MONITORING OF BORATE AND FLUORIDE LEVELS IN SOILS AND CITRUS FRUIT LEAVES IN THE CASTELLÓN CERAMIC DISTRICT ENVIRONMENT

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1. ABSTRACT

Since the beginning of the 20th century, the Castellón province has housed one of the main ceramic production centres in Spain, more than 93% of the Spanish ceramic tile manufacturing industry being concentrated in Castellón as the main economic driver of the province, with the concomitant industrial concentration. Concurrently a series of ancillary industries of high added value developed, closely related to the sector, such as the frit, glaze and ceramic colours subsector and spray-dried powder manufacture. The industry emissions include, in particular, borates associated with the condensation of borate vapours released in ceramic frit fusion and fluorides associated with clay defluoridation in the ceramic body firing process. This study has monitored the evolution of boron and fluorine in the Castellón ceramic district in alluvial as well as calcareous soils and in environments with a predominant ceramic tile as well as glaze industry during the rainfall period 2013–14. As in previous studies, the results indicate higher than normal values in all cases, although the values have decreased with regard to previous years, with boron values being associated with glaze and fluorine values with ceramic tile production environments. The values in citrus fruit leaves exceeded the normal values reported in the literature, though no differences were observed between the winter and summer measurements. The decrease in ceramic tile production and the transition to glazes with a higher firing temperature, less rich in borates in their formulation, as well as the changeover to white tile bodies with a lower fluorine content, would explain the observed decrease, though this decrease has been moderated by the severe drought of the studied period.

2. INTRODUCTION

Since the beginning of the 20th century, the Castellón province has housed one of the main ceramic production centres in Spain, more than 93% of the Spanish ceramic tile manufacturing industry being concentrated in Castellón as the main economic driver of the province, with the concomitant industrial concentration. Concurrently a series of ancillary industries of high added value developed, closely related to the sector, such as the frit, glaze and ceramic colours subsector and spray-dried powder manufacture. The industry emissions include, in particular, borates associated with the condensation of borate vapours released in ceramic frit fusion and fluorides associated with clay defluoridation in the ceramic body firing process (1,2). According to Aucejo et al. (3), the normal values for boron in soils are about 1 mg.Bsoluble/kg in soils and 60 mg/kg in orange tree leaves (dry matter), fluorine values being 2 mg/kg in soils and 15 mg.Fsoluble/kg dry matter in orange tree leaves. (Tables I and II).

	Soil (mg/kg)	Water (ppm)	Leaf (mg/kg)
Normal	0,8-1,29	<0,2	60
Limit	1,3	1	100-130
Reversible	-	1-2	200-250
Acute	-	2	> 250

Table 1. *Acceptable boron concentrations according to Aucejo et al. (3).*

	Soil (ppm)	Water	Leaf (mg/kg)
Normal	2	Not available	15
Limit	-	-	75

Table 2. *Fluorine toxicity according to Aucejo (3).*

3. OBJETIVES

The present study has monitored the evolution of boron and fluorine in the Castellón ceramic district in alluvial as well as calcareous soils and in both predominating ceramic tile and glaze and frit manufacturing industry environments during the rainfall period 2013–14.

4. EXPERIMENTAL

The soil samples were taken in non-farmed areas to a depth of 5 cm. They were passed through a sieve with a 1 mm mesh aperture and dried in air for 72 h. The leachate was obtained by continuous stirring of 20 g air-dried soil in 100 ml distilled water for 20 min. This extraction method provided the quantity of soluble boron and fluorine in the soil (3,4). The boron concentrations were determined with a visible spectrophotometer (Azomethine method) (5). Total boron was obtained by boiling a mixture of 40 g soil in 80 ml distilled water under reflux for 5 minutes (6). On the other hand, total fluorine was determined with an ion-selective electrode after dissolving the samples in NaOH in nickel crucibles (7).

Boron is fixed by organic matter and also by calcite (8,9). Fluorine is fixed by calcium carbonate in the form of insoluble compounds such as fluorite CaF_2 or fluorapatite $Ca_{10}(PO_4)_6F_2$ (10). The bioavailable soluble contents for plants were therefore deemed good indicators of boron and fluorine pollution.

The soils collected were referenced T(Tile), G(Glaze), and T+G (Tile+Glaze) depending on the prevalence of the type of factories in the surrounding area. This study sets out the results of the analysis campaign in the rainfall year 2013–2014, with the following characteristics: samples of December 2013 with rainfall of 0.6 l/m^2 for the calcareous area in the three months prior to sampling and 5.2 l/m^2 for the alluvial area; of June 2014 with 21.8 l/m^2 and 4.6 l/m^2, respectively; and finally the campaign of November 2014 with 0.2 l/m^2 and 20.2 l/m^2 rainfall, respectively, in the previous three months.

