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Arsenic Contamination Levels in Waters, Soils, and Sludges in Southeast Spain

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Arsenic is a trace element which can accumulate in food via contaminated soil, water or air. The atmosphere is one of the most important means by which this element enters the food chain (Nurnberg 1977), being deposited by both dry and wet precipitation.

Arsenic is a heavy metal which is present in all waters, although concentrations may differ considerably in different areas. It normally originates in the arsenopyrite found in some geological formations, but its concentrations can increase when arsenical pesticides are used on soils and crops. The mean As content in soils is generally 6 µg g^{-1} (Fabiani and Nguyen Phu Lich 1984), although this value can increase to 500 µg g^{-1} when the soils are contaminated by mineral and organic arsenical compounds which are still used as pesticides . Moreover, arsenical pesticides which increase the levels of As in soil (Wauchope and McDowell 1984), are then transferred to plants (Marcus-Wyner and Rains 1982). Plants, in turn, can act as vectors of high As concentrations to different animals (Baxter et al. 1983) and the metal finally reaches man, where its serious toxic effects can appear, given its accumulative character (Concon 1988).

The objective of this research was to determine the level of As pollution in water, soil and sludge samples from the Motril area of Southeastern Spain, to establish a base level of contamination to serve as a reference point in further studies. Particular attention was paid to As because of the toxicity of this metal, and the importance of agriculture in this area which necessitates intensive use of arsenical pesticides.

MATERIALS AND METHODS

The samples analyzed were collected in the Mediterranean coastal area of southeastern Spain (Motril) (Figure 1).

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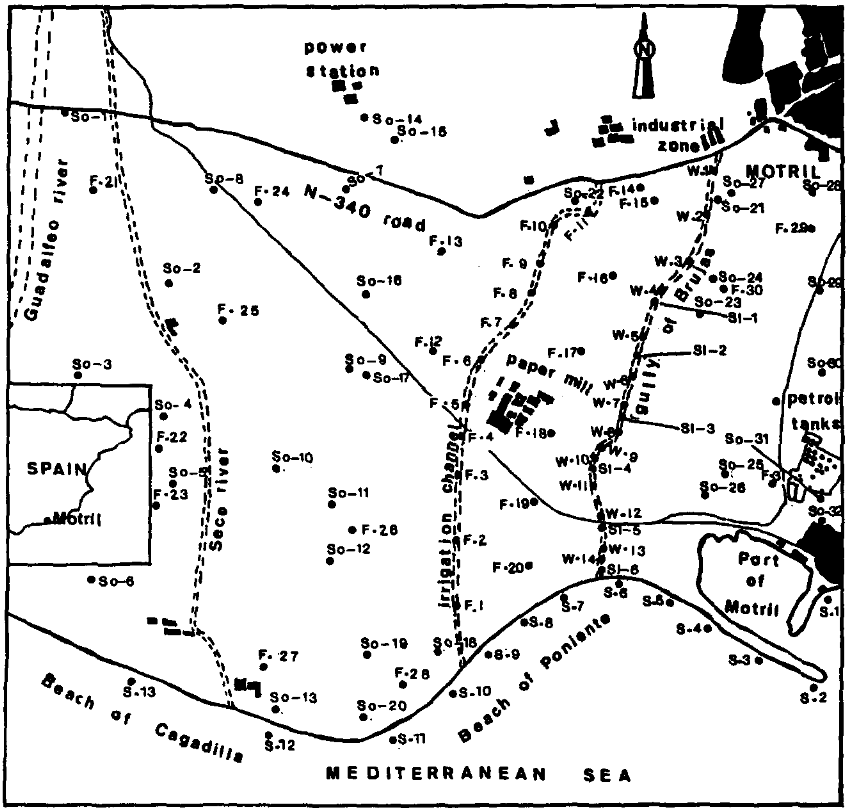

Figure 1. Location of sampling stations (F: freshwater. S: seawater. W: wastewater. So: soil. Sl: sludge).

