**Geochemical distribution and thresholds values determination of heavy metals in stream water in the sub-basins of Vermelho and Sororó rivers, Itacaiúnas River watershed, Eastern Amazon, Brazil**

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Table 1. Physico-chemical parameters and anions in surface water samples.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Parameters | Detection limit (DL) | Unit | Specific  conditions | Method | Maximum holding time |
| 1Dissolved oxygen | 0.1 | mg/L | In situ | HI 98194 multiparameter probe | - |
| 2pH (25°C) | 2 to 13 | - |
| 3Temperature | - | °C |
| 4Specific electrical conductivity | 1.0 | µS/cm |
| 5Redox potential | - | mV |
| 6Total Dissolved Solids (TDS) | 5.0 | mg/L | Cooling at 4ºC | 7 days |
| 7Turbidity | 0.1 | NTU | Nephelometric | - |
| 8Phosphorus total (Ptotal) | 0.01 | mg/L | Sulfuric acid digestion at pH < 2 | 28 days |
| 9Nitrate (NO3-) | 2.2 | Ion chromatography | 28 days |
| 9Sulfate (SO42) | 0.5 |
| 9Fluoride (F-) | 0.05 |
| 9Chloride (Cl-) | 0.5 | 48 hours |

Note: The analytical procedures were adopted accordingly to the SMWW methods (APHA 2012): 4500O G1; 4500H+ B2; 2550 B3; 2510 B4; 2580 B5; 2540 A, B, C, D, E6; 2130 B7; 4500 P-E8; and to the EPA 300.0: 1993, 300.1: 1999, POP PA 032 - Rev. 129.

Table 2. Descriptive statistics of stream water analyses of samples from Vermelho (VSB) and Sororó (SSB) sub-basins during rainy (-R) and dry (-D) seasons. n: number of samples; DL: detection limit; LOL: lower outlier limit; Min: minimum concentration; M: 50th percentile of the data set, also known as median; and Max: maximum concentration. Mean (σ) and standard deviation (SD) were calculated before (BRO) and after (ARO) removing outliers.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | SB - Season | n | DL | n<DL | %<DL | LOL | n≥LOL | %≥LOL | Min | M | Max | BRO | | ARO | |
| σ | SD | σ | SD |
| As | VSB-R | 143 | 1 | 130 | 90.9 | 1.03 | 13 | 9.1 | <1 | <1 | 4.37 | 0.62 | 0.50 | 0.50 | 0 |
|  | VSB-D | 123 | 1 | 114 | 92.7 | 1.26 | 4 | 3.3 | <1 | <1 | 2.8 | 0.61 | 0.42 | 0.50 | 0 |
|  | SSB-R | 75 | 1 | 54 | 72.0 | 1.19 | 21 | 28.0 | <1 | <1 | 3.99 | 0.92 | 0.79 | 0.50 | 0 |
|  | SSB-D | 50 | 1 | 34 | 68.0 | 2.69 | 3 | 6.0 | <1 | <1 | 3.39 | 0.90 | 0.71 | 0.76 | 0.45 |
| Co | VSB-R | 143 | 1 | 66 | 46.2 | 4.90 | 5 | 3.5 | <1 | 1.11 | 9.58 | 1.53 | 1.51 | 1.36 | 1.10 |
|  | VSB-D | 123 | 1 | 62 | 50.4 | 6.67 | 5 | 4.1 | <1 | <1 | 17.7 | 1.74 | 2.38 | 1.38 | 1.32 |
|  | SSB-R | 75 | 1 | 58 | 77.3 | 2.07 | 3 | 4.0 | <1 | <1 | 4.29 | 0.77 | 0.62 | 0.68 | 0.38 |
|  | SSB-D | 50 | 1 | 33 | 66.0 | 3.44 | 2 | 4.0 | <1 | <1 | 4.04 | 0.87 | 0.71 | 0.75 | 0.40 |
