

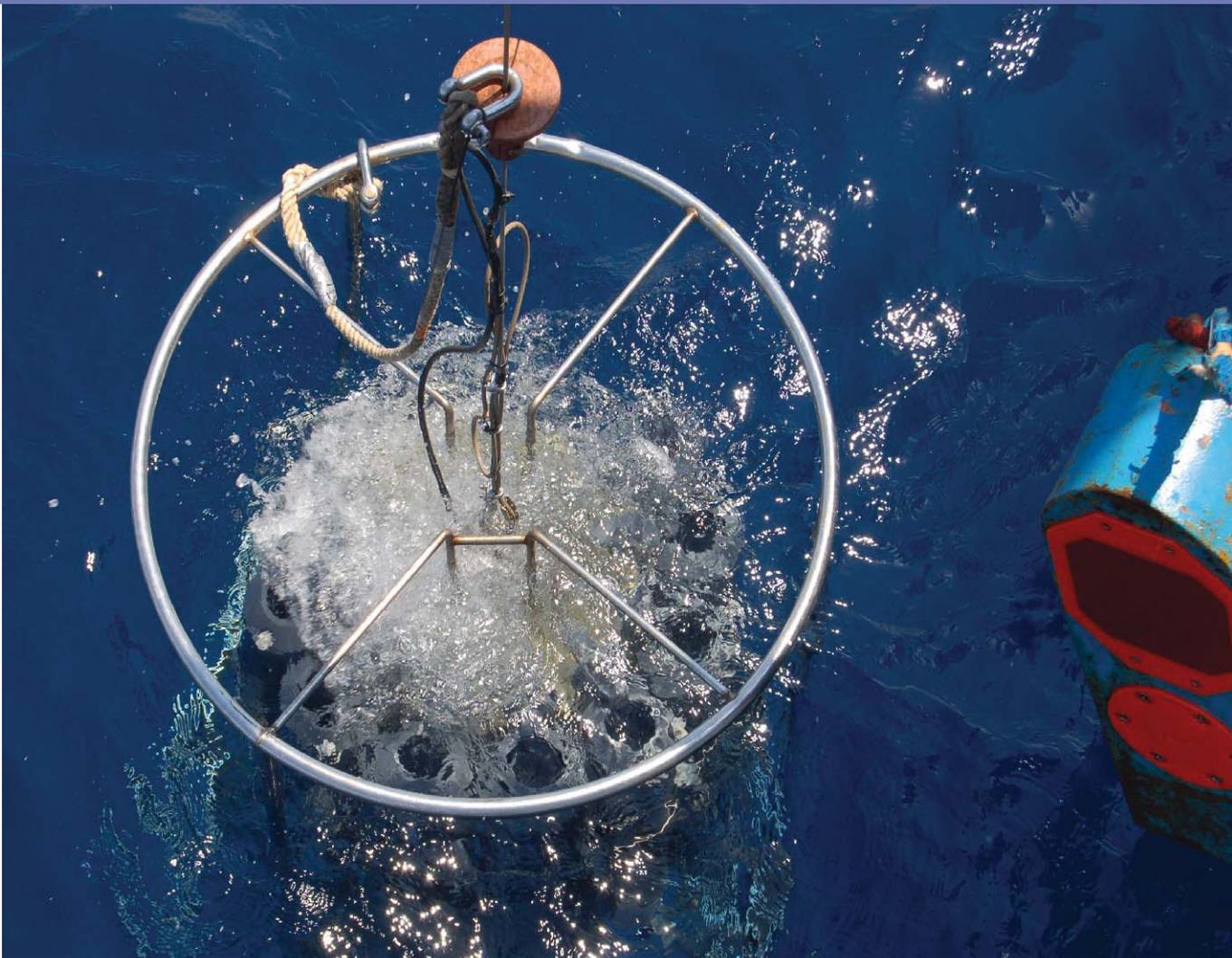


Food and Agriculture Organization
of the United Nations

38

MEDSUDMED - TECHNICAL DOCUMENTS

Report of the MedSudMed Oceanographic
Survey: Libyan continental shelf -
South central Mediterranean Sea
(15 - 30 July 2010)



**REPORT OF THE MEDSUDMED OCEANOGRAPHIC
SURVEY: LIBYAN CONTINENTAL SHELF -
SOUTH-CENTRAL MEDITERRANEAN SEA
(15 - 30 JULY 2010)**

The conclusions and recommendations given in this and in other documents in the Assessment and Monitoring of the Fishery Resources and the Ecosystems in the Straits of Sicily Project series are those considered appropriate at the time of preparation. They may be modified in the light of further knowledge gained in subsequent stages of the Project.

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Preface

The Regional Project “Assessment and Monitoring of the Fishery Resources and the Ecosystems in the Straits of Sicily” (MedSudMed) is executed by the Food and Agriculture Organization of the United Nations (FAO) and funded by the Italian Ministry of Agriculture, Food and Forestry Policies (MiPAAF). The Directorate-General for Maritime Affairs and Fisheries of the European Commission (DG MARE) co-funded the project since October 2012. The Italian Regione Siciliana funded a project aimed at strengthening MedSudMed’s effectiveness on issues related to demersal resources, namely crustaceans, for 18 months, starting from May 2011.

MedSudMed promotes scientific cooperation between research institutions of the four participating countries (Italy, Libya, Malta and Tunisia), for the continuous and dynamic assessment and monitoring of the status of the fisheries resources and the ecosystems in this area of the Mediterranean Sea.

Research activities and training are supported to increase and use knowledge on fisheries ecology and ecosystems, and to create a regional network of expertise. Particular attention is given to the technical coordination of the research activities between the countries, which should contribute to the implementation of the FAO Code of Conduct for Responsible Fisheries and the Ecosystem Approach to Fisheries. Consideration is also given to the development of an appropriate tool for the management and processing of data related to fisheries and their ecosystems.

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The MedSudMed Project publications are issued as series of Technical Documents (GCP/RER/010/ITA/MSM-TD-00) and Scientific Reports (GCP/RER/010/ITA/MSM/SR-00) related to meetings, missions and research organized by or conducted within the framework of the Project.

Comments on this document would be welcomed and should be sent to the Project headquarters:

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Preparation of this document

Oceanographic surveys are probably the most important source of data to investigate the ecology, abundance and spatial distribution of small pelagic fish species, and to detect possible influence of environmental factors on their abundance and distribution. The experts of the countries participating in the FAO Project MedSudMed, during the “MedSudMed Expert Consultation on Small Pelagic Fishes: Stock Identification and Oceanographic Processes Influencing their Abundance and Distribution (Tunisia, October 2003)”, deemed necessary to expand the area covered by oceanographic surveys in the south-central Mediterranean Sea and investigate areas where little or outdated information on eggs and larvae was available. As follow up, cooperative oceanographic and acoustic surveys at sea were organised by the Project in the south-central Mediterranean Sea. Oceanographic surveys were organised in Libyan waters in 2006, 2008 and 2010. After each survey a document summarising participating institutions, methods used and results achieved was prepared and published as MedSudMed Technical Documents.

This document is the final version of the report of the MedSudMed Oceanographic Survey carried out in Libyan waters from 15 to 30 August 2010 on board of the R/V Urania. The document presents the results of the processing of the data collected during the survey. The survey was organised in the framework of the MedSudMed Project in cooperation with the Istituto per l’Ambiente Marino Costiero (IAMC-CNR) of Mazara del Vallo (Italy) and the Marine Biology Research Centre (MBRC) of Tajura (Libya). Other collaborating research institutes involved in the survey and in the data processing are: i) ISMAR-CNR, Istituto di scienze marine, Sezione di Oceanografia Fisica, La Spezia, Italy; ii) Istituto Nazionale di Geofisica e Vulcanologia, La Spezia, Italy; and iii) IAMC – CNR of Messina, Italy. The outcomes of the survey and data processing described in this report contributed to the publication of MedSudMed identification sheets for early life stages of bony fish (MedSudMed Technical document No. 18¹ <http://www.faomedsudmed.org/pdf/publications/TD18.pdf>).

This report is one of outcomes of the MedSudMed Project component on “Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution”. This report is primarily for scientists of the south-central Mediterranean Sea; it can also be of interest for students and professional of fisheries research and management in the Mediterranean Sea region. It is believed to be a contribution to better knowledge on the distribution and abundance of small pelagic fish and of some oceanographic parameters in an area not fully investigated.

¹ FAO MedSudMed 2011. Identification sheets of early life stages of bony fish. Western Libya, Summer 2006. GCP/RER/010/ITA/MSM-18 (MedSudMed Technical Documents n°18). 2011. 251pp.

Acknowledgements

The Libyan Authorities, through the General Authority of Marine Wealth, are gratefully acknowledged for their support. Mr. Nurreidin Essarbout (MBRC, Libya) and Mr. Salvatore Mazzola (IAMC-CNR, Italy) are warmly thanked for the efforts spent and the support provided in the organization of all activities and for making this work possible. Mr. Emanuele Gentile, Master of the R/V Urania and all his crew are thanked for their work. Ms Carolie Bennet is also thanked for the technical revision of the English of the document.

Bonanno A., Zgozi S., Rumolo P., El Turki A., Cuttitta A., Hamza M.A., Basilone G., Uheshi O., Placenti F., Bara M., Genovese S., Assugayer M., De Luca B., Leonardi M., Fontana I., Giacalone G., Azzaro F., Patti C., del Core M., Ceriola L. 2015. Report of the MedSudMed Oceanographic Survey: Libyan continental shelf – south-central Mediterranean Sea (15 – 30 July 2010).

MedSudMed Technical Documents No. 38. GCP/RER/ITA/MSM-TD-38, Rome, 2015: 88 pp.

ABSTRACT

This document is the final version of the report of the MedSudMed Oceanographic Survey carried out in Libyan waters from 15 to 30 July 2010 on board of the R/U Urania. The document presents also the results of the processing of the data collected during the survey. The survey was carried out under the cooperative framework promoted by the FAO MedSudMed Project (Assessment and Monitoring of the Fishery Resources and the Ecosystems in the Straits of Sicily). The main objective of the survey was to collect information on areas of concentration of eggs and larvae of small pelagic fish species and on the mesoscale physical aspects characterizing the area. During the survey, advantage was also taken to collect sediments and water samples to update and/or complement existing information and study the chemical-physical properties of the water masses. The results were expected to complement information gathered during the first and second MedSudMed surveys (August 2006, July 2008) and information available in other part of the MedSudMed area. The main target species for the ichthyoplankton study were anchovy (*Engraulis encrasicolus*) and round sardine (*Sardinella aurita*). An overall description of the sampling scheme, of the area explored and of the methods adopted is provided. The distribution and abundance of eggs and larvae of the main target species anchovy (*Engraulis encrasicolus*) and round sardine (*Sardinella aurita*) in the eastern part of Libyan waters is described. An outline of the composition and abundance of phytoplankton in the area is also provided. The main oceanographic characteristics, including water mass circulation, in the western Libyan waters are illustrated. A description of the trophic status of the waters is provided taking into account nutrients and suspended matter. A description of the content of trace elements and nutrients in the water column complete the information provided in this report.

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1 Introduction

The regional assessment of small pelagic fish stocks and the study of the spatial distribution of the different life stages in relation to environmental parameters are two of the research activities endorsed by the MedsudMed Coordination Committee. These activities are developed in the framework of the MedSudMed Project component “Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution”.

The MedSudMed Project has put considerable effort in the support of scientific cooperation, standardization of methods for sampling and processing data and to conduct activities at regional scale. The Project also supported participating institutes in strengthening capacity in data and samples collection at sea, their processing and statistical analysis. In this line, the Project supported the organization of acoustic, oceanographic and ichthyoplankton surveys in cooperation between the Marine Biology Research Centre (MBRC) of Tajura, Libya and the Istituto per l’Ambiente Marino Costiero (IAMC-CNR) of Mazara del Vallo, Italy. Other Institutes participated in the survey because of their expertise on specific topics. The surveys were instrumental to collect data in areas where little or outdated information on small pelagic fish abundance and distribution and driving oceanographic factors was available. Overall, a series of surveys was carried out in Libyan waters since 2006: oceanographic survey in 2006, 2008 and 2010; and acoustic surveys in 2008 and 2010. The oceanographic survey MedSudMed-10 was conducted on board the Italian R/V “Urania” from 15 to 30 July 2010 in the eastern part of the Libyan waters.

The main scope of the survey was to locate the spawning areas of small pelagic fish species and relate them to the mesoscale physical structures characterizing the area. The results were expected to complement information available in the rest of the Libyan waters and MedSudMed area, where hypothesis were drawn on the transport and retention processes of small pelagic fish eggs. Considering the reproduction period of small pelagic fish in this area, the main target species were anchovy (*Engraulis encrasicolus*) and round sardinella (*Sardinella aurita*). Besides the main scientific target of the survey, advantage was taken to collect sediments and water samples to update and/or complement existing information and to study the chemical-physical properties of the water, such as concentration of nutrients in the water column and trace elements concentration in located spots (i.e. in front of the main cities of the study area). The survey gave the possibility to provide on-the-job training and reinforce cooperation relationships between the Institutes.

Data and samples were processed jointly by the different participating Institutes and, whenever required, training courses were organized. In particular, three training courses were organized in parallel to the data processing and to the preparation of the technical reports that were used as basic material for this document.

This document gives an overview of the work carried out at sea and of the main findings related to ichthyoplankton, oceanography, phytoplankton, organic matters, nutrients, trace elements and meteorology.

2 Objectives and study area

The oceanographic survey MedSudMed-10 was conducted on board the Italian R/V “Urania” from 15th to 30st July 2010 in the eastern part of the Libyan waters and was the fourth survey carried out in cooperation between CNR-IAMC and MBRC under the framework of the FAO MedSudMed Project component on “Small Pelagic Fish: Stock Identification and Oceanographic Processes Influencing their abundance and distribution”. Other institutes participated in the survey, in their capacity as partners of the CNR IAMC.

Research activities on board mainly focused on eggs and larvae of small pelagic fish in part of the MedSudMed study area, in relation to biological and physical processes. Considering the reproduction period of small pelagic fish in this area, the main target species were *Engraulis encrasicolus* (anchovy) and *Sardinella aurita* (round sardine). The study area is shown in Figure 1.

As for previous oceanographic surveys, the main objectives of the study were:

- delineation of the spawning areas of the target species;
- study of the correlation between mesoscale physical structures and the distribution and abundance of small pelagic fish eggs and larvae and zooplankton in the study area;
- measurement of physical parameters with a multiparametric probe;
- analysis of sediments;
- Sampling and analysis of samples of water in the entire water column.

The survey was organized with the aim of collecting data in the in the eastern area of the Libyan waters, as a follow-up to the first survey that covered the western part of the Libyan waters, and to the second survey that covered the Gulf of Syrt. The study area was defined to get a complete representation of regional transport patterns of small pelagic fish eggs and larvae and to identify the oceanographic features that are responsible for retention areas.

The main study area of the MedSudMed-10 Oceanographic survey was comprised between parallels 30° and 33° and meridians 14° and 21° (Gulf of Sirt). Sampling was also carried out along a transect between Capo Passero (Sicily) and Misurata (Libya), and along an offshore transect from south of Crete and Sicily.. The study area including all the stations covered is described in Figure 1 (CTD stations, Bongo 90 and Bongo 40), Figure 2 (sediments and phytoplankton), Figure 3 (water samples for nutrient analysis, isotopes, trace metals, Particulate Organic Carbon [POC], Particulate Organic Nitrogen [PON]).

3 Participating Institutes and Scientific Staff

Scientists from the following research institutions participated in the organization and carrying out of the survey:

1. Istituto per l'Ambiente Marino Costiero (CNR-IAMC), Capo Granitola Section, Italy;
2. Marine Biology Research Centre (MBRC), Tripoli, Libyan Arab Jamahiriya;
3. FAO MedSudMed Project;
4. Istituto per l'Ambiente Marino Costiero (CNR-IAMC), Messina Section, Italy

The following table shows some details on the Scientific staff on board:

	Name	Institution	Role on board
1	Angelo Bonanno	IAMC-CNR	Chief scientist - Oceanography
2	Paola Rumolo	IAMC-CNR	Interdisciplinary measurements
3	Simona Genovese	IAMC-CNR	Interdisciplinary measurements
4	Salem Zgozi	MBRC	Interdisciplinary measurements
5	Monica Calabrò	Università di Palermo	Interdisciplinary measurements
6	Marianna Del Core	IAMC-CNR	Interdisciplinary measurements
7	Marco Barra	IAMC-CNR	Interdisciplinary measurements
8	Francesco Filiciotto	IAMC-CNR	Interdisciplinary measurements
9	Maria Rita Amico	Università di Palermo	Interdisciplinary measurements
10	Germana Borsetta	IAMC-CNR	Interdisciplinary measurements
11	Giovanni Giacalone	IAMC-CNR	Interdisciplinary measurements
12	Akram El Turki	MBRC	Interdisciplinary measurements
13	Biagio De Luca	IAMC-CNR	Interdisciplinary measurements
14	Salvatore Mangano	Università di Palermo	Interdisciplinary measurements
15	Mohamed Hamza	MBRC	Interdisciplinary measurements
16	Maria Bonsignore	Università di Palermo	Interdisciplinary measurements
17	Osama Uheshi	MBRC	Interdisciplinary measurements
18	Mahmoud Bara	MBRC	Interdisciplinary measurements
19	Mohamed Assugayer	MBRC	Interdisciplinary measurements
20	Ali Kahlifa	Libyan Navy	Coast Guard

The shifts on board were organized as follows:

Work shifts		
1st shift 08:00 - 12:00 20:00 - 24:00	2nd shift 12:00 - 16:00 24:00 - 04:00	3rd shift 16:00 - 20:00 04:00 - 08:00
Angelo Bonanno	Giovanni Giacalone	Biagio De Luca
Salem Zgozi	Germana Borsetta	Salvatore Manfano
Maria Rita Amico	Marco Barra	Maria Bonsignore
Francesco Filiciotto	Mohamend Assugayer	Akram El Turki
Mahmoud Bara	Osama Uheshi	Mohamed Hamza
Water sampling	o Nutrients	Simona Genovese
	o Isotopes	Paola Rumolo
	o Metals	Marianna Del Core
	o Microalgy	Monica Calabrò

3. Diary of the survey

1st day: Thursday 15 July 2010 (Messina – Sicily Channel).

The morning was dedicated to administrative formalities for the embarkation of the scientific crew and the instruments. The survey started with a sampling plan alternative because release authorizations to work in Libyan waters were slowed by the application of new rules. In this regard the 05/07/2010 has been formulated the request for permission to the Italian Coast Guard units, to Maristat, in Marisicilia and Maridrografico.

We leave the port of Syracuse at 17:00 with some excellent weather conditions. In the afternoon the Libyan colleagues (Marine Biology Research Centre, Tripoli, Libya) reported that most likely the necessary permits to work in Libyan waters will be released on Sunday, July 18, 2010. Therefore, it was decided to carry out some sampling stations in international waters belonging to the initial program, waiting for communications from Libyan Authorities.

2nd day: Friday 16 July 2010 (Sicily Channel).

Work activities begin at 01:42 UTC at station M1 and proceed along the transect towards Mysurata (M2, M3, M4, M5, M6 Stations). Arriving at the middle line, and having not yet been granted authorization by the Libyan authorities, it was decided to continue the activities of the sampling stations positioned in international waters. The weather conditions are excellent.

3rd day: Saturday 17 July 2010 (Ionian Sea)

At 07:30 UTC the Urania vessel arrived at L111 station. After concluding the sampling activities, we head towards the L118 station, reached at 22:56.

Terminated the sampling transect, the vessel goes to the restart for the activity from station M7. The weather conditions are excellent.

4th day: Sunday 18 July 2010 (Sicily Channel).

The whole day is used to reach the M7 station.

5th day: Monday 19 July (Libyan water)

Excellent weather condition. At 00:29 UTC the vessel arrived at the station M7, and continue along the transect to complete the sampling operations on the M8 and M9 stations.

After having contacted dr. Essarbout, Director of MBRC, we head towards Misurata since the authorizations to work in Libyan waters have been released. The sampling is stopped in order to reach the port of Misurata.

During the transfer, dr. Zgozi informs probably the boarding of staff of the Libyan MBRC and the officer of the Coast Guard will take place the next day.

So it was decided to complete the sampling plane in the stations M10 and M11.

6th day: Tuesday 20 July (Mysurate- Tripoli)

Even today the weather conditions are good; at 08:00 the ship is located in the Anchorage area in front of the port of Mysurata waiting to take onboard the research staff of the MBRC.

At 13:00 hours about dr. Salem Zgozi announces that some of the formal problems prevent their embarkation on the Urania vessel.

After telephone contact, dr. Essarbout, Director of MBRC, suggests the boarding of Libyans researchers directly in Tripoli where can closely follow the procedures..

The Urania vessel moved towards Tripoli. During the transfer the transect “Sicily-Lybia” (M12 station) is completed. The night is used for navigation from Misurata to Tripoli.

7th day: Wednesday 21 July (Tripoli)

At about 10:20 the vessel enters in the Tripoli harbor for boarding the research staff of the MBRC. During the day the procedures for boarding staff of MBRC and Officer of the Coast Guard (Ali Kahlifa Asherbani) are carried out.

The vessel restart from Tripoli harbor at 17:30. Excellent weather conditions.

8th day: Thursday 22 July (Goulf of Syrte)

During the day, the weather conditions remain excellent. The whole day is used to reach the first sampling point. A new sampling plan is designed in relation to the time available and the scientific objectives of the survey (Figure 1, 2 e 3).

9th day: Friday 23 July (Goulf of Syrte- Benghazi)

The vessel arrives at N1 point of the new sampling plan at 03:17 UTC. Although weather conditions is decreased, they still allow to be able to work safely. The sampling N2, N3, N4, N5, N6, N7, N8 and N9 stations are carried out regularly (Table 1)

10th day: Saturday 24 July (Benghazi-Darna)

Sampling operations are continuing on a regular basis during the day and the night. The station N10, N11, N12, N13, N14, N15 and N16 (Table 1) are completed. During the day, the sea is a little rough.

11th day: Sunday 25 July (Darna – Tobruk)

Another day with rough sea. However, the sampling procedures continue. The stations N17, N18, N19, N20 and N21 (Table 1) are completed. Due to worst weather and sea conditions it was decided not to sample the station N22 and continue the sampling plan from the N23 station. The weather conditions improved and we continued to carry out the sampling procedures in the stations N23, N24 and N25.

12th day: Monday 26 July (Tobruk)

During the night stations N28, N27 and N26 are completed. At 09:00 hours the Urania vessel is located in the anchorage waiting to disembark the colleagues of the MBRC.

At the end of the bureaucratic procedures, the customs agents communicate to the Chief of vessel to wait two hours at anchor for the "clearance". Actually, five hours are spent and about 15.00 of Mr. Lamin of the "Ras Al-Hilal Marine Services Company" announces that the ship should enter the port of Tobruk for inspection by Customs officers. Despite various contacts with dr. Essarbout, dr. Zgozi and the same Mr. Lamin, the vessel enters in the harbor at 17 pm. All customs and immigration procedures are performed again. Only at 20.00 the vessel leaves the harbor of Tobruk. We moved towards the station L114 to continue sampling.

13th day: Tuesday 27 July (Tobruk- Ionian Sea)

At 07:52 UTC the ship reaches the station L114 where the acquisition of profiles of oceanographic variables and the sampling of seawater is carried out.

The excellent weather and sea conditions allow to reach the next sampling point (L116) at 07:42 UTC. Then, the vessel moved towards the point L117.

14th day: Wednesday 28 July (Ionian Sea)

The ship arrives at station L117 at 04:58. At the end of the operations the vessel moved towards Palermo.

15th day: Thursday 29 July (Ionian Sea-Strait of Messina)

The entire day is used to sail to Palermo.

16th day: Friday 30 July (Palermo harbor)

The ship arrives in port at 08:00. The day is used bureaucratic procedures for disembarkation of scientific personnel and equipment.

4. Sampling design of the Oceanographic survey MedSudMed-10Diary of the survey

The sampling design of the surveys is shown in the following figures 1, 2 and 3. Since the Libyan-Italian research team adopted a multidisciplinary approach in carrying out the survey, all the research activities performed in the study area are described in three different figures.

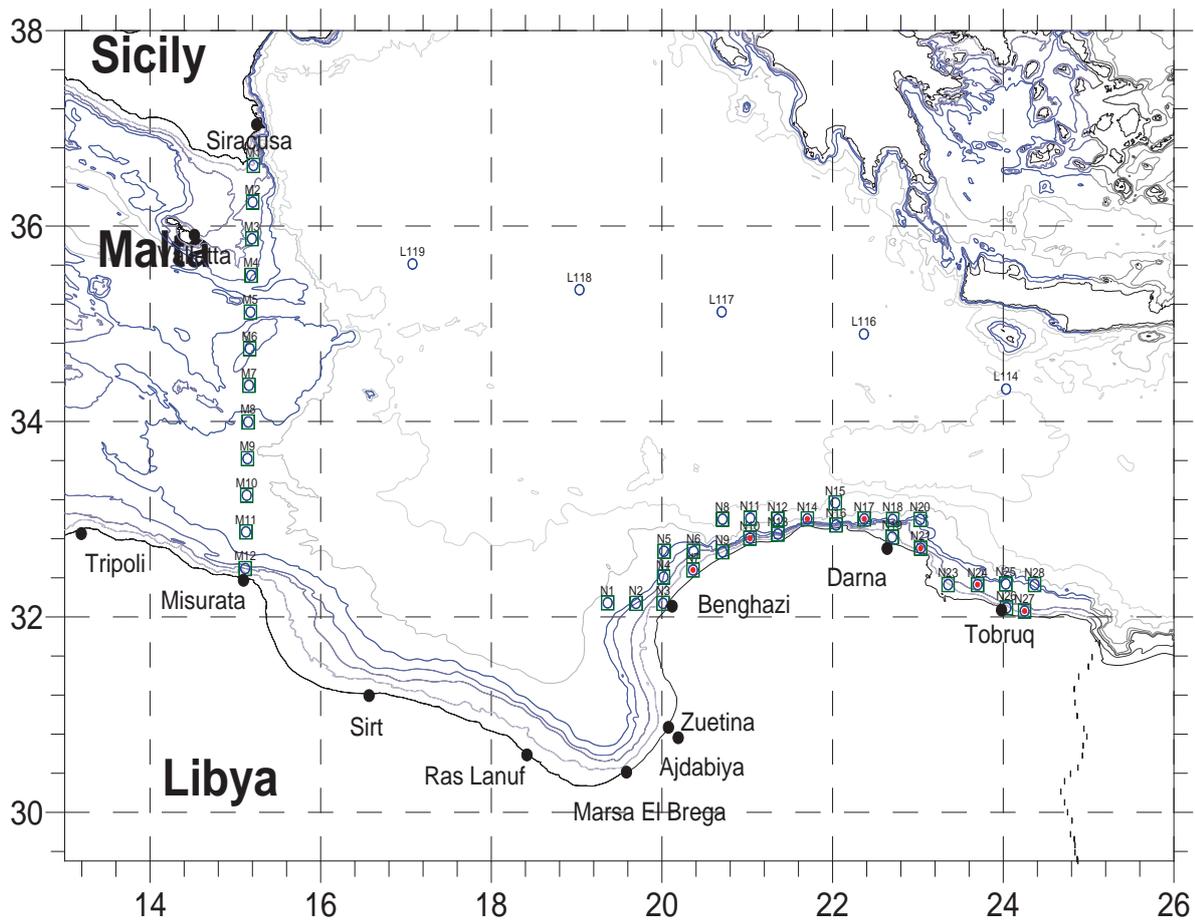


Figure 4.1. Position of CTD (blu circles), Bongo90 (red circles) and Bongo 40 (green squares) stations covered during the MedSudMed-10 survey on board R/V Urania

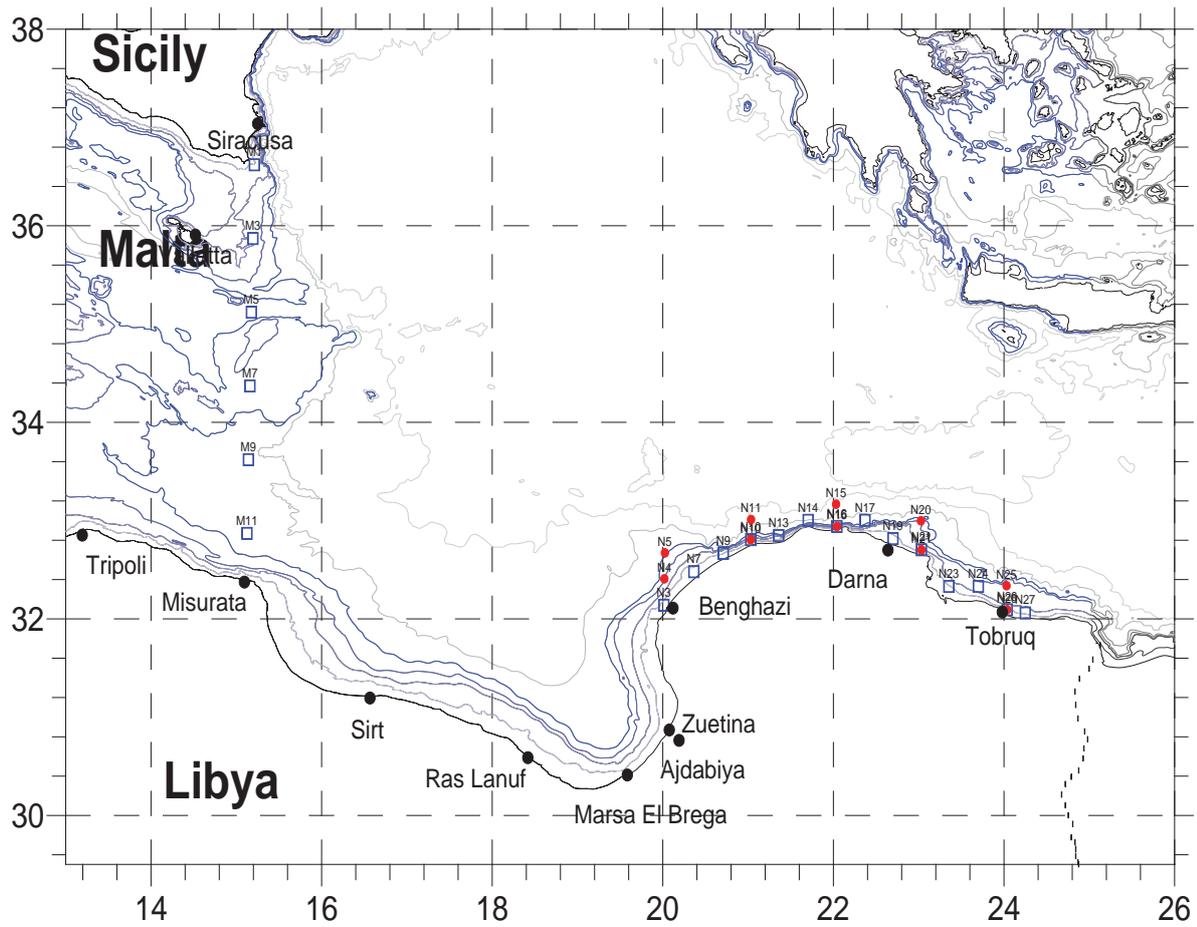


Figure 4.2. Position of the stations where sediments (blue squares), Phytoplankton (red circle) stations covered during the MedSudMed-10 survey on board R/V Urania.

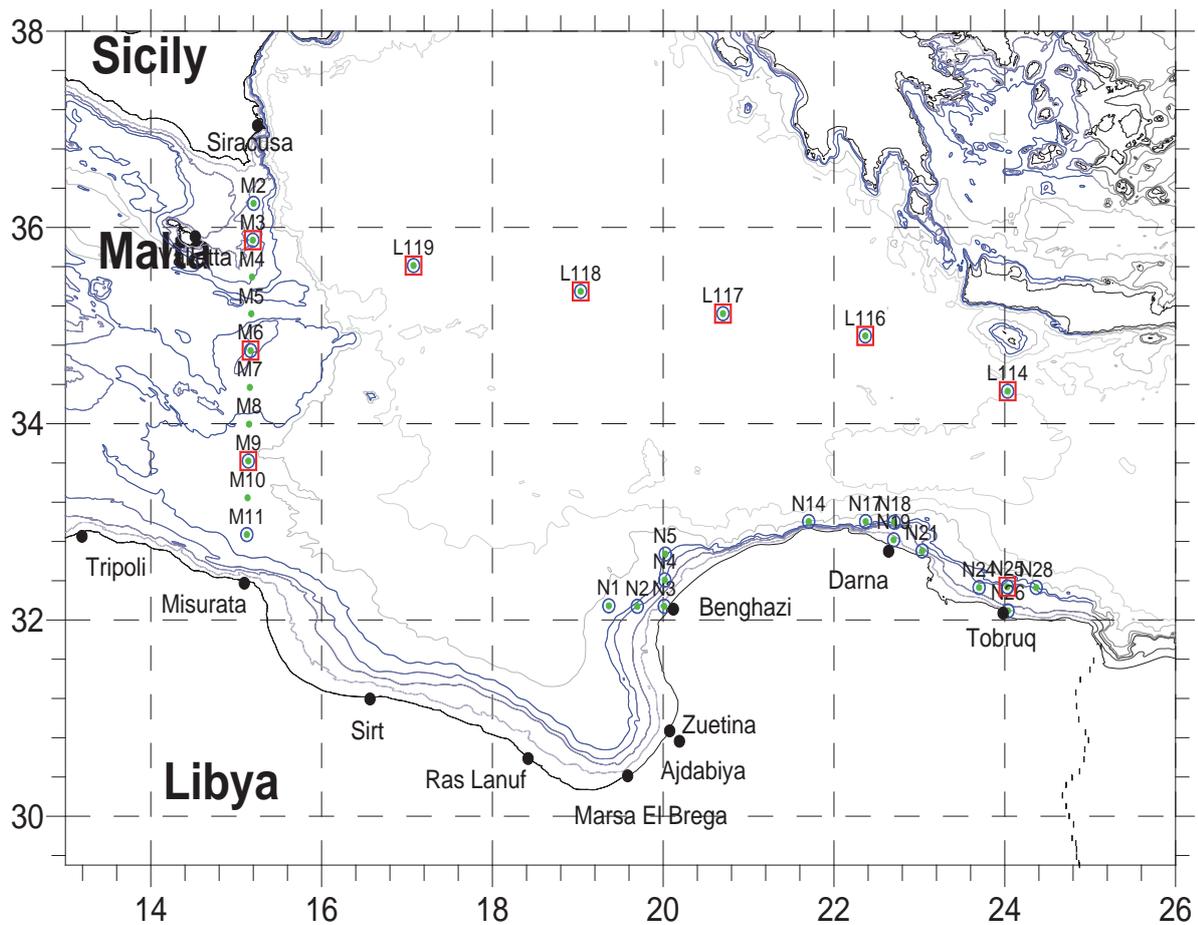


Figure 4.3. Position of the stations where water samples were collected for the analysis of nutrients (green circles), isotopes (blue circle), trace metals (red squares), POC and PON (blue circle).

5. Oceanography

From the oceanographic point of view the Strait of Sicily is a crucial area of the Central Mediterranean (CMED) that separates the eastern and western basins of the Mediterranean Sea. Both basins show different hydrological and biogeochemical characteristics with the eastern basin more oligotrophic than the western one. The main reason for the very low productivity of the eastern Mediterranean sea is the unusual anti-estuarine circulation in the basin in which nutrient depleted surface water (Modified Atlantic Water - MAW) flows in through the straits of Sicily, while more saline Levantine Intermediate Water (LIW) flows out at intermediate depths (200–500 m) carrying dissolved nutrients, including nitrate and phosphate (Krom *et al.*, 2010). The export of nutrients through the intermediate water causes the deep waters of the Eastern Mediterranean Sea (Eastern Mediterranean Deep Water – EMDW) to be more nutrient depleted than deep water in all other parts of the global ocean and to have a N:P ratio of ~28 (Krom *et al.*, 2005). The cause of this latter anomaly is still unclear. The MedSudMed-10 survey permitted to acquire a new set of oceanographic data useful to better understand the water masses circulation in this not fully explored part of the Mediterranean sea.

5.1 Material and methods

During the survey 12 stations were sampled along the Siracusa-Misurata transect, 5 stations in off-shore waters between Crete and Sicily and 27 in the coastal waters between Benghazi and Tobruq.

In all hydrological stations, continuous vertical profiles of conductivity, temperature, pressure and dissolved oxygen were obtained (from the surface to the bottom) by means of a CTD SBE 911plus probe. Data were processed using Seasoft-Win32 software following the Mediterranean and Ocean Data Base instructions (Brankart, 1994).

5.2 Results

The main surface circulation features in the CMED were evaluated by means of the altimeter products (Absolute Dynamic Topography) produced by Ssalto/Duacs and distributed by Aviso, with support from Cnes (<http://www.aviso.oceanobs.com/duacs/>). It permitted to evaluate the patterns of the main circulation streams, i.e. ATC, ALC and AIS as shown in Figure 5.2.1. From this figure there is no evidence of a possible joint path of the AIS and ATC. Actually both streams join in the sea area south-east of Malta and then a unique stream moves towards the northern African coasts.

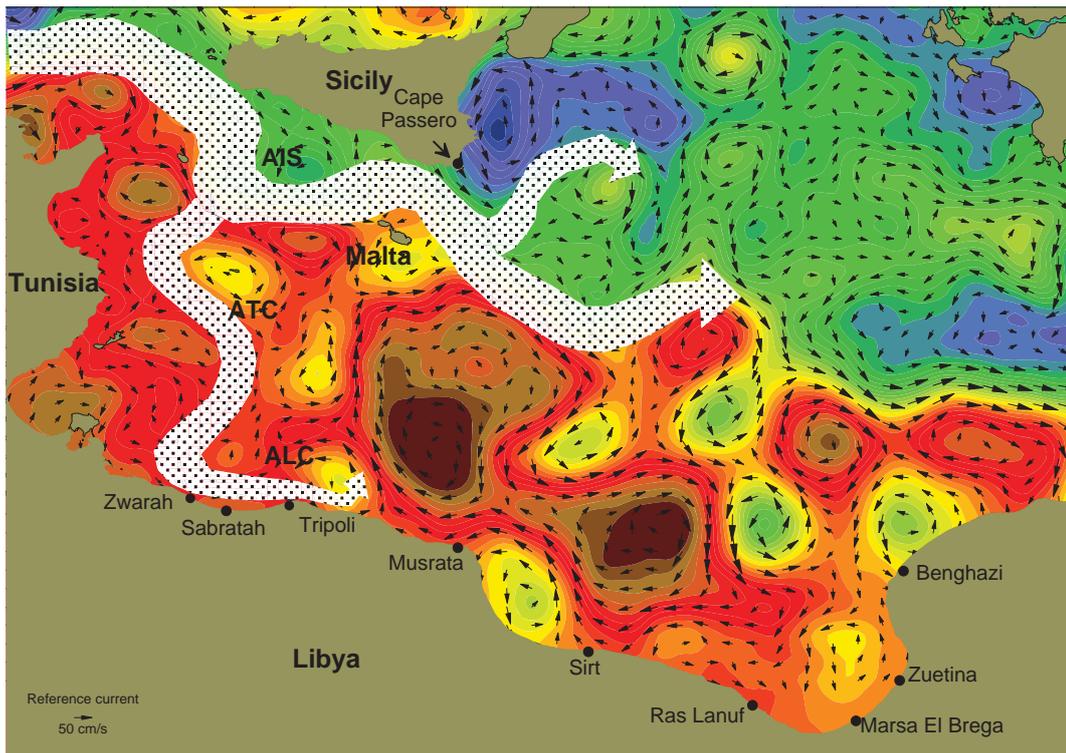


Figure 5.2.1. Mean geostrophic velocity field (Absolute Dynamic Topography by Aviso) estimated in the period 15-30 July 2010. The patterns of the main circulation streams (ATC, ALC and AIS) are evaluated by the Aviso altimeter products.

