Review of Regulatory Policies for Copper and Silver Water Quality Criteria

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by

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I. WATER MANAGEMENT

The 20\textsuperscript{th} century has been plagued with a global water crisis, including the failure to meet basic human drinking water and sanitation needs in a large percentage of the world. This failure arises from economic and political barriers to water access as well as environmental barriers like water scarcity, groundwater pollution, and chemical or bacterial pollution of surface waters (Gleick and Palaniappan, 2010). In light of these crises, researchers have been evaluating the feasibility of solving water crises on global and local scales through political and technological changes.

Peter Gleick’s peak water theory (Gleick and Palaniappan, 2010) has extreme relevance to water management decisions in light of the current water crisis. The peak water theory attempts to predict when the global population’s water use will exceed the peak water production limit relative to the replenishment timeline of the resource. Within the concept of peak water, resources are divided into three different types of water reservoirs: renewable, nonrenewable, and ecological uses. Most relevant to this study is the concept of peak ecological water, which is the point of water contamination where the damage to natural ecosystems causes “the value of ecological services” a waterbody provides society to equal the “value of human services” the use of this water can provide. Further extraction will create more human services while continuing to diminish the value of ecological services provided by that water body (Gleick and Palaniappan, 2010). For water bodies with little recreational or other value to humans, continued extraction and pollution may create inhabitable waters or eradicate the water body all together. Some industrialized countries like the United States are speculated to have already passed
this point of peak ecological water, but revised water policy can stimulate behaviors encouraging sustainable water use for the future (Gleick and Palaniappan, 2010).

Human activities like agriculture and industry introduce novel and often persistent chemical contaminants into aquatic ecosystems. Chemicals are directly discharged into waterways or transported into aquatic ecosystems with runoff following intense rain events. Coupled with natural processes like erosion, these factors contribute greatly to ecosystem degradation (Simeonov et al., 2003). While classic toxicological testing can show the mechanisms and response thresholds of a particular chemical to a test organism, ecosystem-wide effects are often influenced by a suite of other factors like competing compounds or chemical transformations. The properties of chemicals (e.g., hydrophobicity) can lead to biomagnification that can cause toxic effects throughout the food chain. Many of the indirect effects chemical contaminants can have on critical ecosystem functions are still not well researched, including primary production, nutrient retention, and carbon sequestration (Bernhardt et al., 2017). These factors, paired with the natural temporal and spatial variability of water chemistry, require stringent water quality criteria to protect our ecosystems.

In 2012, the Organisation for Economic Co-operation and Development (OECD) called for a “water reform” to update water policies to be more protective, inclusive, and sustainable (OECD, 2012). Ecological water quality criteria for pollutants must utilize toxicity data sets that are representative of natural aquatic communities, requiring the inclusion of the most sensitive taxa to be truly protective of these communities (Brix et al., 2011). In addition, water policies must reflect the types and concentrations of
pollutants that may degrade aquatic ecosystems through the use of water quality criteria derived from data sets continually updated with recent findings.

This study focuses on the level of protection provided by water quality criteria for copper and silver for the novel test organism *Lymnaea stagnalis*. *L. stagnalis* is a widely-distributed aquatic snail and a primary consumer of algae and aquatic plants (Budha *et al.*, 2010). In many ecosystems, this snail serves as an integral part in the diet of fish and crayfish (Stoiber *et al.*, 2016). The freshwater pulmonate snail *L. stagnalis* has been found to be one of the most sensitive species tested to date in terms of chronic metal toxicity (Brix *et al.*, 2011). Both copper and silver are categorized in the highest metal toxicity class (Ratte, 1999), yet available toxicity data about these two metals differs substantially. Copper is both an essential trace nutrient and a relatively well-researched contaminant (Solomon, 2009), while research on silver toxicity only began approximately 25 years ago. Many toxicity modifying factors are still not well known for silver due to a lack of substantial data sets (Ratte, 1999). The unclear effects of water chemistry on silver toxicity make it difficult to extrapolate researched concerns into water quality criteria (Erickson *et al.*, 1996).

To evaluate the effectiveness of current water quality criteria in protecting sensitive species like *L. stagnalis* from copper and silver toxicity, a chronic toxicity study was completed, and the results were compared to water quality regulations in the following jurisdictions: United States, Canada, South Africa, Australia and New Zealand, and the European Union. The United States and Canada provide insight into nationwide water quality regulations in developed nations, while South Africa’s policies
are representative of developing nations. Australia and New Zealand and the European Union represent collaborative water management efforts between multiple nations. By studying the criteria in each jurisdiction, differences in intent, priority, and implementation of water management efforts can be observed for a well-researched contaminant (Cu) and an emerging pollutant of concern (Ag).
II. WATER QUALITY CRITERIA

Water quality criteria are used in water management to protect aquatic ecosystems from anthropogenic inputs of chemical contaminants that may degrade the ecosystem and to establish management objectives for a particular water body or set of water bodies (Yillia, 2012). These management objectives are designed to protect the designated use of the water body (i.e. drinking, recreational, bathing, etc.) with respect to both human needs and natural circumstances (Hart et al., 1999). By doing so, water quality criteria place limits on the amounts and types of pollutants that can be discharged into waterways and guide restoration efforts designed to remedy impaired waterways to meet current regulations (Karr and Dudley, 1987). Currently, most water quality criteria are based off of physico-chemical parameters supplemented with few – if any – biological indicators (Hart et al., 1999).

Chemical risk assessment is a process by which the impacts a chemical may have on the environment can be systematically predicted and described. Chemical risk assessment aims to determine the scope of a potential contaminant’s impact by evaluating which aspects of the ecosystem will be affected by the chemical constituent and to what degree (EPA, 2016). For example, when a chemical enters a waterbody, it interacts with the other chemicals already present in the water, and this can enhance or inhibit its toxicity (Bernhardt et al., 2017). Chemical risk assessment then aims to designate a level of protection to ecological entities that are deemed worthy of protection, which is often based on organisms’ susceptibility, role within the ecosystem, and, frequently, services provided to humans. Managers then utilize this information to predict what
concentrations of the chemical will be dangerous to organisms based on a particular endpoint, acute and chronic effects, and scope of the impact (EPA, 2016).

Bioavailability plays an important role in distinguishing between the total concentration of a chemical in an ecosystem and the fraction of that concentration that can actually affect biota. It has been commonly observed that total contaminant concentrations (especially metals) in water or sediment do not accurately predict ecological effects. Metal bioavailability in water is influenced by a number of different factors, but pH, ambient ion concentration, and dissolved organic carbon are considered most important (DeForest and Van Genderen, 2012). Knowledge of the bioavailability of a particular chemical allows a better prediction of the effects it will have on the biotic community. As a result, bioavailability-based criteria are tailored to the predicted toxicity of a chemical under the conditions in a specific aquatic ecosystem, thus avoiding unnecessarily high or mistakenly low water quality criteria (Allen, 1993).

