IMPROVING THE UNDERSTANDING OF THE DANUBE RIVER IMPACT ON THE STATUS OF THE BLACK SEA

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#WRc plc

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List of Abbreviations

UNDP	The United Nations Development Programme
GEF	The Global Environmental Facility
BSERP	The Black Sea Ecosystems Recovery Project
PIU	The Project Implementation Unit
JTWG	Joint Technical Working Group
BSC	Black Sea Commission
PDF-B	GEF Project Development Fund, Phase B
ICPDR	International Commission for the Protection of the Danube River
BSIMAP	Black Sea Integrated Monitoring and Assessment Programme
DIN	Dissolved Inorganic Nitrogen
N	Nitrogen
AQC	Analytical Quality Control
ISO	International Standard Organisation
NATO	North Atlantic Treaty Organisation
JRC	Joint Research Centre of the European Commission
SD	Secchi depth
DOW	Dissolved Oxygen (as determined by the Winkler titration method)
NH_4	Ammonium
NO_2	Nitrite
NO_3	Nitrate
PO_4	Ortho-phosphate
SiO_4	Silicate
BOD, BOD_5	Biological Oxygen Demand (5 days)
COD	Chemical Oxygen Demand
ANOVA	Analysis of variance
HRPT	High Resolution Picture Transmission
GSFC DAAC	Goddard Space Flight Centre Distributed Active Archive Centre
SeaDAS	SeaWiFS Data Analysis System
PCB	Polychlorinated biphenyl
PNG	Portable Network Graphics format
SeaWiFS	Sea-viewing Wide Field-of-view Sensor
BSMS	Black Sea Main Stream
TSS	Total suspended solids
NW	North-Western
PMA	Pollution Monitoring and Assessment
QA	Quality Assurance
POC	Particulate Organic Carbon,
PN	Particulate Nitrogen
DON	Dissolved Organic Nitrogen
SRP	Soluble Reactive Phosphorus = PO_4-P
DSi	Dissolved Silicate

1. SUMMARY

For the first time, this report makes use of available data to assess the impact of the Danube River on the North Western Shelf of the Black Sea and examines the pragmatism of a series of environmental indicators, originally agreed by the Black Sea-Danube Joint Technical Working Group (JTWG) for doing this. The inability to establish baseline (reference) conditions meant that rather than a true impact assessment, a spatial 'state of the environment' comparative approach had to be adopted.

A large body of evidence is available to suggest that nutrient loads to the Black Sea via the Danube River have fallen substantially over the last 10-15 years. However, the Danube Trans-National Monitoring Network has not been in operation for such a long period of time and the adoption of good quality assurance procedures has meant that only three years worth of nutrient loading data are currently available (a fourth year, 2003, is due to be published soon). This is too short a period to undertake a trend analysis of river loads. However, a number of statistically significant trends (improvements in water quality) have been detected in the Danube River (notably nutrients) over the last 10-15 years, with up to 30% annual reductions (1996-1998) in some (ammonium) concentrations.

Unfortunately, recent improvements in Black Sea water nutrient concentrations have been much less dramatic when average results are considered. Indeed, in direct contrast to the Danube, some Black Sea trends are positive, showing up to 3-5% increases in nutrient concentrations. It is likely that a longer lag period is required before the benefits of reduced riverine nutrient loads to the North Western Shelf will be reflected within the Sea itself, a conclusion which is supported by the recent publication of a nutrient budget for the North Western Shelf (Fig. 3.1). Regardless of these recent results, data presented for one Romanian site (Constanta) show dramatic improvements in orthophosphate concentrations since the mid-1980s (Fig. B.6). This figure shows an overall decrease in nitrate concentrations since the mid-1970s, albeit with an increase in more recent years.

The Danube clearly has had a major historical impact on the North-Western Shelf, but the Sea appears to be recovering as a functional ecosystem, with dissolved oxygen and macrozoobenthos data appearing to be the best indicators of this. However, the Danube appears still to be a significant source of other contaminants – both organic (some PCBs and chlorinated pesticides) and inorganic (heavy metals). Huge capital investment in sewage treatment within the Danube River Basin has improved the situation with regard to nutrients and major organic pollution of the river, but any improvements in heavy metals loads and diffuse sources of pollution are much more difficult to assess, particularly as the current assessment does not involve source apportionment modeling. For this, inputs from other rivers, (local) direct discharges to the marine environment, atmospheric deposition and the historical contribution to surface sediment contamination need to be fully evaluated. However, statements about the impact of the Danube have be taken in context: even for increased levels of those pollutants which are associated with the Danube inflow, sediment concentrations are not massively elevated offshore of where the River enters the Sea; and comparable concentrations of many of these parameters have been recorded at sites that are much less heavily influenced by the Danube. The implication of this is that pollutant export from coastal regions (much smaller areas than that of the Danube Basin) is proportionally greater (on an areal basis) than from the land drained by the Danube.

The use of chlorophyll-a (chl-a) concentrations as an environmental status concentration is critically reviewed. While it is still regarded as a useful indicator, a wide range of factors need to be considered in data interpretation. As an indicator, chl-a concentration requires extensive interpretation and explanation. The use of remote sensing data for estimating chlorophyll results has been a worthwhile exercise, but uncertainty over the temporal and spatial variability of these results when compared with laboratory-measured chl-a introduces a further question mark over their utility.

Macroalgal morpho-functional parameters indicate that the major impact of the Danube is restricted to a relatively small part of the North Western Shelf. This is unlikely to be the case, bearing in mind results from zoobenthos monitoring studies, and is more likely to be a reflection of the very small number of monitoring locations. The macroalgal results should also be treated with caution because they are prone to bias from localized sources of nutrients (e.g. costal sewage treatment works outfalls). Morpho-functional parameter information was the only data available for use in this report, but the Black Sea Commission's Pollution Monitoring and Assessment Advisory Group recently proposed the use of vegetation indicator species (*Zostera marina* and *Cystoseira barbata*) as indicators of trophic status within BSIMAP

Monitoring of phytoplankton and zooplankton populations has not yet produced comparable data from the six Black Sea riparian countries, although it is expected that this situation will improve in the near future. Although there are clear advantages to the identification of phytoplankton taxa, biomass monitoring appears to be considerably more expensive is perhaps a weaker indicator than chlorophyll-a determination. However, if the ratio of diatoms:dinoflagellates is to be used as an indicator of trophic status, with results expressed on a biomass, rather than a cell number, basis, the biomass of individual taxa and taxonomic groups must continue to be measured. The benefits of zooplankton monitoring as an environmental status indicator are unclear at this stage, although such results should help explain variability in phytoplankton/chl-a monitoring results. However, the number, size and biomass of *Noctiluca* spp. (a genus of non-photosynthetic dinoflagelates) are considered important indicators of environmental status. Although in taxonomic terms *Noctiluca* spp are classed as phytoplankters, the large size (300-600 µm) of these organisms means that they are monitored during zooplankton monitoring exercises.

Gross organic loads to (BOD_5) and organic concentrations within (total organic carbon) the Black Sea are necessary indicators of trophic status and of the impact of the Danube River (and other pollutant sources). Monitoring of BOD_5 loads to the sea will continue to be undertaken, but a recent proposal of the PMA Advisory Group to change BOD_5 from a mandatory to an optional parameter (with good reasons), and to maintain total organic carbon as an optional parameter, means that there is a risk of organic status within the Black Sea being ineffectively monitored in future years.

No turbidity or Secchi depth data were available for analysis within this report

The existing Black Sea Integrated Monitoring and Assessment Programme (BSIMAP) is described and factors for consideration in updating this are discussed Proposals to increase the number of biological monitoring metrics for the 2006-2011 BSIMAP are considered. There is a need for some countries to identify appropriate reference sites within the BSIMAP, and a need for more detail regarding what parameters are to be measured and what indicators should be used. Important decisions will need to be made in the near future over updating the Black Sea Information System in terms of whether raw or processed biological data should be reported to the Black Sea Commission.

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2. INTRODUCTION

2.1 Background

Work conducted in the previous GEF PDF-B and Phase I BSERP programmes, and discussion between the ICPDR and the Black Sea Commission via their Joint Technical Working Group has led to the selection of a number of environmental status indicators for the Black Sea. These are considered to be key elements underlying the work of the BSC and its Permanent Secretariat, and thus should play a crucial role in the design of the Black Sea Integrated Monitoring and Assessment Programme (BSIMAP). These indicators are:

1. Nutrient concentrations in the water column – DIN/total N, phosphate/total phosphorus and silicate.
2. Secchi depth
3. Turbidity
4. Chlorophyll-a concentrations
5. Macroalgae (indicative species) presence/absence
6. Dissolved oxygen content
7. Phytoplankton (key taxa, biomass and average volume of cells)
8. Zooplankton (biomass and percentage of key groups, number of *Noctiluca*)
9. Macrozoobenthos (biomass, percentage of key groups)
10. Pollutants (toxicants) – organic and inorganic.

Despite the large capital investments made in the 17 countries represented by the BSC and the ICPDR, no assessment has yet been made of the impact of the Danube River on the Black Sea. Water quality in the Danube River has certainly improved in recent years, with riverine nutrient loads to the Black Sea having fallen substantially during this period (see also Table B.8). A number of studies have greatly helped to quantify and assess the impacts of such reductions on the status of the Black Sea itself, as well as contributing to the selection of indicators (e.g. SCRFEP, 1998; Anon, 1999; Kroiss *et al*, 2005), but individually these studies have either not considered all indicators or have been limited in terms of the area of their assessment.

This document is extremely important from both political and scientific perspectives. It is not anticipated that definitive answers will be produced as a result of the analysis, but an initial investigation of what information the available data are able to provide should be of great interest to both Commissions.

2.2 Aims

This document aims to provide the first holistic use of available data in assessing the impact of the Danube on the Black Sea, focusing on the environmental status (chemical and biological) of the North Western Shelf. In order to do this, the assessment is divided into two parts:

- Danube River inputs (loads) to the Black Sea
- The Environmental status of the North Western Shelf

Data and the conclusions drawn from them are presented, and the current Black Sea Integrated Monitoring and Assessment Programme (BSIMAP) is explained. Finally, a discussion is presented on factors that should be considered in the further development of the BSIMAP.

It is emphasized that not all data sources have been used in this report; only those that were immediately available to the authors.

3. INITIAL ASSESSMENT OF THE DANUBE RIVER ON THE CHEMICAL AND BIOLOGICAL STATUS OF THE BLACK SEA

The conclusions shown in this section of the report are drawn from an assessment of available data undertaken by members of the BSERP, Phase 2 Project Implementation Unit., with further details presented in Appendix B. Where possible, an analysis of historical data is provided in an attempt to look for trends exhibited by each of the indicators. In addition, supporting data has been added from alternative sources to those outlined below.

Unfortunately, due to the paucity of baseline/reference data (see Section 4.3), it has not been possible to provide a true 'impact' assessment of the Danube River on the Black Sea. Instead, results for the majority of indicators are presented as spatial patterns

The following four major sources of data (collated during BSERP, Phase 1) have been used in the current assessment:

- NATO funded Black Sea cruises
- UNDP-GEF funded International Study Group research cruises
- UNDP-GEF funded pilot monitoring exercises
- Recent data gathered as part of the BSERP (Phase 1)

3.1 Danube loads into the Black Sea

Annual pollutant loads from the Danube River to the Black Sea are discussed in detail in Appendix A, with results summarised in Table 3.1, below. The 3-year period for which loads are available is too short a timescale over which to undertake a trend analysis, so no such analysis ha been presented. Thus, even though there appears to have been an increase in ammonium, nitrate and inorganic nitrogen, and a decrease in ortho-phosphate over this period, there is little basis for assuming that these changes represent trends.

Table 3.1 Annual loads of pollutants/contaminants from the Danube River into the Black Sea (2000-2002)

Parameter	2000	2001	2002	Mean (2001-2003)
Suspended solids	5,100,000	3,700,000	5,100,000	4,633,333
NH_4-N	62,100	67,592	71,584	67,092
NO_3-N	252,540	355,852	413,980	340,791
NO_2-N	9,315	8,350	11,212	9,626
Inorganic N[1]	299,000	437,000	493,000	409,667
PO_4-P	6,100	5,200	5,000	5,433
Total P	10,900	13,100		12,000
BOD_5	395,000	303,000	343,000	347,000

[1] Inorganic loads presented in this table differ from the sum of ammonium, nitrate and nitrite loads because of the different calculation methodologies described in Appendix A.

