

Participation of ISMAR-Trieste in the SESAME IT01 and IT02 cruises

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ISMAR Trieste has been involved in the WP2 “Cohordinated acquisition of new multidisciplinary field data in the SES” of SESAME project. Responsible: D. Georgopoulos and A. Zatsepin.

Participation aimed at acquiring the first synoptic collection of new biogeochemical data in the Adriatic and Ionian Seas useful to:

- define the current state of water masses in these basins and their chemical characteristics in late winter early spring conditions
- gather the first dataset of marine carbonate system in these two seas, where good quality data are still very scarce (Medar group 2002-MEDATLAS/2002 database),
- define the current dynamics of biogenic elements (C, N, P, Si) in the dissolved inorganic and organic pools in seawater
- analyze the latitudinal gradient (35° to 45° N) exhibited by biogeochemical properties of the Mediterranean marine ecosystem
- establish a future monitoring frame to study the effects of climate change in the Adriatic and Ionian seas
- coordinate the acquisition of field data in different Southern European Seas required for the ecosystem modelling of the whole Mediterranean.

Collected data cover marine areas under different trophic characteristics, varying from the highly productive shallow North Adriatic continental shelf, characterised by a pronounced seasonal cycle and subjected to strong anthropogenic pressure, to the oligotrophic deep sea environment of the Ionian basin. This feature will permit further analysis of a wide range of effects of climate changes on the marine ecosystem. In particular, the following key processes should be better analysed:

- modification of the marine carbonate system features and CO₂ fluxes at the air-sea interface in the region, as a consequence of climate changes and the increase of air CO₂ concentration
- ecosystem changes and/or degradation due to Ocean Acidification
- the evolution of dense water formation in the Adriatic Sea and their spreading in the Ionian and Eastern Mediterranean basins
- evolution of biogeochemical properties of water masses in these seas in relationship to biological processes and ecosystem structure.

Activity on the field

The personnel of ISMAR-TS participated in 2 campaigns on board of R/V Urania along the Adriatic and Ionian basins (fig 1 and 2):

S-IT01 Adriatic Sea (15-26/02/2008): 30 sampling stations.

S-IT02 Ionian Sea (01-09/03/2008): 16 sampling stations.

taking care of the analysis of the following biogeochemical parameters (gathered by CTD downcasts and bottle sampling):

- Dissolved Oxygen (DO)
- Dissolved inorganic nutrients (NO_3 , NO_2 , NH_4 , PO_4 , $\text{Si}(\text{OH})_4$)
- Dissolved organic nitrogen (DON) and phosphorus (DOP),
- pH_T and Total Alkalinity (TA) + derived parameters

Fig 1 stations map in the Adriatic basin

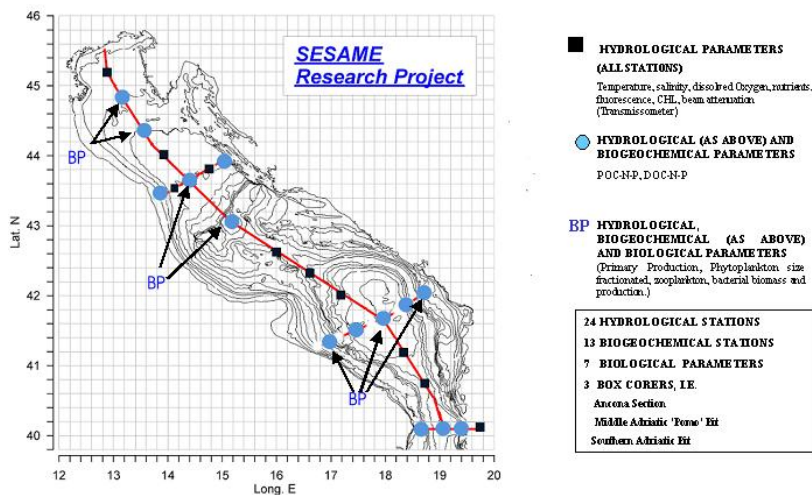
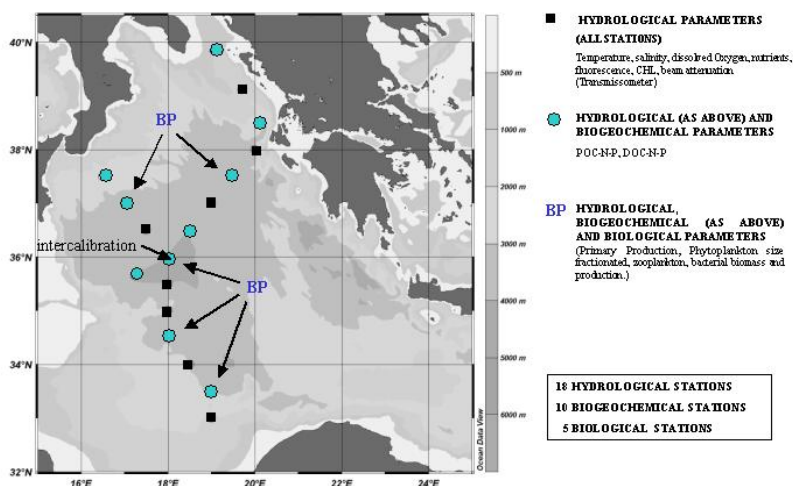


