# Tritium in the World Trade Center September 11<sup>th</sup>, 2001 Terrorist Attack: It's Possible Sources and Fate

P. Parekh, T. Semkow, L. Husain, D. Haines, G. Wozniak, P. Williams, R. Hafner, R. Rabun

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Trends and Recent Achievements

# Tritium in the World Trade Center September 11th, 2001 Terrorist Attack: It s Possible Sources and Fate

P.Parekh, T.Semkow(a), L.Husain(a), D.Haines

Wadsworth Center, New York State Department of Health, Albany, NY, (a) also School of Public Health, University at Albany, State University of New York

- G.Wozniak(b), P.Williams(c)
- (b) Nuclear Science Division, (c) Physical Biosciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA

R.Hafner

Fission Energy and System Safety Program, Lawrence Livermore National Laboratory, Livermore, CA

R.Rabun

Tritium Engineering Department, Westinghouse Savannah River Company, Aiken, SC

#### Abstract

Traces of tritiated water (HTO) were determined at 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  $0.174\pm0.074$  ( $2\sigma$ ) nCi/L of HTO. A split water sample, collected on 9/21/01 from the basement of WTC Building 6, contained  $3.53\pm0.17$  and  $2.83\pm0.15$  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. Tritium is used in self-luminescent emergency EXIT signs. No such signs were present inside the WTC buildings. However, it was determined that Boeing 767-222 aircraft operated by the United Airlines that hit WTC Tower 2 as well as 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. Other possible sources of tritium include dials and lights of fire and emergency equipment, sights and scopes in weaponry, as well as time devices equipped with tritium dials. It was determined that emergency equipment was not a likely source. However, 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 with tritium sights, died in the attack. The weaponry containing tritium was therefore a likely and significant source of tritium. It is possible that some of the 2830 victims carried tritium watches, however this source appears to be less significant that the other two.

The fate of tritium in the attack depended on its chemistry. Any tritium present in the vicinity of 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 a consideration water flow at ground zero. Most of ground zero is encircled by the Slurry Wall, 70 ft deep underground, called a 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. That water would meet and combine 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 water was collecting in the PATH train tunnel and continuously being pumped out to prevent flooding. A 3-Box model of water flow was developed to describe the above scenario.

Considering the uncertainty in the amount of tritium present from sources other than the aircraft, as well as the dynamic character of tritium removal from the site, it is feasible to provide only a qualitative picture of the fate and behavior of tritium at WTC with the limited experimental data available. If the time history of tritium concentration at WTC had been measured, this study could have been a tracer study of water flow at WTC possibly useful to civil engineering.

#### 1. World Trade Center

World Trade Center, the symbol of New York City, had been built in the 1970s and 1980s. It contained 7 buildings designated as WTC 1 through WTC 7 (slide 3). 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 (slide 4). WTC was owned and operated by Port Authority of New York and New Jersey (PANYNJ). It is important to this investigation hat several federal law enforcement agencies were located at WTC (1,2). 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 (slide 5). The modern land to the west of it is actually a fill. 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. 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 (slide 6). 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 11th, 2001 are well known. At 8:45 am, Boeing 767-223ER aircraft operated by the American Airlines, Flight 11, hit WTC Tower 1 causing jet fuel explosion and fire. At 9:03 am, second Boeing 767-222 aircraft operated by the United Airlines, Flight 175, hit WTC Tower 2. Both flights originated in Boston, so the aircraft were full of fuel. WTC 2 collapsed first, lasting 47 min; WTC 1 collapsed next, lasting 103 min (slides 7,8,9).

The collapse of the Towers was studied in detail (3,4) (slide 10). 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 (slide 8), the columns lost their strength causing the structures to collapse semi-vertically (slide 9). 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 were, higher speed of the aircraft at collision (586 mph) compare 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), close to the structural braking point of the aircraft.

The collapsing Towers destroyed other WTC buildings and the debris compacted and destroyed much of the Bathtub (slide 11). The debris from WTC 1 plunged through the center of WTC 6 creating a pit stretching down to the basement of the Bathtub (5). At 5:30 pm, WTC 7 collapsed due to a diesel fuel fire from the tank for New York City emergency team (6). The WTC area is referred to as ground zero.

