

C.M. 1980/E:38

Trace metals (Zn, Cd, Pb, Cu, Sb and Bi) levels (ionic forms and dissolved organic complexes) in the Southern Bight (Belgian coast)

Technique to avoid contamination during sampling and filtration
and to improve representativity

G. GILLAIN, C. DUJCKAERTS and A. DISTECHE

Laboratory of Analytical Chemistry and Laboratory of Oceanology (Chemistry Unit)
University of Liège, Belgium

Trace metals (Zn, Cd, Pb, Cu, Sb and Bi) levels (ionic forms and dissolved organic complexes) in the Southern Bight (Belgian coast)

Technique to avoid contamination during sampling and filtration
and to improve representativity

G. GILLAIN, C. DUYCKAERTS and A. CISTECHE

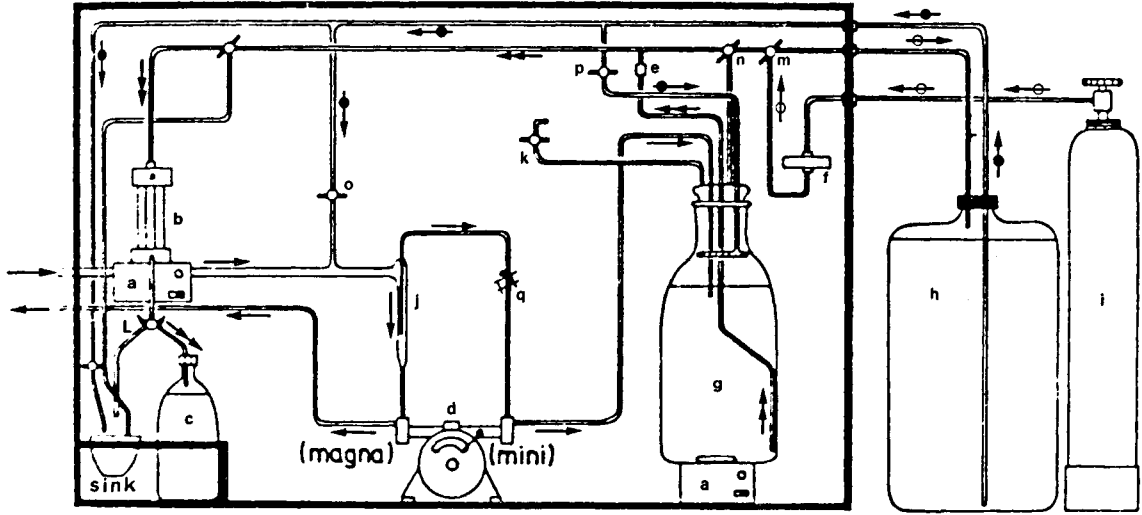
Laboratory of Analytical Chemistry and Laboratory of Oceanology (Chemistry Unit)
University of Liège, Belgium

1.- Optimization of sampling methodology - The problem of contamination and representativity

The difficulties in obtaining non contaminated and representative samples of sea water have been outlined in a previous paper where a short description of the sampling apparatus we recommend can also be found (Gillain et al. (1979a)). The principle is to continuously collect small samples of water from a very large volume delivered by a peristaltic pump and screened from atmospheric pollution besides to try and avoid all possible contamination due to the vessel or any other cause during manipulations. The sampling kit has further been improved and will now be described in more detail together with the precautions to be taken to use it properly.

1.1.- DESCRIPTION OF SAMPLING AND FILTRATION KIT

The kit is schematically represented in fig. 1. It is protected by a wooden box with a lid. The total weight is only 25 kg and the floor space required reduced to a minimum (80 × 70 × 35 cm). Conical flexible polyethylene connectors allow to connect the nitrogen supply, a tridistilled water (Milli-Q) tank and a collector for waste water.



- | | | |
|-----------------------|-------------------------------|-------------------------|
| a) magnetic stirrer | d) peristaltic pump | g) unfiltered sea water |
| b) filtration unit | e) one way valve | h) tridistilled water |
| c) filtered sea water | f) millipore filter (0,22 μm) | i) nitrogen tank |

- ← Sampling circuit
- ← Filtration circuit
- ← Gas circuit
- ← Rinsing circuit

fig. 1.
Diagram of seawater sampling and filtration kit

1.1.1.- THE SAMPLING CIRCUIT (→ in figure 1)

The sampling circuit consists in a double peristaltic pump simultaneously driven by a speed controlled motor and 20 m PVC tube. Speed reducers are fitted on each sides of the motor shaft. At one end a "Magna" pump is driven with a suction height of 9 m and a maximum output of 5 to 6 l/min. The other pump is a "Mini" type, supplying 400 to 500 ml/min depending on the diameter of the internal flexible tubing. It takes water in front of the large pump at point (j) as shown in figure 1.

A small volume of water is thus continuously drawn from the large main flow, the rest of which is returned to sea. The sampled water is stored in a graduated Pyrex container (5 l) [(g) in figure 1], equipped with a magnetic stirrer.

1.1.2.- THE FILTRATION CIRCUIT (→ in figure 1)

The collecting container (g) is fitted with a ground glass stopper with five passages allowing to connect the container to the atmosphere (k) or to the 4 following circuits :

1. the sampling circuit ("Mini" pump)
2. the filtration circuit starting at the bottom of the container
3. the pressurized gas circuit
4. the rinsing circuit from the tridistilled water bottle.

The filtration unit (b) is made from a Pyrex glass tube 120 mm long and 47 mm ϕ fitted in between two PVC lids with silicone seals. The lowest one contains a fritted glass plate supporting the filter. The upper one can easily be removed, sliding upwards, which allows to change the filter. It is fitted with an air-outlet vane and a magnetic rod is suspended to it a few millimeters above the filter to retard clogging by vigorous stirring.

