

## **Response to Public Comments on 8/18/09 Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority (TVA) Kingston Fossil Plant**

**December 2009**

### **I. Introduction**

An EPA Science Panel was charged to assess selenium (Se) effects on the ecosystem. All of the Se data and conclusions drawn in this report will be considered in the ecological risk assessment (ERA) that is currently being conducted for the TVA spill. The Office of Solid Waste and Emergency Response (OSWER) and Risk Assessment Forum have developed guidance documents (e.g. USEPA 1997, 1998) that seek to align the results of site investigations with the needs of risk managers. A common theme of the guidance documents that describe elements of risk-based decision making is the call for the development of a problem formulation early in the process. Problem formulation is a systematic planning step identifying the major factors to be considered and is linked to the regulatory and policy contexts of the assessment. The process of problem formulation has as its products: assessment endpoints, a site conceptual model with working hypotheses, and development of an analysis plan. In the Science Panel review (<http://www.epakingstontva.com>), we prepared a preliminary problem formulation for the site that described what monitoring could be the most beneficial for informing OSWER actions for Se on the site.

After publication of the Science Panel review paper on the Region 4 website, there was a public comment period, during which we received comments from four parties: Drs. Payne, Lemly, and Skorupa, and the Tennessee Valley Authority. This document summarizes the key comments of these four submitters, and provides discussion or responses to them. They are intended for the consideration of those responsible for the risk assessment and cleanup as well as for the commenters and the public. It was not the mandate or intent of the Panel to serve in an ongoing capacity as advisors, but rather to provide our views on these issues at one point in time and based on the information available in summer 2009. In many respects, the data available then is being superseded by the ongoing collection of data, and in some cases we are indicating where that data may be obtained.

Following publication of the Science Panel review paper, additional data were received from Tuberty et al., including analytical results from fish collected in March 2009 and corresponding quality control (QC) data for both January and March fish tissue samples. Additionally, QC data for water and fish samples reported by the State of Tennessee and information on the method detection limit (MDL) and practical quantitation limit (PQL) for surface water samples reported by Ruhl et al. (2009) have since been received. Data from each source evaluated in the report (TVA, State of TN, Ruhl et al. and Tuberty et al.) have equally been reviewed by the Panel.

EPA Region 4 contractors reviewed a subset of data from TVA and TDEC. The TDEC samples consisted of 12 water samples collected between March 24 and May 12, 2009, and five fish samples collected between February 12 and April 1, 2009. All samples were analyzed by ICP-MS. The reviewer found the State of Tennessee Department of Health Environmental Laboratories' validation to be acceptable, with one exception. One water sample the TN State

lab had reported as estimated (i.e., J flagged) was determined to be nondetected (i.e., UJ flagged) due to instrumental baseline instability. The subset of TVA data that were reviewed consisted of 38 water samples collected between January 9 and April 29, 2009, and 33 fish samples collected between January 9 and February 25, 2009. Like TDEC's samples, the TVA samples were analyzed by ICP-MS. All water and fish sample results were found to be acceptable.

The reviews of data made in this document should not be considered as a substitute for extensive data evaluation (typically called 'validation') performed prior to use of analytical data in a Superfund risk assessment. Reviews of data adequacy for risk assessment are usually performed according to USEPA Contract Laboratory Program National Functional Guidelines (OSWER 9240.1-45 EPA 540-R-04-004 October 2004) or other similar sets of guidelines.

The reported MDL for the published data by Ruhl et al. (2009) is 0.5 ug/L and the PQL is 1.6 ug/L. On this basis, the Panel notes that all of the results for total Se, except for one sample report at the MDL, should be considered as non-detects (NDs) because the reported values are below the MDL. Additionally, all data for dissolved Se falling below 0.5 ug/L should be considered as NDs and any data reported between 0.5 ug/L and 1.6 ug/L should be considered as estimated.

The January and March fish tissue data from Tuberty et al. have been reviewed by the Panel as an appendix to this report (see below).

TVA has described, in summary form in its comments, a variety of bioaccumulation and toxicity studies not reviewed by the Science Panel that may contribute to the overall ERA of the areas potentially impacted by the spill. All biotic and abiotic data, including total metal scans and other chemical analyses, will be evaluated in the ERA to determine which metals and/or chemicals potentially pose unacceptable risks to plants and wildlife. In addition, bioassay results and physical/chemical measurements taken in the field will be integrated into the ERA process. As a result of the problem formulation, the ecological effects of contaminants, fate and transport of the contaminants, complete exposure pathways, and ecosystems potentially at risk will be evaluated. (see Appendix F of the Science Panel Review document for a description of the proposed sampling and analysis methodology and the scope of work for a number of these studies. Appendix G provides reviews of this proposed work. TVA noted that this work has been completed, and the data will eventually be posted on the TVA site. <http://www.tva.gov/kingston/index.htm>).

## **II. Summary and Responses to Comments**

### **A. General Comments**

Dr. Payne: "Commentary and conclusions with respect to selenium and its behaviors and impacts in general were sound."

Dr. Lemly: "The review is OK with respect to its designated values for hazardous levels of Selenium in fish and the tiered monitoring strategy."

Dr. Skorupa: “The screening values appropriately and accurately represent current knowledge and the specific trigger values chosen by Sette et al. (2009: Table 3) are scientifically defensible.”

## B. Individual Comments

Bryce Payne, Ph.D. Comments on USEPA Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant, An EPA Science Panel Review Paper. August 18, 2009.

1. Dr. Payne submitted two clarifications for the record with regard to his original letter included as Appendix D in the EPA Science Panel Review Paper.

RESPONSE: Appendix D has been footnoted with Dr. Payne’s comments.

2. Dr. Payne believes that there is little or no chance that a Se contamination problem will be assessable by sampling river water, even if there is substantial bioaccumulation.

RESPONSE: Recognizing the potential shortcomings of water sampling, the Panel has already recommended fish tissue monitoring as part of the Tier 1 measurements to be made along with surface water measurements. The Panel believes that both sources may provide important data.

3. Dr. Payne raises an issue about the bioavailability of particulate Se, citing Presser.

RESPONSE: The Luoma-Presser approach starts from dissolved inorganic Se taken up by algae, which convert it to organic Se, and is bioaccumulated. Since such algae are particles, the accumulated Se is thus organic bio-particulate Se. But it is important not to treat organic Se in that biomass, as modeled by Luoma and Presser, the same as inorganic abiotic particulate Se.

Plants do not absorb particulate Se. And for animals, the direct bioavailability of inorganic Se, whether dissolved or ingested as particulates, is low and so not considered a concern in real-world contamination problems.

4. Dr. Payne notes a disparity between Tuberty’s fish tissue levels and low water levels.

RESPONSE: The Panel acknowledges that the reviewed water levels seem low (See Skorupa comment no 4.), but has not found a basis to question the soundness of the measurements. While as noted, surface water levels may not reflect the bioaccumulation that may occur, the Panel has a number of questions about the reliability of the Tuberty et al. fish tissue analyses (see appendix below).

5. Dr. Payne questions whether 5 ppm, which is the screening level for fish tissue, can be reliably measured in fish.

RESPONSE: The Panel acknowledges that it is challenging to measure levels of 5 ppm and less in fish tissue. But our analysis found that TVA calculated a Method Detection Level (MDL) of 0.7 -1.0 mg/kg and estimated the Maximum Quantification Level (MQL) at about 5 times those levels, i.e. up to 5.0 mg/kg (or 5 ppm). The State of Tennessee Laboratory calculated an MDL of 0.13 mg/kg and found most of its results below the MQL. Thus, while for both of these sets of fish tissue data, the results were considered to be estimated for sample concentrations below the MQL and above the MDL, concentrations in fish tissue in the range of 5 ppm were achievable.

6. Dr. Payne questions whether the fish ovaries and bird eggs would be available in a time frame to evaluate their Se concentrations as called for in Tier 2.

RESPONSE: The Panel acknowledges that unless the ovaries are mature, they may be too small to sample, and so, ovary sampling, like bird egg sampling, may only be done seasonally. It is thus an inherent, acknowledged limitation of that approach. Nonetheless, they are believed to be critically sensitive organs, and so should be measured when they are available. It should also be noted here that our listed concentrations are intended to be below levels associated with actual effects.

7. There is a need for evaluation of the Se in the ash, since it is the source of the problem and the place where the most reliably measurable concentrations are.

RESPONSE: As noted above, the Panel believes that focus on concentrations in air, water, sediments, and target species are an appropriate focus for examining bioavailable Se. As part of the ongoing site monitoring activities, soil and ash samples have been collected and analyzed by the US Fish and Wildlife Service (USFWS) (<http://www.fws.gov/contaminants/examples/Kingston.html>) TVA (<http://www.tva.gov/kingston/solids/index.htm>) and TDEC ([http://www.state.tn.us/environment/kingston/soil\\_ash.shtml](http://www.state.tn.us/environment/kingston/soil_ash.shtml)). Ford and Wilkin (2009, Appendix G of Review) provide commentary on TVA's proposed fly ash sampling and considerations for future monitoring and analyses that has been passed on to TVA.

8. There is a need to identify and correct analytical problems with water and fish tissue monitoring.

RESPONSE: The Panel agrees.

Dennis Lemly, Ph.D., USDA-Forest Service. Comments on USEPA *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant*, An EPA Science Panel Review Paper. August 18, 2009.

1. Dr. Lemly sees the discrepancy in analytical results among investigators, i.e., higher fish tissue levels from Tuberty et al. in comparison to low fish tissue levels from TVA and TDEC as a key issue. He also concludes that the Tuberty et al. data would meet the screening value for Tier 3 fish reproductive studies and for “equal consideration of adaptive management”; and suggests “steps to reduce Se inputs related to activities at the site.”

