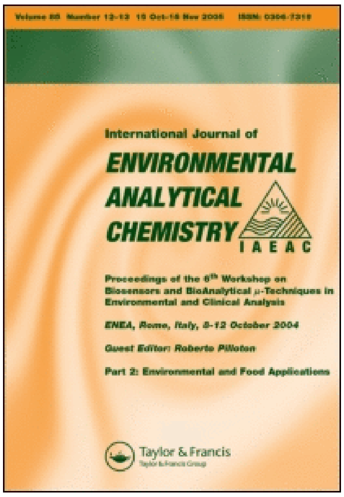

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Levels and Speciation of Heavy Metals in Waters of Valladolid

R. Pardo[a]; E. Barrado[a]; A. Arranz[a]; J. M. Pérez[a]; M. Vega[a]
[a] Deparamento de Química Analitica, Facultad de Ciencias, Universidad de Valladolid, Valladolid, Spain

To cite this Article Pardo, R. , Barrado, E. , Arranz, A. , Pérez, J. M. and Vega, M.(1989) 'Levels and Speciation of Heavy Metals in Waters of Valladolid', International Journal of Environmental Analytical Chemistry, 37: 2, 117 — 123
To link to this Article: DOI: 10.1080/03067318908026891
URL: http://dx.doi.org/10.1080/03067318908026891

Intern. J. Environ. Anal. Chem., Vol. 37, pp. 117–123
Reprints available directly from the publisher
Photocopying permitted by license only

LEVELS AND SPECIATION OF HEAVY METALS IN WATERS OF VALLADOLID*

R. PARDO, E. BARRADO, A. ARRANZ, J. M. PÉREZ and M. VEGA

Deparamento de Química Analítica, Facultad de Ciencias, Universidad de Valladolid, Valladolid, Spain

We have determined the concentration levels of some heavy metals (Hg, Cr(VI), Zn, Cd, Pb and Cu) in fluvial waters of the province of Valladolid (Duero River and its main tributaries) finding values lying on the normal ranges. We have also studied the pattern speciation of Zn, Cd, Pb and Cu in the river Pisuerga, polluted by municipal and industrial effluents, by using the speciation sheme devised by Nürnberg.

KEY WORDS: Heavy metals, speciation, voltammetry, fluvial waters

INTRODUCTION

The knowledge of the concentration in fresh waters of certain metals and metalloids, collectively known as heavy metals: Pb, Hg, Cr, Cd, Cu, Zn and others is today seen as a priority target in industrialized countries, because of their chemical toxicity for aquatic organisms and ultimately man.[1,2] These elements, in contrast with other anthropogenic pollutants, are not biodegradable and undergo a global biogeochemical cycle[3] in which the inland waters (rivers and lakes) play a main role as primary input ways. In all the cases, the heavy metals appear at trace levels (0.1–100 μg/L), but the knowledge of their total concentrations in the water samples is not usually sufficient to ascertain its polluting potential: it is necessary to carry out their speciation, i.e. to elucidate the chemical species in which they actually occur,[4]because the different chemical forms of a given heavy metal have a different behaviour with respect to their accumulation and toxicity towards the living organisms.[5]

Because of their trace level occurrence in waters, the determination of heavy metals (and logically their speciation) implies the use of sensible and reliable analytical methods, which must be also substance-specific for use in speciation studies. Among the ones actually in use, voltammetry is one of the more powerful,[6] for its inherent high sensitivity and low detection limits achieved mainly if "advanced" modes, as Differential Pulse or Stripping Voltammetry, are used. If not all heavy metals are accessible to voltammetry, the technique is very adequate

*Presented at the 18th International Symposium on Environmental and Analytical Chemistry, Barcelona, 5–8 September 1988.

for the determination of Pb, Cd, Cu, Zn, Ni, Co, Se ... , with a Hg-electrode, an Au-electrode being necessary for Hg and As.

There are two ways to carry out the speciation of heavy metals in waters: chemical modelling and experimental determination.[4] Among the schemes available fo the latter approach, the one devised by Nürnberg[7] is one of the more suitable due to the great amount of information provided by the combination of voltammetry and some simple treatments of the examined samples. The Nürnberg scheme makes an operational division in four categories, and is applicable to the speciation of Zn, Cd, Pb and Cu. The scheme is not adequate for Hg or Cr(VI), whose speciation must be carried out in a different way.

The goal of the study described in this paper is to know the overall situation of the province of Valladolid with respect to the presence of heavy metals in its waters. For it, we have first examined the concentration levels of several heavy metals in different rivers of the province (Duero River and its main tributaries). After this global evaluation, we have carried out a diagnostic study of the speciation of Zn, Pb, Cd and Cu in the waters of the main industrial and population centre of the province, i.e. the town of Valladolid. The distribution of the indicated metals in several categories, according to the Nürnberg scheme, is also discussed.