The sea water filtered under pressure (nitrogen) is continuously collected in a polyethylene flask (c) which is used to store the sample. Its stopper has an air-outlet. Excess water is sent to the sink by vane (L).

1.1.3.- THE GAS CIRCUIT (⊖→ in figure 1)

Nitrogen from the pressure tank (i) is released at 0,3 kg/cm² and is filtered through a 0,22 μm Millipore filter (f) to remove dust to reach vanes (m) and (n). Vane (m) sends the gas in the distilled water reservoir for rinsing or to the filtration unit. Vane (n) puts the filtration unit under pressure either directly or through the Pyrex collector (g). This is useful when clogging occurs to empty the filtration unit in order to change the filter. A one way security valve (e) then avoids pressure to be applied to collector (g).

1.1.4.- THE RINSING CIRCUIT (●→ in figure 1)

Tridistilled water (Milli-Q) can be distributed from tank (h) either to the sampling circuit (vane o) or the filtration circuit (vane p). One will notice that the distilled water goes into collector (g) through a sprayer to increase cleaning efficiency and minimize the amount of water needed.

1.2.- CLEANING, SAMPLING, FILTERING, RINSING, STORAGE

1.2.1.- CLEANING

The sampling and filtration kit including the 20 m PVC tube as well as the bottles which will contain the final sea water samples are treated during a week with 6 N HCl. Large amounts of "Milli-Q" water is used for rinsing. The kit is kept filled with tridistilled water until used. The filters (Millipore 0,45 μm) are kept in diethylenetriamine penta-acetic acid (DTPA) 10⁻² M, pH 6 (complexing agent); they are rinsed several times with large volumes of "Milli-Q" water, dried at 50°C, weighed and kept in Petri boxes. Cleaning efficiency is severely followed analytically.

1.2.2.- SAMPLING

Sampling from an oceanographic vessel even with a sophisticated system as described above, means to try and avoid all causes of contamination due to the ship herself. A sea area will be chosen where the ship has not yet been; one will try and find

the best location to put the PVC sampling tube overboard, away from outlets of all sorts, propellers, etc ; the sampling will be carried out with the boat adrift and on the lee side to meet continuously renewed water masses. A telescopic mast 4 m long will be used to hang the tube as far as reasonably permitted from the boat ; the inlet of the sampling tube (protected by a stopper when not used) will be kept at about 2.5 m below the keel (that is at 5 m in our case) ; a lead lest inside a leak proof PVC container is used to keep the tube at depth.

Pumping through the kit, emptied from its distilled water and flushed with nitrogen, is then started the first liters being returned to the sea by closing clamp (q) (see fig. 1). After 10 minutes the collecting container (g) is filled, the pumps are stopped and tridistilled water is sent into the sampling circuit to eliminate residual sea water. The PVC sampling tube is carefully stoppered.

1.2.3.- *FILTERING*

Nitrogen is sent into container (g) where the sea water is continuously stirred and the filtration chamber is filled. Stirring above the Millipore filter is started. Filtration then proceeds under pressure when one opens vane (L) to remove the first ml towards the sink or next to fill the sample storage polyethylene bottle (c). 1 l water in this bottle is in fact representative of 60 l sea water.

Even when the bottle is full filtration is continued until clogging to collect the greatest possible amount of suspended matter, excess water being sent to the sink. The filter is then removed as described above under continuous nitrogen flow to avoid any contamination.

1.2.4.- *RINSING*

After filtration, rinsing is carried out first at the level of the sampling circuit with the pumps in action for a few seconds, continuing with the collecting container and finally with the filtration circuit. After rinsing, a new filter is introduced again under nitrogen flow. The system is then ready for a new operation.

