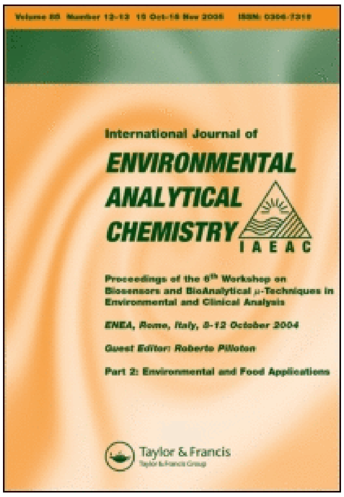

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Determination of Heavy Metal Pollution by ICP and AAS in the Suspended Matter of the Gulf of Cadiz

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DETERMINATION OF HEAVY METAL POLLUTION BY ICP AND AAS IN THE SUSPENDED MATTER OF THE GULF OF CADIZ*

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ICP, GFAAS and FAAS are appropriate techniques for the study of metal pollution related to suspended particulate matter at sea. Metal concentrations detected by these techniques in the Gulf of Cádiz are coherent with other observations.

KEY WORDS: Heavy metal, marine pollution, fluvial suspended matter, sampling, ICP, AAS

INTRODUCTION

The study of pollutant distribution and dynamics is very important in order to evaluate environmental problems. At sea, pollutant dynamics are controlled by hydrodynamics, water circulation and even by sediments dynamics. Metal pollutants have a high affinity for fine solid particles suspended in the water column. Pollution of suspended particles is a good indication of the state of the associated waters.[1] In addition, these particles work as transport agents of the pollutants associated with them. It is possible to learn about pollutant dispersion just by studying their contents in suspended particulate matter.

Normally, during oceanographic cruises, ship availability, sampling methods and filtration systems only allow one to obtain a few milligrams of suspended matter from sea water samples. For this reason it is necessary to use high resolution analytical techniques, as ICP and GFAAS, to analyze heavy metal levels of marine suspended matter.

For this kind of study we chose the Gulf of Cádiz, which is located in the Atlantic SW coast of Spain (Figure 1). Various kinds of industrial activities affect this area and its proximity to the Gibraltar Strait make it an interesting area of study from an environmental point of view.

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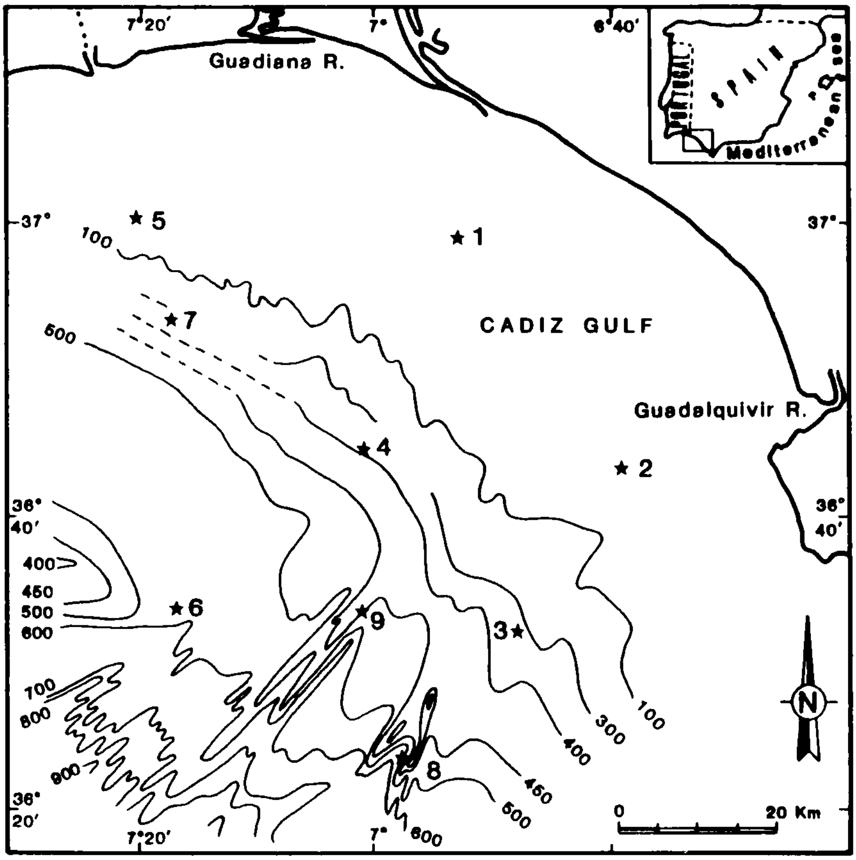

