

**ALTERNATIVE SOURCE APPORTIONMENT IN THE SURROUNDING REGION OF A  
LARGE STEEL INDUSTRY APPLYING *Tillandsia usneoides* AS BIOMONITOR**

Laura Benevides dos Santos, Ana Cristina Almeida, Jose Marcus Godoy\*

*Chemistry Department, Pontifical Catholic University of Rio de Janeiro, Rua Marques de São*

*Vicente 225, Gávea, Rio de Janeiro, RJ, Brazil, CEP 22451-900*

**SUPPLEMENTARY MATERIAL**

**Table S1:** Coordinates of the steelwork stations for its air quality monitoring program

Station	Station Location	Coordinates
EMQAM 1	Adalgisa Nery Municipal School	22° 53' 19.5" S
	Eduardo de Aguiar Filho Street, s/n° Lote 230 - Conjunto	43° 42' 57.5" W
	São Fernando - Santa Cruz - RJ - CEP: 23565-250	
EMQAM 2	Maestro Francisco Mignone School	22° 52' 30,7" S
	Kaiser Abraão Street s/n° - Monte Serrat - Itaguaí - RJ -	43° 46' 13.6" W
	CEP: 23810-560	
EMQAM 3	Barão de Itararé School	22° 55' 37.3" S
	Vitor Dumas Street, s/n° - Largo do Bodegão - Santa	43° 41' 40.8 " W
	Cruz - RJ - CEP: 23550-140	
EMTKCSA 4	Steelwork Meteorological Station	22° 54' 19.4" S
	Internal Street	43° 43' 33.0" W

**Table S2:** Operational conditions, data acquisition modes and other information for the determination of elemental concentration by ICP-MS

Operational Conditions	
Forward power	1400 W
Radiofrequency	27.12 MHz <i>free running</i>
Sample introduction	Cross Flow
Sample flow rate (mL min <sup>-1</sup> )	0.98
Argon flow rates (L min <sup>-1</sup> )	16.0 (plasma)
	0.95 (auxiliary)
Makeup gas (L min <sup>-1</sup> )	0.23
Temperature Spray Chamber	2 °C
Nebulizer pump	0.1 rps
Measured Isotopes	<sup>27</sup> Al, <sup>47</sup> Ti, <sup>51</sup> V, <sup>53</sup> Cr, <sup>55</sup> Mn, <sup>57</sup> Fe,
	<sup>60</sup> Ni, <sup>63</sup> Cu, <sup>66</sup> Zn, <sup>86</sup> Sr, <sup>137</sup> Ba, <sup>208</sup> Pb
Spectral peak processing	Peak hopping
Reading/replicates	3
Number of replicates	3
Integration Time	15 ms

**Table S3:** Analysis of Certified Reference Materials, values expressed as  $\mu\text{g g}^{-1}$  (N=6,  $\pm$  means expanded uncertainty and  $k = 2$ )

Element	Peach Leaves, NIST-1547				Tomato Leaves, NIST-1573a			
	Obtained Value	Reference Value	Z-score	Recovery (%)	Obtained Value	Reference Value	Z-score	Recovery (%)
V	(0.381±0.043)	(0.37±0.03)	0.41	103	(0.845±0.011)	(0.835±0.010)	1.3	101
Cr	(1.19±0.31)	1.00		119	(1.59±0.47)	(1.99±0.06)	-1.7	80
Mn	(89.3±1.3)	(98±3)	5.36	91	(241.2±6.1)	(246±8)	-1.0	98
Fe	(164±20)	(218±14)	-4.46	75	(278±24)	(368±7)	-7.1	76
Ni	(0.55±0.18)	(0.69±0.09)	-1.12	79	(3.53±0.0.81)	(1.59±0.07)	4.8	
Cu	(3.80±0.12)	(3.7±0.4)	0.50	103	(4.68±0.17)	(4.70±0.14)	-0.2	100
Zn	(17.2±1.4)	(17.9±0.4)	-1.03	96	(29.7±3.3)	(30.9±0.7)	-0.7	96
Sr	(52.9±1.5)	(53±4)	-0.04	100	(85.3±6.3)	85		100
Mo	(0.071±0.007)	(0.06±0.08)	2.06	118	(0.518±0.074)	0.46		113
Cd	(0.024±0.000)	(0.026±0.003)	-1.26	93	(1.383±0.032)	(1.52±0.04)	-3.2	91
Ba	(115.0±5.3)	(124±4)	-2.70	93	(61.1±4.1)	63		97
Pb	(0.860±0.029)	(0.87±0.03)	-0.49	99	(0.491±0.091)			

