BASELINE SELENIUM IN SCULPINS RELATED TO THE NORTHEAST BRITISH COLUMBIA COAL ZONE

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ABSTRACT

Selenium (Se) is a contaminant of particular concern for coal mines in British Columbia and elsewhere. The primary concern is uptake of the organic form of Se by fish and water birds, potentially resulting in reproductive impairments of their offspring. Because the primary concern relates to dietary uptake, tissue Se concentrations are measured and compared to tissue threshold reference values (TRVs) to determine whether or not there is a potential risk. However, Se is also an essential element that can be preferentially accumulated by organisms. Thus, background tissue concentrations need to be determined to reduce uncertainties in the application of TRVs. Extensive coal mining development is presently occurring in the northeast of British Columbia (B.C.), Canada, where the rocks are Se-enriched such that natural background concentrations can be elevated. This paper reports on the determination of background Se concentrations in whole bodies of slimy sculpin (*Cottus cognatus*) collected from reference areas both inside and outside the coal zone. Sculpins collected from reference areas within the coal zone generally had higher Se whole body concentrations than those outside the coal zone and consistently exceeded the current B.C. fish whole body draft interim Se guidelines, sometimes also exceeding the 50 % higher USEPA draft fish whole body Se criterion for summer sampling. These data will be useful for assessing potential risks from Se released by coal mining in northeast B.C. and possibly elsewhere.

INTRODUCTION

Selenium (Se) is an essential element but, like all substances, it is toxic at elevated concentrations. It has two different modes of toxic action in the aquatic environment. Acute toxicity occurs at relatively high water-borne Se concentrations via similar mechanisms as the toxic responses of other inorganic substances such as metals. Specifically, uptake occurs via the gills or other respiratory structures with consequent disruption of physiological processes. Available scientific data indicate that chronic toxicity in the aquatic environment to fish and water birds is related not to water column inorganic Se concentrations, but rather to organo-Se body burdens, which are derived from dietary sources (USEPA 1998).

Mining for coal accelerates the natural release of Se from rocks containing naturally elevated concentrations. Determining whether or not Se at particular mines could be hazardous to resident fish and water birds typically involves comparison of measured tissue concentrations to generic tissue threshold reference values (TRVs) (Hamilton 2002; Sappington 2002). However, Se is also a natural essential element that can be preferentially accumulated by organisms. Thus, background tissue concentrations need to be determined to reduce uncertainties in the application of TRVs. This paper reports such determinations for whole bodies of slimy sculpin (*Cottus cognatus*) collected from reference areas both inside and outside the coal zone of northeast British Columbia. This sculpin species has very high site fidelity (Gray et al. 2004) and is currently being used to monitor tissue Se concentrations associated with mining activities at all northeast coal mines (present and proposed), thus the findings of this study are directly applicable to on-going environmental protection efforts.

METHODS

Slimy sculpin were collected opportunistically from reference sites both within and outside the coal zone by a variety of methods by both Ministry of Environment (MOE) personnel and proponents of new coal mines in the region (at the request of MOE). At each site, captured sculpins were placed into individual, labeled, re-sealable plastic bags. Where single fish weighed in excess of 8 g (the minimum weight necessary for total Se and percent moisture analyses), they were placed in individual bags as single tissue samples. In cases where fish were small, and several individuals were required to bring the sample weight to 8 g or greater, samples comprised composites of several fish.

At each site replicate samples were collected; samples collected comprised 1-15 sculpins per sample. Ministry of Environment collected a total of 92 samples at 24 sites. Mine proponents collected a total of 86 samples at 21 sites. An average of 4 samples was collected per site. Limited sampling and analysis was also conducted for other species (mountain whitefish, bull trout, rainbow trout). Those initial results are reported here.

While in the field, samples were held in ice-filled coolers. Once in the laboratory, fork lengths were measured and weights determined. Otoliths were removed for age determinations. After processing, the sculpin samples were stored frozen in their respective sample bags prior to whole body total Se and percent moisture analyses. Note that whole body samples were also analyzed for total metals; however, those results are not reported here.

