water

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*Article*

# Multi-Indices Assessment of Origin and Controlling Factors of Trace Metals in River Sediments from a Semi-Arid Carbonated Basin (the Sebou Basin, Morocco)

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## Supplementary Materials

## Figures

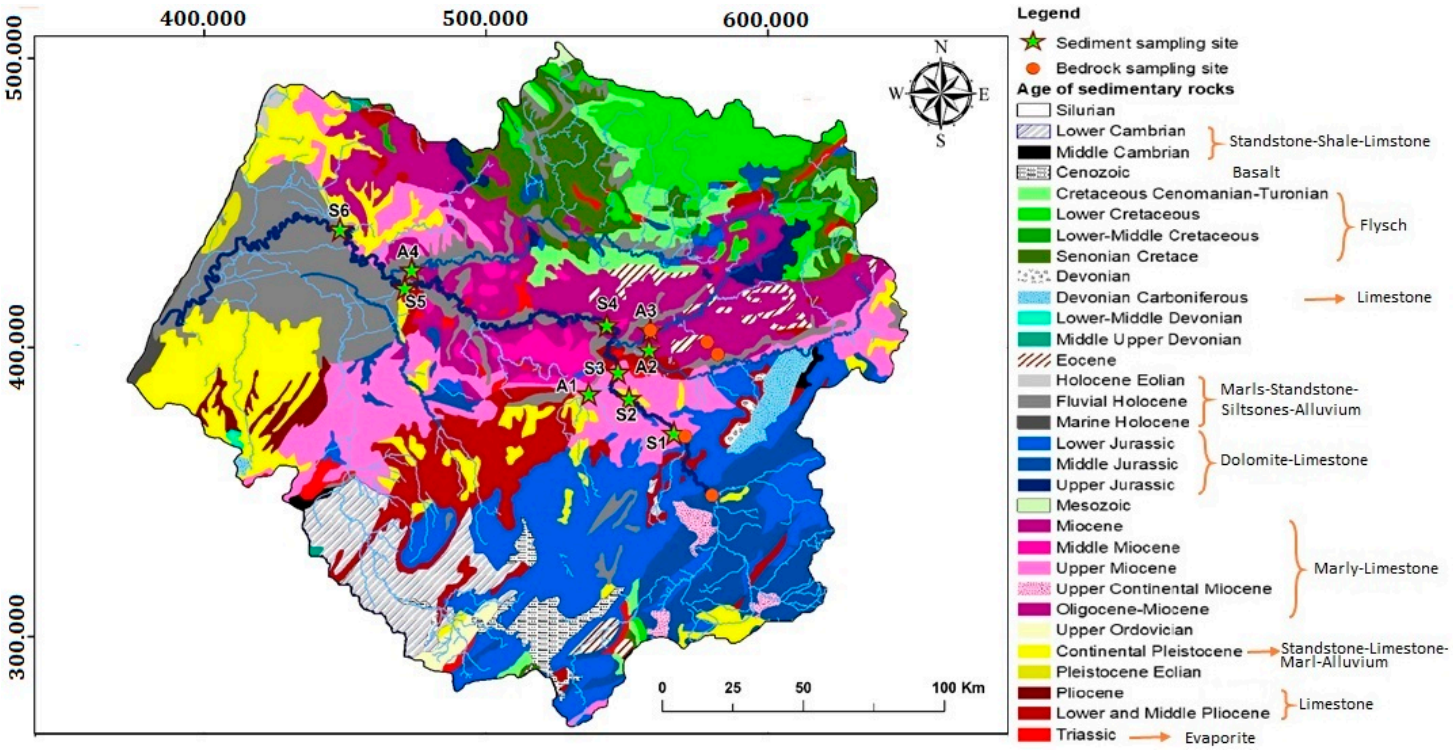


**Figure S1.** Geological map and associated lithology of the Sebou basin (performed using ArcGis software on the basis of the geological map of Morocco 1/1,000,000) ***Source :*** *M. Saadi, E.A. Hilali, M. Bensaïd, A. Boudda, M. Dahmani, Carte géologique du Maroc (1/1,000,000), Ministère de l'Energie et des Mines, Direction de la Géologie. (1985).*