Water samples (31 freshwater, 14 wastewater and 13 seawater) were taken just below the surface in polyethylene bottles. Samples were preserved by the addition of 2 mL of HNO_3 per 100 mL of sample. Arsenic was determined by the hydride generation technique. Previously, 1 mL of 10% (w/v) potassium iodide solution was added to 10 mL of sample to reduce As^{5+} to As^{3+} (Sinemus et al., 1981). The standard addition method was not necessary.

Thirty two soil samples were taken from the agricultural land in the area (top 10-15 cm); six sludge samples were collected from Brujas gully, in the upper layer (0-15 cm) which is expected to have the highest level of As contamination (Steinnes et al. 1989). Samples were dried in thin layers at room temperature for two weeks, passed through a 340-μm pore sieve and frozen at -18°C until analysis. For soils and sludges, we used 100 mg of dried sample and 1.5 mL of concentrated HNO_3 in a microwave acid digestion bomb, according to the method described by Huang et al. (1988). This was heated for 60 sec with the oven at full power, cooled, and then 1.5 mL of HNO_3, 0.7 mL of $HClO_4$ and 0.4 mL of H_2SO_4 were added to the predigested sample. This was then heated in the oven again for three 90 sec periods with 2 min intervals between each. The digest was cooled and, prior to filtration, the resulting solution was diluted to 25 mL with ultrapure water. It was then analyzed, using the standard addition method.

Determination was carried out using a Perkin-Elmer 2380 atomic absorption spectrophotometer equipped with a MHS-10 hydride generation system. The reductant used was $NaBH_4$ 3% in NaOH 1%. The As signal (peak height mode) was measured at 193.7 nm. The detection limit of the method, calculated according to the definition of Long and Winefordner (1983), was 0.082 ng mL^{-1} in water and 0.0445 µg g^{-1} in soil and sludge, respectively. The mean recovery obtained for spiked samples was 100.4% for water, 98.8% for soil and 100.1% for sludge. The accuracy of measured concentrations of As in NBS standard reference material (SRM 2704 Buffalo River sediment) with a certified content of 23.4 ± 0.80 µg g^{-1} gave a result of 23.5 ± 0.50 µg g^{-1} (n = 10). The relative standard deviation was normally better than 9% in the concentration range of the samples analyzed in this manuscript (Table 1).

Table 1. Precision study

Sample	Concentration[a]		RSD[b]
	---µg L^{-1}---	---µg g^{-1}---	
Soil-4	--	26.5 ± 0.56	2.13
Sludge-1	--	13.5 ± 0.79	6.31
Wastewater-12	3.43 ± 0.26	--	8.10
Seawater-4	1.24 ± 0.10	--	8.47

[a] Mean As content ± standard deviation (n = 7)
[b] Relative standard deviation (%)

RESULTS AND DISCUSSION

The mean value of As concentrations in freshwater samples taken from the irrigation channel (Figure 1) was 4.78 µg L^{-1}, whereas for the other stations it was 2.94 µg L^{-1}. Stein et al. (1980) reported a mean concentration of 9.58 µg L^{-1} (range 9.00 to 10.0 µg L^{-1}) in samples from lakes and rivers from the New York City area (U.S.A.), which is higher than the mean of 3.67 µg L^{-1} obtained here (Table 2). Chunguo and Zihui (1988) found levels of 37.77 µg L^{-1} (range 4.00 to 251 µg L^{-1}) in samples from the Xiangjiang River (Zuzou area in China) , which was also higher than the ours. However, Mann and Knobel (1988) reported a mean level of 1 µg L^{-1} for an interval between

ND (not detectable) and 4.00 µg L^{-1} in samples from the Snake River Plain aquifer (Idaho area in U.S.A.), which is below the level determined by us. On the other hand, Freitas et al. (1988) found a mean level in samples from the Tagus River (Western Spain) of 3.20 µg L^{-1}, which is very similar to ours. Moreover, an analysis of more than 700 surface water samples in the U.S.A. showed that in the range of concentrations detected (<10.0 to 1100 µg L^{-1}), 79% of the values were less than 10 µg L^{-1} (Concon 1988).

Table 2. Arsenic concentrations (µg L^{-1}) in water samples from Southeast Spain.

