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Agenda item 12: Harmonization and standardization of IMAP Pollution Cluster Monitoring

Monitoring Guidelines/Protocols for Sampling and Sample Preservation of Sediment for IMAP Common Indicator 17: Heavy and Trace Elements and Organic Contaminant

UNEP/MAP
Athens, 2021

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Annexes

Annex I: UNEP/MAP (2011). UNEP(DEPI)MED WG.365/Inf.9. Manual on sediment sampling and analysis (1.1)
Annex II: References.

Note by the Secretariat

In line with the Programme of Work 2020-2021 adopted by COP21 the MED POL Programme has prepared the Monitoring Guidelines related to IMAP Common Indicators 13, 14, 17 and 20 for consideration of the Integrated Meeting of the Ecosystem Approach Correspondence Groups on Monitoring (December 2020), whilst the Monitoring Guidelines for Common Indicator 18, along with the Monitoring Guidelines related to data quality assurance and reporting are under finalization for consideration of the Meeting on CorMon on Pollution Monitoring planned to be held in April 2021.

These Monitoring Guidelines present coherent manuals to guide technical personnel of IMAP competent laboratories of the Contracting Parties for the implementation of the standardized and harmonized monitoring practices related to a specific IMAP Common Indicator (i.e. sampling, sample preservation and transportation, sample preparation and analysis, along with quality assurance and reporting of monitoring data). For the first time, these guidelines present a summary of the best available known practices employed in marine monitoring by bringing integrated comprehensive analytical practices that can be applied in order to ensure the representativeness and accuracy of the analytical results needed for generation of quality assured monitoring data.

The Monitoring Guidelines/Protocols build upon the knowledge and practices obtained over 40 years of MED POL monitoring implementation and recent publications, highlighting the current practices of the Contracting Parties' marine laboratories, as well as other Regional Seas Conventions and the EU. A thorough analysis of presently available practices of UNEP/MAP, UNEP and IAEA, as well the HELCOM, OSPAR and European Commission Joint Research Centre was undertaken to assist an innovative approach for preparation of the IMAP Monitoring Guidelines/Protocols.

The Monitoring Guidelines/Protocols also address the problems identified during realization of the Proficiency testing being organized by UNEP/MAP-MEDPOL and IAEA for two decades now, given that many unsatisfactory results within inter-laboratory testing may be connected to inadequate laboratory practices of the IMAP/MEDPOL competent laboratories.

In order to support national efforts, this Monitoring Guidelines for Sampling and Sample Preservation of Sediment for IMAP Common Indicator 17 provides the two following Technical Notes: a) Technical Note for the sampling of sediment for the analysis of heavy metals and organic contaminants, capturing the following five Protocols: i) Protocol for the use of a grab for collecting sediments; ii) Protocol for the for the use of a box corer for collecting sediments; iii) Protocol for the use of a multi-corer for collecting sediments; iv)Protocol for the use of a gravity corer for collecting sediments; v) Protocol for the hand collection of sediment with a shovel/scoop and a hand-held corer; b) Technical Note for the preservation of sediment sample to be analysed for heavy metals and organic contaminants, capturing Protocol for the treatment of sediment samples prior to analysis for heavy metals and organic contaminants.

The Monitoring Guidelines/Protocols, including the one related to sampling and sample preservation of sediments for IMAP Common Indicator 17, establish a sound ground for further regular update of monitoring practice for the purpose of successful IMAP implementation.

In accordance with the Conclusions and Recommendations of the Integrated Meetings of the Ecosystem Approach Correspondence Groups on IMAP Implementation (CORMONs) (Videoconference, 1-3 Dec. 2020), and in particular paragraph 22, this Meeting requested the Secretariat to amend this Monitoring Guideline by addressing agreed technical proposals that were described in the Report of the Meeting in line with its agreement to proceed with submission of this document to the Meeting of MEDPOL Focal Points. Requested amendments included technical written suggestions that were provided by several Contracting Parties up to 10 days after the Integrated Meeting of CORMONs. The amended document was shared by the Secretariat on 19 February 2021 for a period of 2 weeks for the non-objection by the Integrated Meetings of CORMONs on the introduced changes. Further to no objection from the Integrated Meeting of CORMONs, this Monitoring Guideline is submitted for consideration of present Meeting of MEDPOL Focal Points.

List of Abbreviations / Acronyms

CI	Common Indicator
COP	Conference of the Parties
CORMON	Correspondence Group on Monitoring
EcAp	Ecosystem Approach
EEA	European Environmental Agency
EC	European Commission
EFSA	European Food Safety Authority
EU	European Union
FAO	Food and Agriculture Organization of the United Nation
HELCOM	Baltic Marine Environment Protection Commission - Helsinki Commission
IAEA	International Atomic Energy Agency
IOC	International Oceanographic Commission
IMAP	Integrated Monitoring and Assessment Programme of the Mediterranean Sea and Coast and Related Assessment Criteria
MAP	Mediterranean Action Plan
MED POL	Programme for the Assessment and Control of Marine Pollution in the Mediterranean Sea
MED QSR	Mediterranean Quality Status Report
OECD	Organisation for Economic Co-operation and Development
OSPAR	Convention for the Protection of the Marine Environment for the North-East Atlantic
PLAN BLEU	Regional Activity Centre of Mediterranean Action Plan
PoW	Programme of Work
QA/QC	Quality Assurance/Quality Control
QSR	Quality Status Report
US EPA	United States Environmental Protection Agency

1 Introduction

1. Determination of the concentrations of targeted heavy metals and organic contaminants in different marine matrices is a key component of the IMAP, since the analytical results will contribute to the assessment of the environmental status of the water body under consideration. Sediment is one of the proposed matrices for the analysis of heavy metals since the establishment of the UNEP/MAP – MED POL Monitoring programme in 1981 (MED POL Phase II), because heavy metals and persistent organic contaminants in seawater tend to become insoluble and precipitate with the particulate fraction on the seafloor. Therefore, since sediment is the ultimate sink of most heavy metals and persistent organic contaminants, which are introduced into the marine environment, their analysis will provide a clear view of the pollution state of the specific water body. Furthermore, in areas with undisturbed sediments, the yearly deposited sedimentary material integrates the pollution load during this specific time period, and the analysis of different sedimentary layers is providing a historical trend of pollution processes in the region.

2. The UNEP/MAP Integrated Monitoring and Assessment Programme (IMAP) (UNEP/MAP, 2019[1]; UNEP (2019a[2]), requires sediment sampling from the top layer of the seafloor, because this layer reflects the recently deposited material, therefore the actual status of pollution at the specific location. The depth of the "recently" deposited sediment varies from one location to another, influenced by the sedimentation rate but also by bioturbation, but in the coastal zone it is usually the top 1 to 5 cm from the seafloor surface. In open sea, the sedimentation rate is lower than in the coastal zone, therefore often the 1st cm of the sediment may be representing several deposition years. It is of paramount importance to collect the undisturbed top layer of the sediment for analysis. Therefore, the use of appropriate sampling equipment is very important, as well as the proper handling during sampling to collect a representative sediment sample.

3. Until now, UNEP/MAP – MED POL pollution monitoring programme was focussing on the marine coastal zone, which was affected by land-based pollution sources. Therefore, sediment sampling was mainly done in relatively shallow waters, although some Contracting Parties were also collecting sediment samples from deeper waters. In a view of extending monitoring to much deeper offshore areas in the framework of the IMAP, sediment collection protocols are also addressing sediment sampling procedures from such offshore environments. Box corers and multiple corers are mostly suitable for such offshore sediment sampling, while gravity corers can be mainly used for tracking historical pollution trends. It has to be underlined that sedimentation rates at offshore sediments are much lower than in the coastal zone, leading to a much lower yearly deposition of sediment material on the seafloor. Therefore, in order to decide on the appropriate sediment depth to be collected for recording recent contaminants' concentrations, as well as on the required sampling frequency in offshore sediments in view of detecting possible changes in contaminants accumulation, the determination of the sedimentation rate at the sampling stations is highly needed.

4. Once a representative sediment sample has been collected, it has to be transported to the laboratory for analysis. However, transportation has to be done in such a way as to avoid any alteration of the physical and chemical characteristics of the sample. Sediment characteristics and contaminants distribution in the sample may be altered if the sediment storage and transportation is not done under specific procedures, in order to avoid sample alteration and cross contamination from the material of the containers and the sampling and transportation environment.

5. The Protocols prepared in the framework of this Monitoring Guidelines for Sampling and Sample Preservation of Sediment for IMAP Common Indicator 17, as provided here-below, describe appropriate methodologies for sampling, processing and storage of marine sediment under controlled conditions to ensure the representativeness and the integrity of the samples. They are not intended to

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[1] UNEP/MAP (2019). UNEP/MED WG.467/5. IMAP Guidance Factsheets: Update for Common Indicators 13, 14, 17, 18, 20 and 21: New proposal for candidate indicators 26 and 27; UNEP (2019).

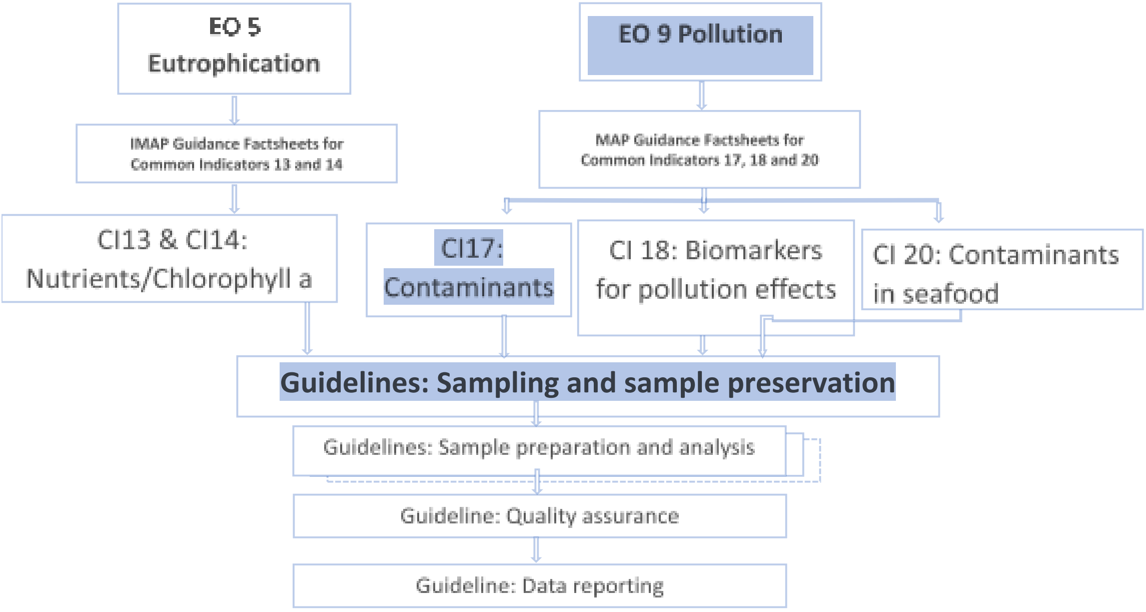
[2] UNEP/MAP (2019a). UNEP/MED WG.463/6. Monitoring Protocols for IMAP Common Indicators related to pollution;

be analytical training manuals, but guidelines for Mediterranean laboratories, which should be tested and modified in order to validate their final results.

6. These Protocols aim at streamlining sediment sampling and sample preservation in order to assure comparable quality assurance of the data, as well as comparability between sampling areas and different national monitoring programmes. They provide a step-by-step guidance on the methods to be applied in the Mediterranean area for sampling and sample preservation of sediments in a view of their subsequent analysis for heavy metals and organic contaminants.

7. In order to avoid unnecessary repetitions, reference is also made to the protocols already published and publicly accessible, which can also be used by the Contracting Parties' competent laboratories participating in IMAP implementation. They build upon the UNEP/MAP (20113) Manual on sediment sampling and analysis (Annex I), as well as similar Guidelines/Protocols for marine sediment sampling which were developed by other Regional Seas Organisations, such as ICES/OSPAR (2018[4]) CEMP Guidelines for Monitoring Contaminants in Sediments and HELCOM (2012[5]) Manual for marine monitoring in the COMBINE programme, as well as EC (2010[6]) Guidance on chemical monitoring of sediment and biota under the Water Framework Directive, given their suitability for application in the context of IMAP. Given the suitability of any of these Guidelines in the context of IMAP, they could be further used by interested IMAP competent Mediterranean laboratories for developing their laboratory specific sampling and sample processing methodologies.

8. The below flow diagram informs on the category of this Monitoring Guideline related to sampling and sample preservation of sediment for IMAP Common Indicator 17 within the structure of all Monitoring Guidelines prepared for IMAP Common Indicators 13, 14, 17, 18 and 20.



Flow Diagram: Monitoring Guidelines for IMAP Ecological Objectives 5 and 9

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[3] UNEP/MAP (2011). UNEP(DEPI)MED WG.365/Inf.9. Manual on sediment sampling and analysis

[4] ICES/OSPAR (2018). CEMP Guidelines for Monitoring Contaminants in Sediments

[5] HELCOM (2012). Manual for marine monitoring in the COMBINE programme. Annex B-13 Appendix 3.: Technical note on the determination of heavy metals and persistent organic compounds in marine sediment

[6] EC (2010). Guidance Document No: 25 Guidance on chemical monitoring of sediment and biota under the Water Framework Directive

2 Technical note for the sampling of sediment for the analysis of heavy metals and organic contaminants

9. Sediment sampling for pollution monitoring aims at the collection of a representative sediment sample from the top layer of the seafloor, because this layer reflects the recently deposited material, therefore the actual status of pollution at the specific location. The depth of the "recently" deposited sediment varies from one location to another, influenced by the sedimentation rate but also by bioturbation. Usually it is recommended (EC, 2010) to sample the top layer of the sediment, from 1 to 5 cm depth, depending on the deposition rate. In open sea, the sedimentation rate is lower than in the coastal zone, while at coastal areas at the vicinity of large rivers the sediment sampling depth for recently deposited sediments could be more than 5 cm. During the initial phase of the IMAP (identification of key sampling sites/stations) sediment sampling should be done every two years, while during the advanced phase (when it is a fully completed MED POL Phase IV implementation with the ongoing reporting of IMAP data sets) sampling should be done every 3 to 6 years, depending on the characteristics of sedimentation areas and the chemical concerned known through previous MED POL assessments (UNEP, 2019).

10. To avoid erroneous sampling, it is of paramount importance to sample the undisturbed top layer (1-5 cm) of the sediment using the appropriate sampling equipment. Box corers are the most appropriate equipment to sample undisturbed top layers sediments in the coastal zone and the open sea, but they are relatively heavy and require adequate shipping facilities. In relatively shallow coastal areas, a grab sampler is a good solution, because it is portable and can be used from a coastal vessel, without special equipment for lowering and lifting the sampler from the seafloor. In very shallow sampling sites with a water depth less than 30 cm, surface sediment samples (5 cm) can be collected with a shovel, spatula or scoop, if no other sampling equipment is available.

11. Sediment monitoring generally addresses the top layer of the sediment because this layer indicates the actual deposited material and the actual status of pollution. Furthermore, the top layers of the sediment form the habitat of benthic organisms and therefore may affect their contaminants' uptake (EC, 2010, UNEP/MAP, 1999[7], UNEP/MAP, 2011). Surface sediments can be collected with grabs and box corers, while gravity corers can be used to collect cores to study historical pollution trends at a specific site. Also, corers could be used in order to collect deeper sediment layers in view of establishing the background concentration of contaminants at a specific area.