Authorities determined that 2830 people died in the attack on the WTC (7), including people onboard the aircraft, 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 (8).

#### 3. Tritium Measurements

It is useful to briefly describe tritium in the environment, which has been reviewed elsewhere (9-11). 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 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 nuclear explosions. 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 (12).

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 a consideration 2 Twin Towers, 110 floors each, and assuming 5 EXIT signs per floor, 10 Ci of <sup>3</sup>H each, would result in a total of 1.1×10<sup>4</sup> 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. Tritium 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 tSIE quench index. The environmental samples had tSIE around 230, corresponding to 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 (slide 12). 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 has 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 has started, and are included for a reference only to show typical results from environmental monitoring of tritium. The 3rd group was requested by EPA Region 2, and by 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 sequence 1, of 0.174±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. It is therefore not an experimental error. 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 (12a). No health implications are known or expected at such low concentrations.

The rest of the results in Table 1 are upper limits. All the errors or limits are at  $2\sigma$ . A note is in order about the limits. While the instrument can deliver an ultralow background, the limits are not determined by the background itself but by its fluctuations. It has been determined that the fluctuations are due to variations of the natural radioactivity content in the glass counting vials. These fluctuations are different from a vial to vial and from a batch to a batch of vials.

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. 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 deposited downwind. The wind direction was approximately northeast during 9/11 and 9/12 (13).

This is seen in slide 13. Therefore, we did some limited environmental sampling in Brooklyn, Queens and south Manhattan. The sequence numbers are 9-20,23 in Table 1, and the location numbers (different from the sequence numbers) are depicted on slide 14. 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), and the detection limit is 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 (11). ZnS is the most widely used phosphor and it is activated by an impurity. ZnS-Ag gives common 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 (14). 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) with 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 (11,14a,14b).

Typical emergency EXIT signs (slide 15) in buildings contain from several to several tens of Ci of tritium. The amount of tritium is regulated per request of a manufacturer. For instance, Mb-microtec ag, registered sealed RLs with Nuclear Regulatory Commission (NRC) up to 50 Ci (14). Typical content of tritium per device is 10 Ci. The examples of RL devices used in airplanes are depicted in slide 16. Each device on an airplane has a regulatory limit of 10 Ci (15).

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 facilitates aiming at night. There are two categories of interest: scopes (slide 17) and night sights (slide 18). The content of tritium depends on the configuration as well as the manufacturer. Trijicon Inc. uses 100 mCi in scopes and 3 capsules 18 mCi each (54 mCi total) in night sights (16). Innovative Weaponry Inc. uses 54 mCi in their PT night sights (17). Meprolight Ltd. uses between 30 to 54 mCi per set of night sights (18).

Tritium in timing devices is used as GTLS or polymer paint (slide 19). NRC regulations limit tritium content per timepiece at 25 mCi for paint (19) and 200 mCi for GTLS (20). The ISO 3157 Standard recommends for paints maximum average activity of 5 mCi per lot and 7.5 mCi per isolated instrument. The US military standard MIL-W-46374F recommends maximum activity of 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 (21). Luminox makes dive watches for US Navy and aviator watches for US Air Force. Consumer models are available. These types of watches are expensive, available through specialty stores only and, therefore, 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. Typical range of tritium activity per timepiece is 0.8-2.7 mCi (22). There is some radiation dose from wearing such watches due to although slow, but measurable tritium release, diffusion through the plastic case and absorption through skin. 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 (23,24). 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 (14). It is characterized by high intensity and long afterglow, and is used in more than 95% of modern luminescent watches instead of tritium paint (22).

#### 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 large source of tritium available. We were informed by PANYNJ authorities that there were no tritium signs at WTC, only photoluminescence ones (25). This is entirely consistent with the 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 (25a). The same activity of tritium was present upon April, 1987 delivery of second Boeing 767 Serial number 22322, Tail Number 767-223ER N334AA, operated by the American Airlines. The United aircraft has not been modified since the delivery, which has not been confirmed for the American aircraft as yet. Including the decay of tritium, the activity from the aircraft was 34.3 Ci at the time of attack.