United States – The United States Environmental Protection Agency (US EPA) created ambient water quality criteria to establish concentrations of chemicals acceptable in freshwater ecosystems. These criteria were created as part of the Clean Water Act of 1972 (UN-Water, 2015) with most aquatic life criteria first established in 1980 (EPA, 2017). At the federal level, these criteria are created as recommendations for states and tribes to consider when adopting water quality criteria, but the adoption of the recommended criteria is not required by law (Yillia, 2012). Instead, states and tribes are required to create water quality criteria that must be submitted to the EPA prior to adoption (Office of the Federal Register, 2017). These criteria are designed to protect
95% of the genera in a given waterbody if exceeded no more than once every three years (EPA, 2007). Water quality criteria are risk-based standards derived for “individual water bodies, such as rivers, lakes, streams, and wetlands.” States often create use designations for water bodies, like recreation or aquatic life, and apply water quality criteria designed to protect this use. Much of US EPA’s regulatory efforts are focused in permitting industrial and municipal discharges to ensure the prevention of toxic pollutant discharges (Yillia, 2012).

The US EPA utilizes two major criteria to regulate potential contaminants in freshwater: the final acute value (FAV) and the final chronic value (FCV). To derive each of these values, US EPA sets a threshold for toxicity datasets that they must include at least one species in eight different families. Chronic data is often limited, but an acute-to-chronic ratio can be calculated for a minimum of three different families as long as a fish, an invertebrate, and an “acutely sensitive freshwater species” have chronic toxicity data represented in the data set. An acute-to-chronic ratio should be calculated for all species for which acute and chronic data is available; the final acute-to-chronic ratio is the geometric mean of these values. Both the FAV and FCV are calculated using EC50 values from individual toxicity tests, meaning the concentration at which adverse toxicity effects are observed in 50% of the test organisms. If the EC50 is not available, alternative parameters are described depending on the type of organism (Stephen et al., 2010).

The FAV is the maximum 24-hour average concentration of a chemical that is unlikely to cause toxic effects. This criterion should be representative of not only the
biological community but also the most sensitive life stages of the species present in a waterbody. Using a data set that meets all minimum requirements set by the US EPA, the species mean acute value (SMAV) should first be derived by calculating the geometric average of all acute values in the data set that meet EPA criteria (e.g., no flow-through tests). For freshwater snails like *L. stagnalis*, the SMAV is calculated using the 96-hour EC50 value, including both the percentage of organisms killed during the toxicity test as well as those organisms with incompletely developed shells. The SMAV should then be used to calculate the genus mean acute value (GMAV) by finding the geometric average of all of the SMAVs in a particular genus. The GMAVs are then ordered highest to lowest and ranked. Then, the cumulative probability of each GMAV is calculated, and the four GMAVs with cumulative probabilities closest to 0.05 are inputted into a logarithmic equation to calculate the FAV (Stephen *et al.*, 2010).

The FCV is the maximum four-day average concentration below which toxic effects are not likely to occur. When data from chronic toxicity tests is available, the FCV criteria can be calculated by following the same process outlined above for the FAV derivation. Alternatively, FCV criteria can be derived by dividing the FAV by the final acute-chronic ratio (FACR). To use the FACR, the ratio must be calculated for each species mean chronic value (SMCV) for which a corresponding SMAV is available. Calculation of the genus mean chronic values (GMCVs) and FCV follow the same methods as for FAV derivation (Stephen *et al.*, 2010).

Traditionally, US EPA water quality criteria for metals are corrected for the modifying effects of water hardness on toxicity. This method plots toxic concentrations
of a particular metal across a range of water hardness, and an empirical regression is then used to derive the water quality criteria. However, this method is best suited to derive criteria for waters that are within the range of test waters used in the toxicity datasets in terms of pH and alkalinity. A water effect ratio (WER) can be calculated to account for differences in bioavailability and toxicity between the target study waters and lab test waters. However, adjusting the criteria on a site-by-site basis through this method can be time and labor intensive (EPA, 2007).

Updated in 2007, US EPA ambient freshwater quality criteria for acute copper toxicity recognize its classification as both a micronutrient for aquatic organisms and a toxic heavy metal at elevated concentrations. The updated criteria account for the effects of increased water hardness on decreasing copper toxicity as calculated through the biotic ligand model (BLM). The BLM derives copper toxicity as a function of the ambient water quality characteristics that can modify how copper interacts with this organism at “sites of toxic action” like gills. The BLM accounts for competitive binding at the gill surface by other cations (e.g., Ca\(^{2+}\), H\(^+\)) and binding of non-biotic ligands (e.g., dissolved organic matter), which can reduce the bioavailability and toxicity of Cu. The BLM model produces species or genera specific criteria to be considered in addition to the overall FAV. Derivation of the FAV utilized a toxicity data set representative of 15 invertebrate species, 22 fish species, and 1 amphibian species. Calculation of the FCV incorporated fewer tests with chronic toxicity data for 6 species of invertebrates and 10 species of fish. The current FAV for copper is calculated using both the BLM and hardness regression methods, while the FCV is derived using the hardness regression
method (Table 1). No hardness-based equation or range of values relative to water hardness is provided for the FCV criteria. Instead, the criteria provided are normalized to the hardness of the test waters (26.1 mg/L CaCO$_3$) (EPA, 2007).

**Table 1:** United States Environmental Protection Agency (US EPA) Ambient Freshwater Quality Criteria for Copper (EPA, 2007)

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Cu Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freshwater site specific final acute value (FAV)</td>
<td>4.67 μg Cu/L</td>
</tr>
<tr>
<td>Final acute-chronic ratio (FACR)</td>
<td>3.22</td>
</tr>
<tr>
<td>Freshwater chronic value (FCV)</td>
<td>1.45 μg Cu/L</td>
</tr>
</tbody>
</table>

US EPA ambient water quality criteria for silver were last updated in 1980 (EPA, 1980). While this criteria does not include the bioavailability specificity that is provided by the Cu BLM, the silver water quality criteria does account for the effect of water hardness on silver toxicity. Silver toxicity is higher in soft waters, but the 1980 dataset lacked sufficient data to create criteria incorporating other factors of silver toxicity including solubility, ambient water ionic composition, and sorption onto sediments. Important to this study, the criteria for silver do not include snail toxicity data. The acute toxicity tests were conducted using ten taxa: one rotifer, two crustaceans, one insect, and six fish species. Derived using fewer species, the chronic toxicity tests only used *Daphnia magna* and *Salmo gairdneri* as test organisms, which is insufficient for derivation of a FCV. The US EPA also considered the acute toxicity of 13 freshwater
plant species, shown to be more resistant to silver toxicity effects than freshwater animals. The water quality criteria for silver (Table 2) are acute criteria that should not be exceeded, though the US EPA recognizes the possibility of chronic toxicity at concentrations as low as 0.12 μg Ag/L (EPA, 1980).

