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TELLUS

A history of atmospheric tritium gas (HT) 1950–2002

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ABSTRACT

Data collected as a part of this study from 1968–2002 and data from other studies from 1950–1967 show that the maximum atmospheric concentration of tritium gas (HT) occurred in the early to mid 1970s, which corresponds to the era of frequent, large underground nuclear tests. These data clearly show that the major source of HT to the atmosphere between 1962 and the early 1990s was the underground testing of nuclear weapons. Samples collected at both our Alaska and Miami stations clearly show marked increases in the autumn of each year between 1970 and 1975 that were associated with large underground explosions conducted by the former Soviet Union at the Novaya Zemlya test site. Other significant sources of HT include accidental releases of HT used in the manufacture and maintenance of nuclear weapons stockpiles, the reprocessing of spent nuclear fuel rods and emissions from nuclear power plants. Since the early 1990s, when underground testing largely ceased, emission estimates from our data agree very well with United Nations estimates of worldwide releases from fuel reprocessing and nuclear power plants, suggesting that the nuclear power industry is now the major source of HT to the atmosphere.

1. Introduction

Hydrogen has three naturally occurring isotopes. Deuterium ($^2_1$H = D) and protium ($^1_1$H) are the two stable isotopes. The radioactive isotope of hydrogen ($^3_1$H = T), tritium, has a half-life of 12.32 yr (Lucas and Unterweger, 2000) and is a very weak beta emitter. Natural sources of tritium are the interaction of cosmic radiation with various atoms in the atmosphere and some additional tritons of direct solar origin. The first confirmation of tritium in nature was the atmospheric tritium gas detected in the early 1950s by two groups (Faltings and Harteck, 1950; Grosse et al. 1951). Later in the decade, Libby and co-workers (Kaufman and Libby, 1954; Begemann and Libby, 1957) started measurements of tritium in natural waters. Östlund and Werner (1962) and Östlund and Dorsey (1977) later improved the measurement techniques. Only estimates are available of the steady-state global tritium inventory before 1954 because of sampling and analytical limitations. The pre-nuclear steady-state global inventory of tritium has been estimated at between 0.5 and 2 kg, and it must have been mainly in the form of water molecules (HTO) with only a small fraction in the form of hydrogen gas (HT). Due to the global circulation pattern of water, most of the tritium resided in the oceans.

Since 1954, the atmospheric picture has changed drastically in that the atmospheric testing of thermonuclear devices by the USA and USSR injected comparatively vast amounts of tritium in the form of HTO into the stratosphere. Estimates are that the 1957–1958 series of tests produced $\sim 3 \times 10^4$ g and the 1961–1963 series (3–5) $\times 10^5$ g of tritium in the form of HTO (UNSCEAR, 2000). The atmospheric tests by the People's Republic of China and by France in the mid 1970s added minor quantities of HTO to the stratosphere. The total amount of HTO released during the history of atmospheric nuclear testing is estimated to be 5.27×10^5 g of tritium (UNSCEAR, 2000).

In the today's atmosphere tritium gas, HT or T_2, is mainly a product of the nuclear power industry, e.g. emissions associated with nuclear power plants and nuclear fuel reprocessing. This paper puts major emphasis on this form of tritium, and to our knowledge our laboratory is currently the only one in the world routinely measuring HT with high enough accuracy to follow variations in the global atmosphere.

1.1. Tritium in the environment

It is not always realized that the three species of tritium-bearing molecules in the environment, namely hydrogen gas, water and hydrocarbons, have very different chemical properties and, therefore, vastly different distribution patterns on Earth. The sources and sinks of the tritiated species are also different, and we shall discuss these separately. It should be noted that our measurement technique does not distinguish between the isotopic configurations of each chemical species. Hence, from now on in this paper "HTO" includes DTO and T_2O, "HT" includes DT and T_2, and

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"CH_3T" includes all volatile gaseous hydrocarbons and possibly the lightest aldehydes and alcohols.

The turnover time of HTO in the lower atmosphere is short, approximately 1 week, and in this form a local release could be rained out within days. In contrast, tritium in the form of hydrogen gas, released for instance from reprocessing of nuclear fuel elements, stays in the atmosphere for several years and eventually spreads around the globe following the pathways of hydrogen (H_2) gas.

Due to the very low energy of the tritium decay and the biological inertness of hydrogen gas, the maximum permissible concentration (MPC) of HT is very high compared with other radioactive substances, including HTO. However, very large amounts of tritium gas will be handled if fusion energy becomes a significant source of energy, and hydrogen gas is notoriously difficult to keep contained under pressure in an industrial environment. It is, therefore, desirable to use the dynamics of the past and present-day anthropogenic HT signal to gain a better understanding of the sources, sinks and average turnover times of atmospheric HT.

1.2. Tritium gas

Measurements on tritium gas in the atmosphere, away from nuclear energy installations, i.e. at levels far below MPC, were made by Ehhalt et al. (1963) and Layton (1969) in the 1960s. They obtained gas samples of the so-called raw neon fraction, which is released from the top of the distillation columns at liquid air factories. This limited the choice of sampling locales to industrial areas. Friedman and Scholz (1974) later made a portable liquid air machine work for collecting atmospheric hydrogen and thereby obtained some mobility. We developed a radically different method for the sampling of tritium, based on first absorbing all water vapour by a molecular sieve, then using palladium metal carried on the molecular sieve to catalytically burn the atmospheric hydrogen gas at ambient temperature, adsorbing the resulting water in the sieve. Adding tritium-free hydrogen from an electrolyser at a known rate results in enough water for tritium analysis and also serves as a continuous control of combustion and recovery in the sampling system. This system has the advantage of being simple and mobile, but requires a very sensitive counting system.

