

# Lawrence Berkeley National Laboratory

## Lawrence Berkeley National Laboratory

### Title

Elevated tritium levels at the World Trade Center

### Permalink

<https://escholarship.org/uc/item/4xq88667>

### Authors

Semkow, Thomas M.

Hafner, Ronald S.

Parekh, Pravin P.

et al.

### Publication Date

2002-05-14

223<sup>rd</sup> American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002  
Division of Nuclear Chemistry and Technology

Proceedings of the Symposium on Radioanalytical Methods at the Frontier of Interdisciplinary  
Science: Trends and Recent Achievements

## **Elevated Tritium Levels at the World Trade Center<sup>ⓧ</sup>**

**Thomas M. Semkow<sup>a,b,ⓧ</sup>, Ronald S. Hafner<sup>c</sup>, Pravin P. Parekh<sup>a</sup>,  
Gordon J. Wozniak<sup>d</sup>, Douglas K. Haines<sup>a</sup>, Liaquat Husain<sup>a,b</sup>, Robert L. Rabun<sup>e</sup>,  
and Philip G. Williams<sup>f</sup>**

<sup>a</sup>Wadsworth Center, New York State Department of Health, Albany, NY 12201

<sup>b</sup>School of Public Health, University at Albany, State University of New York, Albany,  
NY 12201

<sup>c</sup>Fission Energy and Systems Safety Program, Lawrence Livermore National Laboratory,  
Livermore, CA 94551

<sup>d</sup>Nuclear Science Division, E.O. Lawrence Berkeley National Laboratory, Berkeley, CA 94720

<sup>e</sup>Tritium Engineering Department, Westinghouse Savannah River Company, Aiken, SC 29808

<sup>f</sup>Physical Biosciences Division, E.O. Lawrence Berkeley National Laboratory, Berkeley,  
CA 94720

### **Abstract**

Traces of tritiated water (HTO) were detected at [the]World Trade Center (WTC) ground zero after the 9/11/01 terrorist attack. A method of ultralow-background liquid scintillation counting was used after distilling HTO from the samples. A water sample from the WTC sewer, collected on 9/13/01, contained  $0.174 \pm 0.074$  ( $2\sigma$ ) nCi/L of HTO. A split water sample, collected on 9/21/01 from the basement of WTC Building 6, contained  $3.53 \pm 0.17$  and  $2.83 \pm 0.15$  nCi/L, respectively. Several water and vegetation samples were analyzed from areas outside the ground zero, located in Manhattan, Brooklyn, Queens, and Kensico Reservoir. No HTO above the background was found in those samples. All these results are well below the levels of concern to human exposure.

Several tritium radioluminescent (RL) devices were investigated as possible sources of the traces of tritium at ground zero. It was determined that [the]Boeing 767-222 aircraft operated by the United Airlines that hit WTC Tower 2 as well as [the]Boeing 767-223ER operated by the American Airlines, that hit WTC Tower 1, had a combined  $34\{.3\}$  Ci of tritium at the time of impact, contained in emergency signs. WTC hosted several law-enforcement agencies such as ATF, CIA, US Secret Service and US Customs. The ATF office had two weapon vaults in WTC Building 6. Also 63 Police Officers, possibly carrying handguns, died in the attack. The weaponry containing tritium sights was therefore a likely and significant source of tritium. It is possible that some of the 2824 victims carried tritium watches, however this source appears to be less significant than the other two.

The fate of tritium in the attack depended on its chemistry. Any tritium present in the vicinity of [the]jet-fuel explosion or fire would convert to HTO. The molecular tritium is also known to quickly exchange with water adsorbed on surfaces at ambient temperatures. Therefore, the end product of reacted tritium was HTO. A part of it would disperse into the atmosphere and a part would remain on site. The dynamic aspect of HTO removal was investigated taking into consideration water flow at ground zero. Most of ground zero is encircled by the Slurry Wall, 70 ft deep underground, called [the] Bathtub. Approximately three million gallons of water were hosed on site in the fire-fighting efforts, and 1 million gallons fell as rainwater, between 9/11 and 9/21 (the day of the reported measurement). The combined water percolated through the debris down to the bottom of the Bathtub dissolving and removing HTO with it. Th[is] water met and combine[d] with the estimated 26 million gallons of water that leaked from the Hudson River, as well as broken mains, during the same period of 10 days after the attack. The combined 30 million gallons of water {were} collect[ed] in the PATH train tunnel and [were] continuously {being} pumped out to prevent flooding.

A 3-Box model of water flow was developed to describe the above scenario, where Box 0 is the debris, Box 1 the Bathtub, and Box 2 the bottom of the Bathtub plus the PATH tunnel. The model predicts that if the only source of tritium were the airplanes, the deposition factor of HTO at ground zero would have been [3]%. This is consistent, but judged somewhat too high by a comparison with the two known incidents involving tritium and a fire. Therefore, [a] second tritium source [was likely to] have been present, which were the weapons (plus possibly the watches). The model also puts a constraint on the rate of tritium release from the weapons: it would have to be slower than the water flow rate in the Bathtub. Such a mechanism is consistent with a slow tritium release from the devices in the debris due to the lingering fires, followed by an oxidation and removal with the water flow.

## **1. World Trade Center**

The World Trade Center (WTC), the symbol of New York City, had been built in the 1960s through the 1980s. It contained 7 buildings designated as WTC 1 through WTC 7. The most prominent were the 110-floor Twin Towers, WTC 1 - The North Tower built in 1970 and WTC 2 - The South Tower built in 1972. The WTC was owned and operated by [the]Port Authority of New York and New Jersey (PANYNJ). It is important to this investigation that several federal law enforcement agencies were located at the WTC (Miller, 2001; Cummings, 2002). US Customs and the Bureau of Alcohol Tobacco and Firearms (ATF) were housed in WTC 6, also called the US Customs House. US Secret Service and Central Intelligence Agency (CIA) had offices in WTC 7, in addition to the New York City emergency command center.

The original, 1776 Manhattan shoreline went across the WTC complex in the north-south direction. The modern land to the west of it is actually a fill (Overbye, 2001). Since the WTC 1 and 2 had to have deep foundations down to the bedrock, the required engineering solution was achieved by constructing a so called Bathtub. It is surrounded by the Slurry Wall 510 ft × 980 ft, 70 ft deep and 3 ft thick (Lombardi, 2002b). The Slurry Wall prevented leaks from the Hudson River. Besides the foundations of the buildings, the Bathtub contained a Concourse and a 6-level basement underground. On the lowest B6 level there was a tunnel and a station for the Port

Authority Trans-Hudson (PATH) train providing commuting from and to New Jersey under the Hudson River.

