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 reclaimed 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 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
proposed and outlined by Tessier et al.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{7–9}

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.
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).

B. Leaching procedures and reagents

The methods used for sequential trace element extractions are those discussed in detail by Tessier et al. 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. Stratified member: stratified sands and mud deposited in a lake from west to east; mostly under the south end of refilled mine site. |
| Kennon Formation            | 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              | Fining upward stream deposit (cobble beds to silty clay) dominated by cobbles and gravelly sand; 3.7–6.7 m thick; carpets large valley 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-Marlborouunit      | Sandy silt-clay confining bed; glauconitic; compact; encountered beneath Tabb Formation and Mining Fill                                                                                |
| Aquia-Potomac units         | 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 NH\textsubscript{2}OH-HCl in 25% (v/v) CH\textsubscript{3}COONH\textsubscript{4} for 6 h at 96±1 °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\textsubscript{3} and 5 ml of 30% H\textsubscript{2}O\textsubscript{2}, adjusted to pH 2.0 with ultrapure HNO\textsubscript{3} (Seastar Chemicals). The mixture was heated to 85±1 °C for 2 h with occasional agitation. Then, 3 ml of 30% H\textsubscript{2}O\textsubscript{2} (pH 2.0 adjusted with HNO\textsubscript{3}) was added and the mixture was heated again to 85±1 °C for 3 h with occasional agitation. After the mixture was cooled to room temperature, 5 ml of 3.2 M CH\textsubscript{3}COONH\textsubscript{4} in 20% (v/v) HNO\textsubscript{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\textsubscript{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\textsubscript{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 μg/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    | 640.871    | nd             | 2 725.560      | nd           |
| Cd    | 5          | a          | 0.108      | 74.332     | 98.191     | 348.656        | 528.108        | 98.71        |
|       | 6          | a          | 5.307      | 10.231     | 2.750      | 296.623        | 280.744        | 110.29       |
|       | 7          | a          | 0.042      | 0.046      | 16.736     | 1.523          | 255.623        | 250.221      |
|       | 8          | a          | 0.062      | 0.078      | 9.059      | 5.319          | 287.225        | 279.386      |
| Sb    | 1          | 6.472      | 48.354     | 45.847     | 5.486      | 101.534        | 238.342        | 87.14        |
|       | 2          | 6.275      | 117.290    | 85.701     | 6.849      | 161.041        | 303.086        | 102.34       |
|       | 4          | 43.571     | 349.965    | 311.591    | nd         | 866.235        | 173.394        | 92.36        |
|       | 5          | 39.239     | 699.384    | 2 223.193  | 179.158    | 921.440        | 5 066.074      | 80.19        |
| Pb    | 1          | 11.260     | 1 999.360  | 9 271.597  | 2 300.046  | 6 202.777      | 25 326.599     | 78.12        |
| Ti    | 1          | 3.188      | 3.457      | 15.325     | 11.274     | 528.135        | 621.076        | 96.30        |
|       | 2          | 5.204      | 7.084      | 37.733     | 25.468     | 738.915        | 434.725        | 89.75        |
|       | 4          | 5.921      | 7.084      | 37.733     | 25.468     | 738.915        | 434.725        | 89.75        |
| Sb    | 1          | 5.028      | 13.786     | 5.503      | 4.746      | 515.786        | 474.605        | 114.80       |
| Pb    | 1          | 11.260     | 1 999.360  | 9 271.597  | 2 300.046  | 6 202.777      | 25 326.599     | 78.12        |
|       | 2          | 9.060      | 5 340.496  | 17 736.960 | 4 033.203  | 4 827.587      | 33 594.686     | 95.10        |
| Cr    | 1          | 43.920     | 15.808     | 1888.904   | 1 545.616  | 39 454.099     | 37 642.710     | 114.09       |
|       | 2          | 4.127      | 765.766    | 5 300.865  | 8 697.676  | 14 745.079     | 80.66          |             |
|       | 4          | 4.759      | 615.366    | 7 478.567  | 1 773.999  | 9 091.660      | 18 007.325     | 105.31       |
|       | 6          | 1 032.451  | 6 844.099  | 836.929    | 5 032.686  | 18 227.665     | 75.44          |             |
|       | 8          | 4.984      | 792.434    | 5 562.834  | 782.768    | 638.363        | 16 785.683     | 82.10        |
| Fe    | 1          | 0.001      | 0.495      | 9.124      | 0.484      | 27.617         | 39.577         | 95.31        |
|       | 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           |
|       | 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 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 | 25.738 | 33.034 | 102.47 |
| Cd            | 93.70 | 77.32 | 57.30 | 51.11 | 30.003 | 101.06 |
| Sb            | 8.02  | 5.36  | 9.10  | 5.33  | 19.433 | 109.84 |
| Tl            | 13.24 | 9.85  | 12.24 | 5.92  | 19.913 | 129.53 |
| Pb            | 93.55 | 89.68 | 84.89 | 68.65 | 17.795 | 120.87 |
| Cr            | 31.96 | 18.61 | 19.20 | 12.71 | 17.795 | 120.87 |
| Ni            | 44.37 | 35.91 | 33.64 | 23.96 | 17.795 | 120.87 |
| Cu            | 75.29 | 47.72 | 50.10 | 38.59 | 17.795 | 120.87 |
| Zn            | 87.59 | 68.75 | 59.38 | 31.41 | 17.795 | 120.87 |
| As            | 45.96 | 30.64 | 29.35 | 23.47 | 17.795 | 120.87 |

