

Evolution of geochemical anomalies of arsenic in airborne particles from smelting activities: influence on air quality during the period 1999-2014

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Arsenic is a toxic element widely distributed in the Earth's Crust that affects human health. The toxicity of arsenic depends on the oxidation state and molecular form in which this element is included. Cu-smelting has been attributed as one of the main anthropogenic sources of arsenic in airborne particulate matter, and is considered as origin of arsenic contamination episodes around the world.

A temporal series study of arsenic (total concentration and speciation analysis) in atmospheric aerosol was performed over the last sixteen years (1999-2014) at urban background monitoring stations with industrial influence, in Huelva, SW Spain.

Arsenic daily mean concentrations since 1999 to 2014 have been analyzed in TSP, PM10 and PM2.5 fractions. An arsenic speciation study has been performed in TSP during 2000. Also, arsenic speciation was performed in PM10 and PM2.5 samples collected during 2001 – 2002, and 2006-2008. Representative urban background monitoring stations used in this study were Manuel Lois during period 2001-2003 and University Campus station from 2003 to actually.

Total arsenic concentration was determined in the resulting acid digestion of the samples by means of Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) (Querol *et al.* 2001). For arsenic speciation, the samples were extracted using a NH₂OH HCl solution and microwave, and the arsenic species were determined by HPLC–HG–AFS (Oliveira *et al.* 2005).

The annual mean concentration of arsenic determined in PM in the city of Huelva during 2005–2010 exceeds the mean annual 6 ng m⁻³ target value proposed by the European Commission for 2013 (EU, 2008) (Table 1). However, a reduction of arsenic and other elements and compounds related to the industrial activity of metallurgical production (e.g. Cu, Zn, Bi, Pb) has been observed from 2011 to present. Consequently, a clear trend to reduction of the arsenic concentration is manifested with a minimum value in 2014 (2.9 ng m⁻³, between January to August).

The results of arsenic species [As(III) and As(V)] analysis have shown that arsenic is concentrated in the fine size fraction (PM2.5), accounting for 61–91% of PM2.5 in PM10.

In summary, arsenic concentration in PM during 2001–2008 are some years above the target value of 6 ng

As m⁻³ proposed by the European Union, with a manifest reduction in the two last years. The implication for human health indicates that the local population in Huelva is exposed to high levels of arsenic in the air.

Table 1. Mean of PM, arsenic total and arsenic speciation concentration collected at the city of Huelva during 1999 – 2014.

Year	PM fraction (µg m ⁻³)			Arsenic (ng m ⁻³)			Arsenic (III)		Arsenic (V)	
	TSP	PM10	PM2.5	TSP	PM10	PM2.5	PM10	PM2.5	PM10	PM2.5
1999	-	35.0	-	8.9	-	-				
2000	36.0	-	-	7.7	-	-	1.2		10.4	
2001	-	38.0	19.4	-	5.4	4.3	1.2	0.9	6.5	5
2002	-	35.0	19.5	-	4.8	4.2	2.1	1.4	7.8	6.6
2003	-	35.0	21.8	-	4.5	3.6				
2004	-	42.0	26.2	-	4.7	3.0				
2005	-	37.5	19.7	-	10.6	9.2				
2006	-	37.2	17.5	-	10.1	9.1	0.4	0.4	16.1	14.8
2007	-	43.0	21.0	-	6.4	6.0	0.3	0.3	9.6	8.9
2008	-	41.0	19.0	-	7.0	4.6	0.4	0.1	14.9	10.7
2009	-	35.7	21.1	-	6.4	6.8				
2010	-	31.4	22.7	-	6.9	5.8				
2011	-	28.5	22.2	-	4.2	3.8				
2012	-	23.4	22.1	-	3.9	3.4				
2013	-	28.2	17.9	-	4.8	3.7				
2014	-	23.9	16.2	-	2.9	2.0				

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Querol *et al.* (2001). *Atmos. Environ.* **35**, 6407–6419.

Oliveira *et al.* (2005). *Anal. Bioanal. Chem.* **382**, 335–340.