MAREANO Chemistry Program

Description of methods for sampling and analysis of seabed sediments

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INTRODUCTION

The Institute of Marine Research (IMR) and the Geological Survey of Norway (NGU) are responsible for MAREANO's Chemistry Program. IMR and NGU carry out the sampling of seabed sediments, and are responsible for the analysis of these samples on a range of physical- and inorganic chemical parameters, as well as the most relevant types of organic and inorganic environmental contaminants.

This *Methods document* describes the methods used on cruises for the collecting of samples, the methods used for the analyses of these samples at various laboratories, and the methods used for the quality assurance of the results. This document provides the up-to-date method descriptions. The *Methods document* together with the *Chemistry database* represent the documentation for MAREANO's Chemistry Program. Both files are published on www.mareano.no/en/download-data/kjemidata where they are updated each year in January.

SAMPLING

Bathymetric maps, video data and information from shallow seismic surveys (where available) are used in mapping suitable locations for sampling seabed sediments during cruises. The sampling focuses also on localities with fine-grained sediments, because they represent areas with stable sedimentation, and these sediments usually contain the highest levels of environmental contaminants.

The Chemistry Program collects two main types of samples:

1. ***surface sediment*** – single samples of the uppermost sediment layer on the seabed in contact with the water
2. ***sediment core*** – continuous core of sediment from the seabed-surface (in contact with the water) down to a depth of up to 50 cm.

Sampling equipment

A multicorer is used in collecting 6 sediment cores of up to 50 cm in length (Figure 1). Alternatively, a boxcorer (Figure 2) is used in collecting 4-6 shorter cores of seabed sediment. It is necessary to collect several sediment cores, because the various analyses require different pretreatments of the samples as well as a sufficient amounts of sample material.

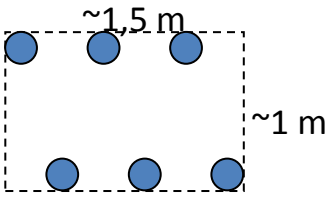

Figure 1. Photo showing the multicorer on deck after sampling. Drawing showing dimensions and placement for the 6 cores.

In 2006 and 2007, a multicorer produced at NGU was used for collecting sediment cores in tubes having an internal diameter of 100 mm. Starting in 2008, a multicorer from KC-Danmark (Model 73.000) is used in the collecting of sediment cores. This multicorer has 6 tubes (transparent PVC-glass) with an internal diameter of 106 mm. Figure 1 shows this multicorer filled with sediment on deck. It is thus possible to collect up to 6 sediment cores at each station, while an approved sampling must provide at least 2 good sediment cores.

A boxcorer (Figure 2) is used for sampling where the multicorer cannot be used. To obtain sediment cores from the boxcorer, tubes from the multicorer are forced down into the sediments resulting in a minimum of 2 (short) sediment cores. It is possible to obtain up to 6 sediment cores from a good sample in the boxcorer. The sediment cores from a boxcorer are processed in the same way as cores from the multicorer (see next section).

