

**ASSESSMENT OF TRACE-ELEMENT IMPACTS ON AGRICULTURAL USE OF
WATER FROM THE DAN RIVER FOLLOWING THE EDEN COAL ASH SPILL**

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SUMMARY AND CONCLUSIONS

A release of approximately 39,000 tons of coal ash into the Dan River on February 2, 2014 has created a need for information on possible effects on agriculture downriver of the spill. This document addresses concerns about impacts of ash-derived trace-element contaminants (e.g. arsenic, lead, copper, etc.) on agriculture in the Dan River Basin.

Assuming that water quality trends along the Dan River can be projected from hundreds of water analyses made during a 40-day period following the spill, we conclude that:

- 1. River water is suitable for use as irrigation water on crops and as drinking water for livestock.**
- 2. Trace-element influx during flooding of agricultural areas will have only a marginal impact on soils and crops.**

This assessment is based on the following observations:

- Total concentrations of trace elements (“total metals”) in Dan River water declined sharply from maximum levels that were typically measured one day after the ash release, and concentrations measured ~2.5 miles downriver of the spill site were equivalent to upstream concentrations within 3 days after the coal-ash release.
- Concentrations of 13 trace elements measured in up to 449 water samples did not exceed adopted standards for surface water used as a drinking water source (Class WS) in more than 90% of samples, and no samples exceeded guidelines adopted (in KY) for drinking-water sources for cattle.
- Mass balance calculations revealed that irrigation or flooding with 10 acre-inches of Dan River water containing trace-elements at the nominal concentrations observed between February 7 and March 14, 2014 would increase total soil concentrations of nearly all of these elements by less than 0.5%, and concentrations in tobacco, corn grain or stover, and fescue would be increased by less than their typical concentration ranges associated with natural variability.

From this data evaluation and an assessment of pathways for trace-element transfer between residual coal ash in the Dan River and agricultural soils and crops, we also provide practical considerations that can be followed as an added precaution to diminish any impacts of the spill on agricultural production.

PRACTICAL CONSIDERATIONS FOR IRRIGATION

- Ensure that irrigation water intakes are near the surface of the Dan River, away from the bottom sediments that could contain coal ash. Surface placement will generally decrease intake of suspended solids that could include ash particles containing trace elements.
- Monitor the USEPA website (www.epa.gov/region4/duke-energy/) or other sources of water-quality information for indications of periodic increases in trace-element concentrations. See, for example “Response Information Updates” and “Surface Water Data” at the USEPA website, recognizing a time delay on the posting of new data.
- Avoid irrigation when the total metal concentrations, total suspended solids, or turbidity, of the Dan River water are elevated above water-quality standards or nominal levels discussed in this report. For example, a rainfall event in the watershed upstream of irrigated land could increase the suspended sediment load, which could possibly include re-suspended ash particles.
- Have agricultural soils and crop tissues tested at least annually, and be specifically mindful of any increases in micronutrients such as copper and zinc in soil or tissue tests.

OVERVIEW OF COAL ASH IN THE DAN RIVER

The February 2, 2014 failure of a stormwater discharge pipe at an ash-storage site at Duke Energy’s Dan River Steam Station in Eden, NC, led to an estimated 39,000 tons of coal ash and 27 million gallons of ash water being released into the Dan River. According to USEPA and Duke Energy officials, clean-up operations over the coming months will remove a portion of the ash from the river. The majority of ash has been dispersed throughout the river between the release site and the Kerr Reservoir downriver. A primary concern about such a coal-ash release is the environmental impacts of potentially toxic trace elements. “Trace elements” generally refer to those elements that occur at very low (part-per-million) concentrations compared with major elements found in rocks and minerals. In environmental monitoring, trace elements are often called “metals” or “heavy metals”.

Figure 1 shows estimated amounts of some trace elements in coal ash particles that were released into the Dan River with the 39,000-ton spill. This assessment is based on measurements of trace elements in coal-ash samples from the Dan River Steam Plant basin from which the release occurred (**see Table 1**). Many of these trace elements are essential to plants or animals at low concentrations, but become toxic when in excess. For example, copper (Cu) and zinc (Zn) are essential to plants and animals, and selenium (Se) and chromium (Cr) are essential for humans, but can become toxic when concentrations in water increase. Of the elements in **Figure 1**, arsenic (As), cadmium (Cd), lead (Pb), selenium (Se), and certain forms of mercury (Hg), chromium (Cr) and barium (Ba) are generally considered to be the most toxic to humans and other mammals (McBride, 1994).

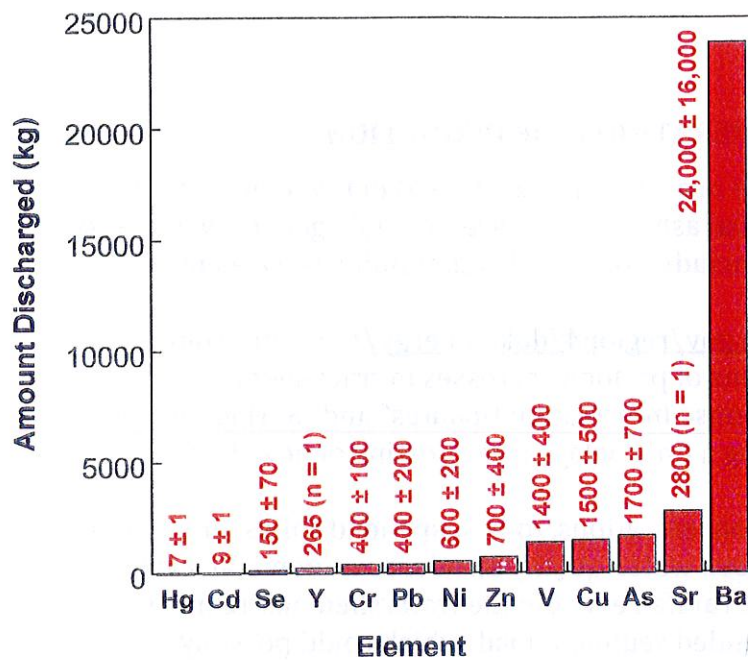


Figure 1. Estimated amounts of various trace elements discharged into the Dan River with 39,000 tons of coal ash. Calculations are based on elemental compositions of ash reported by USEPA for the primary ash basin at the Dan River Steam Station. Numbers associated with bars are calculated means (\pm standard deviations) based on coal ash analyses in **Table 1**.