**Table 2:** United States Environmental Protection Agency (US EPA)

Ambient Freshwater Quality Criteria for Silver (EPA, 1980)

<table>
<thead>
<tr>
<th>Hardness (mg CaCO₃/L)</th>
<th>Acute Silver Criteria (μg Ag/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.2</td>
</tr>
<tr>
<td>100</td>
<td>4.1</td>
</tr>
<tr>
<td>200</td>
<td>13</td>
</tr>
<tr>
<td>Any hardness level</td>
<td>(e^{(1.72 \ln[\text{hardness}]) - 6.52}))</td>
</tr>
</tbody>
</table>

_Canada_ – The Canadian Water Quality Guidelines create criteria for the protection of fresh and marine water, agricultural water, drinking water, recreational water, and industrial supplies. These guidelines establish minimum requirements for water quality that are meant to protect both aquatic ecosystems and human use of these water bodies, and these guidelines can be modified by local governments to best suit their region. Thus, the legislative authority of these guidelines is the provincial or territorial government, not the federal government. Exceptions to this rule are federal lands and exceptionally high quality ecosystems, which are expected to be regulated by the federal guidelines (Yillia, 2012). The guidelines currently do not have legal backing or direct
enforcement but instead are used in “permitting and licensing” procedures. In addition, these guidelines create standards to assess the success of water management efforts throughout Canada. For this purpose, the guidelines present strategies for adapting the generic guidelines on a site-specific basis (CCME, 2003).

The Canadian Water Quality Guidelines (WQG) are single maximum concentrations that should not be exceeded at any time. These values represent a long-term no-effect concentration (NOEC), the highest concentration at which organisms are unlikely to experience adverse toxicity effects. Toxicity data sets used to derive these criteria must be representative of essential parts of the ecosystem, including fish, invertebrates, and plants (CCME, 2003).

To derive these guidelines, chronic, non-lethal toxicity data sets using the most sensitive life stage of an organism are desired for the most chronically sensitive species. From this data set, the most sensitive lowest observed effect level (LOEL) is then multiplied by 0.1, a safety factor, to calculate the WQG. The Guidelines present alternative procedures for calculating the WQG from acute toxicity data sets if chronic data sets are not available (CCME, 2003).

Canadian Water Quality Guidelines for copper, which were established in 1987, are derived as a function of water hardness (Table 3; CCME, 1987).

Revised in 2015, Canadian water quality recommendations for silver currently recognize the modifying effects of hardness, sodium, alkalinity, pH, anions, and dissolved organic carbon on silver toxicity, but these factors have not yet been incorporated into the derivation of water quality criteria. Use of BLM in updating these
criteria is also being researched, but current criteria do not incorporate this technology. Instead, Canadian water quality criteria for silver are derived based on exposure time (Table 4; CCME, 2015B).

Table 3: Canadian Water Quality Guidelines for Copper (CCME, 1987)

<table>
<thead>
<tr>
<th>Hardness (mg CaCO₃/L)</th>
<th>Copper Criteria (μg Cu/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-82</td>
<td>1.2</td>
</tr>
<tr>
<td>82-180</td>
<td>Evaluated using equation below: 0.2e^(0.8545 * ln[hardness]) – 1.465</td>
</tr>
<tr>
<td>Greater than 180</td>
<td>4</td>
</tr>
<tr>
<td>Unknown</td>
<td>2</td>
</tr>
</tbody>
</table>

The derivation of the short-term criteria for silver, which was statistically equal to the long-term exposure criteria, was established using LC50s for several species: six fish, nine invertebrates, and one protozoan. Because of their essential role in silver biogeochemical cycling through the uptake of aquatic silver, two algal species, *C. reinhardtii* and *P. subcapitata*, were incorporated into derivation using the EC50 values. On the other hand, the long-term criteria used a variety of endpoints for the species in the dataset, including maximum acceptable toxicant concentrations (MATCs) for growth and reproduction, LC10s, inhibition concentrations (IC20s) for reproduction, and NOECs for reproduction and dry weight. The following types of species were included in the data
set for the long-term criteria: four fish, two cladocerans, one amphipod, one midge, and one aquatic plant. Neither criterion considered *L. stagnalis* in the derivation of WQGs (CCME, 2015B).

**Table 4:** Canadian Water Quality Guidelines for Silver (CCME, 2015B)

<table>
<thead>
<tr>
<th>Exposure Type</th>
<th>Silver Criteria (μg Ag/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-term</td>
<td>0.25</td>
</tr>
<tr>
<td>Short-term</td>
<td>No recommended guideline*</td>
</tr>
</tbody>
</table>

*No guideline is recommended for short-term exposure as this value is essentially equal to the long-term exposure criteria.

*Australia and New Zealand* – The Australian and New Zealand Environment and Conservation Council (ANZECC) water quality guidelines are designed to protect the value and use of natural aquatic ecosystems. The ANZECC guidelines express environmental indicators as descriptive or narrative statements as well as trigger values of potential contaminants. Designed to licit a management response, these trigger values can be altered to suit the specific ecosystem conditions (e.g., soil type, precipitation regime). These guidelines provide the tools and framework necessary for both governments and the general public (e.g., watershed managers and community groups) to effectively manage and protect aquatic ecosystems. Though the national and state or territorial governments are involved in water quality management, the ANZECC
guidelines encourage water management at the catchment level to adapt the guidelines to local water body characteristics and community needs (Yillia, 2012). This implementation strategy creates guidelines reflecting the level of protection citizens want to give a particular water body. The guidelines also differ based on the type of ecosystem, which includes different levels of disturbed ecosystems, highly disturbed ecosystems that cannot be restored, and ecosystems with high ecological value (ANZECC/ARMCANZ, 2000A).