RESPONSE: The Panel has updated its review of Tuberty’s fish tissue data, based on additional quality control (QC) data and fish tissue data submitted after the last Panel review and found that this data is unreliable from an analytical perspective. Thus, it stands behind its earlier conclusion, that the limited data set of Se concentration in muscle tissue does not support the concept that the spill and subsequent dredging had significantly elevated the levels of Se in the fish tissue to levels that pose a risk to aquatic life, although the paucity of the fish data reviewed was insufficient to rule out this possibility with an adequate level of certainty. However, recognizing that noise is inherent in the analytical methods, it is the Panel’s recommendation that the site coordinators evaluate whether screening values are exceeded by considering the weight of evidence, rather than individual exceedances.

2. Dr. Lemly quotes the Panel review which states “Because of the significant time lag between Se mobilization and biological response, the monitoring strategy should be a systematic effort to track accumulation over time rather than simply collecting fish periodically or when certain concentration screening levels are reached.” p 17. He found it “is important to note that in addition to the lag for accumulation when selenium inputs begin, there will be an overshoot when inputs stop, that is, if concentrations begin to increase toward an "effect/unacceptable" level, they will go even higher before actions to stabilize or reduce them take effect. This is well documented in case examples for fish (Belews Lake) and wildlife (Kesterson National Wildlife Refuge). The resultant "ecosystem inertia" is like trying to stop a moving train.....if you want to stop it and avoid a crash (catastrophic selenium impacts) you have to apply the brake far in advance. It seems to me that's where we are now.....fish Se has moved toward an effect/unacceptable level (based on Dr. Tuberty's data) and now is the time to apply the brake.”

RESPONSE: Recognizing the above issues, the Panel has selected environmentally conservative screening values, such that potential problems are recognized prior to concentrations rising to toxic levels. Furthermore, the Panel also recommends that the site coordinators consider any temporal and spatial patterns that can be discerned in the data.

Joseph Skorupa, Ph.D., U.S. Fish and Wildlife Service. Technical Comments Regarding the Draft Report: on USEPA Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant: An EPA Science Panel Review Paper. August 18, 2009.

1. Dr. Skorupa states that “an ideal monitoring program would be generating fully quantitated data for Se in five compartments: (1) the ash slurry coming out of the river via dredging, (2) the affected water column, (3) the affected sediment, (4) the affected biota, and (5) the affected atmosphere.”

The Panel Review “does not identify a need to implement monitoring of selenium retrieval from the river, *via* dredging, including monitoring the ultimate fate of retrieved Se; especially if there is going to be any return discharge to the river from ash processing facilities. Given the inadequate implementation of water monitoring for mass balance accounting purposes (discussed below), quantitating the back flow of Se out of the river in dredge slurry becomes absolutely essential so that mass fluxes to the water column can be estimated indirectly (assuming that fluxes to sediment and biota will first move thru the water column).”

RESPONSE: The Panel’s Initial Site Conceptual Model identifies all of these exposure sources and targets cited by the commenter (Figure 2). The Panel supports the need for monitoring Se that may be discharged into the river as a result of the dredging, and the proposed TVA testing (Appendix F, Table 3, page 7) includes the sluice channel as the highest potential source for post dredging Se release, as well as sediments. Surface water monitoring, of course, close to the dredging site (i.e., plume), also is aimed at measuring Se release during the dredging.

2. Dr. Skorupa asserts that “the water monitoring program has been inadequate for mass balance accounting (and therefore inadequate for ecological risk assessment) because of MDLs that are simply too high. A non-detect frequency of greater than 90% means we can’t even make educated guesses about Se mass fluxes to the water column. Water analyses currently are being conducted by routine analytical methods not suited to the situation at hand. Those methods were specifically designed with reference to regulatory compliance values ranging from 5-20 ug Se/L. Under the extraordinary circumstances of the Kingston spill, and given the high value to the public of the Watts Bar Reservoir aquatic system, and given that ecological effects from selenium are known to be possible at water column concentrations well below 5-20 ug Se/L (as noted by Sette et al. 2009), non-routine methods for water analyses of Se capable of quantitating concentrations below 1 ug/L should be implemented immediately.”

RESPONSE: The Panel does not agree that a high % of non-detects renders water monitoring inadequate for ecological risk assessment. The Panel has reviewed both TVA and TDEC data which established MDLs of 0.1-3 ug/L, and 1.3 ug/L, respectively. Our recommended level of concern for considering additional testing is 2 ug/L, which while estimated, should, for the most part, be above these MDLs. Careful analyses of these monitoring data are an important and challenging component of monitoring this site.

3. Dr. Skorupa notes that “The National Environmental Methods Index (NEMI; [www.nemi.gov](http://www.nemi.gov)) profile for USEPA method 200.8 reports a MDL of no better than 7.9 ug/L based on a joint EPA-AOAC 13-laboratory round robin validation. This raises the question of how detection limits of 0.1 to 1.3 ug/L as reported for EPA method 200.8 in the data summarized in Sette et al. (2009) have been validated? Does this discrepancy deserve some discussion and/or explanation?”

RESPONSE: The most current revision of EPA Method 200.8 was published in 1994. Advances in the ICP/MS instrumentation and analytical methodology since this publication have led to MDLs which are much less than the 7.9  $\mu\text{g/L}$  reported in the original method. Many accredited laboratories routinely perform MDL studies as part of their certification programs and have reported MDLs as low as 0.1  $\mu\text{g/L}$ . The Panel believes the reported MDLs for Se in water are consistent with the current science. In addition to the MDLs provided in the report, a national CLP laboratory reported an MDL of 0.19  $\mu\text{g/L}$  in the first fiscal quarter of 2009 and an EPA laboratory reported MDLs of 0.08 and 0.19  $\mu\text{g/L}$  in May 2009 and December 2008, respectively.

4. Dr. Skorupa wrote that “I am also perplexed by the large number of non-detects at a reported MDL of 0.1 ug/L. Values below 0.1 ug/L would be typical of rivers in selenium-deficient watersheds (e.g., Maier and Knight 1994). Given the long history of substantive selenium discharges from the Kingston Fossil Plant even before the spill, it seems very odd that the river would be analyzing out in the Se-deficient range. Furthermore, EPA’s mass balance model write-up (Sette et al. 2009: Appendix E) reports “...significant loading [0.5-2 ug Se/L] from outside [upstream, ERM 12.1] the model domain...” that carries through all the way to the Clinch River. Again, if there is significant upstream boundary loading of Se in addition to substantive historical loading from NPDES permitted Kingston Fossil Plant discharges, how can the river be analyzing out in the selenium-deficient range (i.e., <0.1 ug Se/L)? The review comprehensively summarizes available data from water analyses, but should there also be an attempt to evaluate whether those results make sense?”

RESPONSE: The Panel has considered this point, and shares the commenter’s perplexity. The Panel will forward this comment to the site managers for referral to TVA for further consideration in analyzing future water monitoring data.

5. Dr. Skorupa notes that “some stakeholders have claimed that the spatial design of post-spill water sampling at Kingston has been inappropriate ([www.thenation.com/doc/20090420/hearn/](http://www.thenation.com/doc/20090420/hearn/)), thus it seems like some discussion of this topic by Sette et al. (2009) might be warranted.”

RESPONSE: The Panel agrees that the spatial design of water (or any) sampling is an important consideration, but this was among many details of an overall testing plan that we deferred to those responsible for the site cleanup.

6. Dr. Skorupa finds that “The TVA and TDEC fish tissue analyses are inadequate for mass balance accounting due to MDLs that are too high (0.7-1.0 mg/Kg). Background levels of Se in fish tissues are typically about 1-2 mg/Kg, dry mass basis, thus to fully quantitate fish tissue selenium for mass balance accounting, MDLs in the range of 0.2 mg/Kg, dry mass basis, must be achieved.

RESPONSE: Mass balance accounting was not our goal. The Panel maintains that the MDLs in the 1.0 mg/Kg or less, dry mass basis, are sufficient to detect the screening values of interest.

7. The commenter asserts that “Sette et al. (2009) appear to choose the TVA/TDEC results over the Tuberty et al. results without a clearly documented basis for that choice. Resolving the reason(s) for cross team differences in fish tissue results should be conducted independent of water results.

RESPONSE: The Panel has now reviewed additional data from Tuberty et al. related to quality assurance evaluation of fish organ Se data collected in January of 2009 and additional fish data collected in March of 2009. That review is now included as an appendix to this report (see below) and articulates the basis of our analyses of the limitations of that data, including the relative insensitivity of the Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES) method used for analysis, in contrast to the ICP – Mass Spectrometry (ICP-MS) method used by TVA and TDEC.

8. Dr. Skorupa notes that “The proposed tiered monitoring scheme is conceptually sound and case-appropriate. My only recommendation for improvement would be to more precisely define statistically how exceedances of trigger values should be quantified. For water, is exceedance determined on an individual sample basis, on the basis of averages, on the basis of geometric means, on a minimum percentage of violating samples basis, etc, etc.? If using averages, will there be an averaging period? For fish and bird tissues, are there any prescriptions regarding particular species, trophic levels, age classes, genders, etc., etc., that should be sampled? And for fish/birds, just as for water, statistically, what constitutes exceedance of a trigger value? Maybe Sette et al. intended to leave such details to local site managers? If so, this should probably be mentioned.”

RESPONSE: The Panel agrees and endorses a weight of the evidence approach for evaluating exceedances of the screening values, including statistical analyses, and consideration of species, trophic levels, etc. in designing sampling plans. As suggested, we are leaving such details to the site manager.

Tennessee Valley Authority (TVA). 2009. Comments on EPA Science Panel paper, *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant*. August 18, 2009.

