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Potential contaminants at a dredged spoil placement site, Charles City County, Virginia, as revealed by sequential extraction

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Backfills of dredged sediments onto a former sand and gravel mine site in Charles City County, VA may have the potential to contaminate local groundwater. To evaluate the mobility of trace elements and to identify the potential contaminants from the dredged sediments, a sequential extraction scheme was used to partition trace elements associated with the sediments from the local aquifer and the dredged sediments into five fractions: exchangeable, acidic, reducible, oxidizable, and residual phases. Sequential extractions indicate that, for most of the trace elements examined, the residual phases account for the largest proportion of the total concentrations, and their total extractable fractions are mainly from reducible and oxidizable phases. Only Cd, Pb, and Zn have an appreciable extractable proportion from the acidic phase in the filled dredged sediments. Our groundwater monitoring data suggest that the dredged sediments are mainly subject to a decrease in *pH* and a series of oxidation reactions, when exposed to the atmosphere. Because the trace elements released by carbonate dissolution and the oxidation (e.g., organic matter degradation, iron sulfide and ammonia oxidation) are subsequently immobilized by sorption to iron, manganese, and aluminum oxides, no potential contaminants to local groundwater are expected by addition of the dredged sediments to this site. © 2004 American Institute of Physics. [DOI: 10.1063/1.1839111]

I. INTRODUCTION

A former sand and gravel mine site in Charles City County, VA was mined in the 1980s, backfilled with 10 m of sandy mine spoils, and reclaimed to farmland use. The property owner, i.e., the Weanack Limited Land Partners, bulldozed the reclaimed mine-spoils into a diked basin and imported sediments dredged from the upper Potomac River estuary as fill for the excavated basin in order to convert it to high-quality farmland. However, in theory, the addition of these dredged sediments may influence local groundwater quality. First, the back-filling dredged sediments have the potential of becoming a contaminant source because these dredged estuarine sediments may contain contaminants such as heavy metals that could subsequently enter the groundwater. Second, by adding these dredged sediments into the reclamation basin, the *in situ* conditions could change, potentially liberating toxic heavy metals/metalloids to local groundwater. Possible processes that could be induced by the addition of the dredged sediments include: (1) mixing of pore water from the upper Potomac River sediments with the local groundwater, which will affect ionic strength and *pH* of the dredged sediment pore water and local groundwater; (2) infiltration of the dredged sediments by rain (*pH*~5.6),

which will affect the *pH* of the dredged sediment pore water; and (3) oxidizing the dredged sediments by exposing them to the atmosphere and/or by local groundwater, which will also affect the redox conditions of the dredged sediment pore water. Therefore, before developing these dredged sediments into agriculturally productive soils, leachate that exits the sediment disposal site must be monitored and traced. To accomplish this, any potential contaminants from the back-filling sediments must first be determined. In this work, a sequential extraction scheme was used to evaluate the mobility of trace elements in sediment and to reveal any potential contaminants that may be mobilized from the dredged sediments.

The mobility of trace elements in sediments, as well as their potential toxicity, depends on their aqueous and solid-phase speciation and the chemical and physical processes to which these elements are subjected. Sequential extraction procedures have been used to identify the “operationally defined solid-phase speciation” of trace elements in sediments, as a means to evaluate their mobility in the natural environments.¹⁻⁶ To ascertain the potential mobility of any contaminants added to a dredged spoil placement site by back-filling with the Potomac River dredged sediments, batch extractions were performed on the local aquifer sediments and on back-filling sediments dredged from the upper Potomac River estuary. The sequential extraction scheme

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proposed and outlined by Tessier *et al.*⁵ was used to partition trace elements associated with these sediments into the following fractions:

Fraction 1 (Exchangeable phase). Trace elements, which are weakly associated with clays, hydrated oxides of iron and manganese, and humic acids, and are readily mobilized by changes in ionic strength.

Fraction 2 (Acidic phase). Trace elements bound to sediment carbonates, which are susceptible to carbonate dissolution as sediments are acidified.

Fraction 3 (Reducible phase). Trace elements bound to iron and manganese oxides, which will be reduced and solubilized under anoxic conditions (i.e., low Eh).

Fraction 4 (Oxidizable phase). Trace elements in reduced metal complexes or bound to organic matter, which can be released into solution under oxidizing conditions.

Residual phase. Trace elements held within the crystal structure of primary and secondary minerals, which are not expected to be released into the solution over a reasonable time span under natural conditions.

Eight samples of local aquifer sediments and the Potomac River dredged sediments were sequentially extracted using the techniques outlined by Tessier *et al.*⁵ The various batch extraction fluids were subsequently analyzed by inductively coupled plasma mass spectrometry (ICP-MS; Finnigan MAT Element II) for eleven trace elements (Ag, Cd, Sb, Tl, Pb, Cr, Fe, Ni, Cu, Zn, and As). From the analytical results, the percentage of the total concentration of each trace element in each fraction is calculated. The total extractable fractions of trace elements and their “operationally defined solid-phase speciation” are discussed. Finally, any potential mobility of any contaminants from the dredge sediments as *in situ* conditions change following disposal at the replacement site is evaluated.

II. STUDY AREA

The dredged spoil placement site is located in Charles City County, VA (Fig. 1). The site was mined for sand and gravel and backfilled by 10 m of mine spoils with 1 m of natural soil over the fill. In the fall of 2000, backfill mine spoils were excavated and reconfigured into dikes around a large L-shape basin and subsequently used as a disposal basin to receive the sediments being dredged from the upper Potomac River estuary near Alexandria, VA (Figs. 1 and 2). To the north and east of the site, the slope of the ground is steep, forming a scarp. Numerous monitoring wells were installed at the disposal site (Fig. 2) to monitor groundwater quality and to evaluate the potential flow paths.

The distribution of aquifers and aquitards at the study site is complex. The complexity stems from the history of cut-and-fill related to the sand-and-gravel mining at this site and the history of stream incision and valley-infilling caused by Pleistocene sea level fluctuations.⁷⁻⁹ According to our stratigraphic analyses, at least six different geologic units are thought to play significant roles in controlling the flow of groundwater in the study region (Fig. 3). These geologic units are listed in Table I, and include Mining Fill, Kennon Formation, Tabb Formation, Shirley Formation, Nanjemoy-Marlboro unit, and Aquia-Potomac units.⁷⁻⁹

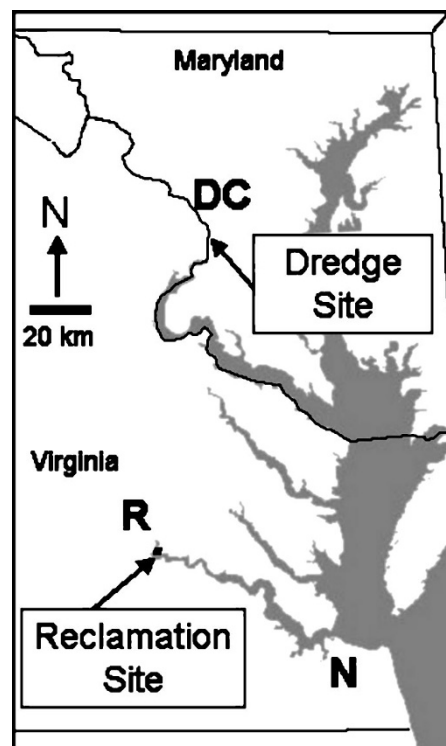


FIG. 1. Map showing location of study area. Sediments dredged from the Potomac River estuary near Washington, DC (DC) are being reclaimed as farmland at the Weanack study site along the James River estuary near Richmond, Virginia (R). Norfolk, Virginia (N) and state boundaries are also shown.