Siracusa – Misurata transect (Stations M) and Crete – Sicily transect (Stations L)

Section of temperature and salinity along the transect from Sicily to Misurata (Figure 5.2.2) and θ -S diagram (Figure 5.2.3) allowed a clear identification of the different water masses during the oceanographic survey. The θ -S diagram for the transect identified the presence of the three main water masses: the AW, occupying the first ≈ 200 m of the water column fresher and warmer than the water masses below, the LIW, located in the portion of the water column between ≈ 200 m and ≈ 500 m depth, with its core located at a mean depth of ≈ 330 m (Figs. 5.2.2d), and the transitional Eastern Mediterranean Deep Water (tEMDW) in the deepest part of the transect.

The EMDW occurs only in the Gulf of Syrte in the deepest layer, with typical features of recently ventilated deep water masses, lower salinity values than the resident deep water, and colder.

In 2010 the presence of Levantine Intermediate Water (LIW), with higher values of salinity, was close to the Libyan coast while in 2008 the core of LIW was located in the middle of the transect Malta – Misurata (see MedSudMed-08 Report).

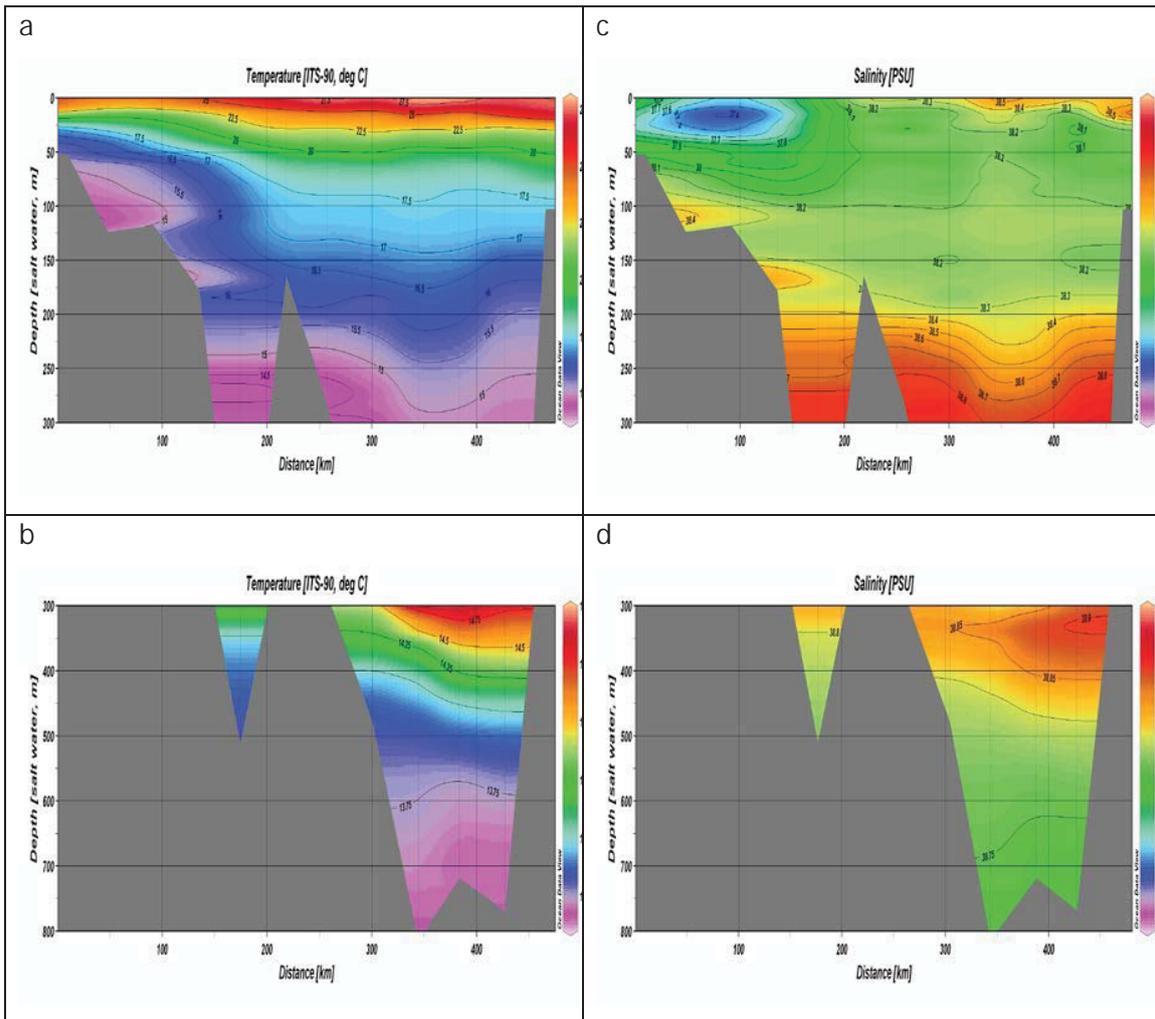


Figure 5.2.2. Vertical sections along the transect from Sicily to Misurata of temperature (a and b) and salinity (c and d) in the survey 2010.

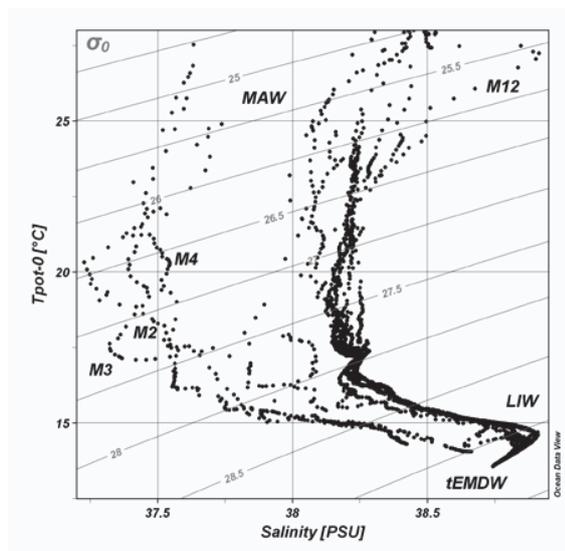


Figure 5.2.3. θ -S diagrams of the CTD casts acquired along the Sicily-Libya transect

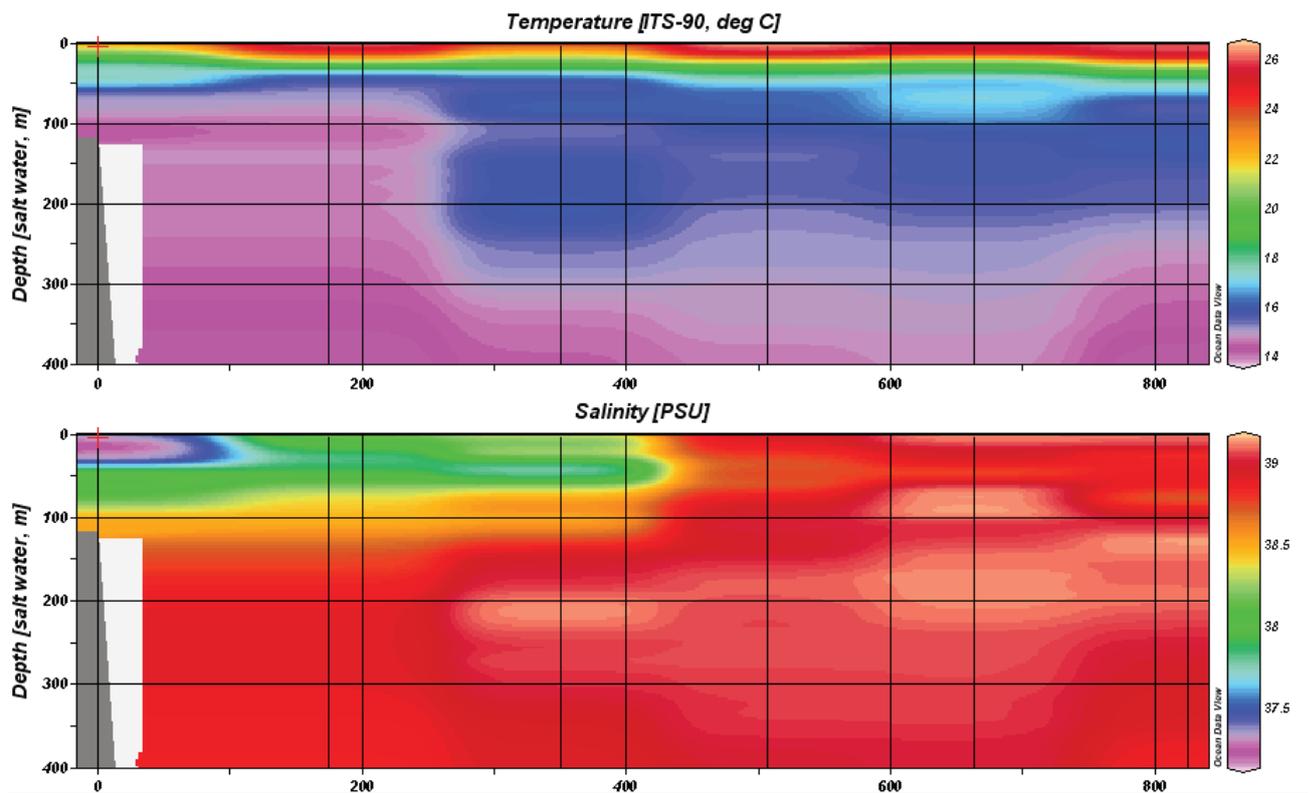


Figure 5.2.4. Vertical sections along the transect from Crete to Sicily of temperature and salinity in the survey 2010.

Section of temperature and salinity along the transect from Crete to Sicily (Figure 5.2.4) highlights the strong thermal stratification and the presence of the AIS flowing eastward. The temperature map (upper panel in Figure 5.2.5) shows a warmer water layer in the southern part of the investigated area.

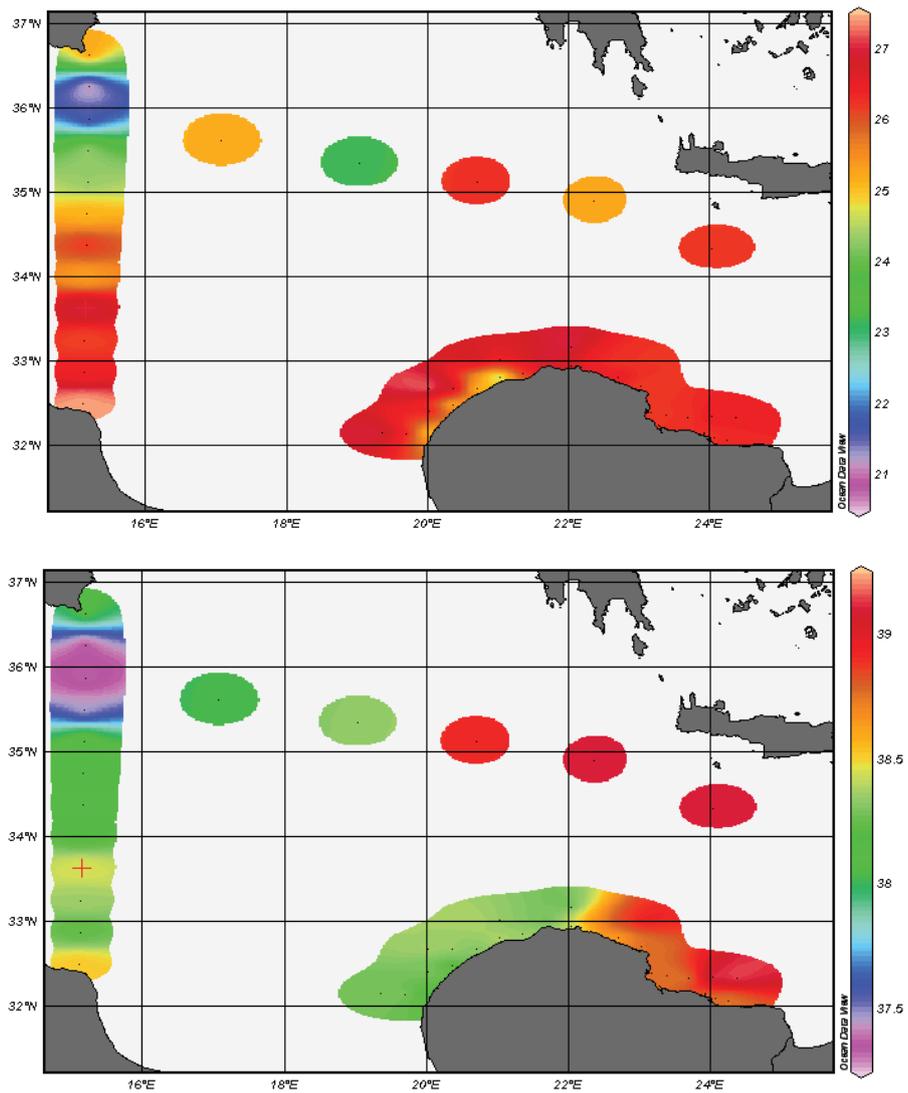


Figure 5.2.5. Maps of temperature and salinity at 10 m depth with all the collected CTD stations in the survey 2010.

The salinity map (Figure 5.2.5) single out the influence of the MAW (Modified Atlantic Water) in the western side of the study area. The vertical profiles of the acquired CTD are reported in Annex 1.

6. Nutrients

The main objectives of the cruise MEDSUDMED-10 were the investigation of the role of nutrients (including the N:P ratios) in marine environment and the identification of a possible terrestrial influence (fluvial contributions, flows of aeolic materials mainly deriving from the Sahara desert and/or from the industrialized European continental area) on primary production through the acquisition of the first geochemical dataset of the study area coupled to chemical and physical parameters determinations in order to assess water masses characteristics.

6.1 Material and methods

During the MedSudMed-10 survey, nutrients were sampled at different depths along the entire water column in 28 stations located along three different transects: i) Transect M (from Siracusa (Sicily) to Misurata (Libya); ii) Transect N (from Benghazi (Libya) to Tobruq (Libya)) and; iii) Transect L (from south of Crete (Greece) to Siracusa (Sicily)). Samples for nutrients analysis were carefully collected directly from Niskin bottles into 60-ml sterile high-density polyethylene bottles previously cleaned with 1M HCl. Sample bottles were rinsed three times with their own volume of sample water and immediately frozen at -20°C. The determination of inorganic nutrients and total phosphorus-nitrogen in seawater were performed through the continuous flow system AutoAnalyzer III (Continuous Flow) Bran + Luebbe. Water samples were completely thawed about 4-12 hours before analysis at room temperature in air or in a water bath (at 40°C) and introduced to the Continuous Flow Analyzer (CFA). CFA uses a multichannel peristaltic pump to mix samples and chemical reagents in a continuously flowing stream to automate colorimetric analysis. By segmenting the sample stream with air bubbles such a system reduces mixing of adjacent samples and enhances mixing of the reagents within the sample stream.

The segmented stream passes through a system of glass coils where mixing and time delays are accomplished. The sample-reagent mixture reacts chemically to produce a colored compound whose light absorbance is approximately proportional to the concentration of nutrient in the sample. Finally the absorbance is measured by a flow-through colorimeter set at the end of the flow path.

The procedures for determination of inorganic nutrients are based on manual methods suitably adapted for an automatic system. All methods are shortly outlined as follows:

- *For the determination of nitrate + nitrite*, nitrate is reduced to nitrite by a copper-cadmium reductor column at pH of 8.0. The nitrite ion then reacts with sulfanilamide under acidic conditions to form a diazo compound. This compound then couples with N-1-naphthylethylenediamine dihydrochloride to form a reddish-purple azo dye and is read at 550 nm.

- *The method for determination of (ortho) phosphate* is based on the colorimetric method in which a blue color is formed by reaction of phosphate, molybdate ion and antimony ion followed by a reduction with ascorbic acid at pH <1. The reduced blue phosphor-molybdenum complex is read at 880 nm.

- *The procedure for determination of soluble silicate* is based on the reduction of silico-molybdate in acidic solution to molybdenum blue by ascorbic acid; oxalic acid is

introduced to the sample stream before the addition of ascorbic acid to minimize interference from phosphate. The complex is read at 820 nm.

- *The procedure for determination of ammonia* uses the Berthelot reaction, in which a blue-green colored complex is formed and measured at 660 nm. A complexing agent is used to prevent the precipitation of calcium and magnesium hydroxides. Sodium nitroprusside is used to enhance the sensitivity of this method. Alternative reagents are given for reaction with salicylate and phenate.

- *For total phosphorous-nitrogen determination*, small modifications were brought at the Bran+Luebbe methodology for on-line sample mineralization. Nitrogen and phosphorous compounds are oxidized with peroxodisulphate to nitrate and ortho-phosphate in a heating bath at 118°C. The determination of ortho-phosphate is then based on the colorimetric method in which a blue is formed by the reaction of phosphate and molybdate followed by reduction with ascorbic acid at an acid pH. The phosphomolybdenum complex is read at 880 nm.

- *Quality control / Quality assurance (QC/OA) routinely employed within the laboratory*

For all analytical determinations calibration standards are prepared using natural seawater of low nutrient content or artificial sea water as sample matrix. The NSW (or ASW) is used as “base” for the analysis of sea water samples and is measured prior to each set of samples run.

6.3 Results

The estimated concentrations of inorganic nutrients and N/P ratios along different transects and depth are reported in Tables 6.2.1, 6.2.2 and 6.2.3. Unfortunately, a bad conservation during the transport caused the loss of some samples (particularly in the transect L).

Vertical distributions

The chemical analysis highlights similar distribution of nitrate concentration with depth in both Transect M and N. In samples collected along Transect M, the nitrate concentration were 0.39 μM from the surface to 200 m, increasing at about 4.52 μM in deep layer (from 200m to bottom). In samples collected in the Transect N, nitrate concentration in surface layer (0-200 m) were 0.52 μM , and 4.24 μM at deep layer (from 200m to bottom) (Figure 6.2.1).

Phosphate (PO_4) and silicates (SiO_4) have a similar trend in column water in both the Transects (M and N). Particularly, mean concentration for the PO_4 in euphotic zone (0 to 200m) were of 0.05 and 0.04 μM , respectively for Transect M and Transect N, while in the deep layer (from 200m to bottom) the values were 0.16 μM and 0.14 μM , respectively. For the SiO_4 , the mean concentrations were 0.84 μM and 0.99 μM in surface layer (from the surface to 200m) and 4.97 and 4.69 μM in deep layer (from 200 m to bottom), respectively for Transect M and N (Figure 6.2.2).

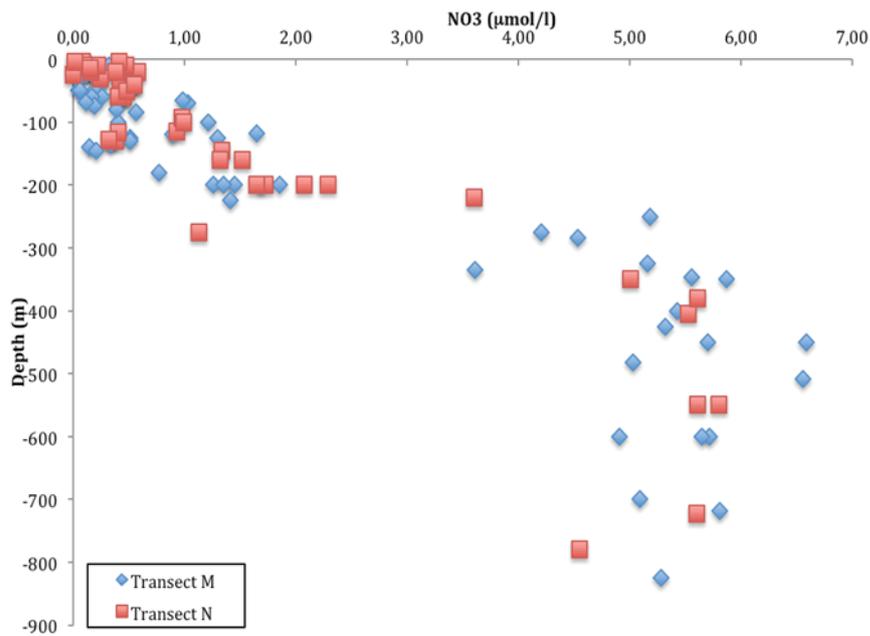


Figure 6.2.1. Nitrate concentration with depth in Transects M and N

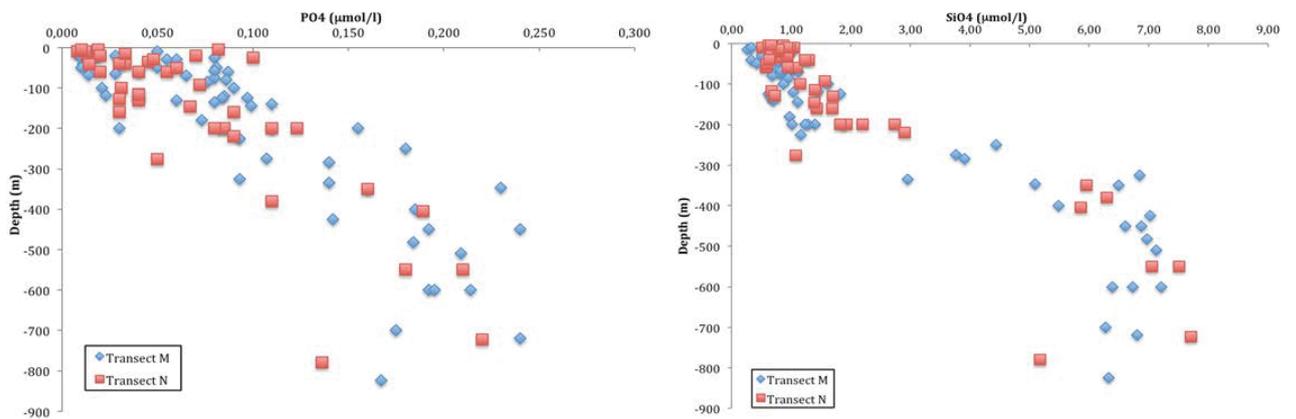


Figure 6.2.2. Phosphate (PO₄) and silicates (SiO₄) trend in column water in Transects M, N

Horizontal distributions

Horizontal distribution of NO₃⁻ in the euphotic layer (0-200m) showed a decrease of concentrations from western samples to eastern samples for both the transects (Figure 6.2.3). However, in the Transect M, excluding M3 station with highest NO₃ concentrations the other values were between 0.1 and 0.5 µmol/l. Contrary, a clear decrease of values from west to east was present in the samples of Transect N. Below the euphotic zone (>200m) nitrate concentration increase with values > 4 µM in both the Transects.

Horizontal PO₄ distribution in surface layer (0-200 m) in the Transect M showed higher average concentration than samples collected in the Transect N. Heterogeneity of distribution was found in SiO₄ distribution except for the stations N2, N4 and N5 with slightly higher values (Figure 6.2.4).

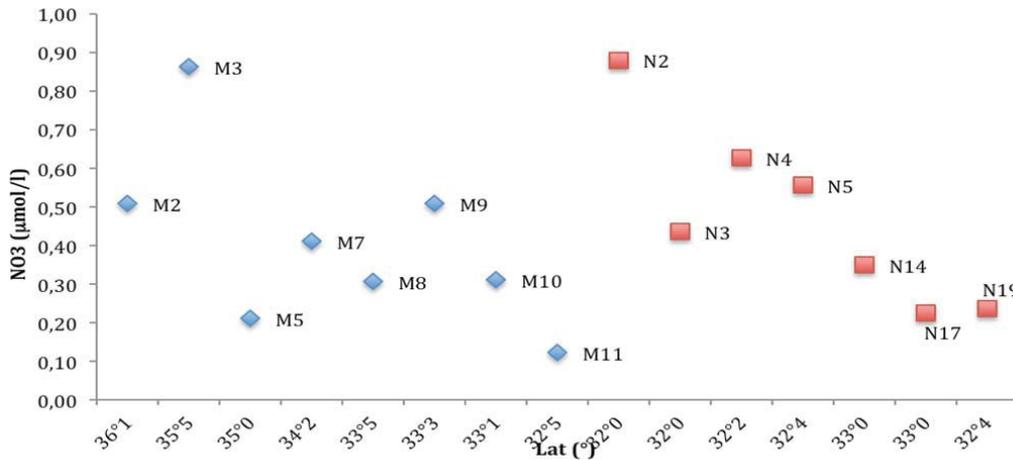


Figure 6.2.3. Horizontal distribution of NO₃⁻ in the euphotic layer (0-200m).

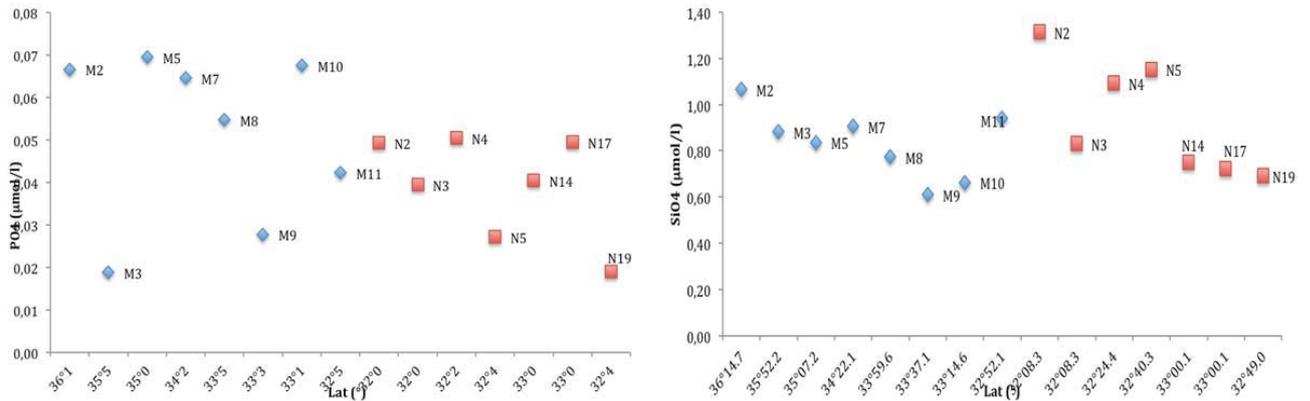


Figure 6.2.4. Horizontal PO₄ distribution in surface layer (0-200 m) in the Transect M.

The measured average N:P was ~10 in surface waters (<200m) while in the intermediate and deep waters, it approximates ~28.8 and 29.6 respectively in the transect M and N. These values according with previous reported values that identify the eastern Mediterranean sea as an ultra-oligotrophic sea where N:P ratio in deep layer is higher than ratio found in deep ocean sea (16:1).

Table 6.2.1. Nutrients concentrations in stations of transect M.

Target	Depth	NO ₂	PO ₄	SiO ₄	NO ₃	N:P
	m	μmol/l	μmol/l	μmol/l	μmol/l	
M2	125	0,06	0,097	1,82	1,30	13,37
	70	<0,01	0,065	1,12	1,03	15,86
	50	<0,01	0,081	0,87	0,04	0,51
	25	<0,01	0,080	0,77	0,02	0,28
	7	<0,01	0,010	0,75	0,15	14,80
M3	118	0,07	0,023	1,45	1,65	71,74
	100	0,05	0,021	1,62	1,21	57,52
	65	<0,01	0,028	0,75	0,98	35,00
	40	<0,01	0,011	0,33	0,24	21,82
	15	<0,01	0,011	0,27	0,24	21,55
M5	20	<0,01	0,028	0,88	0,11	3,93
	50	<0,01	0,050	0,90	0,19	3,80
	100	0,04	0,090	0,87	0,40	4,44
	140	0,11	0,110	0,70	0,14	1,27
	200	0,13	0,155	1,40	1,45	9,35
	250	0,04	0,180	4,44	5,18	28,78
	350	0,05	0,160	6,49	5,87	36,69
	450	0,03	0,192	6,87	6,59	34,32
	509	0,01	0,209	7,12	6,56	31,39
M7	284	0,03	0,140	3,91	4,53	32,39
	200	0,01	0,110	1,28	1,85	16,82
	120	0,16	0,085	1,03	0,89	10,47
	85	0,01	0,076	0,95	0,56	7,37
	60	0,01	0,087	0,98	0,26	2,97
	30	<0,01	0,055	0,84	0,24	4,27
	15	<0,01	0,020	0,74	0,11	5,45
M8	7	<0,01	0,010	0,69	0,01	1,00
	25	<0,01	0,010	0,75	0,11	11,00
	60	<0,01	0,040	0,90	0,16	4,10
	75	<0,01	0,080	0,82	0,19	2,38
	80	0,01	0,086	0,68	0,39	4,53
	125	0,06	0,084	0,62	0,51	6,07
	180	0,03	0,073	0,97	0,77	10,56
	275	<0,01	0,107	3,76	4,21	39,31

Target	Depth	NO2	PO4	SiO4	NO3	N:P
	m	µmol/l	µmol/l	µmol/l	µmol/l	
M9	482	<0,01	0,184	6,96	5,03	27,35
	10	0,01	0,011	0,33	0,20	18,18
	50	0,01	0,010	0,42	0,06	6,00
	130	0,04	0,060	0,68	0,51	8,50
	200	0,03	0,030	1,01	1,26	42,00
	335	0,02	0,140	2,95	3,61	25,79
	400	0,01	0,185	5,48	5,43	29,35
	600	0,01	0,192	6,73	4,91	25,57
M10	824	0,02	0,167	6,32	5,28	31,62
	718	0,07	0,240	6,80	5,81	24,21
	600	0,03	0,214	7,21	5,72	26,73
	450	<0,01	0,240	6,60	5,70	23,75
	347	<0,01	0,230	5,09	5,56	24,17
	225	0,04	0,093	1,16	1,41	15,16
	136	0,12	0,080	0,68	0,33	4,13
	57	<0,01	0,080	0,66	0,39	4,88
M11	30	<0,01	0,060	0,50	0,20	3,33
	10	0,01	0,050	0,82	0,32	6,40
	10	<0,01	<0,01	0,95	0,09	
	25	<0,01	0,014	0,89	0,08	5,80
	68	<0,01	0,014	0,83	0,11	7,91
	145	0,09	0,099	1,10	0,21	2,09
	200	0,01	0,085	1,23	1,35	15,85
	325	<0,01	0,093	6,84	5,16	55,46
425	<0,01	0,142	7,02	5,32	37,46	
600	<0,01	0,195	6,39	5,65	28,97	
700	<0,01	0,175	6,27	5,09	29,07	

Table 6.2.2. Nutrients concentrations in stations N.

Target	Depth	NO ₂	PO ₄	SiO ₄	NO ₃	N:P
	m	µmol/l	µmol/l	µmol/l	µmol/l	
N2	10	<0,01	0,010	0,90	0,02	2,00
	20	<0,01	0,013	0,95	0,58	44,46
	40	<0,01	0,033	1,29	0,51	15,45
	115	0,03	0,040	1,39	0,93	23,25
	160	0,03	0,090	1,43	1,52	16,89
	199	0,02	0,110	1,93	1,72	15,64
N3	35	<0,01	0,045	0,78	0,42	9,31
	20	<0,01	0,017	0,64	0,44	25,71
	10	<0,01	0,014	1,05	0,47	33,57
	5	<0,01	0,082	0,86	0,41	5,04
N4	10	<0,01	0,010	0,52	0,14	14,10
	30	<0,01	0,048	0,93	0,24	5,00
	60	<0,01	0,055	1,08	0,44	8,04
	93	0,03	0,072	1,56	0,98	13,57
	146	0,04	0,067	1,39	1,34	19,93
	200	<0,01	0,123	2,20	2,29	18,59
N5	5	<0,01	0,019	0,62	0,08	4,21
	20	<0,01	0,020	0,76	0,16	7,85
	40	<0,01	0,030	1,23	0,53	17,70
	60	<0,01	0,020	0,94	0,45	22,30
	100	0,02	0,031	1,14	0,99	31,94
	130	0,02	0,040	1,70	0,38	9,43
	160	<0,01	0,030	1,68	1,32	43,83
	200	<0,01	0,085	2,74	2,07	24,38
405	<0,01	0,189	5,85	5,53	29,25	
N14	780	<0,01	0,136	5,17	4,55	33,46
	550	<0,01	0,210	7,51	5,61	26,71
	350	0,01	0,160	5,95	5,01	31,31
	200	<0,01	0,080	1,82	1,65	20,63
	176	0,09	0,050	1,07	1,13	22,60
	117	0,06	0,040	0,67	0,40	10,00
	60	<0,01	0,040	0,58	0,40	10,00
	20	<0,01	0,070	0,78	0,38	5,43
10	<0,01	0,012	0,97	0,22	18,33	

Target	Depth	NO2	PO4	SiO4	NO3	N:P
	m	µmol/l	µmol/l	µmol/l	µmol/l	
N17	10	<0,01	0,008	0,93	0,10	12,50
	25	<0,01	0,100	0,66	0,00	0,00
	51	<0,01	0,060	0,59	0,48	8,00
	128	0,05	0,030	0,72	0,32	10,67
	220	0,04	0,090	2,90	3,60	40,00
	380	0,01	0,110	6,29	5,61	51,00
	550	0,02	0,180	7,05	5,80	32,22
	723	0,02	0,220	7,70	5,60	25,45
N19	41	<0,01	0,014	0,63	0,55	39,07
	15	<0,01	0,033	0,79	0,15	4,55
	5	<0,01	0,010	0,66	0,01	1,00

Table 6.2.2. Nutrients concentrations in stations of transect L.

Target	Depth	NO2	PO4	SiO4	NO3	N:P
	m	µmol/l	µmol/l	µmol/l	µmol/l	
L119	4007	0,01	0,140	6,55	4,45	31,79
	3000	0,05	0,136	7,02	4,68	34,41
	2000	0,03	0,195	7,15	5,77	29,59
	1500	0,02	0,138	6,59	4,62	33,48
	1000	0,04	0,201	7,50	5,39	26,82
	800	0,02	0,190	7,17	6,90	36,32
	600	0,02	0,160	6,17	5,10	31,88
	500	<0,01	0,174	6,06	5,87	33,74

7. Trace elements

The key aims of this report focus on: (a) the influence of atmospheric, coastal and riverine sources on metal concentrations and distributions, (b) the relationship of trace metals with the complex circulation and hydrography of the Eastern Mediterranean Sea, (c) the spatial and temporal variability of dissolved trace metals and their causes and (d) the definition of the distribution of metal concentrations in the Eastern Mediterranean Sea evaluating the potential influence of Eastern basin for the entire Mediterranean Sea.

To achieve these objectives, all the necessary activities have been carried out, ranging from the organization of work onboard the oceanographic cruise MeSudMed-10 to the determination of the considered elements concentrations, obtained through the selection of suitable analytical techniques.

7.1 Materials and methods

The main activities to achieve these objectives were :

- samples collection during the MeSudMed-10 oceanographic cruise;
- samples treatment on board the vessel;
- analysis of samples in the geochemical laboratory.

Samples collection

96 seawater samples were collected in the Central and Eastern Mediterranean Sea during the oceanographic cruise. Such seawater samples (Tab. 7.1.1) were collected in the entire water column of the 9 stations shown in Figure 7.1.1.

Cadmium, Cu, Mo, Ni and Fe dissolved concentrations and Al, Cd, Cu, Fe and Ni in the particulate phase were measured from each sample.

Sampling techniques

To minimise any contamination risk, all apparatus with potential contact with seawater samples (bottles, pipette tips, filtration system etc.) were pre-conditioned as described by Scelfo (1997).

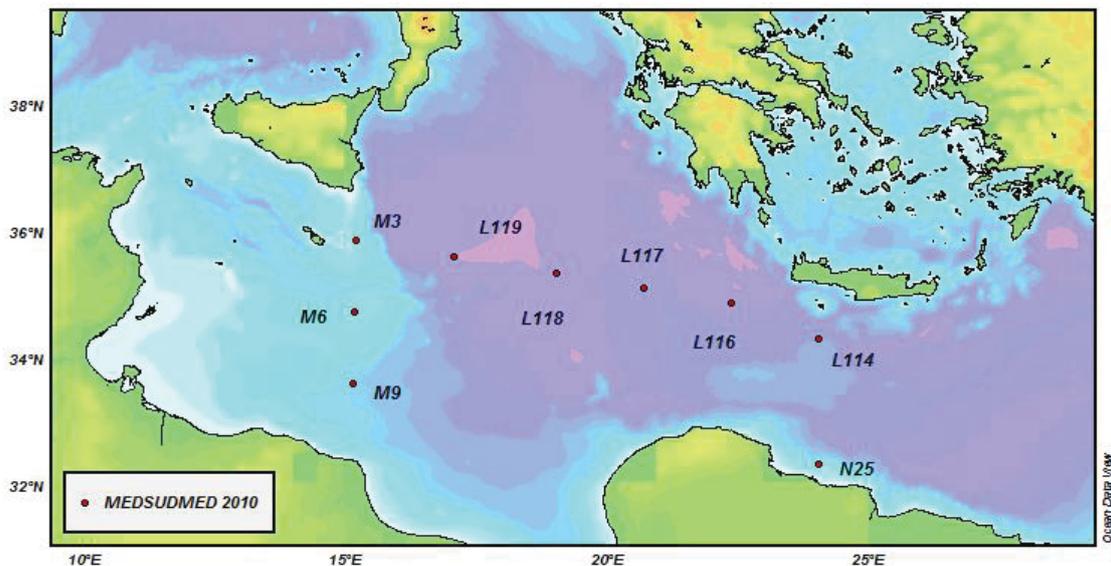


Figure 7.1.1. Sampling stations during the MEDSUDMED oceanographic cruise.

Table 7.1.1. Summary of pole sample sites in the East Mediterranean Sea

Station	Location	Depth (m)	N° samples
M3	15°11.67'E 35°52.20'N	118	5
M6	15°10.10'E 34°44.69'N	164	4
L119	17°04.58'E 35°36.69'N	4007	21
L118	19°02.00'E 35°20.90'N	3694	15
M9	15°08.52'E 33°37.19'N	823	8
N25	24°01.77'E 32°20.25'N	190	5
N26	24°02.25'E 32°05.56'N	50	2
L114	24°02.00'E 34°19.88'N	2176	12
L116	22°22.00'E 34°53.67'N	3007	12
L118	20°42.00'E 35°07.28'N	2791	12

The cleaning procedures involved multi-steps of washing with reagents to remove any source of metal contamination from the bottles walls. Polyethylene and Teflon materials were used ensuring that these metals adsorbed onto the bottles walls are simply removed with acid cleaning. Plastic bottles for seawater sampling were filled up with HNO₃ 10% and placed under hood for 4 days at room temperature. After this time, the bottles were rinsed 2-3 times with ultrapure water and, after drying, singularly, were stored in polyethylene bags until final sampling. Polycarbonate membrane filters, for particulate collection, were pre-weighed, and stored in petri dishes for the transport.

