Supporting Information

**Portable XRF as a rapid determination tool to detect ppm levels of Ni, Zn, As, Se and Pb in human toenails: A South India case study**

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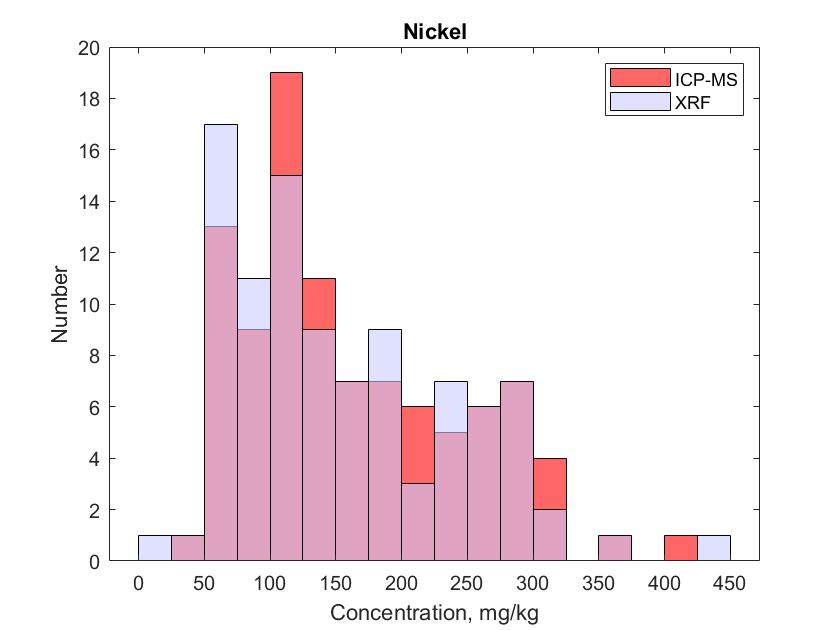
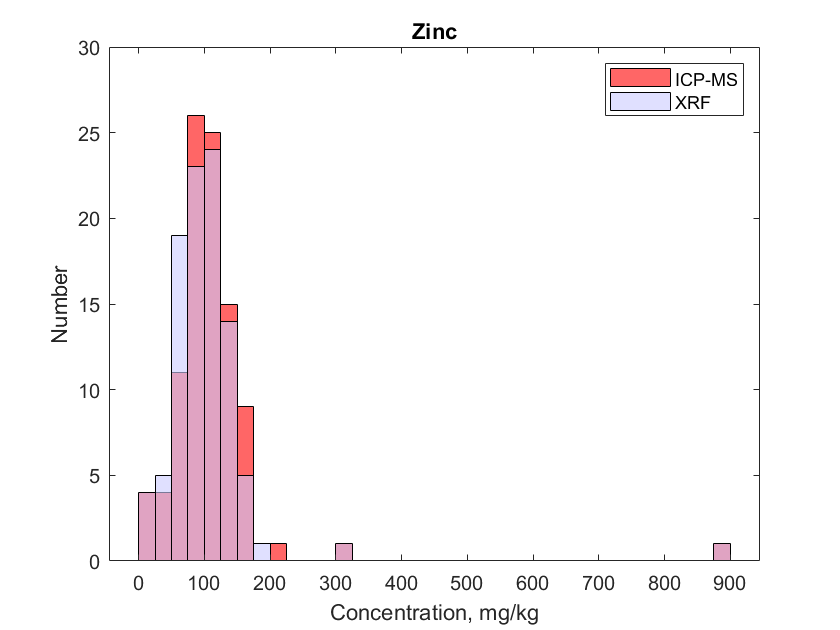
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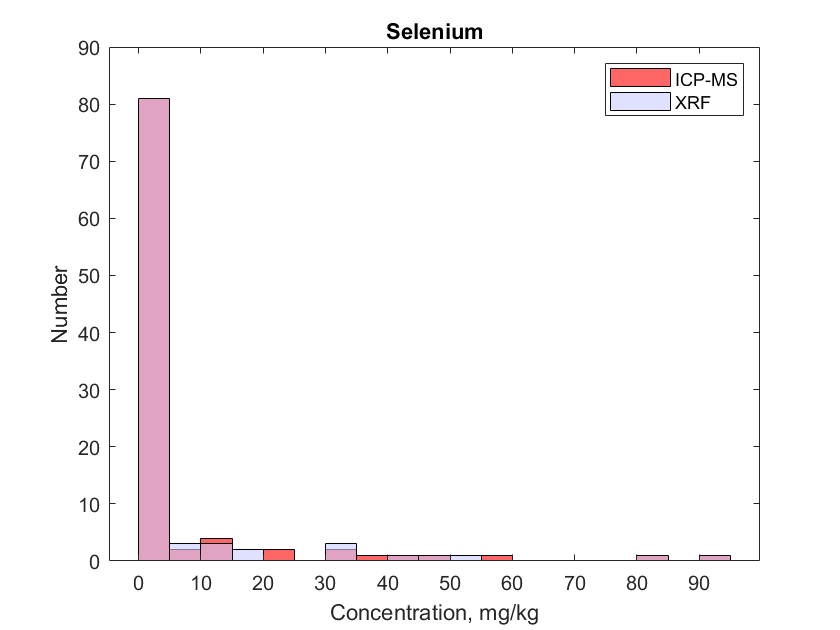
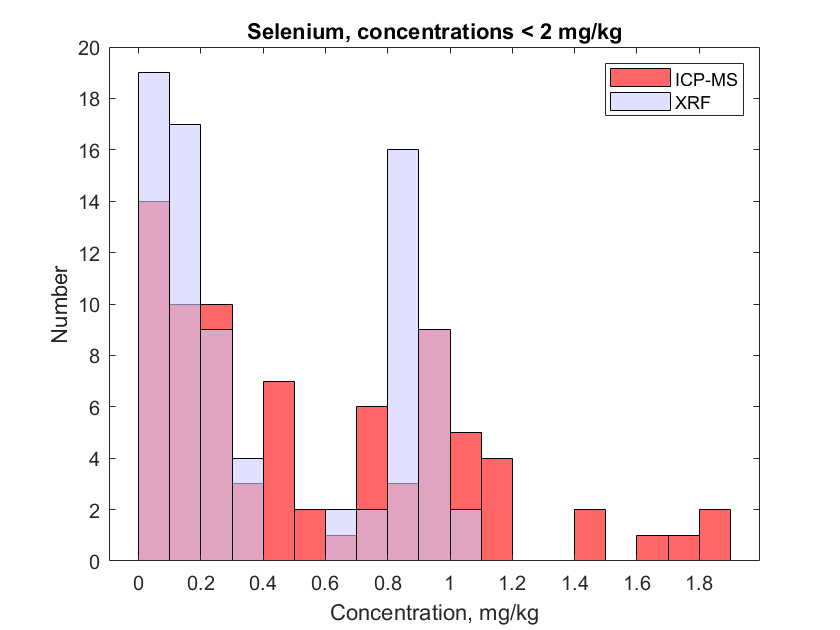
4 Department of Climate Change, Indian Institute of Technology (IIT) Hyderabad, Kandi, TS 502285, India.

