

APPENDIX E

SLAG METALS RELEASE STUDY

A report to the
State of Washington Attorney General Office
Colville Confederated Tribes

Release of Major and Trace Elements from Smelter Slag Separated from the Upper Columbia River

Joseph N. Ryan¹, Sanjay Mohanty, and M. Elise Bingham
Department of Civil, Environmental, and Architectural Engineering, University of Colorado at Boulder

¹ corresponding author: University of Colorado at Boulder, 428 UCB, Boulder, Colorado 80309;
joseph.ryan@colorado.edu

Abstract

The release of a set of major and trace elements from three slag fractions isolated from sediments collected in the upper Columbia River were measured in a series of short-term (3 d) experiments and a long-term (28 d) experiment. The short-term release experiments were conducted to examine the effects of mixing speed, oxic versus near-anoxic conditions, crushing of slag, and pH. The long-term release experiment was conducted under nitrogen-purged near-anoxic conditions with crushed slag fractions in Columbia River water at near-neutral pH. The three slag fractions were isolated by heavy liquid separation from upper Columbia River sediments SCB12A, BSB5A, and DE8C.

The results of the short-term experiment established that (1) mixing speed did not affect the release of major and trace elements from a slag fraction, (2) near-anoxic conditions increased the release of some elements, decreased the release of some elements, and had no effect on the release of some elements relative to oxic conditions, (3) crushing increased the slag surface area and the release of most elements, but had no effect or decreased the release of some elements, and (4) acidic pH (5.4) increased the release of some cationic elements and decreased the release of some anionic elements; basic pH had the opposite effect.

The results of the long-term experiment established that most of the metals present in the slag in measurable concentrations were released to the Columbia River water at concentrations above the concentrations of those elements in the Columbia River water. Relatively high concentrations were observed for the release of iron, aluminum, barium, copper (especially for slag fraction DE8C), lead (especially for slag fraction SCB12A), zinc, and arsenic. Antimony and selenium were released at relatively high levels by slag fraction DE8C.

Introduction

In 1999, the Confederated Tribes of the Colville Indian Reservation in the State of Washington submitted a preliminary assessment petition to the U.S. Environmental Protection Agency (EPA) to survey the upper Columbia River for contamination by hazardous materials [EPA, 2003]. Following the preliminary assessment, the U.S. EPA coordinated an expanded site inspection for upper Columbia River sediment in the river region from the U.S.-Canadian border to the Grand Coulee Dam (Figure 1).

The EPA inspection revealed that the upper Columbia River sediments contained smelter slag and trace element contaminants (arsenic, cadmium, copper, lead, mercury, and zinc). The EPA implicated the Teck Cominco lead-zinc smelter in Trail, British Columbia, as the major source of the slag and trace element contamination. The EPA determined that the contaminants pose a risk to humans who consume fish from and recreate in the upper Columbia River.

The slag found near the U.S.-Canadian border in the upper Columbia River has been identified as relatively fresh smelter slag undergoing chemical weathering (Cox et al., 2002). The U.S. Geological Survey examined the release of trace elements from upper Columbia River by three methods – collection of interstitial water from the sediments, gentle stirring of water above the sediments, and vigorous tumbling of sediments in water [Paulson *et al.*, 2006; Paulson and Cox, 2007]. These techniques found that the sediments released high concentrations of cadmium, copper, lead, and zinc relative to release from reference sediments.

Purpose of this Work

The EPA and U.S. Geological Survey studies indicate that the upper Columbia River sediments are contaminated by slag and trace elements commonly found in slag. The U.S. Geological Survey studies showed that the sediments release these trace elements under conditions that simulate the upper Columbia River environment. The U.S. Geological Survey studies did not demonstrate that the trace elements released from the sediment came directly from the slag in the sediment. We undertook this study to assess the release of trace elements from slag isolated from the river sediments.

The U.S. Geological Survey release experiments were conducted under oxic conditions; under oxic conditions, iron released by the sediments may have been oxidized from ferrous to

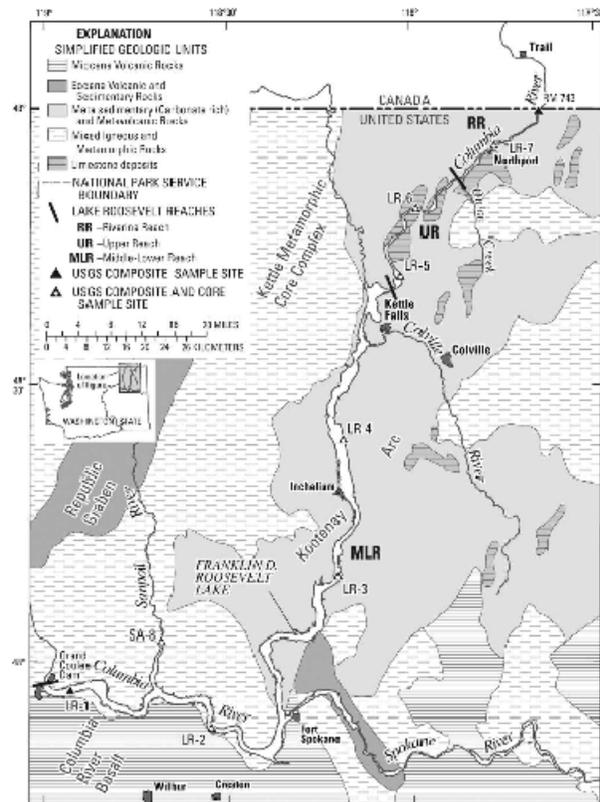


Figure 1. Map showing the upper Columbia River, regional geology, and locations sampled by the U.S. Geological Survey (Paulson et al., 2004).

ferric iron and precipitated as ferric oxyhydroxide. The ferric oxyhydroxide precipitation may have occurred as coating on the sediment and slag grains and caused less release of the many trace elements that adsorb readily to ferric oxyhydroxide surfaces. To avoid the adsorption of trace elements on precipitated ferric oxyhydroxide surfaces, we conducted the slag release experiments under near-anoxic conditions. These near-anoxic conditions may simulate oxidation-reduction conditions that occur at depth in the River sediments.

Methods

Sediment. Sediment samples from the upper Columbia River were delivered to our laboratory in 2 L glass sample jars. The samples were designated as follows:

- SCB12Archive-1.3-3.5 and SCB12A-1.5-3.1 (Figure 2a)
- DE8C-2.25-3.25 and DE8C-3.25-4.25 (Figure 2b)
- BSB5A-1.5-2.3 (Figure 2c)

The numbers at the end of the sample designations represent the depth (in feet) from which the samples were taken. The two SCB (South of the Canadian Border) samples were taken from similar depths in cores collected less than 60 cm apart – these two samples were homogenized for these experiments. The DE samples were taken from the same core at successive depths – these two samples were homogenized for these experiments. The location of the DE samples was not included on the aerial photograph (Figure 2). A single BSB (Black Sand Beach) sample was provided. Each of the sediments had been screened for lead concentration in excess of 100 mg kg⁻¹ and zinc concentration in excess of 2,400 mg kg⁻¹ by x-ray fluorescence.

Slag. Slag was isolated from the sediments using a heavy liquid density separation using methylene iodide

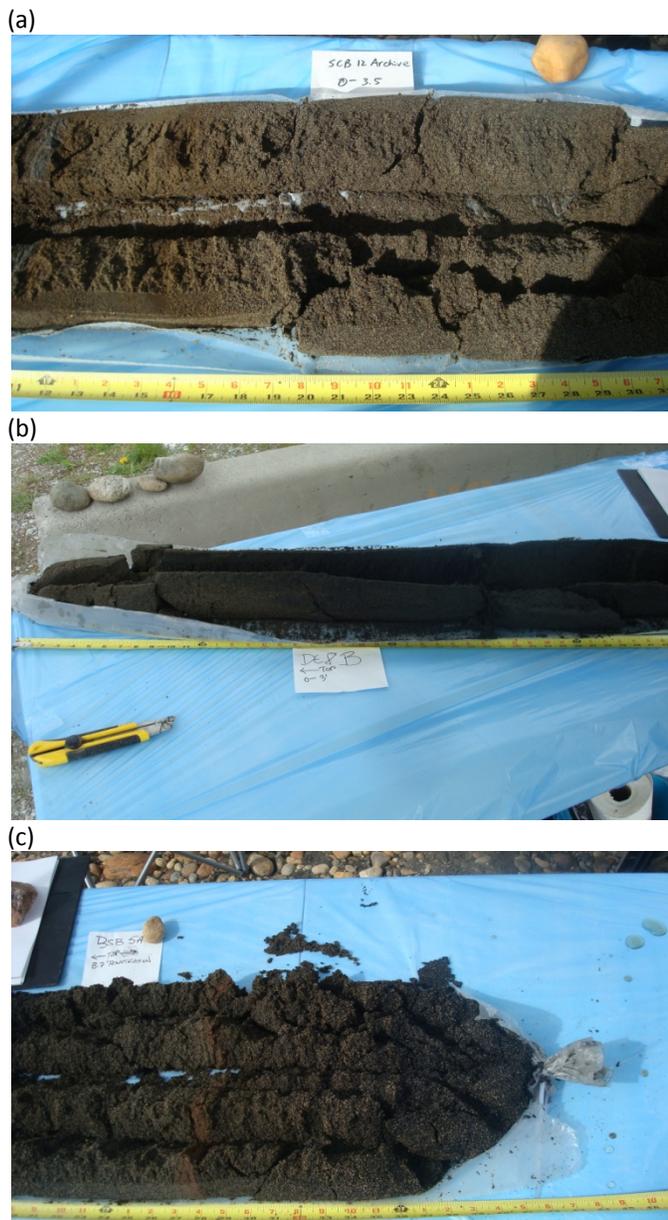


Figure 2. Photographs of sediments collected from the upper Columbia River: (a) sample SCBArchive, (b) sample DE8C, incorrectly labeled as DECB in the photograph, and (c) sample BSB5A.

