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Tritium in Australian precipitation: A 50 year record

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SUMMARY

Tritium in precipitation has been measured in Australia over the past 50 years, as an essential research tool in hydro-climate studies, and to contribute to the Global Network for Isotopes in Precipitation (GNIP). Tritium, a component of the water molecule (HTO), is the only true age tracer for waters. The elevated level of tritium in the environment as a result of last century's atmospheric thermonuclear testing delivers the benefit of tracing groundwater systems over a 100 year timeframe. The concentration of tritium in Australian precipitation reached a maximum of 160 Tritium Units (TU) in 1963, during one of the most intense periods of nuclear weapons testing. From 1963 to present we observe a rapid drop in the concentration of tritium, more than expected from natural decay, and this can be attributed to the wash out of tritium into the oceans and groundwater. Spikes in the tritium level are superimposed over this general trend; the first around 1969, with levels ranging from 39.4 to 84.4 TU was due to French atmospheric weapon testing, and again in 1990, levels peaked between 6.6 and 12.9 TU, which is attributed to tritium leaking from underground tests in the French Pacific. Since 1990 the levels of tritium have declined globally and regionally. Currently the levels of tritium in Australia are stabilising to around 2–3 TU increasing with latitude across the continent, suggesting that today the tritium in precipitation is predominantly natural. The spatial distribution of tritium is presented and found to be dominated by the annual stratosphere–troposphere exchange in combination with latitude and continental effects. A precipitation amount effect is also observed for inland sites.

1. Introduction

Tritium (^{3}H) is the radioisotope of hydrogen with a half-life of 12.32 years (Lucas and Unterweger, 2000). Incorporated directly into the water molecule in the global hydrological system, tritium is the only direct tracer for groundwater dating (Cartwright and Morgenstern, 2012; Morgenstern and Daughney, 2012). Tritium is naturally produced in the atmosphere by cosmic ray spallation of nitrogen. It is also produced anthropogenically by a variety of nuclear activities (CNSC, 2009; Akata et al., 2011). By far the most significant release of tritium into the atmosphere was from atmospheric thermonuclear explosions which introduced tritium directly into the stratosphere, and resulted in an increase across the worldwide distribution (Begemann and Libby, 1957; Martell, 1963). Once in the stratosphere, tritium is rapidly oxidised into tritiated water (HTO) and transferred into the troposphere by stratosphere-to-troposphere transport in spring, where it is rapidly removed by precipitation (Morishima et al., 1985; Ehhalt et al., 2002) and then transported in the environment through the hydrological cycle.

This bomb-tritium input is an effective and useful environmental tracer for studying hydrogeological systems. For several years tritium concentrations in groundwater have been widely applied as a semi-quantitative tool for the identification of modern recharge from the post-1960s thermonuclear era (e.g. Allison and Hughes, 1975; Scanlon et al., 2002; Huang and Pang, 2010; Yangui et al., 2012). Lumped parameter modelling of tritium transport has also been used to quantitatively calculate the mean transit time and mean of the residence time distribution of water through an aquifer (Zuber, 1986; Zuber and Maloszewski, 2001). More recently tritium is increasingly being applied to calibrate and validate three-dimensional groundwater flow and solute transport models of aquifer systems at the regional scale (Orban et al., 2010; Zuber et al., 2011). With a levelling off of bomb-tritium levels in precipitation to natural levels, unique groundwater ages are now being obtained from tritium measurements (Morgenstern et al., 2010; Cartwright and Morgenstern, 2012; Morgenstern and Daughney, 2012).

Tritium concentrations in the atmosphere are known to vary across latitudes and between seasons (Hauglustaine and Ehhalt,

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2002). When atmospheric tritium concentrations are uniform, a continental effect is evident whereby tritium in precipitation at continental sites is higher relative to coastal sites due to (i) the dilution of atmospheric tritium with low concentrations in oceanic water (Momoshima et al., 1991; Vreca et al., 2006), and (ii) a larger proportion of water vapour inland being 're-evaporated', originating from terrestrial evapotranspiration, which generally has higher tritium concentrations than marine vapour. Harries and Calf (1980) measured tritium in Australian ocean waters in the late 1970s and found values ranging from 1 TU in the Southern Ocean south of Tasmania to 3 TU in the Tasman Sea off Sydney. Dilution and mixing of higher concentrations of tritium in rainfall within a water depth of 75 m (Bainbridge, 1963; Kakiuchi et al., 1999) and the efficient removal of tritiated water from the atmosphere by vapour exchange over the ocean (Eriksson, 1965) led to these low levels. Although no measurements have been recorded for the Australian region, the background levels of tritium in water vapour evaporated from the ocean would be slightly lower than these due to isotopic fractionation during evaporation, although fractionation of ~16% (Gat et al., 2001) is close to the measured uncertainty in tritium.

Tritium in precipitation is dominated by a seasonal cycle where a north to south mixing of air masses from the stratosphere to the troposphere occurs in mid-latitudes with a maximum in spring (Gat et al., 2001; Yasunari and Yamazaki, 2009). The time histories of tritium fallout, seasonal variation patterns and the continental effect in Northern Hemisphere stations are comprehensive and well documented in comparison to the Southern Hemisphere.