## **2. The Terrorist Attack**

The events of September 11, 2001 are well known. At 8:46 am, [a]Boeing 767-223ER aircraft operated by the American Airlines, Flight 11, hit WTC Tower 1 causing jet fuel explosion and fire. At 9:02 am, a second [aircraft, a] Boeing 767-222[,] operated by the United Airlines, Flight 175, hit WTC Tower 2. Both flights originated in Boston, so the aircraft were full of fuel, estimated at 10,000 gallons each (AP, 2002). WTC 2 collapsed first, lasting 47 min; WTC 1 collapsed next, lasting 102 min.

The collapse of the Towers was studied in detail (Ashley, 2001; Lipton and Glanz, 2002a; AP, 2002). The floors of the Towers were supported by the steel perimeter columns, while the central columns supported the elevator shafts. If there had been no fire, the Towers would have not collapsed. However, due to the fires, when temperature reached 1500F, the columns lost their strength causing the structures to collapse semi-vertically. By some estimates, the temperatures could have locally reached 1800C from burning of the aluminum bodies of the airplanes. At this temperature, hydrogen gas is evolved from the concrete burning, which fuels further burning. The reasons that WTC 2 collapsed first included the higher speed of the aircraft at collision (586 mph) compare[d] to the speed of the aircraft colliding with WTC 1 (494 mph), as well as noncentral and lower point of impact in the case of WTC 2. The speeds of both aircraft were substantially above the limit at this elevation (287 mph), and close to the structural (or breaking?) point of the aircraft. [does this mean the point at which it would disintegrate?

The collapsing Towers destroyed other WTC buildings and the debris compacted and destroyed much of the Bathtub. The debris from WTC 1 plunged through the center of WTC 6 creating a pit stretching down to the basement of the Bathtub (Slobin, 2001). At 5:30 pm, WTC 7 collapsed due to a diesel fuel fire from the tank for New York City emergency team (Glanz and Lipton, 2002). The WTC area is referred to as ground zero.

Authorities determined that 2824 people died in the attack on the WTC (Lipton and Glanz, 2002b), including 157 people onboard the aircraft. [This total includes] 343 New York City Fire Department firefighters, 23 Officers from the New York City Police Department, 37 Officers from the PANYNJ Police Department, and 3 Officers from the New York Office of Court Administration (IUPA, 2001).

## **3. Tritium Measurements**

It is useful to briefly describe tritium in the environment, which has been reviewed elsewhere (Okada and Momoshima, 1993; Hill and Johnson, 1993; Traub and Jensen, 1995). Tritium is produced naturally in the atmosphere from the reactions of cosmic ray protons and neutrons with N and O nuclei, as well as by ternary fission in geological formations. However, a bulk contribution to environmental accumulation comes from the nuclear explosions in the atmosphere, nuclear fuel cycle, and some from consumer products. The total present-day inventory of tritium in the environment is 19 EBq, only 1.3 EBq of which is attributed to the

natural production (Bennett, 2002). The levels of tritium in the environment have been decreasing steadily due to its decay with a half-life of 12.3 years, since the ban on atmospheric nuclear testing. Tritium occurs in the environment primarily as tritiated water (HTO), and much less as organically bound tritium. Typical current concentrations of HTO in water in the US are 0.1-0.2 nCi/L (EPA, 1997).

The reason we became interested in the subject of tritium at WTC was a possibility that tritium RL devices could have been present and destroyed at WTC. Tritium emergency EXIT signs are often used in public buildings. Taking into consideration 2 Twin Towers, 110 floors each, and assuming 5 EXIT signs per floor, 10 Ci of  $^3\text{H}$  each, would result in a total of  $1.1 \times 10^4$  Ci.

Several environmental measurements were made to confirm or disprove this hypothesis. Water was distilled once from the environmental stationary water samples, and twice from the vegetation samples. 10 ml of such distillate was mixed with 13 ml of Instagel XF cocktail (Packard) in a borosilicate glass vial and measured on an ultralow-background liquid scintillation counter TRI-CARB, model 3170TR/SL by Packard. [The t]ritium end-point beta energy is 18.6 keV. We used the energy window 1-13 keV to maximize signal to background ratio. The background rate was about 2 cpm. The efficiency of the instrument was calibrated using HTO standards as a function of [the]tSIE quench index. The environmental samples had [a] tSIE [value of] around 230, corresponding to [an] efficiency in the range 0.20-0.25.

Four groups of samples were analyzed for tritium as HTO. The results are listed in Table 1. The samples from groups 1 and 2 were measured for 200 min, while from groups 3 and 4 for 100 min. The 1st group consisted of the samples collected by New York State agencies without tritium in mind. They were analyzed for tritium after this investigation had started. The 2nd group consisted of the samples collected especially for this investigation. The 3rd and 4th groups were analyzed for tritium before this investigation started, and are included for reference only to show typical results from environmental monitoring of tritium. The 3rd group was requested by EPA Region 2, and by the New York City Department of Environmental Protection. The 4th group consisted of routine samples measured by this laboratory at the request of Albany County Health Department.

The sequence numbers 1,6,7 in Table 1 are from ground zero and they are all positive. The rest of the results in Table 1 are upper limits. All the errors or limits are at  $2\sigma$ . The sequence 1, of  $0.174 \pm 0.74$  is from the WTC sewer, collected 2 days after the attack, and is just above the detection limit. The sequences 6,7 of about 3 nCi/L are split samples from WTC 6, basement B5, collected 10 days after the attack. Thus tritium was detected in these limited samples at ground zero, but the concentrations are very low. In fact, 3 nCi/L is about 7 times less than the EPA limit in drinking water of 20 nCi/L (CFR, 141.66). No health implications are known or expected at such low concentrations (Hill and Johnson, 1993). As a consequence no additional ground-zero samples were judged necessary.