(CH₂I₂; density 3.325 g cm⁻³ at 20°C). The methylene iodide separation did not affect the surfaces of slag examined for metal toxicity to aquatic organisms [Morrison and Gulson, 2007]; therefore, we assumed that the separation would not affect the release of major and trace elements from the slag. In the separation, we expected that sediment grains would float and slag grains would settle because the density of slag was expected to be high owing to its high iron content – about 20-30% by mass [Sigma Engineering, 1992]. Before the separation, the sediment samples were heated to dryness in glass dishes at 100°C for 32 h and sieved through a 125 µm brass mesh to remove the fine fraction of the sediment. In a fume hood, portions of the sediment (about 50 g) were added to methylene iodide (200 mL) in a separatory funnel (250 mL) and stirred. The grains were allowed to separate for 5 min. The settled slag grains were drained from the bottom of the separatory funnel onto a filter paper (Whatman 2), rinsed with acetone, allowed to dry for 24 h in the fume hood, weighed, rinsed with deionized water, and dried at 100°C for 24-32 h. Microscopic inspection of the separated grains indicated that the settled fraction was predominantly slag. To create fresh surfaces, the slag used in most of the release experiments was crushed using a ceramic mortar and pestle to pass through a 500 µm brass sieve and be retained on a 75 µm brass sieve.

The isolated slag samples were characterized for elemental composition, mineralogy, and surface area. Elemental composition was measured by digestion in a mixture of hydrochloric acid (3.5 mL), hydrofluoric acid (1.5 mL), and nitric acid (2.0 mL) at 95°C for 2 h, cooling, dilution to 50 mL in a boric acid (1.5 wt%) solution, re-heating to 95°C for 15 min, and cooling before analysis of major elements by inductively coupled plasma-atomic emission spectrometry (ICP-AES; ARL model 3410+) and trace elements by inductively coupled plasma-mass spectrometry (ICP-MS; Perkin Elmer SCIEX Elan DRC-e). For ICP-MS, indium was used as an internal standard. Four standards (blank, 100, 500 and 1000 ppb) made by accurately diluting certified standards were used for calibration. For ICP-AES, a blank and three standards made by accurately diluting certified standards were used for calibration. The major elements included aluminum, silicon, sodium, potassium, magnesium, calcium, iron, aluminum, titanium, and manganese. The trace elements included antimony, arsenic, barium, cadmium, chromium, cobalt, copper, lead, nickel, lead, selenium, silver, strontium, thallium, and zinc. The ICP-AES and ICP-MS analyses were done in the Laboratory for Environmental and Geological Sciences at the University of Colorado at Boulder.

Mineralogy was measured by x-ray diffraction (Department of Geological Sciences, University of Colorado at Boulder). Results will be inserted into this report when available.

The surface area of crushed (75-500 µm fraction) and uncrushed slag fractions (whole), with the exception of the uncrushed DE8C slag fraction, which had all been crushed and sieved by the time of the surface area analysis, was measured by five-point BET nitrogen absorption at relative pressures ranging from 0.05 to 0.25 (Micromeritics TriStarII instrument) by Pacific Surface Science (Ventura, CA).

Water. A sample of upper Columbia River water (32 L) was delivered to our laboratory for the experiments. The sample was designated Ryan-SW-001. The sample was delivered on ice and stored in a refrigerator at about 4°C until used in an experiment. The Columbia River water was characterized for major cations and iron (ICP-AES), major anions (ion chromatography; IC), and trace elements and silica (ICP-MS). The major cations and trace elements analyzed in the

river water were the same as those listed above for the slag fraction digestions. Fluoride, chloride, bromide, nitrate, nitrite, sulfate, and phosphate were measured as the major anions. Samples were analyzed as unfiltered and 0.2 μm -filtered (nylon membrane syringe filter, Whatman) to determine total and dissolved concentrations. Alkalinity (Hach digital titrator 16900) and pH (Orion 250A meter, 9107BN combination electrode, calibrated to pH values of 4, 7, 10) were measured in our laboratory.

Experimental Setup. The slag release experiments were conducted in reactors from which oxygen could be purged by bubbling of nitrogen gas. The slag suspensions were held in flasks (polypropylene, 500 mL). The flasks were sealed by rubber stoppers and Teflon[®] tape. The stoppers were pierced to accommodate a nitrogen inlet and outlet and a sample port. Nitrogen (industrial grade, $\text{N}_2 > 99.9\%$, $\text{O}_2 < 10 \text{ ppm}$) was delivered to the flask at pressures of 0.4-0.7 bar through a polypropylene tube submerged to the bottom of the slag suspension. Samples were collected through a polypropylene tube into a polyethylene syringe (30 mL). A new syringe was used for each sample. The flasks were agitated by a shaker table at 100 rpm.

For each slag release experiment, Columbia River water (300 mL) was added to a flask and nitrogen purging was conducted for about 10 h (overnight). To measure the effectiveness of nitrogen purging for removing dissolved oxygen from the water, we measured dissolved oxygen concentration as a function of time over 25 h in a preliminary experiment. Dissolved oxygen concentration was measured using a portable colorimeter (Hach DR890) and vacuum vials for measuring dissolved oxygen in the 1-15 and 0-1 mg L^{-1} ranges (Hach method 8316). The dissolved oxygen concentration decreased from a saturated concentration of 6.5 mg L^{-1} to a minimum plateau at about 0.2-0.3 mg L^{-1} at 4 h. After purging with nitrogen overnight, slag (30 g) was added to the Columbia River water and the release experiment commenced.

Experimental Procedure. Samples were collected from the slag release experiments at roughly doubling time intervals. To collect a sample, the shaker table was turned off, the slag grains were allowed to settle, and a water sample was withdrawn into a syringe. Half of the sample was filtered through a 0.45 μm nylon membrane in a polypropylene housing to determine dissolved concentrations; the other half of the sample was not filtered to determine total concentrations. The total and dissolved subsamples were placed in polyethylene (15 mL) test tubes with screw tops, acidified to a pH of 2(± 0.1) with trace metal-grade nitric acid, and stored at 4°C until analysis. Most of the slag release experiment samples were measured for major ions and trace elements (ICP-AES, ICP-MS), but not major anions. The final sample from each slag release experiment also included a 0.45 μm -filtered, but not acidified, aliquot (15 mL) to be analyzed for major anions (IC).

After each 30 mL sample was collected, 30 mL of Columbia River water was added to the slag suspension to maintain a constant solid:solution ratio. The addition of the fresh Columbia River water diluted the remaining slag suspension; therefore, the concentrations of the released major cations and trace elements were corrected for the dilution using the following equation:

$$C_{corrected} = \frac{C_{m,0}V_s + C_{m,1}(V_0 - V_s + V_a)}{V_0 - V_s + V_a} \quad (1)$$

where $C_{corrected}$ is the concentration corrected for the dilution, $C_{m,0}$ is the concentration measured in the previous sample, $C_{m,1}$ is the concentration measured in the following sample,

V_0 is the initial volume of the slag suspension (300 mL), V_s is the volume of the sample removed (15 mL), and V_a is the volume of the Columbia River water added to replace the sample. The exact volumes removed and added were measured by the difference in masses of the filled and empty syringe. The concentrations of the released major cations and trace elements were also corrected for evaporation of the slag suspension caused by the nitrogen purging using the following equation:

$$C_{corrected} = C_{m,1} \left(\frac{V_0 - V_e}{V_0} \right) \quad (2)$$

where V_e is volume of Columbia River water added to replace the evaporated water. The volume of evaporated water to be replaced was estimated using a mark at the height of the 300 mL slag suspension in each flask.

Slag release experiments were conducted for two durations: 3 d and 28 d. The 28 d release experiment examined the release of major cations and trace elements from the three isolated slag samples, each in duplicate. The 3 d experiments were conducted to examine the effect of three variables – stirring speed, anoxic versus oxic conditions, crushed versus uncrushed slag, and pH – on major cation and trace element release from a single slag sample. The 3 d experiments were conducted on slag separated from the composited SCB12Archive and SCB12A upper Columbia River sediments. The baseline conditions included nitrogen purging, crushed slag, and an initial pH value of about 7.0.

