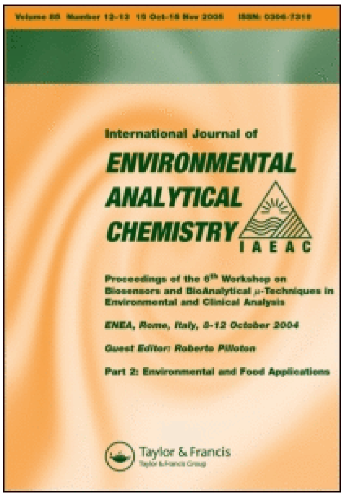


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Trace, Alkaline and Alkaline-Earth Elements in Sea Water Samples from Terra Nova Bay - Ross Sea (ANTARCTICA): A Three-Year Period of Observation

P. Cescon[a]; R. Fuoco[b]; P. Papoff[c]
[a] Dipartimento di Scienze Ambientali, dell'Università Calle Larga, Venezia, Italy [b] Istituto di Chimica Analitica Strumentale del C.N.R., Pisa, Italy [c] Dipartimento di Chimica e Chimica Industriale, Pisa, Italy

To cite this Article Cescon, P. , Fuoco, R. and Papoff, P.(1994) 'Trace, Alkaline and Alkaline-Earth Elements in Sea Water Samples from Terra Nova Bay - Ross Sea (ANTARCTICA): A Three-Year Period of Observation', International Journal of Environmental Analytical Chemistry, 55: 1, 91 — 119

To link to this Article: DOI: 10.1080/03067319408026211

URL: http://dx.doi.org/10.1080/03067319408026211

Intern. J. Environ. Anal. Chem., Vol. 55, pp. 91-119
Reprints available directly from the publisher
Photocopying permitted by license only

TRACE, ALKALINE AND ALKALINE-EARTH ELEMENTS IN SEA WATER SAMPLES FROM TERRA NOVA BAY - ROSS SEA (ANTARCTICA): A THREE-YEAR PERIOD OF OBSERVATION

P. CESCON*, R. FUOCO† and P. PAPOFF‡

**Dipartimento di Scienze Ambientali dell'Università Calle Larga S.Marta 2137, 30123 Venezia, Italy; †Istituto di Chimica Analitica Strumentale del C.N.R. Via Risorgimento 35, 56100 Pisa, Italy; ‡Dipartimento di Chimica e Chimica Industriale dell'Universita Via Risorgimento 35, 56100 Pisa, Italy*

(Received in final form, 3 August 1993)

This report concerns the correlation of the analytical results relevant to some elements obtained in filtered sea water samples collected in Terra Nova Bay and the Ross Sea (Antarctica) during three Italian expeditions. The following ranges of variability of the medians of total concentrations (ng/l) – which include time effect among expeditions and bias effect among participant groups – were found for trace elements (single values refer to elements which were only determined once by one laboratory): Sb (260), As (1.2 10^3), Cd (5–50), Cr (120), Co (4), Cu (110–230), Fe (435–445), Pb (6–52), Mn (15–88), Hg (3), Ni (185–580), Se (30) and Zn (242–265). Speciation studies pointed out that 10–40% of Cd, 15–60% of Cu and 20–50% of Pb were present in the samples as an ASV-labile fraction.

As for alkaline and alkaline-earth elements, the following concentration ranges in surface sea waters, expressed in mM, were found: Li ([1.4–3.0] 10^{-2}), Na (394–480), K(5.1–9.9), Ca (6.4–14.7), Mg (46.2–59.0) and Sr ([7.6–10] 10^{-2}).

Inter- and intra-laboratory data comparison, incorrect results, local variations of concentration, including pollution effects and pack melting effect, are discussed in detail.

KEY WORDS: Antarctica, trace elements, alkaline and alkaline-earth elements, sea water.

INTRODUCTION

This report presents and correlates the results obtained by six participating groups in the chemical characterization of filtered sea water sub-samples, gathered during the 1987–88, 1988–89 and 1989–90 Italian expeditions to Antarctica. These expeditions were performed under the Italian "Programma Nazionale di Ricerche in Antartide", "Impatto Ambientale-Metodologie Chimiche" section.

---

*To whom correspondence should be addressed.

The main goals of the scientific activity of each expedition were:

1987–88 Expedition

a) to measure the total concentration of trace elements of biological interest in sea water samples from Terra Nova Bay and the Ross Sea, including the sea area near the Italian Base, in order to get a preliminary evaluation of the concentrations of the elements considered and to ascertain whether contamination effects occur, and at which confidence level they can be detected and quantified. The following trace elements were taken into consideration: antimony, arsenic, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium and zinc;

b) to measure the distribution of total concentration between ASV-labile and chemically bounded species for some trace elements (cadmium, lead and copper) for each sampling station, and to correlate these concentrations with other biological and chemical parameters;

c) to measure the alkaline (Li, Na and K) and alkaline-earth (Mg, Ca and Sr) element contents in order to get additional information about the representativity of the sample gathered in each sampling station **x** at the time **t**, in relation to space and time variables.

1988–89 Expedition

To verify whether significant variations in trace element content, its speciation and alkaline and alkaline-earth concentrations occur in the sea water of Terra Nova Bay before and after pack ice melting.

1989–90 Expedition

To study the distribution of alkaline and alkaline-earth elements in terms of depth and to confirm for trace elements the results obtained in the previous expeditions.

Table 1 shows for each expedition: the number of sampling stations, the field and laboratory operations, the instrumental techniques employed and the elements determined by the five participating groups.

The correlation of the analytical results, as obtained by the individual groups during the three expeditions, is preceded by a discussion on the random and systematic errors inherent to each analytical procedure. Pollution and seasonal effects are then highlighted and interpreted. Figures 1, 2 and 3 show the location of the sampling stations for the 1987–88, 1988–89 and 1989–90 expeditions respectively.

TRACE ELEMENTS

Definition of the chemical problem

Trace elements are generally present in uncontaminated sea water at concentration levels of a few to hundreds of ng/l, depending on their nature[1]. The accuracy of the analytical data is the most important problem at these extremely low concentration values. It is well known from interlaboratory exercises that when the same sample is distributed in sub-samples and the solution is carefully homogenized in all the containers, the spread of interlaboratory data can be quite large, even at μg/l level, and that for the same laboratory, the relative bias for

Table 1 Number of stations, field and laboratory operations considered, instrumental techniques used and trace elements determined for each participating laboratory.

U.O.	NUMBER OF STATIONS	FIELD OPERATIONS					LABORATORY PRE-CONCENTRATION	INSTRUMENTAL	ELEMENTS	REFERENCES
		FILTERING 0.45μm	ADD HCl pH=2	PRE-CONC.	STORAGE -20°C	STORAGE 4°C	METHOD	TECHNIQUE		
IACES 1987-88	12/12	YES			YES		Electrodeposition on TFME	DPASV	Cd, Cu, Pb	2 5
1988-89	10/10	YES			YES		Electrodeposition on TFME	DPASV	Cd, Cu, Pb	5
1989-90	4/6	YES			YES		Electrodeposition on TFME	DPASV	Cd, Cu, Pb	6
IAFRA 1987-88	12/12	YES		Chelex-100 (batch)	YES		None	AAS/ETA	Cr, Cu, Fe, Ni	7
1988-89	10/10	YES		Chelex-100 (batch)	YES		None	AAS/ETA	Cd, Cu, Fe, Ni	8
IAMEN 1987-88	1/12	YES			YES		Reductive precip. (M1) Hydride gener.& trap(M3) Complex & ion ex.(M2)	GFAAS GFAAS GFAAS	As, Cd, Co, Cu, Ni, Pb, Se, Zn As, Se, Sb Cd, Cu, Fe, Ni	9 9 9
1988-89	1/10	YES			YES		Complex & ion exchange (M4 &M5)	ICP/AES, CV/AAS DPASV, LSCSV	Cd, Cu, Fe, Hg, Mn, Ni, Zn	4
1989-90	1/6	YES			YES		Complex & ion exachange	GFAAS	Cd, Co, Cu, Fe, Ni, Pb	10
IAPAP 1987-88	12/12	YES	YES			YES	Electrodeposition on HDME	DPASV	Cd, Cu, Pb, Zn	3
1988-89	10/10	YES	YES			YES	Electrodeposition on HDME	DPASV	Cd, Cu, Pb	11
1989-90	4/6	YES	YES			YES	Electrodeposition on HDME	DPASV	Cd, Cu, Pb	11
IASAI 1987-88	12/12	YES	YES		YES		Reductive precipitation	GFAAS	Cd, Cu, Ni	12
1988-89	6/10	YES	YES		YES		Reductive precipitation	GFAAS	Cd, Cr, Cu, Mn, Ni	13