Figure 1 Map showing the Gulf of Cádiz and the locations of the stations where water was taken.

In the Gulf of Cádiz, the most important sources of material from the continent are the Guadiana River and the Guadalquivir River. The Tinto Odiel River is also a significant source. Some important mines and relatively big cities and industries are situated in the drainage basin of these fluvial systems. Heavy metal inputs from human activities are transported to the Gulf of Cádiz by these rivers. This area also receives heavy metal inputs from the industries situated along its coast. Some parts of the slope also receive waste from ocean dumping activities.

Suspended particles samples were collected and analyzed by ICP and AAS in order to (1) evaluate metal levels associated with the solid phase suspended in sea water and (2) evaluate the impact on the suspended matter of the heavy metal pollution introduced by man's activities.

EXPERIMENTAL

Water samples were taken with Niskin bottles at different depths in the water column at selected locations in the Gulf of Cádiz (Figure 1). One sample was

Table 1 List of variables statistically analyzed

Suspended matter concentration	SMC
Cobalt	Co
Chromium	Cr
Titanium	Ti
Copper	Cu
Manganese	Mn
Iron	Fe
Zinc	Zn
Lead	Pb
Nickel	Ni
Cadmium	Cd
Quartz	QUA
Feldspar	FEL
Calcite	CAL
Dolomite	DOL
Illite	ILL
Chlorite	CHL
Kaolinite	KAO

taken in waste a few minutes after it was dumped. These samples were vacuum-filtered in Millipore membranes (HAWP04700) that had been previously washed, dried and weighed. Both the volume of filtered water and the weight of particulate matter retained in each membrane were known.

Particulate matter plus the membrane was digested in 5 ml of hot (95 °C) nitric acid for 30 minutes and immediately allowed to almost completely dry. Then, 10 ml of HNO3 (10%) was added and the acid soluble extract was separated by filtration and made up to volume 50 ml. Cd, Co, Cr, Ti, Mn and Cu were analyzed by ICP, Pb and Ni by GFAAS, Fe and Zn by FAAS.

The results of the metal analysis were statistically processed along with the mineralogical components,[2] and the concentration of the suspended matter. A list of the analyzed variables is shown in Table 1. Correlation analysis and factor analysis were done. Sets of active variables of the most significant factors were interpreted.

RESULTS

Metal Distribution

Concentration of heavy metals associated with suspended particles can vary by several orders of magnitude between different stations and depths. Metal concentration for each sample is shown in Table 2. Metals do not show a generalized trend of being more concentrated at any specific depth in the water column.

In the continental shelf all the samples have relatively high concentrations of Pb, Cr and Cu and some of them also have high concentrations of Fe, Mn, Ni and Ti.

Table 2 Metal concentrations detected in the suspended particulate matter in the Gulf of Cádiz. W: waste, ud: undetectable