EXPERIMENTAL

1) Sampling Zone

Valladolid is the central province of the Comunidad of Castilla y León. It is crossed by the Duero River which has several minor tributaries. In the General Study, the sampling sites (A01–A11) were chosen in order to cover the input and output points of the Duero and its affluents (see Figure 1) in the province. The samples were collected in August 1987. In the Speciation Study of Zn, Pb, Cd and Cu, a more limited zone was studied (see inset in Figure 1), covering with 6 sites (NX1–NX6) the pass of the Pisuerga River through the town of Valladolid (capital of the province with several metal industries and 400,000 inhabitants) and its confluence with the Duero River. Three samplings were made during November 1987 (N1Y–N3Y, Y being the sampling site).

2) Apparatus

A Metrohm E-506 Polarecord was used in combination with a Metrohm VA-663 Stand (three electrode operation with a Static Mercury Drop Electrode, an AgCl/Ag reference electrode and a Pt counter-electrode). The Polarecord was provided with a sleeve potentiometer. Temperature was controlled by using a double-wall polarographic cell and a Tamson TC3 thermoregulator operating at 25 °C.

We also used a computer system for acquisition and processing of the polarographic data. Details of the A/D interface are given elsewhere.[8]

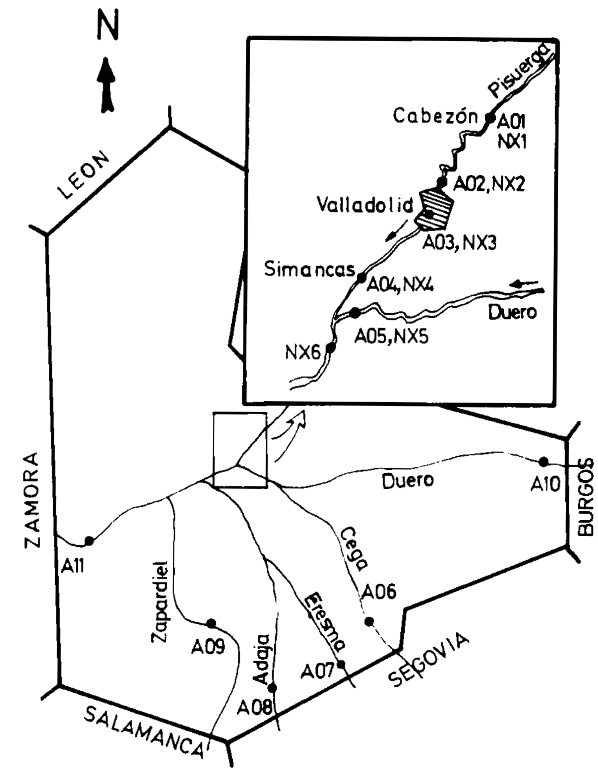

Figure 1 Schematic map of the province of Valadolid. Inset: Area of the Speciation Study. A01–A11: sites for General Study sampling. NX1–NX6: sites for speciation sampling.

3) Reagents

All reagents were of analytical grade and demineralized water was used throughout.

4) Procedures

a) Voltammetric methods Zn, Cd, Pb and Cu were always determined by means of Differential Pulse Anodic Stripping Voltammetry (DPASV). The parameters of the determination were: Potential of deposition -1.2 V, deposition time 90 s (with stirring) + 30 s (rest time) and superimposed potential +50 mV. Table 1 shows the analytical parameters of the determinations in these conditions. To avoid the problems derived from the different analytical matrix of the samples, an automatized standard addition method was used.[8]

b) General study Standard water analysis methods[9] were used to determine the chemical composition of the waters: Conductivity, pH, hardness, hydrogen car-

Table 1 Analytical parameters of the voltammetric determination (DPASV) of heavy metals

Element	*Range* ($\mu g/L$)	*Sensitivity* ($A \cdot mol^{-1} \cdot L$)	*Det. limit* ($\mu g/L$)
Zinc	0–180	0.0940	6.47
Cadmium	0– 20	0.0672	0.63
Lead	0– 30	0.0659	1.42
Copper	0– 30	0.1942	1.06

bonate, chloride, fluoride, nitrate, nitrite, phosphate, calcium, magnesium, sodium, potassium, iron and manganese. With respect to the heavy metals, Hg was determined by Cold Vapour Atomic Absorption and Cr(VI) with diphenylcarbazide. The determination of Zn, Cd, Pb and Cu was carried out as indicated in (a). All metals were determined in samples previously filtered through a 0.45 μm filter (i.e. soluble contents were measured).

