SYNTHESE SURV/1977-1978 : 02

ACTIONS CONCERTEES EN OCEANOLOGIE

RAPPORT D'ACTIVITE

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IV

ANNUAL VARIATION OF Zn, Cd, Pb AND Cu IN SEAWATER AND PARTICULATE MATTER IN THE NORTH SEA(SOUTHERN BIGHT).

by: G.GILLAIN

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INTRODUCTION.

Surface water samples, collected over I year in the North Sea, are analysed for Zn, Cd, Pb and Cu using pulse polarography directly on seawater.(I-I5).

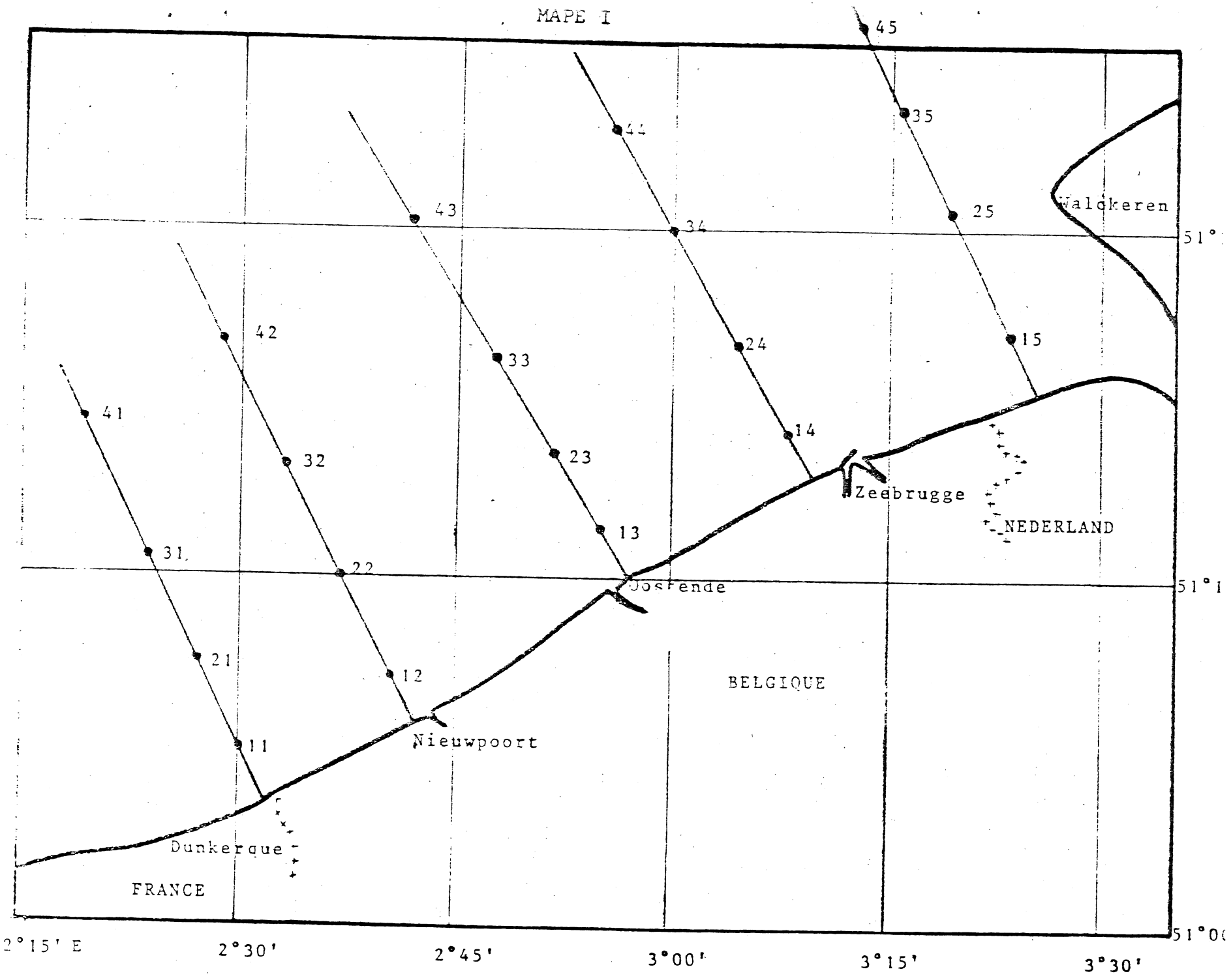
The purpose of these cruises is to achieve a chemical survey of coastal waters of the North Sea.

The location of the stations where samples are collected is summarized in table I and reported on mape I.

