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Abstract

Tungsten (W) is a heavy metal with the potential to impact human health and aquatic ecosystem function. For a long time W was considered an insoluble metal without serious toxicological or environmental effects. However, over the last decade this view has been challenged and discredited as numerous studies have highlighted the toxicological and environmental effects of W. W has recently been nominated as a priority substance by the U.S. National Toxicology Program in 2002, designated an emerging contaminant in 2008 by the U.S. EPA, and listed as a priority chemical for biomonitoring in 2014 by the state of California. W concentrations in urine of WA State citizens are consistently higher than the national average, and elevated W in urine is linked to higher probabilities of stroke, diabetes, peripheral arterial disease, and altered thyroid function. Despite this, W levels in WA waters have not been measured, and controls on W solubility, W speciation, and effects of W on ecosystems are not well-understood. Watersheds of the Pacific Northwest, which are tungsten-rich provide an opportunity to understand how chemical, edaphic, and climatic factors control the solubility and transport of W through watersheds. With the work outlined in this proposal we aim to begin addressing this critical, policy-relevant knowledge gap. Building on recent progress in W analytic chemistry and toxicology, we will test fundamental hypotheses concerning W mobility and speciation in surface waters downstream from W deposits and collect data for an ecotoxicological risk-assessment model. In particular, we will collect and analyze water samples in the areas surrounding tungsten deposits, conduct multivariate statistical analysis in order to biogeochemical factors that control W concentration in samples, and establish a series of laboratory-based dissolution and geochemical experiments to examine and quantify these factors. The proposed study will be the very first study examining tungsten in environmental systems in the State of Washington. As such it will provide badly needed insight into rates and controls on W loading to surface waters, thereby advancing fundamental understanding of hydrogeochemistry providing policy-relevant information to regulatory agencies and policy-makers and supplying important pilot-data that can be used to generate compelling proposals to state and federal funding agencies.

13. Title: Understanding controls on mobility and toxicity of tungsten, an emerging threat to Washington's waters.

14. Tungsten as a state and regional water problem

Tungsten (W) is a heavy metal with the potential to impact human health and aquatic ecosystem function (Strigul et al. 2005). Yet controls on W solubility, speciation, and ecosystem effects are not well-understood. Watersheds of the Pacific Northwest, which are often W-rich (Fig. 1) provide an outstanding opportunity to understand how chemical, edaphic, and climatic factors control the solubility and transport of W through watersheds. With the work outlined in this proposal we aim to begin addressing this critical, policy-relevant knowledge gap.

For a long time W was considered an insoluble metal without serious toxicological or environmental effects (Koutsospyros et al. 2006). However, over the last decade this view has been challenged and discredited as numerous studies have highlighted the toxicological and environmental effects of W (Dermatas et al. 2004, Strigul et al. 2005, Koutsospyros et al. 2006, Bednar et al. 2009a, Strigul 2010). In parallel with this increasing understanding, W has received increasing attention from federal and state regulatory agencies, being nominated as a priority substance by the U.S. National Toxicology Program (NTP) in 2002, designated as an emerging contaminant in 2008 by the U.S. EPA (EPA 2008), and listed as a priority chemical for biomonitoring in 2014 by the state of California (CA biomonitoring 2014).