In the 3 d slag release experiments, the effect of stirring speed was assessed in a preliminary experiment in which stirring of the slag suspensions was done by a magnetic Teflon[®]-coated stir bar (5 cm length) and a stir plate at rates of 50, 100, and 200 rpm. This stirring method resulted in degradation of the Teflon[®] coating on the stir bar and the bottoms of the polypropylene flasks because of the angular nature of the crushed slag. Following this preliminary experiment, we changed the stirring method to the shaker table as described above. The effect of anoxic versus oxic conditions was assessed by conducting one slag release experiment with compressed air bubbling into the flask instead of nitrogen. The dissolved oxygen concentration remained at saturation – about 6.5 mg L⁻¹. The effect of crushing of the slag was assessed by conducting one slag release experiment on uncrushed slag. The effect of pH was assessed by conducting the slag release experiments at initial pH values of 5.4, 6.6, and 10.0. The pH of the Columbia River water was adjusted by addition of nitric acid (0.1 M) or sodium hydroxide (0.1 M).

Two slag-free quality control experiments were performed to ascertain that significant amounts of trace elements were not being released from the experimental vessel in 3 d experiments. The flasks were filled with high-purity water (Millipore Milli-Q, > 18 MΩ cm resistivity) and Columbia River water and no slag was added.

Results

Slag characterization. The fraction of the sediments isolated as slag using the methylene iodide separation ranged from 15 to 34% of the sediments (Table 1). Minerals present in the slag will be added to this report when results are received from the Laboratory for Environmental and Geological Studies at the University of Colorado at Boulder.

The surface areas of the crushed and sieved (75-500 μm) slag fractions were greater than those of the uncrushed slag fractions (Table 1). No uncrushed slag remained for the DE8C sample at the time of the surface area analysis. The DE8C slag fraction had the highest surface area for the crushed and sieved slag fractions.

The separated slag fractions are made up primarily of iron, silicon, calcium, and aluminum (Table 2). There was little variation in the major element composition of three slag fractions.

The most abundant trace elements in the slag fractions include zinc, copper, barium, and lead (Table 3). The concentrations of selenium, silver, and thallium were just above or below the detection limits. The composited SCB12Archive and SCB12A slag fraction contained more lead and zinc than the other two slag fractions. The BSB5A slag fraction contained more antimony, barium, chromium, and copper than the other two slag fractions.

Table 1. Characteristics of the slag fractions isolated from the upper Columbia River sediments.

sediment sample	slag fraction ^a (%)	minerals identified in slag fraction ^b	surface area of slag fraction ^c ($\text{m}^2 \text{g}^{-1}$)
SCB12Archive-1.3-3.5	22.4 \pm 0.6	tbd	4.9 (crushed)
SCB12A-1.5-3.1			-- (uncrushed)
BSB5A-1.5-2.3	34.0 \pm 3.6	tbd	3.9 (crushed) 2.2 (uncrushed)
DE8C-2.25-3.25	15.0	tbd	3.1 (crushed)
DE8C-3.25-4.25			2.3 (uncrushed)

^a one standard deviation for separations of 50 g subsamples of the whole sediment sample; only one 50 g subsample of whole DE8C sediment was separated; others were sieved (125 μm) before separation to improve the separation efficiency.

^b to be determined; analysis not yet complete.

^c crushing was followed by sieving (75-500) for the "crushed" slag fractions, which were used in the 28 d release experiments. The "uncrushed" slag fractions were not sieved.

Table 2. Major element composition of the slag fractions separated from the upper Columbia River sediments by an acid digestion. Element concentrations measured by ICP-AES. Concentrations presented as the average of duplicate measurements.

slag fraction	Al (wt %)	Si (wt %)	Li (wt %)	Na (wt %)	K (wt %)	Mg (wt %)	Ca (wt %)	Fe (wt %)	Ti (wt %)	Mn (wt %)
SCB12Archive-1.3-3.5	3.39	15.2	0.002	0.18	0.47	0.79	8.30	32.0	0.22	0.66
SCB12A-1.5-3.1										
BSB5A-1.5-2.3	3.14	14.6	0.003	0.23	0.46	0.81	8.87	29.0	0.21	0.45
DE8C-2.25-3.25	3.57	14.6	0.001	0.25	0.58	1.14	8.60	29.5	0.29	0.57
DE8C-3.25-4.25										

Table 3. Trace element composition of the slag fractions separated from the upper Columbia River sediments by an acid digestion. Element concentrations measured by ICP-MS. Concentrations presented as the average of duplicate measurements.

slag fraction	As (ppm)	Ba (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Ni (ppm)	Pb (ppm)	Sb (ppm)	Sr (ppm)	Zn (ppm)
SCB12Archive-1.3-3.5	82	1,400	7.9	36	99	1,630	20	1,310	65	211	27,700
SCB12A-1.5-3.1											
BSB5A-1.5-2.3	80	2,180	9.5	47	155	2,680	37	802	244	224	19,600
DE8C-2.25-3.25	65	1,120	8.1	41	92	1,280	29	663	54	242	21,200
DE8C-3.25-4.25											

River water characterization. The major cations and anions of the upper Columbia River water were calcium, magnesium, bicarbonate, and sulfate (Table 4). At the pH of 6.9 ± 0.3 (triplicate measurement) measured in the laboratory, the measured alkalinity is the equivalent of a bicarbonate concentration of about 1.0×10^{-3} M, or about 61 mg L^{-1} . The concentrations of iron, nitrite, bromide, and phosphate were just above or below the detection limits. The most abundant trace elements in the river water were barium and strontium. The dissolved concentrations were similar to the total concentrations, which indicates that colloids (which would be trapped on a $0.2 \mu\text{m}$ filter) were not playing a role in the speciation of the trace elements. Antimony, arsenic, cobalt, lead, silver, titanium, and thallium concentrations were just above or below the detection limits.

Table 4. Major ion composition of the upper Columbia River water sample as total (unfiltered) and dissolved ($0.2 \mu\text{m}$ filtration) samples. Ion concentrations measured by ICP-AES and IC. Concentrations presented as the average of duplicate measurements.

river water	Si (mg L^{-1})	Na (mg L^{-1})	K (mg L^{-1})	Mg (mg L^{-1})	Ca (mg L^{-1})	F ⁻ (mg L^{-1})	Cl ⁻ (mg L^{-1})	NO ₃ ⁻ (mg L^{-1})	SO ₄ ²⁻ (mg L^{-1})	Alk (mg CaCO ₃ L ⁻¹)
total	2.68	1.89	0.73	4.22	17.5	0.068	0.89	0.45	8.58	51.5
dissolved	2.61	1.90	0.69	4.14	17.1	0.064	0.88	0.43	8.44	--

Table 5. Trace element composition of the upper Columbia River water sample as total (unfiltered) and dissolved ($0.2 \mu\text{m}$ filtration) samples. Element concentrations measured by ICP-MS. Concentrations presented as the average of duplicate measurements.

slag fraction	Al (ppb)	Ba (ppb)	Cd (ppb)	Cr (ppb)	Cu (ppb)	Li (ppb)	Mn (ppb)	Ni (ppb)	Se (ppb)	Sr (ppb)	Zn (ppb)
total	7.0	30.0	0.03	2.3	0.72	1.23	0.30	1.00	0.40	88.0	4.0
dissolved	5.5	29.0	0.02	2.6	0.87	1.23	0.15	1.05	0.38	85.0	3.5

Slag release quality control experiments. Two quality control experiments were conducted to determine if the experimental apparatus was contributing any trace elements to (1) upper Columbia River water and (2) high-purity water. After three days in the experimental apparatus, the upper Columbia River water contained the major and trace element concentrations similar to those of the un-reacted river water (Figure 3). Reaction in the experimental apparatus resulted in the appearance of a small amount of arsenic (0.4 ppb) and

increases in the barium and titanium concentrations. Barium and titanium were also released into the high-purity water by the experimental apparatus. The amounts of major and trace elements released in these control experiments was far less than the amounts released by the slag fractions.

