

A record of fallout ^{239}Pu and ^{240}Pu at World Heritage Bathurst Harbour, Tasmania, Australia

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ABSTRACT

This study presents the first measurements of anthropogenic plutonium (^{239}Pu and ^{240}Pu) concentrations and atom ratios ($^{240}\text{Pu}/^{239}\text{Pu}$) for Tasmania, in sediment collected from Bathurst Harbour, in the Tasmanian Wilderness World Heritage Area, Australia. The weighted mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio measured at this site was 0.172 ± 0.007 which is consistent with published data from mainland Australia and global and Southern Hemisphere averages. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios ranged between 0.11 and 0.21 with the earliest recorded $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios being the lowest, suggesting an influence of low atom ratio fallout from nuclear testing in Australia. Post-moratorium fallout $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios were consistent with other records. Lead-210 (^{210}Pb) sediment chronologies indicate sediment accumulation rates have increased since the early part of the 19th century at this location.

1. Introduction

Tasmania, the smallest state (68,000 km²) in Australia, is an island located between 41 and 43°S in the Southern Ocean (Fig. 1). The South West National Park, part of the Tasmanian Wilderness World Heritage Area (Bosworth, 1982; Edgar et al., 2010), is one of only three temperate wilderness areas in the Southern Hemisphere (Edgar et al., 2010). Bathurst Harbour, one of Australia's most pristine estuaries, located on the southern part of Tasmania's west coast, is within this region (Fig. 1). Unlike many estuaries in Australia which have been highly modified since European settlement (Augustinus et al., 2010; Birch and McCreedy, 2009; Mayer-Pinto et al., 2015; Taylor et al., 2004; Townsend and Seen, 2012), Bathurst Harbour is an ideal location to investigate global and regional nuclear testing fallout patterns as it is an estuarine system virtually free of direct anthropogenic impacts.

This paper presents the first measurements of plutonium isotopes and $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios for Tasmania, from the remote and pristine Bathurst Harbour.

1.1. History of nuclear weapons testing and fallout measurements in and around Australia

The detonation of nuclear weapons in the atmosphere between 1945

and 1980 injected a wide range of anthropogenic radionuclides into the stratosphere where they were mixed during latitudinal circulation and globally distributed as fallout (UNSCEAR, 2000). The main periods of testing were 1957–1958 and 1961–1962 in the Northern Hemisphere, and 1966–1970 and 1971–1974 in the Southern Hemisphere (Moroney, 1979). Approximately 7 Mt was detonated in the Southern Hemisphere under the nuclear testing programmes of the British government in Australia and the French government in the South Pacific (UNSCEAR, 2000). The fallout inventory in the Southern Hemisphere was approximately one third of that in the Northern Hemisphere (Hancock et al., 2011; Leslie and Hancock, 2008; UNSCEAR, 2000).

Between the years of 1952–1957 a total of twelve nuclear weapons were detonated by the British Government in Australia, at Maralinga and Emu Field in South Australia, and the Montebello Islands off the coast of Western Australia. There were also “Minor Trials” and “Assessment Trials” from 1953 to 1963 at Emu Field and Maralinga (Symonds, 1985). The total yield of atmospheric nuclear tests in Australia was ~180 kt (Tables 2 and 4, Annex C, UNSCEAR (2000)). The nuclear test sites in South Australia and Western Australia are 2000 km and 3800 km northwest of Tasmania, respectively, and published fallout plume trajectories did not pass over Tasmania (Butement et al., 1957, 1958; Dwyer et al., 1959). However, monitoring stations in Tasmania (at Hobart and Western Junction near Launceston) that collected fallout

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Fig. 1. Location of Study Site, Bathurst Harbour, Tasmania, Australia, showing sediment core locations NB and BH.

using gummed sheets and, in some instances, air filters during the South Australian tests detected radioactivity (measured in $\mu\text{Ci}/\text{m}^2$ and converted to whole body dose) in 1956 after the Buffalo test series (four shots detonated from September–October 1956) (Butement et al., 1958), and in 1957 after the Antler test series (three shots detonated from September–October 1957) (Dwyer et al., 1959). A reservoir at Boyer, Tasmania, recorded a small but detectable increase in radioactivity in water during the Buffalo test series (Butement et al., 1958). These measurements were gross radioactivity measurements using a Geiger counter (Butement et al., 1957) and it was not possible to distinguish the source(s).

Undisturbed soils record fallout input and can be used to provide an average value for a given site. An international study reports fallout $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios ranging from 0.16 to 0.19 with a global average of 0.176 ± 0.014 (Krey et al., 1976). A later study reported latitudinal variation in $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios and proposed a higher atom ratio of 0.185 ± 0.047 for soils of the mid-latitudes of the Southern Hemisphere ($30\text{--}53^\circ\text{S}$) (Kelley et al., 1999). Low $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios in soil from some South American locations have been attributed to tropospheric fallout from French nuclear tests in the South Pacific in the 1960s and 1970s some 7000–8000 km away (Chamizo et al., 2011; Kelley et al., 1999).

Recent studies of Australian soil and sediments (none of which include data from Tasmania) indicate $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios are lower than the global average (0.142 ± 0.003 , Everett et al. (2008); $0.114\text{--}0.165$, Smith et al. (2016); and $0.120\text{--}0.197$, Tims et al. (2013)) particularly those close to the former testing sites in South Australia and Western Australia (Child and Hotchkis, 2013; Johansen et al., 2016, 2019; Tims et al., 2016).

Higher resolution fallout archives, such as ice cores from Antarctica and the Arctic (Koide et al., 1985) and sediment cores from the USA (Krey et al., 1990) indicate global $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios have changed throughout the history of testing, reflecting different source term contributions. According to Koide et al. (1985), before the brief moratorium on weapons testing which commenced in late 1958 and ended in 1961, high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios associated with testing by the United States in the Pacific Proving Grounds (PPG) dominated global fallout, while post-moratorium fallout, before the Partial Test Ban Treaty in 1963, was dominated by lower $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios associated with former Soviet Union tests. The characterisation of stratospheric fallout in the Northern Hemisphere commenced in 1959 (HASL, 1973). Prior to this, the mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio of two stratospheric air filter samples was 0.269 ± 0.006 and estimates from sediment cores during the period of 1952–1958 were $0.185\text{--}0.35$ (Krey et al., 1990).

