

Original

Air quality assessment in urban areas of Gipuzkoa (Spain)

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Objectives: To evaluate the air quality to which a population of 90,000 inhabitants in the province of Gipuzkoa (Basque Country, Spain) is exposed. The population resides in a periurban environment, where industrial activity (11 iron and steel foundries) is scattered among residential areas.**Methods:** Throughout 2006 and 2007, levels of particulate matter less than 2.5 mm in diameter (PM_{2.5}) were quantified and levels of trace elements in PM_{2.5} fraction [cadmium (Cd), arsenic (As), manganese (Mn), copper (Cu), chromium (Cr), nickel (Ni), iron (Fe), lead (Pb), mercury (Hg) and zinc (Zn)] were analyzed. The samples were gathered in seven sampling sites using three high-volume Digitec DAH 80 samplers. Annual and seasonal variability were evaluated for the various contaminants in each valley and PM₁₀ and PM_{2.5} samples were also gathered at the same site for a month, with the goal of analyzing the composition of trace elements in each particle size. Finally, the results were compared with those obtained from the same study area by the Basque Government Air Quality Network equipment.**Results:** The observed PM_{2.5} concentrations (12.2–28.9 µg/m³) were similar to those described in urban environments in large European cities, while mean trace element concentrations were significantly higher. The Mn levels observed in all three valleys indicated the influence of the steel and metal industries on air quality.**Conclusion:** The finding that levels of particulate matter and trace elements in the study area were similar to or higher than those found in metropolitan areas has implications for the evaluation of health risks in populations far from large population centers.

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Evaluación de la calidad del aire en medios urbanos de Gipuzkoa

R E S U M E N

Objetivo: El objetivo del estudio es evaluar la calidad del aire a la que está expuesta una población de 90.000 habitantes de Gipuzkoa que residen en un entorno periurbano, donde las actividades industriales (11 industrias siderometalúrgicas) se entremezclan con zonas residenciales en la propia trama urbana.**Métodos:** Se cuantificaron las concentraciones de partículas de 2,5 mm de diámetro (PM_{2.5}) y se analizaron los elementos traza asociados a PM_{2.5}: cadmio (Cd), arsénico (As), manganeso (Mn), cobre (Cu), cromo (Cr), níquel (Ni), hierro (Fe), plomo (Pb), mercurio (Hg) y zinc (Zn) a lo largo de 2006 y 2007. Las muestras se recogieron a partir de 3 captadores de alto volumen DIGITEL Modelo DAH 80 en 7 puntos de muestreo. Se analizó la variabilidad anual así como la variabilidad estacional de los diferentes contaminantes en cada valle. Asimismo, se recogieron muestras de PM₁₀ y PM_{2.5} con equipos similares durante un mes y en el mismo sitio para analizar la composición de los elementos traza en las diferentes fracciones PM₁₀ y PM_{2.5}. Por último, los resultados fueron comparados con los de los equipos de la Red de Calidad del Aire del Gobierno Vasco ubicados en la misma área de estudio.**Resultados:** Las concentraciones de PM_{2.5} observadas (12.2–28.9 µg/m³) fueron similares a las descritas en entornos urbanos de grandes ciudades europeas. Las concentraciones medias de elementos traza, en cambio, superaron con gran diferencia a las de las ciudades europeas. Las concentraciones de Mn encontradas en los tres valles indican la influencia de la industria siderometalúrgica en la calidad del aire.**Conclusión:** Los resultados de partículas y elementos traza encontrados en el área de estudio presentan valores similares o superiores a las áreas metropolitanas, lo cual tiene implicaciones en la valoración del riesgo en la salud de entornos apartados de los grandes núcleos de población.

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Introduction

Air pollution is an important public health problem, as environmental epidemiology studies have consistently shown. Airborne particulate matter (PM) is currently one of the principal air pollutant health concerns in urban areas. Several epidemiological studies have found consistent associations between

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exposure to ambient particulate matter and adverse health effects, including increased mortality, hospitalization for respiratory or cardiovascular disease, and respiratory symptoms and decreased lung function^{1–3}. Metal exposure, related to industrial emissions or traffic, is associated with heart rate variability⁴, increase in hospital emergency visits for respiratory conditions⁵ and increased risk of lung cancer after long term exposure⁶.

