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Biomonitoring of airborne particulate matter emitted from a cement plant and comparison with dispersion modelling results

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HIGHLIGHTS

- Emissions from the cement plant were confined to the vicinities.
- Prevalent winds had an influence on the dispersion of pollutants.
- Ca, Cd and Pb, pH and EC were identified as biomarkers for the cement plant.
- Building downwash effects were detected by the biomonitors.
- Vehicular traffic emissions could be observed in the biomonitors.

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ABSTRACT

The influence of a cement plant that incinerates industrial waste on the air quality of a region in the province of Córdoba, Argentina, was assessed by means of biomonitoring studies (effects of immission) and atmospheric dispersion (effects of emission) of PM_{10} with the application of the ISC3 model (Industrial Source Complex) developed by the USEPA (Environmental Protection Agency). For the biomonitoring studies, samples from the epiphyte plant *Tillandsia capillaris* Ruíz & Pav. f. *capillaris* were transplanted to the vicinities of the cement plant in order to determine the physiological damage and heavy metal accumulation (Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb). For the application of the ISC3 model, point and area sources from the cement plant were considered to obtain average PM_{10} concentration results from the biomonitoring exposure period. This model permitted it to be determined that the emissions from the cement plant (point and area sources) were confined to the vicinities, without significant dispersion in the study area. This was also observed in the biomonitoring study, which identified Ca, Cd and Pb, pH and electric conductivity (EC) as biomarkers of this cement plant. Vehicular traffic emissions and soil re-suspension could be observed in the biomonitors, giving a more complete scenario. In this study, biomonitoring studies along with the application of atmospheric dispersion models, allowed the atmospheric pollution to be assessed in more detail.

1. Introduction

Even though the atmospheric emission rate limits imposed on industrial facilities have become stricter in recent years, inadequate control measures are still prevalent in the case of many emerging countries. In Argentina, atmospheric studies are few, often poorly performed, and do not always result from governmental initiatives due to environmental studies not being high on the public agenda.

Particulate matter and pollutants in general can be transported by the wind and dispersed by the turbulent movement of air prior to reaching receptors. One of the industries which can cause particulate matter pollution is cement production, with the emission of dust being the main environmental concern in relation to cement manufacture (Isikli et al., 2006).

Cement plants produce a considerable quantity of particulate matter as a result of the continuous feeding of raw materials into the cool end of the cement kiln, processing, and the rapid countercurrent flow of combustion gases over the raw feed. Particles that become entrained in combustion gases are removed from the kiln by exhaust gases and are known as cement kiln dust (CKD) (EPA, 1998), with particle sizes generally varying according to the

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kiln process types and ranging from 0 to 5 μm (approximately clay size) to greater than 50 μm (silt size) (EPA, 1993).

The complex mix of pollutants emitted into the atmosphere as a result of industrial activities is known to affect the physiological and biochemical condition of plants, depending on the type, chemical composition and concentration of the pollutants (Mandre et al., 1999). Previous studies have determined that cement dustfalls are enriched in toxic heavy metals such as As, Pb, Ni, Cr, Cu, Zn, Mn, and Cd, (Adejumo et al., 1994), which can spread throughout a large area by wind, rain, etc. and accumulate on plants, animals and soil, thus ultimately affecting human health (Isikli et al., 2006).

Environmental monitoring studies employing biomonitors can be useful in assessing the atmospheric quality at sites where cement plants are established. These living organisms permit, on the basis of networks, the impact of pollutants on ecosystems to be determined (immision effects) and are of particular importance in the framework of environmental protection measures (Franzle, 2003). Lichens, mosses and some epiphytic plants are widely used in biomonitoring studies of air pollution, either as

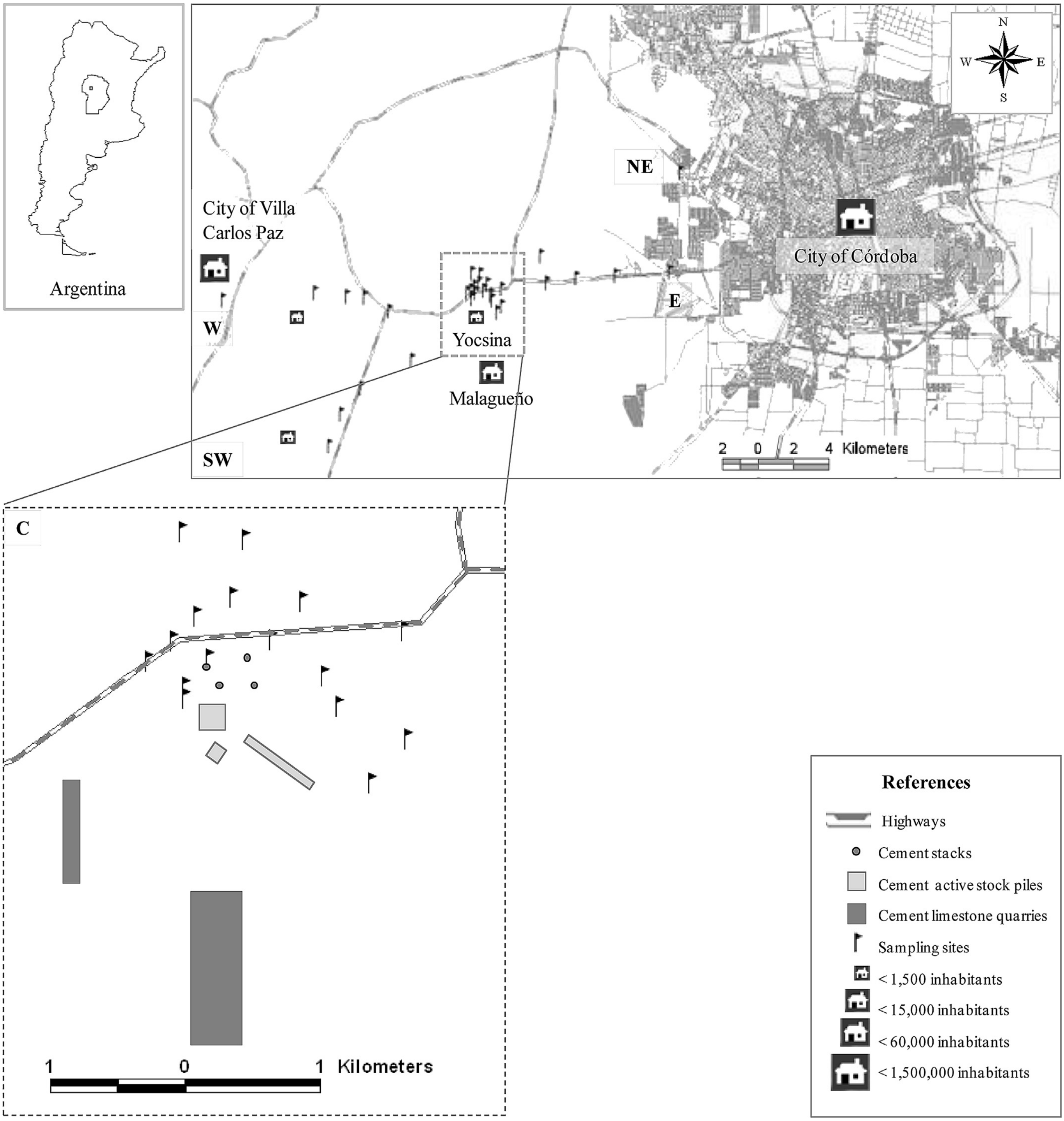


Fig. 1. Location of the study area in the Province of Córdoba, identifying the sampling sites, the cement plant, and categorizing the subareas (NE, SW, E, W, C).

bioindicators of air quality or as bioaccumulators of atmospheric pollutants (Pignata et al., 2002).