A flow path map (Fig. 4), generated from hydrologic head data collected monthly at all monitoring wells and staff gauges, indicates that groundwater radiates in nearly all directions from the elevated replacement site. After leaving the bermed area, groundwater passes through highly permeable beds within the Mining Fill and the Tabb Formation. Water draining from the dredged sediments may take as little as one year to more than a decade to reach surface water bodies, depending upon the sediment permeability, distance, and hydraulic gradient along the flow path.

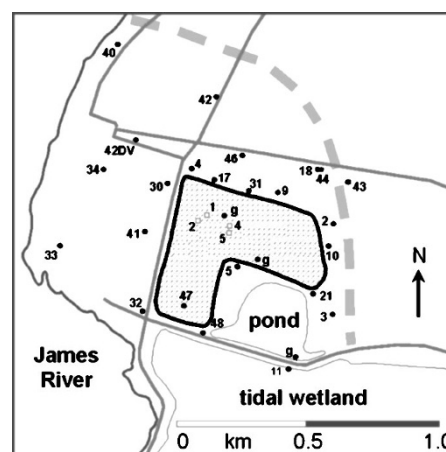


FIG. 2. Locations of L-shaped disposal site (lined), monitoring wells and gauges (solid dots), dredged sediment samples (open rectangles), and the scarp (coarse dash line).

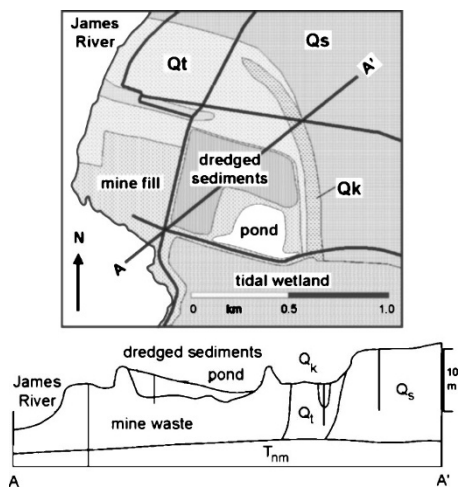


FIG. 3. Schematic geologic map and diagrammatic cross-section of study site. Qs: Shirley Formation; Qt: Tabb Formation; Qk: Kennon Formation. Locations of boreholes (wells) near the transect are shown on the profile.

III. EXPERIMENT

A. Sampling

Eight sediment samples were collected from the local aquifers and the back-filling dredged sediments from the upper Potomac River estuary. Samples 1 and 2 are older dredged sediments from the Potomac River, which were filled onto the replacement site between January and March 2001. Samples 4 and 5 represent the more recent filling dredged sediments, which were filled onto the replacement site between January and March 2002. These four samples were collected from the dredged sediments after they were deposited in the reclamation basin (Fig. 2). Samples 6 and 7 belong to the Tabb Formation. Sample 6 represents shallow sediments developed within the Tabb Formation, and was collected from the well SW 40 core at a depth of 1.1–1.7 m (Fig. 2). Sample 7 is from deeper sediments, taken from the well SW44 core at a depth of 2.7–3.4 m (Fig. 2). Samples 8 and 9 belong to the Shirley Formation. Sample 8 represents shallow sediments, collected from the well SW42DV core at a depth of 0.9–1.5 m (Fig. 2), whereas sample 9 represents deeper sediments, obtained from the well SW43 core of a depth of 2.7–4.3 m (Fig. 2).

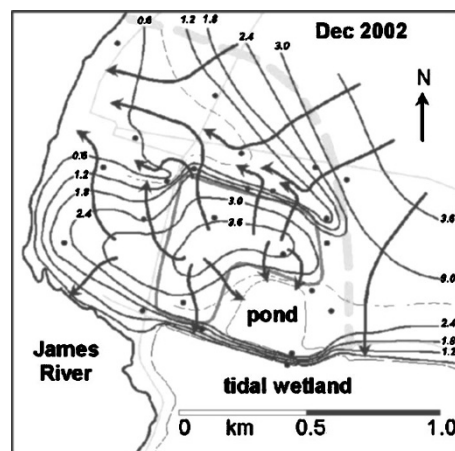


FIG. 4. Map of potentiometric surface and illustrative flow lines for head data collected 15 December, 2002.

The sediment samples were stored at 4 °C prior to batch extractions. Before batch extractions, sediment samples were dried at ~80 °C in a forced air oven and then ground with a wooden roller to pass through a 1 mm sieve and homogenized. 0.5 g sediment samples (dry weight) were used for the initial extraction.

B. Leaching procedures and reagents

The methods used for sequential trace element extractions are those discussed in detail by Tessier *et al.*⁵ In the following, we briefly outline the procedure for each extraction step.

1. Fraction 1: Exchangeable phase

A 0.5 g (dry weight) aliquot of sample was extracted into a 50 ml tube with 8 ml of 1 M CH₃COONa at room temperature and pH 8.2. The mixture was subsequently agitated on a shaker for 1 h.

2. Fraction 2: Acidic phase

The residue from Sec. III B 1 was leached at room temperature with 8 ml of 1 M CH₃COONa adjusted to pH 5.0 with CH₃COOH. The mixture was agitated on a shaker for 5 h.

TABLE I. Hydrostratigraphic unit at a dredged spoil placement site, Charles City County, VA. [Data are from 2002 annual monitoring report (Whittecar—Ref. 15); unit names from Mixon *et al.* (Ref. 7), McFarland (Ref. 8), and Johnson *et al.* (Ref. 9)].

Unit	Description
Mining Fill	Mine spoils placed into old abandoned mine excavation. Commonly 4.6–7.6 m thick, beneath sediment disposal site. Mixed member: poorly sorted mixture of gravel, sand, silt, and clay; deposited by dumping; mostly under north half of refilled mine sites.
Kennon Formation	Stratified member: stratified sands and mud deposited in a lake from west to east; mostly under the south end of refilled mine site. Fining upward stream deposit (gravelly sand to silty clay) dominated by thick clay-rich beds; 1.5–4.6 m thick; fills small recent valleys carved into Tabb Formation beds.
Tabb Formation	Finning upward stream deposit (cobble beds to silty clay) dominated by cobbles and gravelly sand; 3.7–6.7 m thick; carpets large valleys carved by the James River; forms broad terrace surface 4.6–6.1 m elevation.
Shirley Formation	Sand and gravel deposit (6.1 m thick) with silty clay cap (1.5 m thick); forms broad terrace at approximately 9.1–12.2 m elevation, and terrace remnant beneath Shirley Plantation manorhouse
Nanjemoy-Marlbouunit Aquia-Potomac units	Sandy silt-clay confining bed; glauconitic; compact; encountered beneath Tabb Formation and Mining Fill Layered gravelly aquifers and confining beds (42.7+ m thick)

3. Fraction 3: Reducible phase

The residue from Sec. III B 2 was extracted with 20 ml of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% (v/v) CH_3COOH for 6 h at $96\pm 1^\circ\text{C}$. The mixture was agitated every 30 min.