The sequences 2-5 are from roof tanks in South Manhattan near ground zero. The sequences 24-37 are from the south Manhattan water supply. All of these were systems closed to air and they do not show any tritium present [as expected]. There was also a possibility that some

HTO would have been transported with the fire plume during the first several days after the attack and

**Table 1. The results of tritium analysis in New York State.**

| Gr. no | Seq. no | Coll. date 2001 | Spl. type | Sampling location                       | Activity(a) (nCi/L) | Foot-note |
|--------|---------|-----------------|-----------|---|---------------------|-----------|
| 1      | 1       | 9/13            | water     | WTC storm sewer                         | 0.174±74            |           |
| 1      | 2       | 9/18            | water     | Manh., roof tank, 45 Wall St., 30 fl.   | <0.13               | b         |
| 1      | 3       | 9/18            | water     | Manh., roof tank, 111 Broadway, 22 fl.  | <0.13               | b         |
| 1      | 4       | 9/18            | water     | Manh., roof tank, 55 Broadway, 32 fl.   | <0.13               | b         |
| 1      | 5       | 9/18            | water     | Manh., roof tank, 7 Hanover Sq., 29 fl. | <0.13               | b         |
| 1      | 6       | 9/21            | water     | WTC Bldg. 6, basement B5, stairway J3   | 3.53±17             |           |
| 1      | 7       | 9/21            | water     | same                                    | 2.83±15             |           |
| 2      | 8       | 10/25           | grass     | Albany                                  | <0.12               | c,d       |
| 2      | 9       | 10/27           | grass     | Brooklyn, Brooklyn Heights              | <0.21               | c,d       |
| 2      | 10      | 10/27           | water     | Brooklyn, Govanus Canal                 | <0.11               |           |
| 2      | 11      | 10/27           | grass     | Brooklyn, Govanus Park                  | <0.091              | c         |
| 2      | 12      | 10/27           | water     | Brooklyn, English Kills                 | <0.11               |           |
| 2      | 13      | 10/27           | water     | Brooklyn, Prospect Park                 | <0.090              |           |
| 2      | 14      | 10/27           | grass     | same                                    | <0.093              | c         |
| 2      | 15      | 10/27           | water     | Brooklyn, Marine Park                   | <0.11               |           |
| 2      | 16      | 10/27           | grass     | same                                    | <0.090              | c         |
| 2      | 17      | 10/27           | water     | Brooklyn, Paerdegat Basin               | <0.090              |           |
| 2      | 18      | 10/27           | water     | Brooklyn, Coney Island                  | <0.11               |           |
| 2      | 19      | 10/27           | grass     | same                                    | <0.092              | c         |
| 2      | 20      | 10/27           | water     | Queens, Forest Park                     | <0.090              |           |
| 2      | 21      | 10/28           | water     | Poughkeepsie                            | <0.11               |           |
| 2      | 22      | 10/28           | grass     | same, with weeds                        | <0.17               | c,d       |
| 2      | 23      | 11/4            | leaves    | Manhattan, Battery Park                 | <0.12               | c,d       |
| 3      | 24-37   | 9/15            | water     | South Manhattan water supply            | <0.12-0.15          | b         |
| 3      | 38-77   | 9/17            | water     | Kensico Reservoir, Westchester County   | <0.10-0.18          |           |
| 4      | 78      | 9/26            | rain      | Albany County Health Department         | <0.061              | e         |
| 4      | 79      | 10/17           | rain      | same                                    | <0.11               |           |

Footnotes:

a)  $2\sigma$  errors or limits.

b) A system closed to ambient air.

c) Activity given per volume of water extracted from the vegetation.

d) Problems with chemiluminescence/color quench. Measured with instrumental luminescence correction on.

e) The value is the lowest due to low natural radioactivity background fluctuations of the glass vials for this batch.

deposited downwind. The wind direction was approximately northwest during 9/11 and 9/12 (NOAA, 2001). Therefore, we did some limited environmental sampling in Brooklyn, Queens and south Manhattan, which are downwind from ground zero. The sequence numbers are 9-20,23 in Table 1. These samples were taken about 7 weeks after the attack. All the results were zero within the detection limits, which is consistent with the small levels of HTO detected at ground zero.

For sequences 8,9,22,23 there were problems with chemiluminescence/color quench. These samples were measured with the instrumental luminescence correction on. The upper limits for sequences 9,22 are higher because the efficiency was lower due to higher quench (lower tSIE index), the detection limit being inversely proportional to the efficiency.

#### 4. Tritium Radioluminescent Devices

The difference between tritium RL devices and CRT tubes is that  $\beta$  particles from tritium decay, rather than accelerated electrons, generate light in the phosphor (Traub and Jensen, 1995). ZnS is the most widely used phosphor and it is activated by an impurity. ZnS-Ag gives {common} [a] green glow with a decay constant of 0.2  $\mu$ s. ZnS-Cu gives blue-green light and ZnS-(Cu,Mg) gives yellow-orange light (Lulu, 1998). There are two basic types of RL devices: i) gaseous tritium light sources (GTLS) sealed in a borosilicate glass tube, internally coated with the phosphor, and ii) tritium chemically incorporated into a polymer such as polystyrene and mixed with the phosphor. There is no tritium leakage from GTLS, unless broken. There is a small diffusion of tritium from polymers. GTLS are used as airport runway lights at remote airports (Alaska), emergency EXIT and other signs in buildings, emergency EXIT signs, handles, and aisle markers in airplanes, as well as sights in weaponry and markings in time devices. The polymer-based RLs are used in emergency signs and as paints in watches. When the GTLS tubes age, they acquire a small percentage (<2%) of HTO due to radiolytic reactions with the phosphor binder (Niemeyer, 1969; Traub and Jensen, 1995; Wermer, 1995).

Typical emergency EXIT signs in buildings contain from several to several tens of Ci of [molecular] tritium ( $T_2$ ). The amount of tritium is regulated per request of a manufacturer. For instance, Mb-microtec ag, registered sealed RL devices with Nuclear Regulatory Commission (NRC) [containing] up to 50 Ci (Lulu, 1998). Typical content of tritium per device is 10 Ci. The airplane tritium emergency signs have a regulatory limit of 10 Ci (CFR, 32.53).

