Environ Geol (2007) 51:1413–1424
DOI 10.1007/s00254-006-0438-3

ORIGINAL ARTICLE

PM10 and Pb evolution in an industrial area of the Mediterranean basin

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Received: 5 May 2006 / Accepted: 10 July 2006 / Published online: 19 August 2006

Abstract The study area is highly industrialized, with businesses involved in the non-metal mineral products sector and ceramic industries (colors, frits and enamel manufacturing) standing out. Air quality evaluation was performed regarding atmospheric particles (PM10 fraction) and Pb in a Spanish coastal area during 2001 and 2002 in order to compare these values with other areas in the Mediterranean basin. Once the samples were collected, their PM10 fraction concentration levels were determined gravimetrically. A Pb analysis in air pollution filters was carried out by ICP-MS. The seasonal and weekly variabilities of these contaminants were also studied, with the objective of being able to explain their origin and thus minimize their possible damaging effects. A similar evolution of PM10 and Pb was observed in both years of the study. Higher PM10 concentrations have been detected during the months of June and July, lower values between March–May, August and October–December, and intermediate values in January and February. A similar tendency has been observed by other authors in European industrialized cities. Regarding Pb, the monthly mean remains constant during the entire year. In the study area, Pb represents 0.6% as a mean of the total PM10 mass, with a variation range between 0.1 and 5.1%. The major crystalline phases in PM10 were quartz, calcite, dolomite, illite, kaolinite and feldspars.

Keywords Air pollution · PM10 · Pb · Mineralogy · Seasonal evolution · Weekly evolution · Coastal area · Mediterranean basin

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Introduction

The high development reached by our society, due to a constant increase in the demand of consumer goods and from the requirements of technological advances, brings as a consequence an increase in the use of raw materials and their subsequent industrial transformation. All this introduces large quantities of chemical substances into the atmosphere, whose behavior in the natural environment and the effects upon living organisms and material goods are unknown in some cases. Atmospheric pollution is formed by part of industrialized life, and a consequence of industrialized areas' constant development (Boix et al. 2001; Gómez et al. 2005).

The requirement for clean and pure air comes from treating it as a limited and common good, indispensable for life. Earth's atmosphere is finite and its self-cleansing capacity has limits. As such its utilization must be subjected to practices that prevent the deterioration of its quality, from either use or abuse, in such a way that its purity is preserved for a guaranteed normal development of living beings.

Maximum value concentrations admissible for the most characteristics of atmospheric pollutants have been established in the majority of industrialized

countries in the world. These values have been set based on both theoretical and practical studies, on the effects that present levels upon human health, and on what levels may reach in the future. The effects are primarily based on the consideration of epidemiological factors.

The control of atmospheric pollution in Spain was begun in 1972 with the passage of law 38/1972 of December 22 concerning environmental protection. This law caused the appearance of Royal Decrees (RD) and Ministerial Orders (OD) where specific aspects were developed about how to minimize this pollution, establishing atmospheric limit values for the preservation of public health. This initial law was recently modified, with law 16/2002 of July 1 concerning the prevention and integral control of pollution. Once the European Union (EU) was formed, and for Spain to enter as a member, EU legislation has had jurisdiction over the Spanish state in the form of RDs. One of these (Spanish Royal Decree 2002) is the base of this study: RD 1073/2002 of October 18 concerning the evaluation and management of atmospheric air quality regarding sulfur dioxide, nitrogen dioxide, nitrogen oxides, PM10 particles (the fraction of suspended atmospheric particles in sizes up to 10 μm), Pb, benzene and carbon monoxide.

In the present study an assessment of atmospheric air quality was conducted, keeping in mind the atmospheric particulate (PM10 fraction and Pb) in the municipality of Vila-real (Fig. 1), during the years of 2001 and 2002, following the new normative concerning atmospheric air quality of recent implantation, RD 1073/2002. The seasonal variation of concentration levels for these two contaminants was also studied, trying to identify the influences that natural origin emissions, as well as those of anthropogenic origin, have upon the concentrations. Weekly behavior was also analyzed, with the goal of identifying the influences that emissions from developed human activity, fundamentally industrial and traffic origins, might have upon the concentrations in the area.

Description of the study area

The area of the atmospheric study is located in the southwest of the municipality of Vila-real. This industrial city is located in the east of the Castellón province, and is 42 m above sea level in the Plana Baixa Community of the of the province of Castellón, in Spain. The population nucleus resides between two fluvial basins, the River Millars to the north and the Riu Sec to the south. The population of the municipality, according to the Vila-Real City Council, numbers approximately 49,000 inhabitants. There is also a high traffic density in the area, a consequence of the proximity of the population to various community roadways: the AP-7 toll motorway and also the N-340 highway. These two factors cause punctual high concentration peaks of atmospheric particle contaminants.

A simplified image of the location of the industrial areas as well as the most important vehicular roadways in the area of Vila-real is shown in Fig. 1.