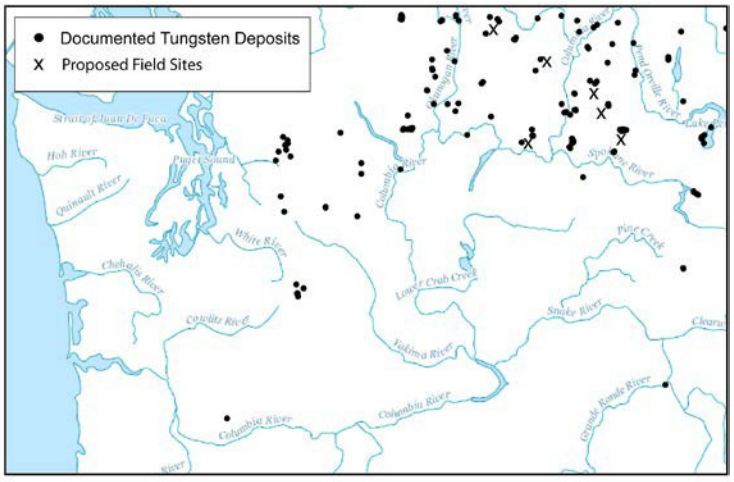

Fig. 1. Locations of tungsten deposits in WA (several of which have been developed as tungsten mines) along with a few likely sampling sites. Data source: USGS

Studies have shown unexpectedly high corrosion rates for metallic W and its alloys in environmental systems, resulting in release of soluble, bioavailable monomeric and polymeric W compounds, polyoxometalates (Strigul 2010). These soluble W compounds are toxic to aquatic organisms, alter nitrogen cycling and enter food chains via uptake by vegetation and aquatic organisms (Strigul et al. 2010). Elevated W in urine (due to elevated W exposure) has been linked to increased probabilities of stroke (Tyrrell et al. 2013), diabetes (Menke et al. 2016), peripheral arterial disease (Navas-Acien et al. 2005), and altered thyroid function (Christensen 2013). Researchers have also speculated about a link between high W exposure and childhood leukemia (Koutsospyros et al. 2006).

Although the U.S. has not yet implemented water quality standards for W, other nations have. For example, in Russia an intensive ecotoxicological research program focused on the effects of W exposure on fish and animal embryos led to the classification of W as a dangerous aquatic contaminant with maximum allowable concentrations of 0.05 mg W L^{-1} for drinking water and 0.0008 mg W L^{-1} for aquatic systems used for fishing (Strigul et. al. 2009a). Although measurements are rare, these concentrations are exceeded in waters draining W-rich deposits in other parts of the American West. W concentrations in ground waters used as drinking water sources around Fallon, NV, ranged from 0.27 to 742 µg L^{-1} (Seiler et al. 2005) and in drinking water across Nevada (Walker and Fosbury 2009) ranged from below the detection limit (3 µg L^{-1}) to a maximum of 610 µg L^{-1} (average 30 µg L^{-1}).

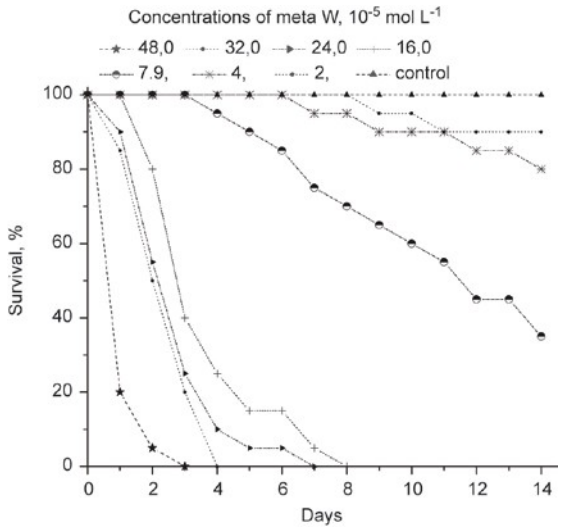

Fig. 2. Survival and mortality of guppies as a function of sodium metatungstate concentration during a 14-day toxicity test (Strigul et al., 2010). Note that significant toxicity due to acute exposure was observed at levels as low as 20 uM/L, which could easily occur in natural waters. At lower levels, tungsten exposure could also have sub-lethal effects on organisms and biogeochemical cycling, as reported by Strigul et al. (2009b).