The sources of HT are very different from those of HTO or H_2. The current major source of HT is probably the reprocessing of nuclear fuel elements, which should release HT together with chemically fission product gases. Releases of HT from the nuclear fuel cycle (reactors and reprocessing plants) from its origin up to 1997 is estimated to be 842 g of T (UNSCEAR, 2000). Another source of HT is accidental releases while handling large amounts of tritium. Large releases, such as one from Savannah, Georgia on 31 December 1975, have been observed as reported by Östlund and Mason (1985). One HT source from the late 1950s to the early 1990s, and as we will argue below, the major source during this time period, was the testing of nuclear devices underground. HT can escape from these tests because there is a limited amount of O_2 available and the remaining HT from fusion devices is not all converted to HTO, as it is during atmospheric testing. Additionally some tritium could be produced by the spallation of heavier nuclides by neutrons (Mason and Östlund, 1974). Once the HT is produced underground it can diffuse through the overlying soil and rock, or can move more quickly along both natural and bomb-produced faults and fractures. It is important to note that almost all underground nuclear tests released radioactive gases to the atmosphere, even if they were considered fully "contained" (Adushkin and Leith, 2001). It has been shown that very marked peaks in tritium gas concentrations at Fairbanks, Alaska in 1973 are clearly correlated with large underground events at the Novaya Zemlya test site (NZTS), in the former USSR (Mason and Östlund, 1974). In some of those cases, $^{37}Ar(t_{1/2} = 34$ days) was also detected by Oeschger in Switzerland (private communication). Many small accidental releases of tritium gas are also probably occurring, for instance in using the gas for biological experiments and for making tritiated compounds by Wilzbach exchange (i.e. exposing organic compounds to tritium gas of very high specific activity). Other sources are fusion energy research, and the manufacturing (and scrapping) of sealed tritium light sources. The latter are used in some watches and in exit signs on some commercial aircraft. Atmospheric testing of thermonuclear weapons did not release any HT.

Other potential sources of HT include any of the recognized sources of H_2 (Novelli et al. 1999), such as fossil fuel combustion, biomass burning and photochemical production from methane (CH_4) and other non-methane hydrocarbons (NMHCs). Fossil fuels will contain virtually no ^3H due to their millions of years of isolation from the atmosphere and the short half-life of ^3H. Although biomass burning will contribute a small amount of HT to the atmosphere it is negligible because the typical T/H ratio in biomass is much lower than the T/H ratio in hydrogen gas. Photochemical oxidation of CH_4 and NMHC may produce a small but significant amount of HT. In any case, anthropogenic emissions of HT are by far the major source of HT to the atmosphere.

The major sinks for atmospheric H_2 are uptake by soils and reaction with OH in the troposphere (Novelli et al. 1999). It has been shown that soils have the ability to oxidize HT (Fallon, 1982; McFarlane et al. 1979). These sinks should also be significant in the global budget of HT, although their strengths have not been estimated. The other significant sink for HT is radioactive decay.

When discussing the sinks, a peculiar complication should be mentioned. Even if the tritium exists in the form of T_2 in the atmosphere, only one of the tritium atoms disintegrates at a time. The leftover atom will be in a chemically hot state and will end up as tritium water, HTO. Thus both T atoms will leave the gaseous state, and the resulting lifetime and rate of disappearance

of tritium gas are different for T_2 and HT. This was pointed out by Mason (1977), and attempts to determine the atmospheric speciation were made in the past years at our laboratory, but with no success.

2. Sampling stations

Samples have been collected at Miami, Florida, USA from 1968 until the present. We regularly sample twice weekly, and the Miami station is the only one with nearly continuous sampling over this time period. Additional samples were collected in Fairbanks, Alaska, USA from 1970–1982, from Mauna Loa, Hawaii, USA from 1971–1977, in Baring Head, New Zealand from 1975–1982 and at Newport, Oregon, USA from 1981–1982.

2.1. Sampling and analytical techniques

The sampling system for atmospheric HT and HTO has been described in Östlund and Mason (1974). The current sampling technique is still basically the same and is described briefly. Since the tritium levels, especially in later years, have been equivalent to only 1 or 2 decays per minute per kg of air we regularly process 9 to 10 kg of air flowing at 4–5 l min^{-1} during a 24-h period. The system employs a small diaphragm pump to deliver airflow to the molecular sieve-based sampling traps. In a location with high atmospheric humidity, such as our current Miami station, a cold-trap is put in before the pump to avoid condensation in the lines and overloading of the sieve trap with water. An electrolysis cell operated by a constant-current power supply is used to add ^{3}H-free H_2 gas to the air stream, so that the H_2 concentration is $\sim$0.2% by volume. The pre-dried mixed gas passes through the molecular sieve trap, where all remaining water species (H_2O, HDO, HTO, etc.) are removed. Then the gases pass through a trap with activated palladium carried on a molecular sieve where the added H_2 plus all atmospheric hydrogen species (H_2, HT, T_2, etc.) are catalytically oxidized and the resulting water is absorbed *in situ*. An electronic mass-flowmeter with an integrator measures the amount of air sampled, and an electronic current integrator–totalizer measures the ampere hours, and thereby the amount of water disintegrated. A 500 g molecular sieve trap can safely absorb about 40 g of water without breakthrough. A 200 g palladium trap may begin to lose its catalytic efficiency when its water content exceeds 8 g H_2O.

The water in each trap was extracted in our Miami laboratory by connecting the trap to a vacuum system, heating it to 500 °C, freezing out the water in a cold finger immersed in dry ice/acetone slush, while pumping with a mercury diffusion pump down to a final vacuum in the 10 μm range. The extracted water is weighed and the weight compared to the weight from the electronic integrator in order to check the combustion efficiency of the palladium trap. An extra portion ($\sim$3 ml) of dead water vapour is usually bled through the hot palladium trap to ensure that the total amount of tritium in that sieve is expelled and the unavoidable water memory ($\sim$100 mg) on the trap contains no detectable tritium.

The water samples collected from the traps are then converted to hydrogen gas and analysed by gas-proportional counting as described in Östlund and Dorsey (1977). A current description of our analytical technique can also be found at our web site (http://www.rsmas.miami.edu/groups/tritium).

3. Results and discussion

3.1. Determination of yearly HT averages and contamination events

In order to obtain a yearly average HT concentration it is ideal to have a station that is not affected by local or regional pollution events. In reality it is difficult to find such a station. Therefore local or regional pollution events must be identified and excluded from the average calculation. These pollution events can range from very small local events (i.e. someone getting close to the sampling intake wearing a tritium watch) to more regional scale events (tritium released through laboratory fume hoods, releases from watch or exit sign production facilities, release from nuclear power plants). Large-scale global pollution events, such as those caused by underground nuclear explosions or large releases from nuclear reprocessing or weapons production facilities, were included in the yearly average HT concentration determinations. It was assumed that individual values, which were not affected by local or regional pollution events, would show an even distribution around the yearly average. Outlying values, presumably caused by local or regional pollution events, were eliminated by applying the momental skewness measure α_3 to each year's data set, and successively eliminating the highest value until an α_3 value of $\leq$1.8 was reached. The last elimination typically resulted in a change in the average smaller than one standard error.