CTD Rosette sampling

Twenty-four “Niskin” bottles, fitted on a rosette with CTD instrumentation, were used for TM sampling. Samples for trace metals were collected in 1L polyethylene pre-cleaned bottles and then filtered through 47 mm, 0.4 µm pore size, polycarbonate membrane filters. Samples, for total dissolved trace metal analysis, were acidified to a pH ~2 with suprapur HNO₃ and stored at room temperature. These samples, filtered and acidified, were returned to its original bottle contained within a plastic bag, while the polycarbonate membrane filters were kept at T= -20°C. A filtered water sample was collected in duplicate for determination of precision related to sampling equipment and analytical procedures.

As above reported, during the sampling, two sets of samples were obtained (dissolved and particulate phase). Below, the preparation of both sets is described.

Dissolved trace metals - Principle of the method

The analytical procedures used to analyse TMs concentration request a preliminary stage of pre-condition of metals present in the sample that, on one side, increases considerably the sensibility limit and, from the other, minimizes interference of the matrix. A mixing of two chelating agents, APDC and DDDC, are used to form metal-carbamate complexes. Chloroform was chosen as the organic solvent for its low solubility in water and high efficiencies in extracting metals.

After chelation, the investigated metals were transformed in no-charge species soluble in the organic solvent, substituting water molecules, to them coordinated, with APDC binding group. The successive extraction of the organic phase in environment acid allows

to eliminate the problems of the instability of the complex and to obtain a stable acid solution that is usable for along time before the instrumental analysis.

Using this technique, it is possible to concentrate the most common metals as Cd, Cu, Mo, Ni and Fe with yields of extraction of the order of 50-100%.

Particulate trace metals - Principle of the method

The method consists in a digestion (mineralization) of material “trapped” in polycarbonate membrane 0,45 μm (following the filtration of 1L seawater) to bring in solution the metals associated with particulate or existing in colloidal and/or in organic form. Particulate matter for trace metals analysis was digested according to a modified total wet digestion method described by Poikāne *et al.* (2005). For this aim, the equipment is configured for the digestion of various types of matrices with the use of particular containers hermetically sealed, resistant to high temperatures, high pressure, and brought in a CEM Microwave Marsfor mineralization process.

To determine the concentrations of elements present in a polycarbonate membrane through the use of the technique of ICP-MS or ICP-OES, the sample must be reduced in an aqueous solution, to be introduced into the instrument. Solutions were prepared in order to ensure:

- a) maintaining in solution all elements of the matrix;
- b) containing all analytes with a concentration that can be detectable by the instrument;
- c) providing fewer interferences.

The mineralization of “these particulate samples”, if associated with the determination of dissolved trace metals, gives an estimate of total trace metals in seawater.

In this study the concentrations of trace metals in particulate and dissolved phases were determined by ICP-MS and ICP-AES (Varian).

7.2 Results

To represent efficiently and synthetically patterns and distribution models of the different TMs in the dissolved phase in terms of ocean dynamics and main driving force, the entire column of water was divided into three layers from the surface to the bottom. Water masses ranging between 0-150 m of depth will be considered as referred to the surface water mass, while the water layer between 300 and ~600 m is integrally considered as intermediate water (LIW). The water mass between 700 m and the sea bottom is considered as Deep Water. This well reflects data and interpretation on hydrographic and hydrodynamic parameters collected on the same sampling stations vertical profiles.

In Table 7.2.1 median values of TMs for the three main water masses at all sampling stations are reported. Due to the lack of data in the literature relatively to the Eastern Mediterranean Sea, these data are compared with values recorded in the Western Mediterranean Sea (Morley *et al.*, 1997; Yi Yong Yoon *et al.*, 1999) and Atlantic Ocean (Morley, 1997; Statham, 1985; Bruggmann, 1985; Flegal, 1995).

The geographical best coverage and vertical sampling reported in this study is sometime not directly comparable with that of datasets available in literature (Morley *et al.*, 1997; Yi Yong Yoon *et al.*, 1999) and represent an important contribution to understanding the ocean chemistry of the Mediterranean Sea.

A number of features immediately emerge from exploration of such new dataset: i) the well-known TMs depletion in surface waters followed by the progressive enrichment with depth typical of the open ocean appears much less pronounced in the Mediterranean basin where a higher variability along the vertical column occurs; ii) due to the short dynamics of 3D water mixing, the Eastern Mediterranean seems to re-distribute impulsive external inputs of trace metals such as Cu, Cd, Fe, Mo, and Ni from river and atmospheric inputs, along the vertical water mass at basin scale; iii) the patterns of classical nutrient-like elements as Cu, Cd and Ni appear primarily driven by lateral transport and vertical mixing processes, rather than biogeochemical cycling. In particular, Cu and Cd show a relatively homogeneous distribution with little variation all along the water column in the whole Mediterranean Sea with higher concentration values with respect to those reported for the global ocean.

The sampling stations can be grouped into two geographic areas for a better understanding of the phenomena affecting TMs distribution: the Levantine basin (from L119 to L114 station) and the Sicily Channel (from M3 to M9 station).

As above mentioned, Cd concentrations are generally higher in the Mediterranean basin than in the open ocean (Morley et al., 1997; Yoon et al., 1999) and maintain a homogenous distribution in the Eastern basin thus confirming a primary role of atmospheric and land inputs on the distribution modes of this elements (Riso et al., 2004).

Tab. 7.2.1 Mean values for dissolved trace metal in the surface, intermediate and deep waters of the Eastern Mediterranean Sea.

Station	Layer	Cd (nMol·L ⁻¹)	Cu (nMol·L ⁻¹)	Ni (nMol·L ⁻¹)	Fe (nMol·L ⁻¹)	Mo (nMol·L ⁻¹)
L114	surface	0,06	1,02	17,61	4,05	92,48
	intermediate	0,05	2,23	3,52	1,90	99,70
	deep	0,19	2,05	12,49	6,19	98,47
L116	surface	0,13	5,25	3,23	26,19	102,26
	intermediate	0,03	3,98	3,14	6,19	93,33
	deep	0,10	1,38	3,68	2,62	102,70
L117	surface	0,17	3,98	7,44	12,62	109,18
	intermediate	0,21	1,93	6,33	6,19	103,43
	deep	0,23	1,96	7,63	4,05	96,01
L118	surface	0,23	33,20	7,27	13,33	104,27
	intermediate	0,34	31,56	8,09	68,10	103,98
	deep	0,21	33,85	7,74	44,15	101,64
L119	surface	0,14	11,35	6,07	14,35	100,19
	intermediate	0,44	2,14	12,25	19,52	104,23
	deep	0,17	11,94	9,40	33,05	102,03

Particularly surface concentrations of $[Cd_d]$ appear to increase westward along the transect from the station 114 to station 119 with the exception of L119, which shows a light decrease of concentrations; the contrary for $[Cd_d]$ in the intermediate waters in the same transect, showing an increase Eastward. In the Sicily Channel stations (M3, M6 and M9), $[Cd_d]$ are homogeneous with a slight increase in the intermediate and deep waters of the M9 station.

Hence, from a first analysis $[Cd_d]$ distribution in the Eastern basin, appears to be not driven by marine biogeochemical processes of uptake by phytoplankton at the surface and successive release by remineralization of organic matter in the deep waters.

$[Fe_d]$ shows a hybrid distribution that can be strongly influenced by both recycling and relatively intense scavenging processes. In fact, like nutrient-type elements, $[Fe_d]$ is observed to be depleted in surface waters (L118 and L119) such as high-nutrient, (Martin and Gordon, 1988; Johnson et al., 1997). In less productive waters of the oligotrophic central gyres, particularly in areas of high dust inputs, $[Fe_d]$ can exhibit surface-water maxima (L116 and L117) more indicative of scavenged elements (Bruland et al., 1994; Measures et al., 1995; Johnson et al., 1997).

Distribution patterns of $[Mo]_d$ are well comparable with those found elsewhere in the world ocean and display a classic conservative behaviour unaffected by biological processes (Collier, 1985; Morris, 1975).

As reported by many authors, $[Mo]_d$ represents an important cofactor for various nitrogen-fixation and nitrate reductase systems (Fogg and Wolfe, 1954; Robson et al., 1986; Mendel, 2005) exhibiting an almost uniform distribution in the oceans. Molybdenum, both in the Sicily Channel stations and in the Levantine basin, shows a relatively low range of variability at the surface, intermediate and deep waters, with concentrations that are comparable to those recorded in the world oceans in the entire water column.

$[Ni_d]$, both in the Levantine basin and in the Sicily Channel, manifests an evident increase of the concentration when compared to the values of the oceanic and Western Mediterranean waters. Although the vertical mixing seems to play a primary role driving vertical distribution of $[Ni_d]$ the behaviour of this element in the L114 shows a typical scavenging-like profile due to the additional inputs in the surface water mass where very elevated values are recorded.

$[Cu_d]$ vertical distribution, in both areas, appears homogeneous along the water column once again confirming the effects of vertical mixing on the distribution modes of this element that loses its typical of open-ocean waters distribution of “nutrient” elements.

The range of variability (1,02-5,25 nMol·L⁻¹) in the different layers is quite low and it is in agreement with data reported in the literature except in the L118 station where not only the column seems to be totally mixed but also high values are recorded.

Hence, a direct comparison with open ocean waters, clearly evidence higher contents and variability along the water column of the Eastern Mediterranean; the dissolved patterns of all elements exclude any biogeochemical control on the element and underline the role of external input as mechanisms of control on the distribution of this element on which, sporadically the hydrographic system (mixing of water column) predominates.

Bibliography

- Bruland K. W., Orians K. J., and Cowen J. P. (1994) Reactive trace metals in the stratified central North Pacific. *Geochim. Cosmochim. Acta* 58, 3171–3182.
- L. Bruggmann, L.G. Danielsson, B. Magnusson and S. Westerlund, Lead in the North Sea and the North East Atlantic Ocean. *Marine Chemistry*, 16 (1985), pp. 47–60.
- Flegal A.R. et al., (1995)- Silver in the Eastern Atlantic Ocean. *Marine Chemistry* 49, 315-320.
- Collier R. W. (1985) -Molybdenum in the Northeast Pacific-Ocean. *Limnol. Oceanogr.* 30(6), 1351–1354
- Fogg G. E., and Wolfe M. (1954) Nitrogen metabolism of bluegreen algae. *Symp. Soc. Gen. Microbiol.* 4, 99–125
- Johnson K. S., Gordon R. M., and Coale K. H. (1997) What controls dissolved iron concentrations in the world ocean? *Mar. Chem.* 57, 137–161.
- Measures C. I., Yuan J., and Resing J. A. (1995) Determination of iron in seawater by flow injection-analysis using in-line preconcentration and spectrophotometric detection. *Mar. Chem.* 50, 3–12.
- Mendel R. R. (2005) -Molybdenum: biological activity and metabolism. *Dalton Trans.*, 3404–3409.
- Morley, N. H., Burton, J. D., Tankere, S. P. C and Martin, J.-M. (1997) Distribution and behaviour of some dissolved trace metals in the western Mediterranean Sea. *Deep-Sea Research II* 44(3–4), 675–691.
- Morris A. W. (1975)- Dissolved molybdenum and vanadium in Northeast Atlantic Ocean. *Deep-Sea Res.* 22(1), 49–54
- Riso et al., (2004)- On the presence of a cadmium-rich subsurface water mass in the western Mediterranean and its influence on the distribution of cadmium in the surface waters. *Marine Chemistry* 87, 15– 22
- Robson R. L. et al., 1986- The alternative nitrogenase of *Azotobacter-Chroococcum* is a vanadium enzyme. *Nature* 322 (6077), 388–390.
- Scelfo, (1997)- A practical handbook for trace metals and ancillary analyses. University of California Environmental Toxicology- Special publication.
- Statham, J.D. Burton and D.J. Hydes, Cd and Mn in the Alboran Sea and adjacent North Atlantic: geochemical implications for the Mediterranean. *Nature* 313 (1985), pp. 565–567.
- Yi-Yong Yoon, Jean-Marie Martin, and Marie Helen Cotté (1999) Dissolved trace metals in the Western Mediterranean Sea: total concentration and fraction isolated by C18 Sep-Pak technique. *Marine Chemistry* 66-129–148
- Statham et al., 1985. P.J.

8. Carbon and Nitrogen Isotopes in Particulate Organic Matter (POM)

Nutrients are essential for the development of primary production. The uptake of nutrients from the biological community determines a distribution gradient in the water column with a heavy loss in the euphotic zone and an increase in deep waters, due to the sinking of the organic material and its further remineralization. Although the Mediterranean is a relatively oligotrophic basin, with the Eastern area more oligotrophic than the Western one, the N:P ratio in deep water is high (~28:1) compared to the adjacent Atlantic Ocean (16:1). This is basically determined by very low concentrations of P in the basin that make it a P-limited system. However, there are different hypotheses to explain why the Mediterranean is a P-limited basin: i) phosphate, but not nitrate, are preferentially removed from the Levantine Deep water (LDW) by Saharan dust absorption (Krom et al., 1991, 1994); ii) there is excess of N due to N₂ fixation in the basin (Bethoux et al. 1992; Sachs and Repeta, 1999; Pantoja et al., 2002) and, iii) the system is enriched with matter flows coming from land (river discharge and aeolian material deriving from the Sahara desert but also from the industrialized European continental area) and from atmospheric inputs (Krom et al., 2004).

The isotopic composition of particulate organic matter (POM) in marine environment constitutes a tracer of surface biogeochemical processes, which may provide insight into physical, chemical and biological factors that govern the magnitude of the flux and the composition of the particulate material settling into deep water. Studies conducted on particles flux and isotopic carbon and nitrogen composition of particulate organic matter, suspended and settling, revealed a tight relation between surface and deep water particles (e.g. Altabet and Deuser, 1985; Voss et al., 1996). However, in some cases, isotopic composition of suspended and sedimenting POM did not likely interact because other sources of organic material exist via land input from the coastal margin or via atmospheric transport.

Particulate organic matter (POM) is known to play an important role in marine nitrogen and carbon cycles (Saino and Hattori, 1980). In particular, PON is mainly derived from phytoplankton, micro-zooplankton, bacteria and detritus. The nitrogen isotopic signature of PON in suspended matter depends on the isotopic fractionation associated with its formation, and in turn upon the isotopic composition of inorganic form of dissolved nitrogenous sources (such as NO₃⁻ 3-7‰, NH₄⁺ 6-8‰, and atmospheric N₂ 0‰; Miyake and Wada, 1967) available for the utilization by phytoplankton.

Variations of the carbon isotopic ratio in POC may result, among principal causes, from changes in the ambient temperature which affect the CO₂ content (e.g. Rau et al., 1996), from the type of autotrophic species (marine and/or terrestrial) or from the number of degradation processes that particles undergo through the successive trophic levels (Rau et al., 1983).

To determinate the principal sources of organic matter along the water column in the central and eastern Mediterranean Sea and to open new scenarios to explain why the eastern Mediterranean is phosphorus limited, a first geochemical dataset was collected. This report is intended to provide the first detailed observations on nutrients concentrations (i.e. nitrate, phosphate and silicate) and on natural isotopic composition of nitrogen and carbon ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) of Particulate Organic Matter (POM) in water samples collected during the MEDSUDMED-2010 oceanographic cruise.

Moreover, this preliminary work represents therefore the first study on both carbon and nitrogen stable isotopes in particulate organic matter in superficial and deep water of the central and southeast Mediterranean Sea.

In what follows, the aims of the cruise, the sampling procedures, the measuring effort and the first obtained results are reported.

8.1 Material and methods

One of the main objectives of the cruise was the identification of possible terrestrial influence on primary production through the acquisition of the first geochemical dataset in the study area coupled to chemical and physical parameters determinations of the water masses.

The cruise took place from 15 to 31 July 2010 on board the R/V Urania in the Central Mediterranean area between the port of Siracusa (Sicily, Italy) and the central and western coasts of Libya (Figure 8.1.1). A group of 29 stations were chosen for determination of nutrients concentration and 24 stations for determination of stable nitrogen and carbon isotopic composition ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) in particulate organic matter (POM). Samples were collected along the entire water column (from surface to the bottom level).

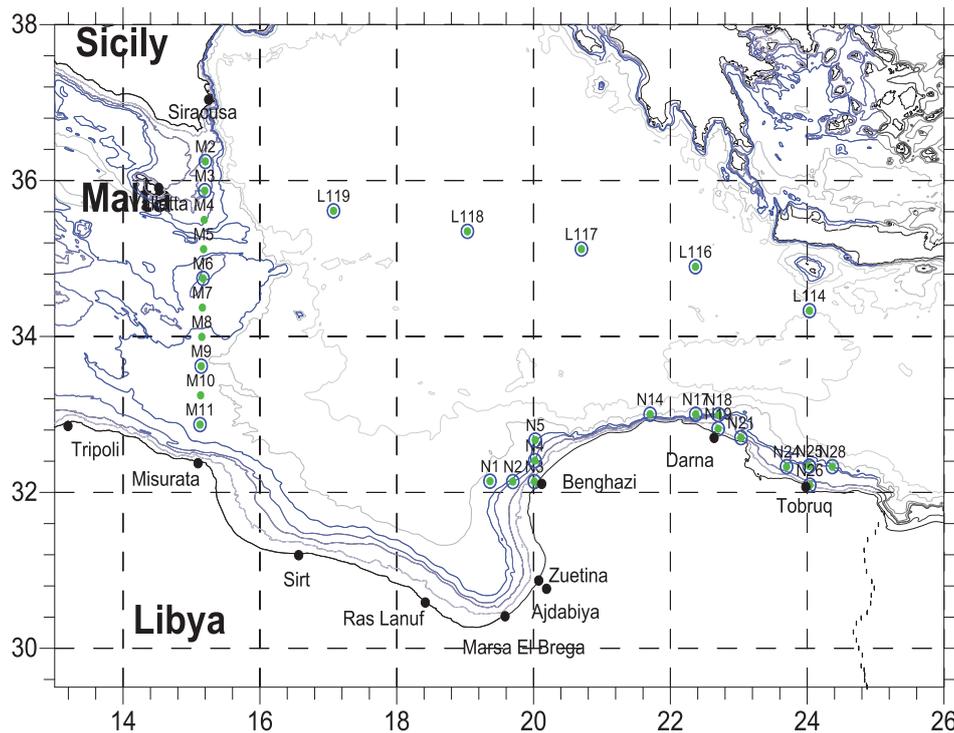


Figure 8.1.1. Position of sampling stations in the study area; the green dots are the stations for nutrients while the blue circles are the stations for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in particulate organic matter (POM).

Twenty four bottles (“Niskin”), fitted on a rosette with CTD instrumentation were used for sea water sampling. Depth levels for samples collection were carefully selected by examining real-time CTD (multiparametric probe) measurements.

All water samples for isotopic analysis were filtered using the Dispensing Pressure Vessel (Millipore) through pre-combusted (450°C for 4h) GF/F filters (25 mm diameter; 0.7 µm pore size). This kind of filtration involved 5-8 l of water for each sample depending on the location and depth level of the water sample. At the end of the process, filters were put in Petri dishes, left for some hours at 60°C (without cover) and finally stored at -20°C.

Determination of $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ in POM

Prior to analysis, filters of POM for isotopic analysis were dried at 60°C, acidified with fumed HCl, and re-dried at 60°C for 24h. After, the filters were stored in desiccators before to carry out the analysis. Filters were then cut into two parts, packed into tin capsules and loaded onto the EA auto-sampler. Duplicate analyses were performed for each sample. The isotopic compositions $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ were determined by a Thermo Electron Flash EA 1112 coupled to a Thermo Electron Delta Plus XP mass spectrometer tuned to carry out high sensitivity analyses.

Acetanilide ($\text{C}_8\text{H}_9\text{ON}$, Thermo Instruments) was used as standard for EA. Carbon and nitrogen calibration curves showed an excellent linearity ($r^2=0.99$ and 0.99 for C_{org} and N_{tot} , respectively ($n=12$)).

For spectrometer readings sample sequences were run with blank cups and known urea standards. Standards were prepared by weighing from 0.5 to 2 mg of analytical grade urea ($\text{CH}_4\text{N}_2\text{O}$ mw=60, C=20% N=46%) of certificated isotopic composition ($\delta^{13}\text{C}$ (‰) = -47,37 vs PDB and $\delta^{15}\text{N}$ (‰) = 0,02 vs AIR). Data quality control was checked by running the reference standard (urea) after each six samples.

Stable isotopes values were reported in ‰ delta notation:

$$\delta(\text{‰}) = \left[\frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right] (1000)$$

where $\delta(\text{‰})$ stands for $\delta^{13}\text{C}$ (‰) or $\delta^{15}\text{N}$ (‰), and R_{sample} and $R_{\text{reference}}$ are the isotopic ratios of the sample and the standard reference respectively. For carbon was used as reference standard the Pee Dee Belemnite (VPDB) and for N air.

8.2 Results

All 29 stations are investigated for suspended $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ of POM. The stations were grouped as follows:

1. Transect M from Siracusa (Sicily- Italy) to Misurata (Libya): M2 - M3 - M6 - M9 and M11.
2. Area N from Benghazi to Tobruq (Libya): N1- N2 - N3 - N4 - N5 - N14 - N17 - N18 - N19 - N21 - N24 – N25 - N26 and N28.
3. Transect L from Creta (Greece) to Siracusa (Sicily- Italy): L114 - L116 - L117 - L118 and L119.

The comparison between nutrients and $\delta^{15}\text{N}$ of PON shows opposite distribution from superface to 50m, while below 50m an increase is releveled in both variables (Figure 2).

A northeast-southeast trend is observed in $\delta^{15}\text{N}$ of PON in the upper 200 m of the Mediterranean Sea (Figure 8.1.3). The $\delta^{15}\text{N}$ of PON is higher in surface waters of the Transect M ($3.2\pm 0.4\text{‰}$) that in the southeast basin corresponding to the Area N ($1.2\pm 1.6\text{‰}$) and the Transect L ($2.2\pm 1.0\text{‰}$).

Below 200m, enrichment of $\delta^{15}\text{N}$ -PON was observed at all sampling sites, averaging $7.6\pm 1.7\text{‰}$ in transect M, $6.5\pm 0.9\text{‰}$ in transect N and $7.3\pm 0.4\text{‰}$ in transect L (Figure 8.1.4).

This increase in $\delta^{15}\text{N}$ of PON with depth has been observed previously and was attributed to isotopic fractionation during bacterial degradation or other heterotrophic activity (Saino and Hattori, 1980; Altabet and McCarthy, 1986; Montoya et al., 1990). Sinking particles trapped at 100m had a $\delta^{15}\text{N}$ values of $4.2\pm 0.5\text{‰}$ (n=5) in transect M, $3.1\pm 0.4\text{‰}$ (n=5) in transect L and $2.3\pm 0.2\text{‰}$ in the transect N (n=11).

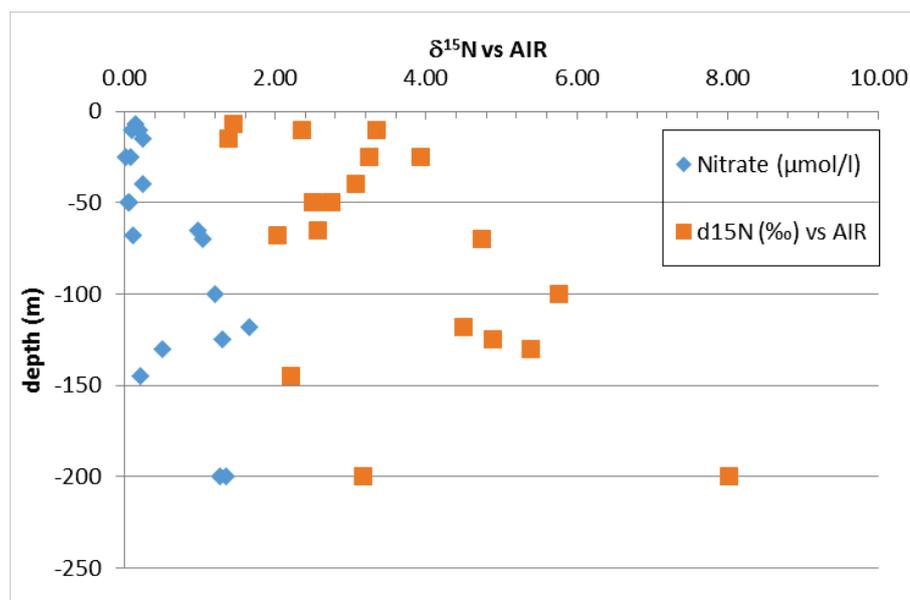


Figure 8.1.2. Vertical distribution of nitrate ($\delta\text{mol/l}$) and $\delta^{15}\text{N}$ PON.

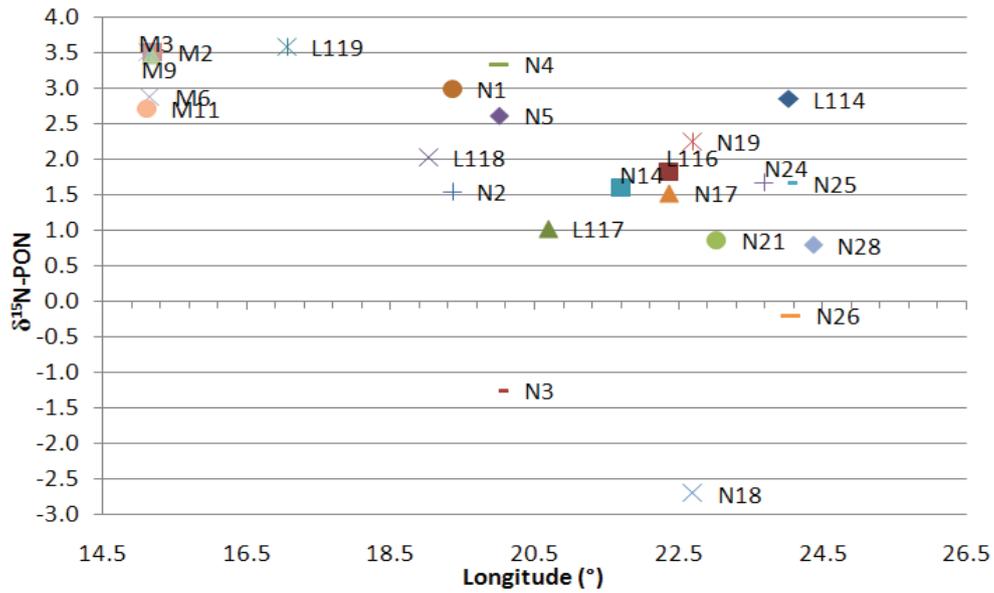


Figure 8.1.3. Longitudinal distribution of $\delta^{15}\text{N-PON}$ in the top 200m in the Mediterranean Sea.

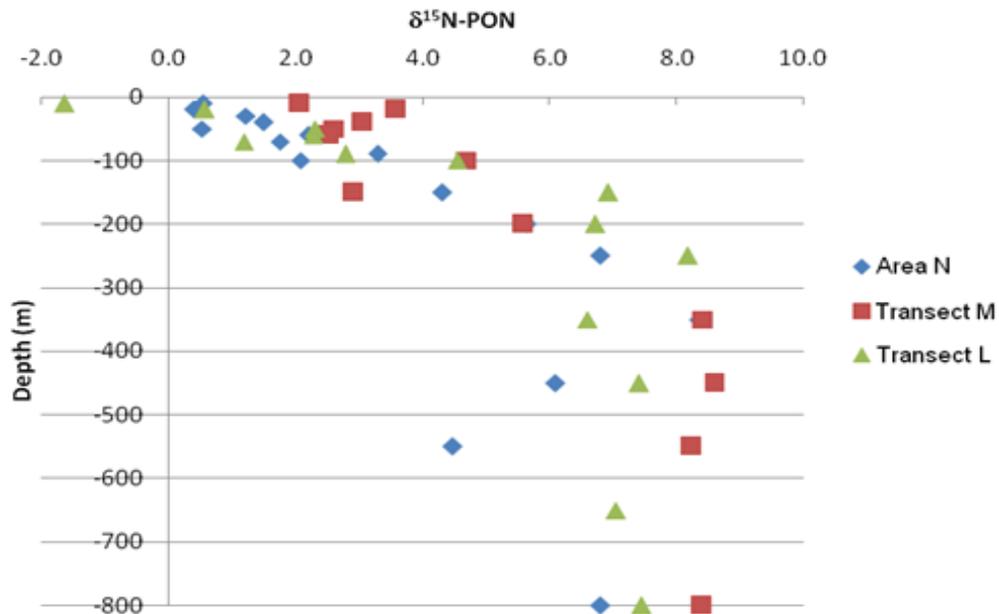


Figure 8.1.4. Distribution of $\delta^{15}\text{N}$ of PON respect to depth in all sites: Transects M, L Area N

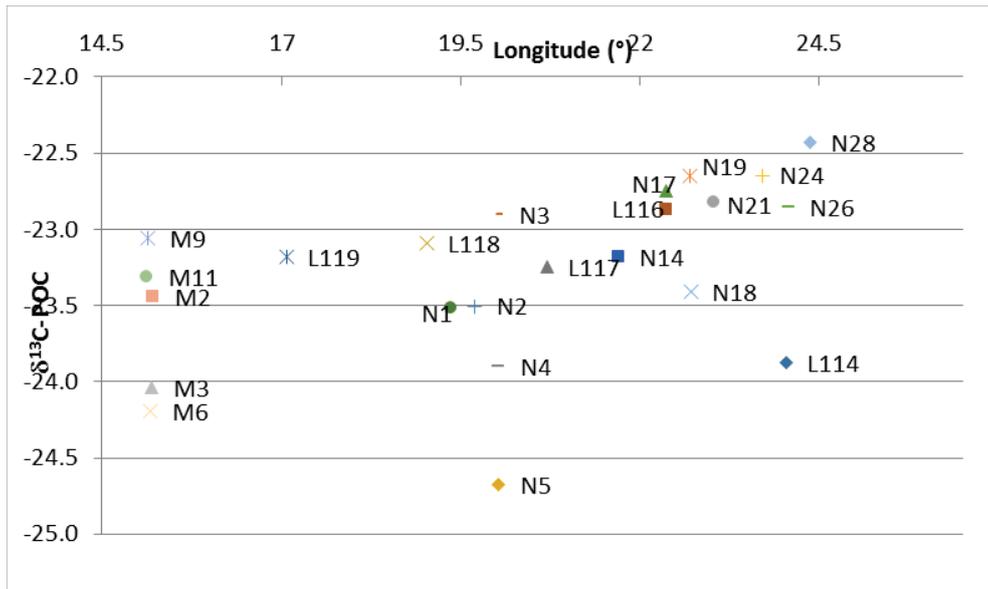


Figure 8.1.5. Longitudinal distribution of $\delta^{13}\text{C}$ -POC in the upper 200m in the Mediterranean Sea.

Large variability of $\delta^{13}\text{C}$ of POC was detected through 100m of depth in all sites. However, the values of $\delta^{13}\text{C}$ of POC were highly variable also below 100m, in relation to different sites (Figure 8.1.6).

Terrestrial organic matter generally has an average $\delta^{13}\text{C}$ value of -27‰ and -28‰ . It is unlikely a noticeable impact of terrestrial organic matter on $\delta^{13}\text{C}$ -POM values observed in the study area. If the influence of terrestrial organic matter were significant, the inner shelf water with a lower salinity should have received more terrestrial organic matter and thus presents lighter $\delta^{13}\text{C}$ values. However, only few values were in the range of terrestrial origin. The $\delta^{13}\text{C}$ values of POM from stations of the Area N (localized near the Libyan coast) were generally heavier than those from open sea stations (Transect L and M).

The relationship between particulate $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values was very weak in all sites ($R^2=0.2$ for Area N, $R^2=0.3$ for Transect L and $R^2=0.07$ for Transect M) likely resulting from the dynamic water mixing (Figure 8.1.7).

This lack of correlation could also indicate different biogeochemical pathways between carbon and nitrogen isotope fractionation in the water column.

Physical parameters collected with CTD probe were coupled to $\delta^{13}\text{C}$ -POC and $\delta^{15}\text{N}$ -PON profiles in order to assess water masses characteristics.

The $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ profiles vs. temperature, show an elevated correlation. However, we found low but positive correlation between $\delta^{13}\text{C}$ values and temperature in the transect L and M ($R^2=0.244$ and $R^2=0.204$, respectively).

An interesting topic is that the lowest $\delta^{13}\text{C}$ values were observed at the same stations where the presence of a cold water mass was detected, so they could be related to the greater isotopic fractionation in low temperature environments. The $\delta^{15}\text{N}$ profiles vs. temperature show more positive correlation in the transect L ($R^2=0.68$) and low but positive in ($R^2=0.356$) transect M and ($R^2=0.234$) in area N.

Our data add new and more detailed geochemical dataset to determinate the principal sources of particulate organic matter along the water column in the eastern Mediterranean Sea. Coupling geochemical data with physical parameters made it possible to assess preliminary water masses characteristics.

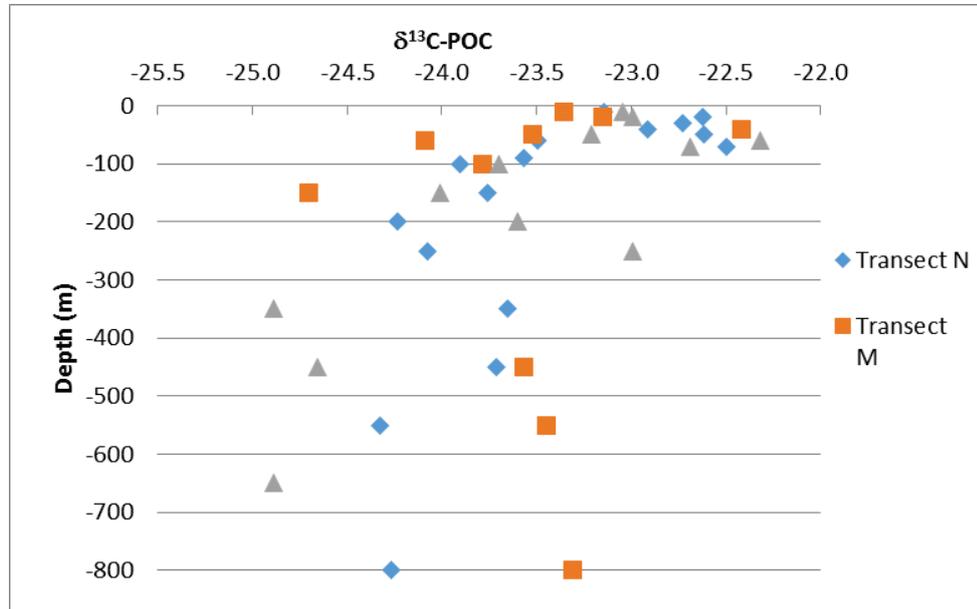


Figure 8.1.6. Distribution of $\delta^{13}\text{C-POC}$ respect to depths in all sites: Transect M, Area N, Transect L

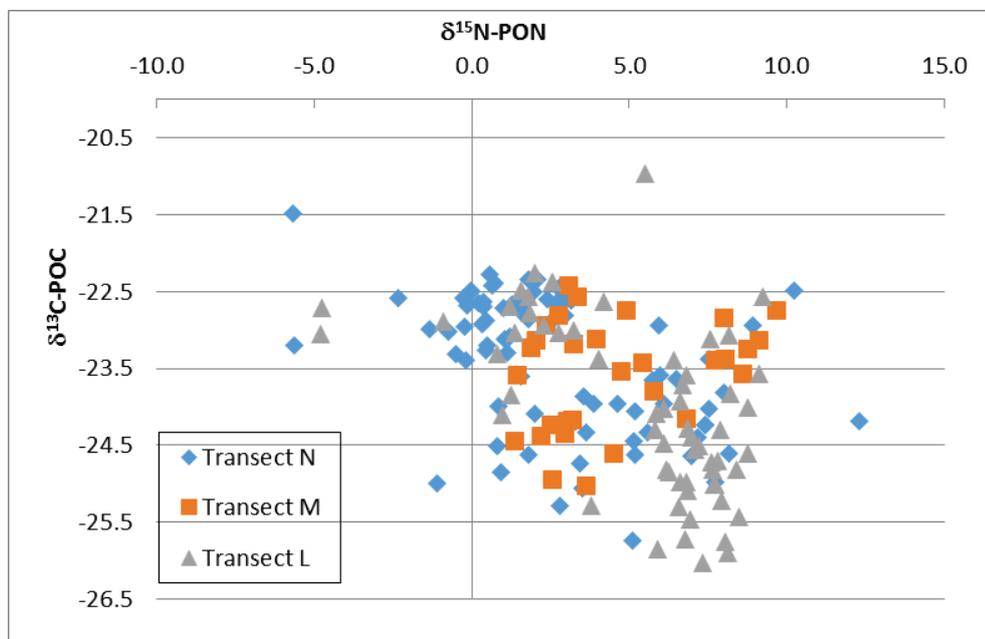


Figure 8.1.7. Relationship between particulate $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values

9. Particulate Organic Matter (POM)

The trophic status of the waters is here described by means of suspended organic matter.

9.1 Material and methods

During the MedSudMed-10 survey, 184 water samples were collected from different depth levels of water column in 24 stations located along three different transects: i) Transect M (from Siracusa (Sicily) to Misurata (Libya)); ii) Transect N (from Benghazi (Libya) to Tobruq (Libya)) and; iii) Transect L (from south of Crete (Greece) to Siracusa (Sicily))(Figure 9.1.1).

Samples of waters were collected with Niskin bottles for the analysis of both POC (Particulate Organic Carbon) and PON (Particulate Organic Nitrogen) concentration.

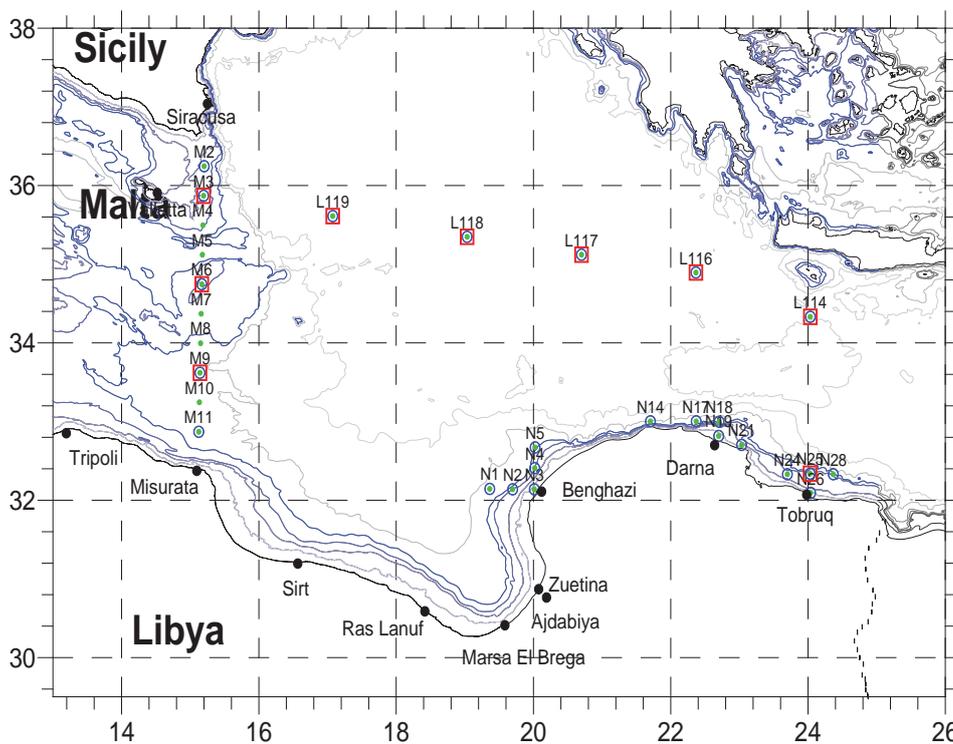


Figure 9.1.1. Position of stations where samples of water were collected for the POC, PON analysis

For TSM (Total Suspended Matter), POC (Particulate Organic Carbon) and PON (Particulate Organic Nitrogen) measurements, suitable quantities of water samples (2000 ml) were before hand screened through a 200 μm net to remove larger zooplankton, and then filtered on pre-combusted (450 $^{\circ}\text{C}$ for 4h) and pre-weighted Whatman GF/F filters (0.75 μm pore size). After filtering, the samples collected on filters were dried (60 $^{\circ}\text{C}$ for 12h) and weighted to calculate the TSM incidence. Subsequently, the filters were exposed to hydrochloric acid fumes for 6h at room temperature (Iseki *et al.*, 1987), to destroy the inorganic carbon, then were dried (60 $^{\circ}\text{C}$, 12h) and rolled into tin discs. Finally POC and PON analyses were performed by a Perkin-Elmer CHN Elemental Analyser (Mod. 2400) at a combustion temperature of 980 $^{\circ}\text{C}$, using Acetanilide as standard.