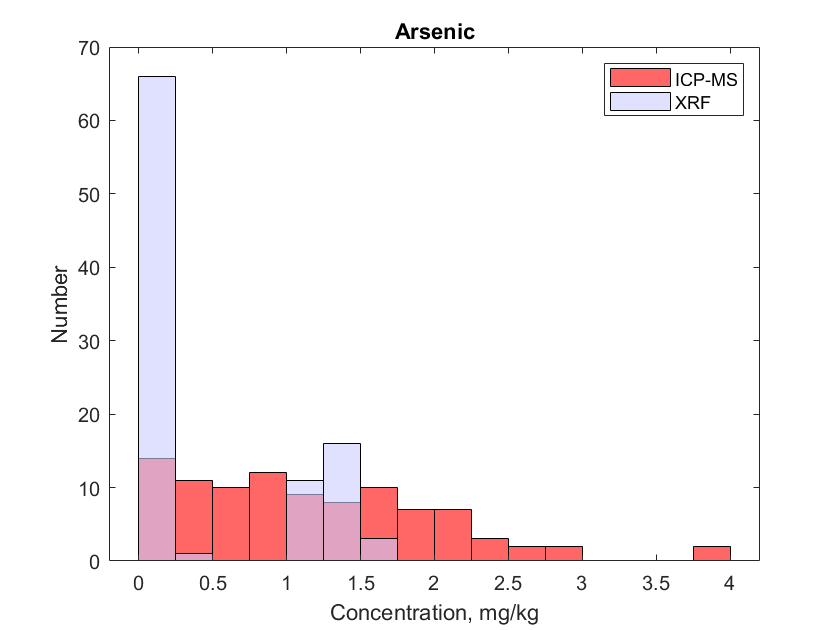
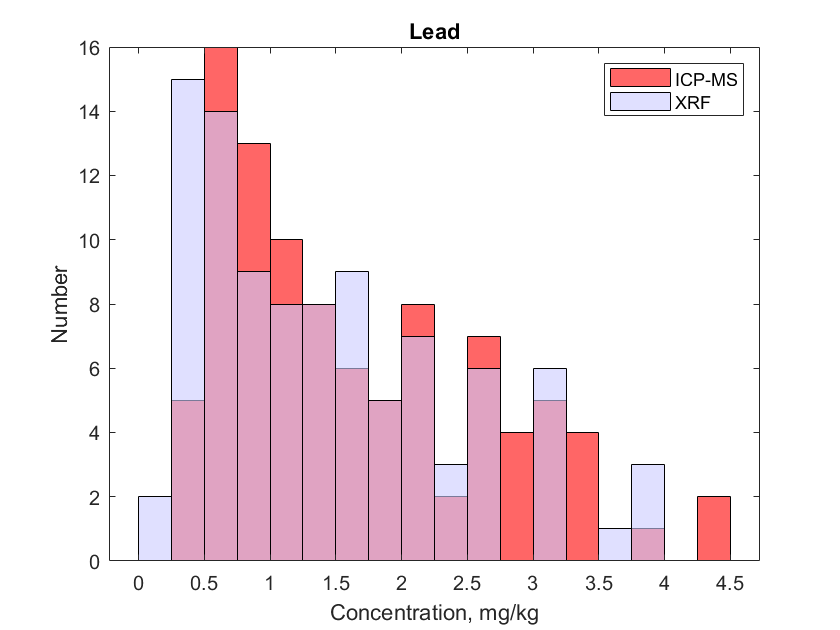
**Table S1.** Demographic characteristic of the study population.