4. Fraction 4: Oxidizable phase

The residue from Sec. III B 3 was extracted with 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 , adjusted to $\text{pH} 2.0$ with ultrapure HNO_3 (Seastar Chemicals). The mixture was heated to $85\pm 1^\circ\text{C}$ for 2 h with occasional agitation. Then, 3 ml of 30% H_2O_2 ($\text{pH} 2.0$ adjusted with HNO_3) was added and the mixture was heated again to $85\pm 1^\circ\text{C}$ for 3 h with occasional agitation. After the mixture was cooled to room temperature, 5 ml of 3.2 M $\text{CH}_3\text{COONH}_4$ in 20% (v/v) HNO_3 was added and the mixture was diluted to 20 ml and agitated for 30 min at room temperature on a shaker.

Between each successive extraction, separation was effected by centrifugation at 10 000 rpm for 10 min. The supernatant was removed and stored in a 50 ml bottle at 4°C until analysis. The residue after each extraction was washed with 8 ml of distilled-de-ionized (18 M Ω cm) MilliQ water (i.e., Q-water). After centrifugation for 10 min, this second supernatant was discarded.

C. Digestion of sediment sample for residual and total trace element analysis

The residue from Sec. III B 4 was first digested in a 50 ml Teflon® beaker with 10 ml of ultrapure HF (Seastar Chemicals). The mixture was subsequently evaporated to near dryness. Then, 10 ml of ultrapure HNO_3 (Seastar Chemicals) was added and again, the mixture was evaporated to near dryness. Subsequently, another 10 ml of ultrapure HF was added and the mixture was evaporated to near dryness. The residue was then dissolved with Q-water and diluted up to 25 ml with Q-water.

Finally, 0.2 g initial sediment sample (dry weight) was digested according to the same procedure for the residual phase and the final solution was diluted to 25 ml with Q-water.

D. Analytical methods

Concentrations of trace elements in extractions, residual phase, and total sediment samples were determined by inductively coupled plasma mass spectrometry (ICP-MS; Finnigan MAT Element II; Dr. Z. Chen, analyst). The detection limits were below 10 ng/L for Ag, Cd, Sb, Tl, and Pb, and below 1 $\mu\text{g/L}$ for Cr, Fe, Ni, Cu, Zn, and As in the extraction fluids. Sequence control blanks and standards prepared from Perkin Elmer multi-element solutions were run regularly during the analyses to monitor the blank level, accuracy, and instrument drift. Analytical precision as relative standard deviation (RSD), estimated from five replicate analyses, is less than 1.0% for Cd, Sb, Tl, Pb, and Ni. For other elements, analytical precision is between 1.0% and 5.2% RSD.

IV. RESULTS AND DISCUSSION

A. Concentrations and recoveries

Concentrations of the analyzed trace elements in the extractions, residual phase, and total sediment samples are given in Table II. The sequential extraction procedure provides satisfactory recoveries, most of which are within 80%–120% (Table II).

B. Total extractable fractions

The total extractable fractions of all trace elements in the sediment samples from the filling dredged sediments and the local aquifer sediments are summarized in the following and in Table III:

- (1) In the dredged sediments, the trace elements Cd, Pb, Cu, and Zn exhibit relatively large total extractable fractions, especially for Cd and Pb, followed by Ni, As, Fe, Ag, and Cr (Table III, Fig. 5). On the other hand, Tl and Sb have low total extractable fractions (Table III, Fig. 5).
- (2) Backfilling dredged sediments have higher total extractable fractions for almost all trace elements examined than the local aquifer sediment samples (Table III, Fig. 5).
- (3) Generally, for the trace elements examined, the more recent filling dredged sediments have higher total extractable fractions than the older dredged sediments (Table III, Fig. 5).
- (4) With exception of Tl and Pb, all trace elements examined exhibit higher total extractable fractions in samples of the local aquifer sediments collected from deeper depths than from the shallow depths (Table III, Fig. 5).

C. “Operationally defined solid-phase speciation” of trace element

Having discussed the general features of the total extractable fractions of trace elements, we now discuss their “operationally defined solid-phase speciation” in the sediments in detail. The percentages of trace elements in the successive extractions are shown in Table IV.

1. Fraction 1: Exchangeable phase

In both the dredged sediments and the local aquifer sediments, exchangeable trace elements are generally found to represent a minor fraction of the total metal concentration of the sediment (Table IV, Fig. 5). The exchangeable fraction is less than 0.5% for most elements. Only Cd has an exchangeable fraction greater than 0.5%, but less than 5.1%, in both the dredged sediments and the local aquifer sediments (Table IV, Fig. 5). Sb and Tl also have more than 0.5% of the exchangeable fraction, but less than 1.3% of the exchangeable fraction in the dredged sediments.

2. Fraction 2: Acidic phase

Although the acid-mobilizable fraction still accounts for a small proportion of the total metal for most of the trace elements in the sediment samples, the filling dredged sediments have higher percentages in fraction 2 than the local aquifer sediments (Table IV, Fig. 5). The higher percentages

TABLE II. Concentrations of trace elements in extractions, residual, and total sediment. (Concentrations are expressed in ng/g of sediment, dry weight, except for Fe, which is in mg/g of sediment, dry weight).