TABLE I

Code of number of stations.		
II	5I°07'20'' N	02°30'I0'' E
2I	5I°II'I0''	02°27'20''
3I	5I°I5'40''	02°23'40"
4I	5I°20'40"	02°I9'20"
I2	5I°I0'30"	02°40'30"
22	5I°I5'00"	02°37'I0"
32	5I°I9'40"	02°33'20"
42	5I°25'00"	02°29'00"
I3	5I°I6'40"	02°54'50"
23	5I°I9'50"	02°52'00"
33	5I°24'00"	02°48'00"
43	5I°30'00"	02°42'00"
I4	5I°2I'25"	03°07'40"
24	5I°25'I0"	03°03'20"

MAPE I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11
Walcheren
Zeebrugge
NEDERLAND
Oostende
Nieuwpoort
BELGIQUE
Dunkerque
FRANCE
51°
51°1
51°0(
2°15' E
2°30'
2°45'
3°00'
3°15'
3°30'

34	5I°30'00"	03°00'00"
44	5I°34'20"	02°55'40"
I5	5I°25'00"	03°24'00"
25	5I°3I'00"	03°I9'20"
35	5I°35'20"	03°I5'40"
45	5I°39'25"	03°I2'25"

Station code number: Ist number= number of the station on the radial,
2^{d} number = number of the radial.

METHODS.

I)Sampling, filtration and storage.(II)

Water samples are collected with a oceanographic reversing bottle at a depth of 3 m and filtered immediately trough Millipore filters (pore size: 0,8 µm) washed in $I0^{-2}$ M DTPA solution and rinsed with tridistilled water before the filtration. One liter of solution is transferred to acid-cleaned high density polyethylene bottles rinsed with seawater which are then stored with the filters(suspended matter) in a deep-freezer(-20°C) until the analysis beguns.

2)Analysis.

a)dissolved metals.

Concentrations of dissolved Zn, Cd, Pb and Cu in North Sea water samples have been mesured at natural pH and acid pH(pH$\sim$3), without and after U.V. irradiations by differencial pulse anodic stripping and using a hanging mercury drop electrode (KEMULA type).
For the purpose of clarity, this technique will be summarized briefly:
a 30 ml seawater sample is added to the electrolytic cell and O_2 is removed with N_2. Zn, Cd, Pb and Cu in the sample are then

deposited by preelectrolysis at -I.200 V for a given period of time(IO-I5 min.) After deposition, the reduced metals in the amalgam are stripped by oxidation and the resulting currents are mesured. The current peaks at approximatively -I.00 V(Zn), -0.60 V(Cd), -0.40 V(Pb) and -0.I2 V(Cu) vs. satured KCl calomel electrode(SCE) are proportionnal to the amount of metal plated into the mercury drop and to the metal concentration in solution. Then 50-I00 µl of metals standard solution are added to the sample and allowed to equilibrate with the seawater components for a period of 5 minutes. The electrolysis and stripping process are repeated and the metal concentration is obtained from the ratio of the peak current of the sample to that of sample plus the standard.

b)particulate metals.

-ashing of the samples(II).

The filters are dried at 60°C and ashed by Low Temperature Asher with micro-wave activated oxygen(LTA Tracerlab).

-analysis of the residue of ashing.

The residue from the LTA ashing is dissolved in two ml of Suprapure concentrated HCl and is transferred to a 50 ml volumetric flask which is filled with distilled water. 30 ml of the final solution are transferred to the cell for the anodic stripping voltammetry(see above).

RESULTS.

a)dissolved metals.

During the period of july 77 to december 77 the variation of dissolved ions, weakly complexed cations and strongly complexed cations in the North Sea have been investigated(tables II to VI and fig. I).
The organically bound metal fraction in the dissolved state is very

CRUISE OF JULY I977

Samples	Zn (ppb)			Cd(ppb)			Pb(ppb)			Cu(ppb)		
	I	2	3	I	2	3	I	2	3	I	2	3
II 270777 I055	5,55	I0,00	27,00	0,40	0,00	0,I4	2,60	I,23	6,08	2,I0	6,40	0,00
4I 270777 I4I0	8,I0	I2,50	20,36	0,36	0,00	0,33	2,20	I,60	9,80	2,70	2,I0	0,00
3I 270777 I300	8,I0	2,87	-	0,I8	0,33	3,50	I,04	I,40	I7,35	I,II	6,3I	6,00
42 270777 I505	4,I8	6,00	20,I7	0,I2	0,00	0,62	I,60	I,68	4,05	2,00	4,48	0,00
44 280777 I550	6,94	I,00	I5,I0	0,I0	0,00	0,I0	2,I8	I,00	4,62	3,80	6,40	0,00
35 280777 2I40	9,44	2,68	-	0,I8	0,00	-	4,68	4,00	-	5,82	9;30	-
I3 270777 I930	9,95	7,42	28,22	0,I3	0,00	0,I0	2,70	4,I0	27,00	2,63	2,I0	5,23
32 270777 I550	8,44	4,I0	-	0,37	-	-	3,I0	5,00	-	3,I8	3,70	-
I4 280777 I8I0	8,20	4,40	0,00	0,I7	0,34	0,00	I,33	I,60	3,00	5,63	4,60	0,00
2I 270777 I2I5	9,90	6,90	0,00	0,I3	0,00	0,39	I,50	5,60	28,00	3,40	9,40	0,00
I2 270777 I745	-	-	-	0,I2	0,00	0,00	2,53	2,00	0,00	I,80	2,00	0,00
45 270777 I830	5,60	I0,80	0,00	0,II	0,20	0,I3	2,30	2,00	I4,30	2,30	3,50	5,85
33 270777 2030	9,62	5,90	II,80	0,I7	0,00	0,00	2,80	I,50	4,40	3,I0	2,20	3,50
I5 280777 I930	I2,60	8,20	I3,40	0,I0	0,07	0,25	I,20	3,00	7,I0	I,50	4,I5	9,20
45 280777 2220	I,70	2,60	9,I0	0,I0	0,20	0,I3	2,I5	5,23	3,05	2,2I	7,52	0,00