Particulate matter is emitted by a wide variety of natural and anthropogenic sources which influence its physical properties (e.g. size, specific surface, density or number-density) and chemical composition⁷. The relative proportions of the different components and the impact on human health are highly variable according to the type of sampling station^{8,9}. For example, air in industrial and metropolitan areas is more contaminated with heavy metals than air in rural areas^{10,11}. According to Nerriere et al.¹², metal traces vary in relation to particle size (PM_{2.5} or PM₁₀). Elements emitted through combustion processes (Ni, V, Pb) are present in higher proportions in PM_{2.5} than in PM₁₀¹³. The main source of particle emissions in urban environments is usually traffic, although in highly industrial areas, traffic pollution may be secondary, depending on the composition of the particles emitted by the industrial activity^{14–16}. Seasonal variability can also be observed in PM metal composition due to fluctuations in emission source¹⁷.

Particulate matter with aerodynamic diameter of less than 2.5 mm (PM_{2.5}) has been proven to be more harmful than PM₁₀, given the greater ease with which it may penetrate the alveoli^{18,19}. Time-series epidemiological studies have highlighted that exposure to PM_{2.5} leads to an increase in morbidity and mortality³. As a consequence, health protection legislation has begun to include smaller particles, an example of this being European Directive 2008/50/EC, which sets a limit of 25 mg/m³ for PM_{2.5} over the course of one year, with target compliance by 2015.

The objectives of this study were: 1) to describe seasonal variation in PM_{2.5} levels in the area of study; 2) to characterize the trace elements composition (Cd, As, Mn, Cu, Cr, Ni, Fe, Pb, Hg and Zn); 3) to analyze the relationship between PM_{2.5} and PM₁₀; and 4) to compare the trace elements in the PM_{2.5} and PM₁₀ fractions.

Methods

Study area and sampling sites

The study area, located in the province of Gipuzkoa (Basque Country, Spain), covers 519 km², including three narrow valleys. The population of the area is approximately 88,000 inhabitants, spread out between 25 small towns. The main activity in the area is the iron and steel industry, with a total of 11 companies in the sector (recorded in the Spanish Emissions and Pollutant Sources Register, EPER-2006). While the industry contributes significantly to atmospheric pollution, another source to be taken into consideration is the traffic, given that roads with high traffic density (between 10,000 and 40,000 vehicles/day) run through all three valleys.

This investigation focuses on analyzing atmospheric pollution in the form of PM_{2.5} and the trace elements associated to these particles, in seven towns with populations ranging between 1,000 and 14,000 inhabitants: Azkoitia and Azpeitia (Urola Medio Valley), Legazpia and Zumarraga (Urola Alto Valley), Beasain, Olaberria and Ataun (Oria Valley). Six of the towns shared very similar air pollution sources (steel foundry and high traffic level) and one, Ataun, was considered as urban background.

Table 1
Method validation statistics

Element	DL (µg/filter)	CL (µg/filter)	Accuracy (%)	Precision (%)
⁵³ Cr	0.57	1.89	7.5	25.7
⁵⁵ Mn	0.41	1.37	9.7	24.8
⁵⁶ Fe	5.82	19.40	4.0	10.7
⁶⁰ Ni	1.60	5.35	12.7	16.4
⁶³ Cu	1.03	2.53	7.0	8.7
⁷⁵ As	0.03	0.09	7.7	8.8
¹¹¹ Cd	0.01	0.05	16.8	28.4
²⁰⁸ Pb	0.81	2.71	4.8	5.1
⁶⁶ Zn	0.92	3.08	6.4	10.2

CL: critical limit; DL: detection limit.