|  |  |  |
| --- | --- | --- |
| **Demographic Characteristics** | | **Number of participants (out of 97)** |
| Age | <35 years | 23 |
| 35-48 years | 37 |
| >48 years | 37 |
| Gender | Male | 35 |
| Female | 62 |
| Education | Educated | 55 |
| Uneducated | 42 |
| Rice consumption | <=300g/meal/day | 68 |
| >300g/meal/day | 28 |
| Water source | Canned water (purchased from shops) | 40 |
| Pipe and other water sources | 57 |
| Secondary exposure | Yes | 32 |
| No | 65 |
| Duration of stay at the site location | <20 years | 28 |
| 20 to 35 years | 36 |
| >35 years | 33 |
| Profession | Pink collared jobs | 37 |
| Blue collared jobs | 43 |
| Other | 17 |
| Income group  (INR per month,  1 USD ~ 74 INR) | < 18000 | 32 |
| 18000 to 33000 | 34 |
| > 33000 | 31 |
| Fish consumption | <=150g/meal/week | 42 |
| 275-450 g/meal/week | 30 |
| >450 g/meal/week | 25 |

**Figure S1.** A sample spectrum from the XRF.

**Figure S2.** Distribution of measured concentrations by the two analysis methods.

**S1.** Concentrations of metal(loid)s in toenails for individual sites

**Table S2.** Mean, standard deviation (S.D.), maximum, minimum and median concentrations (mg/kg) corresponding to each metal measured in toenails. **Site: Sepakkam.**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Concentrations | **Nickel** | | **Zinc** | | **Arsenic** | | **Selenium** | | **Lead** | |
| ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF |
| Mean | 152 | 143 | 106 | 95.5 | 1.20 | 0.490 | 0.576 | 0.389 | 1.73 | 1.44 |
| S.D. | 73.0 | 73.1 | 58.0 | 57.6 | 0.864 | 0.605 | 0.584 | 0.382 | 1.07 | 1.01 |
| Median | 133 | 124 | 102 | 87.6 | 0.944 | 0.065 | 0.383 | 0.181 | 1.58 | 1.28 |
| Maximum | 361 | 353 | 320 | 317 | 2.83 | 1.48 | 1.90 | 0.962 | 4.47 | 3.97 |
| Minimum | 57.3 | 54.2 | 9.35 | 0 | 0.105 | 0.00 | 0.00 | 0.00 | 0.285 | 0.225 |

**Table S3.** Mean, standard deviation (S.D.), maximum, minimum and median concentrations (mg/kg) corresponding to each metal measured in toenails. **Site: Athipattu Pudu Nagar.**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Concentrations | **Nickel** | | **Zinc** | | **Arsenic** | | **Selenium** | | **Lead** | |
| ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF |
| Mean | 222 | 217 | 114 | 108 | 1.03 | 0.641 | 0.588 | 0.493 | 1.62 | 1.46 |
| S.D. | 77.2 | 77.8 | 138 | 137 | 0.684 | 0.663 | 0.424 | 0.400 | 0.808 | 0.881 |
| Median | 238 | 233 | 82.8 | 76.4 | 1.07 | 0.123 | 0.594 | 0.462 | 1.41 | 1.17 |
| Maximum | 417 | 427 | 892 | 887 | 2.69 | 1.56 | 1.46 | 1.03 | 3.78 | 3.83 |
| Minimum | 74.0 | 62.4 | 24.3 | 33.2 | 0.00 | 0.00 | 0.032 | 0.00 | 0.590 | 0.440 |