3.2 Status of the Black Sea

3.2.1 Nutrient concentrations in the water column

No data on total nutrient concentrations were available for analysis. Nitrogen-nutrient data were provided as separate nitrate, nitrite and ammonium data, and analysed as individual parameters, not as dissolved inorganic nitrogen.

Overall, nutrient concentrations in waters of the North-Western Shelf show relatively small differences, perhaps with slightly higher concentrations in the waters off the Bulgarian coast.

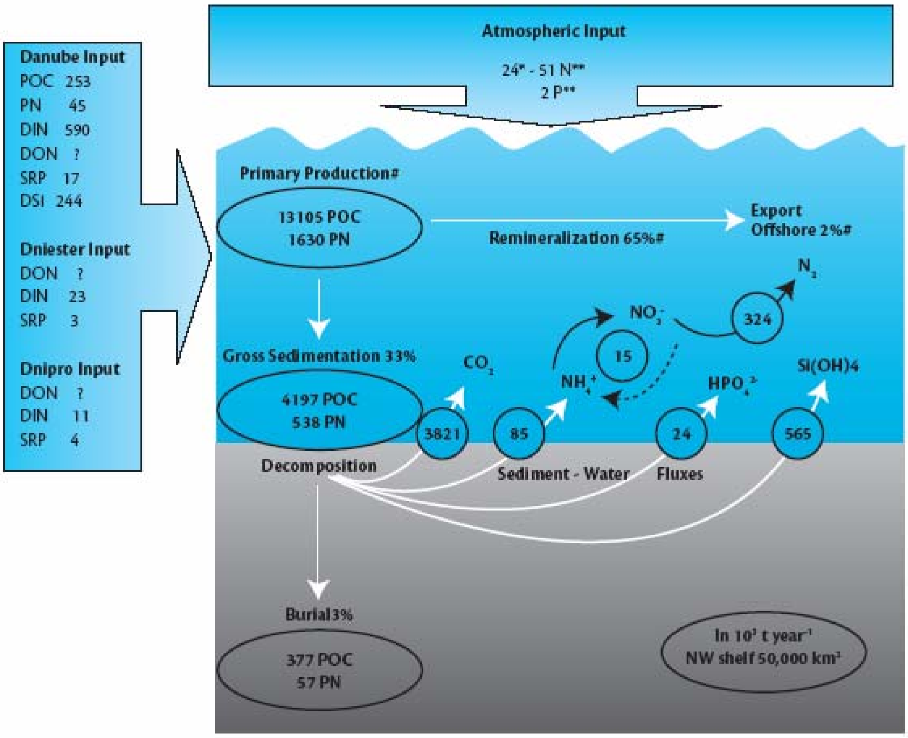
While there is evidence of some nutrient concentrations in the Danube River undergoing a major decrease during the 1990s, (Appendix B, Section B.2.7), these decreases are most apparent for ammonium, with a much smaller (but still statistically significant) improvement for nitrate concentrations at one site over the same period (1996-200). Ammonium typically constitutes only a minor fraction of DIN (comprised predominantly of nitrate), and is an even smaller constituent of total nitrogen. Thus, reductions in ammonium concentrations are probably a better indicator of improved sewage treatment processes and the dissolved oxygen status in the river (i.e. improving substantially) than they are of improving nitrogen contamination. No phosphorus data were available for the Danube River from the data sources used for this analysis.

Nevertheless, it is clear that the reduction in inorganic nitrogen concentrations in the Danube is not reflected in waters of the Black Sea North-Western Shelf. In fact, between 1990 and 2003 the overall picture that emerges is of increasing nitrate concentrations in North Western Shelf waters of Bulgaria, Romania and Ukraine (Table B.7).

Not surprisingly, seasonality occurs in nutrient concentrations, most noticeably for ammonium and nitrate. However, the available Black Sea data did not provide adequate coverage of the colder months of the year (Table B.4), whereas the data available for the Danube River represented all seasons evenly (Table B.5).

A preliminary nutrient balance for the mid-1990s has been prepared for the 50,000 km^2 area of the North-Western Shelf, focusing on inputs from the Danube, Dniester and Dnipro rivers, together with estimates of atmospheric inputs and nutrient recycling within the system itself (Fig. 3.1). Benthic nutrient recycling is a significant internal nutrient source for the pelagic system, sustaining high productivity by the release of phosphorus and nitrogen from the sediment (in the same range as river inputs). The shelf sediments release about twice as much silicon as the load discharged by the Danube. However, the shelf acts also as a sink for nutrients. Perhaps surprisingly, modeled atmospheric nitrogen deposition appears to be of relatively minor importance, amounting to only 4-8% of the river inputs. The importance of nutrient cycling in deeper waters and the contribution of this to the overall nutrient budget has still to be determined. It is clear from this budget just how much greater and more important the Danube is than either the Dneister or the Dnipro as a nutrient source for the North-Western Shelf.

Figure 3.1 Nutrient budget for the North-Western Shelf of the Black Sea during the mid-1990s (Mee, 2005, Mee *et al*, 2005, based on Friedrich *et al*, 2002)



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All fluxes, except for measured river inputs, are calculated for a 50,000 km^2 shelf area. Data marked with # are taken from model calculations in Gregoire & Friedrich (2004) and Gregoire & Lacroix (2003). Danube input represents the average input of 1991-1995 (Cociasu *et al*, 1996) except for POC and PN (Reschke *et al*, 2002). Dniester and Dnipro inputs were taken from Topping *et al* (1999). Literature data on atmospheric inputs reflect high uncertainties; values here are from Sofief *et al* (1994).

3.2.2 Secchi depth

No Secchi depth data were available for the current assessment.

3.2.3 Turbidity

In essence, Secchi depth and turbidity are different measuring techniques for monitoring the same parameter (light penetration through the water column). No turbidity data were available for the current assessment.

3.2.4 Chlorophyll-a

Chlorophyll-a has long been used as an indicator of trophic status of fresh and marine waters, but caution needs to be applied in the comparative analysis of results from different waterbodies or different areas of large waterbodies, such as the Black Sea, since spatial difference may be high. Probably the best example of this variability is from freshwater lakes, where for any given (limiting) nutrient concentration, 95% confidence limits for long-term average chlorophyll-a results are an order of magnitude apart (OECD 1982).

Chlorophyll-a is the only pigment present in all photosynthetic algae and higher plants, and is used as a surrogate of phytoplankton biomass/standing crop when measured spectrophotometrically. Very few data were available on chlorophyll-a measurements, and certainly not enough to make an assessment of the trophic status of the North-Western Shelf in comparison to other areas of the Black Sea. However, a considerable amount of remote sensing chlorophyll data has been collated and processed for the Black Sea. It is these results which are discussed below.

Satellite data does not only include chlorophyll-a, however, it also records other types of chlorophylls and chlorophyll-like substances. A major problem with the use of satellite imagery is, therefore ground-truthing of the satellite data, Remote sensing chlorophyll-a data are usually calibrated/validated against *in-situ* chlorophyll-a, but as the ratio of chlorophyll-a to other types of chlorophyll and chlorophyll-like substances varies from between phytoplankton taxa, at any one time, satellite data provide only an estimate of chlorophyll-a concentrations. The remote sensing chlorophyll maps of the Black Sea presented in this report (e.g. Appendix B, Fig. B.12) show higher concentrations in the Sea of Azov, and along the Bulgarian/Romanian/West Ukrainian coast, where the impact of the Danube would be greatest. Remote sensing data records chlorophyll levels only in the very surface of waterbodies, whereas laboratory-analysed chlorophyll-a levels can be measured for any depth from which water is sampled.

Elevated chlorophyll levels in the Sea of Azov have been explained in terms of the shallow nature of the water. While the reasons underlying this explanation remain unclear, they could also explain (partly at least) the elevated levels in transitional waters of the Danube. Possible reasons for these elevated levels are:

- Carry-over of freshwater phytoplankton into the Black Sea.
- Greater mixing of waters, resulting in increased resuspension of benthic material (including detrital chlorophyll-like substances).
- Possible increases in phytoplankton growth rates (primary productivity) due to increased nutrient concentrations. However, phytoplankton growth is not limited at nutrient concentrations greater than 10 µg/l PO_4-P in the presence of 100 µg/l dissolved inorganic nitrogen. It is paradoxical that above these levels of nutrient concentration, although the rate of growth of phytoplankton does not increase substantially, the standing crop of phytoplankton (and therefore chlorophyll-a) can increase dramatically.
- The shallower the water, the more light that is available to drive planktonic photosynthesis. Thus, the greater the primary productivity in shallow waters and the greater chance of increased chlorophyll levels occurring.

3.2.5 Aquatic vegetation

Two indicator species have been selected for use in the Black Sea: *Cystoseira barbata* (a brown seaweed) and *Zostera marina* (a macrophytic sea grass). No data were available on the distribution of these species within the Black Sea, but their presence/absence will be mandatory BSIMAP mandatory parameters for monitoring during 2006-2011.

However, a methodology using rocky shore macroalgae morpho-functional indices to monitor trophic status has been developed and tested at seven transects in the Sea (Appendix B, Section B.4).

The results of this assessment demonstrate a higher trophic status of rocky shores close to the Danube delta than those further away, but concerns are raised that this methodology is more prone to local influences (e.g. relatively small local discharges) than offshore biological methodologies (e.g. zoobenthos assessments) when investigating the impact of the Danube.

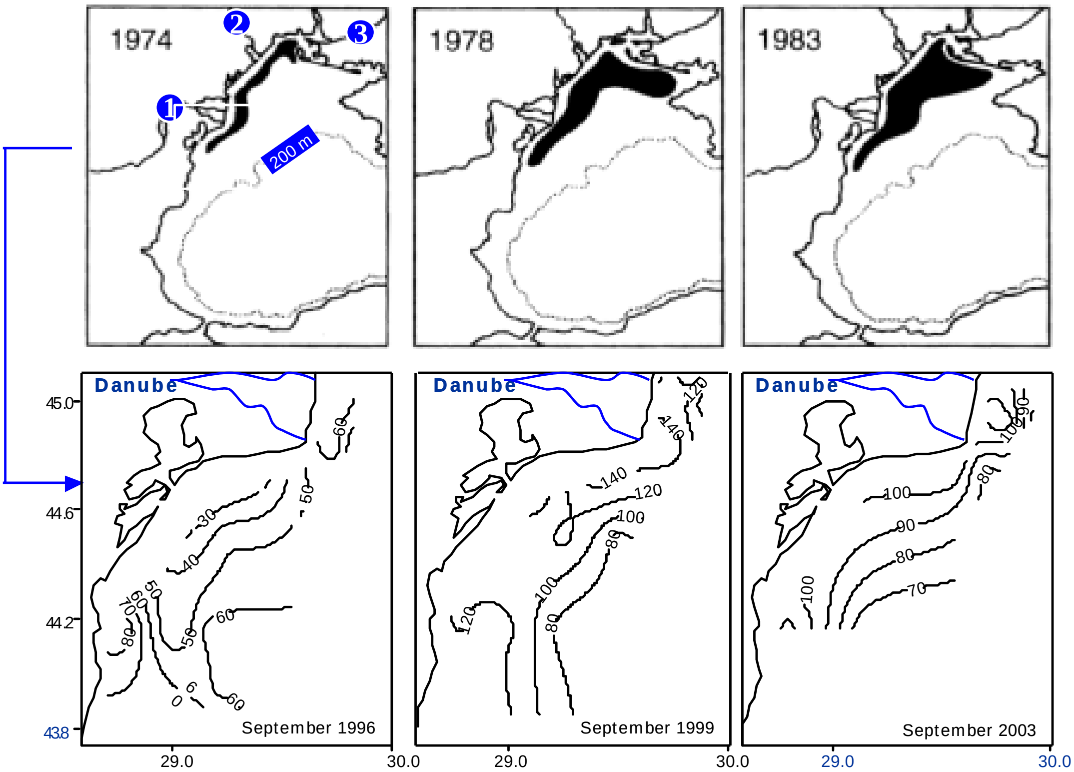
3.2.6 Dissolved oxygen content

During the period 1990-1995, there was minor variability in dissolved oxygen levels in Romanian coastal waters, with annual mean levels of 315-345 µM/l (Appendix B, Table B.3). These data suggest that hypoxia was not a problem during this period, but hypoxia only needs to occur for a very short period of time for ecological damage to occur.

