

Manual for Marine Monitoring in the

COMBINE

Programme of HELCOM

Part C

**Programme for monitoring
of **eutrophication**
and its effects**

Annex C-2

Hydrographic and hydrochemical variables



ANNEX C-2 HYDROGRAPHIC AND HYDROCHEMICAL VARIABLES

NOTE - 31 July 2017

Replaced partly replaced by new guidelines for nutrients ([nitrite](#), [nitrate](#), [ammonium](#), [phosphate](#), [total nitrogen](#), [total phosphorus](#), [silicate](#)), [Secchi depth](#), [hydrogen sulfide](#), [pH](#), and [total alkalinity](#))

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Technical Annex I Temperature and salinity measurements of seawater. Acquisition of CTD data and sampling with rosette CTD sampler

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1. INTRODUCTION

This guideline is to fulfil the aims of the HELCOM monitoring programme. Following variables are measured:

Core variables:

- temperature
- salinity
- oxygen
- hydrogen sulphide
- nutrients: phosphate, total phosphorus, ammonia, nitrate, nitrite, (In the CMP nitrate and nitrite may be measured together), total nitrogen, silicate
- light attenuation

Main variables (In the CMP supporting studies):

- particulate and dissolved matter: POC, PON, POP, DOC, DON, DOP
- humic matter
- pH and alkalinity (only in combination with primary production measurements)
- current speed and direction

2. PURPOSE

As to set the background for all other measurements and to quantify the effects of anthropogenic activities the hydrographic/hydrochemical measurements shall be able to account for

- the winter pool of nutrients,
- annual cycles of hydrographic and hydrochemical parameters,
- space-temporal variations in the distribution of hydrographic and hydrochemical variables below the halocline,
- spatial distribution of salinity, oxygen/hydrogen sulphide and nutrient concentrations in the bottom water,
- water transport between the Baltic and the North Sea as well as between Baltic sub-basins and its effects on hydrographic and hydrochemical parameters,
- the supply of nutrients and nutrient limitation in coastal waters.

3. SAMPLING STRATEGY, EQUIPMENT AND TECHNIQUES

Different sampling techniques are necessary to resolve temporal and spatial variations of different variables. Master information such as position, date, time, weather conditions shall be recorded according to the reporting requirements (see below).

The sampling techniques can be grouped as follows:

Attended measurements: Sampling carried out at the stations with fixed position.

Data on the variables listed above may be collected using a CTD system which is attached to a rosette sampler or a cast of reversing water samplers (e.g., Niskin or Nansen bottles) equipped with reversing thermometers. It is strongly recommended that CTD system is equipped with the fluorometer for recording of chlorophyll-a measurements. The depths at which sampling should take place are as follows (in metres): 1, 5, 10, 15, 20, (25)*, 30, 40, 50, 60, 70, 80, 100, 125, 150, 175, 200, 225, 250, 300, and 400 metres, and as close to the bottom as possible (preferably less than 1 metre from the sediment surface to get near bottom oxygen concentration.) In the CMP, samples should be taken from 1 m below the surface or an integrated sample from 1m to the pycnocline (spring layer) and as close to the bottom as possible (less than 1 m). At least two samples should be collected. For unstratified water less than 10m depth, samples will be taken from 1m or an integrated sample is taken. The regional conditions and circumstances have to be considered, when choosing the sampling depth. National programmes should be coherent. The general description how to take water samples is given in **Technical Annex I**.

[(*) 25 m obligatory in the Kattegat and the Belt Sea]

The sampling depths for pH and alkalinity are those selected for primary production sampling.

Unattended measurements: Sampling carried out at automatic stations or onboard of ships-of-opportunity.

Basically these measurements shall comply with the same standards as the attended measurements. Preferably one or more of those sampling depths mentioned above should be used. However, it is recognised that technical or other reasons, e.g. dynamic conditions, also influence where the samples are taken.

4. PROCEDURES FOR OBSERVATION OR ANALYSIS

4.1 TEMPERATURE

Temperature is to be determined by temperature sensors as on a CTD (as well as in a flow-through system onboard ships-of-opportunity or on an automatic station) or by reversing thermometer. The measurements can be done from different platforms, i.e. research vessels, ships-of-opportunity and fixed platforms.