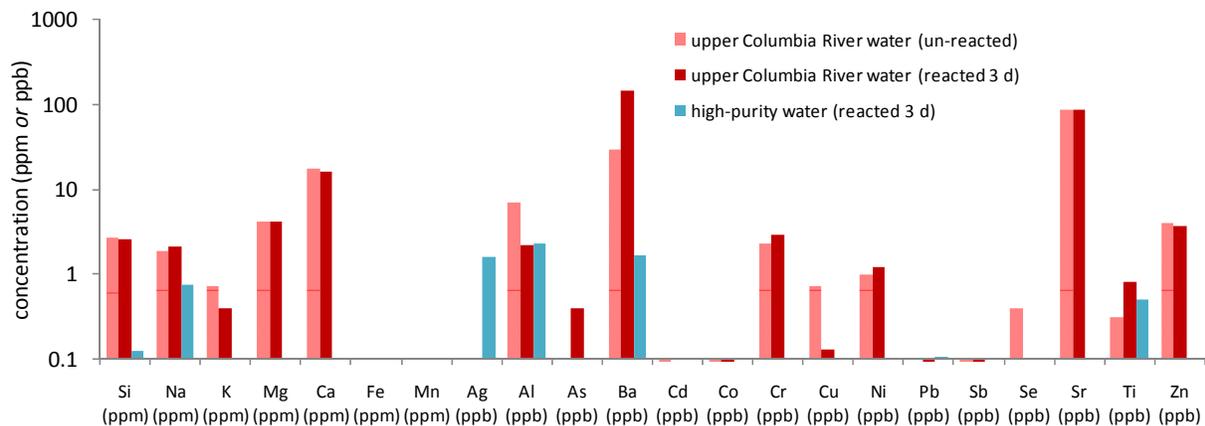


Figure 3. Results of two quality control experiments to assess the amount of major and trace element release from the experimental apparatus into upper Columbia River water (black) and high-purity water (blue) compared with major and trace element concentrations in un-reacted upper Columbia River water (grey). Concentrations measured as below the detection limit plotted as 0.1 on the logarithmic concentration axis.

Three-day slag release experiments. The 3 d experiments were conducted to examine the effect of three variables – stirring speed, anoxic versus oxic conditions, crushed versus uncrushed slag, and pH – on major cation and trace element release from slag separated from the composited SCB12Archive and SCB12A upper Columbia River sediments. For each experiment, we show graphs of release of iron, arsenic, copper, and zinc as a function of time – data for the other major ions and trace elements are available.

Stirring speed did not significantly affect the release of major cations and trace elements from the slag (Figure 4). The grinding caused by the angular slag grains caused degradation of the stir bar and flasks, which resulted in floating plastic particles in the slag suspension. These plastic particles did not appear to affect the release of the major cations and trace elements based on comparison with early release in the 28 d experiment.

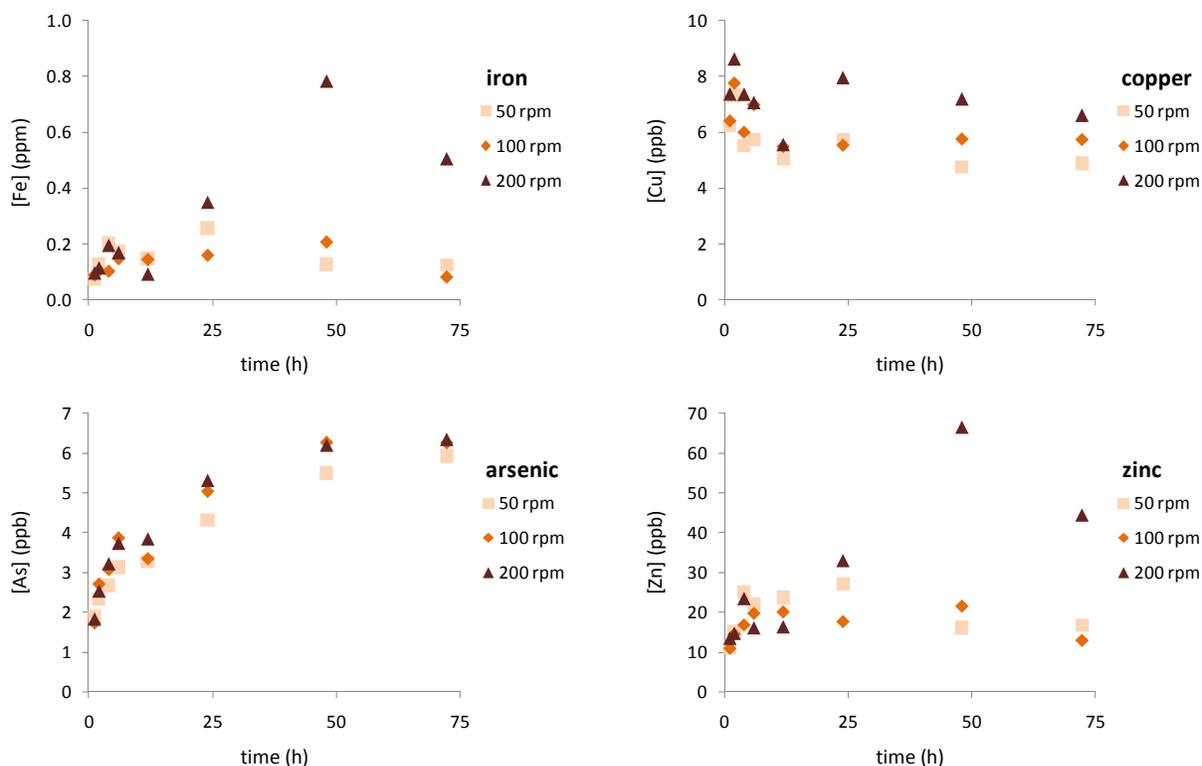


Figure 4. The effect of stirring speed on the release of iron, copper, arsenic, and zinc from the slag separated from upper Columbia River sediment samples SCB12Archive and SCB12A to Columbia River water under nitrogen-purged conditions during a 3 d experiment.

The effect of anoxic versus oxic conditions was assessed by conducting one slag release experiment with compressed air bubbling into the flask instead of nitrogen. The dissolved oxygen concentration remained at saturation – about 6.5 mg L^{-1} – in the air-bubbled flask and decreased to about $0.2\text{-}0.3 \text{ mg L}^{-1}$ in the nitrogen-bubbled flask. The near-anoxic versus oxic conditions did not significantly affect the release of iron, copper (Figure 5), silicon, the major cations, antimony, barium, chromium, lead, manganese, nickel, and strontium (data not shown). For arsenic (Figure 5) and aluminum (data not shown), greater release was observed under the nitrogen-purged near-anoxic conditions. For zinc, greater release was observed under air-bubbled oxic conditions. We expected that the near-anoxic conditions would enhance the release of iron and trace elements typically adsorbed to ferric oxyhydroxide minerals because we assumed that some of the iron in the slag was ferric iron. The lack of a significant effect of near-anoxic versus oxic conditions on iron release suggests that iron is present primarily as ferrous iron.

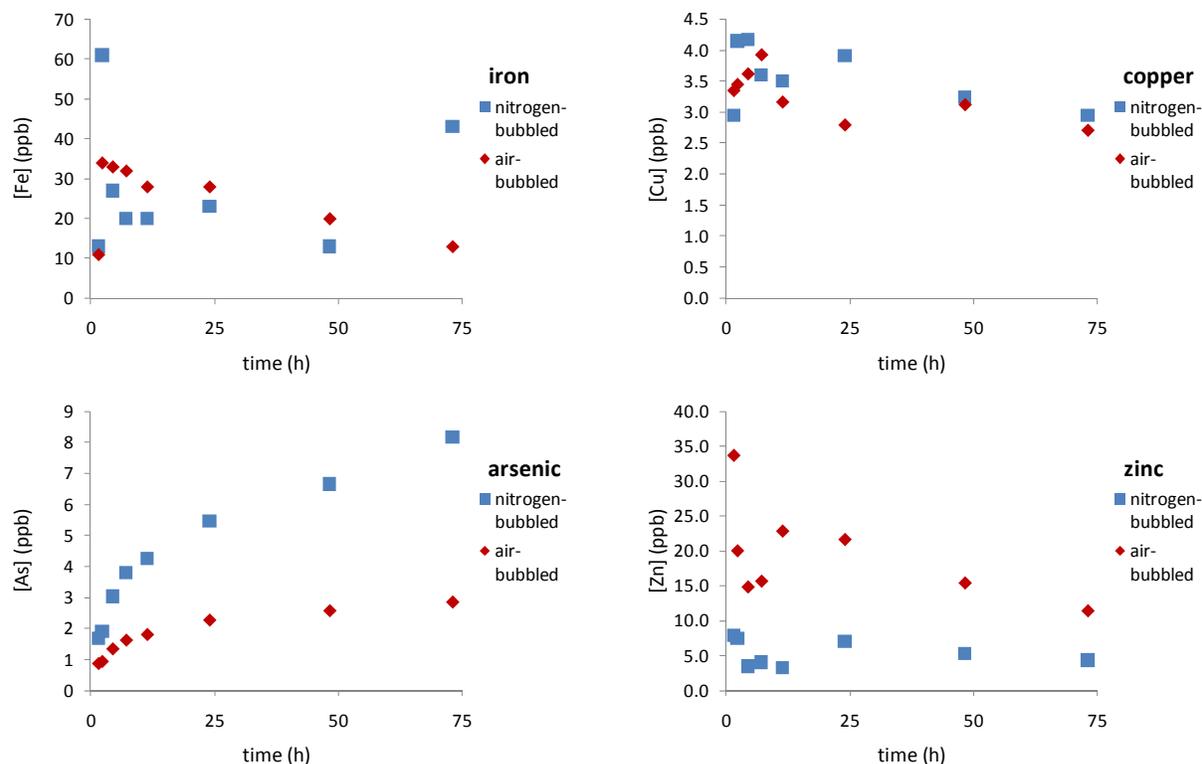


Figure 5. The effect of nitrogen- versus air-bubbling on the release of iron, copper, arsenic, and zinc from the slag separated from upper Columbia River sediment samples SCB12Archive and SCB12A to Columbia River water under nitrogen-purged conditions during a 3 d experiment.