From the early 1970s through the 1980s, tens of thousands of km^2 of the Western Black Sea were under hypoxic conditions (depleted oxygen). Oxygen levels increased throughout the 1990s, evidence of which is presented in Section B.6.2 (Fig. B.20) with regard to mussel community age class distributions. Clearly, the mussel beds have recovered to a large extent, particularly in the North of the North-Western Shelf.

Further evidence of the onset of the increasing degradation of the North-Western Shelf waters throughout the 1970s and early 1980s is shown in Fig. 3.2. The dramatic autumnal recovery in oxygen status during the mid-1990s and early 2000s is illustrated in the lower half of the same figure.

Figure 3.2 Area of oxygen depletion (1974, 1978 and 1983) and percentage oxygen saturation levels (1996, 1999 and 2003) in the North-Western Shelf of the Black Sea (Kroiss 2004)



3.2.7 Phytoplankton

Because of sampling and analytical methodology differences, data from Bulgaria, Romania and Ukraine have not been comparable. However, at a recent workshop in Odessa (15-19August 2005) a first Black Sea Regional phytoplankton intercalibration exercise was undertaken to facilitate comparison of historical data, and agreement was reached over the use of standardised sampling/processing equipment. No formalised lists of key taxa or other phytoplankton trophic status metrics have yet been made, but these are expected as a reported output of the Odessa workshop.

Data are presented in Appendix B (Section B.5) for phytoplankton populations off the coast of Romania, which show a marked change coinciding with the temporary return of eutrophic conditions in 2001. However, the same data also cast doubt on the use of what has been considered one of the most robust phytoplankton trophic status indicators (the diatoms:dinoflagellates ratio), when used in terms of cell numbers. No data on phytoplankton biomass were available to compare results.

3.2.8 Zooplankton

No data were available on zooplankton biomass, percentage of key groups or No of *Noctiluca*. Because of sampling and analytical methodology differences, historical data from Bulgaria, Romania and Ukraine have not been comparable. However, at a recent workshop in Odessa (15-19 August 2005) a first Black Sea Regional zooplankton intercalibration exercise was undertaken to facilitate comparison of historical data, and agreement was reached over the use of standardised sampling/processing equipment. No formalised lists of key taxa or other zooplankton trophic status metrics have yet been made, but these are expected as a reported output of the Odessa workshop.

3.2.9 Macrozoobenthos (biomass, percentage of key groups)

Macrozoobenthos populations of the North Western Shelf are discussed in detail in Appendix B, Section B.6. The Danube Delta region of the Shelf shows clear signs of impact from the Danube itself, although the zoobenthic population is not as heavily impacted there as it is closer to Odessa, where other sources of contamination and disturbance are likely to be the predominant causative factors. Other areas of the North-Western Shelf are less heavily impacted.

While there are still obvious signs of the impact of the Danube, the situation has improved substantially from that in the mid-late 1990s (Appendix B, Section B.6), but a reversal of the status of the zoobenthos ecosystem to that observed in the 1980s and early 1990s is still possible. For example, year 2001 was a dry year, causing reduced mixing of waters and resulting in extensive hypoxia, leading to the death of benthic organisms. In Fig. B.20, for example, recruitment of young mussels in 2001 (1+ for year 2003) was very low in marine areas south of the Danube Delta, but much improved in more northerly waters.

3.2.10 Pollutants

Sediment contamination with organic and inorganic contaminants is discussed in detail in Appendix B, Section B.7. Overall, results indicate an impact of the Danube on coastal sediments of the North Western Shelf, particularly with regard to heavy metals, albeit that any increases in sediment contamination levels are relatively small when considering the catchment area of the Danube compared to the catchment area of coastal land which drains directly into the North Western Shelf.

Levels of contamination at individual sites will reflect land export of contaminants as a result of contaminant production/use in coastal areas, direct discharges to the marine environment, illegal waste dumping at sea and atmospheric deposition, as well as river inputs. While surface sediment samples were used for the vast majority of the analyses presented, there is also the risk of a historical ‘shadow’ reflecting sediment contamination. This is primarily due to bioturbation – mixing of marine sediments by burrowing animals - so older, deeper and possibly more contaminated sediments (reflecting levels occurring before the Danube clean-up programme of the 1990s and early 2000s) may become incorporated into surface sediments.

For a number of chlorinated pesticides (dieldrin, lindane, opp DDD, opp DDT, pp’DDD, pp’DDT, DDMU, op’DDE, pp’DDE and β HCHa) the highest concentrations were found in Ukrainian sediment, with concentrations diminishing in a southerly direction. For two of these contaminants (dieldrin and op’DDE), however, increased concentrations were again recorded in Bulgarian sediments. Elevated levels of HCB, δ HCH, lindane, heptachlor, aldrin and endosulfan were also detected at Bulgarian sites. For three pesticides (cis- and trans-chlordane and *a*-HCH), maximum levels were associated with the Sulina branch of the Danube, although for *a*-HCH, comparable levels were detected at a number of other sites.

The massive level of DDT contamination recorded at one Ukrainian site is considered much more likely to reflect illegal discharges/dumping than land run-off.

PCB concentrations were highest at more northerly sites of the North-Western Shelf. Maximum concentrations of ten PCBs (aroclor 1260, PCBs 149, 153, 170, 174, 177, 180, 183, 187 and 194) were associated with Danube River input via the Sulina Channel. For a further twelve PCBs (aroclor 1254, PCBs 44, 49, 52, 87, 101, 105, 110, 118, 128, 138 and 201) maximum concentrations were recorded in Ukrainian sediment, levels which could also reflect inputs from the Dneister and Dnipro rivers. Sediment concentrations of all PCBs except one (PCB 201) were low in north Bulgarian sediment, but for most PCBs greater contamination was detected in southerly Bulgarian sediments.

For eight metals, highest sediment concentrations are associated with inputs from the Sulina Branch of the Danube Delta, albeit that elevated levels of contamination of some metals (cobalt, nickel copper and aluminium) were also noted in samples from off the coast of southern Bulgaria. A sampling site off the coast of Ukraine also had elevated levels of arsenic. However, as stated for organic contaminants, the Ukrainian result is also likely to reflect greater influence of inputs from the Dnipro and Dneister rivers.

4. THE BLACK SEA REGIONAL INTEGRATED MONITORING AND ASSESSMENT PROGRAMME (BSIMAP)

4.1 Background

The underlying principles of the Convention on Protection of the Black Sea against Pollution imply a holistic approach to monitoring and assessment of the Black Sea ecosystem. These principles have been considered in the development of the Black Sea Integrated Monitoring and Assessment Programme (BSIMAP), which seeks to maximize the use of historical data from previously established monitoring sites for trend analysis, supported by new additional sites to improve the assessment of the current chemical/ecological status of the Black Sea. The main purpose of the BSIMAP is therefore to provide data for 'state of the environment' reporting, but the sites, parameters and monitoring frequencies also reflect data requirements for compliance with other national and international legislation and agreements. The same data should also be suitable for undertaking broad-scale 'impact assessment' investigations of major pollutant and water sources, such as assessing the impact of major rivers (in this case the Danube, the largest river feeding the Black Sea). However, for impact assessments to be undertaken, unimpacted baseline conditions need to be established.

4.2 BSIMAP aims and purposes

A consensus was reached by the BSC institutional network (including its Pollution and Monitoring Advisory Group) that the BSIMAP should:

1. Build on established national monitoring programmes.

2. Be compatible with underlying WFD principles.

3. Utilise standardised, sampling, storage, analytical techniques, assessment methodologies and reporting formats. [Reporting formats have been specified, but are sometimes not followed. Standardised manuals for phytoplankton, zooplankton and zoobenthos are currently being updated and a series of workshops were held during summer/autumn 2005 to promote harmonization of techniques and train workers from all coastal countries. Standardised procedures for nutrient analysis and chlorophyll-a have also been produced.]

4. Include agreed quality assurance/quality control procedures. [These have not yet been fully established. However, a draft mission report from December 2002 (now somewhat out of date), prepared by Dr Stephen de Mora and Dr Oksana Tarasova is included as Appendix G, describing the infrastructure, equipment and staff available (primarily for chemical analysis) in those organisations responsible for Black Sea monitoring in five of the six riparian countries (Georgia is excluded). Limits of detection and accuracy and precision targets are not specified for any parameters.]

   A first regional quality assurance intercomparison exercise was undertaken in 2004 for metals, nutrients, chlorinated pesticides and petroleum hydrocarbons. Seven laboratories from five countries participated (no Turkish laboratories took part in the exercise), albeit with different laboratories participating for different groups of chemicals The results of this exercise remain confidential, but as may be expected from the first exercise of this type, the results suggest that there is a considerable amount of work required by the participating laboratories. During 2005, the Black Sea Commission provided the funds for all countries to participate in the IAEA-MEL Quasimeme chemical quality assurance exercise. Additional quality assurance exercises are planned for 2005/2006 on nutrients in seawater, organic contaminants in sediment and heavy metals in sediment as part of the BSERP.

Preliminary results from plankton intercalibration exercise undertaken during August/September 2005 show a major variability in results obtained by individual laboratories, differences which in large part are probably due to the alternative methodologies and equipment used by individual countries. The workshop on macrozoobenthos, included an intercomparison exercise (again with some important inter-laboratory differences being reported), albeit with full agreement having been reached on a standardised methodology and equipment for use by all six countries.]

5. Be affordable. [The economies of the six countries are all suffering to various extents, with that of Georgia being most depressed. With environmental matters being low on the political agenda, funding for environmental monitoring tends to receive scant political support, so while a comprehensive list of parameters and high monitoring frequencies can be supported technically, from a pragmatic viewpoint, a smaller list of monitoring sites, less expensive parameters and less frequent sampling/monitoring is more likely to achieve governmental funding. Clearly, those countries aiming for EU accession in the near future (Romania and Bulgaria; Turkey at a later date) will need to comply with the monitoring requirements of EU Directives. In general terms, organic compounds are more expensive to analyse for than inorganic compounds, and not all countries have the equipment or technical ability to analyse for them. However, not all countries have the capacity/ability to analyse for some inorganics, e.g. mercury.]

The Black Sea Commission and its advisory bodies/institutional framework believes that to achieve further harmonisation, common environmental quality criteria/objectives should be established and the Black Sea Information System further developed to facilitate regional State of the Environment reporting.

4.3 Reference/baseline conditions

The establishment of baseline (reference) conditions is at the heart of the EU Water Framework Directive (WFD), since all biological monitoring results should be presented in the form of environmental quality indices (EQIs), i.e.:

$$\text{EQI} = \frac{\text{Result at monitoring site}}{\text{Result at reference site}}$$

Reference conditions for impacted sites can be established using three main approaches:

- Status at quasi-pristine (but otherwise comparable) site
- Expert judgment
- Modeling

However, the reality is that the first of these three methods is the most practical and robust, particularly when considering ecological monitoring. The reasons for choosing some individual monitoring site locations remain unclear, although as already indicated, there is a historical justification for many of these sites to enable trend analysis using historical data.

4.4 BSIMAP proposed spatial coverage

Perhaps the most obvious aspect of the BSIMAP is that it is restricted to the Black Sea – there are no monitoring sites in the Sea of Azov. While it is very obviously a transboundary waterbody, both the Ukrainian and Russian governments consider it to be outside of the scope of BSIMAP, despite its influence on the Black Sea. However, some protocols of the Black Sea Commission also cover the Sea of Azov. These include the Black Sea Biodiversity and Landscape Conservation Protocol and the draft revised Protocol for the Protection of the Black Sea against Pollution from Land-Based Sources and Activities.

Article I of the Convention (on the Protection of the Black Sea against Pollution) defines the area of application as the Black Sea proper, with the southern limit constituted by the line joining Capes Kelagra and Dalyan. It also states that the Black Sea shall include the territorial sea and exclusive economic zone of each Contracting Party in the Black Sea. However, any protocol to the Convention may include areas outside of the Black Sea 'proper' for the purposes of that protocol. The Black Sea 'proper' is thus interpreted as excluding the Sea of Azov.

In 2005, the Turkish government funded monitoring at an additional 63 sites (Table 4.1), with many of these sites being relatively unimpacted. Thus, over half of the current BSIMAP sites are now along the Turkish coast, greatly improving the spatial coverage of the integrated programme (see Fig. 4.1, with coordinates shown in Appendix F), albeit with the Ukrainian and Russian coasts still remaining only sparsely covered. Improved spatial coverage of BSIMAP remains an aim of the Black Sea Commission Permanent Secretariat. It is hoped to increase the number of Georgian and Russian monitoring sites in future years.