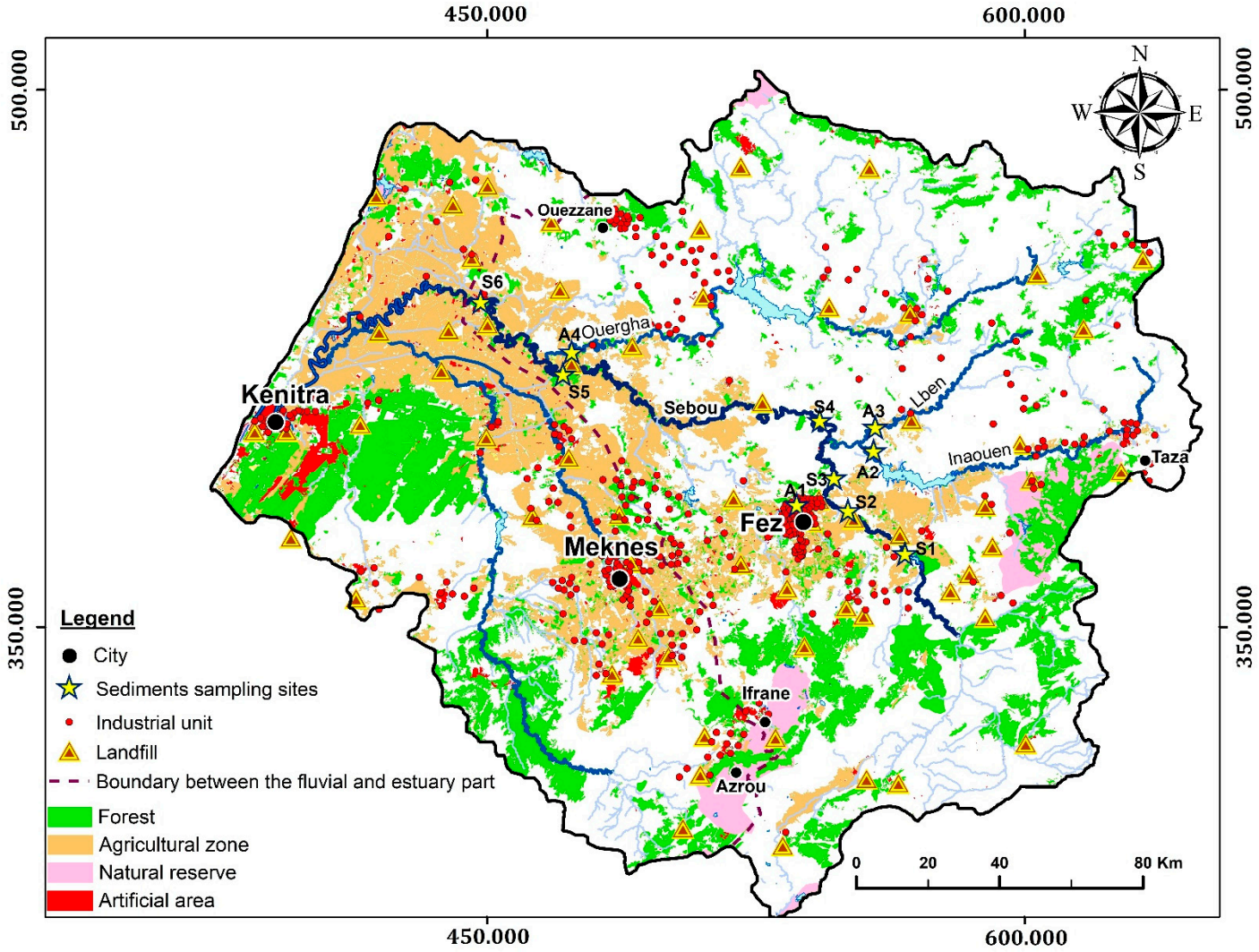


**Figure S2.** Land use (except white areas, which mainly concern mountainous areas, where no information is available) and location of the main anthropogenic activities, assumed to be potential pollution sources at the scale of the whole Sebou Basin.