Table 1. Concentrations of trace elements measured in samples from the ash basin from the Dan River Steam Station compared with concentration ranges reported for soils and fertilizers.

Trace Element	Range of ash conc. (mg/kg) [†]	Mean \pm std. dev. Ash conc. (mg/kg) [†]	Soil concentration range (mg/kg) [‡]	Fertilizer conc. Range (mg/kg) [¥]
As - arsenic	17 - 61	48 \pm 21	4.4 - 7.2	2.7 - 120
Ba - barium	210 - 1110	680 \pm 460	580	no data
Cd - cadmium	<0.08 - 0.29	0.27 \pm 0.04	0.068 - 0.35	0.06 - 8.5
Cr - chromium	6.3 - 14	12 \pm 4	38 - 54	1.0 - 134
Cu - copper	20 - 51	43 \pm 15	7 - 25	1 - 138
Hg - mercury	<0.06 - 0.24	0.21 \pm 0.03	0.01 - 0.09	0.4 - 3.2
Ni - nickel	7.0 - 20	16 \pm 6	6.2 - 19	7.0 - 44
Pb - lead	4.7 - 18	12 \pm 6	9.6 - 34	1.9 - 48.7
Se - selenium	2.3 - 6.4	5 \pm 2	0.39	0 - 13.2
Sr - strontium	79	-----	240	no data
V - vanadium	22 - 48	40 \pm 12	80	no data
Y - yttrium	7.5	-----	25	no data
Zn - zinc	8 - 35	21 \pm 11	12.9 - 96	1 - 235

[†] Range or mean coal ash concentrations (conc.) \pm standard deviations (Std. Dev.) measured by USEPA in four samples collected 6-12 February, 2014. Means for Cd and Hg are for two and three samples with reportable concentrations, respectively; and Sr and Y were reported for only one sample (n = 1).

[‡] Soil concentrations represent the range of means or medians reported in three sources: Pease et al. (2007) (median for Tar-Pamlico sediments), Holgrem et al. (1992) (mean of 163 soil samples across North Carolina), and Sparks (2003) (median for soils sampled across the contiguous U.S.). Single numbers (Ba, Se, Sr, Y, and V) are medians reported in Sparks (2003).

[¥] Overall concentration range reported by Prasad (2008) for urea, ammonium nitrate, ammonium sulfate, superphosphate, and potassium sulfate fertilizers. The actual loading of trace elements on soils depends on both their concentration and the amounts of fertilizer applied.

Trace element concentrations measured in coal ash from the “release” basin are compared in **Table 1** with concentrations in soils and some common agricultural fertilizers. The highest concentrations of arsenic, barium, copper, mercury, and selenium measured in the coal ash samples exceeded the upper concentrations of the ranges shown for soils. However, the upper concentrations of most elements shown in **Table 1** were lower in the coal ash samples than in certain chemical fertilizers. Specifically, the highest concentrations measured in fertilizers exceeded those of the ash for arsenic in ammonium nitrate; cadmium and mercury in all five fertilizers considered (**Table 1** footnote), chromium in superphosphate; copper and zinc in superphosphate and potassium sulfate; nickel in all considered fertilizers except for urea; lead in urea and ammonium nitrate; and selenium in ammonium nitrate and potassium sulfate (Prasad, 2008). However, loading of trace elements on soils depends on both their concentration in the material (e.g., ash or fertilizer) and the amount of material discharged or applied to a soil. In essence, concentrations of trace elements in soils vary, depending on concentrations in the parent material (rocks/sediments) on which the soils formed, and on historical inputs of trace elements with fertilizers, pesticides, biosolids, and other soil amendments.

Possible pathways of trace element movement from coal-ash particles in the Dan River to soils and crops are illustrated in **Figure 2**. The most direct pathways into crops are by root uptake of dissolved elements in soil porewater or by leaf uptake of dissolved elements in irrigation water. Porewater concentrations of trace elements can be directly impacted by dissolved concentrations in irrigation or floodwater, or by release from ash particles applied to the soil or leaves. Soil solids (mineral and organic matter particles) typically have a high affinity to bind trace elements, thereby removing these elements from soil porewater and regulating crop uptake. Uptake and release from soil particles depends not only on total element concentrations, but more importantly on the amounts and types of soil minerals and organic matter, and on soil chemical properties such as pH and oxidation-reduction (redox) potential. In essence, binding of any applied trace elements by soil particles largely regulates their uptake into crops and their possible impacts on crop quality for human or animal consumption.

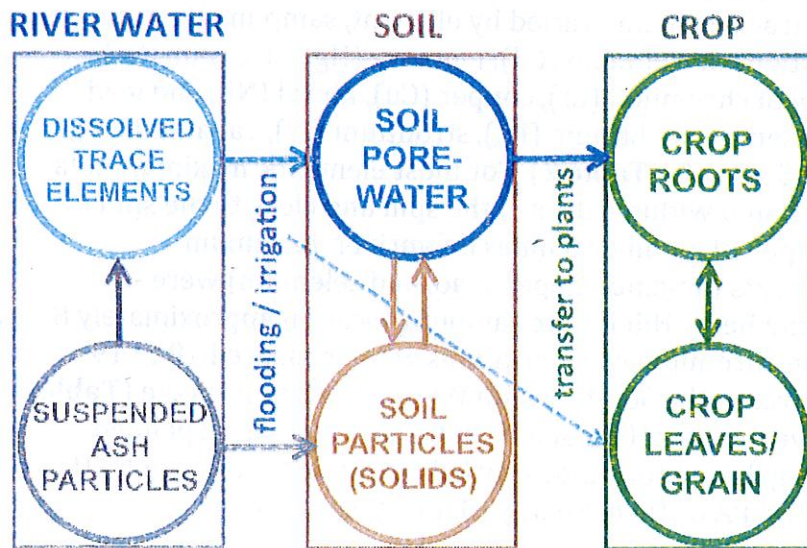


Figure 2. Pathways of trace element transfer from coal-ash impacted river water to soils (via flooding or irrigation) and crops (via soils or direct leaf-water contact).

