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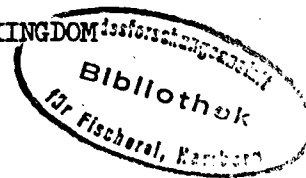
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AN INTERCALIBRATION EXERCISE FOR ANALYSING DISSOLVED TRACE METALS IN SEA WATER BY
MARINE LABORATORIES IN BELGIUM, THE NETHERLANDS AND THE UNITED KINGDOM

by

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INTRODUCTION

In 1971 the International Council for the Exploration of the Sea established a Working Group for the International Study of the Pollution of the North Sea and its Effect on Living Resources and their Exploitation. Several exercises involving the measurement of trace metals in the water of the North Sea by laboratories in Belgium, the Netherlands and the United Kingdom came under the auspices of this working group. To assess the comparability of results produced by these different analytical teams, a series of intercalibration exercises was established to run concurrently with the programmes of field measurements. The following report summarises the results of these tests.

METHODS

Samples were collected by plastic bucket at the sea surface and by Niskin bottle at depth and were immediately filtered prior to storage. Samples collected by Belgium, the Netherlands and the United Kingdom were filtered through Millipore membranes of 0.8, 0.45 and 0.22 μ , respectively. All water was stored deep frozen in polyethylene bottles prior to analysis. The following Institutes participated in the exercise:-

BELGIUM

Free University of Brussels (UVB): Extraction by chelex ion exchange column, measurement by atomic absorption with a graphite furnace.

University of Liège (UL): Anodic stripping voltametry with hanging mercury drop electrode.

NETHERLANDS

Netherlands Institute for Sea Research (NIOZ), Texel: Extraction by MIBK/APDC, measurement by atomic absorption with air/acetylene flame.

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* Free University of Brussels

+ Fisheries Laboratory Lowestoft

UNITED KINGDOM

Institute of Oceanographic Sciences (IOS), Wormley: Extraction by MIBK/APDC, measurement by atomic absorption with air/acetylene flame.

Institute of Marine Environmental Research (IMER), Plymouth: Extraction by chelex ion exchange column, measurement by atomic absorption with air/acetylene flame.

Ministry of Agriculture, Fisheries and Food (MAFF), Lowestoft:

a. Hydrochemistry Laboratory (HL). Extraction by APDC/MIBK, measurement by atomic absorption with air/acetylene flame unless stated otherwise.

b. Fisheries Radiobiological Laboratory (FRL). Extraction by APDC/chloroform, evaporation and resolution in methanol, measurement by atomic absorption with air/acetylene flame.

RESULTS

Data are presented in chronological order. When five or more sets of samples are used in any intercalibration series, tests of significance have been made by student's t-test. Four or less samples are considered too few for valid statistical analysis.

1971

Intercalibration tests were made between the Liège and Lowestoft (FRL) laboratories using samples collected in the southern North Sea by both countries (Table 1). All copper values measured by Lowestoft were markedly lower than those reported by Liège and the discrepancy is statistically significant. With one exception, there was reasonably good agreement for zinc on those samples collected by Lowestoft. The results of the analysis of samples collected by Belgium were not so close. The Lowestoft values were mainly lower than those recorded by Liège, but the discrepancy was barely significant. The cadmium values were in fair agreement, bearing in mind the relatively low levels of this metal.

1973

All samples were collected by Lowestoft and Texel in the southern North Sea. The first series involved intercalibration between Lowestoft (HL) and Texel, (Table 2). Although the basic analytical techniques of both laboratories were similar, the reagent concentrations differed somewhat. The levels of zinc, copper and cadmium measured by Lowestoft were generally lower than those reported by Texel, but the discrepancy was only statistically significant for those samples collected by the latter. The nickel values reported by Lowestoft were generally higher than those of Texel but no statistical difference was proven.