ANZECC guidelines classify both copper and silver as a toxicant and include suggested procedures for monitoring such toxicants. Trigger values for each toxicant are represented as levels of protection, indicating the percentage of species likely to be protected by the regulation. The guidelines also suggest procedures for adopting trigger values based on the ecosystem classification, reserving the 99% level of protection for conservation ecosystems. All trigger values are designed to prevent the effects of chronic toxicity. The “high reliability” values utilize NOECs from chronic toxicity data sets to derive the trigger values, while “moderate reliability” trigger values are calculated from acute toxicity data sets through the use of acute-to-chronic ratios (ANZECC/ARMCANZ, 2000A). To derive the trigger values, short-term sub-chronic tests conducted at the most sensitive life stage of the organism were used in the data sets. While ANZECC guidelines do not readily provide a list of the organisms used to derive each criterion, the freshwater snail *Amerianna cumingii* was used frequently as a bioassay throughout the derivation of all criteria to measure both reproduction and offspring survival (ANZECC/ARMCANZ, 2000B).
ANZECC guidelines consider several toxicity modifying factors relevant to copper, including chemical speciation, but do not provide numerical guidance for these factors. Trigger values for copper are calculated as a function of the level of protection offered for the water body (Table 5). Another set of trigger values for copper have been derived relative to water hardness ranging from 0-400 mg/L CaCO₃ (ANZECC/ARMCANZ, 2000A).

Table 5: Australian and New Zealand Guidelines for Fresh and Marine Water Quality for Copper (ANZECC/ARMCANZ, 2000A)

<table>
<thead>
<tr>
<th>Level of protection (% species)</th>
<th>Trigger value for freshwater (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99%</td>
<td>1.0</td>
</tr>
<tr>
<td>95%</td>
<td>1.4</td>
</tr>
<tr>
<td>90%</td>
<td>1.8</td>
</tr>
<tr>
<td>80%</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Silver is regulated in much the same way as copper. No additional trigger values have been derived for silver relative to any toxicity modifying factors, though generic modifying factors are discussed in the guideline narratives (Table 6; ANZECC/ARMCANZ, 2000A).
Table 6: Australian and New Zealand Guidelines for Fresh and Marine Water Quality for Silver (ANZECC/ARMCANZ, 2000A)

<table>
<thead>
<tr>
<th>Level of protection (% species)</th>
<th>Trigger value for freshwater (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99%</td>
<td>0.02</td>
</tr>
<tr>
<td>95%</td>
<td>0.05</td>
</tr>
<tr>
<td>90%</td>
<td>0.1</td>
</tr>
<tr>
<td>80%</td>
<td>0.2</td>
</tr>
</tbody>
</table>

_South Africa_ – The South African Water Quality Guidelines presents water quality criteria along with information about the potential contaminants, including background concentrations, effects, and treatment options as research permits. These guidelines are divided into different water uses (e.g., drinking, agriculture), and each use is detailed in a separate volume of the guidelines. Suggestions for modifying these guidelines on a local level are included. These suggestions are expected to maintain the same level of protection as the original criteria, and the inclusion of these suggestions makes it easier for water quality managers to adopt effective and practical criteria for their locality (Yillia, 2012). Like the criteria from other jurisdictions, South African water quality criteria are intended to be adopted at a local level.

South African water quality criteria for copper recognize the effects of a number of toxicity modifying factors. For example, copper toxicity increases with decreases in water hardness and dissolved oxygen, and copper toxicity decreases with increases in alkalinity as well as the presence of chelating agents (e.g., zinc, molybdenum, sulfate).
However, copper criteria are only calculated as a function of water hardness. The criteria specify that at least 90% of all dissolved copper measurements must lie within the target water quality range (TWQR) and 100% of measurements must be below the chronic effect value (CEV), the concentration above which chronic toxic effects are likely to be observed in up to 5% of species (Table 7). The TWQR is designed to be added to and subtracted from the CEV to calculate a range of safe long-term concentrations. Copper water quality criteria also include an acute effect value (AEV), the concentration above which acute toxic effects are expected in up to 5% of species (DWAF, 1996A).

The copper water quality criteria also specify conditions in which site-specific water quality criteria must be developed and the data requirements for the development of such criteria. Site-specific criteria should be developed if locally valuable species displaying sensitivity to copper toxicity are not represented in the data sets, the aquatic community is stressed by existing factors (e.g., diseases, other contaminants, or hydrologic characteristics), or if background copper concentrations exceed the TWQR values through natural processes. Data sets utilized to derive site-specific criteria must represent one full year of data and show altering the copper TWQR concentration will not negatively impact the ecosystem (DWAF, 1996A).

South African water quality criteria do not provide any current or historic regulations for silver in natural waters. As a result, silver is currently an unregulated potential contaminant of freshwater ecosystems in South Africa (DWAF, 1996A). However, silver is regulated in the country’s drinking water standards (Pieterse, 1989).
Table 7: South African Water Quality Guidelines for Copper (DWAF, 1996A)

<table>
<thead>
<tr>
<th>TWQR and Criteria</th>
<th>Copper concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water Hardness</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Less than 60 mg/L CaCO₃</td>
</tr>
<tr>
<td></td>
<td>(Soft)</td>
</tr>
<tr>
<td></td>
<td>60-119 mg/L CaCO₃</td>
</tr>
<tr>
<td></td>
<td>(Medium)</td>
</tr>
<tr>
<td></td>
<td>120-180 mg/L CaCO₃</td>
</tr>
<tr>
<td></td>
<td>(Hard)</td>
</tr>
<tr>
<td></td>
<td>Over 180 mg/L CaCO₃</td>
</tr>
<tr>
<td></td>
<td>(Very hard)</td>
</tr>
<tr>
<td>Target Water Quality Range (TWQR)</td>
<td>0.3</td>
</tr>
<tr>
<td>Chronic Effect Value (CEV)</td>
<td>0.53</td>
</tr>
<tr>
<td>Acute Effect Value (AEV)</td>
<td>1.6</td>
</tr>
</tbody>
</table>

**European Union** – The European Union (EU) utilizes the Water Framework Directive (WFD) to create environmental quality standards (EQS) for “priority substances” (Schlekat et al., 2016) as well as to restore and to protect waterbodies by fostering sustainable use practices. One of the major goals of the WFD, outlined in Article 4, is the achievement of “good ecological status (or potential) and good chemical status for surface waters” by 2015 (Yillia, 2012). This objective is common to all EU Member States, as each State is required to adopt the EQS as defined in the WFD (Schlekat et al., 2016). Regardless of this legal requirement, these regulations may have
been implemented unevenly because the enforcement power of the EQS and other pertinent standards remains at the Member State level (Yillia, 2012).