Sampling

Daily PM_{2.5} and Pb, Cr, As, Ni, Cd, Fe, Mn and Cu concentrations were obtained along May 2006 and December 2007. Throughout the study period, 24-h sampling was carried out over a period of 238 days in Urola Medio Valley, 220 days in Urola Alto Valley and 451 days in Oría Valley. Hg content was analyzed in only 25% and Zn content in 17% of the samples. The remainder of the trace elements were analyzed in 100% of samples. Three Digitec DAH 80 high-volume samplers fitted with PM_{2.5} inlets were used to gather the samples. Two of the samplers were rotated monthly between the three valleys, in 6 sampling sites, in order to gather quarterly information for each valley. The third device was continuously at Beasain site, Oría Valley. Two high-volume samplers were installed in parallel in the town of Azkoitia during July 2007, in order to collect both PM₁₀ and PM_{2.5} samples.

Hourly PM_{2.5}/PM₁₀ concentrations were measured at Azpeitia and Beasain during the whole study period by means of β-radiation attenuation method equipments, provided by the Basque Government's Air Quality Network (henceforth 'Network'). In Azpeitia, the high-volume sampler was located in the same place as the Azpeitia-Network equipment and in Beasain, the distance between the two devices (high-volume sampler and Network station) was approximately 500 m. The sampling period was the same for both sets of equipment. Meteorological hourly data was obtained from the both Network's sites.

The Digitec samplers were used at a flow rate of 30.0 ± 1.5 m³/h in ambient conditions for 24 h, thus guaranteeing a quantification limit of 2 µg/m³. Particles were collected on Whatman® QMA 150-mm, quartz-fibre filters. The filters were kept in controlled conditions in the laboratory before and after sampling, which involved monitoring the ambient temperature (20 ± 1 °C) and relative humidity (50 ± 5%) for a minimum of 48 h. The particle matter was weighted using a gravimetric method on calibrated scales with maximum uncertainty of 0.09 mg (K=2).

Chemical analysis

Trace element content was determined by analysis of the filters digested with concentrated nitric acid,* at a temperature of 120 °C for 18 h. The 16% of the filter was used for digestion. The digested samples were processed using an inductively coupled plasma mass spectrometry (ICP-MS) system (Agilent 7500a) with a Babington nebulizer with high tolerance for dissolved solids and a collision cell. Table 1 displays the method validation statistics, including accuracy and precision at the quantification level. The certified reference

* Method validated by ISO17025.

material “Vehicle Exhaust Particulates,” produced by the National Institute of Environmental Studies, was used for validation.

Statistical analysis

Air quality in the study area was evaluated by comparing the mean annual values with the values set by EU Directive 2008/50/EC for PM_{2.5}, 2004/107/EC for As, Cd and Ni and by Directive 1999/30/EC for Pb, Mn, Cr and Hg were compared with the World Health Organization (WHO) proposed values²⁰.

In order to determine annual and seasonal variations of the pollutants in each valley, mean values for each year and season were calculated and compared using ANOVA. Pearson’s coefficient was used to calculate the degree of linear association between different towns located in the same valley. Four linear regression models were constructed using the data from both the Network and the study.

The dependent variable in the first model was the Beasain-Network PM₁₀ and the independent variable was PM_{2.5} from Beasain sampler. The dependent variable for the second and third models was the Azpeitia-Network PM₁₀ and the independent variables were the Network PM_{2.5} and the PM_{2.5} from the sampler, respectively. The fourth model was constructed using the Network-Azpeitia PM_{2.5} as the dependent variable and PM_{2.5} (from Azpeitia sampler) as the independent variable. Finally, the percentage composition of each trace element associated to PM₁₀ and PM_{2.5} was calculated, based on the two samplers installed in Azkoitia.

Results

Table 2 shows the mean PM_{2.5} and trace element concentrations recorded in each monitoring site over the two years of the study. The highest PM_{2.5} concentrations were recorded in the towns in the Urola Medio Valley during 2006. The limit value set by the European Community (25 µg/m³) was exceeded only by Azkoitia in 2006. In general, a fall in PM_{2.5} concentrations was observed between 2006 and 2007, which was significant in the towns of Azkoitia (28.9 µg/m³ in 2006 vs. 12.2 µg/m³ in 2007, a 58% decrease), Azpeitia (23.4 µg/m³ in 2006 vs. 13.6 µg/m³ in 2007, a 42% decrease) and Legazpi (17 µg/m³ in 2006 vs. 12.5 µg/m³ in 2007, a 26% decrease). None of the trace elements exceeded the guideline value. However, the mean Mn concentrations found in Urola Medio, in 2006, and in the Oria Valley, in 2007, are comparable to those found in industrial and not urban environments.

