A Review and Analysis of the Data Provided in or Relevant to the TVA Kingston Dredge Plan and Foreseeable Selenium Contamination Risks

by Bryce F. Payne Jr., PhD* ----- 30 March 2009

I have reviewed and analyzed the selenium and related data in the TVA Dredge Plan to the extent practical given the limited data provided in the plan. Only two specific pieces of selenium data were provided in the Plan: an ash settling pond effluent selenium load of 2.84 lb/day under normal operations (without dredging) and a dredging selenium load based on a single reported extraction of an ash sediment sample extracted with river water. I have presumed from context and table labeling in the plan that the load values are for dissolved selenium though there is no clear indication of the basis for this classification (dissolved, total, or other) in the plan. I have compared the TVA dredge plan approach and data to my own findings regarding selenium in coal fly ash related to the 2005 coal fly ash spill in Pennsylvania as well as data from investigations by other scientists looking at ashes from other sources.

The Selenium Load in the TVA Kingston Ash Settling Pond Effluent

With regard to the 2.84 lb selenium per day load in the ash settling pond effluent, data from the scientific literature indicate the water solubility of selenium in fly ash can range from <1% to almost 70% depending on the ash, burn conditions and other factors that may vary considerably day to day. Using the assumptions in the plan and further assuming a fresh ash total selenium concentration of 3 ppm, the total normal daily operations output of selenium to the ash settling pond would be 6.4 lb per day. The daily effluent load of 2.84 lb/day in the Plan thus would represent a water solubility of 44% of the total selenium load in the fresh ash. This is high, but within the plausible range. If that rate is correct, then another difficulty follows.

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Specifically, a selenium concentration of 8.4 ppb in the ash settling pond effluent is given in the plan as the water concentration equivalent to the 2.84 lb/day load. This concentration is higher than desirable, but not alarming in its own rite. However, as a chronic, practically continuous dosing of selenium over the approximately 50 years of operations at TVA Kingston this discharge would have loaded the Clinch River with over 45,000 lb of selenium, presumably all as fresh ash selenite, a more rapidly toxic form of selenium. This approximates the selenium load at which the collapse of the fish populations in Belews Lake, NC became apparent. The already verified selenium loads in fish tissues (originally reported by Shea Tuberty at Appalachian State University and later confirmed by TDEC) clearly suggest the lower reaches of the Clinch and Emory Rivers and probably parts of Watts Bar Reservoir are suffering the effects of such a load. Any additional selenium load can be reasonably expected to have serious, long-term, harmful effects on the fishery in the Clinch and Emory Rivers and much if not all of Watts Bar Reservoir.

Estimates of Selenium Release
Due to the Planned TVA Kingston Phase I Ash Dredging

The dredge plan states that the toxic metal loads expected to result from dredging were estimated using data from a cursory river water extraction of a sample of spilled ash. The following are stated or apparent from the discussion and other data in the Plan. The extraction was extremely mild, "a quantity of ash was thoroughly mixed with river water and then allowed to settle for 1 hour." Interestingly, the Plan states that the one-hour exposure time was used "To simulate dredging followed by minimum time in the ash pond system". Then two sentences later, "As stated earlier the theoretical retention time in the ash pond is 2.68 days or 64 hours with three dredges in operation." Why a one-hour extraction is considered a reasonable simulation of a settling pond retention time of at least 64 hours is not explained in the Plan. Most who perform water or similar mild extractions of ash use continuous shaking for 12-24 hours, which would certainly seem to provide a better approximation of >64 hours in the ash settling pond. In my work I have favored collection of pore water from raw ash samples. Either of these approaches is more intense, and would appear a more reasonable approach, than the extraction used in the TVA Dredge Plan to estimate the amount of metals likely to be released during dredging.

The manner in which the data are used in the Plan suggest that the ash:water ratio for the extraction in the Plan must have been 15% ash:85% water, the solids concentration in the dredgings used in the Plan calculations. The ash-in-river-water extract was reported in the Plan to contain 10 ppb selenium (presumably dissolved). Using the relevant data in the Plan this can be corrected to a dry basis water solubility of selenium in the spilled ash of approximately 66 ppb. For a one-hour, 15% ash in water extraction this is a high result. In my experience, levels this high indicate that oxidation-releasable selenium could easily range up to several ppm or higher. That is, the mere presence of 66 ppb (dry basis) of easily water extractable selenium in the ash is cause for serious concern, particularly given that the river system probably cannot tolerate any additional selenium. If the aeration/oxidation of the ash associated with the dredging and processing goes as appears likely, and the probable associated release of selenium does occur, the selenium load to the river can be expected to exceed the load anticipated in the dredge plan by 10 to 100 fold, possibly more.

Recently the U.S. Fish and Wildlife Service subjected a sample of spilled ash to a modified Toxic Contaminants Leaching Procedure (TCLP). This is a mild acid extraction in which the sample is shaken in the TCLP extractant typically for about 18 hours. The resulting leachate contained 78 ppb of selenium, almost 8 times more than reported and used in the TVA Dredge Plan. Again, my experience has been that selenium likely to be released by the aeration/oxidation of the ash due to dredging will be 10 to 100 times greater than the TCLP extractable selenium, which was 8 times greater than the amount used in the Plan estimates.