Below detection limit.

aBelow detection limit.

bnd=not determined.
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 |
| | | 5 | 0.00 | 0.02 | 14.26 | 18.84 | 66.88 |
| | Older dredged | 2 | 0.00 | 0.04 | 3.71 | 27.52 | 68.94 |
| | sediments | 1 | 0.002 | 0.003 | 7.29 | 3.45 | 88.71 |
| | Deep local | 7 | 0.01 | 0.00 | 3.00 | 0.89 | 95.80 |
| | aquifer sediments | 9 | 0.02 | 0.03 | 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 | 22.87 | 1.62 | 42.70 |
| | sediments | 1 | 3.12 | 23.28 | 22.07 | 2.64 | 48.89 |
| | Deep local | 7 | 2.23 | 1.34 | 27.97 | 3.00 | 61.27 |
| | aquifer sediments | 9 | 0.25 | 0.28 | 1.29 | 0.82 | 97.43 |
| | Shallow local | 6 | 0.08 | 0.22 | 12.97 | 2.38 | 82.11 |
| | aquifer sediments | 8 | 0.54 | 2.01 | 7.16 | 0.59 | 93.30 |
| 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 | 90.30 |
| | 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 | 2.97 | 0.82 | 97.43 |
| | Shallow local | 6 | 0.25 | 0.28 | 7.16 | 0.28 | 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 | 4.43 | 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 | 0.10 | 0.04 | 4.40 | 3.60 | 91.86 |
| | 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 |
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.\textsuperscript{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...
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., Tissier et al.); 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 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. 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. 5).
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., NH$_3$ + NH$_4^+$) in the Potomac River sediments is ~27.4 mg N/L, as reported by Schlekat et al.\textsuperscript{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:

\[
2\text{NH}_4^+ + 3\text{O}_2 \rightarrow 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+,
\]
\[
\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}_2\text{O} + 2\text{H}^+.
\]
\[
\{\text{CH}_2\text{O}\} + \text{O}_2 \rightarrow \text{H}_2\text{CO}_3,
\]

\[
4\text{FeS}_2 + 15\text{O}_2 + 14\text{H}_2\text{O} \rightarrow 4\text{Fe(OH)}_3 + 16\text{H}^+ + 8\text{SO}_4^{2-}.
\]

These potential reactions would precipitate iron oxides and release hydrogen ions, NO$_3^- +$ 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 NO$_3^- +$ 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, NO$_3^- +$ 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,\textsuperscript{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