Our stations in New Zealand and Oregon were remote enough that outlying values and thus local or regional HT pollution events were never detected (see Östlund and Mason, 1985, for these data). At our Miami station, where we have the longest continuous sampling period and the data from which are used to derive global concentrations, inventories and emissions, it is typical to have several local or regional pollution events per year. In most cases these events are short lived, appearing in only one or two consecutive samples (Fig. 1). During some of 1988 and 1990 we were collecting simultaneous samples from two locations in the Miami area separated by $\sim$6 km. The fact that short-lived increases in HT concentration were observed nearly simultaneously at both of the stations argues against highly localized small pollution events (Fig. 1) and suggests that these increases are due to regional pollution. We attribute most of these short-term events as some type of regional pollution, for example

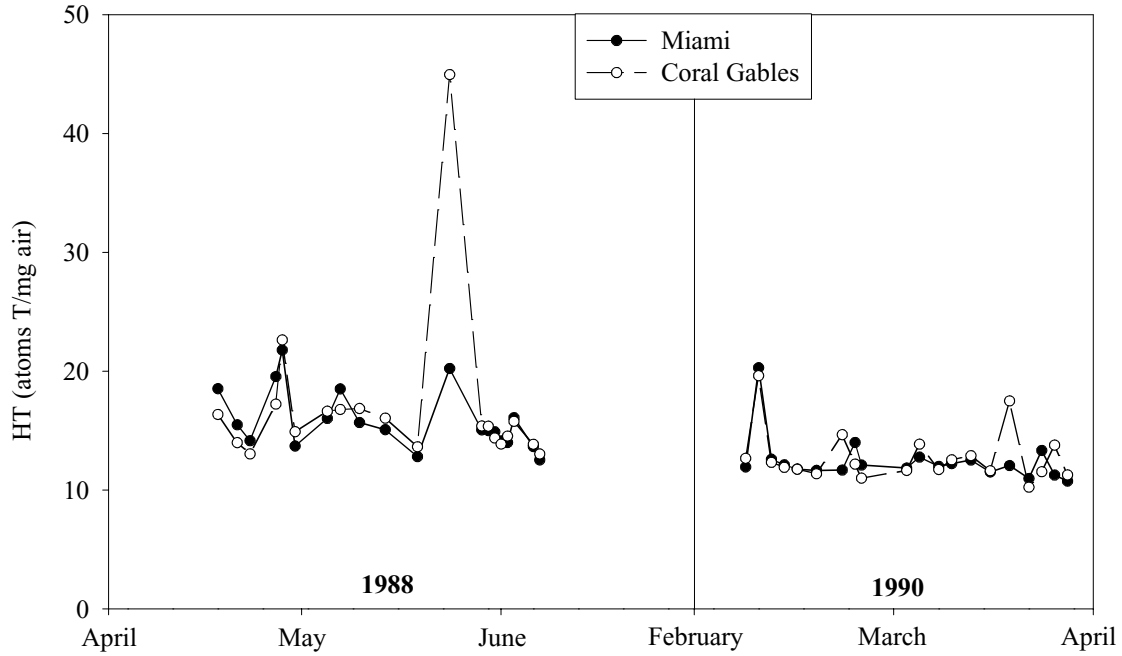

Fig 1. The concentration of HT from simultaneously collected samples from two Miami area locations separated by ∼6 km.

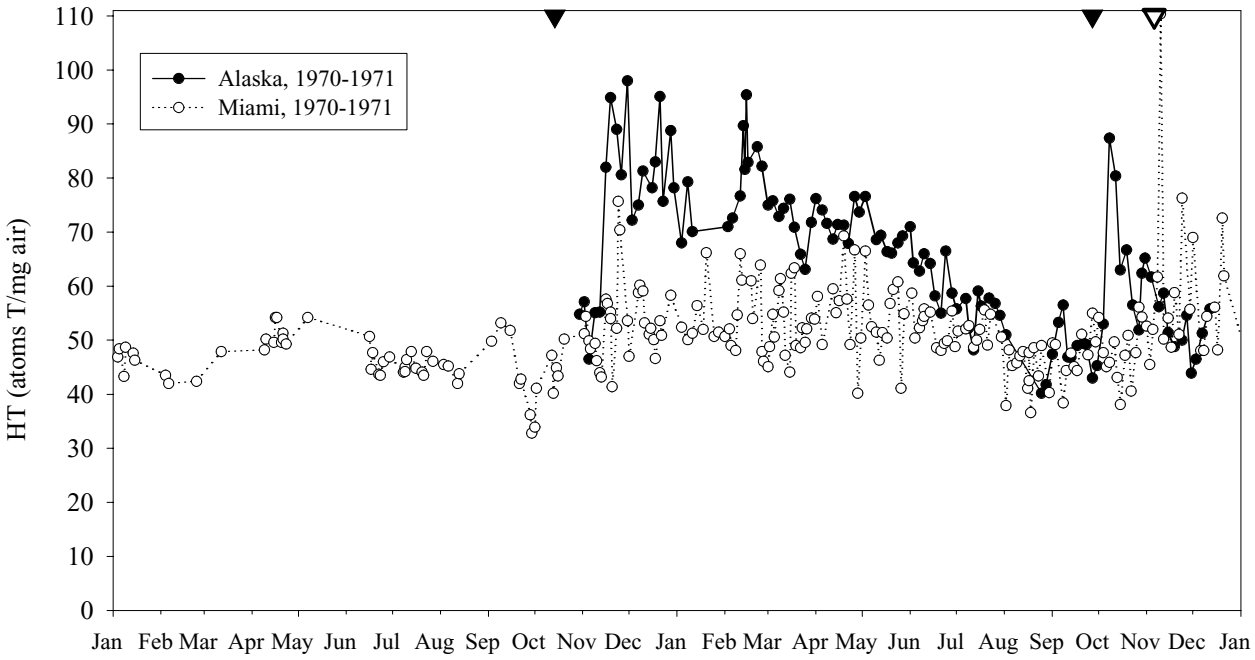

Fig 2. HT concentrations at Miami (open circles, dotted line) and Alaska (closed circles, solid line) from 1970 and 1971. The closed inverted triangles mark large underground nuclear tests at NZTS and the open inverted triangle marks a large underground test at Amchitka Island, Alaska, USA. The test at NZTS on 14 October 1970 was estimated to have released 2 million Ci of radioactive materials (Adushkin and Leith, 2001).

from industrial sources, the breaking of "beta lights", or the Turkey Point nuclear power plant which is located ∼25 km southwest of the Miami station.