GTLS are used extensively in weaponry and are standard equipment in military as well as law enforcement. Of interest to this work are gun sights containing GTLS capsules, either cylindrical or spherical, which facilitate {s} aiming at night. There are two categories of interest: scopes and night sights. The content of tritium depends on the configuration as well as the manufacturer. Trijicon Inc. uses 100 mCi in scopes and 3 capsules [of] 18 mCi each (54 mCi total) in night sights (Trijicon, 2002). Innovative Weaponry Inc. uses 54 mCi in their PT night sights (IWI, 2002). Meprolight Ltd. uses between 30 to 54 mCi per set of night sights (Kinder, 2002).



Tritium in timing devices is used as GTLS or polymer paint. NRC regulations limit tritium content per timepiece at 25 mCi for paint (CFR, 30.15) and 200 mCi for GTLS (CFR, 32). The ISO (1991) Standard recommends for paints [a]maximum average activity of 5 mCi per lot and 7.5 mCi per isolated instrument. The US Military Standard (MIL, 1991) recommends [the]maximum activity [for a] GTLS device as 25 mCi. A major manufacturer of GTLS containing watches is Mb-microtec ag, who offers the watches to the US market under the brand name Luminox. The watches are licensed with NRC under NR-0446-D-103-E up to 100 mCi of tritium, however, the watches on the market contain up to 41 mCi of tritium (Benziger, 2002). Luminox makes dive watches for the US Navy and aviator watches for the US Air Force. Consumer models are available. These types of watches are expensive, available through specialty stores only and, therefore, are not widely worn. There is no radiation dose associated with the GTLS watches, since tritium and its low-energy radiation are entirely contained within the sealed tube.

Less expensive and more popular watches use paint containing tritiated polymer, in plastic casing. A major manufacturer of tritiated paint is Rc Tritec ag. The typical range of tritium activity per timepiece is 0.8-2.7 mCi (Zeller, 2002). There is some radiation dose from wearing such watches due to measurable tritium release, diffusion through the plastic case and absorption through skin, albeit slow. The average whole-body doses range from 2.5 to 4  $\mu$ Sv/y (0.25-0.4 mrem/y), although the skin dose can be larger (Brunner *et al.*, 1996; Sadagopan *et al.*, 1997). However, a new photoluminescent material, Super-LumiNova has been recently developed by Nemoto & Co., based on mixed aluminum oxides and activated with a rare earth element (Lulu, 1998). It is characterized by high intensity and long afterglow, and is used in more than 95% of modern luminescent watches instead of tritium paint (Zeller, 2002).

## 5. Sources and Fate of Tritium at WTC

As described in Section 3, HTO was detected at ground zero, but the concentrations were very low. Several sources of tritium were considered and analyzed, to be consistent with the limited experimental data: i) EXIT signs in the buildings, ii) emergency signs on the airplanes, iii) fire and emergency equipment, iv) weaponry, and v) timepieces.

RL EXIT signs in the buildings would imply [a]large source of tritium available. We were informed by PANYNJ authorities that there were no tritium signs at [the]WTC, only photoluminescent ones (Lombardi, 2001). This is entirely consistent with [our] observations.

It was determined by the Federal Aviation Administration, that Boeing 767 Serial Number 21873, operated by the United Airlines, Tail Number 767-222 N612UA, was delivered in February, 1983 with 43{.2} Ci of tritium in emergency EXIT signs and handles (Sabatini, 2002). The 43{.2} Ci of tritium is contained in 4 emergency EXIT signs (10 Ci each) and 4 emergency slide/raft handles (0.8 Ci each). The same activity of tritium was present upon April, 1987 delivery of a second Boeing 767 Serial number 22322, Tail Number 767-223ER N334AA, operated by the American Airlines. Since neither of these aircraft were modified after the[ir] delivery (Sabatini, 2002; Cashdollar, 2002), the total activity from the aircraft was 34{.3} Ci at the time of attack, accounting for [the]radioactive decay of tritium [was accounted for].

The source of tritium from the airplanes was released at the point of impact with the Towers. Conversion of molecular tritium to HTO in the atmosphere is negligible: the formation of HTO through chemical kinetics is extremely slow (Pan and Rigdon, 1996). Rather, the conversion to HTO in atmospheric transport goes through a stage of deposition of molecular tritium to soil, followed by a microbial and exchange oxidation in soil. HTO is then directly reemitted, or uptaken by plants first and then reemitted into the atmosphere. The combined process results in the measured conversion rates between  $10^{-5}$  and  $10^{-3}$  for downwind distances of up to 15 km.

However, at the point of impact there was an explosive release. Considering the jet fuel explosion and high-temperature fires at the WTC,  $T_2$  was efficiently oxidized to HTO, based on weapon testing data (Gaver, 2002) as well as laser heating experiments (Skinner *et al.*, 2002). This oxide immediately vaporized due to the intense heat. Most of the HTO would be transported in the vapor phase with the wind, since the weather was dry on 9/11/01 (NOAA, 2001). One cannot accurately determine how much HTO condensed on building surfaces and deposited on the ground with the collapse of the buildings, but it would be a small fraction of the 34[.3] Ci available. One indication is barely  $0.174 \pm 0.74$  nCi/L from the WTC sewer, collected 2 days after the attack. Since the overall source was small, it is consistent that the environmental samples collected downwind over 7 weeks after the attack contained no tritium (Section 3).

It is interesting to compare this small release of tritium in the fire with two known accidents involving the release of molecular tritium caused by fire. The first involved a fire in a community building at Council, Alaska, on 9/6/87, where 12 RL light panels for airport runway marking were stored, totaling 3000 Ci of tritium (Jensen and Martin, 1988). It was a free burning fire, which consumed the building in 1 hr. Tritium assessment was done 11 days after the accident. The remaining GTLS tubes were mostly undamaged but disfigured, indicating that all tritium had escaped. No air-borne tritium was detected. All tubes were carefully swiped, and the remaining HTO activity on the tubes amounted to merely  $6.5 \times 10^{-8}$  of that originally present. No HTO was found in bioassay or environmental samples. The release scenario at [the]WTC from the airplanes is consistent with this accident. However, [the]WTC collapsed before complete burning of the buildings, so the fraction of tritium deposited at [the]WTC might be larger. Another incident, involving containers with tens of thousands Ci of tritium, was a fire on a C-124 airplane on the ground at the Wright-Patterson Air Force Base, Dayton, OH, on 10/12/65 (USAF, 1965). That fire was actively extinguished. Elevated levels of HTO were found in bioassay samples, on emergency and fire equipment, clothing, debris, as well as in the neighboring soil and water samples. In comparison with the Alaska incident, the active fire fighting contributed to capturing some of the HTO on site.