EU EQS are only required for priority or priority hazardous substances, a list currently encompassing over 45 constituents (European Commission, 2009). These priority substances are potential problematic contaminants across the entire EU (European Commission, 2016). Other substances may be regulated by Member States on an individual, voluntary basis through the implementation of river basin management plans. Currently, the EU does not list either copper or silver as priority substances (European Commission, 2009), and therefore these metals are regulated at the Member State level.

Member States may regulate additional substances using various EQS for water, sediment, or biological indicators following the procedures outlined in Section 1.2.6 of Annex V of the WFD. To derive these criteria, both chronic and acute data sets must be used for, at minimum, algae and/or macrophytes, daphnia, fish, and other organisms important to the ecosystem. Derivation must also integrate any relevant toxicity modifying factors into the criteria as well as utilize an assessment factor to correct for any uncertainty in the data set. Two methods of data extrapolation are utilized in formation of EQSs. The deterministic method uses an assessment factor to adjust for uncertainties in data sets with known low credibility, while the probabilistic method uses species sensitivity distributions for more credible toxicity data sets from which NOECs can be derived. The probabilistic method results in derivation of NOEC criteria protective of a certain percentage of taxa, generally 95% (European Commission, 2011).
England and Wales utilize water quality standards (WQS) derived by the United Kingdom Technical Advisory Group (UKTAG) for river basin specific contaminants in addition to those EQS set by the EU. These standards are reported as predicted no-effect concentrations (PNEC) for short- and long-term concentrations. UKTAG follows the EU WFD procedures for calculating EQS criteria (UKTAG, 2008).

The short-term PNECs describe the maximum allowable concentration (MAC) of a contaminant at any time. These standards are thus derived from acute toxicity data sets. Long-term PNECs, on the other hand, are derived from chronic toxicity datasets and stated as a yearly average concentration. Environmental agencies utilize the long-term concentration in compliance assessments, while the short-term concentration is treated as a trigger for further examination on exceedances in a particular waterbody. Currently, UKTAG has developed WQS for copper (Table 8) but not silver (UKTAG, 2008).

**Table 8:** England and Wales Water Quality Standards for Copper (DEFRA, 2014)

<table>
<thead>
<tr>
<th>Exposure Type</th>
<th>Copper Concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long-term (annual mean)</td>
<td>1.0*</td>
</tr>
<tr>
<td>Short-term (95 percentile)</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*This standard is expressed as the bioavailable concentration that can be calculated using the UKTAG Metal Bioavailability Assessment Tool.
Another Member State of the EU, Spain currently regulates copper as a preferred substance, meaning a substance which poses a substantial threat to Spanish waters. Copper is regulated through the use of hardness-based criteria to be utilized as an annual average (Table 9). This average represents the maximum acceptable concentration of dissolved copper. At this time, Spain does not regulate silver as a potential water pollutant (Government of Spain, 2015).

**Table 9:** Spanish Environmental Quality Standards for Copper (Government of Spain, 2015)

<table>
<thead>
<tr>
<th>Hardness of water (mg CaCO₃/L)</th>
<th>Copper Concentration (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-10</td>
<td>5</td>
</tr>
<tr>
<td>10-50</td>
<td>22</td>
</tr>
<tr>
<td>50-100</td>
<td>40</td>
</tr>
<tr>
<td>Over 100</td>
<td>120</td>
</tr>
</tbody>
</table>

Germany regulates both copper and silver using EQSs derived from chronic toxicity data sets (Table 10). These standards are designed to be implemented so that concentrations equal to or exceeding half of the EQS value require remediation. Like EU EQSs, these river basin EQSs are legally binding, and compliance is evaluated using yearly average concentrations. Toxicity data sets used to derive the EQSs demonstrate the contaminants’ potential effects on the food web of the ecosystem. The most sensitive values in the data set are multiplied by a compensating factor to correct for the assumed
increased sensitivity of these organisms in the real environment, compared to controlled laboratory settings. For some metals, the detection limit is greater than the EQS value, so EQS are provided as either the soluble concentration (µg/L) or the amount of the substance suspended in the water column relative to the amount in sediment (mg/kg) (Arle et al., 2014).

**Table 10:** German Environmental Quality Standards for Copper and Silver

(Arle et al., 2014)

<table>
<thead>
<tr>
<th>Metal</th>
<th>EQS Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>160 mg/kg*</td>
</tr>
<tr>
<td>Silver</td>
<td>0.02 µg/L</td>
</tr>
</tbody>
</table>

*Suspended sediment concentration

For comparison with the results of this study, the water quality criteria from each jurisdiction are listed below for copper (Table 11) and silver (Table 12). These criteria are applicable to the hardness of the OECD reconstituted freshwater utilized in this study (92.3 mg CaCO₃/L).

**Table 11:** Summary of Chronic Water Quality Criteria for Copper from all Jurisdictions for OECD Reconstituted Freshwater

<table>
<thead>
<tr>
<th>Jurisdiction</th>
<th>Criteria Name</th>
<th>Copper Threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>United States</td>
<td>Final Chronic Value (FCV)</td>
<td>1.45</td>
</tr>
<tr>
<td>South Africa</td>
<td>Chronic Effect Value</td>
<td>1.5</td>
</tr>
<tr>
<td>Jurisdiction</td>
<td>Criteria Name</td>
<td>Silver Threshold (μg/L)</td>
</tr>
<tr>
<td>---------------------------</td>
<td>--------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>European Union</td>
<td>Annual Average Concentration</td>
<td>0.02*</td>
</tr>
<tr>
<td>Australia and New Zealand</td>
<td>95% Level of Protection</td>
<td>0.05</td>
</tr>
<tr>
<td>Canada</td>
<td>Long-Term Criteria</td>
<td>0.25</td>
</tr>
<tr>
<td>United States</td>
<td>Final Chronic Value (FCV)</td>
<td>∞</td>
</tr>
<tr>
<td>South Africa</td>
<td>Chronic Effect Value (CEV)</td>
<td>∞</td>
</tr>
</tbody>
</table>

*Criteria for copper listed from the European Union represent the value used as water quality criteria in Germany.
III. SILVER AND COPPER CHRONIC TOXICITY TO THE SNAIL *LYMNAEA STAGNALIS*

**Introduction:**

Anthropogenic activities like mining and industry greatly affect the amounts of trace metals in the environment. Once in the environment, both essential and nonessential metals have the potential to become toxic if bioavailable concentrations exceed thresholds of toxicity. Aquatic ecosystems are at greater risk of trace metal pollution through transportation by acid rain and flooding (Hare, 1992). The highly mobile nature of trace metal pollutants highlights the importance of water quality criteria derived from reliable toxicity datasets representative of all taxa in natural aquatic communities (Brix *et al.*, 2011)