Geology

The area under study is in the province of Castellón, in the municipality of Vila-real. It is situated near the Mediterranean coast. This area is based on Quaternary materials generated by torrents from the inland massifs (Maestrazgo Range and tributaries from the Sierra de Espadán Range), which have formed lagoons moving closer to the sea. This process is reported to have started at the end of the Tertiary period, as the

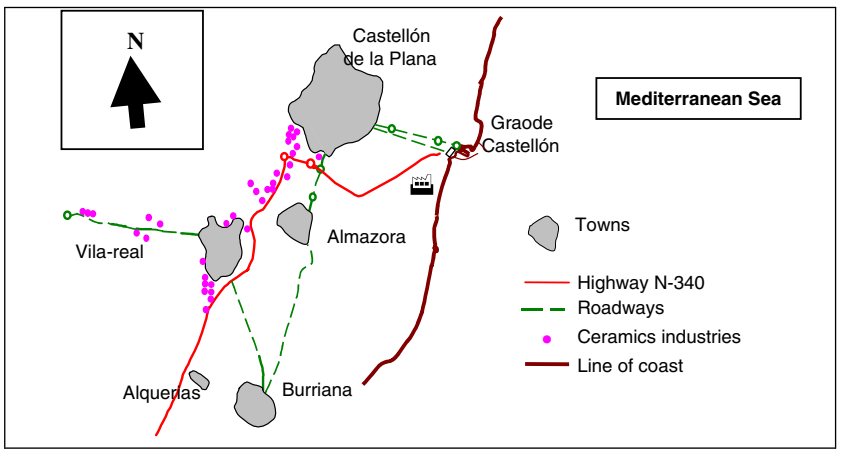

Fig. 1 Location of the primary emission sources in the studied area

Pliocene became the Pleistocene era, favoring a climate suitable for the activities of torrents. The main source of sediments is the River Mijares. The supply of sediments has reduced in the last few years because of regulation in the course of the river.

Socio-economic aspects

The ceramic industry manufacturing floor and wall tiles and a wide sector of services from the ceramic industry forms the main economic activity. Next to this industry is the construction sector followed by the refinery on the coast. Agriculture in the area was once very important, with the cultivation of citrus fruit (oranges) and other fruit trees as well as olives. From the urban center toward the coastal area, many villas and apartment blocks are being built for tourism.

The area to the southwest of Vila-real is highly industrialized, with businesses involved in the non-metal mineral products sector (ceramic floor and wall manufacturing) and chemical industries (ceramic colorants, frits and enamel manufacturing) standing out.

Sampling conditions

The sampling station was installed, conforming to the directives of the implantation of RD 1073/2002, in the urban area of the southwestern portion of Vila-real, specifically within the municipal warehouse installations of this locality (UTM coordinates: X 4425000 Y 746595).

It was located in order to avoid measuring microclimates, in an open area containing at least 500 m^2. There were no restrictions to the air flow around the sampling entrance point, established approximately 3 m above ground level on a special metallic platform. There were no local emission sources nearby, in this way avoiding a distortion of the sample due to the influence of smoke plums of specific contaminants. A PM10 medium volume automatic sampler was used, model IND_LVS3, manufactured by Kleinfitergerät. This device complies with the Spanish normative, adapted to the European Normative UNE-EN 12341:1999 (1999), for the sampling of PM10 particles. It obtained the daily concentration levels of PM10 particles present in the atmosphere, according to the RD 1073/2002 environmental protection law.

The technique consists in blowing air through a PM10 inlet with a vacuum pump. The programmed sampling volume was 2.3 m^3/h during 24-h periods, with a precision of 0.1 m^3/h.

The particulate matter was blown in through the opening circumference between the frame and round cover mounted on top. Within the sampler inlet, the air flow was accelerated by eight impactor nozzles and then directed toward the impacting surface. It was then passed through a filterholder tube. Particles up to 10 μm were trapped on a permeable support, being a 47-mm diameter fiberglass filter. The measurements were daily corresponding to a 24 h sampling period. The air volume was measured through an orifice installed between the filter and vacuum pump. In this way the precision obtained was 0.01 m^3. The device contains a temperature sensor, with a radiation protector that eliminates deviations in the reading due to solar radiation, and also a pressure sensor. Molded polystyrene cassettes were used to protect the filters during transport and storage.

Quartz fiber filters were used in the sampling since they are made with a pure SiO_2 base, with a total absence of additives. As such, they possess great chemical stability during the acid dissolution of the samples for their subsequent chemical analysis, with hardly any loss of filter mass due to chemical reactions in the extreme conditions of acidic gases.

The sampling took place during 2001 and 2002. A total of 333 daily samples of PM10 fractions were collected from the atmospheric particulate.

Determination of PM10 concentration levels and mineralogical composition

Once the samples were collected, their PM10 fraction concentration levels were determined gravimetrically, expressed in micrograms per cubic meter.

Before weighing the filters, whether empty or with sample, they are prepared. They are kept for at least 2 days in a desiccator, controlling their humidity around 50% and the weighing room temperature is kept at 20°C with an air conditioner. With this it is intended to assure equivalent conditions upon weighing the sample as normative UNE-EN 12341:1999 (1999) recommends, relating to the determination of PM10 in ambient air.

The weights of the collected samples are obtained with the use of an analytic scale having a precision of 0.1 mg. The PM10 concentration levels are determined from the sample quantities obtained and the volume of air pumped using the expression:

$$C_{\mathrm{PM10}} = (\mathrm{Pm} - \mathrm{Pv})10^6 / V_{\mathrm{air}}$$

Being C_{PM10}, PM10 concentration in micrograms per cubic meter; Pm, weight of the sampled filter in gram; Pv, empty weight of the filter in gram; V_{air}, volume of air pumped in a cubic meter.