Area		*Continental shelf*			*Upper slope*			*Mid slope*			*W*
Station		*5*	*1*	*2*	*7*	*4*	*3*	*6*	*9*	*8*	
Seabed depth (*m*)		40	40	40	330	370	325	530	450	500	
Metal	*depth*										
Co	Surface	27	78	23	ud	ud	33	ud	ud	ud	107
	300 m							ud	ud	ud	
	Near bottom	30	45	13	71	ud	ud	ud	ud	ud	
Cr	Surface	160	250	130	210	130	260	ud	ud	ud	4280
	300 m							160	240	60	
	Near bottom	90	300	170	40	380	320	40	ud	7	
Ti	Surface	ud	100	ud	ud	240	40	30	140	120	1770
	300 m							ud	ud	ud	
	Near bottom	100	280	ud	ud	ud	90	ud	ud	65	
Cu	Surface	190	620	340	360	200	380	230	250	210	570
	300 m							390	250	280	
	Near bottom	260	470	120	250	300	250	240	ud	230	
Mn	Surface	870	2530	1200	1200	1180	840	1100	980	1320	1610
	300 m							660	140	220	
	Near bottom	880	2080	760	440	350	1130	350	340	210	
Fe	Surface	2.4	4.8	2.9	2.8	4.2	3.3	3.2	2.3	2.9	12.6
	300 m							2.1	0.9	1.0	
	Near bottom	3.8	4.6	2.6	1.8	3.1	2.4	1.1	1.8	4.0	
Zn	Surface	308	289	216	306	340	340	ud	75	ud	1420
	300 m							325	68	950	
	Near bottom	370	257	64	218	590	220	145	269	250	
Pb	Surface	210	910	340	120	500	450	ud	600	130	390
	300 m							ud	ud	ud	
	Near bottom	180	1050	360	ud	500	400	490	ud	300	
Ni	Surface	510	20	20	120	100	190	200	250	200	500
	300 m							180	ud	310	
	Near bottom	60	280	20	520	250	90	110	40	420	
Cd	Surface	ud	ud	ud	ud	ud	ud	ud	ud	ud	ud
	300 m							14	ud	4	
	Near bottom	ud	ud	12	ud	15	5	5	ud	ud	

Maximum concentration of Ti, Cu, Cr, Pb, Fe, Mn and Co were detected in front of the Tinto Odiel River mouth (Co, Cu, Mn and Fe in the surface samples; Cr, Ti and Pb in the near-bottom samples). Maximum concentrations of Ni and Zn were detected in front of the Guadiana River (in the surface level). Maximum concentration of Cd in the shelf was detected in front of the Guadalquivir River.

In the upper slope Pb, Cr and Cu concentrations are still relatively high. Maximum levels of Cr, Ti, Fe, Mn and Pb in this part of the slope were detected in station 4 (central radial); Co, Zn and Ni maximum levels were detected in station 7 (north west radial) and Cu and Cd maximum levels were located in station 3 (south east radial). Ti, Cu, Mn, Fe and Pb maximums were detected in particles from the surface waters, while Co, Cr, Zn, Ni and Cd maximums correspond to particles suspended in near-bottom waters. Maximum locations could indicate that metal dispersion from the shelf to the slope is made more by seaward diffusive processes than by coast-parallel advective processes. During the transport to the upper slope, a clear trend of metal depletion or enrichment in the particles is not observed. In general, metal levels detected in the upper slope are similar to the ones detected in the shelf, except for Ni and Cd. Ni concentration increases and Co concentration decreases with respect to the shelf concentration.

In the mid slope maximum levels of heavy metals decreases and only Fe, Mn and Ti concentration in particles suspended in surface waters are similar to the ones detected in shallower waters. Levels of Cr, Pb, Co, Cu and Zn and levels of Fe, Mn and Ti in near bottom waters decrease with respect to the values detected in the upper slope and shelf. Ni is the only element of which concentration increases seaward. In general, metal levels in the mid slope tend to decrease with respect to the ones detected in the shelf.

Products dumped on that area have high levels of Cr, Ti and Fe and moderately high levels of Co and Ni. However, it is not possible to identify any important anomaly of these elements in suspended particles of the dumping area. Ni concentration increases with respect to shelf concentration but this increase cannot be clearly linked to the waste impact. Ti concentration is relatively high in particles from the surface waters of the slope, but these values are not significantly different from the Ti concentrations detected in other parts of the slope and on the shelf. Statistical analysis of the data is studied in the next section.