Table 4.1 Number of national monitoring sites included in the BSIMAP, with an indication of spatial coverage

Territorial waters of	Pollution hot spots	Sampling sites	Length of coast, km	Average distance (km) represented per sampling site
Bulgaria	9	5	300	60
Georgia	6	5	310	62
Romania	5	21	225	17
Russian Federation	4	5	475	95
Turkey	10	3 (66 from 2005)	1400	466 (21 from 2005)
Ukraine	9	14	1628	116

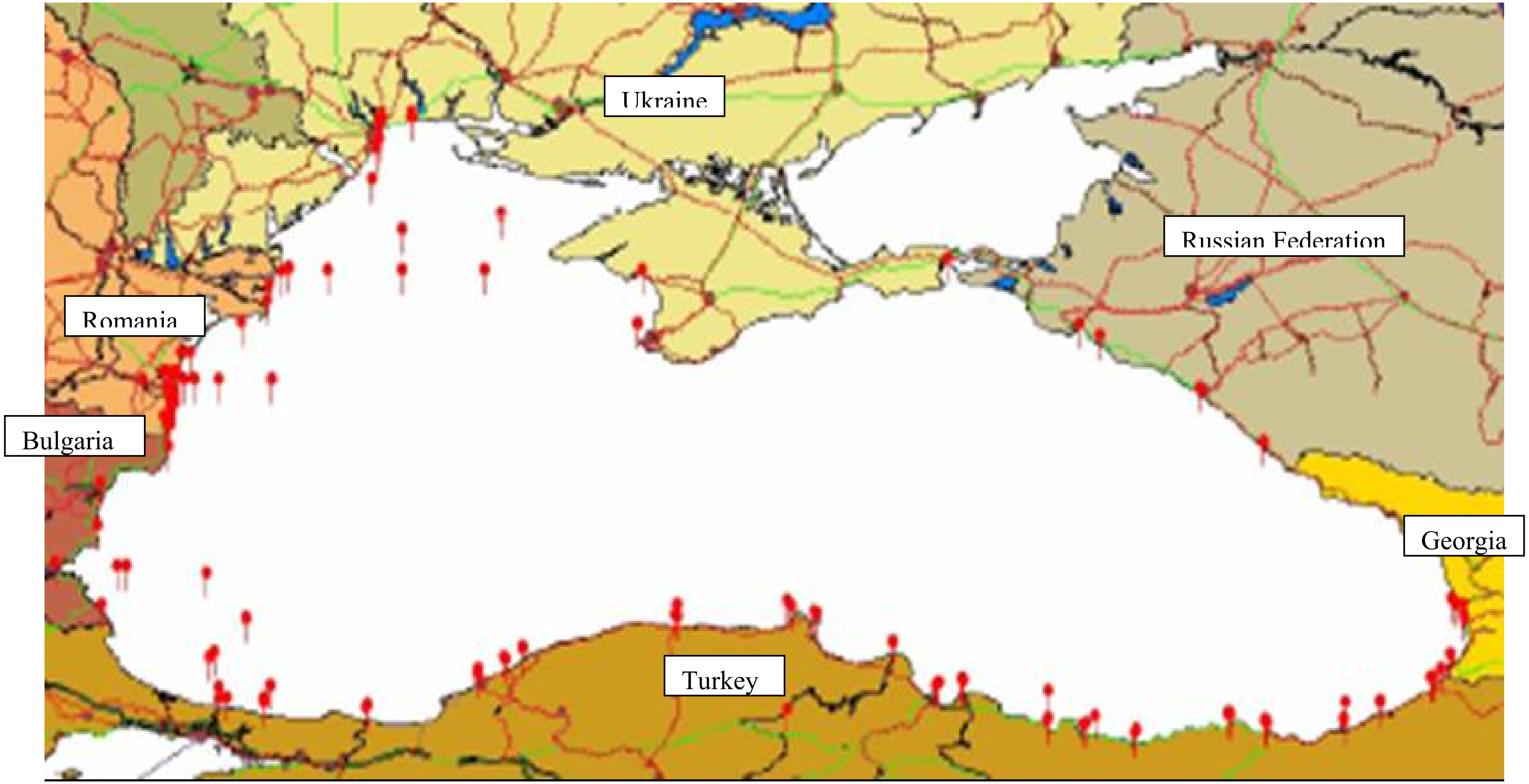
4.5 BSIMAP parameters

A list of compulsory and recommended (optional) parameters has been specified by the BSC Permanent Secretariat. The paucity of national funding for environmental monitoring means that only mandatory parameters are considered in this report, since optional parameters tend to be monitored by few (if any) countries. Mandatory parameters are shown in Appendix H.

This list of compulsory parameters does not fully tie-up with the list of indicators agreed by the JTWG, and detail is sometimes omitted from the recommendations. The recommendations for monitoring in 2005 include phytoplankton as the only mandatory biological parameter.

For nitrogenous nutrients, data are requested for ammonia, nitrite and nitrate, but for reporting purposes it would preferable to add these parameters together to give dissolved inorganic nitrogen (DIN), an accepted surrogate of bioavailable nitrogen, albeit composed overwhelmingly of nitrate. Total nitrogen and total phosphorus are also requested as part of the BSIMAP but, to date, few countries have monitored theses as standard parameters.

Figure 4.1 BSIMAP proposed monitoring sites, 2005



The list of 2005 compulsory parameters does not adequately tie-up with the list of indicators agreed by the Black Sea-Danube JTWG (Section 2), e.g. phytoplankton as the only mandatory biological parameter (Appendix H, Table H.1). However, the revised list of compulsory parameters for 2006-2011 Appendix H, Table H.2), proposed at a recent PMA Advisory Group meeting, much more closely matches the agreed list of indicators, but detail is sometimes missing from both the agreed list of indicators and the specified reporting parameters of the Black Sea coastal countries. For example, no decisions appear to have been made on the format for reporting macrozoobenthos data – although biomass and percentage of key groups has been agreed on as the indicator, should these key groups be taxonomic or functional feeding groups (Appendix B, Section B.6). Alternatively, should a biotic index be used (Section 6.9)? This also poses very large questions for data collation/storage as part of the Black Sea Information System (BSIS): should raw data be quested by the Commission or processed data? Clearly raw data would be of benefit for future development work on indicators. In addition there is still a need to reach agreement on standard taxonomic lists for use by all countries; at present different countries are still calling some taxa by different names.

Monitoring for a limited number of toxic heavy metals (cadmium, copper, mercury and lead) is mandatory within the BSIMAP, which appears appropriate given the limited funding available. However, the addition of other heavy metals should require only a marginal increase in expenditure and is likely to be beneficial for future impact assessment studies. No guidance is presented on whether total or dissolved heavy metals should be monitored – this is an important consideration which should be addressed in terms of loading to the Sea, bioaccumulation and toxicity to marine biota.

4.6 BSIMAP proposed monitoring frequencies

Up until 2005, the BSIMAP specified the same monitoring frequency for all compulsory parameters in all countries (Appendix H). For most of the compulsory parameters (phytoplankton, nutrients, petroleum hydrocarbons, salinity, oxygen balance parameters, suspended solids and physico-chemical parameters) this frequency is set at 4 times per year.

For fish catch statistics annual reporting is required, which again appears pragmatic, given how the data are reported nationally.

For the four heavy metals, a monitoring frequency of only once per year is specified by the Black Sea Commission Permanent Secretariat. This appears to be an extremely low monitoring frequency for analysis of either trends or step changes, and is likely to result in only very large changes being detected at a statistically significant level. However, at a recent meeting of the PMA Advisory Group, during a discussion on whether monitoring of heavy metals in the water column should be mandatory (as opposed to monitoring of sediment contamination), it was stated that the purpose of monitoring the water column was only to define 'background levels' throughout the Sea.

While the Commission specifies a minimum monitoring frequency of 4 times per year for most of the compulsory parameters, Bulgaria aims to samples seven times a year, and will continue to do so, while at the 63 new (2005 onwards) Turkish sites, monitoring will only be undertaken twice a year.

4.7 Recent years BSIMAP reporting

Appendix I shows the maximum number of results reported to the Black Sea Commission for samples collected during the years 2001 (Table I.1) and 2003 (Table I.2) for each of the BSIMAP sites. Sites 51 to 113 (see Appendix F) are excluded from these tables, since formal monitoring only began at those sites during 2005. For Tables I.1 and I.2 results are grouped into the following categories:

- Oxygen balance parameters (including BOD_5, dissolved O_2 [% saturation] and dissolved O_2 [mg/l])
- Nutrients (including ammonia, nitrite, nitrate, silicate and ortho-phosphate – neither total P nor total N are monitored by any laboratory)
- Heavy metals (including cadmium, copper, mercury and lead)
- Organic pollutants (petroleum hydrocarbons)
- Other water column physico-chemical parameters (including temperature, pH, salinity, total suspended solids and Secchi depth)
- Chlorophyll-a

The information in Appendix I therefore represents a rather optimistic view of historical monitoring. For example, if BOD_5 had only been reported on three occasions during 2001, but dissolved oxygen (% saturation and mg/l had both been reported on 10 occasions during that year, then the oxygen balance parameters group would be shown as having been monitored on 10 occasions (250% of the recommended monitoring frequency). The tables show enormous variability in the number of reported data for individual sites and in the types of parameters which were monitored, making the BSIMAP appear rather uncoordinated.

5. CONSIDERATIONS FOR IMPROVING THE COLLECTION AND INTERPRETATION OF BLACK SEA MONITORING DATA

5.1 Funding and equipment

Perhaps the most obvious statement to make is that there is little use in defining or agreeing to a monitoring programme if insufficient funds are made available to measure the minimum (mandatory) monitoring parameters. This funding needs to cover transportation costs (including provision of a boat/ship), monitoring and analytical equipment costs, including consumables, as well as staff costs.

5.2 Relevant and proposed legislation

The most relevant international policies and agreements in terms of monitoring the Black Sea are considered to be the Strategic Action Plan for the rehabilitation and protection of the Black Sea, the Water Framework Directive and the proposed Marine Framework Directive.

5.2.1 Strategic Action Plan for the rehabilitation and protection of the Black Sea

Article 54 of the Black Sea Strategic Action Plan (BSSAP) states that "A Black Sea Monitoring System, based upon biological effects measurements and measurements of key contaminants will be established in compliance with the Bucharest Convention. It will consist of the integration of obligatory monitoring programmes, to be included in the National Strategic Action Plans, and an independent quality assurance system. It is advised that the Istanbul Commission develop such a quality assurance system through its advisory group on Pollution monitoring and assessment by 1998." The Black Sea SAP will shortly be updated for presentation to the Black Sea Commission and the six national governments

5.2.2 Existing European Union directives

Bulgaria and Romania are expected to join the European Union in 2007. Turkey is a candidate country with whom accession negotiations have not yet started. Once these countries have joined the EU they will have to implement the EU legislation relating to marine waters.

The most significant EU policy relating to the water environment is the Water Framework Directive. The Water Framework Directive covers all waters, including inland waters (surface water and groundwater) and transitional and coastal waters up to one sea mile (in terms of monitoring ecological status and for the chemical status also territorial waters which may extend up to 12 sea miles) from the territorial baseline of a Member State, independent of the size and the characteristics.

Member States have to characterise their waters in terms of numbers and types of water bodies, and identify the pressures upon them. A surface water body is defined as a discrete and significant element of surface water such as a transitional water or a stretch of coastal water. The main purpose of identifying "water bodies" is to enable status to be accurately described and compared to environmental objectives. Physical features (geographical or hydromorphological) should be used to identify discrete elements of surface water. A water body should not contain significant elements of different status and must be capable of being assigned to a single ecological status class with sufficient confidence and precision through the Directive's monitoring programmes.

To that end, Member States have to implement monitoring programmes that enable the classification of surface water bodies into one of five classes. Monitoring is termed surveillance, operational or investigative each with defined objectives. Operational monitoring is to be undertaken in water bodies thought to be at risk of failing environmental quality objectives and will focus monitoring on those determinands most relevant to the pressures creating the risk. Surveillance monitoring should include sufficient water bodies to provide an assessment of the overall surface water status within each catchment and sub-catchment of the river basin district: to achieve this water bodies not at risk (i.e. high and good status) and those at risk will have to be monitored. Member States will also have to determine how many monitoring stations are required in each water body (or groups of water bodies) to determine its status.