Mason and Östlund (1974) have correlated two underground nuclear tests at the NZTS (representative latitude of 73°30′N) in 1973 with major increases in HT concentration in Alaska, Hawaii and Miami using some of the same data presented here. In addition we see HT peaks in the autumn of 1970, 1971, 1972, 1974 and 1975 that appear to be correlated with large underground explosions at the NZTS (Figs. 2–4), or Amchitka Island, Alaska,

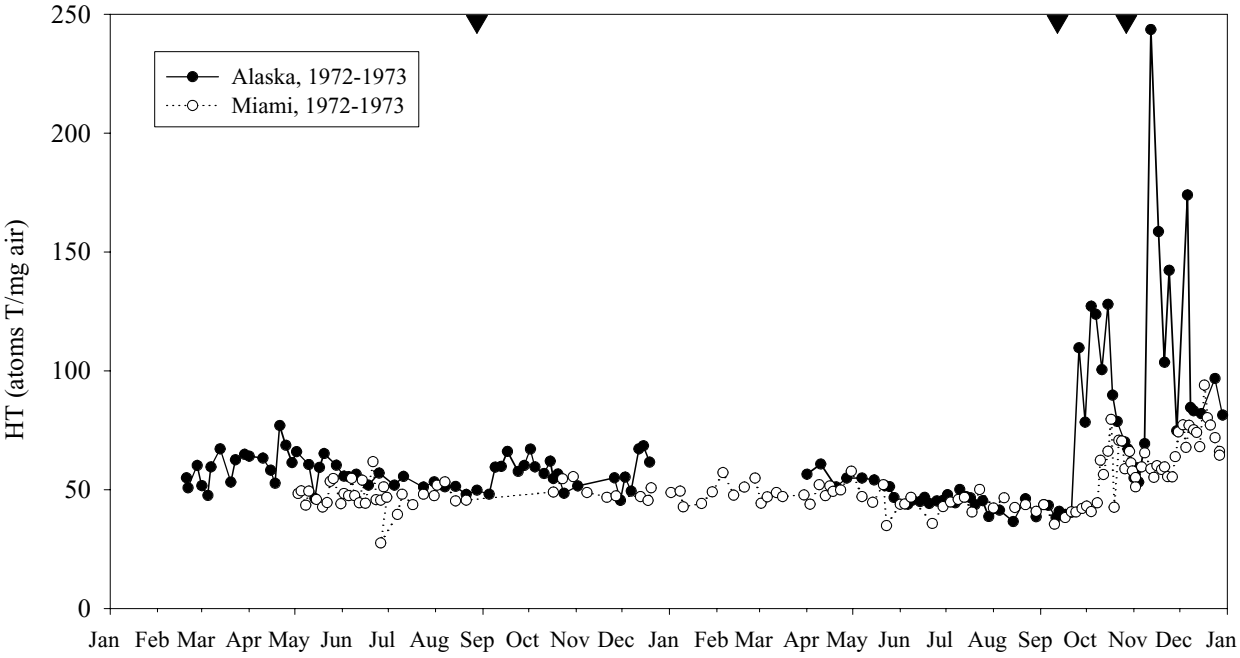

Fig 3. HT concentrations at Miami (open circles, dotted line) and Alaska (closed circles, solid line) from 1972 and 1973. The closed inverted triangles mark large underground nuclear tests at NZTS. The test on 28 August 1972 was reported to have released 1 million Ci of radioactive materials (Adushkin and Leith, 2001).

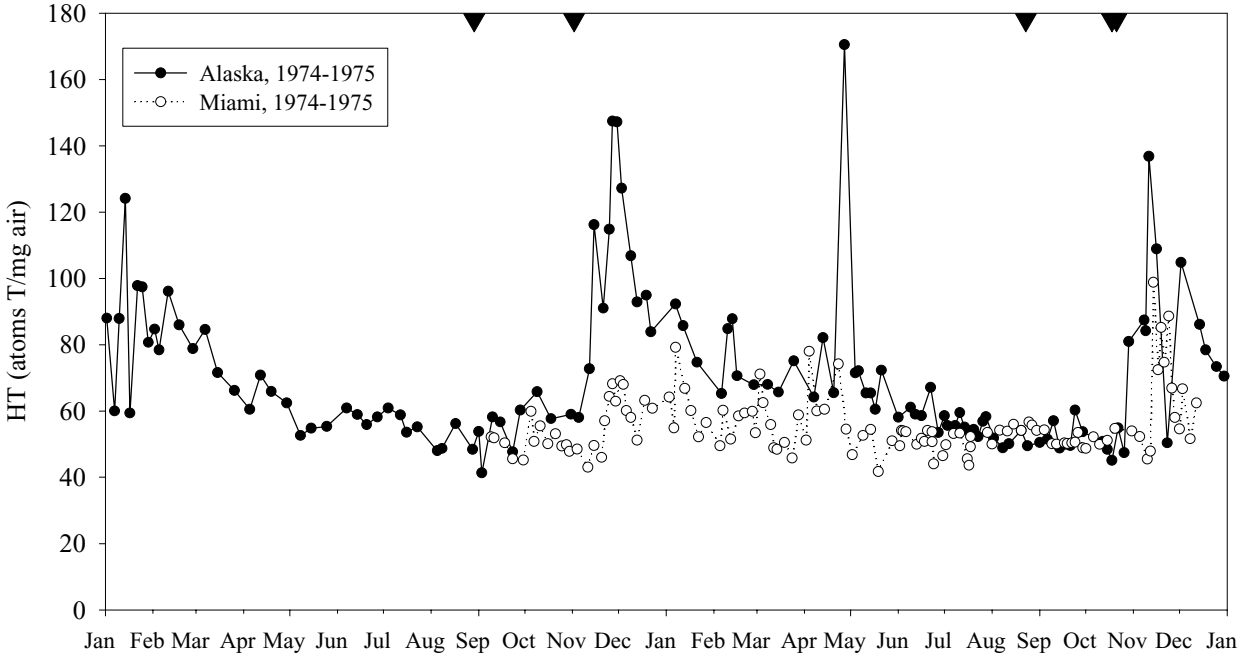

Fig 4. HT concentrations at Miami (open circles, dotted line) and Alaska (closed circles, solid line) from 1974 and 1975. The closed inverted triangles mark large underground nuclear tests at NZTS. The tests on 29 August 1974 and 21 October 1975 were reported to have released 4685 and 297, 297 Ci of radioactive materials, respectively (Adushkin and Leith, 2001).