After the WTC buildings collapsed, fire fighting and rescue operations continued. The fires at ground zero were smoldering for months after the attack (Duenes, 2001). It was determined that 3 million gallons of water were hosed on site in the fire-fighting efforts between 9/11 and 9/21 (the day of the tritium measurement, sequences 6,7 in Table 1) (Headley, 2002). In addition, there were 2 episodes of rain during the same 10 day period after the attack: on 9/14 and 9/20,21 (NOAA, 2001), totaling 0.9 million gallons of water in the Bathtub area. Considering the neighboring area, one can take 1 million gallons from the rain. Therefore, a total of 4 million gallons of water percolated through the debris in the first 10 days and collected at

the bottom of the Bathtub. The percolating water efficiently dissolved that part of the airplane HTO, which was deposited in the building collapse, and carried it to the bottom of the Bathtub.

An engineering assessment determined that there was a [large]water leak into the Bathtub, adding to the rain and hose water. The main leak was from the Hudson River via two WTC cooling water outfall lines, while the two incoming pipes were shut down (Post, 2001a). There were reported leaks from broken water mains (Overbye, 2001; Cho and Post, 2001). There were also problems with the water table due to a hole in the damaged Slurry Wall along the Liberty Street (Post, 2001b). The combined water from rain and hoses as well as the leaks, collecting at the bottom of the Bathtub, transferred into the PATH train tunnel. Water {was} then flow[ed] under the Hudson River to the Exchange Place Station, Jersey City, NJ, since it is lower in elevation than WTC B6 level (Post, 2001a; Overbye, 2001), where it was pumped out. Other pumps were installed (after 9/21) along Liberty Street to stabilize the Slurry Wall, which had moved (Post, 2001b). Based on the pumping records, a total of 30 million gallons of water passed through the Bathtub between 9/11 and 9/21 (Lombardi, 2002a, 2002b). Therefore, 26 million gallons were from the leaks. Even on 10/8/01 there was still some water flowing to New Jersey (Cho and Post, 2001).

HTO collected at the bottom of the Bathtub shared the fate of water and was removed with the flow. The 9/21 HTO sample, reportedly collected from basement B5, sampled that dynamical system close to the bottom of the Bathtub.

It was concluded that fire and emergency equipment could not have been a source of tritium, since such equipment does not typically use tritium RL devices, at least for type of emergency response conducted at [the]WTC.

Weaponry was another likely source of tritium. As described in Section 1, several federal and state law enforcement agencies were housed at WTC, in buildings 6 and 7. ATF had two vaults filled with tactical weapons and guns (Miller, 2001; WPVI, 2001; Gardiner and Hurtado, 2001; note: the ATF vaults were in WTC 6, where our sequences 6,7 were measured). A total of 63 Police Officers died in the attack (IUPA, 2001). They may have been carrying pistols equipped with tritium night sights. In fact, many guns have been recovered from the debris (WPVI, 2001; Gardiner and Hurtado, 2001; Koppel, 2002), some of them in good condition. It would take only 20 weapons destroyed to obtain approximately 1 Ci of tritium (Section 4).

Considering 2824 victims of the attack, tritium watches could have been another source of tritium. Tritium paint watches were less likely, since they contain much less tritium and are generally not used in modern watches (Section 4). However, GTLS-type watches, although expensive, could have been worn by [the]more affluent public of lower Manhattan. In addition, the military-style watches may have been worn by the emergency/law enforcement personnel who perished. It would take a mere 40 GTLS watches to obtain 1 Ci of tritium activity. The GTLS watches can be obtained in specialty stores only. No specialty watch stores were located at WTC (NYNEX, 1996). Some watches (but not necessarily tritium) were recovered from the debris with only minor damage (Koppel, 2002).

On a probability scale, weapons were definitely present at WTC and the law-enforcement types contain tritium night sights by design; tritium watches were possibly present. [The] mechanism of tritium release from either the weapons or watches would have been much different than from the airplanes. Some devices could have been catastrophically destroyed in the buildings collapse, however, surprisingly, many were recovered with minor damage. Many devices would have been subjected to smoldering fires of much lower temperature than the explosive and high-temperature fires up in the Towers (with the exception of possibly the WTC 7 fire). Under such temperatures, GTLS tubes would soften and disfigure, slowly releasing tritium. Some of that tritium would diffuse from the debris and be dispersed in the air, while some would remain trapped in the debris. While oxidation of molecular tritium is slow in the air, tritium is known to adsorb on surfaces and exchange with the adsorbed monolayer of water to form HTO due to a catalytic action of the surface (Traub and Jensen, 1995; Ono *et al.*, 1992; Dickson and Miller, 1992; Antoniazzi *et al.*, 1992) (at elevated tritium concentrations, also radiolytic and hot-atom chemistry effects assist in the oxidation; Wermer, 1995). Consequently, some molecular tritium released in the debris would convert to HTO and be swept with the hose and rain water down to the basement of the Bathtub sharing the fate of HTO from the airplanes, but at much slower time scale. This mechanism resembles leaching of HTO from landfills containing tritium RL devices (Hicks *et al.*, 2000).