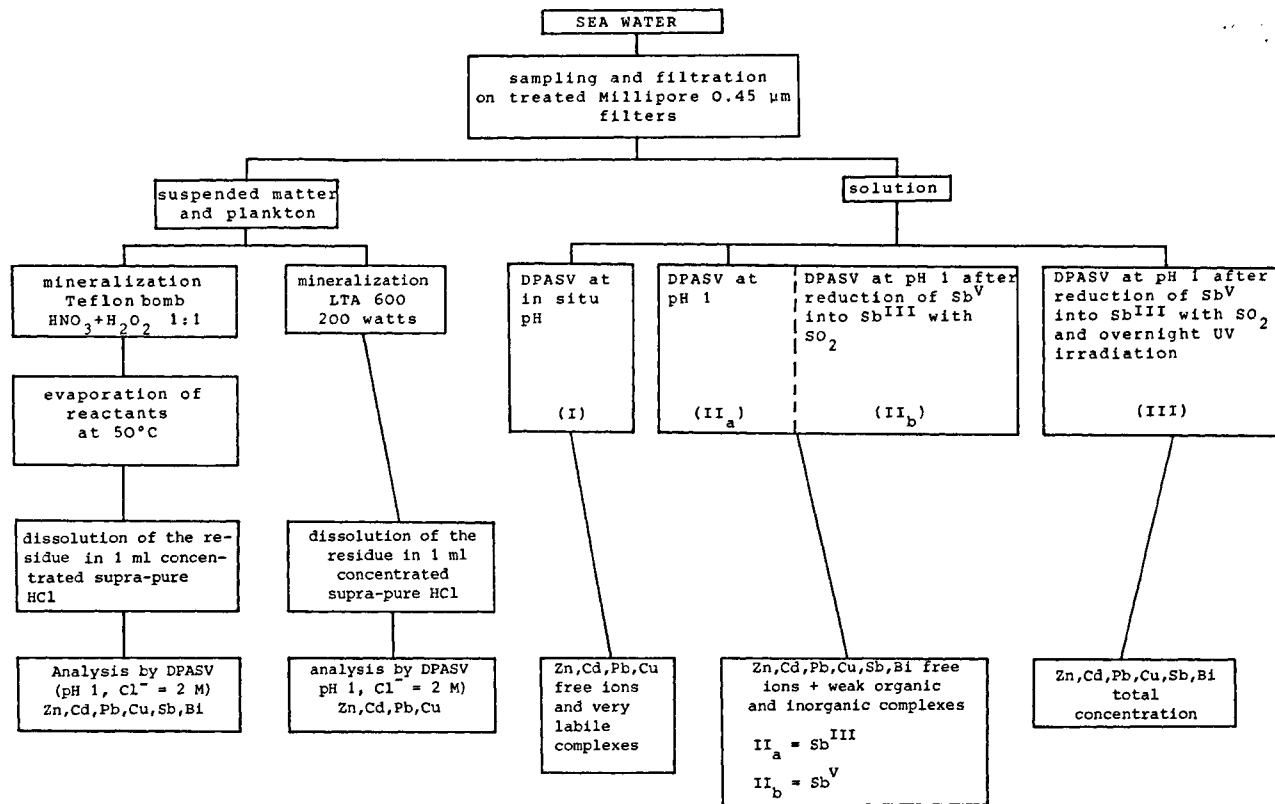


fig. 2.

Analytical protocol to analyse Zn, Cd, Pb, Cu, Sb and Bi in suspended matter, plankton and to study speciation of metals in solution in the water column.

LTA : low temperature ashing (activated O₂).

1.2.5.- STORAGE OF SAMPLES

The 1 l sea water samples are immediately deepfrozen at - 20 °C and thawing is carried out in the laboratory just before analysis.

2.- Analytical methods

Differential pulse anodic stripping voltammetry with hanging mercury drop electrode (DPASV) is used as described earlier (Gillain et al. (1979a,b)). The full analytical protocol is given in fig. 2 but we will in this paper only describe results regarding ionic forms and soluble organic complexes.

3.- Results

The results described in this paper refer to samples collected in October 1979 during a surveyance cruise along the Belgian Coast to detect the distribution of trace metals, the effect of coastal discharges, dumping, rivers (mainly the Scheldt with its estuarian regime), the importance of speciation. The stations are located as indicated in fig.3 along grid lines perpendicular to the coast numbered from 1 to 5.

Going back to the general analytical protocol (fig. 2) it is easy to see that the results expressed in $\mu\text{g}/\text{l}$ given by steps (I), (IIa - IIb) and III, allow to estimate the different species of dissolved Zn, Cd, Pb, Cu, Sb and Bi in sea water passing through Millipore 0.45 μm filters.

The data are given in table 1. The spatial distribution is illustrated by figures 4 to 9.

The fraction detected in step I at *in situ* pH refers rather arbitrarily to ionic species since very labile complexes (probably inorganic) can also be involved. It concerns Zn, Cd, Pb and Cu. Sb and Bi cannot be measured because of hydrolysis of their salts at *in situ* pH.

Table 1
Concentration in $\mu\text{g/l}$

Stations	Zn			Cd			Pb			Cu			Sb			Bi		
	<i>in situ</i> pH	acid pH	UV	<i>in situ</i> pH	acid pH	UV	<i>in situ</i> pH	acid pH	UV	<i>in situ</i> pH	acid pH	UV	acid pH	acid pH + SO ₂	UV + SO ₂	<i>in situ</i> pH	acid pH	UV
	I	II _a	III	I	II _a	III	I	II _a	III	I	II _a	III	II _a	II _b	III	I	II _a	III
11	0.15	0.95	2.97	0.12	0.18	0.30	<0.05	1.10	2.21	0.11	1.05	1.30	n.d.	0.17	0.17		n.d.	n.d.
21	0.21	2.70	4.15	0.03	0.08	0.14	0.22	1.00	2.20	0.20	1.14	1.85	n.d.	0.08	0.10		0.14	0.20
31	0.10	1.10	3.37	0.02	0.14	0.25	0.07	0.40	1.13	0.10	0.25	0.82	n.d.	0.12	0.14		n.d.	n.d.
41	0.10	0.70	6.37	0.02	0.05	0.27	<0.05	0.61	1.03	0.06	0.12	0.70	n.d.	0.12	0.12		n.d.	n.d.
12	0.50	1.10	6.10	0.05	0.05	0.20	0.10	0.30	3.15	0.15	0.40	1.65	n.d.	0.10	0.15		n.d.	n.d.
22	0.75	1.90	3.40	0.08	0.08	0.16	<0.05	0.30	1.40	0.25	0.60	1.20	n.d.	0.14	0.20		n.d.	0.08
32	0.36	1.30	2.40	0.04	0.05	0.10	<0.05	0.35	1.00	0.10	0.40	0.80	n.d.	0.10	0.15		n.d.	n.d.
42	0.10	2.25	4.16	0.02	0.06	0.13	<0.05	0.36	3.02	<0.10	0.10	0.50	n.d.	0.12	0.15		n.d.	0.07
13	0.50	1.23	2.38	0.06	0.10	0.26	0.14	0.75	1.31	0.20	0.40	0.80	n.d.	0.17	0.25		n.d.	< 0.05
23	0.30	1.50	2.05	0.04	0.04	0.06	0.11	0.80	1.22	0.60	0.90	1.20	n.d.	0.12	0.18		n.d.	n.d.
33	0.50	2.12	3.10	0.05	0.10	0.15	0.16	0.80	1.80	0.30	0.80	1.60	n.d.	0.05	0.08		n.d.	n.d.
43	0.20	1.20	3.50	0.05	0.08	0.18	0.08	0.20	1.60	0.06	0.20	0.60	n.d.	0.15	0.25		n.d.	n.d.
14	0.54	1.42	1.70	0.08	0.08	0.10	0.16	0.44	1.20	0.30	0.84	1.32	n.d.	0.26	0.30		n.d.	< 0.05
44	0.30	2.00	4.30	0.03	0.03	0.05	<0.05	0.30	1.80	0.10	0.30	1.20	n.d.	0.18	0.28		n.d.	n.d.
15	0.80	4.50	7.90	0.02	0.08	0.18	<0.05	1.20	1.80	0.12	1.50	2.90	n.d.	0.20	0.23		n.d.	0.10
25	0.30	5.08	5.80	0.05	0.06	0.13	0.07	1.54	3.90	0.54	1.12	1.90	n.d.	0.25	0.26		n.d.	0.08
35	0.50	3.65	6.70	0.02	0.10	0.16	0.08	1.23	3.40	0.15	0.80	0.80	n.d.	0.16	0.20		n.d.	n.d.
45	0.30	2.25	7.18	0.02	0.05	0.14	0.08	1.88	3.23	0.15	0.80	1.42	n.d.	0.10	0.25		n.d.	n.d.