The source of tritium from the airplane(s) 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 (26). Rather, the conversion to HTO in atmospheric transport goes through a stage of deposition of molecular tritium to soil, followed by a microbial or 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 (slides 7,8), T<sub>2</sub> efficiently oxidized to HTO, based on weapon testing data (27) as well and laser heating experiments (28). This oxide immediately evaporized due to the intense heat. Most of HTO would be transported in the vapor phase with the wind, since the weather was dry on 9/11/01 (13). One cannot accurately determine how much HTO condensed on building surfaces and fell to the ground with the collapse of the buildings, but it would be a small fraction of the 54-80 Ci available (slide 9). One indication is barely 0.174±0.74 nCi/L from the WTC sewer, collected 2 days after the attack. Since the overall source was small, it is only 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 the two known accidents involving the release of molecular tritium caused by fire. The first involved a fire in the 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. It was a free burning fire, which consumed the building in 1 hr. Tritium assessment was done 11 days after the accident. The remained GTLS tubes were mostly undamaged but disfigured, indicating that all tritium had escaped. No airborne 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 WTC from the airplanes in consistent with this accident. Another incident involving RL lights was a fire on a C-124 airplane on the ground at Wright-Patterson Air Force Base, Dayton, OH, on 10/12/65 (30). 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 of 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. Slide 20 shows the hot spots in the Bathtub area on 9/16/01 determined from aerial surveys. 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) (31). In addition, there were 2 episodes of rain during the same 10 day period after the attack: on 9/14 and 9/20,21 (13), totaling 0.9 million gallons of water per 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 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 water leak into the Bathtub, in addition to 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 shutdown (32). There were reported leaks from broken water mains (33,34). There were also problems with water table due to a hole in the damaged Slurry Wall along the Liberty Street (35). The combined water from rain and hoses as well as the leaks, collecting at the bottom of the Bathtub (slide 21), transferred into the PATH train tunnel (slide 22). Water was then flowing under the Hudson River to the Exchange Place

Station, Jersey City, NJ, since it is lower in elevation than WTC B6 level (32,33) (slide 5), where it was pumped out. Other pumps were installed (however after 9/21) along Liberty Street to stabilize the Slurry Wall, which has moved (35) (slide 23). Based on the pumping records, a total of 30 million gallons of water passed through the Bathtub between 9/11 and 9/21 (36,37). Therefore, 26 million gallons were from the leaks. Even on 10/8/01 there was still some water flowing to New Jersey (34).

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 that type of emergency response conducted at WTC.

Weaponry was a likely source of tritium. As described in section 1, several federal and state law enforcement agencies were housed at WTC, in building 6 and 7. ATF had two vaults filled with tactical weapons and guns (2,38,39) (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 (8). They may have been carrying pistols equipped with tritium night sights. In fact, many guns have been recovered from the debris (38,39,40), some of them in good condition. It would take only 20 weapons destroyed to obtain approximately 1 Ci of tritium (section 4).

Considering 2830 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 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. Some watches (but not necessarily tritium) were recovered intact from the debris (40).

On a probability scale, weapons were definitely present at WTC and the law-enforcement types contain tritium night sights by default; tritium watches were possibly present. A mechanism of tritium release from either the weapons or watches would have been much different than from the airplanes. Several scenarios were possible. Some devices could have been catastrophically destroyed in the buildings collapse, releasing tritium instantaneously, followed by oxidation in the debris. However, surprisingly, many were recovered with minor damages. Some devices could be subjected to smoldering fires of much lower temperature than the explosive and high-temperature fires up in the Towers (with the exception of possibly 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 from adsorption on surfaces and exchange with the adsorbed monolayer of water to form HTO due to a catalytic action of the surface (11,42,43,44). At elevated tritium concentrations, also radiolytic and hot-atom chemistry effects assist in the oxidation (14b). 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 (45).