Bulgaria and Romania have identified and characterised their water bodies as required by Article 5 of the Water Framework Directive: two coastal water bodies and types were identified along the 300 km of Bulgaria's, and three water bodies and two types identified along the 225 km and Black Sea coastlines (Member States are only required to identify water bodies in coastal waters, not territorial waters). For comparison 556 coastal waterbodies have been identified in the UK along 5167 km of coastline, giving approximately one waterbody per 9.3 km. In Bulgaria and Romania there is an average of one water body per 150 km and 75 km of coastline, respectively.

The European Commission is also developing a Daughter Directive to the Water Framework Directive under Article 16 on environmental quality standards and emission controls for Priority Substances. At the present time environmental quality standards for the concentration of the substances in water (including coastal waters) will be established, but not for concentrations in biota or sediment. The Daughter Directive will re-iterate the need for these substances to be monitored not only in water for determining chemical status and checking compliance with the EQSs, but also for their presence in sediment and biota to demonstrate compliance with the "no-deterioration" objective of the Water Framework Directive (Article 4(1)(i).

Monitoring of surface freshwaters, estuarine, coastal and marine waters is also required for the Nitrates Directives where marine waters are referred to as those in "exclusive economic zones". The geographic extent of marine waters included in the requirements of the Urban Waste Water Treatment Directive is not clear: Annex II, (criteria for the identification of sensitive and less sensitive areas) includes estuaries and coastal waters in terms of sensitive areas, whereas marine water bodies are included in the criteria for less sensitive areas. Coastal waters are defined as "waters outside the low-water line or the outer limit of an estuary". The European Commission has developed informal guidance on monitoring required for the Nitrate's Directive which includes water quality determinands such as nitrate but also relevant biological determinands such as phytoplankton, aquatic vegetation, benthic invertebrates and fish.

The European Commission is also developing guidance on eutrophication for the Water Framework Directive. It compares how eutrophication is understood, defined and assessed in EC Directives, policies, guidance and research, and proposes a new conceptual framework for eutrophication assessment across all water categories and policies. The guidance includes a chapter on monitoring with the aim of integrating the monitoring requirements stemming from the various obligations dealing with eutrophication.

5.2.3 Proposed Marine Framework Directive

The proposed Marine Framework Directive (arising from the Commission's Marine Strategy) would be applicable to all European marine waters under the sovereignty or jurisdiction of the Member States. It would, therefore, cover marine waters within a country's exclusive economic zone (up to 200 nautical miles from the baseline from which the breadth of territorial waters are measured). The strategy is also directed at non-EU countries bordering these areas (presumably including those Black Sea countries that are not EU candidate countries) and at the relevant international organisations in which countries cooperate (e.g. the Black Sea Commission). The objective of the Directive would be to protect, conserve and improve the quality of the marine environment in these marine waters through the achievement of good environmental status within a defined time period. The directive will define/establish ecosystem-based marine regions as the implementation unit. The latter will be defined on the basis of their hydrological, oceanographic and bio-geographic features. Monitoring and assessment programmes will have to be developed for each marine region taking into account existing monitoring and assessment programmes. Monitoring would also be required offshore of territorial waters within economic zones, the delineation of which has not yet been completed by all Black Sea countries. It is, therefore, likely that the geographical extent of monitoring of the Black Sea will have to be increased by at least some of the Black Sea countries.

5.3 Spatial and depth coverage of monitoring stations

Table 4.1 and Appendix F summarise the numbers of stations per country and the average distance represented per sampling site. If the spatial coverage of stations could be increased then new stations should not only be located to detect potential impacts from identified sources (hot spots) such as point source discharges or diffuse inputs via rivers, but also at points further away where impacts are expected to be less. In particular reference sites (see below) should be established against which values of determinands measured at the impacted sites could be compared. The approach used in Romania seems an appropriate one if resources are limited, where stations have been established seaward along a line perpendicular to the coast where the main sources of pollution appear to be. Of course stations further offshore may also be impacted by pollutants carried by the prevailing currents from other parts of the Black Sea. Similarly, the zone of influence of river inputs and major discharges should also be covered by monitoring.

The selection of stations (and determinands to be monitored) would also be facilitated by the approach adopted for the Water Framework Directive, that is transitional and coastal waters are characterised in terms of the types and numbers of water bodies and then the pressures potentially impacting them identified. The identification of pressures includes those arising from point sources along the coast and offshore, diffuse sources such as pollution from shipping and the flows from the larger rivers. This is the process that Romania and Bulgaria have started as candidate EU countries and which Turkey will start at some point in its EU entry negotiations.

The typifying of water bodies helps the comparison of like-with-like when it comes to comparing monitoring results and assessing state from different parts of the same country and across the Black Sea as a whole. For example, comparing the biological community attributes and metrics (such as diversity) from relatively low salinity and shallow parts of the Black Sea with relatively high salinity deep parts of the Black Sea may not be valid and lead to the wrong conclusions about their relative quality. The division of coastal waters in terms of types and potential status could help obtain (through surveillance monitoring) a representative view of quality along the coast rather than just of the worse quality areas.

The physical factors that could be considered in determining whether stations are within water bodies or areas of similar and comparable types would include depth of water, salinity, degrees of exposure and sea bed characteristics (i.e. sedimentary or rocky). The Water Framework Directive working group on intercalibration identified three depths for the identification of comparable types for intercalibration: shallow with a depth of less than 30 m, of intermediate depth 30 to 50 m and deep greater than 50 m. For example, in the Black Sea a ‘natural’ decrease in macrozoobenthic community diversity is observed in the deeper waters of the North-Western Shelf reflecting the greater environmental stress at these depths. In terms of salinity, the least saline parts of the Black Sea are in the North-Western Shelf in relation to the main river inputs. Differences in salinity should be taken into account when monitoring for any biological determinands as aquatic communities will vary in relation to salinity. Nitrate concentrations will also vary in relation to salinity particularly as the rivers are significant sources of nutrients to the Black Sea. Allowing or normalising for salinity will improve the robustness of trend analysis of nitrate concentrations at stations where salinity varies significantly between sampling occasions.

In terms of depth the sampling for some water quality determinands such as nutrients and chlorophyll should take into account the potential vertical stratification of the water column (e.g. presence of a pycnocline) and the varying depths of maximum phytoplankton biomass. For example samples for chlorophyll would ideally be taken throughout the euphotic zone at regular intervals or by taking continuous measurements with a fluorometer. Once a few seasons/years of data have been obtained the results could be statistically assessed to see if there was any opportunity to reduce the number of samples without losing any information (i.e. where maximum chlorophyll concentrations are occurring). As an example, for the Baltic Sea the standard sampling depths for chlorophyll-a are 1 m, 5 m, 10 m, 15 m and 20 m. Samples integrated over 1 to 10 m are also acceptable.

One of key criteria of the present BSIMAP is the affordability of monitoring in each of the countries. It is quite clear that the present monitoring in some of the countries is not adequate to obtain an overview of the state of coastal waters of the Black Sea (and also maybe not for the assessment of all hot spots). As the largest proportion of the total cost of monitoring probably is generally with undertaking sampling (ships, personnel etc.) cruises (compared to the cost of sample analysis) then it might be the better option to undertake sampling at more stations and at an increased number of depths over the water column for water quality samples, rather than increasing the monitoring frequency. In addition, more monitoring stations in the open, offshore waters of the Back Sea (particularly in the North-Western Shelf area and in the deeper central area) would enable a more complete spatial assessment of water quality/ecological status to be made.

No guidance is currently offered to countries on the depth at which water should be sampled. Nutrient and chlorophyll-a concentrations (in particular) will differ with depth, particularly when a summer thermocline is established. The existence of a very obvious halocline in the Black Sea will also result in different concentrations above and below the pycnocline.

5.4 Reference site selection

Stations should ideally be selected in water bodies/areas that represent the least impacted parts of the Black Sea. They should also be selected where possible in a range of types of water bodies/areas to account for any differences in the monitored determinands between stations that arise from natural factors rather than from differences in anthropogenic pressures when comparing monitoring results.

The Water Framework Directive requires Member States to establish type-specific reference conditions which “equate to the values of the biological quality elements for the surface water body reflect those normally associated with that type under undisturbed conditions, and show no, or only very minor, evidence of distortion.” These conditions would be equivalent to high ecological status. Not many Member States will be able to identify and monitor stations and water bodies that are at high ecological status: this may also be the case in the Black Sea as it is effectively isolated from the World Ocean and is very vulnerable to pressures from land-based human sources. However Member States are able to use temporal reference conditions reconstructed from historical records – early 20th century.

If reference conditions are not present in the Black Sea and temporal reference conditions cannot be established, then the least impacted stations could be used for comparisons of relative quality and state. In either case a number of reference stations should be selected to be representative of all the different water types/areas in the Black Sea. In addition, reference stations/conditions can be “shared” by countries in the case where they do not exist in the coastal waters of one country but do so in another. Thus the monitoring results obtained (assuming the same methods and metrics are used) from the reference station in one country, could be used as a baseline for comparison of the results from the impacted station in another country. However, to make the resultant comparison and assessment of results/status valid, the water bodies/areas must be of the same type.

Reference sites/conditions for individual impacted sites are not specified on the BSC website. The proposed inclusion of macrozoobenthos as a mandatory monitoring parameter opens a very large issue in terms of the BSIMAP site selection, since many of the current BSIMAP sites appear to have been selected primarily for water column chemistry/hydrology monitoring. Sediment particle size can make an enormous difference to what taxa live in/on the sediment and the level of contaminants adsorbed onto that sediment. The identification of sediment reference sites therefore remains open. While different sites could be selected for monitoring water column and sediment parameters, the underlying principles of an 'integrated' monitoring programme strongly suggest that the same (vertical) sites should be selected for monitoring all parameters/metrics.

5.5 River inflows

Rivers have been identified as important sources of pollutants into the Black Sea with the Danube, Dnipro and Dniester being the biggest rivers in terms of flow discharging into the North-Western Shelf area of the Black Sea. There appears to be two main reasons for monitoring the main rivers discharging into the Black Sea, to determine the riverine loads entering the sea and to assess the impact of the pollutants in the river water on the Black Sea ecosystem. Black Sea countries undertake some monitoring of riverine loads but as the Black Sea Commission states the data are not always reported in a harmonised way. It would be of value if the quantification of riverine loads (as well as other pollution sources) could be standardised and harmonised to obtain a more accurate assessment of loads entering the Black Sea. Good examples of how this has been undertaken by other Marine Conventions are the RID and PLC guidelines produced by the OSPAR and HELCOM Commissions, respectively. The Danube has a very well established river monitoring network (TNMN) with a load assessment programme that started in 2000 with countries agreeing to use a standard operational procedure for the measurement and calculation of riverine loads from the Danube into the Black Sea. Procedures giving comparable results should be adopted for the assessment of loads at the most downstream points in other major rivers discharging into the Black Sea.

A number of surveys have been undertaken of the North-Western Shelf to assess the impact of river discharges and other pollution sources. Comments have also been made about the spatial coverage of monitoring stations: more stations would be required in BSIMAP to more accurately quantify the impact of major rivers. For example, 60 stations were sampled to assess status if the macrozoobenthic communities into the North Western Shelf (Todorova *et al,* 2004). The potential importance of salinity as a factor influencing water quality determinands and aquatic biological communities has also been discussed earlier.

5.6 Seasonality and sampling frequency

In an ideal situation sampling would be undertaken at a frequency high enough to determine the inherent variability of the monitored determinands in all the different water types/areas in the Black Sea. This implies an initial high frequency of sampling, for example, at least monthly for some of the water quality determinands such as nutrients and chlorophyll. An assessment can then be made as to the optimum frequency to obtain an adequate level of confidence and precision in the information that is required e.g. to detect maximum chlorophyll and nutrient concentrations or to assess average conditions from year-to-year.

Annex V of the Water Framework Directive provides tabulated guidelines in terms of the minimum monitoring frequencies for all the quality elements. The suggested minimum frequencies are applicable to both surveillance and operational monitoring and are generally lower than currently applied in some countries. More frequent monitoring will most likely be necessary in many cases to achieve a reliable assessment of the status of the relevant quality element, but also less frequent monitoring is justified when based on technical knowledge and expert judgment. The Black Sea Commission has considered the Water Framework Directive requirements when proposing monitoring frequencies for the different elements of the BSIMAP.