Fig 2 stations map in the Ionian basin



Analytical methods

The determination of dissolved oxygen (DO) was performed using an automated potentiometric Winkler titration system (Grasshoff, 1983). Samples have been titrated directly on board.

The determination of inorganic nutrients, nitrate plus nitrite (NO₃), reactive phosphorus (PO₄) and reactive silicon (SiO₂), was carried out using one Technicon and one Flow-Solution III autoanalyzer, following equivalent standard colorimetric methods (Grasshoff, 1983).

Dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) have been determined after UV oxidation, by means of an autoanalyzer, following equivalent standard colorimetric methods (Grasshoff, 1983).

pH and Total Alkalinity have been determined according to Byrne et al 1991, and to Hernandez-Ayon et al 1999 respectively.

The remaining derived carbonate system parameters: pCO₂, fCO₂, H₂CO₃, HCO₃⁻, CO₃⁼, DIC (dissolved inorganic carbon), calcium carbonate saturation states (Ω_{Ca} and Ω_{Ar}), Revelle, were computed (by CO2SYS programme, according to Lewis & Wallace 1998) from the experimental measurements of pH and TA as indicated by Dickson et al. 2007 .

Bibliographic references

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- Hernandez-Ayon J.M., Belli S.L., Zirino A., 1999. pH, alkalinity and total CO₂ in coastal seawater by potentiometric titration with a difference derivative readout. *Analitica Chimica Acta* 394, 101– 108.
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pH determination

(A. Luchetta)

Spectrophotometric pH in seawater was measured, following the method recommended in “*Guide to best practices for ocean CO₂ measurements*” by Dickson et al. (2007), at several stations and depths along the cruises (15.02.2008- 9.03.2008, on board of R/V Urania) and reported at 25°C and on the Total scale, hereinafter pH_{25T}.

Sampling

pH was sampled after dissolved oxygen. Each sample was drawn directly from Rosette bottles in cylindrical optical glass 10-cm pathlength cells, which were filled to overflowing and immediately stoppered. After sampling, the cells were stored in the dark, at a constant temperature of about 12°C, until analyses in onboard within a few hours from sampling.

Analytical method.

After sampling and short storage, the cells were immediately stabilised at 25°C and pH measured using a double-wavelength spectrophotometric procedure (Byrne, 1987). The indicator was a solution of m-cresol purple (Riedel-de Haën) prepared in MilliQ water (2 mM).

All the absorbance measurements were obtained in the thermostatted (25±0.05 °C) cell compartment of a VARIAN Cary 50 single beam spectrophotometer. The temperature was controlled with a VARIAN Cary PCB 150 Water Peltier System (0.5L) thermostatic bath.

After blanking with the sampled seawater without dye, 50 µl of the dye solution were added using a calibrated micropipette (Gilson F50). The absorbance was measured at three different fixed wavelengths (434, 578 and 730 nm), pH, on the total hydrogen ion concentration scale, is calculated using the following formula (Clayton and Byrne, 1993):

$$\text{pH}_T = 1245.69/T + 3.8275 + (2.11 \cdot 10^{-3})(35-S) + \log((R_{\text{corr}} - 0.0069)/(2.222 - R_{\text{corr}} \cdot 0.133))$$

where R_{corr} is the ratio of the absorbances (A) of the acidic and basic forms of the indicator, corrected for both the baseline absorbance at 730 nm ($R = (578A - 730A) / (434A - 730A)$) and the volume of dye added (as reported in Dickson et al. 2007), T is temperature in Kelvin scale and S is salinity.