#### General comments

1. While a tiered strategy is a logical scientific approach, the commenter felt that a more aggressive approach is appropriate. TVA's ecological monitoring strategy includes site-specific bioaccumulation and toxicity studies. It also includes assessments of possible effects on populations and community structures and potential effects on reproduction, teratogenesis, and other stress responses at levels ranging from individual organisms to biological communities. TVA has carefully selected the fauna being sampled to ensure all relevant ecological compartments are included and that the strategy focuses on organisms most likely to be exposed or that will provide the most useful information for assessing environmental effects.

RESPONSE: TVA has described, in summary form, a variety of bioaccumulation and toxicity studies that can contribute to the overall ERA of the areas potentially impacted by the spill. These data will eventually be posted on the TVA site, <http://www.tva.gov/kingston/index.htm>.

As scientists, the Panel applauds the collection of any data that are appropriate for assessing these potential effects. All data will be evaluated during the ERA.

2. TVA believes the most effective approach is almost exactly the reverse of the tiered approach suggested in the Science Panel's report. Conducting Tier 2 and 3 monitoring first (but with greater taxonomic diversity), then backing down over time to Tier 1 and 2 monitoring if no significant bioaccumulation and/or adverse health effects are observed is a more pragmatic and defensible strategy.

RESPONSE: The Panel believes that a broad strategy incorporating measurements in water and other media, e.g. air and sediments, along with measurements and testing in target receptors is the best approach. While it supports testing at all tiers without regard to the screening values, there are a number of reasons why a tiered approach may be both practical and necessary. Some testing relies on fish or bird reproduction which is seasonal. Higher tier testing or surveys are more resource intensive, and so will be done less frequently. Water measurements, while they are measures of exposure and not internal measures of dose in the target receptors or measures of toxicity, may be done more frequently and over a wider area.

3. TVA questioned the value of water measurements and use of 2µg/L as a trigger for further testing. The substantial dilution of the Emory and Clinch Rivers may preclude detection of Se being leached into pore waters. Table 3 of the report identifies 5µg/L as EPA's screening value. The water quality and hydrologic setting of the Emory and Clinch Rivers do not indicate that there would be a high rate of Se precipitation and uptake into the food web. This is not a particularly lentic system, nor is the pH very high, nor is there a high organic content layer in the sediment. Consequently, there seems to be insufficient justification for proposing a trigger value for Se in water lower than the one currently in use (5µg/L).

RESPONSE: The screening values do not represent water quality criteria or clean-up targets. They are set at environmentally conservative levels with the intent to encourage moving to the next tier prior to the actual occurrence of biological effects at the site. The Panel's intent is consistent with TVA's previously stated preference for evaluating higher tiers early in the process.

4. TVA questioned the recommended trigger of 8 mg/Kg Se for bird eggs, noting that UDEQ 2008 had recommended a regulatory level of 12 mg/Kg Se in bird eggs, and that a scientist consulted had asserted that the probability of finding deformities in eggs at 8 mg/Kg or even 12 mg/Kg would be so low that more eggs than is feasible would need to be sampled to correlate deformities with those concentrations.

RESPONSE: Again, the screening values are not clean-up targets. Exceeding a screening value does not imply that effects are likely to be occurring. The Panel acknowledges that these comments speak to the conservative nature of the screening level benchmarks used in the tiered monitoring scheme. It is worth restating the intended uses of the screening levels for the reviewers from the document (page 6): "*1) they represent conservative, screening levels such that, when media concentrations from the site are found to be below those values, there is high confidence of no adverse effects occurring*"; also "*2) because they are screening values, the occurrence of exceedances does not indicate that adverse effects are occurring or will occur, only that the margin of safety is sufficiently reduced that further investigation at the Kingston site is thought to be appropriate, considering the resources available to carry out such investigations and level of concern the public has voiced.*" Therefore, the Panel agrees with the TVA reviewer (and outside expert) that if Se concentrations in abiotic or biotic media are found at the levels proposed, there would be little cause for concern for those receptors. As clearly stated in the document, the concentrations recommended in the tiered scheme were not to definitively demonstrate a risk, but rather alert site managers that bioaccumulation is occurring in an important pathway and further investigation MAY BE warranted.

5. TVA notes that "Exposure to nestlings may come thru contaminated diet, and this exposure route should be assessed. TVA's ecological assessment strategy includes analyses of levels of contaminants in mayfly larvae and adults, and levels of contaminants in both egg and hatchlings of tree sparrows, an obligate insectivorous avian species whose adults forage range is limited to approximately 200 meters of their nests."

"Egg-laying reptiles and amphibians also maternally transfer Se to their eggs. It remains unclear as to whether they are more or less sensitive than other egg-laying vertebrates. Consequently TVA has included herpetofauna in our assessments in order to more fully understand ecological impacts of the spill."

"There are several places in the report where fish-eating waterfowl are mentioned as prime indicators of exposure. Insectivorous birds feeding upon emerging insects (e.g., tree swallows) are also at high risk of exposure to Se and other ash-derived elements."

RESPONSE: The Panel appreciates TVA's effort to assess these other target species and exposure pathways. All of the data will be evaluated during the ERA.

6. TVA recognizes that Se is not the only constituent of concern in coal ash, and that in such a complex matrix there may be interactions among multiple constituents that make resultant toxicological outcomes difficult to predict. Because of the complexity of coal combustion wastes, drawing firm conclusions about toxicological effects based solely upon Se concentrations in water or tissue data would be short-sighted.

RESPONSE: Comment noted. The mandate of the Panel was to focus on Se as a toxicant of concern. All of the data will be evaluated during the ERA.

7. TVA also recognizes that in addition to direct toxicity of Se to fish and birds as addressed in this report, there can be indirect effects of coal ash on important ecological receptors. Major events such as the Kingston release may modify microbial communities and invertebrate assemblages, particularly in the benthic community. This has the potential to influence large scale ecological processes, such as nutrient cycling, independent of direct toxicity from trace constituents. In some cases, this could affect key receptor populations due to changes in availability of food resources.

RESPONSE: The Panel agrees. In Appendix G of the Panel Review, the reviewer specifically points out the potential utility of a benthic macroinvertebrate survey/monitoring program.

#### TVA Specific Comments and Edits

1. Page 1, Paragraph 2, the sentence reads as follows: “Chemical analyses for total metals including selenium (Se) and mercury (Hg) are part of the dredging monitoring program.” Suggest revising the sentence to “Chemical analyses for an extensive list of total and dissolved metals including arsenic (As), selenium (Se), and mercury (Hg) are part of the dredging monitoring program.” The last sentence reads as follows: “Additional testing, including toxicity and bioaccumulation tests, will be conducted.” Suggest revising the sentence to “Additional extensive testing, including toxicity and bioaccumulation testing, have been and continue to be conducted.”

RESPONSE: The suggested revision has been made in the report.

2. Page 1, Last Paragraph: The complex flow patterns around the Kingston Fossil Plant (KIF) are such that a comparison of data from the most downstream Emory River surface water location [Emory River Mile (ERM) 0.1] to upstream locations is misleading. Cooling water intake requirements for KIF necessitate drawing water from the Clinch River at approximately Clinch River Mile (CRM) 4 in the upstream direction on the Emory River with subsequent discharge back to the Clinch River above CRM 2.0 such that at during times the lower reach of the Emory is more like the Clinch River than upstream Emory River locations.

3. Page 11, Paragraph 3: The authors state “This subset of data was selected because it was collected at Emory River mile 0.1, a location at high risk for elevated levels for Se because it is located immediately downstream of the spill site”.

RESPONSE: The Panel acknowledges the complexity of flow patterns at this site as described by these comments. This information will be forwarded to the On-Site Coordinators to consider during future monitoring activities.

4. Page 2, Paragraph 1: The sentences read as follow: “The maximum dissolved concentration of lead (Pb) that exceeded the criteria benchmarks was for a sample collected on 04/03/09 and is not consistent with samples collected prior to, or after this date”; and “Further, dissolved Pb concentrations upstream of the spill were found to be higher.” A significant number of spurious dissolved lead detections during the referenced timeframe were traced to a series of lead metal surface water weights; these data have since been rejected during TVA’s data quality assurance procedures.

RESPONSE: The Panel has added a footnote in the text of the report describing this comment.

5. Page 2, Paragraph 3: “However” would be a better word to use in the last sentence in the paragraph immediately preceding section II, instead of “Although.”

RESPONSE: The suggested revision has been made in the report.

6. Page 2, Paragraph 1: The sentence reads as follows: “Further, absolute concentrations are not elevated in the downstream stations as mostly evident by nearly all of the metals having median levels below detection limits.” It appears that the limits should be referred to as “quantitation” or “reporting” limits instead of “detection limits.

RESPONSE: The sentence in the text references any result of an analyte that was reported as a non-numerical result (e.g. ND or < 1.3 ug/L, etc). In some cases the reference values are the minimum reporting levels, and in some cases the values are method detection levels. Reporting limits would have probably been sufficient to relay the message of a non-detect.

7. Page 5, Paragraph 4: The authors suggest that risk to aquatic biota should be determined in the “downstream reaches of the Tennessee River to Watts Bar Dam”, given that the distance from KIF to Watts Bar Dam is approximately 40 river miles, tying impacts to aquatic biota to KIF would be highly uncertain.

RESPONSE: Numerous Superfund sites in the western and southeastern USA (e.g., Clark Fork River, MT; Whitewood Creek, SD; Martin County, KY) clearly demonstrate the ability of fluvial mine wastes (which are heavier and larger particles than those at KIF) to relocate > 100 miles downstream of the point of uncontrolled release. Granted, these releases occurred over a much longer period of time. None-the-less, it would be imprudent to assume that downstream contamination as far as 40 miles is improbable. The Panel proposed the tiered approach to monitoring, in part, to allow a cost-effective assessment of distant downstream locations that could be affected by the spill.