I : Ionic species,

2 : Weakly complexed species,

3 : Strongly complexed species,

CRUISE OF SEPTEMBER 1977

Samples	Zn(ppb)			Cd(ppb)			Pb(ppb)			Cu (ppb)		
	I	2	3	I	2	3	I	2	3	I	2	3
35 070977 I700	2,74	2,29	I0,I8	0,I2	0,00	0,00	I,I0	5,06	I,40	2,63	3,90	4,30
33 050977 I440	I,23	5,42	6,3I	0,63	0,22	0,39	3,I6	I,50	4,39	6,89	5,59	-
I4 060977 I830	I,27	5,92	I6,3I	0,20	0,86	0,00	I,62	3,00	3,47	3,94	9,6I	-
43 050977 I335	-	-	-	0,I6	0,00	0,00	0,57	3,05	0,00	9,33	5,00	0,00
4I 080977 0850	5,3I	-	-	0,24	0,00	0,00	3,45	2,50	6,86	5,57	3,88	0,00
2I 060977 I408	4,68	6,33	I0,I2	0,06	0,20	0,00	I,70	5,00	3,22	2,96	I,76	8,37
34 070977 I340	7,84	7,20	25,80	2,72	I,00	I,96	I,60	3,60	9,98	9,70	-	-
3I 080977 I0I0	2,56	5,04	I7,00	0,30	0,00	0,46	I,3I	5,60	9,60	4,00	2,08	0,00
45 070977 I600	I,42	3,85	5,00	0,I9	0,30	0,00	2,49	7,50	0,00	3,04	2,I0	7,65
44 070977 I430	2,42	7,I3	I8,59	0,44	0,00	0,I5	2,96	I,50	2,I0	4,05	9,36	0,00
42 080977 0735	2,66	5,53	I7,74	0,I4	0,00	0,32	I,32	3,30	9,60	2,I4	9,00	8,90
I2 060977 0840	3,94	2,40	7,60	2,60	0,00	2,20	9,I2	-	-	4,85	8,I0	2,30
I5 0I0977 I940	9,25	8,95	-	0,20	0,00	0,I0	3,03	5,00	0,00	3,96	5,20	0,00
I3 050977 I633	2,00	5,80	3,58	0,23	0,I3	0,I3	4,40	2,70	0,00	7,00	4,70	0,00
32 060977 III0	2,80	8,70	4,I7	0,I5	0,65	0,42	2,I0	5,00	6,00	2,50	5,70	-
II 060977 I555	3,46	9,20	-	0,26	0,I9	-	2,80	3,00	-	5,40	9,I0	-

I : ionic species,

2 : weakly complexed species,

3 : strongly complexed species,

Samples	Zn			Cd			Pb			Cu		
	I	2	3	I	2	3	I	2	3	I	2	8
I3 03I077 I240	46	27	56	0,6I	0,00	0,00	2,38	IO,85	00,00	5,40	6,60	28,50
33 03I077 I030	7	IO	-	0,60	I,20	0,50	I,70	2,20	6,70	6,75	IO,80	I4,75
43 03I077 I4I5	9	7	IO	0,40	0,00	0,00	I,90	I,80	3,60	3,70	2,77	3,50
23 04I077 I4I5	I5	73	36	0,60	0,30	0,20	2,32	6,90	2,40	4,IO	2,60	2,50
II 04I077 I000	69	92	3I	I,65	I,00	I,IO	2,55	6,IO	I2,30	8,I5	9;00	4,20
2I 05I077 I420	42	43	4I	0,44	0,00	0,22	2,I3	I,70	7,70	I,63	4,00	3,60
3I 05I077 I245	290	397	II90	-	-	-	I,50	3,IO	3,90	6,90	4,30	7,75
4I 05I077 II20	IO	23	40	0,I3	0,IO	0,I5	I,30	I,90	2,90	2,25	2,75	4,IO
I2 05I077 I550	T27	53	32	0,70	0,20	0,IO	I,30	2,70	0,00	3,00	3,56	2,45
25 06I077.I400	27	92	26	0,53	0,I4	0,90	0,56	4,I3	0,00	5,70	4,90	0,00
35 06I077.I200	5I	2I	54	0,70	0,00	0,00	I,52	4,30	6,35	2,70	4,30	6,60
45 06I077.II00	227	253	I00	I,30	0,00	0,00	2,30	I,30	I4,80	4,50	2,30	I2,IO
I4 07I077.I300	320	230	I2I	0,96	I,20	0,00	3,50	4,70	-	2,IO	4,80	7,20
24 07I077.II00	2IO	326	I564	I,50	I,50	0,00	5,I6	IO,I6	20,20	3,I4	4,20	2,80
34 07I077.I000	28I	I96	697	0,50	I,00	I,00	4,IO	5,00	5,80	2,20	4,60	II,00
44 07I077.0900	54	97	24	I,40	I,20	I,05	3,00	4,I3	3,40	2,30	3,00	2,IO
Cap gris nez I9I077 II30	6,35	6,80	IO,65	0,I8	0,20	0,00	I,60	I,70	I,40	4,85	2,80	2,90
Hansweert 2II077 0930	-	-	-	0,45	0,20	0,60	2,25	I,77	3,00	3,70	2,30	6,00