| Cr | VSB-R | 143 | 1 | 82 | 57.3 | 3.94 | 15 | 10.5 | <1 | <1 | 32.7 | 1.85 | 3.45 | 0.99 | 0.76 |
|  | VSB-D | 123 | 1 | 86 | 69.9 | 1.76 | 20 | 16.3 | <1 | <1 | 85.7 | 2.38 | 8.84 | 0.63 | 0.29 |
|  | SSB-R | 75 | 1 | 30 | 40.0 | 4.64 | 2 | 2.7 | <1 | 1.24 | 11.6 | 1.49 | 1.53 | 1.30 | 0.90 |
|  | SSB-D | 50 | 1 | 42 | 84.0 | 1.07 | 8 | 16.0 | <1 | <1 | 37.8 | 1.57 | 5.42 | 0.50 | 0.00 |
| Cu | VSB-R | 143 | 1 | 45 | 31.5 | 11.4 | 6 | 4.2 | <1 | 1.66 | 19.3 | 2.94 | 3.41 | 2.44 | 2.40 |
|  | VSB-D | 123 | 1 | 44 | 35.8 | 5.84 | 9 | 7.3 | <1 | 1.35 | 45.9 | 2.48 | 5.03 | 1.52 | 1.11 |
|  | SSB-R | 75 | 1 | 19 | 25.3 | 7.35 | 5 | 6.7 | <1 | 1.46 | 40.4 | 2.66 | 5.36 | 1.50 | 0.85 |
|  | SSB-D | 50 | 1 | 27 | 54.0 | - | 0 | 0 | <1 | <1 | 4.02 | 1.17 | 0.93 | 1.17 | 0.93 |
| Fe | VSB-R | 143 | 0.02 | 0 | 0 | 9.45 | 5 | 3.5 | 0.82 | 3.56 | 19.1 | 3.99 | 2.44 | 3.63 | 1.45 |
|  | VSB-D | 123 | 0.02 | 0 | 0 | 7.73 | 4 | 3.3 | 0.36 | 1.55 | 16.3 | 2.27 | 2.18 | 1.98 | 1.37 |
|  | SSB-R | 75 | 0.02 | 0 | 0 | 11.90 | 2 | 2.7 | 1.81 | 4.28 | 14.9 | 4.54 | 1.92 | 4.30 | 1.22 |
|  | SSB-D | 50 | 0.02 | 0 | 0 | 5.53 | 3 | 6.0 | 0.57 | 1.94 | 7.12 | 2.27 | 1.40 | 2.01 | 0.95 |
| Mn | VSB-R | 143 | 0.001 | 0 | 0 | 1.04 | 8 | 5.6 | 0.03 | 0.22 | 3.74 | 0.33 | 0.42 | 0.25 | 0.18 |
|  | VSB-D | 123 | 0.001 | 0 | 0 | 0.61 | 27 | 22.0 | 0.02 | 0.17 | 5.90 | 0.62 | 1.09 | 0.18 | 0.12 |
|  | SSB-R | 75 | 0.001 | 0 | 0 | 0.71 | 5 | 6.7 | 0.03 | 0.20 | 2.12 | 0.28 | 0.30 | 0.21 | 0.13 |
|  | SSB-D | 50 | 0.001 | 0 | 0 | 2.64 | 4 | 8.0 | 0.02 | 0.62 | 9.14 | 0.99 | 1.48 | 0.64 | 0.46 |
| Ni | VSB-R | 143 | 1 | 53 | 37.1 | 6.25 | 15 | 10.5 | <1 | 1.51 | 16.8 | 2.40 | 2.88 | 1.57 | 1.24 |
|  | VSB-D | 123 | 1 | 56 | 45.5 | 5.01 | 11 | 8.9 | <1 | 1.09 | 20.7 | 1.88 | 2.72 | 1.20 | 0.88 |
|  | SSB-R | 75 | 1 | 14 | 18.7 | 5.25 | 1 | 1.3 | <1 | 1.61 | 5.25 | 1.68 | 0.87 | 1.63 | 0.77 |
|  | SSB-D | 50 | 1 | 31 | 62.0 | 11.2 | 1 | 2.0 | <1 | <1 | 11.2 | 1.15 | 1.59 | 0.94 | 0.66 |
| Pb | VSB-R | 143 | 1 | 103 | 72.0 | 2.70 | 2 | 1.4 | <1 | <1 | 9.21 | 0.83 | 0.86 | 0.76 | 0.46 |
|  | VSB-D | 123 | 1 | 110 | 89.4 | 1.07 | 13 | 10.6 | <1 | <1 | 3.65 | 0.65 | 0.51 | 0.50 | 0 |
|  | SSB-R | 75 | 1 | 36 | 48.0 | 6.57 | 2 | 2.7 | <1 | 1.13 | 9.52 | 1.28 | 1.34 | 1.09 | 0.69 |
|  | SSB-D | 50 | 1 | 43 | 86.0 | 1.0 | 7 | 14.0 | <1 | <1 | 1.69 | 0.62 | 0.31 | 0.50 | 0.00 |
| Sn | VSB-R | 143 | 1 | 83 | 58.0 | 6.07 | 14 | 9.8 | <1 | <1 | 22.4 | 2.30 | 3.62 | 1.26 | 1.23 |
|  | VSB-D | 123 | 1 | 37 | 30.1 | 25.3 | 1 | 0.8 | <1 | 1.88 | 25.3 | 2.25 | 2.59 | 2.07 | 1.53 |