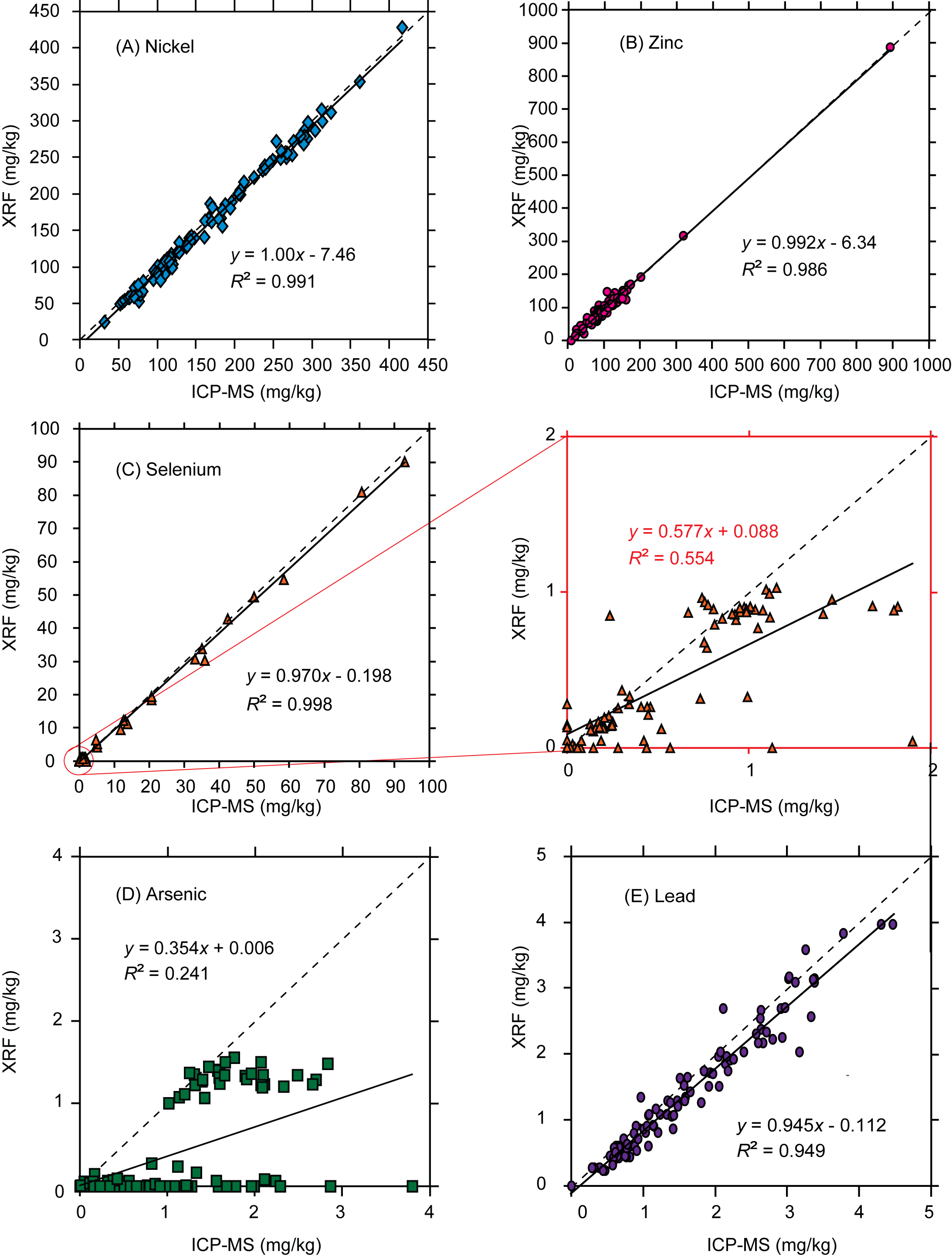
**Table S4.** Mean, standard deviation (S.D.), maximum, minimum and median concentrations (mg/kg) corresponding to each metal measured in toenails. **Site: Avurivakkam.**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Concentrations | **Nickel** | | **Zinc** | | **Arsenic** | | **Selenium** | | **Lead** | |
| ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF | ICP-MS | XRF |
| Mean | 92.0 | 86.6 | 119 | 116 | 1.33 | 0.00 | 21.6 | 20.5 | 1.55 | 1.39 |
| S.D. | 31.4 | 32.4 | 20.7 | 21.6 | 0.991 | 0.00 | 26.2 | 25.6 | 1.16 | 1.07 |
| Median | 95.4 | 89.4 | 113 | 107 | 1.14 | 0.00 | 12.6 | 11.3 | 0.963 | 1.07 |
| Maximum | 166 | 166 | 168 | 166 | 3.80 | 0.002 | 93.0 | 90.2 | 4.31 | 3.97 |
| Minimum | 31.8 | 23.9 | 86.7 | 89.2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.315 | 0.225 |

**S2. Pearson’s regression results**

**Table S5.** Statistical parameters from the comparison between XRF and ICP-MS results (Pearson’s correlation), where *x* is the ICP-MS measurement and *y* is the XRF measurement.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Metal** | **Model equation** | **Correlation** | **Adjusted *R2*** | **95% CI (lower bound, upper bound)** | | **Difference (%)** |
| **Beta** | **Intercept** |
| **Ni** | *y*=1.00*x*-7.46 | 0.996 | 0.991 | 0.983, 1.02 | -11.0, -3.92 | 4.32 |
| **Zn** | *y*=0.992*x*-6.34 | 0.993 | 0.986 | 0.967, 1.02 | -9.81, -2.86 | 6.48 |
| **As** | *y*=0.354*x*+0.006 | 0.491 | 0.241 | 0.226, 0.483 | -0.180, 0.191 | 65.0 |
| **Se** | *y*=0.970*x*-0.198 | 0.999 | 0.998 | 0.960, 0.980 | -0.366, -0.030 | 6.32 |
| **Pb** | *y*=0.945*x*-0.112 | 0.974 | 0.949 | 0.900, 0.990 | -0.198, -0.027 | 12.4 |



