Association of State and Territorial Solid Waste Management Officials
Federal Facilities Research Center
Policy & Technology Focus Group

FINAL

Tungsten Issues Paper
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TABLE OF CONTENTS

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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. Tungsten/nylon 5.56 mm small arms range ammunition (referred to as "green ammunition") was introduced at the Massachusetts Military Reservation (MMR) during the training year 1999-2000 to replace the lead-based projectile. Tungsten was originally thought to be less soluble and more environmentally friendly than lead. 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 tungsten/nylon 5.56 mm ammunition has been shipped to numerous installations across

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)

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.

This PTFG Tungsten Issues Paper is intended to serve as a source of information to assist State and Territorial program managers tasked with jumpstarting policy deliberations dialogues. 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 is a "living document" and will be updated as new information becomes available. Go to the PTFG Tungsten Issues Paper on the ASTSWMO website 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.

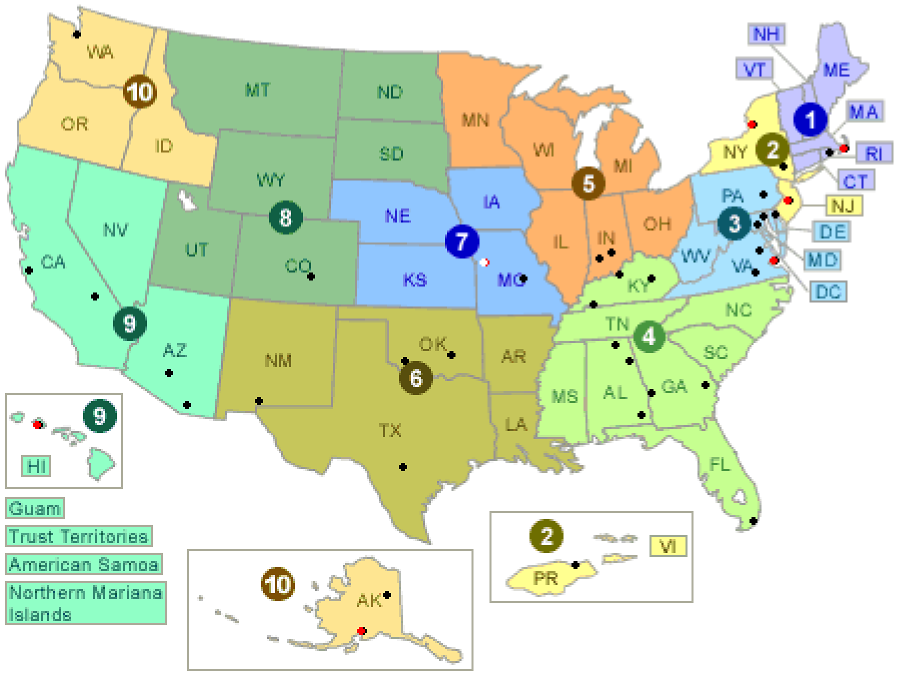
Quickly evolving technological advances in the fate and transport, toxicological, and analytical testing arenas, coupled with the lack of federal and State standards, are some of the challenges posed by this unique constituent that has been introduced at some federal facilities' small arms ranges. While 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). The map below illustrates military facilities known to have shipped or received tungsten/nylon bullets.



NOTE: The installations shown on the above map were provided by the U.S. Army Defense Ammunition Center, Munition Items Disposition Action System, updated 2005.

The tungsten dilemma stems from knowledge of potential impacts to human health and the environment (fate and transport mobility issues as well as potential adverse health outcomes), yet the lack of federal and State drinking water, soil and/or groundwater cleanup standards at this time make it difficult for regulators to trigger assessment and cleanup actions at sites.

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 the Massachusetts MMR can be found at http://www.mass.gov/guard/E&RC/index.htm.

3.0 FATE AND TRANSPORT

Recent laboratory studies and field investigations suggest that tungsten may be much more mobile than previously thought. 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. The 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 2008b). 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 2008b; 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 TOXICITY AND HEALTH EFFECTS

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).

One case of tungsten poisoning has been reported after accidental ingestion. After drinking a mixture of beer and wine that had been rinsed in a hot gun barrel, a man experienced nausea, seizures, signs of encephalopathy, moderate renal failure, and extensive tubular necrosis with anuria by day two. After five months, the individual had fully recovered (Haneke 2003).

No direct link has been made between the cancers and tungsten. Tungsten has not been 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).

Potential risk from perinatal exposure to tungsten is also a concern, as animal studies have shown that tungsten can cross the placental barrier and is transferred in milk. Animal studies are now a priority for testing under the National Toxicology Program (ATSDR 2005).

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).

6.0 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 2008b). In addition, Massachusetts is using 1-2 ppm in soil and 15 ppm in groundwater as action levels for tungsten.

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)

7.0 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 at the MMR 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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