|  | SSB-R | 75 | 1 | 53 | 70.7 | 3.84 | 3 | 4.0 | <1 | <1 | 5.91 | 1.00 | 1.05 | 0.83 | 0.64 |
|  | SSB-D | 50 | 1 | 8 | 16.0 | 13.3 | 3 | 6.0 | <1 | 2.51 | 19.3 | 3.40 | 3.54 | 2.62 | 1.62 |
| V | VSB-R | 143 | 1 | 53 | 37.1 | 7.58 | 8 | 5.6 | <1 | 1.66 | 18.9 | 2.19 | 2.42 | 1.75 | 1.42 |
|  | VSB-D | 123 | 1 | 48 | 39.0 | 5.80 | 10 | 8.1 | <1 | 1.42 | 31.1 | 2.24 | 3.62 | 1.46 | 1.09 |
|  | SSB-R | 75 | 1 | 14 | 18.7 | 5.20 | 2 | 2.7 | <1 | 1.52 | 8.67 | 1.72 | 1.19 | 1.58 | 0.77 |
|  | SSB-D | 50 | 1 | 31 | 62.0 | - | 0 | 0 | <1 | <1 | 2.89 | 0.92 | 0.63 | 0.92 | 0.63 |
| Zn | VSB-R | 143 | 1 | 51 | 35.7 | 52.7 | 4 | 2.8 | <1 | 7.12 | 517.0 | 14.41 | 44.35 | 9.78 | 11.00 |
|  | VSB-D | 123 | 1 | 4 | 3.3 | 61.0 | 3 | 2.4 | <1 | 9.03 | 109.0 | 14.39 | 15.60 | 12.53 | 9.76 |
|  | SSB-R | 75 | 1 | 2 | 2.7 | 63.6 | 5 | 6.7 | <1 | 15.30 | 151.0 | 22.54 | 24.00 | 17.47 | 11.74 |
|  | SSB-D | 50 | 1 | 0 | 0 | 68.4 | 5 | 10.0 | 1.2 | 11.25 | 170.0 | 26.28 | 38.88 | 14.79 | 14.34 |

Note: Concentration values of Fe and Mn are expressed in mg/L, and for the other elements in μg/L. Data below DL were replaced by ½ of the DL value. Cd, Hg and Mo were not exhibited because they presented more than 98% of the overall data <DL. ‘-’ Value not applicable.

Table 3. Threshold values obtained from various statistical methods [Median + 2 MAD, Tukey's inner fences (TIF), cumulative probability (CP) distribution diagrams, iterative 2σ technique (I2σ) and calculated distribution function (DF)] for 11 elements in stream water of the Vermelho (VSB) and Sororó (SSB) sub-basins during rainy (-R) and dry (-D) seasons of 2017.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Element | SB - Season | Regul. | Possible threshold values based on GBI data | | | | | Number of exceedances above | | | | | |
| SWC1 | MMAD | TIF | CP | I2σ | DF | SWC1 | MMAD | TIF | CP | I2σ | DF |
| As | VSB-R | 10 | <1 | <1 | - | - | - | 0 | 13 | 13 | - | - | - |
|  | VSB-D | <1 | <1 | - | - | - | 0 | 9 | 9 | - | - | - |
|  | SSB-R | <1 | - | - | - | - | 0 | 21 | - | - | - | - |
|  | SSB-D | <1 | 2.00 | - | - | - | 0 | 16 | 4 | - | - | - |
| Co | VSB-R | 50 | 2.68 | 3.80 | 2.31 | - | 2.28 | 0 | 22 | 12 | 24 | - | 25 |
|  | VSB-D | <1 | 3.66 | 3.46 | - | - | 0 | 61 | 14 | 14 | - | - |
|  | SSB-R | <1 | <1 | - | - | - | 0 | 17 | 17 | - | - | - |
|  | SSB-D | <1 | 2.04 | - | - | - | 0 | 17 | 2 | - | - | - |
| Cr | VSB-R | 50 | <1 | - | - | - | - | 0 | 61 | - | - | - | - |
|  | VSB-D | <1 | - | - | - | - | 1 | 37 | - | - | - | - |
|  | SSB-R | 3.28 | 3.66 | 1.59 | 1.94 | 2.57 | 0 | 5 | 4 | 23 | 16 | 10 |
|  | SSB-D | <1 | - | - | - | - | 0 | 8 | - | - | - | - |