1.2. Application of fallout radionuclides to sedimentation studies

Naturally occurring lead-210 (^{210}Pb , half-life 22.3 years (Baum et al., 2009)) has been widely used for dating recent sediments since it was first described (Goldberg, 1963). The three most common ^{210}Pb dating models are Constant Flux Constant Sedimentation (CF:CS) (Krishnaswamy et al., 1971), Constant Rate of Supply (CRS) (Appleby and Oldfield, 1978) and Constant Initial Concentration (CIC) (Robbins, 1978). Each model has its own set of assumptions that need to be considered when selecting an appropriate model (Appleby, 2001).

An independent age marker tied to a well-documented local or global event such as fallout radionuclides from nuclear weapons testing can be used to support or even calibrate ^{210}Pb derived ages (Appleby, 2001; Smith, 2001). Fallout radionuclides are often preserved in sedimentary records, and changes in concentrations and isotopic ratios that have occurred in fallout over time can be used as age markers (Hancock et al., 2011; Koide et al., 1985; Tims et al., 2010). It is critical that the sedimentary record and the sectioning interval enables sufficient resolution for the main features to be clearly distinguished.

^{137}Cs , with a half-life of 30.07 years (Baum et al., 2009), has been widely used to support ^{210}Pb chronologies (Battarbee et al., 2002; Christensen and Zhang, 1993; Edgington et al., 1991; Lockhart et al., 1995; von Gunten et al., 1997; Wan et al., 1987; Zwolsman et al., 1993), including in Australia (Gell et al., 2005; Gerritse et al., 1998; Pfitzer et al., 2004). Nearly two half-lives have elapsed since the peak release of ^{137}Cs in 1963 and the typical measurement technique for ^{137}Cs , gamma spectrometry, often requires large sample masses. Some high-resolution sedimentary studies, including this one, cannot supply the sample mass required for ^{137}Cs measurements without losing temporal resolution. Therefore, an alternative age marker is desirable.

Plutonium isotopes, ^{239}Pu and ^{240}Pu , have longer half-lives (24,100 and 6560 years respectively (Baum et al., 2009)) in comparison to ^{137}Cs , and it has been demonstrated that plutonium in undisturbed lacustrine sedimentary records are a good proxy for correlating depth of deposition with global nuclear fallout (Crusius and Anderson, 1995; Olivier et al., 2004; Sakaguchi et al., 2004). Plutonium will transfer almost quantitatively to soils and terrestrial sediments (Hakonson et al., 1981) as well as saline sediments (Hancock et al., 2011; Sholkovitz and Mann, 1984), making it a suitable candidate for erosion and sedimentation studies.

The use of high sensitivity mass spectrometry techniques such as Accelerator Mass Spectrometry (AMS; Fifield et al. (1996); Hotchkis et al. (2010)), Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS; Zheng and Yamada (2005)) and Thermal Ionisation Mass Spectrometry (TIMS; Cooper et al. (2000)) now mean that plutonium isotopic ratios can be measured in addition to plutonium concentrations at ultra-low levels in environmental materials. AMS is well suited to the analysis of low concentrations of plutonium (pg/g – fg/g range) such as is found in the sediments from areas with low fallout deposition, which is the case in the Southern Hemisphere. This is due to the technique's ability to discriminate between interferences such as isobaric molecular ions and abundant adjacent mass ions to enable accurate determination of ^{239}Pu in samples with complex matrices (Child et al., 2008). This means plutonium isotopic analysis is a viable alternative to ^{137}Cs for verifying ^{210}Pb chronologies, but it has rarely been applied to Southern Hemisphere estuarine sediments (Hancock et al., 2011).

2. Materials and methods

2.1. Study area

Bathurst Harbour ($43^\circ 20' 33'' \text{S}$, $146^\circ 10' 32'' \text{E}$) in the remote south west of Tasmania is only accessible on foot, by boat or light aircraft. It has a surface area of approximately 46 km^2 , maximum depth of 7 m and catchment of ca. 2000 km^2 (Fig. 1). The harbour is joined to the Southern Ocean via Bathurst Channel, which is a narrow, deep channel

that opens up at Port Davey. The region has a cool, wet climate with an annual rainfall of 2100 mm (BOM, 2019b) and an annual mean wind speed of 33 km h⁻¹ that is predominantly from the northwest (BOM, 2019a). Areas to the north west of Bathurst Harbour have a history of mining with the longest operation being the Mount Lyell Copper mine at Queenstown, which is 150 km north west of Bathurst Harbour. Cu-rich sulphide deposits were mined from the 1890s and the extracted ore was processed on-site using various smelting techniques until the late 20th century (McQuade et al., 1995). A small scale alluvial tin field mine (1 km²), accommodation huts and an unsealed airstrip built in the mid to late 1950s exist in a sub-catchment of Bathurst Harbour. Mining at this location has been continuous since the 1930s, however freshwaters entering Bathurst Harbour from this and other tributaries have not been found to contain elevated levels of trace and major ions (Mackey et al., 1996). Instead, trace element concentrations in Bathurst Harbour sediments indicate the site receives atmospheric input from regional activities such as Queenstown (Saunders et al., 2013), which has also been demonstrated for other lakes within the World Heritage Area (Schneider et al., 2019), as well as mining operations on the Australian mainland and more generally, due to global industrialisation.

2.2. Core collection

Sediment cores were collected from two locations in Bathurst Harbour (Fig. 1) in March 2007. The first sampling location, NB (43°18'39.4"S, 146°10'3.6"E), was in North Bay, near the North River inlet. It was chosen as it was protected from strong winds and mixing currents. The water depth was 5 m and a 35.5 cm core was extracted. The second sampling site, BH (43°20'35.2"S, 146°11'1.7"E), was chosen because of its proximity to the centre of Bathurst Harbour. Water depth was 7 m and the total length of a core retrieved was 36 cm.

Sediment core collection and sub-sampling were carried out using a messenger-operated gravity corer and a vertical-type extruder (Glew et al., 2001). At the time of collection evidence of laminations or burrowing biota were not observed. Each core was sectioned at 0.5 cm intervals on-site after collection in order to minimise disturbance of unconsolidated sediments. All samples were analysed at the Australian Nuclear Science and Technology Organisation (ANSTO).