As an alternative to biomonitoring studies, emission sources can be assessed by means of dispersion modelling analyses, with the widespread application of atmospheric dispersion models reflecting the current lack of atmospheric studies and the need for predictive tools in decision making in order to protect human health. The model applied in the present study was ISC3, which was developed by EPA as a regulatory application for estimating ambient concentrations. This model was used here for assessing the atmospheric dispersion of PM_{10} emissions from an industrial complex dedicated to the manufacture of cement (emission effects).

In Argentina, there are currently seventeen cement plants, of which two are located in the province of Cordoba and generate 2.700.000 t/year (metric tonnes), representing 16.3% of the national cement production (Schvarzer and Petelski, 2005).

The objective of the present study was to assess the air pollutant emissions from a cement plant located in the province of Cordoba, Argentina by means of particulate matter (PM_{10}) dispersion modelling (effects of emission) and biomonitoring studies (effects of immission).

2. Materials and methods

2.1. Study area description and location of sampling sites

Fig. 1 shows the location of the sampling sites. The study area covered several towns, but had its focal point in Yocsina (designated in this study as C), which is located 18 km SW of Cordoba city. This town has a population of 5000 inhabitants and has developed an industrial profile, mainly due to its cement plant. The area presents a heterogeneous topography, ranging from 420 to 1020 m a.s.l (Fig. 2) with the east direction (E) from the cement plant corresponding to one of the principal accesses to the city of Cordoba, presenting an intense and constant vehicular traffic of approximately 1852 vehicles/hour (unpublished results, Municipality of Cordoba, 2012). Heading towards the west (W) is Villa Carlos Paz city, located at the beginning of a geological formation that may represent a topographic boundary with the area under study. In the north-east direction from the cement plant (NE), agricultural activities are found, with soybean and wheat being the principal crops cultivated in this area. The south (S) and southwest direction (SW) lead to the limestone quarries associated with the cement plant, beyond which are located private residential areas and agricultural fields. Potential PM and heavy metal sources identified in the study area are: industrial activities (cement plant), vehicular traffic, and agriculture. The sampling sites were chosen with a radial distribution surrounding the cement plant (C) and with linear distributions to assess the effects of prevailing winds (NE and SW) and the influence of Cordoba city and Villa Carlos Paz (E and W, respectively).

2.2. Meteorological variables in the study area

For most air modelling studies, five years of hourly data from a representative national weather service station is recommended.

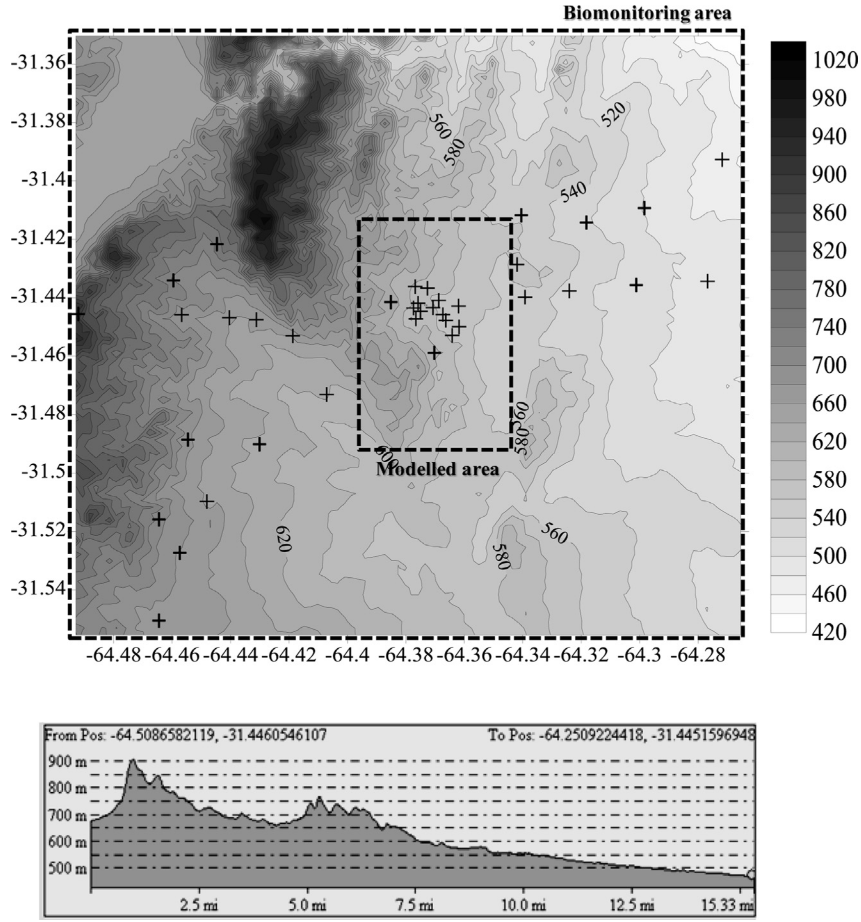


Fig. 2. DEM and topographic profile of the biomonitoring and modelled areas under study. **Footnote**: The icons represent the location of sampling sites and the dashed lines delimit the biomonitoring and modelled areas.

Wind roses were elaborated to illustrate flow vectors (wind blowing to) for the period 2006–2012 from data provided by the National Weather Service (2012), Córdoba airport station, which is located at approximately 12 km NE of the study area. Information regarding meteorological data validation can be found at Supplementary material (Fig. S1). From the wind rose (Fig. 3), it can be seen that the leading wind directions were those blowing to SSW, S and SW, and this also could be observed during the biomonitoring exposure periods: "spring, 2009" and "summer, 2010" (Fig. 4). In spring, there were fewer episodes of calm periods (26%) compared to the summer season (42%), and stronger winds coming from the S were more frequent.