If CTD system is used, both temperature profile and temperature values at the moments when water samplers are tripped should be stored. Handling and calibration of CTD is described in Technical Annex I. Reversing thermometers should be calibrated using standard facilities at least once every two years. Mercury thermometer readings should be corrected using the Sverdrup formulae, as given by La Fond (1951). If digital reversing thermometers are used, one should follow the manufacturer's recommendations.

Unattended measurements require special consideration according to (UNESCO, 1993; Rantajärvi and Leppänen, 1994).

The required accuracy for thermometers and sensors used is $\pm 0.05^{\circ}\text{C}$, in CMP 0.1°C .

4.2 SALINITY

Salinity is to be determined by conductivity and temperature sensors as on a CTD (as well as in a flow-through system onboard ships-of-opportunity or on an automatic station) or from water samples by a laboratory salinometer. The measurements can be done from different platforms, i.e. research vessels, ships-of-opportunity and fixed platforms.

Handling and calibration of CTD is described in Technical Annex 1 to this document and in Annex B-9 Appendix 1. Samples for the determination of salinity must be collected with care, in order to ensure that no salt crystals are trapped in the cap. Sample bottles which ensure negligible evaporation must only be used, this has to be validated by each laboratory. Samples should be analysed using a salinometer that has been carefully standardised using IAPSO Standard Seawater. It is important that other kinds of standard seawater should be calibrated against the IAPSO Standard Seawater and not against a KCl standard on which IAPSO Standard Seawater is calibrated. It is also important to follow closely the manufacturer's recommendations on salinometer use.

In order to compute salinity values from salinometer conductivity ratio values, only the International Oceanographic Tables Vol. 3 (UNESCO, 1981) or related algorithms (UNESCO, 1988) should be used. The values produced by using either of these publications are derived from the Practical Salinity Scale 1978, and are, therefore, in practical salinity units. The algorithms should also be used to compute density values from the Equation of State for Seawater 1980. Density and other derived physical quantities may also be obtained using the Tables published in (UNESCO, 1987).

Salinity determinations from water samples can be carried out on shore, provided that the analyses are carried out within a few weeks after sampling.

The required accuracy for salinity is 0.05 psu, in CMP 0.1 psu.

4.3 OXYGEN

The basic method for the determination of oxygen concentration is the Winkler method (Grasshoff et al., 1983). The oxygen sensors may be used, however it is highly recommended to take water samples in areas with low oxygen concentration (below $2\text{ cm}^3/\text{dm}^3$).

Samples for the determination of oxygen concentration should be collected using appropriate water samplers, especially when collecting near bottom samples to ensure that sample is taken within one metre from the sediment surface. Oxygen sample must be the first one taken from the water sampler and the reagents should be added immediately.

Oxygen samples may be stored for up to 24 hours after adding the reagents and after complete fixation. The bottles should be kept in the dark and any change in temperature should be avoided. The bottles can be stored under a waterlock for up to one month.

If oxygen sensors are used (e.g., attached to the CTD), regular checks of the reproducibility of the sensor have to be carried out by titration of water samples by the Winkler method. At least the surface reading has to be calibrated. Oxygen sensors cannot be properly calibrated against moist air (100% saturation). Oxygen sensors may be poisoned by hydrogen sulphide. If a sensor has been lowered into hydrogen sulphide containing water, it must be checked immediately.

Minimum analytical requirements are as follows; detection limit 0.02 cm³/dm³, accuracy 0.03 cm³/dm³, for CMP 0.1 cm³/dm³.

4.4 HYDROGEN SULPHIDE

For small amounts, use the colorimetric method (Fonselius, 1983) and for large amounts, use dilution or volumetric titration according to Fonselius, 1983.

Hydrogen sulphide samples of moderate concentrations (<300 µM) may be stored for several days after adding the reagents. The bottles should be kept in dark and any change in temperature should be avoided.

Minimum analytical requirements are: simply note, by smelling at the water sample, if hydrogen sulphide is present or not.