The effect of crushing of the slag was assessed by conducting one slag release experiment on uncrushed slag. The size range of the crushed slag was 75-500 μm . Without crushing, less than 5% of the slag passed through a 500 μm sieve. For iron, arsenic (Figure 5), aluminum, cobalt, lead, and manganese (data not shown), release from the crushed slag exceeded release from the uncrushed slag. For copper (Figure 6), silicon, the major cations, antimony, chromium, nickel, selenium, and strontium (data not shown), release from the crushed and uncrushed slag was similar. For zinc (Figure 6) and barium (data not shown), release from the uncrushed slag exceeded release from the crushed slag.

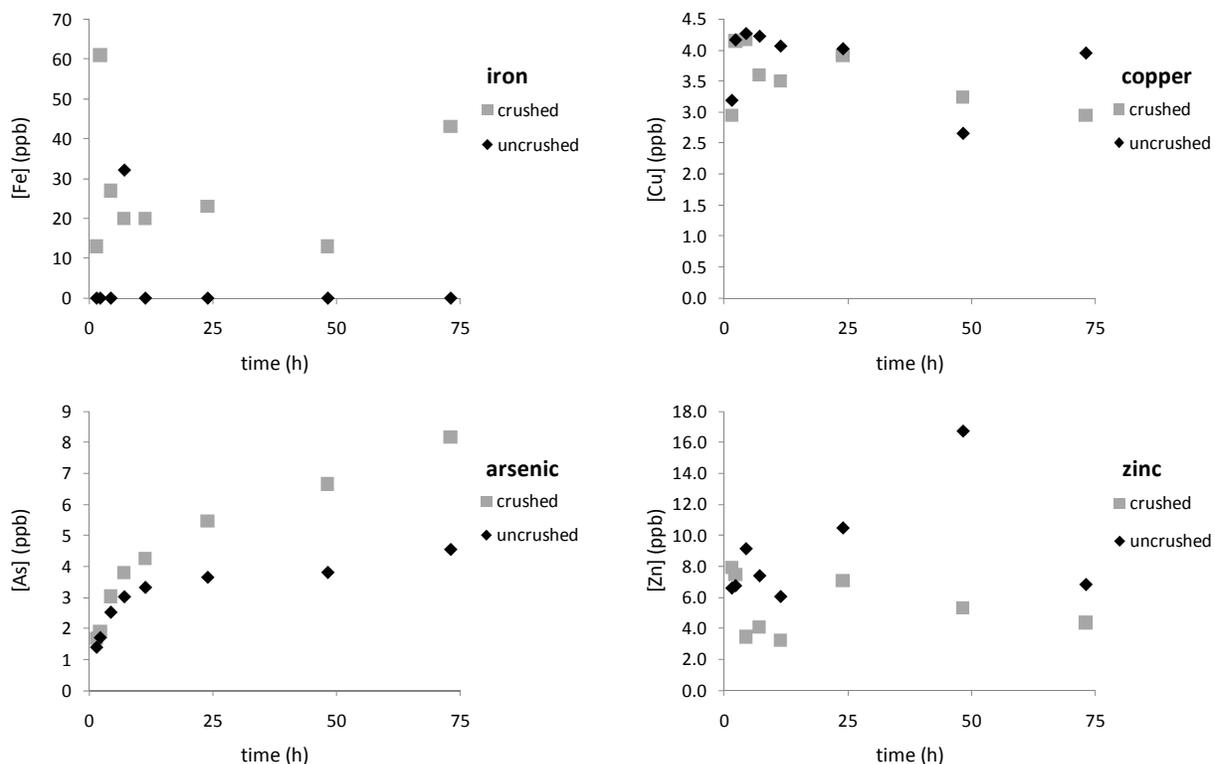


Figure 6. The effect of nitrogen- versus air-bubbling on the release of iron, copper, arsenic, and zinc from the slag separated from upper Columbia River sediment samples SCB12Archive and SCB12A to Columbia River water under nitrogen-purged conditions during a 3 d experiment.

The effect of pH was assessed by conducting the slag release experiments at initial pH values of 5.4, 6.6 (the baseline condition), and 10.0. The lower pH increased the release of iron, zinc (Figure 7), the major cations, barium, cobalt, manganese, and strontium (data not shown) relative to the pH 6.6 baseline condition. The lower pH decreased the release of arsenic (Figure 7), aluminum, and chromium (data not shown) relative to pH 6.6. The lower pH had no clear effect on the release of copper (Figure 7), silica, antimony, lead, and nickel (data not shown).

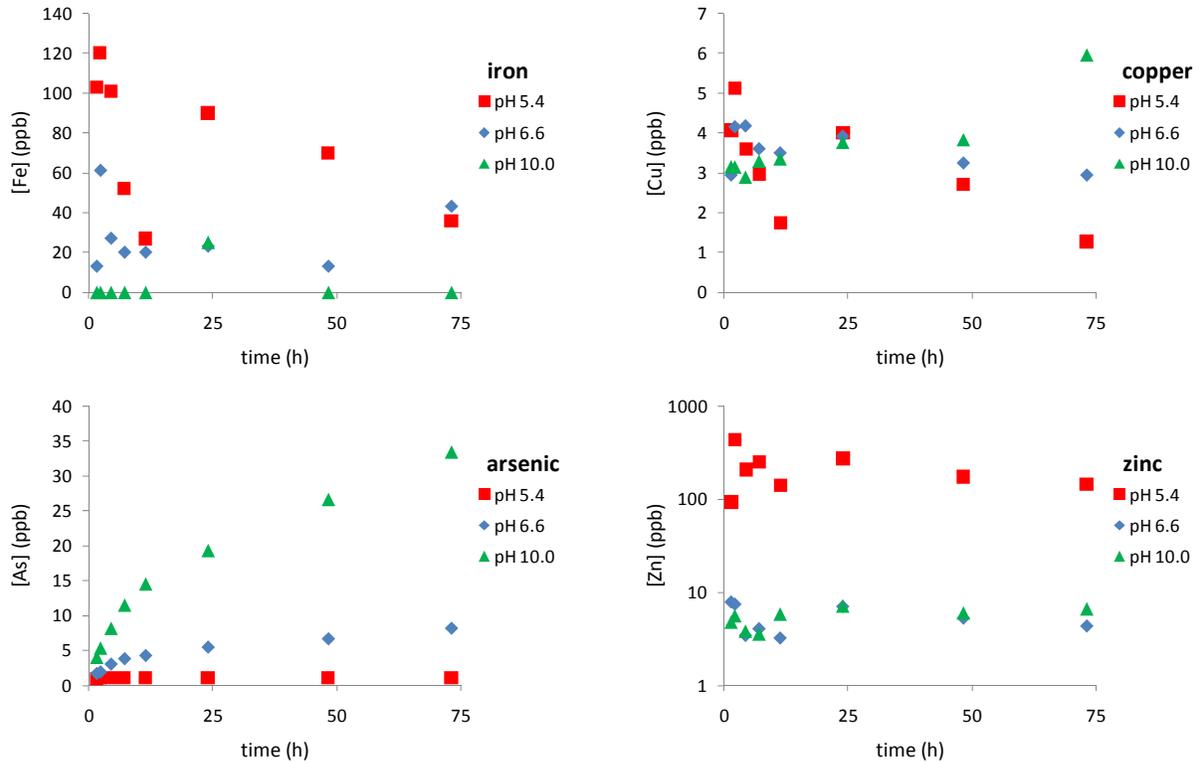


Figure 7. The effect of pH on the release of iron, copper, arsenic, and zinc from the slag separated from upper Columbia River sediment samples SCB12Archive and SCB12A to Columbia River water under nitrogen-purged conditions during a 3 d experiment. The concentrations for zinc are shown on a logarithmic axis to distinguish the low concentrations at pH values of 6.6 and 10.0 from zero.

Twenty-eight-day release experiment. For the 28 d release experiments, we examined the release of major cations and trace elements from the slag fractions separated from the three upper Columbia River sediments into the Columbia River water at a pH value of about 7 under nitrogen-purged, near-anoxic conditions. The results for all of the major cations and trace elements are presented as a function of time in Figures 9-12. For most elements, the graphs show the concentration of the Columbia River water before introduction of the slag fractions; for some elements that were not detected in the Columbia River water at concentrations above detection limits, the detection limits are shown.

The fraction of the major and trace element release was quantified as a ratio of the mass of the element released to the Columbia River water to the mass of the element in the slag fraction:

$$f_{\text{release}} = \frac{C_w^{\text{max}} V_0}{C_{\text{slag}} M_{\text{slag}}} \quad (3)$$

where C_w^{max} is the maximum average concentration of the element for duplicates in the Columbia River water during the 28 d experiment, V_0 is the volume of water in the 28 d experiment (300 mL), C_{slag} is the concentration of the element in the slag, and M_{slag} is the mass of slag added to the 28 d experiment (30 g). The fraction released was not calculated for

selenium, silver, and thallium, which were not found above the detection limits for these elements in the slag fractions.