n.d.: below detection limit (< 0.05 $\mu\text{g/l}$)

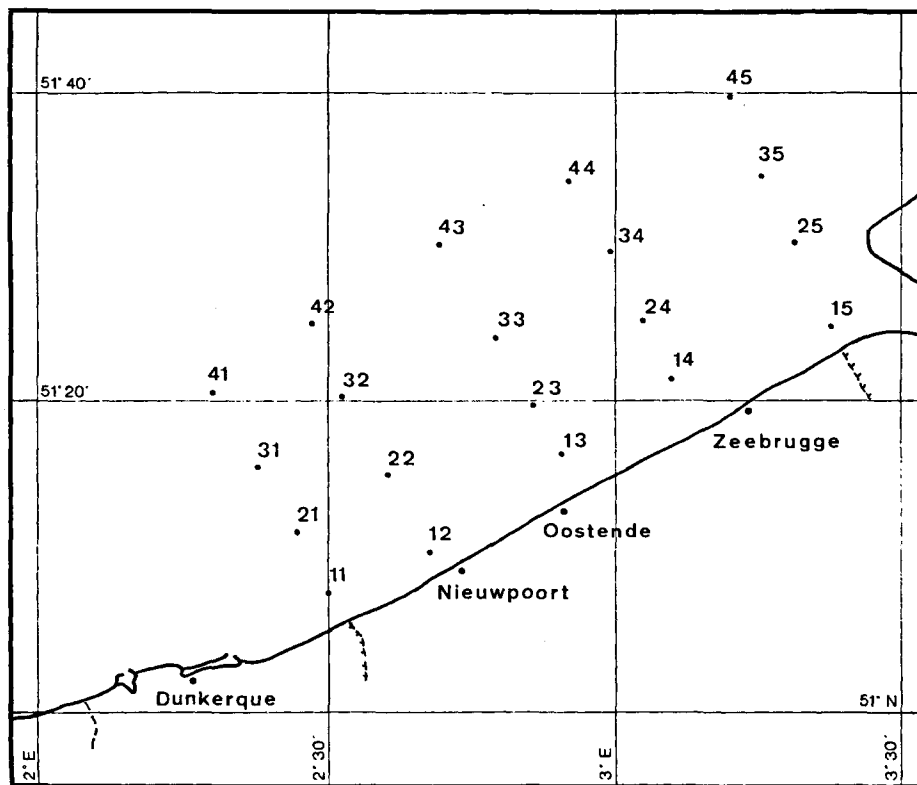


fig. 3.

Location of sampling stations in the North Sea (Belgian coast)

The difference between the results obtained in steps IIa (acid pH) and I corresponds to weak complexes. In the case of Sb and Bi, the ionic form cannot be dissociated from weak complexes, IIa gives the sum of the two forms.

Regarding Zn, Cd, Pb, Cu and Bi the IIB step gives after treatment by SO_2 and DPASV at acid pH values identical to those obtained in step IIa. But the IIB data for Sb correspond to the sum of Sb^{III} and Sb^{V} .

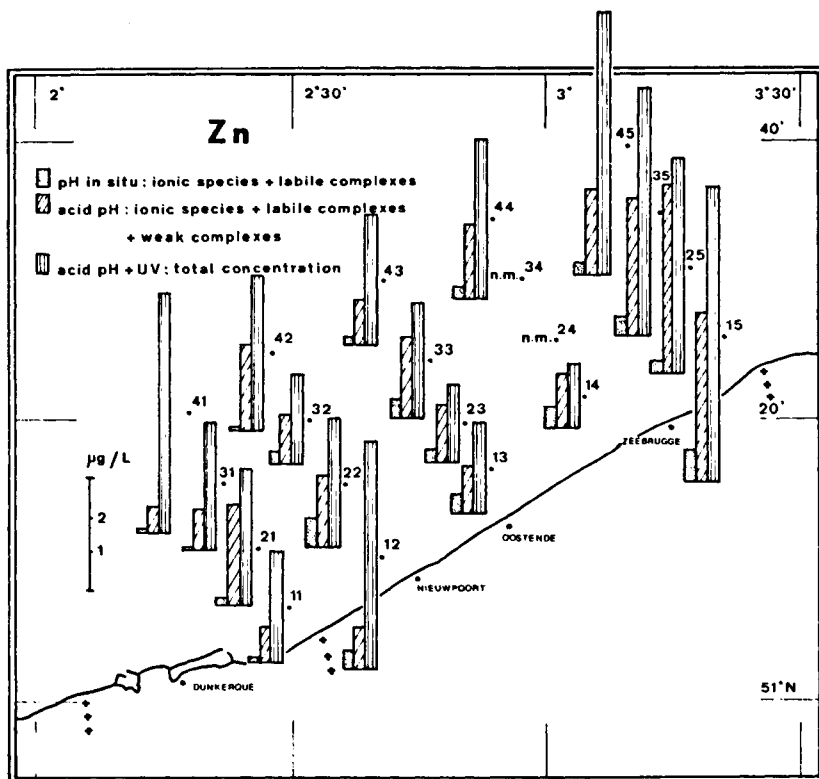


fig. 4.