2.3. Brief description of the cement plant

The cement plant began operating in 1963 and currently has a production capacity of 1,200,000 t (metric tonnes) of cement and 540,000 t of clinker per year (Schvarzer and Petelski, 2005). The major PM emission sources from the production process include: limestone quarries and active stockpiles (area sources), clinker grinding and cooling, and cement grinding (point sources). Since 1994, the cement plant has utilized a technology named "blending", which consists of a retrofit of industrial waste with the aim of using it as an alternative fuel and diminishing the costs due to a high consumption of natural gas (resulting in 25% alternative fuels and 75% conventional fuels).

2.4. Biological material and sample preparation

Plants of *Tillandsia capillaris* Ruíz & Pav. f. *capillaris* were collected at Dique la Quebrada, Province of Córdoba, located 38 km NW from the capital city. This natural reserve is considered to be an unpolluted site, where the baseline compositions of these plants have remained practically unchanged over the years. *T. capillaris* has been previously employed in other biomonitoring studies carried out by our research group and has been shown to act as a good biomonitor of response and accumulation in the assessment of atmospheric quality (Pignata et al., 2002; Wannaz et al., 2012). More information regarding this biomonitoring species can be found at Supplementary material.

2.5. Active biomonitoring and exposure periods

Net bags containing 8-10 plants were prepared according to (Wannaz et al., 2006) and transplanted to the study area ($n = 3$ bags/site). These were placed 3 m above ground level and exposed for 3 (September 20th–December 21st, 2009) and 6 months (September 20th–March 20th, 2009/2010) at 30 sites. Once

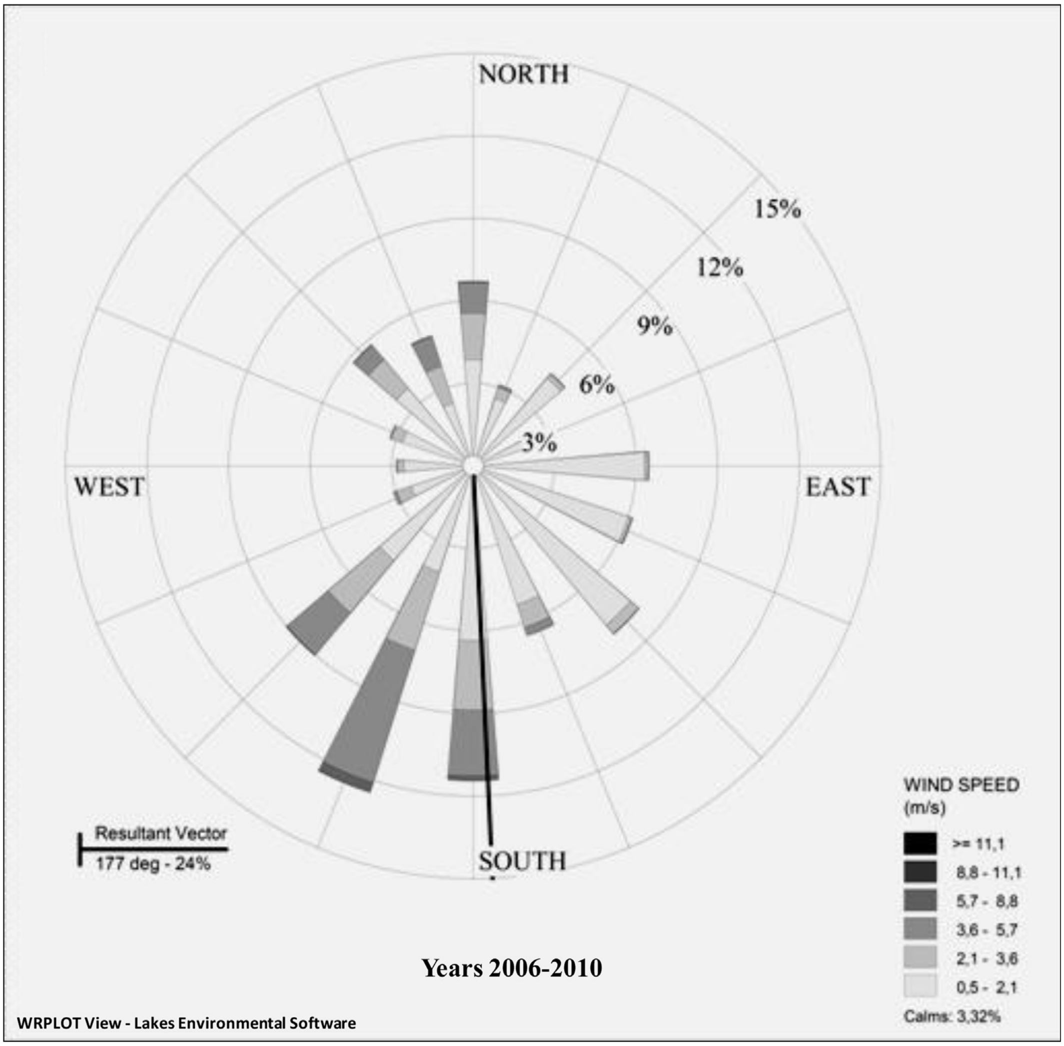


Fig. 3. Wind rose for the period 2006–2012. Data provided by the National Weather Service, Córdoba airport station.