Statistical analysis

Heavy metal concentrations and mineralogical components,[2] of the suspended particulate matter were statistically analyzed. A total of 18 variables were considered (Table 1). A correlation matrix showing the coefficients of correlation between all the pairs of variables is represented in Figure 2. This matrix shows very high correlation coefficients (>0.90) among Ti, Cr and Fe and lower correlation coefficients (0.50–0.70) of Co with Fe, Cr and Ti and of Mn with Co, Fe and Pb. The elevated correlation index among Ti, Cr and Fe could be defined by their high concentration in the dumped wastes, while lower correlation coefficients of Co/Fe, Cr, Ti and Mn/Co, Fe, Pb could be defined by the multi-source littoral pollution.

There is no correlation between metals and concentration of suspended matter. This means that pollution of suspended particles is not exclusively located in areas where suspended matter concentration is high, as at the mouths of the rivers. It is also important to point out that no correlation exists between heavy metals and mineralogical phases. This observation is consistent with the fact that metal ions were integrated in the suspended matter by absorption, complexation or precipitation processes that take place mainly on the surface of the suspended particles.[1] Near the coast and near the sea bed, a large fraction of the suspended matter are

	SMC	Co	Cr	Ti	Cu	Mn	Fe	Zn	Pb	Ni	Cd	QUA	FEL	CAL	DOL	ILL	CHL	KAO
SMC	1.00																	
Co	0.07	1.00																
Cr	−0.05	0.65	1.00															
Ti	−0.01	0.65	0.97	1.00														
Cu	−0.17	0.02	0.13	0.03	1.00													
Mn	0.16	0.50	0.26	0.37	−0.08	1.00												
Fe	0.04	0.71	0.90	0.93	0.13	0.58	1.00											
Zn	−0.28	0.04	−0.15	−0.18	−0.05	−0.46	−0.30	1.00										
Pb	0.36	0.40	0.15	0.20	0.28	0.67	0.37	−0.21	1.00									
Ni	−0.13	0.39	0.38	0.39	0.10	0.02	0.34	0.09	−0.10	1.00								
Cd	−0.27	−0.17	−0.03	−0.09	0.09	0.05	−0.04	−0.05	−0.12	−0.10	1.00							
QUA	−0.38	0.20	0.47	0.45	−0.03	0.15	0.42	−0.21	−0.18	0.17	0.26	1.00						
FEL	−0.10	−0.05	−0.09	−0.10	−0.02	0.02	0.00	−0.17	−0.05	−0.04	−0.09	0.05	1.00					
CAL	−0.21	−0.08	0.20	0.26	−0.15	0.06	0.14	−0.20	−0.35	0.16	0.38	0.29	−0.28	1.00				
DOL	−0.23	−0.22	−0.08	−0.14	−0.07	−0.23	−0.20	−0.04	−0.27	−0.17	−0.07	0.42	−0.14	−0.04	1.00			
ILL	0.31	−0.02	−0.28	−0.31	0.10	−0.17	−0.31	0.33	0.30	−0.18	−0.30	−0.72	−0.42	−0.58	−0.15	1.00		
CHL	0.39	0.06	−0.25	−0.25	0.05	0.05	−0.17	0.34	0.39	0.04	−0.26	−0.65	−0.35	−0.54	−0.27	0.77	1.00	
KAO	0.51	0.10	−0.23	−0.22	0.25	0.05	−0.11	0.22	0.45	−0.13	−0.24	−0.62	−0.33	−0.57	−0.30	0.76	0.83	1.00
	SMC	Co	Cr	Ti	Cu	Mn	Fe	Zn	Pb	Ni	Cd	QUA	FEL	CAL	DOL	ILL	CHL	KAO

Figure 2 Correlation matrix showing the coefficients of correlation between different pairs of variables.

Table 3 Contribution of the variables to the two first factors

Variable	*Factor 1*	*Factor 2*
SMC	−0.327	0.464
Co	0.420	0.704
Cr	0.743	0.502
Ti	0.756	0.530
Cu	−0.029	0.195
Mn	0.344	0.577
Fe	0.723	0.646
Zn	−0.361	−0.089
Pb	−0.098	0.757
Ni	0.348	0.233
Cd	0.225	−0.317
QUA	0.793	−0.221
FEL	0.149	−0.196
CAL	0.551	−0.335
DOL	0.094	−0.443
ILL	−0.797	0.390
CHL	−0.723	0.528
KAO	−0.713	0.581

polymineral composite particles[3,4] that were covered by organic and/or Fe/Mn oxy-hydroxide coatings, so metal content in suspended matter does not have to be related with any of their single mineral components although clay minerals and organic tests are highly interactive with them.