In terms of Marine Conventions, HELCOM defines frequent and highly frequent monitoring stations (some high frequency stations are sampled up to 26 times/year or even more often) that have recommended sampling frequencies higher than the minimums given by the Water Framework Directive and Nitrates Directive. However a common theme between those Directives that require monitoring of marine waters and other Marine Conventions that could be incorporated into BSIMAP is the recognition that sampling should be targeted to specific times of year for some of the determinands (e.g. nutrients in winter and chlorophyll during maximum chlorophyll production). There is also a common theme in a number of European Directives and international agreements of ensuring that monitoring results are fit for purpose and this implies that different frequencies would be required for different quality elements, different water categories (transitional, coastal and open marine waters) and different water bodies. As examples: Member States have to achieve acceptable levels of precision and confidence in the monitoring results and subsequent assessments (Water Framework Directive); Contracting Parties have to determine optimum sampling frequencies, for example, to confirm maximum winter nutrient concentrations have been determined (OSPAR) or to detect changes in concentrations over 10 years (MEDPOL).

The analysis of historical datasets on water quality indicates clear seasonality in relation to dissolved oxygen, ammonium, nitrate and silicate concentrations. In these cases the detection of significant trends in quality over time might be improved by aggregating data not only annually but also for specific seasons such as winter for nitrate. Sampling for nitrate and other nutrients, however, should ideally be undertaken throughout the year.

Benthos shows considerable numerical variability over a year due to larval recruitment and mortality. The results of repeated surveys are more easily compared if they are carried out at the same time of year, for example within +/- 3 weeks of an agreed date or the date of the first annual survey. For the North Sea the best time to sample in order to avoid the largely ephemeral larval recruitment is the first six months of the year. However, because of bad winter weather the sampling period April to June is generally used. In the Baltic Sea sampling is undertaken in May or June in Finland and Sweden, and in August in Latvia. OSPAR recommends sampling to be undertaken between June and September. The recommended sampling period for BSIMAP is in April and then again in September/October: this is consistent with approaches adopted in other seas.

5.7 Historical data availability for trend analysis

The data sets compiled and assessed for this report have provided some good quantitative information on the state of, and trends, in the North-Western Shelf area. The historical data would also be useful in determining the spatial and temporal variability of some of the monitored determinands: this would be useful if additional monitoring stations and revised monitoring frequencies were to be considered for BSIMAP. It would also be worth considering including some of the stations used in the various research cruises in BSIMAP to maintain the already available time series.

5.8 Sources and types of current and historic pollutants

The impact of as many major pollution sources as possible should be monitored as far as is possible under BSIMAP bearing in mind the affordability to do so in each of the countries. The cruise to screen pollutants in sediments revealed some very interesting results in terms of the relatively high contamination levels of some substances (some pesticides, some heavy metals, and PCB) found at a few locations off the coasts of Bulgaria and Ukraine. The concentrations of some substances are in or above the ranges used as Ecotoxicological Assessment Criteria (EAC) by OSPAR. EACs are defined as concentration levels of a substance above which concern is indicated, and have been used by OSPAR to identify possible areas of concern and to indicate which substances might be a target for priority action. Whilst the applicability to the Black Sea of EACs developed for the NE Atlantic is not known, the significance of the detected contamination should be further investigated and if possible the monitoring of contaminants in sediment and biota should be considered for inclusion as mandatory elements in the BSIMAP.

5.9 Pollution impacts

One of the aims of monitoring is to determine the impact of pollution. In terms of the Water Framework Directive this would be expected when pollutants were causing the degradation of ecological and chemical status to be less than good. Ecological status is monitored and assessed in terms of defined biological quality elements: these elements are included as either mandatory or optional elements of BSIMAP. The results obtained from BSIMAP when compared to appropriate reference levels/conditions would give a measure of impact. For example the assessment of macrozoobenthos in the North-Western Shelf has detected pollution effects.

The European Commission is in the process of developing environmental quality standards for Priority Substances: compliance with these standards will equate to the achievement of good chemical status. At the present time, annual average and maximum allowable concentration standards for the water phase in inland surface waters and other surface waters (presumably transitional and coastal waters) are being proposed. There are no standards yet being proposed for the substances in sediment and biota. These standards could be applied to BSIMAP monitoring results once they are available.

In addition, the use and possible adaptation to Black Sea conditions (if technically necessary) of the Background/reference concentrations, and Ecotoxicological Assessment Criteria developed and used by OSPAR for assessing the significance of monitoring undertaken in its Convention area could be used (see also Section 5.8). In the longer term it may also be possible to use direct biological effects measurements such as oyster embryo water bioassays and whole sediment bioassays with amphipods and annelids: such measurements have been used in the OSPAR Convention area.

5.10 Data analysis and interpretation

The importance of robust statistical techniques for assessing spatial differences and temporal trends in water quality data sets have been demonstrated by the analysis undertaken on historical datasets in Appendix B.2. For example, significant seasonality was found in some of the nutrient data sets. Such periodicity in data sets needs to be understood and accounted for if valid trend assessments are to be undertaken. The targeting of monitoring to specific times of year and to specific types of water body (e.g. in terms of depth and salinity) might also serve to reduce some of the inherent variably of the measured determinands. There are well established, robust and accepted statistical methods for trend analysis such as the Mann-Kendall Statistics used by the European Environment Agency to detect significant trends in marine water quality datasets used in its indicators. It is expected that appropriate statistical methods will be used by the BSC for the analysis of data arising from the BSIMAP.

6. INDICATORS OF STATUS OF THE BLACK SEA

The JTWG has selected a number of indicators for presenting the data and information collected under the BSIMAP. The successful use of indicators requires a proper definition of each indicator in terms of aspects such the data required, its availability, reliability and robustness, subsequent data manipulation and analysis, and the policy and environmental relevance of the indicator. The production of more thorough definitions for each of the proposed BSIMAP indicators should be considered, particularly in relation to the monitoring (and its affordability) that would be required for each of the indicators. Short comments on each of the selected indicators are provided in the following paragraphs.

6.1 River inputs (loads)

The ICPDR has agreed to monitor for and provide results to the black Sea Commission on Danube River loads to the Black Sea for the following parameters:

- Total suspended solids
- Nitrate
- Nitrite
- Ammonium
- Total nitrogen
- Ortho-phosphate
- Total phosphorus
- BOD_5
- Cadmium
- Copper
- Mercury
- Lead

In order to better determine the impact of the Danube on the Black Sea, monitoring is required to produce similar estimates of other river inputs to the Sea.

6.2 Nutrient concentrations in the water column

This is one of the core set indicators for the European Environment Agency (EEA) and is updated annually through data collected using EIONET-Water. The concentrations of total oxidised nitrogen (nitrate plus nitrite), orthophosphate and the N/P ratio in the uppermost 10 m of the water column during winter are used for the formulation of the indicators. The trends in concentrations at stations in the coastal zone (<20 km) are calculated and maps of most recent concentrations in the coastal and open sea (>20 km) presented.

HELCOM has an equivalent indicator based on the spatial distribution of the winter nutrient pool, based on dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) concentrations in the 0 to 10 m water layer, and the DIN:DIP ratio

The proposal to develop an indicator of nutrients in the water column for the Black Sea based on DIN/total N, phosphate/total phosphorus and silicate is consistent with the indicators successfully used by other international organisations. The determinands for the formulation of this indicator are mandatory parameters as part of the current and proposed future (2006-11) BSIMAP. These include:

- Nitrate
- Nitrite
- Ammonium
- Ortho-phosphate
- Total N

- Total P

6.3 Secchi depth and turbidity

HELCOM has an indicator on water transparency in the Baltic Sea based on the summer (June-September) Secchi depth collected during monitoring cruises. Secchi depth is relatively easy to measure and such data collected over time will give useful information on how transparency is changing over time, for example in response to changes in phytoplankton production in relation to nutrient loads and/or to suspended sediment loads in the water column. Secchi depth and suspended solids are also mandatory parameters for inclusion in BSIMAP, 2005. Turbidity was dropped from the BSIMAP in 2003 and replaced with total suspended solids. The importance of Secchi depth as an indicator was re-emphasised at a recent Black Sea PMA Advisory Group meeting, as was the very low cost of equipment required for monitoring.

6.4 Chlorophyll

The EEA also has a core set indicator based on the trends and status of summer concentrations of chlorophyll concentrations in transitional, coastal and marine waters. However, because of confounding factors such as variations in freshwater discharge, hydro-geographic variability of the coastal zone and internal nutrient cycling in water, biota and sediments, trends in chlorophyll *a* concentrations can sometimes be difficult to demonstrate and interpret in relation to the nutrient reduction measures taken.

For the EEA indicator, the concentration of chlorophyll *a* is expressed as µg/l in the uppermost 10 m of the water column during summer. The uppermost 10 m often represents an almost homogenous surface layer of the water column above any pycnocline, but not the euphotic zone which can vary considerably between areas. Specific data on euphotic zone depth is often not available. Summer is defined as the period May-September, except in the Baltic Sea north of latitude 59º N, where summer is defined as the period June-September.

Chlorophyll a is also one of the mandatory parameters for inclusion in BSIMAP, 2005, and will be proposed as a mandatory parameter for 2006-2012.

HELCOM also has an indicator based on chlorophyll concentrations: July-August mean concentration from daily data from the SeaWiFS satellite. Remote sensing images certainly provide a very user-friendly overview of trophic status, but it is important not to confuse such results with chlorophyll-a analysis, the requirement of chlorophyll-a monitoring for calibration/validation purposes and the many factors that need to be considered in interpreting such images (Section 3.2.4; Appendix B.5).

6.5 Aquatic vegetation

Macroalgae and angiosperms are included as a quality element for the monitoring and assessment of the ecological status of coastal waters under the Water Framework Directive. At present very few EU countries have classification schemes based on these elements compatible with the WFD.

Seagrasses are a common biological element along the European coastline. Their absence or deterioration along some Mediterranean coasts is indicative of serious environmental degradation due to tourism, urban or industrial pollution. The extent of *Posidonia oceanica* meadows covering the whole of the coastal waters in the Mediterranean Sea and *Zostera marina* covering the NE Atlantic Ocean, the North Sea, Baltic Mediterranean and Black Seas make them suitable pan-European indicators of ecological status. The depth limit of their distribution and density of roots have been suggested as appropriate indicators/metrics in assessing ecological quality status/changes at a European level.

6.6 Dissolved oxygen content

The EEA has developed an indicator based on the frequency of hypoxia in close-to-bottom waters. It based on the relative frequency of oxygen concentrations in bottom water (May-November) below 2 mg/l, which is defined as hypoxic conditions reported to have adverse effects on the benthic community. Dissolved oxygen concentrations throughout the water column are requested as part of the EEA's EIONET-Water priority data flow.

Zones of seasonally low oxygen in the bottom waters of the north western shelf have been detected for many years: the extent of these in Romanian coastal waters has more recently decreased. The indicator is thus of direct relevance to assessing the status of the Black Sea. However whilst dissolved oxygen is a mandatory parameter for BSIMAP, hypoxia (however this is defined) is not, and so it is not clear whether relevant data for the formulation of this indicator will be forthcoming from the BSIMAP.

The dissolved oxygen status of water is determined by many factors, and while eutrophication (nutrient enrichment) is principally considered to have been the underlying cause of historical hypoxic events, gross organic enrichment (from allochthanous and autochthanous sources) has been the principal causative factor. In 2005, BOD_5 is a compulsory parameter while TOC (total organic carbon) is an optional BSIMAP parameter. However, in future years, it is proposed to make BOD_5 optional, and to propose that TOC is made compulsory by the year 2011. This would leave the BSIMAP without a mandatory indicator/measure of gross organic pollution, the major factor underlying the ecological degradation of the Sea during the 1970s-1980s, for a period of up to five years.

6.7 Phytoplankton

Phytoplankton total density (No. of cells per ml or litre of water) is a poor indicator of trophic status, since different taxa have very different biovolumes and dominant taxa change throughout the course of the year. Phytoplankton biomass is a much better indicator of trophic status, but this is a lengthy and costly parameter to measure and only includes phytoplankton of >2 μm in size. Thus, chlorophyll-a content is probably a better indicator of overall phytoplankton biomass (standing crop), since this includes the chlorophyll-a content of all phytoplankton. Chlorophyll-a, phytoplankton total density and biomass are mandatory parameters for the BSIMAP.