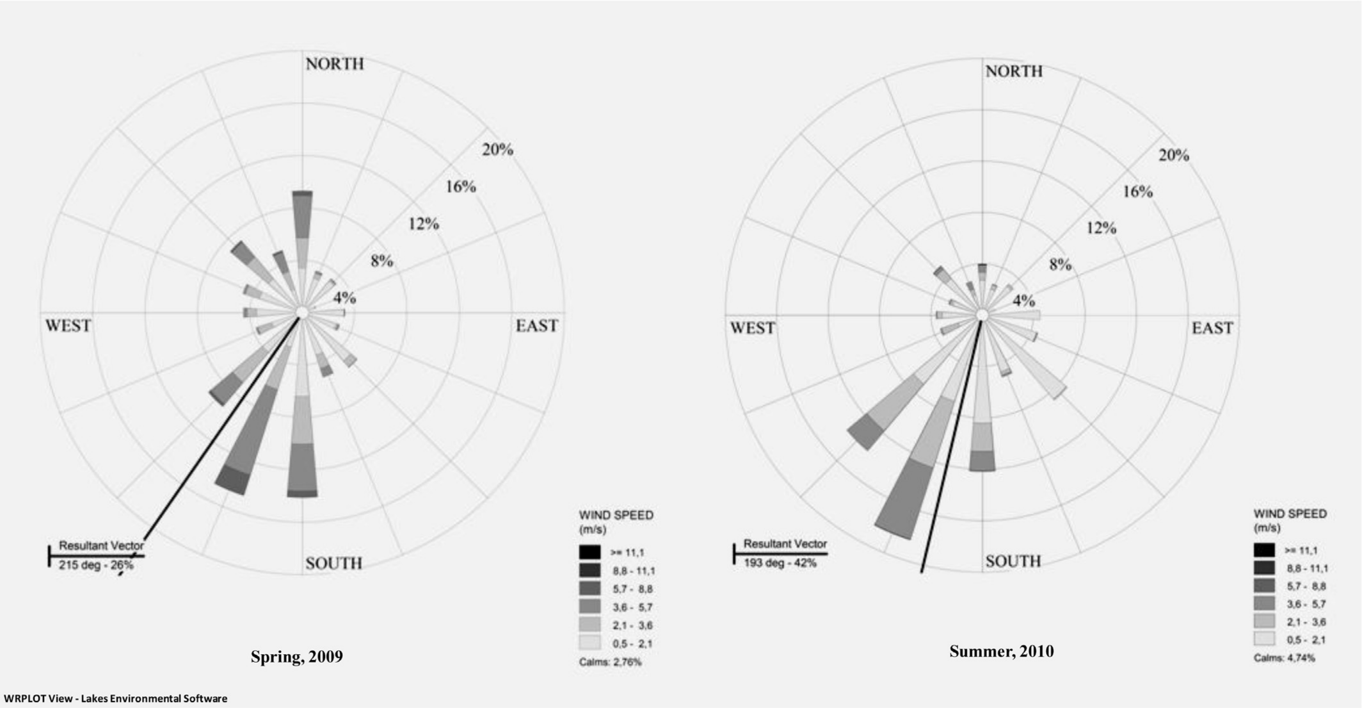


Fig. 4. Seasonal wind roses corresponding to the biomonitoring exposure periods (Spring, 2009 and Summer, 2010). Data provided by the National Weather Service, Córdoba airport station.

the exposure periods had been concluded, plants were carefully collected and placed in paper bags. For the 3-month period, part of the material was separated to determine the pH_1, EC_1 (electric conductivity), water and sulphur content, whereas the rest was kept in plastic vials at −15 °C in the dark for subsequent physiological determinations. For the 6-month period, part of the material was separated to determine pH_2 and EC_2, and the remainder was taken to constant weight in a stove at 45 °C for two weeks for heavy metal content determinations. The same procedures were used on basal samples to evaluate the physiological damage and heavy metal accumulation in order to obtain baseline conditions.

2.6. Physiological determinations

Three sub-samples of *T. capillaris* were taken from each sampling site once the exposure period had elapsed. Quantification of chlorophyll a (Chl-a), chlorophyll b (Chl-b), phaeophytin a (Ph-a), phaeophytin b (Ph-b), carotenoids (Carot), malondialdehyde (MDA), hydroperoxy conjugated dienes (HPCD), sulphur content (S) and dry weight/fresh weight ratio (DW/FW) was performed using procedures already described by Pignata et al. (2002). A Foliar Damage Index (FDI) was also calculated, which combines the variations in certain individual chemical parameters (biomarkers) to assess stress due to atmospheric pollution (Pignata et al., 2002). More information of this index can be found in Supplementary material.

2.7. Determination of heavy metal content

For heavy metal content, 2.5 g of dry weight of *T. capillaris* leaf samples were reduced to ashes in a muffle furnace at 450 °C for 4 h. These ashes were dissolved with concentrated HNO_3 (65% Merck, Germany), and after being individually covered with plastic film, the samples were kept for 24 h in the dark. Following this, the samples were filtered twice, the second time with a 2 μm filter paper (Munktell, Germany), and brought to a final volume of 25 mL with ultrapure water, before being transferred to a 50 mL dark flask. The acid solutions were analyzed by flame atomic absorption spectrometry (FAAS) to determine the concentrations of Ca, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb, and the results were expressed as $\mu g\ g^{-1}$ DW.

2.8. Quality control of samples

In order to assess the digestion procedure and to check the accuracy of the determination of the heavy metals, laboratory blanks and two replicate samples of certified reference material of oriental tobacco leaves “CTA-OTL-1” (Institute of Nuclear Chemistry and Technology) were prepared and ran every ten samples following the same treatment. Values for all blank samples were near to or less than the detection limits of FAAS, and the results were between 79% (Fe) and 92% (Zn) of the certified values, with the coefficients of variations (CV) $\leq$ 16% (Table S1 –Supplementary material).

2.9. Statistical analyses

Statistical analyses were based on the mean values of determinations performed on the three sub-samples obtained at each sampling point. Assumptions for normality were tested using the Shapiro–Wilk test (S–W), and non-normal distributed variables were LOG_{10} transformed before carrying out parametric statistics. A correlation analysis was applied to evaluate the relationships among the heavy metal enrichment factors and proximity to the cement plant (Pearson correlation coefficient). An analysis of variance (ANOVA) was performed for each parameter considering the different areas (C, NE, E, W and SW), and when the ANOVA null hypothesis was rejected (significance level $<$ 0.05); post-hoc comparisons were performed to determine differences between pairs of means (Least Significant Difference, LSD). A principal component analysis (PCA) was used to identify possible

Table 1
Descriptive statistics for the heavy metal accumulation and physiological damage in *T. capillaris* samples exposed at the cement plant in Córdoba, Argentina.

Variable	Units	*n*	Mean	S.E.	% C.V.	Minimum	Maximum
Cu	μg g^{-1} DW	54	14.69	0.56	28.14	8.33	29.70
Zn	μg g^{-1} DW	54	29.21	0.89	22.41	20.48	44.46
Ni	μg g^{-1} DW	54	6.23	0.24	28.68	3.67	12.42
Cd	μg g^{-1} DW	54	0.32	0.04	97.25	0.00	1.64
Mn	μg.g^{-1} DW	54	118	3	19	74	161
Pb	μg g^{-1} DW	54	6.89	0.48	51.25	2.55	22.67
Fe	μg g^{-1} DW	54	2728	95	25.63	1447	4971
Ca	μg g^{-1} DW	54	13,722	1899	101.71	3390	85,603
Chl-a	mg g^{-1} DW	90	1.65	0.06	35.62	0.34	2.81
Chl-b	mg g^{-1} DW	90	0.74	0.03	36.84	0.14	1.30
Ph-a	mg g^{-1} DW	90	1.92	0.07	33.85	0.50	3.49
Ph-b	mg g^{-1} DW	90	0.77	0.03	33.03	0.20	1.39
Carot.	mg g^{-1} DW	90	0.32	0.01	39.19	0.04	0.57
HPCD	μmol g^{-1} DW	90	12.82	0.64	47.46	1.94	28.54
MDA	nmol g^{-1} DW	90	112	3	27	71	229
S	mg g^{-1} DW	90	1.22	0.04	32.78	0.51	2.41
Ph-a/Chl-a	–	90	1.01	0.02	14.83	0.84	1.43
Chl-b/Chl-a	–	90	0.44	0.01	8.04	0.31	0.52
DW/FW	–	90	0.27	0.01	24.16	0.19	0.42
FDI	–	90	2.10	0.08	38.23	0.47	4.47
pH_1	–	90	7.10	0.06	7.64	5.95	8.40
EC_1	μS cm^{-1} ml^{-1} g^{-1} FW	90	0.41	0.02	58.42	0.08	1.27
pH_2	–	48	6.86	0.10	9.73	5.68	8.44
EC_2	μS cm^{-1} ml^{-1} g^{-1} FW	48	0.69	0.12	116.18	0.19	3.89

S.E. = Standard Error; % C.V. = percent Coefficient of Variation.

atmospheric pollution sources and the associations between the different sites.