The effectiveness of current water management regulations in protecting ecosystem integrity can be evaluated by comparing the effects of a well-researched, essential metal to those of a lesser-researched, nonessential metal on a benchmark organism. Contaminants of emerging concern may have outdated or nonexistent regulations, leaving aquatic ecosystems unprotected from potential toxic effects. Often, these contaminants are underrepresented in toxicity studies, so the risks associated with these chemicals are not properly evaluated. In contrast, well-researched contaminants typically have up-to-date water quality criteria that incorporate toxicity modifying factors to predict and mitigate the pollutants effects (Sauvé and Desrosiers, 2014). In this study, *Lymnaea stagnalis*, a freshwater pond snail, will be used as a benchmark organism to
measure the chronic toxicity of copper (Cu) and silver (Ag) over a 28-day period to compare the results between metals and to current water quality criteria. Chronic metal (Co, Pb, Ni) toxicity studies have shown that *L. stagnalis* may be the most sensitive species tested so far (Brix *et al.*, 2011)

Copper is a naturally-occurring element in the earth’s crust and surface waters, with background concentrations ranging from 0.20-30 μg/L (EPA, 2007). A component of jewelry, electrical wiring, and automobile parts, copper has been used by humans for over 6,000 years (Solomon, 2009). Compared to other industries, mining contributes a large amount of copper pollution to the environment. In fact, the concentration of copper in water can be as high as 200,000 μg/L near mining areas (EPA, 2007). Copper can also be introduced into the environment through the use of copper-based algaecides, corrosion of infrastructure, and wastewater treatment plants. It is estimated that anthropogenic sources comprise 33-60% of the global input of copper in the environment (DWAF, 1996A).

An essential metal, copper is used by plants and animals as a micronutrient (Solomon, 2009), but at high concentrations, copper can serve as a sodium (Na+) antagonist (Brix *et al.*, 2011). By disturbing sodium/potassium transfer in organisms (EPA, 2007), copper can have negative and potentially lethal effects on the cardiovascular and nervous systems of aquatic organisms (Solomon, 2009). Previous copper toxicity studies show *L. stagnalis* to be relatively insensitive to acute copper toxicity, possibly due to the high Na+ loss the snail normally undergoes when ejecting extracellular fluid to shrink its body into its shell. However, *L. stagnalis* has recently
been found to be one of the most sensitive species to chronic copper exposure. A chronic toxicity study conducted by Brix et al. (2011) found the hardness-based water quality criteria used in the United States to be ineffective in protecting L. stagnalis, with 83% reduction in growth in water with 7.0 μg/L Cu and 100% fatality with 13 μg/L Cu (Brix et al., 2011).

Silver, on the other hand, is a much less researched contaminant than copper. Naturally-occurring silver can be found in pure forms and ore forms, but aquatic environments do not have significant background concentrations of silver (EPA, 1980), measured at approximately 0.01 μg/L in unpolluted waterways and 0.01-0.1 μg/L in industrial or urban areas (Howe and Dobson, 2002). Silver is used in a variety of anthropogenic products like photographic materials, mirrors, jewelry, alloys, and electroplating (EPA, 1980). Recent technological advancements have led to the increased use of silver in the form of silver nanoparticles (Stoiber et al., 2016). Silver has unique antibacterial properties enabling the element to disrupt vital metabolic processes within bacterial cells (EPA, 1980), and thus silver nanoparticles utilize these antibacterial properties in a variety of applications, potentially increasing silver concentrations in aquatic ecosystems (Stoiber et al., 2016).

The monovalent form of silver (Ag+) is the most common in aquatic ecosystems and the focus of this study. Silver has been shown to be one of the most toxic metals to freshwater organisms in its soluble form, with toxicity affected by both water hardness and chloride concentration (EPA, 1980). Many toxicity databases utilized to derive water quality criteria lack enough data to create well-supported, protective water quality criteria.
for this element. Even in countries that currently regulate silver, like the United States, criteria often lack enough data to account for toxicity modifying factors (EPA, 1980).

To compare the toxicity of copper and silver to aquatic organisms, *L. stagnalis* was used as a sensitive model organism. For a 28-day period, *L. stagnalis* was exposed to varying concentrations of both copper and silver. Each snail was monitored every four days to measure survival, and all remaining snails were weighed at the end of the study to measure growth rates. These results were then analyzed for significant differences between both the concentrations of the metals as well as the metals themselves. Results of this study were then compared to existing water quality criteria in the United States, Canada, South Africa, Australia and New Zealand, and the European Union to determine the level of protection offered to *L. stagnalis* by these regulations.

**Methods:**

*Test organism* – This study used the freshwater pulmonate snail *L. stagnalis* as the model organism. *L. stagnalis* is widely distributed, and this species is a major part of the diet of several fish and crayfish. In addition to dermal and gill exposure to metals, the small size of these snails increases the likelihood that *L. stagnalis* will encounter minute metal particles both suspended in the water and sorbed onto its food (Stoiber et al., 2016). For this experiment, laboratory-reared snails less than 72 hours old were used. Upon hatching, these snails were transferred to reconstituted freshwater to become acclimated to the test water conditions; all reconstituted freshwater was prepared according to OECD guidelines (OECD, 2007). At the start of the experiment, the snails weighed an average of 1.3 mg (dry weight).
**Test solutions** – 7000 mL of each test solution were prepared prior to the onset of the experiment. Copper was added to the solutions in the form of copper chloride (CuCl₂) to reach the desired concentrations. Copper toxicity was tested using concentrations of 0 (control), 2, 4, 8, 16, and 32 μg/L Cu. Silver was added to the reconstituted freshwater in the form of silver nitrate (AgNO₃) to create the test solutions of 0 (control), 2, 4, 8, 16, and 32 μg/L Ag.

**Study design** – Ten snails per treatment were individually placed in 250 mL containers with 100 mL of test solution. Every four days, the snails were briefly removed from the containers so the test solutions could be replenished. At each water change, any snail mortality was recorded. Snails were fed spinach *ad libitum* continuously throughout the experiment. Any remaining spinach in the beaker was disposed of and replaced at each water change. The snails were held for 28 days in an incubator at 20°C on a 12-12 hour light-dark cycle for the duration of the study.

At the end of the 28-day period, the remaining snails were individually placed in centrifuge tubes and frozen for 48 hours. The snails were then dried for 24 hours and then weighed in the centrifuge tubes to determine growth rate over the test period.