It is important to realize that the quality of Dan River water could change over time if properties such as flow conditions, temperature or redox state change substantially. Ongoing data collection by the USEPA, Duke Energy, and other agencies is evaluating the dissolved concentrations (filtered samples) and total concentrations (unfiltered samples) of elements at multiple points downriver of the spill site. Total concentrations include trace elements that are dissolved and those associated with any suspended ash and soil particles in the river. Coal ash itself is a complex material that consists of crystalline minerals and noncrystalline aluminosilicate glass that are inherited from coal or formed during combustion (Ward and French, 2006). Although the ash particles do not readily dissolve in water, trace elements can be released from the particles over time. Different crops (tobacco, corn, grasses, etc.) take up different trace elements from soils to different degrees (Kabata-Pendias, 2011).

Over time, residual ash will become mixed with or buried under new sediment deposited into the Dan River, effectively forming a sediment cap on the ash. Although this cap can serve as a barrier to trace element migration from buried ash into the overlying river water, disturbance of the sediments, e.g., under high flow conditions or by sediment-dwelling organisms could re-suspend ash particles. Also, trace elements that dissolve from the buried ash can diffuse through the cap over time and into the overlying water. Ongoing monitoring of total and dissolved trace elements in the Dan River will help to reveal periods of concern with respect to using the river for irrigation water.

TRACE ELEMENT CONCENTRATIONS IN DAN RIVER WATER

Table 2 summarizes total concentrations of various trace elements measured in up to 449 unfiltered surface-water samples collected by USEPA or Duke Energy at multiple locations downriver of the coal-ash spill between Feb. 2 and Mar. 19, 2014. Some of the USEPA data are available on their website (www.epa.gov/region4/duke-energy/ - accessed 4/15/2014), and the rest were provided to us by both organizations. The USEPA samples were collected at multiple locations between the coal-ash spill site and the South Boston, VA water intake located approximately 70 miles downriver. Duke Energy samples were taken between the spill site and the Henderson, NC water intake on John H. Kerr Reservoir.

Measured concentrations of trace elements varied by element, sampling location, and time. Maximum total concentrations of cadmium (Cd), mercury (Hg), selenium (Se), and yttrium (Y) were $\leq 5 \mu\text{g/L}$; those of chromium (Cr), copper (Cu), nickel (Ni), and lead (Pb) were $< 50 \mu\text{g/L}$; and those of arsenic (As), barium (Ba), strontium (Sr), vanadium (V), and zinc (Zn) were between 50 and 530 $\mu\text{g/L}$ (**Table 2**). For most elements, maximum total concentrations in river water were found within 4 days of the spill and close to the spill site, e.g., at the spill outfall or at Draper's Landing 2.5 miles downriver. Maximum concentrations of several trace elements (arsenic, copper, lead, and selenium) were measured the day after the spill at the Berry Hill Bridge sampling location approximately 8 miles downriver. Maximum zinc and chromium concentrations were measured 18 to 19 days after the spill, 68 miles downriver at the South Boston Water Treatment Intake (**Table 2**). In addition to trace elements, river water pH ranged from 6.5 to 7.8, total suspended solids (TSS) ranged from 5 to 855 mg/L, and turbidities varied between 3.3 and 676 NTU across samples analyzed by either USEPA or Duke Energy (data not shown).

Overall, concentrations of elements shown in Table 2 exceeded the adopted standards for surface waters used for drinking water (Class WS) in less than 10% of all samples. It is noteworthy that the stretch of the Dan River between the spill site and the first crossing of the Virginia border has a less restrictive water use classification (Class C) (NCDENR, 2013). Concentrations of barium, cadmium, mercury, nickel, lead, and strontium never exceeded their adopted standards in the samples analyzed. For 65 measurements of surface-water samples reported by Duke Energy during the month of March 2014, no samples exceeded the adopted WS water-quality standards for arsenic, cadmium, chromium, copper, lead, selenium, or zinc. ***In summary, the quality of Dan River water was in compliance with adopted standards for surface waters used as drinking water for the vast majority of samples taken over time from different sampling locations.***

TEMPORAL TRENDS IN DAN RIVER TRACE-ELEMENT CONCENTRATIONS

Figure 3 shows total trace-element concentrations and suspended solids or turbidities of Dan River surface water analyzed by USEPA upriver and downriver of the coal-ash spill site during a 16-day period following the 2 Feb. 2014 spill. Concentrations of trace elements measured over time in downriver samples declined sharply from their maxima within the first 5 days after the spill, and were thereafter essentially the same as concentrations in upriver samples. In nearly all cases, the downriver concentrations were less than the practical quantitation limit or “reportable limit” (**Table 2**) after 6 Feb. 2014. Total suspended solids showed an analogous sharp decline. Dissolved trace-element concentrations measured in filtered water samples (data not shown) were less than the total concentrations in unfiltered samples (**Figure 3**), indicating that a significant portion of the trace elements were bound with ash particles. Much of the sharp decline in trace-element concentration in **Figure 3** is probably due to a 29% rise in the Dan River gauge height (2.56 to 3.29 ft.) and corresponding 47% increase in flow rate (discharge increased from 1130 to 1660 cubic feet per second) measured between 2 - 4 February near Wentworth, NC (USGS, 2014). USEPA officials (19 March 2014 teleconference) indicated that the high river stage carried much of the released ash downriver.

Analyses of Dan River surface-water samples collected at the Berry Hill Bridge over time showed that total concentrations of trace elements were greatest 1 to 2 days after the spill, then declined sharply within the next 3 days (**Figure 4**). Trace-element concentrations followed trends in suspended solids (reported as “suspended residues”), suggesting that much of the initial trace-element load was in suspended ash particles. For example, zinc in filtered samples shown in **Figure 4** was always less than 3 µg/L, whereas total zinc was greater than 20 µg/L the day after the spill. Similar to data shown in **Table 2** for multiple locations, total concentrations of most elements other than zinc at the Berry Hill site were below or near Duke Energy’s detection limits (1-3 µg/L) as of 12 March 2014.