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

A 3-Box model has been developed to quantify water flow and tritium removal (Fig. 1, slide 24). Box 0 describes the debris, from which HTO is assumed to be removed at a rate  $\lambda$ . The Bathtub is divided into two boxes. Box 1 consists of 6/7 of the void volume of the Bathtub, through which the hose and rain water flows. Considering that the Bathtub was at least 50% destroyed and filled with the debris from the buildings (46) (slide 23), we assume its porosity of 0.1 (note: for instance, a porosity of close packed spheres is 0.26). Using the data described in the previous sections, we calculate a flow rate  $f_1=1.51\times10^6$  L/day and void volume  $V_1=8.49\times10^7$  L. A flow time constant  $s_1=f_1/V_1=1.78\times10^{-2}$  1/day. We take the B6 level with the PATH tunnel (slide 22) as Box 2 and assume its porosity of 0.3, since the damage was less. This yields:  $f_2=1.14\times10^7$  L/day,  $V_2=4.25\times10^7$  L, and  $s_2=f_2/V_2=0.267$  1/day.

The 3-Box model was solved through the differential equations. Using also the approximation  $s_2 >> s_1$ , the following equation describes the measured HTO concentration  $c_2$ 

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

where  $A^0$  is the total HTO activity and t is the time (slide 25).

Calculating  $\lambda$  and  $A^0$  from eq. (1) requires at least two measured concentrations  $c_2$  at different times, which was not available. However, it is useful to consider two limits:  $1^\circ$  when  $\lambda >> s_1$ , where HTO removal is controlled by the water flow in Box 1, and  $2^\circ$  when  $s_1 >> \lambda$ , where HTO removal is controlled by the transfer rate from the debris. In case  $1^\circ$ , one obtains a limit from eq. (1) (slide 25)

$$A^{0} = c_{2} f_{2} \left( \frac{1}{s_{1}} + t \right). \tag{2}$$

Using  $c_2$ =3.18 nCi/L, t=10 days, and the values  $s_1$  and  $f_2$  give above, one obtains  $A^0$ =2.40 Ci from eq. (2). This scenario would be appropriate for the source from the airplanes, since tritium was in HTO form and its removal from the debris would be controlled by the flow rate. Taking the total tritium activity from the two airplanes 34.3 Ci, implies HTO deposition fraction of 7%. This fraction appears to be high, indicating that other sources of tritium were present.

For case 2° one obtains a limit from eq. (1) (slide 25)

$$A^0 = \frac{c_2 f_2}{s_1 \lambda t} \ . \tag{3}$$

One cannot solve eq. (3) uniquely with one value of  $c_2$ . There is, however, a constraint  $s_1 >> \lambda$ . Taking, for instance,  $\lambda=0.1s_1$  would imply  $A^0=114$  Ci. Such activity of tritium could be generated by 2280 weapons, 50 mCi each. This is on a high side and, therefore, such a mechanism alone was not feasible. It thus shows that the weapons/watches could not have been a major contributor to the measured  $c_2$ , if tritium release from them was slow. However, these sources could have two components, a catastrophic release in buildings collapse, similar to tritium from the airplanes, followed by a slow release. This points to several tritium sources, as described in section 5, and eq. (1) should be used for each source separately.

#### 7. Conclusions

There were two sources of tritium at WTC: from the aircraft signs and from the gun sights (plus possibly watches). The limited measurements and modeling are consistent with an instantaneous (catastrophic) creation of HTO from the aircraft signs, deposition of a small fraction of it at ground zero and water-flow controlled removal from site. The modeling suggests that the contribution from the aircraft alone is too low to explain the measurement. The weapon/watch source could have had two components: i) catastrophic release in building collapse followed by a rapid oxidation to HTO and flow-controlled removal as for the aircraft source; ii) slow release due to lingering fires. The modeling suggests that component ii) could not have been a major contributor to the measured concentration of HTO, or its release could not have been much slower than the rate of flow removal.