c) Speciation study: (c.1) Labile species The pH of the filtered samples was adjusted at 4.7 (acetic acid/acetate buffer) and the concentrations of Zn, Pb, Cd and Cu determined by the method given in (a).

c.2) H^+ exchangeable species The pH of another water aliquot is adjusted at 2 (with hydrochloric acid), and the concentrations determined as above.

c.3) Strong inert species A water aliquot is treated with concentrated nitric and perchloric acids (1 mL of each for 25 mL of sample) gently heating to destroy the Dissolved Organic Matter (DOM). The measurement of the heavy metals was carried out after neutralization of the excess of acid and adjustment of pH until 4.7.

c.4) Species bonded to suspended matters An unfiltered sample is treated as indicated in (c.3), and the heavy metals measured after neutralization and adjustment of pH until 4.7.

Obviously each category includes all the previous ones, so in each case the actual value was calculated by subtracting the one corresponding to the category immediately above.

RESULTS AND DISCUSSION

1) General Study

The goal of this explanatory study was to determine the heavy metal concentration of the province waters. Simultaneously, a series of chemical major constituents of these waters were determined, in order to build a database for future speciation studies. For the sake of simplicity they are not shown in this paper, but all values found lay on their normal ranges.

Because of the tentative nature of this previous General Study, only dissolved concentrations of Hg, Cr, Zn, Cu, Cd and Pb were determined. The results appear

Table 2 Dissolved heavy metal contents in waters of the province of Valladolid (General Study)

Site	*Heavy metal*[a]				
	Hg	*Zn*	*Cd*	*Pb*	*Cu*
A01	—	11.4	—	16.1	1.8
A02	1.3	41.4	—	6.2	—
A03	—	22.1	1.2	3.1	—
A04	—	46.6	4.5	12.5	—
A05	—	18.0	6.5	11.8	2.3
A06	1.0	10.7	0.6	2.5	—
A07	5.1	—	—	1.0	—
A08	2.2	23.9	2.1	5.1	—
A09	5.5	55.7	5.0	17.6	14.1
A10	—	42.1	1.3	—	—
A11	—	20.5	—	1.3	1.6
Maximum allowed	1	5,000	5	50	1,500

[a]Results in μg/L.

in Table 2 (all Cr(VI) values were null and are not shown). We have also included the maximum allowed values of the analyzed heavy metals as given by the Spanish water legislation.[10] As can be observed, the global situation with respect to the examined heavy metals can be described as being within the normality, though some sampling sites presented values for Hg higher than the ones allowed. In all the cases, the situation can be explained by the low waters in the sampling sites at the time of the sampling (mid-summer in a very dry region).

2) *Speciation Study*

The sample zone for the speciation study was chosen because it represents the main industrial and populated centre of the province, having a greater probability of existence of pollution problems derived from the presence of heavy metals. Six sites (see Figure 1) were located: Point No. 1 is upstream from the town and reasonably represents the normal state of the Pisuerga River (at least for the heavy metals). Point No. 2 includes the effluents of the industries located on the river and above the town. Point No. 3 corresponds to the pass of the river through the town of Valladolid, whereas point No. 4 is located downstream and corresponds to the state of the river after the recollection of the municipal and industrial polluting effluents. Points No. 5 and 6 are both on the Duero River, before and after respectively of its confluence with the Pisuerga River.

The results found are summarized in Table 3 and Figure 2. Table 3 shows the mean global percentages of each speciation category, as well as the mean total content, for the four examined metals (Zn, Cd, Pb and Cu). Figure 2 is a development of Table 3 showing the mean percentage of each category *versus* the sampling site. All values lay within the maximum allowed, and no visible

Table 3 Summary of the mean speciation pattern of zinc, cadmium lead and copper

Speciation category	*Heavy metal (%)*			
	Zn	*Cd*	*Pb*	*Cu*
Labile	15.3	37.2	6.7	3.5
H^+ exchangeable	13.3	14.7	18.7	14.1
Strongly inert	7.0	13.8	20.1	61.2
Suspended matter	64.4	34.3	54.5	21.2
Total content[a]	106.7	1.2	9.6	13.2

[a]Mean of the Speciation Study in μg/L.