9.2 Results

The estimated values of TSM, POC, PON and C/N ratio for different transects are reported in Tables 9.2.1, 9.2.2 and 9.2.3. For the Transect M, Total Suspended Matter (TSM) values were in the range 4.20 - 9.04 mg/l. Higher values were found in deep samples (>200m) than in the surface samples (<200m). Except for the station M3 with highest TSM value (9.04 mg/l) at the depth of 110m, means TSM values were 5.43 ± 0.61 for samples collected to depth >200m and 4.84 ± 0.56 in euphotic layer (<200m) (Figure 9.2.1).

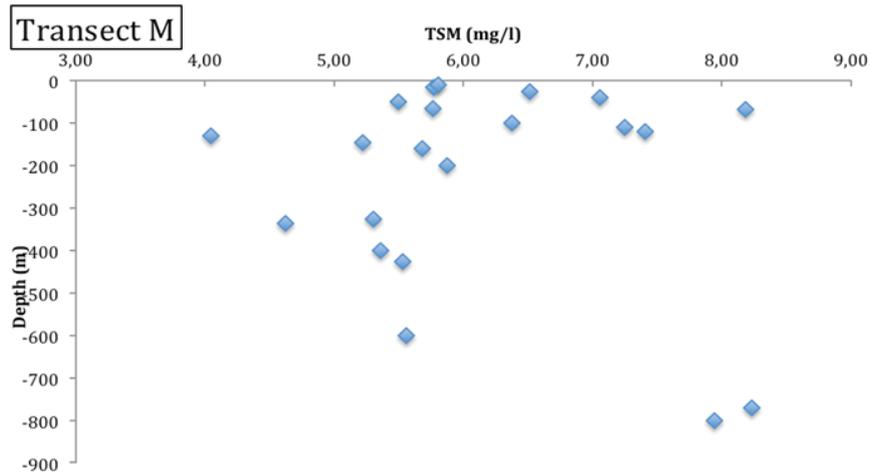


Figure 9.2.1. Total Suspended Matter (TSM) values vs. depth.

The POC and PON values (mean $51.39 \mu\text{g/l}$ and $8.58 \mu\text{g/l}$, respectively) were not particularly high, but higher than those we had found in our previous investigations in the Sicily Channel. The highest POC values were recorded in the euphotic layer ($98.65 \mu\text{g/l}$) and lowest in deep sea ($13.15 \mu\text{g/l}$ at 600m) (Figure 9.2.2).

Both high correlation between PON and POC values ($R^2=0.81$) and the wide range of values of C/N (max 8.23 and min 4.04) showed a general condition of equilibrium between the trophic components (autotrophy, heterotrophy, detritus) (Figure 9.2.3).

Along the Transect N, Total Suspended Matter (TSM) values were in the range 3.78 - 9.12 mg/l (Figure 9.2.4). Higher values were found in surface samples (<200m) than in the deep waters (>200m). The stations N25, N26 and N28 showed highest TSM values (8.17, 9.06 and 9.12 mg/l, respectively), likely due to the proximity of these stations to Tobruq city. Excluding these values the means of TSM values was 5.08 ± 0.66 (Figure 9.2.5).

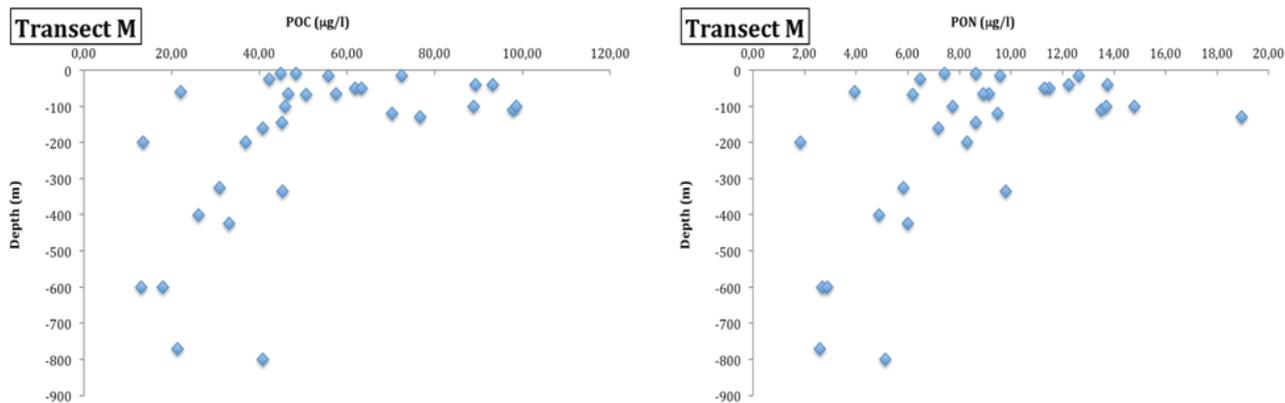


Figure 9.2.2. Distribution of Particulate Organic Carbon and Particulate Organic Nitrogen values vs. depth.

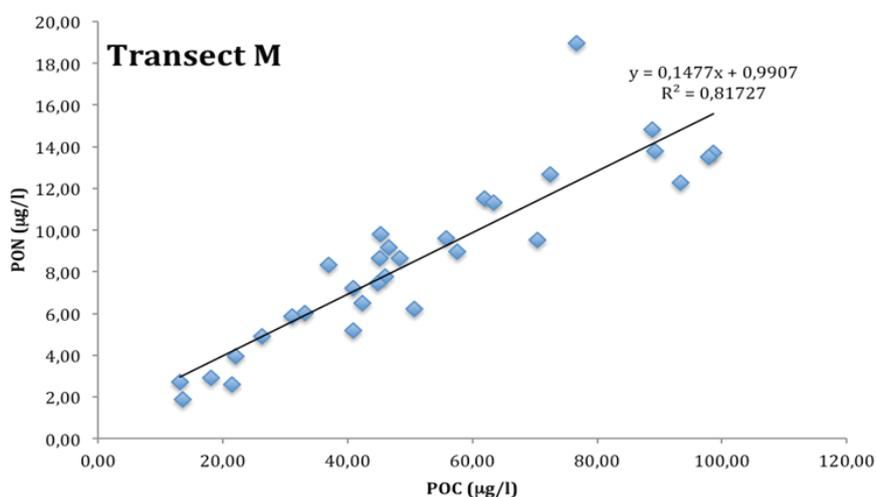


Figure 9.2.3. Correlation between Particulate Organic Carbon and Particulate Organic Nitrogen

The range of POC values (min 5.50 µg/l and max 179.90 µg/l) and PON values (min 1.45 µg/l and 24.15 µg/l) in the samples of the transect N were wide (Figure 9.2.5). This variability was probably due to the position of the samples collected. Overall, the samples were sampling near the coast, in the sites were the influence of the land is very high.

Moreover, also the low correlation between POC and PON ($R^2=0.63$ – Figure 9.2.6) evidenced the presence of more sources that contributed to this variability.

Eventually, high C/N ratio (>10) found in the samples collected in the transect N are additional consequence of land input. Generally the C/N ratios >10 are attributed to organic matter of terrestrial origin while ratio between 4 and 8 are indicative of organic matter of marine source (Meyers, 1978). Moreover, a good efficiency level of the autotrophic compartment was found where mean C/N values ranged between 6 and 8, while mean C/N values, ranging between < 6 indicate the prevalence of heterotrophic activities.

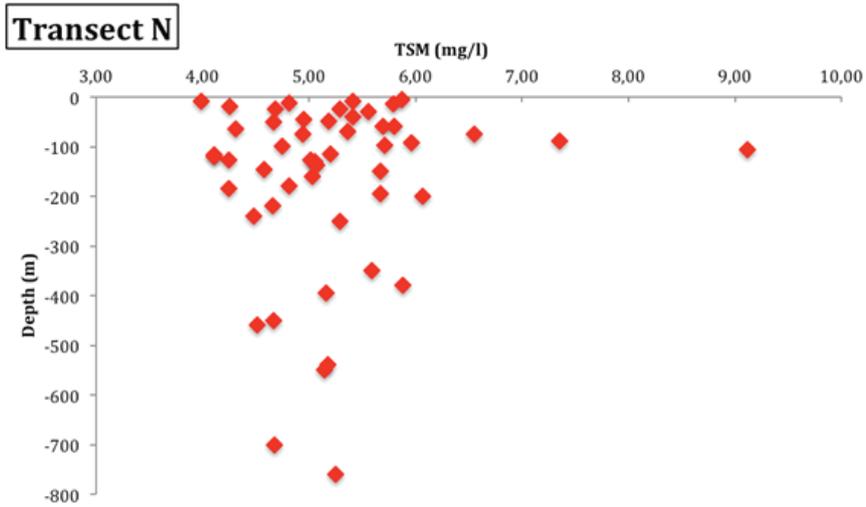


Figure 9.2.4. Total Suspended Matter (TSM) values with depth

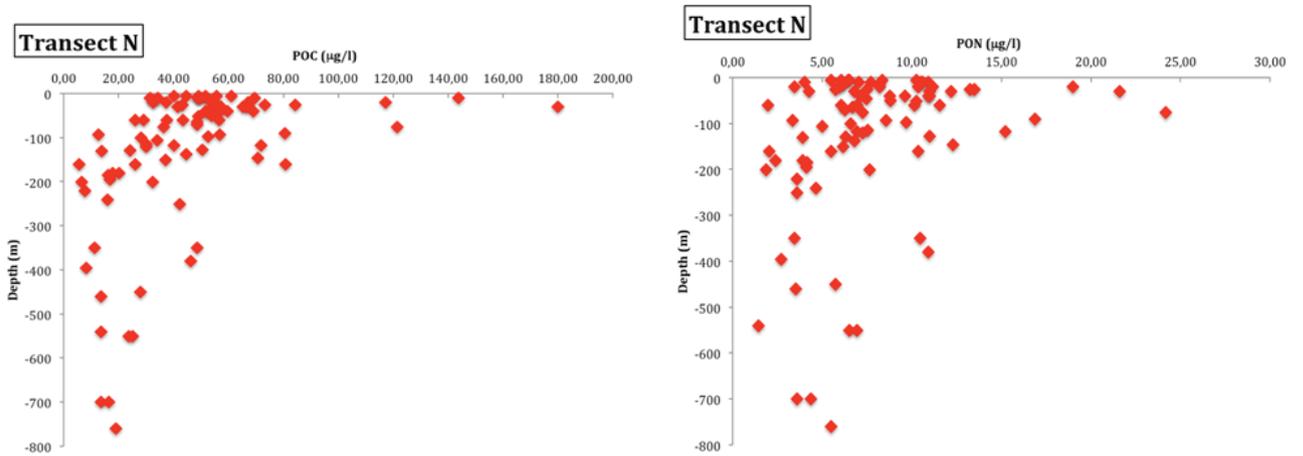


Figure 9.2.5. Distribution of Particulate Organic Carbon and Particulate Organic Nitrogen vs. depth.

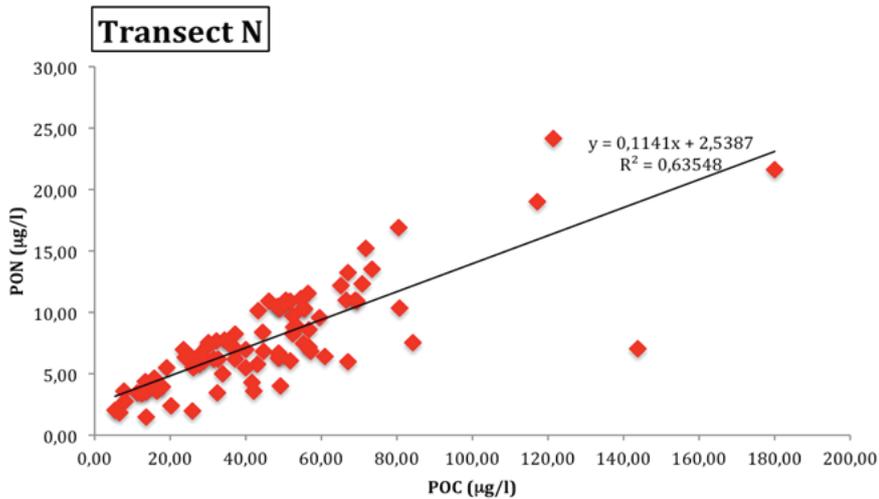


Figure 9.2.6. Correlation between Particulate Organic Carbon and Particulate Organic Nitrogen.

In the Transect L, Total Suspended Matter (TSM) presented a wide range of values between 3.11 mg/l and 7.25 mg/l (Figure 9.2.7). The TSM values were meanly higher in deep samples (5.18 mg/l for samples >200m) than in surface samples (4.65 mg/l for samples <200m) (Figure 9.2.8)

The range of POC (min 1.65 $\mu\text{g/l}$ and max 179.30 $\mu\text{g/l}$) and PON values (min 1.00 $\mu\text{g/l}$ and 29.20 $\mu\text{g/l}$) in the samples of the transect L were wide due also to the depth of the samples collectioned that in some stations reached the 4000m. The distribution of the POC and PON values with the depth showed a decrease from the surface to the bottom (Figure 9.2.9).

However, high correlation between POC and PON ($R^2=0.85$ – Figure 9.2.10) and C/N ratio between 1.65 and 13.45 were indicative of a general condition of equilibrium between the trophic components (autotrophy, heterotrophy, detritus). In particular, in the western station (L119) mean C/N values (9.02) were indicative of a good efficiency level of the autotrophic compartment where mean C/N values ranged between 6 and 10. Contrary, ratio slightly lower (ranging between 4.35 and 5.71) found in the other stations, indicated the prevalence of eterotrophic activities.

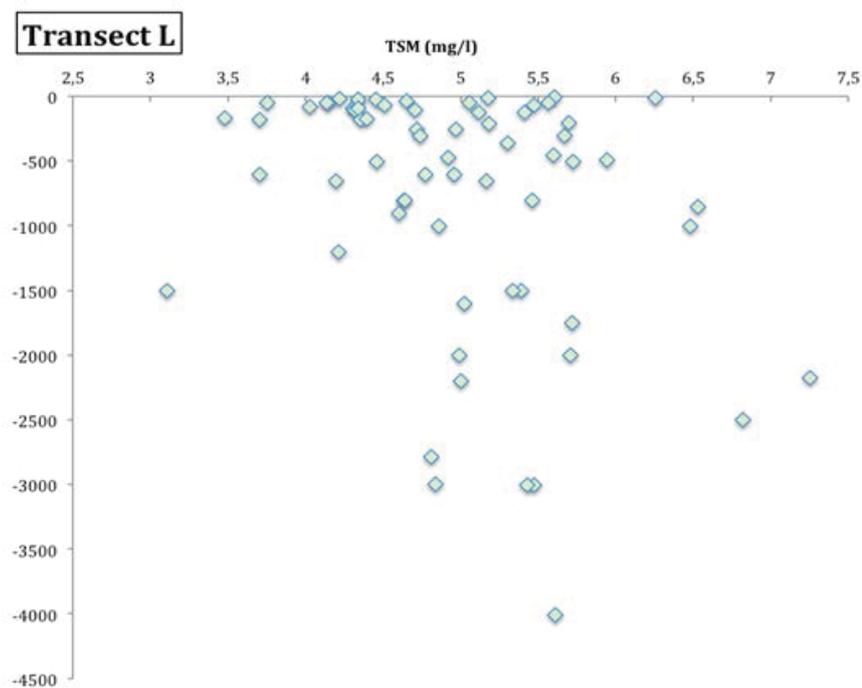


Figure 9.2.8. Total Suspended Matter (TSM) values with depth along the transect L.

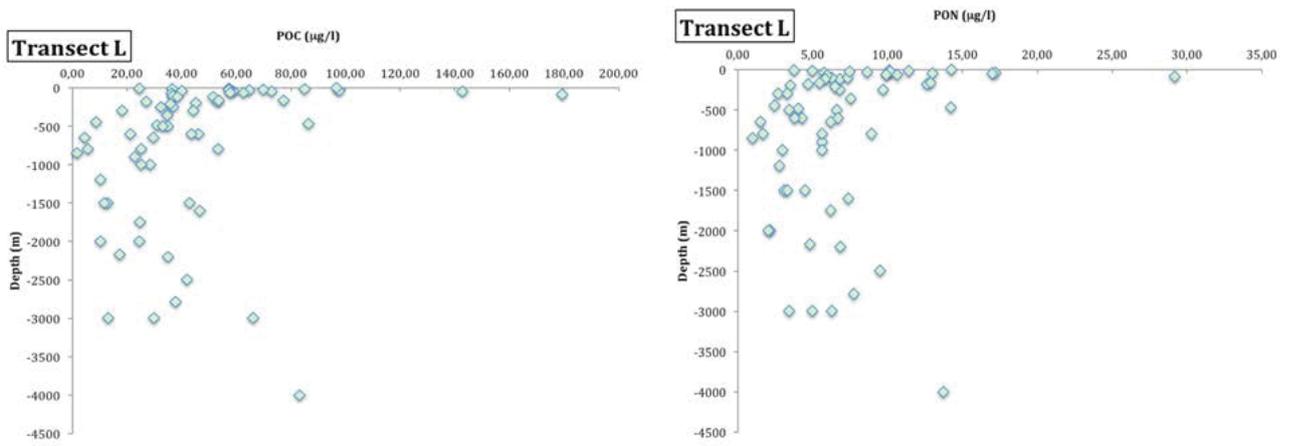


Figure 9.2.9. Distribution of Particulate Organic Carbon and Particulate Organic Nitrogen vs. depth.

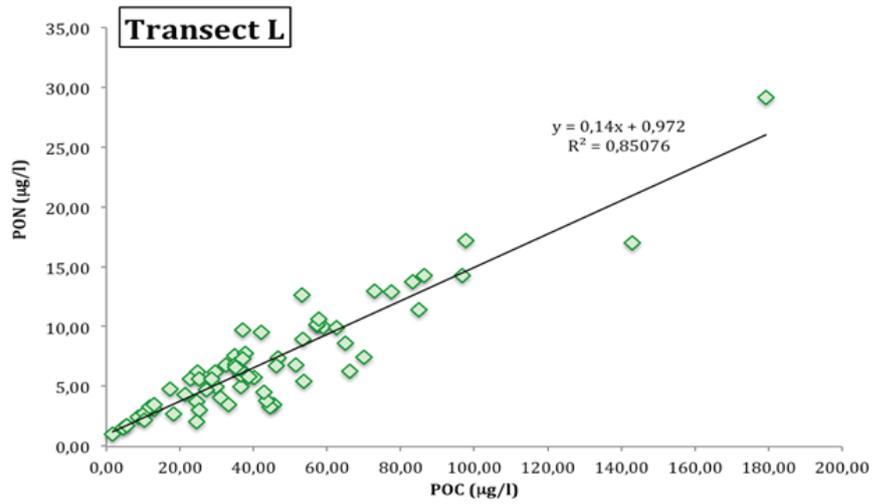


Figure 9.2.10. Correlation between Particulate Organic Carbon and Particulate Organic Nitrogen.

Tables 9.2.1. Estimated values of Total Suspended Matter (TSM), Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON) and C/N ratio in the transect M.

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
M2	15	5.11	72.45	12.65	5.73
	40	4.30	89.30	13.75	6.49
	65	4.93	46.65	9.15	5.10
	100	4.20	88.85	14.80	6.00
	120	***	70.35	9.50	7.41
M3	15	4.72	55.80	9.60	5.81
	40	4.96	93.30	12.25	7.62
	65	4.40	57.50	8.95	6.42
	100	5.81	98.65	13.70	7.20
	110	9.04	97.90	13.50	7.25
M6	50	5.70	61.95	11.50	5.39
	60	4.48	22.10	3.95	5.59
	100	5.79	45.95	7.75	5.93
	160	5.43	40.91	7.20	5.68
M9	10	4.22	48.35	8.65	5.59
	50	4.97	63.40	11.30	5.61
	130	4.62	76.65	18.95	4.04
	200	5.82	37.00	8.30	4.46
	335	5.13	45.30	9.80	4.62
	400	4.57	26.25	4.90	5.36
	600	5.08	13.15	2.70	4.87
	800	5.97	40.90	5.15	7.94
M11	10	4.85	44.85	7.45	6.02
	25	5.13	42.35	6.50	6.52
	68	4.67	50.75	6.20	8.19
	145	4.22	45.15	8.65	5.22
	200	4.31	13.50	1.85	7.30
	325	5.48	31.05	5.85	5.31
	425	4.92	33.20	6.00	5.53
	600	6.37	18.10	2.90	6.24
	770	5.92	21.40	2.60	8.23

Tables 9.2.2. Estimated values of Total Suspended Matter (TSM), Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON) and C/N ratio in the transect N.

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
N1	10	3.99	143.80	7.05	20.40
	20	4.26	37.30	8.20	4.55
	45	4.95	55.30	7.45	7.42
	120	4.02	30.05	7.25	4.14
	160	5.03	80.75	10.35	7.80
	240	4.49	15.90	4.65	3.42
	450	4.67	27.85	5.75	4.84
	700	4.68	16.50	3.60	4.58
N2	10	5.62	48.75	10.50	4.64
	20	5.56	117.10	19.00	6.16
	40	5.42	51.70	10.90	4.74
	115	5.20	30.10	7.55	3.99
	160	5.72	26.15	5.50	4.75
	185	4.25	16.20	4.15	3.90
N3	5	5.87	55.65	10.25	5.43
	10	5.19	69.50	10.90	6.38
	20	5.31	67.20	5.95	11.29
	30	5.56	179.90	21.60	8.33
N4	10	6.69	31.55	6.15	5.13
	30	5.83	66.55	11.00	6.05
	60	5.59	37.50	6.95	5.40
	93	5.96	12.60	3.35	3.76
	146	4.58	70.75	12.30	5.75
	195	5.68	16.90	4.10	4.12
N5	5	4.50	40.05	5.50	7.28
	20	4.94	54.55	11.15	4.89
	40	4.65	59.60	9.60	6.21
	60	5.80	29.10	6.05	4.81
	100	4.75	28.15	6.60	4.27
	130	5.06	13.85	3.90	3.55
	160	5.68	5.50	2.05	2.68
	200	6.07	6.60	1.85	3.57
	395	5.17	8.15	2.70	3.02
N14	10	4.10	34.35	7.70	4.46

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
	20	4.64	55.25	10.35	5.34
	60	4.33	56.55	11.55	4.90
	117	4.11	71.85	15.20	4.73
	176	6.55	121.35	24.15	5.02
	200	5.98	32.40	7.65	4.24
	350	5.59	48.60	10.45	4.65
	550	5.15	23.60	6.95	3.40
	760	5.25	19.10	5.50	3.47
N17	10	4.94	49.90	10.60	4.71
	25	5.90	67.05	13.25	5.06
	51	4.67	48.95	10.25	4.78
	128	4.25	24.15	6.30	3.83
	220	4.66	7.75	3.60	2.15
	380	5.89	46.20	10.90	4.24
	550	4.96	25.15	6.50	3.87
	700	3.78	13.55	4.35	3.11
N18	12	4.81	52.60	8.20	6.41
	25	4.69	73.35	13.50	5.43
	60	4.82	43.35	10.15	4.27
	97	5.71	52.60	9.70	5.42
	127	5.02	50.55	11.00	4.60
	180	4.82	17.90	3.90	4.59
	350	5.16	11.35	3.45	3.29
	460	4.52	13.65	3.50	3.90
N19	5	5.52	44.60	8.35	5.34
	15	5.79	32.65	6.16	5.30
	30	4.50	65.15	12.20	5.34
N21	5	3.87	61.10	6.43	9.50
	25	4.81	84.25	7.51	11.22
	40	4.34	52.75	8.78	6.01
	50	5.19	53.70	8.79	6.11
	75	4.94	36.40	7.26	5.01
	90	7.36	80.55	16.89	4.77
N24	25	5.07	43.10	5.75	7.50
	40	4.77	56.80	7.15	7.94

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
	64	4.31	48.65	6.70	7.26
	117	4.83	40.15	6.95	5.78
	138	5.07	44.70	6.80	6.57
	150	5.67	37.15	6.15	6.04
N25	5	8.17	51.75	6.05	8.55
	30	5.61	41.65	4.25	9.80
	70	5.37	48.70	6.25	7.79
	93	5.13	56.85	8.55	6.65
	180	9.06	20.25	2.40	8.44
N26	9	5.41	49.15	4.00	12.29
	30	4.92	57.25	6.80	8.42
N28	5	3.93	48.95	6.50	7.53
	20	5.20	32.60	3.45	9.45
	40	4.84	69.00	11.00	6.27
	60	5.31	25.95	1.95	13.31
	106	9.12	34.00	5.00	6.80
	250	5.30	42.25	3.60	11.74
	540	5.18	13.60	1.45	9.38

Tables 9.2.3. Estimated values of Total Suspended Matter (TSM), Particulate Organic Carbon (POC), Particulate Organic Nitrogen (PON) and C/N ratio in the transect L.

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
L114	20	4.34	36.55	5.00	7.31
	46	3.75	97.60	17.20	5.67
	90	4.31	***	***	***
	122	5.41	51.40	6.80	7.56
	180	4.36	53.20	12.65	4.21
	250	4.97	36.90	9.70	3.80
	450	5.60	8.57	2.46	3.48
	650	4.20	4.45	1.52	2.93
	850	6.53	1.65	1.00	1.65
	1200	4.21	10.20	2.78	3.67
	1750	5.72	24.75	6.20	3.99
2176	7.25	17.35	4.80	3.61	
L116	15	4.22	84.95	11.40	7.45
	37	4.65	64.85	8.65	7.50

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
	50	5.06	58.90	10.00	5.89
	104	4.32	37.00	6.30	5.87
	170	4.39	77.35	12.90	6.00
	250	4.72	32.50	6.80	4.78
	490	5.94	30.95	4.05	7.64
	653	5.17	29.55	6.20	4.77
	900	4.60	22.80	5.65	4.04
	1500	3.11	12.95	3.10	4.18
	2500	6.82	41.95	9.50	4.42
	3007	4.84	29.75	5.00	5.95
L117	12	6.26	24.45	3.75	6.52
	45	4.15	40.10	5.75	6.97
	77	4.03	36.45	5.95	6.13
	180	3.71	27.00	4.70	5.74
	360	5.30	34.80	7.55	4.61
	470	4.92	86.40	14.25	6.06
	600	3.70	21.35	4.30	4.97
	800	5.46	25.25	5.65	4.47
	1600	5.02	46.66	7.38	6.32
	2200	5.00	34.95	6.85	5.10
2791	4.81	37.75	7.75	4.87	
L118	10	5.18	57.25	10.10	5.67
	25	4.34	57.25	10.20	5.61
	50	4.14	72.90	13.00	5.61
	65	5.47	57.70	10.65	5.42
	105	4.71	36.90	7.35	5.02
	210	5.18	35.90	6.50	5.52
	300	4.74	18.25	2.70	6.76
	500	4.46	35.10	6.60	5.32
	600	4.96	46.10	6.70	6.88
	800	4.64	5.55	1.70	3.26
	1000	6.48	28.50	5.65	5.04
	1500	5.39	11.60	3.30	3.52
	2000	5.71	10.25	2.15	4.77
3000	5.47	13.00	3.45	3.77	

Station	Depth	TSM mg/l	POC µg/l	PON µg/l	C/N
L119	5	5.61	96.77	14.27	6.78
	25	4.46	69.95	7.45	9.39
	48	5.57	142.80	17.00	8.40
	66	4.51	62.60	9.90	6.32
	90	4.34	179.30	29.20	6.14
	120	5.12	38.55	5.85	6.59
	168	3.48	53.55	5.45	9.83
	200	5.70	45.30	3.50	12.94
	300	5.67	44.40	3.30	13.45
	500	5.73	33.20	3.45	9.62
	600	4.77	43.50	3.80	11.45
	800	4.64	53.40	8.95	5.97
	1000	4.86	25.10	3.00	8.37
	1750	5.34	42.80	4.50	9.51
	2000	4.99	24.50	2.05	11.95
	3000	5.43	66.15	6.30	10.50
4007	5.61	83.20	13.75	6.05	

10. Phytoplankton

Phytoplankton plays key roles in global biogeochemical cycles, particularly in the carbon-carbonate cycle (Honjo, 1976; Westbroek, 1991; Westbroek et al., 1994). Phytoplankton plays key roles also in the sulphur cycle as they produce dimethylsulphoniopropionate (DMSP), the precursor of dimethyl sulphide (DMS) (Keller et al., 1989; Malin and Kirst, 1997) which, in turn, may influence climate through stimulating cloud formation and influencing the Earth's radiative balance (Charlson et al., 1987; Simó and Pedrós-Alió, 1999). Some algae are known to produce stable lipid compounds which can be used as a tool to evaluate paleoclimatic changes (Volkmen et al., 1980; Brassell et al., 1986). These properties, together with the fact that the ubiquitous species *Emiliania huxleyi* is a recognized bloom forming alga (Holligan et al., 1993), confirm that the phytoplankton is an important role as active biogeochemical and climatic agents.

Coccolithophores are unicellular planktonic algae belonging to the phylum Haptophyta, and have been one of the most important contributors to calcium carbonate production in the oceans since the Middle-Late Mesozoic. Most phytoplankton species need both sunlight and nutrients from deep in the ocean. The ideal place for them is on the surface of the ocean in an area where plenty of cooler, nutrient-carrying water is upwelling from below. In contrast, the coccolithophores prefer to live on the surface in still, nutrient-poor water in mild temperatures. Coccolithophores do not compete well with other phytoplankton. They do not need a constant influx of fresh food to live. They often thrive in areas where their competitors are starving. Typically, once they are in a region, they dominate and become more than 90 percent of the phytoplankton in the area.

Coccoliths are not normally harmful to other marine life in the ocean. The nutrient-poor conditions that allow the coccolithophores to exist will often kill off much of the larger phytoplankton. Many of the smaller fish and zooplankton that eat normal phytoplankton also feast on the coccolithophores. In nutrient-poor areas where other phytoplankton are scarce, the coccolithophores are a welcome source of nutrition.

The coccolithophores' short-term effect on the environment is somewhat more complex. This effect again has to do with the formation of their coccoliths and the chemical reaction involved in the process. The chemical reaction that makes the coccolith also generates a carbon dioxide molecule, a potent greenhouse gas, from the oxygen and carbon already in the ocean. While much of the gas is sucked back in by the coccoliths (all plants take in carbon dioxide for food) some of it escapes into the atmosphere and immediately becomes part of the greenhouse gas problem. Scientists are concerned in the short term that greenhouse gases will cause the upper layers of the ocean to become more temperate and stagnant. This would increase the number of coccoliths in the world, which would produce more greenhouse gas.

Diatoms are photosynthesising algae, they have a siliceous skeleton (frustule) and are found in almost every aquatic environment including fresh and marine waters, soils, in fact almost anywhere moist. They are non-motile, or capable of only limited movement along a substrate by secretion of mucilaginous material along a slit-like groove or channel called a raphe. Being autotrophic they are restricted to the photic zone (water depths down to about 200m depending on clarity). Both benthic and planktic forms exist. Diatoms are formally classified as belonging to the Division Chrysophyta, Class

Bacillariophyceae. The Chrysophyta are algae which form endoplasmic cysts, store oils rather than starch, possess a bipartite cell wall and secrete silica at some stage of their life cycle. Diatoms are commonly between 20-200 microns in diameter or length, although sometimes they can be up to 2 millimetres long. The cell may be solitary or colonial (attached by mucous filaments or by bands into long chains). Diatoms may occur in such large numbers and be well preserved enough to form sediments composed almost entirely of diatom frustules (diatomites), these deposits are of economic benefit being used in filters, paints, toothpaste, and many other applications.

Diatoms are divided into two Orders. The Centrales (now called the Biddulphiales) which have valve striae arranged basically in relation to a point, an annulus or a central areola and tend to appear radially symmetrical, and the Pennales (now called Bacillariales) which have valve striae arranged in relation to a line and tend to appear bilaterally symmetrical. The valve face of the diatom frustule is ornamented with pores (areolae), processes, spines, hyaline areas and other distinguishing features. It is these skeletal features which are used to classify and describe diatoms, which is an advantage in terms of palaeontology since the same features are used to define extant species as extinct ones. The classification system developed by Simonsen (1979) and further developed by Round et al. (1990) is currently the most commonly accepted. Diatoms commonly found in the marine plankton may be divided into the centric diatoms including three sub-orders based primarily on the shape of the cells, the polarity and the arrangement of the processes. These are the Coscinodiscineae, with a marginal ring of processes and no polarity to the symmetry, the Rhizosoleniineae with no marginal ring of processes and unipolar symmetry, and the Biddulphiineae with no marginal ring of processes and bipolar symmetry. The pennate diatoms are divided into two sub-orders, the Fragilariineae which do not possess a raphe (araphid) and the Bacillariineae which possess a raphe.

Diatoms have been well studied both in their natural habitat and in cultures by biologists and there is therefore a wealth of knowledge on their biology and ecology. The protoplast of diatoms consists of a cytoplasmic layer that lines the interior of the frustule and surrounds a large central vacuole, within the cytoplasmic layer there is a diploid nucleus and two to several pigment-bearing plastids (the site of photosynthesis). The diatom frustule is often likened to a pill-box or agar dish with an epitheca (larger upper valve), and a hypotheca (smaller lower valve). The vertical lip or rim of the epitheca is called the epicingulum, and the epicingulum fits over (slightly overlaps) the hypocingulum of the hypotheca. The epicingulum and hypocingulum with one or several connective bands make up the girdle. Many diatoms are heterovalvate, i.e., the two valves of the frustule are dissimilar. This is most obvious within the family Achnantheaceae where one valve has a raphe and the other does not, and the Cymatosiraceae where one valve has a tubular process and the other does not. Chain-forming species with cells linked together by siliceous structures may, in addition, have separation valves. These valves are morphologically different from the valves within the chain. Therefore, one species may have four morphologically distinct types of valves.

Dinoflagellates are microscopic, unicellular, flagellated, often photosynthetic protists, commonly regarded as "algae" (Division Dinoflagellata). They are characterized by a transverse flagellum that encircles the body (often in a groove known as the cingulum)

and a longitudinal flagellum oriented perpendicular to the transverse flagellum. This imparts a distinctive spiral to their swimming motion. Both flagella are inserted at the same point in the cell wall, by convention defining the ventral surface. This point is usually slightly depressed, and is termed the sulcus. In heterotrophic dinoflagellates this is the point where a conical feeding structure, the peduncle, is projected in order to consume food. Dinoflagellates possess a unique nuclear structure at some stage of their life cycle a dinokaryotic nucleus (as opposed to eukaryotic or prokaryotic), in which the chromosomes are condensed. The cell wall of many dinoflagellates is divided into plates of cellulose ("armor") within amphiesmal vesicles, known as a theca. These plates form a distinctive geometry/topology known as tabulation, which is the main means for classification.

Both heterotrophic and autotrophic dinoflagellates form a significant part of primary planktonic production in both oceans and lakes. Most dinoflagellates go through moderately complex life cycles involving several steps, both sexual and asexual, motile and non-motile. Some species form cysts composed of sporopollenin (an organic polymer), and preserve as fossils in the sedimentary record. Often the tabulation of the cell wall is somehow expressed in the shape and/or ornamentation of the cyst.

Silicoflagellates are a small group of unicellular heterokont algae, found in marine environments. In one stage of their life cycle, they produce a siliceous skeleton, composed of a network of bars and spikes arranged to form an internal basket. These form a small component of marine sediments, and are known as microfossils from as far back as the early Cretaceous. There is one living genus, *Dictyocha*, with two commonly recognized species. There are also several extinct genera, but their classification is difficult, since skeletons may show diverse forms within each living species. *Dictyocha* has one golden-brown chloroplast and a long flagellum extended into a wing-like shape. The skeleton-bearing stage is uninucleate, with many microtubule-supported projections, and there are also uninucleate and micronucleate stages that do not produce skeletons, but how they relate to each other is poorly understood. The cell structure places the silicoflagellates in a group called the axodines. They are usually treated as an order, called the Dictyochales by botanists and the Silicoflagellida by zoologists.

Silicoflagellates skeletons usually comprise 1-2% of the siliceous component of marine sediments; they are thus much less abundant than diatoms. However, they are widely distributed throughout the world ocean.

The quantitative analysis focuses on Coccolithophyceae species, hence supplementing previous work carried out at MBRC on diatoms, silicoflagellates and dinoflagellates (Tufail, 1981). Coccolithophyceae should be identified at level of genera and species.

10.1 Material and methods

Phytoplankton samples have been collected during the survey in the ten stations shown in Figure 10.1.1.

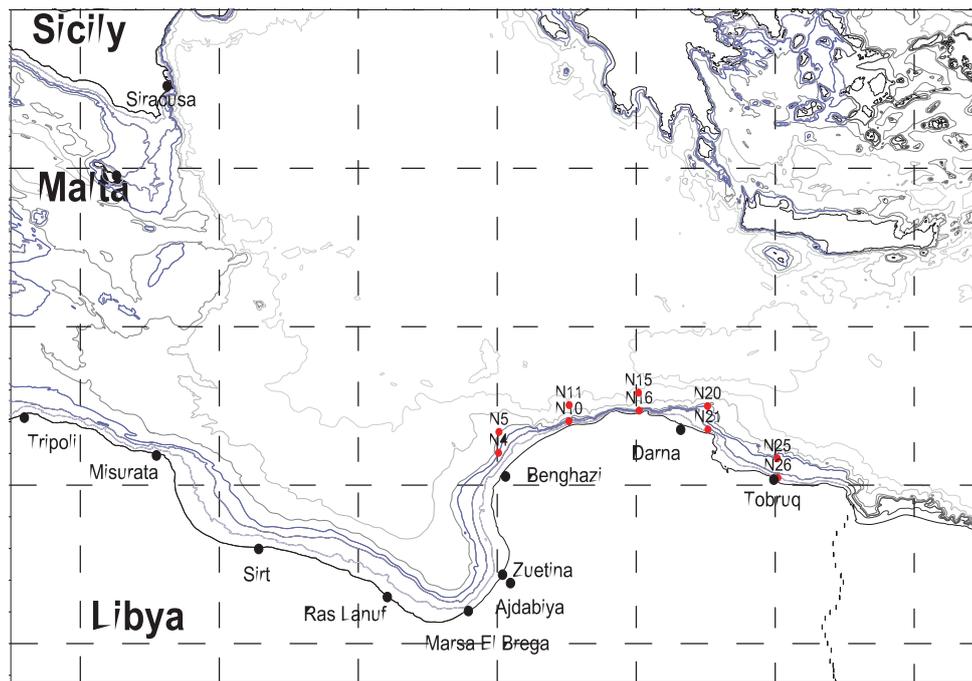


Figure 10.1.1. Position of stations for Phytoplankton collection.