USA (Fig. 2). These types of pollution event were generally of longer duration than the regional ones discussed above, sometimes lasting for 1 to 2 months. This suggests that in addition to the HT that was probably emitted nearly instantaneously from these large explosions, significant amounts of HT were released more slowly for several days to several weeks after the explosion. Mason and Östlund (1974) show that the HT concentration for the 1973 peaks in Alaska decreases with a time constant of

47 days, and suggest that there must be more than just an instantaneous release of HT. In general the peaks in HT concentration after large tests are easily discernible at our Alaska site, and readily discernible in most cases at our Miami site. Mason and Östlund (1974) also report discernible peaks in HT at Mauna Loa in 1973 associated with NZTS tests, but similar peaks were not observed in other years. This may be due to the fact that the Mauna Loa station is at an elevation of 3399 m, which is above the trade wind inversion and the partial confinement of HT below this inversion causes the HT peak to be damped to such as extent that it is not readily observable.

Additional evidence for a Northern Hemisphere source of HT in 1974 and 1975 comes from data collected along a transect from California to New Zealand to Antarctica aboard the USNS *Pvt. John R. Towle* in late 1974 and again in early 1976. Elevated concentrations of HT were observed between 11 and 32°N in both years (Fig. 5) suggesting that there was a relatively large Northern Hemisphere source during this time. This source could be the large underground explosions at NZTS on 29 August and 2 November 1974 and 23 August, 18 October and 21 October 1975. A large HT release of ∼19 g T from the United States Department of Energy (USDOE) Savannah River Site (SRS, representative latitude of ∼32°N) on 31 December 1975 (Jacobson, 1976) could also explain some of the Northern Hemisphere increase seen in the 1976 transect. Due to favourable weather conditions we believe that we also saw this release at our Miami site on 7 January 1976 when HT concentrations were 376 atoms T mg^{-1} air compared to 67 and 55 atoms T mg^{-1} air observed 2 days before and 2 days after, respectively. There have been other documented large HT releases associated with USDOE activities on 2 May 1974 (50 g T) from SRS (Marter, 1974) and Lawrence Livermore National Laboratory (LLNL) on 21 January 1965 (37 g T) and 6 August 1970 (31 g T) (Tate, 1999), although these releases are not readily discernible in our data.

3.2. *Global concentration, inventory, emissions and sources of HT*

Tritium data from this work are presented from 1968 to 2002. Pre-1968 data were obtained from various reports (Grosse et al. 1954; Begemann and Friedman, 1959; Gonsior, 1959; Fireman and Rowland, 1961; Gonsior and Friedman, 1962; Ehhalt, 1966; Begemann and Friedman, 1968; Layton, 1969; Friedman and Scholz, 1974). We use the Miami average tritium gas concentration in atoms of tritium per mg of air, as representative of the Northern Hemisphere from 1968 onwards because this is where we have the longest continuous data set. Before 1968 the Northern Hemisphere average concentration is determined from averaging the concentrations from the various reports cite above. Interhemispheric differences in HT concentration were determined

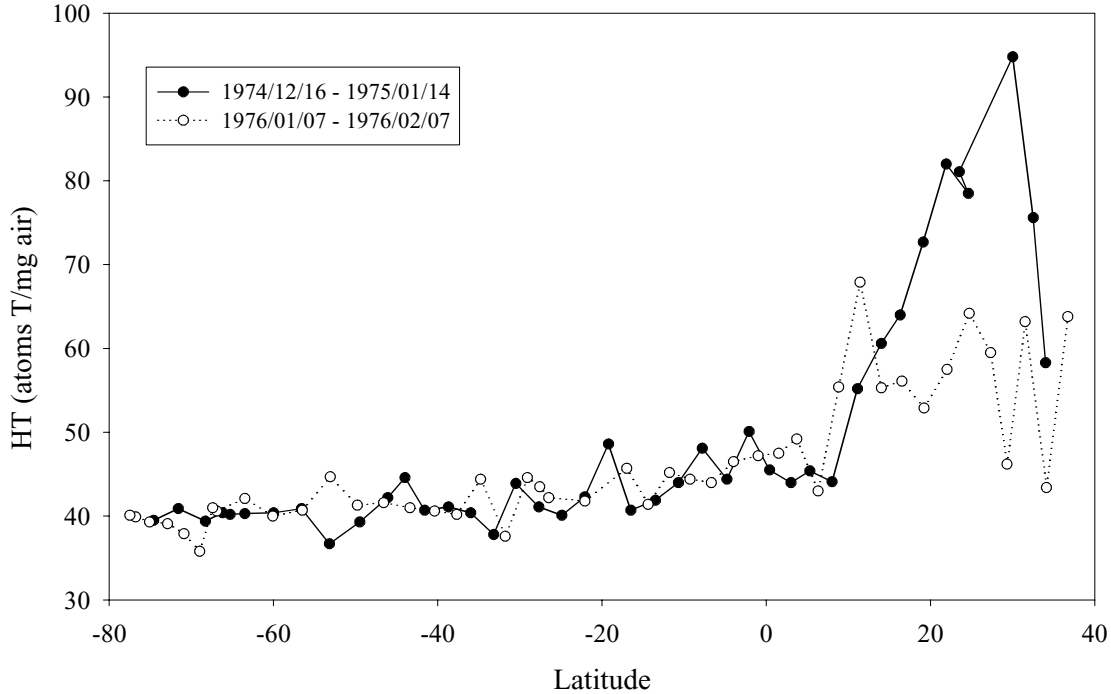

Fig 5. The tropospheric concentration of HT with latitude from two transects across the Pacific Ocean between 16 December 1974 and 14 January 1975 (dark symbols, solid line) and 7 January 1976 and 7 February 1976 (open symbols, dotted line). HT concentrations are greater between 11 and 34°N compared with the more southerly stations in both transects probably due to contamination events associated with underground nuclear tests at NZTS on 29 August and 2 November 1974 and 23 August, 18 October and 21 October 1975 (Adushkin and Leith, 2001). A large HT release from the SRS on 31 December 1975 could also explain some of the Northern Hemisphere increase seen in the 1976 transect.