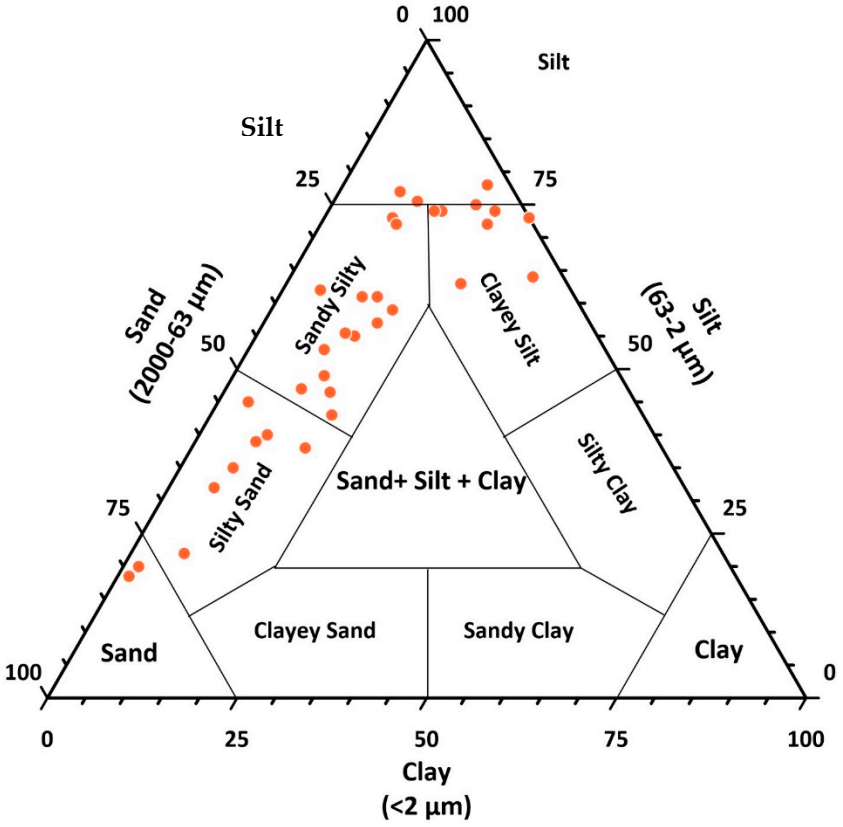


**Figure S3. a.** Shepard's classification of Sebou basin sediments (particle size < 2mm).

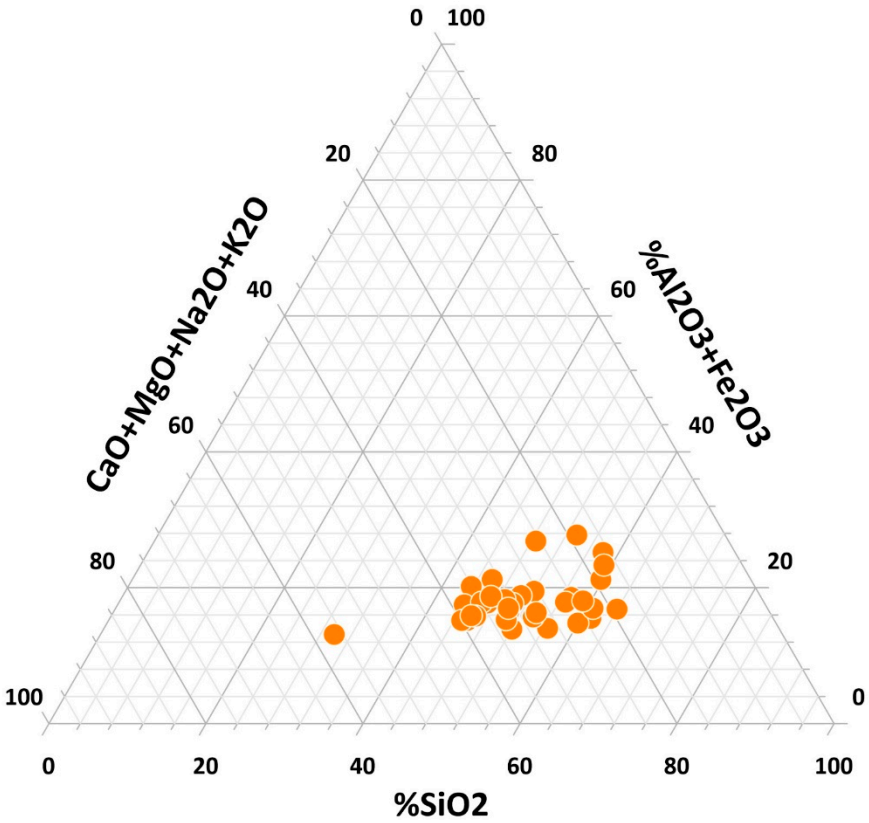


**Figure S3. b.** Ternary plot of major elements in river bottom sediments from the Sebou basin.

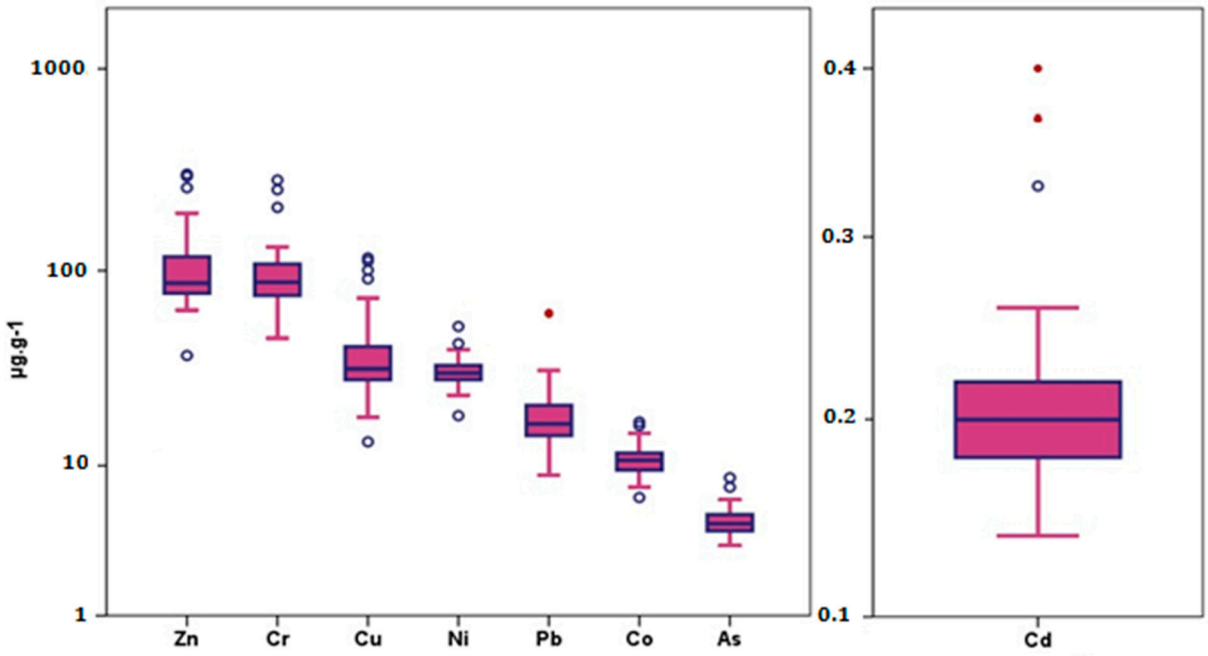


**Figure S4.** Box plot of the TM concentrations in bottom sediments from the Sebou basin. Note that concentrations are expressed in log, except for Cd.

