A Procedure for Developing Ecosystem Loading Limits (TMDLs) for Selenium in Watersheds Affected by Gold Mining in Northern Argentina

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BACKGROUND

The Argentina Federal Secretary of Natural Resources oversees a wide array of mining operations conducted on public lands. Recently, selenium has emerged as a contaminant issue associated with several gold mines in the northern mountain ranges. The Secretary's Office contacted me and requested assistance interpreting selenium concentrations and possible impacts on fish, and formulating environmental quality goals to protect aquatic life. I conducted a technical review of environmental data collected by the mining companies, applied my Protocol for hazard assessment of selenium (Lemly, 1995), and concluded that their was a substantial risk of toxic impacts to fish in streams and wetlands near active and inactive mines.

I provided guidelines for interpreting residues of selenium in fish and aquatic habitats (Lemly, 1993a), but this still left an important issue unaddressed, namely, what regulatory procedures and processes should be used to reduce selenium pollution. This report gives technical guidance by laying out an assessment method that provides the contaminant-specific information necessary for selenium. The next step in resolving the environmental aspect of the problem in Argentina is for the Secretary to develop and issue a contaminant management plan that meets regulatory requirements and also protects fish and wildlife resources. That plan can be both responsive and effective if the Total Maximum Daily Load (TMDL) approach is used. The objective of TMDLs is to identify all pollution sources and then allocate/regulate discharges to meet the water quality needs of aquatic life within a basin. The TMDL process will be necessary to determine the ecological capacity of the various watersheds for selenium,

and set limits on how much can be safely discharged into downstream receiving waters and wetlands. Because of selenium's unique biogeochemical cycle, it's propensity to bioaccumulate and cause teratogenic deformities and reproductive failure in wildlife, and it's long-term persistence in the environment (Lemly, 1985, 1993b, 1997; Lemly and Smith, 1987), special procedures are required to set environmentally safe TMDLs for this contaminant. The method I provide here satisfies all of the necessary requirements. The hazard assessment procedures and interpretive guidelines used in the method have all been published in the peer-reviewed literature. This methodology can be used as a technical framework by the Secretary's Office as it moves forward with the gold mining selenium contamination issue. The resulting TMDLs will be environmentally safe, meet federal regulatory requirements, and afford protection to fish and wildlife resources.

PROCEDURE

The method presented here is structured to answer two basic questions:

(1) Is selenium impairing the water body based on biological criteria, and

(2) If so, what amount of selenium load reduction is necessary to correct the problem.

A 7-step procedure can be used to answer these questions and develop environmentally safe TMDLs for selenium. The basic premise in this approach is that selenium concentrations be kept below levels that threaten the reproduction of fish and aquatic birds.

Step 1): Delineate and characterize the hydrological unit (HU) of concern.

TMDLs for selenium should be based on an assessment of the degree of toxicological hazard to fish and wildlife, which is influenced by the hydrology of the site under consideration. The physical area from which measurements are taken to evaluate selenium concentrations and biological threats/effects, i.e., the database for setting TMDLs, must encompass more than an isolated segment of a river, a tributary stream, etc. Because of hydrological connections between the various aquatic habitats that may be present in a watershed basin – wetlands, rivers, streams, lakes, and impoundments – the toxic threat from selenium contamination is also connected. For example, a TMDL that is set for a stream or river where low bioaccumulation occurs may result in seemingly harmless concentrations becoming a problem in downstream impoundments or in off-channel bays and wetlands where bioaccumulation is greater.

The hydrologically connected parts of a basin that are downgradient of a selenium input (natural or anthropogenic selenium source), extending to the point at which new sources of low-selenium water dominate the hydrology and lower concentrations below levels of concern (e.g., confluence with a larger tributary or river, spring or groundwater inflow), should be the area evaluated and given a specific TMDL, not isolated parts (Figure 1). Thus, a hydrological unit (HU) should be identified and used as the "site" for the purpose of setting TMDLs. Importantly, TMDLs derived is this manner will reflect the transport and bioaccumulation of selenium within the entire HU rather than simply focusing on a small, artificially designated segment of the system. Failure to use a HU approach can set the stage for significant biological

problems and undermine the intended outcome of the TMDL process. Consult Lemly (1999) for more information on the rationale and justification for using HU's.