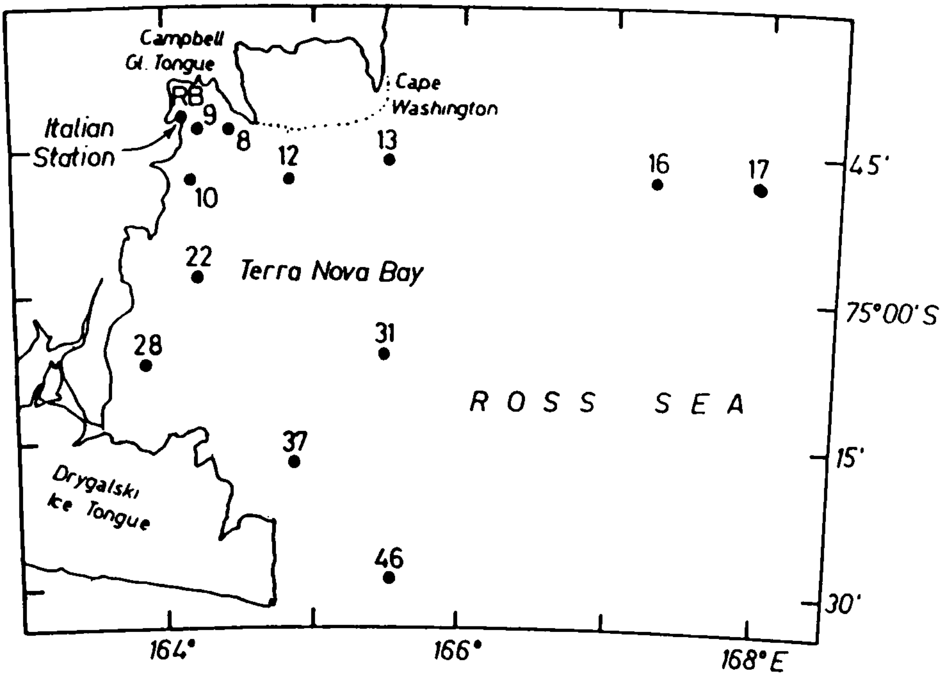


Figure 1 Sampling stations for the 1987–88 Expedition in Antarctica.

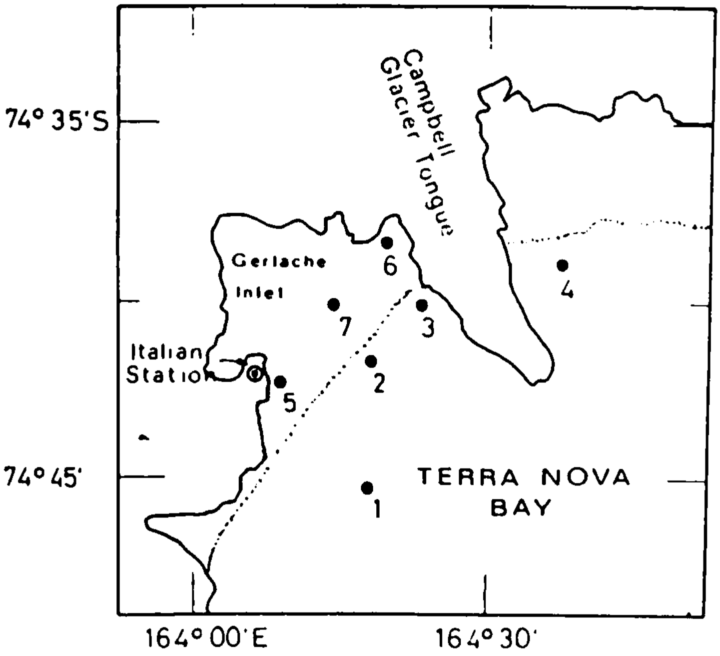


Figure 2 Sampling stations for the 1988–89 Expedition in Antarctica.

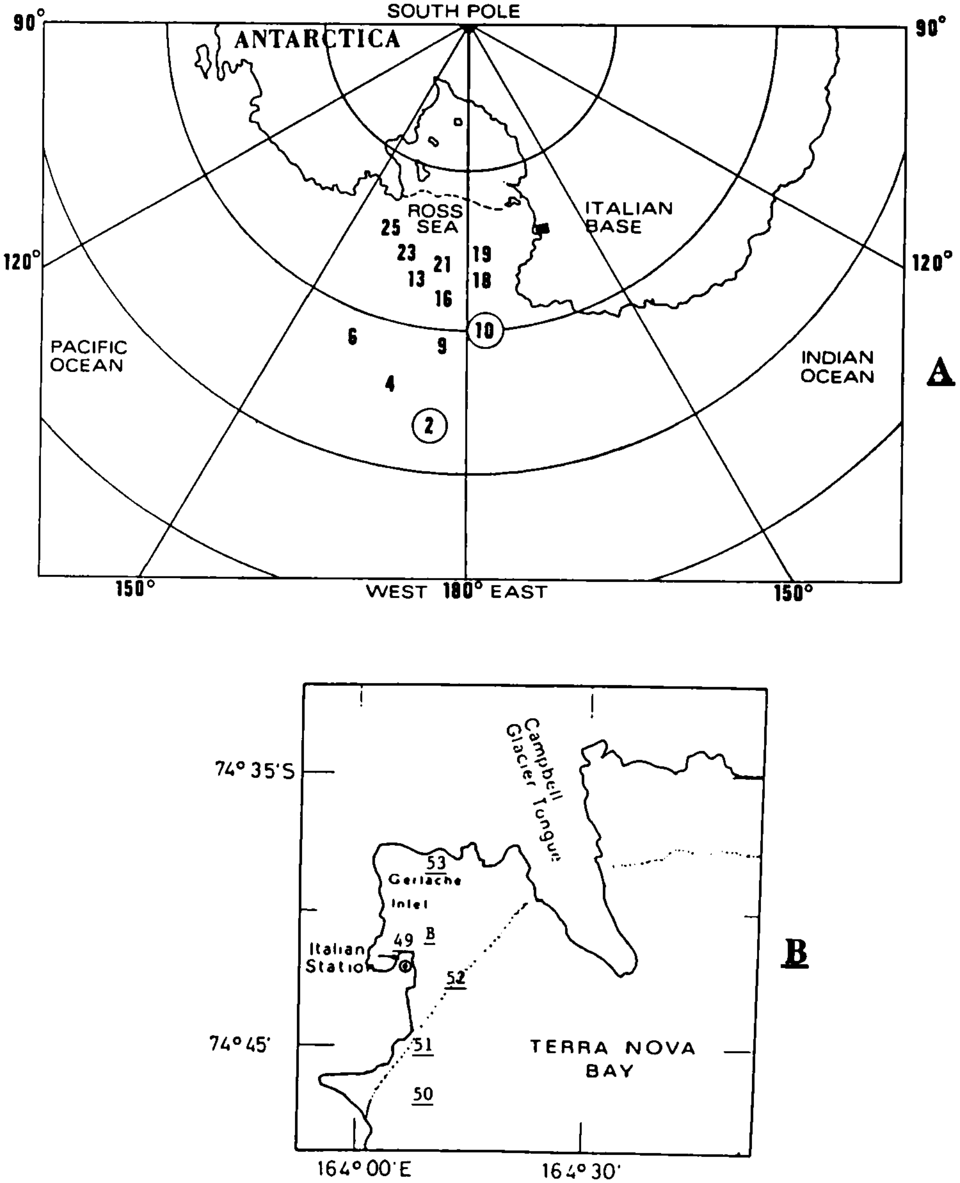


Figure 3 Sampling stations for the 1989–90 Expedition in Antarctica:
A) off-shore sampling stations (the numbers within circles refer to stations where depth profile was done);
B) in-shore sampling stations.

different samples appears to be to some extent chaotic and unrelated to the analyte concentration in the sample. In the characterization of sea water, apart from estimating the true concentration value of the analyzed sample, another source of uncertainty is the lack of a priori knowledge of the extent of variability, due to space and time effects, in the chemical composition of the sample in the sampling sites.