Dissolved metal concentration
Distribution of Zn along the Belgian coast in October 1979

Finally step III (SO_2 + UV treatment, analysis at acid pH) allows to find the total concentrations of the six elements.

The difference between the concentrations detected in step III and (IIa - IIb) corresponds to strong complexes.

The results for Sb lead to the conclusion that this metal is dissolved mainly as Sb^{V} . The percentage of Sb complexed by organic matter can be estimated to vary between 20 and 40 % of the total metal concentration.

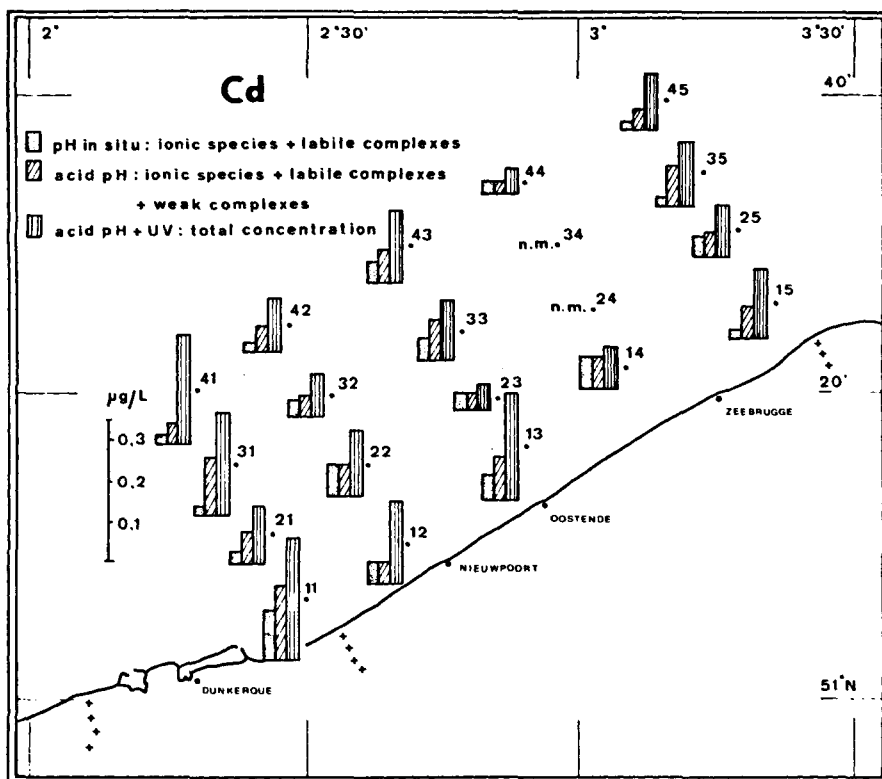


fig. 5.

Dissolved metal concentration
Distribution of Cd along the Belgian coast in October 1979

The data for Bi show concentrations often below detection limit ($< 0,05 \mu\text{g}/\text{l}$) ; a few results have been obtained after UV treatment on samples collected close to the coast (grid points 21, 22, 13, 14) and in the vicinity of the Scheldt estuary (grid points 15, 25). This might indicate that Bi diffuses from the coast and is rapidly diluted or removed by unknown processes from the water column offshore.

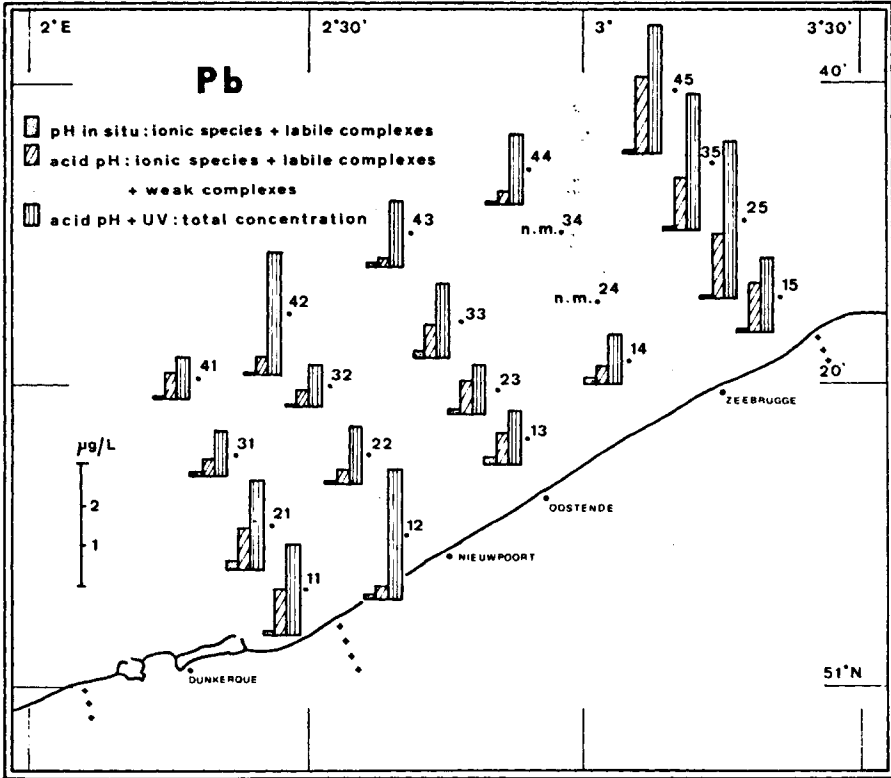


fig. 6.
Dissolved metal concentration
Distribution of Pb along the Belgian coast in October 1979

For Zn and Pb they appear to be rather uniformly distributed, although some maxima are found along grid lines 5 and at some other grid points (12, 41 and 42). This probably reflects coastal and estuarine influence.