**Table S4:** Median referring to composite samples of biomonitoring stations, 1<sup>st</sup> sample collection, values in  $\mu\text{g g}^{-1}$

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Sb	Ba	Pb
PUC-Rio	444	25	1.2	1.7	38	717	1.1	17	76	19	1.5	1.1	19	3.4
EMQAM 1	1924	102	7.3	7.6	163	3230	2.6	21	117	30	2.6	1.2	35	9.4
EMQAM 2	1545	86	4.2	4.3	79	2562	2.0	25	104	25	2.4	1.1	28	7.4
EMQAM 3	2898	168	6.5	5.5	100	4210	2.7	25	136	30	3.0	1.7	43	8.8
EMTKCSA 4	3666	237	41	45	1268	16222	3.8	18	231	100	2.8	1.2	46	25

**Table S5:** Median referring to composite samples of biomonitoring stations, 2<sup>nd</sup> sample collection, values in  $\mu\text{g g}^{-1}$

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Ba	Pb
PUC-Rio	780	49	1.7	1.9	50	1160	1.4	13	82	20	22	4.4
EMQAM 1	747	40	2.6	2.8	74	1507	1.0	5.6	44	11	11	3.0
EMQAM 2	914	54	2.1	2.9	53	1300	1.3	7.6	43	10	13	3.1
EMQAM 3	1316	72	2.8	2.6	40	1478	1.3	7.6	50	12	17	2.9
EMTKCSA 4	2021	125	26.2	20.1	750	9426	2.4	6.0	119	61	22	8.7

**Table S6:** Median referring to composite samples of biomonitoring stations, 3<sup>rd</sup> sample collection, values in  $\mu\text{g g}^{-1}$

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
PUC-Rio	510	31	1.5	1.4	32	632	1.1	9.0	72	15	1.6	16	3.0
EMQAM 1	657	38	3.0	3.3	66	1362	1.1	5.2	40	9.8	2.1	10	3.0
EMQAM 2	616	35	2.0	2.5	46	1106	1.7	7.9	39	9.7	2.5	11	3.5
EMQAM 3	990	60	2.9	2.5	28	1183	1.4	6.0	42	8.3	2.7	15	2.5
EMTKCSA 4	2625	199	52	39	1278	15342	3.2	7.8	162	110	1.5	34	13

**Table S7:** Median referring to composite samples of biomonitoring stations, 4<sup>th</sup> sample collection, values in  $\mu\text{g g}^{-1}$

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
PUC-Rio	488	31	1.3	1.4	38	641	1.1	10	62	17	1.6	20	3.2
EMQAM 1	1156	63	4.1	4.6	114	2135	1.4	10	84	20	2.1	23	5.4
EMQAM 2	908	54	2.4	2.6	76	1425	1.4	15	85	22	2.1	27	4.7
EMQAM 3	2005	109	4.6	4.2	68	2313	2.1	15	87	22	2.3	33	5.4
EMTKCSA 4	2357	175	40	30	954	12423	2.8	11	222	96	1.7	33	14

**Table S8:** Median referring to composite samples of biomonitoring stations, 5<sup>th</sup> sample collection, values in  $\mu\text{g g}^{-1}$