The PM10 statistical values obtained during the 2 years of study are presented in Table 1. Very similar statistical values were obtained in the 2 years of study. This indicates that the concentration level variation is very similar during the two periods. The highest PM10 value detected in 2001 (212 μg/m^3) occurred on 07/05/01 and in 2002 (119 μg/m^3); this occurred on the days 02/13/02 and 02/14/02. The lowest value (4 μg/m^3) in 2001 was measured on 03/02/01 and in 2002 this happened on both 04/07/02 and 12/03/02.

Studies taking place in various industrialized cities by Houthuijs et al. (2001) in central and eastern Europe, and by Querol et al. (2002) and Viana et al. (2003) detected PM10 values in Spain in the same range variation as those observed in Vila-real.

The standard deviation is high in the 2 years, indicating that there is significant dispersion of the PM10 concentration levels obtained, observed in Fig. 2.

The PM10 concentration levels follow a similar behavior during the 2 years of study (Fig. 2). This is something already shown in the statistical values obtained. Even so, the values detected during 2001 were slightly higher than those measured in 2002.

A Siemens D-5000 X-ray diffractometer was used for the mineral analysis of the PM10 filters. The operating conditions were Cu K_α radiation, 36-kV voltage, 26-mA current, Ni filter, 2-mm incidence slit, and 0.2-mm detector slit (Gómez et al. 2002).

Table 1 Statistical values of PM10 concentration levels

PM10 (μg/m^3)		
Sampling conditions	24-h cycles at 2.3 m^3/h	
	2001	2002
Total number of collected samples	183	150
Minimum recorded value	4	4
Maximum recorded value	212	119
1st quartile (25%)	33	35
Mean	52	51
Median	48	49
3rd quartile (75%)	66	66
95th percentile	105	93
Standard deviation	31	24

Seasonal evolution

Even though no significant seasonal variation was observed, the tendency is to detect high PM10 values during the months of June and July, lows from March to May and October to December, and intermediate highs from January to February (Table 2).

The PM10 level increases during the months of June and July are possibly due to a decrease in precipitation (Fig. 3), provoking a lesser cleansing effect upon the atmosphere (Bergametti et al. 1989), and as such a greater contaminant concentration.

The highest temperatures (Fig. 4) were also recorded during these months, drying the Earth and promoting the resuspension of dolomite calcareous substrate in the area (Gómez et al. 2001).

On the other hand, the mixing layer, which is the lowest part of the troposphere where contaminants are free to move about, increases its width and facilitates the mix of air masses that originate in North Africa in ow layers (Kubilay and Saydam 1995). This is a result of the turbulence generated in the low layers of the atmosphere, appearing as long distance material intrusion episodes that bring forth a PM10 concentration increase.

During the months of January and February consistently high PM10 concentration levels were detected. This is a typical tendency in European

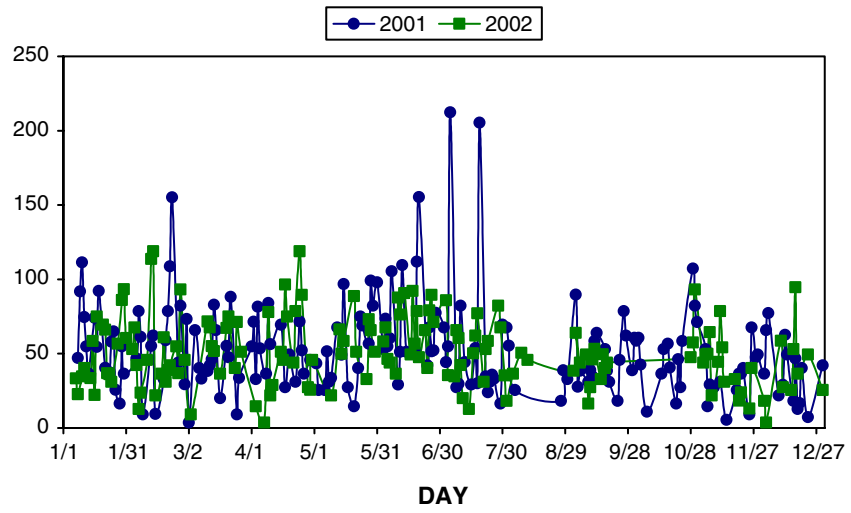

Fig. 2 PM10 levels in micrograms per cubic meter during 2001 and 2002

Table 2 Monthly PM10 values during 2001 and 2002

Month	PM10 (μg/m^3)			
	2001		2002	
	Mean	Range	Mean	Range
January	58	16–111	50	22–93
February	61	9–155	52	13–119
March	47	4–88	54	9–75
April	53	27–84	53	4–119
May	55	15–99	56	22–89
June	71	29–155	65	37–92
July	59	16–212	51	13–86
August	40	18–68	38	18–41
September	47	18–90	42	16–64
October	52	11–107	66	48–93
November	34	5–68	40	13–79
December	38	7–77	39	4–95

industrialized urban areas (Tsitouridou et al. 2003). This is due to the greater anthropogenic emissions, consequence of an energy demand increase, and greater combustion of fossil fuels for heating and other domestic or industrial uses. There is also an increase in the traffic density. Harrison et al. (1997) detected a contribution produced by traffic up to 32% in winter versus 23% in summer in the cities of the United Kingdom, making the study concentrations detected in winter and summer comparable. These same tendencies were observed by Artiñano et al. (2001) in Spanish cities and Manoli et al. (2002) in Greek cities.