Metal	Sample No.	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Residual phase	Total sediment	Recovery (%)
Ag	1	0.071	0.108	24.282	13.151	295.500	272.972	122.03
	2	a	0.258	26.423	194.766	491.561	693.362	102.83
	4	a	a	258.351	1 640.871	nd ^b	2 725.560	nd
	5	a	0.108	74.332	98.191	348.656	528.108	98.71
	6	a	a	5.307	1.010	243.375	240.755	103.72
	7	0.029	a	10.231	2.750	296.623	280.744	110.29
	8	0.042	0.046	16.736	1.523	255.623	250.221	109.49
	9	0.062	0.078	9.059	5.319	287.225	279.386	108.00
	Cd	1	6.472	48.354	45.847	5.486	101.534	238.342
2		6.275	117.290	85.701	6.849	161.041	303.086	124.44
4		43.571	349.965	311.591	106.501	nd	866.235	nd
5		39.239	699.384	2 223.193	179.158	921.440	5 066.074	80.19
6		0.400	1.678	10.813	2.650	91.395	100.167	106.76
7		3.998	8.867	64.063	7.605	104.854	174.981	108.23
8		0.669	2.506	16.212	2.968	102.618	121.542	102.82
9		3.568	8.871	44.786	4.804	98.115	173.394	92.36
Sb		1	5.028	13.786	5.503	4.746	515.786	474.605
	2	6.710	28.956	7.883	4.863	483.815	519.791	102.39
	4	8.204	29.122	12.983	7.455	nd	720.023	nd
	5	6.312	18.481	7.257	4.735	649.543	632.068	108.58
	6	1.372	1.554	3.924	2.673	544.855	478.999	115.74
	7	1.581	1.727	3.974	3.330	532.943	485.434	111.97
	8	0.517	1.481	5.382	3.878	649.343	644.756	102.46
	9	0.845	1.681	7.016	4.484	530.655	454.094	119.95
	Tl	1	3.188	3.457	15.325	11.274	528.135	621.076
2		3.522	5.351	22.836	17.036	349.515	443.725	89.75
4		5.204	7.084	37.733	25.468	nd	569.952	nd
5		2.678	4.336	22.136	15.267	406.490	468.313	96.28
6		1.246	1.148	22.210	13.809	350.623	398.097	97.72
7		1.505	1.265	10.337	9.181	507.974	427.184	124.13
8		0.995	0.802	19.498	8.158	396.546	444.724	95.79
9		2.806	2.093	19.205	9.198	408.756	400.062	110.50
Pb		1	11.260	1 999.360	9 271.597	2 300.046	6 202.777	25 326.599
	2	9.060	5 340.496	17 736.960	4 033.203	4 827.587	33 594.686	95.10
	4	14.420	5 434.827	32 087.274	11 519.033	nd	52 435.338	nd
	5	129.663	31 102.512	91 037.459	14 546.412	15 745.862	189 134.779	80.66
	6	4.127	765.766	5 330.865	869.676	4 659.941	15 741.670	73.88
	7	4.759	615.366	7 478.567	1 773.999	9 091.660	18 007.325	105.31
	8	4.984	1 032.451	6 844.099	836.929	5 032.686	18 227.665	75.44
	9	4.741	792.434	5 562.834	782.768	6 638.363	16 785.683	82.10
	Cr	1	9.250	676.057	4 144.599	3 533.393	57 449.183	61 441.193
2		6.695	904.332	5 931.275	4 631.480	48 271.178	53 827.594	110.99
4		8.988	1 302.097	11 276.499	9 805.180	nd	70 072.496	nd
5		9.102	855.133	5 642.895	4 230.704	46 970.601	51 356.518	112.37
6		12.017	25.631	3 194.288	1 929.951	40 754.522	38 091.117	120.54
7		7.660	42.031	6 567.750	3 158.592	50 648.430	59 552.998	101.46
8		16.475	27.106	4 848.704	1 396.597	43 903.636	51 437.231	97.58
9		43.920	15.808	1 888.904	1 545.616	39 454.099	37 642.710	114.09
Fe		1	0.001	0.495	9.124	0.484	27.617	39.577
	2	3.3E-5	0.505	10.108	0.737	23.525	31.584	110.42
	4	4.3E-5	0.326	11.235	1.817	nd	38.392	nd
	5	4.3E-5	0.606	10.228	0.718	23.674	31.623	111.39
	6	a	0.001	6.469	0.484	29.853	34.569	106.47
	7	6.7E-5	0.001	4.964	0.334	17.561	22.729	100.58
	8	2.6E-4	0.001	8.664	0.356	25.631	36.269	95.54
	9	1.1E-5	0.002	6.770	0.464	19.486	26.629	100.35

TABLE II. (Continued.)

Metal	Sample No.	Fraction 1	Fraction 2	Fraction 3	Fraction 4	Residual phase	Total sediment	Recovery (%)
Ni	1	32.781	1 169.294	4 853.280	2 054.761	25 738.313	33 034.089	102.47
	2	27.933	1 857.217	6 498.011	2 316.266	21 107.574	28 958.351	109.84
	4	46.143	1 794.210	9 930.939	3 878.025	nd	35 266.273	nd
	5	40.443	1 628.284	6 406.030	2 813.551	19 433.457	30 003.451	101.06
	6	44.151	35.639	1 456.371	1 601.098	19 913.320	17 795.148	129.53
	7	186.767	503.479	8 233.408	1 412.784	23 452.670	32 684.564	103.38
	8	58.319	44.355	1 856.858	810.413	22 698.592	23 392.666	108.87
	9	26.250	114.256	2 307.372	1 272.209	17 232.591	16 453.127	127.35
	Cu	1	53.019	1 188.204	3 758.365	5 944.153	17 415.774	29 436.611
2		49.178	1 773.634	4 434.530	8 870.600	15 064.632	27 370.758	110.31
4		109.659	3 729.499	11 020.389	22 689.878	nd	49 870.074	nd
5		34.285	1 427.713	4 967.171	7 551.255	15 315.070	27 577.567	106.23
6		15.007	83.844	2 938.981	1 822.681	20 064.779	18 926.953	131.69
7		25.881	932.864	16 554.675	3 301.967	15 848.147	33 243.183	110.29
8		13.493	75.531	3 035.225	990.290	18 085.262	21 602.361	102.77
9		19.182	175.868	4 095.619	1 431.143	11 754.839	14 271.972	122.45
Zn		1	102.805	2 748.999	16 884.517	5 534.190	55 179.058	89 011.596
	2	45.126	15 607.008	42 838.627	7 910.451	45 422.619	102 402.318	109.20
	4	300.531	46 232.551	143 051.392	32 983.708	nd	254 094.253	nd
	5	86.802	18 314.012	61 859.848	7 562.907	39 928.454	125 067.801	102.15
	6	6.174	103.943	5 986.605	5 559.082	57 102.705	60 814.605	113.06
	7	37.223	1 530.869	31 940.336	9 076.450	55 298.628	89 163.105	109.78
	8	15.069	133.418	7 826.604	3 432.023	55 492.337	70 172.591	95.34
	9	7.089	319.206	13 012.595	6 488.597	51 448.571	59 903.783	118.98
	As	1	28.328	151.934	1 232.778	34.054	4 719.936	5 499.051
2		29.745	201.669	1 544.199	93.879	4 500.311	4 431.341	143.74
4		19.041	219.711	2 713.633	331.686	nd	7 145.773	nd
5		47.221	267.051	1 943.043	148.682	5 445.426	5 496.017	142.86
6		a	12.706	108.269	a	7 268.973	6 212.311	119.08
7		34.574	68.575	2 191.545	169.113	10 166.936	10 736.104	117.65
8		10.537	20.510	154.292	a	7 677.608	8 578.925	91.76
9		a	10.850	311.100	a	5 635.792	4 953.477	120.24

^aBelow detection limit.^bnd=not determined.

TABLE III. Total extractable fractions of trace elements in the dredged sediments and the local aquifer sediments. (Note: Because there are no data for the residual phase of Sample 4, percentages of trace elements in the successive extractions were calculated assuming the recoveries of all metals are 100%.)