Samples in the second series were collected in the southern North Sea by Lowestoft and distributed between Brussels, Liège and Lowestoft (HL) (Table 3). Apart from the sample collected on station K6, zinc values showed reasonably good agreement. The copper results were not so uniform: Lowestoft values were lower than those reported by Brussels which in turn were lower than those reported by Liège and

the discrepancies were statistically significant. However, when Elskens (1973) compared copper results of the same two Belgian laboratories on 20 samples collected in the southern North Sea no statistical variation was proven. The cadmium values in the present series analysed by the two Belgian laboratories did not statistically differ. The Lowestoft values, however, were significantly lower than the Belgian results.

Samples of Atlantic water were collected by Lowestoft west of Scotland to intercalibrate the two Lowestoft laboratories (Table 4). There was no statistically significant difference between the copper, cadmium and zinc results of the two laboratories. Nickel was omitted since most of the values fell below the detection limit of $0.4 \mu\text{g}/\text{l}$. Several pairs of analyses showed a relatively large discrepancy. However, compared with the North Sea these oceanic levels of metal are low and often near the analytical limit of detection where background "noise" is often relatively large in relation to the amount of metal present.

1974

During much of the year the intercalibration tests were orientated towards collecting a relatively small number of samples but subdividing them so that each laboratory analysed replicate subsamples. Thus, reproducibility of the technique was also assessed.

Table 5 shows the results from samples collected by Lowestoft in the southern North Sea and distributed between Brussels, Liège, Lowestoft and Texel. Most sets of zinc values showed fair agreement. However, the samples from station 6 which were analysed by Liège showed a higher zinc content than those reported by the other participants. The mean zinc value of the sets of samples analysed by both Belgian laboratories at station 10 would have been closer to the other three sets had not some abnormally low values been recorded among the replicates.

Texel and both Lowestoft laboratories showed fairly good agreement for copper. The values reported by Brussels were slightly higher than the other three sets. The two samples analysed by Liège, however, reported markedly higher copper values than the other analysts.

The cadmium values showed rather poor agreement, with Liège recording higher values than the other participants. However, the results as a whole must be treated as inconclusive in view of the relatively low level of cadmium present. Similarly the intercalibration of nickel was also inconclusive since most levels were near the limit of detection. However, the relatively good agreement between the three sets analysed on station 24 where levels were significantly higher than in the other samples was encouraging.

Table 6 shows the results of an intercalibration between Lowestoft (HL) and Plymouth (IMER) on samples collected in the Thames Estuary and English Channel by Lowestoft. On this occasion Lowestoft analysed cadmium by means of an HGA 74 graphite furnace. Plymouth passed one 5 litre sample from each station through an ion exchange column, whereas ten replicate 1 litre subsamples were analysed separately by Lowestoft. Agreement between the two sets on zinc and cadmium was good. (The rather poor reproducibility of cadmium on the Lowestoft sample 19 was later traced to a faulty graphite furnace tube). The copper values recorded by Lowestoft, however, were approximately twice the levels reported by Plymouth and the cause of this discrepancy is not apparent.

Samples collected by Lowestoft west of Ireland and in the south west approaches to the English Channel were used to intercalibrate the techniques of Lowestoft (HL) and Wormley (IOS). On this occasion Lowestoft analysed both cadmium and nickel on the graphite furnace. Table 7 shows reasonably good agreement for copper. The zinc values reported by Wormley were generally higher than Lowestoft, although this trend was not statistically significant. The levels of both nickel and cadmium were near or below the limit of detection. On the whole, the agreement between the two participants was acceptable bearing in mind the low level of metal present in this oceanic water.

During September an international team of analysts assembled in the Netherlands at Texel in order to participate in a metal intercalibration workshop. Laboratories represented were Brussels, Liège, Texel and Lowestoft (FRL and HL). Samples for intercalibration were collected in the southern North Sea by RV CORELLA of the Lowestoft laboratory.