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#### References

- 1. S.Cummings. WTC Complex: 6WTC, 7WTC. www.patriotresource.com, 2002.
- 2. J.Miller. Digging for gold, guns and drugs. abcnews.go.com, 10/3/01.
- 3. S.Ashley. When the Twin Towers Fell, www.sciam.com, 10/9/01.
- 4. E.Lipton, J.Glanz. First Tower to fall was hit at higher speed, study finds. www.nytimes.com, 2/23/02.
- 5. S.Slobin. W.T.C.: Clearing the debris. www.nytimes.com, 10/13/01.
- 6. J.Glanz, E.Lipton. Burning diesel is cited in fall of 3<sup>rd</sup> tower. www.nytimes.com, 3/2/02.
- 7. Remains of 11 firefighters, 2 civilians found at ground zero, www.cnn.com, 3/13/02.
- 8. List of Officers missing or killed in the line of duty during the attacks in New York. www.iupa.org, 2002.

- 9. S.Okada, N.Momoshima. Overview of tritium: characteristics, sources, and problems. Health Phys. 65 (1993) 595-609.
- 10. R.L.Hill, J.R.Johnson. Metabolism and dosimetry of tritium. Health Phys. 65 (1993) 628-647.
- 11. R.J.Traub, G.A.Jensen. Tritium radioluminescent devices. Health and safety manual. Pacific Northwest National Laboratory Report PNL-10620 (UC-610), Richland, WA (1995).
- 12. Environmental radiation data. Environmental Protection Agency. Report 81. EPA-402-R-97-004 (1997).
- 13, 12a. Maximum contaminant levels for radionuclides. 40 CFR Part 141.66.
- 14, 13. Local climatological data. National Oceanic and Atmospheric Administration, September 2001.
- 15, 14. B.Lulu. Luminous watch hands. www.timezone.com, 11/19/98.
- 16, 14a. R.G.Niemeyer. Tritium loss from tritium self-luminous aircraft exit signs. Oak Ridge National Laboratory Report ORNL-TM-2539, Oak Ridge, TN (1969).
- 17, 14b. J.R.Wermer. Assessment of commercial self-luminous exit signs containing tritium: Final Report Task 1. Westinghouse Savannah River Company Report WSRC-TR-0311Aiken, SC (1995).
- 18, 15. Luminous safety devices for use in aircraft: Requirements for license to manufacture, assemble, repair or initially transfer. 10 CFR Part 32.53.
- 19, 16. www.trijicon.com, 2002.
- 17. Innovative Weaponry, Inc., personal communication, 3/18/02.
- 18. K.Kinder, Kimber of America Mfg., Inc., personal communication, 3/19/02.
- 19. 10 CFR Part 30.15.
- 20. 10 CFR Part 32 I.4 and 32.22.
- 21. J.Benziger, Mb-microtec ag, personal communication, 3/19/02.
- 22. A. Zeller, Rc Tritec ag, personal communication, 3/18/02.
- 23. P.Brunner et al., Health Phys. 70 (1996) 484-487.
- 24. G.Sadagopan et al., Rad. Prot. Dos. 72 (1997) 49-53.
- 25. F.J.Lombardi, PANYNJ, personal communication, 12/10/01.
- 25a. N.A. Sabatini, Federal Aviation Administration, personal communication, 3/26/02.
- 26. P.Y.Pan, L.D.Rigdon, LA-UR-96-2953.
- 27. J.M.Gaver, Savannah River Site, US Department of Energy, personal communication, 1/30/02.
- 28. C.H.Skinner et al., J. Nucl. Mater., in press (2002).
- 29. G.A.Jensen, J.B.Martin, PNL-6523 (1988).
- 30. AFR 11-30 (1965).
- 31. T. Headley, Fire Department of New York, personal communication, 2/12/02.
- 32. N.M.Post, www.enr.com, 9/17/01.
- 33. D.Overbye, New York Times, 9/18/01.
- 34. A.Cho, N.M.Post, www.enr.com, 10/8/01.
- 35. N.M.Post, www.enr.com, 10/29/01.
- 36. F.J.Lombardi, PANYNJ, personal communication, 1/28/02.
- 37. F.J.Lombardi, National Engineers Week 2002 Banquet, Fishkill, NY, 2/19/02.
- 38. abclocal.go.com, 10/5/01.
- 39. S.Gardiner, P.Hurtado, seattletimes.nwsource.com, 10/6/01.
- 40. abcnews.go.com, and T.Koppel, Nightline, 3/11/02.