8. Page 6, Paragraph 4: A reference should be provided for the statement that "Se is unlikely to bioaccumulate to a hazardous level if the filtered fraction of water samples is below 2 ug/L."

RESPONSE: This statement is referenced from Lemly, A.D. and J.P. Skorupa. 2007. Technical Issues Affecting the Implementation of US Environmental Protection Agency's Proposed Fish Tissue-Based Aquatic Criterion for Selenium. *Integrated Environmental Assessment and Management*, 3: 552-558

9. Page 7, Paragraph 1: References should be provided for the Tier 2 screening levels presented.

RESPONSE: The Panel notes the ambiguity between the text on Page 7 and the appropriate citation in Table 3. The text on Page 7 attributes the 10 mg/kg-dw screening value to ovary tissue, while the citation in Table 3 attributes the screening value to fish eggs, Ohlendorf et al., 2008. This ambiguity, however, reflects the interchangeable use of the tissues in review articles regarding critical tissue burdens in either eggs or ovaries. Species sensitivity distributions of Se in critical reproductive tissues will often include values for both eggs and ovaries on the same plots. Indeed, it is not unreasonable to consider that eggs being produced in the ovaries will reflect concentrations in those tissues.

10. Page 9, Paragraph 2: The authors state "TVA water samples were analyzed by multiple analytical laboratories". TVA has only used Test America once the problems with Microbac were discovered.

RESPONSE: Initial review of the data by the Panel did include data from Microbac. In this context, "multiple analytical laboratories" refer to two laboratories. As described in the next comment, TVA water samples were split and analyzed by multiple NELAP accredited analytical laboratories.

11. Page 9, Paragraph 3: The sentence reads as follows: "TVA water samples were analyzed by multiple analytical laboratories using EPA Method 200.8 for total and dissolved fractions." Suggest revising the sentence to "TVA water samples were split and analyzed by multiple NELAP accredited analytical laboratories using EPA Method 200.8 for total and dissolved fractions."

RESPONSE: The suggested revision has been made in the report.

12. Page 32, Table 2: The table reports the Microbac Laboratories' data for the 47 original samples of fly ash—that data did not pass TVA's validation process and was subsequently rejected, with retained samples being re-analyzed by another laboratory. The re-analyses were not available to provide to the review panel, and the new data is just now being posted to the TVA website to replace the Microbac data.

RESPONSE: Fly ash data reported by TVA are presented in Table 1 of the report. A footnote has been added to Table 1 regarding analytical results for the 47 fly ash samples reported by TVA as described in this comment.

13. Page 10, Paragraph 1: sentences read as follow: “It must be noted here that there is no quality control information provided within the publication, especially information detailing the laboratory's established MDLs. Typical ICP-MS MDLs are around 0.5 ug/L with MQLs and Practical Quantitation Limits (PQLs) approximately five times this concentration.” Perhaps additional information should be requested from Ruhl *et al.* to allow more definitive statements to be made relative to these data.

RESPONSE: At the Panel's request, Ruhl *et al* have provided further information regarding their procedures. The information received from Ruhl on 10/18/2009 indicates the MDL for the published data is 0.5 ug/L and a PQL of 1.6 ug/L. Based on this, all of the results for total Se, except for one sample report at 0.5 ug/L, should be considered as non-detects (NDs) because the reported values are below the MDL. All data for dissolved Se falling below 0.5 ug/L should be considered ND and any data reported between 0.5 ug/L and 1.6 ug/L should be considered as estimated. A footnote has been added to the text in this regard and data in Appendix B have been qualified as described.

14. Page 10, Paragraph 4: The authors state “TVA did not report MQL values...and therefore all the detections of Se in the sample should be considered estimated”. This is incorrect; analytical results are reported to the MQL therefore, all reported results have a high degree of certainty in their quantitation.

RESPONSE: This was an oversight in review of the data. MQLs were reported at approximately twice the MDL. The report should have stated that results between the MDL and MQL should be considered estimates. Values above the MQL should not be qualified. The text in the report has been revised to reflect this correction.

15. Page 17, Last Paragraph: The sentence reads as follows: “The sediment elutriate tests that use coal ash and waters taken directly from the site may provide useful information on the concentration and species of Se released during the suspension and oxidation of coal ash resulting from dredging activities that could be used in geochemical modeling.” The U.S. Army Engineer Research and Development Center has recently completed this work and its findings should be included in this report.

RESPONSE: Appendix F has been footnoted to reflect this comment and a link to the U.S. Army Engineer Research and Development Center Report has been added.

16. Page 28, Figure 2: The cross mark for soil in inverts is located in between two rows.

RESPONSE: This has been corrected in the report.

17. Page 29, Figure 3: The MDL legends for the lines in Figure 3 are reversed (TDEC has the higher detection limit)

RESPONSE: This has been corrected in the report.

18. Appendix B: This appendix should be updated with validated data at the time this document goes to press.

RESPONSE: Appendix B contains data that were available to the Panel at the time of review. Notes have been added to Appendix B to reflect the Panel's review of the QC data from the State of TN and Ruhl *et al.*

19. Appendix C: TDEC should be requested to provide data validation reports and/or a description of how its data were validated.

RESPONSE: Notes have been added to Appendix B to reflect the Panel's review of the QC data from the State of TN.

20. Appendix F: The work represented by this work plan has already been completed and the findings of that work should be included in this report.

RESPONSE: Appendix F has been footnoted to reflect this comment and a link to the TVA website has been added.

### **III. References**

USEPA. 1997. Ecological Risk Assessment Guidance for Superfund: Process for Designing and Conducting Ecological Risk Assessments. Interim Final. U.S. Environmental Protection Agency, Solid Waste and Emergency Response. EPA 540-R-97-006. June.  
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## APPENDIX

### **Review of Analytical Methodology and Results of Fish Organ Samples taken by Tuberty et al. from the TVA Ash Spill Site**

Tuberty et al. (2009) submitted to EPA results of January and March 2009 selenium analyses of fish organs from fish taken from the Emory, Clinch, and Tennessee River systems near the TVA fly ash spill site. Based on issues identified in the Panel's August 2009 review related to the sensitivity of the analytical method used on the January fish samples, the investigators provided additional information and fish data (March data), but they were received too late for our August review. Tuberty et al. submitted the final analytical results and accompanying quality control (QC) data. A review of this data was performed at EPA's Office of Emergency Management and EPA's Region 4 Analytical Support Branch in Athens, Georgia. Selenium has been the focus of an EPA science panel tasked with review of analytical data, issues, and actions taken by EPA, TDEC, TVA, and Tuberty et al. concerning the ash spill. This review only focuses on data supporting Tuberty et al.'s selenium fish tissue results received too late for the earlier Science Panel Review.

Tuberty et al. (2009) have collected 12 fish (5 species) from 2 sampling locations along the Emory River in January 2009 and 59 fish (5 species) from 6 sampling locations including 3 sites identified as reference locations along the Emory, Clinch and Tennessee Rivers in March 2009. Analyses of samples collected in January were conducted on tissues and organs including gastric caecum, muscle, stomach, liver, ovary, testes and spleen (62 tissue samples were analyzed). Analyses of samples collected in March were conducted on either muscle tissue or gonads (98 tissue samples were analyzed). These data are presented in Appendix C of the December 2009 EPA Science Panel Review Paper *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant* (<http://www.epakingstontva.com>).

Methodology: All fish organ samples were analyzed using Inductively Coupled Plasma – Atomic Emission Spectrometry (ICP-AES). ICP-AES is a well established analytical tool for analyzing numerous inorganic metals, including selenium, in environmental matrices. EPA has published two primary methods that utilize ICP-AES: for analysis of metals in water, EPA Method 200.7; and in aqueous and solid matrices, Method SW 846 6010C. The estimated detection limit for Method 200.7 is listed as 75 ug/L, and an estimated instrument detection level (IDL) of 50 ug/L for Method SW 846 6010C. The concentration of selenium found in the majority of the fish samples is well below 50 ug/L (concentration in the sample digestate which is not corrected for sample mass). Given these low selenium concentrations, the fact that the sample masses are extremely small, and that ICP-AES is subject to interference from aluminum, iron, and broadband carbon emission interferences at low concentrations, there is concern by EPA that the ICP-AES technique is not a sensitive enough technique to use for fish organ analysis for Se at low levels. A more appropriate technique would be the use of ICP-Mass Spectrometry (ICP-MS) using EPA Method 200.8 or SW 846 Method 6020A.

Detection/Reporting Limits: Tuberty et al. has provided data for establishment of Instrument Detection Levels (IDL), as opposed to a Method Detection Limit (MDL). IDLs are typically lower than the MDL and should not be used as reporting limits (EPA 6010C, Section 9.3). It is

unclear how the laboratory is using the IDL to qualify results. There are instances in the data reported in which the selenium concentration (in the digestate) is lower than the laboratory reported IDL of 5.99 ug/L. The laboratory should have established a Method Detection Limit (MDL) and a Reporting Limit (RL) to use with a tissue matrix instead of the IDL. The MDL provides an indication of data reliability at low concentrations. The RLs provide an indication of the uncertainty of results. Any result falling below the RL and above the MDL should be assumed to be an estimated value only.