Substitute HU for the term "water body" used by states and EPA in their TMDL documentation, and use the entire HU as a "mixing zone" for the purpose of evaluating potential selenium transport and bioaccumulation. Characterize and map the aquatic system of the HU using available information in combination with field reconnaissance to identify/verify hydrological connections. Identify all aquatic habitats within the HU: wetlands, streams, rivers, off-channel bays, lakes, reservoirs, other impoundments; map their spatial and gradient/hydrological relationships, i.e., know what flows where, and into/out of what. Obtain information on trophic status, prevailing sediment type (organic, inorganic, mixed), and volume replacement times or flushing rates for lakes, reservoirs and other impoundments, bays off main-stem rivers, and wetlands; describe general level of primary productivity (low-oligotrophic, moderate-mesotrophic, high-eutrophic), predominant flow regime (slow, moderate, swift), and dominant sediment characteristics (depositional, erosional, particle size, organic, inorganic, mixed) of flowing-water habitats. Large rivers merit special attention in order to identify, map, and describe the variety of habitats that may be present, e.g., main-stem, off-channel bays, seepage or floodplain wetlands, etc. Characterize fish and wildlife uses (feeding, spawning, nesting, migration, etc.) and identify biota of special concern, i.e., endangered or threatened species, management priorities, and selenium-sensitive species (e.g., centrarchid fishes, Lepomis sp., Micropterus sp.; waterbirds such as stilts, Recurvirostra sp.; and ducks, Anas sp.). Also, identify habitats where

bioaccumulation would likely be greatest (e.g., wetlands, lakes, reservoirs and other impoundments, and off-channel backwater areas of rivers).

Step 2): Determine if selenium is present at hazardous levels in the HU.

Gather information on selenium concentrations. If there is no recent monitoring data (within the past 3 years), or if the data do not satisfy the following requirements, then it will be necessary to collect and analyze new samples. Selenium concentrations are needed for 5 ecosystem components: water, sediments, benthic macroinvertebrates, fish eggs, and aquatic bird eggs (use fish/bird tissue to egg conversion factor of 3.3 if no eggs are available; i.e., tissue concentration X 3.3 = approximate egg concentration; Lemly and Smith, 1987). If bird eggs **OR** fish eggs cannot be obtained (but not both missing), a 4-component assessment can be done. Collect a minimum of 10 samples of each component in each major habitat type present in the HU (stream, river, off-channel bay, wetland, lake, reservoir, other impoundment). Make sure to designate sampling sites throughout the HU to provide adequate spatial coverage. Maintain high quality assurance/quality control in all sampling and analysis; document QA/QC procedures for future reference. Evaluate selenium concentrations with hazard assessment protocol (Lemly, 1995 for 5-component datasets; Lemly, 1996 for 4-component datasets) to determine the hazard rating. A rating of low, moderate, or high hazard indicates that the TMDL process should continue. A rating of either minimal or no hazard indicates that TMDL calculations are not necessary, but the HU should be monitored by applying the assessment protocol to selenium measurements made on a 3-year interval.

If monitoring reveals that hazard has increased above the minimal level, TMDL reductions are needed.

Step 3): Determine selenium sources, concentrations, and discharge volumes.

Identify all possible sources of selenium (agricultural, industrial, petrochemical, mining, etc.) and map them in the HU, noting their proximity/discharge to specific habitat types, i.e., wetlands, streams, rivers, reservoirs, etc. Determine/verify selenium concentrations from each source using existing data or by analyzing new samples; determine/estimate average discharge volume from each source. Calculate total existing selenium loading rate to the HU (kg/day).

Step 4): Estimate the retention capacity of the HU for selenium.