Based on the trends shown in **Figures 3 and 4**, we conclude that the first 3 or 4 days after the spill reflect the worst-case scenario for surface water quality. Therefore, our following estimates of soil and crop loading are based on irrigation water from the Dan River having a “nominal” total concentration of 5 µg/L for all elements considered, and for comparison, a worst-case scenario of 50 µg/L. Because mercury and cadmium were essentially always below reportable concentrations in river-water samples and are typically very low in soils, these elements were excluded from our soil loading calculations.

Table 2. Summary of total trace-element (total metal) concentrations measured in up to 477 samples of surface water collected from the Dan River near or downriver of the Dan River Steam Station coal-ash spill site between 5 February and 3 March 2014 (60 USEPA samples) and between 2 February and 19 March 2014 (389 Duke Energy samples).

Element	Class WS Surface Water Standard†	Range of reported concentrations (µg/L)		Date and location of maximum measured concentration ‡		% of samples exceeding* Class WS Surface Water Standard (see col. 2)
		USEPA	Duke Energy	USEPA	Duke Energy	
As - arsenic	10 µg/L	<1 - 183	<1 - 35.3	2/18/14 Duke OC	2/3/14 - BHB	29%
Ba - barium	1.0 mg/L	23 - 530	no data	2/3/14 DLDS	-----	100%
Cd - cadmium	2 µg/L	<0.7 to <1	<1	2/3/14 DLDS	-----	0.4%
Cr - chromium	50 µg/L	<2.5 - 15	<1 - 12.7	2/3/14 DLDS	2/21/14 SBWTI	67%
Cu - copper	7 µg/L	2.3 - 46	<1 - 34.3	2/3/14 DLDS	2/3/14 - BHB	80%
Hg - mercury	0.012 µg/L	<0.0002 - <0.2	<0.05	N/A	-----	0%
Ni - nickel	25 µg/L	<5 - 21	no data	2/3/14 DLDS	-----	25%
Pb - lead	25 µg/L	<1 - 23	<1 - 15.6	2/3/14 DLDS	2/3/14 - BHB	47%
Se - selenium	5 µg/L	<1 - <5	<1 - 5.2	N/A	2/3/14 - BHB	7.1%
Sr - strontium	14 mg/L	47 - 260	no data	2/3/14 DLDS	-----	100%
V - vanadium	-----	<5 - 67	no data	2/3/14 DLDS	-----	38%
Y - yttrium	-----	<3 - 3.2	no data	2/6/14 SBWTI	-----	3.4%
Zn - zinc	50 µg/L	5.6 - ~167	<5 - 43.1	2/15/14 Duke OA	2/20/14 SBWTI	71%

† NCDENR (2007) standard for Class WS surface waters used as drinking water supplies are more restrictive for some elements than the actual Class C classification of the Dan River between the spill site and the nearest Virginia border crossing downriver (NCDENR, 2013). No standards were listed for V or Y.

‡ Duke OC-Duke Outfall C (at spill site); Duke OA-Duke Outfall A (at spill site); DLDS-Draper Landing Downriver of spill site; BHB = Berry Hill Bridge (NC); SBWTI = South Boston (VA) Water Treatment Intake (N/A = not applicable - no reportable element concentrations measured).

* Reportable concentrations (practical quantitation limits) or detection limits: **Duke Energy:** <0.05 µg/L for Hg; <1 µg/L for As, Cu, Pb, Cr, and Cd; <1 or <3 µg/L for Se; and <5 µg/L for Zn. **USEPA:** <0.0002, 0.1, or 0.2 µg/L for Hg; <0.7, <0.5 or <1 µg/L for Cd; <1 or <2 µg/L for Pb; <1, <2, or <5 µg/L for As; <1 or <5 µg/L for Se; <2 or <5 µg/L for Ni; <2.5 or <10 µg/L for Cr; <3 µg/L for V; <3 or <25 µg/L for Y; and <10 µg/L or lower for Zn and Cu. The total number of samples in which specific elements were analyzed (USEPA + Duke Energy) are As-449, Ba-56, Cd-445, Cr-449, Cu-449, Hg-57, Ni-60, Pb-449, Se-449, Sr-40, V-60, Y-29, and Zn-449.