12. Under this technical Note, the Guideline for Sampling and Sample Preservation of Sediment for IMAP Common Indicator 17 provides the following IMAP Protocols:

- Protocol for the use of a grab for collecting sediments;
- Protocol for the for the use of a box corer for collecting sediments;
- Protocol for the use of a multi-corer for collecting sediments;
- Protocol for the use of a gravity corer for collecting sediments;
- Protocol for the hand collection of sediment with a shovel/scoop and a hand-held corer.

13. These Protocols are based on methods for sediment sampling and processing developed by UNEP/MAP (Annex I: UNEP/MAP (2011), UNEP(DEPI)MED WG.365/Inf.9. Manual on sediment sampling and analysis), EC (2010) Guidance Document No 25, HELCOM (2012) Technical note on the determination of heavy metals and persistent organic compounds in marine sediment, and ICES/OSPAR (2018) CEMP Guidelines for Monitoring Contaminants in Sediments. In each protocol the operation and the proper deployment and recovery of the sampling equipment is presented, and

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[7] UNEP/MAP (1999). MED POL Phase III. Programme for the assessment and control of pollution in the Mediterranean Region.

guidelines are provided for the appropriate taking of the sediment sample in order to preserve its integrity and to avoid contamination.

2.1 Protocol for the use of a grab for collecting sediments

a. <u>Grab operation</u>

14. A tightly closing grab, which is handled with care, can collect relatively undisturbed surface sediment samples. Grabs are not the preferable sampling equipment for collecting undisturbed sediment samples because their penetration in the sediment may disturb the recently deposited sediment layers. However, grabs may provide a workable sampling solution in relatively shoal waters, which are out of the reach of an oceanographic vessel, or when an oceanographic vessel equipped with a box corer is not available. A light-weight hand-held grab is suitable for collecting approximately 250 ml of sediment, which is an appropriate volume for sediment analysis (Figure 1).

Figure 1. Van Veen Grab

15. To improve the sampling procedures the sampling vessel should be equipped with some sampling facilities, such as a winch, davit or other such lifting equipment. However, in very shallow coastal waters (for example less than 20 m depth) a small hand-held grab can be used with success from a small boat.

16. The grab is lowered locked-open and upon hitting the sediment’s surface the lock is released and the grab’s jaws are closing penetrating thus into the sediment to a depth depending on the size and the weight of the grab, as well as the hardness of the sediment.

17. Grabs can be used efficiently in sand or consolidated sediments collecting a good volume of undisturbed sample. On the other hand, in hard clays the grab may not be able to penetrate the hardened sediment, while in un-consolidated soft sediments the grab will sink through the top layer disturbing sediment stratigraphy.

b. <u>Taking the sample</u>

18. The water depth at the sampling station should be recorded before the deployment of the grab in order to ensure that appropriate wire/rope length is available.

19. During the descent of the grab through the water column it is important to control the speed of deployment, to allow the grab arriving at the sediment floor jaws-first. If the grab falls aside on the sediment, sampling will be unsuccessful and the grab has to be lifted, locked-open again and lowered once more. Controlling the speed of the grab’s deployment will keep the wire stretched and the grab in a vertical position, as needed.

20. Another factor affecting the successful deployment of the grab is the existence of near-bottom currents that may deflect the grab from the vertical line, resulting in unsuccessful sampling. Additional weight on the grab sampler, as well as longer wire than the actual depth at the station, may be needed.

21. Once the grab is closed at the sediment floor it has to be lifted to the surface. At this stage it is important to avoid any leakage of fine-grained sediment from the grab. If the grab is well designed, no loss of collected sediment should occur. However, leakage can occur if the grab is not tightly closed because of ill-design or because of partial closure of the jaws, caused by obstruction from coarse material (for example coarse sand or shell).

22. When the grab is lifted on-board it has to be positioned on a clean surface and handled with care to ensure that no alteration of the sediment characteristics will occur because of contamination.

i) Pose the grab on a clean surface (plastic).

ii) Visually inspect the collected sample from the small trap doors on top of the grab to make sure that the sediment collected is undisturbed. If water is trapped on the top of the sediment remove it using a glass tube or allow to be slowly drained in order to avoid washing off the top fine-grained layers that may be present.

iii) Record the visual characteristics of the sediment, such as grain size (fine or coarse grained), colour, smell and the presence of organisms. Taking a photo of the collected sediment is also recommended, in order to keep a visual record of the collected sample. If required, you can measure additional parameters, such Eh and pH.

c. Avoiding contamination

23. Grabs are made of metal therefore the best solution for trace metal determinations is to use a stainless-steel grab and, as an additional precaution, use plastic tools to collect subsamples from the central part of the sample, avoiding the sediment which is in contact with the grab’s walls. If possible, use grabs with Teflon coatings on all surfaces that come into contact with the sediment. The use of lowering cables coated with plastic (polyethylene) or of synthetic ropes will further minimize possible contamination.

24. After the water is drained, open the grab carefully on a clean and metal-free area (for example a plastic sheet) to collect the samples for heavy metal analysis. For the analysis of organic contaminants, the grab should be open in a dust-free area avoiding contact with possible sources of contamination from organic pollutants (such as exhaust gases).

25. Remove with a plastic or stainless-steel spoon the top layer, which is representing recent sedimentation. The depth of this layer may vary from 1 to 5 cm depending on the sedimentation rate in the sampling site and has to be decided by the institution that is responsible for the sampling.

26. It is important to ensure that enough sediment material is collected to allow for analysis of heavy metals, organic contaminants, as well as additional sediment analyses (such as grain size). The EC Guidance on sediment sampling (EC, 2010) suggests to collect 50 ml of wet sediment for heavy metal analysis. Taking into consideration that a small hand-held grab can collect approximately 250 ml of sediment, it is a suitable equipment to collect sediment samples for contaminants’ analysis at shallow waters. When a larger grab is used, the collected sediment provides enough material for further analysis.

27. Surface sediment samples are transferred into wide-mouth, pre-cleaned containers:

i) Zip-lock bags, plastic (polyethylene, polypropylene), or glass are suitable container’s materials for sediments to be analysed for heavy metals;

ii) Glass or aluminium are suitable container's materials for sediments to be analysed for organic contaminants.

28. Containers and zip-lock should be filled to the top to reduce the likelihood of oxidation during transport.

29. Sediment samples have to be stored at 4°C in a cooler box and transported to the laboratory for further processing and analysis.

Protocol for the use of a box corer for collecting sediments

a. Box corer operation

30. A box corer is a sediment sampling equipment, which collects large diameter undisturbed cores, from which replicate sub-samples may be collected by a hand-operated corer (Figure 2). Box corers are relatively heavy and are operated from a ship with appropriate equipment (heavy winch) in water depths more than 3 m (EC, 2010). Usual models collect sediment samples with a penetration of 0.75 m with a surface of 0.25 m^2, although there are smaller box corers available on the market. The big advantage of box corers is that they collect a virtually intact sediment core. If properly handled box corers operate efficiently in all kinds of bottoms, hard, soft or unconsolidated, retrieving undisturbed sediment cores. Therefore, if available, they are the preferable equipment for sediment sampling.

Figure 2. Box corer

b. Taking the sample

31. The water depth at the sampling station should be recorded before the deployment of the box corer in order to ensure that appropriate wire length is available.

32. The box corer is armed (locked-open) and is lowered from the ship with a controlled speed to allow the corer arriving upright at the sediment floor. Controlling the speed of the box corer's deployment will keep the wire stretched and the equipment in a vertical position, as needed. Another factor affecting the successful deployment of the box corer is the existence of near-bottom currents that may deflect it from the vertical line, resulting in unsuccessful sampling. Additional weight on the box corer, as well as longer wire than the actual depth at the station, may be needed.

33. Upon arriving at the sediment's surface, the box corer is penetrating the sediment depending on the hardness of the bottom.

34. Once the core box is filled with sediment, the winch operator slowly recovers the lifting wire and box corer ensuring the lowering of the cutting edge of the spade into the sediment to close the bottom of the box.

35. Once the box corer is lifted on board it has to be positioned on a clean area and secured.

i) Visually inspect the collected sample from the inspection door on top of the box corer to make sure that the spades have are closed tightly and the sediment collected is undisturbed.

ii) Siphon the supernatant water off the sample with a plastic or glass tube and stored it in pre-cleaned bottles, if additional seawater analysis is planned.

iii) Record the visual characteristics of the sediment, such as grain size (fine or coarse grained), colour, smell and the presence of organisms. If required, you can measure additional parameters, such Eh and pH.

36. Record the depth of the core penetration in order to decide if the sampling can be considered successful (appropriate sediment penetration).

c. <u>Avoiding contamination</u>

37. Box corers are made of metal (usually stainless steel) therefore they have to be handled with care, to avoid contamination in the determination of heavy metals. Once the box corer is open on a clean area on the deck of the ship, subsamples can be taken by hand-held plastic coring tubes for metal analysis, and by metallic tubes for organic contaminants analysis. The diameter of these coring tubes depends on the surface of the sediment retrieved with the box corer, as well as the number of subsamples required. The depth of the sediment retrieved for analysis may vary from 1 to 5 cm depending on the sedimentation rate in the sampling site and has to be decided by the institution that is responsible for the sampling. In all cases it is important to ensure that enough sediment material is collected to allow for analysis of heavy metals, as well as additional sediment analyses (such as grain size). The EC Guidance on sediment sampling (EC, 2010) suggests to collect 50 ml of wet sediment for heavy metal analysis and 250 ml for the analysis of organic contaminants. All tools for handling sediment for metal analysis should be made by plastic tools, while metallic tools have to be used for handling sediment for organic contaminants' analysis.

38. Sediment sub-samples are transferred into wide-mouth, pre-cleaned containers:

i. Plastic (polyethylene, polypropylene) or glass are suitable container's materials for sediments to be analysed for heavy metals;
ii. Glass or aluminium are suitable container's materials for sediments to be analysed for organic contaminants.

39. Containers and zip-lock bags should be filled to the top to reduce the likelihood of oxidation during transport.

40. If the contaminants profile will be studied, the cores collected from the box-corer have to be sliced on board to preserve their integrity. If un-sliced cores are transported in horizontal position, the profile characteristics may be lost because of mixing of layers. On the other hand, if cores are transported in vertical position, they may be compacted because of vibration altering the thickness of core's depositional layers. The core sub-samples are transferred to pre-cleaned containers: plastic (polyethylene, polypropylene) or glass are suitable container's materials for sediments to be analysed for heavy metals, while glass or aluminium are suitable container's materials for sediments to be analysed for organic contaminants.

41. Samples have to be stored at 4°C in a cooler box and transported to the laboratory for further processing and analysis.

2.2 Protocol for the use of a multi-corer for collecting sediments

a. Multi-corer operation

42. A multi-corer is a sediment sampling equipment, with several corers joined together (usually 4 to 12 corers) (Figure 3). The multi-corer is lowered from a ship and when it touches the seafloor, its weight pushes the assembled cores into the sediment. When the multi-core is lifted, individual corers' tops and bottoms are closed in order to bring an undisturbed sediment on board. Multi-corers are relatively heavy and can be operated from a ship with appropriate equipment (heavy winch) in water depths more than 3 m, as well as in offshore waters (EC, 2010). Usual models collect sediment cores of 0.7 m length and a coring tube diameter 0.1 m, although there are smaller multi-corers available in the market. The big advantage of multi-corers is that they collect several virtually intact sediment cores, which can be used for the analysis of different parameters (heavy metals, organic contaminants, grain sizes, etc.). Multi-corers can also be used for dating sediment layers. If properly handled multi-corers operate efficiently in all kind of bottoms, hard, soft or unconsolidated, retrieving undisturbed sediment cores.

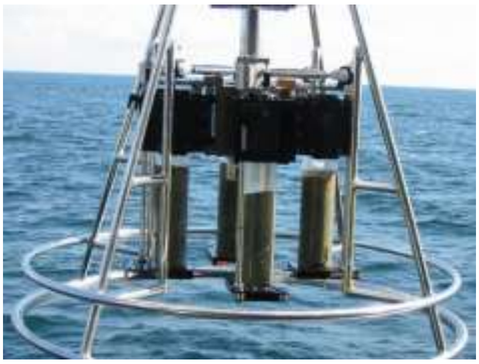

Figure 3. Multiple corer

b. Taking the sample

43. The water depth at the sampling station should be recorded before the deployment of the multi-corer in order to ensure that appropriate wire length is available.

44. The multi-corer is armed (locked-open) and is lowered from the ship with a controlled speed, in order to arrive at the bottom in an upright position.

45. During the descent of the multi-corer through the water column it is important to control the speed of deployment, to allow the corer arriving upright at the sediment floor. A speed of descent of 1 m/s is considered appropriate for the deployment of the device. Controlling the speed of the multi-corer's deployment will keep the wire stretched and the equipment in a vertical position, as needed.

46. Upon arriving at the sediment's surface, the individual corers are penetrating the sediment driven by the weights. Penetration depth depends on the hardness of the bottom.

47. Once the cores have penetrated the sediment, the winch operator slowly recovers the lifting wire and multi-corer, and upon detaching from the sediment, the core tubes are sealed, being capped both top and bottom, preserving the integrity of the samples, and the multi-corer is recovered to the surfaces.

48. Once the multi-corer is lifted on board it has to be positioned on a clean area and secured.

i) Visually inspect the collected cores to make sure that both ends of the coring tubes are properly closed and the sediment collected is undisturbed;
ii) Siphon the supernatant water off the samples with a plastic or glass tube and stored it in pre-cleaned bottles, if additional seawater analysis is planned;
iii) Record the visual characteristics of the sediment, such as grain size (fine or coarse grained), colour, smell and the presence of organisms. If required, you can measure additional parameters, such Eh and pH;
iv) Record the depth of the core penetration in order to decide if the sampling can be considered successful (appropriate sediment penetration).

c. Avoiding contamination

49. Multi-corers have coring tubs made of plastic (acrylic or polycarbonate) for heavy metal analysis or stainless steel for organic contaminants or granulometric analysis. Therefore, appropriate coring tubes should be used for specific measurements. The sizes of the individual coring tubes vary, however usual models collect sediment cores of 60-70 cm length with a coring tube diameter of 10 cm. The depth of the sediment which represents the surface, recently deposited material may vary from 1 to 5 cm depending on the sedimentation rate in the sampling site and has to be decided by the institution that is responsible for the sampling. However, in all cases it is important to ensure that enough sediment material is collected to allow for analysis of heavy metals, as well as additional sediment analyses (such as grain size). The EC Guidance on sediment sampling (EC, 2010) suggests to collect 50 ml of wet sediment for heavy metal analysis and 250 ml for the analysis of organic contaminants. As an example, if the top 5 cm are retrieved from a coring tube with an internal diameter of 10 cm, the sediment volume collected is 390 cm^3.

50. Multi-corers can also be used to collect deeper sediment layers cores for dating historic pollution trends. The length of the core is restricted to 70-100 cm, which may be enough for recent pollution studies. All sediment handling tools for metal analysis, including core slicer to retrieve specific sediment layers, should be made by plastic, while metallic tools have to be used for handling sediment samples for organic contaminants’ analysis. Samples are transferred into pre-cleaned containers: plastic bags or containers for heavy metal analysis and glass or aluminium for organic analysis.

