

Supplementary information

Table S1. Mean concentrations and standard deviation (SD) for the analyzed certified reference material PACS-2 with recoveries (%) related to the certified values (National Research Council of Canada).

| Element | Certified reference values for CRM PACS-2 | | Analyzed PACS-2 | | | |
|---------|-------------------------------------------|---------------------------|-------------------------------------------|---------------------------|---|--------------|
| | mean concentration (mg kg ⁻¹) | SD (mg kg ⁻¹) | mean concentration (mg kg ⁻¹) | SD (mg kg ⁻¹) | N | Recovery (%) |
| Be | 1.00 | 0.20 | 1.03 | 0.10 | 4 | 103 |
| Na | 34 500 | 1 700 | 33 925 | 2 023 | 4 | 98 |
| Mg | 14 700 | 1 300 | 14 111 | 3 300 | 4 | 96 |
| Al | 66 200 | 3 200 | 65 361 | 14 559 | 4 | 99 |
| P | 960 | 40 | 1 000 | 65 | 4 | 104 |
| K | 12 400 | 500 | 11 509 | 2 543 | 4 | 93 |
| Ti | 4 430 | 320 | 4 424 | 263 | 4 | 100 |
| V | 133 | 5 | 132 | 9 | 4 | 99 |
| Cr | 90.7 | 4.6 | 88 | 5 | 4 | 98 |
| Mn | 440 | 19 | 443 | 30 | 4 | 101 |
| Fe | 40 900 | 600 | 39 561 | 3 624 | 4 | 97 |
| Co | 11.5 | 0.3 | 11.4 | 0.8 | 4 | 99 |
| Ni | 39.5 | 2.3 | 39.6 | 2.5 | 4 | 100 |
| Cu | 310 | 12 | 309 | 16 | 4 | 100 |
| Zn | 364 | 23 | 380 | 28 | 4 | 104 |
| As | 26.2 | 1.5 | 25.9 | 1.3 | 4 | 99 |
| Se | 0.92 | 0.22 | 0.87 | 0.80 | 4 | 95 |
| Sr | 276 | 30 | 279 | 42 | 4 | 101 |
| Mo | 5.43 | 0.28 | 5.40 | 0.33 | 4 | 99 |
| Ag | 1.22 | 0.14 | 1.53 | 0.48 | 4 | 126 |
| Cd | 2.11 | 0.15 | 2.13 | 0.08 | 4 | 101 |
| Sn | 19.8 | 2.5 | 19.5 | 0.3 | 4 | 99 |
| Sb | 11.3 | 2.6 | 11.5 | 0.7 | 4 | 102 |
| Pb | 183 | 8 | 180 | 15 | 4 | 98 |
| U | 3 | | 2.5 | 0.4 | 4 | 83 |

Table S2. Results of HERFD-XANES linear combination fits.

| | Br speciation (in molar % of Br) | | Sum | R factor |
|--------------------------|-----------------------------------------|---------------------|------------|-----------------|
| | Aromatic Br | Inorganic Br | | |
| STO_1-2 | 84 | 14 | 98 | 0.00287 |
| STO_5-6 | 84 | 15 | 99 | 0.00211 |
| STO_9-10 | 82 | 16 | 98 | 0.00365 |
| STO_17-18 | 81 | 15 | 96 | 0.00289 |
| STO_23-24 | 86 | 14 | 100 | 0.00226 |
| STO_23-24 (replicate) | 87 | 13 | 100 | 0.00226 |

Table S3: Radiocarbon ages obtained in core STO (bulk sediment exclusively).