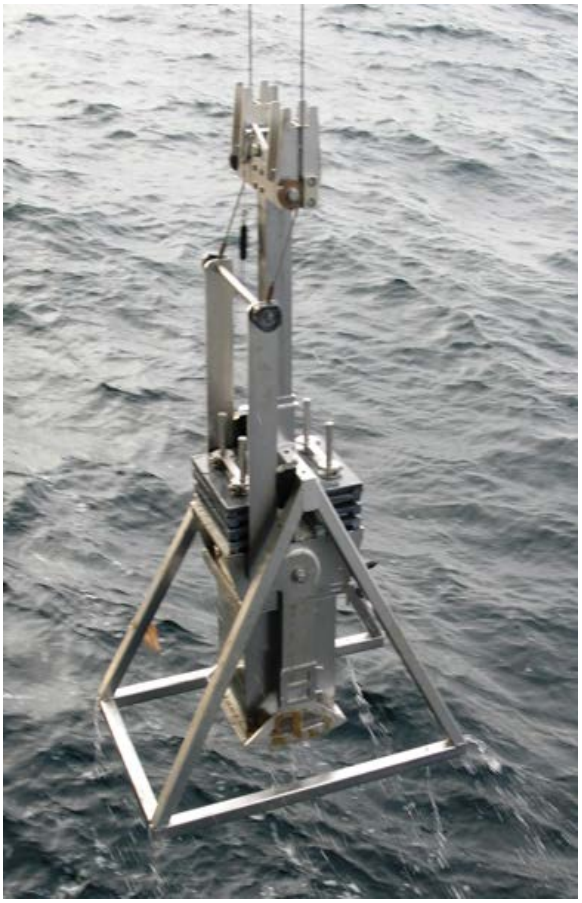

Figure 2. Boxcorer being recovered.

Figure 3. Van Veen grab.

Sometimes a Van Veen grab (Figure 3) is used in collecting samples of surface-sediment when it is not possible to use other equipment.

Selecting samples from sediment cores

The multicorer has 6 fixed positions for the sample tubes (marked 1-6). These positions correspond to the numbers 1-6 in the decklog. This identification is used throughout the logging, sample identification and reporting. The same procedure is used when working with a boxcorer, except that the cores taken from a boxcorer are numbered randomly.

1. Following the recovery of the multicorer, the need for a repeated lowering of the equipment is assessed. This assessment is made everytime at every station by the responsible geologist/chemist who is on duty. The minimum requirement for a successful sampling is the recovery of 2 sample tubes filled with sediment (corresponding to cores A and B below), but preferably 6 filled sample tubes where possible. If the multicorer was handled wrongly (e.g. too-high speed, stopped prematurely, etc.) or there were technical problems, a new attempt at lowering the rig may be made. But if unsatisfactory results with the multicorer are caused by other, more risky factors, such as the local composition of the seabed (e.g. rock, gravel or coarse sand) or bad weather, it may be better to stop using the multicorer in order to protect the equipment which is designed for soft sediments.

   At each station, up to 3 attempts may be made at sampling with the multicorer. The person responsible for sampling must check the results from sampling with the grab and boxcorer, before the multicorer is employed. These results are recorded in the deck log and are used to decide on whether or not to employ the multicorer. Furthermore, when the boxcorer provides a good quality sample, it must remain on deck for possible sampling of sediment cores. This latter situation may arise when the multicorer does not provide acceptable recovery, and in particular when the station is deemed important for environmental analyses.

2. The sample tubes are washed on the outside while still in place in the multicorer. This is done to provide good visible inspection of the tube's contents.

3. A photograph is taken of each sample tube filled with sediment and with water standing atop the sediment. A ruler along the full length of the tube and a label with the tube-ID should also show in the photograph.

4. The length of each sediment core is measured and recorded in the deck log.

5. The sample tubes with the sediment cores are removed from the multicorer, after which they are processed as described below. The sequence of sample tubes with sediment cores is determined by the quality and length of each sediment core, with quality referring to the sediment not having been disturbed during sampling, and a column of water remaining atop the sediment in the sample tube.
   - Core A: the longest core is selected for inorganic chemistry (grain size, TC-TOC-TS, metals), and for possible dating by ^{210}Pb and ^{137}Cs, and potentially by ^{14}C. This sediment core is sliced in subsamples onboard the ship.
   - Core B: the next-longest core is selected for organic chemistry. This sediment core is sliced in subsamples onboard the ship.
   - Core C: selected for XRI and possible scanning of the core (gamma, magnetic susceptibility). This sample tube is sealed at the bottom and over top of the water column (atop the sediment), and stored upright. Archive storage is done at NGU's National Drill Core and Sample Centre (NBPS) in Løkken. X-ray inspection (XRI) is used to reveal any sedimentary structures or bioturbation, providing important information for the selection of sediment cores for analyses.
   - Core D: selected as a backup core for NGU. This sediment core is sliced in subsamples onboard the ship.
   - Core E: selected for storage (sediment archive). The whole core is sealed and stored as described for Core C.
   - Core F: selected for storage (sediment archive). The whole core is sealed and stored as described for Core C.