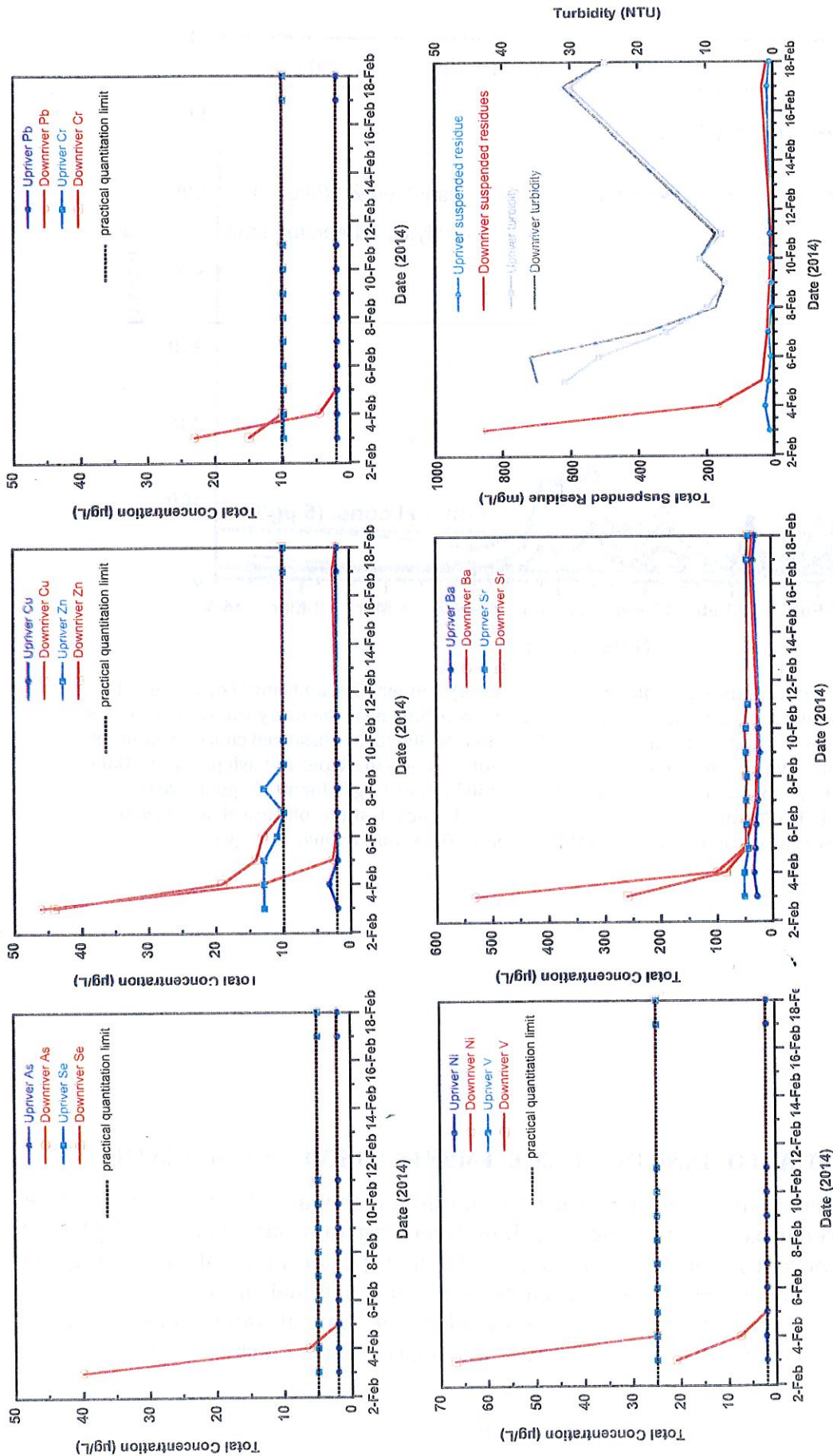


Figure 3. Temporal trends in total (unfiltered) concentrations of arsenic (As), selenium (Se), copper (Cu), zinc (Zn), lead (Pb), chromium (Cr), nickel (Ni), vanadium (V), barium (Ba), and strontium (Sr), along with suspended solids (reported as "suspended residues") and turbidity of Dan River surface-water samples collected by USEPA upriver ("Hwy 14") and 2.5 miles downriver ("Draper Landing") of the coal-ash spill site. In all cases, concentrations of trace elements and total suspended solids were equivalent in upriver and downriver samples within 4 days of the spill. In most cases, measurements were reported as being below the practical quantitation limit for the analytical technique used to analyze each element (Data source: USEPA).

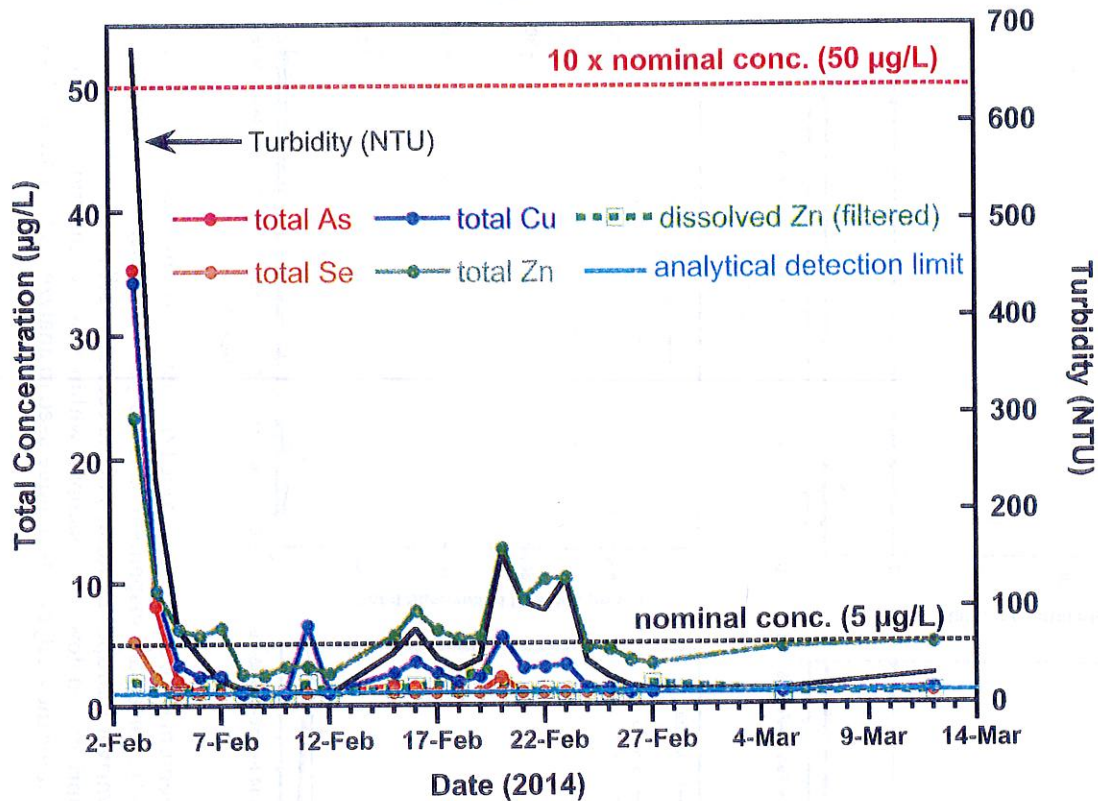


Figure 4. Total concentrations of arsenic (As), selenium (Se), copper (Cu), and zinc (Zn), along with turbidity measured in Dan River water samples collected over time near the Berry Hill Bridge 8 miles downriver of the coal-ash spill site near the Virginia border. Included are dissolved concentrations of Zn in filtered samples, which indicated that most of the total Zn was in suspended ash particles. Data falling on the blue line representing an analytical detection limit of 1 µg/L for all elements were reported as <1 µg/L. The “nominal” and “10 x nominal” total concentrations of trace elements were used in mass-balance calculations shown in Tables 3 and 4 (Data source: Duke Energy).