Because W pollution standards have not been established in the US, W concentrations are not monitored by the State of Washington, and almost nothing is known about the spatial distribution, dynamics, or effects of W in the waters of Washington State or throughout the American West. This is a problem because there are reasons to suspect that W delivery to WA surface waters and associated ecosystem and human health impacts are significant. The State of Washington has a large number of W-rich deposits, which are part of a W-rich geologic zone extending across the American West (Fig. 1, Culver and Broughton 1945, Kerr 1946, Bunning 1985). Some of this W finds its way into Washingtonians, who, on average, have urine W concentrations significantly higher than the national average (Fig. 3, WNT 2017). In addition to the high background geological W in several regions of WA, W exposure and mobilization also occurs through use of purchased goods. Global W use has nearly tripled in the past 20 years (Fig. 4; USGS 2017) for applications such as lighting (filaments), welding electrodes, steel tools, solar energy devices, electrical contacts, fishing weights, hunting and military ammunition, automobile engines, transmission and tire studs. An unknown, but potentially significant, fraction of this W makes it back into the environment through landfill pollution, road pollution (in the case of automotive applications), and direct dispersal (e.g. via unrecovered ammunition).

By starting to quantify W delivery to surface waters and developing an initial understanding of the important controls on this delivery, our proposed research will address an important knowledge gap with great relevance to multiple stakeholders, including the citizens of WA (and especially the tribes on whose lands many of WA's W deposits lie), state and federal monitoring and regulatory agencies such as WA Departments of Ecology and Health, USGS, US EPA, and others.

15. Statement of results and benefits

The proposed work will provide badly needed insight into rates and controls on W loading to surface waters, thereby advancing fundamental understanding of hydrogeochemistry and providing policy-relevant information to regulatory agencies and policy-makers. Building on recent progress in W analytic chemistry and toxicology, we will test fundamental hypotheses concerning W mobility and speciation in surface waters downstream from W deposits and collect data that could eventually inform ecotoxicological risk-assessment models. In so doing, this proposal directly addresses the following priority topic identified by the State of Washington Water Research Center: ***understanding fate and transport of nutrients and emerging contaminants in the environment.***

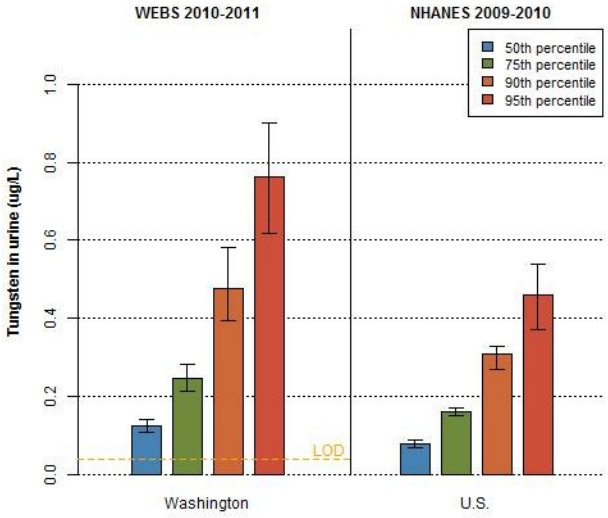

Fig. 4. Results of biomonitoring survey of tungsten (W) in urine conducted by the Washington State Department of Health showing that W concentrations urine of WA State citizens are consistently higher than the national average (Washington Tracking Network (WTN 2017)). Elevated W in urine is linked to several diseases such as stroke, diabetes, peripheral arterial disease, and altered thyroid function (Section 14).

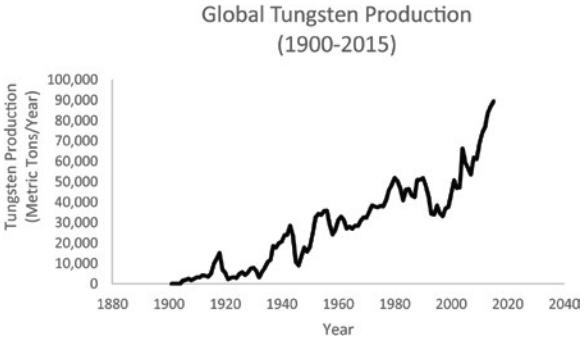

Fig. 4. Global tungsten production for use in industrial and household products showing marked increase during the industrial revolution and an acceleration in recent decades.