2.10. Selection of biomarkers from this cement plant

Using the statistical and bibliographical analyses of the physiological variables and heavy metal accumulation (Skórzyńska-Polit et al., 1998; Mandre et al., 1999; Isikli et al., 2006; Branquinho et al., 2008) biomarkers of this cement plant were selected in order to identify the effects of immission and to compare them with the emission effects.

2.11. Atmospheric dispersion modelling of PM_{10} with ISC3

To assess the PM_{10} atmospheric dispersion in the study area (EPA, 1995; Abdul-Wahab, 2006; NPI, 2008), the ISCST3 model (Industrial Source Complex Short Term, third version) was utilized (Schuhmacher et al., 2004). The ISC Short Term model uses hourly meteorological data records to define the conditions for plume rise, transport, diffusion, and deposition. It then estimates the concentration or deposition value of each source and receptor combination for each hour of input meteorology, and the user-selected short-term averages can then be calculated (EPA, 1995).

The results from the biomonitoring studies and the PM_{10} predicted average concentrations were represented graphically using the IDRISI Selva GIS and Imagery Processing software.

3. Results and discussion

3.1. Biomonitoring studies employing T. capillaris (effects of immission)

3.1.1. Descriptive statistics

The mean, minimum and maximum values were calculated and compared with similar scenarios, with Table 1 showing these descriptive statistics for the heavy metal accumulation and physiological damage in *T. capillaris* samples transplanted to Yocsina. Bermudez et al. (2012) analyzed the elemental composition of bulk deposition samples in the Province of Córdoba and found that Yocsina had the highest deposition rates for Ca, with differences being up to 2 orders of magnitude greater than the rest of the sampling areas. In the present study, the Ca accumulation in *T. capillaris* was of one order of magnitude higher at sites located in the vicinities of the cement plant. With respect to the concentration of Cd, this ranged from 0.03 to 1.64 μg g^{-1} DW, with these values being higher than others reported in woody plant species, which ranged from 0.001 μg g^{-1} DW (*Gmelina arborea*) to 0.130 μg g^{-1} DW (*Mangifera indica*) (Princewill and Adanma, 2011) and those in grass (0.085–0.186 μg g^{-1} DW) or *Piptatherum* sp. (0.00–0.06 μg g^{-1} DW) around cement factories in Konya, Turkey (Onder et al., 2007) and Vallcarca, Spain (Schuhmacher et al., 2009), respectively. Furthermore, the concentrations of Cu, Mn, Ni, Pb and Zn were higher than those found in herbage samples collected in the vicinities of a cement plant in Spain (Schuhmacher et al., 2002). The S (2.235 ± 0.107 mg g^{-1} DW) and Zn (57.25 ± 17.98 μg g^{-1} DW) concentrations found in *T. capillaris* samples exposed for 3 and 6 months, respectively, at an industrial site in the Province of Cordoba by Bermudez et al. (2009) were higher than the values obtained in this study, Fe (1829 ± 185 μg g^{-1} DW) was significantly lower, and Mn values (118.10 ± 16.15 μg g^{-1} DW) were similar.

3.1.2. Heavy metal enrichment factors

The calculation of the heavy metal enrichment factors (EFs) in samples of *T. capillaris*, either in relation to baseline conditions (EF_B), or local/background soil composition (EF_{TS}), have been used to evaluate emission sources of metals (natural or anthropogenic). Information regarding EF calculations can be found in Supplementary material. The topsoil heavy metal compositions from the study area and at a local site were used in order to take into account the regional geochemistry as well as to be able to speculate on the origin of the elements (Table S2). Figs. S2 and S3 illustrate the mean EF_B and EF_{TS} values for heavy metals as a whole and between sites. By considering the scale proposed by Frati et al. (2005), the EF_B values revealed a severe accumulation of Cd (C, E and SW) and accumulations of Ca (C), Mn (all sites), Cu (all sites), Cd (NE) and Pb (C and E). The mean EF_{TS} values for all the elements under study were greater than 3, suggesting an anthropogenic input. Significantly higher EFs were found for Cu, coinciding with

Table 2
Correlation matrix for heavy metal enrichment factors (EF_B), pH and EC measured in *T. capillaris* leaves, considering distance from the cement plant in Córdoba, Argentina (Pearson Correlation Coefficient).

	pH_1	EC_1	EF Cu	EF Zn	EF Ni	EF Cd	EF Mn	EF Pb	EF Ca	EF Co	pH_2	EC_2	Dist. C.
pH_1	1												
EC_1	**0.63*****	1											
EF Cu	ns	ns	1										
EF Zn	ns	ns	0.39**	1									
EF Ni	ns	ns	**0.86*****	ns	1								
EF Cd	**0.77*****	**0.59*****	0.33*	ns	0.33*	1							
EF Mn	ns	ns	ns	0.48**	ns	ns	1						
EF Pb	**0.57*****	**0.53*****	0.41**	**0.50*****	0.35*	**0.72*****	ns	1					
EF Ca	**0.71*****	**0.79*****	ns	ns	ns	**0.82*****	−0.32*	**0.65*****	1				
EF Co	**0.50*****	0.31*	**0.59*****	0.37*	**0.50*****	**0.55*****	0.35*	**0.61*****	0.32*	1			
pH_2	**0.65*****	0.41**	ns	ns	ns	**0.65*****	−0.33*	ns	0.48**	ns	1		
EC_2	0.36*	ns	ns	ns	ns	0.39**	ns	ns	**0.49*****	ns	**0.59*****	1	
Dist. C.	**−0.53*****	−0.36*	0.33*	**0.53*****	ns	−0.47**	0.39**	ns	−0.48**	ns	**−0.55*****	ns	1

*Significant at 0.05 probability level. **Significant at 0.01 probability level.
***Significant at 0.001 probability level. ns: not significant. pH_1 and EC_1: measured at the 3-month exposure period. pH_2 and EC_2: measured at the 6-month exposure period. Dist. C: Distance from Cement Plant (km).

results found by Bermudez et al. (2012) in bulk deposition samples at 10 different sites located in the province of Córdoba (including our study area). This may indicate that Cordoba is being affected by large concentrations of Cu, probably due to vehicular traffic emissions.