The results of the intercalibration of analytical techniques are shown in Tables 8 and 9. The analyses of zinc and copper by the three participants who used organic solvent extraction (HL, FRL and NIOZ) showed fair agreement on most sets of samples, although the difference in mean copper values between Lowestoft (HL) and Texel showed marginal statistical significance. The Belgian team did not analyse all samples. However, two out of three sets of samples analysed by Liège reported copper and zinc values higher than those analysed by solvent extraction. Similarly, Brussels reported two out of three zinc values and all three copper values higher than those analysed by solvent extraction.

The cadmium and nickel results were inconclusive, due as on earlier occasions to the relatively low level of these metals in the samples, coupled with poor precision of nickel analysis by atomic absorption. (Nickel was not analysed by the Belgian team).

DISCUSSION

Of the metals intercalibrated the levels of cadmium and nickel was generally too low for a valid comparison of techniques. However, the use of a graphite furnace in the atomic absorption system improved the lower limit of detection of both metals by approximately an order of magnitude compared with the flame technique.

Of the samples analysed by solvent extraction, the copper values reported by HL at Lowestoft were mainly lower than those measured by Texel (Tables 2, 5 and 8). The nature of the discrepancy is obscure since both laboratories cross-checked their respective copper standards and found good agreement. The remaining intercalibration of solvent extraction techniques did not show any consistent discrepancies, although individual methods varied in the concentration of reagents and the nature of solvent. The Texel workshop demonstrated this feature well, where analysts working side by side reported small differences, the nature of which varied from sample to sample. Such differences must be related to the analytical degree of precision rather than inherent features of any one technique or team.

Unfortunately the number of trials comparing different basic techniques was rather small. However, the ion exchange technique of Brussels generally gave higher copper values than the solvent extraction methods (Tables 3 and 5), whereas the ion exchange procedure of Plymouth reported markedly lower copper values compared with Lowestoft (Table 6). Similarly the electro-chemical technique employed by Liège showed higher copper values compared with the extraction method (Tables 3 and 5), although this feature was not so marked during the Texel workshop (Table 8). Muzzarelli and Rocchetti (1974) have discussed the analysis of copper in relation to analytical techniques. They believe that a significant fraction of copper is bonded to organic compounds and that certain techniques such as solvent extraction at the pH of sea water do not analyse this fraction. Duyckaerts and Gillain (1974) have made similar proposals in relation to copper measured by anodic stripping voltammetry.

In addition to the above intercalibration tests, reference must be made to similar trials reported by Brewer and Spencer (1972) and Macaulay (1974) who showed large discrepancies between laboratories measuring trace metals in sea water. Clearly further investigation is required concerning analytical techniques for measuring trace metals in sea water, particularly in relation to the selective analysis of different species.

Any of the techniques used in the present study would be adequate for locating major areas of pollution. However, with the possible exception of zinc, the uniformity of data is not adequate to permit a comparison of values obtained by different basic techniques, particularly in the case of oceanic water where levels are often near detection limits.

In addition to analytical techniques, the method of water collection and storage is of paramount importance. Although not reported upon here, some comparison of methods of sampling and filtration was made during the above trials. The type of filtration unit and the pore size of the membrane filter was sometimes shown to influence the amount of "dissolved" metal measured. Further investigations are necessary to fully elucidate the nature of this effect.

An expanded intercalibration programme to include sample collection, storage and analysis is being planned under the auspices of the ICES Working Group on Pollution Baseline and Monitoring Studies in the Oslo commission and ICNAF Areas. Full participation in this project is essential both for the success of future international metal surveys and to further understanding of the many remaining unsolved problems.

SUMMARY

Laboratories in Belgium, the Netherlands and the United Kingdom participated in an intercalibration of analytical techniques which included anodic stripping voltammetry and atomic absorption by solvent extraction and ion exchange resin. The metals intercalibrated were copper, zinc, cadmium and nickel. The latter two, however, were generally too near the limit of detection for a meaningful comparison. Most solvent extraction methods gave comparable results, although some variation in copper was reported. The anodic stripping method and sometimes the ion exchange technique gave copper values higher than by solvent extraction. Speciation of the metal was thought to be relevant to such discrepancies. Further intercalibration, both of sample collection and storage in addition to methods of analysis, is proposed to help solve the many problems still remaining.