I: Ionic species; 2: weakly complexed species; 3: strongly complexed species

CRUISE OF NOVEMBER 1977

Samples	Zn			Cd			Pb			Cu		
	I	2	3	I	2	3	I	2	3	I	2	3
I3 23II77 0930	-	-	-	0,3I	0,I7	0,00	I,78	0,90	I,80	5,20	I0,70	0,00
I4 23II77 I200	3,50	I0,50	47,50	0,24	0,34	0,I0	I,20	2,60	I,60	0,56	2,00	3,I0
34 23II77 I4I5	I,80	8,20	9,90	0,I0	0,I7	I,40	I,33	2,00	3,2I	I,43	2,I0	I,40
22 24II77 II35	I,55	7,I0	20,90	0,I4	0,38	0,40	I,62	5,35	6,80	3,50	3,20	2,00

I : ionic species

2 : weakly complexed species,

3 : strongly complexed species,

CRUISE OF DECEMBER 1977

Samples	Zn			Cd			Pb			Cu		
	I	2	3	I	2	3	I	2	3	I	2	3
II.I4I277.IC30	9,40	34,00	25,50	0,52	0,34	0,00	I,20	3,55	I,00	3,50	2,00	I,20
2I.I4I277.I2I5	8,50	IO,IO	4I,65	0,22	0,00	0,38	0,94	4,68	I5,00	2,42	2,32	I2,50
I2.I5I277.I200	IO,IO	4,I5	24,00	0,20	0,00	0,I6	2,00	5,25	6,40	2,60	3,IO	2,80
22.I5I277.I240	7,00	5,90	60,20	0,IO	0,80	I,00	I,00	3,20	20,80	3,70	5,25	IO,IO
42.I5I277.I355	3,50	3,40	28,50	0,30	0,20	0,50	I,30	I,60	I,80	2,I5	3,20	I,50
43.I2I277.I300	8,40	20,50	44,80	0,75	0,20	0,00	2,IO	I,50	2,00	4,70	3,30	2,30
I5.I3I277.II05	I5,40	25,80	I6,50	I,00	0,00	0,00	0,90	3,40	4,20	6,35	0,00	0,00
44.I6I277.I235	4,86	IO,50	5,70	0,23	0,00	0,00	I,40	3,90	I2,40	7,IO	-	-
45.I3I277.I330	5,20	2,20	I2,50	0,27	0,I8	0,00	3,I5	I,55	2,00	6,50	3,IO	I5,20
24.I6I277.II20	4,20	I5,36	IO,60	0,32	0,50	0,60	3,50	2,60	3,IO	7,40	4,IO	3,IO
I3.I2I277.I345	33,40	33,30	0,00	0,50	0,00	0,00	2,IO	3,00	4,00	4,70	0,00	0,00
I4.I6I277.IO33	5,40	3,50	II,00	0,46	0,00	0,40	I,00	3,70	6,50	5,00	2,50	0,00
35.I3I277.I430	9,20	20,90	0,00	0,50	0,40	0,90	2,I5	2,00	4,00	5,IO	2,80	3,I5
25.I3I277.I225	6,80	5,IO	4,IO	0,35	0,00	0,40	I,23	3,00	20,00	2,70	I,70	2,00
33.I2I277.I350	8,70	5,70	22,00	0,II	0,20	2,00	I,00	2,00	I3,20	0,80	I,20	0,80