POTENTIAL LOADING OF TRACE ELEMENTS TO SOILS VIA IRRIGATION

Table 3 summarizes mass balance calculations on annual soil enrichment by trace elements for scenarios of 10 acre-inches of Dan-River irrigation water being applied at total element concentrations of either 5 µg/L or 50 µg/L. (An example calculation is given at the end of this document.) These concentrations reflect nominal and 10x nominal concentrations discussed above with respect to **Figure 4**. Annual water needs of crops are approximately 10 inches for wheat, 16 inches for tobacco, and 17 inches for soybeans, and

actual irrigation needs will depend on rainfall levels for a given year. Data on soil trace-element concentrations in the Dan-River basin are lacking. Thus, to make an assessment on a worst-case basis from available data, we used as reference values in **Table 3** the lowest of the median or mean concentrations reported for soils or sediments in North Carolina or the contiguous 48 U.S. states. Trace elements in irrigation water from the Dan River could be present in suspended ash or soil particles, or in dissolved forms. Particulate and dissolved trace elements have different pathways for reaching crops (**Fig. 2**).

Table 3. Concentrations of trace elements in ash and soils, and estimated enrichment (%) of agricultural soils with trace elements at total concentrations of 5 µg/L (nominal – see Fig. 4) or 50 µg/L (10x nominal) if 10 acre-inches of water from the Dan River were applied as irrigation water or discharged to a field as flood water. Cadmium and mercury were excluded because cadmium was detectable/reportable in only one water sample and mercury was never reportable (Table 2).

Trace Element (“metal”)	Reference soil concentration (mg/kg) [†]	Annual increase (%) in soil concentration [†] from 10 acre-in./yr. of irrigation water containing		Soil concentration range of concern (mg/kg) [‡]
		Element at nominal concentration (5 µg/L)	Element at 10 x nominal concentration (50 µg/L)	
As - arsenic	4.4	0.22%	2.2%	15 - 20
Ba - barium	580	0.002%	0.02%	400 - 600
Cr - chromium	38	0.03%	0.3%	50 - 450
Cu - copper	7	0.14%	1.4%	60 - 500
Ni - nickel	6.2	0.16%	1.6%	20 - 60
Pb - lead	9.6	0.1%	1.0%	20 - 300
Se - selenium	0.39	2.5%	25% [‡]	3 - 10
Sr - strontium	240	0.004%	0.04%	no data
V - vanadium	80	0.01%	0.1%	100 - 340
Y - yttrium	25	0.04%	0.4%	no data
Zn - zinc	12.9	0.08%	0.8%	100 - 300

[†] Reference soil concentrations are the lowest of the range shown in Table 1, and the annual increase is based on this reference concentration.

[‡] Maximum Se concentration measured in 485 water samples was 5.2 µg/L (Table 2), making a 50 µg/L scenario unlikely.

[‡] Ranges of “Maximum Allowable Concentrations” (MAC) for soil trace elements in agricultural soils, where available; with ranges for Ba, Se, and V reflecting ranges of “Trigger Action Values” (TAV) (Kabata-Pendias, 2011). The range for Cr is the MAC for Cr(III), whereas the TAV reported for Cr(VI) is 3-25 mg/kg.

Scenario calculations in **Table 3** show that the soil concentration of a given trace element (other than selenium) would increase by ≤0.22% per year relative to our selected soil reference concentration for an application of 10 acre-inches per year of river-water containing a total concentration of 5 µg/L of a trace element. Selenium would be enriched by 2.5% per year under this scenario, making it an element of greatest potential concern. If the total concentration of any trace element in the river water was at a concentration of 50 µg/L – a scenario that we consider unlikely based on trends in measurements since the spill (**Table 2, Figures 3 and 4**) – then soil concentrations would increase 10-fold faster, ranging from 0.02% per year for barium to 25% per year for selenium (**Table 3**). It is important to recognize that actual enrichment rates of soils with trace elements from irrigation water depend on the concentrations of these elements both in the river water and in the soil before irrigation water is applied.

Table 3 includes soil concentrations of trace elements that are considered to be a concern, i.e., “maximum allowable concentrations” (MAC) or “trigger action values” (TAV). For the most part, these concentrations mostly exceed the soil concentrations shown in **Tables 1 and 3**. Although it is highly undesirable to add trace elements up to these excessive concentrations, they are included in **Table 3** to give a perspective on the significance of our calculated enrichment rates. If 5 µg/L of trace elements (other than Ba, Sr, and Y) were added with 10 acre-inches of irrigation water each year, it would take between 267 years (for Se) and >19,000 years (for Zn) for the soil concentration to increase from the reference concentration in **Table 3** to the low end of the MAC or TAV range shown. These times would be shortened if the soil or water concentrations were higher. For example, it would take 10 to 27 years to increase soil Ni and Se concentrations (respectively) to the MAC or TAV for a soil containing these elements at the high end of the range reported in **Table 1** and for irrigation water at 50 µg/L of each element. *These scenario calculations illustrate that farmers should stay aware of potential issues of excessive soil enrichment with trace elements by staying informed about river water quality, especially during the irrigation season.*

In addition to total concentrations in soils, impacts of trace elements on crop concentrations are affected by soil porewater concentrations (**Figure 2**). For the most part, the trace elements listed in **Table 3** should be strongly bound in soil solids. Thus, modest increases in total concentration are expected to have only a marginal, if any, effect on plant uptake of an element. Because soils and soil-crop interactions are highly variable, it is difficult to quantify the magnitude of effects without direct measurements. Annual soil test analyses would provide insights to potential increases in plant-available trace elements that are reported in such tests, particularly copper and zinc.