6. Processing Cores A and D (sliced for inorganic analyses):
   a. The sediment core is transferred to the slicer and is measured again. This measuring is necessary because some of the sediment may waste when transferring the core from the sample tube to the slicer.
   b. The measured length is recorded on the sampling form together with information on the sediment's consistency and other data.
   c. The core is carefully cranked up to the opening in the slicer without disturbing the sediment surface. The sediment's top 1-cm-thick layer must protrude out of the slicer.
   d. Photograph the top surface together with a label identifying the cruise, sampling station and sample tube. (Figure 4).
   e. The core is sliced in 1-cm-thick sections using a plastic tray (not a metal tray!). A description of the sediment in each section is recorded in the deck log.
   f. The sample section (subsample) is transferred directly into a plastic bag with a zipper-lock. The bag is sealed with a minimum of air in the bag.
   g. The bags are identified with printed labels (waterproof material and ink) containing: cruise-number, station-number, sampling-equipment|equipment-number|core-number, sample depth from-to in duplicate, and NGU's unique sample-number.
   h. All plastic sample bags from one core are packed together in a cardboard box which is identified with cruise-number, station-number, sampling-equipment|equipment-number|core-number, and this box is stored in the ship's freezer room. If space allows, subsamples from two cores can be packed together (separated by a sheet of paper) in one cardboard box. All cardboard boxes containing frozen samples for inorganic analyses are shipped to NGU upon completion of a cruise.

Figure 4. Top 1-cm of sediment core protruding from the core slicer. Surface sample for inorganic analyses.

7. Processing Cores C, E and F (stored whole):
   a. These sediment cores are sealed in the sample tubes with a plastic lid and grey tape, registered on the sampling form, and stored as cool as possible in an upright position on deck and secured against falling and soiling. These cores are not to be frozen because freezing will likely destroy sediment structures. Meanwhile it is important to have a complete water column in the tube atop the sediment in order to avoid any disturbances to the sediment. Each tube is identified with cruise-number, station-number, sampling-equipment|equipment-number|core-number written on the tube's lid.

8. Processing of Core B (slices for organic analyses):
   a. The sediment core is transferred to the slicer and is measured again. This measuring is necessary because some of the sediment may waste when transferring the core from the sample tube to the slicer.
   b. The measured length is recorded on the sampling form together with information on the sediment's consistency and other data.
   c. The core is carefully cranked up to the opening in the slicer without disturbing the sediment surface. The sediment's top 1-cm-thick layer must protrude out of the slicer.
   d. Photograph the top surface together with a label identifying the cruise, sampling station and sample tube.
   e. The core is sliced in 1-cm-thick sections using a metal tray (not a plastic tray!). (Figure 5). A description of the sediment in each section is recorded in the deck log.
   f. Each sample section (subsample) is packed in aluminum foil. Each sample should be wrapped as tight as possible in the foil, but without squeezing out or losing any material. Take care in particular with the surface sample because of the high water content.
   g. Identify each aluminium package with an adhesive label (use a pencil not a marker) containing multicorer-number, station-number, date, core-number, and sample-depth from-to in duplicate.
   h. Each foil-wrapped sample is placed inside a small plastic bag without any further identification.
   i. All small plastic bags with individual samples are collected inside a bigger plastic bag which can contain about 10 individual samples. Each of the bigger plastic bags is identified with multicorer-number, station-number, date, and core-number.
   j. Repeat point g until all samples from one core are packed.
   k. Collect all bigger plastic bags from one core in a box, mark the box, and store the box in the ship's freezer room. All cardboard boxes containing frozen samples for organic analyses are shipped to IMR upon completion of a cruise.