A key part of the TMDL process for selenium is to estimate retention capacity (RC). This will determine the sensitivity of the HU to selenium and, thereby, serve as an indicator of how much selenium the system can tolerate. For the purposes of this paper, RC is defined as the propensity of a system to accumulate and conserve selenium. Components of RC include bioaccumulation, detrital retention, physical and chemical sequestration, and recycling within the HU. The more that selenium is held within a HU – whether incorporated in biota, deposited in sediments, etc., – the higher the RC. It is necessary to know RC in order to develop an environmentally sound TMDL because the higher the RC, the lower the TMDL has to be to prevent toxic threats to fish and wildlife.

To a large extent, RC depends on the degree of bioaccumulation and internal recycling in the HU, which is reflected in (1) primary productivity, (2) water flow regime, and (3) sediment type. From the characterization of HU done in Step 1 (above), information on these three factors should be available for each aquatic habitat. Use the matrix in Table 1 to assign each of these factors a separate RC rating; low, medium, or high. A rating should be done for each distinct habitat in the HU, i.e., each main-stem river, off-channel bay, stream, wetland, lake, reservoir, and other impoundment.

An overall RC rating for each habitat is determined by combining the three factor ratings as follows:

3 low ratings = low RC

2 low and 1 medium = low RC

2 low and 1 high = medium RC

2 medium and 1 low = medium RC

2 medium and 1 high = medium RC

3 medium ratings = medium RC

2 high and 1 low = medium RC

2 high and 1 medium = high RC

3 high ratings = high RC

The final RC rating for the HU should be set equal to the highest individual habitat rating. For example, if there are two habitats with low RC and one with medium RC, the final RC rating for the HU is medium.

Step 5): Calculate the total allowable selenium load.

Begin by plugging the hazard rating from Step 2, and the RC from Step 4, into the matrix in Table 2. The table indicates the appropriate amount of load reduction needed: small, medium, or large. The total existing selenium load should be reduced by 10% if the amount designated is small, 25% if it is medium, and 50% if it is large. Subtract the indicated amount from the total existing selenium loading rate (kg/day) calculated in Step 3. This will yield the total allowable selenium load for the HU.

Step 6): Allocate total allowable selenium load among discharge sources.

Designate allowable discharges making sure to keep habitat type and sensitive species in mind. For example, it would be inappropriate to allow the largest loading to occur in habitats occupied by priority species (threatened or endangered, or management priority), selenium-sensitive species (e.g., centrarchid fishes, Lepomis sp., Micropterus sp.; waterbirds such as stilts, Recurvirostra sp.; and ducks, Anas sp.), or where bioaccumulation would likely be greatest (e.g., in a wetland, lake, reservoir, or off-channel backwater area of a river).

Step 7): Monitor to determine effectiveness of selenium load reduction in meeting environmental quality goals.

The objective of the TMDL process is to keep selenium concentrations below levels that are toxic to biota. Therefore, it is important to use environmental quality goals as a guide in follow-up effectiveness monitoring. For this purpose, I recommend that the following guidelines be used as maximum allowable selenium concentrations (Lemly, 1993a, 1995):

Water = 2 µg/l, filtered samples (0.45 µm)

Sediment = 2 µg/g dry weight

Benthic invertebrates = 3 µg/g dry weight

Fish tissues: whole body = 4 µg/g dry weight

skeletal muscle (skinless fillets) = 8 µg/g dry weight

liver = 12 µg/g dry weight

ovary and eggs = 10 µg/g dry weight

Aquatic bird tissues: liver = 10 µg/g dry weight

eggs = 3 µg/g dry weight

These guideline values represent concentrations that are protective of fish and wildlife reproduction. Monitor selenium residues annually, and apply hazard assessment protocols (same as for Step 2) to determine if hazard is reduced to either the minimal or no hazard level. If it is, then no further load reductions are necessary –

conduct environmental monitoring every 3 years. If it isn't, repeat Step 5 to determine the additional amount of selenium load reduction necessary, implement load reduction, and monitor annually. The entire TMDL process is summarized in Figure 2.