Two separate chemical analytical laboratories conducted the analyses, with some overlap (16 samples split and analyzed by both laboratories) to compare results. Both laboratories achieved a level of detection of 0.1 µg/g ww [wet weight]. There were some differences in analytical methods. ALS (conducting analyses for proponents) digested their samples with a nitric acid/peroxide mixture, and analyzed the extracts with HVAAS. Maxxam (conducting analyses for MOE) digested their samples with nitric and hydrochloric acids and analyzed the extracts with ICPMS. Both laboratories met their internal data quality objectives.

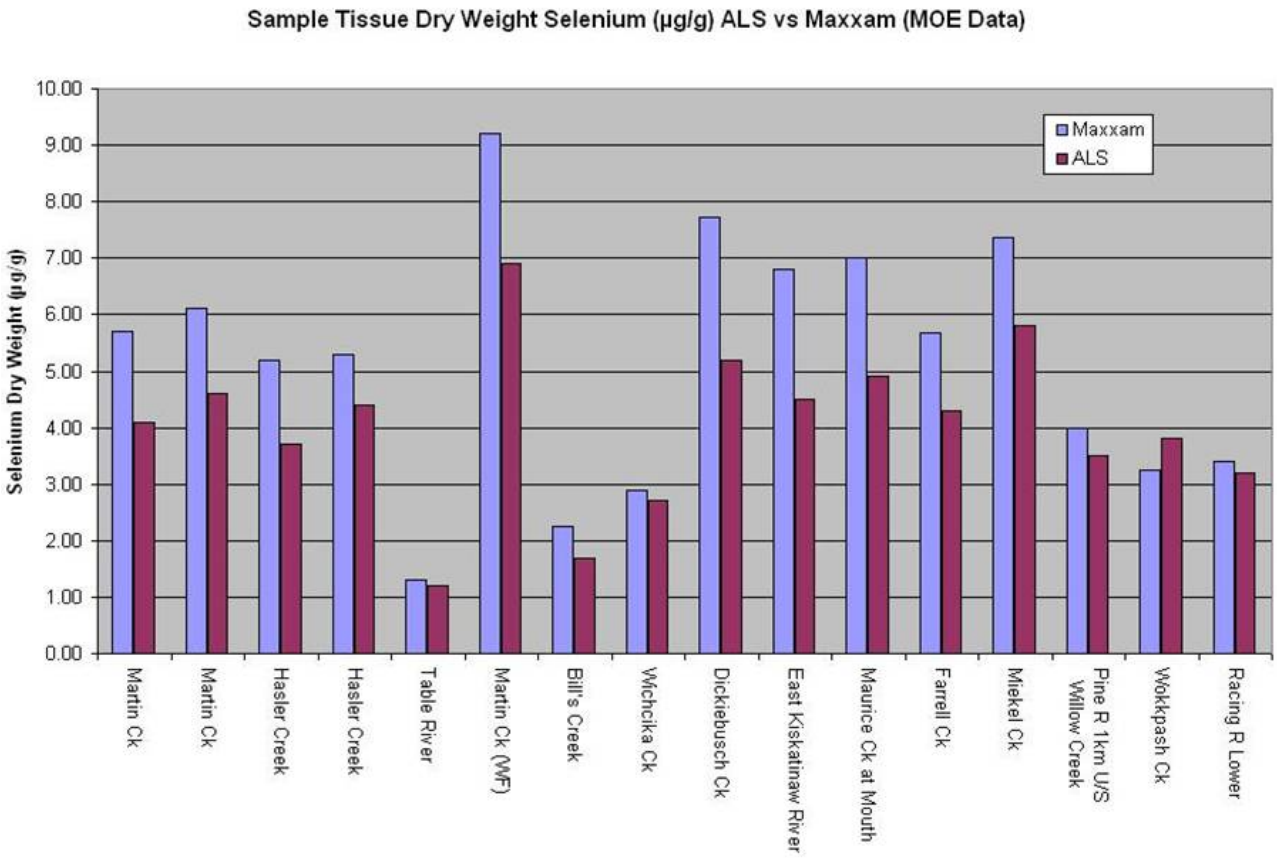
RESULTS AND DISCUSSION

Similar results were obtained by the two different analytical laboratories (Figure 1). The relative standard deviations ranged from 4 to 29%, averaging 17% (n=16), indicating good comparability between the two data sets. All but one split sample pair showed consistent direction of variation between laboratories, suggesting a systematic difference in Se recoveries.