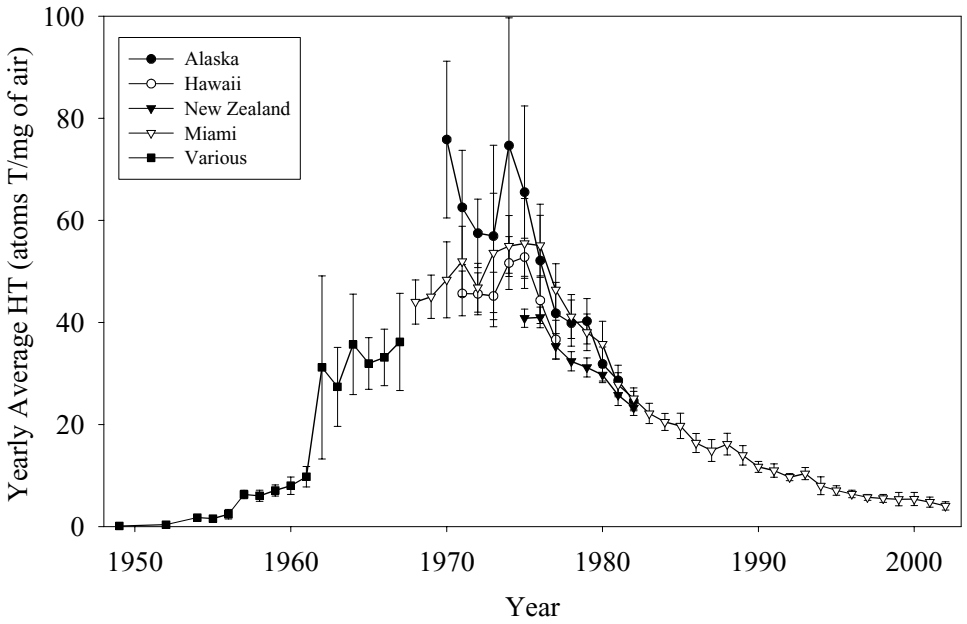

Fig 6. The yearly average atmospheric concentration of HT from 1949 to 2002. Data from all stations from 1968 to 2002 were collected as part of this study. Before 1968 data were obtained from various locations by various investigators as follows: 1949 (unknown; Fireman and Rowland, 1961), 1952 (Buffalo, New York; Grosse et al. 1954), 1954 (Buffalo, New York; Begemann and Friedman, 1959), 1955 and 1956 (New York and Germany; Begemann and Friedman, 1959; Gonsior, 1959), 1957 and 1958 (Germany; Gonsior, 1959; Gonsior and Friedman, 1962); 1959 (Germany; Gonsior and Friedman, 1962); 1960 (Indiana and Germany; Begemann and Friedman, 1968; Gonsior and Friedman, 1962), 1961 and 1962 (Germany; Begemann and Friedman, 1968), 1963–1966 (Indiana; Layton, 1969); 1967 (Colorado; Friedman and Scholz, 1974). Error bars are the standard deviation of multiple measurements made in each year.

by comparing our New Zealand data from 1975–1982 with the Miami data. The interhemispheric difference, with the Southern Hemisphere concentration lower, ranged from 26.4% in 1975 and steadily decreased to 7.2% in 1981 and 1982. In order to calculate the yearly global inventory of HT we use the measured difference between our New Zealand and Miami yearly averaged concentration data between 1975 and 1982, after 1982 and before 1962 we assume the interhemispheric difference was 7.2%, and between 1962 and 1974 we assumed an interhemispheric difference of 25%. The larger interhemispheric difference that we measured during the mid 1970s and we assume occurs from 1962 to 1974, is probably due to the large Northern Hemisphere source from underground testing during that time.

An examination of the yearly average atmospheric tritium gas concentration (Fig. 6) and inventory in (Fig. 7) clearly indicates that the maximum global amount of HT was observed between 1974 and 1976, more than 10 yr after the USA and USSR stopped atmospheric nuclear testing. It also appears that the predominant source of HT between 1970 and 1976 was in the high latitudes of Northern Hemisphere, because the Alaska data had a greater amount of HT than our other stations. This scenario is consistent with underground thermonuclear tests, particularly those in the former Soviet Union at the NZTS, contributing a relatively large amount of HT to the atmosphere during this time period. The geological conditions at this test site resulted in relatively large volumes of gases being produced that were particularly difficult to contain underground, and there were a number of tests that leaked significant amounts of radioactive isotopes to the atmosphere (Adushkin and Leith, 2001).

The yearly HT atmospheric inventory data (Fig. 7) can be used to determine the yearly emission of tritium if the loss rates of the major HT sinks are known via the following equation:

$$\mathrm{d}I/\mathrm{d}t = E - L_{\mathrm{OH}} - L_{\mathrm{soil}} - L_{\mathrm{rad}}$$

where all terms are in grams of tritium, $\mathrm{d}I/\mathrm{d}t$ is the change in tritium inventory from the previous year and L is the loss of tritium due to reaction with OH, uptake by soils and radioactive decay. Estimates of the major sink partial turnover times for atmospheric H_2 can be derived from Novelli et al. (1999) (Table 1). These turnover times can be used to derive partial turnover times for HT if the isotope fractionation factor is known. Ehhalt et al. (1989) have measured the HT fractionation factor for the reaction with OH. The isotope fractionation factor for soil uptake has not been measured to our knowledge so we have estimated it (0.819) based on the relative difference in HD (0.606) and HT (0.526) fractionation factors for the OH reaction (Ehhalt et al. 1989) and the measured HD fractionation factor (0.943) for soil uptake (Gerst and Quay, 2001). These partial HT lifetimes are presented in Table 1 and along with the radioactive lifetime to arrive at a combined atmospheric lifetime for HT of ∼2 yr.