One could potentially make use of the lowest, non-zero, calibration standard to establish a reporting level. It appears that from the January set of data, Tuberty et al. performed a complete six-point calibration analysis per 20 samples, with the low calibration standard set at 10ug/L. To appropriately establish 10 ug/L as the reporting level, the laboratory should have analyzed a verification check sample (approximately 10ug/L or lower selenium standard subjected to the same digestion and analytical procedures as the samples) for comparison against the calibration curve. It should be noted that this is a critical step, as the data indicates the lab's 10 ug/L calibration standard has an intensity only approximately 2 to 5 times greater than the analytical blanks analyzed with each set of calibration standards (see EPA Method 6010C, Section 10.1.3.1).

For the March data, it appears that Tuberty et al. sometimes used a 10 ug/L low calibration standard, but more often used a 50 ug/L low calibration standard for sample batches (batches of 20 samples). Without the analysis of check standards analyzed at or below the low calibration standards, a high level of uncertainty exists for results falling below the low calibration standards.

Spiked Analysis: The laboratory performed a Laboratory Fortified Blank (LFB), a Matrix Spike (MS) and Matrix Spike Duplicate (MSD) for every group of 20 samples. While these are required QC parameters within the analytical methods, the laboratory should have spiked all of these at concentrations that more appropriately matched the concentration of the samples analyzed. Even the LFB, which was spiked at a concentration of 200 ug/L, is approximately 10 times more concentrated than the samples themselves. At the concentrations of the LFB and the MS/MSD very little useful information can be gained as to the accuracy and precision of results at the levels reported in these samples. Also, it does appear that MS/MSD samples were analyzed from a single sample digestate, and not as separate samples. Separately weighed out fish organ samples should have been spiked and processed through the complete digestion process and analyzed as separate samples.

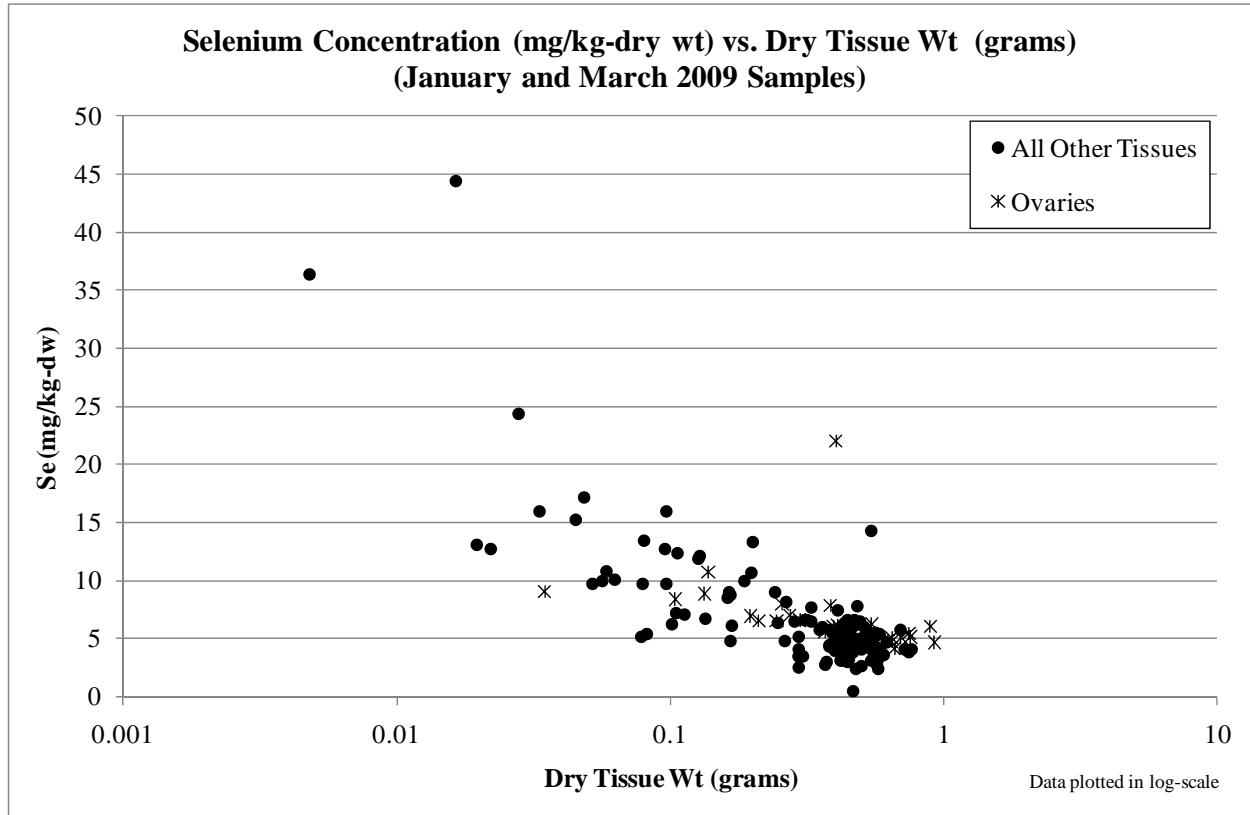
Duplicate Analysis: Duplicate analyses were run every 20 samples. However, it again appears that the lab did not actually weight out separate portions of a fish organ and process them through the digestion and analytical processes. It appears that only two separate aliquots of a single sample digestate were analyzed. This gives no useful information as to the precision and uncertainty of the preparation and analysis. Because of the very limited sample sizes, low concentration levels, and the fact that we may be making decisions based upon certain screening values, it is extremely important that the uncertainty around each analytical result is known.

Sample Mass: The ICP-AES and ICP-MS methods usually call for approximately 5 gram samples. This reduces uncertainty and increases the instrument signal being measured. However, these sample masses are not obtainable on some fish organ dissections. Sample composites would be necessary to obtain the larger sample mass for some fish. It is very important to be able to estimate the uncertainty on each individual result, especially in dealing with decisions based on screening values. While there are literature references of analysis of fish organ samples with masses on the order of 0.1 - 0.5 grams, one should question these results unless replicate analysis is performed on multiple aliquots of the fish organ (with each aliquot taken through the complete analytical process – not just replicates of the digestate of a single sample). An observation of these data shows a trend in which the final sample concentration (ug/kg) increases as the sample mass decreases. This is shown in Figure 1 below in which the concentration of selenium (mg/kg dry weight) for each sample is plotted against the sample mass (grams). This plot of data seems to indicate that selenium concentrations are tending to increase when sample masses fall below 0.5 grams. This indicates a level of uncertainty in the results based solely on sample mass, and may indicate a situation of systematic low level selenium contamination during sample collection, processing, and/or analysis. Again, when dealing with screening values (especially data involving ovaries), this is important information to have.

Based upon the review of this data, the following conclusions and recommendations are made:

1. Because of the low Se concentrations in these samples, ICP-AES should not be used unless there is an exhaustive comparability study between ICP-AES and ICP-MS methods to demonstrate equivalency of the data. This type of study should include, but not be limited to, the following items:
  - a. ICP-AES analysis should be performed in which calibration check sample analysis is made at concentrations similar to those found in the samples.
  - b. LCS should be spiked at concentration levels similar to concentrations found in the samples.
  - c. MS and MSD should be spiked at concentrations similar to concentrations found in the samples, and must be made on separate aliquots of tissue (do not just spike a single digestate).
  - d. Tissue samples should be composited to achieve sample sizes greater than 0.5 grams.
  - e. Interference check samples should be analyzed to determine interferences.
2. Results of samples in which the sample mass is less than 0.5 grams should be rejected completely.
3. All January results in which the digestate concentration is less than 10 ug/L should be rejected, and all March results in which the digestate concentration is less than 50 ug/L should be rejected.
4. All results in which the digestate concentration is less than 200 ug/L should be flagged as inconclusive (the only potential low concentration verification check sample would be the LFB, which is spiked at a concentration of 200 ug/L).
5. All remaining results should be flagged as estimated.

Figure 1



## PUBLIC COMMENTS

Bryce Payne, Ph.D. Comments on USEPA Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant, An EPA Science Panel Review Paper. August 18, 2009.

William Sette, Ph.D.  
Science Panel Review Chair

Dr. Sette,

At the 'suggestion' (see below) of Mr. Robert Tanner of the Senate Committee on Environment and Public Works Staff I am forwarding the following comments on the recently released "Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant".

First, I would like to offer two clarifications for the record with regard to my letter to Robert Tanner which was included in the Review Paper as Appendix D.

1. I stated that selenium was oxidized to selenate under coal combustion furnace conditions. This statement intentionally oversimplified the combustion chemistry. Selenate exists only as an anion, with no stable molecular form. Hence, though the intense oxidizing conditions in many combustion furnaces may be appropriate for selenate to be the prevalent valence state (my point in the original letter), and though data suggests some selenium does exist in some coal ashes as selenate, the vast majority exists as selenite. This is due to the fact that the highest oxidation state of selenium that occurs as a stable, free molecular form is selenium (IV) in selenium dioxide. The free existing molecular form will be the form most likely to become involved in the condensing amorphous glass that is coal fly ash, and the literature documents this, selenite being the predominant form of selenium in coal fly ash.

Ultimately whether the selenium initially in the coal fly ash is present as selenite or selenate is of no import with respect to the selenium transformations otherwise described in my letter to Mr. Tanner. The only implication of the foregoing is that selenite is released to be adsorbed by the secondary oxyhydroxide minerals on aged coal fly ash, instead of selenate being released, then transforming to selenite under ash storage redox conditions, then adsorbing on the secondary minerals. The issue of concern is that selenite adsorbed on the secondary minerals during ash storage will undergo oxidation to selenate when redox conditions change to those under which selenate is the stable form, as I have proposed will happen when ash is dredged or moved and redistributed over wider areas of the river/reservoir by high water flows.