Funding will be used to directly support one MS student (Phil Steenstra) and one undergraduate researcher, thereby addressing the SWWRC goal of training future scientists. Steenstra will work with an interdisciplinary mentoring committee, including PI Dr. Nikolay Strigul (Asst. Prof., WSU Vancouver, mathematician/biologist), Co-PI Dr. John Harrison (Assoc. Prof., WSU Vancouver, biogeochemist), and at least one additional faculty member. Consequently, this work will foster interdisciplinary and inter-institutional collaborations. Funding from the USGS 104b program would support key measurements that are not currently planned under existing grants. As W is a well-established roadside pollutant, this research will also contribute toward a sustained WSU research program on the topic of green stormwater infrastructure and important support for students and a pre-tenure WSU faculty member (Strigul).

Prior USGS 104b funding to Harrison has resulted directly in more than $1.3 million in external NSF and USACE funding to WSU (see Harrison's CV) and has contributed indirectly to several other successful proposals. In addition, the 104b funding has directly supported the

training of 5 MS students and 2 PhD students, and has directly resulted in 8 peer reviewed publications to date, with more in preparation, 4 MS theses, and 2 PhD theses (Papers: Harrison et al. 2009, Martin and Harrison 2009, Deemer et al. 2011, Deemer et al. 2012, Henderson and Deemer 2012, Bellmore et al. 2015, Norton et al., 2017, Deemer et al. 2015, MS theses: Goodwin 2010, Deemer 2010, Norton 2017, and PhD theses: Bellmore 2014, Deemer 2016). The data collected for this project will be used to support new, collaborative follow-up proposals to multiple external agencies and programs. Future research foci will likely include: GIS mapping of W distribution in aquatic system in the State of Washington, extended experimental studies to understand and predict factors that control W mobility and W fluxes among different environmental domains, and modeling of W fate and transport in environmental systems including quantitative ecotoxicological risk assessment. Potential target agencies include: NSF Low Temperature Geochemistry, the USGS 104c Program, Washington Department of Ecology, Portland Bureau of Environmental Services, Oregon Department of Environmental Quality, Oregon Watershed Enhancement Board, Washington Department of Transportation, Oregon Department of Transportation, and Department of Defense's Strategic Environmental Research and Development Program (SERDP).

Results will be disseminated by publication, presentation, and outreach. This proposal would directly support 1 MS thesis, 1 undergraduate research assistantship, up to 2 peer-reviewed publications (one on dissolution dynamics of W and one on watershed controls of W loading to surface waters), and a MS student presentation at the Society of Environmental Toxicology and Chemistry (SETAC) North America Meeting.

16. Project nature, scope, and objectives

Our **long term objective** is to understand W geochemistry and the fate, transport, and effects of W in aquatic systems. In this initial study, we propose to use a combination of spatial analysis, field sampling coupled with state-of-the-art measurement techniques, and controlled laboratory experiments to address the following research question: ***What environmental variables co-vary with and control tungsten concentrations and delivery to surface waters, both in bulk and by chemical species?*** In the remainder of this section we outline our general approach to addressing this question (with a timeline). We then further elaborate upon the specific techniques and approaches we will use (Section 17).