Together with the soil extract with water 1:5, parameters such as conductivity, pH, hardness, nitrates (ultraviolet spectrophotometry 205 nm) (10) and sodium (flame spectrophotometry) were also measured. Total carbonates were also measured as % $CaCO_3$ using the Bernard calcimeter. All measurements were triplicated.

In five of the samplings in the farming area with orange groves, a sample of leaves was collected. To prepare the leaves, 5 g leaves were cut into small pieces of 3x3 mm. The samples were dried in an oven at 110ºC for two days and calcined at 550ºC for 6 h (11). The ash was dissolved in HCl 0,1 M with 6h continuous stirring and the final solution was filtered to obtain a volume of 100 ml water, which was used for leaf boron and fluorine analysis by the azomethine and selective electrode methods indicated above.

The Castellón ceramic district is located in an area rich in clays from the Permian-Triassic period with very low calcite content (mining is done at Moró by open-pit mining) and Cretaceous-Paleogene clays (open-pit mines at Araia and Mas Vell) (12). The soils of the Castellón industrial district are all located in Castellón province. The geology of this province is characterised by a Quaternary alluvial area and a Cretaceous-Paleogene calcareous pre-coastal area. The geographic coordinates of the samples are given in Table III (calcareous pre-coastal area) and Table IV (alluvial coastal area) (13). In addition, a sample from outside the ceramic district, from the Sierra d'Espadà mountain range, whose location is also indicated in Table IV, was studied as a reference sample (BLANK). The present study is a follow-up to the studies conducted by Sorlí et al. (14).

Sample	Classification (T=Tile, G=Glaze)	Geographic coordinates Long.	Lat.
1	T	00º04’41.60”W	39º59’02.10”N
2	T	00º04’31.00”W	39º59’10.70”N
3	T	00º06’60.00”W	40º00’70.00”N
4	T+G	00º07’35.20”W	40º00’53.10”N
5	G	00º09’01.70”W	40º02’04.00”N
6	T	00º08’38.20”W	40º02’23.20”N
7	T+G	00º11’11.30”W	40º03’54.40”N
8	G	00º11’45.30”W	40º03’35.30”N
9	T+G	00º11’30.80”W	40º03’17.20”N
10	T	00º11’12.40”W	40º02’48.70”N

Table 3. *Sample locations in the calcareous pre-coastal area.*

Sample	Classification (T=Tile, G=Glaze)	Geographic coordinates Long.	Lat.
1	T+G	0° 9' 46.1766"N	39°50'28.6146"W
2	T+G	0° 9' 52.4334"N	39 50'30.8112"W
3	T+G	0° 10' 3.615"N	39°50'14.7732"W
4	T+G	0° 9' 54.1908"N	39° 50' 9.8484"W
5	BLANCO	0°14' 37.536"N	39° 49'45.7068"W
6	T+G	0° 9' 54.4212"N	39 50'28.3554"W
7	T+G	0° 10' 2.4558"N	39° 50' 12.876"W

Table 4. *Sample locations in the alluvial coastal area.*

5. RESULTS AND DISCUSSION

The results obtained for the boron and fluorine contents (soluble and total contents in the soils, as well as the measurements made on citrus fruit leaves) are summarised in the "a" tables of Tables V to X. The results of the studies conducted on the other parameters of these samples are detailed in the corresponding "b" tables of Tables V to X.

5.1. PRESENCE OF BORON

5.1.1. SOLUBLE BORON

Boron is one of the eight essential micronutrients for the healthy growth of harvests, its deficiency being a widespread problem in relatively wet farming areas. The importance of excess boron in soils, particularly important in arid soils, has only recently drawn greater attention. The threshold between boron deficiency and toxicity is very narrow. On the other hand, the natural global deposition of boron by erosion and atmospheric deposition is considered to be higher than that emitted by glass and other industries such as those associated with ceramic glazes (15), which can in certain cases produce local excesses of the micronutrient.

As indicated previously, the quantity of soluble boron is the bioavailable boron in the soil for plants and is ultimately the currently relevant boron with regard to plant health. The values measured, together with the historical values of Sorlí et al (14), are shown in Figure 1 (right).

It may be observed, first, that the values measured in the ceramic district always exceeded the limit value of 1,3 mg/kg of Aucejo et al., and they also exceeded the value measured in the reference soil outside the district, which ranges between 3 and 0,7 mg/kg in the period analysed.