2. My estimate that the portion of total selenium that would be in a soluble form in fresh coal fly ash (dry, directly from the furnace) was developed from indirect data. Since writing the letter to Mr. Tanner I have encountered credible reports in the literature that the actual portion of total selenium that is initially soluble (water extractable) ranges from less than 1% to greater than 40% for different coal ashes. This clearly suggests more potential for selenium contamination of water bodies receiving coal fly ash slurry water than my earlier crude estimates.

Let me proceed to comments on the Panel's review. I will try to be brief.

My impression was that the commentary and conclusions with respect to selenium and its behaviors and impacts in general were sound.

I regret that your panel did not contact me for clarifications regarding my letter to Mr. Tanner on the transformations and behavior of selenium that become likely if dredging proceeds as it has to date, or if ash is spread downstream by high water flows. Among the important implications of the conceptual ash/selenium model I have tried to communicate is that there is little or no chance that a selenium contamination problem

will be assessable by sampling river water. Indeed, it may never be measured at apparently alarming levels in water samples even after bioaccumulation has become substantial.

Along the same line, it is my recollection that an accepted selenium ecotoxicological model uses selenium associated with particulates, not in water or not just in water, as the primary driving factor for projecting food chain bioaccumulation of selenium (You may want to contact Dr. Theresa Presser of the USGS for more information in this regard.) Further, if one accepts the reported selenium in water data from the Kingston sampling efforts, then selenium levels in the water are low. One is then faced with two possibilities. Either the Tuberty et al fish tissue data are correct or the TVA-TDEC fish tissue data are. If the Tuberty et al data are correct, then there is substantial fish tissue accumulation of selenium occurring even though water selenium levels are low.

That brings me to the effectively summary dismissal of the Tuberty et al data by the Review Panel. I have had numerous exchanges with Dr. Tuberty regarding the methods and attention to execution that are routinely used by his group. I respectfully submit that minimally the Review Panel should have called for a rigorous effort to resolve the clear conflicts in results that have been consistently present in the selenium data, and for that matter results for other analytes, since spill related sampling began. The apparently irreconcilable differences between the Tuberty et al data and the TVA-TDEC data are critically important. If the Tuberty et al data are closer to correct, then the suggested 3-Tiered monitoring approach should already be at Tier 3.

With regard to the 3-Tiered monitoring approach, given the foregoing and the lag times, etc. for selenium bioaccumulation as cited in the Panel Review and elsewhere, it is hard to understand how such an approach is proposed to be protective of the fishery and related sensitive wildlife in the potential ultimate ash spill impact area. Tier 1 suggests the a criterion of 2 ppb selenium in filtered water samples or 5 ppm in fish tissue for progressing to Tier 2. As previously discussed reliance on water and not particulate selenium levels is questionable. At present the ability of the various monitoring efforts to reliably measure 5 ppm in fish tissue or particulates must be regarded as in doubt. Therefore, it seems unlikely that transition to Tier 2 would occur until actual conditions are worse than Tier 1 anticipates.

If transition to Tier 2 is deemed necessary, then there would be a risk of another delay in that fish ovaries and bird eggs are needed for the selenium Tier 2 assessment. That is, if the season of recognition of the need to move to Tier 2 is not coincident with the sampling availability of fish ovaries or bird eggs, then the suspected selenium problem will continue on its trajectory until samples can be collected, and that goes without considering lab turn around times once the samples are collected. Tier 3 timing could suffer the same built-in seasonality problem, though this could perhaps be functionally overcome if lab turn around times for Tier 2 samples were short enough.

Finally, to put it simply, if there is a selenium problem in the subject case, the source of the problem is the ash, and the highest and, hence, most reliably measurable concentrations of selenium are in the ash. Since the spill began there appears to have been a reluctance to develop definitive data on the actual amounts and forms of selenium in the ash. Though a number of rational arguments can be made as to how to undertake such an ash evaluation effort, there can surely be no doubt that such information is needed.

On the other hand, without a credible effort to identify and correct the apparent analytical problems that have afflicted water and fish tissue monitoring efforts since the spill, there is little hope that analytical data for the ash would add anything other than more additional contentiousness to the situation.

Sincerely,  
Bryce Payne, PhD

Dennis Lemly, Ph.D., USDA-Forest Service. Comments on USEPA Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant, An EPA Science Panel Review Paper. August 18, 2009.

Dr. Sette,

I have a few comments on the "Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant".

The review is OK with respect to its designated values for hazardous levels of selenium in fish and the tiered monitoring strategy.

A key issue I see is the discrepancy in analytical results among the investigators.

Sole reliance on TVA/TDEC data leads to an entirely different (benign) conclusion of existing conditions and the need for "adaptive management with respect to activities at the site".

Once Dr. Shea Tuberty's data are confirmed (and I am confident that they will be), tissue levels will be shown to be "hazardous" and meet the trigger for Tier 3 fish reproductive studies.....far beyond the Tier 1 trigger for "equal consideration of adaptive management".

The report needs language more precisely attune with the environmental implications of conditions beyond Tier 1. For example, this statement would be quite appropriate ecologically....."With respect to fish and wildlife health risks, movement beyond Tier 1 monitoring should trigger steps to reduce selenium inputs related to activities at the site".

An important point came to mind when I read this statement in the summary on page 17.....

Because of the significant time lag between Se mobilization and biological response, the monitoring strategy should be a systematic effort to track accumulation over time rather than simply collecting fish periodically or when certain concentration screening levels are reached.

It is important to note that in addition to the lag for accumulation when selenium inputs begin, there will be an overshoot when inputs stop, that is, if concentrations begin to increase toward an "effect/unacceptable" level, they will go even higher before actions to stabilize or reduce them take effect. This is well documented in case examples for fish (Belews Lake) and wildlife (Kesterson National Wildlife Refuge). The resultant "ecosystem inertia" is like trying to stop a moving train.....if you want to stop it and avoid a crash (catastrophic selenium impacts) you have to apply the brake far in advance. It seems to me that's where we are now.....fish Se has moved toward an effect/unacceptable level (based on Dr. Tuberty's data) and now is the time to apply the brake.

Once the questions about Dr. Tuberty's data are resolved, it would be sensible and wise for the Panel to issue an addendum that (1) fine-tunes the language for Post-Tier 1 adaptive management response, and (2) acknowledges that existing conditions are at Tier 3.....far worse than initially assessed using TVA/TDEC data alone. As the Panel Chair, are you prepared and willing to issue such an addendum??

Dennis Lemly

Joseph Skorupa, Ph.D., U.S. Fish and Wildlife Service. Technical Comments Regarding the Draft Report: on USEPA *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant: An EPA Science Panel Review Paper*. August 18, 2009.

Technical Comments Regarding the Draft Report: *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant: An EPA Science Panel Review Paper* [hereafter, Sette et al. 2009]

Commenter: Joseph Skorupa, U.S. Fish and Wildlife Service

Setting the stage: The Kingston coal ash spill was estimated to have released about 5.4 million cubic yards of ash sludge, about 3 million cubic yards of which entered the Emory River (source: Davinna Marraccini, EPA). The ash sludge was estimated to contain an average of 6.4 mg/kg Se and the bulk density was estimated at 1.66 kg/L (Sette et al. 2009: Appendix E). Thus, at 764.554858 L/cubic yard, about 3.8 billion kg of ash sludge entered the Emory River containing a total mass load of about 24,368 kg of Se. Freshwater aquatic ecosystems are extremely sensitive to excessive selenium mass loading, thus the primary goal of post-spill environmental monitoring and risk assessment should be to achieve as complete an accounting as possible of the fate of the Se mass load that went into the river. At its simplest first cut, how much of the Se that went into the river is coming back out via the dredging operation and what is the fate of the Se, if any, missing from the ash coming out of the river. The missing Se can be expected to be partitioned between the water column, atmosphere, sediment, and biota. Thus, an ideal monitoring program would be generating fully quantitated data for Se in five compartments: (1) the ash slurry coming out of the river via dredging, (2) the affected water column, (3) the affected sediment, (4) the affected biota, and (5) the affected atmosphere.

Selenium retrieval: Sette et al. (2009) does not identify a need to implement monitoring of selenium retrieval from the river, via dredging, including monitoring the ultimate fate of retrieved Se; especially if there is going to be any return discharge to the river from ash processing facilities. Given the inadequate implementation of water monitoring for mass balance accounting purposes (discussed below), quantitating the back flow of Se out of the river in dredge slurry becomes absolutely essential so that mass fluxes to the water column can be estimated indirectly (assuming that fluxes to sediment and biota will first move thru the water column).

Water monitoring: To date the water monitoring program, even if accepted at face value, has been inadequate for mass balance accounting (and therefore inadequate for ecological risk assessment) because of MDL's that are simply too high. A non-detect frequency of greater than 90% means we can't even make educated guesses about Se mass fluxes to the water column. Water analyses currently are being conducted by routine analytical methods not suited to the situation at hand. Those methods were specifically designed with reference to regulatory compliance values ranging from 5-20 ug Se/L. Under the extraordinary circumstances of the Kingston spill, and given the high value to the public of the Watts Bar Reservoir aquatic system, and given that ecological effects from selenium are known to be possible at water column concentrations well below 5-20 ug Se/L (as noted by Sette et al. 2009), non-routine methods for water analyses of Se capable of quantitating concentrations below 1 ug/L should be implemented

immediately. Many commercial labs have this capability; one that I am familiar with is Frontier Geosciences, Inc.; also there are a number of university and government labs with such capability. Contacts such as Dr. Gregory Cutter (academia) and Dr. David Naftz (USGS) could be very helpful to TVA/TDEC/EPA in this regard.