Samples of waters were collected with Niskin bottles in selected stations for the analysis of calcareous phytoplankton (Coccolitophyceae). About 2 liters of sea water were filtered, using a vacuum pump, onto polycarbonate Nucleopore filters of 0.2 μm pore size and 47 mm diameter. Each filter membrane was rinsed with distilled water immediately after filtration in order to remove all traces of sea salt. All membranes were stored in plastic Petri dishes, until preparation for the Polarized Microscope, and dried in an oven at 40 – 60 $^{\circ}\text{C}$ for several hours. The seawater was filtered with an accuracy of ± 0.1 l. To investigate the total thickness of the photic zone we have selected these depth intervals: 0, -25, -50, -75, -100, -150 and -200 meters.

For light microscope analyses a piece of filter membrane cut along its radius was mounted onto a glass slide using Norland Optical Adhesive and fixed beneath a cover slip. A similar sized piece of filter membrane was mounted onto an aluminium stub using carbon tape and coated with 15 nm of gold for subsequent analysis in the SEM. Cell counts were carried out with a Leica DM2500 polarizing light microscope (LM) using 100X objectives. The area represented by one field of view is 0.04521 mm^2 . Calculation of the observed filtration area relies on the positioning accuracy of the stage and the accuracy with which the area of one field of view can be calculated. The area of observation is the sum of the area of all single fields of view. This is easily estimated and controlled with LM. It is important that single fields of view do not overlap to prevent double counting of specimens.

The number of coccolithophore cells in 1 l of water was calculated using the following equation:

$$CD = \frac{A*N}{a*v}$$

where

CD = cell density (cells/l water);

A = filtration area;

N= total number of cells counted;

a = analysed area;

v = volume of water filtered.

The results of the analysis are reported in the following tables.

Sampling Station	Sampling Depth [m]	Total Coccolithophores l-1	A. robusta l-1	B. bigelowii l-1	C. leptoporus l-1	Calciosolenia spp l-1	C. cristatus l-1	C. binodata l-1
ST N5	5	4201	0	0	0	0	0	326
ST N5	25	2024	0	0	0	0	0	72
ST N5	50	1286	0	0	0	0	0	0
ST N5	75	3754	0	0	0	43	0	0
ST N5	100	12741	0	0	225	730	0	0
ST N5	150	1976	94	31	0	0	0	0
ST N5	200	1751	45	0	0	0	0	0
ST N25	5	7166	0	0	0	43	85	0
ST N25	25	8899	0	0	0	0	0	74
ST N25	50	12107	0	0	0	63	63	63
ST N25	75	15428	0	0	0	71	0	0
ST N25	100	11660	213	0	71	1635	0	0
ST N25	150	3429	335	0	0	0	0	0
ST N25	200	1056	127	0	0	0	0	0
ST N15	5	2981	0	0	0	0	0	557
ST N15	25	8144	0	0	48	0	0	485
ST N15	50	11612	0	0	0	0	0	0
ST N15	75	12868	71	0	0	0	0	71
ST N15	100	5656	0	0	0	126	0	32
ST N15	150	8154	162	0	0	0	0	0
ST N15	200	3981	190	0	0	0	0	47
ST N11	5	1362	0	0	0	0	0	154
ST N11	25	2922	0	0	0	0	0	156
ST N11	50	11660	0	0	0	0	0	0
ST N11	75	3213	0	0	0	0	0	0

Sampling Station	Sampling Depth [m]	Total Coccolithophores l-1	A. robusta l-1	B. bigelowii l-1	C. leptoporus l-1	Calciosolenia spp l-1	C. cristatus l-1	C. binodata l-1
ST N11	100	3907	0	0	45	0	0	180
ST N11	150	7414	0	0	0	102	0	0
ST N11	200	9043	228	0	0	0	0	0
ST N20	5	11144	53	0	0	53	53	0
ST N20	25	9171	0	0	0	0	43	128
ST N20	50	8148	0	0	0	0	0	0
ST N20	75	13407	0	0	0	0	0	0
ST N20	100	8905	53	0	0	427	0	373
ST N20	150	7636	0	0	0	0	0	0
ST N20	200	853	0	0	0	0	0	0
ST N21	5	7849	0	0	0	0	0	85
ST N21	25	7166	0	0	0	0	0	85
ST N21	50	11475	0	0	0	0	0	0
ST N21	75	6612	0	0	0	0	0	43
ST N21	100	8062	0	0	0	0	0	43
ST N10	5	768	0	0	0	0	0	43
ST N10	25	1365	0	0	0	0	0	43
ST N10	50	938	0	0	0	0	0	43
ST N10	75	1252	0	0	0	0	78	0
ST N4	5	2831	0	0	0	0	0	0
ST N4	25	6313	0	0	43	0	0	213
ST N4	50	2602	43	0	0	0	0	0
ST N4	75	4308	43	0	0	0	0	0
ST N4	100	15186	256	0	0	0	0	0
ST N4	150	7294	43	0	0	0	0	0
ST N4	200	640	0	0	0	0	0	0
ST N26	5	8148	0	0	0	0	0	43
ST N26	25	9214	0	0	0	0	0	85
ST N26	50	7934	0	0	0	0	0	43
ST N16	5	2815	0	0	0	0	0	171
ST N16	25	3071	0	0	0	0	0	213
ST N16	50	14148	0	0	0	0	0	0
ST N16	75	10375	0	0	0	0	0	0
ST N16	100	6569	43	0	0	469	0	43

Sampling Station	Sampling Depth [m]	C. mediterranea l-1	Cricosphaera spp l-1	D. tubifera l-1	E. huxleyi l-1	F. profunda l-1	Gephyrocapsa spp l-1	G. oceanica l-1
ST N5	5	0	0	130	65	0	0	0
ST N5	25	0	0	434	0	0	0	0
ST N5	50	0	0	0	68	0	0	0
ST N5	75	0	0	256	213	85	0	0
ST N5	100	0	0	0	9710	1066	0	0
ST N5	150	0	0	0	753	1035	0	31
ST N5	200	0	0	0	718	718	0	45
ST N25	5	0	0	43	2602	128	0	0
ST N25	25	0	0	110	2758	0	0	0
ST N25	50	0	0	63	1568	0	0	0
ST N25	75	0	0	569	2702	71	0	0
ST N25	100	0	0	71	6470	427	71	71
ST N25	150	0	0	0	627	1882	0	0
ST N25	200	0	0	0	127	760	0	0
ST N15	5	0	0	170	994	0	0	0
ST N15	25	0	0	679	1115	0	48	48
ST N15	50	0	0	711	1896	79	0	0
ST N15	75	0	0	711	498	0	0	71
ST N15	100	0	0	885	1201	63	0	0
ST N15	150	0	0	0	702	5778	0	54
ST N15	200	0	0	0	1232	2085	0	0
ST N11	5	0	0	0	103	0	0	0
ST N11	25	0	0	117	993	0	0	0
ST N11	50	0	0	640	2062	0	0	0
ST N11	75	0	0	55	609	0	0	0
ST N11	100	0	0	359	943	90	0	45
ST N11	150	0	0	51	3149	3047	0	0
ST N11	200	0	0	57	1365	6768	0	0
ST N20	5	0	0	53	4266	0	0	0
ST N20	25	0	0	85	3669	0	0	0
ST N20	50	0	0	341	1365	0	0	0
ST N20	75	0	0	457	4494	0	229	0
ST N20	100	0	0	107	5759	53	0	0
ST N20	150	0	0	0	1792	5332	0	0
ST N20	200	0	0	0	299	555	0	0
ST N21	5	0	0	256	4223	0	0	0

Sampling Station	Sampling Depth [m]	C. mediterranea l-1	Cricosphaera spp l-1	D. tubifera l-1	E. huxleyi l-1	F. profunda l-1	Gephyrocapsa spp l-1	G. oceanica l-1
ST N21	25	0	0	85	3199	0	0	0
ST N21	50	0	0	384	2304	0	0	0
ST N21	75	0	0	299	1749	0	0	0
ST N21	100	0	0	171	1962	0	0	0
ST N10	5	0	0	0	0	0	0	0
ST N10	25	0	0	171	0	0	0	0
ST N10	50	0	0	43	213	0	0	43
ST N10	75	0	0	0	117	39	0	0
ST N4	5	0	0	151	76	0	0	0
ST N4	25	0	0	1152	1664	0	0	0
ST N4	50	0	0	43	427	0	0	0
ST N4	75	0	128	0	1621	810	0	0
ST N4	100	0	0	0	1024	13480	0	0
ST N4	150	0	43	384	810	5460	0	0
ST N4	200	0	0	0	299	256	0	0
ST N26	5	0	0	43	2986	0	0	0
ST N26	25	43	0	85	4095	0	0	0
ST N26	50	0	0	213	3370	0	0	0
ST N16	5	0	0	171	981	0	0	0
ST N16	25	0	0	299	341	0	0	0
ST N16	50	0	0	995	3697	0	0	0
ST N16	75	0	0	685	2686	0	0	0
ST N16	100	0	0	640	2176	171	0	0

Sampling Station	Sampling Depth [m]	G. flabellatus l-1	H. carteri l-1	O. fragilis l-1	Pontosphaera spp l-1	R. clavigera l-1	R. xiphos l-1	S. apsteinii l-1
ST N5	5	0	33	0	0	0	0	0
ST N5	25	0	36	0	0	0	0	0
ST N5	50	0	0	0	0	0	0	0
ST N5	75	0	128	0	0	213	43	0
ST N5	100	56	112	0	0	281	0	0
ST N5	150	0	0	0	0	0	0	31
ST N5	200	45	0	0	0	0	0	0
ST N25	5	0	0	0	0	43	213	0
ST N25	25	0	0	0	0	184	331	0
ST N25	50	0	125	0	0	63	565	0
ST N25	75	0	0	0	0	71	640	0
ST N25	100	71	0	0	0	0	0	0
ST N25	150	293	84	0	0	0	0	0
ST N25	200	0	0	0	0	0	0	0
ST N15	5	0	0	0	0	0	24	0
ST N15	25	0	0	0	0	48	436	0
ST N15	50	0	395	0	0	79	79	0
ST N15	75	0	71	0	0	71	569	0
ST N15	100	0	126	0	32	348	32	32
ST N15	150	162	108	0	0	108	0	0
ST N15	200	190	0	0	0	0	0	0
ST N11	5	0	0	0	0	0	0	0
ST N11	25	0	0	0	0	0	97	0
ST N11	50	0	71	0	0	284	853	0
ST N11	75	0	0	0	0	55	55	0
ST N11	100	0	180	0	0	359	45	0
ST N11	150	152	152	0	0	51	0	0
ST N11	200	284	57	0	57	0	0	0
ST N20	5	0	0	0	0	53	160	0
ST N20	25	0	0	0	0	85	1408	0
ST N20	50	0	43	0	0	128	683	43
ST N20	75	0	0	0	0	152	609	0
ST N20	100	0	53	53	0	53	107	0
ST N20	150	213	0	0	0	0	0	0
ST N20	200	0	0	0	0	0	0	0
ST N21	5	0	0	0	0	171	0	0

Sampling Station	Sampling Depth [m]	G. flabellatus l-1	H. carteri l-1	O. fragilis l-1	Pontosphaera spp l-1	R. clavigera l-1	R. xiphos l-1	S. apsteinii l-1
ST N21	25	0	0	0	0	85	0	0
ST N21	50	0	0	0	0	512	469	0
ST N21	75	0	43	0	0	128	725	0
ST N21	100	0	43	0	0	85	683	43
ST N10	5	0	0	0	0	0	0	0
ST N10	25	0	0	0	0	43	0	0
ST N10	50	0	43	0	0	85	0	0
ST N10	75	0	39	0	0	39	0	0
ST N4	5	0	0	0	0	0	38	0
ST N4	25	0	43	0	0	0	171	0
ST N4	50	0	384	0	0	128	0	43
ST N4	75	0	171	0	0	128	43	0
ST N4	100	341	0	0	0	0	0	0
ST N4	150	341	43	0	0	0	0	0
ST N4	200	0	0	0	0	0	0	0
ST N26	5	0	0	0	0	0	0	0
ST N26	25	0	0	0	0	43	43	0
ST N26	50	0	0	0	0	171	171	0
ST N16	5	0	0	0	0	0	0	0
ST N16	25	0	0	0	0	0	0	0
ST N16	50	0	71	0	0	213	782	0
ST N16	75	0	0	0	0	0	579	0
ST N16	100	0	43	0	0	85	213	0

Sampling Station	Sampling Depth [m]	Syraco sphaera spp l-1	S. tumularis l-1	S. histrica l-1	S. pulchra l-1	U. tenuis l-1	U. sibogae l-1	Hothe r l-1	T. heimi i l-1	Holococcoli thophores spp l-1
ST N5	5	0	0	0	0	0	0	0	0	3647
ST N5	25	0	0	0	36	217	0	0	0	1229
ST N5	50	0	0	0	0	68	0	0	0	1151
ST N5	75	0	0	0	213	0	43	0	85	2517
ST N5	100	0	0	0	449	0	0	0	281	112
ST N5	150	0	0	0	0	0	0	0	63	0
ST N5	200	0	0	0	0	0	0	0	45	180
ST N25	5	43	0	0	128	0	43	0	0	3797
ST N25	25	147	0	0	294	110	0	0	0	4891

Sampling Station	Sampling Depth [m]	Syracosphaera spp l-1	S. tumularis l-1	S. histrica l-1	S. pulchra l-1	U. tenuis l-1	U. sibogae l-1	Hotheor l-1	T. heimi l-1	Holococcolithophores spp l-1
ST N25	50	0	0	0	63	816	0	63	0	8594
ST N25	75	0	0	0	569	4195	142	0	71	6399
ST N25	100	0	0	0	71	71	0	71	0	2346
ST N25	150	0	0	0	0	0	42	0	0	167
ST N25	200	0	0	0	42	0	0	0	0	0
ST N15	5	0	0	0	0	0	0	24	0	1212
ST N15	25	0	0	0	291	630	48	0	0	4266
ST N15	50	0	0	0	79	3081	0	0	0	5214
ST N15	75	0	0	0	142	4479	71	0	142	6043
ST N15	100	0	0	0	379	980	0	0	253	1422
ST N15	150	0	0	54	216	216	0	0	108	594
ST N15	200	0	0	0	0	0	0	0	0	237
ST N11	5	0	0	0	0	0	0	0	0	1105
ST N11	25	0	0	0	0	19	0	0	0	1539
ST N11	50	0	0	0	355	1635	0	0	71	5759
ST N11	75	0	0	0	55	55	0	0	55	2327
ST N11	100	0	0	0	90	90	0	0	180	1482
ST N11	150	0	0	0	152	0	0	0	102	559
ST N11	200	0	0	0	0	0	0	0	57	228
ST N20	5	107	0	0	53	107	0	0	0	6185
ST N20	25	171	0	0	171	171	128	0	0	3114
ST N20	50	0	0	0	256	1450	0	0	43	3839
ST N20	75	229	0	0	533	1676	0	229	76	4799
ST N20	100	107	0	0	480	107	53	53	53	1066
ST N20	150	0	0	0	43	0	43	0	171	213
ST N20	200	0	0	0	0	0	0	0	43	0
ST N21	5	85	0	0	85	0	43	0	0	2901
ST N21	25	0	0	0	0	43	0	0	0	3669
ST N21	50	0	0	0	43	1280	0	0	0	6484
ST N21	75	43	0	0	128	1578	0	43	0	1834
ST N21	100	85	0	0	85	2858	0	43	43	1962
ST N10	5	0	0	0	0	0	0	0	0	725
ST N10	25	0	0	0	85	0	0	0	0	1024
ST N10	50	0	0	0	85	0	0	0	0	384
ST N10	75	39	0	0	39	0	0	0	39	861
ST N4	5	0	0	0	0	0	0	0	0	2567

Sampling Station	Sampling Depth [m]	Syracosphaera spp l-1	S. tumularis l-1	S. histrica l-1	S. pulchra l-1	U. tenuis l-1	U. sibogae l-1	Hothe r l-1	T. heimi i l-1	Holococcolithophores spp l-1
ST N4	25	0	0	0	0	597	0	0	0	2431
ST N4	50	0	0	0	85	0	0	0	43	1450
ST N4	75	0	0	0	128	85	0	0	85	1152
ST N4	100	0	0	0	0	0	0	0	256	85
ST N4	150	0	43	0	43	0	43	0	85	43
ST N4	200	0	0	0	0	0	0	0	43	85
ST N26	5	0	0	0	0	85	0	0	0	4991
ST N26	25	43	0	0	213	85	0	0	43	4479
ST N26	50	43	0	0	43	85	0	0	0	3797
ST N16	5	0	0	0	0	0	0	0	0	1493
ST N16	25	0	0	0	0	0	0	0	0	2218
ST N16	50	0	0	0	71	1564	0	0	0	6754
ST N16	75	105	0	0	316	1738	0	0	53	4266
ST N16	100	43	0	0	171	810	43	0	85	1621

11. Ichthyoplankton

The Ichthyoplankton distribution in the Libyan waters was little investigated in the past. Only in recent years in the framework of the MedSudMed Project three oceanographic surveys have been conducted and permitted to acquire samples and information for characterizing, in terms of species composition, the Ichthyoplankton structure in the Libyan waters. The first survey was carried out in summer 2006 in the westernmost area of the Libyan waters. The second survey covered the area of the Gulf of Sirt up to Benghazi. With the oceanographic survey performed in summer 2010 the easternmost area was completed. These three surveys permitted to have a basic image of the Ichthyoplankton spatial distribution even though they were performed in three different periods.

11.1 Material and method

Samples Collection

Biological samples were collected by means a Bongo 40 net with a 200 μm mesh size for both mouths of the frame and Bongo 90 net with a 1000 μm mesh size for both mouths (Figure 11.1.1). Flow meters were used in each net (General Oceanic's, mod. 2030R). A depressor was used during the net hauling to enhance the stability of the nets. The lowering speed of the net was 0.75 m/s and the ascending speed 0.33 m/s. The Bongo 40 net hauls described an oblique trajectory from the surface to 100 m depth or to the bottom in areas where depth was less than 100 m, at a constant speed of 2 knots with a cable inclination of about 45 degrees. 124 samples were collected, using a regular sampling grid of 12 nm. The Bongo 40 net hauls was carried out in specific layers in the water column to collect further Ichthyoplankton samples.

Samples were fixed immediately after collection and preserved in a 4% buffered formaldehyde seawater solution; the recognized individual larvae were conserved in liquid nitrogen.



Figure 11.1.1 Bongo 90 during sampling operation.

b. Samples Processing

Ichthyoplankton composition was estimated for the Bongo 40 and Bongo 90 nets on samples coming from one of the two mouths of each net.

11.2 Results

Some details of the larvae sorting for the biological stations (Bongo 40 and Bongo 90) are reported in the following Tabs. 11.2.1 and 11.2.2.

Table 11.2.1. Number of the most abundant species and family of Larvae collected during the survey.

	Number of Bongo 40 stations	Number of unidentified eggs	Number of <i>Vinciguerria powerii</i> larvae	Number of <i>Vinciguerria</i> Spp. larvae	Number of <i>Cyclothone</i> Spp. larvae	Number of GOBIDAE larvae	Total number of larvae
GSA 21 (Eastern waters of Libya)	124	555	31	37	124	56	316

Table 11.2.2. Number of larvae per species/family.

Species/Family	Number of larvae
<i>Myctophum punctatum</i>	1
<i>Vinciguerria powerii</i>	31
<i>Vinciguerria nimbaria</i>	6
<i>Vinciguerria attenuata</i>	13
<i>Lestidiops jayakari</i>	
<i>pseudosphyraenoides</i>	2
<i>Lampanyctus crocodilus</i>	9
<i>Coris julis</i>	1
<i>Chromis chromis</i>	2
<i>Electrona risso</i>	4
<i>Lampanyctus pusillipus</i>	2
<i>Gnathophis mistax</i>	1
<i>Ceratoscopolus maderensis</i>	3
<i>Echelus myrus</i>	1
<i>Engraulis encrasicolus</i>	1
<i>Vinciguerria</i> Spp	37
<i>Myctophum</i> Spp	4
<i>Cyclothone</i> Spp	124
<i>Arnoglossus</i> Spp	2
GOBIDAE	56
TUNNIDAE	2
CONGRIDAE	3
CENTRACANTIDAE	6
GADIDAE	1
BLENNIDAE	2
ECHENEIDE	2

The distribution maps of the collected eggs and the most abundant species and family are reported in the following figures.

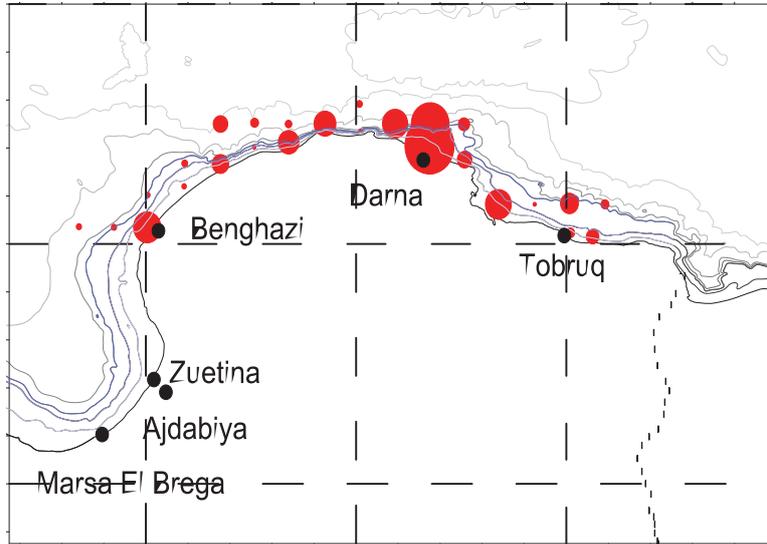


Figure 11.2.1: Number of non-identified eggs; range 0 – 74 eggs.

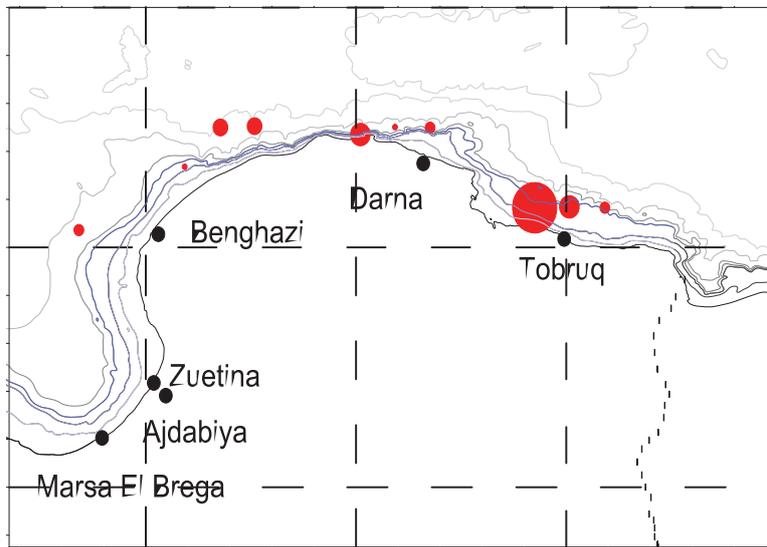


Figure 11.2.2 Number of *Vinciguerria powerii* larvae (from 1 to 9 specimens).

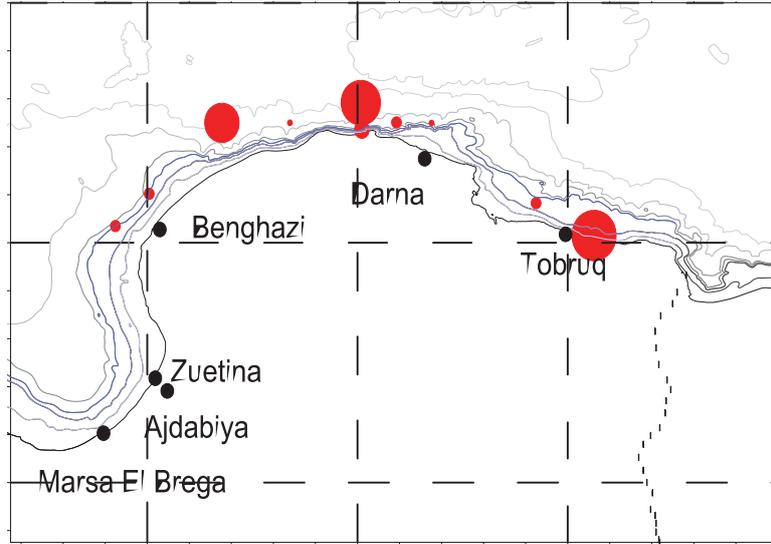


Figure 11.2.3 Number of *Vinciguerria Spp.* larvae (from 1 to 9 specimens).

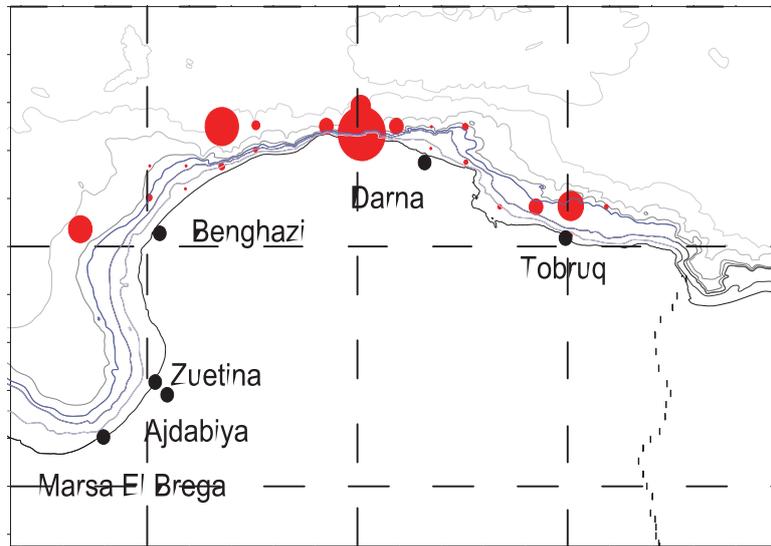


Figure 11.2.4 Number of *Cyclothone Spp.* larvae (from 1 to 24 specimens).

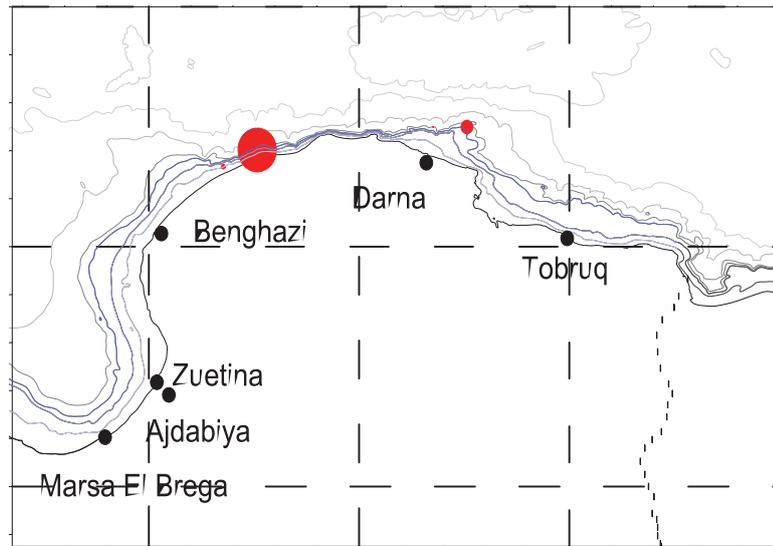


Figure 11.2.4 Number of GOBIDAE larvae (from 1 to 39 specimens).

12. Notes, recommendations and acknowledgments

The survey was conducted in cooperation with several institutes. MBRC scientists were involved in the work shifts and participated in the discussions on sampling design wherever changes had to be made. Moreover, the survey was an occasion to increase the technical skills of those who had limited experience in this type of field work. As mentioned above, a set of samples was sent to the MBRC during the survey and at the end of the survey a copy of electronic data was given to the Libyan focal point (CTD, base maps, coordinates of the stations, navigation data).

The survey was conducted successfully. The decisions regarding the operations to be conducted on board were made in agreement with the MBRC staff who was involved in all stages of the data collection, sampling conservation and analysis. No particular problem was encountered during the survey, which allowed for smooth performance of the work and rigorous data collection.

Captain Emanuele Gentile and all his crew are gratefully acknowledged for their willing participation and the interest they showed in the scientific survey “MedSudMed-10”. It is important to underline the high professionalism and readiness of the R/V Urania crew who participated in all the activities in synergy with the scientists. All the crew showed great willingness and flexibility, allowing the scientists to conduct activities in secure conditions and to overcome unexpected events.

The particular sensitiveness and helpfulness of the whole crew with the scientists of the MBRC and the Libyan coast guard needs to be underlined and acknowledged.

13. References

Altabet M.A. and J.J. McCarthy (1985). Temporal and spatial variations in the natural abundance of $\delta^{15}\text{N}$ in PON from a warm-core ring. *Deep-Sea Research*, **32**, 755–772.

Altabet M.A. and W.G. Deuser (1985). Seasonal variations in $\delta^{15}\text{N}$ natural abundance in the flux of particulate matter to the deep ocean. *Nature*, **315**, 218–219.

Bethoux, J.P., Morin, P., Madec, C., Gentili, B. (1992). Phosphorus and nitrogen behavior in the Mediterranean Sea. *Deep-Sea Research II*, 39 (9), 1641–1654.

Krom, M.D., Herut, B., Mantoura, R.F.C., (2004). Nutrient budget for the eastern Mediterranean: implications for P limitation. *Limnology and Oceanography*, 49, 1582–1592.

Krom, M.D., Kress, N., Brenner, S., Gordon, L.I., (1991). Phosphorus limitation of primary productivity in the Eastern Mediterranean-Sea. *Limnology and Oceanography*, 36, 424–432.

Miyake Y. and E. Wada (1967) The abundance ratio of $^{15}\text{N}/^{14}\text{N}$ in marine environments. *Records of Oceanographic Works in Japan*, **9**, 37–53.

Montoya, J. P., Horrigan, C. G., McCarthy, J. J. (1990). Natural abundance of $\delta^{15}\text{N}$ in particulate nitrogen and zooplankton in Chesapeake Bay. *Mar. Ecol. Prog. Ser.* 65: 35-61

Pantoja, S., Repeta, D.J., Sachs, J.P., Sigman, D.M., (2002). Stable isotope constraints on the nitrogen cycle of the Mediterranean Sea water column. *Deep-Sea Research I*, 49, 1609–1621.

Rau, G. H., Mearns, A. J., Young, D. R., Olson, R. J., Schafer, H. A., Kaplan, I. R. (1983). Animal $\delta^{13}\text{C}$ correlates with trophic level in pelagic food webs. *Ecology* 64(5):1314-1318

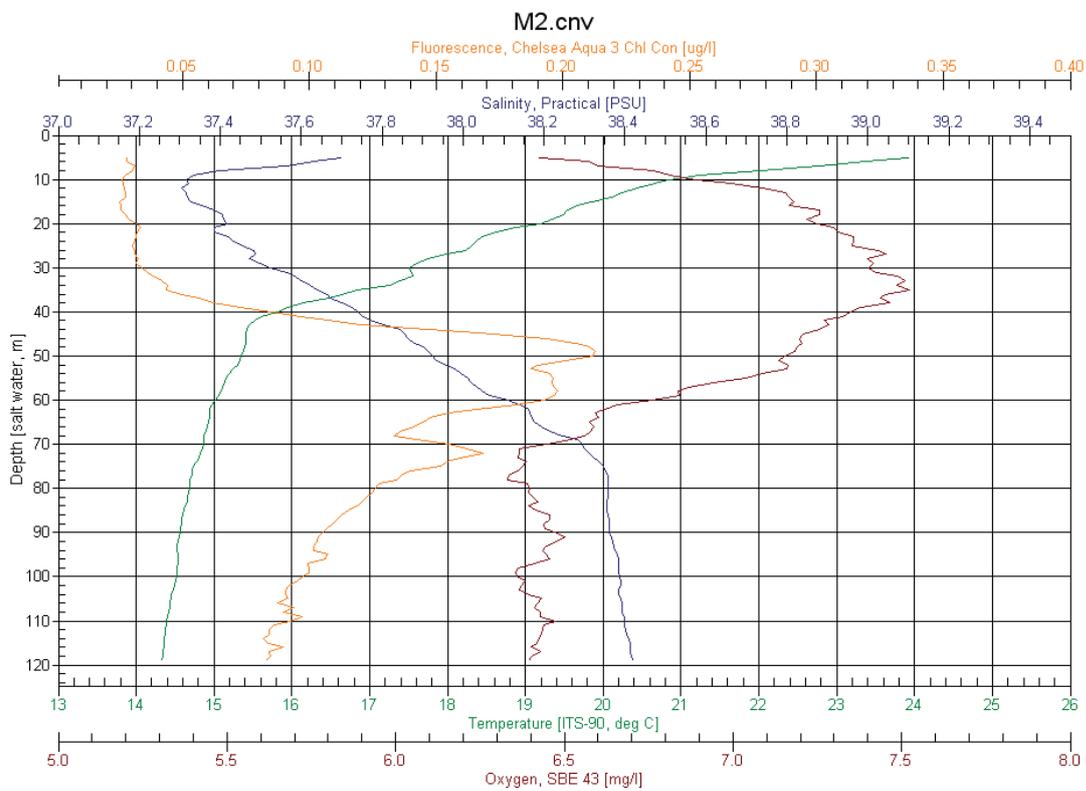
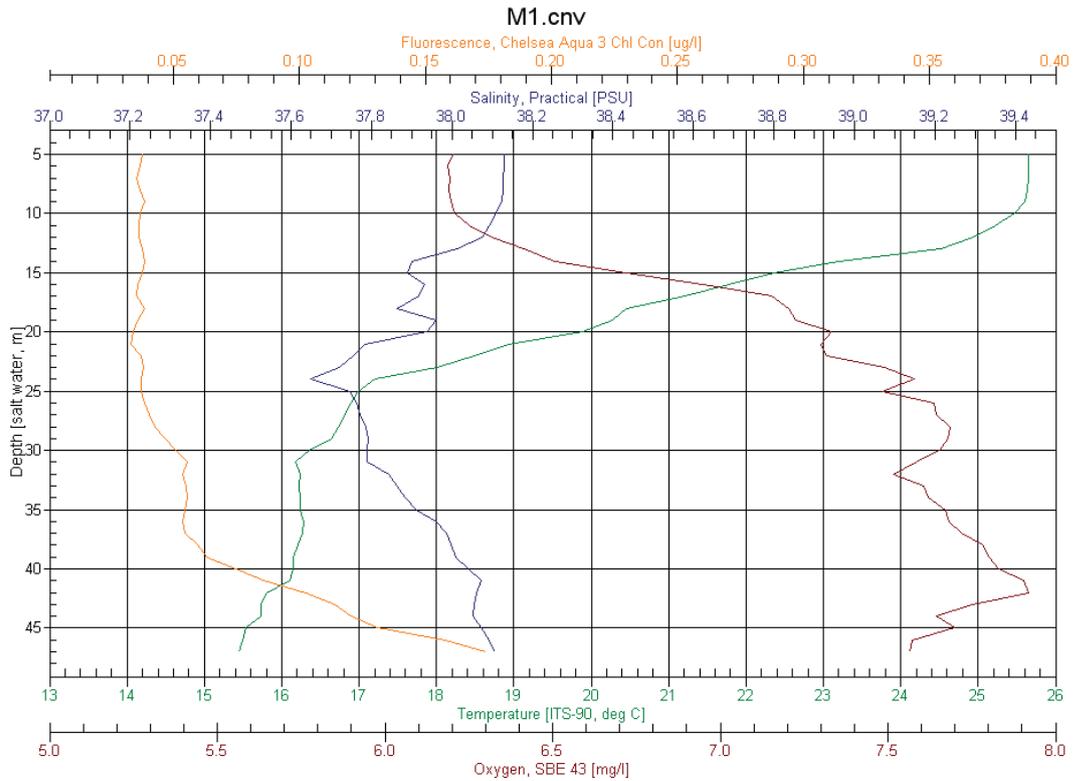
Rau, G.H., Low, C., Friederich, G.E., Pennington, J.T., Chavez, F.P., (1996). $\delta^{13}\text{C}$ -POM and $\delta^{15}\text{N}$ -POM seasonal variations in Monterey Bay, CA: effects of CO_2 and NO_3 supply/demand. EOS 76, OS199.