This observation is not confirmed for Cd and Cu which show significant concentration differences from point to point.

The amounts of Zn, Cd, Pb, Cu involved in organic complexes often correspond to an important fraction of the total concentration with great variations from point to point : 12 to 87 % for

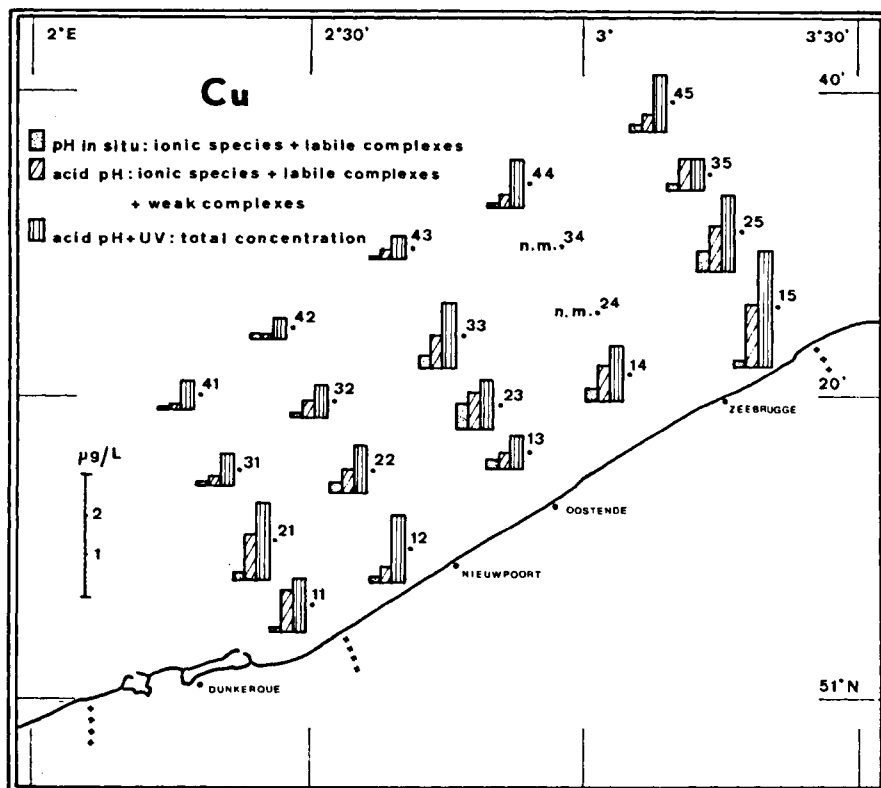


fig. 7.

Dissolved metal concentration
Distribution of Cu along the Belgian coast in October 1979

Zn, 20 to 80 % for Cd, 33 to 87 % for Pb, 20 to 83 % for Cu. This is of great importance in the study of the fate of heavy metals in the sea, their relative toxicity and is closely connected to the study of organic matter.

Although the grid covers some regions of dumping of important quantities of chemicals in solution containing heavy metals, no heavily polluted zone can be detected. Rate of dispersion is of course very high in well mixed shallow waters.

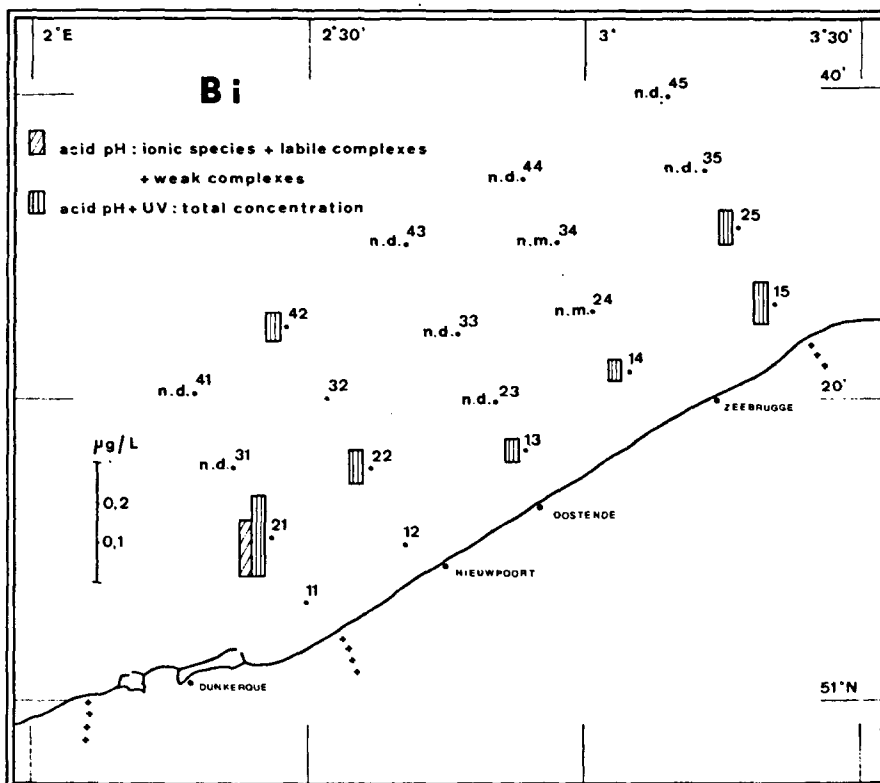


fig. 8.