The data on soluble boron in Figure 1 show that the alluvial area (referenced T+G) displays higher values in the period considered (with an average of about 6 mg/kg), followed by the calcareous samples T+G with a similar average in the period. The values are lower in the calcareous samples of the T environment and it is surprising that in this period, the calcareous samples associated with the glaze and frit production environment G exhibit lower values than the Alluvial and T+G environments. The few G samples and the difficulty of isolating this type of environment in the industrial space analysed could be the cause of this result. In any event, the T environment free of glaze production always displays lower values, which would corroborate the association of the presence of soluble boron with glaze and frit production.

The analysis of the historical values in calcareous T and G environments, and to a greater extent in T+G, with very low values in 2002–2003, confirms, in 2014, the increase observed in 2012–13. The frit and glaze producers have declared a progressive increase in production since 2011 (18) with 20% higher production than in the years 2000–2004. This increase in production, as well as the increase in the use of boron in frit and glaze composition as a substitute for lead, would explain the historical rise in the detected presence of boron. In the alluvial area (albeit with a shorter time perspective), a reduction in the values of soluble boron is observed in 2014 with respect to 2013.

The studied period has been an extremely dry period with rainfall that in the 3 months prior to sample collection was never, in cumulative form, more than 22 l/m^2. Drought mitigates the elimination of soluble boron and it should therefore induce an increased presence of boron in soils, which may be clearly observed in the historical series in this study, but not in the 2014 series compared with the rainier 2012–13 series.

5.1.2. TOTAL BORON

Total boron is the sum of the soluble boron and the partially immobilised boron in the form of low-solubility compounds in the soils, preferentially calcium and magnesium borates, which can be extracted by boiling under reflux with water (9). The values measured, together with the values of previous studies (16), are reported in Figure 2 (right).

It may be observed that the values measured in the ceramic district usually exceed the value measured in the reference soil from outside the district, which ranges from 9 to 1 mg/kg in the period analysed.

The data on total boron in Figure 2 show that higher values are found in the alluvial area in the period considered (with an average of about 18 mg/kg) followed by the T+G calcareous samples with an average value in the period of 10 mg/kg. The values are slightly lower in the calcareous samples of the G environment and the lowest values are those of the calcareous samples associated with the tile production environment, T. As in the case of soluble boron, the T environment free of glaze production always exhibits lower values, corroborating the association of the presence of boron with glaze and frit production. Moreover, the greater concentration in the soils is associated with a greater soil exposure, evidenced by the highest soluble boron values, as well as a greater capability of the sedimentary calcite, which is finer and more reactive (Figure 4), to fix calcium and magnesium borates in alluvial soils.

Earlier data are only available in the case of the alluvial area (16). Figure 2 on the alluvial area exhibits a certain consistency in the values of about 18 mg/kg. The extreme drought, with rainfall that in the 3 months prior to sample collection never exceeded, in cumulative form, 22 l/m^2 in the studied period, does not allow the boron "washing effect" by the rain to be observed. However, in the calcareous area, a decrease in total boron is observed in this period, which is not as clear as in the case of the previously discussed soluble boron.

5.1.3. BORO IN CITRUS FRUIT LEAVES

In 5-6 of the sampling points with citrus fruit plantations, a study was performed of the presence of boron in citrus fruit leaves (Citrus reticulate tree, Clemenules variety).

The values obtained exceed the normal values for boron of 60 mg/kg indicated in the literature (3), being located at limit values (about 150 mg/kg) and often at the reversible damage values (about 250 mg/kg) of Table I. In addition, the values are always higher in the alluvial than in the calcareous area, matching the detected higher values in this area for soluble boron and total boron. The quantity of samples analysed does not allow differentiation between the exposure environments considered in this study or between the seasons of the year.

5.2. PRESENCE OF FLUORINE

The total fluorine content in soils normally lies in the range 150 to 400 mg/kg, though values can be measured of about 1000 mg/kg in areas with highly fluoridated clay. Fluorine is found in the soil in form of fluorite CaF_2, fluorapatite $Ca_{10}(PO_4)_6F_2$, or cryolite Na_3AlF_6. None of these minerals is very soluble in water, which is why the bioavailable quantity of fluorine is low. Fluorine concentration and distribution in soils around aluminium facilities have been widely studied (4) but few studies have been conducted on ceramic environments (3,14).