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Sample	Position	Zn $\mu\text{g}/1$		Cu $\mu\text{g}/1$		Cd $\mu\text{g}/1$		
		MAFF (FRL)	UL	MAFF (FRL)	UL	MAFF (FRL)	UL	
Belgium	M 11	51°51'N 03°47'E	6.0	4.2	2.4	5.3	0.45	0.18
	M 12	" 03°28'E	3.6	7.0	1.3	8.0	0.20	0.26
	M 13	" 03°09'E	3.0	8.4	1.0	7.5	0.70	0.17
	M 14	" 02°52'E	1.2	5.0	0.8	15.0	0.30	0.20
	M 15	" 02°33'E	2.9	8.0	1.1	10.0	0.10	0.41
		t 2.444	.1 > p > .05	t 4.219	.02 > p > .01	t 0.754	.6 > p > .5	
MAFF	B 1	53°33'N 00°08'W	5.9	6.5	1.9	5.7	0.20	0.17
	C 4	53°22'N 01°45'E	1.9	2.6	0.4	4.4	0.20	0.17
	C 5	53°23'N 02°28'E	2.5	10.0	0.4	8.0	0.30	0.20
	D 4	52°37'N 02°47'E	1.9	2.2	1.1	5.7	0.05	0.16
	E 4	51°38'N 01°53'E	5.3	5.5	1.2	6.3	0.50	0.27
		t 1.316	.3 > p > .2	t 7.335	.01 > p > .001	t 1.013	.4 > p > .3	

Table 1 Intercalibration of analyses of selected trace metals in water from the North Sea: Belgium (UL) and United Kingdom (FRL): 1971

Sample	Position	Zn $\mu\text{g}/1$		Cu $\mu\text{g}/1$		Cd $\mu\text{g}/1$		Ni $\mu\text{g}/1$		
		MAFF (HL)	NIOZ	MAFF (HL)	NIOZ	MAFF (HL)	NIOZ	MAFF (HL)	NIOZ	
NIOZ	T 5	53°00'N 04°48'E	10.7	21.4	3.4	7.6	0.1	0.4	2.3	1.8
	T 7	53°00'N 04°51'E	8.9	10.0	2.9	7.0	0.1	0.4	1.1	0.8
	T 9	53°01'N 04°51'E	12.4	16.1	5.7	8.0	0.1	0.4	0.5	0.8
	T 11	53°02'N 04°54'E	6.7	10.6	3.1	4.6	0.1	0.4	0.5	< 0.3
	T 13	53°03'N 04°53'E	10.1	16.7	3.8	6.2	0.1	0.3	0.5	0.3
		t 3.196	.05 > p > .02	t 5.432	.01 > p > .001	t 14.0	p < .001	t 1.633	.2 > p > .1	
MAFF	A 1	55°39'N 01°43'W	6.8	3.0	0.8	1.2	0.1	0.2	1.9	< 0.3
	B 1	55°01'N 01°24'W	7.4	6.2	0.8	1.2	0.1	0.3	0.6	< 0.3
	C 6	55°27'N 00°36'E	3.9	4.1	0.4	1.6	0.1	0.2	0.8	0.4
	I m	53°38'N 00°09'W	13.3	16.7	3.1	2.2	0.6	0.6	7.6	3.8
		t 0.233	.9 > p > .8	t 0.633	.6 > p > .5	t 2.449	.1 > p > .05	t 2.141	.2 > p > .1	

Table 2 Intercalibration of analyses of selected trace metals in water from the North Sea: Netherlands (NIOZ) and United Kingdom (HL): 1973