The concept "Negative Oxygen" is a convenient way to express the amount of oxygen utilized for producing hydrogen sulphide by reduction of sulphate ions $2(\text{CH}_2\text{O}) + \text{SO}_4^{2-} \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O} + \text{S}^{2-}$. Assuming simple stoichiometry ($\text{S}^{2-} + 2\text{O}_2 \rightarrow \text{SO}_4^{2-}$) sulphide may be converted into "negative oxygen" in order to get comparable equivalents by multiplying the hydrogen sulphide result by two (one molecule of H₂S is equivalent with two molecules of oxygen). To convert from µmol/l of sulphide to cm³/dm³ of oxygen, multiply the µmol -result by the factor -0.044. This simplification, however, may not completely reflect natural conditions, because other oxidizable sulphur compounds may possibly be produced in significant amounts by microbial sulphate reduction under anoxic conditions.

4.5 NUTRIENTS

The determination of nutrients is based on colorimetric methods (c.f. Grasshoff *et al.*, 1983, Kirkwood, 1996).

Minimum analytical requirements are as follows:

- Detection limit µmol/l Accuracy requirements (IZI score <2)

- medium-high-low concentration
- phosphate 0.02 12% 25%
- nitrite+nitrate 0.1 12% 25%
- nitrite 0.02 12% 25%
- ammonia 0.1 12% 25%
- silicate 0.1 12% 25%

Low concentration can be defined as being within a factor of 20 of the respective detection limits.

The use of IZI score was established during QUASIMEME LPS (Laboratory performance studies). A IZI=2 was considered a minimum requirement for a satisfactory analysis. A IZI score 1 should be attainable.

It is recommended that interlaboratory intercomparison tests for nutrients should be carried out on a regular basis. Standard stock solutions containing concentrations $> 1 \text{ mmol/dm}^3$ may be stored for about an year if kept in DURAN glass ampoules, except for nitrite and silicate. Stock solution for nitrite may be stored for maximum half a year and glass ampoules should not be used for silicate.

It is strongly recommended that all laboratories participate in QUASIMEME II Proficiency Testing Programme.

Nutrient standard solutions are also recommended to be compared on a regular basis to either "Sagami Industrial Standards" or to primary standards which have been confirmed using Sagami standards or by intercalibration.]

Total nitrogen [Total nitrogen means nitrogen compounds measured after peroxy-disulphate oxidation.]

The peroxy-disulphate oxidation (Koroleff, 1983) with consecutive determination of the nitrate based on colorimetric methods (cf. Grasshoff *et al.*, 1983, Kirkwood, 1996) should be used.

Total phosphorus and total nitrogen

As an alternative for the methods listed above for total nitrogen, use digestion according to Valderrama (1981) and Koroleff (1983), for both total nitrogen and total phosphorus.

Silicate

Preference should be given to the ascorbic acid method by Koroleff (1983). Other methods intercalibrated within QUASIMEME can also be used.

Corrections for turbidity, salinity or hydrogen sulphide

Details are given in Part B, Annex B-9 and Annex B-10.

When nutrients are analysed using various kinds of autoanalyzers, the effect of sample turbidity is often omitted. The cuvettes of autoanalyzers are often too short to register the small error caused by turbidity. In

precise work with cuvettes longer than 2-3 cm, the turbidity of the sample should be measured when analysing phosphate and nitrite and also nitrate if a cadmium coil is used as reductor instead of cadmium grains.

4.6 PARTICULATE AND DISSOLVED MATTER

Particulate organic carbon and nitrogen (POC and PON), concentrated on filters, is measured using the high-temperature combustion technique after filtration on a 0.7 µm filter. Recommended filtered amount is 500 cm³ for open sea samples. Filters have to be burnt off at 450C for 4 hours prior to use. In order to avoid sedimentation and adsorption of particles onto the walls of the sample bottle, filtration within 2 hours is recommended. Blank filters are prepared by filtering water of the highest available purity under the same conditions as the samples. For calibration purposes dry acetoanilide standards, containing a well defined amount of carbon and nitrogen, are prepared.

The dissolved fraction (DOC/DON) is measured using a TOC analyzer (HTCO method according to Sugimura and Suzuki (1988) either directly on a filtrate (preferable technique) or on the untreated sample and calculated as the difference between the total and particulate fractions. In both cases inorganic carbon has to be removed by acidification to pH 4 and purging with an inert gas for 10 minutes prior to analysis.