2.3. Physical properties

The grain size distribution, in particular the percentage of clay (<2 µm) and silt (<63 µm) sized particles, in each sediment interval was measured using a Malvern Mastersizer S Laser Particle Size Analyser with a 300 R F lens, 0.05–900 µm detection range and a beam length of 2.40 mm. Approximately 0.2 g of bulk wet sample was used and duplicate measurements were taken. Each sample was dispersed in water, transferred to the dispersion unit, stirred and subjected to ultrasonic agitation before being pumped into the detection cell.

Moisture content was determined by heating each sample in an oven to constant weight (typically overnight) at 105 °C. Dry bulk density for each sediment interval was calculated as the dry mass per unit wet volume using the moisture content and an estimated sediment particle density of 2.5 g/cm³ (Avnimelech et al., 2001; Walling et al., 2002). Sediment interval depths were converted to cumulative dry masses using the sediment slice midpoint according to Appleby (2001) in order to account for sediment compression due to burial and sampling.

2.4. ²¹⁰Pb sediment dating

Approximately 2 g of dry sample was used for ²¹⁰Pb dating. Fifteen samples from the NB core and 25 samples from the BH core were chemically processed to separate and purify ²²⁶Ra and ²¹⁰Po (Harrison et al., 2003; McMinn et al., 1997). Sediments were spiked with ²⁰⁹Po and ¹³³Ba yield tracers and digested with a combination of HNO₃, HCl and H₂O₂. Polonium was auto-deposited onto polished silver disks and

Ra/BaSO₄ was collected on a filter paper as a micro-precipitate. Chemical yields exceeded 60% and 70% for Po and Ra/Ba, respectively. Alpha sources of ²²⁶Ra and ²¹⁰Po were measured in ORTEC Octète Plus chambers fitted with low-background ULTRA-AS ion-implanted silicon detectors. Energy and efficiency calibrations for each alpha detector were performed using stainless steel electroplated sources of ²³⁶U and ²⁴³Am. The CF:CS model was used to calculate sediment ages and mass accumulation rates in both cores.

The subtraction of ²²⁶Ra (proxy for supported ²¹⁰Pb) from ²¹⁰Po (proxy for total ²¹⁰Pb) gives excess ²¹⁰Pb (²¹⁰Pb_{ex}; Appleby (2001)). In this study ²²⁶Ra values were variable and an alternative estimate of supported ²¹⁰Pb was used as described in section 3.2.

2.5. Plutonium measurements

Plutonium isotopes were measured in 10 dried samples from the BH core. This core was selected because the site was considered to better represent the entire catchment, rather than being influenced by one or more of the tributaries and had the longer sedimentation history. Approximately 1 g of each sample was transferred into a 50 mL porcelain crucible and approximately 2 pg of NIST ²⁴²Pu tracer SRM 4334G was added. The samples were ashed at 800 °C (Farr et al., 2004) for 3 h. The ashed residues were refluxed with 15 mL of aqua regia at 80 °C for 8 h (Sill, 1975). The leachate was separated and heated to dryness, and the residual salts dissolved in 2 M HNO₃. This solution was applied to an Eichrom TEVA/UTEVA ion exchange resin column to yield a purified plutonium fraction which was then dispersed in 2.5 mg of iron oxide. Samples were then loaded into AMS target holders for measurement. Further details on this method, its validation and quality control parameters are described in Child et al. (2008).

The ANTARES AMS facility at ANSTO was utilised to perform the plutonium isotopic measurements. The facility consists of a 9 MV FN Tandem accelerator with a dedicated heavy ion beamline (Hotchkiss et al., 2000). PuO⁻ ions are generated using a negative ion sputter source and accelerated to 4 MV. The 5+ charge state was selected for analysis after argon gas stripping. Target plutonium isotopes (239, 240, 242) were cycled into the detector using synchronous high and low energy electrostatic switching. The data were corrected for dead time losses in the detector and normalised to an in-house isotopic ratio standard composed of NIST SRM 4330B ²³⁹Pu, NIST SRM 4338a ²⁴⁰Pu and NIST SRM 4334H ²⁴²Pu. The multiple sets of data were then averaged to provide a final measure of the Pu concentrations and atom ratios.

3. Results

Tables 1 and 2 show the naturally occurring ²²⁶Ra, a proxy for supported ²¹⁰Pb, and ²¹⁰Po, a proxy for total ²¹⁰Pb, as well as datasets of cumulative dry mass, grain size and ²¹⁰Pb_{ex} used for the age models for NB and BH cores respectively.

3.1. Physical properties

Sediments from both sites were predominantly silt size or smaller (<63 µm) with the NB core averaging 78% < 63 µm material and the BH core averaging 82% < 63 µm material. The BH core had a horizon of predominantly sand material at 3.82–3.96 g/cm² (14–15 cm). The NB core had a larger dry bulk density range (0.091–0.341 g/cm³) compared to the BH core (0.205–0.304 g/cm³). The NB core had a higher moisture content range (71.7–91.3%) compared to the BH core (74.3–83.6%).

3.2. Naturally occurring radionuclides: ²²⁶Ra, ²¹⁰Po and establishing natural sedimentation rates using ²¹⁰Pb_{ex}

²²⁶Ra (proxy for supported ²¹⁰Pb) in the NB and BH cores exhibited variability. ²²⁶Ra in the NB core ranged from 1.97 to 21.70 Bq/kg and

Table 1Physical data, ^{210}Pb data, CF:CS derived ages for the NB sediment core.