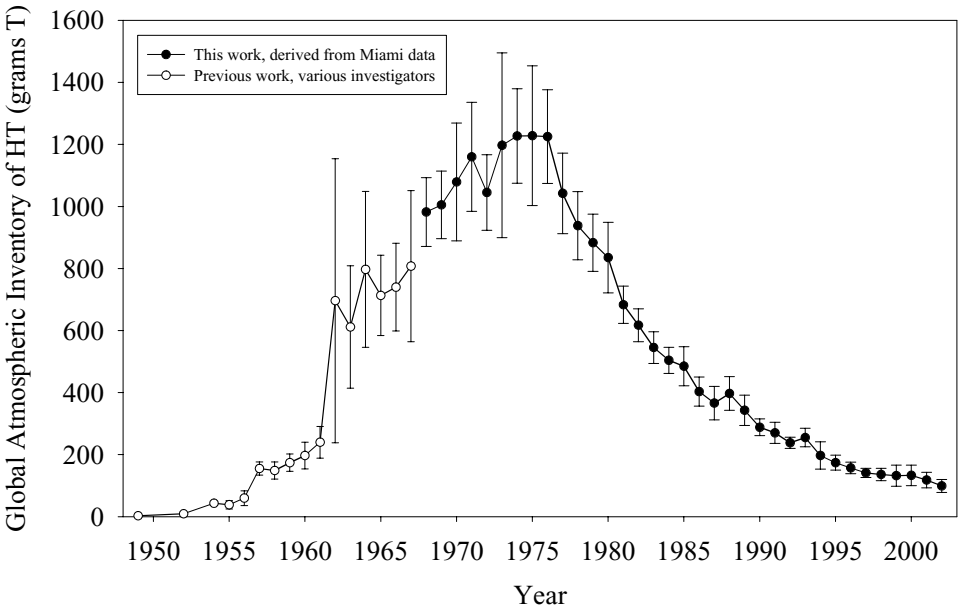

Fig 7. The global atmospheric inventory of HT from 1949–2002, derived from the various reports and Miami data presented in Fig. 6. The inventory values were determined using an atmospheric mass of 5.14×10^{21} g and from data collected in the Northern Hemisphere. Error bars are derived from the standard deviation of the average HT concentration given in Fig. 6.

Table 1. Partial and combined atmospheric turnover times for H_2 and HT

	τ_{OH} (yr)	τ_{soil} (yr)	τ_{rad} (yr)	τ_{atm} (yr)
H_2	8.2 ± 2.2	2.8 ± 1.0		2.1 ± 0.7
HT	15.5 ± 4.1	3.4 ± 1.2	17.94 ± 0.02	2.4 ± 0.9

Lifetime values for H_2 were derived from data presented in (Novelli et al. 1999). The partial turnover times for HT reacting with OH and taken up by soils were calculated from the corresponding H_2 partial turnover times and the corresponding isotope fractionation factors of 0.526 (Ehhalt et al. 1989) and 0.819. The HT fractionation factor for the soil reaction was estimated from the relative difference in HD and HT fractionation factors for the OH reaction (0.606 and 0.526, Ehhalt et al. 1989) and the published HD fractionation factor for soils (0.943, Gerst and Quay 2001). The 17.94 yr partial turnover time for radioactive decay of HT is based upon a half-life of 12.32 yr.

Emissions of HT (Fig. 8) calculated with these partial turnover times and the tritium inventory (Fig. 7) indicate a relatively slow but steady increase in HT emissions between the early 1950s and 1961 when there were many atmospheric thermonuclear tests of varying intensity and numbers, but only a few underground tests. There is a noticeable increase in HT inventory and emission in 1957, which may be related to the United States beginning to experiment with shaft and tunnel underground explosions. Three out of the five 1957 underground tests were in unstemmed (open to the atmosphere) shafts (Mikhailov, 1999), and almost certainly released radioactive gases to the atmosphere. The lack of correlation between HT emissions and the large number of atmospheric explosions before 1961 confirms that atmospheric tests were not a direct source of significant amounts of HT to the atmosphere, as has already been pointed out by Östlund and Mason (1974, 1977). A more likely explanation for the relatively steady increase in the 1950s is the accidental release of tritium associated with its increasing production and handling for thermonuclear bomb development. Between 1961 and 1962, the number of underground nuclear tests more than tripled (Fig. 8) and this corresponds with a large increase in HT concentration (Fig. 6), inventory (Fig. 7) and emission (Fig. 8) observed in 1962. In general, relatively high emissions of HT between 1957 and the early 1990s (Fig. 8) coincide with the era of underground nuclear testing, suggesting that these tests were an important source of HT during that time. Between 1963 and 1976 the correlation between the number of underground tests and HT emission is not as good as it is between 1976 and the early 1990s. We suggest that in the earlier time period, both the USA and USSR were improving the containment of underground explosions and that HT emissions were dominated by a relatively small number of "leaky" tests. There is a very good correlation in the first half of the 1970s between the total yield of underground tests and HT emissions that supports our earlier claim that several large-yield tests at the NZTS dominated HT emissions during this time. Between 1976 and the early 1990s containment techniques were better developed and there were presumably not as many "leaky" tests. The United States defines successful containment as "such that a test results in no radioactivity detectable off-site as measured by normal monitoring equipment, and no unanticipated release of radioactivity on site within a 24-h period following execution"