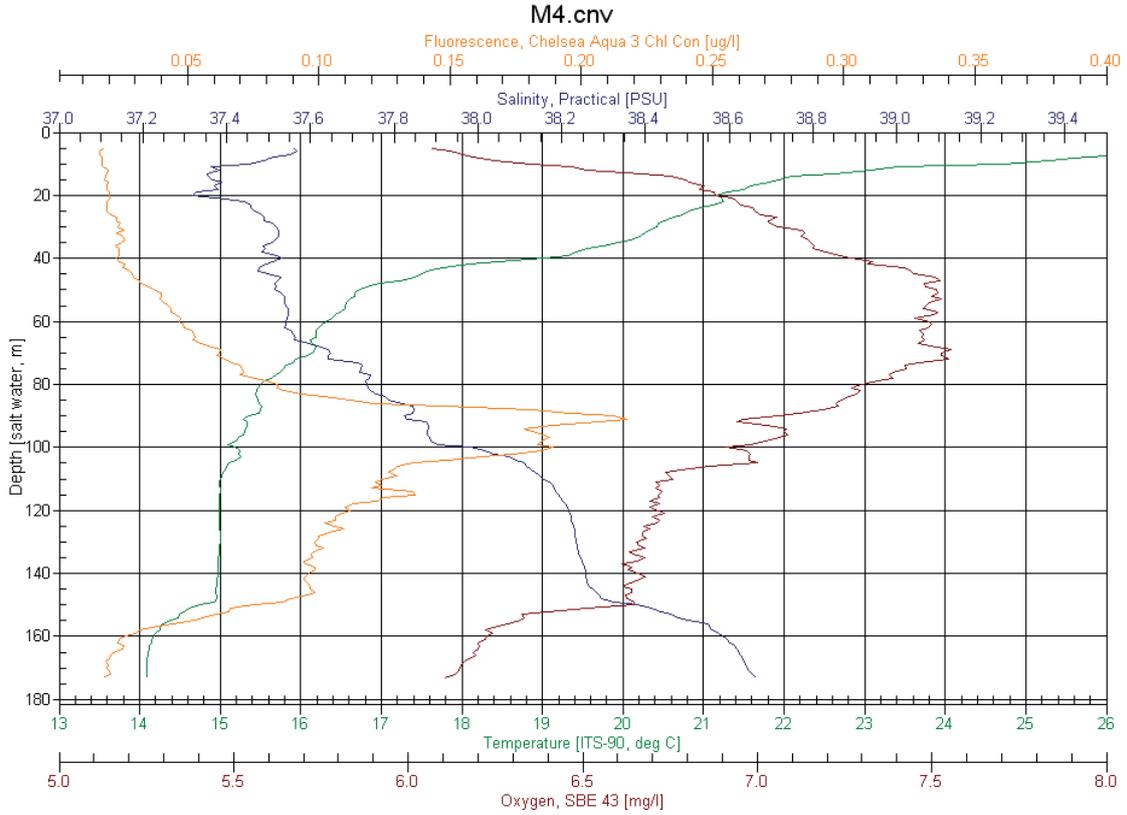
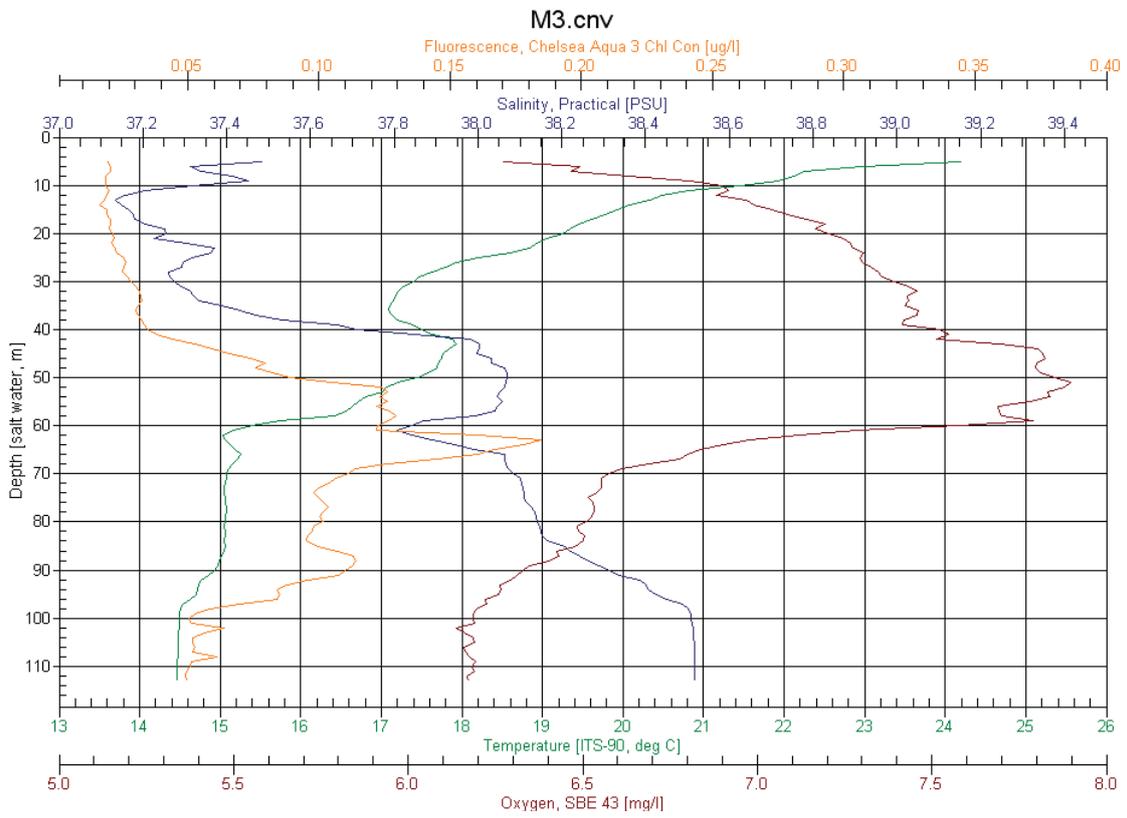
Sachs J. P. and Repeta D. J. (1999). Oligotrophy and nitrogen fixation during eastern Mediterranean sapropel events. *Science* 286, 2485-2488.

Saino T. and A. Hattori (1980). $\delta^{15}\text{N}$ natural abundance in oceanic suspended particulate matter. *Nature*, **283**, 752–754

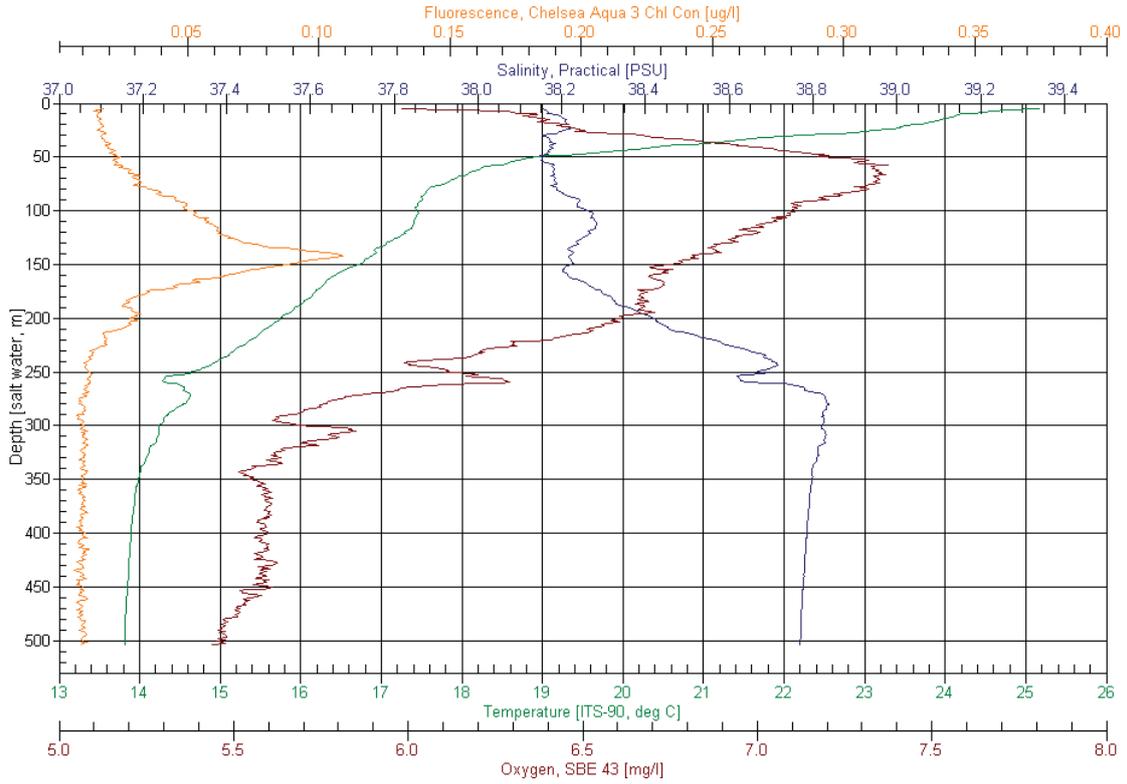
Voss, M., Altabet, M.A., Bodungen, B.V.,(1996). $\delta^{15}\text{N}$ of sedimenting particles as indicator of euphotic zone processes. *Deep-Sea Research I*, 43, 33 - 47.

CTD Profiles for each station of the "MedSudMed-10" Oceanographic Survey

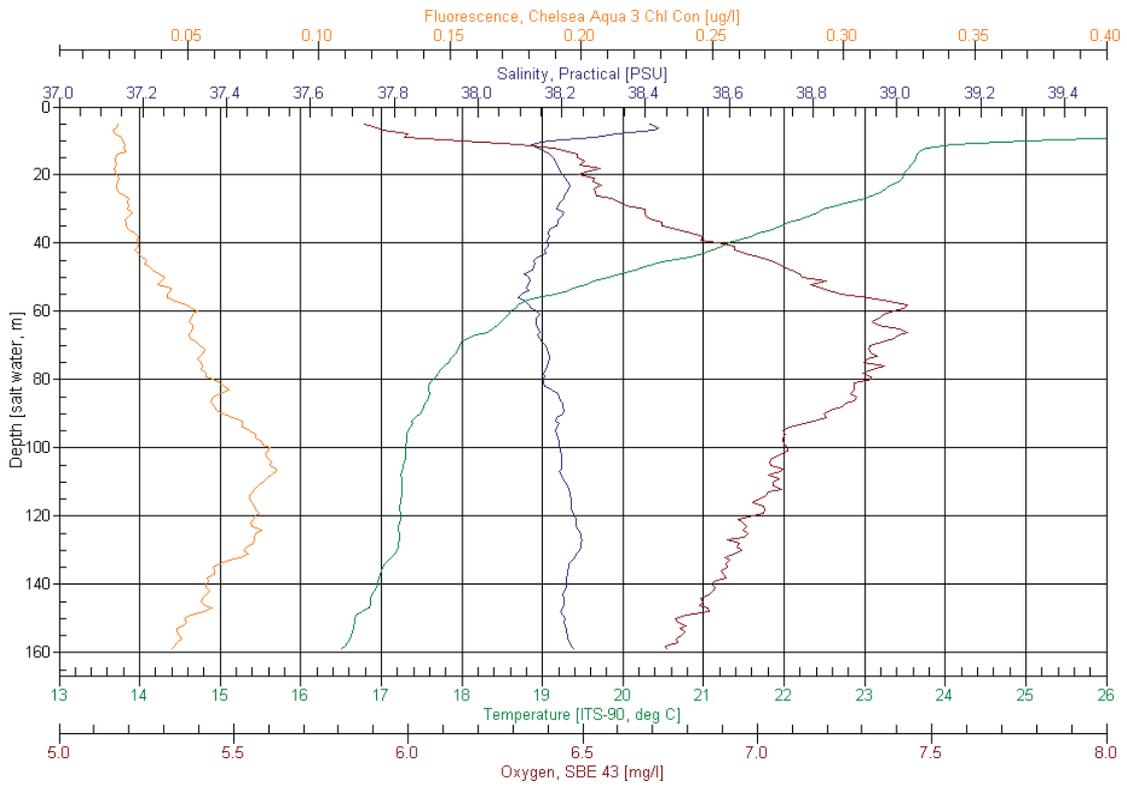




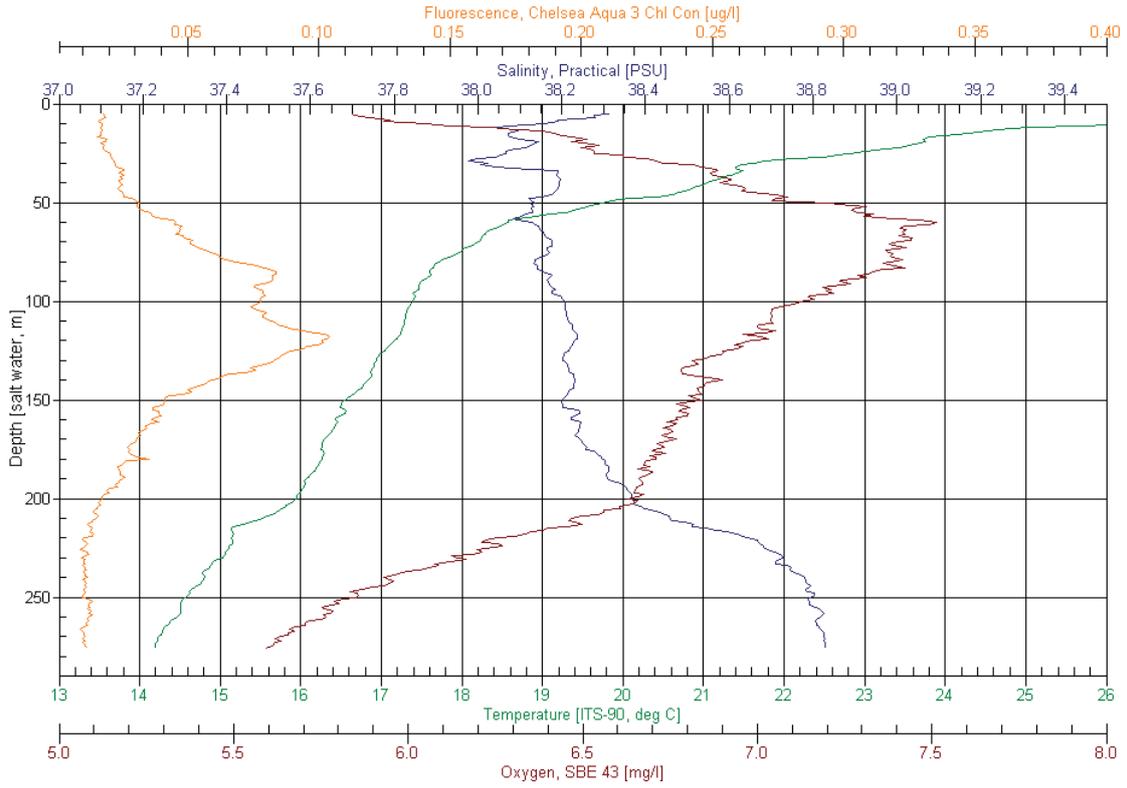
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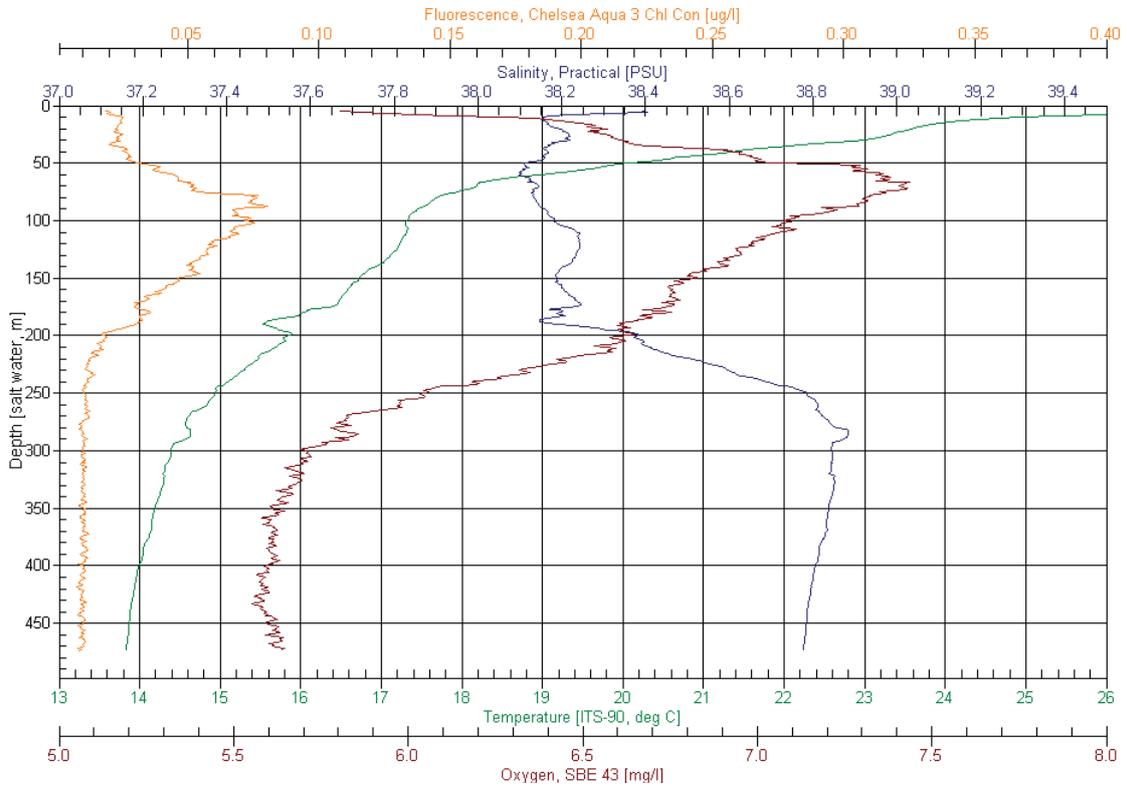
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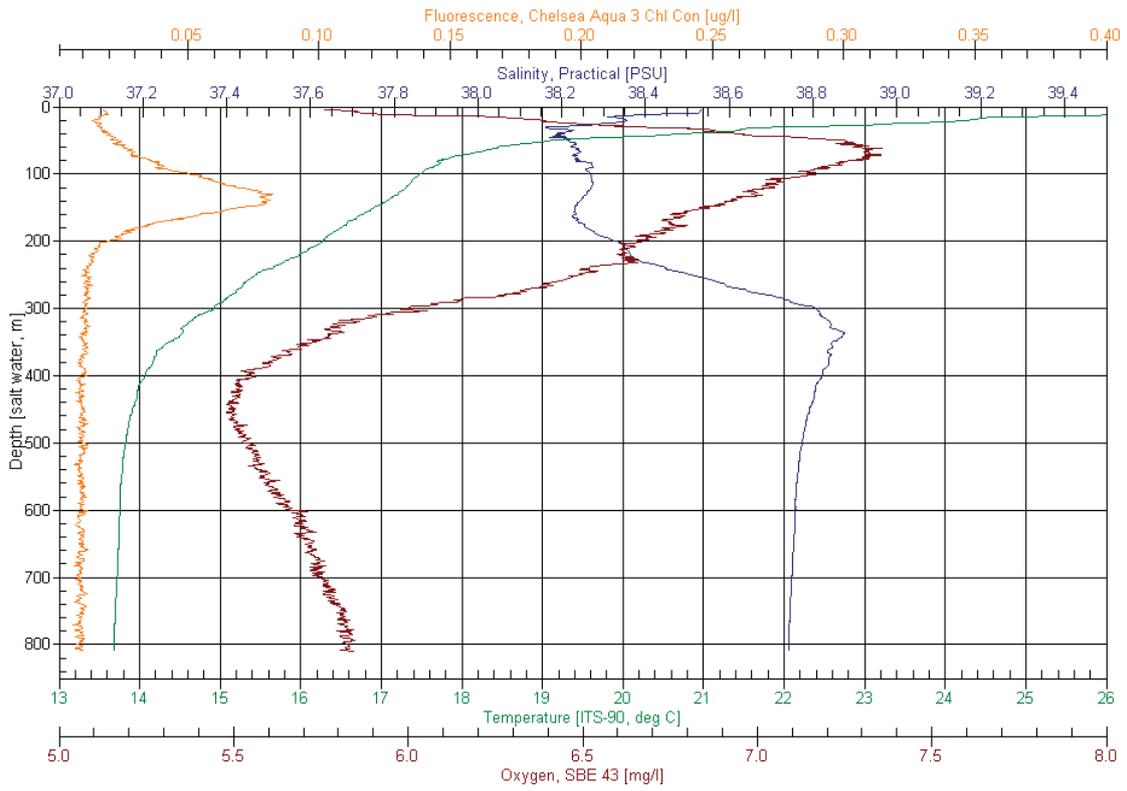
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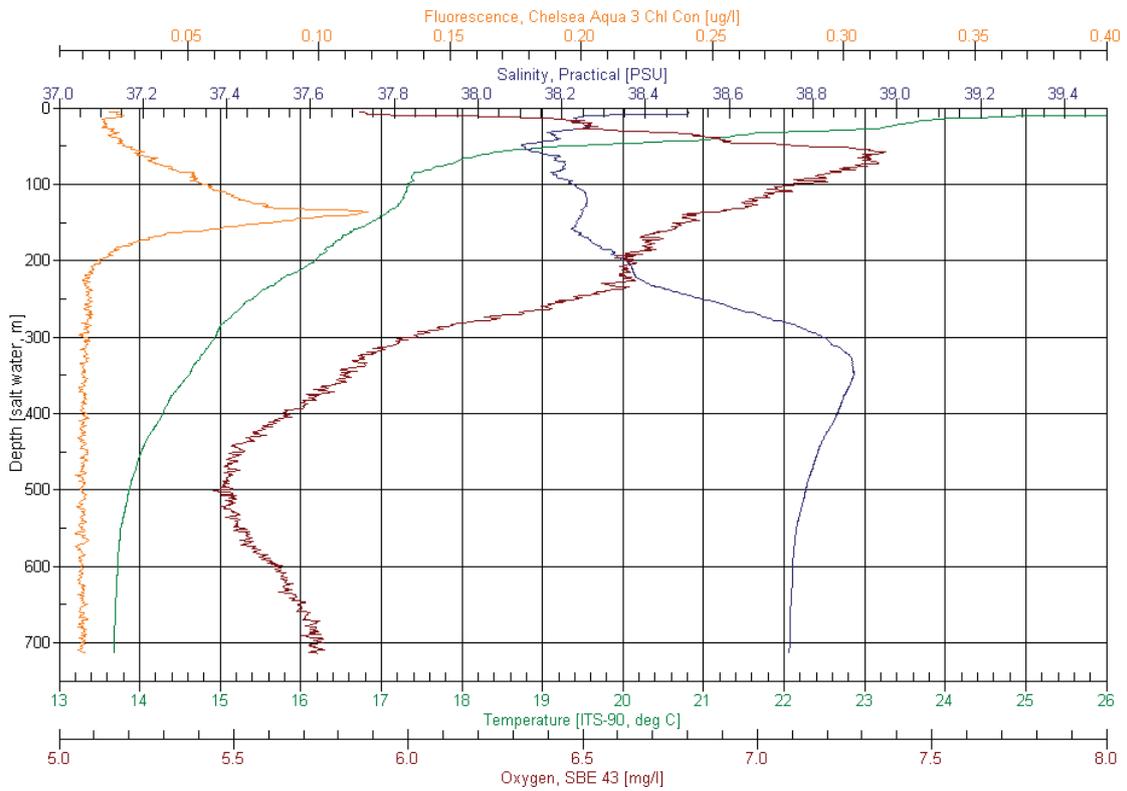
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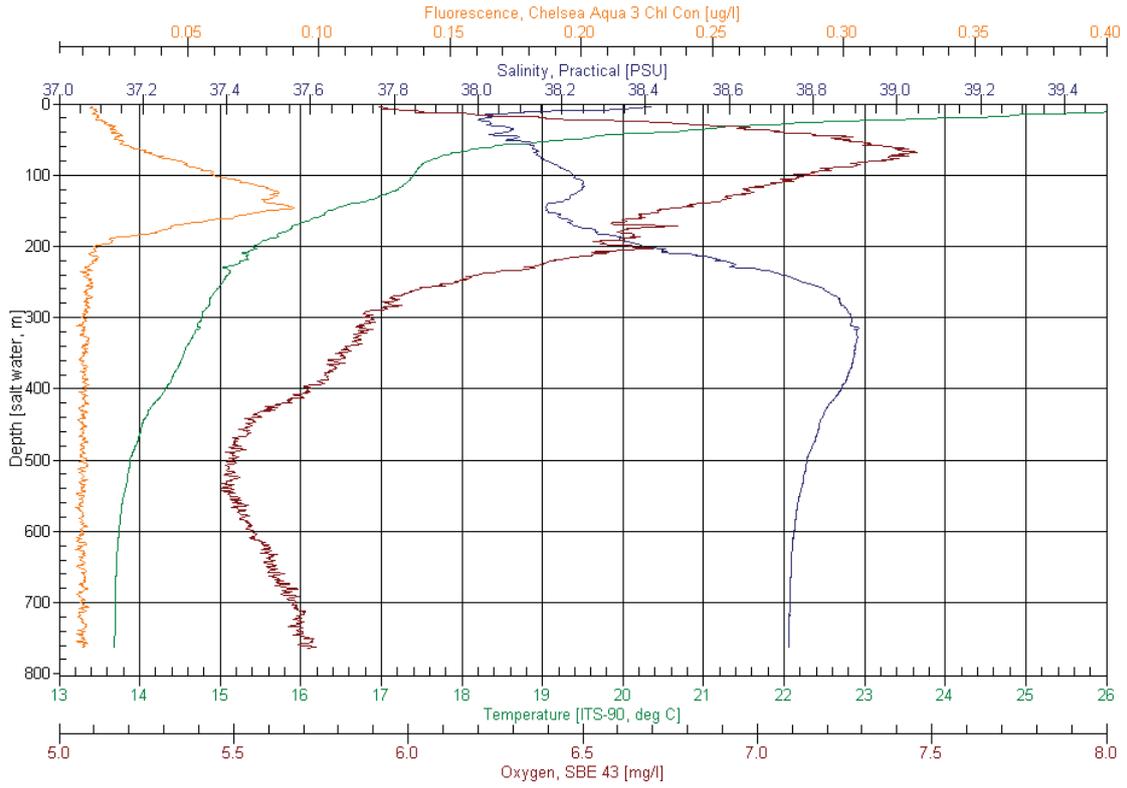
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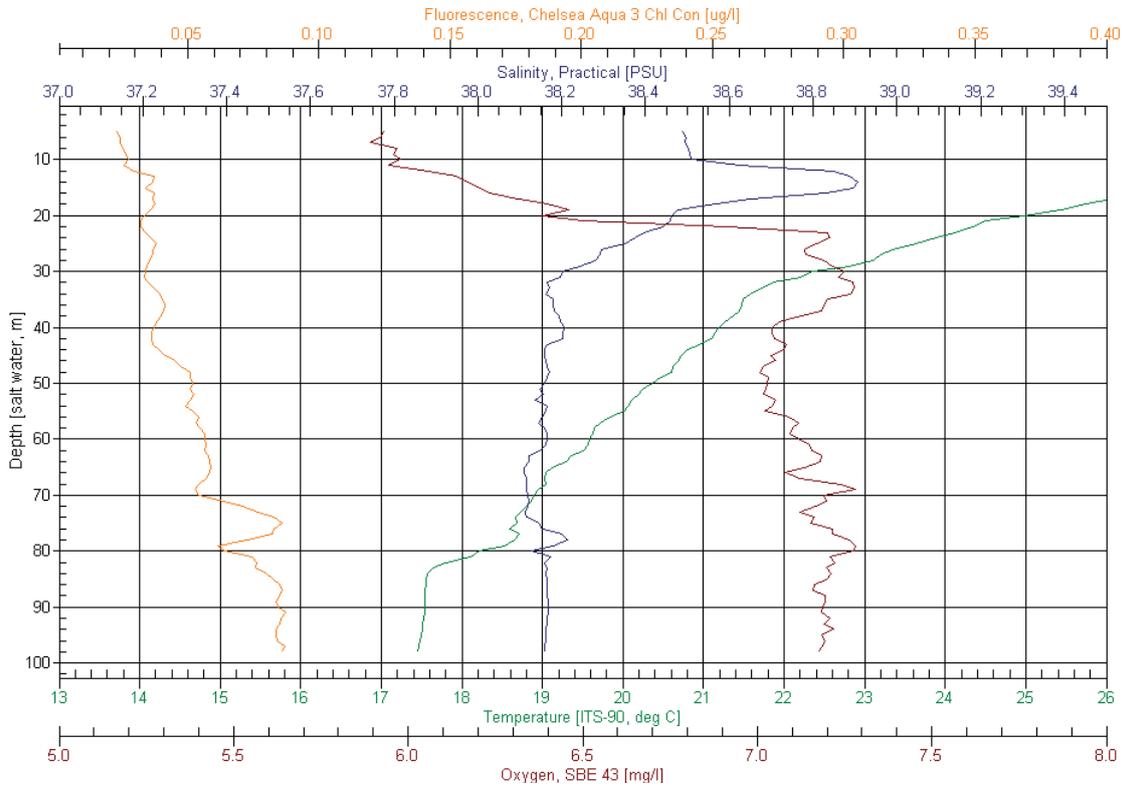
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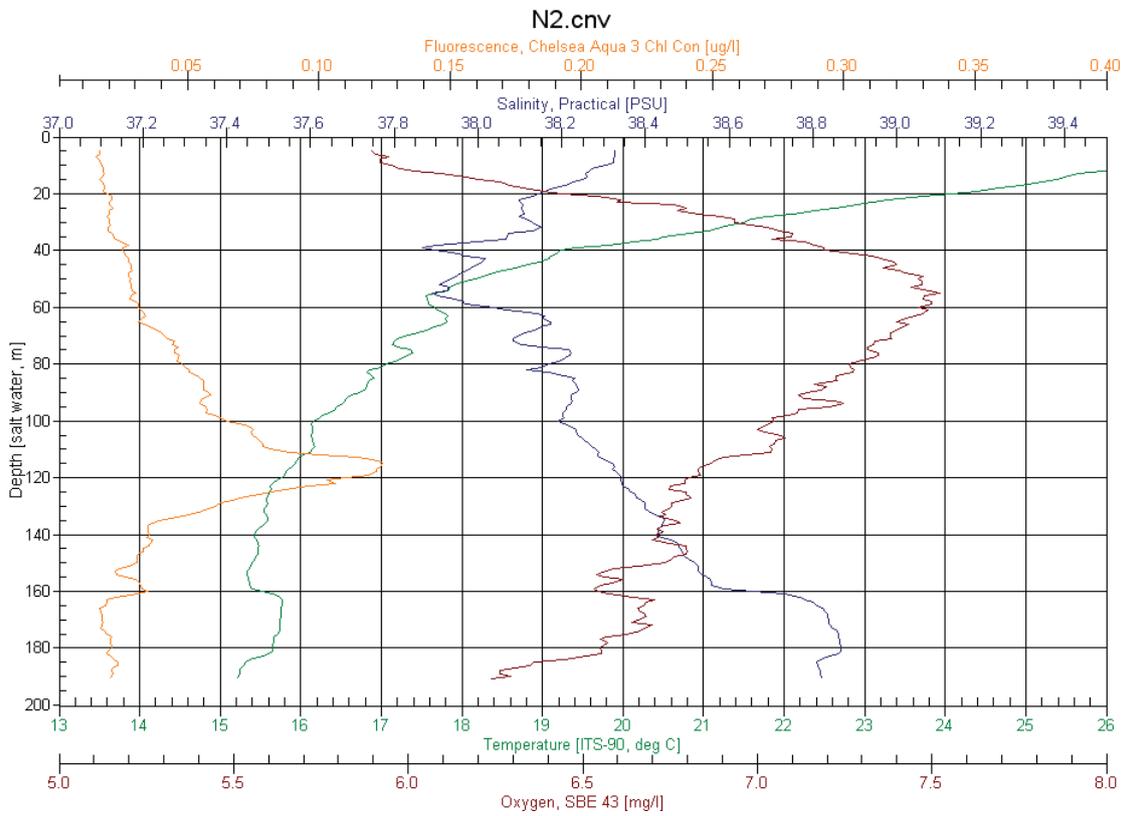
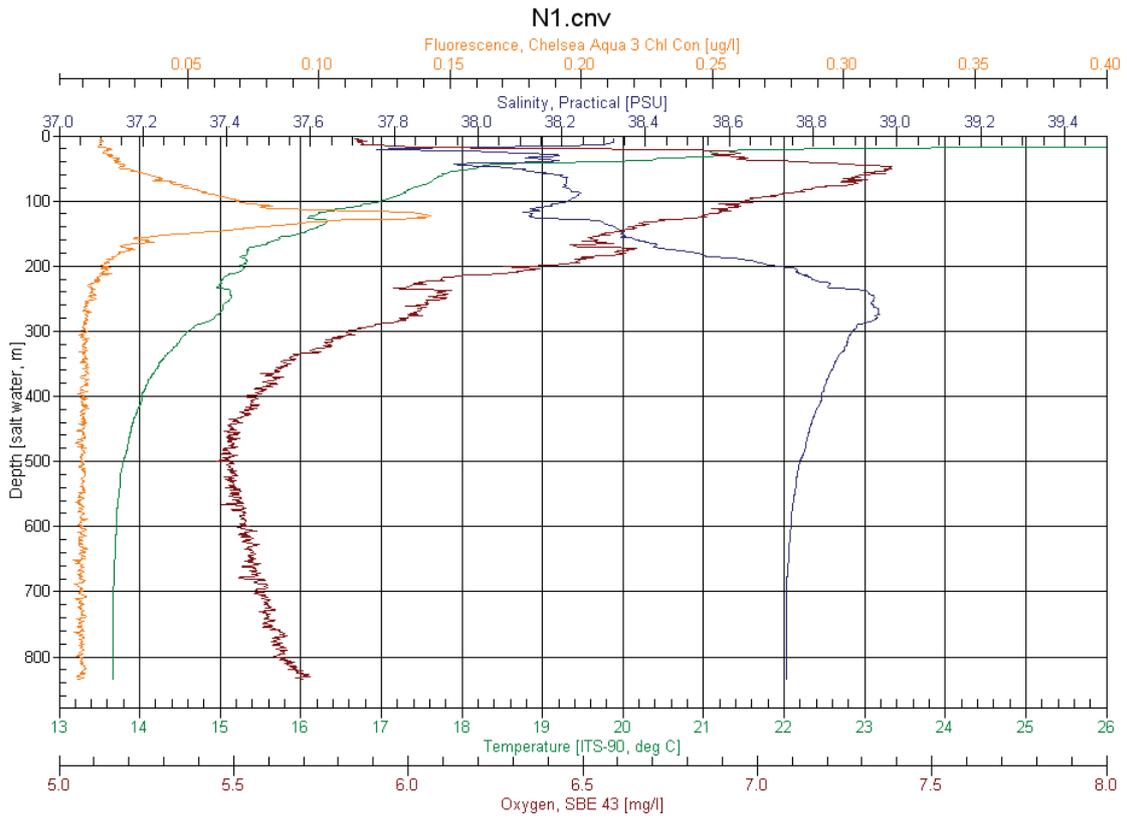


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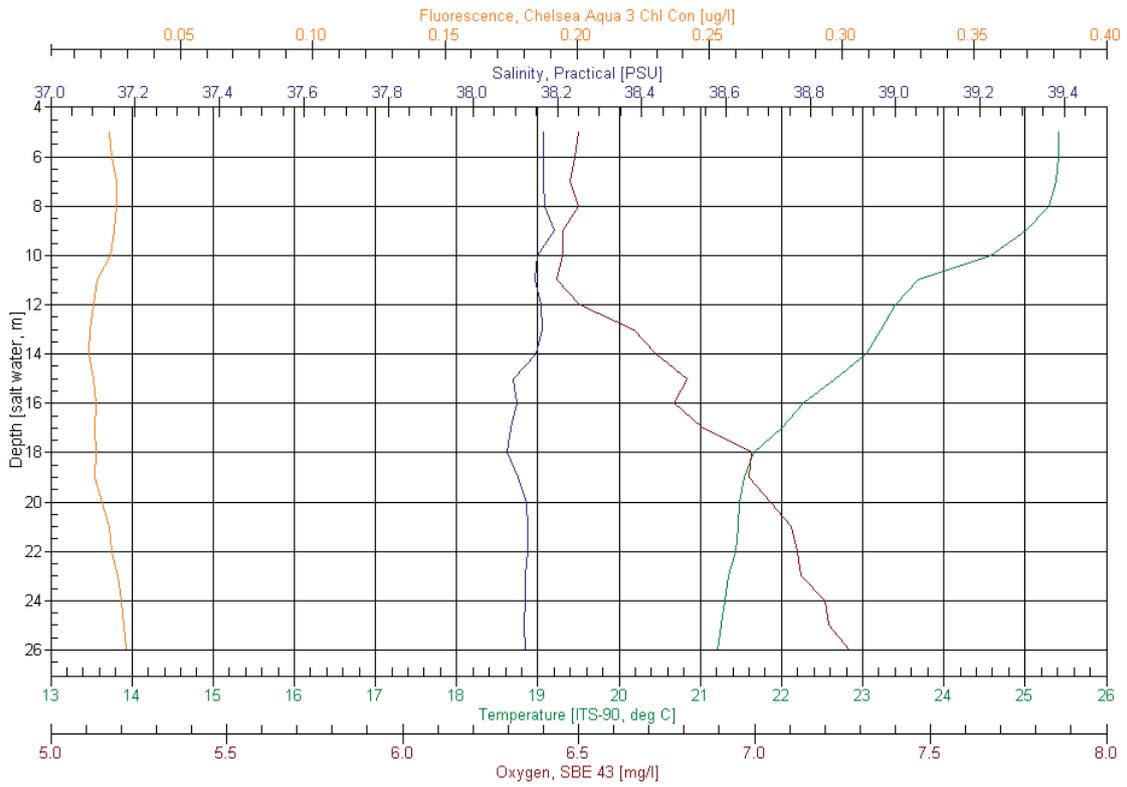


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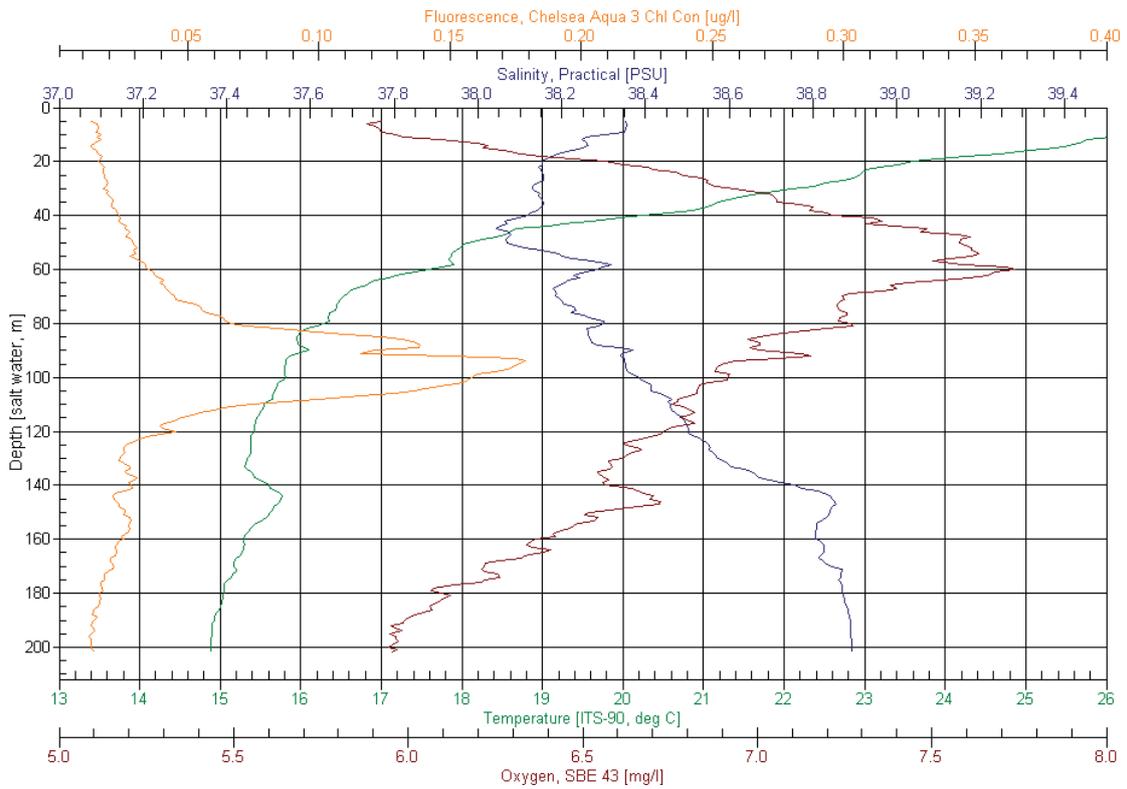




