Association of State and Territorial
ASTSWMO
Solid Waste Management Officials

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Federal Facilities Research Center
Policy & Technology Focus Group

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EXECUTIVE SUMMARY

The Association of State and Territorial Solid Waste Management Officials (ASTSWMO) is a non-profit trade organization supporting the environmental agencies of the States and Territories. The Association's mission is "to enhance and promote effective State and territorial waste management programs, and affect national waste management policies". In 2007, the Policy & Technology Focus Group (PTFG) of ASTSWMO's Federal Facilities Research Center began researching tungsten issues and the inherent challenges and impacts of tungsten assessment and remediation on existing cleanup programs being implemented at federal facilities in the United States.

In the context of military training at active small arms ranges located at federal facilities, lead projectiles have typically served as the ammunition of choice in support of the military's training/readiness mission. The U.S. Army introduced Tungsten/nylon 5.56 mm small arms range ammunition (referred to as "green ammunition") in the mid-1990s as a replacement for lead ammunitions. Tungsten was initially thought to be less soluble and more environmentally friendly than lead.

The tungsten/nylon 5.56 mm ammunition has been shipped to numerous installations across the country, with an estimated 90 million bullets sold to the military for their use (USADAC 2005). The implications of use of the so-called "green ammunition" have triggered numerous research efforts aimed at understanding potential health, fate and transport, assessment, and cleanup strategies for this constituent.

TUNGSTEN QUICK FACTS

What is tungsten?
Tungsten (W), Chemical Abstracts Service (CAS) #7440-33-7, is a solid, white- or grey-colored metal that occurs naturally in rocks and soil as a trace mineral. While relative inert, ferrotungsten (the principal alloy of tungsten) is used to make alloys given it has the highest melting point of all metals. Tungsten powder is used as a lead replacement in bullets.

What is the problem with tungsten?
Tungsten dissolves readily in water and is mobile under some field conditions, challenging initial assumptions with regard to tungsten's fate and transport characteristics. Other concerns include data (occupational, animal studies, cancer clusters) indicating adverse non-cancer and cancer health effects and risk outcomes.

How is tungsten used?
Tungsten alloys are good conductors of electricity, and used primarily to increase the toughness and strength of steel. The most common tungsten product, cemented tungsten carbide, is used to make grinding wheels and cutting or forming tools. Tungsten powder is used as a lead replacement in bullets. However, firing of a tungsten/nylon bullet introduces tungsten and other projectile related metals into the environment.

How does exposure to tungsten affect human health?
The toxicology of tungsten depends on the route of administration, the solubility of the constituent and the duration of exposure. Occupational exposure via the inhalation pathway has revealed elevated levels of pulmonary fibrosis (scarring of the lung tissue) and other effects including asthma and inflammation of the nose tissues. Research also suggests that the combination of tungsten and other substances can be linked to the development of lung cancer. Some animal data suggests that tungsten could cause adverse developmental and reproductive effects (including the kidneys as a target organ). Information from Nevada has drawn attention to tungsten's potential toxicity as exhibited in the Fallon Nevada cancer cluster.
(Edel, J. et al.; USCDC 2003)

This paper is intended to serve as a source of information to assist State and Territorial program managers tasked with jumpstarting policy deliberations dialogues at sites that have or are suspected of having tungsten contamination. The PTFG is not responsible for errors or omissions in the text or for an erroneous, outdated or non-working Uniform Resource Locator (URL) links.

This paper is the 2nd version to the original Tungsten Issues Paper published in December 2008. This is a "living document" and will be updated as new information becomes available. Visit the ASTSWMO Federal Facilities Research Center Publication Page at http://astswmo.org/publications_federalfacilities.htm to access the most up-to-date version.

1.0. INTRODUCTION

The PTFG of the Federal Facilities Research Center Subcommittee of ASTSWMO has developed this document in the spirit of helping readers bridge the gap between policy and technology issues emerging at federal facility sites currently or potentially contaminated with tungsten.

Quickly evolving technological advances in the fate and transport, toxicological, and analytical testing arenas, coupled with the lack of federal and State standards, are some of the challenges posed by this unique constituent that has been introduced at some federal facilities' small arms ranges. While a substantive body of information currently exists for tungsten, in recent years advancements have been made, which have drastically changed the original position of the scientific community with regard to fate and transport, analytical testing and toxicology.

2.0 THE TUNGSTEN DILEMMA

The use of tungsten at small arms ranges represents the military's effort to develop and utilize a bullet with environmental protection in mind, while providing soldiers with the opportunity to attain necessary marksmanship qualifications. Conversely, firing a tungsten/nylon bullet serves as a release mechanism, introducing tungsten and other related constituents into the environment.

Over the past years, soil and groundwater samples collected at certain small arms ranges have demonstrated that tungsten is very mobile and soluble once it is released into the environment. In addition, limited yet important health studies have also revealed that tungsten may pose risks to humans and ecological receptors, as noted in the U.S. Environmental Protection Agency's (EPA's) Integrated Risk Information System (IRIS) 2008 Agenda: Literature Searches and Request Information. This information is the U.S. EPA's first documented step in its evaluation of this constituent (U.S. EPA 2008a).