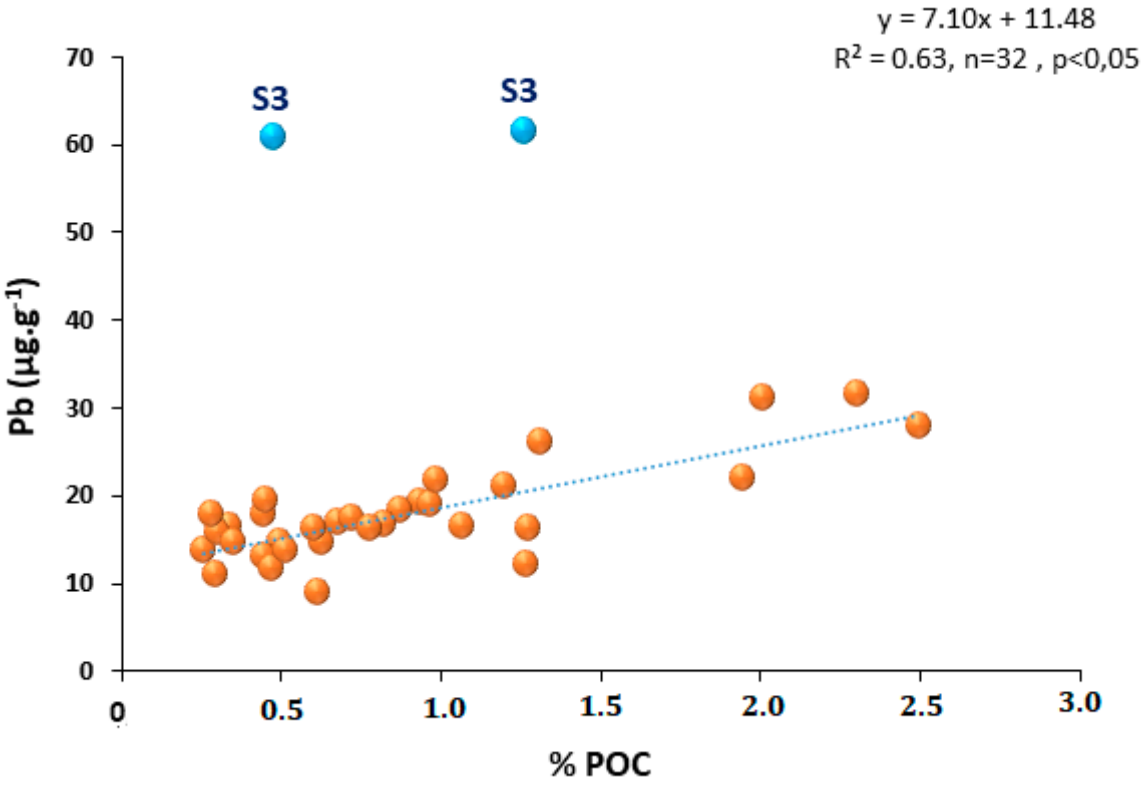


**Figure S5.** Relationship between Pb total content (µg.g$^{-1}$) and particular organic matter (% POC) for samples from all campaigns (Spring: March 2018 and April 2019 and summer: July 2018 and July 2019); n= 32 (outliers S3 sampled in April and July 2019 were not included).