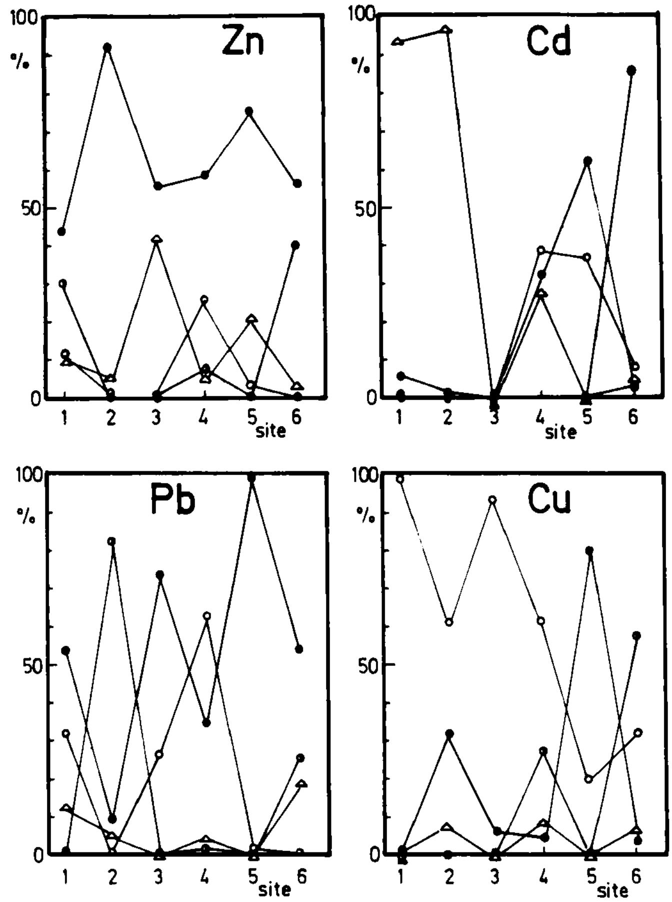

Figure 2 Mean percentage of each speciation category for Zn, Cd, Pb and Cu *versus* the sampling sites. (●) suspended matter; (○) strongly inert; (◑) H^+ exchangeable; (△) labile.

correlation was found between the speciation pattern and the sampling sites, the two rivers (Duero and Pisuerga) having similar behaviour. However, we can point out some considerations for each examined metal.

2.1) Zinc The higher concentrations corresponded to the site immediately downstream of the town (point No. 4). The metal always appeared distributed between the dissolved state and the suspended matter. In the dissolved state the main amount corresponds to the categories of labile and H^+ exchangeable species. This behaviour is in accordance with the usual trends for zinc speciation, because this metal has little affinity for the DOM, main complexing agent for the formation of strongly inert species in fluvial waters.

2.2) Cadmium In many of the examined sites, the cadmium concentrations found were lower than the detection limit of the analytical technique. In the rest of the cases the cadmium presence did not follow any fixed rule, and appeared almost totally in the dissolved state as labile species in the same way as the chemically similar zinc.

2.3) Lead All the results found were lower than the maximum allowed, the highest being the ones at site No. 4 (as for lead). With respect to its speciation, lead was found mainly in the suspended matter. In the dissolved state the preferred category was the strongly inert, due to its affinity for the DOM.

2.4) Copper This metal was found in values very inferior to the maximum legislated. Its speciation trend is similar to the one for the lead, i.e. the metal is mainly present in the suspended matter and bonded to DOM as strongly inert species, in the dissolved state. Its presence does not follow any visible trend.

We can conclude that the heavy metals do not present a serious pollution problem in the waters of the province of Valladolid, even in its more polluted zone. The pattern speciation found for Zn, Cd, Pb, and Cu is very similar to that predicted from the bibliographical sources, for similar types of waters.[5]

Acknowledgements

This work was supported by a grant from the Consejeria de Fomento of the Junta de Castilla y León.

References

1. G. G. Leppard (Ed.), *Trace Element Speciation in Surface Waters* (Plenum Press, New York, 1983).
2. J. W. Patterson and R. Passino (Eds.) *Metals Speciation, Separation and Recovery* (Lewis Pub. Inc., Michigan, 1987).
3. H. W. Nürnberg, in *Electrochemistry in Research and Development* (R. Kalvoda and R. Parsons, Eds.) (Plenum Press, New York, 1985), pp. 121–149.
4. T. M. Florence, *Talanta* **29**, 345 (1982).
5. M. Smies, in *Trace Element Speciation in Surface Waters* (G. G. Leppard, Ed.) (Plenum Press, New York, 1983), pp. 177–191.
6. H. W. Nürnberg, *Pure Appl. Chem.* **54**, 853 (1982).
7. H. W. Nürnberg, *Fresenius Z. Anal. Chem.* **316**, 557 (1983).
8. R. Pardo, E. Barrado, M. L. Tascón and M. D. Vázquez, *Quím. Anal.* (in the press).
9. *Standard Methods for the Examination of Water and Wastewater*, APHA-AWWA-WPCF (American Public Health Association, Washington, 1985), 16th ed.
10. R. D. 1423/1982 de 18 de Junio, (B.O.E. 29-6-82).