This information, coupled with knowledge of numerous shipments delivered at approximately 40 installations nationwide, has compelled the military to abandon the production of tungsten/nylon bullets and look to other "green ammunition" alternatives, including resuming lead bullet firing. In 2005, Army officials indicated that as many as 90 million tungsten/nylon bullets had been used at training ranges across the nation (USADAC 2005).

Since 2008, researchers and environmental professionals have obtained additional knowledge concerning fate and transport specific to tungsten and technologies used to remediate tungsten contamination. Several agencies are continuing to conduct studies to determine potential impacts to human health and the environment, and to date findings are still not conclusive. As a result, federal and most States have yet to promulgate drinking water, soil and/or groundwater cleanup standards, which continue to make it difficult for regulators to trigger assessment and cleanup actions at sites.

> ***TUNGSTEN USE AT MMR***
>
> The U.S. Army introduced tungsten ammunition at the Massachusetts Military Reservation (MMR) during the training year 1999-2000 to replace the lead-based projectile. In 2006, use of tungsten/nylon bullets in Massachusetts ceased per the Governor's Office cease and desist order. This was due to concerns with regard to tungsten's mobility in the environment and possible impacts on the sole source aquifer underneath the MMR (Clausen, Jay L. et al 2007).
>
> The Massachusetts MMR experience may be useful for other States in need of a roadmap that aims to evaluate and assess the use of tungsten/nylon bullet use at training ranges within their States. Information concerning MMR and Massachusetts Department of Environmental Protection's (MA DEP) activities concerning tungsten can be found at:
>
> 1. MA DEP. 2006. Fact Sheet: Tungsten and Tungsten Compounds.
>
> 2. http://states.ng.mil/sites/MA/about/installations/edwards/default.aspx.

3.0 FATE AND TRANSPORT

Under certain conditions tungsten metal can readily oxidize and dissolve as tungstate ions when in contact with water. Laboratory studies found that the dissolution process was accompanied by significant reductions in pH and dissolved oxygen concentration (Dermatas et al 2004; Lasssner and Schubert 1999). At low pH the relatively large dissolved tungsten concentrations (over 400 mg/L) may be due to the formation of even more soluble polytungstate ions. The presence of iron also appeared to enhance tungsten dissolution (Dermatas et al 2004).

Tungsten has not been detected in the vast majority of surface and ground waters of the United States, with the exception of areas near mines and natural deposits. An investigation of tungsten in groundwater detected dissolved concentrations ranging from 0.27 to 742 ug/L. The highest tungsten concentrations were correlated with higher pH, which was attributed to the fact that the anions formed have decreasing adsorption with increasing pH (Seiler et al 2005).

Of the most significance with respect to federal facilities is the detection of dissolved tungsten in groundwater in the vicinity of small arms ranges, which have been using tungsten-based ammunition (Clausen et al 2007). Recent studies suggest that tungsten powder used in the Army's tungsten/nylon projectiles form oxide coatings that are soluble in water. Soil pore-water underlying the bullet collection areas had relatively high levels of tungsten (up to 400 mg/L) at depths up to 65 cm. The presence of tungsten (up to 560 ug/L) in a down gradient monitoring well indicates that tungsten is mobile through the local sandy, acidic, aerobic soils. Tungsten does not appear to be retarded by sorption, which may be due to the low clay content of the local soils (Dermatas et al. 2004).

4.0 SAMPLING AND ANALYSIS

The sampling and analysis processes for tungsten are still evolving. For example, in the Commonwealth of Massachusetts, a number of analytical studies have been conducted to investigate, delineate, characterize, and assess the chemistry of tungsten in the environment. With extensive research being done for the various applications of sampling and analysis, the PTFG has found that the processes are not prevalent and/or standardized. However, the entities that are performing these investigations have made exceptional progress on an elemental compound that is by far more challenging to analyze than most others.

To date, the use of different types of sampling techniques has not been an issue with regard to characterizing a specific media. There are four types of matrices involved; groundwater, surface water, surface and subsurface soil, and air. Lysimeters, submersible pumps, and inertial pumps were found to be the most common equipment used for groundwater sampling. No specific references could be found for the equipment being used for surface water, surface and subsurface soil, and air sampling collection, but specific information could be found to suggest that not all types of equipment would be applicable for use.

Tungsten analysis is still in the developmental and optimization stage. For screening purposes, x-ray fluorescence seems to be the most common type of equipment used. For definitive data, inductive coupled plasma, ultraviolet-visible spectrometer, atomic absorption, and spectrophotometer seem to be the most commonly used tools. The methods utilized for aqueous and solid matrices are the SW-846 Methods 6010 and 6020. However, the analytical methods preparation and analysis have been modified to accommodate the difficult nature of tungsten (Clausen, Jay L. et al 2007; U.S. EPA 2009). For air matrix, the National Institute for Occupational Safety and Health (NIOSH) Method 7074 is the preferred method for analysis. Researchers have found that the characteristics of tungsten, and in an elemental compound state, have not been fully understood. This further complicates the digestion and analysis procedures, but progress is and will continue to be made (U.S. EPA 2009; USCDC 1994).