Sample	Soluble boron (mg/kg)	Total boron (mg /kg)	Leaf boron (mg /kg)	Soluble fluorine (mg /kg)	Total fluorine (mg /kg)	Leaf fluorine (mg/kg)	Calcimetry (%$CaCO_3$)
1(T)	7	13		1,3	279,4		10,1
2(T)	6	13	163,6	2,5	188,1	62,3	6,3
3(T)	5	12		0,95	93,1		7,4
6(T)	5	16		1,6	92,1		22,2
10(T)	6	20	226,6	0,95	94,4	67,3	23,9
T weighted average	*5,7*	*12,7*		*1,3*	*125,2*		*12,3*
4(T+G)	5	8	146,3	0,6	92,4	83,9	21,1
7(T+G)	9	18		1,3	285,0		24,5
9(T+G)	7	23		1,9	190,0		10,0
T+G weighted average	*7,0*	*18*		*1,3*	*190*		*21,1*
5(G)	10	11		0,95	185,2		18,8
8(G)	11	17		2,9	380,0		8,7
G weighted average	*10,0*	*14*		*1,93*	*283*		*8,7*
BLANK	*3*	*8*		*0,63*	*93,9*		*1,8*

***Table V.a**. Boron and Fluorine CALCAREOUS AREA (**DECEMBER 2013**, 0,6 l/m^2 in the previous three months)*

Sample	Conduct. (μS)	pH	Total hardness ($mgCaCO_3/kg$)	Na^+ (mg /kg)	K^+ (mg /kg)	NO_3^- (mg/kg)
1(T)	1134	6,28	630	15	157	80
2(T)	284	6,68	270	8	31	80
3(T)	565	6,48	450	13	63	105
6(T)	278	6,72	270	10	5	95
10(T)	480	6,52	360	10	17	105
T weighted average	*443*	*6,56*	*360*	*11*	*37*	*93*
4(T+G)	297	6,69	360	9	10	75
7(T+G)	362	6,64	180	11	31	100
9(T+G)	318	6,43	360	7	21	90
T+G weighted average	*318*	*6,64*	*360*	*9*	*21*	*90*
5(G)	270	6,69	180	10	15	100
8(G)	523	6,32	360	11	44	95
G weighted average	*397*	*6,50*	*270*	*10,5*	*29,5*	*97,5*
BLANK	*362*	*6,54*	*180*	*15*	*26*	*100*

***Table V.b**. Other parameters CALCAREOUS AREA (**DECEMBER 2013**, 0,6 l/m^2 in the previous three months)*

Sample	Boron (mg/kg)	Total boron (mg/kg)	Leaf boron (mg/kg)	Fluorine (mg/kg)	Total fluorine (mg/kg)	Leaf fluorine (mg/kg)	Calcimetry
12(T+G)	10	35	288,7	1,3	94,1	65,1	2,3
13(T+G)	8	16	213,9	1,3	93,1	40,0	5,4
14(T+G)	15	40		1,6	92,8		2
15(T+G)	9	25		1,3	188,9		2
16(T+G)	6	22		0,6	93,3		3,7
Weighted average	*9*	*27,3*		*1,3*	*93,5*		*2,2*
BLANK	*3*	*8*		*0,63*	*93,9*		*1,8*

Sample	Boron (mg/kg)	Total boron (mg/kg)	Leaf boron (mg/kg)	Fluorine (mg/kg)	Total fluorine(mg/kg)	Leaf fluorine (mg/kg)	Calcimetry
1(T)	2,0	5,9		4,75	95,0		7
2(T)	1,7	5,2	169,3	3,8	93,9	62,3	15
3(T)	1,2	5,8		2,85	94,4		31
6(T)	1,3	5,0		2,85	94,6		38
10(T)	8,9	11,4	158,4	0,95	93,5	67,3	38
T weighted average	*1,7*	*5,6*		*3,2*	*94,3*		*28*
4(T+G)	1,9	4,4	81,7	0,95	94,6	83,9	17
7(T+G)	6,7	9,0		11,4	189,2		23
9(T+G)	7,0	13,1		3,8	95,0		13
T+G weighted average	*6,7*	*9,0*		*3,8*	*95,0*		*17*
5(G)	1,2	4,5		1,9	95		38
8(G)	2,9	12,9		2,85	94,2		19
G weighted average	*2,05*	*11*		*2,4*	*94,6*		*28,5*
BLANK	*2,4*	*8,7*		*0*	*93,8*		*7*

Table VII.a. *Boron and Fluorine CALCAREOUS AREA (**June 2014**, 21,8 l/m^2 in the previous three months)*