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
PUC-Rio	706	47	2.4	2.3	63	1022	<LQ	19	105	29	2.0	27	4.7
EMQAM 1	1064	66	3.4	4.2	104	1772	<LQ	14	101	23	1.7	23	5.3
EMQAM 2	1214	78	3.0	3.8	82	1653	<LQ	17	116	28	2.0	30	5.9
EMQAM 3	2909	210	7.1	6.4	103	3427	2.1	19	144	30	2.2	48	7.4
EMTKCSA 4	3338	299	47	56	1407	18109	2.7	14	243	99	1.5	40	15

LQ = Limit of Quantification

**Table S9:** Median referring to composite samples of biomonitoring stations, 6<sup>th</sup> sample collection, values in  $\mu\text{g g}^{-1}$

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
PUC-Rio	687	48	1.6	2.2	44	1024	1.1	13	77	22	2.2	24	4.6
EMQAM 1	568	37	2.1	2.8	69	1156	<LQ	5.8	57	14	1.3	14	2.8
EMQAM 2	757	43	1.5	2.2	41	1053	1.3	6.3	43	11	1.3	13	3.1
EMQAM 3	1299	93	3.2	3.4	46	1865	1.7	7.0	47	12	1.4	22	3.5
EMTKCSA 4	1133	102	17	16	433	6283	1.4	4.8	85	40	1.0	19	6.1

LQ = Limit of Quantification

**Table S10:** Obtained enrichment factor, 1<sup>st</sup> sample collection (bold = values higher than 100)

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Sb	Ba	Pb
EMQAM 1	<b>333</b>	<b>312</b>	<b>494</b>	<b>343</b>	<b>324</b>	<b>351</b>	<b>133</b>	24	54	59	67	3	85	<b>178</b>
EMQAM 2	<b>248</b>	<b>247</b>	<b>245</b>	<b>147</b>	<b>106</b>	<b>257</b>	77	48	37	33	54	0	49	<b>119</b>
EMQAM 3	<b>553</b>	<b>575</b>	<b>433</b>	<b>222</b>	<b>160</b>	<b>487</b>	<b>140</b>	47	78	57	96	54	<b>130</b>	<b>160</b>
EMTKCSA 4	<b>726</b>	<b>857</b>	<b>3245</b>	<b>2496</b>	<b>3211</b>	<b>2163</b>	<b>233</b>	6	<b>203</b>	<b>431</b>	80	7	<b>142</b>	<b>635</b>

**Table S11:** Obtained enrichment factor, 2<sup>nd</sup> sample collection (bold = values higher than 100)

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Ba	Pb
EMQAM 1	<0	<0	52	49	48	30	<0	<0	<0	<0	<0	<0
EMQAM 2	17	12	26	51	7	12	<0	<0	<0	<0	<0	<0
EMQAM 3	69	48	65	37	<0	27	<0	<0	<0	<0	<0	<0
EMTKCSA 4	<b>159</b>	<b>156</b>	<b>1447</b>	<b>955</b>	<b>1411</b>	<b>713</b>	73	<0	45	<0	<b>208</b>	98



**Table S12:** Obtained enrichment factor, 3<sup>rd</sup> sample collection (bold = values higher than 100)

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
EMQAM 1	29	23	<b>103</b>	<b>142</b>	<b>108</b>	<b>115</b>	2	<0	<0	<0	36	<0	<0
EMQAM 2	21	14	37	82	47	75	55	<0	<0	<0	59	<0	<0
EMQAM 3	94	93	94	85	<0	87	29	<0	<0	<0	73	<0	<0
EMTKCSA 4	<b>415</b>	<b>540</b>	<b>3408</b>	<b>2786</b>	<b>3938</b>	<b>2326</b>	<b>193</b>	<0	<b>126</b>	<b>626</b>	<0	<b>115</b>	<b>332</b>