As time goes on and research continues, it is likely that the analytical approaches will be standardized. The developmental process is being performed in concert with the development of risk factors to help define the exposure risks. This will hopefully prevent premature promulgation of action levels before the optimization and standardization of the analytical system is developed.

5.0 REMEDIAL TECHNOLOGIES

Potential treatment methods to address tungsten contamination are still being developed. For soils, phytoremediation and chemical recover/soil washing, and electrokinetic remediation (in situ) have been studied. “Ice electrode” technology has been researched for water contamination (EPA 2009). Further research is recommended.

6.0 IMPACTS TO HUMAN HEALTH AND ENVIRONMENT

Human exposure to tungsten and its compounds occurs most commonly in occupational settings. The possible exposure pathways are inhalation, ingestion, dermal and eye contact. Occupational inhalation exposure to tungsten is known to affect the eyes, respiratory system, skin and blood. Most of the tungsten that enters the body is rapidly eliminated in urine and feces. Studies have found that the tungsten that is retained is predominantly stored in the bones (ATSDR 2005).

Several agencies and independent researchers have studied potential impacts to human health and the environment. Currently, tungsten is not classified for carcinogenic effects by the Department of Health and Human Services, the International Agency for Research on Cancer, or the U.S. EPA (ATSDR 2005). The June 2005, the Armed Forces Radiobiology Research Institute published the results of its four year study to study long-term health effects of shrapnel from combat operations containing tungsten, nickel and cobalt alloy. The study provided the following conclusions (FHPI 2010):

> The health effects of tungsten/nickel/cobalt alloy pellets warrant further investigation, and it is too early to draw definitive conclusions from the results. Scientific research has shown that some chemicals that cause cancer in rats do not cause cancer in humans. For this reason, one study in rodents is not enough evidence to indicate that people will or will not develop cancer as a result of embedded fragments. More research is needed to see if similar effects might be expected in humans.

DoD is currently considering a few options to follow up on the study, which include a confirmation study of AFRRI’s research, a similar study on a different animal, and related studies with a different tungsten alloy (FHPI 2010).

Environmental effects of tungsten are limited and more studies are warranted. Tungsten powder mixed with soils at rates higher than 1% (on a mass basis) results in death of a substantial portion of the bacterial component and an increase in the fungal biomass. Tungsten in soil also causes the death of red worms and plants (ATSDR 2005).

7.0 FEDERAL AND STATE REGULATORY GUIDELINES

A federal drinking water standard has not been established for tungsten. Interestingly, the Soviet Union established a 50 ppb drinking water limit (MA DEP 2006). However, the NIOSH and the American Conference of Industrial Hygienists have established a recommended exposure limit of 5 milligrams per cubic meter (mg/m3) as the time-weighted average over a 10-hour work exposure and 10mg/m3 as the 15 minute, short-term exposure limit for airborne exposure to tungsten (ATSDR 2005; NIOSH 2007; NJDHSS 2000). The Occupational Safety and Health Administration recommends an exposure limit of 5 mg/m3 to insoluble compounds of tungsten and 1 mg/m3 limit of exposure to soluble compounds in construction and shipyard industries (ATSDR 2005; U.S. EPA 2009).

In addition to the lack of regulations or guidelines regarding tungsten in drinking water, U.S. EPA does not have regulations or guidelines regarding tungsten concentrations in the ambient air or soil (MA DEP 2006). U.S. EPA has not classified tungsten or tungsten compounds for carcinogenicity, nor has the U.S. EPA derived reference concentrations (RfCs) or reference doses (RfD) for tungsten or tungsten compounds. U.S. EPA regulates the effluent discharge of tungsten at primary tungsten facilities and tungsten or cobalt at secondary tungsten and cobalt facilities processing tungsten or tungsten carbide scrap raw materials (ATSDR 2005).

8.0 CONCLUSIONS

The tungsten/nylon bullet was first introduced as “green ammunition” in the late 1990’s after the U.S. EPA ordered the military to halt the use of lead ammunition due to environmental concerns. The “green” bullet was thought to be more benign than lead ammunition because tungsten was believed to be nontoxic and insoluble. This “green ammunition” is now under the same scrutiny after the discovery of tungsten contamination in groundwater at MMR. Concerns with tungsten contamination are not only at MMR, but at other firing ranges across the country where the ammunition has been shipped and may have been fired. As a result, there has been an increase in research efforts aimed at understanding potential health, fate and transport, assessment, and cleanup strategies for this constituent.

This paper was designed to help bridge the gap between policy and technology issues emerging at federal facilities currently or potentially contaminated with tungsten and related compounds. The intent was to capture information available on tungsten at this time while recognizing the challenges posed by this emerging contaminant. Although advancements have been made in the areas of fate and transport, analytical testing and toxicology, the need for additional research is obvious. As with other ASTSWMO “living documents,” updates and revisions to the paper will be done as new information becomes available. The most current version of the paper can be found on ASTSWMO’s web site.

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