51. In order to preserve the integrity of cores, it is preferable to slice them on board and to store the samples of the different sediment layers. If un-sliced cores are transported in horizontal position, the profile characteristics may be lost because of mixing of layers. On the other hand, if cores are transported in vertical position, they may be compacted because of vibration altering the thickness of core’s depositional layers

52. Sediment samples are stored at 4 ^{o}C on board in a cooler box and are transported to the laboratory for further processing and analysis.

2.3 Protocol for the use of a gravity corer

a. Gravity corer operation

53. A gravity corer consists of a metallic corer tube with a plastic internal liner and attached weights that enables penetration into the sediment (Figure 4). The gravity corer is used for taking relatively long cores to study sediment layers. It is a heavy equipment (could be hundreds of kilograms), which is usually operated from a ship equipped with a heavy winch for relatively deep waters. Smaller gravity corers may be available but, they also need a boat and a winch to be handled. Gravity corers are mostly used to study contaminants’ variation between sediment layers, or to record pre-industrial background concentrations of contaminants, rather than studying recent pollution

changes. They can be used in both coastal and offshore sediments, taking into consideration the respective sedimentation rates, in order to evaluate the analytical results.

Figure 4. Gravity corer

54. The gravity corer is lowered from a ship and when it touches the seafloor, its weight pushes the corer tube into the sediment. Penetration depth depends on the hardness of the bottom and the weight added on top of the corer's tube. It has to be noted that because of the gravity-driven penetration of the corer into the sediment and the relatively small diameter of the coring tube, the retrieved sediment layers may be compressed and/or stretched, which may result in misleading geochronology results.

b. Taking the sample

55. The water depth at the sampling station should be recorded before the deployment of the gravity corer in order to ensure that appropriate wire length is available.

56. During the descent of the corer through the water column it is important to control the speed of deployment, to allow the corer arriving upright at the sediment floor. Controlling the speed of the gravity corer's deployment will keep the wire stretched and the equipment in a vertical position, as needed.

57. Once the corer has penetrated the sediment, the winch operator slowly recovers the lifting wire and when the corer is lifted from the seafloor the "orange peel" closing system prevents the loss of the collected sediment, preserving the integrity of the sediment layers.

58. Once the gravity corer is lifted on board it has to be positioned on a clean area and secured.

i) Remove the inner liner of the corer and record the visual characteristics of the sediment, such as grain size (fine or coarse grained), colour, smell and the presence of organisms. If required, you can measure additional parameters, such Eh and pH.

ii) Record the depth of the core penetration in order to decide if the sampling can be considered successful (appropriate sediment penetration).

iii) Slice the core using a core slicer, according to predefined sections. Surface sediment, which represents recent deposition, may correspond to the upper 1 - 5 cm, according to the sedimentation rate in the area, while the core intervals, which correspond to past deposition times will be defined by the leading scientist.

c. Avoiding contamination

59. Gravity corers collect only one core at a time, therefore if a plastic liner is used the collected sediment can be used for heavy metal analysis only. Stainless steel or Teflon liners can be used for collecting sediments for organic contaminants analysis. The depth of the sediment which represents the surface, recently deposited material may vary from 1 to 5 cm depending on the sedimentation rate in the sampling site and has to be decided by the institution that is responsible for the sampling. It is

important to ensure that enough sediment material is collected to allow for analysis of heavy metals, as well as additional sediment analyses (such as grain size). The EC Guidance on sediment sampling (EC, 2010) suggests to collect 50 ml of wet sediment for heavy metal analysis and 250 ml for the analysis of organic contaminants.

60. Gravity corers are mainly used to collect deeper sediment layers for dating historic pollution trends. All sediment handling tools for metal analysis, including core slicer to retrieve specific sediment layers, should be made by plastic, while metallic tools have to be used for handling sediment samples for organic contaminants' analysis. Samples are transferred into pre-cleaned containers: plastic bags or containers for heavy metal analysis and glass or aluminium or other non-contaminating material for organic analysis.

61. In order to preserve the integrity of cores, it is preferable to slice them on board and to store the samples of the different sediment layers. If un-sliced cores are transported in horizontal position, the profile characteristics may be lost because of mixing of layers. On the other hand, if cores are transported in vertical position, they may be compacted because of vibration altering the thickness of core's depositional layers

62. Sediment samples are stored at 4 ºC on board in a cooler box and are transported to the laboratory for further processing and analysis.

2.4 Protocol for hand collection of sediment with a shovel/scoop and a hand-held corer

a. <u>Hand shovel/spatula operation</u>

63. In mud flats or in very shallow water zones with a water depth less than 30 cm, surface sediment samples (5 cm) can be collected with a shovel, spatula or scoop, if no other sampling equipment is available (Figure 5). This method can be used to collect both unconsolidated and consolidated sediment; however, it is more accurate when used in relatively calm waters. The person who will take the sample has to walk with care into the water, avoiding disturbing the site to be sampled and using a shovel/spatula/scoop he/she collects the desired thickness of the sediment. The depth of the sediment which represents the surface, recently deposited material may vary from 1 to 5 cm depending on the sedimentation rate in the sampling site, and it has to be decided by the institution that is responsible for the sampling. It is important to ensure that enough sediment material is collected to allow for analysis of heavy metals, as well as additional sediment analyses (such as grain size). The EC Guidance on sediment sampling (EC, 2010) suggests collecting 50 ml of wet sediment for heavy metal analysis and 250 ml for the analysis of organic contaminants.

64. The sample collected is transferred to a pre-cleaned container. The excess water should be removed before closing the container with the sediment sample.

Figure 5. Hand-held scoop sediment sampler

b. Avoiding contamination

65. To avoid contamination during sampling the sampling utensil (shovel/spatula/scoop) has to be made of plastic for heavy metal analysis and of stainless steel for organic contaminants analysis. The containers used to store the sediment samples should be pre-cleaned and made of plastic for heavy metal analysis or of metal/glass for organic contaminants analysis.

66. Sediment samples are stored at 4 °C on board in a cooler box and are transported to the laboratory for further processing and analysis.

3 Technical note for the preservation of sediment sample to be analysed for heavy metals and organic contaminants

67. After collection wet sediment samples have to be treated in order to be preserved unaltered until transfer to the analytical laboratory for heavy metals analysis. Sediment sample preservation include: i) Storage of wet samples on board; ii) Wet sieving to collect the grain size fraction < 2 mm, which will be further analysed for organic contaminants; iii) Freeze drying to prepare the sample for the analysis and iv) Homogenization and storage of dried sediments. Wet sieving may also include an additional step to define the percentage (weight) of the silt and clay fraction of the sediment (< 63 μm), which is a useful parameter in assessing pollution in sediments. For the processes, the Protocol includes all necessary precautions to avoid cross-contamination of the sediment samples from tools, equipment and the laboratory environment.

68. The IMAP Protocol 3.1. addresses the treatment of sediment samples prior to analysis for heavy metals and organic contaminants.

3.1 Protocol for the treatment of sediment sample prior to analysis

a. Storage of wet samples on board

69. Upon collection wet samples have to be stored on board in such a way as to preserve them from deterioration that will affect the subsequent analysis of contaminants. Keeping the samples in low temperature (at 4 °C) and away from light and air (as much as possible) will slow down oxidation and bacterial activity, helping in maintaining sediment's initial characteristics. The first few hours after sampling are the most critical for changes to occur in the sample, therefore preservation steps should be taken, where possible, immediately upon sample collection (HELCOM 2012).

b. Wet sieving

70. Sediment texture may differ among locations, from very fine clay in the open sea to coarse sandy sediments close to the shoreline. Finer sediments indicate net depositional areas, which are preferable sampling stations for studying pollution impact, while coarse sand, pebbles or rocky substrates are not favourable sampling locations. For pollution studies, the most informative fraction of the sediment is the silt and clay fraction (< 63 μm) because contaminants are mainly associated with finer particles (EC 2010, ICES/OSPAR 2018) and coarser sediments (sand fraction) have much lower concentrations of heavy metals and organic contaminants. Therefore, the distribution of contaminant's concentrations in sediments will generally follow the distribution of fine-grained sediments. However, sieving over 63 μm mesh adds another step in the processing of the sample and, consequently, an additional source of potential contamination. Also, sieving over 63 μm mesh may be influenced by the unsuccessful disaggregation of particle conglomerates, which may affect the efficient quantitative segregation of silt + clay from the sand fraction.

71. The IMAP Common Indicator Guidance Fact Sheets (UNEP, 2019) requires the separation of the sediment fraction less than 2 mm, as the appropriate sediment fraction for the determination of heavy metals and organic contaminants. Also, an additional sieving over a 63 μm mesh is requested, in

order to record the percentage of the silt and clay fraction in the sediment. This data will be used for normalizing contaminants concentrations in the whole sediment (< 2 mm) for the grain-size effect, evaluating pollution levels and comparing between areas with different sediment texture.

72. Upon arrival on board, sediment samples should be wet sieved using a 2 mm mesh-size sieve as soon as possible in order to remove large detritus and benthic organisms, which may affect the sediment characteristic during subsequent sample handling and processing (storage, freezing or ultrasonic treatment) (EC, 2010).

73. It is preferable to use seawater from the sampling site for wet sieving in order to avoid any possible alteration of the sediment equilibrium (such as adsorption or desorption of metals). If this is not possible, wet sieving could take place in the laboratory using seawater with approximately the same salinity with the sampling location. Sieving over 63 μm mesh, if not implemented on board, it can be done in the laboratory.

74. For heavy metal analysis, sieving for both 2 mm and 63 μm mesh sizes may be carried out using sieves made of polymer (PVC or acrylic rim, with nylon or polyester mesh).

75. For organic contaminants analysis sieving may be carried out using sieves made of stainless steel (rim and mesh).

76. The sediment material is placed on the mesh, water is poured, and the sieve is moved manually. For the processing of larger numbers of samples, sieves may be placed on vibrator tables. Clays often tend to form larger lumps if dried, therefore wet sieving should be done when the sediment is still wet. In case the sediment is becoming dry, it has to be pre-soaked in seawater for at least 2 hours to disaggregate the lumps (EC, 2010). However, this procedure may result in the release of contaminants, which are adsorbed on particles' surface and should be avoided, if possible. In case that pre-soaking is needed, use seawater from the sampling area and sieve disaggregated particles as soon as possible.

77. For heavy metal analysis, the sieved sediment is collected with a plastic spatula and stored in a plastic container for further processing (drying). For organic contaminants analysis the sieved sediment is collected with a stainless-steel spatula and stored in a glass or aluminium container.

c. Drying

78. Prior to the instrumental detection, sediment samples must be dried. For metal (except volatile mercury) analysis, sediments should be freeze-dried, which is the preferable procedure. Alternatively, the sediments may be dried at any temperature below 105°C until constant weight. For mercury analysis, to minimise losses due to evaporation, a sediment sub sample could be air dried at temperature <50°C (EC, 2010).

79. For organic compounds analysis drying procedures depends on the compounds to be analysed. For chlorinated hydrocarbons sediments can be freeze-dried taking care to avoid determinant loss through evaporation by keeping the temperature in the evaporation chamber below 0°C (OSPAR, 2018). For PAH determination, freeze-drying sediment samples may be a source of contamination due to the back-streaming of oil vapours from the rotary vacuum pumps. Furthermore, drying the samples may result in losses of the lower molecular weight, more volatile PAHs through evaporation. To protect sediments samples during freeze drying from cross-contamination from particles and vapours, the sample containers could be covered with a lid or filter paper perforated with a small hole (HELCOM, 2012).

d. Homogenization and storage of dried sediments

80. After drying, the samples are homogenized using a ball mill and are stored in a cool and dark place, for further analysis. Temperature is the most important factor affecting the samples, from the time of sample collection through handling to the final analyses. Also, contamination from the laboratory's air should be avoided.

81. Freeze-dried sediment samples can be stored in pre-cleaned wide-mouth bottles with a screw cap. Samples intended for the analysis of metals can be stored in plastic or glass containers. For mercury analysis, samples must be stored in acid-washed borosilicate glass or quartz containers, as mercury can move through the walls of plastic containers. Samples intended for the analysis of organic contaminants must be stored in amber glass, stainless steel or aluminium containers (EC, 2010).

82. Containers with sediment samples should be archived and kept in storage after the completion of the analysis, in order to be used as a replicate sample in case crosschecking of the results are required or additional determinations are needed in the future. Freeze-dried sediments remaining after analyses could be are stored in the original sample bottle, closed with an airtight lid to protect against moisture. When stored in a cool, dark place, samples may be archived and stored for 10-15 years (EC, 2010).

Annex I

UNEP(DEPI)MED WG.365/Inf.9. Manual on sediment sampling and analysis (1.1)

United Nations
Environment
Programme

UNEP(DEPI)MED WG.365/Inf.9
November 2011
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MEDITERRANEAN ACTION PLAN

Consultation Meeting to Review MED POL Monitoring Activities
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MANUAL ON SEDIMENT SAMPLING AND ANALYSIS

UNEP/MAP
Athens, 2011

TABLE OF CONTENTS

1. Introduction

Within the Regional Seas Program of UNEP, many scientists are concerned about sediment sampling and analysis and therefore there is an increasing demand for the reliable analysis of both organic and inorganic pollutants in sediments. On the other hand, the sampling strategy set prior to the monitoring activity is critically important and should be established with caution in order to represent the sampling site and achieve the statistical objectives of a trend monitoring programme.

The need for a revision of the trend monitoring programme in sediments was raised during the Second Review Meeting of MEDPOL Phase III Monitoring Activities (Saronida, 2003), after a first examination of the sediment monitoring data was made by an expert, and it was recommended by the meeting to revise the existing strategy (UNEP(DEC)/MED WG.243/4). Afterwards, an expert meeting to revise the strategy for trend monitoring of pollutants in coastal water sediments was organized in April 2005 (Athens) and the meeting report (UNEP(DEC)/MED WG.273/2) considered important recommendations for the revision.

Dr Jean-Pierre Villeneuve (IAEA/MESL) drafted the initial version of the manual aimed at presenting the state-of-the-art in sediment monitoring in coastal waters. It fully took into account the recommendations of the expert meeting on both sampling strategy and analysis. A detailed section on sampling instruments and sample handling is also included in the manual, because it was observed in the training courses organized by MED POL and IAEA/MEL that there is a lack of knowledge on different sampling instruments and the sampling/sample pretreatment techniques. The draft manual was discussed at the Third Review Meeting of MEDPOL Phase III Monitoring Activities (Palermo, December 2005) and further comments of the meeting were incorporated in the present text. The section on normalization procedures was revised by Dr Barak Herut (IOLR, Israel). The section on ^{210}Pb dating was written by Dr. Joan-Albert Sanchez-Cabeza (Universitat Autònoma de Barcelona, Spain).

It is a considerable demand on resources to sample and analyze sediments, so, in order to facilitate the work of the laboratories in charge of monitoring, two different approaches (see the Conclusion) are indicated for sampling, sieving and analyzing the samples: the minimum requirement and the state-of-the-art, then laboratories could use the way that would correspond better to their needs and to their budgets.

2. Sampling design

2.1 Objectives

Sediments have an important role to play in the monitoring of the environment as they are considered as the final sink of most contaminants. Marine sediments are closely inter-related to other compartments of the environment. Therefore, their use in monitoring should be part of an integrated monitoring programme.