In order to establish inter-element relationships in the exposed biomonitoring samples (EF_B), Pearson correlation coefficients were calculated and are presented in Table 2 in the form of a correlation matrix. Cd, Ca, pH_1, pH_2 and EC_1 were negatively correlated with distance from the cement plant (km), with these elements also being positively correlated with each other. These results coincided with Branquinho et al. (2008) who also found decreasing Ca values with increasing distance from a cement mill by using two biomonitoring species. There was a strong correlation between Cd and Ca ($r = 0.82$), suggesting that this element derived from cement plant emissions (Isikli et al., 2006). Pb was positively correlated with Cd and Ca, and also with Co, EC_1, Zn and Cu, indicating that Pb originated from more than one source of atmospheric pollution (Wannaz et al., 2012). Furthermore, Cu and Ni were positively correlated, although it still needs to be evaluated if these relationships had an agricultural and/or industrial origin.

The EF_B and EF_{TS} showed similarities in the ANOVA analyses between subareas (NE, SW, E, W and C) (Table 3), implying that same effects were being observed, and also that there was a strong air/plant–soil interaction. Mn, Ni and Cu did not present significant differences between sites, whereas Cd, and Ca were highly enriched in the vicinities of the cement plant. The high correlation between Cd and Ca may be explained by the fact that Cd was taken up by plants, using the paths of Ca transport (Skórzyńska-Polit et al., 1998). It is therefore reasonable to suppose that the presence of Cd in the study area was determined by the Ca levels occurring in plant cells. The Ca values did not significantly differ between C and NE, indicating a dispersion of this element (mostly) towards both these directions. In fact, Ca is not only emitted from stacks (point sources) but also from area sources (fugitive dust emissions), which are generated at ground level by wind re-suspension (Abdul-Wahab, 2006). Zn showed significant values (E, NE and SW), and was probably related to vehicular traffic emissions, considering that the highest values were found towards the E, one of the main accesses to Córdoba city, which is characterized by elevated vehicular flux. Pb was significantly enriched at most of the sites, especially at C and E, indicating that Pb was not only explained by the cement plant but also probably originated from traffic emissions (Wannaz et al., 2012).

There were two sites at C which showed elevated heavy metal content for most of the elements studied, compared to the average

Table 3
ANOVA analysis of heavy metal enrichment factors with basal samples (EF_B) and local topsoils (EF_{TS}) in *T. capillaris* exposed at the cement plant in Córdoba, Argentina, between the subareas NE, SW, E, W and C. The LSD Test was applied when significant differences were found ($p < 0.05$).

	Element	C	SW	NE	E	W	ANOVA
		Mean ± S.E.	Mean ± S.E.	Mean ± S.E.	Mean ± S.E.	Mean ± S.E.	p − value [a]
EF_B	Ca	1.41 ± 0.10 a	0.61 ± 0.27 b	0.87 ± 0.27 ab	0.72 ± 0.22 b	0.51 ± 0.17 b	***
	Mn	1.60 ± 0.06	1.77 ± 0.16	1.55 ± 0.16	1.69 ± 0.13	1.77 ± 0.10	0.5386
	Co	0.45 ± 0.02 a	0.40 ± 0.05 ab	0.36 ± 0.05 ab	0.38 ± 0.04 ab	0.35 ± 0.03 b	*
	Ni	0.85 ± 0.04	0.78 ± 0.11	0.67 ± 0.11	0.75 ± 0.09	0.77 ± 0.07	0.4751
	Cu	1.45 ± 0.06	1.28 ± 0.17	1.35 ± 0.17	1.34 ± 0.14	1.21 ± 0.11	0.4076
	Zn	0.45 ± 0.02 b	0.48 ± 0.06 ab	0.52 ± 0.06 ab	0.64 ± 0.05 a	0.44 ± 0.04 b	*
	Cd	4.84 ± 0.34 a	2.24 ± 0.90 b	1.18 ± 0.90 b	2.14 ± 0.73 b	1.00 ± 0.57 b	***
	Pb	1.25 ± 0.07 a	1.07 ± 0.17 ab	1.00 ± 0.17 ab	1.27 ± 0.14 a	0.87 ± 0.11 b	*
EF_{TS}	Mn	4.01 ± 0.15	4.44 ± 0.40	3.90 ± 0.40	4.23 ± 0.33	4.44 ± 0.26	0.5409
	Co	6.28 ± 0.21 a	5.61 ± 0.56 ab	4.95 ± 0.56 b	5.35 ± 0.46 ab	4.71 ± 0.36 b	**
	Ni	5.94 ± 0.29	5.39 ± 0.77	4.66 ± 0.77	5.23 ± 0.63	5.33 ± 0.49	0.4752
	Cu	33.01 ± 1.48	29.21 ± 3.91	30.81 ± 3.91	30.44 ± 3.19	27.50 ± 2.47	0.4069
	Zn	6.02 ± 0.32 b	6.38 ± 0.85 ab	6.87 ± 0.85 ab	8.51 ± 0.70 a	5.88 ± 0.54 b	*
	Cd	10.84 ± 0.74 a	5.02 ± 1.96 b	2.64 ± 1.96 b	4.13 ± 1.60 b	2.17 ± 1.24 b	***
	Pb	7.67 ± 0.41 a	6.56 ± 1.07 ab	6.14 ± 1.07 ab	7.81 ± 0.88 a	5.32 ± 0.68 b	*
	n	30	4	4	6	10	