Based on our own prior work (e.g. Strigul et al. 2005) and work by others (Section 18) using W alloys and soluble W compounds (not naturally occurring W-rich minerals), we anticipate that factors such as pH, Eh, temperature, concentrations of Mo, Fe and Mn and other metals, and water hardness will control solubility and mobility of W in aquatic systems. Of particular interest is the possibility that the dissolution of W-containing minerals leads to local acidification, which in-turn facilitates the formation and release of soluble PW. To evaluate the impact of several of these potential controls on W mineral solubility and speciation and to elucidate potential mechanisms for W dissolution, we will implement a laboratory-based solubility assay. In this experiment, we will build on past experience studying dissolution of W alloys (e.g. Dermatas et al. 2004, Strigul et al. 2005, Strigul et al. 2009b) to develop a factorial experiment in which the solubilities of W-rich minerals are evaluated across a pH range, in the presence of other elements naturally associated with W. Results of a planned early round of field sampling from streams draining watersheds with W-rich underlying geology (Fig. 1), including water characteristics (e.g. pH) and chemical concentrations of co-occurring minerals (e.g. Fe and

Mn) will inform the design of these experiments, so that experiments are carried out using field-representative concentrations and pH values. The results of this controlled experiment will provide insight into the relative importance of potential controls on W solubility and speciation, which we will use to interpret field data on W concentrations. In addition, multivariate analysis of field samples (sampling design described in section 18 below) should allow us to identify and rank different factors according to their relative importance for W controls. Overall, the W mineral solubility experiments conducted in concert with field sampling will allow us to test hypotheses concerning drivers of W speciation and biogeochemistry while building a dataset that can be used as pilot data for larger, follow-up proposals.

Although it is useful to understand controls on bulk W solubility and mobility, this is not sufficient if one wants to evaluate the human health and ecosystem impacts of W. Rather, one must understand controls on W speciation. Our previous research using aquatic organisms (fish, daphnia, and algae) and communities showed that polytungstates (PW) are much more toxic than monotungstates (MW) (Strigul et al. 2009a, 2010). LD-50 concentrations obtained in acute toxicity tests with fish, daphnia, algae, plants, red worms and microorganisms for PW were hundreds of times lower than the corresponding values for MW. Until recently, quantification of W chemical species was not possible, but recently developed analytical methods, such as size exclusion chromatography (SEC) interfaced with inductively-coupled plasma mass spectrometry (ICP-MS; Bednar et al. 2009a, 2009b, available in Harrison's lab) have allowed researchers to characterize the distribution of W species in environmental samples and to gain additional insights, for example demonstrating that PW evolves during dissolution of metallic W. Despite this recent progress, data on W speciation and geochemistry in environmental systems are still lacking. In particular, there is almost no information about rates of, and controls on, dissolution of naturally occurring W minerals. To address this knowledge gap, we plan to quantify W species in a subset of the samples we collect from both the laboratory experiments and the field observations.

Table 1. Timeline of proposed activities

Activity	Sp 2018	Su 2018	Fa 2018	W 2018/'19 Future
Lab-Based Tungsten Solubility Testing	<-----	------>		
Establish sites (O) and collect Water Samples (X)	OX	X		
Chemical and Data Analysis			<------	--->
Meeting Talk (X) and paper preparation			<------	----X---------->
External proposal(s), future work				<--------- ------>

Additional, follow-up experiments may include the following tasks, depending on the results of field sample analysis and dissolution experiments: dissolution/precipitation rate depending on different factors (for example, pH and Eh) and development of Pourbaix diagrams, quantifying precipitation reactions of mono- and poly-tungstates with hydroxides of iron and manganese, and quantitative analysis of competitive interactions between tungstates and molybdates. Several, mostly overlooked, publications in Russian from the 1970s and 1980s on dissolved W in the environment (reviewed in Strigul et al. 2009a) provide motivation for these experiments. These studies indicate: 1) W and Mo are positively correlated with Eh level and correlated negatively with pH, 2) precipitation of W by calcium has a minor effect on W mobility in aquatic systems, compared to precipitation by oxides and hydroxides of manganese, and 3) iron hydroxides precipitate W ions in water, and this should be a major factor restricting dispersion of W.