From an analysis of all the data obtained by the five participating laboratories, the primary goal, as mentioned in the introduction, was to estimate both the most reliable total soluble concentration interval of trace elements and, for some of them, how this concentration is shared between labile and chemically bounded species (speciation), in each station during the 1987–88, 1988–89 and 1989–90 expeditions. From data correlations among stations for each expedition, and among expeditions and stations, information can then be obtained about time and space effects on the homogeneity of sea water. As far as speciation is concerned, note that Biologists, who are an important class of users of data on the chemical composition of sea water, consider total concentrations as gross, first level information in the interpretation of the effects of trace elements on biota. Apart from the experimental difficulties associated with this approach, their final concern is how this total concentration is shared between free (hydrated) metal ions and other metal-containing chemical species, and which chemical and physical characteristics these metal-containing compounds present. The solution to this kind of problem (speciation) requires particular care in obtaining and processing experimental results. It was tackled by the IACES group which reached a remarkably high level of qualification before the start of the Italian research program in Antarctica.

The strategy

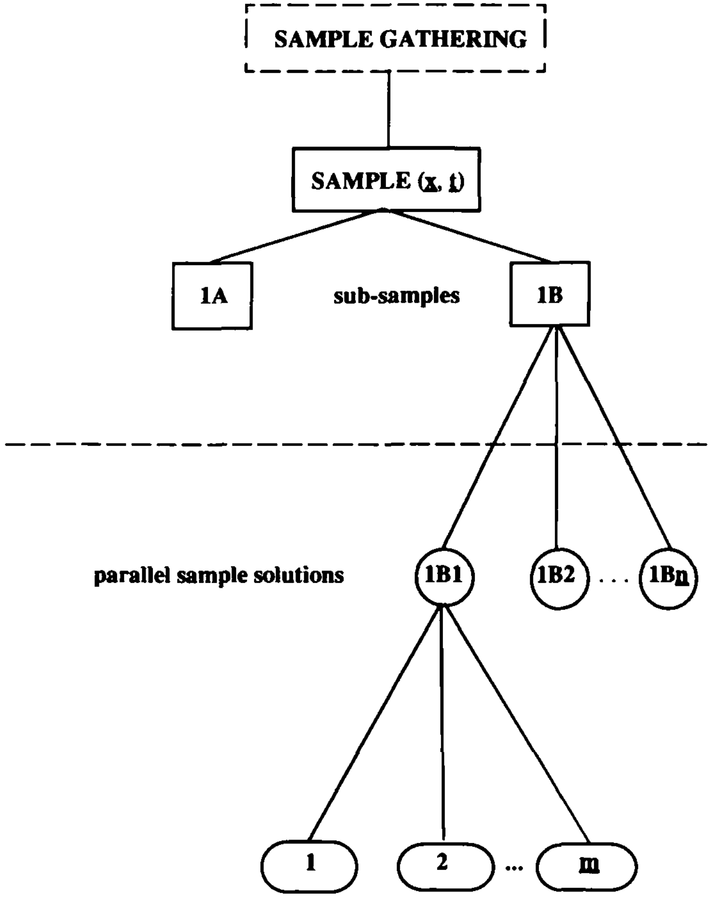
The strategy followed by the Environmental Impact Research group had two main objectives:

1) to establish a permanent laboratory in Antarctica where all the preliminary manipulations of the samples, such as filtration, pre-concentration, acidification, etc., along with particular analyses (depending on the instrumentation and skilled operators available each time) can be performed;
2) to send the sub-samples to Italy to all the participating laboratories, in accordance with the pre-treatment procedures individually suggested and using containers which were pre-conditioned by each laboratory. The more the procedures are different, from pre-treatment to analysis, the higher the possibility is to distinguish between systematic and random effects.

Figure 4 shows the sequence of steps from sampling to measurements performed both in Antarctica and in the laboratories. When required, each laboratory received two parallel sub-samples **A** and **B** for each sampling point (see point **1** in Figure 4). The sub-samples were conditioned, stored in pre-cleaned containers and shipped back to the participants, in accordance with their specific instructions.

Total concentrations of trace elements

Data interpretation, in terms of absolute concentration of trace elements and effects of distance, depth and time of sampling, requires a preliminary estimate, for each analyte **i**, of



FIELD OPERATIONS

Filtration, acidification and pre-concentration as required, storage in pre-cleaned containers at required temperature.

POINT 1) Conditioned sub-samples (A and B) sent to each of the five participating laboratories. Laboratory No. 1 is consider as an example.

LABORATORY OPERATIONS

POINT 2) n parallel sample solutions prepared in the participating laboratory from a sub-sample, and ready for the instrumental analysis according to the selected laboratory procedure(s). Sample 1B is consideres as an example.

POINT3) m aliquots of a parallel sample solution analyzed according to the selected procedure(s)

Figure 4 Schematic sequence of sample distribution from sampling to the analysis performed in each of the five participating laboratories.

the effect of the different steps of sample handling and analysis on the mean value $\mathbf{X}_{m,i}$ and on the overall sample standard deviation **s**. Systematic measurements were thus performed in order to quantify the:

i) *reproducibility of the measured concentration of analyte **i** in the sample solution:* **m** aliquots of the same sample solution, which contains a known amount of sub-sample and is ready for instrumental analysis after physical and chemical treatments, are analyzed by using the same procedure in the same laboratory. In this case, the spread of the found concentrations $\mathbf{X}_i$ is directly related to the reproducibility of the instrumental measurement (see point **3** in Figure 4);

ii) *reproducibility of the replicate measurements of a sub-sample:* the same sub-sample is divided into **n** sub-sub-sample which are individually treated by suitable physical-chemical procedures giving rise to **n** sample solutions. These sample solutions are analyzed **m** times in the same laboratory by using the same overall procedure. In this case, the spread of the mean values $\mathbf{X}_{m,i}$ depends on the concomitant effects of the reproducibility of both measurement and sample preparation procedures (see point **2** in Figure 4);

iii) *reproducibility of the replicate measurements by analyzing several aliquots of the same sub-sample with different procedures*: in this way, once the interval of confidence at the selected confidence level for $\mathbf{X}_{m,i}$ has been estimated, it is possible to obtain information on the presence of systematic errors (see point **2** in Figure 4);

iiii) *reproducibility of* $X_{m,i}$ *among sub-samples in the same laboratory:* by using the same analytical procedure, aliquots of sub-samples **A** and **B** are each analyzed m times in order to check whether $\mathbf{X}_{miA}$ is equal to $\mathbf{X}_{miB}$ at the desired confidence interval (see point **1** Figure 4). Effects due to physical-chemical processes which may change the chemical composition of the sample can be then highlighted.

In addition to the procedure described in point **iii)**, the bias is estimated by comparing the data obtained by the analyses of the sub-samples **A** and **B** in different laboratories according to their own procedures (see point 1 in Figure 4). The risk of obtaining data whose amount of bias is completely unknown, decreases by increasing the skillfulness of the laboratories which perform the analyses following their tested procedures. In this respect it must be mentioned that the five laboratories were selected on the basis of their previous experience in trace element determination in natural waters.

Storage effects on bias Systematic measurements were performed to evaluate the storage effects on trace element content in sea water samples both stored at natural pH, for speciation studies, and at pH=2 by adding HCl or HNO_3, for total concentration determination.

In experiments performed in filtered sea water samples at natural pH^2, the total concentration of lead was measured:

i) immediately after manual and teflon pump sampling:

ii) after storage at −20°C for 5–10 months.

From these results, no contamination due to the teflon pump was observed. For most of the stations (1987–88 expedition) a decrease in the total lead concentration after storage, which is roughly proportional to the concentration and is about 20%, was observed as a trend; while an increase of 20 to 55% in the total cadmium concentration was found for the same storage conditions. The latter was explained as an effect on the accuracy of the measurements of both the total metal concentration to total ligand concentration ratio and the concentration range used for standard additions.

From experiments performed on NASS-2 certified sea water sub-samples poured into five pre-cleaned containers and analyzed after thermal and chemical treatment[3], it was found that:

i) the concentrations of Cd, Pb and Cu, as found before pouring the sea water aliquots into the containers (29, 39 and 110 ng/l respectively), underwent an average increase of 10% for Cd, 15% for Pb and 5% for Cu during the first day.

ii) no further changes were observed after storing at 4°C for six months.