POTENTIAL UPTAKE OF TRACE ELEMENTS BY CROPS FOLLOWING IRRIGATION

Soils will typically regulate the transfer of trace elements between irrigation water and crops. However, any irrigation water sprayed directly on the crops that does not run off the leaves to the soil (a minor amount) can leave residual trace elements in dissolved or particulate forms (**Figure 2**). We made mass-balance calculations to gain insights on the potential loading of trace elements to above-ground parts of three crops if 50% of trace elements applied to a crop at either 5 or 50 µg/L in 10 acre inches of irrigation water accumulates in these parts (**Table 4**). Specifically, these mass-balance calculations assume that (1) the total (dissolved + particulate) concentration of a given trace element in irrigation water is 5 or 50 µg/L; (2) 100% of trace elements in ash particles dissolve during the cropping season; (3) all added trace elements remain 100% plant-available (labile); (4) roots take up 100% of each element non-selectively; and (5) 50% of each element is translocated from roots to the above-ground plant parts being considered (leaves/stems or grain). It is important to note that these mass balance calculations are intended to determine which trace elements at nominal or elevated concentrations in Dan River water could be of most concern with respect to crop concentrations. In reality, a significant portion of any applied trace element is expected to remain in ash particles or be bound to soil particles (**Fig. 2**), thereby diminishing actual crop uptake. Moreover, the actual uptake of trace elements by roots and translocation to aboveground biomass varies by element and crop, and depends on the element’s mobility in the plant (Kabata-Pendias, 2011).

Table 4. Mass-balance calculations of potential enrichment of trace-elements in aboveground crop biomass components if 10 acre-inches of Dan River water containing either 5 µg/L (nominal case) or 50 µg/L (10 x nominal case) of a given trace element were applied to a field, and 50% of the applied trace element accumulated in tobacco leaves, corn grain or stover, or fescue biomass. The range of reference concentrations of specific elements generally reflects concentrations in non-contaminated crops.

Irrigation Scenario	Increase in trace-element concentration per unit biomass (typically leaf or grain) for the given water concentration (mg/kg)‡			
	Tobacco	Corn Grain	Corn Stover	Fescue
Nominal water concentration (5 µg/L water)†	2.3	0.5	0.6	0.8
10 x nominal water concentration (50 µg/L water) †	23	5.4	6.3	8.1
	Reference concentration range (mg/kg biomass or grain)			
	Tobacco	Corn Grain	Corn Stover	Fescue Hay
As - arsenic	1.1-4.5	1.85	0.01-1	0.28-0.33
Ba - barium	72-3000	no data	10-100	2-13¥
Cd - cadmium	0.77-7.02	<0.002-0.34	0.05-0.2	0.07-0.32
Cr - chromium	<0.1-3.45	0.24-0.41	0.05-1	0.5 -3.4
Cu - copper	14.9-21.1	0.89-3.6	5-25	4.3-10.5
Hg - mercury	no data	0.0017-0.073	no data	0.01 - 0.1
Ni - nickel	<2-4	0.3-1.2	0.1-10	0.13-1.7
Pb - lead	0-200	<0.003-2.9	3-5	0.36-4.6
Se - selenium	2-4	0.05-0.085	0.5-5	0.013-0.11
Sr - strontium	29.7-49.5	0.06-0.4	13-22	6-37
V - vanadium	1.06-1.65	no data	0.62-3.6	no data
Y - yttrium	no data	no data	0.01-3.5¥	0.01-3.5¥
Zn - zinc	16.8-30.5	14-34	20-100	27-47

† See Fig. 3 for "nominal" water concentration. Increases in biomass concentrations are based on yields of 2500 lbs. tobacco/acre (Matthew Vann, NCSU Tobacco Extension Specialist - personal comm.); and 150 bu. corn/acre at 70 lbs./bu., 4.5 tons corn stover/acre, or 3.5 tons fescue per acre (Osmond and Kang, 2008).

‡ Data sources for crop concentrations: **Tobacco** - As, Ba, Cu, Pb, Se (Tso, 1990 for leaves or commercial tobacco); Cd, Cr (Chiba and Masironi, 1992); Ni, Sr, V, Zn (Iskander et al., 1986 for cigarette samples). **Corn grain** - As (mean from one study), Hg, Se (corn+sweet corn), Sr (Kabata-Pendias, 2011); Cd, Cu, Ni, Pb, Zn (Wolnik et al., 1985); Cr (Yu-kui et al., 2009). **Corn stover** - As, Ba, Cd, Cr, Cu, Ni, Se, Zn (Pais and Jones, 1997 for corn leaves); Pb (Kabata-Pendias, 2011); Sr, V (Sadiq and Hussain, 1993-pot expt.). **Fescue hay** - As, Cd, Cr, Cu, Hg, Ni, Pb, Se, Sr, Zn based on ranges for "grasses" (Kabata-Pendias, 2011).

¥ Overall concentration range of Ba and Y in plants reported by Kabata-Pendias (2011).

As shown in **Table 4**, 10 acre-inches of irrigation water applied at trace-element concentrations of 5 µg/L could increase the concentrations of some elements in some crops by levels in excess of their maximum expected concentration. The most notable cases are arsenic in fescue (0.8 mg/kg added with irrigation water compared with up to 0.33 mg/kg observed in fescue grown on non-contaminated soils), selenium in corn grain and fescue, and vanadium in tobacco. Although typical crop cadmium and mercury concentrations would be exceeded in the "5 µg/L" irrigation scenario, the concentrations of these elements in Dan-River water were almost always <1 µg Cd/L and <0.2 µg Hg/L. If 50% of trace elements at a concentration of 50 µg/L in irrigation water were transferred into leaves, grain, or stover of the crops in **Table 4**, then maximum "normal" concentrations reported for these crops could be exceeded by one to two orders of magnitude. ***These scenario calculations indicate that arsenic, chromium, nickel, lead, and selenium of the elements in Dan River water of most concern, and caution should be used in irrigation scheduling when concentrations of these elements (or cadmium or mercury) in the Dan River significantly exceed the 5 µg/L level.***

POTENTIAL LOADING OF TRACE ELEMENTS TO SOILS BY FLOODING

Another concern about potential impacts of the Dan-River coal ash spill on agriculture in the river basin regards discharge of ash particles onto land with flooding. To evaluate impacts of flooding, we considered a worst-case scenario of a maximum total suspended solids concentration of 855 mg/L, as measured in Dan River water 1 day after the spill (**Figure 3**). If land in the basin were flooded with 10 acre-inches of river water containing 100% ash at this concentration (i.e., no suspended soil particles), then 1 ton/acre of ash would be distributed to the land. Considering the >25-fold drop in total suspended solids within 3 days after the spill (**Figure 3**), we consider 1 ton/acre to be the maximum likely loading rate with floodwater.