*Can the water monitoring conducted to date be taken at face value?*

The National Environmental Methods Index (NEMI; [www.nemi.gov](http://www.nemi.gov)) profile for USEPA method 200.8 reports a MDL of no better than 7.9 ug/L based on a joint EPA-AOAC 13-laboratory round robin validation. This raises the question of how detection limits of 0.1 to 1.3 ug/L as reported for EPA method 200.8 in the data summarized in Sette et al. (2009) have been validated? Does this discrepancy deserve some discussion and/or explanation?

I am also perplexed by the large number of non-detects at a reported MDL of 0.1 ug/L. Values below 0.1 ug/L would be typical of rivers in selenium-deficient watersheds (e.g., Maier and Knight 1994). Given the long history of substantive selenium discharges from the Kingston Fossil Plant even before the spill, it seems very odd that the river would be analyzing out in the Se-deficient range. Furthermore, EPA's mass balance model write-up (Sette et al. 2009: Appendix E) reports "...significant loading [0.5-2 ug Se/L] from outside [upstream, ERM 12.1] the model domain..." that carries through all the way to the Clinch River. Again, if there is significant upstream boundary loading of Se in addition to substantive historical loading from NPDES permitted Kingston Fossil Plant discharges, how can the river be analyzing out in the selenium-deficient range (i.e., <0.1 ug Se/L)? Finally, leaching tests of Kingston fly ash performed for the U.S. Fish and Wildlife Service indicated Se concentrations as high as about 70 ug Se/L in the leachate (Steve Alexander, USFWS, file data). Are conditions so different in the river compared to the leaching test conditions that Se which is readily leached out in the lab, wouldn't be leached out at all in the field; not even enough to get the river above the selenium-deficient range? Sette et al. (2009) comprehensively summarize available data from water analyses, but should there also be an attempt to evaluate whether those results make sense? Of course, if we had measures of the back flow of Se in dredge slurry and thereby could determine how much, if any, mass load is missing, then we could most likely also definitively answer whether water results that commonly come in at <0.1 ug Se/L make sense?

Sette et al. (2009) also did not evaluate the spatial design of water sampling efforts. Sound environmental monitoring requires both appropriate analytical chemistry methods, and a spatially appropriate sampling design. I bring this up only because some stakeholders have claimed that the spatial design of post-spill water sampling at Kingston has been inappropriate ([www.thenation.com/doc/20090420/hearn/](http://www.thenation.com/doc/20090420/hearn/)), thus it seems like some discussion of this topic by Sette et al. (2009) might be warranted.

Fish tissue monitoring: As with the water monitoring program, the TVA and TDEC fish tissue analyses are inadequate for mass balance accounting due to MDL's that are too high (0.7-1.0 mg/Kg). Background levels of Se in fish tissues are typically about 1-2 mg/Kg, dry mass basis, thus to fully quantitate fish tissue selenium for mass balance accounting, MDL's in the range of 0.2 mg/Kg, dry mass basis, must be achieved. Such MDL's are routinely achieved for Se in biological tissues by commercial contract laboratories working for the U.S. Fish and Wildlife

Service, and have been achieved consistently for more than 20 years. This is routine performance that doesn't require "new" or special technology to achieve. I'd be happy to put TVA and TDEC in touch with personnel at the U.S. Fish and Wildlife Service's Analytical Control Facility for further details.

Analytical sensitivity considerations aside, it seems premature to draw inferences from the fish monitoring to date... which Sette et al. (2009) also ultimately seem to conclude by noting that nothing can yet be conclusively ruled out regarding current risk status among fish. Notwithstanding that ultimate conclusion, Sette et al. also seem to be endorsing the TVA/TDEC fish sampling results even though there have been clear differences in results between TVA/TDEC and Tuberty et al. that would have meaningfully different implications regarding the current risk status of fish. Sette et al. (2009) appear to choose the TVA/TDEC results over the Tuberty et al. results without a clearly documented basis for that choice. Basic principles of fair scientific protocol would seem to require that such a choice not be put in writing, or even inferred, unless it can be clearly substantiated. Normally differences between two or more teams would be resolved by thorough presentation and evaluation of the pros and cons of each team's analytical methods and QA/QC documentation, and/or cross-laboratory blind checks using sample remainders (as necessary), and/or independent third laboratory blind validation analyses of sample remainders (as necessary). If remainders are not available from past samples, then a new, joint sampling event with cross team splitting and analyses of samples would be called for. Sette et al. (2009) did not present an evaluation of any such cross comparison components before appearing to choose the low fish tissue results of TVA/TDEC over the higher results of Tuberty et al. For example, did any or all teams employ collision cell technology to account for potential interference effects? Did any or all teams analyze NBS certified tissues, and if so did they achieve similar levels of performance on those analyses? Have any or all teams shared samples with, or had samples analyzed by, other laboratories or by more than one analytical method? It is essential that a plausible explanation for the meaningfully different results between different teams be clearly resolved before any data are censored or any data are preferentially retained. It should also be evaluated whether all the results might be valid and differ between teams to the extent they do simply due to differences in fish species, tissues, timeframes, and specific locations being sampled by different teams.

Resolving the reason(s) for cross team differences in fish tissue results should be conducted independent of water results which themselves seem potentially problematic in this case, i.e., lower fish numbers shouldn't necessarily be chosen as more valid solely because water numbers are believed to be low. Even if the water numbers are valid, water concentrations can be low because there is little mass loading of selenium to the water column (in which case fish would be expected to also be low), or they can be low because selenium loading to the water column is rapidly removed by primary producers (in which case low water concentrations and elevated fish concentrations could co-occur). Water concentrations, under the right circumstances, can be disconnected from fish tissue concentrations, that's precisely why EPA has moved away from selenium criteria based solely on water concentrations and toward criteria that also incorporate direct measures of fish tissue.

Se media screening values: The screening values appropriately and accurately represent current knowledge and the specific trigger values chosen by Sette et al. (2009: Table 3) are scientifically defensible.

Proposed tiered monitoring scheme: The proposed tiered monitoring scheme is conceptually sound and case-appropriate. My only recommendation for improvement would be to more precisely define statistically how exceedances of trigger values should be quantified. For water, is exceedance determined on an any individual sample basis, on the basis of averages, on the basis of geometric means, on a minimum percentage of violating samples basis, etc., etc.? If using averages, will there be an averaging period? For fish and bird tissues, are there any prescriptions regarding particular species, trophic levels, age classes, genders, etc., etc., that should be sampled? And for fish/birds, just as for water, statistically, what constitutes exceedance of a trigger value? Maybe Sette et al. intended to leave such details to local site managers? If so, this should probably be mentioned.

Conclusion: Overall, I concur with most of Sette et al.'s (2009) draft report, but with the major exception of several core analytical chemistry issues linked to what's required for complete mass balance accounting of the truly massive quantity of Se that entered the Emory River and for resolving conflicting fish tissue results to date. In my opinion, much of the analytical performance so far has simply been too insensitive to be very useful for authoritative ecological risk assessment. I also believe that the required additional sensitivity could be gained at very reasonable, if any, extra analytical costs. Furthermore, I think that monitoring the back flow of Se in the dredge slurry should be a fundamental component of the monitoring program, a piece that as far as I can tell is currently missing and also being overlooked by Sette et al. (2009). It seems to me, that at a very minimum, the public deserves monitoring that tells us definitively how much selenium is in the water and in the fish; that doesn't just "ballpark" the answers... especially when there's really no technical or financial barrier that must be overcome to get to real answers. Commercial contract labs exist that do this stuff at the necessary analytical sensitivities on a routine basis.

Citations:

Maier, K.J., and A.W. Knight. 1994. Ecotoxicology of selenium in freshwater systems. *Rev. Environ. Contam. Toxicol.*, 134:31-48.

Tennessee Valley Authority (TVA). 2009. Comments on EPA Science Panel paper, *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant*. August 18, 2009.

TVA Comments on EPA Science Panel paper, *Review of Potential Selenium Issues Following a Coal Ash Spill at the Tennessee Valley Authority Kingston Fossil Plant*

## General Comments

TVA agrees with and supports the general conclusions that the available data:

- Indicate no adverse ecological impacts to the river systems at this time,
- Do not support the concept that the spill and subsequent dredging have increased levels of Se in water enough to pose a risk to aquatic life,
- Indicate that most metals and metalloids are not readily leaching from the ash spilled into the Emory River. (We suggest tempering that statement by pointing out that the substantial dilution of the Emory and Clinch Rivers may preclude detection of selenium being leached into pore waters.)

TVA agrees with the general thrust of the report that concentrations in biological tissues are much more important for assessing selenium mobilization and impacts to aquatic systems than are water concentrations. In addition, those data will be much easier to interpret in the long run. Consequently, in addition to analysis of water, ash, and sediments, TVA's monitoring strategy includes a substantial biological monitoring component.

The Science Panel's recommendation for using exceedances of Se screening values to trigger more intensive investigations ("If elevated levels are noted in surface water and/or fish tissue monitoring, a tiered strategy is outlined for possible additional monitoring of water, fish and birds, and subsequent offspring.") is a logical scientific approach. However, the magnitude of the spill at Kingston, the level of public and regulatory scrutiny of TVA's response, and the urgency of the need for sound scientific data to accurately assess environmental impacts requires a much more aggressive approach.

In this case, TVA believes the most effective approach is almost exactly the reverse of the tiered approach suggested in the Science Panel's report. Conducting Tier 2 and 3 monitoring first (but with greater taxonomic diversity), then backing down over time to Tier 1 and 2 monitoring if no significant bioaccumulation and/or adverse health effects are observed is a more pragmatic and defensible strategy. A well-structured, systematic monitoring program is necessary to track possible bioaccumulation and associated physiological effects over time and to provide early detection so actions can be taken to mitigate or eliminate adverse effects. Because it takes a significant amount of time for most biological effects to occur, this approach has the additional benefit of allowing TVA to determine with certainty whether cleanup activities have been effective.