Figure 5. Top 1-cm of sediment core protruding from the core slicer. Surface sample for organic analyses.

9. Upon arrival to port, all boxes with Cores B are shipped frozen to IMR, and all boxes with Cores A and D are shipped frozen to NGU. All sealed sample tubes with whole sediment cores are shipped unfrozen to NGU.

10. All completed sampling forms are archived at NGU while copies of these forms are sent to IMR upon completion of each cruise.

ANALYSES

The analyses carried out on samples of seabed sediment are divided between IMR and NGU as follows:

- Hydrocarbons (PAH and Total Hydrocarbon Content - THC), PBDE, and chlorinated contaminants (PCB and pesticides) are analysed by IMR,
- Inorganic components (main- and trace elements incl. heavy metals and barium) and other sediment parameters (grain size, Total Carbon – TC, Total Organic Carbon – TOC, Total Sulphur – TS) are analysed by NGU. In addition, NGU is responsible for:
  - Analyses of ^{210}Pb and ^{137}Cs, used for dating of sediments, carried out by the Gamma Dating Centre (GDC) at the University of Copenhagen, Denmark.
  - Analysis of ^{14}C, used for dating of sediments, carried out by the ^{14}CHRONO Centre (14CC) at Queen's University in Belfast, Ireland.

Grain size, TC-TOC-TS and metals

These analyses are carried out by NGU's Laboratory using accredited methods (Table 1). Sample preparation includes freeze-drying and measuring the moisture content of each sample. Aliquots of freeze-dried sample are used in determining grain size (by Coulter and gravimetry) and TC-TOC-TS (by LECO), and in acid-extraction for subsequent elemental analyses (by ICP-AES and CV-AAS).

For quality control, two standard samples (natural materials: marine sediments from the Trondheim fjord and from Nordkynn) are added for each set of 30 samples in all batches. This is particularly important when comparing results from different batches of analyses.

Table 1. Methods used in analyses of MAREANO samples – NGU.

Analytical method	Parameters analysed	Operator	Instrument	Description of method Accredited: yes/no
Freeze drying	Moisture content	NGU	Hetosicc freeze dryer CD 53-1	NGU-SD 7.2 – no
Grain size analysis	< 2.000 – 0,4 µm > 2.000 µm using gravimetric measurement (not accredited)	NGU	Coulter LS 200	NGU SD 5.11 – yes
LECO	Total carbon (TC), Total organic carbon (TOC) Total sulphur (TS)	NGU	Leco SC 444	NGU SD 2.14 – yes NGU SD 2.15 – yes NGU SD 2.16 – yes
Acid extraction		NGU	CertoClav Sterilizer GmbH CV-EL 18LGS	extraction with 7 N HNO_3 in an autoclave (using Norwegian Standard - NS 4770) – yes
ICP-AES	Cr, Cu, Ni, Zn, Li, Pb, Cd, As and 25 main- and trace elements	NGU	ICP-AES Perkin Elmer Optima 4300 Dual View	Method described in NGU-SD 2.11: *ICP-AES - analyse av ekstrakter* – yes
CV-AAS	Hg	NGU	CETAC M-6000A Hg Analyzer.	Method described in NGU-SD 2.13: *Atomabsorp-sjonsanalyse (CV-AAS) av Hg i ekstrakter* – yes
	^{210}Pb dating, ^{137}Cs analysis. ^{14}C dating	External - GDC External – 14CC		No No

Hydrocarbons, brominated flame retardants and chlorinated contaminants

These analyses are carried out by IMR's Laboratory. Accredited methods are used for the analysis of polycyclic aromatic hydrocarbons (PAH) in whole sediment cores, and for the analysis of total hydrocarbon (THC) in samples of surface sediment (Table 2). Brominated flame retardants (poly-brominated diphenyl ether – PBDE) and chlorinated contaminants (PCB and selected pesticides) are only analysed in a selection of surface sediment samples.