## 6. Modeling of Water Flow and Tritium Removal from Ground Zero

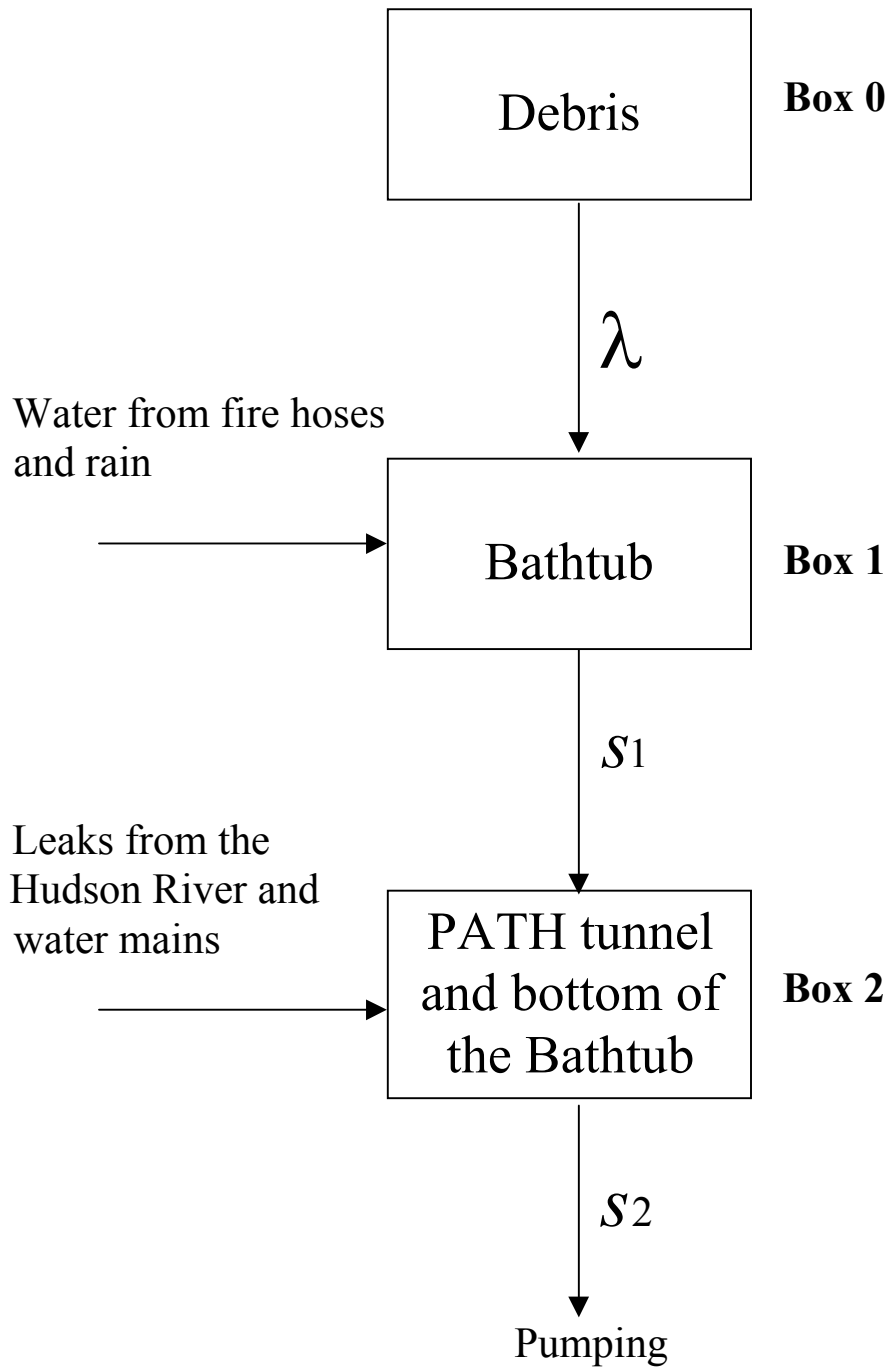
A 3-Box model was developed to quantify water flow and tritium removal, depicted on Fig. 1. Box 0 describes the debris, from which HTO is assumed to be removed at a rate  $\lambda$ . The Bathtub is divided into Boxes 1 and 2.

Box 1 consists of 6/7 of the void volume of the Bathtub, through which the hose and rain water flowed. Using the data described in the previous sections, one can calculate an experimental flow rate  $f_1=1.51 \times 10^6$  L/day through Box 1. Considering that the Bathtub was at least 50% destroyed and filled with the debris from the buildings (Post, 2001c), one could assume its air porosity of 0.1 (note: for instance, a porosity of close packed spheres is 0.26). With such porosity, the void volume can be calculated as  $V_1=8.49 \times 10^7$  L. It would take  $V_1/f_1=56$  days for such volume to propagate through Box 1. The experimental volume of  $1.51 \times 10^7$  L of water would not have even reached the bottom of the Bathtub in 10 days. One can conclude that the water could not have filled the air porosity completely and what really mattered was the water, not the air porosity. Water would flow through filled small pores, however, it would flow only on the surfaces of larger voids. A reasonable estimate of the water void volume can be made by equating it to the experimental volume of water that is known to have flowed in 10 days,  $V_1=1.51 \times 10^7$  L. This yields a water flow time constant  $s_1=f_1/V_1=0.1$  1/day for Box 1.

One can take the B6 level with the PATH tunnel as Box 2 and assume its air porosity [is] 0.3, since the damage was less. One could estimate an upper limit for the water porosity as 0.1. Its exact value is less important, since the experimental water flow rate through Box 2,  $f_2=1.14 \times 10^7$  L/day  $\gg f_1$ . This yields  $V_2=1.42 \times 10^7$  L, and the water flow time constant  $s_2=f_2/V_2=0.803$  1/day for Box 2.

The following differential equations describe tritium propagation through the three boxes at ground zero.

$$\frac{dA}{dt} = -\lambda A, \quad (1a)$$



$$\frac{dc_1}{dt} = \frac{\lambda}{V_1} A - s_1 c_1, \quad (1b)$$

$$\frac{dc_2}{dt} = \frac{f_1}{V_2} c_1 - s_2 c_2, \quad (1c)$$

where  $t$  is the time,  $A$  is [the] total tritium activity in the debris and  $c_1, c_2$  are HTO concentrations in Boxes 1 and 2, respectively. Equations (1) are linear, 1<sup>st</sup> order, of which (1b,c) are inhomogeneous. They can be solved with standard methods (Margeneau and Murphy, 1976). Using also an approximation  $e^{-s_1 t} \gg e^{-s_2 t}$ , the following equation describes the measured HTO concentration  $c_2$  at the bottom of the Bathtub

$$c_2 = \frac{s_1 \lambda A^0}{V_2} \frac{1}{s_1 - \lambda} \left( \frac{1}{s_2 - \lambda} e^{-\lambda t} - \frac{1}{s_2} e^{-s_1 t} \right), \quad [(2)]$$

where  $A^0$  is the total HTO activity in the debris at time zero.

