

SUPPLEMENTARY MATERIAL

Arsenic and trace metals in water and sediment of the Velhas River, Southeastern Iron Quadrangle region, Minas Gerais, Brazil

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Table 1S. Operational conditions and parameters of ICP-MS

| Parameter | |
|--|--|
| Nebulizer spray chamber | Cyclonic glass |
| Nebulizer | Meinhard concentric. Type C |
| RF power (W) | 1500 |
| Plasma gas flow rate (L min ⁻¹) | 16 |
| Auxiliary gas flow rate (L min ⁻¹) | 1.10 |
| Nebulizer gas flow rate (L min ⁻¹) | 1.02 |
| Replicates | 3 |
| Isotopes | ⁷⁵ As, ¹¹¹ Cd, ⁵⁹ Co, ⁵² Cr, ⁶³ Cu, ⁶⁰ Ni, ²⁰⁸ Pb and ⁶⁶ Zn |

Table 2S. BCR protocol

| Shaking | Time (h) | Temp. (°C) | Vol. (ml) ^a | Extractants | Fraction | Step |
|---------------------|----------|------------|------------------------|---|-------------------------------|------|
| 40 rpm | 16 | 22 ± 5 | 32 | CH ₃ COOH 0.11 mol L ⁻¹ | Exchangeable and acid-soluble | 1 |
| 40 rpm | 16 | 22 ± 5 | 32 | NH ₂ OH·HCl 0.5 mol L ⁻¹ (pH 1.5) ^b | Reducible | 2 |
| Occasional | 1 | 22 ± 5 | 8 | H ₂ O ₂ 8.8 mol L ⁻¹ (pH 2) ^b | Oxidizable | 3 |
| Occasional | 1 | 80 ± 5 | | | | |
| Occasional | 1 | 80 ± 5 | 8 | H ₂ O ₂ 8.8 mol L ⁻¹ (pH 2) ^b | | |
| 40 rpm | 16 | 22 ± 5 | 40 | NH ₄ OAc 1 mol L ⁻¹ (pH 2) ^b | | |
| Microwave digestion | | | 12 | Aqua regia (HCl/HNO ₃ , 3:1) | Residual | 4 |

^a Related to sample weight of 0.8 g.

^b pH values adjusted with concentrated nitric acid.

Table 3S. Analytical figures of merit for the quantitative determination of As, Cd, Co, Cr, Cu, Ni, Pb and Zn by ICP-MS

| Parameters | Isotopes | | | | | | | |
|--|------------------|-------------------|------------------|------------------|------------------|------------------|-------------------|------------------|
| | ⁷⁵ As | ¹¹¹ Cd | ⁵⁹ Co | ⁵² Cr | ⁶³ Cu | ⁶⁰ Ni | ²⁰⁸ Pb | ⁶⁶ Zn |
| Limit of detection ^a (µg L ⁻¹) | 0.07 | 0.03 | 0.01 | 0.05 | 0.07 | 0.08 | 0.04 | 0.09 |
| Limit of quantification ^b (µg L ⁻¹) | 0.21 | 0.09 | 0.03 | 0.15 | 0.21 | 0.24 | 0.12 | 0.27 |
| Linear correlation coefficient (r) | 0.999 | 0.998 | 0.999 | 0.998 | 0.999 | 0.999 | 0.998 | 0.999 |
| Calibration range (µg L ⁻¹) | 0.1–100 | 0.1–100 | 0.1–100 | 0.1–100 | 0.1–100 | 0.1–100 | 0.1–100 | 0.1–100 |
| Measurement precision ^c (%) | 1.2 | 1.7 | 1.1 | 1.5 | 1.9 | 1.4 | 1.2 | 1.6 |

^a LOD = three times the average of the standard deviation of ten blanks divided by the slope of analytical curve.

^b LOQ = 3 × LOD.

^c Coefficient of variation obtained from n = 10 measurements of a standard solution containing 10 µg L⁻¹ of each element.