Trace element	The dredged sediments				The local aquifer sediments			
	Recent filling		Older		Deep		Shallow	
	No. 4	No. 5	No. 2	No. 1	No. 7	No. 9	No. 6	No. 8
Ag	69.68	33.12	31.06	11.29	4.20	4.81	2.53	6.70
Cd	93.70	77.32	57.30	51.11	44.64	38.73	14.53	17.89
Sb	8.02	5.36	9.10	5.33	1.95	2.57	1.72	1.70
Tl	13.24	9.85	12.24	5.92	4.20	7.53	9.87	6.91
Pb	93.55	89.68	84.89	68.65	52.06	51.83	59.93	63.40
Cr	31.96	18.61	19.20	12.71	16.18	8.24	11.24	12.53
Fe	34.84	32.79	32.55	26.79	23.18	27.08	18.89	26.03
Ni	44.37	35.91	33.64	23.96	30.59	17.75	13.61	10.88
Cu	75.29	47.72	50.10	38.59	56.77	32.74	19.50	18.53
Zn	87.59	68.75	59.38	31.41	43.51	27.82	16.95	17.05
As	45.96	30.64	29.35	23.47	19.51	5.40	1.64	2.34

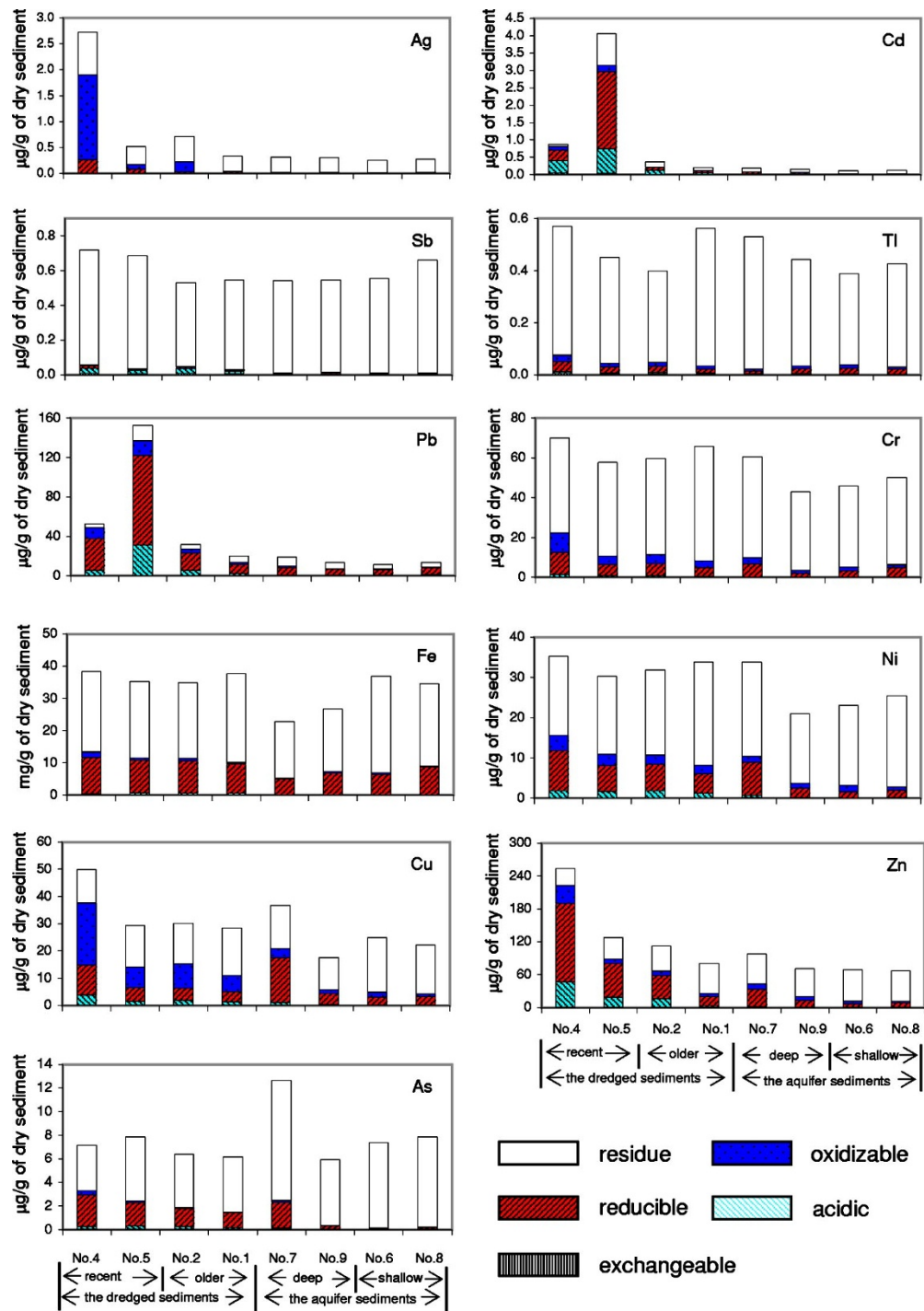


FIG. 5. “Operationally defined solid-phase speciation” of trace elements in the dredged sediments and the local aquifer sediments presented in absolute concentration.

in fraction 2 are especially evident for Cd, Pb, and Zn, whose acid-mobilizable fractions account for an appreciable proportion of the total metal in the filling dredged sediments: 17.2%–40.4% Cd; 10.1%–20.4% Pb; 3.4%–18.2% Zn; (Table IV, Fig. 5). Cu, Sb, Ni, and As also have 2.5%–7.5% of acidic phase.

3. Fraction 3: Reducible phase

With the exception of Sb and Tl, the reducible fraction of trace elements accounts for a large proportion of the total

metal concentrations in both the filling dredged sediments and local aquifer sediments (Table IV, Fig. 5). In general, reducible trace element fractions exhibit higher proportions of the total metals in the filling dredged sediments than in the local aquifer sediments (Table IV, Fig. 5).

4. Fraction 4: Oxidizable phase

With the exception of Sb and As, whose oxidizable fractions are low (less than 2.0% in most of samples, Table IV, Fig. 5) and Cu and Ag, whose oxidizable fraction is larger in

TABLE IV. Percentages of trace elements in the successive extractions for both the dredged sediments and the local aquifer sediments. (Note: Because there are no data for the residual phase of Sample 4, percentages of trace elements in the successive extractions were calculated assuming the recoveries of all metals are 100%.)