| Cu | VSB-R | 50 | 4.62 | 7.45 | 3.56 | 1.47 | 3.56 | 0 | 28 | 16 | 33 | 76 | 33 |
|  | VSB-D | 3.53 | 4.64 | 2.95 | 2.00 | 2.80 | 0 | 14 | 11 | 22 | 40 | 25 |
|  | SSB-R | 3.46 | 4.36 | 2.6 | 2.61 | 2.82 | 0 | 6 | 5 | 12 | 12 | 12 |
|  | SSB-D | <1 | 3.27 | - | - | - | 0 | 23 | 3 | - | - | - |
| Fe | VSB-R | - | 6.50 | 7.87 | 6.22 | 5.74 | 5.95 | - | 10 | 5 | 10 | 15 | 13 |
|  | VSB-D | 3.23 | 4.13 | 1.99 | 2.07 | 2.67 | - | 20 | 17 | 39 | 39 | 28 |
|  | SSB-R | 6.93 | 7.89 | 5.16 | 6.21 | 6.57 | - | 3 | 2 | 24 | 6 | 4 |
|  | SSB-D | 3.61 | 4.24 | 2.49 | 2.84 | 3.41 | - | 8 | 4 | 13 | 11 | 8 |
| Mn | VSB-R | 0.1 | 0.50 | 0.66 | 0.44 | 0.37 | 0.44 | 112 | 20 | 14 | 24 | 33 | 24 |
|  | VSB-D | 0.28 | - | 0.22 | 0.20 | 0.30 | 96 | 42 | - | 50 | 52 | 40 |
|  | SSB-R | 0.42 | 0.50 | 0.22 | 0.31 | 0.40 | 60 | 12 | 7 | 35 | 19 | 14 |
|  | SSB-D | 1.45 | 1.94 | 0.67 | 1.32 | 1.39 | 43 | 6 | 5 | 24 | 7 | 7 |
| Ni | VSB-R | 25 | 3.65 | - | 4.36 | 1.88 | - | 0 | 25 | - | 18 | 54 | - |
|  | VSB-D | 1.49 | 3.76 | 2.97 | - | 2.22 | 0 | 46 | 13 | 16 | - | 24 |
|  | SSB-R | 2.90 | 3.58 | 1.81 | 3.10 | - | 0 | 6 | 1 | 33 | 2 | - |
|  | SSB-D | <1 | 2.76 | - | - | - | 0 | 19 | 1 | - | - | - |
| Pb | VSB-R | 10 | <1 | 1.90 | 1.82 | - | - | 0 | 40 | 7 | 7 | - | - |
|  | VSB-D | <1 | - | - | - | - | 0 | 13 | - | - | - | - |
|  | SSB-R | 2.48 | 3.08 | 1.60 | 1.87 | 2.37 | 0 | 5 | 4 | 16 | 11 | 6 |
|  | SSB-D | <1 | - | - | - | - | 0 | 7 | - | - | - | - |
| Sn | VSB-R | - | <1 | 4.05 | 6.28 | - | - | - | 60 | 22 | 12 | - | - |
|  | VSB-D | 5.91 | 6.26 | 3.3 | 3.16 | - | - | 4 | 4 | 24 | 26 | - |
|  | SSB-R | <1 | 1.87 | - | - | - | - | 22 | 9 | - | - | - |
|  | SSB-D | 4.38 | 5.22 | 3.43 | 4.44 | 5.07 | - | 8 | 6 | 12 | 8 | 6 |
| V | VSB-R | 100 | 4.47 | 5.13 | 2.12 | 2.31 | - | 0 | 16 | 11 | 42 | 41 | - |
|  | VSB-D | 3.59 | 4.25 | 2.26 | 2.18 | 3.06 | 0 | 17 | 12 | 30 | 33 | 22 |
|  | SSB-R | 2.75 | 3.34 | 2.08 | 2.79 | 2.83 | 0 | 6 | 4 | 20 | 6 | 6 |
|  | SSB-D | <1 | 2.45 | - | - | - | 0 | 19 | 2 | - | - | - |
| Zn | VSB-R | 180 | 25.00 | 37.00 | 23.3 | - | 18.68 | 1 | 19 | 8 | 19 | - | 28 |
|  | VSB-D | 18.66 | 34.82 | 9.17 | 12.08 | 17.27 | 0 | 30 | 7 | 60 | 41 | 34 |
|  | SSB-R | 31.13 | 44.23 | 32.2 | 24.75 | 29.90 | 0 | 14 | 9 | 12 | 20 | 16 |
|  | SSB-D | 29.51 | - | 24.5 | 19.0 | 23.75 | 0 | 11 | - | 11 | 14 | 12 |

Note: Concentration values of Fe and Mn are expressed in mg/L, and for the other elements in μg/L. Data below detection limit (DL) were replaced by ½ of the DL value. Regul. – Regulations; SWC1 = maximum values for Class 1 fresh water (CONAMA 357/05). ‘-’ technique not applicable to the analyzed data set.