I : ionic species,

2 : weakly complexed species,

3 : strongly complexed species,

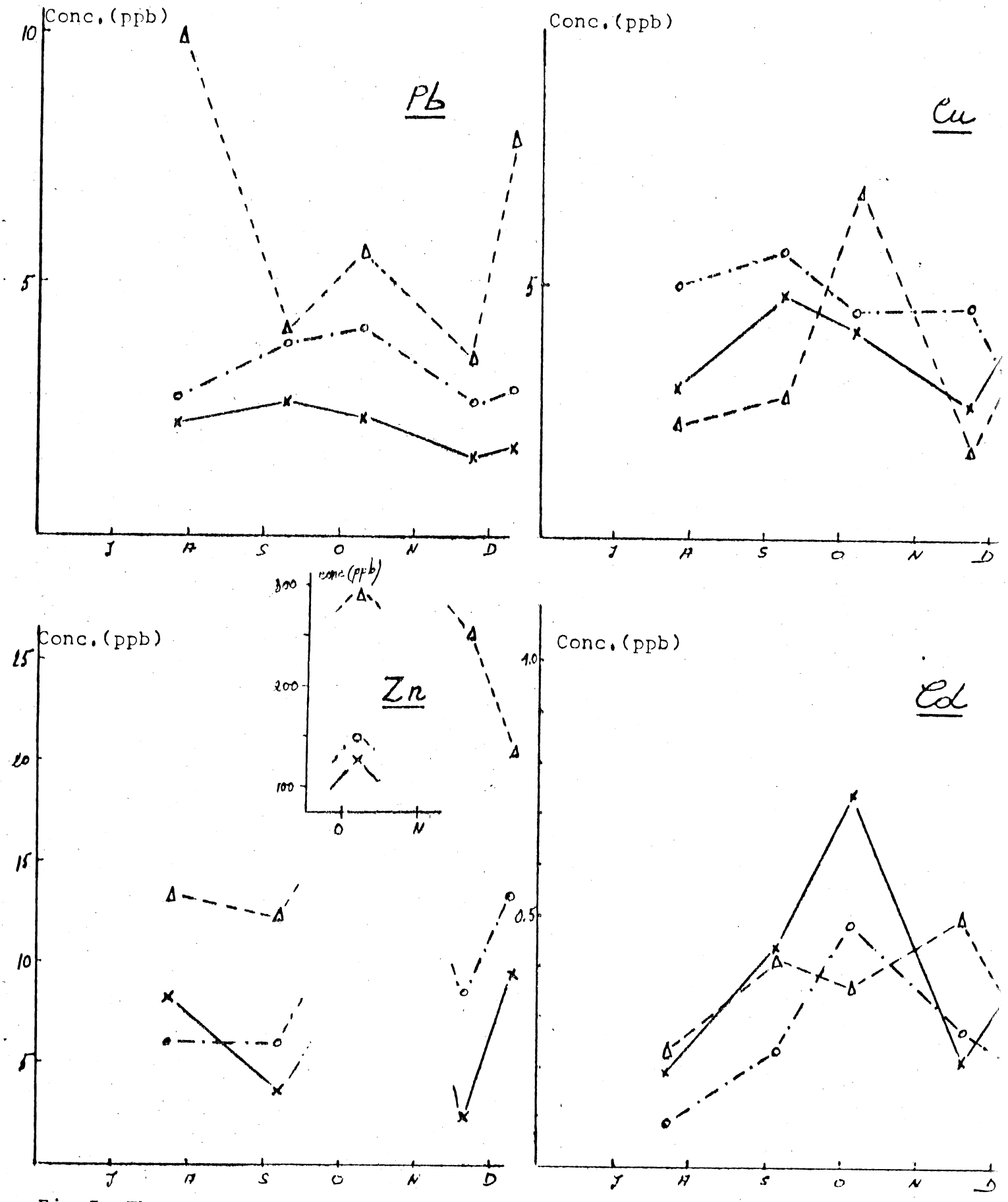


Fig.I: The concentrations of Zn, Cd, Pb and Cu in surface water of North Sea collected over I year period.
- x - ionic species; - o - weakly complexed species; - - strongly complexed species.

Suspended Matter

concentration ppm(dry weight)

Samples	Zn(ppm)	Cd(ppm)	Pb(ppm)	Cu(ppm)
25.300377.I330	I99	2,9	49	64
II.3I0377.II45	I40	0,9	26	-
3I.3I0377.I540	-	0,06	52	94
2I.3I0377.I240	3500	I0	800	4I00
I4.260477.II00	I	-	I	36
25.280477.II50	I74	0,9	26	-
35.280477.I430	225	0,5	44	-
I4.230577.I030	336	0,2	60	87
24.230577.I200	5I5	I,6	7I	I43
34.230577.I400	I33	0,5	29	I47
44.230577.I3I5	-	-	-	-
I2.240577.I030	277	0,I0	86	393
22.240577.II30	I64	0,4	8	23
II.260577.II35	87	3,2	46	II4
2I.260577.I230	3496	3,7	540	-
3I.260577.I430	-	I4,7	94	I25
4I.260577.I345	8I	0,6	II	9I
34.280577.I400	225	0,5	43	-
II.270777.I055	I6	8,8	-	2I4
2I.270777.I2I5	I07	I7	II4	297
3I.270777.I300	40	0,7	II0	I66

concentration ppm(dry weight)