Calculating  $\lambda$  and  $A^0$  from Eq. (2) requires at least two measured concentrations  $c_2$  at different times, which w[ere] not available. In spite of this drawback, it is useful to consider two limits: 1<sup>o</sup> when  $\lambda \gg s_1$ , where HTO removal is controlled by the water flow in Box 1, and 2<sup>o</sup> when  $s_1 \gg \lambda$ , where HTO removal is controlled by the transfer rate from the debris. In case 1<sup>o</sup>, one obtains from Eq. (2)

$$A^0 = \frac{c_2 f_2}{s_1} e^{s_1 t}. \quad (3)$$

Using  $c_2=3.18$  nCi/L,  $t=10$  days, and the values  $s_1$  and  $f_2$  give[n] above, one obtains  $A^0=0.98\{5\}$  Ci from Eq. (3). This scenario is appropriate for the source term from the airplanes, since such tritium was in HTO form in the debris and its removal would be controlled solely by the flow rate. Taking the total tritium activity of 34\{3\} Ci from the two airplanes, implies an upper limit for the HTO deposition fraction of [3]%. This fraction, although the right order of magnitude, appears to be somewhat high by {a} comparison with the two tritium fire incidents described in Section 5, indicating that another source of tritium was present.

For case 2<sup>o</sup> one obtains from Eq. (2)

$$A^0 = \frac{c_2 f_2}{\lambda(1 - e^{-s_1 t})}. \quad (4)$$

One cannot solve Eq. (4) uniquely with one value of  $c_2$ . There is, however, a constraint  $s_1 \gg \lambda$ . Taking, for instance,  $\lambda=0.1s_1$  would imply  $A^0=5.7\{4\}$  Ci. Such activity of tritium could be generated by 115 weapons (plus any watches), 50 mCi each. Such a slow release of tritium from the weapons subjected to smoldering fires is thus an entirely reasonable scenario, however it appears to be somewhat too high and would require a complete destruction of 115 weapons and a quantitative tritium capture as well as a conversion to HTO. Taking  $\lambda$  even smaller would further

overestimate this tritium source. Therefore, such a mechanism alone [is] not [sufficient] and another tritium source must have been present, which were the airplanes.

## 7. Conclusions

34{.3} Ci of tritium were released from the two Boeing 767 on impact with the Twin Towers at the World Trade Center. The limited measurements and modeling are consistent with an instantaneous (catastrophic) creation of HTO from the aircraft emergency signs, deposition of a small fraction of it at ground zero and water-flow controlled removal from the site. The modeling suggests that the contribution from the aircraft would imply the HTO deposition fraction of [3]%, a value which is judged somewhat too high. Therefore, the source term from the airplanes alone is insufficient to explain the measurements and modeling.

Several weapons were present and destroyed at [the]WTC. The modeling is also consistent with the second tritium source from the weapon sights (plus possibly tritium watches) where tritium was slowly released from the debris in the lingering fires, followed by an oxidation and removal with the water flow. Such a limiting case would require a minimum of 115 weapons and a quantitative capturing of tritium. Therefore, such a mechanism alone [seems in]sufficient, which indicates that the weapon/watch source complemented the airplane source.

## Acknowledgments

The following individuals are highly acknowledged for their substantial contributions to the overall success of this work: E. Regilski and C. Schwenker, New York State Department of Health, for their help in the sample analysis and measurements; J. Cashdollar and N. Sabatini, Federal Aviation Administration, for the estimation of tritium activity onboard the aircraft; D. Dischino, Bristol-Myers Squibb Corporation, for scientific discussion regarding tritium; T. Headley, Fire Department of New York, for estimating of water flow rate due to fire fighting at WTC; F. Lombardi, Port Authority of New York and New Jersey, for estimating of the total water flow rate at WTC as well information about emergency EXIT signs at WTC; J. Gaver, US Department of Energy, and C. Skinner, Princeton Physics Plasma Laboratory, for their expertise on tritium chemistry at high temperatures.

## References

⚠Disclaimer. The statements and conclusions in this paper are those of the authors and not necessarily those of either the New York State Department of Health State, or State University of New York, Lawrence Berkeley National Laboratory, Lawrence Livermore National Laboratory, Westinghouse Savannah River Company. The mention of commercial vendors, products, and news media in connection with the work reported herein is not to be construed as either actual or implied endorsement of such vendors, products, or media.

✉Corresponding author. Address: Thomas Semkow, Wadsworth Center, New York State Department of Health, Empire State Plaza, Albany, NY 12201-0509. Email: semkow@wadsworth.org.



- Antoniazzi A.B., Shmayda W.T., Surette R.A. (1992). Decontamination of stainless steel. *Fusion Tech.* **21**: 867-871.
- AP (2002). Engineers study WTC collapse. Associated Press, New York Times, [www.nytimes.com](http://www.nytimes.com), 4/30/02.
- Ashley S. (2001). When the Twin Towers Fell. Scientific American, [www.sciam.com](http://www.sciam.com), 10/9/01.
- Bennett B.G. (2002). Worldwide dispersion and deposition of radionuclides produced in atmospheric tests. *Health Phys.* **82**: 644-655.
- Benziger J. (2002). Mb-microtec ag, personal communication, 3/19/02.
- Brunner P., Schneider P., Scheicher H., Seyerl G., Kurnik P., Ennemoser O., Ambach W. (1996). Tritium intake by exposure to plastic case watches. *Health Phys.* **70**: 484-487.
- Cashdollar J. (2002). Federal Aviation Administration, US Department of Transportation, personal communication, 4/23/02.
- CFR (30.15). Certain items containing byproduct material. US Code of Federal Regulations, 10 CFR Part 30.15.
- CFR (32). License applications for certain items containing byproduct material. US Code of Federal Regulations, 10 CFR Part 32, RIN 3150-AF76.
- CFR (32.53). Luminous safety devices for use in aircraft: Requirements for license to manufacture, assemble, repair or initially transfer. US Code of Federal Regulations, 10 CFR Part 32.53.
- CFR (141.66). Maximum contaminant levels for radionuclides. US Code of Federal Regulations, 40 CFR Part 141.66.
- Cho A., Post N.M. (2001). Crews shore damaged subways. Engineering News Record, [www.enr.com](http://www.enr.com), 10/8/01.
- Cummings S. (2002). WTC Complex: 6WTC, 7WTC. Patriot Resource, [www.patriotresource.com](http://www.patriotresource.com).
- Dickson R.S., Miller J.M. (1992). Sorption of tritium and tritiated water on construction materials. *Fusion Tech.* **21**: 850-855.
- Duenes S. (2001). Hot spots linger at ground zero. New York Times, [www.nytimes.com](http://www.nytimes.com), 10/2/01.
- EPA (1997). Environmental radiation data. US Environmental Protection Agency. Report 81. EPA-402-R-97-004.
- Gardiner S., Hurtado P. (2001). Billions in stocks, bonds found in WTC rubble. Seattle Times, [seattletimes.nwsourc.com](http://seattletimes.nwsourc.com), 10/6/01.
- Gaver J.M. (2002). Savannah River Site, US Department of Energy, personal communication, 1/30/02.
- Glanz J., Lipton E. (2002). Burning diesel is cited in fall of 3<sup>rd</sup> tower. New York Times, [www.nytimes.com](http://www.nytimes.com), 3/2/02.
- Headley T. (2002). Fire Department of New York, personal communication, 2/12/02.
- Hicks T.W., Wilmot R.D., Bennett D.G. (2000). Tritium in Scottish landfill sites. Galson Science Report 014-2, Rutland, UK.
- Hill R.L., Johnson J.R. (1993). Metabolism and dosimetry of tritium. *Health Phys.* **65**: 628-647.
- ISO (1991). Radioluminescence for time measurement instruments – specifications. ISO 3157, International Organization for Standardization, Geneva, Switzerland.
- IUPA (2001). List of Officers missing or killed in the line of duty during the attacks in New York. International Union of Police Associations, [www.iupa.org](http://www.iupa.org).