17. Methods, procedures, and facilities

We will conduct a series of experiments and field observations to assess major parameters that influence W occurrence in aquatic systems in Washington near natural deposits. We will employ a GIS map of tungsten deposits (Fig 1.) based on USGS Mineral Resources Data System (MRDS, accessed 2017) in conjunction with other publicly available data (e.g. data from USGS and WA Dept. of Ecology sites) to identify water sampling locations. In situ (in the case of pH) and laboratory analysis of water samples will provide us with the initial set of parameters to conduct experiments on W solubility and mobility.

Field sample collection and data analysis

We will twenty to twenty-five streams that are likely to have high W loading due to W-rich underlying geology (Fig. 1). Although we have identified candidate streams, we will further refine our site selection to ensure that sites have similar elevations, slopes, and climate characteristics. We will focus on sites with active stream gauges so that estimates of W loads (kg W/yr) will be possible in follow-up studies. We will sample each stream a minimum of two times, once at the beginning of the project and once during summer base flow. We anticipate that precipitation should lead to a substantial increase of W concentration in streams; Zaguzin et al. (1980) reported that daily monitoring revealed a more than 10-fold increase in W concentration in streams draining W ore deposits during precipitation periods, from average concentrations of 10 $\mu g\ L^{-1}$ to 80-120 $\mu g\ L^{-1}$.

At each site (at least 20 total) and time point (at least 2 for each site), we will measure pH, Eh, W concentration, temperature, and the concentration of other metals associated with W. If time and resources permit, we will also measure dissolved organic carbon to see whether that plays a role in W solubility as well, as it is possible that chelation plays a role in controlling W solubility, as has been shown with many other metal ions (Schlesinger and Bernhardt 2013). With the data from our samples, we will conduct correlation analysis, simple and stepwise multiple regression analyses and principal components analyses to test for significant relationships between W concentrations and other water and watershed characteristics. For water, independent variables will include pH, Eh, organic carbon concentration, hardness, temperature, and concentrations of other metals. For watersheds, we will test for relationships between W concentrations and underlying geology, climate characteristics such as precipitation and temperature, and other available characteristics likely to control W delivery to surface waters.

Laboratory solubility assays

Based on field-observed in-stream water chemistry (pH values) we will design and carry out a series of controlled experiments on W solubility and mobility. These experiments will be conducted according the Organization for Economic Cooperation and Development (OECD) 105, Water Solubility Test. The OECD 105 test guidelines are in agreement with the Toxic Substances Control Act, TSCA (in particular, with 40 CFR 799.6784 - TSCA water solubility: Column elution method; shake flask method), and are accepted by EPA. Following these guidelines, we will measure solubility of the 4 most commonly occurring W minerals: scheelite,

wolframite, ferberite and huebnerite. Based on the results of these tests we will conduct either a column elution test or a shake flask test for minerals which solubility is above 10^{-2} g L^{-1}. Samples of these minerals will be pulverized and added to buffered HCl or NaOH solutions with initial pH values of 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, and 8.5 (with the pH range subject to modification based on field-measured pH values; n=3 flasks for each pH). At the end of the incubation period (and periodically over the course of each incubation, as necessary) flasks will be sampled for pH, Eh, and dissolved oxygen. Then eluent will be filtered and concentrations of dissolved tungsten, iron, calcium, manganese, organic carbon, and other metal concentrations will be determined. pH, Eh, and dissolved oxygen will be measured using standard laboratory equipment and concentrations of W and other metals in solution will be measured using an Agilent Inductively Coupled Plasma Mass Spectrometer (ICP-MS) available at WSU, Vancouver (Harrison Lab). This experiment will be completed twice: once at 20 °C (approximate mean summer water temperature) and once at 5 °C (approximate mean winter water temperature). This will allow us to observe how W mineral solubility varies as a function of field-relevant pH and temperatures. Relationships observed in the lab will be compared with field-observed relationships between pH, temperature, and W concentrations. In a subset of samples from both the lab and field studies (ones with high dissolved W concentrations) we will use size exclusion chromatography along with ICP-MS to quantify W. This work will be done in consultation with, Dr. Anthony Bednar, from the USA CoE Environmental Laboratory in Mississippi, who is an expert in the relevant techniques and a collaborator of PI Strigul.