Sample	Conduct. (μS)	pH	Total hardness ($mgCaCO_3/kg$)	Na^+ (mg /kg)	K^+ (mg /kg)	NO_3^- (mg/kg)
1(T)	569	6,54	450	44	1,7	80
2(T)	666	6,96	360	52	2,2	80
3(T)	816	6,89	540	54	2,8	105
6(T)	657	6,54	450	46	1,3	95
10(T)	673	6,57	360	51	1,2	105
T+G weighted average	*665*	*6,7*	*405*	*50*	*1,7*	*93*
4(T+G)	696	6,62	450	49	0,9	75
7(T+G)	892	6,7	450	94	9,3	100
9(T+G)	876	6,49	360	41	0,8	90
T+G weighted average	*605*	*6,62*	*450*	*49*	*0,9*	*90*
5(G)	560	6,67	270	49	1,5	100
8(G)	953	6,76	450	110	11	95
G weighted average	*757*	*6,70*	*360*	*80*	*6,25*	*97,5*
BLANK	*362*	*6,31*	*270*	*50*	*1.6*	*100*

Table VII.b. *Other parameters CALCAREOUS AREA (**June 2014**, 21,8 l/m^2 in the previous three months)*

Sample	Boron (mg/kg)	Total boron (mg/kg)	Leaf boron (mg/kg)	Fluorine (mg/kg)	Total fluorine(mg/kg)	Leaf fluorine (mg/kg)	Calcimetry
12(T+G)	7,6	13,0	290,1	1,9	94	43,5	9
13(T+G)	9,6	16,9	262,5	1,9	93	78,9	5
14(T+G)	5,3	25,5		2,85	94		7
15(T+G)	3,9	7,0		1,90	184		18
16(T+G)	4,1	10,9		0,95	373		4
weighted average	*5,7*	*13,6*		*1,9*	*124*		*7*
BLANK	*2,4*	*9,1*		*0*	*93*		*7*

Table VIII.a. *Boron and Fluorine ALLUVIAL AREA (**JUNE 2014**, 4,6 l/m^2 in the previous three months)*

Sample	Na^+ (mg/kg)	K^+ (mg/kg)	Total hardness ($mgCaCO_3$/kg)	Nitrates (mg/kg)	Conduc. (µS)	pH
12(T+G)	52,7	2,2	180	98	451	6,52
13(T+G)	49,8	1,5	180	80	420	6,44
14(T+G)	105	3,4	720	111	1517	6,19
15(T+G)	56,8	2,0	270	100	421	6,09
16(T+G)	9,8	1,6	450	100	1053	6,35
weighted average	*53,1*	*1,9*	*300*	*99,3*	*633*	*6,27*
BLANK	*9,3*	*1,6*	*270*	*100*	605	6,31

Table VIII.b. *Other parameters ALLUVIAL AREA (**JUNE 2014**, 4,6 l/m^2 in the previous three months)*

Sample	Boron (mg/kg)	Total boron (mg/kg)	Leaf boron (mg/kg)	Fluorine (mg/kg)	Total fluorine(mg/kg)	Leaf fluorine (mg/kg)	Calcimetry
1(T)	3,9	*4,6*		4,75	559		10
2(T)	4,4	*5,9*	173,5	3,8	376	21,2	10,5
3(T)	3,5	*6,6*		2,85	279		24,7
6(T)	0,99	*1,4*		2,85	184		32,9
10(T)	2,7	*4,4*	130,6	0,95	189	101,7	31,6
T weighted average	*3,4*	*4,9*		*3,2*	*281,3*		*22,3*
4(T+G)	5,1	*7,3*	223,6	0,95	185	40,6	53,7
7(T+G)	5,4	*7,4*	36,6	11,4	380	21,0	46,1
9(T+G)	4,5	*6,9*		3,8	285		15,7
T+G weighted average	*5,1*	*7,3*		*3,8*	*285*		*46,1*
5(G)	1,9	*5,5*		1,9	278		20,9
8(G)	4,9	*5,7*		2,85	475		35,0
G weighted average	*3,4*	*5,6*		*2,4*	*377*		*28,0*
BLANK	*0,7*	*1,1*		*0*	*94*		*6*

Table IX.a. *Boron and Fluorine CALCAREOUS AREA (**NOVEMBER 2014**, 0,2 l/m^2 in the previous three months)*

