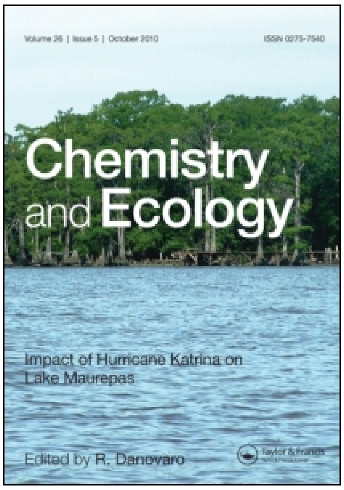

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Separation of Organic Materials and Metallic Elements from Marine Waters by the Operation of Gas-Bubble Extraction

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A laboratory experimental investigation was conducted to define the action of rising bubbles with respect to heavy-metal enrichment at the sea surface. Analytical data (HMDE—differential pulse anodic stripping voltammetry technique) show possible enrichments of organic-bound Zn, Cu, Cd and Pb at the top of a laboratory bubble-extraction column filled with water samples collected in the Southern Tyrrhenian Sea. In consideration of analogy between natural and laboratory bubble-extraction processes, laboratory results, i.e., enriched-over-original concentration ratios, make it possible to assess the intrinsic heavy-metal flotation capability in marine waters.

INTRODUCTION

A fractional part of the organic materials dissolved in marine waters escape homogeneous bulk distribution and spontaneously segregate at interfaces (adsorption). At the air–sea interface, besides convection and molecular diffusion, a particular mechanism of this segregation process is the transport at the interface of air bubbles rising through the bulk liquid (foam separation and non-foaming bubble separation) (Liss, 1975).

In addition to surface active substances, air bubbles also convey colloidal particles to (or close to) the air–sea surface layer (microflotation).

On the other hand, organic matter, either dissolved or in colloidal suspension, interacts with heavy-metal elements, by forming various types of bond (Mantoura, 1981). Thus, some heavy metals undergo the same transport processes as those characteristic of organic substances (ion flotation).

Moreover, the separation of electrical charge, involved in the act of breaking the air bubble at the sea surface, may induce a destabilization of colloidal suspensions (flocculation). The fate of bound heavy metals is a distribution between soluble and particulate organic matter. Particulate organic matter itself may also be subjected to bubble attachment (precipitate flotation).

Ultimately, the processes summarized above are responsible for several effects. Among these, there is the excess transfer (concentration or fractionation) of organic materials and metallic elements from sea water to the atmosphere, in the form of marine aerosol. Thus, for example, storms over polluted coastal areas may produce metals/organics-rich aerosols and result in objectionable inland transport of toxic substances.

Various aspects of these natural physico-chemical processes are not yet clear, and, to obtain a better knowledge, it is necessary to establish some new indices of significance together with the relevant measurement protocols. The objective is to assess the ability of marine-water constituents to enter a given process, i.e., to follow a given distribution pathway in the natural basin.

As a contribution to the studies outlined above we report, in this note, flotability data for specific metallic elements (namely, Zn, Cu, Cd, and Pb) and suggest the adoption of a global index reflecting the overall intrinsic metal-flotation capability. The measurements were made in laboratory on water samples collected in the Southern Tyrrhenian Sea.

EXPERIMENTAL

Sea-water sampling. Sampling was carried out with a polyethylene 50-dm^3 sampler, immersed at 1-m depth (Loglio *et al.*, 1981a). No chemical compound was added to the original samples, and no preliminary operation was performed.

Gas-bubble extraction of heavy-metal elements. Sea-water samples were subjected to non-foaming gas bubble extraction.

Essentially, the (whole-glass) apparatus was set up with a separating funnel, collecting vessel, at the top of a column, which functioned as a gas-bubble mobile-bed extraction chamber. A hydrodynamic trap device, between funnel and column, prevented axial dispersion or back-mixing (Loglio *et al.*, 1981b). Gas bubbles were generated with a G3 porous-glass disc, at the bottom of the column.

The sea-water volume processed was $V_A = 12.7$ dm^3 and the enriched-water volume was $V_B = 0.2$ dm^3 ($V_A/V_B = 63.5$). Pure nitrogen was allowed to flow through the extraction column for about 1 hour, with a flow rate of 5–8 dm^3/hour, at room temperature. The operation was performed in batch mode, shortly after sample collection whilst still aboard ship.

Enriched samples, as well as portions of original samples, were stored at 4 – °C temperature.

Determination of heavy-metal elements. Heavy metals were determined on unfiltered fractional parts of the original and of the enriched samples, using the differential pulse anodic stripping voltammetry technique.