Moreover, thermal inversions occur during winter, promoting an accumulation of contaminating particles in the layers of the troposphere near the Earth. This phenomenon makes the transport in these layers under these circumstances occur very slowly. As a consequence there is an increase in the concentration of contaminants (Monn et al. 1995).

During the periods of October to December and March to May the lowest PM10 levels were detected. This was due to atmospheric instability, a change in the global climatic conditions, decreasing in this way the frequency of North African air mass arrivals (decreasing the mixing layer), increasing precipitation and producing a greater washing effect in the atmosphere.

Röösli et al. (2002) also proved this type of seasonal variation in suspended particle levels' characteristic in industrialized urban areas in various Swiss cities, as did Gómez et al. (2001) in the ceramic cluster of Spain.

Weekly evolution

Another important point in the study of atmospheric contamination of a heavily industrialized urban area is the weekly evolution of PM10 concentrations.

A reduction in the PM10 concentration is clearly visible on weekends with respect to the averages occurring on weekdays. The mean reduction observed during 2001 is 50% and in 2002 it was 41%. Also detected similar mean annual reductions of 54% in urban industrialized cities.

Because of this, the conclusion is drawn that a great portion of the emission of PM10 particles into the atmosphere has anthropogenic origins, owing in great measure to the superposition of emissions coming from the human activities. When anthropogenic activities cease or decrease their rate, as is the case on weekends, the particle contamination in the area decreases.

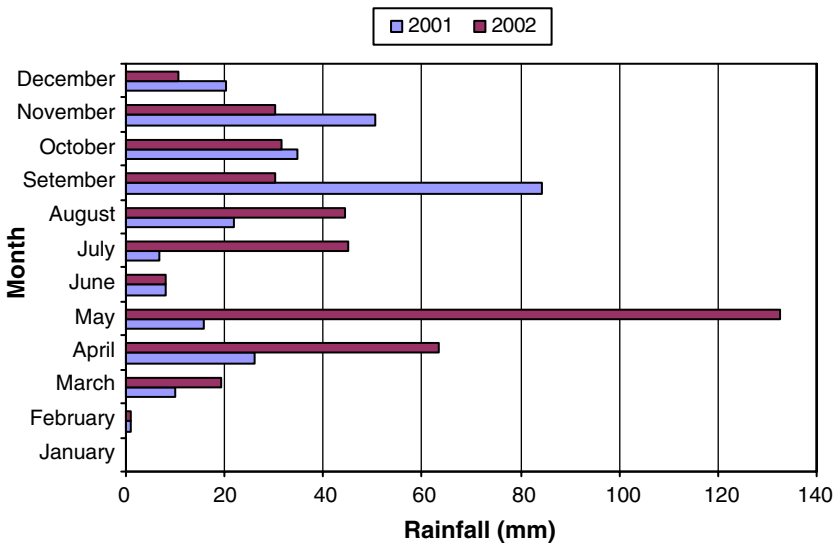

Fig. 3 Monthly rainfall (source: Vila-real City Hall Meteorological Station)

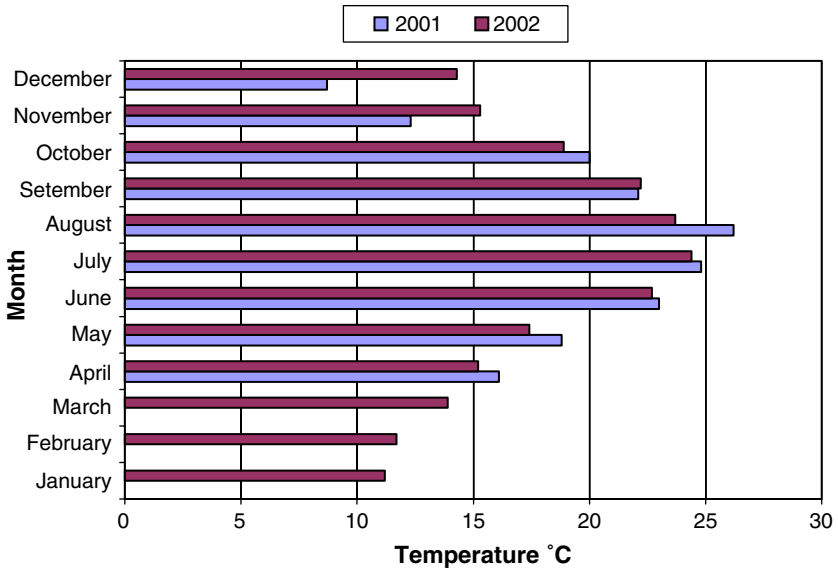

Fig. 4 Monthly mean temperatures (source: Vila-real City Hall Meteorological Station)

PM10 air quality study

The air quality values due to the PM10 contaminant are shown in Table 3. They were obtained during the 2 years of study concerning the limit values established by legislation for each year from European Directive 1999/30/CE and passed on to the Spanish state by RD 1073/2002.