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|c|c|c|}
\hline
Trace element & USEPA MCLs\textsuperscript{a} for drinking-water & Baseline analyses\textsuperscript{b} & SDS2\textsuperscript{c} & SDS3\textsuperscript{c} & SW3\textsuperscript{d} & SW3\textsuperscript{e} & SDS2\textsuperscript{f} & SDS3\textsuperscript{f} & SW3\textsuperscript{g} & SW3\textsuperscript{g} \\
\hline
Ag & 0.1 & bdl & bdl & bdl & bdl & bdl & bdl & bdl & bdl & bdl \\
Cd & 0.005 & bdl & bdl & bdl & bdl & bdl & bdl & bdl & 0.00065 & bdl \\
Sb & 0.006 & bdl & 0.054 & bdl & bdl & bdl & bdl & bdl & 0.0055 & bdl \\
Tl & 0.002 & bdl & bdl & bdl & bdl & bdl & bdl & bdl & bdl & bdl \\
Pb & 0.015 & bdl & 0.048 & 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 & 0.013 & 0.026 & 0.014 \\
Cu & 1.3 & bdl & 0.039 & bdl & bdl & 0.0064 & bdl & bdl & bdl & bdl & 0.0051 & 0.019 & 0.0077 \\
Zn & 5.0 & bdl-0.16 & 0.088 & 0.056 & 0.03 & 0.016 & 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 \\
NO$_3^- +$ 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 \\
\hline
\end{tabular}
\caption{Concentrations of trace elements (mg/L) in groundwaters from the monitoring wells after the placement of the dredged sediments at the replacement site.}
\end{table}

\textsuperscript{a}USEPA maximum contaminant levels for drinking water are based on the data provided by Fetter (Ref. 11), except for new As MCL.
\textsuperscript{b}Baseline 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.
\textsuperscript{c}Samples Analyzed by Gascoyne Laboratories, Inc.
\textsuperscript{d}The collection date of the groundwater samples.

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 in-bound dredged sediments were all initially the dark bluish black color seen at the center of the aggregate.
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.

ACKNOWLEDGMENTS

This study was funded by Weanack Limited Land Partners, Inc. as part of a grant to W.L.D., G.R.W., and K.H.J. Special thanks go to Charles Carter for advice and historical land-use information. We also wish to thank Dr. Z Chen and Dr. C. Jones for ICP-MS analysis and Ms. J. Daniels, Ms. N. McGinnis, and Mr. W. Bounds for assistance with sample collection.

1 A. D. K. Banerjee, Environ. Pollut. 123, 95 (2003).
2 X. Feng, Y. Hong, B. Hong, and J. Ni, Environ. Geol. 39, 372 (2000).
3 X. Li and I. Thornton, Appl. Geochem. 16, 1693 (2001).
4 J. Nyamangara, Agric., Ecosyst. Environ. 69, 135 (1998).
5 A. Tessier, P. G. C. Campbell, and M. Bisson, Anal. Chem. 51, 844 (1979).
6 R. van Ryssen, M. Leermakers, and W. Baeyens, Environ. Sci. Policy 2, 75 (1999).
7 R. B. Mixon, C. B. Berquist, Jr., W. L. Newell, and G. H. Johnson, U.S. Geological Survey, Miscellaneous Investigations Series Map I-2033, 1989.
8 E. R. McFarland, U.S. Geological Survey, Water Resources Investigations Report 99-4093, 1999.
9 G. H. Johnson, L. W. Ward, and P. C. Peebles, in Geological Excursions in Virginia and North Carolina: Southeastern Section—Geological Society of America Field Trip Guidebook, edited by G. R. Whittecar (1987), pp. 189–218.
10 R. M. Hassirson, D. P. H. Laxen, and S. J. Wilson, Environ. Sci. Technol. 15, 1378 (1981).
11 C. W. Fetter, Contaminant Hydrogeology (Prentice Hall, Upper Saddle River, NJ, 1999), p. 500.
12 L. W. Hall, W. S. Hall, S. J. Bushong, and R. L. Herman, Aquatic Toxicology 10, 73 (1987).
13 C. E. Schlekat, B. L. McGee, D. M. Boward, E. Reinharz, D. J. Velinsky, and T. L. Wade, Estuaries 17, 334 (1994).
14 J. A. Davis and D. B. Kent, Rev. Mineral. 23, 177 (1990).
15 G. R. Whittecar (unpublished).