This study presents an extensive tritium data set, extending back to 1962, collected from a network of stations throughout Australia. The aim is to construct a more detailed picture of fallout distribution and identify the influence of thermonuclear weapons testing in the Southern Hemisphere. The tritium composition in monthly rainfall will also be used to examine temporal and spatial variability across the continent and ascertain how these phenomena have changed as the tropospheric tritium levels have gradually decreased; thereby providing tritium reference data for hydrology studies in Australia.

2. Methods

2.1. Sampling stations

Since 1960 monthly precipitation samples have been collected for ^{3}H analysis from various meteorological stations throughout Australia under the International Atomic Energy Agency (IAEA)/World Meteorological Organisation (WMO) program now known as the Global Network of Isotopes in Precipitation (GNIP), and independently by the Australian Nuclear Science and Technology Organisation (ANSTO), previously known as the Australian Atomic Energy Commission (AAEC). This paper presents the tritium dataset collected by the AAEC/ANSTO since 1970 (Calf et al., 1976a, 1977; Calf and Stokes, 1979, 1981, 1983, 1985, 1987). Data prior to this time was obtained from the GNIP database (IAEA/WMO, 2006). The locations of the sampling stations which have operated throughout Australia are shown in Fig. 1.

Site locations and the time-span of monthly sample collections at each meteorological station are listed in Table 1. The tabulated data is restricted to the collection stations with a relatively complete record.

In Australia, the most extensive datasets with the longest continuous sampling period(s), spanning 1962 until present, are for two meteorological stations: Brisbane and Darwin. An additional four stations, Adelaide, Alice Springs, Melbourne and Perth, also commenced operation in the early 1960s under the IAEA/WMO program. In 1970 the AAEC independently established a network of 16 meteorological sampling stations, duplicating the existing six IAEA/WMO sites and adding an additional 10 locations in NSW, Queensland and Tasmania. In 1979, Cape Grim (Tasmania), which is Australia's baseline station, was added to the IAEA/WMO network. Sampling was discontinued in 1983 at Bundaberg, Charleville, Claredale, Hobart, Ryde and Toowoomba, and the AAEC took over responsibility for the IAEA/WMO network in Australia; duplicate sampling ceased at this time. At the end of 1991 the network was further downsized to four locations; Brisbane, Cape Grim, Darwin and Melbourne; in 1999 collection in Melbourne ceased. Since 2005 monthly precipitation samples have been collected from the Alice Springs, Brisbane, Cape Grim, Darwin, Melbourne and Perth stations for tritium analysis. In 2006 nine new precipitation sampling stations were established by ANSTO, primarily for $\delta^{2}H$ and $\delta^{18}O$ analyses, at Adelaide, Charleville, Cobar, Kyeemagh, Meekatharra, Mildura, Mount Isa, Wagga Wagga and Woomera. Because analytical capacity for tritium is limited, only a few samples from these sites have been analysed, and the remainder will be archived.

For overlapping collection periods, the r^2 value between the GNIP and ANSTO datasets for each site was greater than or equal to 0.81. However the agreement between the two datasets for Perth was poorer; with a r^2 value of 0.6, which was influenced by six samples (two months in each year) between 1970 and 1972. The six samples either had a large concentration for the ANSTO data and a lower concentration for the GNIP data, or vice versa. As these are historical data, insufficient information precludes a reason for the discrepancy.

2.2. Sampling method

Precipitation was sampled on a calendar month basis at locations outlined in Table 1. Historical records suggest that both the IAEA/WMO and the AAEC programs used similar sampling methods, consisting of a composite sampler comprised of a funnel in a large glass or steel collector. No technique to prevent evaporation of the sample appears to have been used in these samplers up to 2005. In 2005–2006 the precipitation isotope sampling network in Australia was revised with daily rain gauge samples composited manually from a standard rain gauge into a HDPE bottle over each month. This reduces potential evaporative losses compared with the previous technique.

2.3. Analytical technique

Tritium activity in a composite of the total precipitation at a station during each month has been determined at the low level tritium laboratory, at AAEC/ANSTO since 1971. Currently tritium is measured on a 9.00 g ± 0.05 g distilled and electrolytically enriched sample, using a sample to Perkin Elmer Ultimagold uLLT scintillant ratio of 0.69:1 by volume. The samples are counted for between 1000 and 2000 min on a Perkin Elmer 1220 Quantulus scintillation counter, to give a detection limit of 0.13–0.21 TU (2011 samples); NIST reference materials are used to calibrate the counter.

The standard error of measurement for samples analysed prior to 1990 has been reported as ±0.5 TU. As the tritium levels have steadily decreased since then and the mean tritium concentration in precipitation is now ~2 TU in the southern hemisphere there has been a need to achieve a higher level of sensitivity. The combined standard uncertainty (1 σ) in the measurements is typically reported at ~6% of the tritium concentration which corresponds to ~0.15 TU. The improvement in the quantification limit and the uncertainty has been achieved by gradually optimising the methodology and sampling systems described in Calf et al. (1976b). Improvements in counting statistics have been achieved by