Table 3 Air quality values concerning PM10 in 2001 and 2002

Period	PM10 Limit value μg/m^3	Actual Vila-real urban station value
Daily limit value[a]	70 without exceeding more than 35 times a year	36 exceedances
Annual limit value[a]	46.4	52.0
Daily limit value[b]	65 without exceeding more than 35 times a year	42 exceedances
Annual limit value[b]	44.8	51.0

[a] Values to achieve during 2001 by European Directive 1999/30/CE

[b] Values to achieve during 2002 by European Directive 1999/30/CE and Royal Decree 1073/2002

Unifying criteria to be able to compare these results, the evaluation of the obtained data referring to the established limit values for 2005 is presented in Table 4.

There is a slight improvement in air quality in 2002 (Table 4). However, if these concentration levels continue, the air quality levels will not be achieved in 2005, the end of the adaptation period of the new normative. Artiñano et al. (2001) reached the same conclusion in various Spanish cities. The days of exceeded higher values of this guide value for each day of the week is presented in Table 5.

During the 2 years of the study (2001–2002), exceedances of the PM10 guide value were mainly produced during the first days of the week, on working days. A few exceedances that occur on weekends are also observed. This is further evidence that leads us to believe that the origin of atmospheric contamination from PM10 particles is in great measure due to anthropogenic activities in the study area.

Mineralogical composition of PM10

XRD analyses show that the major crystalline phases in the ambient air particles were quartz SiO_2, calcite

Table 4 Comparison of air quality due to PM10 during the two years of study

Period	PM10 limit value μg/m^3	Actual Vila-real urban station value	
		2001	2002
Daily limit value	50 without exceeding more than 35 times a year	87 exceedances	70 exceedances
Annual limit value	40.0	52.0	51.0

Table 5 Days of exceedances of the 50 μg/m^3 guide value for each day of the week

Day	2001 (%)	2002 (%)
Monday	25.3	27.1
Tuesday	26.4	27.1
Wednesday	21.8	21.4
Thursday	19.5	15.7
Friday	1.1	0.0
Saturday	1.1	0.0
Sunday	4.6	8.6

$CaCO_3$, dolomite $CaMg(CO_3)_2$, illite $K(Al,Mg)_3SiAl_{10}(OH)$, kaolinite $Al_2Si_2O_5(OH)_4$, feldspars $(Na_3Ca)(AlSi)_4O_8$, gypsum ($CaSO_4$ $2H_2O$), and halite (NaCl).

Both quartz and clay minerals are related with the re-suspension of soil particles (Boix et al. 2001; Moral et al. 2005). Also calcite and dolomite have a natural origin in the calcareous dolomitic mountains close to the Vila-real plains (Gomez et al. 2005). There are two large limestone and dolomite quarries to the west of the city, as well as clay quarries which support the ceramic industry, the main industrial activity in the province of Castellon.

Halite is directly related to the coastal location of the sampling sites. Gypsum particles have both natural and anthropogenic origins, since the mineral is frequently present in the soils of the study area (Moral et al. 2005).

Determination of Pb concentration levels in PM10

The Pb levels in the PM10 samples were determined by ICP-MS. The equipment utilized is a PerkinElmer model Elan-6000, with a 3,600 lines/mm holographic network, 1-m focal distance, 0.26 nm/mm linear dispersion, 27.12 MHz frequency, and 1.60 kW maximum power.

The instrumental technique allows a rapid form of determining the Pb levels after dissolution of the sample. The dissolution is obtained by acid digestion in hermetic Teflon recipients.

To determine the possible Pb traces that the reagents and quartz filter fibers might contain, giving rise to sample contamination, digestions with only reagents (blank reagents) and filters without a sample (blank filters) were performed. In the validation of the results the SRM 1648 ''urban particulate matter'' pattern was used, whose composition is particulate matter of anthropogenic origin collected in an industrialized urban atmosphere and adequate for use as a reference standard.

With the values obtained in parts per billion from the aforementioned technique described, the Pb concentration levels were determined, keeping in mind the possible traces that the reagents and quartz fiber filters utilized in the collection of samples may contain. The values are expressed in micrograms of Pb in PM10 per cubic meter of air. The statistical values of the Pb obtained during the 2 years of study are presented in Table 6.

Practically, equal statistical values were obtained during the 2 years of study. There is stability in the temporal variation of the Pb concentration levels comparing the 2 years in the control area. Even if the measured values for each year are considered individually, the standard deviation obtained each year is high, even becoming a value close to the mean (Table 6). Then there is a significant dispersion of the detected values. The highest value detected in 2001 (1.04 μg/m^3) occurred on July 3, and in 2002 (1.13 μg/m^3) it was on May 9. The lowest value in 2001 (0.04 μg/m^3) was measured on August 30, while in 2002 (0.01 μg/m^3) this took place on June 16.

Pb values in the PM10 fraction of the atmospheric particulate obtained during 2001 and 2002 are present in Fig. 5.

The evolution of Pb levels is similar during the 2 years of study (Fig. 5) except during the months of May and December. The values obtained during 2002 were lower than those detected during 2001, with the exception of the same two previously mentioned months, that were higher.