Dissolved metal concentration
 Distribution of Bi along the Belgian coast in October 1979

We will finally compare the results obtained in 1979 with our actual sampling method with those resulting from the analysis of samples collected using other techniques during october cruises carried out in the same region since 1972.

Fig. 10 shows that from 1972 until 1977 included the values for Zn, Cd, Pb and Cu are rather high and that dispersion is important.

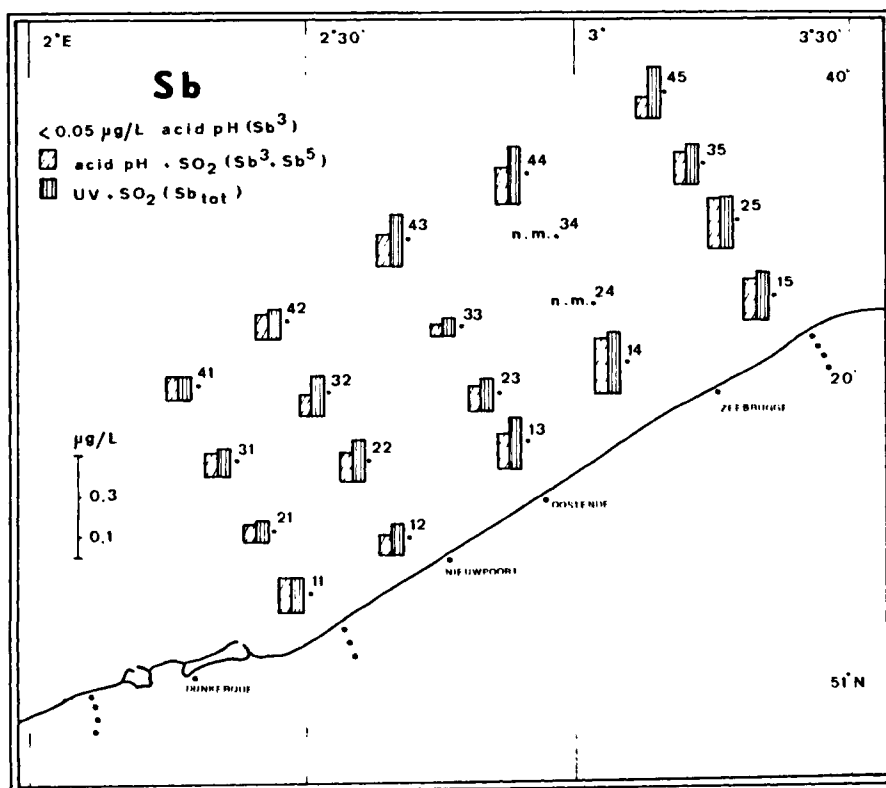


fig. 9.

Dissolved metal concentration
Distribution of Sb along the Belgian coast in October 1979

From 1978 on, one observes a progressive and important diminution of the concentrations and a reduction of dispersion.

This, we believe, is due to several steps taken to avoid contamination during sampling and filtration.

In 1978, the samples for routine work were still collected with a Niskin bottle as during the preceding years, but filtration by suction was replaced by filtration under pressure. In

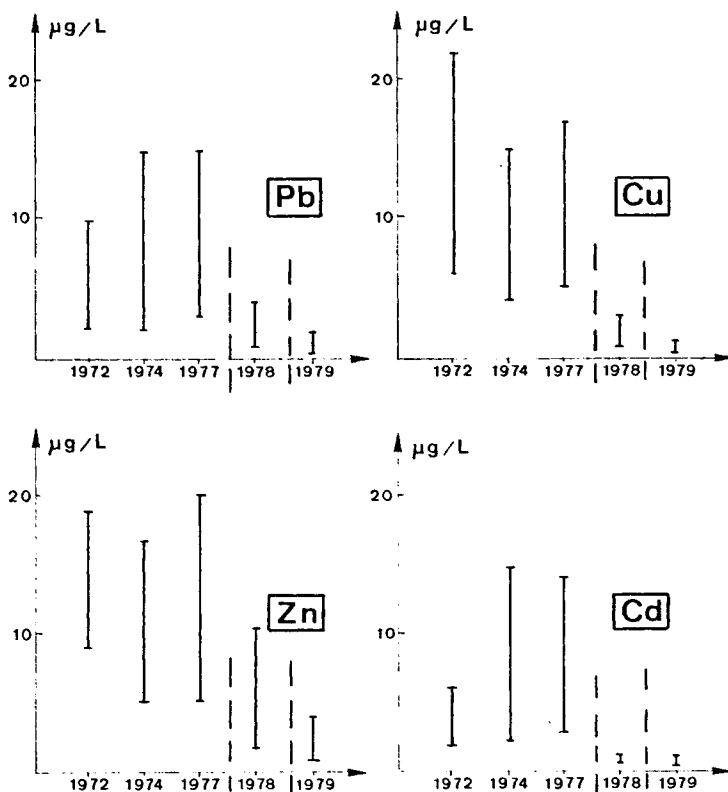


fig. 10.

Zn, Cd, Pb, Cu concentrations measured during cruises along the Belgian coast in October 1972, 1974, 1977, 1978, 1979. Broken line indicate improvement of filtering technique (under pressure instead of suction) in 1978, of sampling and filtering system in 1979.