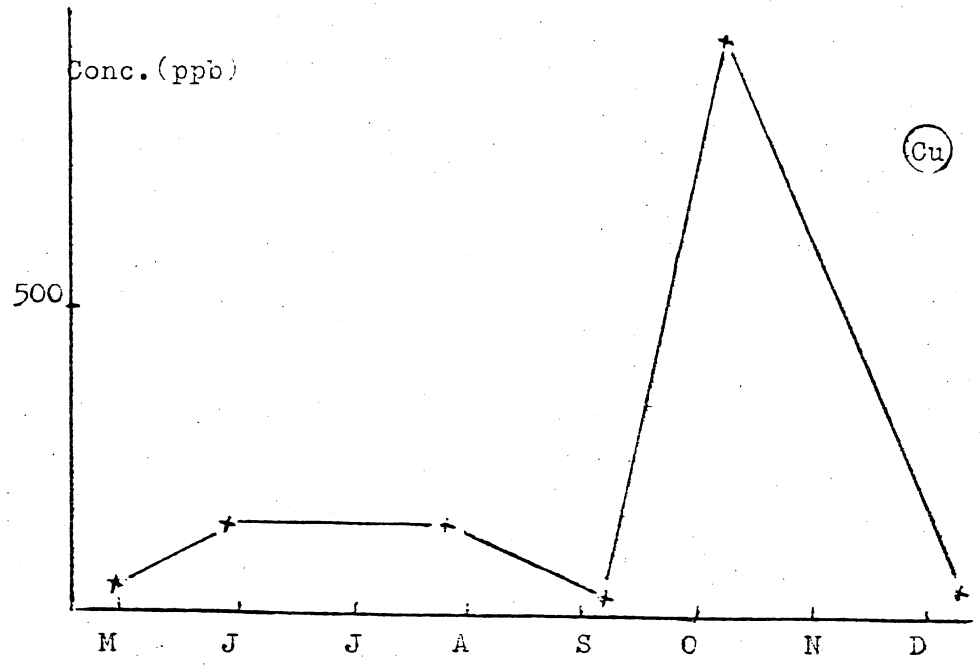
Samples	Zn(ppm)	Cd(ppm)	Pb(ppm)	Cu(ppm)
4I.270777.I4I0	334	7,3	46	I03
I2.270777.I740	25	0,3	I7	30
42.270777.I455	8I	0,5	32	I88
I3270777.I9I5	I	0,4	I72	I6
33.270777.2030	235	2,5	46	I50
43.270777.I8I0	I66	I,5	39	-
I4.280777.I8I0	I66	I,5	39	-
24.280777.I725	I42	0,I	6	9
44.280777.I550	I53	0,6	58	98
35.280777.2I40	-	-	-	-
45.280777.2220	II90*	2,I	253*	I94
I3.050977.I630	I74	0,8	93	332
33.050977.I340	I50	I,2	76	250
43.050977.I335	I	0,7	I08	70
II/060977.I550	-	-	-	-
I2060977.0840	I66	-	54	I74
I4.060977.I830	536	5	I76	I57
I5.070977.I940	I230*	3,5	45	98
24.070977.I230	250	6	80	264
34.070977.I340	268	6I*	54	2I0
35.070977.I700	I0I	2,4	23	I07
44.070977.I430	485	I,4	95	200
45.070977.I600	343	0,5	93	57

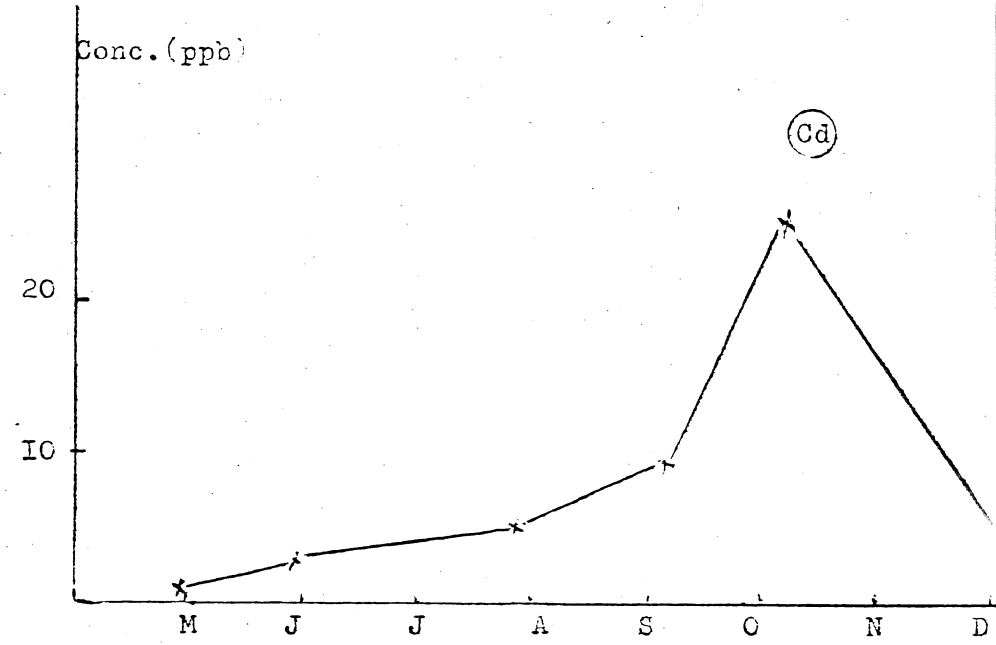
concentration ppm(dry weight)