**Figure S3.** Linear regression between measurements of metal concentrations in toenails using XRF and ICP-MS.

**S3. Normality/Lognormality tests, histograms and QQ plots of measurement values (normal and lognormal scales) obtained by ICPMS and XRF**

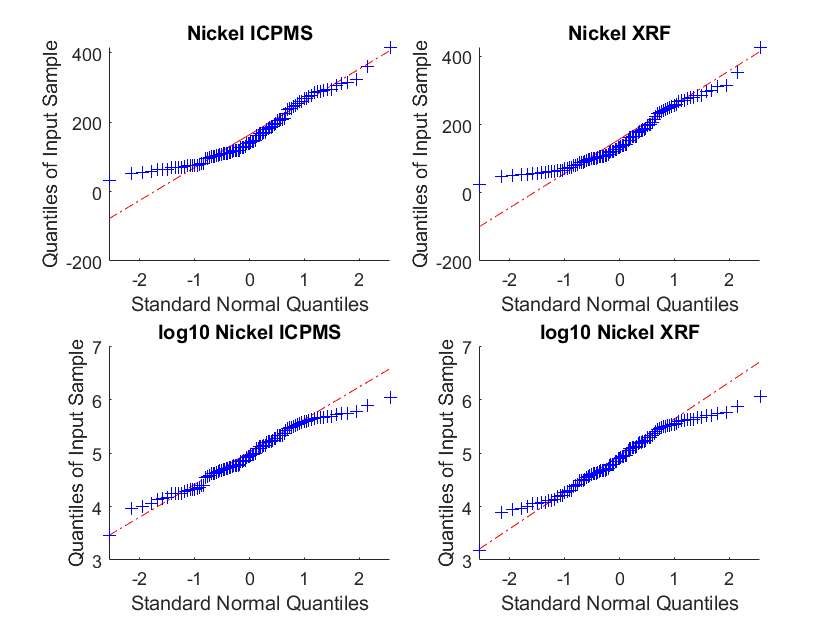
**Table S6.** Test for normality / log-normality (*Kolmogorov-Smirnoff test*)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **ICP values** | **Log-ICP values** | **XRF values** | **Log-XRF values** |
| **Nickel** | **Yes** | **Yes** | **Yes** | **Yes** |
| **Zinc \*** | No | No | No | **Yes** |
| **Arsenic** | No | **Yes** | No | No |
| **Selenium** | No | No | No | No |
| **Lead** | **Yes** | **Yes** | **Yes** | **Yes** |

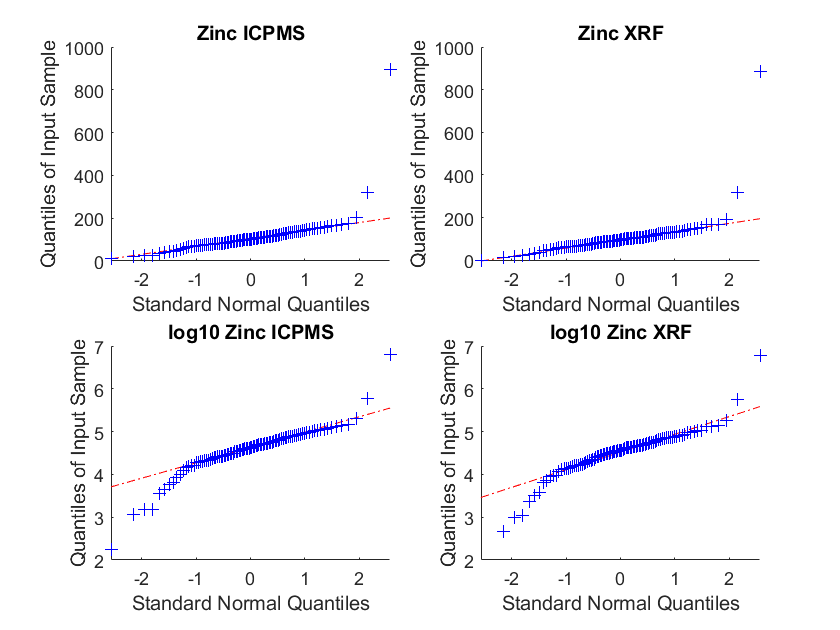
\* Distributions became normally or lognormally distributed once the highest measured value of ~880 mg/kg (compared to a median of ~105 mg/kg was removed)