- 41. NYNEX Directory, April 1665-March 1996.
- 42. F.Ono et al., Fusion Tech. 21 (1992) 827-832.
- 43. R.S.Dickson, J.M.Miller, Fusion Tech. 21 (1992) 850-855.
- 44. A.B.Antoniazzi et al., Fusion Tech. 21 (1992) 867-871.
- 45. T.W.Hicks et al., Galson Science 014-2 (2000).
- 46. N.M.Post, www.enr.com, 10/8/01.

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

Gr.	Seq.	on	Coll. date 2001	_	Sampling location	Activity (nCi/L)	Foot- note
1	1	20	9/13	water	WTC storm sewer	0.174±74	a
1	2	21	9/18	water	Manh., roof tank, 45 Wall St., 30 fl.	< 0.13	ь
1	3	22	9/18		Manh., roof tank, 111 Broadway, 22 fl.	< 0.13	b
1	4	22	9/18	water	Manh., roof tank, 55 Broadway, 32 fl.	< 0.13	b
1	5	23	9/18	water	Manh., roof tank, 7 Hanover Sq., 29 fl.	< 0.13	Ъ
1	6	20	9/21	water	WTC Bldg. 6, basement B5, stairway J3	3.53±17	a
1	7	20	9/21	water	same	2.83±15	a
2	8		10/25	grass	Albany	<0.12	c,d
2	9	1		grass	Brooklyn, Brooklyn Heights	< 0.21	c,d
2	10	2			Brooklyn, Govanus Canal	< 0.11	,
2	11	4		grass	Brooklyn, Govanus Park	< 0.091	С
2	12	9	10/27	water	Brooklyn, English Kills	< 0.11	
2	13	6	10/27	water		< 0.090	
2	14	6	10/27	grass	same	< 0.093	c
2	15	11	10/27	water	Brooklyn, Marine Park	< 0.11	
2	16	11		grass	same	< 0.090	c
2	17	13			Brooklyn, Paerdegat Basin	< 0.090	
2	18	10	10/27	water	Brooklyn, Coney Island	< 0.11	
2	19	10	10/27	grass	same	< 0.092	c
2	20	15	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	19	11/4	leaves	Manhattan, Battery Park	< 0.12	c,d
3	24-37	7	9/15	water	South Manhattan water supply	<0.12-0.15	
3	38-77	7	9/17	water	Kensico Reservoir, Westchester County	<0.10-0.18	
4	78		9/26	rain	Albany County Health Department	<0.061	е
4	79		10/17	rain	same	<0.11	

# Footnotes

- a)  $2\sigma$  error.
- 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.

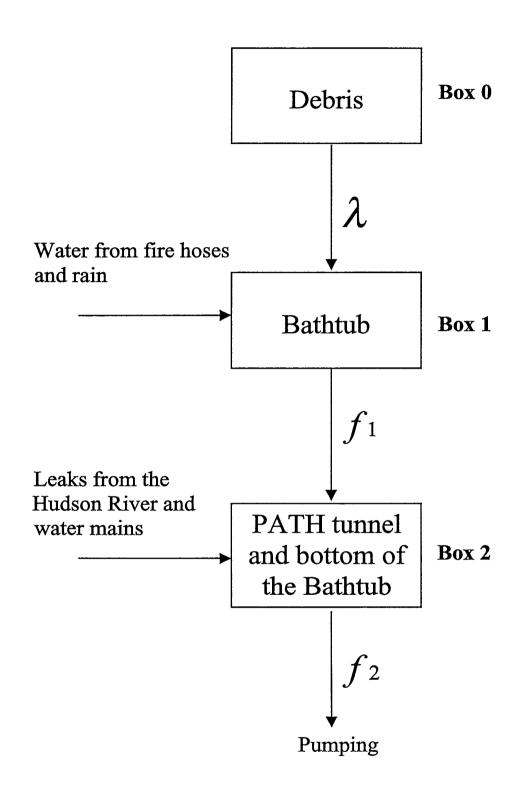


Fig. 1. Model of water flow and tritium removal from the WTC.  $\,$