4.7 HUMIC MATTER

Humic matter is measured on ordinary water samples using fluorescence spectroscopy at 350/450 nm excitation/emission wavelength (Coble et al, 1990; Wedborg et al, 1994). Samples can be stored in the dark for at least 2 weeks. It is strongly recommended that calibration is always carried out with a quinine sulphate solution in 0.5 M H₂SO₄ in order to ensure comparability between different projects. If true humic substance units are sought, a humic substance standard has to be prepared for every sea area.

4.8 LIGHT ATTENUATION

Vertical light attenuation is measured using a Secchi disc or an irradiance metre (400-700 nm).

Secchi depth should be measured at all stations whenever possible, i.e. in day light and when the sea is relatively calm. Light attenuation shall always be measured if primary production measurements are performed. The methods for measuring light attenuation are described in Annex C-5, Phytoplankton Primary Production, Chapter 7.

4.9 PH

pH should be measured, by the electrometric method with glass electrodes. Measurement should be made according to Grasshoff et al. (1983), Poisson et al. (1990) or UNESCO (1987) using thermostated samples. The temperature correction should be made using the temperature coefficient by Gieskes (1969). pH sensors (e.g., attached to a CTD) are also allowed.

Remarks: No depth correction should be applied because the pressure coefficient is not precisely known.

4.10 ALKALINITY

Alkalinity should be determined by potentiometric titration. Today most methods are according to Bradshaw et al. (1981) or a similar method, where the evaluation is done by curve fitting either before or after the equivalent point. The definition of the alkalinity is shown in Dickson (1981).

4.11 CURRENT SPEED AND DIRECTION

The information on water transport between the Baltic and the North Sea as well as between Baltic sub-basins is of great importance for the budget calculations. Therefore it is recommended to perform current measurements in the transition areas. Preferably measurements from fixed platforms or at buoy stations should be carried out and appropriate current meters should be used. Manufacturer recommendations must be followed. Data treatment according to UNESCO (1991; 1993).

5. QUALITY ASSURANCE

The QA programme should ensure that the data are fit for the purpose for which they have been collected, i.e. that they satisfy detection limits and levels of accuracy compatible with the objectives of the monitoring programme (c.f. text above).

Concerning QA and sampling c.f. Technical Annex I.

Concerning QA and chemical variables c.f. Part B.

6. REPORTING REQUIREMENTS

To be provided at a later stage.

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TECHNICAL ANNEX I TEMPERATURE AND SALINITY MEASUREMENTS OF SEAWATER. ACQUISITION OF CTD DATA AND SAMPLING WITH ROSETTE CTD SAMPLER

INTRODUCTION

Temperature and salinity can be considered the most important parameters in Physical Oceanography because of their conservative characteristics. By means of these two parameters one can identify the water masses, their evolution and propagation, even though other parameters such as chemical, biological or sedimentological, are extremely useful.

Ocean circulation is still, to a large extent, deduced from the density field which is defined by the temperature and salinity fields. Particular care must be taken in measuring these two parameters and especially the salinity whose variations, at low temperatures, have a greater influence on the density determination.

Previous method for measuring salinity was the Knudsen titration method, based on the assumption of the almost constant composition of sea water. The chlorinity of the sample was determined by titration with silver nitrate, and then the relationship $S = 0.030 + 1.8050 Cl$ gave the salinity expressed in grams per kg seawater. This method was used until the 1950's and after that was gradually substituted with the laboratory salinometer. With this instrument the salinity is determined by measuring the conductivity of the sea water sample and comparing it, directly or indirectly, to the conductivity of the "standard seawater".

In the 1960's and 1970's the era of "in situ" measurements started by means of profilers, called CTDs because the standard configuration is formed by Conductivity, Temperature and Depth(pressure) sensors. The introduction of CTD systems introduced new problems in computing salinity from the observed variables, conductivity, temperature and pressure. This led to the development of a new algorithm for salinity, "The practical salinity scale 1978"(PSS 78) and further "The International Equation of State of Seawater 1980" (UNESCO, 1981).

Salinity determination by titration is no longer scientifically acceptable. The bench salinometers are still used, and moreover they are recommended to be used for the control and calibration of the CTD conductivity sensor during cruises.