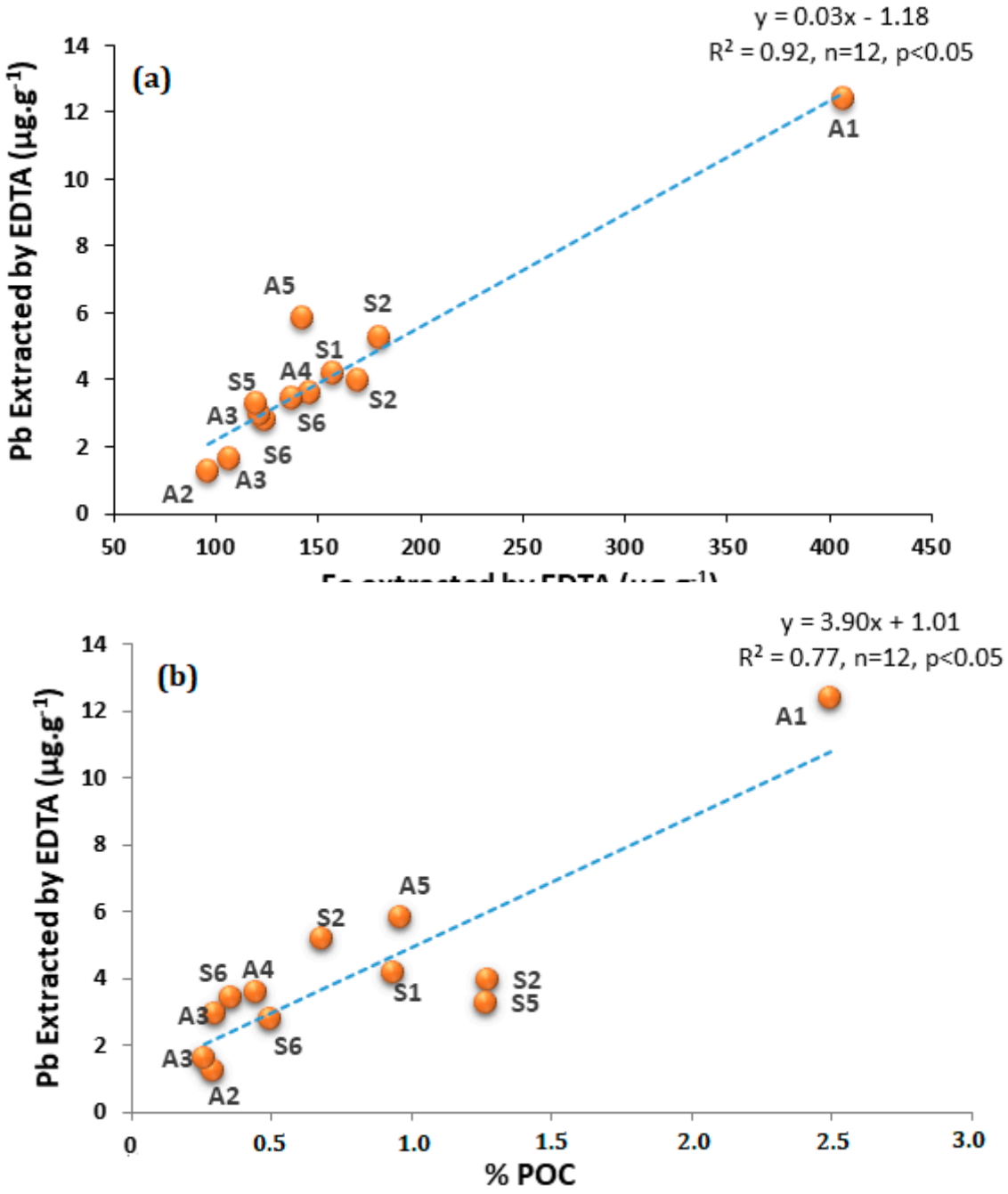


**Figure S6.** Relationships between labile fraction of Pb extracted by EDTA with (a) labile fraction of Fe (µg.g$^{-1}$) and (b) POC (%).

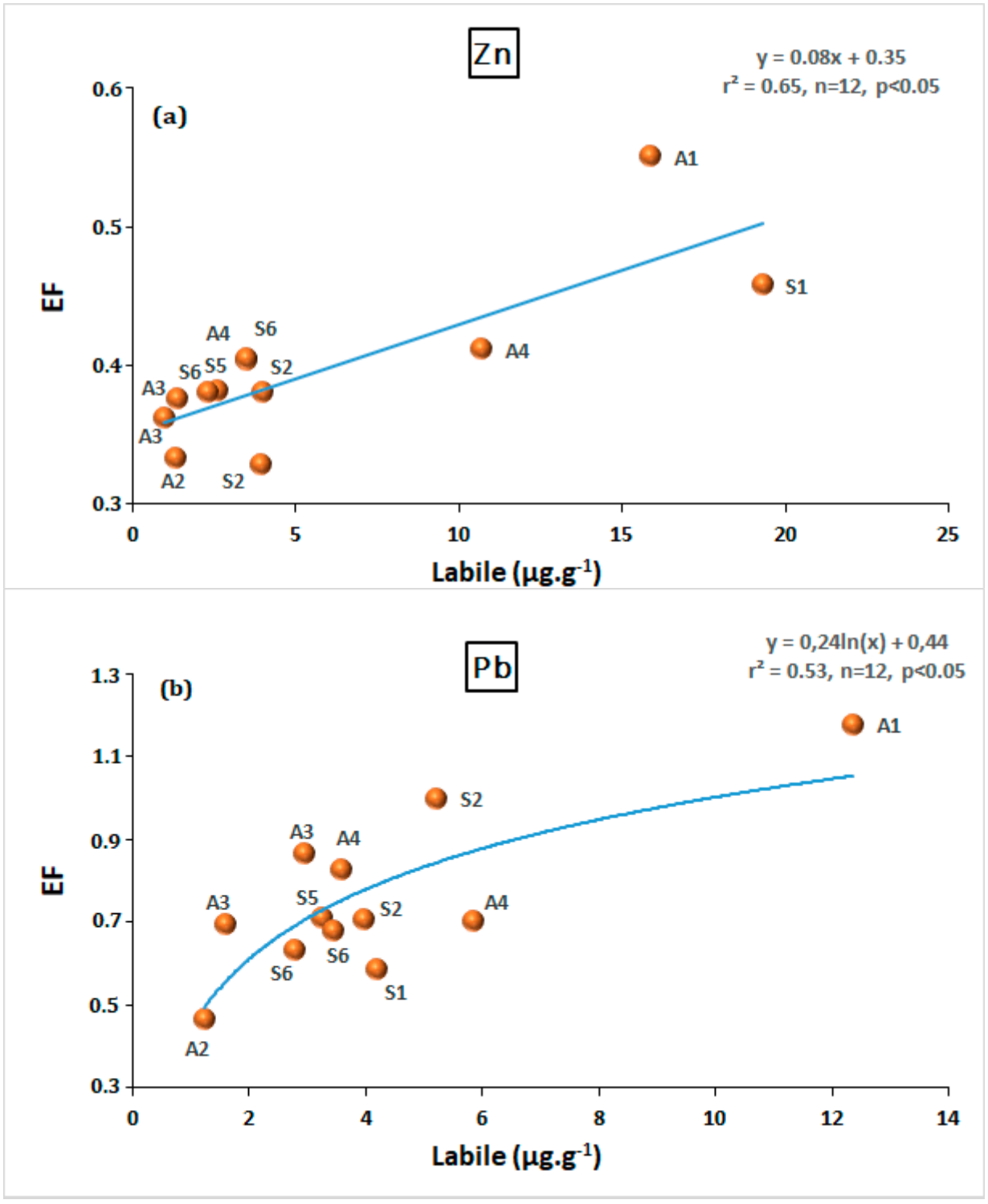


**Figure S7.** Relationships between the enrichment factor (EF) and the labile fraction extracted by EDTA (µg.g$^{-1}$) for (a) Zn and (b) Pb.