The EEA has also developed an indicator on the harmful algae phenomenon based on the premise that an observed increase in harmful algae events may be due to nutrient enrichment from increasing anthropogenic inputs. The indicator is formulated from the number of recorded amnesic (ASP), diarrhoetic (DSP) and paralytic shellfish poisoning (PSP) events. The monitoring of harmful algae events is not included in BSIMAP and it is not known whether they are monitored under the auspices of others in the Back Sea.

At a workshop on developing indicators of eutrophication for the Black Sea; Istanbul, 25-30 September 2000, a series of phytoplankton indicators were recommended, of which it is proposed to use the following:

- Population species composition (on both a number and biomass basis)
- Diatoms:dinoflagellates ratio (on both a number and biomass basis)
- Total biomass (with a view to replacing this by chlorophyll-a analysis in the longer term

6.8 Zooplankton

Zooplankton is not included as one of the quality elements of the Water Framework Directive and is only known to be included in the monitoring of one other sea area (the Baltic Sea as part of HELCOM's eutrophication monitoring programme). Nevertheless, at a workshop on developing indicators of eutrophication for the Black Sea; Istanbul, 25-30 September 2000, the following series of zooplankton indicators were recommended:

- Total mesozooplankton biomass (mg/m^3)
- Biomass of *Noctiluca scintillans* in total mesozooplankton (% of total zooplankton biomass)
- Density of neustonic copepods (Pontelidae family) ($No./m^3$)
- Number of polychaete larvae expressed as a percentage of the total number of meroplankton
- Growth rate (production) of dominant species per day

There are no known examples of the use of zooplankton indicator species used by other countries/organisations, but the following list of zooplankton indicator species have been suggested for use in the Black Sea:

Indicators of worsening conditions

PROTOZOA:	*Noctiluca scintillans* (=*N. miliaris*)
SCYPHOMEDUSA:	*Aurelia aurita* and *Rhizostoma pulmo*
CLADOCERA:	*Pleopis polyphemoides*

Indicators of improvement conditions

CLADOCERA:	*Penilia avirostris*, *Pleopis tergestina* and *Evadne spinifera*
MONSTRILOIDA:	*Monstrilla grandis*, *Monstrilla helgollandica* and *Monstrilla longiremis*
CALANOIDA:	*Pontella mediterranea, Anomalocera patersoni*, *Labidocera brunescens* and *Centropages kroyeri pontica*
CYCLOPOIDA:	*Oithona minuta*
ISOPODA:	*Idothea ostroumovi*
DECAPODA:	*Macrura* (shrimps) and *Brachiura* (crabs)

6.9 Zoobenthos

A variety of soft bottom fauna tools are used in most EU countries to assess the ecological quality status of transitional and coastal waters. It is also a required quality element for the Water Framework Directive. Among the statistical metrics and indicators used by European countries for assessing the ecological quality of soft bottom communities, univariate methods like the number of species, number of exotic species, abundance, biomass and the Shannon diversity index H' seem to be shared by most countries. Most of the different expressions of the "indicator organism" concept (e.g. presence/absence of sensitive species) are closely related. Indicator taxa could, therefore, be regarded as the second most commonly used approach. Biotic indices are also used by some countries such as Norway (Indicator Species index), Sweden (Benthic Habitat Quality Index), Greece (Bentix index) and UK (Infaunal Trophic Index).

This is, therefore, a highly used and recommended indicator for assessing the status of coastal waters. At present it is only an optional parameter for BSIMAP, although it is intended for monitoring of it to become compulsory in future years.

Emphasis has been placed on monitoring of macrozoobenthos, rather than meiobenthos in the Black Sea Region. Biomass/number and percentage of key groups have been specified as the monitoring metric, but decisions still need to made on what the key groups are and the pragmatism of using/developing a zoobenthos biotic index for the Black Sean requires investigation.

6.10 Pollutants

As described in Section 5.2.2, the Water Framework Directive and its Article 16 Daughter Directive will require the monitoring of Priority Substances and other pollutants in water, and most probably in biota and sediment as well. These elements will, therefore, be required in the coastal monitoring programmes of the three EU candidate countries from the Black Sea area. At present the monitoring of pollutants in sediment and biota is only optional in BSIMAP even though significant sediment contamination has been found in the North-Western Shelf area. It should be noted that the EQSs for metals in coastal waters will be expressed as dissolved concentrations, and for other substances total concentrations will be used. This should be borne in mind for the monitoring of seawater for the mandatory pollutants (cadmium, copper, mercury and lead) included in BSIMAP. From 2006 monitoring of sediments for these heavy metals, chlorinated pesticides and PCBs will be made mandatory parameters within BSIMAP.

The EEA and HELCOM both present indicators of hazardous substances in marine biota. In the case of HELCOM, PCB, DDT compounds and mercury concentrations in different age classes of the Baltic Herring are presented. For the EEA indicators, cadmium, mercury, lead, DDT, lindane, PCB concentrations in herring, cod and mussels are used.

Oil pollution has been recognised as an important issue in the Black Sea. Petroleum hydrocarbons are included as mandatory parameters for inclusion in BSIMAP. The data arising from this monitoring could be used to formulate an appropriate indicator. The EEA and HELCOM also have indicators of oil pollution based on illegal oil discharges monitored by aerial surveillance.

APPENDIX A – DANUBE RIVER LOADS INTO THE BLACK SEA

A.1 Overview of data used – the Trans-National Monitoring Network

In order to have a regular assessment of the water quality of the Danube River as prescribed by the Danube River Protection Convention (DRPC), the Danube countries established a Trans-National Monitoring Network (TNMN) in the Danube River Basin. According to the DRPC the Contracting Parties shall cooperate in the field of monitoring and assessment. To achieve this aim they have, e.g.:

- Harmonised or made comparable their monitoring and assessment methods, in particular in the field of river quality
- Developed a concerted monitoring system and procedures, including communication and data processing facilities
- Implemented joint programmes for monitoring the riverine conditions in the Danube catchment area concerning both water quantity and quality, sediments and riverine ecosystems, as a basis for the assessment of transboundary impacts.

The TNMN was designed in 1993 and formally launched in 1996, the main objective being to allow a good overall view of the water quality (pollution) status and the long-term development of pollution loads in major rivers of the Danube basin. The network includes eleven national border cross-sections of the Danube itself. The responsibility for TNMN was assigned to the Monitoring, Laboratory and Information Management Expert Group (MLIM EG) of the ICPDR. In line with the implementation of the EU Water Framework Directive TNMN is currently being revised to ensure full compliance with the provisions of the WFD.

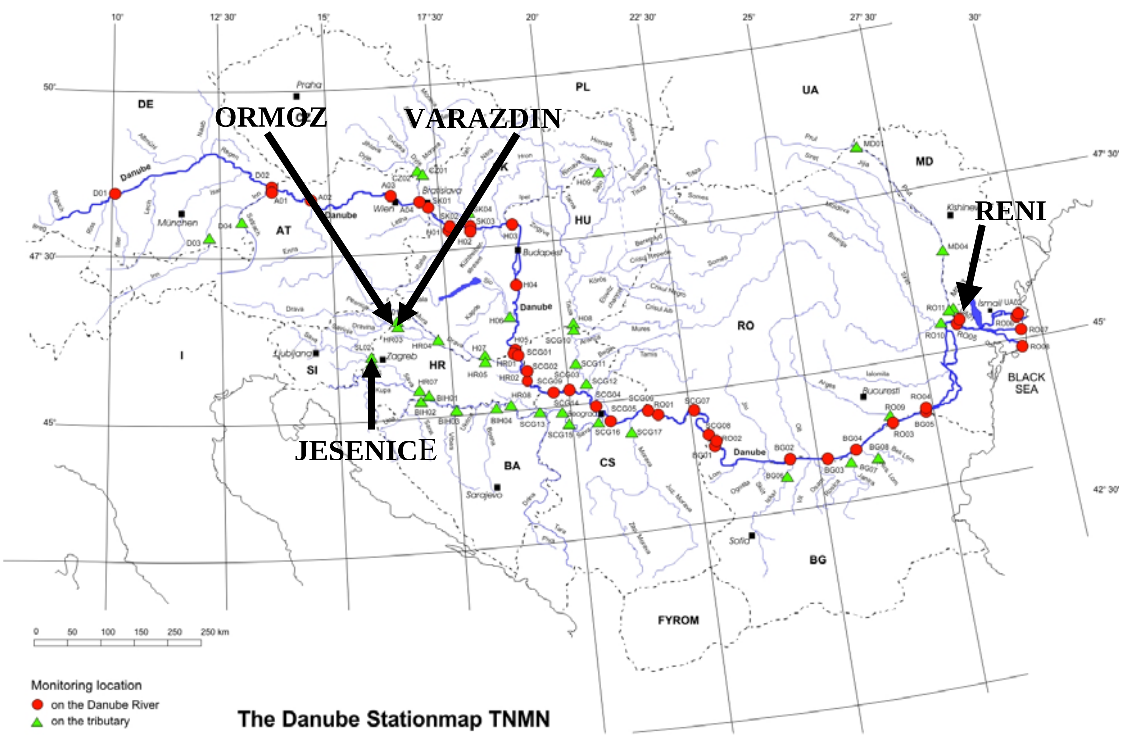
As with the BSIMAP (Section 4), the TNMN monitoring network is based on national surface water monitoring programmes. TNMN sampling sites were selected according to the following criteria:

- Sites located just upstream/downstream of an international border
- Sites located upstream of confluences between the Danube and its main tributaries or between main tributaries and larger sub-tributaries (for the calculation of mass balances)
- Sites located downstream of the largest point sources
- Sites located at major drinking water supply abstraction points

This resulted in the initial selection of 61 TNMN monitoring sites. Territory of former Yugoslavia was not included in the network when it was first devised (due to war conditions), but Serbia and Montenegro joined the TNMN in 2001, increasing the number of sites to 79 (Fig. A.1). To date, no data have been provided by Bosnia and Herzegovina, and Ukraine provided data only for 1998 and 1999.

Each monitoring location may have up to three sampling points, located on the left side, right side or in the middle of a river. More than one sampling point was proposed for selected monitoring locations in the middle and lower part of the Danube River and for large tributaries such as the Tisza and Prut rivers. The minimum sampling frequency is 12 times per year for chemical determinands in water and 2 times per year for biological parameters.

Figure A.1 Danube Trans-National Monitoring Network (TNMN) sites



The analytical methodologies applied for the analysis of TNMN samples are based on a list containing reference and optional analytical methods. The National Reference Laboratories (NRLs) have been provided with a set of ISO standards, which were recommended for the reference methods. However, taking into account current practice in environmental analytical methodologies in the EU, individual laboratories are now free to choose their own analytical procedure(s), provided they are able to demonstrate that the method(s) in use meet(s) the required analytical performance criteria. Therefore, the minimum concentrations expected and the tolerance required for the measurements have been defined for each determinand in order to enable laboratories to determine the acceptability of their preferred analytical methods. The quality of the TNMN data is regularly checked by a basin-wide analytical quality control (AQC) programme organized by the ICPDR.

A.2 Load assessment

Load assessment in the Danube River is necessary to estimate the influx of polluting substances to the Black Sea and to provide an information basis for both policy development and assessment. The load assessment programme started in 2000.

MLIM EG has agreed on the following principles/procedures for the load assessment:

- In-stream loads are calculated for: BOD_5, inorganic nitrogen, ortho-phosphate-phosphorus, dissolved phosphorus, total phosphorus, suspended solids and - on voluntary basis – chlorides;
- The minimum sampling frequency in sampling sites selected for load calculation is set at 24 per year;
- In case of several sampling sites in the profile, an average concentration at the location is calculated for each sampling event.
- For values “below the limit of detection”, the limit of detection value is used in further calculations.
- Average monthly concentrations are calculated thus:

$$C_m\,[mg.l^{-1}] = \frac{\sum_{i \in m} C_i\,[mg.l^{-1}]\,.\,Q_i\,[m^3.s^{-1}]}{\sum_{i \in m} Q_i\,[m^3.s^{-1}]}$$

where: C_m = average monthly concentrations
C_i = concentrations in the sampling days of each month
Q_i = discharges in the sampling days of each month

- Monthly loads are calculated thus:

$$L_m\,[tonnes] = C_m\,[mg.l^{-1}]\,.\,Q_m\,[m^3.s^{-1}]\,.\,days\,(m)\,.\,0.0864$$

where Lm = monthly load
Qm = average monthly discharge

  - If discharges are available only for the sampling days, Q_m is calculated from those discharges.
  - In case of months without measured values the average of the products $C_m.Q_m$ in the months with sampling days is used.