On comparing the mean levels of trace elements in 2006 and 2007 for each valley, a significant decrease was observed (p < 0.05) in the concentrations of all trace elements in the Urola Medio Valley and a significant increase (p < 0.05) in Mn, Pb, As and Fe concentrations in the Oria Valley. In Urola Alto Valley, Ni was the only metal to display a significant decrease (p < 0.05) between 2006 and 2007, in both towns.

Table 3 shows the seasonal variation per year in the main pollutant levels for all towns. Significant differences (p < 0.05) were observed between the seasonal means for all pollutants; the highest concentrations in 2006 were registered in autumn except for PM_{2.5} with the highest levels in winter and in 2007, the highest mean values were registered in autumn and winter, and the lowest in summer in both years. During the winter months, winds of SSW and ENE prevailed in Beasain-Network, and WSW/SW/SSW and NE/ENE in Azpeitia and during the summer months, ENE in Beasain and NE/ENE in Azpeitia.

In general, all the air pollutants gathered in the same valley showed high correlations. Levels at different sites from in Urola Medio (Azkoitia and Azpeitia) showed good correlation levels for

Table 2 Mean concentrations of PM_{2.5} (mg/m³) and trace elements (ng/m³) per year, for each town

Site	Valley	n _{year}	PM2.5 (µg/m ³)		Cr (ng/m ³)		Ni (ng/m ³)		Cd (ng/m ³)		Mn (ng/m ³)		Pb (ng/m ³)		As (ng/m ³)		Fe (ng/m ³)		Cu (ng/m ³)		Zn (ng/m ³) ^a		Hg (ng/m ³)	
			2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007	2006	2007
Azkoitia	Urola Medio	N ₂₀₀₆ = 55 N ₂₀₀₇ = 56	28.9	12.2 ^b	22.7	6.8 ^b	7.9	4.3 ^b	0.8	0.2 ^b	124	23.3 ^b	224	43 ^b	1.5	0.8 ^b	1074	227 ^b	23.6	11.2 ^b	74.1	0.1	0.0	0.0
Azpeitia		N ₂₀₀₆ = 82 N ₂₀₀₇ = 140	23.4	13.6 ^b	12.7	5 ^b	4.9	3.4 ^b	0.5	0.2 ^b	76.6	20.5 ^b	129	31 ^b	1.1	0.8 ^b	737 ^b	205	18.1	11.5 ^b	80	0.0	0.0	0.0
Zumarraga	Urola Alto	N ₂₀₀₆ = 82 N ₂₀₀₇ = 58	17.5	16.3	13.8	8.9	6.8	3.1 ^b	0.9	0.9	55.2	57.3	148.8	164	0.8	0.8	481	427.6	16.1	13.7 ^b	328.7	0.0	XX	0.0
Legazpi		N ₂₀₀₆ = 83 N ₂₀₀₇ = 109	17	12.5 ^b	4.5	3.9	2.5	2.2 ^b	0.5	0.4	23.3	16.5	56.7	34.6 ^b	0.4	0.3 ^b	240.2	186.2 ^b	7.1	9	79.6	0.0	0.0 ^b	0.0
Beasain	Oria	N ₂₀₀₆ = 241 N ₂₀₀₇ = 174	19.2	18.6	18.9	19.7	6.9	6.9	0.7	0.7	52.6	69.4 ^b	74.1	96.5 ^b	1.4	1.8 ^b	502.2	596.6 ^b	37.2	41.2	370	0.0	0.0	0.0
Olaberría		N ₂₀₀₆ = 61 N ₂₀₀₇ = 130	19.5	17.9	18.4	19.3	6.9	7.2	0.7	0.9	58.9	104.4 ^b	83.3	113.3	1.5	2.3 ^b	577.2	790 ^b	39	48.2	315.1	0.0	0.2 ^b	0.0
Ataun		N ₂₀₀₆ = 60 N ₂₀₀₇ = 105	14.6	14.4	5.6	9.6 ^b	3.1	4.2	0.2	0.3	10.2	31.2 ^b	20.3	42.1 ^b	0.4	0.9 ^b	152.1	263 ^b	7.2	18.2 ^b	171	0.0	0.1 ^b	0.0

^a Mean Zn concentration was calculated on the basis of n=30.