Table 4S. Arsenic and trace metals (in milligrams per kilogram; average of three repetitions \pm standard deviation) quantities recovered from the sediments by application of the BCR sequential extraction method

| S1 | | | | | | |
|----|-----------------|-----------------|------------------|------------------|-------------------|------------------|
| | Step | | | | PT | (%) ^a |
| | 1 | 2 | 3 | Residual | | |
| As | 0.73 \pm 0.16 | 0.49 \pm 0.03 | 0.23 \pm 0.10 | 29.20 \pm 0.92 | 30.80 \pm 0.28 | 100 |
| Cd | 1.56 \pm 0.36 | 1.06 \pm 0.17 | 0.50 \pm 0.11 | 2.47 \pm 0.31 | 6.30 \pm 0.10 | 89 |
| Co | 4.49 \pm 0.15 | 5.10 \pm 0.30 | 1.72 \pm 0.43 | 10.13 \pm 0.12 | 19.25 \pm 0.11 | 111 |
| Cr | 1.23 \pm 0.09 | 5.49 \pm 0.29 | 18.25 \pm 0.12 | 85.68 \pm 0.18 | 133.15 \pm 0.35 | 83 |
| Cu | 0.68 \pm 0.07 | 4.49 \pm 0.35 | 1.27 \pm 0.17 | 21.73 \pm 0.42 | 28.70 \pm 0.70 | 98 |
| Ni | 2.23 \pm 0.28 | 3.92 \pm 0.30 | 4.95 \pm 0.17 | 34.39 \pm 0.57 | 45.50 \pm 0.60 | 100 |
| Pb | 0.48 \pm 0.14 | 1.49 \pm 0.34 | 0.22 \pm 0.07 | 2.10 \pm 0.46 | 4.45 \pm 0.10 | 97 |
| Zn | 3.39 \pm 0.14 | 4.02 \pm 0.18 | 9.12 \pm 0.24 | 2.72 \pm 0.15 | 20.50 \pm 0.40 | 94 |

| | Step | | | | PT | (%) ^a |
|----|-----------------|-----------------|------------------|-------------------|-------------------|------------------|
| | 1 | 2 | 3 | Residual | | |
| As | 0.68 \pm 0.12 | 3.27 \pm 0.14 | 2.08 \pm 0.50 | 37.13 \pm 0.12 | 44.65 \pm 0.13 | 97 |
| Cd | 1.44 \pm 0.47 | 1.56 \pm 0.16 | 0.81 \pm 0.17 | 1.48 \pm 0.56 | 5.80 \pm 0.50 | 91 |
| Co | 5.07 \pm 0.91 | 7.66 \pm 0.11 | 2.33 \pm 0.78 | 8.20 \pm 0.16 | 20.20 \pm 0.60 | 115 |
| Cr | 1.69 \pm 0.06 | 5.81 \pm 0.12 | 18.99 \pm 0.16 | 105.44 \pm 0.31 | 151.50 \pm 0.37 | 87 |
| Cu | 0.84 \pm 0.13 | 7.37 \pm 0.17 | 1.41 \pm 0.41 | 38.50 \pm 0.10 | 55.05 \pm 0.95 | 87 |
| Ni | 3.18 \pm 0.12 | 5.23 \pm 0.14 | 5.49 \pm 0.47 | 37.91 \pm 0.25 | 53.45 \pm 0.29 | 97 |
| Pb | 0.48 \pm 0.05 | 2.56 \pm 0.06 | 0.12 \pm 0.03 | 8.86 \pm 0.78 | 11.20 \pm 0.15 | 106 |
| Zn | 0.71 \pm 0.08 | 9.44 \pm 0.05 | 6.43 \pm 0.19 | 6.53 \pm 0.63 | 23.20 \pm 0.17 | 100 |

| | Step | | | | PT | (%) ^a |
|----|-----------------|------------------|------------------|-------------------|-------------------|------------------|
| | 1 | 2 | 3 | Residual | | |
| As | 0.27 \pm 0.04 | 4.53 \pm 0.85 | 44.84 \pm 0.29 | 158.61 \pm 0.40 | 206.70 \pm 1.25 | 101 |
| Cd | 1.04 \pm 0.21 | 1.36 \pm 0.33 | 0.74 \pm 0.12 | 2.76 \pm 0.41 | 6.15 \pm 0.50 | 96 |
| Co | 4.86 \pm 0.05 | 7.39 \pm 0.21 | 3.73 \pm 0.08 | 10.78 \pm 0.06 | 27.35 \pm 0.11 | 98 |
| Cr | 1.27 \pm 0.12 | 6.31 \pm 0.02 | 21.22 \pm 0.44 | 136.63 \pm 0.56 | 186.55 \pm 0.33 | 89 |
| Cu | 0.17 \pm 0.03 | 7.23 \pm 0.31 | 3.86 \pm 0.11 | 36.31 \pm 0.10 | 62.85 \pm 0.65 | 76 |
| Ni | 3.06 \pm 0.26 | 5.06 \pm 0.08 | 6.07 \pm 0.07 | 51.36 \pm 0.13 | 72.15 \pm 0.27 | 91 |
| Pb | 0.57 \pm 0.02 | 2.13 \pm 0.10 | 0.08 \pm 0.02 | 1.87 \pm 0.02 | 4.75 \pm 0.10 | 98 |
| Zn | 4.52 \pm 0.18 | 20.51 \pm 0.10 | 10.12 \pm 0.33 | 14.58 \pm 0.35 | 53.15 \pm 0.25 | 94 |