## SM Tables

**Table S1.** Mineralogical composition of the clays in the Sebou Basin sediments collected at the stations Machraa Bel Ksiri, Azib, Soltane and M'jara [29], which correspond respectively to the stations S6, the upstream of station S5 and the upstream of the station A4 of the present study.

| | | | | Mineralogy of clay | | | |
|---|---|---|---|---|---|---|---|
| | **Date of sampling** | **River** | **Sampling Site** | **Kaolinite (%)** | **Illite (%)** | **Chlorite (%)** | **Inter 10-14sm (%)** |
| **Sediment** | 11/09/1997 | Sebou | Mechraa Bel Ksiri outfal (S6 present Study) | - | 25 | 14 | 61 |
| | 15/11/1997 | | | - | 19 | 11 | 70 |
| | 11/01/1996 | Sebou | Azib Es Soltan station located upstream of S5 (present study) | 11 | 18 | 9 | 62 |
| | 15/12/1996 | | | 11 | 14 | 8 | 67 |
| | 26/01/1997 | | | 8 | 14 | 5 | 73 |
| | 05/03/1997 | | | 7 | 15 | 6 | 72 |
| | 01/05/1997 | | | 13 | 19 | 6 | 62 |
| | 11/10/1996 | Ouergha | M'jara station located upstream of A4 (present study) | 5 | 45 | 16 | 34 |
| | 15/12/1996 | | | 21 | 25 | 13 | 41 |
| | 26/01/1997 | | | 9 | 20 | 23 | 48 |
| | 05/03/1997 | | | 20 | 30 | 22 | 28 |
| | 01/05/1997 | | | 20 | 30 | 15 | 35 |

**Table S2.** Different types of industries located in the Sebou basin.

| Industry type | Production | Polluting agent | Location | Receiving environment |
|---|---|---|---|---|
| Paper mill | Paper pulp | Cd, Pb,Hg | Sidi yahya | Sebou River |
| | Paper | | Kenitra | |
| | | | Meknes | |
| Tannery and handicraft | Leather | Cu, Cr | Meknes | - |
| | | | Fez | Fez River |
| | Pottery<br>Porcelain<br>Carpet | Cu, Cr, Pb | Fez | Fez River |
| Textile | Fabrics | Cr, Pb, Cu | Fez | Fez River |
| Agro-Food | Milk | Organic matter | Kenitra | Sebou River |
| | | | Fez | Fez River |
| | | | Meknes | - |
| | Sugar | | Sidi Allal Tazi<br>Machraa Bel Ksiri | Sebou River |
| | | | Dar El gueddar<br>i<br>Sidi Slimane | Beht River |
| | | | Fez | Fez River |
| | Oil | | Fez | Fez River |
| | | | Taza | - |
| | | | Meknes | Boufkrane River |
| | | | Kenitra | Sebou River |
| | | | Sidi Kacem | - |
| | Canned goods | | Meknes | Boufkrane River |
| | Fresh yeast<br>Olive oil<br>Drinks | | Fez | Fez River |
| | Mineral water | | | Sebou River |
| Cement plants | Building materials | Pb | Fez | Fez River |
| | | | Meknes | Boufkrane River |
| Slaughterhouse | Meat | Organic matter | Fez<br>Meknes<br>Kenitra<br>Khmisset<br>Taza<br>Sidi Kacem | Diffuse |
| Others | Plastic tubes<br>Equipment in Cu, concrete and silver metal and glass | Cr, Cu, Zn | Fez | Fez River |
| | Bulbs | Sn,Pb | | Sebou River |

**Table S3.** Chemical composition of total major and trace elements of the bedrocks sampled in the Sebou basin.

| | μg.g$^{-1}$ | | | | | | | | mg.g$^{-1}$ | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Rocks type** | **As** | **Cd** | **Co** | **Cr** | **Cu** | **Ni** | **Pb** | **Zn** | **Si** | **Al** | **Fe** | **Mn** | **Mg** | **Ca** | **Na** | **K** | **Ti** | **P** |
| **Limstone** | 3.04 | 0.66 | 0.70 | 9.53 | 3.00 | 5.56 | 3.47 | 63.37 | 22.67 | 4.12 | 2.50 | <LD | 2.89 | 371.40 | <LD | 1.17 | 0.28 | <LD |
| **Dolomite** | <LD | 0.02 | 0.28 | 3.45 | <LD | <LD | <LD | <LD | 2.76 | 1.17 | 1.48 | <LD | 127.74 | 219.29 | 0.16 | 0.43 | <LD | <LD |
| **White** | 2.80 | 0.29 | 7.93 | 53.19 | 31.22 | 28.56 | 8.15 | 67.58 | 142.78 | 34.92 | 20.53 | 0.26 | 10.60 | 203.64 | 2.20 | 10.30 | 2.18 | 0.70 |
| **Marl** | 3.38 | 0.14 | 5.41 | 32.31 | 11.39 | 16.58 | 7.11 | 40.43 | 230.74 | 21.15 | 13.23 | 0.18 | 17.75 | 137.98 | 3.96 | 7.07 | 1.64 | <LD |
| **Evaporite** | 3.68 | 0.19 | 5.01 | 21.00 | 7.60 | 13.31 | 5.73 | 32.35 | 114.09 | 9.48 | 10.90 | 0.24 | 29.15 | 238.94 | 1.33 | 3.16 | 0.77 | 0.48 |
| **Limstone** | 0.82 | <LD | 0.74 | 3.76 | 2.55 | < LD | 1.43 | < LD | 7.48 | 1.65 | 2.97 | 0.27 | 2.48 | 385.66 | 0.54 | 0.55 | <LD | <LD |
| **Mean** | 2.74 | 0.26 | 3.34 | 20.54 | 11.15 | 16.00 | 5.18 | 50.93 | 86.75 | 12.08 | 8.60 | 0.24 | 31.77 | 259.48 | 1.64 | 3.78 | 1.22 | 0.59 |