Trace element	Sample No.		Exchangeable	Acidic	Reducible	Oxidizable	Residual
Ag	Recent filling	4	0.00	0.00	9.48	60.20	30.32
	dredged sediments	5	0.00	0.02	14.26	18.84	66.88
	Older dredged	2	0.00	0.04	3.71	27.32	68.94
	sediments	1	0.002	0.003	7.29	3.95	88.71
	Deep local	7	0.01	0.00	3.30	0.89	95.80
	aquifer sediments	9	0.02	0.03	3.00	1.76	95.19
	Shallow local	6	0.00	0.00	2.13	0.40	97.47
	aquifer sediments	8	0.02	0.02	6.11	0.56	93.30
Cd	Recent filling	4	5.03	40.40	35.97	12.29	6.30
	dredged sediments	5	0.97	17.22	54.73	4.41	22.68
	Older dredged	2	1.66	31.10	22.72	1.82	42.70
	sediments	1	3.12	23.28	22.07	2.64	48.89
	Deep local	7	2.11	4.68	33.83	4.02	55.36
	aquifer sediments	9	2.23	5.54	27.97	3.00	61.27
	Shallow local	6	0.37	1.57	10.11	2.48	85.47
	aquifer sediments	8	0.54	2.01	12.97	2.38	82.11
Sb	Recent filling	4	1.14	4.04	1.80	1.04	91.98
	dredged sediments	5	0.92	2.69	1.06	0.69	94.64
	Older dredged	2	1.26	5.44	1.48	0.91	90.90
	sediments	1	0.92	2.53	1.01	0.87	94.67
	Deep local	7	0.29	0.32	0.73	0.61	98.05
	aquifer sediments	9	0.16	0.31	1.29	0.82	97.43
	Shallow local	6	0.25	0.28	0.71	0.48	98.28
	aquifer sediments	8	0.08	0.22	0.81	0.59	98.30
Tl	Recent filling	4	0.91	1.24	6.62	4.47	86.76
	dredged sediments	5	0.59	0.96	4.91	3.39	90.15
	Older dredged	2	0.88	1.34	5.73	4.28	87.76
	sediments	1	0.57	0.62	2.73	2.01	94.08
	Deep local	7	0.28	0.24	1.95	1.73	95.80
	aquifer sediments	9	0.63	0.47	4.34	2.08	92.47
	Shallow local	6	0.32	0.30	5.71	3.55	90.13
	aquifer sediments	8	0.23	0.19	4.58	1.92	93.09
Pb	Recent filling	4	0.03	10.36	61.19	21.97	6.45
	dredged sediments	5	0.08	20.39	59.67	9.53	10.32
	Older dredged	2	0.03	16.72	55.52	12.62	15.11
	sediments	1	0.06	10.11	46.86	11.63	31.35
	Deep local	7	0.03	3.24	39.43	9.35	47.94
	aquifer sediments	9	0.03	5.75	40.37	5.68	48.17
	Shallow local	6	0.04	6.58	45.84	7.48	40.07
	aquifer sediments	8	0.04	7.51	49.77	6.09	36.60
Cr	Recent filling	4	0.01	1.86	16.09	13.99	68.04
	dredged sediments	5	0.02	1.48	9.78	7.33	81.39
	Older dredged	2	0.01	1.51	9.93	7.75	80.80
	sediments	1	0.01	1.03	6.30	5.37	87.29
	Deep local	7	0.01	0.07	10.87	5.23	83.82
	aquifer sediments	9	0.10	0.04	4.40	3.60	91.86
	Shallow local	6	0.03	0.06	6.96	4.20	88.76
	aquifer sediments	8	0.03	0.05	9.66	2.78	87.47
Fe	Recent filling	4	0.00	0.85	29.26	4.73	65.16
	dredged sediments	5	0.00	1.72	29.04	2.04	67.21
	Older dredged	2	0.00	1.45	28.98	2.11	67.45
	sediments	1	0.00	1.31	24.19	1.28	73.21
	Deep local	7	0.00	0.01	21.71	1.46	76.82
	aquifer sediments	9	0.00	0.01	25.33	1.74	72.92
	Shallow local	6	0.00	0.00	17.57	1.31	81.11
	aquifer sediments	8	0.00	0.00	25.00	1.03	73.97

TABLE IV. (Continued.)

Trace element	Sample No.		Exchangeable	Acidic	Reducible	Oxidizable	Residual
Ni	Recent filling	4	0.13	5.09	28.16	11.00	55.63
	dredged sediments	5	0.13	5.37	21.13	9.28	64.09
	Older dredged	2	0.09	5.84	20.43	7.28	66.36
	sediments	1	0.10	3.45	14.34	6.07	76.04
	Deep local	7	0.55	1.49	24.37	4.18	69.41
	aquifer sediments	9	0.13	0.55	11.01	6.07	82.25
	Shallow local	6	0.19	0.15	6.32	6.95	86.39
	aquifer sediments	8	0.23	0.17	7.29	3.18	89.12
Cu	Recent filling	4	0.22	7.48	22.10	45.50	24.71
	dredged sediments	5	0.12	4.87	16.96	25.78	52.28
	Older dredged	2	0.16	5.87	14.69	29.38	49.90
	sediments	1	0.19	4.19	13.25	20.96	61.41
	Deep local	7	0.07	2.54	45.15	9.01	43.23
	aquifer sediments	9	0.11	1.01	23.43	8.19	67.26
	Shallow local	6	0.06	0.34	11.79	7.31	80.50
	aquifer sediments	8	0.06	0.34	13.67	4.46	81.47
Zn	Recent filling	4	0.12	18.20	56.30	12.98	12.41
	dredged sediments	5	0.07	14.34	48.42	5.92	31.25
	Older dredged	2	0.04	13.96	38.31	7.07	40.62
	sediments	1	0.13	3.42	20.99	6.88	68.59
	Deep local	7	0.04	1.56	32.63	9.27	56.49
	aquifer sediments	9	0.01	0.45	18.26	9.10	72.18
	Shallow local	6	0.01	0.15	8.71	8.08	83.05
	aquifer sediments	8	0.02	0.20	11.70	5.13	82.95
As	Recent filling	4	0.27	3.07	37.98	4.64	54.04
	dredged sediments	5	0.60	3.40	24.75	1.89	69.36
	Older dredged	2	0.47	3.17	24.24	1.47	70.65
	sediments	1	0.46	2.46	19.99	0.55	76.53
	Deep local	7	0.27	0.54	17.35	1.34	80.49
	aquifer sediments	9	0.00	0.18	5.22	0.00	94.60
	Shallow local	6	0.00	0.17	1.47	0.00	98.36
	aquifer sediments	8	0.13	0.26	1.96	0.00	97.64

the filling dredged sediments (more than 20.0% in most of the dredged sediments, Table IV, Fig. 5), oxidizable fractions also account for 2.0% to ~20.0% of the total metals for most of the trace elements in both the filling dredged sediments and local aquifer sediments. In general, the relative mobility in terms of the percentage of the oxidizable trace elements follows the order of the recent filling dredged sediments (placed on site in 2002) > the older dredged sediments (placed on site prior to 2002) > the deep local aquifer sediments > the shallow local aquifer sediments (Table IV, Fig. 5).

5. Fraction 5: Residual phase

For most of the trace elements examined the residual fractions account for the largest proportion of the total metals in the sediments (Table IV, Fig. 5). In some cases, mainly found in the filling dredged sediments, the concentrations of Pb, Cd, Zn, and Cu in the residual phase are lower than those observed in the reducible and oxidizable phases (Table IV, Fig. 5).

D. The potential contaminants revealed by sequential extractions

To become a potential contaminant in drinking water, a particular trace element must be able to be mobilized. The mobility of trace elements in sediments mainly depends upon its solid-phase speciation and the chemical and physical processes to which it is subject. We first discuss the mobility of trace elements examined as related to their “operationally defined solid-phase speciation.” Then, we discuss the possible changes of *in situ* conditions occurring at the replacement site after disposal of the dredged sediments and the effect of these potential changes on the mobility of trace elements examined.

It is generally agreed that the mobility of trace elements decreases approximately in the order of the extraction sequence, i.e., exchangeable > acidic > reducible > oxidizable > residual.^{1,3,10} The exchangeable phase is weakly associated with the sediments and is the easiest to mobilize by increasing ionic strength of sediment pore water under natural conditions. The acidic phase, bound to carbonate, is also relatively easy to mobilize by lowering the pH of sediment pore water. Many natural processes such as the infiltration of acid

TABLE V. Monthly *pH* and conductivity in groundwaters from the monitoring wells after the placement of the dredged sediments at the replacement site. Also included are *pH* and conductivity in upper Potomac River waters. (Note: Data for upper Potomac River waters are from Hall *et al.*—Ref. 12.)