Factor analyses show obvious relations among different variables. Active variables that define a factor are the ones whose contribution is >0.5 in absolute value.[5] In this case the two first factors are statistically dominant (59% of the total variance). The first factor is defined by a set of variables (Cr, Ti, Fe, QUA and CAL) with a positive contribution and by a set of variables (ILL, CHL and KAO) with a negative contribution (Table 3). The former set of variables represent crystalline biogenic particles (silicious and carbonate biogenic tests), which are dominant in surface waters of the slope, and also represent the pollution of the waste dumped in the surface waters of the slope, which have high concentrations of Cr, Ti and Fe. In contrast, active variables with a negative contribution to first factor represent crystalline detritic particles suspended in the shelf and in the near-bottom layer (bottom nepheloid layer) of the slope, which are principally made up by clay minerals (ILL, CHL and KAO).

The sample with a maximum contribution to this factor is the one taken just when the waste was dumped. In Figure 3 it is possible to appreciate that samples with positive contribution to this factor are the ones taken in surface waters of the slope (except 4), while samples with negative contribution are the ones taken in the shelf waters and in the near-bottom and intermediate waters of the slope. Positive contribution of the particles suspended in surface waters of the slope is mainly due to the biogenic nature of them. These particles do not seem to be significantly polluted by the dumped waste.