Sample	Number of samples	Mean	Range
Freshwater	31	3.67	0.87-9.50
Wastewater	14	2.16	0.77-4.35
Seawater	13	1.49	0.45-3.67

In wastewater samples collected from the gully of Brujas, a mean concentration of 2.16 µg L^{-1} was detected (Table 2). A mean As concentration of 3.40 µg L^{-1} was noted at stations collected downstream from the paper mill which was almost three times higher than that found upstream (Figure 2). In this sense, and by means of a statistical study using the Student t-test we found statistically significant differences ($p < 0.01$) in the As levels at these two groups of sampling stations. This could be associated with the fact that at the level of the paper mill there is a municipal wastewater outlet, which may have been responsible for the increase in As concentration downstream.

Arsenic concentrations in seawater samples were similar, with a mean value of 1.49 µg L^{-1} (Table 2). This is within the 1.00 to 8.00 µg L^{-1} range of normal concentrations of this element in seawater samples (Fabiani and Nguyen Phu Lich 1984). Ishikawa et al. (1987) found mean concentrations of 3.14 µg L^{-1} in seawater near the coast at Nakaminato (Ibaraki area in Japan), and 0.63 µg L^{-1} in the open sea at Onagawa (Miyagi area in Japan). Concon (1988) refers to several studies in which levels between 2.00 and 5.00 µg L^{-1} were found in seawater samples.

In general, the levels of As found in water were not elevated and were comparable to those determined by others.

The average As concentration in soil samples of 16.75 µg g^{-1} (Table 3) was higher than the mean value (6.00 µg g^{-1}) recorded in the earth's crust (Reilly 1980). Ure et al. (1979) reported a mean concentration of 8.37 µg g^{-1} (range

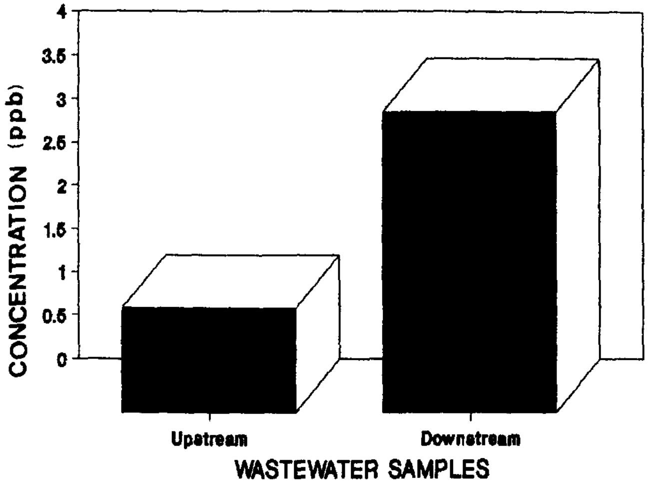

Figure 2. Average concentrations of As upstream and downstream from the paper mill in samples taken in the gully of Brujas.

4.60 to 26.0 µg g^{-1}) in Scottish soils. Wiersma et al. (1986) found a mean concentration of 11.00 µg g^{-1} in different types of soil in Holland, and also referred to other studies, which were never greater than those obtained in this study. In Southern Norway Steinnes et al. (1989) determined an As concentration of 4.00 µg g^{-1} in soils of this zone, which is lower to ours.

The average As level in sludge samples was 15.94 µg g^{-1} (Table 3). This is higher than the average As level of 9.00 µg g^{-1} found in the sediments of the Tagus River (Western Spain) by Freitas et al. (1988).

Table 3. Arsenic concentrations (µg g^{-1}, dry weight) in soil and sludge of Southeast Spain.

Sample	Number of samples	Mean	Range
Soil	32	16.75	8.75-34.5
Sludge	6	15.94	11.5-23.2

In view of the As concentrations determined in soil and sludge in this study, it can be said that they are higher than normal in non-contaminated areas, which does not suggest the existence of some degree of contamination in the areas examined, since comparison data are not normalized for grain size effects. Moreover, As levels are fairly variable in different geographic regions, even those remote from pollution. In soil, this fact could be related to the agricultural nature of the area, whose climatological conditions allow several harvests per year, thus making necessary a more intensive use of arsenical pesticides.

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