The complete data set for sculpin whole body dry weight concentrations is shown in Figure 2. Coal zone sculpin whole bodies contained significantly more Se ($P<0.001$) than those outside the coal zone; sculpin whole body Se was directly related to coal seams absent mining of those seams, which latter would increase natural Se releases. In Figure 2 the sculpin data are also compared to the Ministry of Water, Land and Air Protection (now Ministry of Environment) (2001) interim draft whole body guideline (4.0 µg/g dw [dry weight] based on 75% moisture) and the USEPA (2004) draft fish whole body criteria (5.85 µg/g dw for summer sampling [EPA

revised] and 7.91 µg/g dw for winter sampling [EPA guideline]). Coal zone sculpin whole body Se concentrations usually ranged between the B.C. (4 µg/g dw) and USEPA (7.9 µg/g dw) TRVs. The 2001 B.C. draft interim guideline was exceeded in the majority of cases, indicating that this value is highly conservative, at least for this fish species and is thus not a useful TRV for assessing the hazard of whole sculpin Se concentrations. The USEPA (2004) winter draft criterion (7.91 µg/g dw) was less commonly exceeded, but was exceeded both in one unimpacted watershed and in one watershed associated with past coal extraction. This indicates that, while this TRV has generic utility, there may be instances where higher site-specific TRVs will be warranted. The limited overlap shown in Figure 2 between whole body Se concentrations inside and outside the coal zone might be explained in terms of small sample size (one replicate) or by minor adjustments to the coalfield boundary.

Figure 1. Comparison of sculpin Se concentrations obtained by the two different analytical laboratories for the same samples.



Se concentrations in sculpin whole bodies were not related to fish lengths over the mean range tested (45 to 100 mm; data not shown). There was a good relationship between length and body weight (Figure 3). Concentrations of Se in the sculpin whole bodies were not age related (data not shown).

A comparison of whole body dry weight concentrations in coal zone slimy sculpin to other local species (limited data, usually of juveniles) is shown in Figure 4. While Se concentrations in mountain whitefish *(Prosopium williamsoni)* were similar to those of the higher levels in slimy sculpins, concentrations in bull trout

(Salvelinus confluentus) and rainbow trout *(Oncorhynchus mykiss)* were lower and similar to the 2001 B.C. interim draft whole body guideline (4.0 µg/g dw [dry weight] based on 75% moisture).

Slimy sculpins have a very broad distribution in Canada, are relatively easily collected (high densities in many locations), are small-bodied (facilitating whole body analyses), have short life-spans (4-5 years), mature early, have low mobility (they lack swim bladders and are territorial), and are not a protected or favored sport species. They have extremely high site fidelity (Gray et al. 2004), which is important relative to comparisons between exposure routes and sources, and they are useful indicators of metal bioavailability related to possible adverse effects (Dubé et al. 2005). Thus, they are being used extensively in the northeast of B.C. for monitoring Se accumulation related to coal mining activities. The results of the present study both support their continued use for this purpose and provide a basis for developing site-specific whole body sculpin Se tissue guidelines (TRVs) based on reference (background data) using procedures outlined by Chapman (2005).

Figure 2. Sculpin whole body Se concentrations ranked by fish from both outside and inside the coal zone and compared to applicable Se whole body TRVs. See text for additional explanation.