| Laboratory Code | Depth (cm) | Sample type | ¹⁴ C age (yr BP) | Age 2σ range (cal. yr BP) |
|--------------------|------------|----------------|-----------------------------|------------------------------|
| SacA-29799 | 17 - 18 | Bulk sediment | modern | (excluded) |
| SacA-57983 | 25 - 26 | Bulk sediment | 4275 ± 30 | (excluded) |
| SacA- 29800 | 28 - 29 | Bulk sediment | 775 ± 30 | 649 - 725 |
| RICH-28155 | 39 - 40 | Organic remain | 1577 ± 26 | (excluded) |
| RICH-28156 | 39 - 40 | Organic remain | 1290 ± 26 | 1073 - 1116 |
| SacA- 29801 | 47 - 48 | Bulk sediment | 1835 ± 30 | 1693 - 1752 |
| RICH-28157 | 50 - 51 | Organic remain | 2101 ± 28 | 1993 - 2096 |
| SacA-57984 | 52 - 53 | Bulk sediment | 4265 ± 30 | (excluded) |
| SacA- 29802 | 62 - 63 | Bulk sediment | 3545 ± 30 | 3691 - 3888 |
| SacA-57985 | 77 - 78 | Bulk sediment | 1215 ± 30 | (excluded) |
| RICH-28181 | 77 - 78 | Organic remain | 700 ± 25 | (excluded) |
| SacA-29803 | 78 - 79 | Bulk sediment | 965 ± 30 | (excluded) |

Figure S1: Br HERFD-XANES spectra for an aliphatic Br compound (Bromoeicosane), an aromatic Br compound (Bromophenol) and inorganic Br (NaBr). The energy position of the maximum of the white line and first oscillation are shifted by 0.5 eV and 1.6 eV, respectively, between aliphatic and aromatic Br.

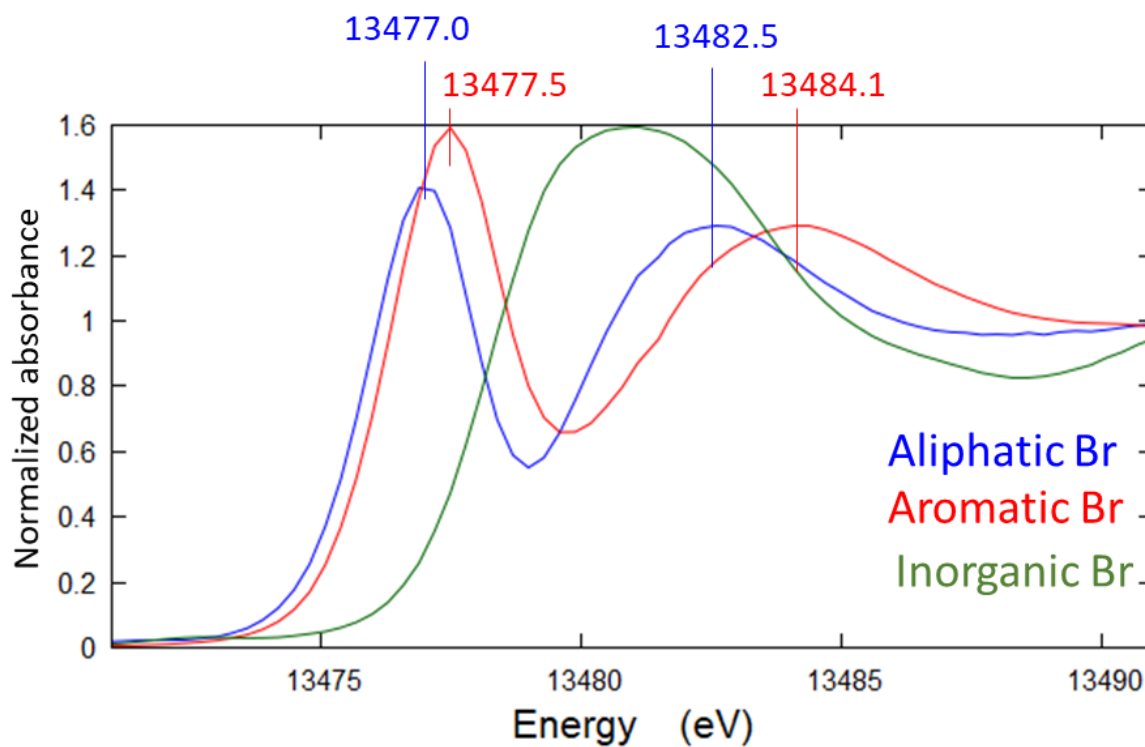


Figure S2: Satellite image (google earth image) of a part of the Saitoco wetland where ancient irrigation canals are easily identifiable.