The samples are air-dried at room temperature, and a certain amount (usually 10 g) of dry material is used for analysis. Internal standards are added to the sample batches for the analysis of PAH (7 deuterated PAHs with different molecular weight), of PBDE (PBDE-139 and ^{13}C-labelled PBDE-209), and of chlorinated contaminants (PCB112). For the analysis of THC an external standard (base oil HDF200) is used.

The sediment is subjected to extraction (using accelerated solvent extraction – ASE), treatment with copper (to remove sulphur), and to cleaning (using silica solid-phase extraction columns). For the analysis of PBDE and PCB an extra cleaning is carried out directly in the ASE-cell using alumina. Subsequent to cleaning, the extracts are dissolved in a known volume of solvent, followed by analysis as described in Table 2. The analytical data obtained by IMR are combined with those from NGU to provide an overall interpretation of results.

Table 2. Methods used in analyses of MAREANO samples – IMR.

Analytical method	Parameters analysed	Operator	Instrument	Description of method
GC-MS	PAH (48 compounds)	IMR	Dionex ASE300; GC HP-6890 with Agilent N-5975 mass spectrometer (EI-SIM mode)	Accredited IMR method O21
GC-FID	Total hydrocarbon (THC)	IMR	Dionex ASE300; GC HP-6890 with flame-ionization detector (FID)	Accredited IMR method O22
GC-MS	Brominated flame retardants (26 PBDE compounds)	IMR	Dionex ASE300; GC HP-6890 with Agilent N-5973 mass spectrometer (NCI-SIM mode)	Non-accredited method
GC-ECD	PCB (10 compounds), HCH (3 isomeres), HCB, TNC, DDT (3 compounds), dieldrine	IMR	Dionex ASE300; GC HP-6890 with micro-ECD detector	Non-accredited method

Chemistry database

The results from all the analyses carried out on MAREANO's samples of seabed sediment, and on equivalent samples collected by IMR in 2003-2004 (before MAREANO officially started in 2005), are assembled in the *Chemistry Database*. This database consists of a downloadable Excel-file published on MAREANO's website. The database is updated each year in January.

The *Chemistry Database* contains an INFO-page with detailed meta-data on all analyses carried out in MAREANO's Chemistry Program.

QUALITY ASSURANCE

The results of all analyses carried out by NGU's Laboratory and by the external laboratories are reviewed prior to reporting and publication. This includes comparing results from similar analyses on different batches of samples using two internal standards (marine sediments from the Trondheim fjord and from Nordkynn). These standards are inserted for each 30 samples in all sample batches.

Results from the isotope analyses used for dating are evaluated together with other inorganic chemistry data and other available information (e.g. video, shallow seismics, XRI).

Quality control for the accredited methods used by IMR's Laboratory follow the requirements specified by Norwegian Accreditation (NS-EN ISO/IEC-17025). These same requirements are also used by IMR for its non-accredited analytical methods, including:

- Regular participation in inter-laboratory comparison tests (SLP) organised by Quasimeme twice each year for PAH, PBDE and chlorinated contaminants in sediments, and by Setoc twice each year for THC in sediments. The results from SLP-exercises may not exceed the uncertainty for each method.
- Regular analyses of NIST-certified reference materials for selected PAH-compounds and chlorinated contaminants in sediment, including registration of these results in the control account. Deviation of the results with regard to the certified value may not exceed the uncertainty of the analytical method.
- The use of IMR's Laboratory internal reference material (LRM) – a sediment sample that is analysed every time for all reported compounds or with every new preparation of samples. The results are registered in a control account and may, over time, not deviate from the established average-value with more than 3 standard deviations for each run.
- The results are verified and, if necessary, corrected for values obtained for blanks that are analysed in each of the sample batches.

In addition, the final data reported by each laboratory are evaluated against other available information, such as known environmental aspects and geographical considerations, including e.g. content of TOC and comparison with other cores or samples from the same area.