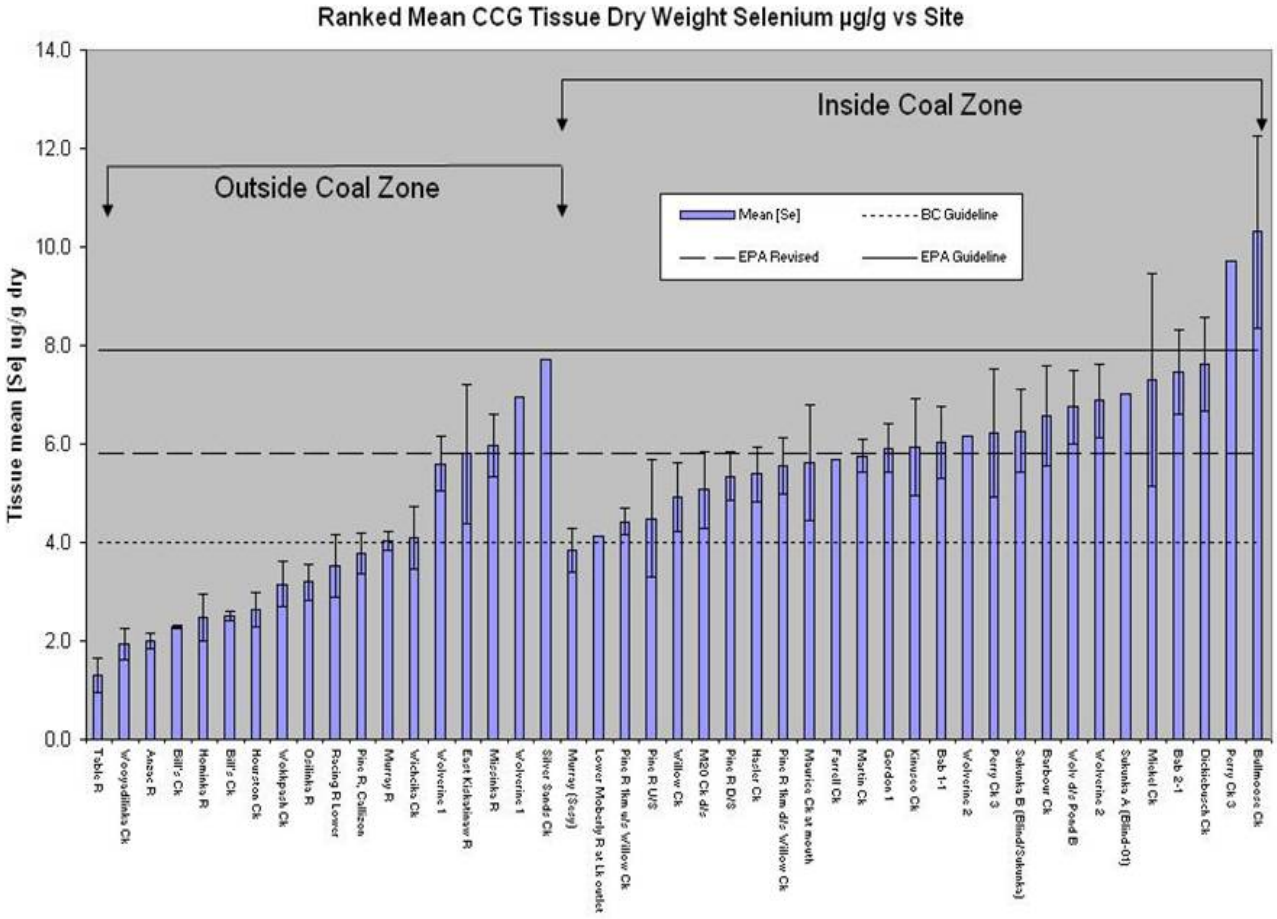


Figure 3. Sculpin length compared to weight.