**Data analysis** – The US EPA Toxicity Relationship Analysis Program (TRAP) was utilized to establish a relationship between the observed effects on mortality and growth rates to the exposure concentrations (EPA, 2015). Using a triangular tolerance distribution analysis, the LC50 concentrations were derived from both the silver and copper survival data. The growth data were analyzed with a threshold sigmoid regression to generate EC50s for both copper and silver.
Results:

*Copper* – Unexpectedly high mortality rates were observed in the controls, but survival was relatively stable between the 2 μg/L and 16 μg/L treatments before a sharp increase in mortality in the highest concentration (Figure 1). Analysis conducted using the TRAP program calculated an LC50 of 24 μg/L (Table 13).

![Graph showing survival of Lymnaea stagnalis exposed to increasing concentrations of copper](image)

**Figure 1:** Survival of *Lymnaea stagnalis* exposed to increasing concentrations of copper (28 d exposure). Each point represents the survival of 10 replicate snails. The solid line shows the concentration-response relationship determined by TRAP (EPA, 2015).
Snail growth rates declined in a typical dose-response relationship as copper concentration increased (Figure 2). The heaviest snails were observed at an intermediate treatment (4 μg/L), while snails in the 32 μg/L treatment were the lightest. An EC50 of 22 μg/L was calculated for reduced growth in *L. stagnalis* (Table 1).

**Figure 2:** Average growth rates in *Lymnaea stagnalis* exposed to increasing copper concentrations (28 d exposure). Each point represents the average final weight of 10 replicate snails. The solid line shows the concentration-response relationship determined by TRAP (EPA, 2015).
Silver – Snail survival during the chronic silver toxicity test showed little variation between concentrations (Figure 3). This consistent survival at even the highest concentration (32 μg/L) prevented the calculation of an LC50 within the test concentrations. Thus, the LC50 is >32 μg/L and an unbound NOEC was estimated as 32 μg/L, though the concentration could be higher.

Figure 3: Survival of *Lymnaea stagnalis* exposed to increasing concentrations of silver (28 d exposure). Each point represents the survival of 10 replicate snails. The solid line shows the concentration-response relationship determined by TRAP (EPA, 2015).

Snails grew at slower rates with increasing concentrations of silver, and snails in all concentrations >5 μg/L had grown to much smaller sizes than snails exposed to
control conditions (Figure 4). Due to the snail response at low concentrations, the TRAP model did not provide a great fit for the threshold sigmoid regression analysis. This analysis generated an EC50 of 5.8 μg/L, but due to the poor fit, confidence intervals could not be accurately estimated (Table 13).

**Figure 4**: Average growth rates in *Lymnaea stagnalis* exposed to increasing silver concentrations (28 d exposure). Each point represents the average final weight of 10 replicate snails. The solid line shows the concentration-response relationship determined by TRAP (EPA, 2015).
Table 13: Summary of Water Quality End Points Derived from Chronic Toxicity Tests

<table>
<thead>
<tr>
<th>Metal</th>
<th>LC50 (μg/L)</th>
<th>EC50 (μg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>24 (16-32)</td>
<td>21 (7.9-36)</td>
</tr>
<tr>
<td>Silver</td>
<td>&gt;32</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Values in parentheses represent the 95% confidence interval.

Discussion:

*Copper* – The EC50 and LC50 calculated for copper show the sensitivity of *L. stagnalis* to chronic copper toxicity. Both growth and survival were negatively affected at similar concentrations of Cu (21-24 μg Cu/L). The small difference between these values indicates that high mortality rates and low growth rates will most likely occur in conjunction with high copper exposure. For this reason, elevated copper concentrations may pose a serious risk to *L. stagnalis* if allowed to persist over extended periods of time.

Compared to results from previous studies with other bioassays, *L. stagnalis* appears to be moderately sensitive to copper toxicity. Cladocerans like *Daphnia longispina, Acantholeberis curvirostris, Bosmina longirostris,* and *Scapholeberis* species have been shown to experience adverse effects from copper toxicity at significantly lower concentrations with EC50s for these taxa below 15 μg/L (Bossuyt and Janssen, 2005).

Several species of mussels have also been tested for copper toxicity. Juvenile oyster mussels are sensitive to copper toxicity, with a calculated EC50 of 12 μg/L. Rainbow mussel and Fatmucket juveniles are less sensitive than oysters (EC50s of 17 and 21 μg/L, respectively) but still more sensitive than *L. stagnalis* in this test (Wang et al., 2007).
While these studies vary in terms of water hardness, the taxa provide insight into the relative sensitivity of *L. stagnalis* and its use as a bioassay.

Previous chronic toxicity studies using *L. stagnalis* show the snail to be more sensitive to the chronic toxic effects of copper than demonstrated in this study. With the endpoint of snail survival, a 28-day chronic toxicity test conducted using *L. stagnalis* produced an EC20 of 5.6 μg/L. This same study produced an EC20 relative to snail growth of 1.8 μg/L, signaling that *L. stagnalis* may be the most sensitive species studied thus far in terms of chronic copper toxicity (Brix *et al.*, 2011). These results are at odds with the results of this study. More chronic toxicity tests using *L. stagnalis* are required to confidently identify the sensitivity of the species.

The United States, Canada, South Africa, and Australia and New Zealand implement chronic Cu water quality criteria between 1.45-6.25 μg/L. Because the observed EC50 and LC50 for copper are much higher than these criteria, *L. stagnalis* is likely to be protected by the enforcement of these current regulations. However, jurisdictions within these countries are not always required to adopt the recommended standards, as is the case in the United States (Office of the Federal Register, 2017). Site-specific water quality criteria thus must be regulated to ensure protection of sensitive species like *L. stagnalis*.

Because copper is not yet listed as a Priority Substance, Member States within the European Union are not currently required to adopt water quality standards for copper, and existing copper regulations within the EU are variable. England and Wales utilize the chronic criteria of 1.0 μg/L of bioavailable copper, but if localities within these
jurisdictions cannot effectively measure bioavailable copper through community resources, the implementation of this criterion, while protective of *L. stagnalis*, may prove ineffective. Other countries like Spain permit much higher copper concentrations. Spain adopted a long-term copper criteria of 40 μg/L for regulation, but this concentration of copper is almost twice the EC50 and LC50 observed for *L. stagnalis* in this study.