18. Related Research

In recent years W's toxicological and environmental effects have received significant attention in different research areas such as the U.S. Army's Green Ammunition Program, biomedical studies, and an investigation of Fallon, Nevada's childhood leukemia cluster (Strigul 2010). The study proposed here focuses on flux of mobile W compounds from natural W deposits, which has not been investigated before. In the early 2000s, W was investigated as part of the U.S. Army's Green Ammunition Program wherein the goal was to identify less toxic alternatives to lead-based ammunition. This program focused on dissolution of W alloys, W toxicology and ecotoxicology and its mobility around shooting ranges (Dermatas et al. 2004, Strigul et al. 2005, Bednar et al. 2009a, 2009b). Important discoveries made in the course of these studies included the following: 1) W alloys readily dissolve in soils and aquatic systems under common environmental conditions and migrate with surface and groundwater, 2) dissolved W is often a complex mixture of MW and PW; these compounds are bioavailable, often toxic and accumulate in plants and animals, 3) PW are much more toxic than MW. Several independently developed biomedical projects examined solubility of metallic W used in W based implants and other biomedical devices and soluble W monomeric and polymeric compounds as antimicrobial and diabetic drugs (Strigul 2010). These projects confirmed high solubility and corrosion of metallic W and development of highly toxic PW under physiologically relevant conditions (Strigul 2010).

However, to our knowledge, very little work has been done to quantify W occurrence in natural waters or to examine controls on W mobility and speciation in watersheds. Furthermore, little is known about dissolution of W-rich minerals because most of the work to-date has focused on W in metallic form or W-rich alloys. The focus of this proposal is on geochemical controls on W leaching to aquatic systems near W deposits. The ecotoxicological data is also

based on laboratory experiments with aquatic and soil-plant systems artificially contaminated by metallic W compounds (Strigul et al. 2005, 2009). There are only few relevant studies on W fate and transport in waters around W deposits, and most of these have focused on hydrothermal biochemistry or are now quite old. Krainov (1973), who reviewed the scant data available at that time, stated that W mobility has been underestimated by geochemists and geologists, and that substantial concentrations of W compounds typically occur in the following natural water environments: 1. groundwater near W deposits, 2. alkaline thermal waters of crystalline rocks, 3. carbonaceous waters of crystalline rocks, and 4. alkaline lakes in proximity to W deposits. Several other studies published in Russian, including Zaguzin et al., 1980 (reviewed in Strigul et al. 2009a) proposed that iron hydroxides precipitate W ions in water and that this should be the major factor restricting dispersion of W. Iron- and manganese- oxidizing bacteria can also destroy the crystalline structure of W-rich wolframite, and facilitate the release soluble W compounds. These largely overlooked studies (see Strigul at al. 2009a) are consistent with more recent studies using W alloys to examine factors controlling W solubility and transport (Strigul 2010). The breakdown of W containing minerals is accompanied by local acidification that may facilitate the formation and release of soluble PW. Our proposed experiments and field observations will allow us to test this hypothesis.

The proposed study will be the first study examining tungsten in WA watersheds (previous work by Strigul was conducted during his tenure at Stevens Tech, NJ prior to his WSU appointment). Based on the scant data available from other parts of the American West, which have shown W concentrations in surface waters draining W-rich soils (Koutsospyros et al. 2006, Seiler et al. 2005, Walker and Fosbury 2009), we expect that W is a common element in aquatic systems draining WA W deposits, with the potential to influence ecosystems and water quality. Overall, we anticipate that this work will provide novel important information concerning this emerging pollutant in the State of Washington.

19. Training potential of project

As noted above, this project will directly support the training of 1 MS student (Phil Steenstra), at least 1 undergraduate student.

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