The concentrations of the alkali and alkaline earth cations – Li, Na, K, Mg, Ca, Sr, and Ba – are shown as a function of time for the 28 d experiments in Figures 9 and 10. The release of lithium and sodium approximately doubled the concentrations of these cations in the Columbia River water (Tables 4 and 5). The release of barium increased the barium concentration by a factor of 5-10 relative to the barium concentration in the Columbia River water (Table 4). The potassium, magnesium, and strontium concentrations decreased below the concentrations initially present in the water (Tables 4 and 5), which suggests that potassium, magnesium, and strontium were adsorbed to the slag. Calcium concentrations were initially at or greater than the calcium concentration in the Columbia River water and they decreased to concentrations at or below the Columbia River water calcium concentration (Table 4). Relative to the amount of these cations in the slag fractions, the amount released ranged from about 0.1-0.3% for lithium, potassium, and calcium to about 2% for sodium (Table 6). The release data for potassium are quite inconsistent, probably because the slag fractions contained very little potassium (Table 2) and amount released was often measured as below the potassium detection limit for ICP-AES (0.09 ppm). The differences between the amounts released for the three slag fractions were minor with the exception of low potassium in BSB5A (many samples measured as below the detection limit) and high magnesium and strontium in BSB5A in the two samples near the end of the 28-d experiment.

Silicon release from the three slag fractions, which is shown with the major cations in Figure 9, increased slowly over the 28 d of the experiment from the concentration present in the Columbia River water (2.7 ppm; Table 4) to about 4 ppm. Each of the three slag fractions released similar concentrations of silicon and about the same fraction of total silicon in the slag fractions, about 0.03% (Table 6).

Table 6. Fraction of release of major and trace elements during the 28 d experiment calculated as the ratio of the mass of the major element released to the mass of the major element composition of the slag fraction.

slag fraction	Al (%)	Si (%)	Li (%)	Na (%)	K (%)	Mg (%)	Ca (%)	Fe (%)	Ti (%)	Mn (%)
SCB12Archive-1.3-3.5	0.0022	0.029	0.077	1.8	0.13	0.50	0.21	0.0017	0.0022	0.0007
SCB12A-1.5-3.1										
BSB5A-1.5-2.3	0.0019	0.028	0.096	2.1	0.13	0.52	0.23	0.0012	0.0012	0.0014
DE8C-2.25-3.25	0.0023	0.031	0.22	1.5	0.11	0.34	0.33	0.0022	0.0009	0.0020
DE8C-3.25-4.25										

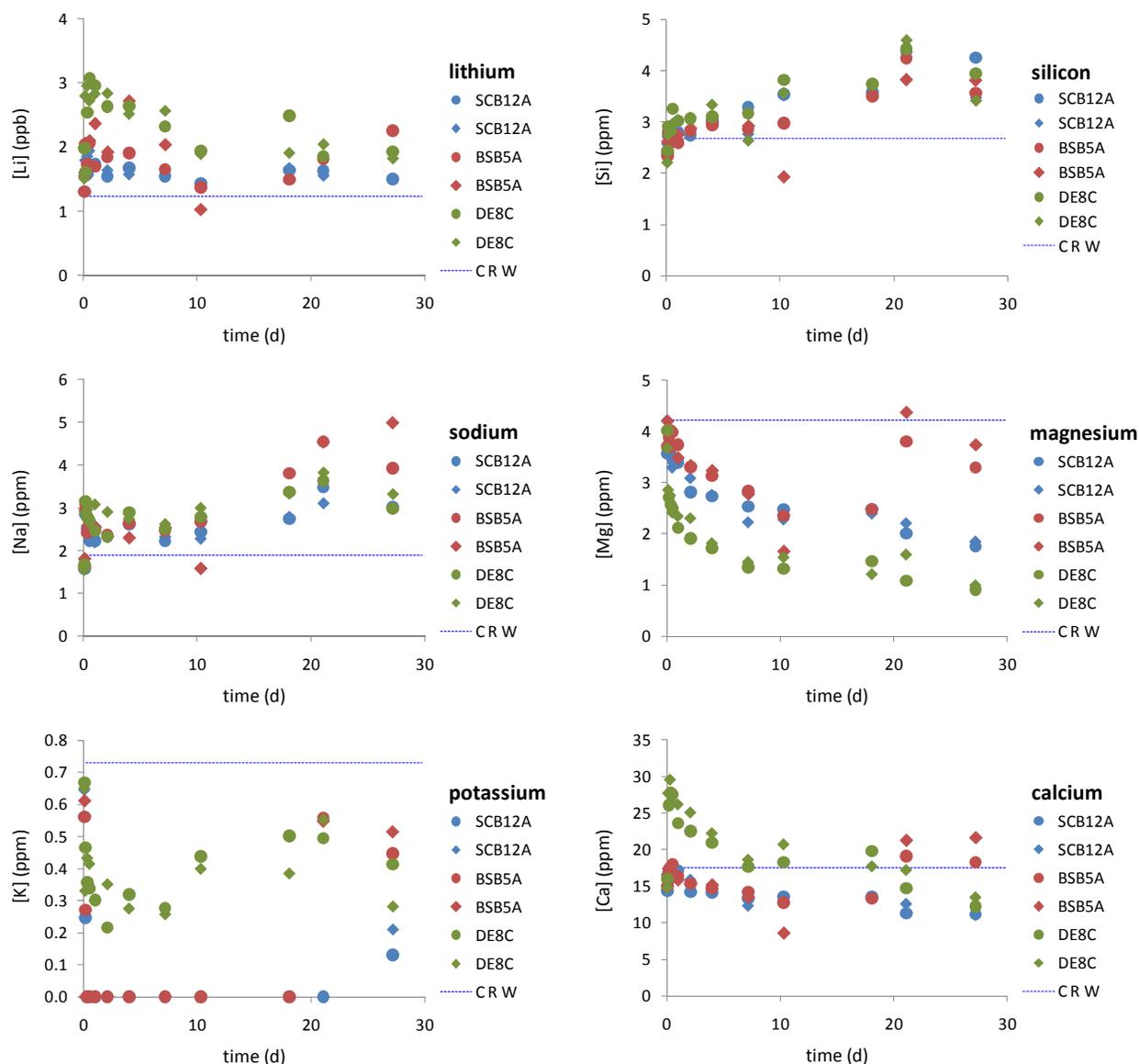


Figure 9. The release of lithium, sodium, potassium, calcium, magnesium, and silicon from the slag separated from upper Columbia River sediment samples to Columbia River water under nitrogen-purged conditions during 28 d experiments. Duplicate results shown for each of the three slag fractions: SCB12A (composite of SCB12Archive and SCB12A), BSB5A, and DE8C. Measurements below the detection limits are shown as concentrations of zero. Horizontal dashed line shows concentration of elements in Columbia River water (C R W) or detection limit (dl).

The concentrations of iron, aluminum, manganese, and titanium are shown as a function of time for the 28 d experiments in Figure 10. In the Columbia River water, these elements were measured at concentrations just above (aluminum) or at the detection limits (iron, manganese, and titanium); therefore, the concentrations measured in the 28 d release experiment represent release of these elements. Each of these metals increased rapidly in concentration in the first few days of the release experiment and increased more gradually over longer time, which suggests an approach to equilibrium. For each of the metals, the agreement between the concentrations measured in the duplicate experiments becomes poorer over time. Some

results in the 21 d and 28 d samples have been submitted for re-analysis. The fractions of iron, aluminum, manganese, and titanium released by the slag fractions range from about 0.001 to 0.002% for all three slag fractions (Table 6).