QQ-Plots

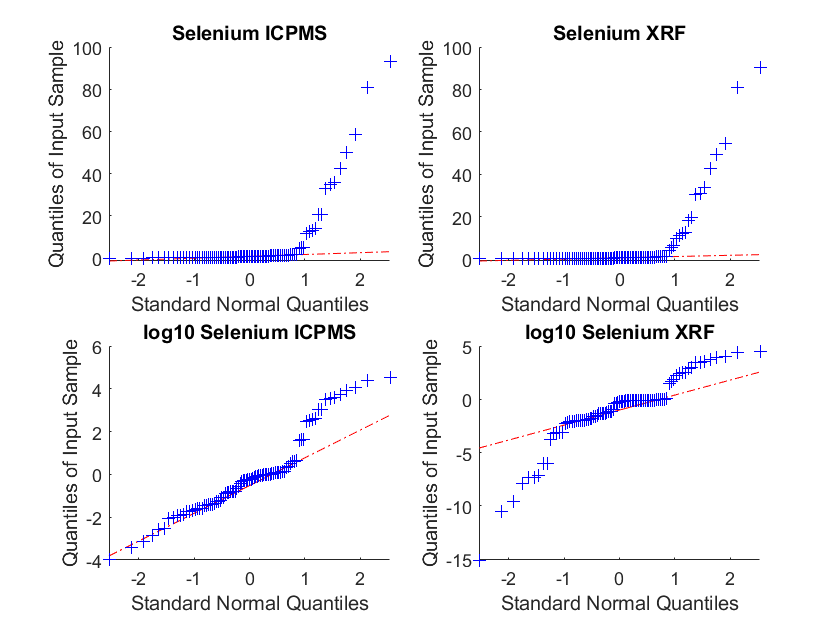
1. Nickel



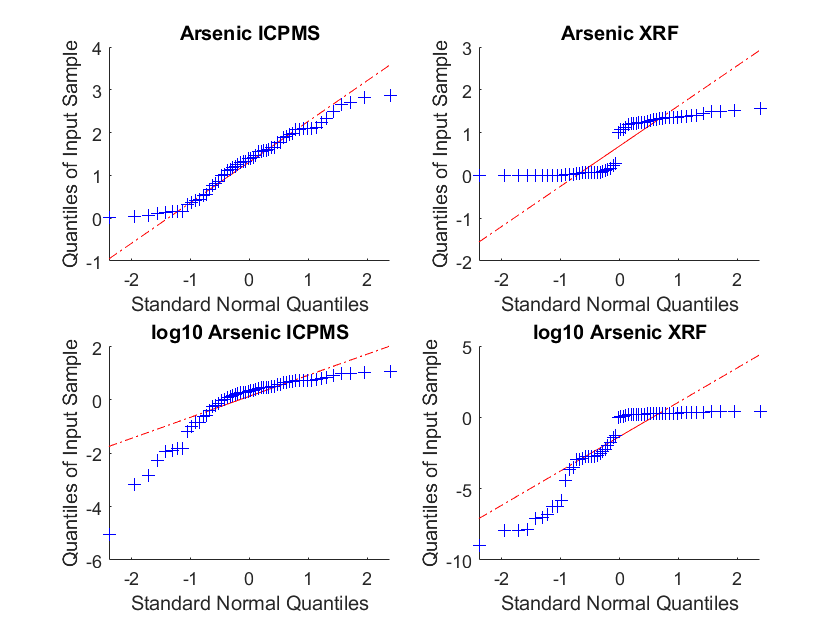
1. Zinc



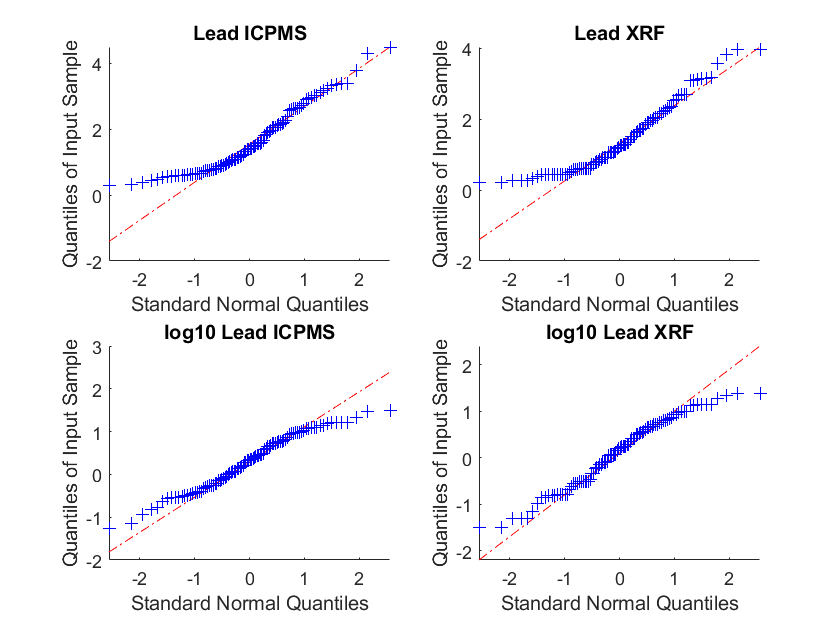
1. Selenium



1. Arsenic



1. Lead



**Figure S4.** QQ-plots for distribution of toenail metal(loid) concentrations

**S4. Results of Passing Bablok regression analysis for individual sites**

**Table S7.** Statistical parameters from the Passing Bablok analysis of XRF and ICP-MS measurements. Results are the parameters of the equation *y* = *a* + *bx*, where *x* is the ICP-MS measurement and *y* is the XRF measurement expressed as median and 95% confidence interval (CI). **Site: Sepakkam**.