Sample	Position	Zn $\mu\text{g}/1$			Cu $\mu\text{g}/1$			Cd $\mu\text{g}/1$		
		MAFF (HL)	UVB	UL	MAFF (HL)	UVB	UL	MAFF (HL)	UVB	UL
MAFF L 5	52°37'N 03°12'E	5.5	5.5	3.2	0.7	1.9	3.7	0.05	0.17	0.65
J 1	51°29'N 00°58'E	5.5	5.7	8.7	1.4	3.3	11.6	0.15	0.87	0.55
K 6	51°22'N 03°01'E	9.8	3.5	12.3	1.2	3.0	5.4	0.04	0.73	0.80
L 2	51°01'N 01°30'E	3.6	4.6	4.7	0.4	1.6	10.7	0.10	0.40	0.67
J 10	52°03'N 04°04'E	7.9	6.9	7.2	1.2	2.8	3.5	0.06	0.69	0.62
		t	p		t	p		t	p	
	MAFF v UVB	0.932	.5-.4		10.478	< .001		4.118	.02-.01	
	MAFF v UL	0.749	.5-.4		3.406	.05-.02		10.086	< .001	
	UVB v UL	1.042	.4-.3		2.539	.1-.05		0.625	.7-.6	

Table 3 Intercalibration of analyses of selected trace metals in water from the North Sea: Belgium (UVB and UL) and United Kingdom (HL): 1973

Sample	Position	Zn $\mu\text{g}/\text{l}$		Cu $\mu\text{g}/\text{l}$		Cd $\mu\text{g}/\text{l}$			
		HL	FRL	HL	FRL	HL	FRL		
33	Surface	58°00'N	09°58'W	1.9	1.5	0.6	0.2	0.06	0.07
	950 m			1.9	2.6	0.1	0.1	0.07	0.09
	1900 m			1.9	3.1	0.1	0.3	0.09	0.02
34	Surface	56°30'N	10°31'W	1.6	2.4	0.1	0.3	0.01	0.02
35	Surface	57°00'N	11°00'W	1.9	0.9	0.2	0.2	0.01	0.05
	1200 m			1.5	4.0	0.1	0.2	0.04	0.10
	2400 m			2.1	1.7	0.3	0.1	0.09	0.08
36	Surface	57°00'N	10°00'W	3.0	3.9	0.3	0.2	0.01	0.30
37	Surface	57°00'N	09°00'W	1.8	1.0	0.1	0.2	0.01	0.04
	65 m			2.0	1.0	0.3	0.1	0.03	0.05
	130 m			2.3	0.7	0.1	0.2	0.04	0.04
				t = 0.221	.9 > p > .8	t = 0.319	.8 > p > .7	t = 1.735	.2 > p > .1

Table 4 Intercalibration of analyses of selected trace metals in water from the Northeast Atlantic: United Kingdom (HL x FRL): 1973