| | Step | | | | PT | (%) ^a |
|----|-----------------|-----------------|------------------|-------------------|-------------------|------------------|
| | 1 | 2 | 3 | Residual | | |
| As | 0.58 \pm 0.09 | 1.76 \pm 0.28 | 23.61 \pm 0.46 | 111.41 \pm 1.34 | 131.60 \pm 0.50 | 103 |

| | | | | | | |
|----|--------------|--------------|--------------|---------------|---------------|----|
| Cd | 0.97 ± 0.16 | 1.25 ± 0.35 | 0.25 ± 0.06 | 3.75 ± 0.56 | 6.75 ± 0.50 | 92 |
| Co | 1.39 ± 0.17 | 9.48 ± 0.93 | 13.53 ± 0.26 | 23.03 ± 0.78 | 56.30 ± 0.12 | 84 |
| Cr | 1.07 ± 0.32 | 6.43 ± 0.78 | 23.81 ± 0.27 | 248.87 ± 0.27 | 302.50 ± 2.57 | 93 |
| Cu | 0.56 ± 0.18 | 6.75 ± 0.13 | 4.14 ± 0.11 | 35.28 ± 0.81 | 58.25 ± 0.95 | 79 |
| Ni | 1.38 ± 0.17 | 5.06 ± 0.14 | 42.23 ± 0.58 | 87.19 ± 0.19 | 140.10 ± 0.31 | 97 |
| Pb | 0.63 ± 0.07 | 1.28 ± 0.23 | 0.51 ± 0.17 | 2.97 ± 0.29 | 5.50 ± 0.50 | 98 |
| Zn | 16.90 ± 0.22 | 32.96 ± 0.25 | 9.47 ± 0.47 | 28.63 ± 0.59 | 89.80 ± 1.40 | 98 |

PT pseudo-total digestion, ^aRecuperation in percentage.

Table 5S. Values of arsenic and trace metals (mg kg⁻¹)^a extracted from the reference material SRM 2704 (Buffalo River Sediment)

| | Steps | | | | VC ^b | (%) ^c |
|----|--------------|--------------|--------------|---------------|-----------------|------------------|
| | 1 | 2 | 3 | Residual | | |
| As | 1.19 ± 0.06 | 5.06 ± 0.05 | 0.31 ± 0.01 | 15.79 ± 0.19 | 23.4 ± 0.8 | 95 |
| Cd | 0.78 ± 0.07 | 0.38 ± 0.03 | 0.25 ± 0.02 | 1.39 ± 0.03 | 3.45 ± 0.22 | 81 |
| Co | 1.09 ± 0.01 | 1.31 ± 0.02 | 0.66 ± 0.08 | 9.09 ± 0.06 | 14.00 ± 0.6 | 87 |
| Cr | 2.20 ± 0.02 | 17.33 ± 0.06 | 22.19 ± 2.43 | 90.16 ± 3.09 | 135.00 ± 5 | 98 |
| Cu | 4.21 ± 1.20 | 3.63 ± 0.20 | 2.14 ± 0.50 | 87.41 ± 0.12 | 98.6 ± 5.0 | 99 |
| Ni | 6.54 ± 0.30 | 13.00 ± 0.20 | 5.34 ± 0.01 | 16.59 ± 0.18 | 44.1 ± 3.0 | 94 |
| Pb | 3.69 ± 0.04 | 66.97 ± 1.11 | 8.44 ± 0.66 | 73.78 ± 0.20 | 161 ± 17 | 93 |
| Zn | 60.38 ± 0.32 | 84.44 ± 1.67 | 1.13 ± 0.12 | 272.28 ± 0.56 | 438 ± 12 | 95 |

^aMean of 3 repetitions ± standard deviation; ^bCertified value for the reference material; ^cRecuperation in percentage.



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