- IWI (2002). Innovative Weaponry, Inc., personal communication, 3/18/02.
- Jensen G.A., Martin J.B. (1988). Investigation of fire at Council, Alaska: A release of approximately 3000 curies of tritium. Pacific Northwest National Laboratory Report PNL-6523, Richland, WA.
- Kinder K. (2002). Kimber of America Mfg., Inc., personal communication, 3/19/02.
- Koppel, T. (2002). Ground zero. American Broadcasting Corporation, Nightline, abcnews.go.com, 3/11/02.
- Lipton E., Glanz J. (2002a). First Tower to fall was hit at higher speed, study finds. New York Times, www.nytimes.com, 2/23/02.
- Lipton E., Glanz J. (2002b). A nation challenged: forensics; DNA science pushed to the limit in identifying the dead of Sept. 11. New York Times, www.nytimes.com, 4/22/02.
- Lombardi F.J. (2001). Port Authority of New York and New Jersey, personal communication, 12/10/01.
- Lombardi F.J. (2002a). Port Authority of New York and New Jersey, personal communication, 1/28/02.
- Lombardi F.J. (2002b). Response at ground zero - role of Engineers. National Engineers Week 2002, Fishkill, NY, 2/19/02.
- Lulu B. (1998). Luminous watch hands. Power Reserve, Inc., www.timezone.com, 11/19/98.
- Margeneau H., Murphy G.M. (1976). The mathematics of physics and chemistry. Krieger Publishing Co., Huntington, NY.
- MIL (1991). Watch, wrist: general purpose. US Military Specification MIL-W-46374F, Naval Publications and Forms Center, Philadelphia, PA.
- Miller J. (2001). Digging for gold, guns and drugs. American Broadcasting Corporation, abcnews.go.com, 10/3/01.
- Niemeyer R.G. (1969). Tritium loss from tritium self-luminous aircraft exit signs. Oak Ridge National Laboratory Report ORNL-TM-2539, Oak Ridge, TN.
- NOAA (2001). Local climatological data. National Oceanic and Atmospheric Administration, US Department of Commerce, September 2001.
- NYNEX (1996). NYNEX Directory for New York Metro Area. April 1995 - March 1996.
- Okada S., Momoshima N. (1993). Overview of tritium: characteristics, sources, and problems. *Health Phys.* **65**: 595-609.
- Ono F., Tanaka S., Yamawaki M. (1992). Sorption and desorption of tritiated water on paints. *Fusion Tech.* **21**: 827-832.
- Overbye D. (2001). Engineers tackle havoc beneath Trade Center. New York Times, www.nytimes.com, 9/18/01.
- Pan P.Y., Rigdon L.D. (1996). Tritium oxidation in atmospheric environment. Los Alamos National Laboratory Report LA-UR-96-2953, Los Alamos, NM.
- Post N.M. (2001a). Engineers plan assessment and new support for WTC foundation perimeter walls. Engineering News Record, www.enr.com, 9/17/01.
- Post N.M. (2001b). WTC 'Bathtub' stabilization begins. Engineering News Record, www.enr.com, 10/29/01.
- Post N.M. (2001c). Half of WTC 'Bathtub' basement damaged by Twin Towers' fall. Engineering News Record, www.enr.com, 10/8/01.
- Sabatini N.A. (2002). Federal Aviation Administration, US Department of Transportation, personal communication, 3/26/02.
- Sadagopan G., Sadarangani S.H., Nambi K.S.V, Krishnamoorthy T.M., Venkataraman G.

- (1997). Radiological safety aspects of Indian watches containing tritium. *Rad. Prot. Dos.* **72**: 49-53.
- Skinner C.H., Gentile C.A., Carpe A., Guttadora G., Langish S., Young K.M., Shu W.M., Nakamura H. (2002). Tritium removal from codeposits on carbon tiles by a scanning laser. *J. Nucl. Mater.* **301**: 98-107.
- Slobin S. (2001). W.T.C.: Clearing the debris. New York Times, [www.nytimes.com](http://www.nytimes.com), 10/13/01.
- Traub R.J., Jensen G.A. (1995). Tritium radioluminescent devices. Health and safety manual. Pacific Northwest National Laboratory Report PNL-10620 (UC-610), Richland, WA.
- Trijicon (2002). Trijicon, Inc., [www.trijicon.com](http://www.trijicon.com).
- USAF (1965). Health physics sampling results, C-124 incident. Bio-environmental Engineering Branch, US Air Force Hospital Wright-Patterson Report AFR 11-30, Wright-Patterson Air Force Base, OH.
- Wermer J.R. (1995). Assessment of commercial self-luminous exit signs containing tritium: Final Report – Task 1. Westinghouse Savannah River Company Report WSRC-TR-0311, Aiken, SC.
- WPVI (2001). World Trade Center rubble holds buried secrets. [abclocal.go.com](http://abclocal.go.com), WPVI, Philadelphia, PA, 10/5/01.
- Zeller A. (2002). Rc Tritec ag, personal communication, 3/18/02.