Until a few years ago, temperature measurements were done with reversing mercury thermometers. Now, generally, CTD profilers are used together with reversing digital thermometers with platinum thermoresistors. In some CTD systems, a combination of a thermistor, which has a rapid response time, with a platinum thermometer, which has a slower but more stable response and is inherently more accurate, is employed.

Methods have been developed to compensate for different time constants of the sensors of the CTD system, mainly by low pass filtering. Guidelines on how to handle CTD data have been introduced (UNESCO, 1988, UNESCO, 1991).

In conclusion, the T and S measurements changed from a discrete to an almost continuous type. Generally the data acquisition speed is 24 Hz, which means 24 samples of each parameter every second. In this way, high resolution in the description of the thermohaline structure of water masses is obtained.

The gain in the accuracy of the measurements is from +/-0.02 PSU for titrations to +/- 0.005 PSU for CTDs and from +/-0.02 ° C for mercury reversing thermometers to +/- 0.004 ° C for CTDs.

Particular mention must be made of the automatic temperature and salinity acquisition systems, for the great quantity of information (time series) that they give, although there is a certain loss in precision. These systems are normally used in moorings together with current meters, sediment traps, etc. Particular instruments in this category are the thermo-salinometers. These instruments can achieve good quality measurements, and since data acquisition is autonomous, they can be used much more widely, for example, on board passenger and commercial ships but for surface samples only.

MATERIALS REQUIRED

EQUIPMENT

A CTD probe preferably equipped with double sensors of temperature and conductivity since this configuration will be a guarantee of no loss of data and a quality check of the data. A broad- beamed altimeter or a bottom switch is recommended in order to be able to go very close to the bottom but still ensure security of the instrumentation.

Other sensors recommended are the oxygen sensor, fluorometer, transmissometer, scatterometer and PAR (Photosynthetically Available Radiation).

A Rosette multisampler with capacity of 12 or, better, 24 bottles of at least 1.7 l volume.

Water sampling bottles. The water samplers shall be clearly marked with individual numbers. This will facilitate logging of any malfunctions, in most cases leakages.

A laboratory salinometer with thermostatic bath and an accuracy better than ± 0.002 PSU.

At least two reversing digital platinum thermometers with traceable calibration.

Personal Computers for the data acquisition and for the data processing.

An analogical tape recorder for a playback of the cast (optional).

SUPPLIES

Bottles for salinity samples. Glass bottles with stoppers with plastic under-stoppers are recommended. Particular care must be taken in closing the salinity bottle samples. Do not completely fill the bottles since

thermal expansion can cause damage to the stopper or bottle. Before storage wash the bottles with fresh water.

Vials of standard seawater for the salinometer calibration (35 PSU, P series) and for the in house quality control (10 PSU, H series).

PROCEDURES

DATA ACQUISITION

There are many protocols for CTD measurements (WOCE, 1991, UNESCO, 1994, UNESCO, 1988). Starting from what is suggested by the previous protocols and taking into account the field experience from the BMP, the following protocol is proposed.

When the CTD is on deck turn on and note the CTD pressure and temperature on the log book (see the CTD station log sheet given in **Attachment 1**).

The CTD and Rosette package must be lowered a few meters below the sea surface for at least two minutes before starting the measurements. This is of special importance if using an oxygen sensor. After a few minutes the CTD is brought back to near the surface and the measurement starts. If the sea state is rough it is recommended to start the downcast from a few meters below the sea surface to prevent the bubbles of the breaking waves entering the conductivity cell.

It is recommended to keep the lowering speed as constant as possible and between 40 and 120 cm/s.

If the CTD is equipped with an Altimeter or a bottom switch, lower the CTD and Rosette package as close to the bottom as possible. Enter in the log book the distance to bottom, CTD depth and sonic depth and all the other information required by the CTD log.

Preferably the rosette bottles should be fired at the selected depths during the up-cast as to be able to obtain an undisturbed ctd profile during the down-cast.

The first bottle, to be closed near bottom, must be equipped with two reversing thermometers. It is recommended to use the new reversing digital platinum thermometers, and in this case, waiting for at least 15 seconds before starting the recovery.

Almost all the data acquisition software creates a Bottle file (a file with pressure, temperature and conductivity values measured at the moment of firing the bottle, or an average around that moment), nevertheless it is recommended to write on the CTD log the bottle number and the pressure, temperature and salinity displayed by the unit, at the moment of firing the bottles as to ensure a correct bottle firing sequence.