If 1 ton/acre of ash containing trace elements at the mean concentrations shown in **Table 1** were mixed into the top 10 cm of soil, then soil concentrations would increase relative to our reference soil concentrations in **Table 3** by the following amounts (also see assumptions in **Table 3**):

- 0.08 mg As/kg soil (1.8% increase),
- 1.1 mg Ba/kg (+0.2%)
- 0.0005 mg Cd/kg (+4.5%)
- 0.02 mg Cr/kg (+0.1%)
- 0.071 mg Cu/kg (+1%)
- 0.0003 mg Hg/kg (+2.8%)
- 0.027 mg Ni/kg (+0.4%)
- 0.02 mg Pb/kg (+0.2%)
- 0.008 mg Se/kg (+2%)
- 0.07 mg V/kg (+0.1%), and
- 0.04 mg Zn/kg (+0.3%).

As discussed above, we consider such loading rates to produce a marginal increase in soil concentrations, particularly if such flooding events are infrequent. ***Thus, impacts of Dan-River flooding on crop production and crop quality should be negligible.***

From an agronomic perspective, coal ash has been examined for use as a soil amendment to improve soil texture and water holding capacity of sandy soils, to increase cation exchange capacity (CEC), and to supply lime, phosphorus (P), potassium (K), and calcium (Ca) when applied at appropriate rates. For these evaluations, coal ash was applied at rates ranging from 5 to ≥ 50 tons/acre, depending on desired changes in pH, nutrients, or physical properties (Plank et al. 1975, Pathan et al., 2003). ***From that perspective, an infrequent addition of 1 ton ash/acre with flooding would also have marginal impacts on agricultural soils in the Dan River basin.***

DAN RIVER WATER QUALITY AND LIVESTOCK

The summary of water-quality samples for the coal-ash impacted Dan River (**Table 2**) can be used to judge possible impacts of river water used as a source of drinking water for livestock. For example, **Table 5** provides maximum recommended concentrations of a number of the trace elements that are considered safe for livestock (from Saltanpour and Raley, 1999, based on National Academies of Science and Engineering water quality criteria). In all cases, the recommended water-quality standards for livestock are 4- to 480-fold greater than those of Class WS surface waters used as sources for human drinking water. ***Based on the maximum measured concentrations of these elements in Dan-River water after the coal ash spill (Table 2), none of the samples analyzed by USEPA or Duke Energy exceeded these maximum recommended concentrations for livestock drinking water.***

Table 5. Maximum recommended concentrations of trace elements in drinking water for livestock (from Saltanpour and Raley, 1999), compared with adopted standards for Class WS surface waters used as drinking water for humans (from Table 2). Livestock guidelines are reported here in units of micrograms per liter ($\mu\text{g/L}$) to be consistent with the Class WS standards.

Element	As	Cd	Cr	Cu	Hg	Pb	Se	V	Zn
Upper-limit guideline ($\mu\text{g/L}$)	200	50	1,000	500	10	100	50	100	24,000
Class WS Standard ($\mu\text{g/L}$)	10	2	50	7	0.012	25	5	no data	50

EXAMPLE MASS BALANCE CALCULATIONS

This section shows examples of the calculations made to prepare data in Tables 3 and 4, and to assess effects of river sediment deposition with flood waters. The units used in these calculations are consistent with concentration units that are typically reported for trace elements in water ($\mu\text{g/L}$) and soils (mg/kg)

Trace Element Deposition with Irrigation Water

- 1 acre-inch of water = 102,790 Liters (L) (~27,000 gallons)
- We assumed for this calculation that any applied trace elements would be distributed evenly throughout the top 10 cm of soil. Assuming a bulk density of $1,300 \text{ kg/m}^3$ of topsoil (~50% porosity), then the top 10 cm of 1 acre of soil would weigh 526,110 kg.
($1 \text{ acre} = 4,047 \text{ m}^2 \times 0.1 \text{ m} = 404.7 \text{ m}^3 \times 1,300 \text{ kg/m}^3 = 526,110 \text{ kg soil}$)
- Applying 1 acre-inch of water containing $50 \mu\text{g/L}$ (0.05 mg/L) of trace element would apply 5,140 mg of the trace element.
($0.05 \text{ mg/L} \times 102,790 \text{ L} = 5,140 \text{ mg trace element}$)
- Distributing this 5,140 mg of trace element into 526,110 kg of soil would increase the soil concentration by 0.0098 mg/kg .
($5,140 \text{ mg}/526,110 \text{ kg soil} = 0.0098 \text{ mg/kg}$)
- If, during a growing season, 10 acre-inches of irrigation water containing $50 \mu\text{g/L}$ of a given trace element is applied to a field, then the soil concentration could increase in the top 10 cm by approximately 0.1 mg/kg .
($10 \text{ acre inches} \times 0.0098 \text{ mg/kg increase per acre inch} = 0.098 \text{ mg/kg}$)

Trace Element Uptake By Crops – Example calculation for tobacco

- Assume a tobacco yield of 2,500 lbs. per acre
- Applying 10 acre-inches of irrigation water (1,027,900 L) containing $5 \mu\text{g element/L}$ (any element) adds 5,140 mg element ($5.14 \times 10^6 \mu\text{g}$).
- Assuming that the soil binds none of the added element, the roots take up all added element, and all of the element is translocated into the harvested tobacco leaves; then leaf concentration would increase by $5,140 \text{ mg element}/(2,500 \text{ lbs. per acre}/2.204 \text{ lbs. per kg}) = 4.53 \text{ mg/kg leaf biomass}$.

Sediment Deposition with Flood Water – Example calculation

- Assume that river water contains 855 mg/kg of total suspended coal ash (equivalent to the maximum observed total suspended solids (TSS) one day after the spill at the Draper Landing site 2.5 miles downriver of the spill - Figure 3).
- Assume that the Dan River floods a field with 10 acre inches of water.
- The total ash loading to the soil would be
 $10 \text{ acre-in} \times 102,790 \text{ L/ac-in} \times 855 \text{ mg/L} \times (1 \text{ kg}/1,000,000 \text{ mg}) \times (2.205 \text{ lb.}/1 \text{ kg}) = 1,938 \text{ lb. ash/acre} \approx 1 \text{ ton ash per acre}$.

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