Depth Interval (cm)	Cumulative Dry Mass ^a (g/cm ²)	^{210}Po (total ^{210}Pb proxy) (Bq/kg)	^{226}Ra (supp. ^{210}Pb proxy) (Bq/kg)	Excess ^{210}Pb ^b (Bq/kg)	Clay <2 μm (%)	Mud <63 μm (%)	Dry Bulk Density (g/cm ³)	Moisture Content (%)	CF:CS Ages (years)	Calendar Age ^c (year)
0.0–0.5	0.03	206.7 $\pm$ 5.8	3.6 $\pm$ 0.7	198.3 $\pm$ 6.8	2.68	79.23	0.091	91.4	1 $\pm$ 0	2006
1.0–1.5	0.17	183.2 $\pm$ 6.3	21.7 $\pm$ 1.6	174.2 $\pm$ 7.2	3.19	79.04	0.188	83.1	4 $\pm$ 1	2003
2.0–2.5	0.38	169.0 $\pm$ 5.4	3.0 $\pm$ 0.4	160.5 $\pm$ 6.5	2.97	77.55	0.218	80.7	9 $\pm$ 2	1998
5.0–5.5	1.05	104.1 $\pm$ 4.5	10.3 $\pm$ 0.9	94.9 $\pm$ 5.6	3.39	82.93	0.233	79.5	26 $\pm$ 4	1981
7.0–7.5	1.54	54.7 $\pm$ 3.2	2.2 $\pm$ 0.5	45.5 $\pm$ 4.7	3.23	80.60	0.255	77.9	38 $\pm$ 6	1969
10.0–10.5	2.35	38.0 $\pm$ 1.6	19.9 $\pm$ 1.5	28.7 $\pm$ 3.8	3.13	78.64	0.282	75.9	58 $\pm$ 9	1949
12.0–12.5	2.90	27.9 $\pm$ 1.0	2.0 $\pm$ 0.4	18.5 $\pm$ 3.6	3.19	78.20	0.273	76.6	71 $\pm$ 12	1936
15.0–15.5	3.74	23.8 $\pm$ 0.9	6.3 $\pm$ 0.5	14.4 $\pm$ 3.6	2.86	74.50	0.282	75.9	91 $\pm$ 15	1916
17.0–17.5	4.31	9.4 $\pm$ 0.5	2.8 $\pm$ 0.4	–	2.97	80.61	0.296	74.9	–	–
20.0–20.5	5.19	14.2 $\pm$ 0.8	6.8 $\pm$ 0.7	–	3.05	75.22	0.285	75.7	–	–
22.0–22.5	5.80	5.6 $\pm$ 0.4	2.6 $\pm$ 0.3	–	3.33	79.56	0.333	72.2	–	–
25.0–25.5	6.79	11.0 $\pm$ 1.0	9.7 $\pm$ 0.8	–	2.88	71.24	0.327	72.7	–	–
27.0–27.5	7.46	4.2 $\pm$ 0.3	2.6 $\pm$ 0.3	–	3.57	84.20	0.341	71.7	–	–
30.0–30.5	8.48	11.1 $\pm$ 0.8	6.6 $\pm$ 0.6	–	3.39	77.33	0.341	71.7	–	–
33.0–33.5	9.48	10.3 $\pm$ 1.0	18.5 $\pm$ 1.3	–	2.97	77.35	0.323	73.0	–	–

– Not calculated as $^{210}\text{Pb}_{\text{ex}}$ was at or below the dating horizon.

ND not determined.

^a Cumulative dry mass calculated according to Appleby (2001).

^b Calculated as described in text, corrected to core collection date: March 13, 2007.

^c Calendar ages calculated from CF:CS ages.

there were three horizons of elevated activity concentration at 0.17, 2.35 and 9.48 g/cm² (1.0–1.5, 10.0–10.5 and 33.0–33.5 cm, see Table 1). ^{226}Ra in the BH core ranged from 2.84 to 14.93 Bq/kg. Due to variability in the ^{226}Ra values, supported ^{210}Pb was estimated using average ^{210}Po (proxy for total ^{210}Pb) values at the base of each core. Estimated supported ^{210}Pb for the NB core was 9.41 g/m², calculated using ^{210}Po values from and below 4.31 g/m² (17.0–17.5 cm). In the BH core, estimated supported ^{210}Pb was 16.76 Bq/kg using ^{210}Po values from and below 3.69 g/m² (13.5–14.0 cm). $^{210}\text{Pb}_{\text{ex}}$ was then calculated by subtracting the estimated supported ^{210}Pb described above from ^{210}Po values above 4.31 g/m² and 3.69 g/m² in NB and BH core respectively.

Fig. 2A shows $^{210}\text{Pb}_{\text{ex}}$ against cumulative dry mass for the NB sediment core. $^{210}\text{Pb}_{\text{ex}}$ between 0 and 3.74 g/cm² (0.0–15.5 cm) were used to calculate ages and a single zone of mass accumulation was used for the CF:CS model.

Fig. 3A shows $^{210}\text{Pb}_{\text{ex}}$ against cumulative dry mass for the BH sediment core. The vertical trend in $^{210}\text{Pb}_{\text{ex}}$ activities in the top part of the profile indicates a surface mixing layer down to 0.61 g/cm² (2.0–2.5 cm) and sediments above this layer were excluded from the age models. $^{210}\text{Pb}_{\text{ex}}$ between 0.61 g/cm² and 3.31 g/cm² (2.0–12.5 cm) were used to calculate ages. In the CF:CS model two zones of mass accumulation, above and below the inflection point at 2.49 g/cm² (9.0–9.5 cm), were used.

The ages calculated using the CF:CS dating model are shown in Tables 1 and 2 for the NB and BH cores respectively. Sediments recovered from the northern part of Bathurst Harbour (NB core) revealed ages of up to 91 $\pm$ 15 years (Fig. 2B), while sediments recovered from the centre (BH core) were up to 135 $\pm$ 25 years old (Fig. 3B). The CF:CS single zone mass accumulation rate for the NB core was 0.041 $\pm$ 0.003 g/cm²/yr. The CF:CS upper and lower mass accumulation rate zones for the BH core were 0.036 $\pm$ 0.002 g/cm²/yr and 0.013 $\pm$ 0.002 g/cm²/yr respectively. The BH core was subsequently used for plutonium measurements for reasons outlined in section 2.5.

3.3. Plutonium isotope concentrations

Activity concentrations for the plutonium isotopes ^{239}Pu and ^{240}Pu are shown in Table 3 and Fig. 4A. Plutonium was measured above the instrumental background in all samples analysed (i.e. equivalent to calendar years 1941 ($\pm$ 11) - 1978 ($\pm$ 5) using the CF:CS model). The peak in ^{239}Pu and ^{240}Pu activity concentration occurred at 5.0–5.5 cm. The $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios are in Table 3 and Fig. 4B and ranged from 0.11 $\pm$ 0.03 and 0.11 $\pm$ 0.02 (8.5–9.0 cm and 8.0–8.5) to 0.21 $\pm$ 0.01 (7.0–7.5 cm).