The apparatus was a AMEL 741 Multipolarograph with a Hewlett Packard 7040 A X–Y recorder. The measurement cell, of a standard type, was made of glass, with a hanging mercury drop electrode (Metrohm E410), saturated Hg_2SO_4 (reference electrode) and Pt (auxiliary electrode). The support electrolyte was an acetic buffer (pH = 4.7), previously purified by mercury cathode electrolysis. The solution was stirred with a Metrohm 504 stirrer. The nitric and perchloric acids used in the wet combustion of the samples were Suprapur Merck (Cellini-Legittimo *et al.*, 1980).

RESULTS

Table I provides typical results, obtained on twelve seawater samples collected in different locations (Ischia–Procida route, 1-m depth, Southern Tyrrhenian Sea, April 1981 Ischia oceanographic cruise). The metals investigated are Zn, Cu, Cd and Pb.

In particular, the table reports either the concentration, *c*, of each

TABLE I

Heavy-metal concentration, *c*, found in water samples collected in Southern Tyrrhenian Sea (at 1-m depth, along the Ischia–Procida route—April 1981 Ischia Oceanographic Cruise): A) Original sample; B) Bubble-enriched sample.

Sample label		Zn		Cu		Cd		Pb	
		c	c_B/c_A	c	c_B/c_A	c	c_B/c_A	c	c_B/c_A
		μg/dm^3		μg/dm^3		μg/dm^3		μg/dm^3	
1	A	11	2.9	6.8	0.9	0.05	16	0.05	18
	B	32		6.4		0.8		0.9	
2	A	17	1.1	8.0	0.8	0.8	1.2	0.05	30
	B	19		6.3		1.0		1.5	
3	A	2.0	6.5	0.8	9.3	0.05	10	0.05	1.0
	B	13		7.5		0.5		0.05	
4	A	14	0.8	3.7	1.6	1.1	0.7	0.5	0.8
	B	12		5.8		0.8		0.4	
5	A	3.0	7.0	5.2	1.1	0.05	14	0.6	6.3
	B	21		5.5		0.7		3.8	
6	A	11	1.2	2.7	2.2	0.05	24	0.05	50
	B	13		6.1		1.2		2.5	
7	A	5.0	2.2	4.8	2.9	0.6	2.7	—	—
	B	11		14		1.6		—	
8	A	6.0	1.8	3.5	3.4	0.05	22	0.5	10
	B	11		12		1.1		5.2	
9	A	—	—	0.8	15	0.05	22	0.05	20
	B	—		12		1.1		1.0	
10	A	21	1.5	2.3	5.6	—	—	0.6	6.6
	B	32		13		—		4.0	
11	A	3.0	2.3	1.8	3.9	—	—	0.05	24
	B	7.0		7.0		—		1.2	
12	A	15	0.7	2.3	4.3	1.0	0.9	—	—
	B	10		10		0.9		—	

specific element, as found in the original sample (A) and in the enriched sample (B), and the concentration ratio, c_B/c_A.

The flotability percentage, F, can be calculated from these data with the relationship

$$F = \{1 - [c_A - (\Delta c \cdot V_B/V_A)]/c_A\} \times 100,$$

where V_A and V_B denote the volume of A and of B, respectively, and Δc the excess concentration of B over that of A.

The tabulated values are affected by the rather large error inherent in the manipulation of heterogeneous samples, containing particles of various sizes (this error dominates the measurement error, $\delta = 10\%$). However, with respect to metal enrichment, we can consider the ratio values $c_B/c_A < 2$ meaningful (hence, values $c_B/c_A < 2$ indicate no metal stripping).

As can be seen in the table, metals were definitely enriched in 25 of 43 cases. In general, the amount of metal stripped was not more than 40%, but in one case reached 80%. Each element is extracted to a different extent from different samples. Moreover, the enrichment varies from one element to another, even in the same sample.

CONCLUDING REMARKS

Heavy metals may be enriched to different extents when different seawater samples are subjected to the laboratory operation of non-foaming gas-bubble extraction.

Bearing in mind the operating procedure used, the enrichment concentration observed derives from the contributions of all the unit processes noted in the introduction, viz., foam separation, non-foaming bubble separation, microflotation, ion flotation, flocculation, precipitate flotation.

Since no chemicals are added, naturally-occurring substances, and man-made substances, if any, are enriched solely by virtue of the actual inner metal-binding/flotation/adsorption properties of the natural system.

The laboratory processes used are analogous to those acting in nature, and all are driven by rising bubbles, which are known to be ubiquitously present in the oceans.

The laboratory operation described does not simulate natural conditions exactly, but the concentration-ratio value, c_B/c_A (or the flotability-percentage value, F) certainly reflects the overall intrinsic capacity for enrichment of the subsurface layer by the element investigated. Thus, c_B/c_A (or F) may be assumed as a global rationale measure or index for the assessment of surface aspects of marine-water quality.

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