			Local groundwaters									
Upper Potomac River waters			Well	Date								
				3/03	4/03	5/03	6/03	7/03	8/03	9/03	11/03	12/03
<i>pH</i>	Station 1	7.46–9.12	SDS2	6.60	5.64	5.59	5.74	5.30	5.29	5.38	5.36	5.11
	Station 2	7.29–8.11	SDS3	6.52	5.63	5.62	5.69	5.43	5.45	5.56	5.41	4.87
			SW30	6.62	5.94	5.78	5.97	5.58	5.58	5.76	6.03	5.99
	Station 3	7.13–8.76	SW31	6.89	5.71	5.48	5.82	5.26	5.26	5.36	5.29	5.30
Conductivity ($\mu\text{S}/\text{cm}$)	Station 1	140–240	SDS2	187	181	177	184	162	172	173	214	215
	Station 2	180–260	SDS3	332	139	149	146	153	144	109	147	130
			SW30	1176	340	265	302	319	226	308	546	546
	Station 3	150–280	SW31	495	232	234	237	222	230	191	343	247

rain and the degradation of organic matter can result in slow lowering of the *pH* of sediment pore water. Trace elements in the reducible and oxidizable phases are thought to be more strongly bound to Fe/Mn oxides/oxyhydroxides and organic matter, respectively (e.g., Tessier *et al.*⁵), and thus are not easily mobilized under steady-state, natural conditions. Trace elements in the residual phase are strongly bound, or held, within mineral crystal structure, and thus are almost impossible to be mobilized under the natural conditions.

At the dredged spoil placement site, the exchangeable and acidic phases only account for a small proportion of most of the trace elements examined. Indeed, only Cd, Pb, and Zn have an appreciable extractable proportion from the acidic phase in the filling dredged sediments (Table IV). Cu, Sb, Ni, and As also have 2.9%–7.7% of exchangeable and acidic phases (Table IV). Therefore, our data suggest that, of the trace elements examined, Cd, Pb, and Zn are most likely to be mobilized into local groundwater at the replacement site. Cu, Sb, Ni, and As are relatively less mobile than Cd, Pb, and Zn, although small fractions of these elements can still be mobilized if *pH* changes at the replacement site. Other trace elements, such as Cr, Fe, Ag, and Tl, would not be mobilized unless the redox conditions of the dredged sediments have been changed at the replacement site.

Because the residual phase is difficult to mobilize, the overwhelming dominance of the residual fraction for these trace elements (Table IV, Fig. 5), except Pb, Cd, Zn, and Cu, indicates that trace elements are strongly bound, or held, within mineral crystal structure, and are thus not easily mobilized under the natural conditions. Based on total extractable fractions (Table III, Fig. 5), the possibility for these trace elements to be mobilized from the dredged sediments may follow the order of Cd, Pb>Cu, Zn>Ni, As, Fe>Ag, Cr>Tl, Sb. Higher total extractable fractions for almost all trace elements examined in the dredged sediments than in the local aquifer sediment samples (Table III, Fig. 5) indicate that the trace elements examined here are more likely to be liberated from the dredged sediments than from the local aquifer sediments under the natural conditions.

The mobility of trace elements ultimately depends upon the changes of *in situ* conditions occurring at the replacement site. Table V lists monthly groundwater data for *pH* and conductivity from two upgradient monitoring wells (SDS2

and 3) and two downgradient monitoring wells (SW 30 and 31). Although we have no data for *pH* and conductivity for the pore water in the dredged sediments from the upper Potomac River, Hall *et al.*¹² reported some *pH* and conductivity data for upper Potomac River waters, which are close to the dredged site (Table V). Compared to conductivity for the upper Potomac River water (Table V), the local groundwaters have slightly higher conductivities. Because the exchangeable trace elements only account for a minor fraction of the total element concentration of the dredged sediments, the slight increase in ionic strength (indicated by the slightly higher conductivities) is not sufficient to release trace elements from the dredged sediments into local groundwater at the dredged spoil placement site. Therefore, we do not anticipate any trace element mobilization at this site owing to the change in ionic strength of local groundwaters. However, local groundwaters have much lower *pH* values than the upper Potomac River waters (Table V). Thus, the changes in *pH* are notable for the dredged sediments. Moreover, monthly *pH* data for the local groundwaters indicate that *pH* slightly decreases with time. Low *pH* in local groundwaters is a common problem due to oxidation of sulfides in the Shirley and Tabb Formation at old mining exposures. According to analysis data for the dredged sediments by Virginia Cooperative Extension Soil Testing Laboratory at Virginia Polytechnic Institute and State University, there are 2%–5% of carbonates in the dredged sediments. The changes in *pH* to which the dredged sediments are subject will result in some carbonate dissolution. Considering their acidic fractions, an appreciable proportion of Cd, Pb, and Zn and some Cu, Sb, Ni, and As may be mobilized by carbonate dissolution.

Because the reducible and oxidizable trace elements account for most of the total exchangeable fractions of trace elements in the dredged sediments, we suggest that oxidation of the dredged sediments may mobilize the trace elements examined in this study, as well as other components of the sediments. When the upper Potomac River sediments were dredged and dumped into the replacement site, a considerable portion was exposed to the atmosphere. As they dried the sediments formed coarse polygonal cracks as much as 0.5 m deep. Along these exposed surfaces, the dark bluish gray sediments altered to a pale gray and then to a tan (Fig.

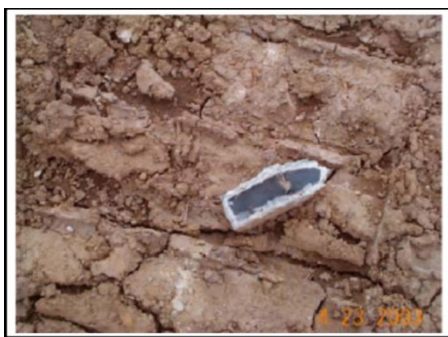
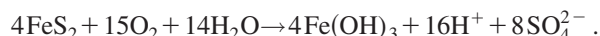
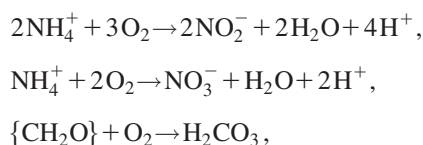


FIG. 6. Prismatic dredged sediment pulled from approximately 76.2 cm deep in the soil. Note the distinct oxidation of both the surface sediments under the aggregate and the oxidation rind around the aggregate itself. The inbound dredged sediments were all initially the dark bluish black color seen at the center of the aggregate.