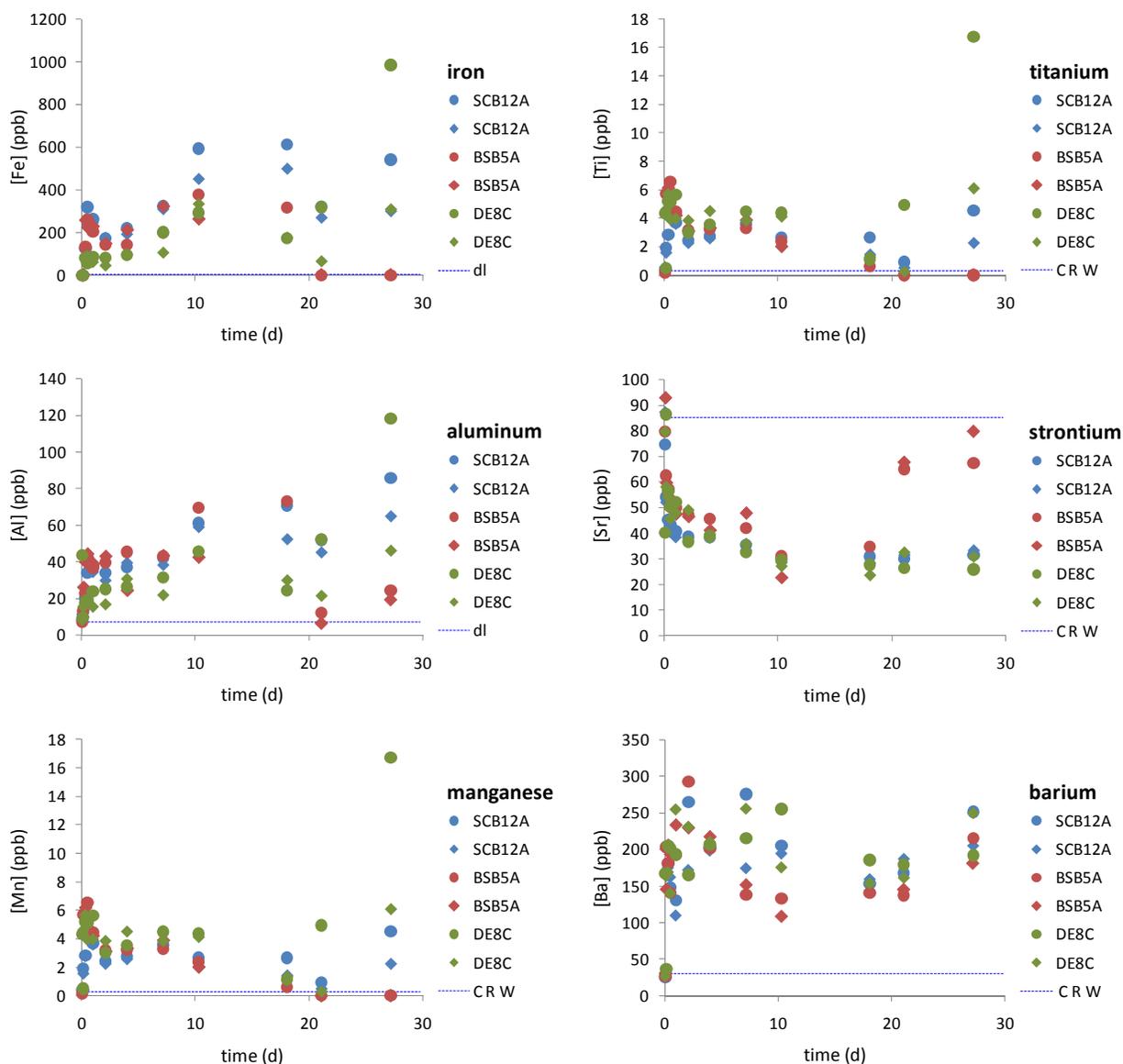


Figure 10. The release of iron, aluminum, manganese, titanium, strontium, and barium from the slag separated from upper Columbia River sediment samples to Columbia River water under nitrogen-purged conditions during 28 d experiments. Duplicate results shown for each of the three slag fractions: SCB12A (composite of SCB12Archive and SCB12A), BSB5A, and DE8C. Measurements below the detection limits are shown as concentrations of zero. Horizontal dashed line shows concentration of elements in Columbia River water (C R W) or detection limit (dl).

The concentrations of six transition metals – cadmium, cobalt, copper, nickel, lead, and zinc – are shown as a function of time for the 28 d experiments in Figure 11. For most of these metals, the concentrations in the release experiments are above the concentrations in the Columbia River water with the exception of cadmium in the DE8C slag fraction and nickel in all of the slag fractions. Most of these metals displayed rapid increases in concentration in the first few days of the release experiment

and more gradual increases, or in some cases, decreases, over longer time. For some metals (e.g., zinc, the disparity between concentrations measured in duplicate experiments became greater with time. Relatively high fractions of nickel were released from the slag fractions (Table 7) relative to the other transition metals. The DE8C slag fraction released much more copper than the other two slag fractions and the copper released was a greater fraction of the total copper in this slag fraction. The SCB12A slag fraction released more cadmium, lead, and zinc than the other slag fractions and these metals were released as a greater fraction of the total amount of these metals in the slag fraction.

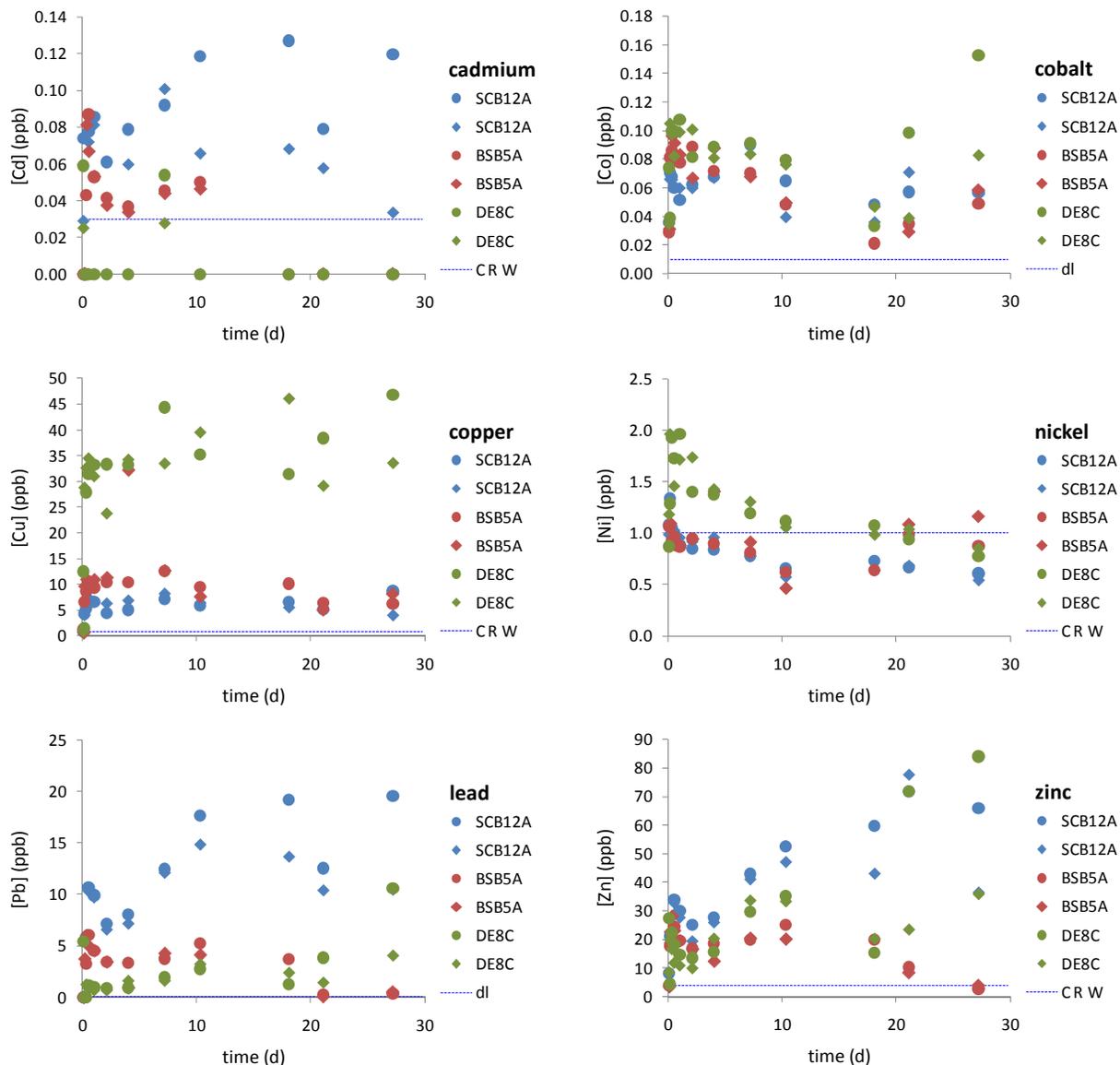


Figure 11. The release of cadmium, cobalt, copper, nickel, lead, and zinc from the slag separated from upper Columbia River sediment samples to Columbia River water under nitrogen-purged conditions during 28 d experiments. Duplicate results shown for each of the three slag fractions: SCB12A (composite of SCB12Archive and SCB12A), BSB5A, and DE8C. Measurements below the detection limits are shown as concentrations of zero. Horizontal dashed line shows concentration of elements in Columbia River water (C R W) or detection limit (dl).