Preliminary Results

A few preliminary profiles of pH_T at stations in the Ionian basin are shown below (in fig 3).

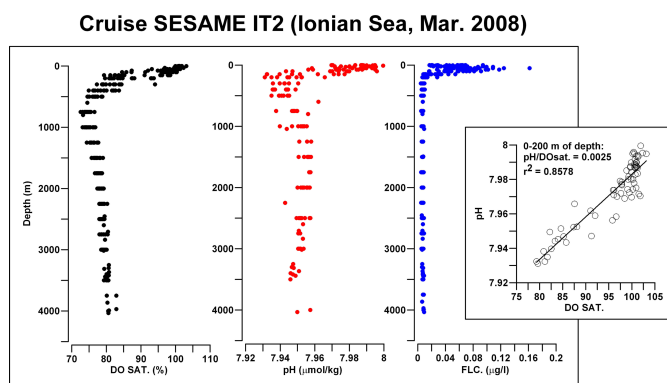


Fig 3

Accuracy

In order to check the accuracy of the pH measurements, samples of CO₂ reference material (CRM, *batch n° 100*, distributed by A.G. Dickson from the Scripps Institution of Oceanography, SIO) were analyzed. Once per leg, five to thirteen samples from a CRM bottle (*batch 100*, certified chemical characteristic for salinity 33.351; phosphate, 0.54 $\mu\text{mol kg}^{-1}$; silicate, 1.5 $\mu\text{mol kg}^{-1}$; nitrate, 1.15 $\mu\text{mol kg}^{-1}$; nitrite 0.00 $\mu\text{mol kg}^{-1}$; total alkalinity $2232.36 \pm 0.84 \mu\text{mol kg}^{-1}$; and total dissolved inorganic carbon $2021.65 \pm 0.42 \mu\text{mol kg}^{-1}$) were drawn carefully to avoid bubbles and analyzed every day for pH using the spectrophotometric method. The corresponding theoretical $\text{pH}_{\text{T}25}$ value for this batch is 7.907, using the dissociation constant from Merbach et al. (1973) refitted by Dickson & Millero (1987). Results of CRMs measurements analyzed for pH are shown in Table 1. In Table 2 results of our measurements against Tris buffer solution in synthetic seawater (home made TRIS, $\text{pH}_{\text{T}} = 8.093$) are shown.

Table 1. Mean standard deviation (STD) values for the CRM batch 100 determination on pH. N stands for the number of measurements and ΔpH is the difference between the theoretical value using the Merbach et al. (1973) constants.

Date	$\text{pH}_{\text{T}25}$	STD	N	ΔpH
15 Feb – 8 Mar 2008	7.896	0.004	23	- 0.011

Table 2. Mean standard deviation (STD) values for the Tris buffer solution in synthetic seawater determination on pH. N stands for the number of measurements and ΔpH is the difference between the theoretical value using the Merbach et al. (1973) constants

Date	$\text{pH}_{\text{T}25}$	STD	N	ΔpH
15 Feb – 8 Ma 2008	8.083	0.008	16	- 0.010

Reproducibility

A few times during the cruise, when time was available, several samples were collected from the same Niskin bottle and were analyzed (Table 3). The mean of the STD on 30 replicates is ± 0.002 , which could be considered as the reproducibility of our pH measurements.

Table 3. Characteristics of the replicate samples taken along the cruise, the mean standard deviation (STD) and number of bottles collected from each bottle for the pH analysis.

Date	Station	Pressure (dbar)	salinity	$\text{pH}_{\text{T}25}$	STD	N° repl
15/02/2008	SIT1-A01	10	38.218	7.932	0.001	4
20/02/2008	SIT1-A07	40	38.486	7.968	0.002	3
23/02/2008	SIT1-A16	1000	38.737	7.946	0.002	3
26/02/2008	SIT1-A23	301	38.859	7.956	0.001	3
03/03/2008	SIT2-I06	3365	38.733	7.959	0.002	5
03/03/2008	SIT2-I08	300	38.913	7.956	0.003	4
08/03/2008	SIT2-I10	3418	38.738	7.963	0.001	3
06/03/2008	SIT2-I17	3	38.432	8.006	0.002	5

Total Alkalinity determination

(A.Luchetta, C. Cantoni)

Total Alkalinity (TA) was analysed after a few months from sample collection by potentiometric titration in an open cell with a difference derivative readout (Hernandez-Ayon et al., 1999).