By far the most important step in designing of the sampling strategy of the monitoring programmes is the strict definition of the objectives of the programme concerned where the objectives should be put as detailed, specific and quantifiable as possible. To this end, a number of important factors should be taken into account, including the nature of the control measure, the contaminant concerned, the nature and location of the inputs, statistical aspects of sampling and analysis etc.

In addition, a trend monitoring programme should permit statistical comparison of the concentration of contaminants between sites (spatial distribution), highlighting areas with high concentrations of contaminants that are of concern. It is anticipated that a temporal trend monitoring programme for trace metals will at a minimum have 90% power to detect a 5% per year change over a period of between 15 and 20 years.

2.2 Sampling sites

Within MED POL monitoring programmes basically two site typologies are considered: Hot spots and coastal waters. As a matter of definition, coastal zone trend monitoring is done through a network of selected fixed coastal stations, with parameters that contribute to the assessment of trends and the overall quality status of the Mediterranean Sea. This type of monitoring is carried out on a regional basis. Trend monitoring of “hot spot” areas is done at intensively polluted areas and high risk areas where control measures have to be taken. These areas are designated by local authorities according to some common definitions provided by WHO-MED POL.

The definition of hot spots and coastal areas as regards sediment trend monitoring could be specified as follows:

- Hotspots are the most polluted sites as recorded using sediments and all such sites should be monitored (NB: these may not necessarily always be the same as the identified MED POL hot spots)
- Coastal sites are sites mainly located in the near shore coastal waters and a limited number of representative stations should be selected for state assessments.

Both hotspot and coastal areas are suitable for monitoring contaminants’ content in sediments, however, only sedimentary basins with positive accumulation can be considered for monitoring. Coastal areas with sedimentation rates higher than ~5 mm/year are suitable for annual monitoring, whereas areas of lower accumulation rates should be monitored at a lower frequency. Sensitive areas for biological life and protected areas within the near shore coastal waters are also recommended to be included in the monitoring network

2.3 Sampling stations

Sample sites are normally chosen on a broad grid network or transects. It is recommended that at least **three** stations be chosen along the sediment distribution gradient of a selected site to include hot spot and the near-shore coastal area. While doing so, nearby sensitive areas for biological life should also be included in the network.

In an example case, ”O” marks sampling stations in the grid below and “hot spot” station is marked by “Δ”. The arrow is pointing in the direction of the residual current (distances are indicated in nautical miles).

It could be recommended to limit the number of stations for data quality assurance purpose, however, the selected station(s) should be representative for the hot spot and the other area of interest.

It is also recommended to examine the selected site for sedimentary purposes as an initial step of the work in order to identify the sediment structure of the whole area as well as the sedimentation rates. Fine and regular sedimentation sites are experienced as more favourable for monitoring purposes.

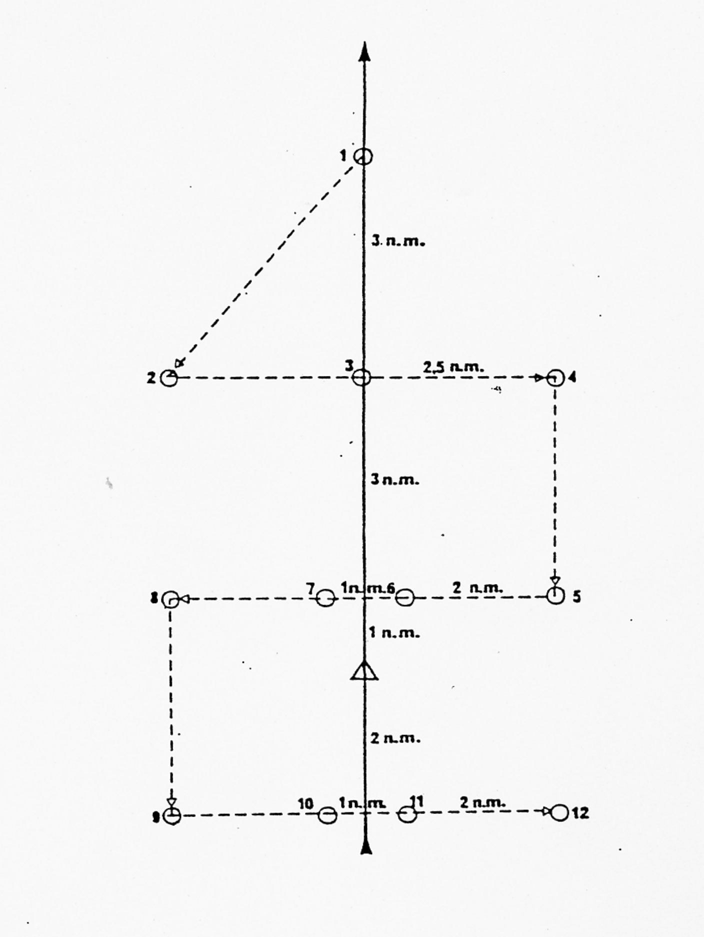


Figure 1: Example case for sampling.

2.4 Number of samples

Multiple samples have to be collected at each station in order to achieve the statistical sensitivity of sampling. It was recommended to take at least **three** samples at each station area (ex: for an area with app. 10 m depth and 10 m radius). In the pilot phase of the programme (first five years) **five** samples for each station is recommended to better understand the sampling variability if it is not known from previous monitoring efforts. Pooling of individual samples is not recommended especially in the pilot phase in order to achieve the field variability, which is an essential parameter for power analysis and trend tests.

2.5 Sampling layer

For spatial trend monitoring at a distribution gradient, surface sediments (uppermost 5 mm) should be sampled both at hot spots and near-shore waters.

For temporal trends, it is recommended to either sample the upper 5 mm at coastal near-shore stations or use core sediments and sample a sediment-depth profile, provided the sedimentation rate is known. However, this will depend on the specific situation.

2.6 Sampling frequency

As a basis and general rule, it is recommended that the sampling frequency is adapted considering the sedimentation rate.

It is generally accepted that for monitoring temporal trends at hotspot stations with high sedimentation rates (>5 mm/year), the sampling frequency can be initially set as annual or more frequent. If the sedimentation conditions are very variable at selected hot spots other frequencies could be adopted. If sampling of deeper layers at near-shore coastal waters is adopted for temporal trends, then sampling frequency could also be reduced according to the accumulation rate at the site. Sampling frequency could also be reduced when parameters are close to or below the quality targets.

In monitoring programmes of seasonal sampling, special attention should be given to sites significantly affected by river sediment input, in which accumulation rates may change seasonally following flood events. Additional attention should be paid to local conditions such as compaction, bioturbation and re-suspension events.

3. Sampling instruments and sample handling

3.1 Sampling instruments

The type of sampling equipment required for sediment surveys is dependent upon the contaminants of interest and on the information requested. Samples of surface sediment taken from a grab can be used to provide an assessment of the present levels of contamination in an area. The use of a more sophisticated sampler, such as a box-corer, would add reliability to the sample, but also would increase the operating cost of the survey. The type of sampler should be chosen among the followings:

Sediment samplers could be divided roughly into 2 different techniques: grab sampling which collects surface and near surface sediments and coring which collects a column of the subsurface sediment and could be required to establish the historical pattern of the contamination. In all grab and core operations, a slow approach to the sea floor should be ensured to avoid the creation of “bow wave” that disturbs the sediment-water interface prior to sampling. In some circumstances, it would be, also, possible to have the samples collected by divers using either glass or Teflon beakers.

3.1.1 Grab sampler

Undisturbed surface sediment samples can provide an immediate assessment of the present levels of contamination in the area in relation to the textural and geo-chemical characteristics of the sediment. The sampler used must consistently collect relatively undisturbed samples to a required depth below the sediment surface and of sufficient volume to permit subsequent analyses.

The Van Veen grab is among the most commonly used grab samplers. With this bottom sampler, samples can be extracted from any desired depth. While it is being lowered, both levers are locked wide apart whereby the jaws are open. Upon making contact with the waterbed, the locking mechanism is released and when the rope is pulled out to raise the sampler, the jaws close.

The small model (Figure 2), with a surface of 250 cm^2, made of stainless steel has a weight of approximately 5 kg and could be hand-operated from a small vessel. It is not recommended for greater water depth. The main problem with this sampler is that it is sometimes difficult to recover the surface layer of the sediment, so this type of sampler could be used only in case a coring device is not available.

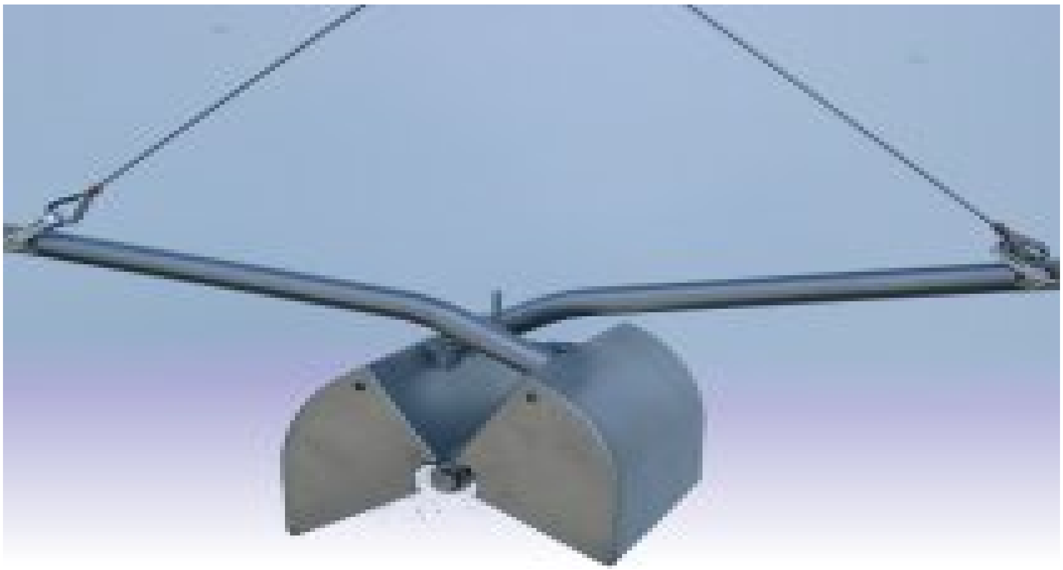


Figure 2: Van Veen grab operated manually (picture from Hydro-Bios, Germany).

There are other models of Van Veen grab, which are winch-operated, with a weight up to 80 kg. These models are presented in the **annex** to this document**.**

3.1.2 Corer

Sediment subsurface samples are often taken using barrel or box corers to determine the change in lithology and chemical composition with depth in order to assess environmental changes in metal fluxes with time. Cores are usually collected in areas of fine-grained sediments but specialized corers are available for coarse-grained sediments.

The main types of corers having cylindrical barrels are the gravity corer (Figure 3) which free-falls from the ship and penetrates the sea floor by gravity, and the piston corer which is released a set distance above the sea floor, penetrates the sediment by free fall, and sucks the sediment into the core barrel by an upward moving piston as the core is retrieved.

Figure 3: Gravity corer (picture from Hydro-Bios, Germany).

For trace metal analysis, plastic core liners are placed inside the core barrels to contain the sediment core sample and to avoid the problems of extrusion and contamination that occur in unlined barrels. When this kind of liner is used, care should be taken for collecting the sample for organic compounds determination, the sample should be collected at the inner part of the core at about a cm from the wall of the plastic liner. In general, the greater the diameter of the liner, the less will be the amount of distortion of the subsurface sediment by the corer penetrating the sediments. Core liners with internal diameters > 50 mm are usually satisfactory for obtaining samples for geochemical purposes.

After the corer is retrieved, the liners are capped at the bottom; the liner is removed from the barrel; the top is capped, and the core stored in a vertical position until all the water inside the liner has risen to the top. The liner is cut off at the sediment - water interface, capped and placed in a deep freezer or a cold room (4°C) for transport to the laboratory. Visual observations and measurements of sediment core samples should include information on the site number and location, depth, time, core length, lithology, stratigraphy, and any distortions in sediment layers.

In the laboratory, core sampling is best carried out by extruding the core upwards and slicing off layers (~ 1 cm) using a non-contaminating cutter (e.g. stainless steel, plexiglass or splitting the plastic core liners lengthwise, avoiding the smeared zone around the inside of the core liners and sampling the interior section of the core.

In order to check the repeatability of the sampling, more than one sediment sample can be collected within the same area. This can be done with the multi-core sampler (Figure 4). After analyzing the different samples, an estimation of the standard deviation due to sampling can be estimated.

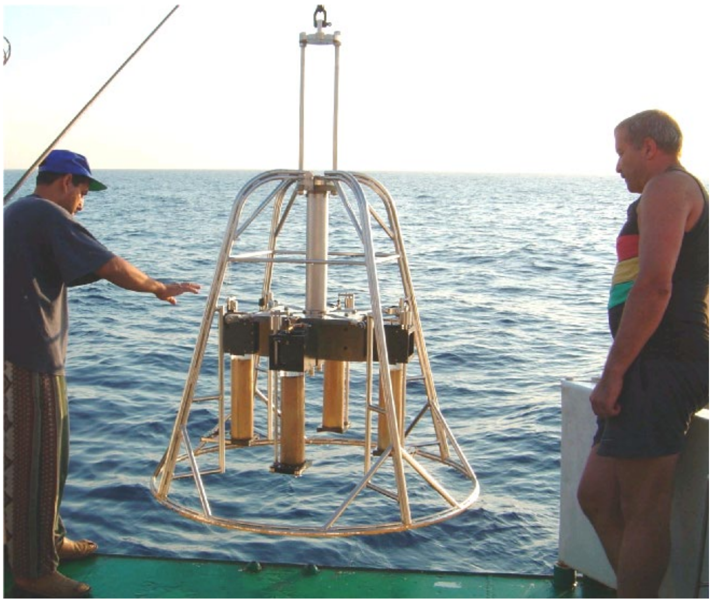


Figure 4: Multi-core sampler.

3.1.3 Box corer

Rectangular sampling devices which obtain cores about 15-25 cm square and 15-60 cm deep are known as box corers (Figure 5) and can be recommended for detailed sampling at or below the sediment-water interface. The advantage of the various types of box or square corers is that they can recover the surface sediment and fauna virtually intact. They can be sub-sampled by inserting several 5 cm diameter tubes into them. However, when sub-sampling is used, the core material should be taken from the mid-part of the core to avoid any “edge effects”. Such samples are treated in the same way as the core samples described above.

Figure 5: Box corer.

3.2 Sample handling

The procedure outlined below assumes that these samples will be collected from a vessel equipped with the basic collection facilities such as a winch, or other such lifting equipment and adequate refrigerated storage space.

Regardless of the equipment chosen for the sampling, it is useful to know the water depth at each station before starting the sampling. The purpose is to ensure adequate cable length for operation of the correct equipment and to control the speed of entry of the sampler into the sediment. The speed of deployment of the sampler can be critical to good operation and sample recovery. It is also useful to have some understanding of the currents at the sampling site. Strong near-bottom currents can lead to poor equipment deployment, deflect a grab sampler, or require a long cable/wire to be deployed. Care should be taken to ensure that the weight of the sampler is adequate for working at the particular current conditions.