4. Discussion

4.1. Establishing sedimentation rates in Bathurst Harbour

Where sedimentation rates have remained constant, $^{210}\text{Pb}_{\text{ex}}$ plotted logarithmically (as in Figs. 2A and 3A), will produce a straight line. Deviations from a straight line, or non-monotonic features indicate changes in sedimentation rates, sediment focussing, interruptions to sediment accumulation and/or sediment mixing (Appleby, 2001). A near-vertical decrease in $^{210}\text{Pb}_{\text{ex}}$ was observed in the top 0.61 g/cm² (2.0–2.5 cm) of the BH core which is suggestive of either sediment mixing or extremely rapid sedimentation in that portion of the core. There have not been any recent (i.e. last 10 years) land use changes or environmental events in the catchment that would support the theory of rapid sedimentation nor was there a marked change in the composition of sediment during this period (Table 2). Therefore, it has been interpreted as fixed depth, surface sediment mixing and excluded from the sediment dating models. It was likely caused by physical effects such as wave action rather than aquatic vegetation or burrowing biota; neither of which were observed during core collection nor sampling. Sediments in surface mixing zones are subject to mixing until, through burial, they exceed the finite depth of mixing and continue to be buried without further disturbance. This will be discussed below in the interpretation of the plutonium data.

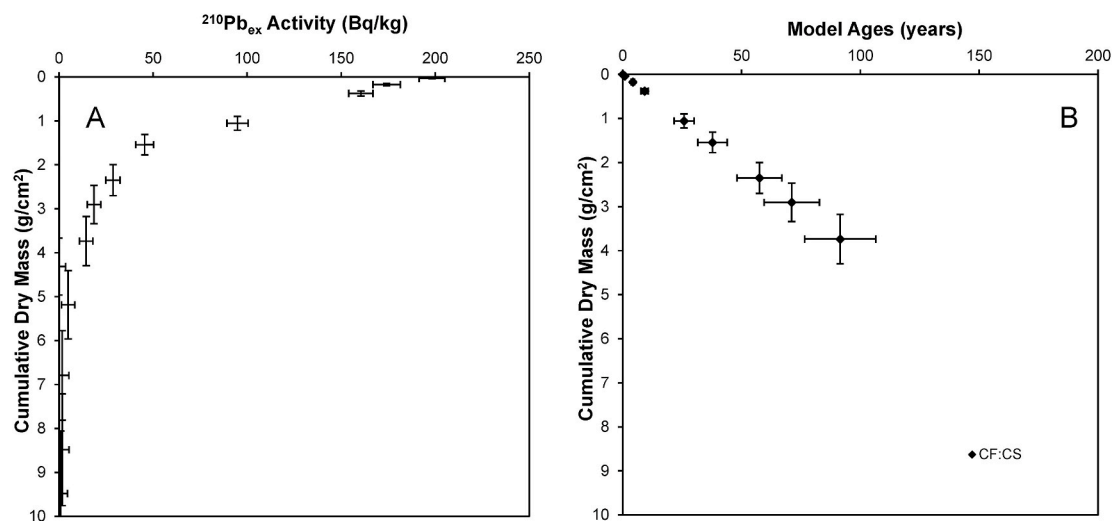
Both core sites revealed different sediment accumulation patterns; the NB site recorded a constant mass accumulation rate of 0.041 $\pm$

Table 2Physical data, ^{210}Pb data, CF:CS derived ages for the BH sediment core.

Depth Interval (cm)	Cumulative Dry Mass ^a (g/cm ²)	^{210}Po (total ^{210}Pb proxy) (Bq/kg)	^{226}Ra (supp. ^{210}Pb proxy) (Bq/kg)	Excess ^{210}Pb ^b (Bq/kg)	Clay <2 μm (%)	Mud <63 μm (%)	Dry Bulk Density (g/cm ³)	Moisture Content (%)	CF:CS Ages (years)	Calendar Age ^c (year)
0.0–0.5	0.07	353.3 $\pm$ 13.7	6.4 $\pm$ 0.8	339.2 $\pm$ 14.1	3.70	83.34	0.304	74.3	mixed layer	ND
1.0–1.5	0.34	324.2 $\pm$ 11.0	9.8 $\pm$ 1.1	308.0 $\pm$ 11.3	2.85	84.14	0.241	78.9	mixed layer	ND
2.0–2.5	0.61	359.1 $\pm$ 8.1	4.0 $\pm$ 0.6	350.4 $\pm$ 8.7	4.42	93.32	0.293	75.1	mixed layer	ND
2.5–3.0	0.76	333.2 $\pm$ 10.9	2.8 $\pm$ 0.5	318.9 $\pm$ 11.3	3.61	80.43	0.293	75.1	21 $\pm$ 3	1986
3.0–3.5	0.90	321.2 $\pm$ 6.1	6.0 $\pm$ 0.6	311.6 $\pm$ 6.8	4.43	93.88	0.288	75.4	25 $\pm$ 4	1982
3.5–4.0	1.05	258.4 $\pm$ 9.1	7.6 $\pm$ 0.8	243.6 $\pm$ 9.6	3.38	81.09	0.281	75.9	29 $\pm$ 5	1978
4.0–4.5	1.18	277.9 $\pm$ 7.9	6.3 $\pm$ 0.9	267.3 $\pm$ 8.6	4.85	94.04	0.259	77.6	33 $\pm$ 5	1974
5.0–5.5	1.41	202.7 $\pm$ 8.6	8.0 $\pm$ 1.3	186.3 $\pm$ 9.0	3.66	92.73	0.205	81.8	40 $\pm$ 6	1967
5.5–6.0	1.53	188.2 $\pm$ 4.2	4.0 $\pm$ 0.8	175.5 $\pm$ 5.1	4.61	94.16	0.274	76.5	43 $\pm$ 7	1964
6.5–7.0	1.81	125.7 $\pm$ 3.5	5.7 $\pm$ 0.9	109.8 $\pm$ 4.5	4.51	90.90	0.279	76.1	51 $\pm$ 8	1956
7.5–8.0	2.09	126.4 $\pm$ 3.2	5.4 $\pm$ 0.5	112.3 $\pm$ 4.3	4.82	95.30	0.281	75.9	59 $\pm$ 9	1948
8.5–9.0	2.35	106.5 $\pm$ 3.6	6.4 $\pm$ 0.6	90.5 $\pm$ 4.5	2.86	76.09	0.249	78.3	66 $\pm$ 11	1941
9.0–9.5	2.49	80.4 $\pm$ 2.2	3.5 $\pm$ 0.3	65.2 $\pm$ 3.5	4.16	92.68	0.297	74.8	70 $\pm$ 13	1937
10.0–10.5	2.77	46.7 $\pm$ 2.5	9.0 $\pm$ 1.1	30.0 $\pm$ 3.7	3.35	86.81	0.252	78.1	92 $\pm$ 17	1915
11.5–12.0	3.17	31.0 $\pm$ 1.7	7.7 $\pm$ 0.8	14.3 $\pm$ 3.2	2.85	76.14	0.288	75.5	124 $\pm$ 23	1883
12.0–12.5	3.31	24.0 $\pm$ 0.7	3.9 $\pm$ 0.4	7.4 $\pm$ 2.8	3.89	92.07	0.273	76.6	135 $\pm$ 25	1872
13.5–14.0	3.69	17.1 $\pm$ 1.1	7.1 $\pm$ 0.7	–	2.85	79.46	0.235	79.4	–	–
14.0–14.5	3.82	20.2 $\pm$ 0.7	10.2 $\pm$ 1.0	–	0.35	13.03	0.272	76.6	–	–
14.5–15.0	3.96	17.1 $\pm$ 0.6	8.3 $\pm$ 0.8	–	1.59	48.62	0.277	76.3	–	–
15.0–15.5	4.08	17.7 $\pm$ 1.6	11.5 $\pm$ 1.1	–	2.83	84.20	0.226	80.1	–	–
16.0–16.5	4.33	10.7 $\pm$ 0.6	7.9 $\pm$ 0.8	–	2.98	83.99	0.281	76.0	–	–
20.0–20.5	5.31	17.2 $\pm$ 1.9	9.7 $\pm$ 1.2	–	3.13	83.79	0.210	81.4	–	–
25.0–25.5	6.42	16.2 $\pm$ 1.9	10.4 $\pm$ 1.1	–	3.11	82.74	0.231	79.7	–	–
30.0–30.5	7.71	19.1 $\pm$ 1.5	11.6 $\pm$ 1.1	–	2.99	86.38	0.284	75.7	–	–
33.0–33.5	8.57	15.5 $\pm$ 1.3	14.9 $\pm$ 1.3	–	2.90	83.23	0.294	75.0	–	–