Sample	Position	Zn $\mu\text{g}/1$					Cu $\mu\text{g}/1$					Cd $\mu\text{g}/1$					Ni $\mu\text{g}/1$		
		MAFF HL	MAFF FRL	UVB	UL	NIOZ	MAFF HL	MAFF FRL	UVB	UL	NIOZ	MAFF HL	MAFF FRL	UVB	UL	NIOZ	MAFF HL	MAFF FRL	NIOZ
6	51°50'N 02°55'E	3.2	2.7	3.0	7.8	1.2	0.5	0.4	1.8	9.9	0.6	0.05	0.10	0.09	0.32	< 0.2	2.3	0.7	< 0.3
		3.2	2.7	2.5	6.4	1.4	0.5	0.3	1.7	8.0	0.4	0.05	0.10	0.10	0.30	< 0.2	2.3	0.7	< 0.3
		3.4	2.7	2.9	7.0	1.4	0.5	0.3	1.7	11.8	1.0	0.10	0.20	0.10	0.32	< 0.2	1.7	0.4	< 0.3
		3.1	2.7	2.9	7.1	1.7	0.5	0.3	1.7	8.9	0.4	0.10	0.20	0.08	0.33	< 0.2	1.7	0.6	< 0.3
		3.2	2.4	2.9	11.3	1.4	0.4	0.4	2.1	13.6	0.4	0.05	0.10	0.09	0.33	< 0.2	1.9	0.3	< 0.3
Arith mean		3.2	2.6	2.8	7.9	1.4	0.5	0.3	1.8	10.4	0.6	0.07	0.14	0.09	0.32	-	1.9	0.5	-
10	52°03'N 04°04'E	10.2	10.0	4.4	10.2	7.5	1.0	1.0	2.4	7.0	0.6	0.20	0.20	0.38	0.48	< 0.2	2.7	1.4	0.4
		10.0	11.0	8.8	9.2	7.5	1.0	1.0	3.0	5.5	0.6	0.20	0.20	0.25	0.48	< 0.2	3.1	1.7	0.4
		10.0	12.1	2.5	2.5	8.4	1.0	1.0	2.5	6.0	0.6	0.20	0.20	0.35	0.34	< 0.2	2.2	1.5	0.4
		10.2	12.3	9.4	10.6	8.0	1.0	1.0	2.3	5.0	0.6	0.20	0.20	0.35	0.35	< 0.2	2.2	1.6	0.4
		10.2	10.0	0.1	12.4		1.0	1.5	2.7	7.5		0.20	0.20	0.40	0.48	< 0.2	2.2	1.6	
Arith mean		10.1	11.1	6.4	9.0	7.9	1.0	1.1	2.6	6.2	0.6	0.20	0.20	0.35	0.43	-	2.5	1.6	0.4
5	50°37'N 00°46'E	3.5	1.2	1.3		2.2	0.1	0.3	1.2		1.2	< 0.05	0.1	0.2		< 0.2	< 0.4	0.4	< 0.7
		2.6	1.1	1.8		2.6	0.2	0.3	2.3		0.3	< 0.05	0.1	0.2		< 0.2	< 0.4	0.4	< 0.7
		2.3	4.8	1.4		2.0	0.2	0.3	1.8		0.2	< 0.05	0.1	0.2		< 0.2	0.4	0.4	< 0.7
		3.1	2.1	2.0		2.0	0.1	0.3	1.4		0.6	< 0.05	0.1	0.2		< 0.2	< 0.4	0.4	< 0.7
		2.5	1.1	1.8		2.6	0.1	0.3	1.4		0.6	< 0.05	0.1	0.2		< 0.2	0.4	0.4	< 0.7
Arith mean		2.8	2.1	1.7		2.3	0.1	0.3	1.6		< 0.05	0.1	0.2		-	0.4	0.4	< 0.7	
24	51°29'N 00°46'E	21.4	17.5	19.6		25.0	2.1	1.8	4.6		3.4	0.3	0.4	0.4		0.2	5.1	5.0	7.4
		21.2	17.5	20.1		22.5	2.1	1.9	4.3		2.8	0.3	0.7	0.3		0.2	5.1	5.0	8.1
		21.2	18.1	21.1		22.2	2.2	2.0	4.2		3.0	0.3	0.4	0.3		0.2	5.1	5.5	8.1
		22.7	18.8	20.7		21.8	2.5	2.2	4.2		2.8	0.3	0.6	0.3		0.3	5.6	5.5	7.4
		20.8	18.1	20.1		22.4	2.4	1.9	4.3		3.4	0.3	0.5	0.3		0.3	4.6	5.0	7.4
Arith mean		21.5	18.1	20.8		22.8	2.3	2.0	4.3		3.1	0.3	0.5	0.3		0.2	5.1	5.2	7.7

Table 5 Intercalibration of analyses of selected trace metals in water from the North Sea: Belgium (UVB and UL), Netherlands (NIOZ) and United Kingdom (HL and FRL): 1974