On-board, the sediments contained in the grab sampler require attention to ensure that essential components are neither lost nor contaminated through improper handling. The most critical sampling and storage techniques relate to the avoidance of chemical contamination and change in the physico-chemical characteristics of the sediments. Special steps should be taken to minimize contamination of the samples. For trace metal determinations, the use of a stainless steel grab sampler with Teflon coatings on all surfaces that come into contact with sediments, and polyethylene coated lowering cables are highly recommended. All samples should be collected into cleaned plastic (inorganic samples) or glass vials or aluminum containers (organic samples).

The actual collection procedure is quite simple:

i. Prepare all sample containers for organic analysis by cleaning with solvent and heating in oven at 250 °C overnight.

ii. Clean the sediment grab thoroughly with hot soapy water, rinse with tap water. Avoid placing the grab sampler on the open deck, keep in a large plastic or aluminum tub while not in use.

iii. Clean a large sized plastic or aluminum tub depending on the destination of the sample.

iv. Cock the grab sampler.

v. Haul sampler on-board.

vi. Initially, a visual inspection should be made of the sample by means of the small trap doors on top of the grab to ensure that the sample has been collected in an undisturbed state and to determine if there is water on top of the sample. If water is present, it can be siphoned off with a glass tube or slowly drained so as not to wash the sample unduly.

Note : Plastic bags or wide-mouth jars (polypropylene or borosilicate glass) should be used for temporary storage of sediments for trace metal analysis. Prior to their use, containers and glass or plastic parts associated with the sampling equipment should be cleaned with detergent and acid then rinsed with metal-free water. For trace organic analysis samples should be stored in cleaned wide-mouth borosilicate glass or aluminum containers. The samples should be stored frozen, or at a sufficiently low temperature (~ 4°C) to limit biological and chemical activity. It is recommended that a minimum sub-sample size be 50 grams.

vii. Once the top of the sediment is exposed, visual estimates of grain-size (coarse, medium, fine grained), color, and the relative proportions of the components should be made and recorded. By inserting the appropriate electrodes into the sample, *in situ* measurements can be made, such as pH.

viii. Most fine-grained sediments usually have a thin, dark yellowish brown surface layer resulting from the oxidization of iron compounds at the sediment-water interface. Since in most cases this layer represents the material being deposited at the present time, it should be sampled carefully with a non-contaminating utensil such as a plastic spatula for trace metals determination and a stainless steel one for organic compounds determination. About 10-30 g should be placed in a numbered polyethylene vial for trace metal analysis and in glass or aluminum container for organic analysis, sealed and frozen for transport to the laboratory.

ix. After the surface layer has been sampled, the grab can be opened and an additional sample, representative of the subsurface, can be obtained. Observations of this material should include color and textural characteristics. To ensure a representative sample, about 100 to 200 grams (or even more) should be collected and placed in a numbered vial. The sample should be frozen quickly for return to the laboratory. Larger samples of about 1 kg are required for admixtures of gravel, sand and mud.

x. Store all sediment samples deep-frozen or, at least, under refrigeration (4°C) until they are transported to the laboratory.

3.2.1 Taking part of the sample for analysis

Depending on the analysis required and on the material of the sampler (plastic liner for corer), the collection of sediment should follow an agreed protocol. The main idea being to avoid contact with plastic liner for organic compounds and contact with stainless steel for trace elements analysis.

The distribution of sediment depending on the analysis to be performed is indicated in Figure 6.

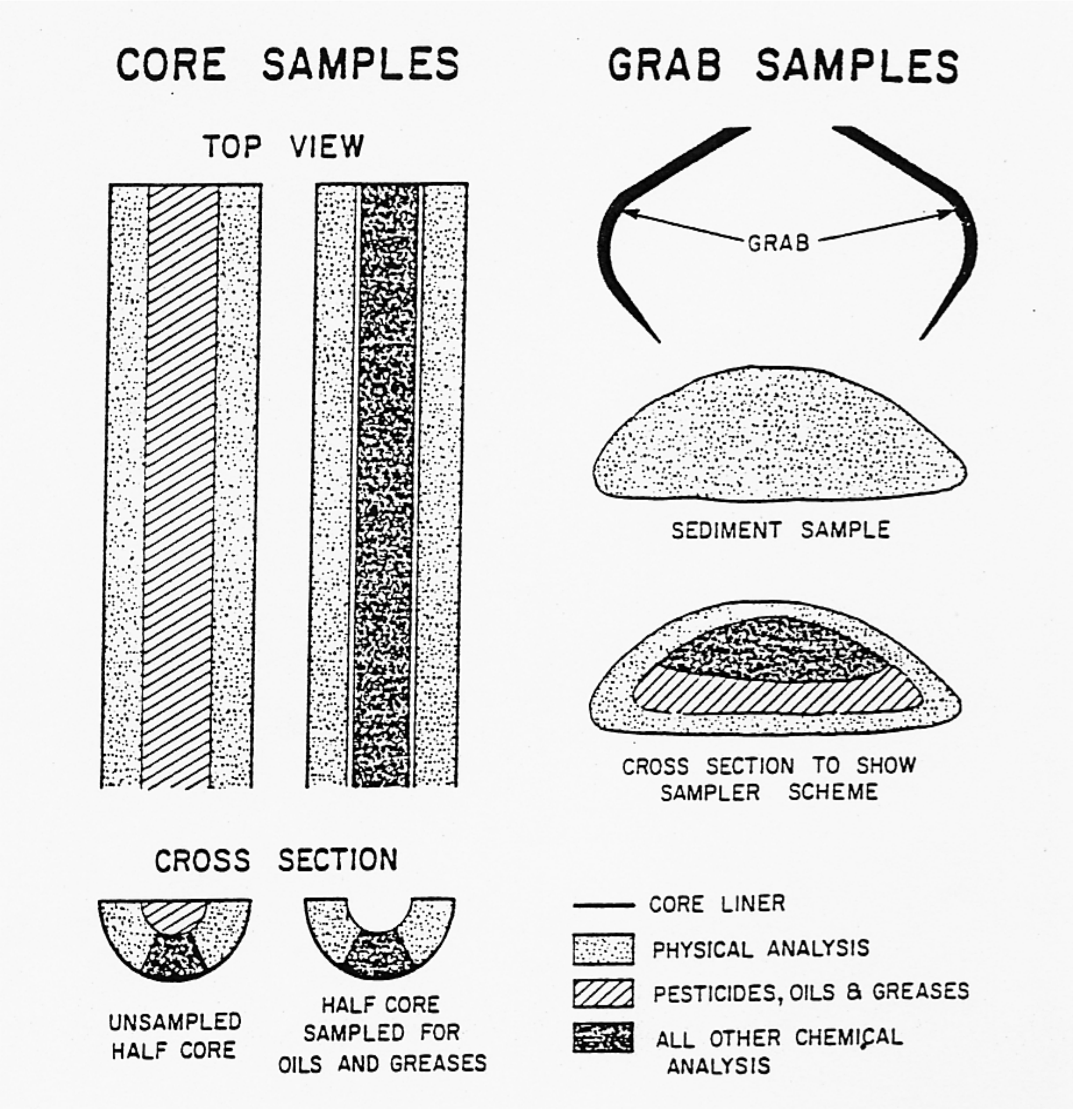


Figure 6: Collection of sediment according to analysis required.

3.2.2 Pre-treatment of the sample

(i) Freeze-drying:

After collection, the sediment samples are transferred into pre-cleaned aluminum boxes or pre-cleaned aluminum paper for organic analysis or into plastic bags for trace element analysis and deep-frozen (or at least kept refrigerated at about 4°C during the transport to the laboratory in order to avoid the bacterial degradation in case of petroleum hydrocarbon analysis).

When in the laboratory, the sediment samples should be deep-frozen at -20°C and, when frozen, freeze-dried in a freeze-dryer. But it is always interesting to archive part of the sample in order to be able to re-analyze it in case of suspected contamination during the analytical process. So, before freeze-drying, one half of the sample should be stored, as such, in the deep-freezer for future reference (in this case it could be interesting to have a -80°C deep-freezer).

In order to proceed with minimal risk of contamination in the freeze-dryer, the samples should be covered with aluminum paper with some pins holes to let the water vapor evacuate and reduce the eventual cross-contamination.

Contamination from the freeze-dryer and from the vacuum pump should be monitored by freeze-drying, with all batch of samples, a portion of clean Florisil. By analyzing the Florisil it is, then, possible to check if the freeze-dryer does not contaminate the samples.

The samples could be weighed before and after freeze-drying in order to access the ratio of dry/wet weight for each sample.

Note: for frozen sample there is no storage limit in time, for freeze-dried samples, if the samples are kept in the **dark**, in a **cool place** (20°C) and with **Teflon tape** around the neck of the bottles to avoid the humidity to enter in the sample, the limit of conservation could be on the order of 10-15 years without deterioration of the sample.

(ii) Sieving:

After freeze-drying the sediment samples could be sieved in order to remove the small gravels, pieces of branches and shells. Before sieving, it is recommended to sort out, with stainless steel forceps (for organic analysis), or with plastic ones (for trace metal analysis), from the sediment sample the small pieces of shells, branches and leaves that could be present in the sample in order to avoid contamination by extra materials. To do that, the samples are transferred to the top sieve of a sieving machine and the machine is activated. Doing so, the sediment will be disaggregated and not crushed.

The question of sieving is very delicate, as many possibilities exist. Some may sieve at 1 or even 2 mm (pre-sieving), only to remove the small pieces of shells, leaves and branches while others may sieve at 250 µm. In most cases, sieving the sediments through a 63 µm sieve in order to separate the silt and clay from the sand and coarser material is both useful and practicable and it is a widely adopted procedure. However, sieving is not recommended for fine and homogeneous sediments, usually found in the zones with high sedimentation rates where the content of the contaminants will be highest because of their wealth of fine particles for which the contaminants have a particular affinity. Obviously, when it is not possible to find fine sediments, sieving can be recommended to extract the finest particles.

Ideally, the sample could be sieved at 63 µm and the two fractions (less than 63 µm and more than 63 µm) could be analyzed. Even in some cases, sieving at 20 µm is undertaken and 3 fractions are, then, analyzed: more than 63 µm, between 20 µm and 63 µm and less than 20 µm.

Since sieving may also cause contamination problems in the samples (basically for the organic contaminants), many steps of sieving should be avoided -if possible- and it may even be recommended to sieve only from 250 µm before organic contaminant analysis.

For spatial trend monitoring sieving is not a critical issue; however, sieving from <1 or <2 mm in the field is recommended to take place directly after sampling or after the freeze-drying step.

For temporal studies sieving is recommended over 63 µm. However, the important thing is to achieve programme consistency and therefore, it is not recommended to switch to any other fraction if all set criteria in terms of sufficient trend detection are met by a laboratory that is using a whole fraction (e.g. less than 1 or 2 mm) for temporal studies.

A preferable approach is to minimize pre-treatment procedures and unify them for all types of metal/organic analyses and monitoring programmes, both spatial and temporal. Accordingly, sieving to less than 63 µm should be avoided since dry sieving is not reproducible whereas wet sieving is complicated and may introduce the following faults: (i) metal release due to the use of water with different pH and salinity; (ii) mineral (carbonates) dissolution when distilled water is used; (iii) contamination during the sieving and the successive drying.

It is therefore recommended to use one-step dry sieving of the less-than-1 mm fraction in order to perform the analyses on total (bulk) sediment. The rationale for this recommendation is as follows:

(i) Better representation of all relevant size fractions; in some sites coarser fractions (generally, fine and medium sand) are dominant and may contain a significant portion of the total metal (or pollutant).
(ii) Simple to handle.
(iii) Applicable for a wide range of sedimentary provinces and suits a multi-national monitoring programme for the Mediterranean countries.
(iv) Facilitates the use of elemental normalizers (see below).
(v) Avoids potential contamination that might be introduced via wet sieving and successive drying.

(iii) Wet sieving:

Some laboratories use wet sieving techniques. One of the problems that occurs with this technique is the possibility of contamination for organic samples as the material used for this wet sieving method is plastic (silicone tubing and plastic tubes with nylon nets). Another factor that has to be taken into consideration in using the wet sieving technique is the time consumed. The wet sieving method could, however, be used for trace metal work and in well-equipped and staffed laboratories.

Note: If wet sieving is applied, it is recommended to perform it on board using in-situ seawater and thus avoid using in-lab fresh or distilled water in order to prevent metal release and mineral dissolution (see above). However, wet sieving should not be applied on board if there are technical limitations and potential contamination from vessel oils and metal corrosion or from local polluted seawater.

(iv) Archiving:

Archiving sediment (and biota) samples is a must in QA/QC procedures. All samples should be kept for the duration of the monitoring in order to be able to come back to any of them, or to all of them, in case of problems.

Archives should consist of different parts: the first one being the sample wet and deep-frozen as it has been collected. This archive will be used in case of contamination that can appear during the freeze-drying process. So, one part of the original sample can be extracted again, even wet and dried with sodium sulfate, if it appears that the freeze-dryer had contaminated the sample.

Then when the sample has been dried, and an aliquot has been analyzed, the remaining sediment sample should be kept in a glass bottle, with Teflon tape around the closing system (that should be aluminum for organic and plastic for trace metal) to protect against the moisture and then, stored in a cupboard in the dark and cool place. This way, the sample archived can be stored for 10-15 years, so, for the duration of the monitoring program.

4. Normalization factors

4.1 Background

Pollutants tend to be associated with the fine particles of marine sediments due to the relatively higher surface area and the compositional characteristics of the fine particles. Both phyllosilicates and organic matter, which have a chemical affinity to trace elements and organic pollutants, are concentrated in the clay (less than 2 μm) and fine silt (2–20 μm) fractions. Most other minerals, including feldspars and heavy minerals, are found in the fine and coarse (20 - 63 μm) silt fractions, whereas the sand fraction (63 μm – 2 mm) mainly consists of carbonate (calcite, aragonite, dolomite) and/or silica (quartz, opal) minerals. Exceptions to this are coastal sediments of mafic and ultra-mafic terrains.

The metals of considerable environmental impact are As, Pb, Hg, Cd, Zn and Cu. Other metals, such as Mo, Ni, Cr and Co, may reflect anthropogenic input resulting from local quarrying and industrial activities. Anthropogenic Cd and Hg have a stronger affinity to organic matter than to clays, whereas natural Ni and Cr may be related to heavy minerals in certain sedimentological provinces. In order to detect anomalous concentrations of anthropogenic origin it is necessary to normalize the results by a physical or a chemical factor. Some elements may have background concentrations below or near the limit of detection for chemical analysis. Therefore, it has been shown that there is no single normalizing factor that can cope with all pollutant metals in all types of coastal sediments, or even in a single type. Comparing the results to average crust, or upper crust, concentration has been shown to be of limited value for this purpose (Loring and Rantala, 1992; Covelli and Fontolan, 1997) and therefore it is not discussed here.

4.2 Review of normalization methods

4.2.1 Physical normalization

The carbonate and silica mineral groups naturally contain negligible amounts of trace metals and therefore serve as diluents of the marine sediments. Removal of much of those diluents should: a) enhance the analytical capability of detecting low-concentration pollutants; and b) enable comparison between samples on a compositional basis of improved homogeneity. Consequently, choosing the less-than-20 μm or less-than-63 μm fraction for analysis, as mentioned in document UNEP(DEC)MED WG.273/2 (Anavissos meeting report, May 2005), seems like an adequate solution for normalization. Several marine sediment studies of trace elements and their isotopic composition, especially of Nd and Sr, preferred to analyze the less-than-20 μm fraction for geochemical purposes (e.g., Innocent et al., 2000; Krom et al., 2002). However, we are not aware of any such studies for environmental purposes. An essential difficulty in using this size fraction is that it excludes the contribution of trace elements in heavy minerals, and therefore the adequate evaluation of background values. Sieving the less-than-20 μm fraction is also technically problematic since it needs in-lab wet sieving with water of different pH and salinity, consumes more time and hence the process is more prone to both metal loss from the sample and contamination. Therefore, if physical normalization is adopted, the less-than-63 μm fraction is preferable to the less-than-20 μm fraction for environmental studies, as has been suggested in the Anavissos meeting report (May, 2005), though some of the difficulties remain.