When the CTD is back on the deck, note on the CTD log the pressure and temperature. The pressure value must be approximately the same as that read before the cast, differences are due to thermal and mechanical hysteresis of the pressure sensor. Do not use deck pressure as offsets to correct pressure. Deck pressure should only be used as consistency check against laboratory-measured historical drift. Flush the sensors with freshwater and deionized water to prevent formation of salt crystals. The conductivity cell

must be kept as clean as possible. Do not touch the inside walls of the conductivity cells or the electrode surface with hands or any other physical means. Protect the CTD from the direct sun radiation and each sensor according to the specific manufacturer's instructions.

Before samples are drawn from a water sampling bottle, one must make sure that it is not leaking. This is done by opening the tap without opening the air vent on the top of the bottle. The bottle is tight if no water comes out of the tap. Leakages should be logged.

When all samples have been taken the water sampling bottle must be emptied for remaining seawater and the CTD be flushed again with fresh water.

Note on the CTD log all particular events that happened during cast.

Make a backup of the data immediately at the end of the cast, before carrying out another operation.

MAINTENANCE

At the termination of a cruise the CTD underwater unit must be thoroughly washed with freshwater. The water sampling bottles must be filled with (or if possible dipped in) freshwater as to prevent any formation of saltcrystals inside the bottles.

Between cruises (and whenever environmental conditions require it) it is important that the CTD underwater unit and rosettsampler are stored in a way that prevents contamination.

CALIBRATION

Temperature, conductivity and pressure sensors must be calibrated before and after a long cruise, or at least once a year by sending them to the manufacturer or to a calibration centre. It is very important to keep the calibration series of each conductivity and temperature sensor to reconstruct the drift history of each sensor.

During the cruise a check of the temperature sensor must be made at every cast by means of a pair of reversing thermometers mounted on a bottle fired in a well mixed layer. A number of salinity samples (preferably from all water bottles or at least from well mixed layers) must be taken to cover the range of temperatures, salinities and pressures encountered on each cast in order to check the conductivity sensor which drifts sufficiently to require field calibration.

The salinity values obtained by the laboratory salinometer must be inverted to an *in situ* conductivity using the CTD temperature and pressure. The conductivity values so obtained will be compared to the CTD conductivity values (for more details see the UNESCO, 1988).

DATA PROCESSING

Attention must be paid to data processing in order to consider the change of temperature standard from T68 to T90 ($T68 = 1.00024 T90$). Software, for the CTD data acquisition and processing, that manufacturers

give to the customer together with the instruments, generally follow the UNESCO recommendations (UNESCO, 1988).

They can be summarised in the following steps.

1. Convert the digitised voltages or frequencies measured by the sensors to physical units.
2. Correct the data by applying the calibration coefficients, the pressure offset and the "slop" and "offset" correction coefficients deduced from laboratory calibrations and salinity bottles samples.
3. Time lag correction. The sensors have very different time responses, the pressure and conductivity are fastest, followed by the temperature, while the oxygen is slowest. Oxygen must be advanced for a few seconds relative to pressure. Similarly, the temperature must be advanced relative to pressure in order to reduce salinity spikes. Particular care must be taken in this operation.
4. Mark "bad" the scans with values which deviate by more than a given number of standard deviations. Also the scans reversing values of pressure or with a CTD velocity less than a given limit must be marked "bad."
5. Apply different kinds of filters to smooth spikes in the data. Particular care must be taken to avoid displacement in the data.
6. If in the CTD configuration there is the oxygen sensor, compute the oxygen.
7. Average the data every 0.1 decibar.
8. Compute salinity, density and other oceanographic parameters.

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ATTACHMENT 1: CTD STATION LOG

Country Ship Station name Station number
 File name
 Cruise Date Operator CTD nr

CTD offset control	On deck press	On deck temp
Before lower		
After lower		

Position	Latitude	Longitude	Time	Sonic depth
Start				
Bottom				
End				

Water samples CTD raw data from deck unit

Btl depth	Btl nr	press	temp	salinity	salinity samples nr	Thermom. nr	Temperature

Comments : _____