Sample	Position	Zn $\mu\text{g}/\text{l}$		Cu $\mu\text{g}/\text{l}$		Cd $\mu\text{g}/\text{l}$	
		MAFF HL	IMER	MAFF HL	IMER	MAFF HL	IMER
1	51°29'N 01°58'E	6.1	6.4	1.17	0.50	0.23	0.25
		6.7		1.17		0.23	
		6.1		1.22		0.22	
		6.6		1.17		0.22	
		5.7		1.19		0.22	
		5.9		1.13		0.20	
		6.2		1.17		0.23	
		6.4		1.17		0.21	
		6.5		1.13		0.22	
		6.1		1.13		0.19	
		Arith mean				6.2	
19	49°25'N 00°37'W	3.2	3.5	0.42	0.20	0.24	0.17
		3.8		0.50		0.21	
		3.3		0.46		0.39*	
		3.5		0.50		0.26	
		2.2		0.46		0.17	
		2.9		0.42		0.09	
		3.2		0.42		0.05	
		3.2		0.42		0.23	
		3.1		0.43		0.23	
		2.9		0.42		0.14	
Arith mean		3.1		0.44		0.20	
62	49°19'N 05°13'W	3.4	3.4	0.45	0.13	0.15	0.15
		2.5		0.35		0.10	
		2.6		0.30		0.11	
		2.9		0.20		0.12	
		2.9		0.25		0.11	
		2.7		0.25		0.10	
		3.4		0.20		0.09	
		2.7		0.16		0.09	
		3.3		0.21		0.09	
		2.8		0.36		0.11	
Arith mean		2.9		0.27		0.11	

Table 6 Intercalibration of analyses of selected trace metals in water from the English Channel and Thames Estuary: United Kingdom (HL and IMER): 1974.

* Omit value mean = 0.18

Sample	Position	Zn $\mu\text{g}/\text{l}$		Cu $\mu\text{g}/\text{l}$		Cd $\mu\text{g}/\text{l}$		Ni $\mu\text{g}/\text{l}$	
		MAFF HL	IOS	MAFF HL	IOS	MAFF HL	IOS	MAFF HL	IOS
12. Surface	54°18'N 11°12'W	0.9	1.2	0.42	0.55	0.05	0.02	0.07	< 0.05
13. 180 m	53°41'N 11°16'W	0.8	1.0	0.37	0.38	< 0.02	0.02	0.04	< 0.05
14. Surface	53°01'N 11°44'W	1.4	2.2	0.42	0.56	< 0.02	< 0.01	0.07	< 0.05
15. 105 m	52°50'N 10°40'W	3.2	2.2	0.22	0.70	< 0.02	0.05	0.02	< 0.05
16. Surface	52°21'N 11°52'W	0.8	0.8	0.42	0.48	< 0.02	0.02	0.02	< 0.05
17. 455 m	51°30'N 11°36'W	0.5	2.6	0.25	0.26	< 0.02	0.01	0.04	0.23
18. Surface	60°00'N 11°00'W	0.3	1.1	0.29	0.30	< 0.02	0.01	0.04	0.20
19. 410 m	50°00'N 11°00'W	0.4	0.8	0.26	0.29	< 0.02	0.01	0.05	0.17
20. Surface	49°27'N 10°04'W	0.7	0.8	0.30	0.27	< 0.02	0.01	0.07	0.06
21. 155 m	48°53'N 09°06'W	0.6	1.2	0.25	0.20	< 0.02	< 0.01	0.07	0.17

$t = 1.739 \quad .2 \quad p > .1$
 $t = 1.625 \quad .2 > p > .1$

Table 7 Intercalibration of analyses of selected trace metals in water from the Northwest Atlantic: United Kingdom (HL x IOS): 1974