From the above findings, in spite of the uncertainty in the estimation of the true μ values from the $X_{m,i}$ ones, a different trend in exchange mechanism between the sample and the walls of the container can be seen:

— in frozen samples stored at neutral pH during the conditioning time period of sample melting at room temperature, trace elements could be competitive to bivalent and monovalent ions, relating to the major and minor components of the sea water, in exchanging with the container walls. At constant concentrations of these components, the amount of trace elements released to the container seems to be proportional to their individual concentration in the sample;

— in acidified samples (HCl 10^{-2}M), hydrogen ion is adsorbed preferentially on the walls of the container. In this condition trace elements, still present as impurities on the walls after cleaning, are released to the sample which reaches equilibrium in a short time.

In the case of pre-concentration on the field, the effect of storage can be ignored since in this case the release from the container is relatively insignificant.

Reproducibility of measurement repetition and replicate The size of the sample standard deviation of measurement repetition s_M and of the overall standard deviation s_T of measurement replicates – which includes the irreproducibility s_{st} of physical and chemical procedures for sample solution preparation ($s_T^2=s_M^2+s_{st}^2$) – were measured for different concentrations of each trace element according to the different procedures. In the case of chromatographic analysis, the measurements performed by directly injecting aliquots of a sub-sample (see point 1, Figure 4) have to be considered replicates since the physical-chemical processes of separation and enrichment of analytes are performed on the chromatographic device on-line with the detector chain.

The coefficient of variation of the measurement repetition (CV_M) generally ranged between 3% and 6% for the different laboratories, which is very satisfactory considering the level of analyte concentrations. As for replicate measurements, particularly when chemical and thermal treatments are required in the sample treatment procedures, the relevant coefficient of variation (CV_T was about five times greater than CV_M, as shown in Table 2, where some examples of reproducibility are reported concerning blanks and reference sea water samples (for which no blank correction is required). We cautiously estimate that CV_T is about 15%, regardless of the laboratory and the procedure, which corresponds to a confidence interval of ± 19% around the mean value at 5% level of significance (α) for five replicates.

Table 2 Blank and certified sea water (NASS-2) concentrations (C, ng/l), and coefficients of variation (CV) for measurement repetition and replicate in the determination of some trace elements as found in different laboratories by different procedures (RM = replicate measurements; MR = measure repetition).

ELEMENT / LABORATORY	CADMIUM		LEAD		COPPER		NICKEL		COMMENTS	REFERENCES
	C	CV	C	CV	C	CV	C	CV		
IACES	**2**	**23**	**19**	**16**	---	---	---	---	**Blank, three RM**	**2** **5**
	32	**3**	**40**	**6**	**105**	**6**			**NASS-2, five MR**	**2**
IAFRA	---	---	---	---	**20**	**50**	**530**	**4**	**Blank, six RM**	**7**
IAMEN	**2**	**7**	**6**	**24**	**47**	**7**	**17**	**18**	**Blank, four RM**	**10**
IAPAP	**31**	**16**	**42**	**14**	**118**	**8**	---	---	**NASS-2, five RM**	**3**
	25	**20**	**50**	**16**	**77**	**14**	---	---	**Blank, five RM**	**3**
	27	**3**	**48**	**3**	**90**	**4**	---	---	**Blank, five MR**	**11**
IASAI	**4**	**25**	**60**	**12**	---	---	**44**	**25**	**Blank, three RM**	**13**

Biases among different analytical procedures used in the same laboratory. Aliquots of the same sub-sample were analyzed by using different analytical procedures[4]. In particular, two different chelating compounds were used, 8-hydroxyquinoline (8-OXINE) and 1-(2-thiazolylazo)-2-naphthol (TAN), to pre-concentrate the analytes in a chromatographic micro-column before ICP detection, and three different electrochemical methods, namely linear sweep and differential pulse cathodic stripping voltammetry (LSCSV and DPCSV), differential pulse anodic stripping voltammetry (DPASV). The interesting results obtained show that the probability **P** that two different procedures lead to similar results depends on the procedures and on the analyte considered. For instance, for the procedures of columns 1 and 4 in Table 3, $\mathbf{P}_{1,4}$ is higher than 90% for copper and lower than 1% for zinc and for procedures of columns 1 and 2,$\mathbf{P}_{1,2}$ is higher than 90% for cadmium, 50% for manganese, 15% for copper and lower than 0.1% for zinc.

Comparison of analytical results within and among laboratories. From the above results[4] – obtained by the same operator who analyzed aliquots of the same sub-sample in the same laboratory – is evident that the problems related to the choice of the most reliable procedure and to the estimate of the bias of individual procedure are difficult to solve whenever trace elements are concerned. These problems are expected to increase when different sub-samples are analyzed in different laboratories. The size of the differences among laboratories will be considered in the next section. We may anticipate that the results obtained by all the groups contain an unknown amount of bias. No criteria are available which single out each time the result that contains the lowest amount of bias. Even where most of the data are inside a narrow interval, the relevant frequency cannot be considered as a proof that the true value μ is close to them. Besides, by considering the high qualification of the groups in trace analysis, it is very probable that μ is inside the interval of all data found. In spite of this, it will be shown later that even when different procedures in different laboratories are used to analyze a series of samples, relative variation among samples obtained in each laboratory, i.e. the $\mathbf{X}_i/\mathbf{X}_{m,n}$ values ($\mathbf{X}_{m,n}$=median or mean value between the n stations considered), can be usefully utilized for inter- and intra- laboratory data comparison and to recognize local variations of concentration, individual incorrect results, and to get information regarding the extent of correlation between data.

RESULTS AND DISCUSSION

Table 4 shows the lowest and the highest median concentrations found by the participating groups for each element in the three expeditions[3,4,7,8,9,11,12,13] along with the available oceanic and Antarctic ranges reported in literature[1]. The single concentration values refer to those elements which were determined by only one laboratory generally for only one expedition. For this reason they are only indicative of the content in sea water samples and thus preclude any specific comment. The median value was preferred to the mean one in order to minimize the effect of extreme values, even though median and mean practically coincided in many cases, and because the mean value is generally associated with the assumption that all the differences between $\mathbf{X}_i$ values are randomly distributed. Tables 5,6 and 7 show the concen-

Table 3 Total concentrations (ng/l) of some trace elements measured in the same sea water sample (SW1, 1988–89 expedition) by different analytical procedures performed in the same laboratory[4]. The coefficients of variation are reported in brackets.

ELEMENT	ANALYTICAL PROCEDURE				
	ICP		DPCSV	DPASV	LSCSV
	8-OXINE	TAN			
CADMIUM	19 (31%)	20 (50%)	---	---	---
COPPER	200 (15%)	260 (15%)	292 (12%)	200 (5%)	---
IRON	400 (8%)	340 (6%)	---	---	277 (11%)
MANGANESE	16 (25%)	13 (38%)	---	---	---
NICKEL	390 (15%)	490 (4%)	---	---	437 (8%)
ZINC	320 (9%)	200 (5%)	---	450 (7%)	---

Table 4 Total concentration ranges (ng/l) of trace elements in Antarctic sea water samples as obtained by considering the lowest and the highest median value found by the participating groups. The single values refer to the elements determined by only one group. (The values in brackets refer to only one or two stations).