Sample	Conduct. (µS)	pH	Total hardness ($mgCaCO_3/kg$)	Na^+ (mg /kg)	NO_3^- (mg/kg)
1(T)	375	5,70	180	52	94
2(T)	424	5,92	270	16	102
3(T)	561	6,11	450	36	99
6(T)	546	6,33	360	52	98
10(T)	495	6,77	360	44	94
T weighted average	*487*	6,1	330	44	97
4(T+G)	*363*	6,39	270	43	37
7(T+G)	*1015*	6,45	540	45	103
9(T+G)	*616*	6,70	360	42	96
T+G weighted average	*616*	*6,45*	*360*	*43*	*96*
5(G)	*444*	6,49	180	85	92
8(G)	*714*	6,66	360	64	97
G weighted average	*579*	*6,58*	*270*	*75*	*95*
BLANK	*593*	*7,14*	*360*	*74*	*99*

***Table IX.b**. Boron and Fluorine ALLUVIAL AREA (**NOVEMBER 2014**, 20,2 l/m^2 in the previous three months)*

Sample	Boron (mg/kg)	Total boron (mg/kg)	Leaf boron (mg /kg)	Fluorine (mg/kg)	Total fluorine (mg/kg)	Leaf fluorine (mg /kg)	Calcimetry
12(T+G)	5,0	24,4	314,5	7,6	188	43,9	10,8
13(T+G)	8,8	23,7	290,7	4,75	93	60	5,0
14(T+G)	7,6	10,3		2,85	186		6,9
15(T+G)	8,3	24,3		5,7	280		22,8
16(T+G)	6,7	12,2		1,9	189		5,9
weighted average	*7,5*	*20,1*		*4,4*	*188*		*7,9*
BLANK	*0,7*	*1,1*		*0,95*	*94*		*6*

***Table X.a**. Boron and Fluorine ALLUVIAL AREA (**NOVEMBER 2014**, 20,2 l/m^2 in the previous three months)*

Sample	Na^+ (mg/kg)	Total hardness (mg/kg)	Nitrates (mg/kg)	pH	Conduc. (µS)
12(T+G)	65	270	95,1	6,94	522
13(T+G)	57	360	95,2	6,92	573
14(T+G)	61	540	92,8	6,91	830
15(T+G)	47	360	94,2	7,11	471
16(T+G)	67	720	96,5	6,90	1021
weighted average	*61*	*420*	*94,8*	*6,97*	*630*
BLANK	*74*	*360*	*99*	7,14	593