Seasonal evolution

No significant seasonal evolution was observed (Table 7). The monthly mean remains practically constant during the entire year. In 2001 the highest monthly mean was detected during February and July,

Table 6 Statistical values of Pb concentration levels in PM10

Lead (μg/m^3)		
Sampling conditions	24-h cycles at 2.3 m^3/h	
	2001	2002
Total number of analyzed samples	79	99
Minimum recorded value	0.04	0.00
Maximum recorded value	1.04	1.13
1st quartile (25%)	0.14	0.12
Mean	0.26	0.25
Median	0.22	0.20
3rd quartile (75%)	0.30	0.33
95th percentile	0.60	0.61
Standard deviation	0.19	0.21

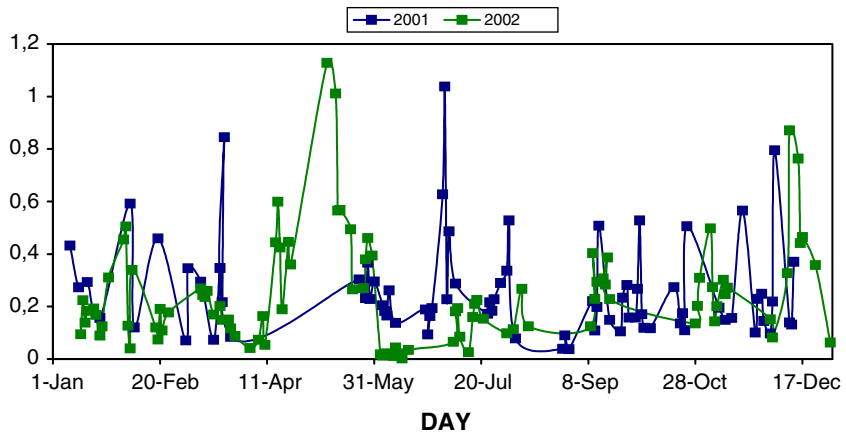

Fig. 5 Evolution of Pb levels (micrograms per cubic meter) during the 2 years of study

Table 7 Monthly values of Pb in PM10 during 2001 and 2002

Month	Lead (μg/m^3)			
	2001		2002	
	Mean	Range	Mean	Range
January	0.29	0.16–0.43	0.22	0.09–0.67
February	0.39	0.12–0.59	0.21	0.04–0.50
March	0.28	0.07–0.84	0.19	0.09–0.27
April	–	–	0.28	0.04–0.60
May	0.29	0.23–0.37	0.55	0.27–1.13
June	0.18	0.09–0.26	0.02	0.00–0.04
July	0.38	0.17–1.04	0.14	0.03–0.22
August	0.18	0.04–0.53	0.15	0.10–0.27
September	0.21	0.10–0.51	0.28	0.12–0.40
October	0.24	0.11–0.53	0.22	0.14–0.31
November	0.22	0.11–0.57	0.28	0.14–0.50
December	0.29	0.10–0.80	0.39	0.06–0.87

while in 2002 this occurred in May. The lowest monthly mean in 2001 occurred in June and August, and for 2002 this was in July and August. During the rest of the year the monthly means are similar.

Even so, it can be said that in months with maximum temperatures there are lower concentrations of Pb (about 0.15 μg/m^3), except for July 2001 and May 2002. During the months of lowest temperatures the monthly means remain stable, about 0.23 μg/m^3.

The same tendency was detected by Marcazzan et al. (2001) in Italy and Röösli et al. (2002) in Switzerland. The explication they give is linked to the origin of Pb, which has vehicular traffic as its primary contributor, from automobiles that still function with leaded gasoline, and from industrial processes. Holidays occur in summertime and so many businesses either limit or stop production in their installations, and this decreases the circulating traffic. In the study area this phenomenon is produced to a lesser degree because not all businesses there close their installations, instead working in the entire year continuously. It is because of this reason that the tendency is not detected in such a marked manner like in other areas.

On the other hand, Pastuszka et al. (2003) observed a summertime variation in Polish cities contrary to that found by the aforementioned authors. There the minimum values were detected in winter. The author explains this by saying that the population in Poland uses public transportation massively in winter instead of private firms. This reduces the circulating traffic density and decreases one of the most important sources of Pb.

The differences in the seasonal variation of Pb levels found in different countries under study assist in concluding that ambient air contamination from Pb depends in a great measure upon the habits of the population in the area measured.

Another interesting point to know is how the Pb and PM10 concentrations are related. The Pb in the samples collected in the study area represent, as a mean, some 0.6% of the total PM10 mass, with a variation range between 0.1 and 5.1%. Marcazzan et al. (2001) found in Milan's (Italy) air a mean percentage between 2 and 3%.

The evolution of Pb along with the evolution of the PM10 fraction of the particulate matter during the 2 years of study is presented in Figs. 6 and 7.

It is observed that the evolution of PM10 and Pb concentration levels is similar during the 2 years of study, except during the months of May and December, 2002, where peaks of Pb and low PM10 concentrations were detected.