ELEMENT	1987-88 EXPEDITION	1988-89 EXPEDITION		1989-90 EXPEDITION	LITERATURE DATA			
		SW	PW		Ocean	Ref	Antarctica	Ref
ANTIMONY	260	-----	-----	-----	100 - 140	1	-----	--
ARSENIC	1.210^3	-----	-----	-----	10^3 - 210^3	1	-----	--
CADMIUM	17 - 44	19 - 50	40 - 75	5 - 20	0.2 - 100	1	16 - 55	5
CHROMIUM	-----	120	115	-----	100 - 250	1	-----	--
COBALT	4	-----	-----	(3)	0.6 - 6	1	-----	--
COPPER	110 - 174	140 - 230	100 - 185	115 - 148	80 - 350	7	20 - 310	7
IRON	427 - 435	(370) - 445	920	(810)	150-310^3	7	-----	--
LEAD	7 - 52	8 - 30	10 - 29	6 - 22	1 - 35	1	4 - 6	2
MANGANESE	-----	(15) - 88	-----	----	10 - 160	1	-----	--
MERCURY	3	-----	-----	-----	0.5 - 2	1	-----	--
NICKEL	350 - 580	185 - (440)	180 - 195	(230)	200-310^3	7	-----	--
SELENIUM	30		-----	-----	40 - 180	1	-----	--
ZINC	242 - 265	(260)	-----	-----	5 - 600	1	-----	--

Table 5 Total concentration (ng/l) of copper in Antarctic sea water samples. (The values in brackets refer to only one or two stations) (n.d. = not detectable)

1987-88 EXPEDITION						1988-89 EXPEDITION						1989-90 EXPEDITION					
SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI	SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI	SAMPLING STATIONS	IACES	IAFRA	IAMEN	IAPAP	IASAI
8	254	160	--	237	110	1SW	305	120	200(M4)	150	140	31/20	120	--	--	141	--
9	178	110	--	176	150				260(M5)			32/0.5	109	--	148	95	--
10	184	n.d.	--	279	58	2SW	182	240	--	90	--	33/0.5	132	--	--	105	--
12	102	120	--	141	--	3SW	146	140	--	130	180	34/0.5	130	--	--	--	--
13	165	n.d.	--	144	110	4SW	107	120	--	290	--	35/0.5	99	--	--	135	--
16	102	130	--	123	139	5SW	160	120	--	170	150	36/0.5	32	--	--	--	--
17	89	n.d.	--	130	40	6SW	67	200	--	140	--						
22	89	n.d.	--	157	--	7SW	116	140	--	160	140						
28	133	360	--	184	55	5PW	175	50	--	150	180						
31	191	n.d.	--	192	230	6PW	128	110	--	140	--						
37	102	120	--	264	98	7PW	99	100	--	130	190						
46	127	n.d.	--	172	115												
mean	--	--	125(M1)	--	--												
mean	--	--	124(M2)	--	--												
MEDIAN VALUE	130	125	125	174	110	SW	146	140	(230)	150	145		115	--	(148)	120	--
						PW	128	100	--	140	185						

Table 6 Total concentration (ng/l) of lead in Antarctic sea water samples. (The values in brackets refer to only one or two stations)

1987-88 EXPEDITION						1988-89 EXPEDITION						1989-90 EXPEDITION					
SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI	SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI	SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI
8	13	--	--	76	--	1SW	4	--	--	31	--	31/20	8	--	--	30	--
9	24	--	--	50	--	2SW	8	--	--	30	--	32/0.5	7	--	18	23	--
10	13	--	--	73	--	3SW	19	--	--	40	--	33/0.5	5	--	--	20	--
12	7	--	--	72	--	4SW	4	--	--	18	--	34/0.5	6	--	--	--	--
13	7	--	--	71	--	5SW	19	--	--	43	--	35/0.5	6	--	--	15	--
16	5	--	--	54	--	6SW	11	--	--	23	--	36/0.5	4	--	--	--	--
17	30	--	--	38	--	7SW	7	--	--	30	--						
22	8	--	--	41	--	5PW	9	--	--	21	--						
28	7	--	--	35	--	6PW	10	--	--	38	--						
31	5	--	--	45	--	7PW	16	--	--	29	--						
37	6	--	--	39	--												
46	6	--	--	55	--												
mean	--	--	34(M1)	--	--												
MEDIAN VALUE	7	--	34	52	--	SW	8	--	--	30	--		6	--	(18)	22	--
						PW	10	--	--	29	--						

Table 7 Total concentration (ng/l) of cadmium in Antarctic sea water samples. (The values in brackets refer to only one or two stations)

1987-88 EXPEDITION						1988-89 EXPEDITION						1989-90 EXPEDITION					
SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI	SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI	SAMPLING STATION	IACES	IAFRA	IAMEN	IAPAP	IASAI
8	27	--	--	55	120	1SW	39	50	19(M4)	27	35	31/20	8	--	--	19	--
9	21	--	--	30	105				20(M5)			32/0.5	10	--	8	31	--
10	29	--	--	52	28	2SW	40	50	--	31	--	33/0.5	5	--	--	22	--
12	17	--	--	42	34	3SW	39	60	--	33	42	34/0.5	3	--	--	--	--
13	21	--	--	39	50	4SW	12	20	--	21	--	35/0.5	4	--	--	15	--
16	9	--	--	34	40	5SW	26	30	--	15	28	36/0.5	3	--	--	--	--
17	11	--	--	25	51	6SW	13	70	--	20	--						
22	10	--	--	21	95	7SW	12	10	--	25	30						
28	15	--	--	37	35	5PW	75	40	--	55	50						
31	16	--	--	41	44	6PW	78	50	--	51	--						
37	17	--	--	38	45	7PW	40	40	--	64	55						
46	45	---	--	39	40												
mean	--	--	14(M1)	--	--												
mean	--	--	40(M2)	--	--												
MEDIAN VALUE	17	--	27	38	44	SW	26	50	(19)	25	32		5	--	(8)	20	--
						PW	75	40	--	55	52						

trations of copper, lead and cadmium respectively for each sampling station in the three expeditions. These elements were measured by the greatest number of laboratories. Table 8 shows, as an example, the normalized concentration of Cd relevant to the 1987–88 and 1988–89 expeditions.

It is now possible to evaluate the size of $\Delta\mathbf{R}$ under which the differences of $\mathbf{R}_i$ are statistically significant or not. Remembering that three replicate measurements were performed for each sample and assuming that $X_{m,n}$ is a constant with a CV of 15%, differences of **R** values among stations (vertical columns of Table 8) or among groups (horizontal lines) higher than 30% are considered statistically highly significant at 0.05 significance level. Table 8, where reduced data for cadmium are shown, highlights that many data obtained by different groups become inter-comparable and that the possibility to identify outliers increases the higher the number of participants is. If these findings are not artifacts, the assumption can be made that:

i) the main sources of differences among laboratories' results are systematic errors. Probably, sample storage and manipulation play the most important role.

ii) the size of these errors – in the range of concentrations observed – is proportional to the concentration: $X_m=b'S$, where b' is the apparent sensitivity of the method including the systematic error part, specific to each group;

iii) using reduced data, referred to $X_{m,n}=b'S_{m,n}$, effects of systematic error are cancelled out.

Table 8 Comparison of normalized total concentration of cadmium in Antarctic sea water samples referred to the median value, for four partecipating laboratories.

1987-88 EXPEDITION					1988-89 EXPEDITION				
SAMPLING STATION	IACES	IAFRA	IAPAP	IASAI	SAMPLING STATION	IACES	IAFRA	IAPAP	IASAI
8	1.60	--	1.41	2.86	1 SW	1.00	1.11	0.93	0.92
9	1.23	--	0.77	2.50	2 SW	1.03	1.11	1.07	--
10	1.70	--	1.33	0.67	3 SW	1.00	1.33	1.14	1.11
12	1.00	--	1.08	0.81	4 SW	0.31	0.44	0.72	--
13	1.23	--	1.00	1.19	5 SW	0.67	0.67	0.52	0.74
16	0.53	--	0.87	0.95	6 SW	0.33	1.56	0.69	--
17	0.65	--	0.64	1.21	7 SW	0.31	0.22	0.86	0.79
22	0.59	--	0.54	2.26	5 PW	1.92	0.89	1.90	1.32
28	0.88	--	0.95	0.83	6 PW	2.00	1.11	1.76	--
31	0.94	--	1.05	1.05	7 PW	1.03	0.89	2.21	1.45
37	1.00	--	0.97	1.07					
46	2.65	--	1.00	0.95					

On the basis of these statistical findings and considering all the data available, it was possible to draw the following conclusions:

1) Stations Nos. 16, 17 and 22 (Figure 1) have the lowest Cd concentration, about one half of the median value, followed by station No. 28. This fact is not supported by any sea water dilution effect as highlighted by the alkaline and alkaline-heart element contents found at the same stations. It may have come from local biological activity[1]. Station Nos. 12, 31, 37 and 46 which are upstream and far from the Italian Base, have the same concentration of cadmium within the reproducibility of the analytical procedures used. Finally, station Nos. 8, 9 and 10 (1987–1988 expedition), which are located in the proximity of the Italian base, have significantly higher trace element concentrations, and show sound evidence of a pollution effect (P is generally higher than 99%). This pollution effect was not at all apparent in the 1988–1989 expedition, as shown by the results from station Nos. 2SW, 3SW and 5SW (Figure 2), which are located in the same area as station Nos. 8,9 and 10. Station No. 31 seems to have an abnormally high cadmium concentration. It is therefore likely that the natural concentration of Cd in Antarctic sea water is the one found at station No. 46. Biological activity or pollution effects may change this concentration in some places by a factor of two.
2) When considering the effect of pack ice melting on trace element content in sea water (1988–89 expedition), a different behaviour emerges between cadmium, iron, manganese, nickel and all the other elements. The concentrations of cadmium, iron, manganese and nickel are three to four times higher in the samples collected under the pack than in those collected in the same sampling stations after pack ice melting, while the content of all the other trace elements remains constant. For cadmium, this depletion is explained by taking into account the great increase in biological activity after pack ice melting, while photosynthesis is precluded under the pack. This seems to be in agreement with Bruland's hypothesis in explaining the low cadmium concentration detected in the surface waters of the Pacific Ocean[1].
3) Cadmium and lead median concentrations (Table 4) decrease from the first to the third expedition. This trend can be partly due to real changes in sea water content. Very likely, as far as concentrations at ng/l level concern, it is due to some extent to the improvement in both the instrumentation and the laboratory working conditions in the Italian Base and on board the ice-breaker, which permitted us the performance of all the chemical and physical pre-treatments of the samples more safely and efficiently. As for cadmium, the sharp decrease in its lowest median concentration for the third expedition was correlated once again with an increase in biological activity[5], the decrease in the labile fraction is more rapid than the total concentration. Non time dependence was found for the other elements considered.
4) The narrowest concentration ranges are observed for iron (371–445 ng/l) and zinc (242–260 ng/l) (Table 4).
5) The median concentration intervals shown in Table 4 are always within the interval reported in literature for oceans and the Antarctic sea. The size of these experimental intervals depends on the bias of each analytical procedure used, and, the lower the concentration of analyte in the sample, the larger the interval. As previously mentioned, we do not give mean values since the hypothesis that the individual set of data is normally distributed around the true mean value was not considered in this case.

Speciation of trace elements.

The speciation procedure adopted was based on titration by a metal ion of the organic ligands present in the untreated sample. Before titration and after each addition, DPASV measurements with a TFME were made on the sample, and the metal peak currents were recorded and plotted against the added metal concentration. Typically, a total of 8–12 standard additions, within a suitable interval, were made for each titration. After each addition, a 25-min. period was allowed to pass before the voltammetric measurement was started in order to obtain equilibrium in the complexation reactions. Lead, cadmium and copper were taken into consideration.

Below, the results are summarized, along with some comments, while the data from each sampling station for each expedition are reported in Tables 9, 10 and 11.

Lead speciation

Expedition: 1987–88
Samples: surface sea water
Total lead content: 5–24 ng/l
Inorganic lead content (ASV-labile): 20–50% of total lead content
Organic ligand content: 0.3–0.9 nM
Conditional pK (mean value): 9.7
Comments:
— No significant difference in total lead content was observed after uv irradiation;
— a linear relationship between ligand and chlorophyll content was observed.

Table 9 Total and ASV-labile cadmiun concentration (ng/l), ligand concentration (nM) and conditional stability constant obtained in Antarctic sea water samples.

1987-88 EXPEDITION					1988-89 EXPEDITION				
SAMPLING STATION	C_{Cd}	[Cd']	C_L	log K'_{cond}	SAMPLING STATION	C_{Cd}	[Cd']	C_L	log K'_{cond}
8	27	8.0	0.66	9.6	1 SW	39	28	1.59	8.7
9	21	9.7	0.55	9.6	2 SW	40	30	0.29	9.5
10	29	9.7	0.51	9.8	3 SW	39	27	1.06	9.2
12	17	9.7	0.25	9.5	4 SW	12	6.7	1.37	8.8
13	21	4.9	0.57	9.9	5 SW	26	5.5	0.86	9.7
16	9	4.2	0.51	9.9	6 SW	13	4.0	1.33	9.3
17	11	6.1	0.43	9.8	7 SW	12	3.4	0.43	9.8
22	10	5.6	0.36	9.4	5 PW	75	51	0.51	9.6
28	15	7.9	0.21	9.6	6 PW	78	46	2.10	9.0
31	16	5.7	0.27	9.9	7 PW	40	13	1.48	9.3
37	17	12	0.13	9.6					
46	45	31	0.12	--					

Table 10 Total and ASV-labile lead concentration (ng/l), ligand concentration (nM) and conditional stability constant obtained in Antarctic sea water samples.

1987-88 EXPEDITION				
SAMPLING STATION	C_{Pb}	[Pb']	C_L	log K'_{cond}
8	13.1	2.9	0.49	9.9
9	23.6	5.6	0.62	9.8
10	12.6	3.5	0.91	9.8
12	7.3	3.5	0.25	9.5
13	6.6	2.1	0.30	9.7
16	5.4	2.7	0.40	9.8
17*	29.6	12.4	0.32	9.7
22	7.9	3.9	0.47	9.4
28	7.0	3.1	0.74	9.3
31	5.2	2.1	0.35	9.8
37	5.6	2.1	0.27	9.5
46	6.0	3.3	0.39	9.8

***Contaminated sample.**

Cadmium speciation.

Expedition: 1987–88

Samples: surface sea water collected after pack ice melting

Total cadmium content: 9–45 ng/l

Inorganic cadmium content (ASV-labile): 23–70% of total cadmium content

Organic ligand content: 0.1–0.7 nM

Conditional pK (mean value): 9.7

Comments: — No significant difference in total cadmium content was observed after uv irradiation of samples;

— a negative and a positive linear correlation between cadmium and both phosphate and nitrate concentrations was observed for coastal and offshore samples respectively;

Table 11 Total and ASV-labile copper concentration (ng/l), ligand concentration (nM) and conditional stability constant obtained in Antarctic sea water samples.

1988-89 EXPEDITION				
SAMPLING STATION	C_{Cu}	[Cu']	C_L	log K'_{cond}
1SW	305	13	33	8.2
2SW	182	11	30	8.3
3SW	146	8.1	23	8.5
4SW	107	6.0	33	8.3
5SW	160	2.6	35	8.7
6SW	67	1.2	29	8.8
7SW	116	3.9	23	8.7
5PW	175	2.5	30	8.9
6PW	128	1.1	32	8.5
7PW	99	3.0	40	8.8

— no clear relationship between ligand content and chlorophyll was observed.

Expedition: 1988–89
Samples: surface sea water under the pack
Total cadmium content: 40–78 ng/l
Inorganic cadmium content (ASV-labile): 33–67% of total cadmium content
Organic ligand content: 0.5–2.1 nM
Conditional pK (mean value): 9.3

Samples: surface sea water after ice melting
Total cadmium content: 12–40 ng/l
Inorganic cadmium content (ASV-labile): 21–75% of total cadmium content
Organic ligand content: 0.3–1.6 nM
Conditional pK (mean value): 9.3

Comments:

- No significant difference in total cadmium content was observed after uv irradiation;
- cadmium content in sea water samples collected under the pack was three to five times higher than in the corresponding samples collected after ice melting. A quite remarkable decrease in both total and labile cadmium concentrations with respect to sampling period were also observed. This effect was mostly confined between December and January when algae bloom occurs. This cadmium depletion in surface water may be a result of interaction with biological systems;
- a high variability of ligand content without a clear spatial pattern was observed.

Copper speciation.

Expedition:	1988–89
Samples:	surface sea water collected under the pack
Total copper content:	99–175 ng/l
Inorganic copper content (ASV-labile):	14–30% of total copper content
Organic ligand content:	30–40 nM
Conditional pK (mean value):	8.7
Samples:	surface sea water collected after the pack ice melting
Total copper content:	67–304 ng/l
Inorganic copper content (ASV-labile):	16–61% of total copper content
Organic ligand content:	23–35 nM
Conditional pK (mean value):	8.5

ALKALINE AND ALKALINE-EARTH METALS

Definition of the chemical problem.