Table 7. Fraction of release of trace elements during the 28 d experiment calculated as the ratio of the mass of the major element released to the mass of the major element composition of the slag fraction.

slag fraction	As (%)	Ba (%)	Cd (%)	Co (%)	Cr (%)	Cu (%)	Ni (%)	Pb (%)	Sb (%)	Sr (%)	Zn (%)
SCB12Archive-1.3-3.5	0.18	0.15	0.013	0.0023	0.024	0.0046	0.054	0.012	0.20	0.35	0.0024
SCB12A-1.5-3.1											
BSB5A-1.5-2.3	0.091	0.11	0.0076	0.0017	0.023	0.0042	0.030	0.0068	0.089	0.35	0.0012
DE8C-2.25-3.25	0.16	0.21	0.0044	0.0029	0.023	0.033	0.061	0.0099	2.3	0.31	0.0015
DE8C-3.25-4.25											

The concentrations of the remaining trace elements – four of which are oxyanions (arsenic, antimony, chromium, and selenium) and two of which behave as transition metals (silver and thallium) – are shown as a function of time for the 28 d experiments in Figure 12. For antimony, arsenic, chromium, and selenium, the concentrations in the release experiments are above the concentrations in the Columbia River water. For silver and thallium, concentrations just above or mostly below the detection limits of ICP-MS were measured both in the release experiments and in the Columbia River water. Arsenic displayed a more consistent pattern of release during the 28 d experiment than most other trace elements – the order of release for the slag fractions is SCB12A > DE8C > BSB5A. The BSB5A slag fraction released the lowest fraction of the total arsenic in the slag (Table 7). Antimony and selenium were released at much higher concentrations by the DE8C slag fraction, but for antimony, not because there was more antimony in the DE8C slag, but because a higher fraction of the antimony was released. The fraction of selenium released could not be determined because the selenium concentration in the slag fractions was below the detection limit. The three slag fractions released chromium at similar concentrations and at similar fractions of the total chromium in the slags.

The major anions released by the slag fractions were measured by ion chromatography at the conclusion of the 28 d experiments (Table 8); these anions were not measured over time. The alkalinity was not measured for these samples. For fluoride, chloride, and sulfate, the concentrations released from the slag fractions into Columbia River water exceeded the concentrations present in the Columbia River water; for nitrate, the concentration released was less than that of Columbia River water for two slag fractions. The BSB5A slag fraction released more chloride and sulfate than the other slag fractions, and the DE8C slag fraction released less sulfate than the other slag fractions. The pH of the slag release solutions increased by about 0.4-0.6 pH units during the 28 d release experiments (Table 8). The initial pH was similar to that of the Columbia River water. Nitrogen purging was probably responsible for some of the pH increase because the purging would remove carbon dioxide. The duplicate experiments for each slag fraction displayed similar initial and final pH values.

Table 8. Concentrations of major anions released from the slag fractions into Columbia River water at the end of the 28 d experiments compared to the composition of the upper Columbia River water (also presented in Table 4) and the initial and final pH for the 28 d release experiments.

28 d release / river water	F ⁻ (ppm)	Cl ⁻ (ppm)	NO ₃ ⁻ (ppm)	SO ₄ ²⁻ (ppm)	pH initial/final ^a
SCB12Archive-1.3-3.5/SCB12A-1.5-3.1	0.21	1.09	0.22	23.6	6.71 / 7.25 6.65 / 7.12
BSB5A-1.5-2.3	0.18	1.78	0.60	19.2	6.92 / 7.31 6.89 / 7.39
DE8C-2.25-3.25/DE8C-3.25-4.25	0.15	1.12	0.22	12.8	6.83 / 7.42 7.10 / 7.56
total, Columbia River water	0.068	0.89	0.45	8.58	6.9±0.3

^a initial and final pH values for duplicate experiments

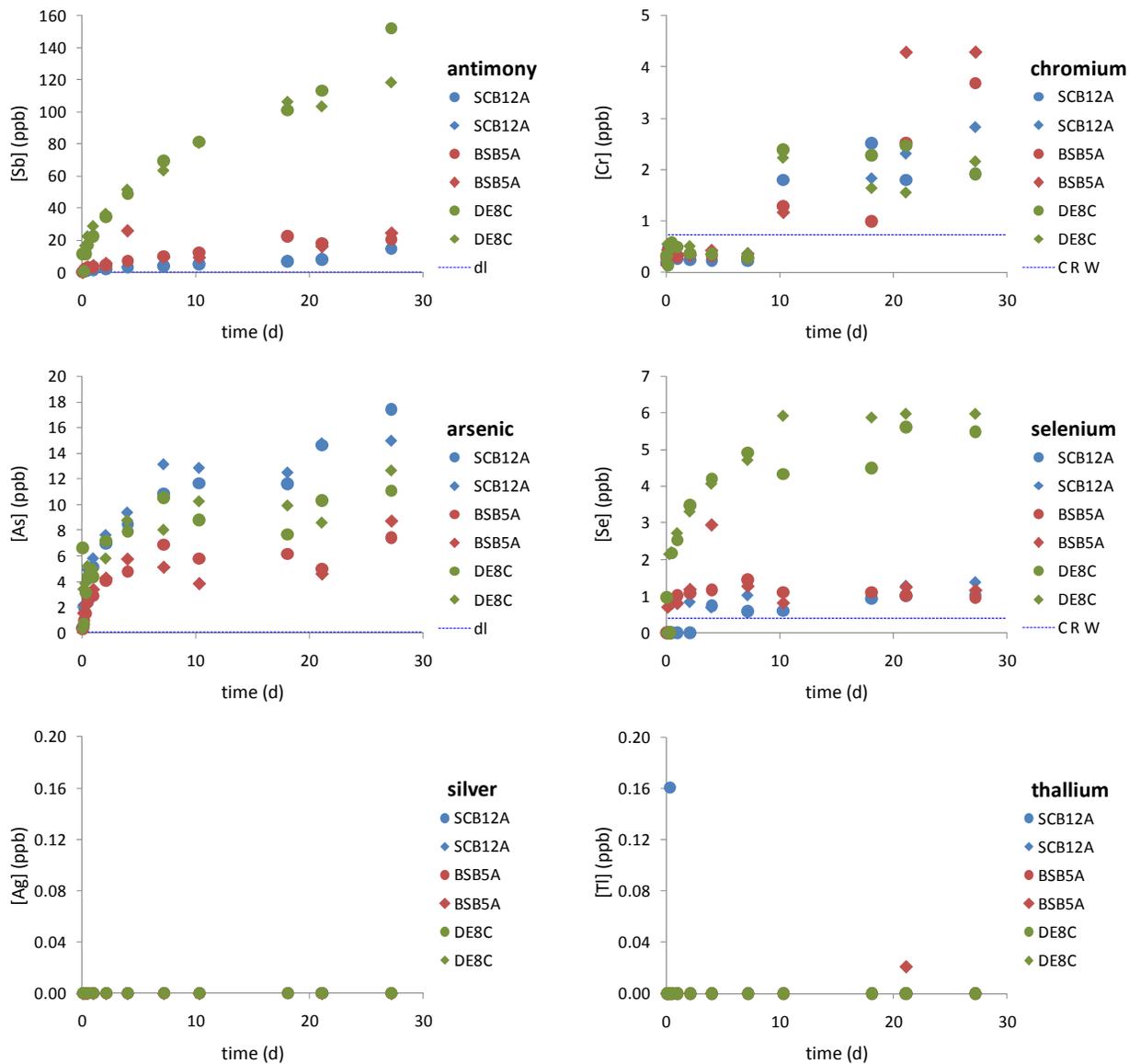


Figure 12. The release of antimony, chromium, arsenic, selenium, silver, and thallium from the slag separated from upper Columbia River sediment samples to Columbia River water under nitrogen-purged conditions during 28 d experiments. Duplicate results shown for each of the three slag fractions: SCB12A (composite of SCB12Archive and SCB12A), BSB5A, and DE8C. Measurements below the detection limits are shown as concentrations of zero. Horizontal dashed line shows concentration of elements in Columbia River water (C R W) or detection limit (dl). No horizontal line shown for silver and thallium because nearly all samples were measured below the detection limit.

References

- Cox S.E., Bell P.R., Lowther J.S., VanMetre P.C., 2004. Vertical Distribution of Trace-Element Concentrations and Occurrence of Metallurgical Slag Particles in Accumulated Bed Sediments of Lake Roosevelt, Washington. Scientific Investigations Report 2004-5090, U.S. Geological Survey, 70 pp.
- EPA, 2003. Upper Columbia River Expanded Site Inspection Report Northeast Washington, TDD: 01-02-0028. Report, Region 10, START-2, U.S. Environmental Protection Agency, March 2003.
- Morrison A.L. and Gulson B.L., 2007. Preliminary findings of chemistry and bioaccessibility in base metal smelter slags. *Science of the Total Environment* **382**, 30-42.
- Paulson A.J. and Cox S.E., 2007. Release of elements to natural water from sediments of Lake Roosevelt, Washington, USA. *Environmental Toxicology and Chemistry* **26**(12), 2550-2559.
- Paulson A.J., Wagner R.J., Sanzolone R.F. and Cox S.E., 2006. Concentrations of Elements in Sediments and Selective Fractions of Sediments, and in Natural Waters in Contact with Sediments from Lake Roosevelt, Washington, September 2004. Open-File Report 2006-1350, U.S. Geological Survey, 84 pp.
- Sigma Engineering, 1992. Lower Columbia River distribution of slag and the impact on fish habitat. Report, Sigma Engineering, Ltd., Vancouver, BC, Canada.