Weekly evolution

In the study of the reduction of Pb concentration levels on non-working days versus working days, only the annual mean for each group of days is considered once the monthly mean levels were detected to be practically equal during all months. In Table 8 the averaged data of Pb concentration levels in PM10 are presented

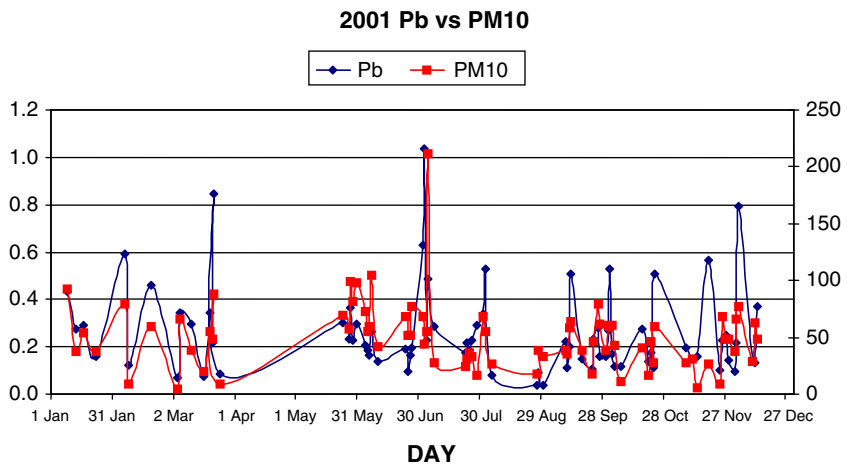

Fig. 6 Evolution of Pb and PM10 levels (micrograms per cubic meter) during 2001

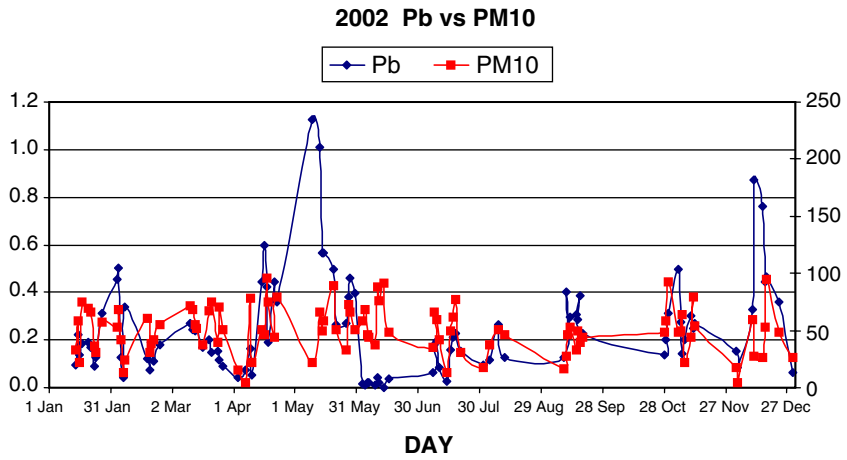

Fig. 7 Evolution of Pb and PM10 levels (micrograms per cubic meter) during 2002

corresponding to working and non-working days. The mean reduction is calculated, in percentages, of this contaminant on non-working days.

A reduction in Pb concentration levels is clearly visible on non-working days with respect to working days. The reduction is greater during 2001 than 2002. Just the same as in the case of PM10, a great portion of the Pb in the atmosphere has anthropogenic origins, and its concentration is guided by social habits. In the case of PM10 the reductions are less (50% in 2001 and 41% in 2002).

The comparisons of ''working/non-working day concentration'' ratios of monthly PM10 and Pb are shown in Figs. 8 and 9 for the 2 years of study. Larger ratios mean there are larger reductions on non-working days for the contaminant concentration studied.

It can be observed that the PM10 ratio is greater than that of Pb, except for the months of March, August, November and December in 2001; in 2002 this was in May, July and August. In general, PM10 suffers a greater reduction than Pb on non-working days.

According to studies conducted by various authors (Dulac et al. 1987; Allen et al. 2001), Pb is found in greater concentrations in the smallest atmospheric particulate fraction (< 0.61 μm, 69.4%, Fernández et al. 2001). This fraction presents greater dwelling

Table 8 Pb statistical values ($\mu g/m^3$) on working days versus non-working days

	Working days		Non-working days		Reduction	
	2001	2002	2001	2002	2001	2002
Mean	0.29	0.26	0.15	0.22	47%	15%
Max.	1.04	1.13	0.29	0.76		
Min.	0.04	0.002	0.07	0.01		

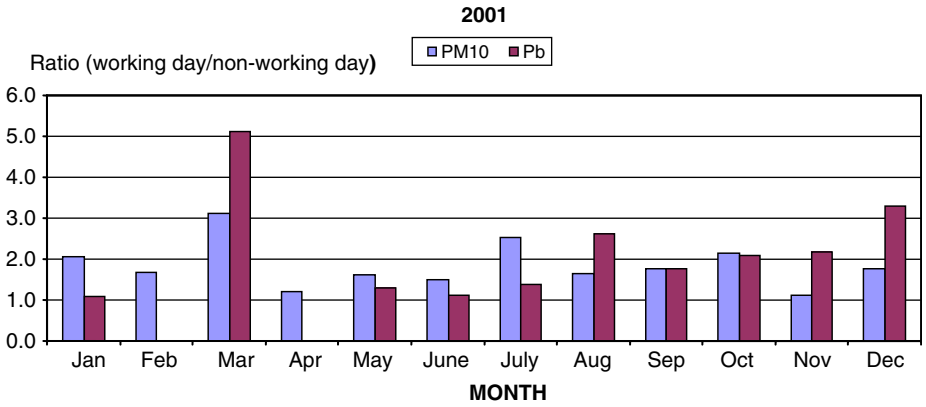

Fig. 8 Workday/non-working day comparison ratios of monthly mean concentrations of PM10 and Pb in 2001