^b p < 0.05.

Table 3
Mean PM_{2.5} and trace elements concentrations by season

Season	N	PM _{2.5} (µg/m ³)		Cr (ng/m ³)		Ni (ng/m ³)		Cd (ng/m ³)		Mn (ng/m ³)		Pb (ng/m ³)		As (ng/m ³)		Fe (ng/m ³)		Cu (ng/m ³)	
		p	p	p	p	p	p	p	p	p	p	p	p	p	p	p	p		
2006																			
Spring	141	22.5	< 0.000	14.9	0.001	5.8	0.001	0.8	0.005	56.5	0.003	87.2	< 0.000	1.0	< 0.000	539.7	0.013	17.7	< 0.000
Summer	232	20.0		12.8		5.0		0.6		48.0		84.1		0.9		478.1		19.6	
Autumn	202	18.2		19.7		7.3		0.8		75.6		140.8		1.5		662.8		39.2	
Winter	29	23.1		14.3		7.3		0.5		49.3		87.2		1.6		492.1		37.1	
2007																			
Spring	133	16.9	< 0.000	11.8	< 0.000	4.6	< 0.000	0.6	0.015	60.3	< 0.000	73.7	0.025	1.2	< 0.000	500.8	< 0.000	24.7	< 0.000
Summer	175	12.7		4.8		2.6		0.5		27.4		68.1		0.7		252.6		11.9	
Autumn	181	15.3		12.8		5.2		0.5		51.4		67.1		1.4		408.3		28.0	
Winter	178	18.1		18.2		7.1		0.7		72.1		99.6		1.8		608.7		43	

Table 4
PM_{2.5} and PM₁₀ linear regression models

Town: ln (particles)	r	β	SE	p	Adjusted R ²
Beasain					
ln (PM ₁₀) Network	0.843				
Intercept		0.620	0.09	< 0.001	0.710
ln (PM _{2.5}) Study		0.933	0.03	< 0.001	
Azpeitia					
ln (PM ₁₀) Network	0.914				
Intercept		0.529	0.08	< 0.001	0.8469
ln (PM _{2.5}) Network		0.936	0.03	< 0.001	
ln (PM ₁₀) Network	0.886				
Intercept		0.737	0.09	< 0.001	0.785
ln (PM _{2.5}) Study		0.836	0.03	< 0.001	
ln (PM _{2.5}) Network	0.936				
Intercept		-0.102	0.07	0.175	0.936
ln (PM _{2.5}) Study		1.061	0.03	< 0.001	

all trace elements ($0.7 < r < 0.8$) except Fe ($r \approx 0.5$). In Oria Valley, a high degree of correlation was observed between Beasain and Olaberria sites (correlations of 0.8–0.9 for all metals and PM_{2.5}) and between Beasain and Ataun (r values between 0.6 and 0.7 for all trace elements, except Ni and Cd, $r=0.5$). A more moderate correlation was noted between Olaberria and Ataun (r values between 0.5 and 0.6, except Ni and Cd, $r=0.4$). The level of association between the towns in the Urola Alto Valley (Zumarraga and Legazpi) was low ($0.2 < r < 0.5$).

The percentage content of each trace element in PM₁₀ and PM_{2.5} was calculated from 2 high-volume samplers placed in Urola Medio Valley. Significant differences ($p < 0.05$) were found in the percentages of Pb, Fe, Ni and Cr between the particle sizes. The percentage composition of Pb is greater in PM_{2.5} than in PM₁₀, whilst the percentage of Fe, Cr and Ni is greater in PM₁₀. Mn and Cu, however, were distributed equally between both fractions.