**Table S13:** Obtained enrichment factor, 4<sup>th</sup> sample collection (bold = values higher than 100)

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
EMQAM 1	<b>137</b>	<b>103</b>	<b>214</b>	<b>222</b>	<b>198</b>	<b>233</b>	35	3	35	17	28	14	66
EMQAM 2	86	72	84	83	99	<b>122</b>	31	53	37	28	33	35	45
EMQAM 3	<b>311</b>	<b>251</b>	<b>247</b>	<b>194</b>	78	<b>261</b>	92	50	41	28	43	67	68
EMTKCSA 4	<b>384</b>	<b>462</b>	<b>2899</b>	<b>1991</b>	<b>2391</b>	<b>1837</b>	<b>165</b>	9	<b>257</b>	<b>452</b>	4	66	<b>341</b>

**Table S14:** Obtained enrichment factor, 5<sup>th</sup> sample collection (bold = values higher than 100)

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
EMQAM 1	51	39	41	88	64	73	NC	<0	<0	<0	<0	<0	13
EMQAM 2	72	66	26	68	30	62	NC	<0	10	<0	0	12	26
EMQAM 3	<b>312</b>	<b>345</b>	<b>192</b>	<b>184</b>	62	<b>235</b>	NC	<0	38	2	11	76	59
EMTKCSA 4	<b>373</b>	<b>536</b>	<b>1844</b>	<b>2380</b>	<b>2118</b>	<b>1672</b>	NC	<0	<b>132</b>	<b>237</b>	<0	49	<b>212</b>

NC = Not Calculated

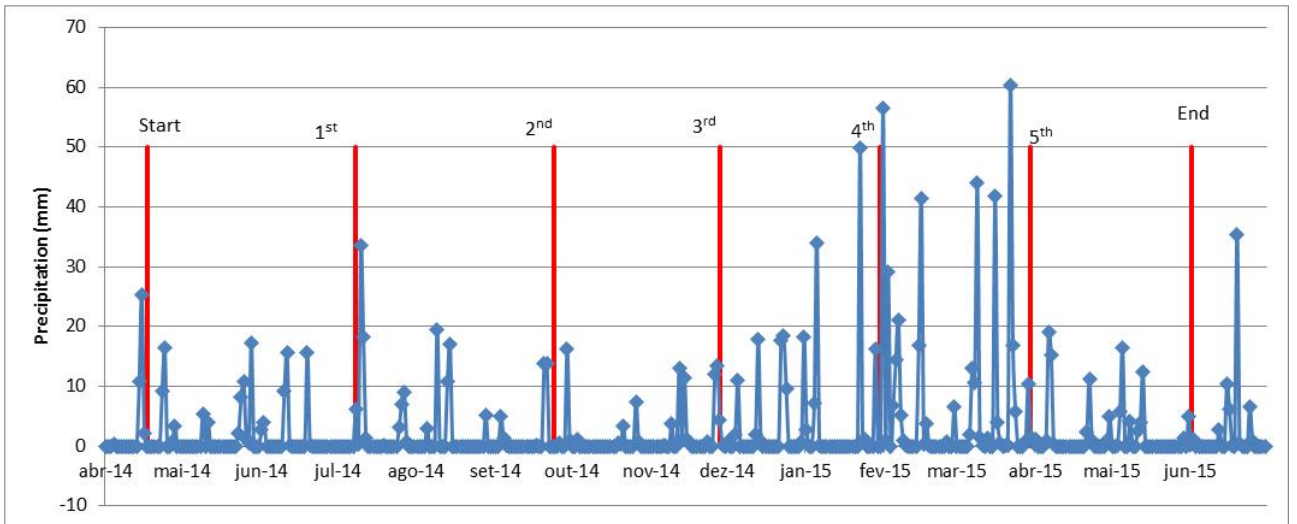
**Table S15:** Obtained enrichment factor, 6<sup>th</sup> sample collection (bold = values higher than 100)