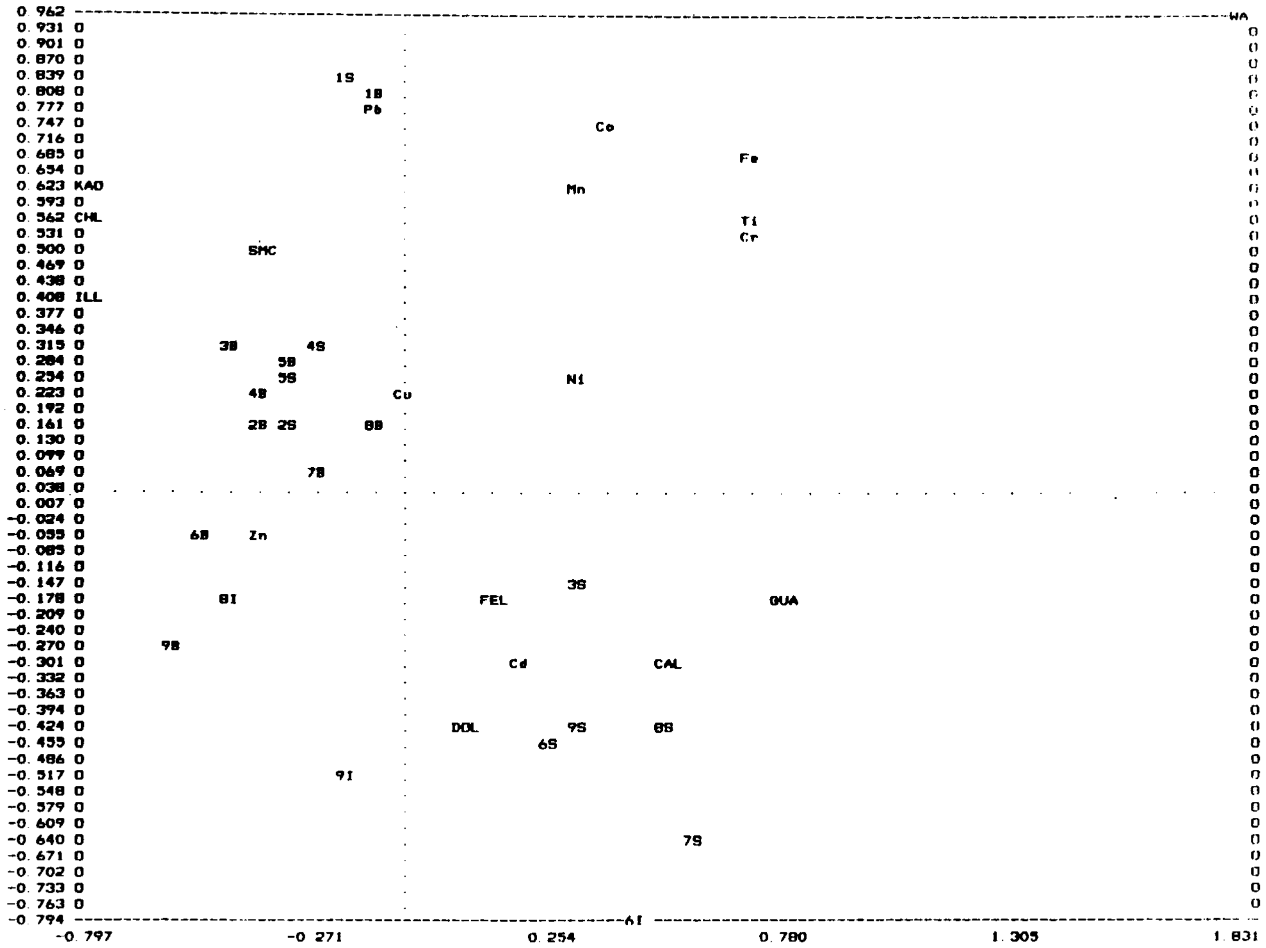

Figure 3 Binary diagram showing the distribution of samples and variables as a function of their contribution to the first factor (X-coordinate) and their contribution to the second factor (Y-coordinate).

The second factor is defined by Co, Ti, Mn, Cr, Fe, Pb, CHL and KAO. All the active variables have a positive contribution to this factor (Table 3). This group of variables represents the littoral pollution, which affects mainly the suspended particles in the shelf waters and in the near-bottom waters of the upper slope. In the shelf, the samples with the highest contribution to this factor are the ones taken in Station 1 (Figure 3), located in front of the Tinto Odiel River mouth. The samples from the shelf and the near-bottom waters of the upper slope have a positive contribution to the second factor. Samples from surface water of the upper and mid slope and from intermediate and near-bottom waters of the mid slope have a negative contribution to this factor, specially the samples from the west part of the slope, which are less affected by the Gulf of Cádiz pollution due to the Atlantic eastward flow.

CONCLUSIONS

In the Gulf of Cádiz, the littoral zone receives supplies of different metal concentrations from several source areas. The littoral pollution has been statistically defined by Co, Ti, Mn, Cr, Fe and Pb. Maximum concentrations of these elements were detected in front of the Tinto Odiel River. This is the most polluted of the sampled stations. Littoral pollution is detected in particles suspended in the shelf and in the slope waters.

Waste dumped in the mid slope area is clearly defined by the high levels of Fe, Ti and Cr. However, no important anomaly has been detected in the metals concentration of particles suspended in the dumping area waters which could be clearly associated with, dumping activities. In general metal concentrations of suspended matter from the mid slope waters decrease with respect to the ones detected in shallower waters.

Metal distribution could indicate that seaward diffusive processes are more effective in the dispersion of metals from the shelf to the slope than coast-parallel advective processes. In fact, metals seem to be dispersed along with particles independently of the SPM concentration in the water column. A clear trend of depletion or enrichment of metals in the suspended particles has not been observed at any depth in the water column.

References

1. V. Förstner and G. T. W. Wittmann, *Metal Pollution in the Aquatic Environment* (Springer Verlag, Berlin, Heidelberg, New York (1980).
2. A. Palanques, F. Plana and A. Maldonado, *Acta Geológica Hispánica* (in press).
3. J. P. Syvitski and J. W. Murray, *Mar. Geol.* **39**, 215 (1981).
4. J. R. Schubel. In: *Proc. of a Pollutant Transfer by Particulates Workshop*, Seattle (L. Kimrey and R. Burns, eds) pp. 53–142 (1982).
5. M. A. Olade, E. E. Upkong and A. H. van de Kraats, *Geol. in Mijn* **58**(3), 341 (1975).