Figure S3: Core lithology and total elemental concentration – depth profiles (from top to bottom) of bromine (Br), bromine over Organic carbon ration (Br:C_{org}), selenium (Se), mercury (THg), lead (Pb), copper (Cu), and antimony (Sb) in sampled Saitoco core.

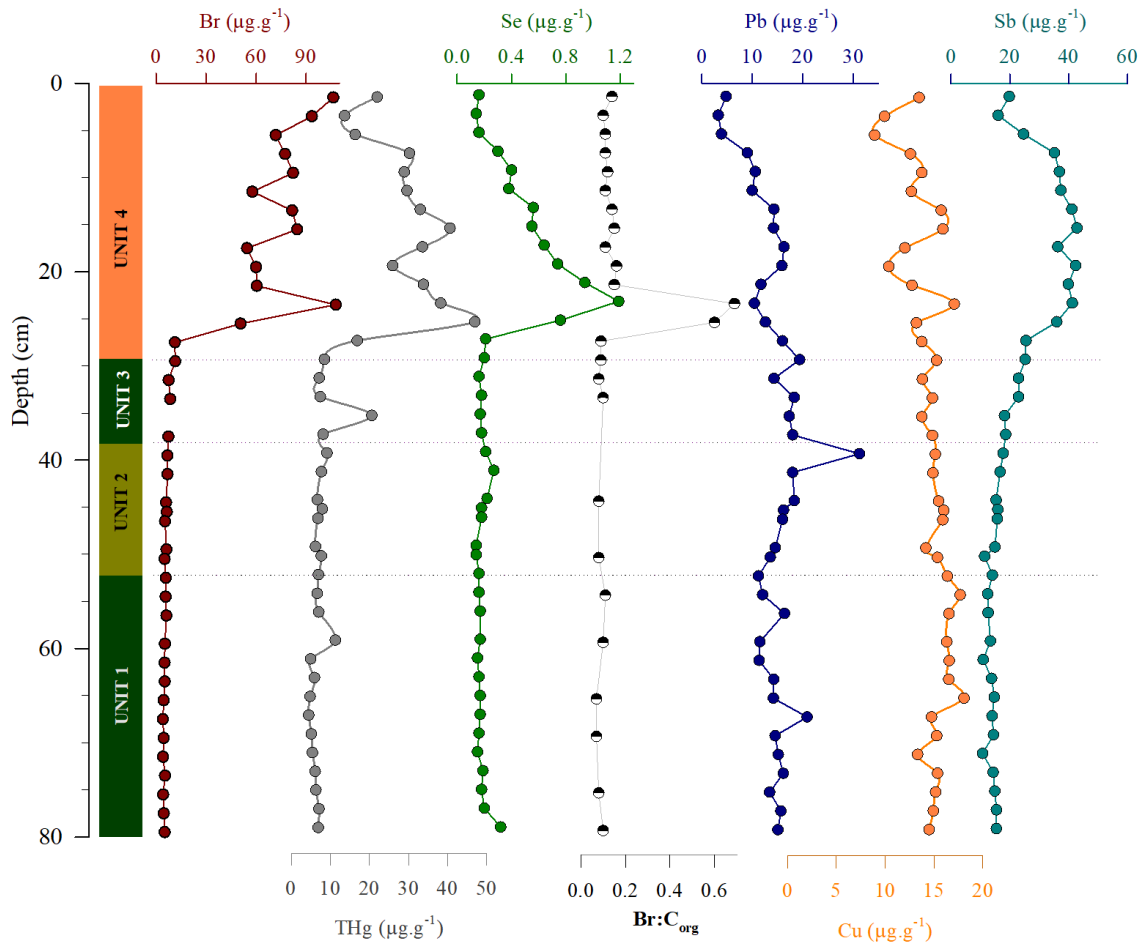


Figure S4: Pb, Cu, Sb and Ti concentrations and accumulation rates (ARs) record in the Saitoco record. Because of the significant minerogenic fraction in the core, both concentrations and ARs show high levels in the entire record, except a decline in the most organic part (Unit 4) of the record.