***Table X.b**. Other parameters ALLUVIAL AREA (**NOVEMBER 2014**, 20,2 l/m^2 in the previous three months)*

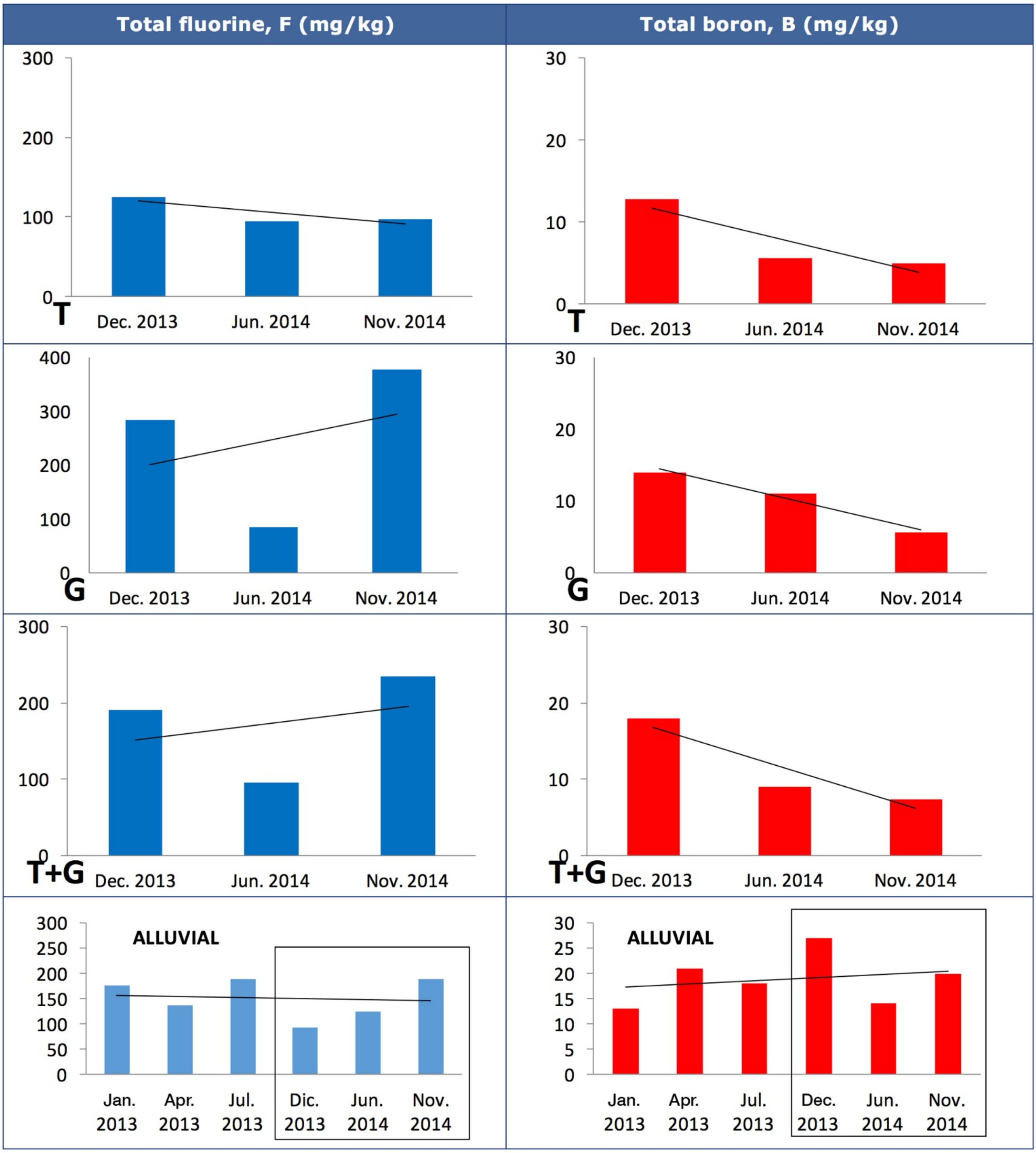

Figure 2. *Evolution of the average values of TOTAL Fluorine and B in the soils with the characteristics indicated (this study and previous values (14)) with trend lines.*

5.2.1. SOLUBLE FLUORINE

The measured average values of bioavailable soluble fluorine in the soil compared with the historical values of Sorlí et al. (14) are shown in Figure 1 (left).

It may be observed, first, that the values measured in the ceramic district always exceeded the limit value of 2 mg/kg of Aucejo et al., and they also exceeded the value measured in the reference soil from outside the district, which ranges from 0 to 0,6 mg/kg in the period analysed.

The data on soluble fluorine in Figure 1 show that the values are low in the alluvial as well as in the calcareous G environments (between 2 and 3 mg/kg) as opposed to the calcareous T and T+G environment with values between 4 and 5 mg/kg indicating the association of fluorine with the presence of tile manufacturing factories.

Analysis of the historical values in all the studied environments and types of soil confirms, in 2014, the decrease already observed in 2012–13 and in all the historical period. The drop in tile production (from 650 Mm^2/year in 2000–2003 to just 324 Mm^2 in 2009 and rising to 404 Mm^2 in 2012 and 420 Mm^2 in 2013) (19), and the increase in porcelain tile production, which uses white-firing clays that are poor in fluorine, could explain the weak drop in fluorine in the soils. However, in the period analysed, a small rise is observed in 2014 with respect to 2013 in all the environments.

5.2.2. TOTAL FLUORINE

Total fluorine is the sum of soluble fluorine and of immobilized fluorine in the form of fluorite CaF_2 and fluorapatite $Ca_{10}(PO_4)_6F_2$ with low solubility. The values measured, together with the values of previous studies (16), are shown in Figure 2 (left).

It may be observed that the values measured in the ceramic district remain within normal levels and are always lower than 400 mg/kg (4), though they are usually higher than the value measured in the reference soil from outside the district, which provides steady values of about 93 mg/kg in the period analysed.

The data on total fluorine in Figure 2 show that the T alluvial and calcareous area exhibit lower and steadier values over time in the period considered (with an average of about 100 mg/kg), followed by the T+G calcareous samples with an average value in this period of 150 mg/kg. The values are higher in the calcareous samples from the G environment. The total fluorine concentration seems to be highly conditioned by soil genesis and the studies conducted do not enable this to be linked to the industrial emissions.

5.2.3. FLUORINE IN CITRUS FRUIT LEAVES

The values obtained, detailed in Tables V to X, in the 5-6 sampling points with citrus fruit plantations (Citrus reticulate tree, Clemenules variety), exceed the normal values for fluorine of 15 mg/kg indicated in the literature (3), being located at limit values (75 mg/kg) in the calcareous area (with values of about 70 mg/kg). In the alluvial area, the detected values are lower, reaching values of about 40–50 mg/kg. Excess fluorine produces damage similar to that of excess boron in citrus fruit: marginal yellowing, burning of leaf edges and tips as well as chlorosis. The quantity of analysed samples does not allow differentiation between the exposure environments considered in this study or between seasons of the year.