As an alternative approach to the same issue, one can consider that the amount of selenium subject to potential release from the spilled ash must be something less than the total amount of selenium in the ash. Previous experience with fly ash in Pennsylvania, confirmed by recent SEM studies of the TVA Kingston ash (S.Tuberty and S.Carmichael at Appalachian State University), indicate a substantial portion of the total selenium is probably now associated with secondary minerals and subject to oxidation and release during dredging. There apparently have been no direct determinations of actual total selenium content of the spilled ash, but at present 3 ppm seems to be the value accepted by TDEC as reasonable. Assuming total selenium is 3 ppm, then for each 1 million tons of ash

dredged there will be 3 tons or 6000 lb of total selenium, a substantial portion of which is likely to be released. It appears unclear how much ash will actually be dredged during Phase 1, but 2 million tons seems a reasonable approximation. At the maximum dredge rates discussed in the plan of about 9,000 cubic yards per day (3,000 cubic yards per day per dredge with a possibility of 3 dredges running simultaneously), Phase 1 will take at least 220 days. That is, it would not be unreasonable to expect that a major fraction of all the selenium loaded into the river over the last 50 years could be added again in as little as 220 days of dredging as planned. The fact that Phase I dredging will probably take much longer than 220 days does not reduce the selenium risk posed because selenium is strongly conserved in the aquatic biota and sediment, and will bioaccumulate in fish and water birds regardless of whether the release occurs over 8 months or 18 months. Because the available selenium data are so limited, the preceding should be regarded as a conservative estimate of the likely release of selenium. The data needed to prepare a confident estimate have not been developed, or have not been made available.

It might be argued that an additional load of perhaps only a few thousand pounds of selenium would be minor in comparison to that already loaded into the river over the last 50 years of operations, and, therefore, would be likely to have no ill effects. This argument, however, fails to recognize:

- There apparently is no actual or useful selenium data for the past 50 years, not for total in the ash and not for selenium in the NPDES discharge water.
- The Dredge Plan estimate of 2.84 lb selenium per day loaded into the river by normal operations is of unknown or unspecified origin, and, though plausible, would suggest total selenium in the ash could be considerably higher than has been reported to date.
- Recently developed selenium data for the ash appears to be in dispute.
- There simply is no data at all on secondary minerals and adsorbed selenium in the spilled ash.
- The fish in the river already carry critical selenium burdens, in excess of 10 ppm (average) across different species and tissues.

Given this lack of quality, relevant selenium data, it must be recognized that the daily operational load of selenium into the river over the last 50 years could well have been considerably less than 2.84 lb per day. The fish tissue levels, however, confirm that even if the historical daily selenium load were lower, it has still been too heavy for the fishery. If the fish have accumulated the present selenium burden even though the NPDES discharge load was considerably lower than 2.84 lb/day, then the potential release of selenium due to dredging would be an even greater risk than suggested in the preceding paragraphs.

Serious consideration also needs to be given to the opposite possibility, the likelihood that the actual selenium levels in the spilled TVA Kingston ash are currently being underestimated. Underestimation is a serious possibility given that no appropriate data have been developed for the spilled TVA Kingston ash, and the TCLP results obtained by the FWS suggest the total selenium is likely greater than the presently accepted estimate of 3 ppm. The selenium data in a 1998 scientific paper (B. P. Jackson and W. P. Miller in the Journal of Analytical Atomic Spectrometry) provide a solid basis for an alternative, initial estimate of the total amount of selenium in the spilled ash and historically in the settling pond effluent. That 1998 investigation determined the total and water-soluble selenium levels in 23 different coal fly ashes from power plants in the southeastern U.S. Twenty-three different ashes is a large enough sample to provide a reliable estimate of an average value for coal fly ashes from southeastern U.S. plants. Given that the spilled ash was accumulated over the better part of 50 years of TVA Kingston operations, it is likely that the typical selenium level in the spilled ash is close to the average value of the 23 ashes in the 1998 study. That is, given the lack of direct TVA Kingston data, the data from the 1998 study should provide a reasonable estimate of likely selenium concentrations in the spilled ash. The 1998 study data showed an average total selenium concentration of 21 ppm and a water-soluble selenium concentration of 2.7 ppm. These likely values for selenium originally in the now spilled ash suggest the average daily historical selenium load in the ash settling pond effluent would have been around 6 lb/day. This estimate raises the likely historical selenium load into the Clinch and Emory Rivers and Watts Bar Reservoir due to discharge of the TVA Kingston ash settling pond effluent to 90,000 pounds. The 1998 study data indicate the total selenium of which a major portion could be released by aeration/oxidation due to Phase I dredging might well be over 80,000 lb, and if the same dredging approach were applied

to the other 3 million tons or so of ash that Phase I will leave in the river the total amount would rise to 200,000 pounds.

Complicating the situation further is the fact that an impending selenium release will probably not be apparent in water monitoring data for a month or more after dredging begins. Even then, it will not be noticed if monitoring points are not properly selected and carefully monitored. Among the sampling points currently being monitored, the settling pond effluent will likely be the first to be appreciably affected by the expected selenium release. Unfortunately the high and noisy chemical, especially selenium, background at this sampling point could make early detection difficult if not impossible. By the time a selenium release does become detectable a large amount will already be undergoing oxidation that will lead to release. In practical terms that oxidation process will be unstoppable, and, once in the river system, the released selenium will not be recoverable. The TVA Dredge Plan contains other data that need similar scrutiny. However, at this time the selenium threat appears sufficiently severe to require immediate and appropriate assessment at least in conjunction with or, preferably, before full scale dredging proceeds. This is a large, real world risk and an opportunity to acquire data to prevent possible destruction of the Watts Bar Reservoir system fishery that can be expected to result from the planned dredging, and to gather data that would enable economically and environmentally responsible protection of other fisheries all over the U.S. while enabling more responsible use of coal as an economically essential fuel.

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