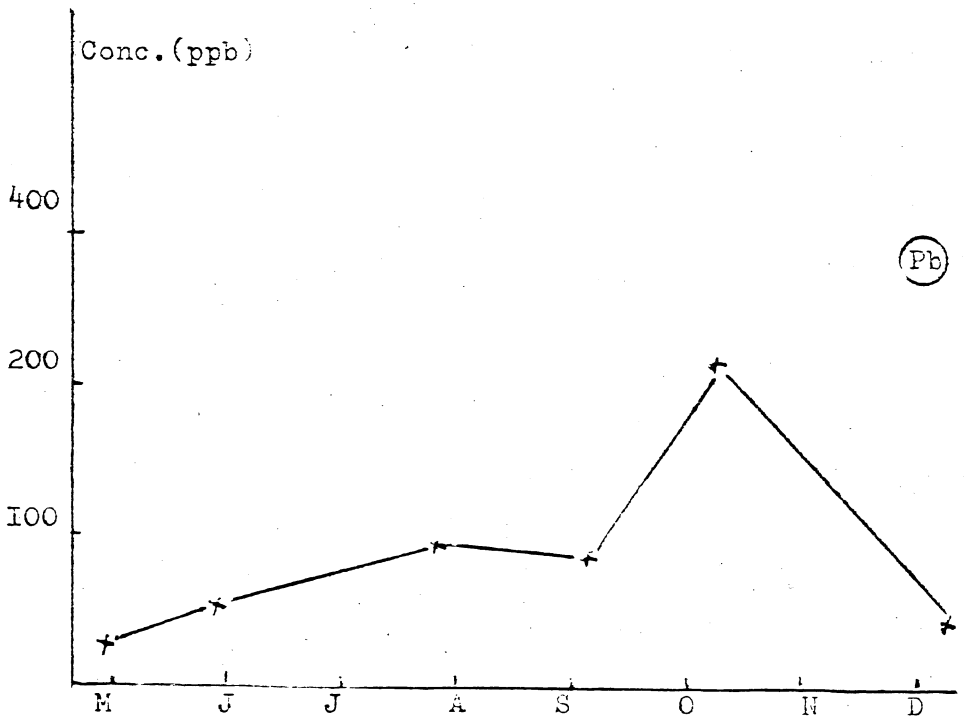
Samples	Zn(ppm)	Cd(ppm)	Pb(ppm)	Cu(ppm)
3I.080977.I0I0	II4	0,5	I5	90
4I.080977.0850	350	20*	75	430*
42.080977.0735	257	2,8	I0	I73
I3.03I077.I240	34	37*	I7	I55
23.03I077.I4I5	340	II0*	I23	343
33.03I077.I745	422	I	I6	548*
43.03I077.I550	833	20*	I25	837*
II.04I077.I045	494	63*	I06	407*
II.05I077.I550	400	0,7	77	364*
2I.05I077.I420	375	I6*	69	II03*
3I.05I077.I250	2I40*	2	338*	2I82*
4I 05I077.II20	I296*	84*	I87	I724*
I5.06I077.I500	I364*	I4*	I54	I32
35.06I077.I200	I505*	5,5	99	I35
45.06I077.II00	426	8,6	I47	I39
I4.07I077.I300	27	I2*	II4	I57
24.07I077.II00	260	0,5	II6	99
34.07I077.I000	2672*	27,5*	65I*	923*
44.07I077.0900	2I38*	5	I034*	5648*
I3.I2I277.I045	55	I,3	II	I8
23.I2I277.II45	I28	0,8	I08	45