TVA's ecological monitoring strategy includes site-specific bioaccumulation and toxicity studies. It also includes assessments of possible effects on populations and community structures and potential effects on reproduction, teratogenesis, and other stress responses at levels ranging

from individual organisms to biological communities. TVA has carefully selected the fauna being sampled to ensure all relevant ecological compartments are included and that the strategy focuses on organisms most likely to be exposed or that will provide the most useful information for assessing environmental effects. This multi-faceted ecological monitoring program is designed so its results will either improve our confidence in the Science Review Board's conclusions, or it will identify ecological impacts before they become problematic so TVA and other agencies can address them expeditiously.

TVA considers some of the Science Panel report's recommended "action levels" as very conservative. EPA should provide additional information on the basis for those recommended trigger levels. The recommended screening value for water, 2 ug/L, is lower than the current Ambient Water Quality Criteria (5 ug/L). Table 3 of the report identifies 5 ug/L as EPA's screening value. The water quality and hydrologic setting of the Emory and Clinch Rivers do not indicate that there would be a high rate of Se precipitation and uptake into the food web. This is not a particularly lentic system, nor is the pH very high, nor is there a high organic content layer in the sediment. Consequently, there seems to be insufficient justification for proposing a trigger value for selenium in water lower than the one currently in use (5 ug/L).

With respect to the recommended trigger of 8 mg/kg Se for bird eggs – the Science Panel for the Utah Department of Environmental Quality (referenced in the report as UDEQ 2008) recommended a regulatory level of 12 mg/kg Se in bird eggs. Although the Science Panel report referenced this work, for some reason it is not in the table of screening values (Table 3). Presumably the 8 mg/kg value was selected based on the likelihood of finding embryo deformities in eggs contaminated at that level. TVA has consulted with Dr. Anne Fairbrother, a well-respected authority on toxicological effects of selenium on biota. Dr. Fairbrother indicates that the probability of finding deformed embryos at 8 mg/kg Se is so low that you would have to look at every egg (i.e., more eggs than is feasible for analysis) to have any statistical power in your analysis. She indicates that even at 12 mg/kg, the probability of finding deformities is only a maximum of 10%, which would still require a large sample size to find a statistically significant correlation of deformities with selenium contamination. More information is needed on the panel's selection of such a low value.

While egg concentrations of Se can be a sensitive metric for assessing risks of adverse effects of selenium, in some migratory birds it is likely that a more significant exposure of the young to ash constituents will occur after hatching. For individuals of those species nesting and foraging nearest the Kingston spill, the principal route of exposure of nestlings to Se and/or other constituents of ash probably is not through the eggs from which they were hatched, but through diet (i.e., the adult birds bringing contaminated prey--fish, mayflies, and other insects-- to them). Some contaminants do not readily transfer to the egg, but are readily transferred via the diet. Because the nestling period and the weeks immediately following fledging (when feather growth and trace element elimination via that pathway slows or stops) are sensitive developmental windows for birds, assessments of ecological impacts should examine this route of exposure. TVA's ecological assessment strategy includes analyses of levels of contaminants in mayfly larvae and adults, and levels of contaminants in both egg and hatchlings of tree sparrows, an obligate insectivorous avian species whose adults forage range is limited to approximately 200 meters of their nests.

The report highlights the importance of evaluating Se concentrations in fish and fish-eating waterfowl at the site, but egg-laying reptiles and amphibians also maternally transfer Se to their eggs. It remains unclear as to whether they are more or less sensitive than other egg-laying vertebrates. Consequently TVA has included herpetofauna in our assessments in order to more fully understand ecological impacts of the spill.

There are several places in the report where fish-eating waterfowl are mentioned as prime indicators of exposure. Insectivorous birds feeding upon emerging insects (e.g., tree swallows) are also at high risk of exposure to Se and other ash-derived elements.

TVA understands that the committee's charge was to focus on selenium; however we recognize that selenium is not the only constituent of concern in coal ash, and that in such a complex matrix there may be interactions among multiple constituents that make resultant toxicological outcomes difficult to predict. Because of the complexity of coal combustion wastes, drawing firm conclusions about toxicological effects based solely upon Se concentrations in water or tissue data would be short-sighted.

TVA also recognizes that in addition to direct toxicity of Se to fish and birds as addressed in this report, there can be indirect effects of coal ash on important ecological receptors. Major events such as the Kingston release may modify microbial communities and invertebrate assemblages, particularly in the benthic community. This has the potential to influence large scale ecological processes, such as nutrient cycling, independent of direct toxicity from trace constituents. In some cases, this could affect key receptor populations due to changes in availability of food resources.

### **Specific technical comments and editing errors**

1. Page 1, Paragraph 2, the sentence reads as follows: "Chemical analyses for total metals including selenium (Se) and mercury (Hg) are part of the dredging monitoring program." Suggest revising the sentence to "Chemical analyses for an extensive list of total and dissolved metals including arsenic (As), selenium (Se), and mercury (Hg) are part of the dredging monitoring program." The last sentence reads as follows: "Additional testing, including toxicity and bioaccumulation tests, will be conducted." Suggest revising the sentence to "Additional extensive testing, including toxicity and bioaccumulation testing, have been and continue to be conducted."

2. Page 1, Last Paragraph: The complex flow patterns around the Kingston Fossil Plant (KIF) are such that a comparison of data from the most downstream Emory River surface water location [Emory River Mile (ERM) 0.1] to upstream locations is misleading. Cooling water intake requirements for KIF necessitate drawing water from the Clinch River at approximately Clinch River Mile (CRM) 4 in the upstream direction on the Emory River with subsequent discharge back to the Clinch River above CRM 2.0 such that at during times the lower reach of the Emory is more like the Clinch River than upstream Emory River locations.

3. Page 2, Paragraph 1: The sentences read as follow: “The maximum dissolved concentration of lead (Pb) that exceeded the criteria benchmarks was for a sample collected on 04/03/09 and is not consistent with samples collected prior to, or after this date”; and “Further, dissolved Pb concentrations upstream of the spill were found to be higher.” A significant number of spurious dissolved lead detections during the referenced timeframe were traced to a series of lead metal surface water weights; these data have since been rejected during TVA’s data quality assurance procedures.
4. Page 2, Paragraph 3: “However” would be a better word to use in the last sentence in the paragraph immediately preceding section II, instead of “Although.”
5. Page 2, Paragraph 1: The sentence reads as follows: “ Further, absolute concentrations are not elevated in the downstream stations as mostly evident by nearly all of the metals having median levels below detection limits.” It appears that the limits should be referred to as “quantitation” or “reporting” limits instead of “detection limits.
6. Page 5, Paragraph 4: The authors suggest that risk to aquatic biota should be determined in the “downstream reaches of the Tennessee River to Watts Bar Dam”, given that the distance from KIF to Watts Bar Dam is approximately 40 river miles, tying impacts to aquatic biota to KIF would be highly uncertain.
7. Page 6, Paragraph 4: A reference should be provided for the statement that "Se is unlikely to bioaccumulation to a hazardous level if the filtered fraction of water samples is below 2 ug/L."
8. Page 7, Paragraph 1: References should be provided for the Tier 2 screening levels presented.
9. Page 9, Paragraph 2: The authors state “TVA water samples were analyzed by multiple analytical laboratories”. TVA has only used Test America once the problems with Microbac were discovered.
10. Page 9, Paragraph 3: The sentence reads as follows: “TVA water samples were analyzed by multiple analytical laboratories using EPA Method 200.8 for total and dissolved fractions.” Suggest revising the sentence to “TVA water samples were split and analyzed by multiple NELAP accredited analytical laboratories using EPA Method 200.8 for total and dissolved fractions.”
11. Page 10, Paragraph 1: sentences read as follow: “It must be noted here that there is no quality control information provided within the publication, especially information detailing the laboratory's established MDLs. Typical ICP-MS MDLs are around 0.5 ug/L with MQLs and Practical Quantitation Limits (PQLs) approximately five times this concentration.” Perhaps additional information should be requested from Ruhl *et al.* to allow more definitive statements to be made relative to these data.

12. Page 10, Paragraph 4: The authors state “TVA did not report MQL values...and therefore all the detections of Se in the sample should be considered estimated”. This is incorrect, analytical results are reported to the MQL therefore, all reported results have a high degree of certainty in their quantitation.
13. Page 11, Paragraph 3: See comment 2 above. The authors state “This subset of data was selected because it was collected at Emory River mile 0.1, a location at high risk for elevated levels for Se because it is located immediately downstream of the spill site”.
14. Page 17, Last Paragraph: The sentence reads as follows: “The sediment elutriate tests that use coal ash and waters taken directly from the site may provide useful information on the concentration and species of Se released during the suspension and oxidation of coal ash resulting from dredging activities that could be used in geochemical modeling.” The US Army Engineer Research and Development Center has recently completed this work and its findings should be included in this report.
15. Page 28, Figure 2: The cross mark for soil in inverts is located in between two rows.
16. Page 29, Figure 3: The MDL legends for the lines in Figure 3 are reversed (TDEC has the higher detection limit)
17. Page 32, Table 2: The table reports the Microbac Laboratories’ data for the 47 original samples of fly ash—that data did not pass TVA’s validation process and was subsequently rejected, with retained samples being re-analyzed by another laboratory. The re-analyses were not available to provide to the review panel, and the new data is just now being posted to the TVA website to replace the Microbac data;
18. Appendix B: This appendix should be updated with validated data at the time this document goes to press.
19. Appendix C: TDEC should be requested to provide data validation reports and/or a description of how its data were validated.
20. Appendix F: The work represented by this work plan has already been completed and the findings of that work should be included in this report.