Nevertheless, utilizing physical normalization by wet sieving might suffer from the following disadvantages: a) any sample manipulation is vulnerable to contamination; b) drying the sediment in an oven or freeze drier, a common practice (Loring and Rantala, 1992; Barbanti and Bothner, 1993), is an obstacle for sample desegregation before wet sieving. Ultrasonic treatment is needed in order to facilitate desegregation, which in turn may cause transfer of pollutants from solid to solution (Barbanti and Bothner, 1993); c) in cases of highly variable mineralogical composition, especially in the sand fraction, the normalization would not reflect this variability. Therefore, most environmental studies dealing with polluting metals use the total sample composition, where "total" generally means the less-than-2, or 1 mm fraction (Loring and Rantala, 1992).

An alternative approach for utilizing physical normalization may be applied in areas where preliminary data indicates that all, or almost all, trace elements and pollutants reside in the less-than-63 μm fraction. In such cases the chemical analysis should be performed on a bulk sub-sample whereas grain-size analysis should be performed on another sub-sample. The chemical results are presented after normalization to the less-than-63 μm fraction.

4.2.2 Chemical normalization by a representative element or elements

Chemical normalization has the following advantages: a) a single analytical procedure is practiced for the determination of all required elements, the pollutants and those used for normalization; b) minimal manipulation of the sample minimizes contamination; c) the chosen element, or elements, supposedly normalizes both the grain size and the composition variability.

The element most used for marine sediment normalization is aluminum (Al) since it represents aluminosilicates, the main group of minerals generally found in the fine sediment fractions. Aluminum supposedly: a) derives from detrital minerals, transported from the continent to the sea; b) has negligible anthropogenic input; c) behaves conservatively in normal marine environments. Therefore, Al is expected to normalize for grain-size and for mineralogical variability (Bertine and Goldberg, 1977; Din, 1992; Hanson et al., 1993; Daskalakis and O'Connor, 1995; Covelli and Fontolan, 1997, among others). Another advantage of Al is its easy, precise and accurate chemical determination.

Lithium (Li) has been shown to serve as a better normalizing element than Al in marine sediments enriched with 2:1 phyllosilicates, as in the North Sea where sediments derive from eroded glacier material (Loring, 1990). This element, which generally is not contributed by anthropogenic activity, has been recently found to be superior to Al in a Mediterranean study (Aloupi and Angelidis, 2001) but inferior to Al and to Fe in another Mediterranean study (Covelli and Fontolan, 1997). Loring and Rantala (1992) recommended determining at least Li and/or Al. Rubidium is similar to Li in its geochemical behaviour. As a trace substitute for K it may represent phyllosilicates, feldspars and some heavy minerals and it is not thought to result from anthropogenic activities. It has been used successfully in a few environmental studies in the UK (Allen and Rae, 1987; Grant and Middleton, 1990), but apparently not elsewhere.

Iron (Fe) has been successfully used for normalization in several studies (Rule, 1986; Sinex and Wright, 1988; Blomquist et al., 1992; Herut et al., 1993; Daskalakis and O'Connor, 1995; Schiff and Weissberg, 1999). However, it has been suggested that remobilization and precipitation can lead to changes in the pollutant/Fe ratio in anoxic sediments (Schiff and Weissberg, 1999). The latter are hardly expected to be found in Mediterranean sediments of open coasts.

A few studies used scandium (Grousset et al., 1995; Ackerman, 1980) and cesium (Ackerman, 1980), or also cerium, beryllium and europium (Herut et al., 1997), as the normalizing element. Since each of these elements may cause analytical difficulties, they are currently not recommended to be used on a routine basis.

4.2.3 Modes of chemical normalization

Chemical normalization by an element is to be performed by one of the following methods:

(i) By comparing the samples, suspected to be polluted, to nearby non-polluted samples of similar texture, mineralogical and major chemical composition. Background concentrations of the non-polluted samples can be established from surface sediments of other regions or from deep core samples of the same region, below the level of anthropogenic intervention. The potential pollutant concentrations should be compared with background averages in order to calculate the enrichment factor (EF) as follows:

$$(1) \quad EF = \frac{X(s)/N(s)}{X(b)/N(b)}$$

where X is the element and N the chemical normalizer (e.g. Al/Fe/Li) concentration; (s) is the sample; (b) is the background value. The evaluation of the EF value taken for estimating pollution should consider both natural variability and analytical errors (especially if the background concentrations were determined in/by another laboratory and/or analytical device).

(ii) By comparing the measured pollutant and chemical normalizers (or multi-element normalizers, Herut and Sandler, 2007) to their relationships in non-polluted (background) sediments, which have a linear relationship at the 95% confidence level, or better, and a high significance ($P<0.001$). The regression equation should follow either **$y = ax$** (x is the normalizing element) or **$y = ax + b$** (Loring and Rantala, 1992; Herut et al., 1995; Covelli and Fontolan, 1997; Roach, 2005). An estimate of the anthropogenic fraction and the ratio between the measured and predicted values (y) can be defined, where the predicted value is within the range of $1 \pm 2\sigma$.

(iii) By calculating the regression line between contaminant and normalizer through a pivot point, which is the concentration of both elements in a non-polluted sand fraction (Kersten and Smedes, 2002) of a selected standard sediment composition. This approach has been adopted by OSPAR (OSPAR/JAMP, 2002; OSPAR, 2005) and is presented in detail in Herut and Sandler (2007).

In summary - Aluminum (Al) and total organic carbon (TOC) determinations should be obligatory. If possible, the determination of Fe and Li as additional normalizers is recommended in order to better assess basin-wide spatial and temporal trends. The most practical normalization approach for the Mediterranean at this stage is the use of the linear regression equations.

The lack of standardized datasets for the Mediterranean prevents defining ‘pivot values’ and the use of the OSPAR chemical normalization approach. It is recommended that a standard analysis be performed for the areas to be monitored including: i) grain-size distribution in order to obtain the relations between physical and chemical normalizers; ii) heavy metal concentration in natural non-contaminated sand fraction; iii) mapping the chemical normalizers (Al, Fe, Li, TOC) range for selecting the proper standard sediment composition; iv) assessment of errors associated with the normalization approach.

4.3 Particle size analysis

Particle size analysis may be performed in order to better characterize the sediment nature and the sedimentological regime of the region monitored. The methods for fractionation into grain size can be found in UNEP/IOC/IAEA (1995) and in Loring and Rantala (1992).

The most time-efficient and robust way to obtain particle size analyses is by a laser-diffraction analyzer. There are many laser-diffraction analyzers on the market, such as the Malvern Mastersizer, the Coulter LS Particle Size Analyzer, or the Microtrac S3500 Analyzer. Laser diffraction is used to detect particle sizes in the range of ~ 0.1 to 2000 µm equivalent spherical diameter (depending on the instrument) using light scattering theory. The refractive and absorption indices for the material must be known for accurate measurements to be made.

Laboratories in which continuous grain-size counters (e.g. Mastersizer) are not available should follow Figure 6. The grain size distribution below 63 µm is determined by one of the sedimentation methods.

Sedimentation methods are based on the application of Stokes' Law, which describes the terminal velocity for an isolated sphere settling in a viscous liquid under the influence of an accelerating force such as gravity. Sedimentation techniques can be cumulative or incremental. In the cumulative method, the rate at which the particles settle is determined, typically, by weighing the mass of settled particles at a certain depth over time. In the incremental method, the change in concentration or density of the material with time is measured at known depths, typically using optical or X-ray sensing. Sedimentation methods are best suited to particles in the range 2-50 µm and, therefore, may not be appropriate for bulk sediment. Temperature must be accurately controlled in order to keep viscosity constant. Incremental sedimentation techniques can be carried out using instruments such as the X-ray SediGraph, manufactured by Micrometrics.

Laboratories equipped with continuous grain-size counters should dry sieve a freeze-dried sub-sample according to the instrumental analytical range (old instruments – below 250 µm; new – below 1 or 2 mm).

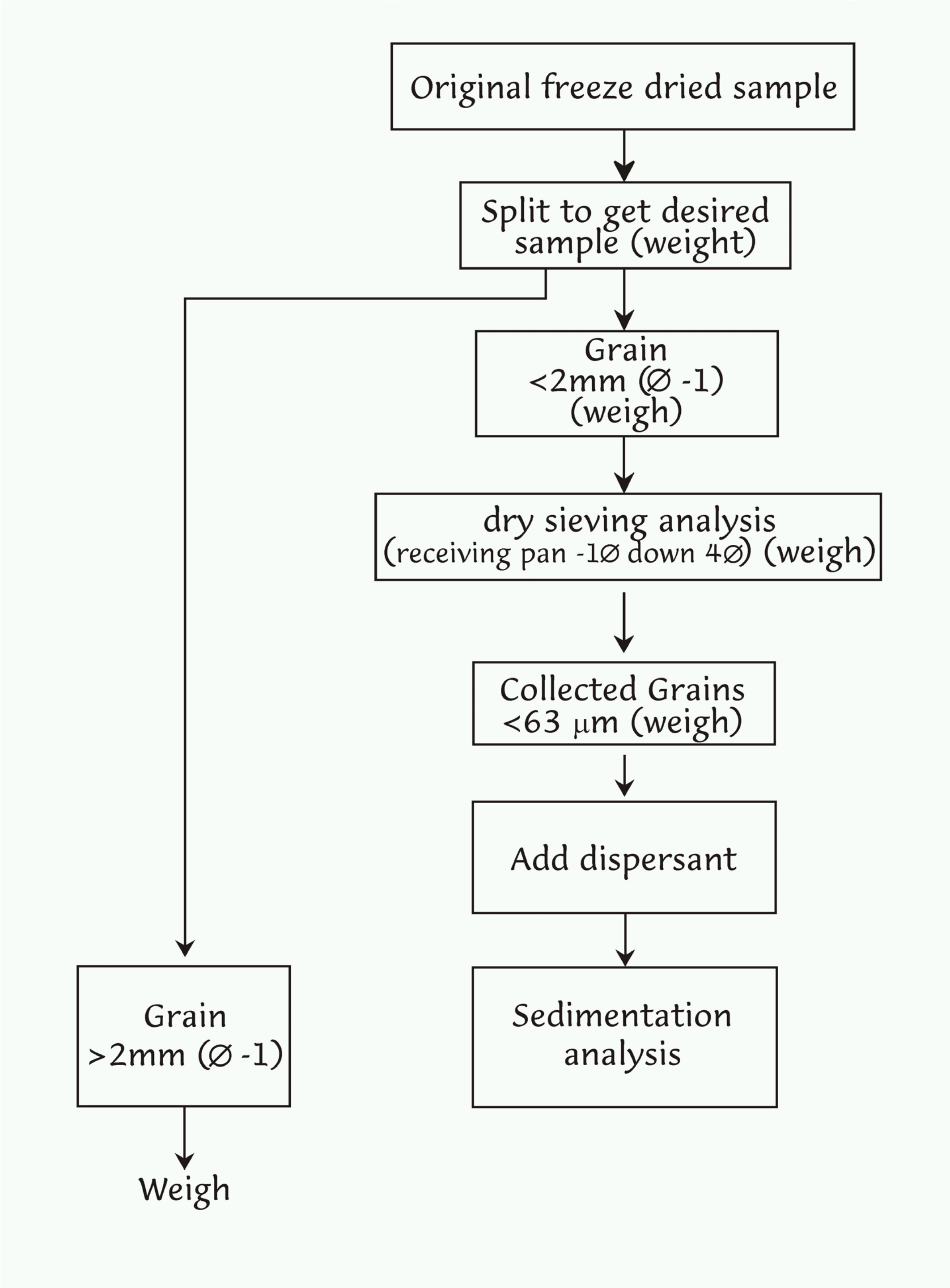


Figure 7: Sequence of steps for the grain size separation of a sediment sample (Please note that 2 mm grain size stands also for 1 mm).

4.4 Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC)

Organic material interacts strongly with both organic and inorganic contaminants. The organic carbon is one of the measures of the organic material. Another parameter would be the determination of lipids, or lipid-like material. The measurement of the hexane extractable organic matter (or HEOM) is also a normalising variable.

The carbonate content (inorganic carbon) of the sediment is generally considered as a dilution factor of the main phases carrying the contaminants and should, also be determined.

Total inorganic carbon (or carbonates) are obtained by the difference of data:

$$\text{TIC (\%)} = \text{TC (\%)} - \text{TOC (\%)}$$

(i) Preparation of samples

Samples for TC analysis are weighed (mg) in tin boats and directly analysed. Samples for TOC analysis are weighed (mg) in tin capsules and acidified with H_2PO_4 1M until the inorganic carbon is removed (3 times in 8 hours intervals to the oven at 55°C). Tin boats and capsules are folded and pressed before the analysis.

(ii) Procedure

Analyses could be done with automatic analyser (such as Elementar “VARIO EL” Instrument) in CN mode. For the mass determination of C and N, an oxidation of the sample followed by the reduction of nitroxides is realized, coupled to chromatographic glass column separation and thermal conductivity detection for CO_2 and N_2.

Note: In case a CHN analyser is available and used for the TC-TOC analysis, Total Nitrogen and Total Organic Nitrogen can be measured simultaneously which can provide a general insight of the lability of organic matter, simply based on the C/N ratio.

(iii) Quality control

Acetanilide standard (C_8H_9NO) is used as a correction factor for accurate and precise measurements (71.1 % C and 10.4 % N) and to control instrumental stability.

The precision of TOC and TC measurements in the samples depends in numerous random factors such as: weighing, use of an acidification step, sample structure (i.e. matrix), concentrations, as well as the instrumental noise. Coefficients of variation (% RSD) must be calculated for each pair of determination, specially, for TOC analysis, which includes an acidification step.

Alternative method to estimate Organic Material in case a CHN Analyser is not available:

The Organic Matter (OM) content in sediments can be measured with the following method:

a) Put the (wet) sediment sample in oven at 60°C for 24 hours (up to constant weight).
b) Weight approximately 1 g of dry sediment (precision 0.01 mg) in a small porcelain boat.
c) Put the sediment for ignition into a furnace at 450°C for 3 hours.
d) Weight the sediment after ignition (precision 0.01 mg).

The Organic Matter (OM) content is equivalent to the percentage of Loss of Weight (LOI %)

$$LOI\ \% = (W_{dry} – W_{ign}) \times 100 / W_{dry}$$

Where:

LOI % = Loss on Ignition (equivalent to the total Organic Matter)
W_{ign} = Weight after ignition
W_{dry} = Weight of dry sediment before ignition

5. Analytical techniques for organic compounds

Before proceeding to the analysis, an aliquot will be taken from the bulk sample and in order to be sure that what is analyzed is representative of the collected sample, the sediment sample should be well homogenized. This could be done in a specialized laboratory homogenizer, but it could be done, more simply, with a spatula, taking care of mixing well the sediment sample before collecting the 10 g aliquot (for organic) or the 1-2 g aliquot (for trace metal) for the extraction.