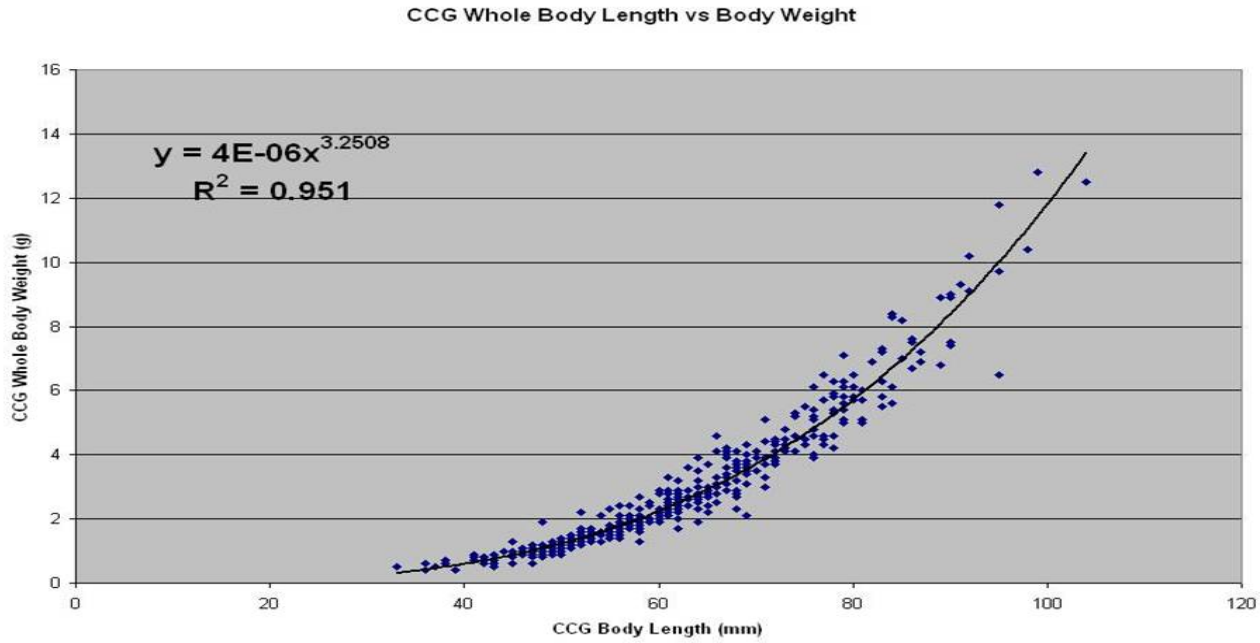
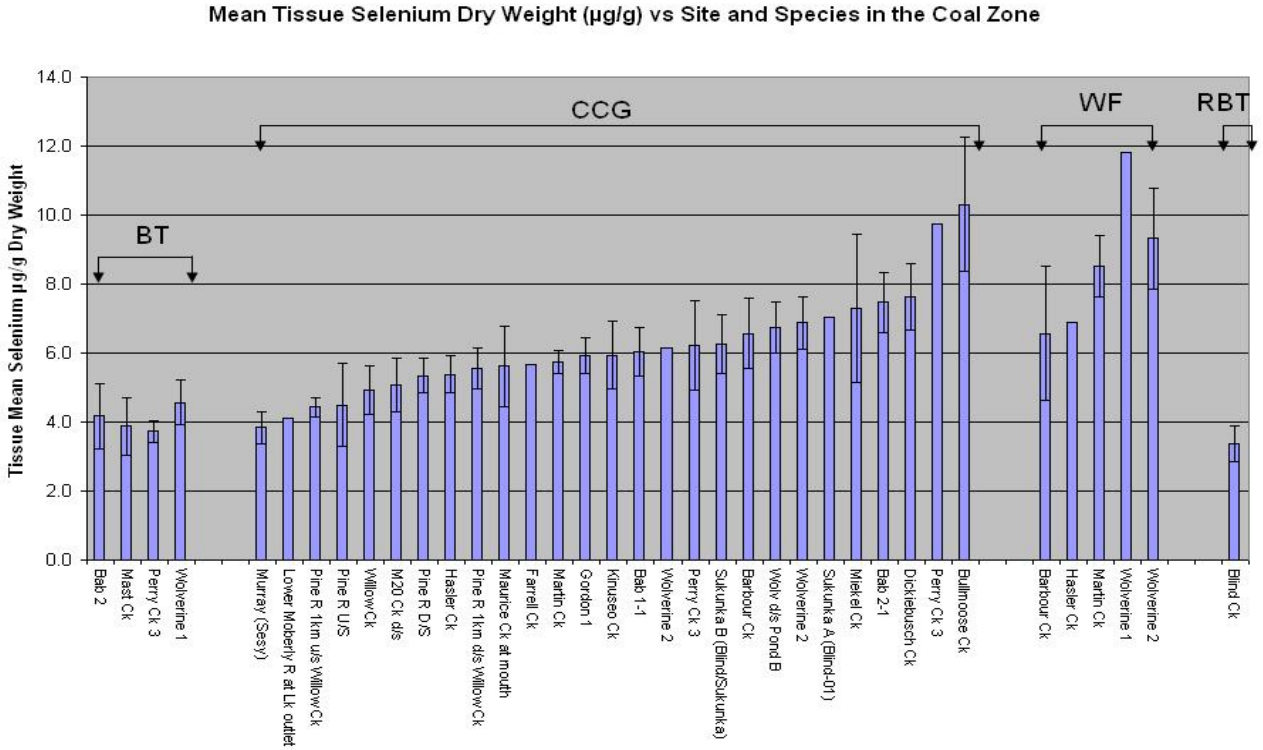


Figure 4. Whole body, mean tissue Se dry weight concentrations (ug/g) versus site and species inside the coal zone.



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