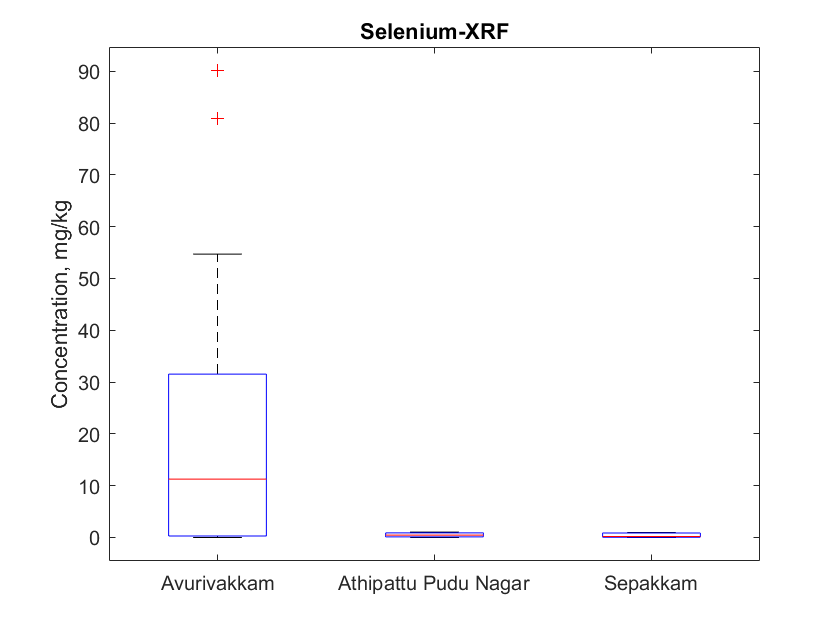
|  |  |  |
| --- | --- | --- |
| **Element** | ***a***  **median (95% CI)** | ***b***  **median (95% CI)** |
| **Ni** | -7.07 (-11.66, -3.49) | 0.999 (0.975, 1.03) |
| **Zn** | -6.33 (-9.76, -1.93) | 0.979 (0.922, 1.02) |
| **Se** | 0.011 (-0.006, 0.049) | 0.628 (0.484, 0.881) |
| **As** | -0.135 (-0.244, -0.007) | 0.568 (0.220, 0.694) |
| **Pb** | -0.070 (-0.199, 0.008) | 0.972 (0.863, 1.09) |

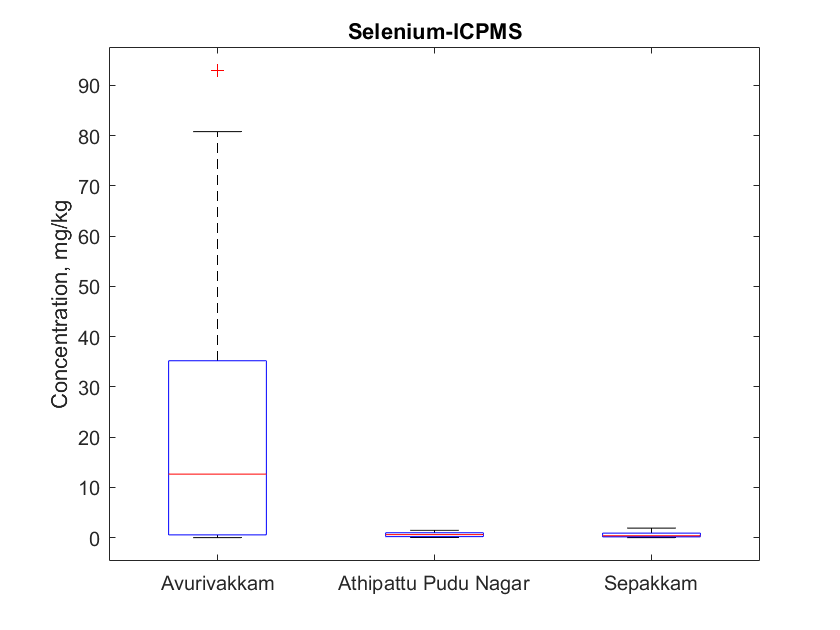
**Table S8.** Statistical parameters from the Passing Bablok analysis of XRF and ICP-MS measurements. Results are the parameters of the equation *y* = *a* + *bx*, where *x* is the ICP-MS measurement and *y* is the XRF measurement expressed as median and 95% confidence interval (CI). **Site. Atipattu Pudu Nagar**.