- Not calculated as $^{210}\text{Pb}_{\text{ex}}$ was at or below the dating horizon.

ND not determined as this sediment was part of the mixed layer.

^a Cumulative dry mass calculated according to Appleby (2001).^b Calculated as described in text, corrected to core collection date: March 13, 2007.^c Calendar ages calculated from CF:CS ages.**Fig. 2.** North Bay (NB) core A) $^{210}\text{Pb}_{\text{ex}}$ versus cumulative dry mass B) CF:CS derived ages versus cumulative dry mass.

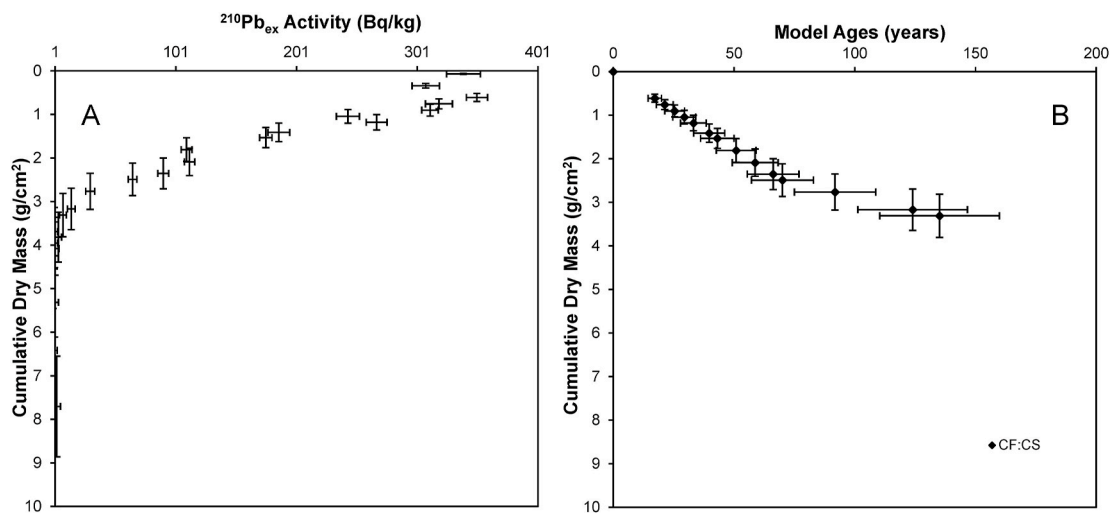


Fig. 3. Bathurst Harbour (BH) core A) $^{210}\text{Pb}_{\text{ex}}$ versus cumulative dry mass B) CF:CS derived ages versus cumulative dry mass.

Table 3

^{239}Pu and ^{240}Pu activities and $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio determined for the BH sediment core.

Depth Interval (cm)	Cumulative Dry Mass (g/cm²)	^{239}Pu Activity (Bq/kg)	^{240}Pu Activity (Bq/kg)	Combined $^{239+240}\text{Pu}$ Activity (Bq/kg)	$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio	Calendar Age (year)	Calendar Age Range (year)
3.5–4.0	1.05	1.45 ± 0.12	0.74 ± 0.08	2.19 ± 0.14	0.14 ± 0.02	1978	1973–1982
4.5–5.0	1.30	1.47 ± 0.12	0.81 ± 0.09	2.28 ± 0.15	0.15 ± 0.01	1971	1964–1977
5.0–5.5	1.41	1.79 ± 0.15	1.16 ± 0.12	2.95 ± 0.19	0.18 ± 0.01	1967	1961–1974
5.5–6.0	1.53	1.75 ± 0.14	1.15 ± 0.11	2.90 ± 0.18	0.18 ± 0.01	1964	1957–1971
6.0–6.5	1.67	1.39 ± 0.13	0.95 ± 0.12	2.34 ± 0.17	0.19 ± 0.01	1960	1952–1968
6.5–7.0	1.81	1.14 ± 0.10	0.84 ± 0.09	1.98 ± 0.13	0.20 ± 0.01	1956	1948–1964
7.0–7.5	1.95	0.92 ± 0.08	0.71 ± 0.08	1.63 ± 0.12	0.21 ± 0.01	1952	1943–1962
7.5–8.0	2.09	0.59 ± 0.07	0.33 ± 0.05	0.92 ± 0.08	0.15 ± 0.03	1948	1939–1958
8.0–8.5	2.22	0.51 ± 0.04	0.21 ± 0.02	0.72 ± 0.05	0.11 ± 0.02	1945	1934–1955
8.5–9.0	2.35	0.22 ± 0.03	0.09 ± 0.02	0.30 ± 0.04	0.11 ± 0.03	1941	1930–1951