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Table 1. Retention capacity (RC) ratings for selenium in aquatic systems based on habitat type and general biological/physical characteristics.

	Habitat Type		
	Stream, Main-Stem River	Lake, Reservoir, Off-Channel Bay, Impoundment	Wetland
Productivity			
High (eutrophic)	High	High	High
Moderate (mesotrophic)	Medium	Medium	Medium
Low (oligotrophic)	Low	Low	Low
Flow			
Swift	Low	Low	Low
Moderate	Medium	Medium	Medium
Slow	High	High	High
Sediment			
Inorganic	Low	Low	Low
Mixed	Medium	Medium	Medium
Organic	High	High	High

Table 2. Amount of selenium load reduction necessary for a hydrological unit (HU) based on hazard rating and retention capacity (RC).

	Hazard Rating		
	Low	Moderate	High
RC of HU			
Low	Small	Medium	Large
Medium	Medium	Medium	Large
High	Medium	Large	Large

Figure 1. Illustration of the "hydrological unit" concept. Arrows indicate the relative concentrations of selenium. The interconnected parts of a unit may include several types of aquatic habitats; for example, a main-stem river, an off-channel wetland, and a reservoir. The hydrological connections transport selenium throughout the unit and thus greatly influence its bioaccumulation potential. Because of this, the entire hydrological unit should be the "water body" that is used to develop a TMDL for selenium.

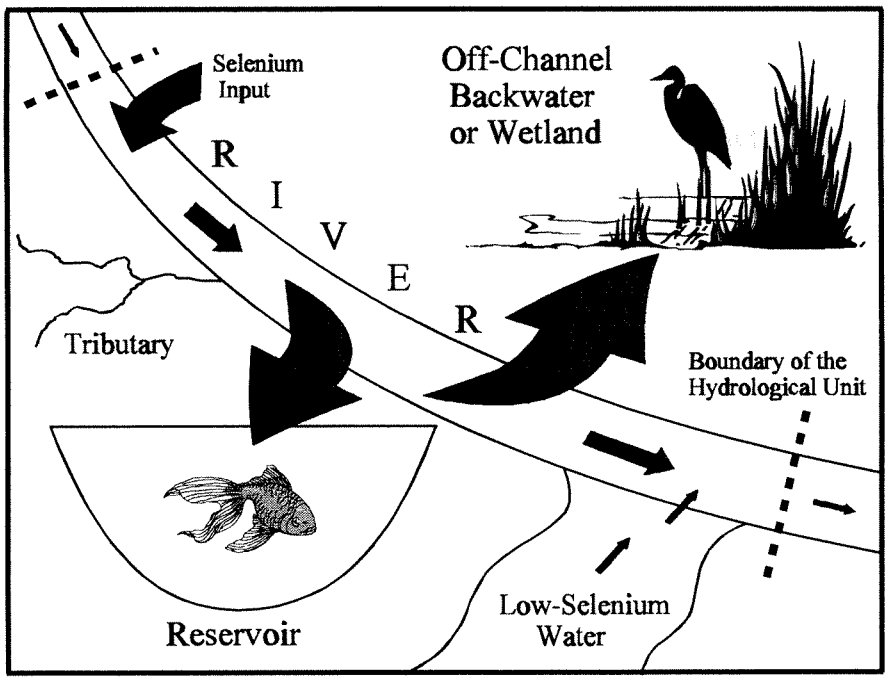

Figure 2. Steps in the TMDL process for selenium.

TMDL DECISION TREE FOR SELENIUM

Delineate and characterize the Hydrological Unit (HU)

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Measure selenium (Se) concentrations and determine hazard level

–	–
Low, moderate, or high hazard	Minimal or no hazard
–	–
Determine existing Se Load	Monitor Se concentrations

–

Estimate retention capacity of HU

–

Determine allowable Se load

–

Prescribe and implement Se load reduction

–

Monitor effectiveness of load reduction

–	–
Environmental Goals met	Goals Not met
–	–
Monitor Se concentrations	Further load reduction
	–
	Monitor Se concentrations