Failing to protect sensitive organisms like *L. stagnalis* from the toxic effects of copper can greatly impact the entire freshwater ecosystem due to their importance in the food chains (Stoiber *et al.*, 2016). While copper has been shown to have a low biomagnification capacity in aquatic food webs (DeForest and Van Genderen, 2012), copper toxicity may lead to indirect ecosystems effects. Sensitive species like *L. stagnalis* and *D. magna* demonstrate direct toxic effects from metal contaminants like copper, and this direct toxicity can facilitate changes in species abundance throughout the ecological community. Species that feed on these sensitive organisms may experience declines in abundance if the population of preferred food sources is significantly reduced from copper toxicity. In addition, the absence of *L. stagnalis* may lead to disproportionate increases in other herbivores as these species are released from competition with *L. stagnalis* (Fleeger *et al.*, 2003).

*Silver* – While the LC50 calculated for *L. stagnalis* is greater than 32 μg/L, the EC50 is much lower at 5.8 μg/L. *L. stagnalis* showed dramatic weight decreases between 4 and 8 μg/L that remained low as the concentration of silver increased. While high silver concentrations may not cause widespread lethal effects on *L. stagnalis*, decreased
growth rates indicate negative impacts on bodily function that may translate into population level impacts. Slow population growth can reduce fecundity and effectively decrease species abundance. In addition, behavioral differences in defense mechanisms can occur as a result of toxicant exposure. Inefficient predator avoidance can cause both declines in prey populations as well as increased biomagnification intensity throughout the food web (Fleeger et al., 2003).

Understanding of the chronic effects of silver toxicity is greatly limited due to only a small number of completed studies. Chronic silver toxicity studies show *L. stagnalis* to be moderately sensitive to silver compared to other bioassays. EC50s calculated for *Daphnia magna* show adverse effects on growth rates at 8.02 μg/L and reproduction at 6.17 μg/L (Bianchini and Wood, 2008). Early life cycle chronic toxicity studies conducted by the US EPA using rainbow trout show negative effects at concentrations between 0.09-0.17 μg/L (EPA, 1980). To better determine the relative sensitivity of *L. stagnalis*, additional chronic toxicity tests for silver must be completed using a wider selection of organisms.

Regardless of potential negative impacts at low concentrations of silver, several jurisdictions within this study have not yet adopted silver water quality criteria. Silver is not currently considered a “Priority Substance” by the EU WFD, and England, Wales, and Spain do not currently regulate aquatic silver concentrations. Although silver mining has been a substantial industry in South Africa since the 1880s (Reeks, 2012), this country has not yet developed water quality criteria for silver. Failure to effectively regulate gold mining caused extensive toxic water pollution in South Africa over the last
130 years (Jamasmie, 2016), and proactively deriving water quality standards for silver can prevent similar environmental disasters.

While the United States does regulate silver through the use of acute water quality criteria, no guideline has been provided for chronic exposures. In fact, the US EPA has acknowledge the possibility of chronic toxic effects at silver concentrations as low as 0.12 μg/L but still failed to provide a protective guideline. Because it was created in 1980 and has not been subsequently updated (EPA, 1980), US EPA silver criteria do not incorporate scientific insight into the toxicity of silver that have been discovered in the last 25 years. While many toxicity modifying factors affecting silver toxicity require further research (Ratte, 1999), the use of such an outdated criteria for a toxic pollutant conflicts with the EPA’s goal of protecting 95% of species in a waterbody. In addition, this criterion was derived using toxicity data from only ten species and without toxicity data for any snails (EPA, 1980), an integral part of aquatic food webs.

Canada, Germany, and Australia and New Zealand all utilize long-term water quality criteria for silver concentrations between 0.02-0.25 μg/L. These criteria fall significantly below the EC50 calculated for L. stagnalis in this study. As a result, L. stagnalis is most likely protected by the implementation of these criteria.

Water Management – The derivation of water quality criteria from the most up-to-date toxicity data sets is only one aspect of an effective water management plan. Criteria protective of 100% of species in an ecosystem are not effective if not properly implemented and enforced.
One major factor affecting water management plans is the required adoption of the provided water quality criteria. States are not required to adopt the US EPA water quality criteria, though the EPA does have to approve all state water quality standards before implementation. In addition, all state water quality criteria must be proven to be sufficient to meet the use designation for the applicable water bodies (Stephen et al., 2010). Similarly, South African and ANZECC water quality guidelines are designed to be adapted to local waterways (DWAF, 1996A; ANZECC/ARMCANZ, 2000A). When modified, South African water quality guidelines must offer the same level of protection to an ecosystem that was intended by the original criteria (DWAF, 1996A). ANZECC guidelines provide a framework by which to modify the provided water quality criteria. However, ANZECC guidelines have no formal legal standing (ANZECC/ARMCANZ, 2000A). Member States must adopt the specified EQSs for “Priority Substances” in the EU, but Member States retain the right to regulate non-priority substances as needed (European Commission, 2009). While these strategies allow for the generation of more specific water quality standards for waterbodies, spatial variability in requirements can also lead to uneven protection of water resources between states or localities. In this sense, water quality standards represent a trade-off between specificity of criteria and uniformity of regulations.

The European Union’s monitoring requirements for compliance with water quality criteria are limited to a yearly average concentration. While this average must include data from all seasons of the year (European Commission, 2009), it is not necessarily representative of the full range of concentrations that may threaten biota in
the water body. This study and others (Brix et al., 2011; Bianchini and Wood, 2008; EPA, 1980; Bossuyt and Janssen, 2005; Wang et al., 2007) show the potential of both copper and silver to cause death and/or reduced growth rates at concentrations less than 32 μg/L. Anthropogenic activities like mining and urbanization increase the levels of these pollutants differentially throughout the year, and extreme fluctuations in concentrations of copper and silver may be hidden by an annual average value. Utilizing a series of frequent, long-term water monitoring requirements will create a better understanding of the concentrations of silver and copper actually in the waterway and thus further direct management activities within the EU as well as within other jurisdictions.

Both silver and copper can have severe toxic effects on aquatic ecosystems. Increased use and production of nanoparticle technologies and further mining activities will increase the amounts of these metals in our ecosystems, necessitating an efficient response in water management. Copper presents a greater risk to aquatic ecosystems, as concentrations have been reported as high as 200,000 μg/L in mining areas (Solomon, 2009). Silver concentrations generally only range between 0.01-0.1 μg/L in polluted waterways near industrial or urban areas (Howe and Dobson, 2002), thus remaining well below reported EC50s. Yet the risk of these chemicals may change with technological advancements, as the increased use of silver nanoparticles is likely to increase the amount of silver in aquatic ecosystems (Stoiber et al., 2016). Water management must reflect these changes in ecological risk. Water quality criteria that represent the most sensitive
taxa and utilize the most up-to-date scientific information and toxicity data sets can be an invaluable tool in preventing ecosystem impairment.
**BIBLIOGRAPHY**