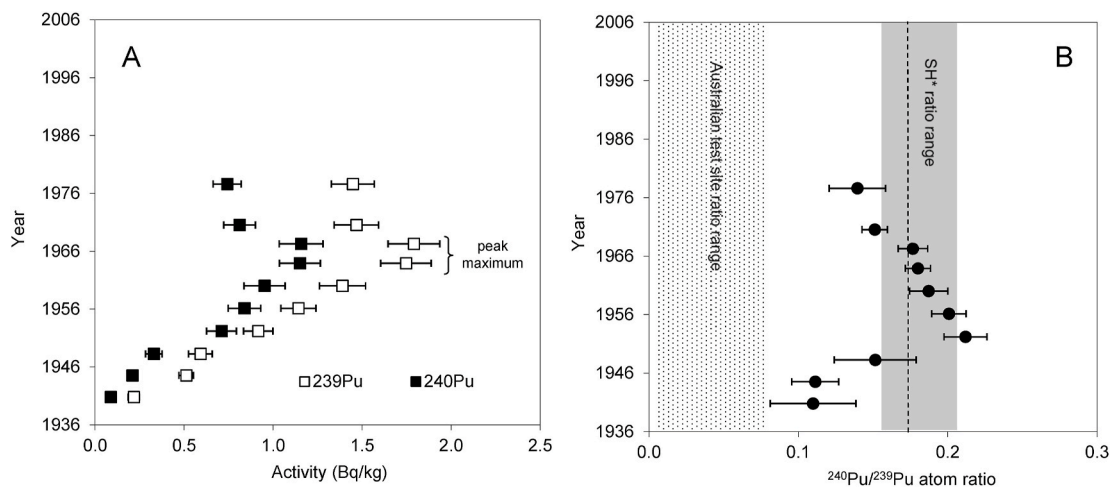


Fig. 4. BH core A) ^{239}Pu and ^{240}Pu activities versus CF:CS derived calendar age B) $^{240}\text{Pu}/^{239}\text{Pu}$ isotopic ratio versus CF:CS derived calendar age. Error bars indicate analytical uncertainty based on $n = 1$. Dotted line represents average global ratio for soils (Krey et al., 1976), diagonal line shading represents the Southern Hemisphere range measured in soil excluding sites in South America influenced by tropospheric fallout from French testing (Kelley et al., 1999) and dotted shading indicates the range of ratios measured at Australian Nuclear Test Sites (Child and Hotchkis, 2013; Johansen et al., 2014, 2016, 2019).

$0.003 \text{ g/cm}^2/\text{yr}$, ($r^2 = 0.96$) while the BH site revealed an increase in sedimentation from 1937 (± 11) from $0.013 \pm 0.001 \text{ g/cm}^2/\text{yr}$ ($r^2 = 0.98$) to $0.036 \pm 0.002 \text{ g/cm}^2/\text{yr}$ ($r^2 = 0.97$).

Church et al. (2006) report the average rise in sea level across Australia between 1920 and 2000 to be 1.2 mm per year. Recent observations in the Port Davey estuary, which includes Bathurst Harbour,

consider sea level rise to be the mechanism responsible for increases in bank erosion (Bradbury, 2011) which may explain the increase in mass accumulation rate. Land use changes in the catchment (tin mining in the 1930s and unsealed airstrip constructed in the 1950s) may also have contributed to the mass accumulation rate increase.

4.2. Plutonium isotope concentrations, inventories and atom ratios

Sediment accumulation without disturbance should preserve a nuclear fallout inventory, and a proposed Southern Hemisphere plutonium inventory using ^{137}Cs values (UNSCEAR, 2000) and $^{137}\text{Cs}/^{239+240}\text{Pu}$ ratios (Koide et al., 1982) has been described by Hancock et al. (2011). The proposed year of maximum fallout in the Southern Hemisphere is 1964 (Hancock et al., 2011) and the date of first detection of fallout plutonium in the southern latitudes (30–40°S) is estimated to be 1953–1954 (Leslie and Hancock, 2008).

In this study, plutonium was detected above the instrumental background of the AMS technique in every sample analysed from the BH core with ^{210}Pb derived ages ranging from the years 1941–1978 (Fig. 4A). The peak in plutonium spans the years 1964 (± 7)–1967 (± 6) which overlaps with the year of maximum fallout in the Southern Hemisphere, 1964 (Hancock et al., 2011).

The broad shape of the fallout peak indicates there has been some sediment mixing or migration of plutonium in the core. Additionally, there are two plutonium data points with ages older than the expected year of first detection in the 30°–40°S region, 1953–1954 (Leslie and Hancock, 2008) also suggesting mixing of plutonium-labelled sediment or migration of plutonium. This is likely a product of sediment mixing that occurred during initial deposition, at the sediment/water interface (as observed in the $^{210}\text{Pb}_{\text{ex}}$ data and described in section 4.1). The input of fallout plutonium was not constant over time, unlike the assumption for $^{210}\text{Pb}_{\text{ex}}$, and sediment mixing effectively stretches the fallout signal and flattens the peak prior to burial. Fallout plutonium older than the date of first appearance has been observed elsewhere and attributed to small but measurable diffusion of plutonium. This impacts the first appearance of the fallout age marker, but not the maximum fallout peak age marker (Crusius and Anderson, 1995; Woodward et al., 2017).

The plutonium atom ratios recorded at a given location comprise a mixture of global input as well as regional and local input, if present. The $^{240}\text{Pu}/^{239}\text{Pu}$ pre-moratorium atom ratios recorded at Bathurst Harbour are between 0.11 ± 0.03 – 0.15 ± 0.03 with the older atom ratios being the lowest. This is not consistent with pre-moratorium global fallout atom ratios which were characteristically high. Furthermore, the highest atom ratios were observed in the early years (1952–1954) when the United States PPG high yield, surface detonated weapons accounted for >90% of global fallout (Koide et al., 1985). PPG sites have typical $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of >0.3 (Muramatsu et al., 2001) and Southern Hemisphere ice cores from Antarctica recorded pre-moratorium $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios of between 0.19 and 0.34 with the older atom ratios being the highest (Koide et al., 1985). However, the twelve atmospheric nuclear tests carried out in Australia during the pre-moratorium period have distinctive low atom ratios: 0.01–0.025 at Emu Field (Child and Hotchkis, 2013); 0.05–0.07 at Taranaki, Maralinga (Johansen et al., 2014, 2016); and 0.027–0.053 at the Montebello Islands (Child and Hotchkis, 2013; Johansen et al., 2019). Therefore, the pre-moratorium fallout record from Bathurst Harbour is most likely a combination of fallout from nuclear testing in Australia with distinctive low $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios as well as global fallout with distinctive high $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios.