6. OTHER PARAMETERS

Generally speaking, the evolution of the measurements performed of the control parameters in the soils indicates consistent values with the following general trends:

a) The calcimetry values in the calcareous area are almost always above 20% $CaCO_3$, evidencing its strongly limestone character, in contrast with the frank alluvial soils of the industrial estate of Nules with calcimetry values between 1,8% and 8,5% $CaCO_3$

b) Despite the previous point, the pH of the 1:5 extract of calcareous soils is slightly more acid, displaying values in the range 6,3–6,7 compared with values between 6,6 and 6,8 of the alluvial soils, probably related to carbonation during stirring and the presence of humic acids of coniferous forest species, abundant in this environment, which acidify the soil (19) as well as to the more reactive character of fine sedimentary calcite particles (see Figure 4).

c) The hardness values are lower in the calcareous area than in the alluvial area as carbonate solubility is low and the calcite present in floods, with a smaller particle size (Figure 4), is more solubilisable.

d) By way of example, Figure 3 plots the variation of hardness with pH for the series of December 2013. A slight reduction in hardness is always observed with pH, which, on being of little significance (as the pH values move in a narrow margin of 6,6–6,8), suggest that pH is regulated by other factors in addition to total hardness.

e) The conductivity values of the 1:5 extract are maintained between 300 and 700 μS in every case, not great differences being observed between the two environments.

f) The values for sodium remain in the range 9 to 60 mg/kg with variations even for the reference soil. The values are slightly higher in the alluvial area. The sodium–conductivity trend line (Figure 3 shows that for the December 2013 series), which is not necessarily linear, indicates that the conductivity of the soils generally increases with the presence of sodium, providing measurement consistency.

e) The values for the nitrates are about 100 mg/kg, indicating that non-farmed soils are involved, as the values would otherwise be much higher (19).

7. CONCLUSIONS

The study conducted in the rainfall year 2013–2014 of samples of soils and citrus fruit leaves in industrial estates of the ceramic Castellón district, in a pre-coastal industrial estate where calcareous soils predominate as well as in a coast industrial estate with an alluvial character, enable the following conclusions to be drawn:

1. The values of soluble boron in soils always exceed the limit value given in the literature (1,3 mg/kg), with greater presence in the alluvial area and their preferential association with glaze and frit production. The increase of the soluble boron concentration, already detected in 2013, is confirmed in the calcareous area with respect to the historical studies of 2000–2003; however, it descends in 2014 with respect to 2013, despite the extreme drought that would have favoured boron build-up in the soils. The frit and glaze producers have declared a progressive increase in production since 2011, with 20% higher production than that of the years 2000–2004. This increase in production, as well as the increase in the use of boron in frit and glaze compositions as substitution for lead, would explain the historical rise in the detected presence of boron.

2. The values of total boron always exceed the value measured in the reference soil from outside the district, which ranges from 9 to 1 mg/kg in the period analysed. Higher values are found in the alluvial area associated with a greater exposure and a greater capability of the sedimentary calcite to fix calcium and magnesium borates in the alluvial soils. The calcareous area exhibits a decrease in total boron in this period, which is not so clear in the case of soluble boron.

3. The values of boron in citrus fruit leaves (Citrus reticulate, Clemenules variety) exceed the normal values of 60 mg/kg for boron indicated in the literature. The values are also always higher in the alluvial area than in the calcareous one, matching the higher values of soluble boron and total boron detected in this area.

4. The average values measured of bioavailable soluble fluorine in the soil always exceed the limit value of 2 mg/kg given in the literature and the association of fluorine with the presence of tile manufacturing factories is noted. The analysis of the historical values confirms, in 2014, the decrease already observed in 2012–13. The reduction in tile production (from 650 Mm^2/year in 2000–2003 to just 324 Mm^2 in 2009, rising to 420 Mm^2 in 2013) and the increase in porcelain tile production, which uses white-firing clays that are poor in fluorine, would explain the weak decrease in fluorine in the soils.

5. The total fluorine values measured in the ceramic district are always within the normal range and less than 400 mg/kg (4), though they are usually higher than the value measured in the reference soil from outside the district, which provides steady values of about 93 mg/kg in the period analysed. The total fluorine concentration seems to be highly conditioned by soil genesis and the studies conducted do not allow this to be associated with the industrial emissions.

6. The values obtained in citrus fruit leaves (Citrus reticulate, Clemenules variety) exceed the normal values of 15 mg/kg for fluorine indicated in the literature, these being 70 mg/kg in the calcareous area and 40–50 mg/kg in the alluvial area.

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