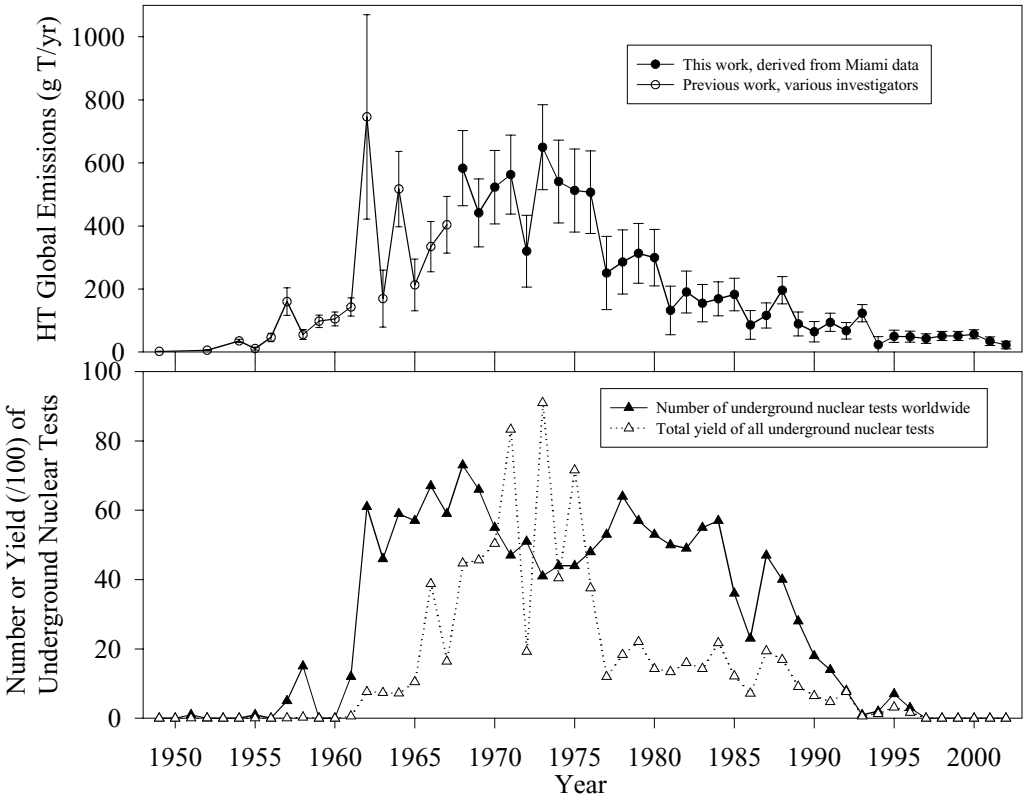

Fig 8. Emissions of HT per year from 1949–2002 (top panel) and the number and total yield of underground nuclear tests (bottom panel) per year throughout the world. Error bars are the propagation of the errors associated with the inventory change, and the OH, soil and radioactive loss rates.

(Adushkin and Leith, 2001). There were also radioactive gas releases associated with post-test sampling. What this means is that nearly all underground nuclear tests resulted in the release of radioactive gases including tritium, regardless of whether they were considered "fully contained" (Schoengold et al. 1996).

The lower correlation between the number of underground tests and HT emission between 1963 and 1976 compared with after 1976 could also be explained by globally significant releases of HT associated with USDOE weapons stockpile activities during the earlier time period. There were short duration releases of 37 and 31 g of tritium in 1965 and 1970 from LLNL and 50 and 19 g of tritium in 1974 and 1975 from SRS. These point releases account for a significant portion of the 213, 523, 540 and 512 g T respectively that we calculate for total global releases in those years. Presumably better handling techniques in later years have led to the reduction of these large releases.

Starting in the early 1970s the nuclear power industry (fuel rod reprocessing, power plants) has also emitted HT to the atmosphere in significant quantities (UNSCEAR, 2000). The UNSCEAR (2000) HT emission estimates are given as 5-yr totals between 1970 and 1994, with a 3-yr total from 1995–1997. Before 1970 HT emissions from the nuclear power industry were insignificant (UNSCEAR, 2000). A comparison between our emission estimates and the UNSCEAR estimates (Fig. 9) clearly shows that the nuclear power industry was the major source of HT to the atmosphere between 1990 and 1997. It is clear that before 1990 the nuclear power industry was not the major source of HT and, as we have suggested previously, underground nuclear testing was probably the dominant source between the late 1950s and early 1990s.

4. Conclusions

The data presented here clearly show that HT concentrations in the atmosphere have been greatly influenced by human activities since the 1950s. Sharp rises in HT concentration, inventory and emission are clearly associated with the number and yield of underground nuclear tests and these tests appear to be responsible for a majority of HT emitted to the atmosphere between the 1950s and early 1990s. Since the early 1990s HT emissions from the nuclear power industry appear to be dominant. Significant quantities of HT were not emitted by aboveground nuclear testing because large increases in HT did not occur until after large scale atmospheric testing ceased. Large increases in HT concentration during the first half of the 1970s at Miami and especially Alaska suggest a high Northern Hemisphere source and correlate very well with large yield underground tests conducted at NZTS.

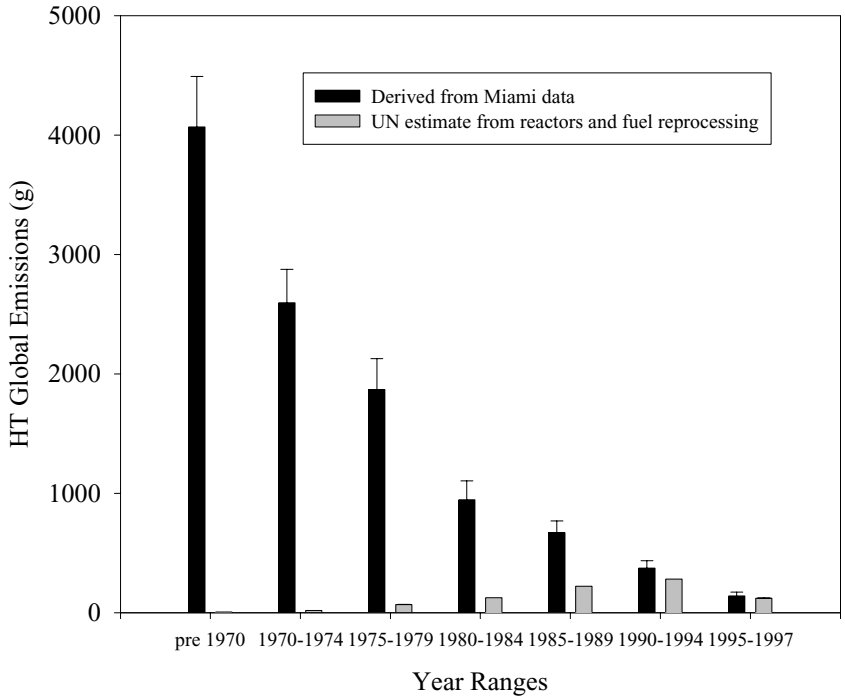

Fig 9. A comparison of the emissions of HT from this work and the United Nations estimate of the emissions from the nuclear power industry.

We plan to continue to monitor HT concentrations because the potential for increases in HT emissions exist with the further development of commercial fusion power, the proposed start-up of the SRS Tritium Extraction Facility in 2007, and possibility of large HT releases associated with the tritium production and underground tests by countries that are actively developing nuclear weapons programs.

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