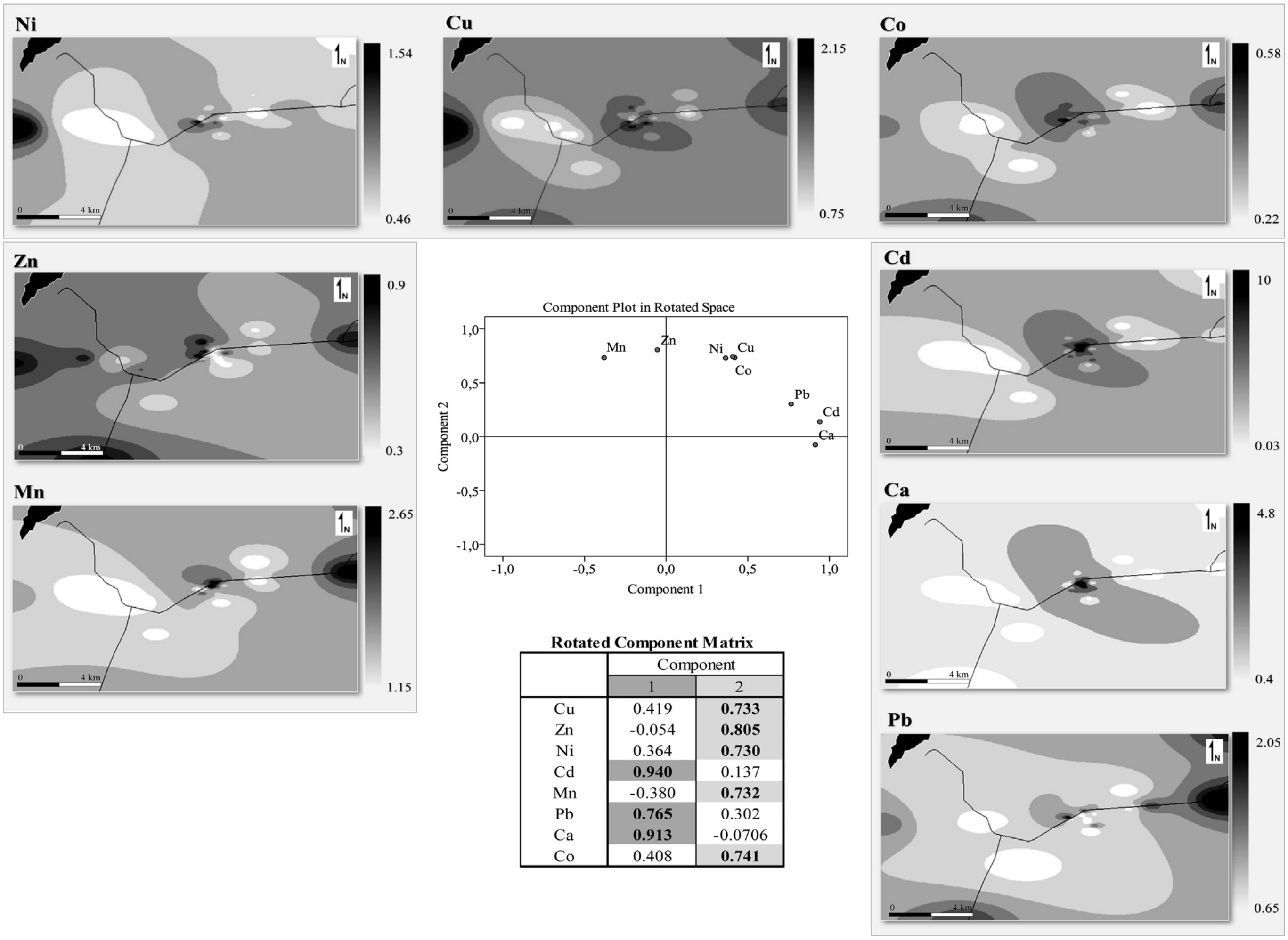
*Significant at 0.05 probability level. **Significant at 0.01 probability level.
***Significant at 0.001 probability level. n: number of samples/site. No data for Ca at EF_{TS}.
[a] Values on each horizontal line followed by the same letter do not differ significantly ($p = 0.05$).

values found at the rest of the sites (Table S3). These sites were located nearest to the clinker cooler stack, at 90 (site 1) and 350 m (site 2), and were probably affected by stack downwash. Generally, the most important source of atmospheric emissions from cement stacks is from the clinker kilns, and when these kilns use organic waste as alternative fuels, the emissions contain heavy metals and their compounds, HF, HCl, dioxins and furans (Schuhmacher et al., 2002). Site 1 was more enriched in heavy metals than site 2, having the highest levels of Ca, Cd and Pb which were greater than 100% of the mean values of C. In contrast, site 2 had increased percentage values but below 100%, with the highest values found for Cd, Zn and Pb. Also, the high Zn values were possibly due to traffic (this site was located only 50 m from the highway). There was a gradient from site 1 to 2, for Cd, Ca and Pb, with Mn having the lowest values, implying that the cement plant probably had few stack emissions of this element.

In Fig. 5, the results are presented of a Principal Component Analysis (PCA) from the heavy metal enrichment factors (EF_B) along with isoconcentration maps to identify possible atmospheric pollution sources and the associations between the different sites, with varimax rotation being applied to differentiate the sources better. The Kaiser–Meyer–Olkin measure of sampling adequacy (KMO) was 0.706, indicating strong correlations. For the variance, 73% was explained by 2 factors, with factor 1 being mainly represented by Cd, Ca and Pb (coefficients > 0.7). The isoconcentration maps show that these elements were directly related to the cement plant emissions with a visible local effect occurring. However, it is also noticeable that the eastern direction was affected, probably due to vehicular traffic emissions, although at minor proportions (coefficients < 0.3). Factor 2 was mainly represented by Zn, Mn, Co, Ni and Cu (coefficients > 0.7), with the isoconcentration maps revealing that these elements were more distributed throughout the study area (this is also noticeable from the ANOVA analysis for Ni, Cu and Mn), and may have originated from vehicular traffic emissions (braking toll gate) and/or soil re-suspension. As Cu, Co and Ni were also related to factor 1 (coefficients < 0.4), they therefore were also associated to the cement plant emissions albeit at minor proportions. Concerning vehicular traffic, according to the European Environmental Agency (EEA, 2007) the major traffic related metal emission sources are brake linings (Cu > Zn > Pb > Ni > Cd), tyre rubbers (Zn > Cu > Pb > Ni > Cd) and asphalt wear (Zn > Pb > Cu > Ni > Cd).

3.1.3. *Physiological damage*

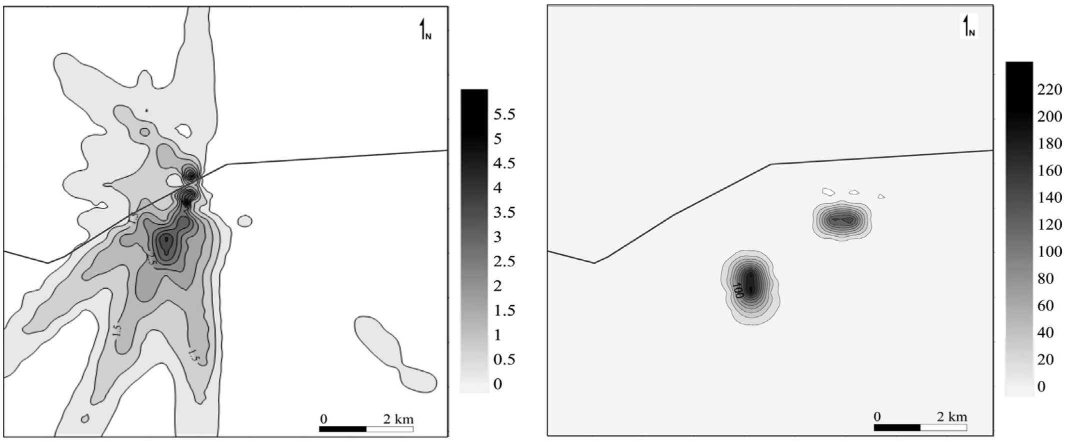
Table S4 shows the ANOVA analysis for physiological damage among the different subareas considered in this study. The FDI and EC_1 values were similar, with the maximum significant values occurring at C, followed by the E direction, whereas Chl-a and carotenoids both had their lowest values in the C and W directions. Prajapati (2012) postulated that the decrease in total chlorophyll content in the exposed leaves may be attributed to the alkaline condition developed by the solubilization of chemicals present in



Rotated Component Matrix

	Component	
	1	2
Cu	0.419	**0.733**
Zn	-0.054	**0.805**
Ni	0.364	**0.730**
Cd	**0.940**	0.137
Mn	-0.380	**0.732**
Pb	**0.765**	0.302
Ca	**0.913**	-0.0706
Co	0.408	**0.741**

Fig. 5. Principal Component Analysis with Varimax rotation and isoconcentration maps for heavy metal enrichment factors (EF_B) in *T. capillaris* leaves.