Sampling and storage.

Seawater samples for TA were collected after pH samples, in 300 ml borosilicate bottles, poisoned with 200 μL meric chloride, sealed with grease (silicone) and stored in the dark, at constant temperature of about 12 °C, until analysis in our laboratory (ISMAR-Trieste) on shore. Samples were filled to overflowing and immediately stoppered. All the stations and depths that were sampled for pH were sampled also for TA.

Analytical method

TA was measured using an automatic potentiometric titrator "685 Metrohm", controlled by pc and TIAMO programme, with a Pt combined electrode (Metrohm 6.0262.100), in a thermostatted (25 ± 0.01 °C) compartment. The temperature was controlled with a HAAKE F6 (5L) thermostatic bath. The system is coupled with a 5.0 mL burette or exchangeable unit. Potentiometric titrations were carried out with hydrochloric acid (HCl= 0.1 N) in artificial seawater (salinity 35.00; 35.0 g/L sodium chloride). Concentrations are given in $\mu\text{mol kg}^{-1}$. The 0.1 N hydrochloric acid was prepared mixing 0.5 mol (18.231 g) of commercially HCl supplied by Riedel-deHaën® (Fixanal 38285) with 5 L of artificial seawater (prepared with MilliQ plus 175.000 g of sodium chloride). The HCl normality is exactly referred to 20°C.

Accuracy

CRM analyses were performed in order to control the accuracy of our TA measurements (Figure 2). The titrating HCl solution was calibrated against samples of CO₂ certified reference material (*batch n° 83*, distributed by A.G. Dickson from the Scripps Institution of Oceanography, SIO). Accuracy was checked by the titration of replicates of CRM (batch 83, certified chemical characteristic for salinity, 34.611; phosphate, 0.33 $\mu\text{mol kg}^{-1}$; silicate, 1.9 $\mu\text{mol kg}^{-1}$; nitrate, 0.61 $\mu\text{mol kg}^{-1}$; nitrite 0.01 $\mu\text{mol kg}^{-1}$; total alkalinity 2286.34 ± 0.61 $\mu\text{mol kg}^{-1}$; and total dissolved inorganic carbon 2055.57 ± 0.37 $\mu\text{mol kg}^{-1}$), obtaining an experimental average AT value of 2286.3 ± 2.9 $\mu\text{mol kg}^{-1}$.

Reproducibility

Regarding the reproducibility of our measurements, two times along the cruise when enough water and time was available, we collected several replicates from the same Niskin bottle (Table 4). In addition, several samples (15) have been collected twice: 11 replicates provided STD < 1.0 μM and 15 exhibited STD < 2.0 μM .

Considering all performed replicates, STD = ± 2.0 can be considered as the reproducibility of TA measurements.

Table 4. Characteristics of the replicate samples taken along the cruise, the mean and standard deviation (STD) and number of analysis performed from each bottle for the TA analysis.

Date	Station	Niskin	Depth	Salinity	TA $\mu\text{mol kg}^{-1}$	STD	N
15/02/2008	SIT1-A01	12	10	38.218	2667.7	1.6	8
20/02/2008	SIT1-A07	5	40	38.486	2641.1	1.4	6
19/02/2008	V33	8	26	38.544	2696.7	0.5	2
23/02/2008	SIT1-A14	21	2	38.696	2634.0	2.0	2
23/02/2008	SIT1-A14	1	150	38.600	2638.1	0.4	2
23/02/2008	SIT1-A15	1	993	38.729	2655.2	0.9	2
23/02/2008	SIT1-A15	13	500	38.756	2642.7	0.4	2
23/02/2008	SIT1-A15	16	10	38.758	2640.0	1.7	2
23/02/2008	SIT1-A15	20	2	38.758	2629.7	0.8	2
24/02/2008	SIT1-A17	1	1214	38.723	2637.6	0.5	2
23/02/2008	SIT1-A16	15	500	38.757	2649.6	0.6	2