The analytical part can be found in the Reference Methods for Marine Pollution Studies published by UNEP. All these Reference Methods are available, free of charge, from IAEA-MEL/MESL.

With a set (one for 10 samples, as a minimal requirement) of sediment samples extracted, sediment Reference Material should be extracted to check the quality of the data produced (UNEP/IOC/IAEA/FAO, 1990).

5.1 Chlorinated pesticides and PCBs.

The analytical method for chlorinated pesticides and PCBs in sediment samples, can be found in UNEP/IOC/IAEA, 1996.

5.2 Petroleum hydrocarbons.

The analytical method for petroleum hydrocarbons can be found in UNEP/IOC/IAEA, 1992.

5.3 Organophosphorus pesticides

The analytical method for organophosphorus pesticides in sediment samples can be found in UNEP/FAO/IOC/IAEA, 1997.

6. Analytical techniques for trace metals

For trace elements, in general, the analytical methods can be found in UNEP/IOC/IAEA, 1995.

For mercury: in UNEP/IAEA, 1985 and UNEP/IOC/IAEA, 1985.

7. Sediment radiochronology with ^{210}Pb

One of the main objectives of surface sediment monitoring is to obtain time series that allow to derive the presence or absence of temporal trends due to anthropogenic pressure. However, monitoring programmes are often not long enough to produce valid assessments. Sediments integrate pollution signals and dated sediment cores may provide a reliable record of pollution levels (e.g. Sanchez-Cabeza and Druffel, 2009). Although radiocarbon is used to study impacts extending back millennia, the most suitable tracer for pollution studies is ^{210}Pb because its half-life (22.23 y) allows suitable dating for the last 100 years, when most of the anthropogenic impact has occurred.

^{210}Pb is a natural radionuclide of the ^{238}U radioactive chain with a half-life of $T_{1/2}$ = 22.23 ± 0.12 yr (DDEP, 2010). It is commonly assumed that *supported* ^{210}Pb in old (> 150 yr) sediments is in equilibrium with its parent radionuclide ^{226}Ra. In recent sediments, ^{210}Pb in disequilibrium with ^{226}Ra is named *excess* (or *unsupported*) ^{210}Pb ($^{210}Pb_{ex}$). The total ^{210}Pb concentration in sediments is usually measured i) by gamma spectrometry (46.5 keV line; Schelske et al., 1994), or ii) alpha spectrometry, through its daughter radionuclide when equilibrium is guaranteed (Sanchez-Cabeza et al., 1998). ^{226}Ra (supported ^{210}Pb) is usually determined by i) gamma spectrometry (352 keV line of ^{214}Pb in equilibrium) or ii) liquid scintillation (Sanchez-Cabeza et al., 2010). If the full ^{226}Ra profile is not available, a mean ^{226}Ra concentration can be i) computed as the mean ^{210}Pb in the core bottom if at least 3 sections show an approximately constant concentration, within the measuring uncertainty (Binford, 1990) or ii) estimated by extrapolation of ^{210}Pb in the bottom sections if the profile shows there an exponential behaviour. Then, $^{210}Pb_{ex} = {}^{210}Pb - {}^{226}Ra$.

The use of $^{210}Pb_{ex}$ to date sediment cores has been used in a large variety of studies. Since ^{210}Pb was first used to date ice cores (Goldberg, 1963), several authors have developed models that adapt to different sedimentary conditions. These models, used to date undisturbed sediments, can be deduced from a single fundamental equation (Krishnaswamy et al., 1971), which relates excess $^{210}Pb_{ex}$ concentration in sediment, its flux to the sediment surface and mass accumulation rate.

7.1. Basic information

$^{210}Pb_{ex}$ decays following the radioactive decay law. If both the sediment accumulation and the $^{210}Pb_{ex}$ flux to the sediment surface were constant, and there were no processes that redistribute $^{210}Pb_{ex}$ in the sediment, the profile of the $^{210}Pb_{ex}$ concentration along the core should be a pure exponential curve (Figure 8). These conditions are not commonly met, but the described models allow obtain good dates in many cases. Some needed physical constants and sampling details are:

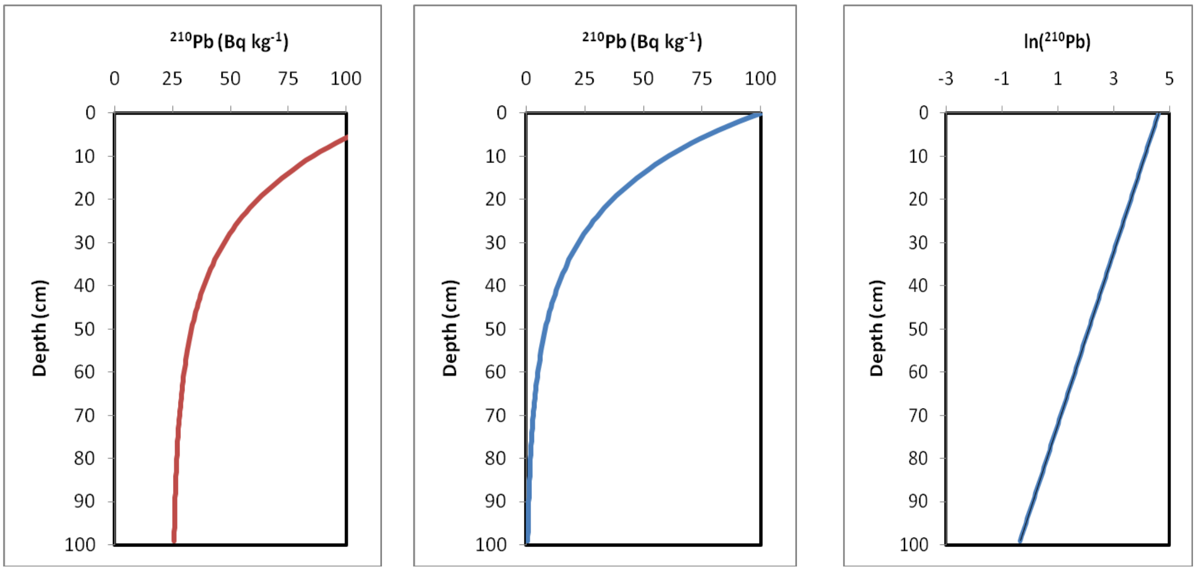


Figure 8. Ideal total ^{210}Pb (left), excess ^{210}Pb (centre) and its logarithm (right).

$T_{1/2} = 22.23 \pm 0.12\ yr$ (DDEP, 2010): ^{210}Pb half-life (yr)

$\lambda = 0.03118 \pm 0.00017\ yr^{-1}$: ^{210}Pb disintegration constant (yr^{-1})

$T(0)$: sampling date (A.D.)

φ : internal core diameter (m)

S : core cross-section (m^2), calculated as $S = \pi\left(\frac{\varphi}{2}\right)^2$.

As different models use similar quantities and constants, a unified notation has been proposed (Sanchez-Cabeza and Ruiz-Fernandez, in press). For example, C_i is the ^{210}Pb$_{ex}$ mean concentration of section *i*, assigned to the geometric centre of the section. Then C_1 is the top section and C_2 is the section below. In the Constant Flux (CF) model, equations refer to quantities in infinitesimal layers *(i)*, derived from calculation. We use *(i)* to refer to the consecutive number of the surface cut (layer) when sampling. For example, *(0)* refers to the core surface and *(1)* to the first surface cut below the surface (usually of the order of 1 cm). For brevity, we define only quantities referred to either sections or layers (usually, section quantities are computed as means of layer quantities). To take into account sediment compaction dating must be performed as a function of mass depth *m* (kg m^{-2}) and not depth *z* (m):

- *z(i)* : depth of layer *(i)* (m), experimentally determined. Note that *z(0)=0* m.
- Δz_i : width of section *i* (m), where $\Delta z_i = z(i) - z(i-1)$
- Δm_i : dry mass of section *i* (kg), experimentally determined
- *m(i)*: mass depth of layer *(i)* (kg m^{-2}), where $m(i) = \sum_{j=1}^{j=i} \frac{\Delta m_j}{S}$.

If we only know the section dry bulk densities ρ_j (kg m^{-3}), the mass depths *m(i)* can also be calculated as $m(i) = \sum_{j=1}^{j=i} \rho_j \Delta z_j$. The mean dry bulk density of section *j* is easily computed as $\rho_j = \frac{\Delta m_j}{S\, \Delta z_j}$.

Some time related quantities are:

- $t(i)$: time elapsed since formation of layer *(i)* (yr). Note that *t(0) = 0* yr
- $T(i)$: calendar age of layer *(i)* (A.D.), which is calculated as $T(i) = T(0) - t(i)$.

The CF model refers to ^{210}Pb deposits (or activity per unit area):

- *ΔA$_i$* : ^{210}Pb$_{ex}$ deposit in section *i* (Bq m^{-2}), computed as $\Delta A_i = \frac{C_i\, \Delta m_i}{S}$
- *A(i)* : accumulated deposit below layer *(i)* (Bq m^{-2}), computed as $A(i) = \sum_{j=i+1}^{j=\infty} \Delta A_j$
- *I = A(0)* : core ^{210}Pb$_{ex}$ inventory (Bq m^{-2})

There is a large variety of definitions that describe sedimentation rates (linear or massic). The following are recommended:

- *s* : sediment accumulation rate – SAR (m yr^{-1}).
- *r* : mass accumulation rate – MAR (kg m^{-2} yr^{-1}). Sediment and mass accumulation rates (SAR and MAR) are proportional: $r = s \cdot \rho$

When a sediment layer *(i)* is formed, the ^{210}Pb$_{ex}$ incorporated can be calculated as (Krishnaswamy et al., 1971):

$$C(i, t=0) = \frac{f(i)}{r(i)} \qquad (1)$$

This is the basic expression on which the dating models are based. If MAR increases, the concentration decreases and the ^{210}Pb signal is diluted. If MAR decreases, the concentration increases and the ^{210}Pb signal is enriched. Therefore, ^{210}Pb$_{ex}$ profiles are not pure exponential functions when accumulation rates are variable.

7.2. Dating models

Dating models are used to i) obtain the section/layer age as a function of depth (*t*), ii) calculate accumulation rates (*s, r*) and iii) estimate sediment mixing rates (not reviewed here). The models have been recently reviewed by Sanchez-Cabeza and Ruiz-Fernandez (in press) and the more useful and commonly used models are described here.

7.2.1. Constant Flux and Sedimentation model (CFCS)

It is recommended that the dating experiment starts with the use of this model, commonly used in the literature to estimate mean accumulation rates. The Constant Flux and Constant Sedimentation model (CFCS; Crozaz et al., 1964; Krishnaswamy et al., 1971; Koide et al., 1973; Brugam, 1978; Appleby and Oldfield, 1983) is based on two hypotheses, (i) that the flux to the sediment surface (*f*) is constant and that the mass accumulation rate (*r*) is constant. In these conditions equation 1 leads to:

$$\frac{f}{r} = C_0 \qquad (2)$$

The decay of ^{210}Pb as a function of time (and hence time) allows us to deduce the CFCS equation:

$$C_i = C_0\, e^{-\lambda m_i / r} \qquad (3)$$

This equation indicates that, when the CFCS hypotheses are met, a purely exponential decrease of C_i with depth should be observed (Figure 1, centre). This can be easily assessed by plotting the ^{210}Pb$_{ex}$ profile in a logarithmic scale as a function of the MAR (Figure 1, right), and then perform a linear regression between (Crozaz et al., 1964) the logarithm of ^{210}Pb$_{ex}$ concentration (ln C_i) and the mass depth m_i:

$$\ln C_i = \ln C_0 - \frac{\lambda}{r} m_i \qquad (4)$$

From the regression line equation obtained with a spreadsheet (*y* = *a* + *bx*) the intercept is $a = \ln C_0$ and the slope is $b = -\lambda / r$, then we can calculate $C_0 = e^a$ and, more importantly, $r = -\lambda / b$. From the regression uncertainties of *a* and *b* the uncertainties of C_0 and *r* can be easily derived. When the CFCS hypotheses are met, the purely exponential behavior of C_i *vs.* m_i allows to estimate ages. From the derived MAR, and assuming that *t(0) = 0 yr*, the age *t(i)* can easily be derived from $t_i = T(0) + \frac{m_i}{r}$. When the profile is piecewise linear, showing two or more linear segments (Goldberg et al., 1977; Brugam, 1978), we may derive mean MAR for each segment.

7.2.2. Constant Flux model (CF)

The Constant Flux model (CF; Robbins, 1978; Smith and Walton, 1980; Appleby and Oldfield, 1983; Binford, 1990; Carroll and Lerche, 2003) is widely known as the Constant Rate of Supply model (CRS; Goldberg, 1963; Crozaz et al., 1964; Krishnaswamy et al., 1971; Appleby and Oldfield, 1978; Appleby, 2001 and 2008; Sanchez-Cabeza et al., 2000). The fundamental hypothesis is that the ^{210}Pb$_{ex}$ flux to the sediment surface is constant (*f*). The age of layer *(i)* can be calculated as:

$$t(i) = \frac{1}{\lambda} \ln \frac{A(0)}{A(i)} \qquad (5)$$

where *A(i)* is the ^{210}Pb$_{ex}$ accumulated deposit below layer *(i)* and that, therefore, *t(i)* is the age of the infinitesimal layer *(i)*, not of a section. The mean age of a section, can be estimated as the mean of its upper and lower layers. *A(0)* is the $^{210}Pb_{ex}$ core inventory and the $^{210}Pb_{ex}$ flux to the sediment surface is $f = \lambda A(0)$.

Garcia-Orellana et al. (2006a) evaluated the ^{210}Pb annual atmospheric flux to the Western Mediterranean from the analysis of 12 soil cores collected from coastal and island sites. The ^{210}Pb fluxes ranged from 34 ± 3 to 121 ± 12 Bq m^{-2} yr^{-1}, with an average of 75 Bq m^{-2} yr^{-1}, and were strongly correlated ($R^2 = 0.95$) with mean annual rainfall. These results can be used to assess the degree of $^{210}Pb_{ex}$ (and therefore fine particles) focussing in a particular area. In general, $^{210}Pb_{ex}$ inventories should be similar or higher than the expected atmospheric flux. Inventories below the expected atmospheric flux could indicate an incomplete inventory, due to erosion or removal of part of the sedimentary column by sedimentary events. Specific studies could be carried out to determine this value in specific regions (e.g. Sanchez-Cabeza et al., 2007).

The MAR can be calculated as:

$$r(i) = \frac{\lambda A(i)}{C(i)} \tag{6}$$

and then $s = r / \rho$. Mean section values can be calculated as the mean of their upper and lower layers.

7.2.3. Incomplete inventory

The use of the CF model requires the knowledge of the core $^{210}Pb_{ex}$ inventory, but this is sometimes not possible. The most common case is when the core length is too short and the ^{210}Pb profile does not reach the base value. In these cases it is recommended to use the CFCS model to obtain mean accumulation rates in the sampled segment and to estimate the missing inventory below layer *(j)* as (Appleby, 1998) $A(j) = \frac{r.C(j)}{\lambda}$. Then, one can calculate the inventory from the accumulated deposit to the incomplete core bottom ($\delta(A)$) and then the total inventory is $A(0) = \delta A + A(j)$. With this value we can now use the CF model described above.