**Table S4.** Comparison of the mean TM content of the Sebou sediments measured in this study with previous studies.

| | | μg.g$^{-1}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Authors** | **location** | **Zn** | **Cr** | **Cu** | **Ni** | **Pb** | **Co** | **As** | **Cd** |
| This study | Sebou basin | 111.83 | 101.23 | 41.05 | 31.40 | 20.27 | 10.95 | 4.95 | 0.21 |
| Haida (2000) [1] | | 72.32 | 78.42 | 22.39 | 28.95 | - | 14.44 | - | - |
| Azzaoui (1986) [2] | | 92.93 | - | 40.03 | 52.60 | 20.23 | - | - | - |
| This study | S3 | 279.67 | 243.98 | 103.20 | 30.17 | 61.07 | 7.15 | 4.82 | 0.39 |
| Hayzoun 2014 [3] | Downstream the confluence of the Fez tributary with the Sebou river | 236.00 | 115.00 | 171.00 | 46.00 | 100.00 | - | - | - |
| Amri et al 2007 [4] | | 220.00 | 170.00 | 112.00 | 40.00 | 73.00 | 9.00 | - | - |

**Table S5.** Spearman correlation coefficients between total concentrations of major elements, trace metals, and POC (excluding outliers).

| | Si | Fe | Mn | Mg | Ca | Na | K | Al | Zn | Cr | Cu | Ni | Pb | Co | As | Cd | POC | P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Si** | 1.00 | | | | | | | | | | | | | | | | | |
| **Fe** | .38* | 1.00 | | | | | | | | | | | | | | | | |
| **Mn** | **.50**** | **.58**** | 1.00 | | | | | | | | | | | | | | | |
| **Mg** | **−.50**** | −0.05 | −0.15 | 1.00 | | | | | | | | | | | | | | |
| **Ca** | **−.80**** | **−.73**** | **−.55**** | 0.28 | 1.00 | | | | | | | | | | | | | |
| **Na** | **.89**** | 0.30 | .40* | **−.50**** | **−.60**** | 1.00 | | | | | | | | | | | | |
| **K** | 0.07 | **.66**** | **.56**** | 0.06 | −.43* | 0.00 | 1.00 | | | | | | | | | | | |
| **Al** | .38* | **.94**** | **.58**** | 0.01 | **−.78**** | 0.26 | **.75**** | 1.00 | | | | | | | | | | |
| **Zn** | 0.32 | **.71**** | **.67**** | 0.18 | **−.62**** | 0.10 | **.70**** | **.73**** | 1.00 | | | | | | | | | |
| **Cr** | 0.33 | **.91**** | **.60**** | 0.30 | **−.77**** | 0.12 | **.70**** | **.93**** | **.78**** | 1.00 | | | | | | | | |
| **Cu** | 0.28 | .45* | **.74**** | **.68**** | −0.34 | 0.34 | .46* | .44* | **.52**** | **.54**** | 1.00 | | | | | | | |
| **Ni** | 0.33 | **.89**** | **.81**** | .47* | **−.66**** | 0.23 | **.76**** | **.87**** | **.78**** | **.90**** | **.69**** | 1.00 | | | | | | |
| **Pb** | −0.23 | 0.26 | −0.20 | .40* | −0.09 | −0.34 | 0.35 | 0.33 | **.54**** | .43* | 0.00 | 0.26 | 1.00 | | | | | |
| **Co** | **.56**** | **,90**** | **.73**** | −0.13 | **-.77**** | .47** | **.60**** | **.81**** | **.66**** | **.78**** | **.57**** | **.86**** | 0.22 | 1.00 | | | | |
| **As** | **−.51**** | 0.12 | −0.31 | 0.19 | 0.21 | **−.65**** | 0.14 | 0.05 | 0.18 | 0.12 | −.42* | 0.03 | **.49**** | 0.05 | 1.00 | | | |
| **Cd** | −0.32 | −0.26 | −0.29 | **.57**** | 0.34 | −.38* | −0.10 | −0.20 | 0.16 | −0.10 | 0.06 | −0.05 | 0.26 | −.39* | 0.21 | 1.00 | | |
| **POC** | −0.34 | 0.01 | −0.14 | **.50**** | 0.07 | −.36* | 0.11 | 0.12 | 0.13 | 0.33 | −0.10 | 0.07 | **.58**** | −0.21 | 0.15 | 0.26 | 1.00 | |
| **P** | −0.10 | −0.26 | −0.24 | 0.33 | 0.12 | −0.14 | −0.10 | −0.11 | .40* | 0.20 | 0.17 | 0.13 | 0.17 | −0.35 | −0.14 | **.58**** | 0.26 | 1.00 |

