combined for a total ^{14}C production of 10.4 PBq, based on the combined power output and the information in Table 2.

Table 4: List of operational reactors in North America [WNA, 2005], along with their ^{14}C production, annual increases, and forms available for release by reactor type.

Reactor type	No. of reactors (end of 2004)	Lifetime production, PBq	Projected increase 2004	%available for release(*)
PWR	78	2.11	0.10	24%
BWR	27	0.97	0.05	32%
HWR	17	7.35	0.32	88%
Total	**122**	**10.43**	**0.47**	**68%**

(*) "Forms available for release" are the dissolved CO_2 species (H_2CO_3, HCO_3^-, CO_3^{2-}) plus their exchanged forms on resins.

The 17 operating reactors in Canada are all HWRs. Including the 5 reactors in lay-up state, these reactors have produced a combined total of 2066 TWe-h of electricity [WNA, 2005]. Using the ^{14}C production rates (Table 2), this corresponds to a combined total of 7.35 PBq, or ~33% of the total man-made production from nuclear reactors. Most of it is available for release, e.g., 6.5 PBq or 29% of total production from nuclear reactors. Most of this inventory was produced in the moderator, and currently sits on ion exchange resins.

Projected increases are approximately 0.32 PBq/year, based on the year 2003 and 2004. From this calculated value, 0.28 PBq/y is available for release, and it currently sits on resins. An earlier lifetime production for Canadian reactors gave an estimate of 3.6 BPq on resins (available for release), 10 years ago [ACRP, 1995]. Assuming a constant production rate of 0.28 PBq/y for the 10 years after this estimate, this value plus our projection amounts to 6.4 PBq, which is very close to the value above. It is encouraging to note, however, that with implementation of appropriate waste management practices, only 0.06 PBq (~2%) were reported as released from these reactors in the period 1993-2002, in gaseous or liquid release [CNSC, 2003].

5. Future trends and conclusions.

The estimates provided in this paper have been compiled from recent sources that are readily available. For the purpose of accurate inventory control, production rate estimates from irradiated components should be further examined for recent reactor operations. Updated numbers of isotopic abundance of target nuclides should be used in future calculations, as the ^{14}C content is directly proportional to the number of target isotopes. Such use should be done with caution, however, as the data is sparse, and the isotopic abundance could change along with operation of the reactors (e.g, with need to upgrade heavy water at a given reactor).

Management of wastes containing ^{14}C forms that are available for release (resins from HWRs) should be prioritized over other ^{14}C-bearing wastes as different forms of ^{14}C bearing waste present different levels of potential for environmental releases.

Although ^{14}C in the environment is not at a level to pose a threat to public health, this radioisotope has characteristics which could be a concern if released. The current inventory continues to grow annually, along with the nuclear power production. If a long-term storage

strategy is adopted, wastes will accumulate in storage facilities, along with the associated potential for emissions. Although the dose impact on global scale appears small, local impact from ^{14}C release from a storage or disposal facility could reach a significant level, causing potential public health issues unless appropriate waste management measures are in place. At present, management is adequate but it should be borne in mind that resins (which contain most of the ^{14}C inventory in Canada) are not designed to hold contaminants for centuries or millennia. Source term studies (fundamental chemical exchange and its rates) should be done to ensure adequate long-term containment (storage), or for disposal.

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