|  |  |  |
| --- | --- | --- |
| **Element** | ***a***  **median (95% CI)** | ***b***  **median (95% CI)** |
| **Ni** | -4.76 (-17.26, 5.90) | 0.99 (0.948, 1.05) |
| **Zn** | -2.28 (-10.60, 9.07) | 0.952 (0.830, 1.03) |
| **Se** | -0.038 (-0.066, -0.014) | 0.937 (0.890, 0.981) |
| **As** | -0.062 (-0.256, 0.019) | 0.887 (0.620, 1.04) |
| **Pb** | -0.244 (-0.438, -0.131) | 1.07 (0.973, 1.18) |

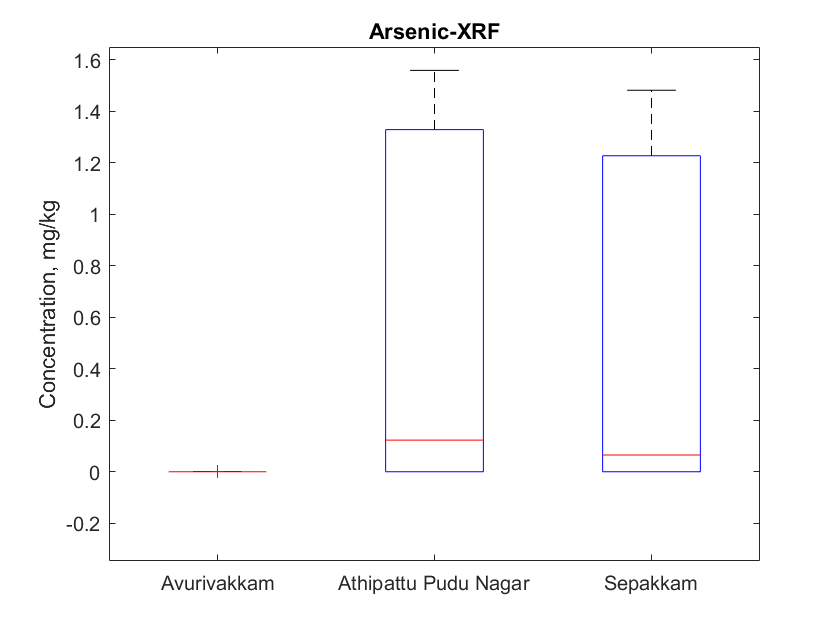
**Table S9.** Statistical parameters from the Passing Bablok analysis of XRF and ICP-MS measurements. Results are the parameters of the equation *y* = *a* + *bx*, where *x* is the ICP-MS measurement and *y* is the XRF measurement expressed as median and 95% confidence interval (CI). **Site. Avurivakkam**.

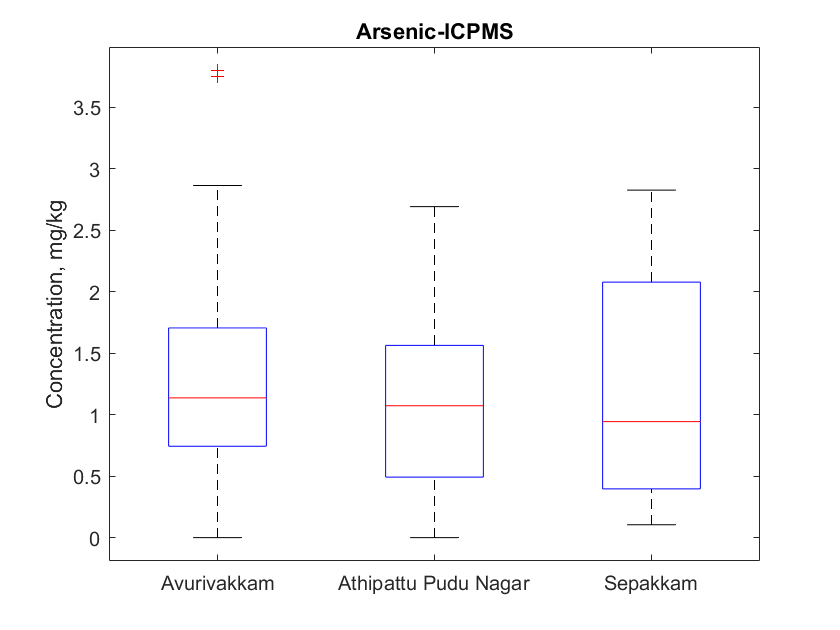
|  |  |  |
| --- | --- | --- |
| **Element** | ***a***  **median (95% CI)** | ***b***  **median (95% CI)** |
| **Ni** | -6.98 (-11.71, -1.26) | 1.02 (0.958, 1.09) |
| **Zn** | -5.99 (-38.34, 14.50) | 1.00 (0.819, 1.28) |
| **Se** | -0.180 (-0.565, -0.050) | 0.964 (0.931, 0.999) |
| **As** | 0.00 (0.00, 0.000) | 0.00 (0.00, 0.00) |
| **Pb** | -0.164 (-0.223, -0.123) | 0.947 (0.910, 0.984) |





**Figure S5.** Boxplot for XRF and ICP-MS determined selenium concentrations at each individual site.





**Figure S6.** Boxplot for XRF and ICP-MS determined arsenic concentrations at each individual site.