6) as oxidation progressed throughout the new soil profile. According to analyses of sediment samples being barged to the replacement area (analyzed by Gascoyne Labs Inc., Baltimore, MD), dredged sediments contained between 50 and 150 mg/kg dry sediment of sulfate, up to 200 mg/kg dry sediment of sulfide, and up to 2% total organic carbon. Pore water total ammonia (i.e., $\text{NH}_3 + \text{NH}_4^+$) in the Potomac River sediments is ~ 27.4 mg N/L, as reported by Schlekot *et al.*¹³ from the same location that the dredged sediments were excavated. When ammonia, organic matter, and iron sulfide (e.g., FeS_2) are oxidized in the dredged sediments at the replacement site, the following geochemical reactions may be expected:



These potential reactions would precipitate iron oxides and release hydrogen ions, $\text{NO}_3 + \text{NO}_2$, dissolved inorganic carbon (DIC), and sulfate into local groundwaters. In addition, the incomplete degradation of organic matter (large molecular) in the dredged sediments may also produce some soluble small molecular organic matter. However, the acidity released by these oxidation reactions would be offset by carbonate buffering reactions. Therefore, after deposition of the dredged sediments at the study site, we expect some levels of increase in $\text{NO}_3 + \text{NO}_2$, DIC, DOC, and sulfate concentrations in local groundwaters, but little if any change of pH.

Our monitoring data for local groundwater verify that these potential geochemical reactions have occurred at the study site (Tables V and VI). Table V indicates that pH only slightly decreases in the monitoring groundwaters with time. Table VI shows that, compared to the baseline analyses, $\text{NO}_3 + \text{NO}_2$, and TOC generally increase. Total iron shows higher concentrations at the first post-baseline monitoring analyses but thereafter, iron generally decreases with time in local groundwaters. The oxidation of ammonia, organic matter, and iron sulfides may release the oxidizable trace elements (fraction 4 in sequential extractions) into local groundwaters. However, considering that iron, manganese, and aluminum oxides exhibit strong adsorption affinity because of their reactivity and large specific surface area,¹⁴ we do not anticipate these reactions would result in any significant water quality risk. Instead, the trace elements released by the proposed mechanism are subsequently absorbed by newly produced iron, manganese, and aluminum oxides and become immobile as long as conditions remain oxidic.

Besides their mobility, the environmental significance of these trace elements is also controlled by their absolute concentrations in the dredged sediments. Figure 5 compares the

TABLE VI. Concentrations of trace elements (mg/L) in groundwaters from the monitoring wells after the placement of the dredged sediments at the replacement site.

Trace element	USEPA MCLs ^a for drinking-water	Baseline analyses ^b	SDS2 ^c			SDS3 ^c			SW30 ^c			SW31 ^c		
			4/20/02 ^d	10/19/02	10/26/03	4/20/02 ^d	10/19/02	10/26/03	4/20/02 ^d	10/19/02	10/26/03	4/20/02 ^d	10/19/02	10/26/03
Ag	0.1	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Cd	0.005	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.00065	bdl	0.00058	bdl
Sb	0.006	bdl	0.054	bdl	bdl	bdl	bdl	bdl	bdl	0.0055	bdl	bdl	0.0071	bdl
Tl	0.002	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Pb	0.015	bdl	0.048	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.012	0.0052
Cr	0.1	bdl-0.004	0.03	0.0048	0.0035	0.04	0.0098	0.0035	bdl	bdl	bdl	0.015	0.036	0.018
Fe	0.3	2.1-8.1	50	6.3	1.4	5.7	1.7	5	bdl	bdl	bdl	8.7	37	15
Ni	0.1	bdl-0.009	0.028	0.0096	0.0058	0.03	0.012	bdl	bdl	bdl	bdl	0.013	0.026	0.014
Cu	1.3	bdl	0.039	bdl	bdl	0.0064	bdl	bdl	bdl	bdl	bdl	0.0051	0.019	0.0077
Zn	5.0	bdl-0.16	0.088	0.56	0.03	0.16	0.2	0.03	bdl	0.03	0.03	0.062	0.120	0.049
As	0.01	bdl	0.0079	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
$\text{NO}_3 + \text{NO}_2$	11.0+1.0	bdl-0.11	1.1	0.15	bdl	1	2.8	0.55	bdl	bdl	0.18	7.5	4.5	10
Total sulfide	...	bdl	2	bdl	bdl	1.7	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
SO_4	250.0	7-76	...	43	33	...	44	26	...	29	55	...	39	43
TOC	...	1.0-3.1	9.4	3.8	1.8	3.7	3.8	3.7	2.1	2.8	3.4	<1.0	1.7	1.0

^aUSEPA maximum contaminant levels for drinking water are based on the data provided by Fetter (Ref. 11), except for new As MCL.

^bBaseline analyses are the concentration ranges for trace elements in a set of local groundwaters collected prior to placement of the dredged sediments at the replacement site.

^cSamples Analyzed by Gascoyne Laboratories, Inc.

^dThe collection date of the groundwater samples.

total concentrations of trace elements and the concentrations of each extractable fraction in the dredged sediments to those in the local aquifer sediments. Pb, Cd, Zn, Ag, and Cu have higher total concentrations and higher concentrations of extractable phases in the dredged sediments than in the local aquifer sediments (Fig. 3). By comparison, As, Cr, Ni, and Sb have similar total concentrations in both the dredged sediments and the local aquifer sediments, but their concentrations in the extractable phase are higher in the dredged sediments than in the local aquifer sediments.

The “operationally defined solid-phase speciation” of the trace elements examined, their absolute concentrations in the dredged sediments, and the changes in *in situ* conditions indicate that some trace elements, especially Cd, Pb, and Zn, may be released from the dredges sediments. However, because the trace elements released by carbonate dissolution and the oxidation (e.g., organic matter degradation, iron sulfide oxidation, and ammonia oxidation) are subsequently immobilized by sorption to iron, manganese, and aluminum oxides, these trace elements would not be released into local groundwaters. Therefore, no potential contaminants to local groundwater are expected as revealed by sequential extractions. Our sequential extraction results are generally consistent with our groundwater monitoring results (Table VI). On 8 May, 2000 (prior to placement of the dredged sediments), local groundwater samples were collected from wells around the L-shape replacement site. The analyses of these samples represent the baseline groundwater chemistry at the replacement site. After the dredged sediments were filled into the site, local groundwater samples were collected on different dates and analyzed for the same trace elements (Table VI). The groundwater monitoring data do not clearly indicate that any trace elements were released into local groundwaters from the dredged sediments, because the concentrations of monitoring elements are very low and inconsistent with time. Compared to baseline analyses, only a slight increase was observed in concentrations for some elements in some local groundwater samples. Almost all the concentrations of monitoring elements are below USEPA maximum contaminant levels (MCLs) for drinking water. Only one monitoring well (SDS2) had a high Pb concentration of 0.048 mg/L at the first, post-baseline monitoring analyses (4/20/2002). But later analyses at SDS2 indicate very low levels of Pb in groundwater from the well (Table VI).

V. CONCLUSIONS

Our sequential extraction results show that the dredged sediments have higher total extractable fractions for almost

all trace elements examined and relatively high concentrations for some trace elements, compared to the local aquifer sediments, which indicates that the trace elements are more likely to be mobilized from the dredged sediments than from the local aquifer sediments. However, the overwhelming dominance of the residual fraction for these trace elements, except Pb, Cd, Zn, and Cu, indicates that trace elements are not easily mobilized under the natural conditions. Moreover, under an oxidizing condition, the trace elements released from the dredged sediments by carbonate dissolution and the oxidation (i.e., organic matter degradation, iron sulfide, and ammonia oxidation) are subsequently absorbed by newly produced iron, manganese, and aluminum oxides and become immobile. No potential contaminants to local groundwater are expected to be released from the dredged sediments.

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