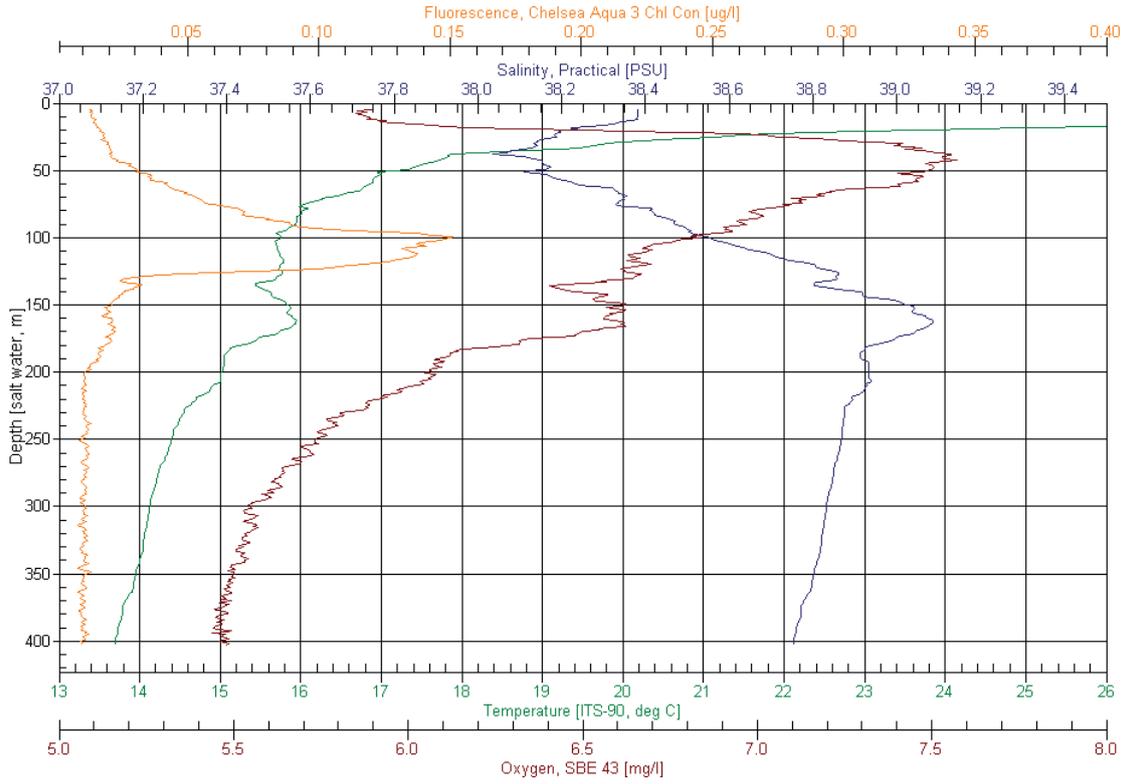
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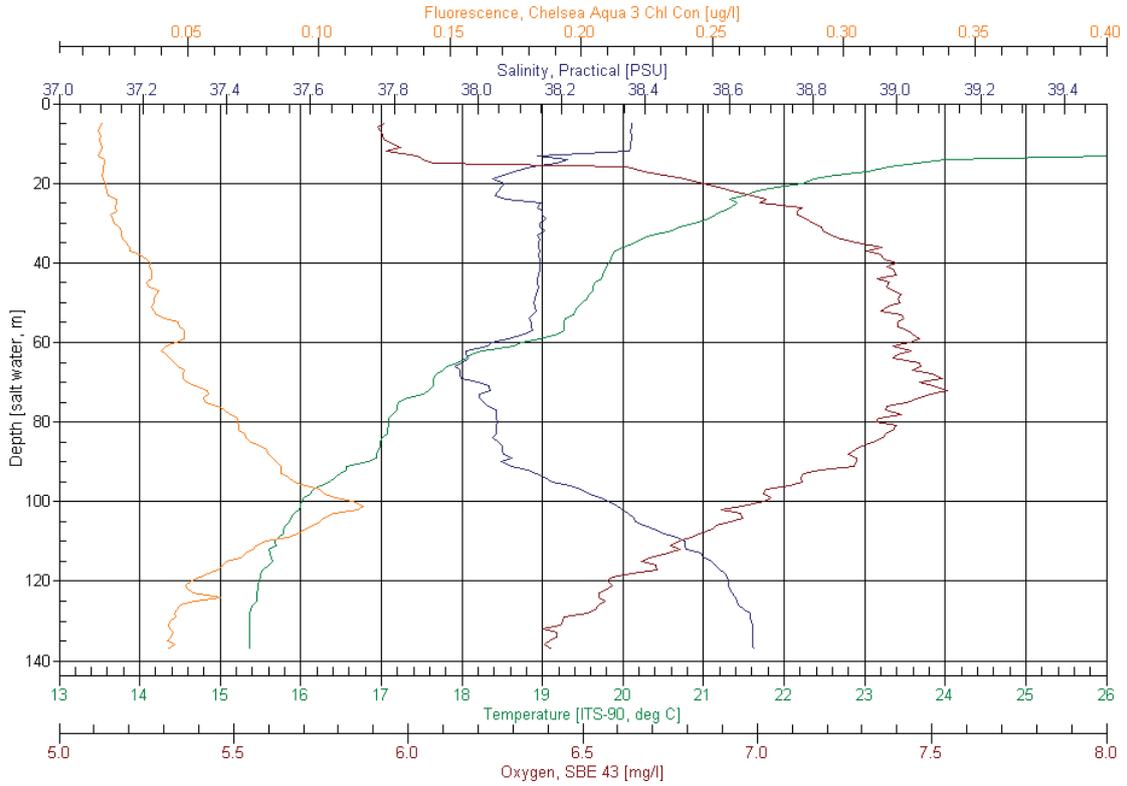
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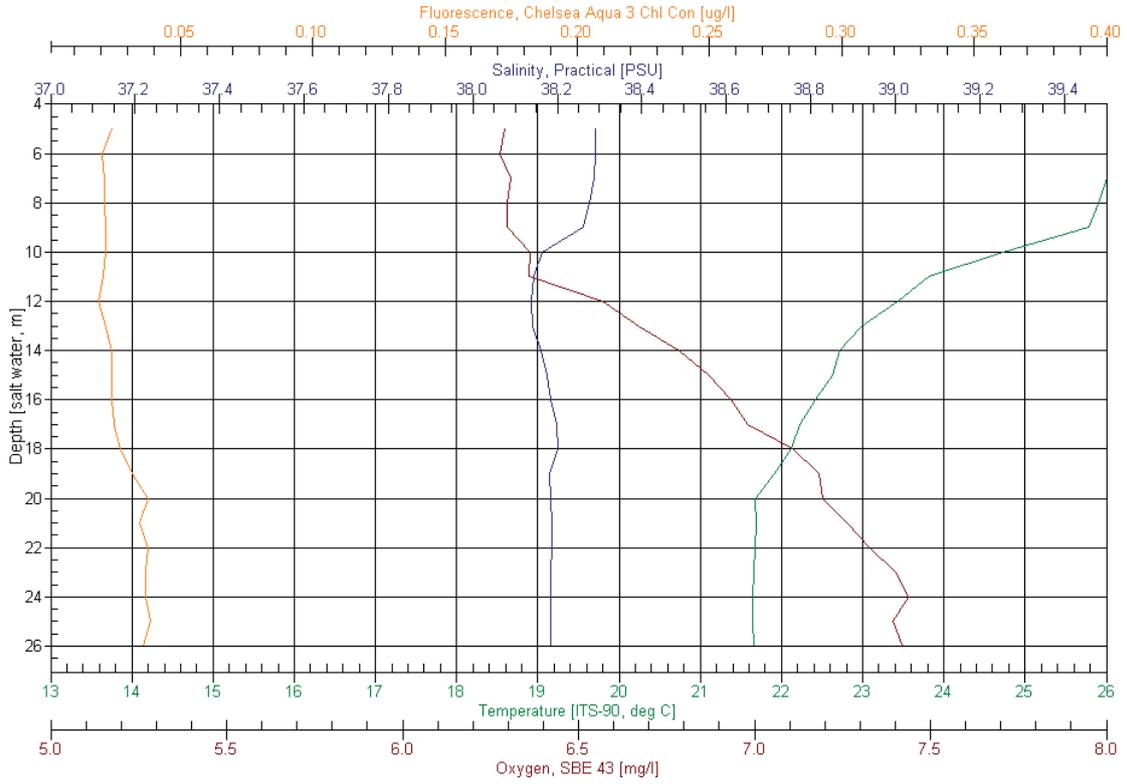
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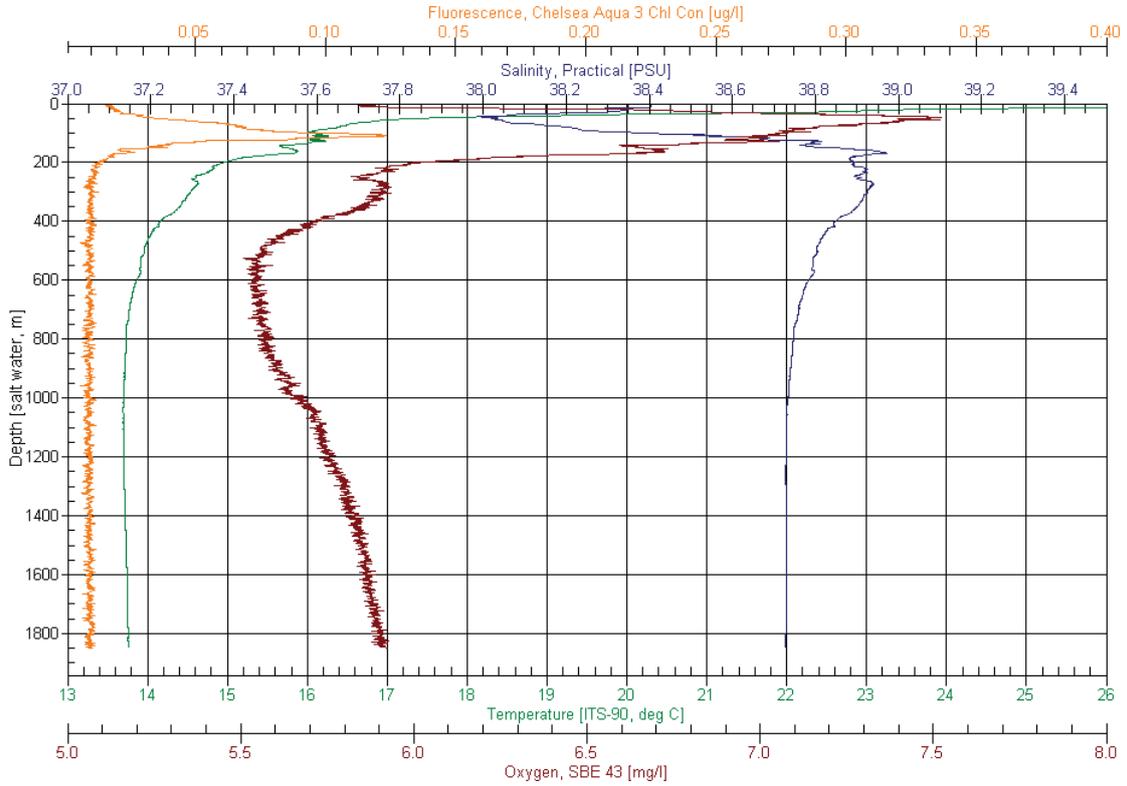
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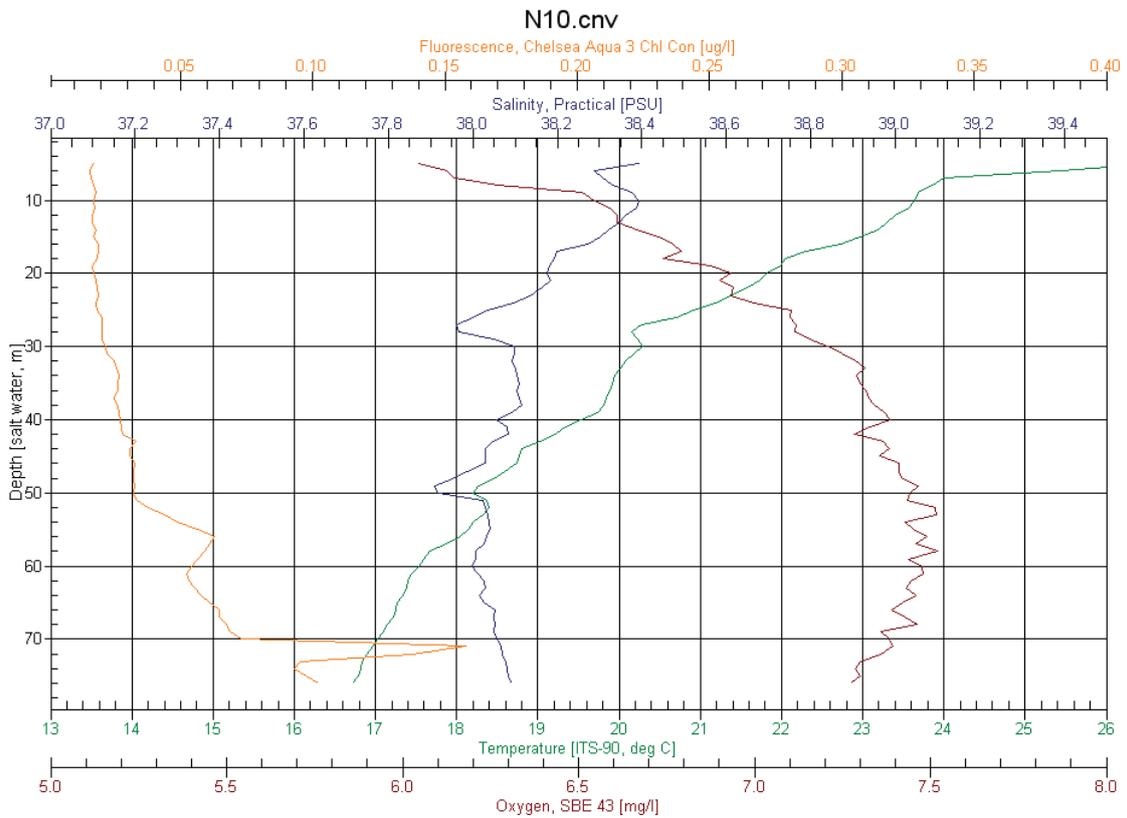
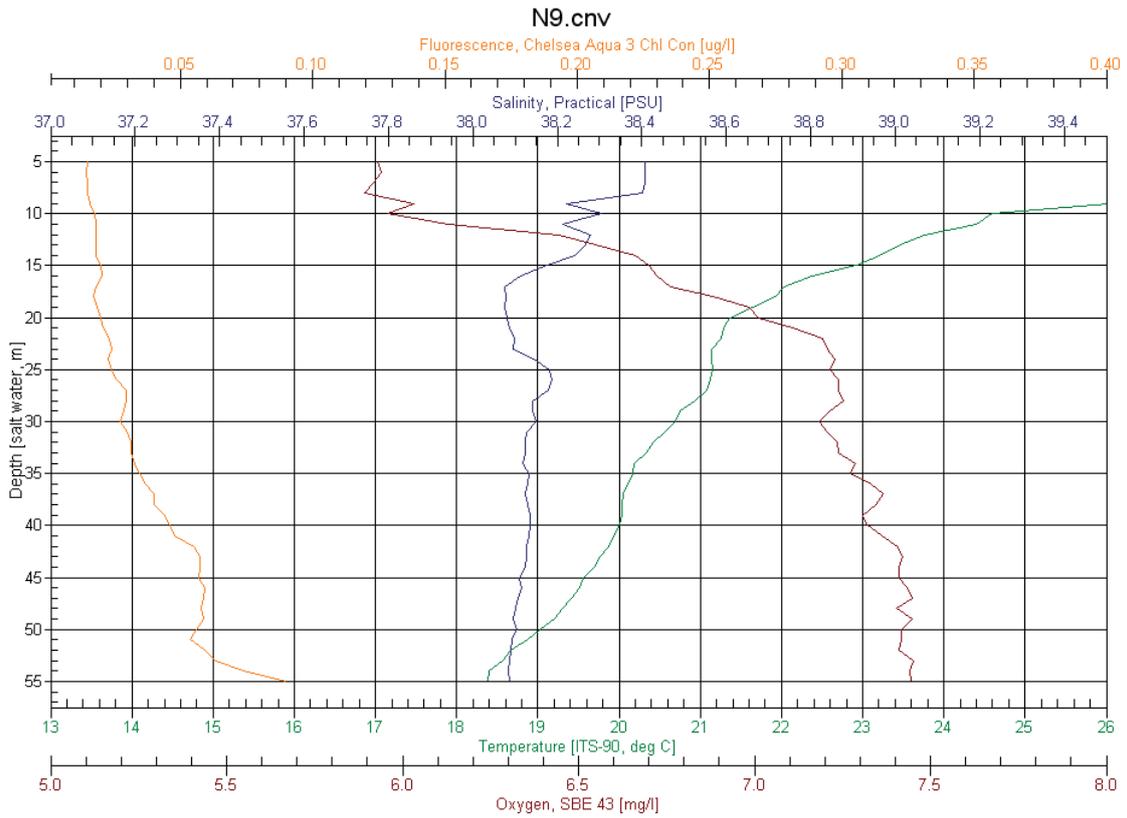


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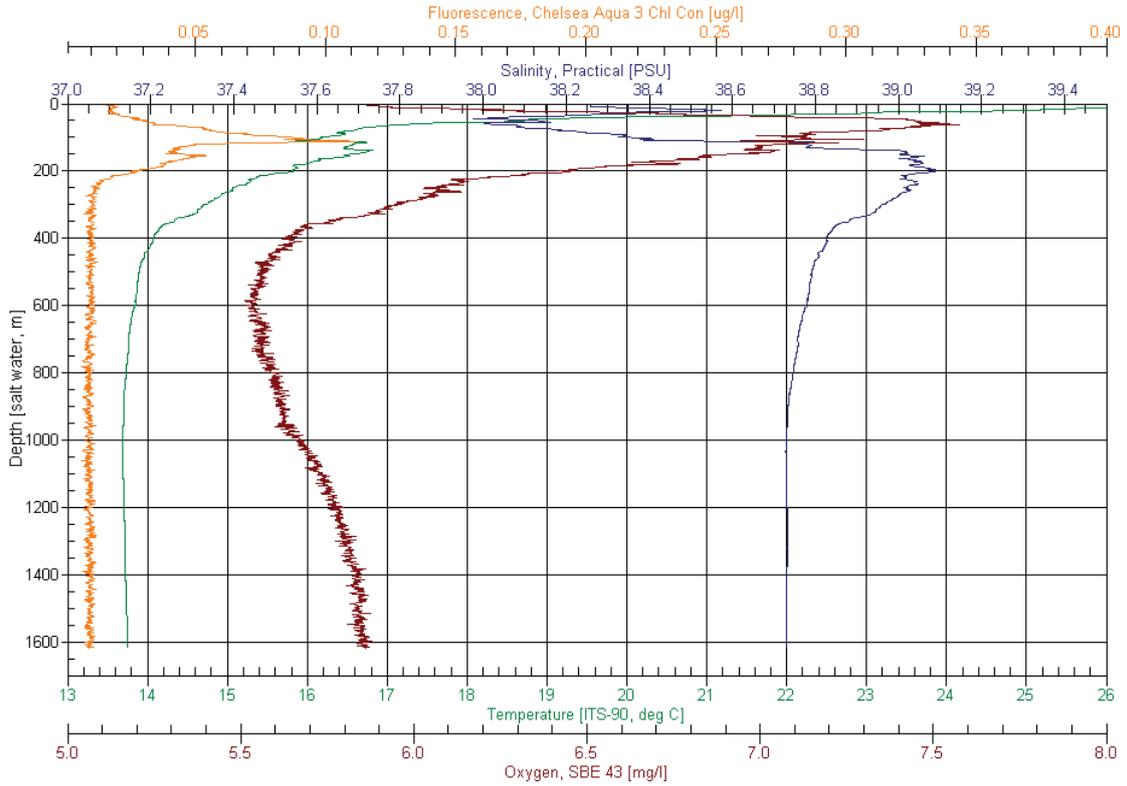


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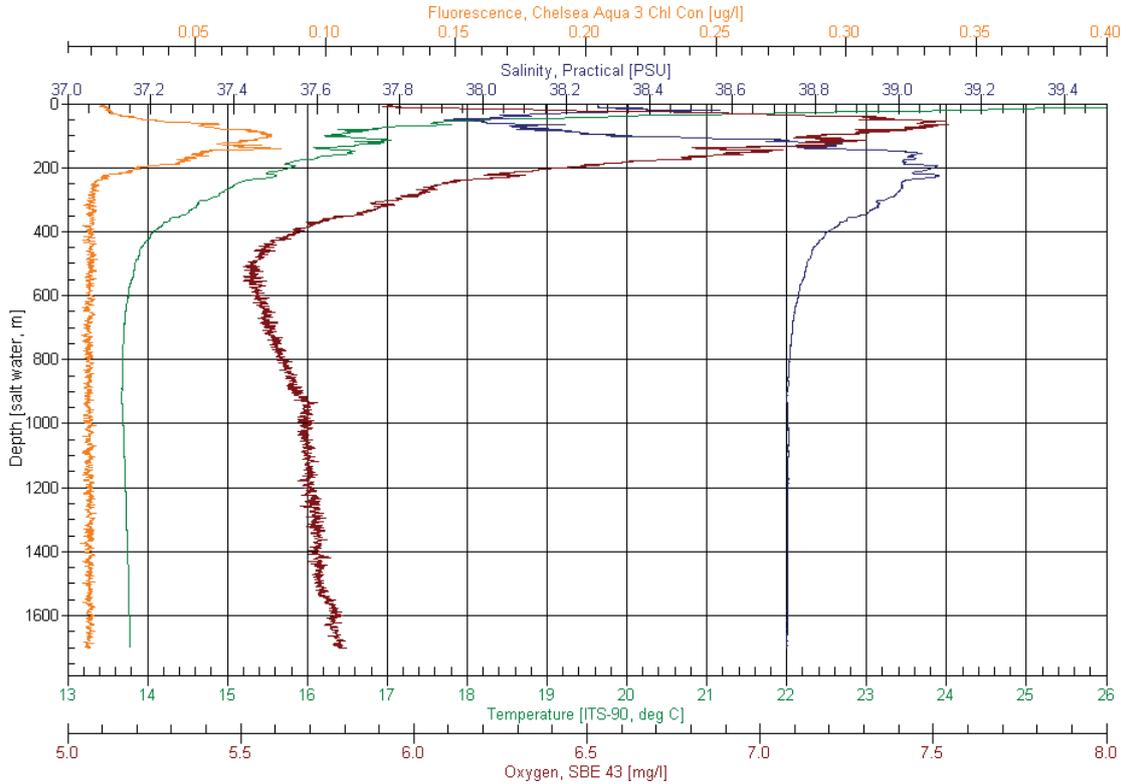