Sample	Position	Zn $\mu\text{g}/\text{l}$				Cu $\mu\text{g}/\text{l}$				Cd $\mu\text{g}/\text{l}$				Ni $\mu\text{g}/\text{l}$						
		MAFF		UVB	UL	MAFF		UVB	UL	MAFF		UVB	UL	NIOZ	MAFF		NIOZ			
		HL	FRL			HL	FRL			HL	FRL				HL	FRL				
Marsdiep	52°58'N 04°46'E	3.5	4.7			5.0	1.2	0.8			2.3	0.05	0.20			< 0.1	< 0.4	< 0.4	< 0.3	
		3.5	4.2			4.0	1.1	0.8			1.7	0.06	0.30							
		3.1				13.0*	1.0				2.2	0.05								
		3.3				3.4	1.1				6.7*	0.05								
		3.6				4.5	1.1				1.5	0.04								
Arith mean																				
		3.4	4.4			4.2	1.1	0.8			1.9	0.05	0.15			< 0.1	< 0.4	< 0.4	< 0.3	
Offshore Den Helder	52°56'N 04°20'E	0.8	3.3			1.8	0.1	1.1			0.5	0.07	0.10			< 0.1	< 0.4	1.3	0.5	
		0.8	1.0			1.3	0.1	0.2			0.5	0.06	0.04			< 0.1		0.05	0.5	
		0.8				1.0	0.1				0.5	0.07				< 0.1			0.5	
Arith mean																				
		0.8	2.2			1.4	0.1	0.6			0.5	0.07	0.07			< 0.1	< 0.4	0.7	0.5	
Inshore Den Helder	52°54'N 04°37'E	4.2	3.3	3.8	6.0	3.9	0.6	0.9	2.0	0.5	1.2	0.07	0.20		0.05	< 0.1	< 0.4	1.4	1.2	
		5.5	3.7			3.4	0.6	1.2				1.3	0.09	0.08			< 0.1		1.4	1.0
		4.0				3.0	0.6					1.1	0.08				< 0.1			0.5
Arith mean																				
		4.6	3.5	3.8	6.0	3.4	0.6	1.0	2.0	0.5	1.2	0.08	0.14		0.05	< 0.1	< 0.4	1.4	0.9	
Inshore Ijmuiden	52°31'N 04°38'E	4.5	4.2	6.6	4.2	4.0	1.0	0.6	3.2	3.1	1.0	0.05	0.30	< 0.04	0.35	0.03	1.0	1.0	1.4	
		4.5	4.6			4.4	0.8	0.6				1.1	0.00	0.06			0.03	1.0	1.0	1.4
		4.2				4.4	0.8					1.1	0.03				0.03	1.0		1.1
Arith mean																				
		4.4	4.4	6.6	4.2	4.3	0.9	0.6	3.2	3.1	1.1	0.03	0.18	< 0.04	0.35	0.03	1.0	1.0	1.3	
Offshore Ijmuiden	52°45'N 04°38'E	2.3	3.1	7.8	8.5	2.0	0.5	< 0.3	0.9	2.5	0.6	0.00	0.03	0.00	0.01	0.00	3.0	1.0	1.0	
		1.5	2.8			2.5	0.5	< 0.3				0.6	0.00	0.02			0.00	3.0	0.8	1.2
		1.5				2.5	0.5					0.6	0.00				0.00	3.0		1.2
Arith mean																				
		1.8	3.0	7.8	8.5	2.3	0.5	< 0.3	0.9	2.5	0.6	0.00	0.02	0.00	0.01	0.000	3.0	0.9	1.1	

Table 8 Results of an international intercalibration workshop on the analyses of selected trace metals in water from the North Sea. Texel, September 1974

* Value omitted from mean

Laboratories	Copper		Zinc	
	t	p	t	p
HL v FRL	0.113	> .9	1.071	.4>.3
HL v NIOZ	3.280	.05>.02	0.331	.8>.7
FRL v NIOZ	2.000	.2>.1	2.484	.1>.05

Table 9 Statistical analysis of copper and zinc values measured by Netherlands and the United Kingdom laboratories during the international intercalibration workshop, Texel, September, 1974