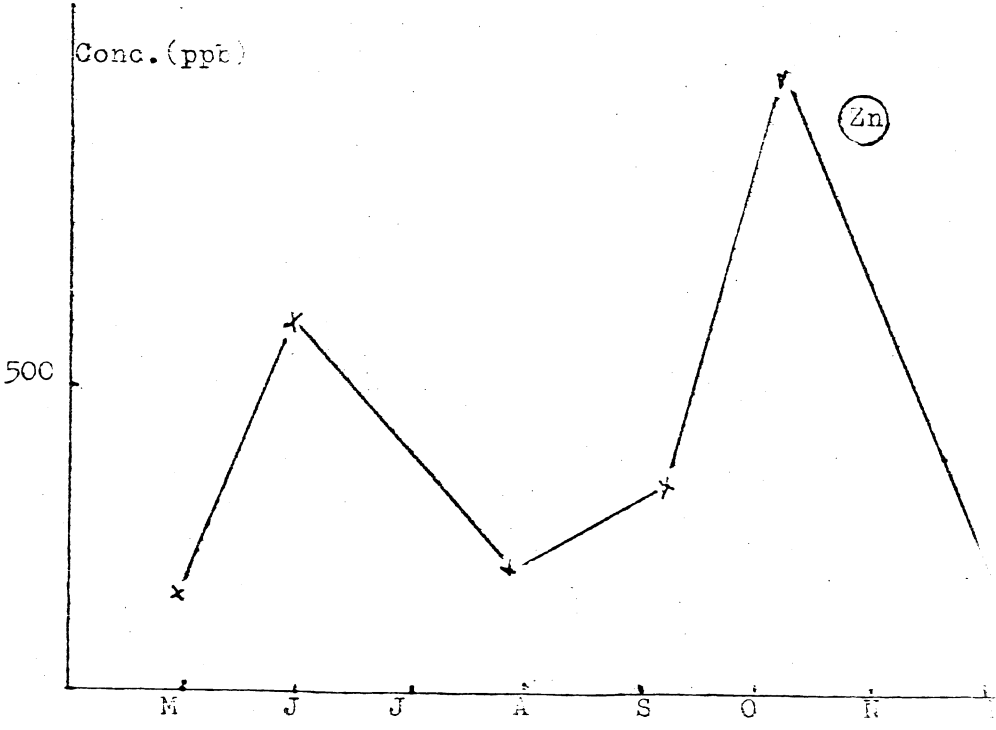
concentration ppm (dry weight)

Samples	Zn(ppm)	Cd(ppm)	Pb(ppm)	Cu(ppm)
33.I2I277.I350	3I	0,7	I2,5	34
43.I2I277.I300	68	0,4	I28	62
I5.I3I277.II25	I36	3,2	84	5I
25.I3I277.I225	II4	3,2	50	-
35.I3I277.I430	89	0,05	73	56
45.I3I277.I340	42	0,3	I2	25
II.I4I277.I030	I5	0,5	8	II
2I.I4I277.I205	56	2,2	II	45
3I.I4I277.I445	I8	0,4	3	I3
4I.I4I277.I345	I3	0,4	I5	49
I2.I5I277.I200	49	0,3	58	46
22.I5I277.I240	36	I,2	7	72
32.I5I277.I450	5	0,3	I2	25
42.I5I277.I400	20	3	IO	28
I4.I6I277.I030	256	0,5	-	-
24.I6I277.II20	9I	0,I	47	33
44.I6I277.I235	32	0,2	5	8


Conc.(ppb)
Cu
500
M
J
J
A
S
O
N
D


Conc.(ppb)
Cd
20
10
M
J
J
A
S
O
N
D


Conc.(ppb)
Pb
400
200
100
M
J
J
A
S
O
N
D


Conc.(ppb)
Zn
500
M
J
J
A
S
O
N

important, however with considerable variations: 47-70% for Zn, 22-46% for Cd, 38-67% for Pb and I8-44% for Cu of the total dissolved metal. Higher levels for all of the metals are observed in the vicinity of the estuary(radial 5), on the radial I and in the coastal waters. The highest concentrations of Zn and Cd dissolved in seawater have been in samples collected during october 77, without significant changes for the other metals. This increase of Zn and Cd concentrations during this period are real and not due to contamination during the sampling. This situation is similar in july and december for Pb.

b)particulate metals.

Time variations in the particulate concentrations of Zn, Cd, Pb and Cu in the surface waters of the North Sea are presented in figure II and table VII.

As in the water samples, the highest values generally occurring in the vicinity of the estuary(points I5,35,45,34,44), Dunkerque(points 2I,3I, 4I,II) and the coast(points I3,23), increase to maximum mean values in autumn(october) and this is followed by a sharp drop to minimum concentrations between december and february.

These high levels are represented by obvious peaks in figure II and identified by an asterisk in table VII.

Unlike those in the water samples, the levels of all metals investigated in the particulate matter do tend to increase simultaneously in october.

CONCLUSION.

The increased levels observed for the metals(particulate and dissolved) during the cruise in october, coinciding with a period of high

productivity, suggests that plancton could be an additionnal factor leading to spacial complexity in the distribution of the metals. However, in some instances higher values occured independently for the metal and not for the others. For exemple, on points II,4I,42,44, and I3 during july, Zn increases without significant changes in the other metals. The situation was similar in october on points II,2I, I3,23 and I4 for particulate Cd.

This fact could very well be related to differences in the lability of each element. However, we think that the factors governing the concentrations of soluble and particulate metals in the coastal waters in the North Sea are variable and more complex; metal levels in coastal surface waters appear to us to be more dependent on industrial dumping(points 34 and 23) and domestic waste than on biological factors.

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