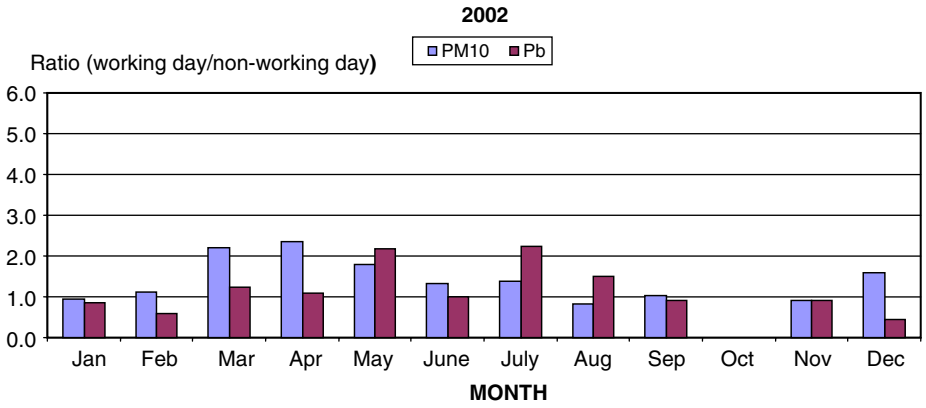

Fig. 9 Workday/non-working day comparison ratios of monthly mean concentrations of PM10 and Pb in 2002

times in the atmosphere than do larger fractions, causing Pb concentrations to be more homogenous over time and the differences between working and non-working days to be less significant.

Study of air quality regarding Pb in PM10

The evaluation of air quality regarding Pb in PM10 (Directive 1999/30/CE, RD 1073/2002) in the study area is shown in Table 9.

Unifying criteria so as to be able to compare the obtained results of Pb concentration levels (Table 10), the evaluation of the data referring to the established limit values in pending legislation for 2005 is conducted, which are more restrictive.

Table 9 Air quality values regarding Pb in PM10 during 2001 and 2002

Period	Pb limit value ($\mu g/m^3$)	Actual Vila-real urban station value
Annual[a]	0.95	0.26
Annual[b]	0.80	0.25

[a] Values to be met during 2001

[b] Values to be met during 2002

A slight improvement in air quality is observed in 2002 as opposed to 2001 when referring to this quality index. The mean annual values obtained in the 2 years of study are below the limit to comply with in 2005. The guide value exceedance days for each day of the week are shown in Table 11. These percentages again indicate that the highest Pb concentration levels are produced on working days, alluding to its origin being mainly anthropogenic.

Conclusions

A similar evolution of both contaminants (PM10 and Pb) was observed in both the years of the study, with

Table 10 Comparison of air quality regarding Pb in PM10 during 2001 and 2002

Period	Pb limit value ($\mu g/m^3$)	Actual Vila-real urban station value	
		2001	2002
Annual	0.50	0.26	0.25

Values to be met during 2005

Table 11 Days of exceedances of the 0.5 μg/m^3 guide value for each day of the week

Day	2001 (%)	2002 (%)
Monday	20.0	25.0
Tuesday	40.0	25.0
Wednesday	10.0	25.0
Thursday	30.0	12.5
Friday	0.0	0.0
Saturday	0.0	0.0
Sunday	0.0	12.5

an exception in the case of Pb in the months of May and December, 2002, where high Pb levels were detected while PM10 concentrations were low.

Although no significant seasonal variation was observed in the studied contaminants, a tendency occurred while detecting higher PM10 concentrations during the months of June and July: low values between March–May and October–December, and intermediate values in January and February. This same tendency has been observed by other authors in the European industrialized cities.

Regarding Pb, the monthly mean remains constant during the entire year, even though there is a slight tendency to detect low values along with high temperatures. Upon comparing the seasonal variation of Pb with areas studied by other authors, some or no similarities were found, depending upon the characteristics of the area studied and the habits of the people living there.

The weekly evolution tendency is clear; there is an obvious reduction in concentration levels of the two contaminants during the non-working days, which indicates their sources are primarily anthropogenic. PM10 suffers greater reductions than Pb on non-working days, this fact is due to Pb being found primarily in smaller particulate fractions. These present longer dwelling times in the atmosphere, so this concentration is more homogenous and makes the differences between working and non-working days to be less significant.

It was shown that, in the study area, Pb represents 0.6% as a mean of the total PM10 mass, with a variation range between 0.1 and 5.1%.

Taking the evaluation of the effected air quality into account, the detected Pb levels are very much below the guide values for the protection of human health, established by RD 1073/2002. As far as PM10 is concerned, the legislated quality indices established were not met during the 2 years of the study. Moreover, if recent trends are any indication of what is yet to come, neither will the requisites that this indicates be met in 2005, the end of the compliance period of the Royal Decree. In light of these results, and given that PM10 levels are primarily due to anthropogenic activity occurring in the area, institutions both public and private, as well as the population in general, must become conscious of the problems of air quality and take corrective measures to reduce the emissions of contaminants into the atmosphere in order to alleviate the effects that these could cause upon material goods, plants, animals, and most importantly, upon human health.

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