Pearson's linear correlation between the Network's PM₁₀ (continuous measurement) series and the PM_{2.5} study series for Beasain was $r=0.86$, with an adjusted R² value of 0.71 (Table 4). In Azpeitia the linear correlation between the Network's two continuous samplers (PM₁₀ and PM_{2.5}) was 0.91; and between the Network's PM₁₀ and the study's PM_{2.5}, 0.87. The adjusted R² values were 0.85 and 0.78 respectively. The correlation between the Network's PM_{2.5} and the study's PM_{2.5} was 0.98, with an adjusted R² value of 0.94.

Discussion

In general, the concentrations of PM_{2.5} observed in the study area (12.2–28.9 µg/m³) were lower than those set by the

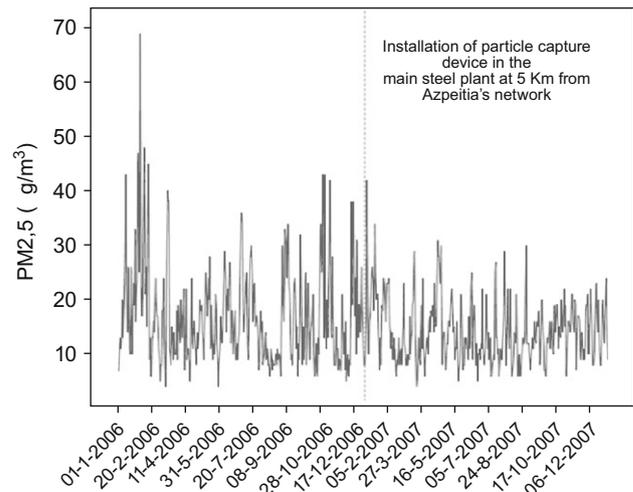


Figure 1. Azpeitia's Network PM_{2.5} time serie (01/01/2006–31/12/2007).

European Community; the limit of 25 µg/m³ was exceeded only in Urola Alto Valley, in 2006. PM_{2.5} values were lower in 2007 than in 2006 in all locations, which could be attributed to a range of factors such as, for example, more favourable weather conditions (a higher percentage of rainy days). With regard to trace element content associated to PM_{2.5} there is not any regulation. The only existing guideline values for trace elements are associated to PM₁₀ and not to PM_{2.5}. Therefore this study was based only on descriptive analysis of trace elements.

In this case, similar behaviour was observed among towns located in the same valley. The notable drop in PM_{2.5} and associated trace elements observed in the Urola Medio Valley, for example, could be due to the installation of a particle capture device in January 2007 in the main steel plant in Azkoitia and to the termination of the plant's activity in July 2007. This could also be the reason for the different seasonal variations observed for all pollutants between two years. While the distance between this plant and the sampling site in either town is considerable (1.5 km to Azkoitia and 4.5 km to the Azpeitia sampler), the prevailing SW/NE (nocturnal drainage) winds transport the pollutants throughout the valley, evidence that can be found in the high correlation between the two sites (Pearson r values between 0.7 and 0.8). Fig. 1 shows Azpeitia-Network PM_{2.5} time-series of the whole period study.

The trace element levels in Beasain, Olaberria and Ataun (Oria Valley) also show similar behaviour. In this case an increase in Fe, Pb, As and Mn concentrations was observed in the three sites between 2006 and 2007. The wind direction data explains the

The high degrees of correlation obtained between the $PM_{2.5}$ values from the high-volume samplers installed specifically for this study and the Network's PM_{10} and/or $PM_{2.5}$ values, indicate that the data gathered by both methods—gravimetric analysis and β -radiation attenuation method—are comparable in our area of investigation.

In general, the levels of particles found in the study area—a group of small towns with high levels of industrial activity—are similar to or higher than those of European cities while levels of analyzed trace elements are higher than those registered at other non-industrialized European cities. This has implications for the evaluation of health risks in environments that might be considered, in principle, as less polluted.

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