Snow, ice and lake waters in Antarctica may hold many salts of sea water origin. Since a group of participants in the Italian expeditions in Antarctica were concerned with the chemical characterization of these matrices, it was decided to get precise information about the alkaline and alkaline-earth metal concentrations in sea water samples and their depth profile. Moreover, the measurement of alkaline and alkaline-earth element content may allow one to get additional information about the representativity of the sample volume, gathered in the point x at the time t with respect to time and spatial variable; this is important in trace element data interpretation.

Table 12 Total average concentration (C, mM) of alkaline and alkaline-earth elements and relative concentration to sodium (R_{Na}) in Antarctic surface water samples. Literature data[1] are referred to open sea at 35‰ salinity.

ELEMENT	1987-88 EXPEDITION			1988-89 EXPEDITION		1989-90 EXPEDITION		LITERATURE DATA	
	IAPAP		IATRI	IAPAP		IAPAP			
	C, mM	R_{Na}	C, mM	C, mM	R_{Na}	C, mM	R_{Na}	C, mM	R_{Na}
LITHIUM	$2.3\ 10^{-2}$	$5.5\ 10^{-5}$	--	$2.5\ 10^{-2}$	$5.5\ 10^{-5}$	$2.35\ 10^{-2}$	$5.3\ 10^{-5}$	$2.5\ 10^{-2}$	$5.3\ 10^{-5}$
SODIUM	417	1	--	450	1	444	1	468	1
POTASSIUM	6.6	$1.58\ 10^{-2}$	15.	7.33	$1.62\ 10^{-2}$	9.3	$2.10\ 10^{-2}$	10.2	$2.2\ 10^{-2}$
MAGNESIUM	55.7	0.133	53.5	54.9	0.122	52.8	0.120	53.2	0.114
CALCIUM	9.4	$2.25\ 10^{-2}$	9.8	11.5	$2.55\ 10^{-2}$	9.7	$2.18\ 10^{-2}$	10.3	$2.2\ 10^{-2}$
STRONTIUM	--	--	$8.3\ 10^{-2}$	--	--	--	--	$9.0\ 10^{-2}$	$1.9\ 10^{-4}$

RESULTS AND DISCUSSION

In Table 12 the mean concentrations of the elements are shown for the three expeditions, as found by different authors[11,14,15,16] along with literature data for open sea at constant salinity (35%)[1]. Relative concentrations $\mathbf{R}_{Na}$, referred to sodium, are also shown. Tables 13, 14 and 15 show sodium concentration in each sampling station for the three expedition and relative concentrations of Li, K, Mg and Ca referred to sodium one for the 1988–89 and the 1989–90 expedition respectively. Five replicates were generally performed on a sub-sample. Parallel sub-samples were also individually analyzed for estimating the relevant bias. In spite of the significant variations in absolute concentrations, relative concentrations are quite constant with the exception of potassium which presents, in the case of the first two expeditions, absolute and relative concentration values which are abnormally low. Whether this result is due to artifacts or to a real change in concentration cannot at present be interpreted.

The average CVs, estimated for each element, were different depending on whether the first two expeditions or the last one is considered, owing to the differences in the procedures used. In the first case (five replicates) the CV average was: Li (1.5), Na (0.6), K (1.0), Mg (1.0) and Ca (2.0). In the second case (three replicates): Li (5), the other elements (0.5). It was then possible to compare:

i) for each element, through the analysis of $\mathbf{X}_i$ (and $\mathbf{X}_i/\mathbf{X}_{m,i}$) values, whether among station variations are statistically significant or not;

ii) for each station, through the analysis of $\mathbf{X}_i/\mathbf{X}_{m,i}$ values, whether variations are consistent with dilution with melt ice or not. The final comparison among expeditions allows us to get information about the time and space effect on the representativity of the sample gathered. Thus, while the characterization of the Antarctica sea water is best expressed by the interval of concentration as found between all the stations considered, it seemed worthwhile to find out whether variations in element concentrations can be assumed to be due to external events or not.

As in the case of trace elements, comparison among relative data was found to be useful in order to obtain direct information on: i) the extent of variations in the concentration for each element among stations: by comparing the ratio values $\mathbf{R}_i=\mathbf{X}_{m,i}/\mathbf{X}_{m,i,r}$ (where $\mathbf{X}_{m,i,r}$ is the reference concentration for the element "i"); ii) the nature of the variation for each station among elements: by the ratio values $\mathbf{R}_{st}=\mathbf{X}_{m,i}/\mathbf{X}_{m,r}$ (where $\mathbf{X}_{m,r}$ is the concentration of the reference elements "r" found at the same station).

From the error propagation theory, the following are statistically highly significant: i) differences $\Delta\mathbf{R}_i$ between pairs of $\mathbf{R}_i$, or $\Delta\mathbf{R}_{st}$ between pairs of $\mathbf{R}_{st}$, higher than 3 and 4.5% respectively for magnesium, potassium and calcium; ii) $\Delta\mathbf{R}_i$ or $\Delta\mathbf{R}_{st}$ higher than 13% for calcium and lithium.

On this assumption, using the IAPAP data of the 1988–89 expedition (Table 14) relevant to the effect of pack-ice melting and inter-station distances in a small area, and those of the 1989–90 expedition (Table 15) relevant to depth profile and inter-station distances in a large area, it was found that:

1) sea water samples drawn under pack-ice present higher $\mathbf{R}_{st}$ for calcium and magnesium, and lower ones for potassium than in the absence of pack-ice. No effect was observed for the remaining alkaline elements;

Table 13 Total concentration of sodium (mM) in Antarctic sea water samples.

EXPEDITION 1987-88			EXPEDITION 1988-89		EXPEDITION 1989-90	
SAMPLING STATIONS	IAPAP	IATRI	SAMPLING STATIONS	IAPAP	SAMPLING STATIONS	IAPAP
8	423	--	1SW	458	4/20	471
9	436	--	2SW	450	6/05	471
10	428	--	3SW	480	9/20	468
12	423	--	4SW	455	18/20	465
13	399	--	5SW	453	19/20	459
16	411	--	6SW	447	23/20	461
17	394	--	7SW	438	25/20	460
22	419	--	5PW	450	49/05	418
28	421	--	6PW	444	50/05	449
31	428	--	7PW	441	52/05	438
37	413	--			10/20	455
46	409	--			10/50	459
					10/100	463
					10/300	468
					10/600	469
					10/1000	470
					10/1300	472

Table 14 Relative concentrations (R_{st}) of Li, K, Mg and Ca referred, for each station, to Na concentration. PW and SW notation refer to samples collected before and after pack ice melting respectively during the 1988–89 Italian expedition in Antarctica.

SAMPLING STATIONS	Lithium	Potassium	Magnesium	Calcium
SW 1	0.057×10^{-3}	0.0164	0.122	0.024
SW 2	0.056	0.0158	0.121	0.026
SW 3	0.056	0.0157	0.120	0.025
SW 4	0.056	0.0158	0.120	0.022
SW 5	0.054	0.0168	0.121	0.019
SW 6	0.054	0.0168	0.120	0.024
SW 7	0.053	0.0162	0.121	0.026
PW 5	0.058	0.0131	0.122	0.033
PW 6	0.054	0.0141	0.127	0.029
PW 7	0.053	0.0168	0.131	0.030
SW mean R_{st}	5.5×10^{-5}	0.0161	0.120	0.026
CV	2.5%	2.5%	0.6%	10%

Table 15 Coefficient of variation (CV) of mean concentration on three replicate measurements, concentration ratios $[M_i]/[Na_i]$ (R_{st}) and $[M_i]/[M_m]$ (R_i) of alkaline and alkaline-earth elements in Antarctic sea water samples collected during the 1989–90 Italian expedition. (Depth is expressed in meters)