Site	Al	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Sr	Sn	Ba	Pb
EMQAM 1	<0	<0	30	28	57	13	NC	<0	<0	<0	<0	<0	<0
EMQAM 2	10	<0	<0	3.8	<0	2.8	12	<0	<0	<0	<0	<0	<0
EMQAM 3	89	97	98	58	3.3	8.2	49	<0	<0	<0	<0	<0	<0
EMTKCSA 4	65	<b>115</b>	<b>925</b>	<b>658</b>	<b>876</b>	<b>514</b>	20	<0	9.5	79	<0	<0	<0

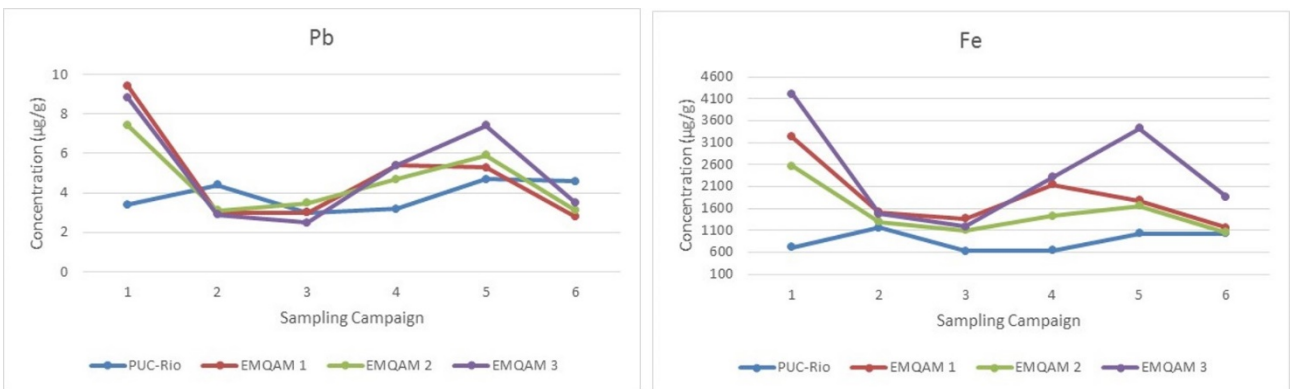
NC = Not Calculated

**Table S16:** Pearson correlation coefficients for the elemental concentrations in samples of biomonitors installed in the steelwork monitoring stations and the Steelwork's Meteorological Station (values significant at 95% level)

	<b>Al</b>	<b>Ti</b>	<b>V</b>	<b>Cr</b>	<b>Mn</b>	<b>Fe</b>	<b>Ni</b>	<b>Cu</b>	<b>Zn</b>	<b>Sr</b>	<b>Sn</b>	<b>Ba</b>	<b>Pb</b>
<b>Al</b>	1				0.52 1	0.79 3							
<b>Ti</b>		1	0.61 2	0.71 4				0.74 2	0.95 0				
<b>V</b>		0.61 2	1	0.96 3			0.93 3	0.89 7	0.61 3		0.58 7	0.96 2	0.58 6
<b>Cr</b>		0.71 4	0.96 3	1			0.86 5		0.75 1		0.60 7	0.86 7	0.61 5
<b>Mn</b>	0.52 1				1	0.85 9							
<b>Fe</b>	0.79 3				0.85 9	1							
<b>Ni</b>			0.93 3	0.86 5			1	0.87 6		0.60 1		0.97 5	0.68 5
<b>Cu</b>		0.74 2	0.89 7	0.94 5			0.87 6	1	0.75 5		0.56 9	0.85 0	0.71 2
<b>Zn</b>		0.95 0	0.61 3	0.75 1				0.75 5	1				
<b>Sr</b>							0.60 1			1		0.58 7	0.88 5
<b>Sn</b>			0.58 7	0.60 7				0.56 9			1		
<b>Ba</b>			0.96 2	0.86 7			0.97 5	0.85 0		0.58 7		1	0.62 8
<b>Pb</b>			0.58 6	0.61 5			0.68 5	0.71 2		0.88 5		0.62 8	1



**Figure S1:** Daily precipitation and sampling periods (red bars)



**Figure S2:** Lead and iron concentration according to the sampling campaign