Point sources

Point and area sources

Fig. 6. Predicted average PM_{10} concentration values (μg m^{-3}) emitted from point and total sources of the cement plant corresponding to the biomonitoring exposure period (September–March 2009/2010). Results obtained from the application of the ISC3 model.

the dust particles. Related to this, dust deposition on leaf surfaces alters their optical properties, and the amount of light available for photosynthesis.

The greatest S values in this study were identified at E, resulting from urban emissions coming from the city of Cordoba. Therefore, despite the fact that S is a pollutant emitted from cement plants (Schuhmacher et al., 2004) in our case the influence of vehicular traffic appeared to be stronger. Similar results were also found by Branquinho et al. (2008) using exposed lichens in the vicinities of a cement plant, and by Carreras and Pignata (2002) who worked at the same plant as the present study.

3.2. *Atmospheric dispersion modelling of PM_{10} emissions from the cement plant (emission effects)*

3.2.1. *Emission rate calculations*

The PM_{10} estimated emission rates were classified as point sources (4 stacks) and area sources (6 active stockpiles and 2 limestone quarries). Information regarding emission rate calculations can be found at Supplementary material. Table S5 shows the resulting emission rates obtained through the emission factor estimation technique. Stacks had the highest values of emission rates however, when considering the emission areas, the limestone quarries and active stockpiles were the major PM_{10} sources.

3.2.2. *ISCST3 input data*

The ISCST3 model was run for PM_{10} emissions from the cement plant, considering a wide-ranging Cartesian grid of 9 km with a resolution of 400 m × 400 m. Another Cartesian sub-grid of 800 m was created, with a resolution of 200 m × 200 m covering the adjacent area of the stacks and 22 buildings were also included for building aerodynamic downwash calculations. The model required the following meteorological variables for the 7-year study period: wind speed (m s^{-1}); wind vector flow (degrees); temperature (k); Pasquill stability class (1–6); and mixing height (m). A rural dispersion was chosen for the model and the PM_{10} pollutant type was analyzed. Flagpole receptor heights for 554 receptors were set at 3 m on elevated terrain (m a.s.l.), with the aim of analyzing concentration values (μg m^{-3}) that could later be compared with the exposed biomonitors (at 3 m). The model was set up for concentration values over 24 h and the biomonitoring exposure period. All runs included 2 source groups consisting of 4 point sources (cement stacks) and 8 area sources (6 active stockpiles and 2 limestone quarries).

3.2.3. *Isoconcentration maps*

In order to compare the PM_{10} concentration values predicted from the atmospheric dispersion model with WHO atmospheric standards (2005), an isoconcentration map was elaborated to represent the summary of the highest concentration obtained over 24 h for 7 years. These results (expressed in μg m^{-3}) are shown in Fig. S4, which gives the total PM_{10} emissions from the cement plant for the 7-year study period (2006–2012), representing the overall and average PM_{10} impact from the cement plant. There were no significant variations found in the PM_{10} concentration or dispersion values modelled over the 7 years (data not shown). It is clear that the greatest PM_{10} values obtained were from the area sources, which were large exposed areas where the dust was re-suspended by the wind. The area sources, in particular the main limestone quarries, generated the maximum emissions in the study area and showed a markedly local effect, with emissions occurring above ground level. The PM_{10} levels were within acceptable limits at approximately 800 m from the main limestone quarry and at 100 m from active stockpiles and the smaller quarries.

3.3. *Relationship between biomonitoring studies and atmospheric dispersion modelling*

Fig. 6 illustrates isoconcentration maps that represent the summary of the averaged concentration values by receptors (μg m^{-3}), obtained for point and total sources during the exposure period from September to March 2009/2010. An impact from stack emissions was observed in the vicinities, which was certainly due to building downwash, considering that the 4 stacks were exceedingly close to large buildings. The model revealed that the emissions from area sources were also confined to the vicinities, without any significant dispersion being shown at the rest of the study area. This was also observed in the biomonitoring study, which identified Ca, Cd and Pb, pH and EC as biomarkers of this cement plant with markedly local effect. Building downwash effects were also detected by the biomonitors, since the highest EFs for the cement plant were observed in C, with two sampling sites (towards the north direction) having the highest values in this study for the heavy metals associated with this cement plant.

Towards E, high levels of other heavy metals indicated that the atmospheric source was not just the cement plant (vehicular traffic). Although the effects from other sources were not considered in the model, vehicular traffic emissions and soil re-suspension were revealed by the biomonitors, thus allowing a more complete scenario to be formed. The heavy metals Zn, Cu, Ni, Mn and Co were mainly related to these sources.

4. Conclusions

The use of biomonitors allowed obtaining a more complete scenario of the atmospheric quality in the region, since different atmospheric sources could be identified and characterised. Ca, Cd and Pb, pH and EC were identified as biomarkers of this cement plant, while Zn, Cu, Ni, Mn and Co were mainly related to vehicular traffic emissions and soil re-suspension. The application of the atmospheric dispersion model ISC3, gave information regarding the behaviour of the cement plant, main contributor of PM_{10} emissions in the area. This model permitted it to be determined that the emissions from the cement plant (point and area sources) were confined to the vicinities, without significant dispersion in the study area. Building downwash effects were detected by the biomonitors, since the highest EFs were observed in C, with two sampling sites (towards the north direction) having the highest values in this study for the heavy metals associated with this cement plant.

Further studies will include on the one hand, the total fraction of heavy metals and trace elements in order to identify and characterize the different atmospheric sources in the study area in more detail, and on the other hand, measured PM_{10} concentrations in order to validate the results obtained in the model.

It is important to emphasize the fact that, as alternative tools for developing atmospheric monitoring studies, biomonitors and the application of atmospheric dispersion models can be useful when applied together, in order to permit more robust and improved predictive atmospheric studies.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.10.020.

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