ELEMENT / SAMPLING STATIONS/DEPTH	Lithium			Sodium			Potassium			Magnesium			Calcium		
	CV	$[M_i]/[M_M]$	$[M_i]/[Na_i]$ x 10^3	CV	$[M_i]/[M_M]$	$[M_i]/[Na_i]$	CV	$[M_i]/[M_M]$	$[M_i]/[Na_i]$	CV	$[M_i]/[M_M]$	$[M_i]/[Na_i]$	CV	$[M_i]/[M_M]$	$[M_i]/[Na_i]$
10/20	5.2	0.960	0.052	0.27	0.989	1.00	0.56	1.000	0.0213	0.06	0.999	0.119	0.48	0.990	0.022
10/50	4.7	0.976	0.052	0.07	0.999	1.00	0.19	1.013	0.0213	0.30	1.017	0.120	0.47	1.007	0.022
10/100	5.7	0.996	0.053	0.40	1.007	1.00	0.48	1.004	0.0210	0.12	1.021	0.120	0.71	1.021	0.022
10/300	4.2	1.012	0.053	0.28	1.019	1.00	0.28	1.024	0.0212	0.05	1.031	0.119	0.20	0.998	0.022
10/600	5.1	1.029	0.054	0.19	1.020	1.00	0.21	1.029	0.0212	0.55	1.030	0.119	0.44	1.025	0.022
10/1000	3.8	1.037	0.054	0.27	1.022	1.00	0.50	1.020	0.0210	0.27	1.035	0.120	0.32	1.018	0.022
10/1300	4.3	1.082	0.056	0.08	1.026	1.00	0.58	1.024	0.0210	0.24	1.037	0.119	0.50	1.078	0.023
49/0.5	6.2	0.878	0.052	0.28	0.909	1.00	0.15	0.899	0.0208	0.53	0.912	0.118	0.77	0.913	0.022
50/0.5	4.5	0.992	0.054	0.20	0.976	1.00	0.40	0.969	0.0209	0.20	0.980	0.119	0.38	0.982	0.022
52/0.5	6.1	0.988	0.056	0.30	0.952	1.00	0.40	0.951	0.0210	0.34	0.965	0.120	0.46	0.960	0.022
18/20	5.2	1.021	0.054	0.36	1.010	1.00	0.31	1.014	0.0211	0.72	0.990	0.116	0.45	1.012	0.022
19/20	5.8	1.008	0.054	0.16	0.998	1.00	0.49	0.995	0.0210	0.75	0.999	0.118	0.31	1.000	0.022
23/20	5.1	1.017	0.054	0.68	1.003	1.00	0.60	0.998	0.0209	0.44	1.009	0.119	0.47	0.993	0.022
25/20	4.2	1.004	0.054	0.31	1.002	1.00	0.41	0.989	0.0208	0.41	1.006	0.119	0.43	1.013	0.022
4/20	6.5	1.029	0.054	0.26	1.024	1.00	0.13	1.040	0.0214	0.84	0.988	0.114	0.54	1.031	0.022
9/20	5.3	0.992	0.054	0.07	1.018	1.00	0.71	1.006	0.0208	0.53	0.987	0.114	0.43	0.976	0.021
6/0.5	4.8	0.980	0.051	0.26	1.026	1.00	0.23	1.026	0.0211	0.33	0.993	0.114	0.92	0.982	0.021
R mean			**0.053**						**0.0210**			**0.118**			**0.022**

2) absolute concentrations of each element were found to vary no more than 4% among stations at constant depth;
3) the concentration of each element considered increases as the depth for the same water column increases, from surface to 1300m. The maximum variation observed was 3–4%;
4) the relative concentrations $\mathbf{R}_{st}$ of each element with reference to sodium seem to be independent of both water column depth and inter-station distances. The sample standard deviation relevant to all the $\mathbf{R}_{st}$ values available for each element, except K, Ca and Mg in the PW stations of the 1988–89 expedition (Table 14), are statistically insignificant. For instance, in the case of magnesium, the molar ratio Mg/Na was found to have a CV of 0.7%.

The average $\mathbf{R}_{st}$ values for the 1988–89 and 1989–90 expeditions along with those calculated by literature data at constant salinity are respectively:

Li: $5.5\ 10^{-5}$, $5.3\ 10^{-5}$ and $5.2\ 10^{-5}$; K: 0.016, 0.021 and 0.022; Mg: 0.121, 0.119 and 0.120; Ca: 0.025, 0.022 and 0.022. Once again, magnesium presents the highest reproducibility of $\mathbf{R}_{st}$ values for different expeditions and different oceans.

These findings shows that:

1) the average $\mathbf{R}_{st}$ values obtained by us in different expeditions, or taken from literature for open sea waters at constant salinity, appear to be constant for each alkaline and alkaline-earth element considered, regardless of the depth and the sampling station position, provided that fresh water streams are absent. The experimental evidence that differences in $\mathbf{R}_{st}$ values observed for different sampling conditions are completely covered by random errors of the analytical procedure used, means that the variations of the absolute concentrations of the elements observed as a function of the sampling conditions occur by dilution of sea water by rain or, as in the case of Antarctica, by snow or ice melting; so that relative concentrations of alkaline and alkaline-earth elements remain constant;
2) if the effect of water column depth on the absolute element concentrations – about 4% from surface to 1,300 meters depth – was not an isolated phenomenon, then vertical mixing of sea water seems to be quite weak;
3) the analytical procedures based on ion chromatography are confirmed to be precise and accurate. The fact that reproducibility of $\mathbf{R}_{st}$ values was sometimes better than expected, as calculated by the error propagation theory (see magnesium) means that some sort of compensation throughout the different steps of data manipulation occurs;
4) the relative alkaline and alkaline-earth element concentrations measured at each sampling station are representative of the whole system with a maximum oscillation of ±4%: i.e., accurate and precise measurements of sodium or magnesium concentrations can allow us to calculate the concentrations of the other elements by the available $\mathbf{R}_{st}$ values.

Acknowledgements.

We wish to express our sincere appreciation to the researchers of the "Environmental Impact – Chemical Methodologies" team for their accurate and skillful work, and to the technical staff of the Italian expeditions in Antarctica of 1987–88, 1988–89 and 1989–90 for their indispensable help during sample collection. This work was financially supported by ENEA (Rome) under the Italian Research Programme in Antarctica.

References

1. K. W. Bruland in "*Chemical Oceanography*", (J. P. Riley, R. Chester, Eds., Academic Press, London 1983) Vol. 8, Chapt. 45.
2. G. Capodaglio, G. Toscano, G. Scarponi and P. Cescon, *Ann. Chim. (Rome)*, **79**, 543–559 (1989).
3. M. Betti, R. Fuoco and P. Papoff, *Ann. Chim. (Rome)*, **79**, 689–699 (1989).
4. E. Mentasti, V. Porta, O. Abollino and C. Sarzanini, *Ann. Chim. (Rome)*, **81**, 343–355 (1991).
5. G. Capodaglio, G. Toscano, G. Scarponi and P. Cescon, *Ann. Chim. (Rome)*, **81**, 277–296 (1991).
6. G. Capodaglio, G. Toscano, G. Scarponi and P. Cescon, *Proceedings of the Second Meeting on "Environmental Impact – Chemical Methodologies"* (Venice, 26–28 May 1992) pp. 39–45.
7. F. Baffi, F. Soggia, R. Frache and A. M. Cardinale, *Ann. Chim. (Rome)*, **79**, 607–616 (1989).
8. R. Frache, F. Baffi, B. Cosma, A. Mazzucotelli, C. Bottinelli, F. Sena and F. Soggia *Proceedings of "Environmental Impact in Antarctica", C.N.R.* (Rome 8–9 June 1990) pp. 37–46.
9. E. Mentasti, V. Porta, O. Abollino and C. Sarzanini, *Ann. Chim. (Rome)*, **79**, 629–637 (1989).
10. V. Porta, O. Abollino, C. Sarzanini and E. Mentasti, *J. Analytical Atomic Spectroscopy*, **6**, 119–122 (1991).
11. P. Papoff and M. Onor, *Intern. J. Environ. Anal. Chem., in press.*
12. G. Saini, C. Baiocchi and P. Bertolo, *Ann. Chim. (Rome)*, **79**, 713–721 (1989).
13. G. Saini, C. Baiocchi and P. Bertolo, *Ann. Chim. (Rome)*, **81**, 317–324 (1991).
14. C. Triulzi, A. Mangia, A. Casoli, S. Albertazzi and F. Nonnis-Marzano, *Ann. di Chim. (Rome)*, **79**, 723–733 (1989).
15. P. Papoff, M. Betti, M. Onor and G. Giovannoni, *Ann. Chim. (Rome)*, **81**, 297–304 (1991).
16. P. Papoff and M. Onor, *Proceedings of the Second Meeting on "Environmental Impact – Chemical Methodologies"* (Venice, 26–28 May 1992) pp. 53–59.