1979 the new sampling kit described here, which began to be tested in 1978 [see Gillain et al. (1979a)] but in a less sophisticated form, was systematically used with further obvious improvement of the results.

For the same geographical site our actual data are comparable to results obtained in August 1976 by Mart (table 2) along a line Ostend - Den Helder. Sampling was carried manually at 50 cm depth from a small rubber boat using plastic bottles attached to

Table 2

Geographical locations	Date of sampling	Analytical method	Concentration, µg/l						References
			Zn ⁺⁺	Cd ⁺⁺	Pb ⁺⁺	Cu ⁺⁺	Sb ³⁺ + Sb ⁵⁺	Bi ⁺⁺⁺	
<u>North Sea</u>									
Belgian coast	oct. 1979	DPASV pH=1	0,70 - 5,10	0,030-0,180	0,20 - 1,90	0,10 - 1,50	0,05 - 0,26	< 0,05	GILLAIN (this paper)
Belgian coast	aug. 1976	DPASV pH=2	-	0,024-0,110	0,10 - 2,60	0,34 - 2,00	-	-	MART (1976)
Dutch coast	1975-1976	DPASV pH=2,7	3,00 -20,10	0,100-0,300	1,70 - 3,30	1,00 - 2,50	-	-	DUINKER and KRAMER (1977)
Atlantic	1963	activation	-	-	-	-	0,11 - 0,58	-	SCHUTZ and TUREKIAN (1965)
Irish Sea	1965	extraction MIBK + colorimetry	-	-	-	-	0,13 - 0,40	-	PORTMAN and RILEY (1966)
English Channel	1965	ion exchange + emission spectroscopy	-	-	-	-	-	0,025	PORTMAN and RILEY (1966)
Irish Sea								0,039	
North Atlantic Ocean								0,033	
South Atlantic Ocean	1960	id.	-	-	-	-	-	0,017	BROOKS (1960)
Pacific Ocean	1973	ASV	-	-	-	-	-	0,020-0,11	FLORENCE (1974)

Note : DPASV = Differential pulse anodic stripping voltammetry
MIBK = Methylisobutylketon
ASV = Anodic stripping voltammetry

a telescopic plastic rod to avoid contamination. Heavy sea conditions make this method quite hazardous and considerably limits its use.

Other data are available for a nearby region, along a line in front of the Rhine Estuary. They are reported by Duinker and Kramer (1977) and are higher. It is difficult to tell whether this can be due to contamination or reflects the Rhine output. Bottles were used for sampling, but filtration was carried out under pressure (nitrogen).

Regarding Sb and Bi data are scarce and comparison can only be made with results obtained with other analytical techniques and in very different locations (table 2). However the order of magnitude seems to be correct. It is obvious that in the case of Sb and Bi contamination problems are much less acute than for Zn, Cd, Cu and Pb, which find a variety of use in ship building.

In conclusion one can only say that sampling is the most hazardous step in detecting trace metals at the levels found in sea water. It is believed that the new sampling and filtering technique presented here meets the requirements for water sampling at moderate depth, allows to work from large or small research vessels, even in rough conditions. It could easily be adapted to be fed under nitrogen pressure from slightly modified Niskin bottles for deep sea operations.

Needless to say it looks obvious to the authors that a proper evaluation of trace metal levels to assess pollution for instance or to understand chemical processes in the sea (complexation is one example) will only be achieved for eventual comparisons with other marine regions if analysts come together to intercalibrate not only their analytical tools but also, and this is urgent, their sampling procedures.

References

- BROOKS, R.R. (1960). The Use of Ion-Exchange Enrichment in the Determination of Trace Elements in Sea Water. *Analyst*, 85, 745-748.
- DUINKER, J.C. and KRAMER, C.J.M. (1977). An experimental study on the speciation of dissolved Zn, Cd, Pb, Cu in River Rhine and North Sea water by differential pulsed anodic stripping voltammetry. *Mar. Chem.*, 5, 207-228.
- FLORENCE, T.M. (1974). Determination of Bi in marine samples by anodic stripping voltammetry. *J. Electroanal. Chem.*, 49, 255.
- GILLAIN, G., DUYCKAERTS, G. and DISTECHE, A. (1979a). The determination of trace metals in sea water and suspended matter by classical anodic stripping (Zn, Cd, Pb, Cu) or differential pulse anodic stripping voltammetry with a hanging mercury drop electrode (Zn, Cd, Pb, Cu, Sb and Bi). An approach to speciation. In : Rapports des journées d'études 1979. Actions de recherche concertées. Action interuniversitaire. Océanologie. Services du Premier Ministre. Programmation de la Politique Scientifique, Bruxelles, pp. 123-132.
- GILLAIN, G., DUYCKAERTS, G. and DISTECHE, A. (1979b). Direct and simultaneous determinations of Zn, Cd, Pb, Cu, Sb and Bi dissolved in sea water by differential pulse anodic stripping voltammetry with a hanging mercury drop electrode. *Anal. Chim. Acta*, 106, 23-37.
- MART, L. (1979). Doctorat thesis, RWTH, Aachen.
- PORTMAN, J.E. and RILEY, J.P. (1966). The determination of Bi in sea and natural water. *Anal. Chim. Acta*, 34, 201-210.
- PORTMAN, J.E. and RILEY, J.P. (1966). The determination of Sb in natural water with particular reference to sea water. *Anal. Chim. Acta*, 35, 35-41.
- SCHUTZ, D.F. and TUREKIAN, K.K. (1965). The investigation of the geographical and vertical distribution of several traces elements in sea water using neutron activation analysis. *Geochim. Cosmo. Acta*, 29, 259-268.