The two highest $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios recorded at Bathurst Harbour (0.21 ± 0.01 and 0.20 ± 0.01) correspond to the years 1952 ± 9 and 1956 ± 8 , and represent $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios immediately before, during and after the moratorium on nuclear testing between 1958 and 1961. These ratios are a combination of higher ratio fallout from the earlier PPG tests and lower ratio fallout from the former Soviet Union tests. Fallout from former Soviet Union tests in 1961–1962 influenced Southern Hemisphere fallout as these tests injected material into the polar stratosphere with circulation and residence times being between 0.5 and 2 years depending on whether debris entered the lower or upper polar stratosphere (Peterson, 1970).

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios at Bathurst Harbour stabilise around 0.19 ± 0.01 to 0.18 ± 0.01 between 1960 (± 8) and 1967 (± 6) and are

representative of contemporary global fallout ratios from the period of maximum testing before the Partial Test Ban Treaty in 1963 (Koide et al., 1982, 1985). The youngest $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios (corresponding to years 1971 (± 6)–1978 (± 5)) then decline to 0.15 ± 0.01 and 0.14 ± 0.02 , and likely contain a contribution of tropospheric fallout from the French government tests in the South Pacific from 1966 to 1974 at Mururoa and Fangataufa atolls (UNSCEAR, 2000). $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios from French testing in Polynesia are low (0.03 – 0.05 ; Chiappini et al. (1999)) and input of tropospheric debris has been reported for 20°–40°S in South America (Chamizo et al., 2011).

The mean plutonium ratio, weighted with total plutonium concentration, was calculated for comparison with surface soil studies. The weighted mean $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratio at Bathurst Harbour is 0.172 ± 0.007 which is lower but within the error proposed for soils from 30 to 53 °S (0.185 ± 0.047 ; Kelley et al., 1999). It is consistent with measurements of Australian soils from the same study (Brisbane 0.1768 ± 0.0027 and Melbourne 0.1716 ± 0.0014), and more recent $^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios observed in surface soil and surface sediment from mainland Australia locations, which indicate nuclear testing in Australia may have had a broader impact on plutonium ratios across the continent than initially thought (Everett et al., 2008; Smith et al., 2016; Tims et al., 2013). Tims et al. (2013) report an atom ratio range of 0.120–0.197 for Eastern Australian sites in Queensland, New South Wales, Victoria and the Australian Capital Territory. Smith et al. (2016) report a range of 0.114–0.165 for the Sydney Basin, New South Wales, and Everett et al. (2008) report an average atom ratio of 0.149 ± 0.003 for the Herbert River Catchment in Queensland.

$^{239+240}\text{Pu}$ activity concentrations in Bathurst Harbour sediments ranged from 0.30 ± 0.04 to 2.95 ± 0.19 Bq/kg. These are higher than published data for other Southern Hemisphere locations within the Australian east coast and Tasman Sea region. Estuarine sediment cores collected from Moreton Bay, Queensland, 1900 km to the north-northeast of Bathurst Harbour, had $^{239+240}\text{Pu}$ concentrations that ranged from 0.009 Bq/kg to 0.062 Bq/kg (estimated based on graphed data from Sanders et al. (2016)). A study of sediment cores from one freshwater New Zealand location, Lake Okaro (2600 km to the north-east), and three estuarine Australian locations: Stokes Inlet (2400 km northwest); Hinchinbrook (2800 km north); and Gippsland (650 km north-northeast) present $^{239+240}\text{Pu}$ concentrations that range from 0.05 to 1.1 Bq/kg (estimated based on graphed data from Hancock et al. (2011)). The mass accumulation rates in Bathurst Harbour are 1–3 orders of magnitude lower than the other sites discussed. Assuming fallout plutonium transfers quantitatively to sediments, sites where sediment is accumulating more slowly will have higher concentrations of fallout radionuclides in comparison to sites with higher accumulation rates.

Plutonium isotope inventories (Pu_i) are a record of the relative amounts of plutonium deposited at a site and were estimated to be $^{239}\text{Pu}_i = 18.0 \pm 0.5$ Bq/m², $^{240}\text{Pu}_i = 11.0 \pm 0.4$ Bq/m² and $^{239+240}\text{Pu}_i = 29.0 \pm 0.6$ Bq/m² for Bathurst Harbour. Calculated $^{239+240}\text{Pu}_i$ values in freshwater and estuarine sediments for four Australian and New Zealand sites range between 9.9 ± 0.7 and 280 ± 5 Bq/m² (Hancock et al., 2011). In this study, the site closest to Bathurst Harbour was the Gippsland site with $^{239+240}\text{Pu}_i$ values for the three lakes within the Gippsland Lakes system being 51 ± 6 , 58 ± 5 and 9.9 ± 0.7 Bq/m². The Bathurst Harbour $^{239+240}\text{Pu}_i$ of 29 ± 0.6 Bq/m² is within that range.

5. Conclusions

This study presents the first record of anthropogenic plutonium concentrations from nuclear weapons testing fallout in Tasmania, Australia, from sediment collected from a remote and near-pristine estuary in the Tasmanian Wilderness World Heritage Area.

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios ranged from 0.11 to 0.21, with early pre-moratorium ratios lower than other temporal records demonstrating there was likely input from nuclear testing in Australia in addition to global fallout. The weighted mean ($\pm$ standard error) of all measured

$^{240}\text{Pu}/^{239}\text{Pu}$ atom ratios was 0.172 ± 0.007 which is within the range of global values and a number of other Australian locations.

A surface mixing layer caused some stretching of the plutonium record as demonstrated by the broad peak maximum correlating to the year of maximum fallout and the presence of plutonium below of the year of first appearance of fallout radionuclides in the Southern Hemisphere.

Contemporary rates of sediment accumulation, established using the ^{210}Pb CF:CS dating model, ranged between 0.036 and 0.041 g/cm²/yr, while prior to the early part of the 19th century, the sedimentation accumulation rate was 0.013 g/cm²/yr.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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