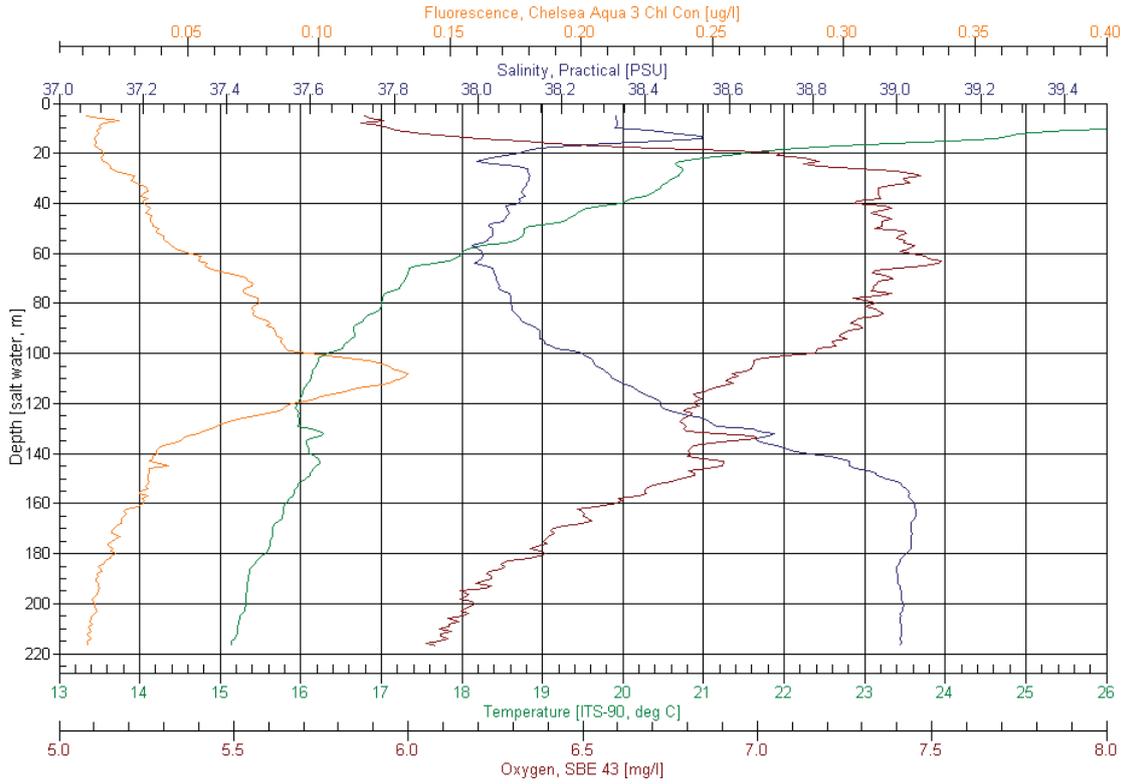
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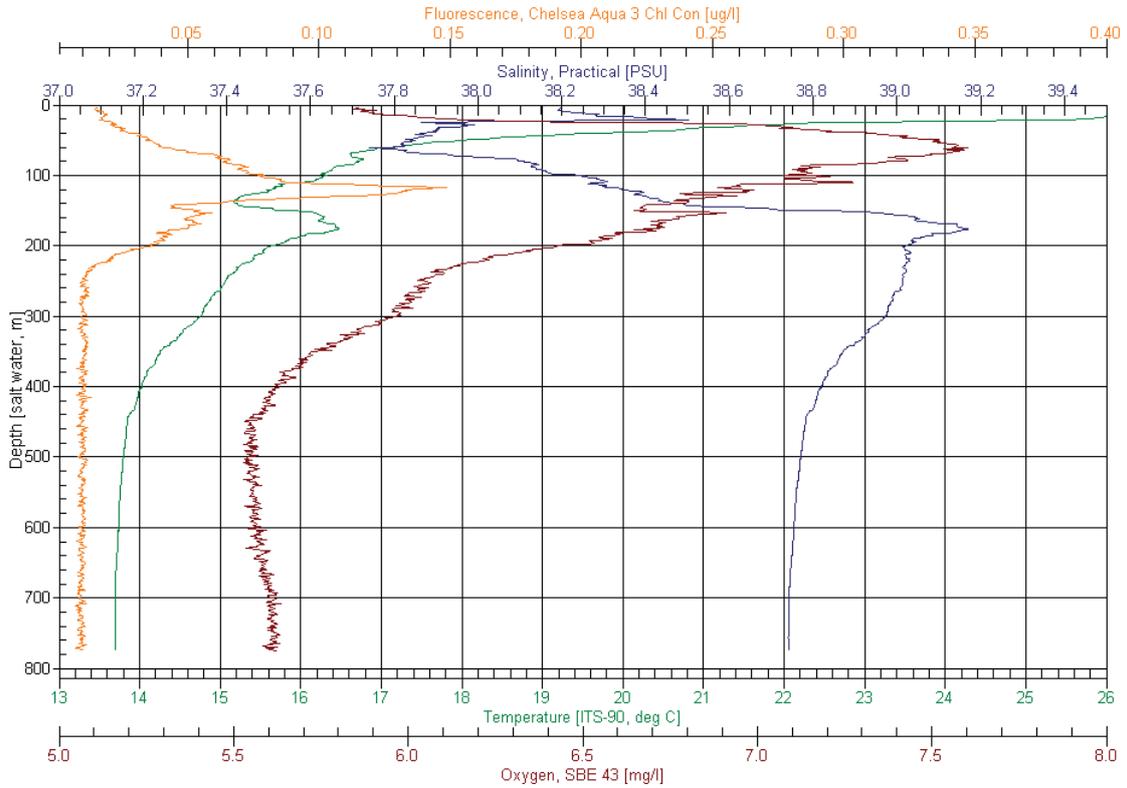
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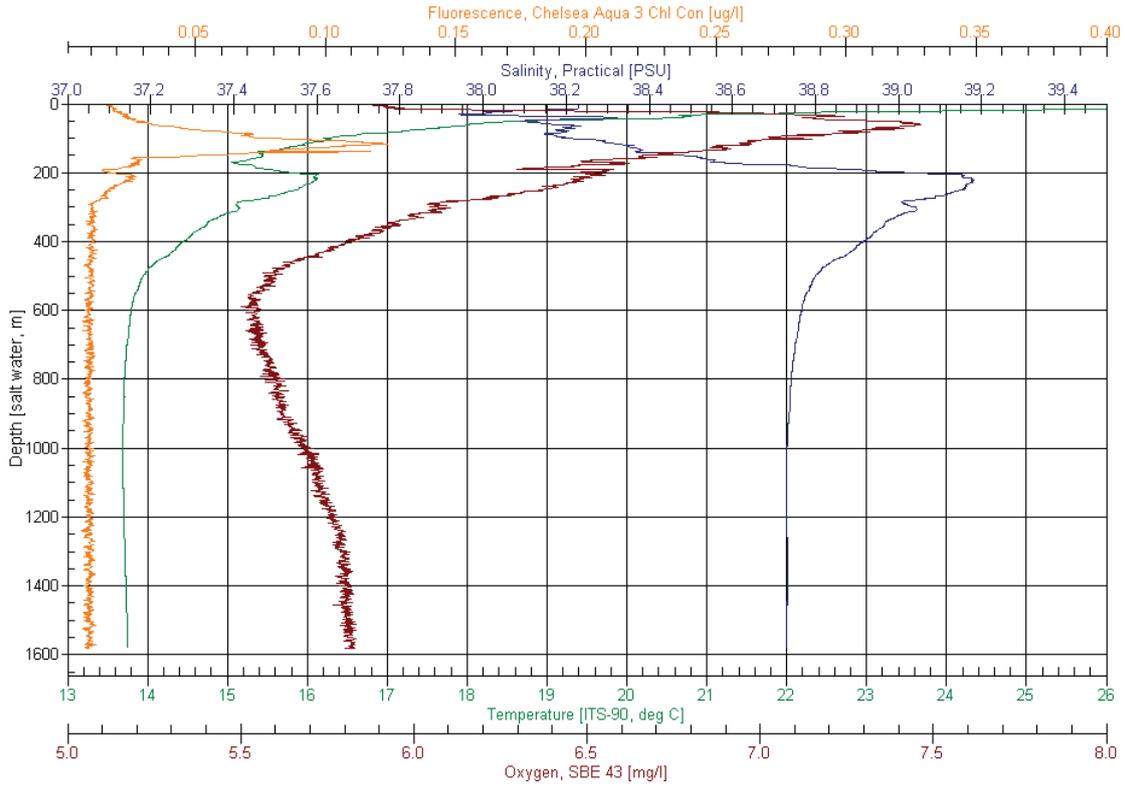
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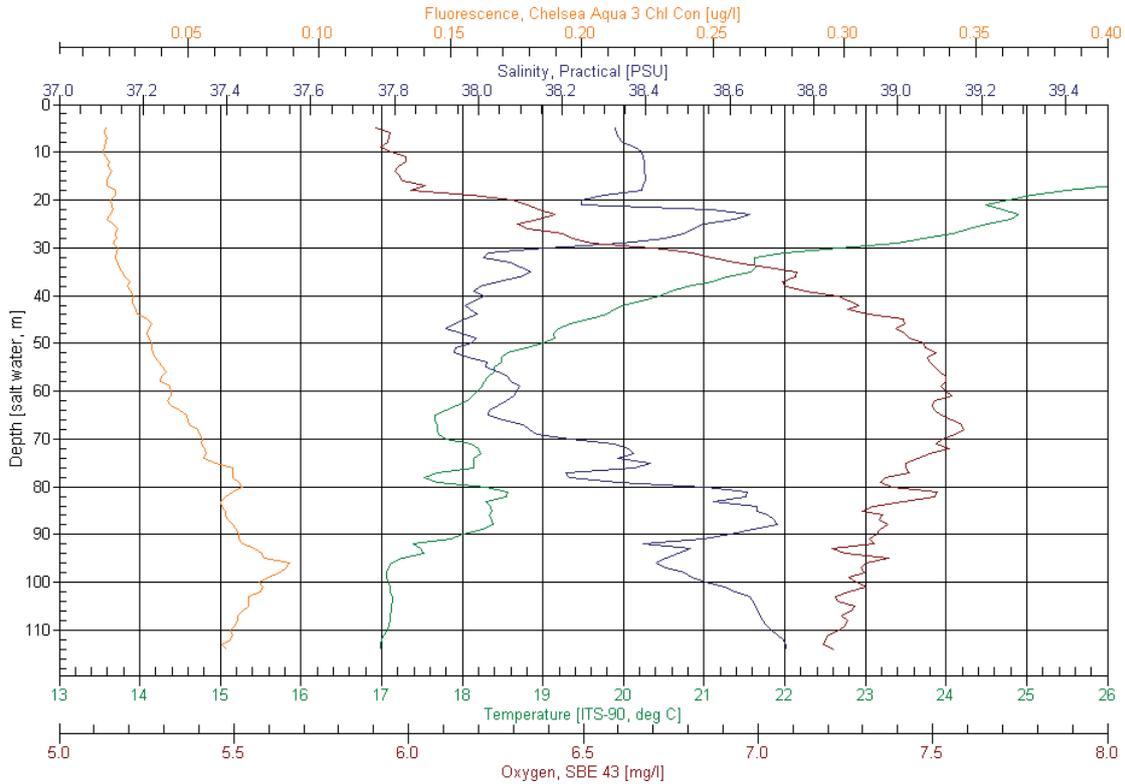
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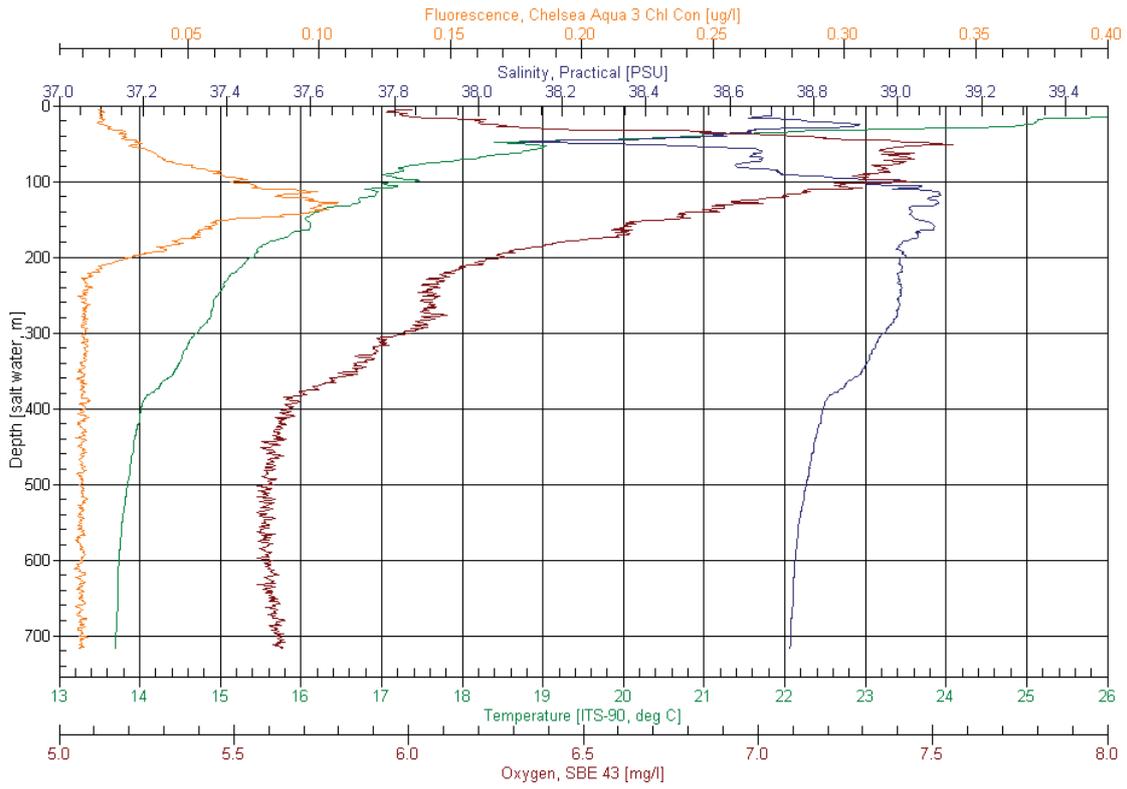
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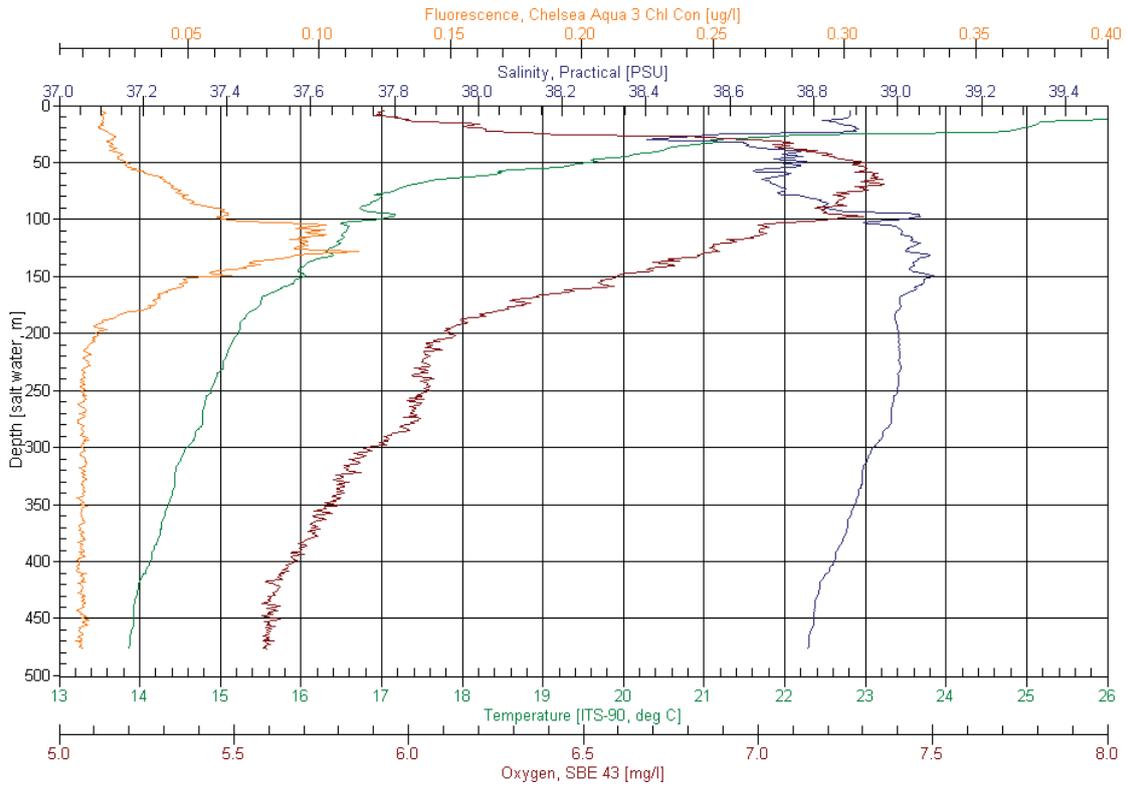
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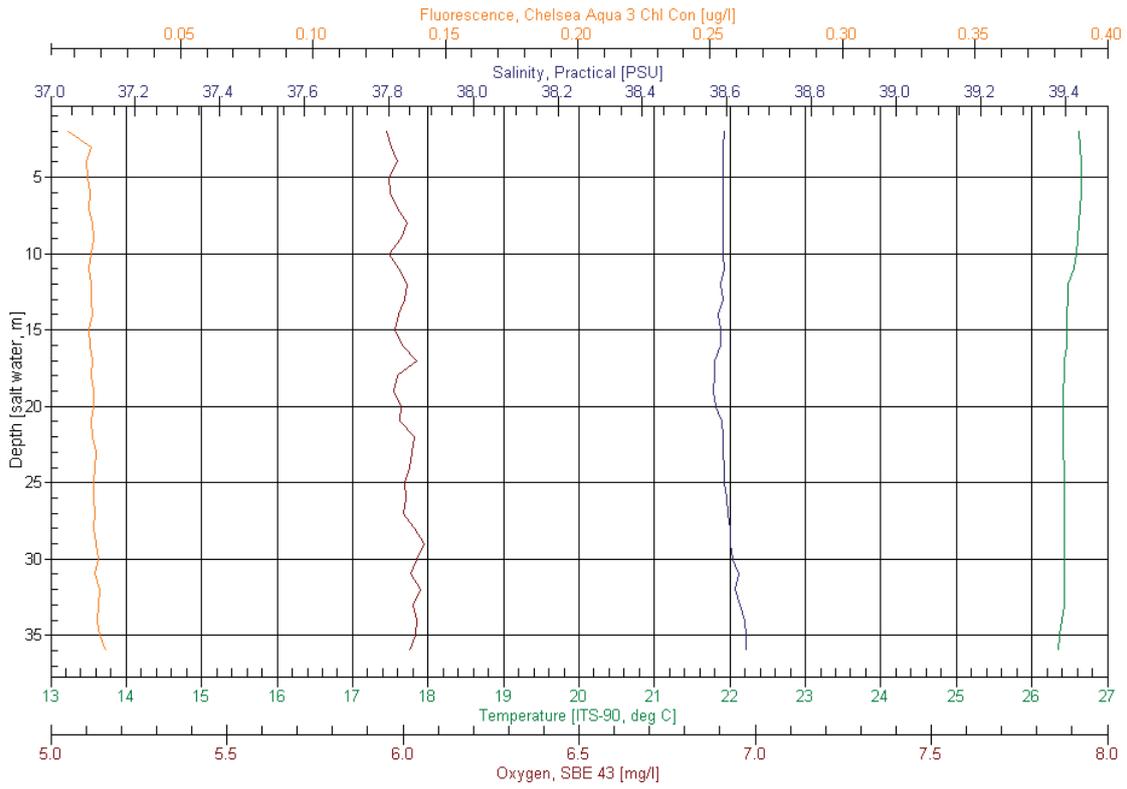
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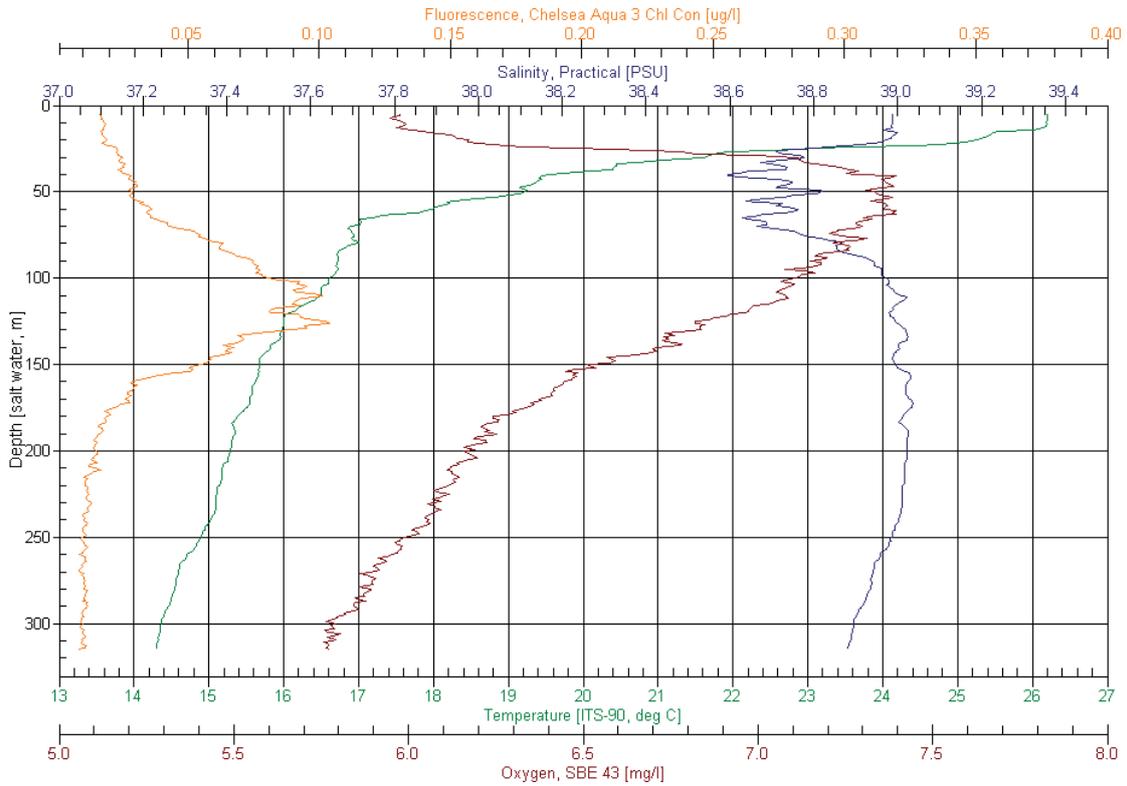
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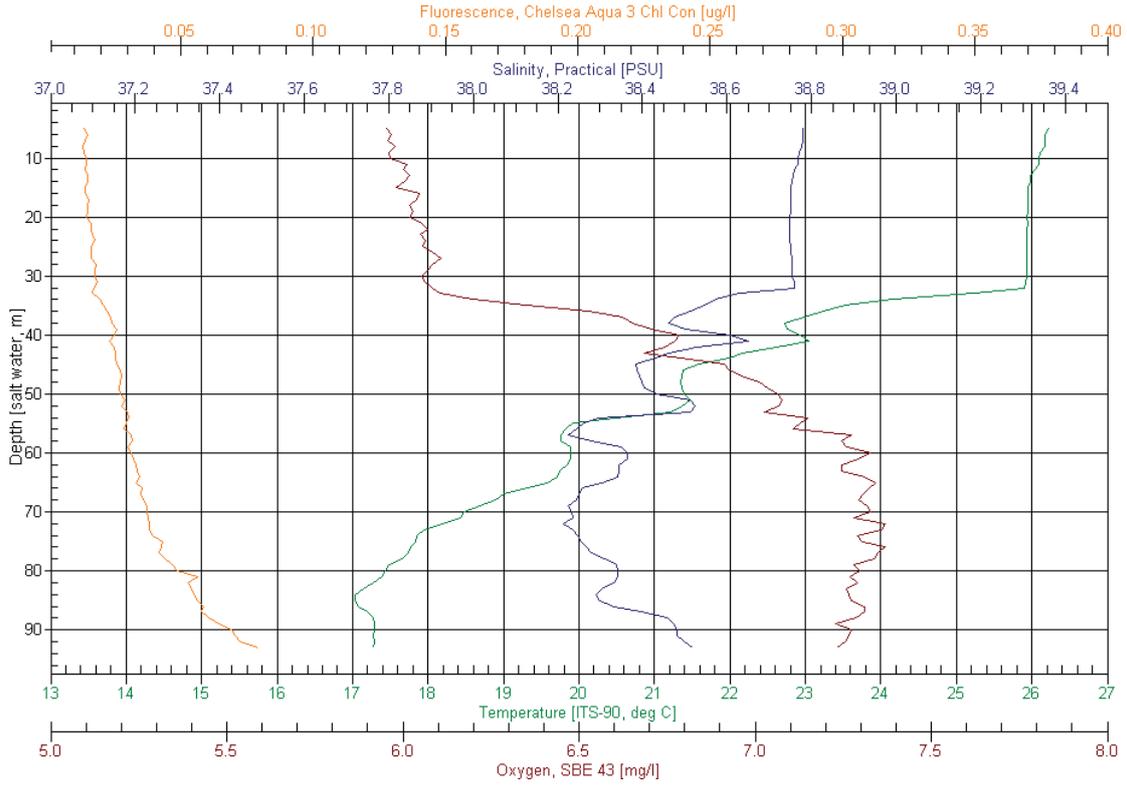
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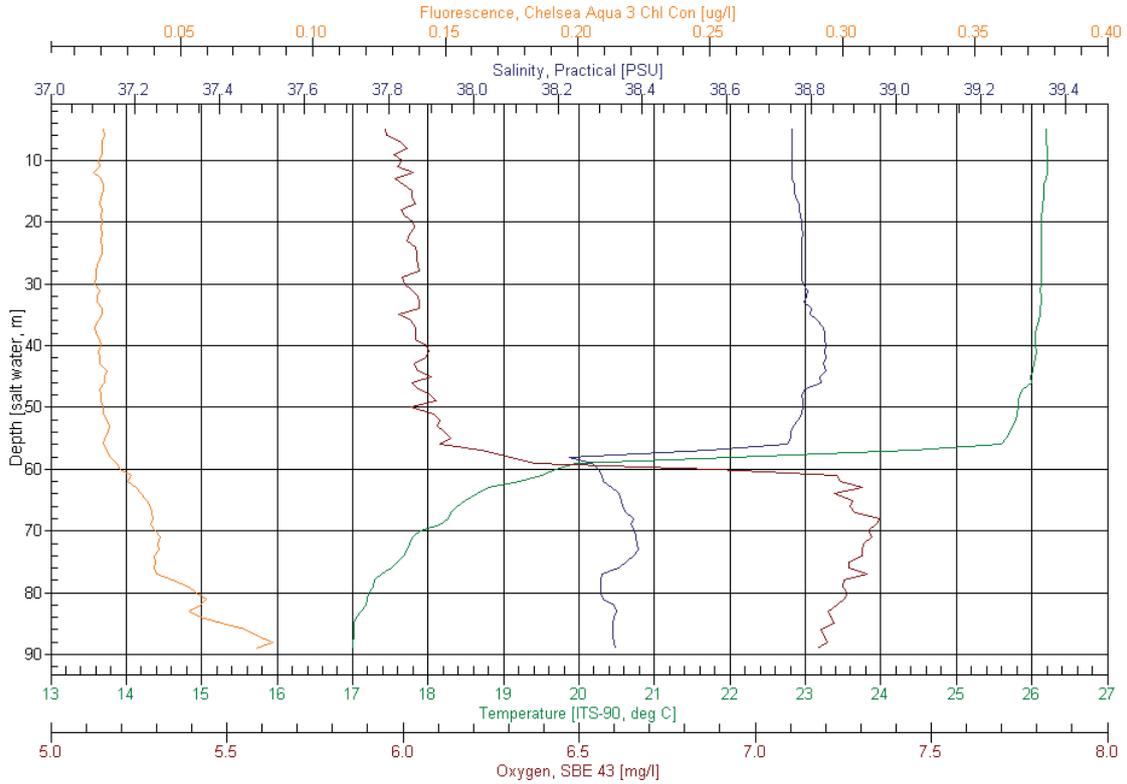
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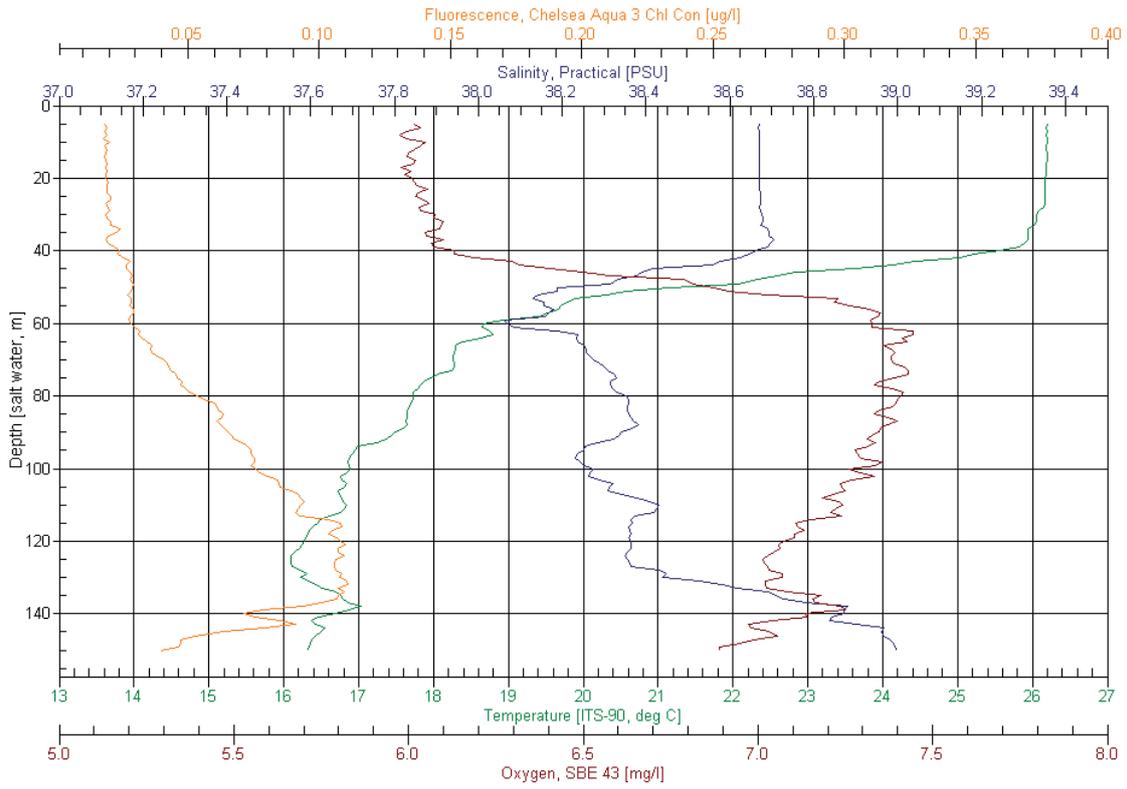
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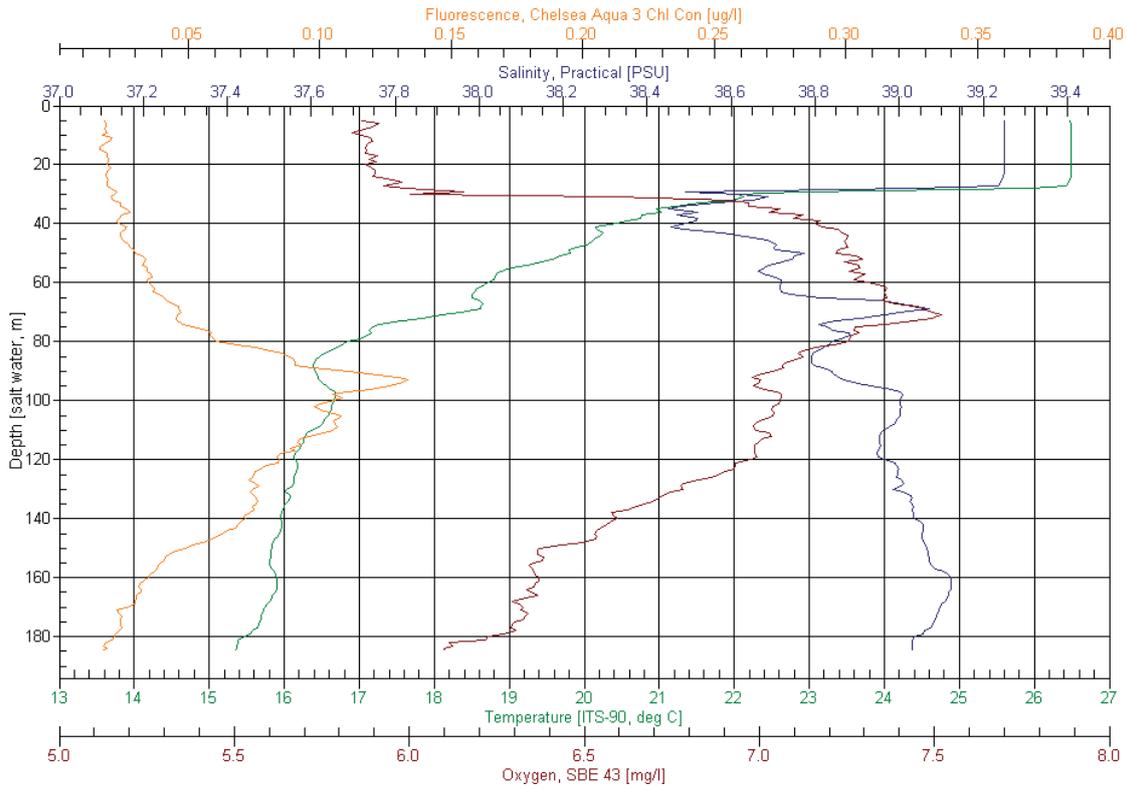
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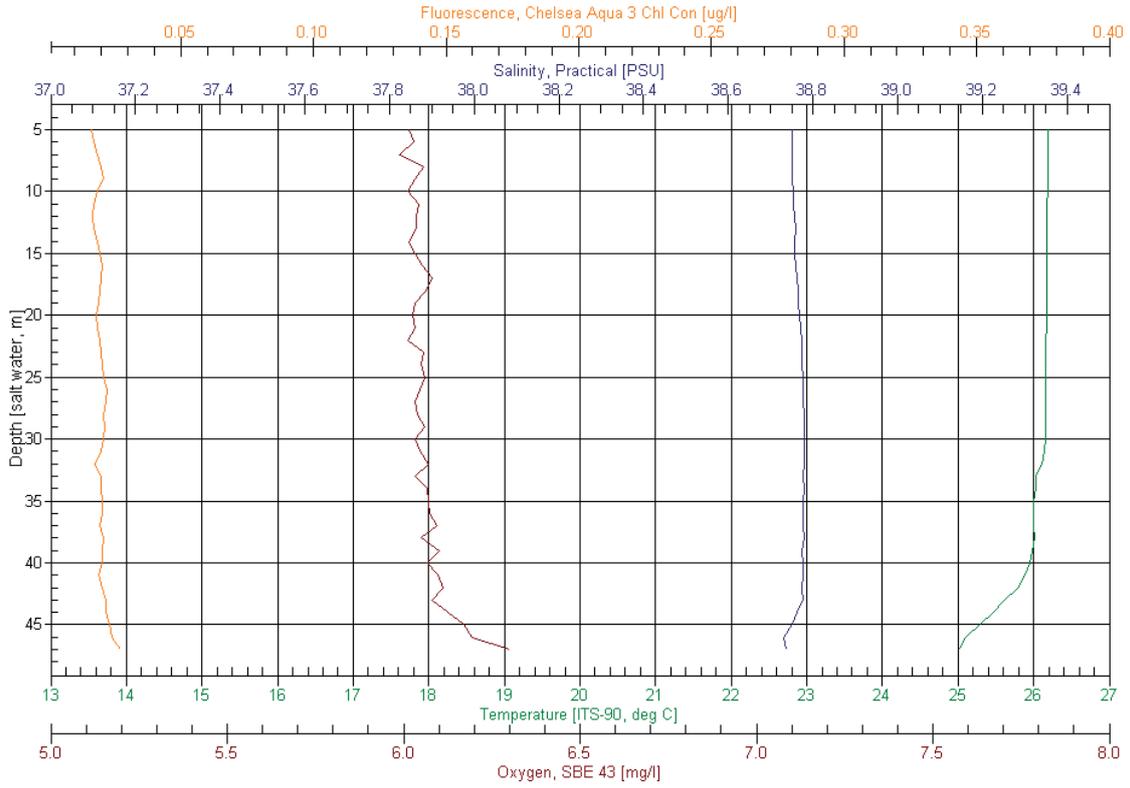
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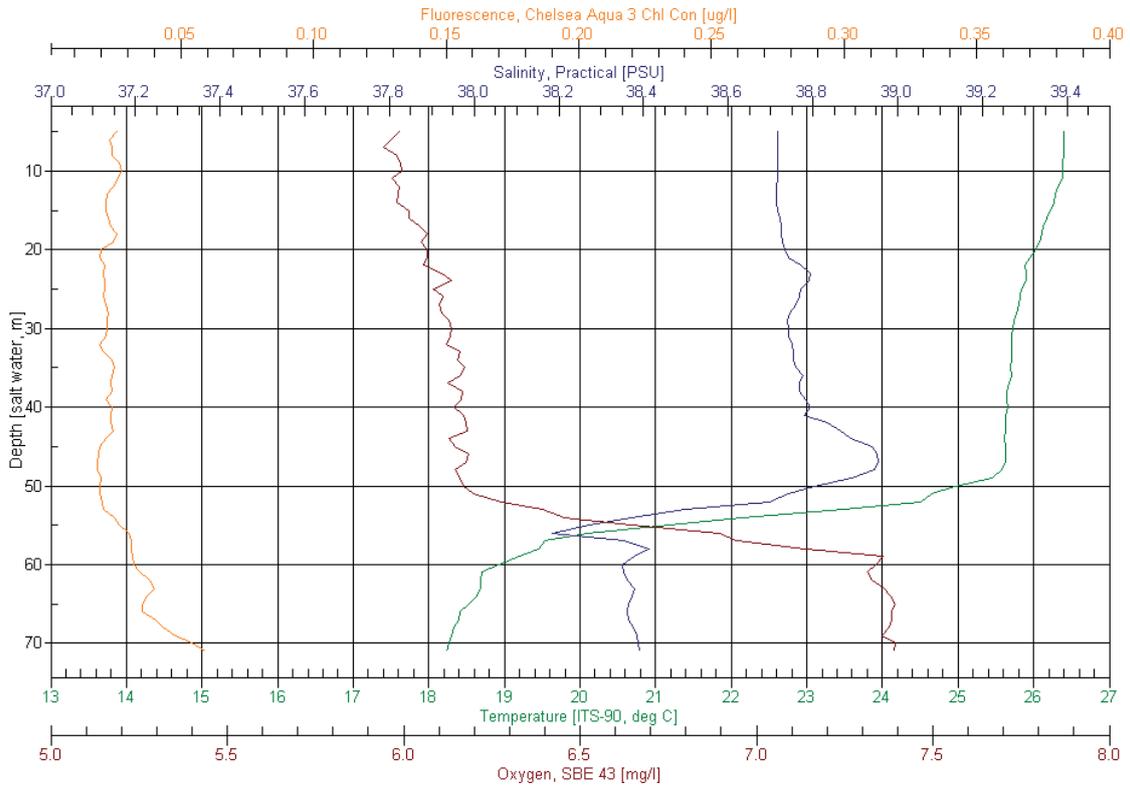
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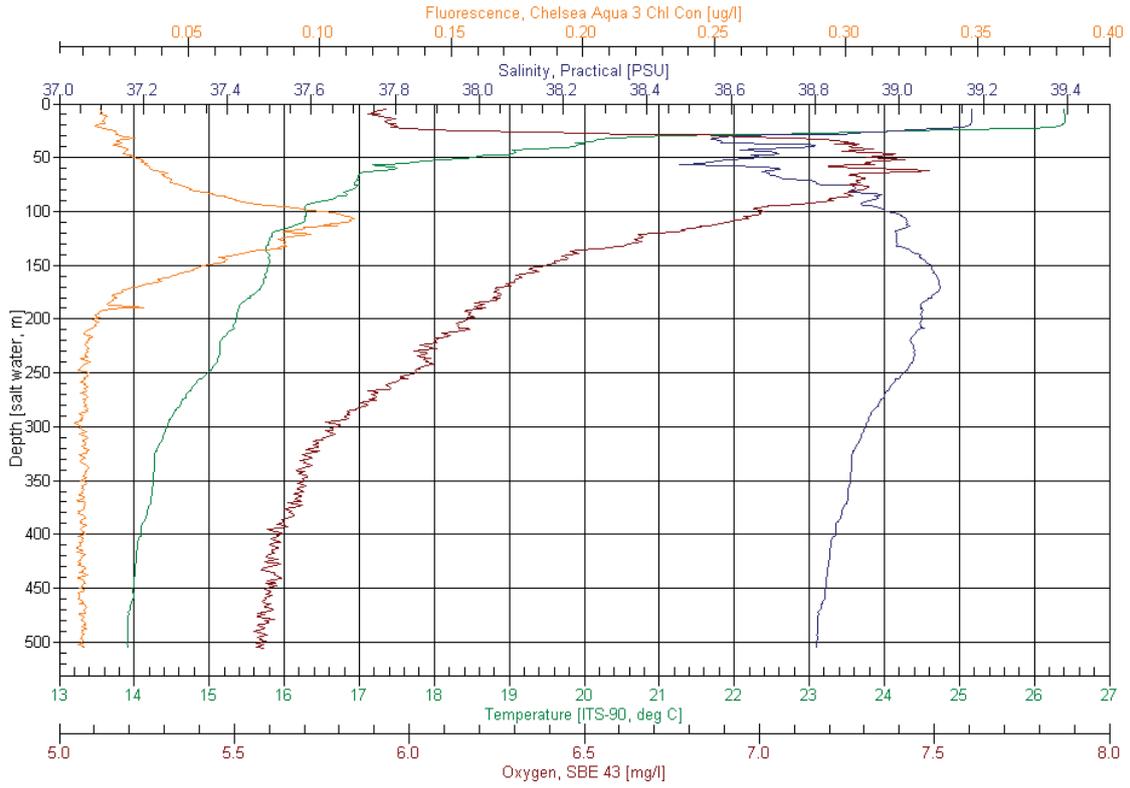
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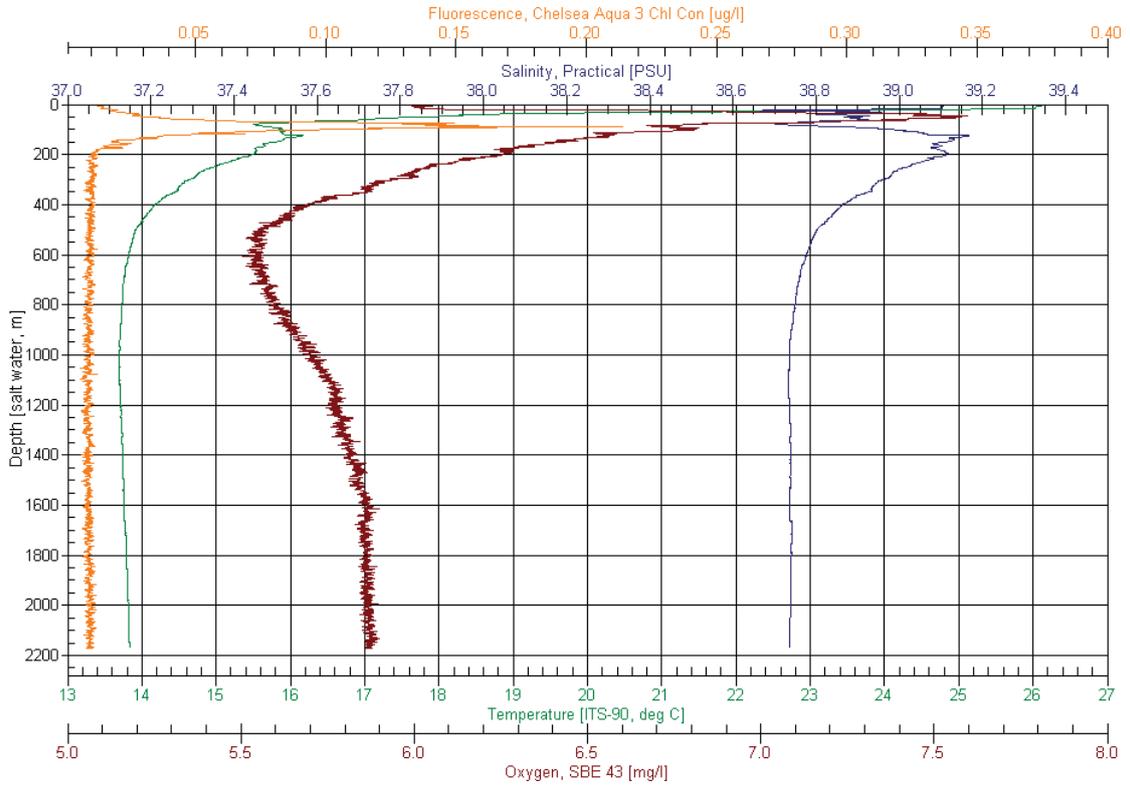
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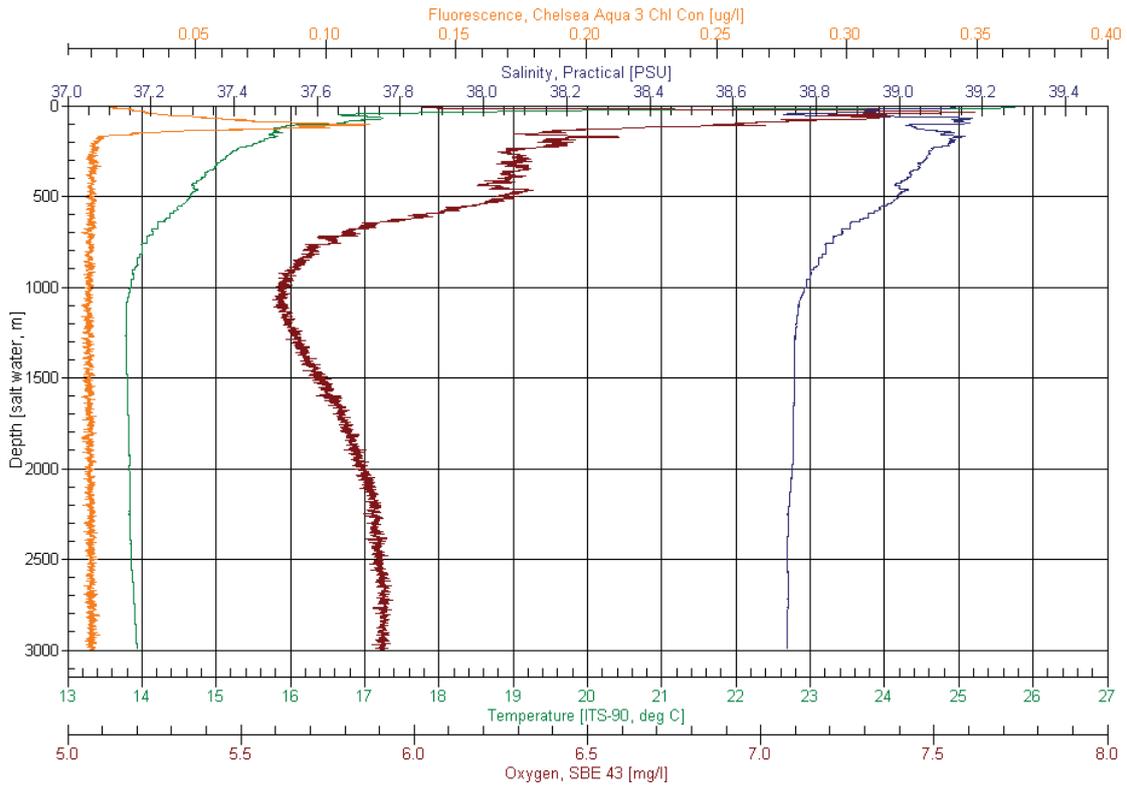
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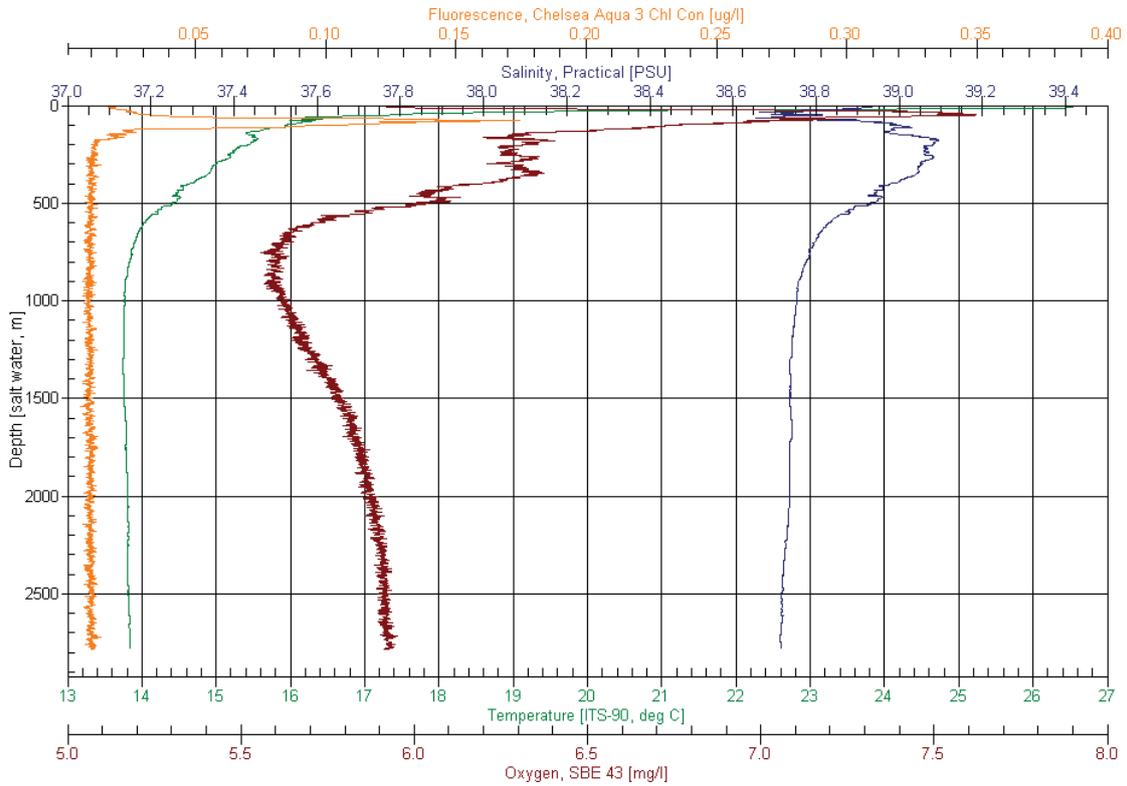
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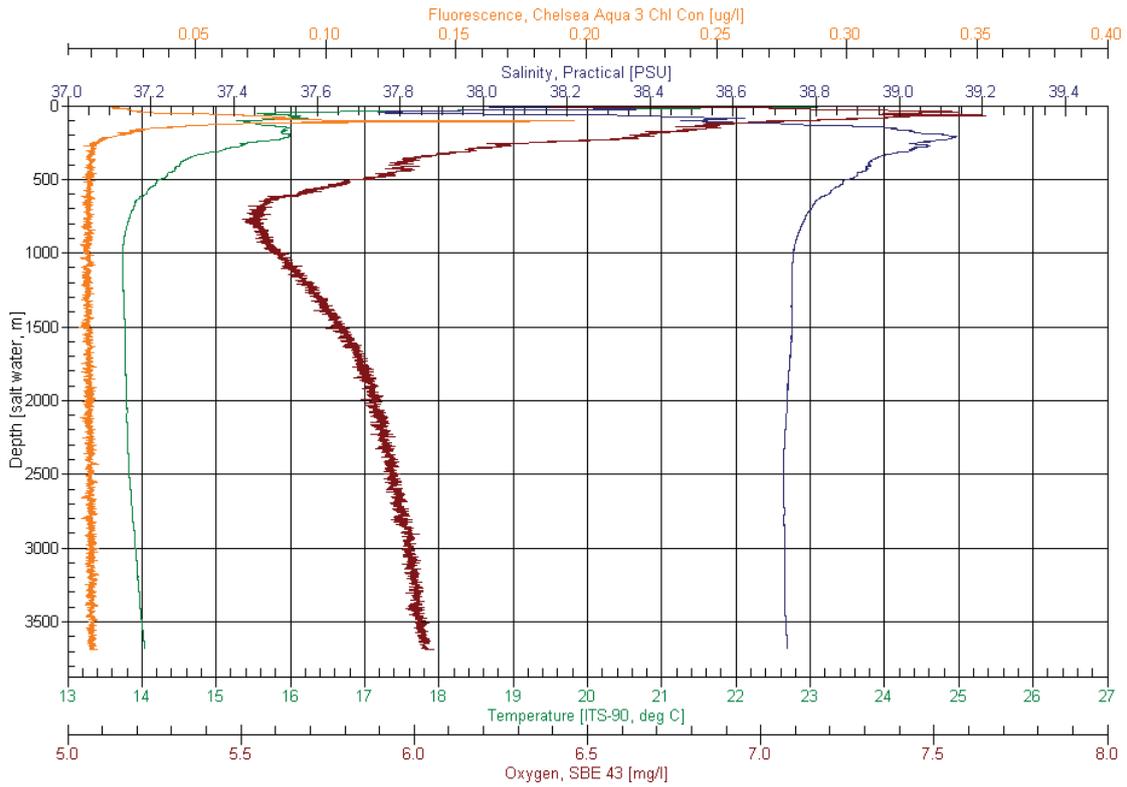
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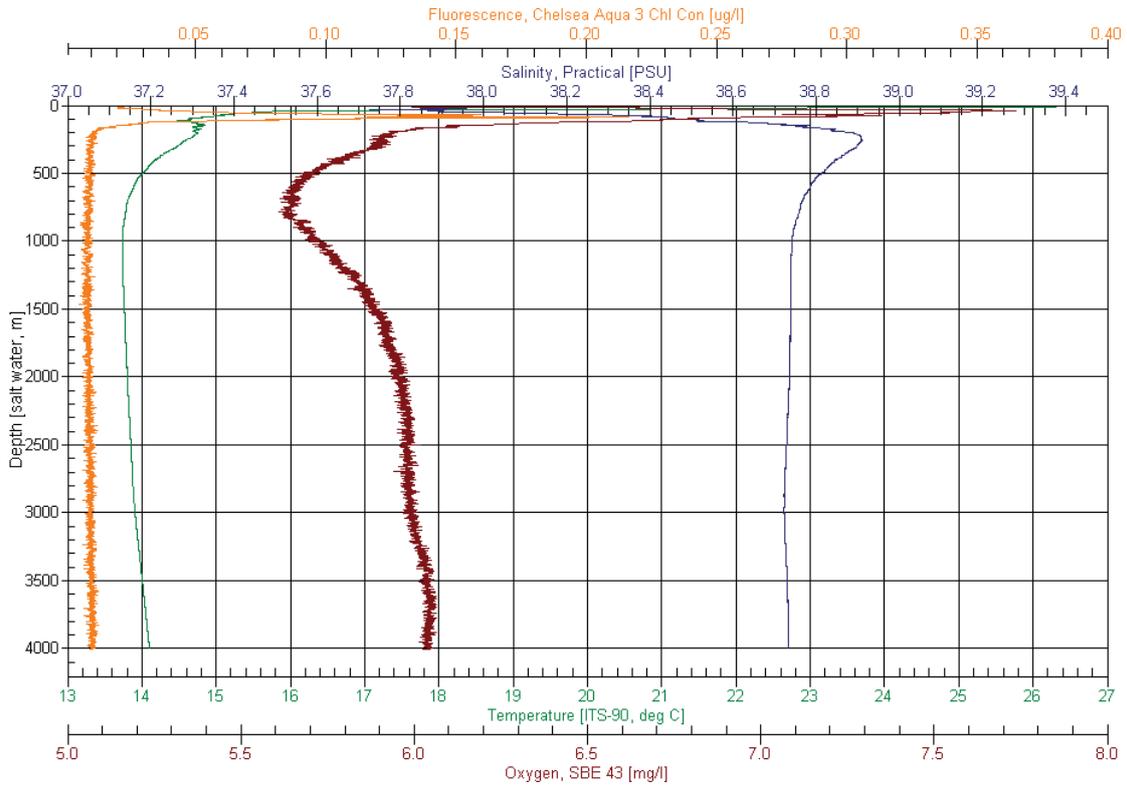
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L118.cnv



L119.cnv



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