** The correlation is significant at the 0.01 (bilateral)

* The correlation is significant at the 0.05 (bilateral)

**Table S6.** Correlation matrix for parameters used in the PCA: mean concentrations of major elements and trace metals content of particular organic matter (POC), Coarse Silts (CS), Fine Silts (FS) and Clays. In bold, p<0.05.

| | Zn | Cr | Cu | Ni | Pb | Co | As | Cd | Si | Al | Fe | Mn | Mg | Ca | Na | K | Ti | P | POC | CS | FS | Clays |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Zn** | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| **Cr** | **0.79** | 1.00 | | | | | | | | | | | | | | | | | | | | |
| **Cu** | **0.97** | **0.77** | 1.00 | | | | | | | | | | | | | | | | | | | |
| **Ni** | 0.20 | −0.14 | 0.20 | 1.00 | | | | | | | | | | | | | | | | | | |
| **Pb** | **0.94** | **0.88** | **0.89** | −0.04 | 1.00 | | | | | | | | | | | | | | | | | |
| **Co** | **−0.55** | **−0.73** | **−0.53** | **0.66** | **−0.70** | 1.00 | | | | | | | | | | | | | | | | |
| **As** | 0.02 | −0.33 | −0.12 | 0.04 | −0.02 | 0.04 | 1.00 | | | | | | | | | | | | | | | |
| **Cd** | **0.87** | **0.93** | **0.84** | −0.19 | **0.93** | **−0.84** | −0.10 | 1.00 | | | | | | | | | | | | | | |
| **Si** | −0.28 | −0.06 | −0.25 | 0.30 | −0.24 | 0.49 | **−0.70** | −0.33 | 1.00 | | | | | | | | | | | | | |
| **Al** | −0.31 | −0.42 | −0.38 | **0.65** | −0.38 | **0.86** | −0.03 | **−0.61** | **0.68** | 1.00 | | | | | | | | | | | | |
| **Fe** | −0.28 | −0.43 | −0.34 | **0.69** | -0.36 | **0.86** | −0.02 | **−0.60** | **0.67** | **0.98** | 1.00 | | | | | | | | | | | |
| **Mn** | **−0.76** | −0.49 | **−0.70** | 0.03 | **−0.69** | 0.49 | −0.40 | **−0.63** | **0.57** | 0.34 | 0.39 | 1.00 | | | | | | | | | | |
| **Mg** | 0.30 | 0.14 | 0.29 | **−0.54** | 0.35 | **−0.52** | 0.28 | 0.26 | **−0.55** | **−0.50** | −0.48 | **−0.55** | 1.00 | | | | | | | | | |
| **Ca** | 0.18 | 0.07 | 0.17 | −0.33 | 0.16 | **−0.51** | **0.58** | 0.34 | **−0.94** | **−0.75** | **−0,74** | −0.39 | 0.32 | 1.00 | | | | | | | | |
| **Na** | −0.28 | −0.06 | −0.18 | 0.21 | −0.24 | 0.45 | **−0.80** | −0.32 | **0.92** | **0.52** | **0.53** | **0.58** | −0.44 | **−0.86** | 1.00 | | | | | | | |
| **K** | **−0.54** | **−0.59** | **−0.61** | 0.35 | **−0.57** | **0.68** | 0.45 | **−0.60** | 0.03 | **0.54** | **0.50** | 0.30 | **−0.54** | 0.04 | −0.01 | 1.00 | | | | | | |
| **Ti** | −0.25 | −0.35 | −0.32 | **0.55** | −0.30 | **0.76** | −0.10 | **−0.54** | **0.74** | **0.97** | **0.95** | 0.28 | −0.39 | **−0.84** | **0.58** | 0.38 | 1.00 | | | | | |
| **P** | **0.73** | **0.95** | **0.70** | −0.16 | **0.79** | **−0.75** | −0.25 | **0.92** | −0.19 | **−0.51** | **−0.55** | **−0.54** | 0.07 | 0.24 | −0.22 | **−0.50** | −0.47 | 1.00 | | | | |
| **POC** | 0.43 | 0.22 | 0.47 | 0.13 | 0.26 | −0.13 | 0.00 | 0.21 | −0.27 | −0.11 | −0.17 | **−0.66** | 0.46 | 0.06 | −0.26 | −0.40 | −0.08 | 0.29 | 1.00 | | | |
| **CS** | 0.42 | 0.45 | 0.49 | 0.06 | 0.49 | −0.21 | **−0.58** | 0.43 | 0.45 | −0.04 | 0.01 | 0.02 | −0.13 | −0.39 | **0.57** | −0.39 | 0.07 | 0.28 | −0.25 | 1.00 | | |
| **FS** | 0.10 | 0.18 | 0.06 | −0.24 | 0.07 | −0.29 | 0.32 | 0.16 | **−0.59** | −0.32 | −0.41 | **−0.51** | 0.39 | 0.49 | **−0.61** | −0.01 | −0.38 | 0.35 | **0.64** | **−0.71** | 1.00 | |
| **Clays** | **−0.70** | **−0.84** | **−0.76** | 0.19 | **−0.76** | **0.60** | 0.46 | **−0.78** | 0.02 | 0.41 | 0.44 | **0.54** | −0.25 | 0.00 | −0.13 | **0.56** | 0.32 | **−0.78** | −0.36 | **−0.62** | −0.11 | 1.00 |

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