Alternatively, if a reference date *(t)* is known to happen at layer *(i)*, we can calculate the inventory below that layer as $A(j) = \frac{\delta A}{e^{\lambda t} - 1}$ and then we can proceed as before (Appleby, 1998).

7.2.4. Mixed sediments

The main hypothesis of sediment dating is that the system is closed. This requires that $^{210}Pb_{ex}$ is not affected by redistribution processes. Mixed sediments do not provide useful information for reconstruction studies, although some information on mean accumulation rates below the mixed segment and other geochemical properties may be obtained.

The mixed segment (sometimes named SML, Single Mixed Layer) can be easily identified by the presence of an approximately constant ^{210}Pb activity (Figure 9). Below the mixed segment, the profile usually decreases exponentially and, therefore, the CFCS model can be used to derive MAR and SAR. Although some authors also use the CF model below the mixed segment, caution must be taken as, assuming that mixing is the result of a continuous process, the apparent time span of the mixed segment should be taken into consideration when estimating age uncertainties. If a quadratic propagation scheme is used, any age will have an uncertainty larger that the time span covered by the mixed segment and, therefore, its utility will be compromised. Mixed sediments should only be used to estimate mean accumulation rates.

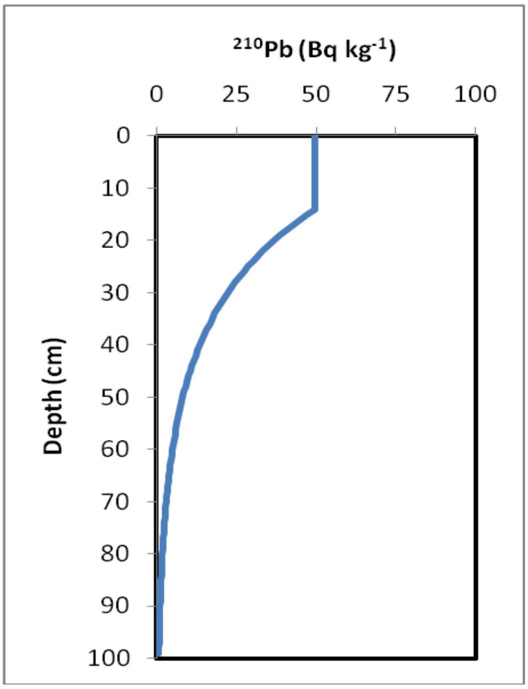


Figure 9. Mixed sediment. Notice the constant ^{210}Pb concentration at the surface.

7.3. Age model validation

The models shown are robust and have been successfully used many times. However, the complexity of most real situations (and particularly marine environments) is such that none of the models can be assumed appropriate without validation (Schottler and Engstrom, 2006). Traditionally, some global fallout radionuclides such as ^{137}Cs, ^{239,240}Pu and ^{241}Am are used. These three radionuclides should show a 1963 time mark in undisturbed sediments, corresponding to its maximum tropospheric concentration, and ^{137}Cs may reflect an additional time mark in 1986 due to the Chernobyl accident (e.g. Sanchez-Cabeza et al., 1999). Other time markers can be used to validate the age models, including for example:

- Volcanic eruptions may leave ash layers deposited in very short periods (Arnaud et al., 2006).
- Extreme events, such as floods, earthquakes and tsunamis, may leave distinct sedimentary deposits identified as abrupt changes of accumulation rates and various geochemical signatures (van den Bergh et al., 2003; Tuttle et al., 2004; Garcia-Orellana et al., 2006b).
- Changes in the type of accumulated particles (due to changes in land use, fires or other major catchment events) may be revealed by magnetostratigraphy (Oldfield and Appleby, 1984).
- The change in quantity and type of pollen grains may be related to changes in soil use in the catchment areas (Clark and Patt, 1984).

- Abrupt changes in known pollution sources (such as the opening or closure of a large industry) may be identified in polluted areas (Palanques et al., 1998; Diaz-Asencio et al., 2009).

7.4. Suggested procedure

If the $^{210}Pb_{ex}$ profile shows one or more exponential segments (linear segments in a logarithmic plot), mean MAR and SAR for each segment can be estimated by using the CFCS model. Although ages could also be estimated from MAR, the most realistic ^{210}Pb dating model is the CF model and is the one recommended to derive layer (and/or section) ages.

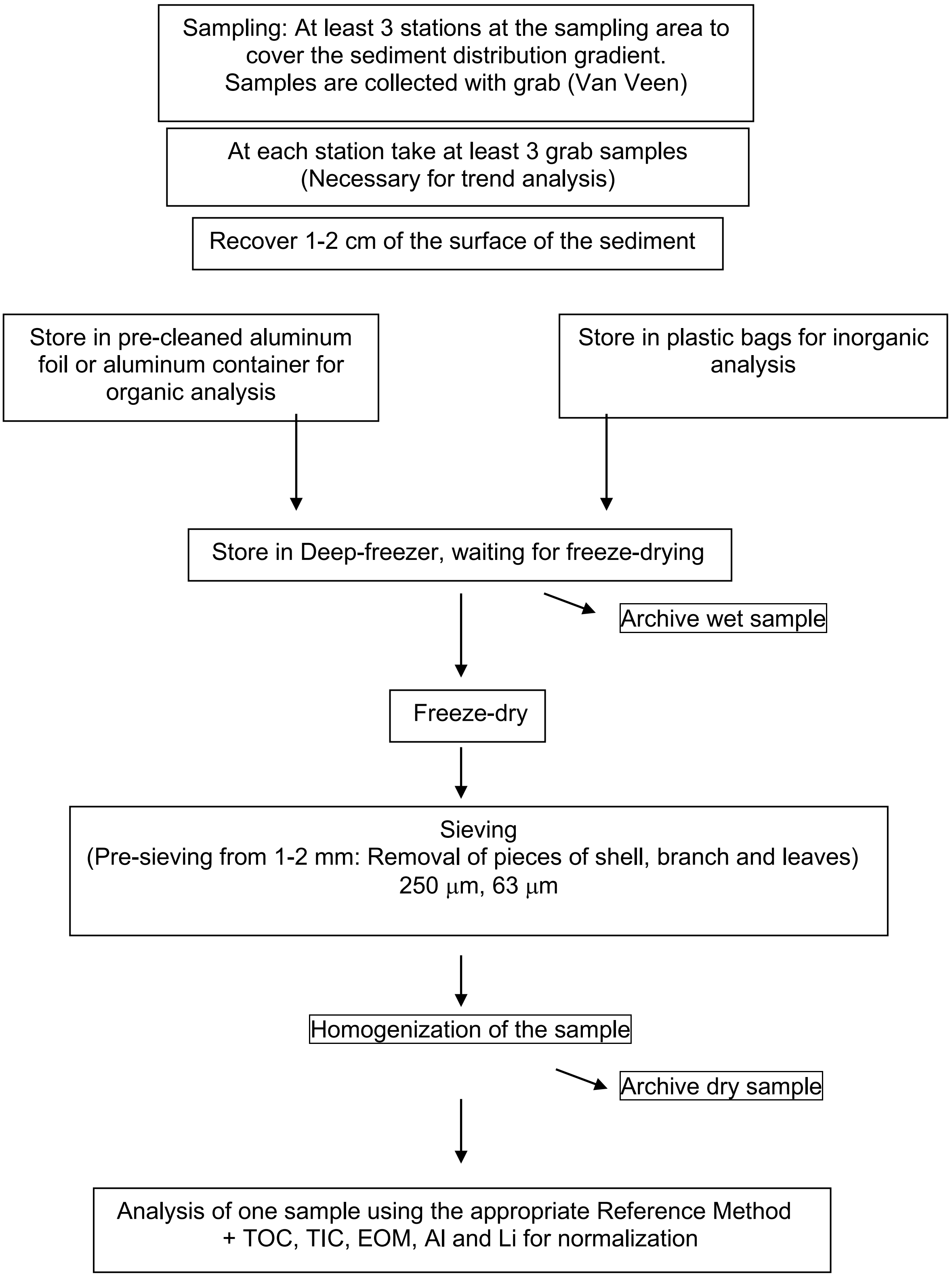
One procedure that could be useful in many cases is:

- From observations, calculate all basic parameters and variables.
- Observe the $^{210}Pb_{ex}$ profile, looking for deviations from the ideal exponential decay and formulating working hypothesis. If the core appears to be mixed, its use to reconstruct environmental conditions would be compromised and only MAR and SAR should be derived.
- Use the CF model to calculate the $^{210}Pb_{ex}$ flux to the surface sediment and compare it with other sediment cores and atmospheric fluxes. A deficit would imply sediment erosion and, therefore, its use to reconstruct environmental conditions would be compromised.
- Obtain the core age-model and section accumulation rates by using the CF model. Validate the CF age model.
- Obtain the MAR and SAR for each layer by using the CF model. Obtain the MAR and SAR for each section as the mean of 2 consecutive layers.
- Obtain mean accumulation rates (MAR and SAR) by using the CFCS model.
- If the $^{210}Pb_{ex}$ profile shows good linearity and the CF model cannot be validated, ages could be estimated form the MAR and massic depth by using the CFCS linear regression equation.

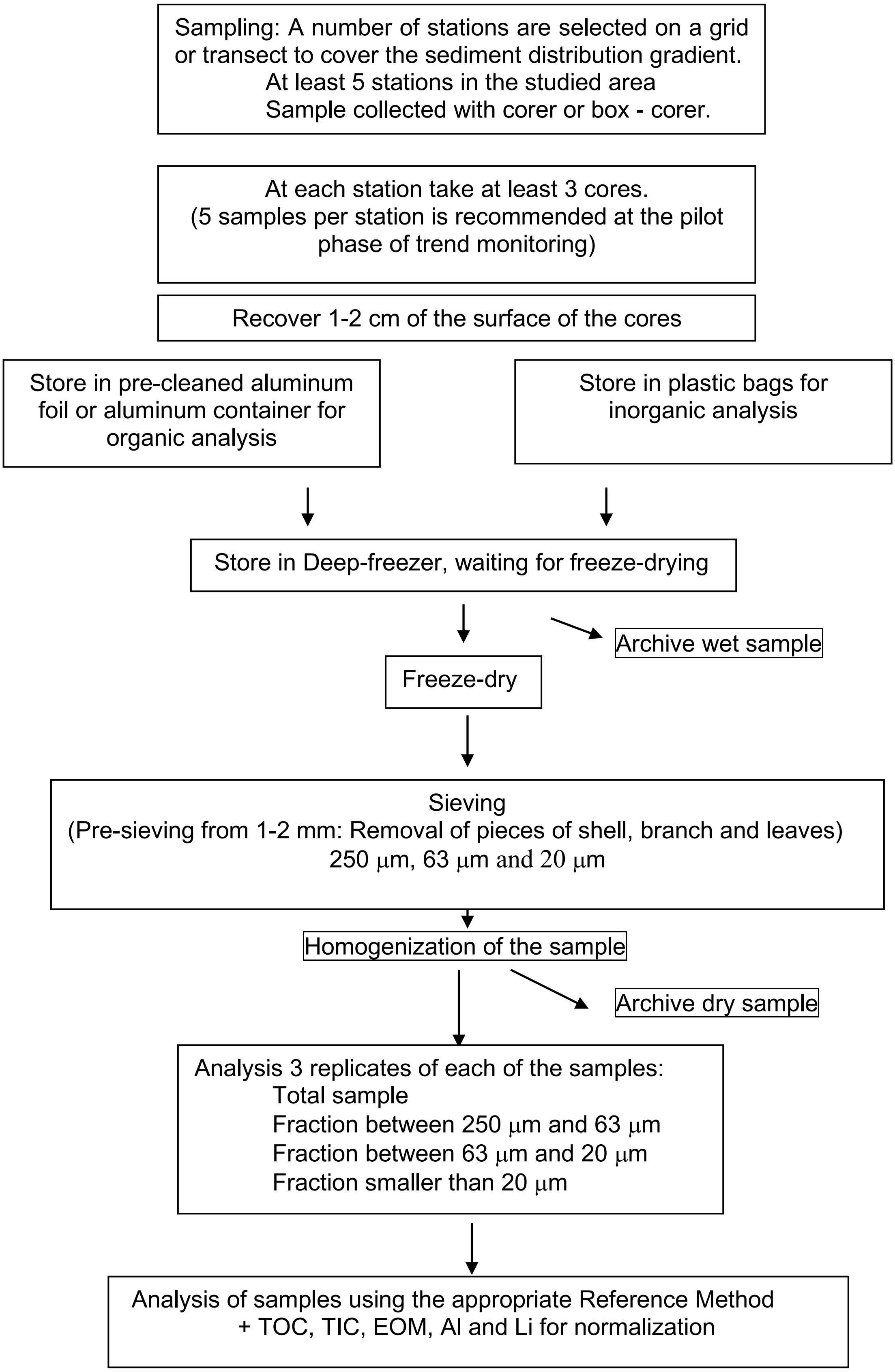
8. Conclusions

We can consider two different approaches to the sediment sampling for monitoring projects. They follow the schematics below depending on the budget and the manpower of the laboratories. One of the methods is a minimum requirement and the other would be the “state-of-the-art” methodology.

First approach (easiest and cheapest one):



Second approach (complete procedure):



Sampling: A number of stations are selected on a grid or transect to cover the sediment distribution gradient.
At least 5 stations in the studied area
Sample collected with corer or box - corer.

At each station take at least 3 cores.
(5 samples per station is recommended at the pilot phase of trend monitoring)

Recover 1-2 cm of the surface of the cores

Store in pre-cleaned aluminum foil or aluminum container for organic analysis

Store in plastic bags for inorganic analysis

Store in Deep-freezer, waiting for freeze-drying

Sieving
(Pre-sieving from 1-2 mm: Removal of pieces of shell, branch and leaves)
250 µm, 63 µm and 20 µm

Analysis 3 replicates of each of the samples:
Total sample
Fraction between 250 µm and 63 µm
Fraction between 63 µm and 20 µm
Fraction smaller than 20 µm

Analysis of samples using the appropriate Reference Method
+ TOC, TIC, EOM, Al and Li for normalization

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Annex

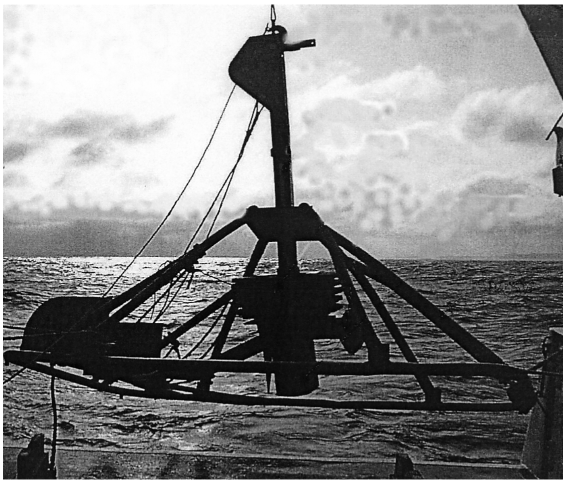
Pictures of some sediment sampling devices.

Large grab sampler
(picture: S. de Mora)

Shipeck grab sampler.

Bottom sampler Ekman-Birge
(picture: Hydro-Bios, Germany).

Gravity core sampler
(picture: S. de Mora)



Reineck corer

Annex II

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