- The annual load is calculated as the sum of the monthly loads:

$$L_a\,[tonnes] = \sum_{m=1}^{12} L_m\,[tonnes]$$

A.3 Reporting of loads to DBS JTWG

The ICPDR Secretariat proposed two ways of reporting the Danube pollution loads to the DBS JTWG. The standard way is to use the results from the most downstream site of the ICPDR load assessment programme, which is located at Reni. For the determinands currently not included in the load assessment programme, the loads can be calculated using the average annual discharge values and the average annual concentration of a particular determinand at the Reni sampling site.

The Monitoring, Laboratory and Information Management Expert Group (MLIM EG) of the ICPDR agreed to use for reporting to the DBS JTWG the available results from the ICPDR load assessment programme. For this purpose the data from the most downstream site of the load assessment programme, which is located at Reni, are used. However, some parameters suggested by the DBS JTWG for the Danube loads reporting procedure were not included in the ICPDR load assessment programme until 2005. For these parameters the use of an alternative load assessment method (using the average annual discharge values and the average annual concentration of a particular determinand at the Reni sampling site) was considered. This alternative procedure was found by the MLIM EG to be applicable only to nutrients. The MLIM EG did not recommend applying this alternative method for the calculation of loads of heavy metals due to possibility of increased fluctuations as the frequency required for the load assessment method is higher that that used in common TNMN programme.

For future reporting to the Black Sea-Danube JTWG, the MLIM EG agreed to include all parameters proposed by BSC into the ICPDR load assessment programme starting from 2005 (for the sampling site at Reni). An inevitable precondition for this upgrade is the availability of AQC results in the responsible laboratory. For the assessment of heavy metals both filtered and non-filtered samples should be analysed. Silicate has been included into the reporting procedure on the presumption that the satisfactory AQC results will be achieved. In 2005 Romania has reported to the MLIM EG that the new load monitoring programme at Reni is being carried out as planned.

The Danube loads reported to the DBS JTWG until now are shown below (Table A.1). Data for 2003 have been collected and will be sent after their official approval by the ICPDR at its Ordinary Meeting in December 2005.

Table A.1 Annual loads from the Danube River to the Black Sea, 2000-2002

Parameter	TMNM mean	Calculated load	TNMN load
2000			
Suspended solids			5,100,000 tonne
NH_4-N	0.3 mg/l	62,100 tonne	
NO_3-N	1.22 mg/l	252,540 tonne	
NO_2-N	0.045 mg/l	9,315 tonne	
Inorganic N			299,000 tonne
PO_4-P			6,100 tonne
Total P			10,900 tonne
BOD_5			395,000 tonne
2001			
Suspended solids			3,700,000 tonne
NH_4-N	0.34 mg/l	67,592 tonne	
NO_3-N	1.79 mg/l	355,852 tonne	
NO_2-N	0.042 mg/l	8,350 tonne	
Inorganic N			437,000 tonne
PO_4-P			5,200 tonne
Total P			13,100 tonne
BOD_5			303,000 tonne
2002			
Suspended solids			5,100,000 tonne
NH_4-N	0.332 mg/l	71,584 tonne	
NO_3-N	1.92 mg/l	413,980 tonne	
NO_2-N	0.052 mg/l	11,212 tonne	
Inorganic N			493,000 tonne
PO_4-P			5,000 tonne
Total P			No data
BOD_5			343,000 tonne

APPENDIX B - STATUS AND TRENDS IN QUALITY OF THE NORTH-WESTERN SHELF OF THE BLACK SEA

B.1 Overview of data used

The datasets used in this Appendix were generated/collated from the following BSERP activities during 2003-2004:

1. **Pilot monitoring exercises**: three sampling exercises took place on Oct - Dec 2003 with key indicators plus some extra indicators totaling 22 indicators. The objective was to extend the historical knowledge with new data. Data from Turkey are not yet available, but from Georgia, Bulgaria, Romania, Ukraine and Russia the data do exist. The AQC is currently under consideration for future pilot monitoring. However the countries prefer to use their own AQC systems. The project is insisting that a standardized methodology is being used.

2. **Historical data collection**: a project was undertaken at the request of the BSC Secretariat. 7 issues were included: air emissions including green houses, priority pollutants, accident pollution discharge of wastewater, river discharges, state of the coastal zone, bathing water quality, disasters. However, the contracts provided extensive data sets, which have been used in the current exercise.

   Water quality data from four monitoring sites in the Danube River (see Fig. A.1) were provided by the ICPDR in mid-2004:

   - L1330/SL02, at Sava river, Jesenice, right bank values
   - L1390/SL03, at Drava river, Ormoz , left bank values
   - L1290/HR03, at Drava river, Varazdin, middle of river values
   - L0430/RO05, at Danube, Reni, left, middle and right bank values.

3. **International Study Group**: 2 cruises were organized: (i) benthic cruise October 2003 from Bulgaria, (ii) hydrology and chemistry cruise May 2004. Macrophytes were not monitored during the benthic cruise. A number of core samples taken during the benthic cruise were sent to IAEA, Monaco for analysis and screening of pollutants. Results of these analyses are also presented.

   Reference was made on the historical database available from NATO study. Data are available from 1950 until 1990. BSERP team undertook trend analysis.

   The current report is based on information, which has been generated within BSERP Phase I research programme, pilot monitoring exercise and historical data collection. BSERP will make an inventory of the data/information available and present metadata to the meeting participants at the 5th meeting.

4. **Remote Sensing**: remote sensing images produced by the Joint Research Centre (JRC) of the European Commission.

B.2 Nutrient and oxygen concentrations in the water column

B.2.1 Data used

Analysis and statistical processing of the water quality data started with analysis of the data as collected by the BSERP, Phase 1. This allows common characteristics of the water quality data to be identified. These characteristics allow the selection of subsequent data analysis procedures.

B.2.2 Representativeness and outliers

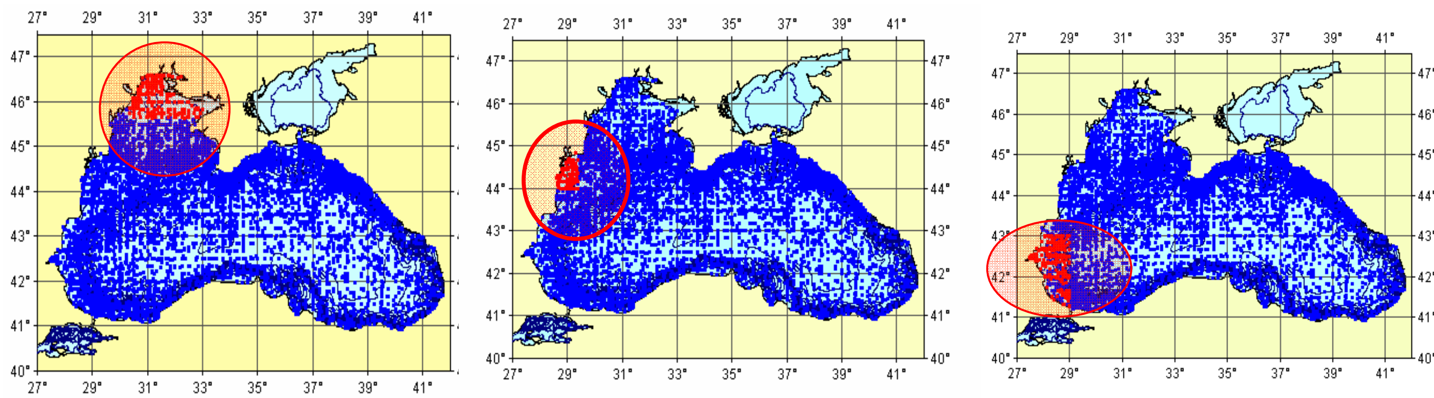
Outliers, those values which differ substantially from others in the data set, often cause concern or alarm. They should not. Outliers are often dealt with by complete exclusion from the analysis or changing them to a median/mean value calculated following their exclusion from the respective data set(s). The latter is useful in a case when the number of samples is a limiting factor for the data processing and evaluation. Treatment of outliers should be carried out prior to describing the data, or prior to some of the hypothesis test procedures, which are carried out during statistical analysis of the water quality data.

There are several methods to identify outliers within a data set, such as graphical methods, frequencies test, mini-maxi check, etc. There are also statistical tests to define whether a data unit represents an outlier. Rosner's test is a statistical procedure to detect various types for outliers. The test has been carried out after checking out how the data provided fit the statistical requirements. Outliers detected within the dataset are presented in 0.

B.2.3 Monitoring sites/areas

The data presented linear time-series of the water quality parameters (a detailed list of parameters are presented onwards in the text) for four monitoring stations located on the main stream of the Danube River for the period 1996-2000 (L1330, L1390, L1290, L0430) and in the North-Western Shelf of the Black Sea (Ukraine, Romania and Bulgaria; Fig. B.1).

Figure B.1 Monitoring sites in Ukrainian, Romanian and Bulgarian marine waters



The number of samples for each location/area is presented in Table B.1, below.

Table B.1 Number of water quality samples for each location/area (1990-2003)

Area or site	Dissolved oxygen (DOW)	Ammonium nitrogen ($N-NH_4$)	Nitrite nitrogen ($N-NO_2$)	Nitrate nitrogen ($N-NO_3$)	Ortho-phosphate (PO_4)	Silicate (SiO_4)	Total number
Ukraine	418	141	428	328	589	558	**2576**
Romania	834	933	997	981	988	974	**5796**
Bulgaria	204	273	324	222	330	228	**1591**
Sava River Jesenice, Slovenia	0	70	0	81	0	0	**232**
Drava River, Ormoz, Slovenia	0	71	0	81	0	0	**231**
Drava River, Varazdin, Hungary	0	54	0	59	0	0	**173**
Danube River, Reni, Romania	0	199	0	199	0	0	**791**
Total	**1456**	**1741**	**1749**	**1951**	**1907**	**1760**	**11390**

B.2.4 Descriptive statistics of data analysed

1990/1995-2000/2003

Descriptive statistical parameters are provided for the water quality parameters shown in Table B.1 These include: sample size, mean, minimum, maximum, standard deviation, variance, range, sum, standard error of the mean, kurtosis and skewness with their standard errors. Details on the principal descriptive statistics for all sites/areas are shown in Table B.2, with further details presented in Appendix C (Tables C.1-C.7). For the period 1990-2003 for the North-Western Shelf of the Black Sea and for the period 1995-2000 for the selected monitoring sites in the Danube River, ammonium concentrations were similar (except for site L0430). However, nitrate concentrations in Sea waters were considerably lower than those in the Danube (Table B.2).

Table B.2 Descriptive statistics for all sites/locations (1990/1995-2000/2003)

	DOW, µM/l		NH_4, µM/l		NO_2, µM/l		NO_3, µM/l		PO_4, µM/l		SI, µM/l	
	Av.[2]	StD.	Av.	StD.	Av.	StD.	Av.	StD.	Av.	StD.	Av.	StD.
Ukraine (1)	313.508	53.320	2.893	3.269	0.272	0.271	2.454	5.541	0.356	0.584	12.022	13.634
Romania (2)	326.740	57.844	4.350	3.643	0.732	0.455	5.777	4.646	1.192	2.582	11.686	11.894
Bulgaria (3)	332.590	49.108	5.505	8.429	1.108	1.700	8.446	8.120	1.153	2.150	7.317	5.244
L1330	-	-	7.848	5.510	-	-	108.258	17.928	-	-	-	-
L1390	-	-	6.096	4.080	-	-	79.429	22.201	-	-	-	-
L1290	-	-	5.582	3.881	-	-	89.479	41.894	-	-	-	-
L0430	-	-	24.639	16.557	-	-	114.479	44.715	-	-	-	-

Individual years

[2] Av. – Mean value, StD. – Standard Deviation.

Estimates presented above are very general and show limited dynamics of nutrient concentrations either in Sea waters or in the Danube River. In order to provide an insight into the dynamics of those concentrations within the given period a more thorough analysis has been carried out. Results of the analysis for the marine areas are presented in Table B.3. Nutrient concentrations in waters of the North-Western Shelf are presented in Figure B.2- B.4.

Figure B.2 Dynamics of nutrient and oxygen concentrations in North-Western Shelf waters of the Black Sea during 1990-2003. Ukraine (Area 1)

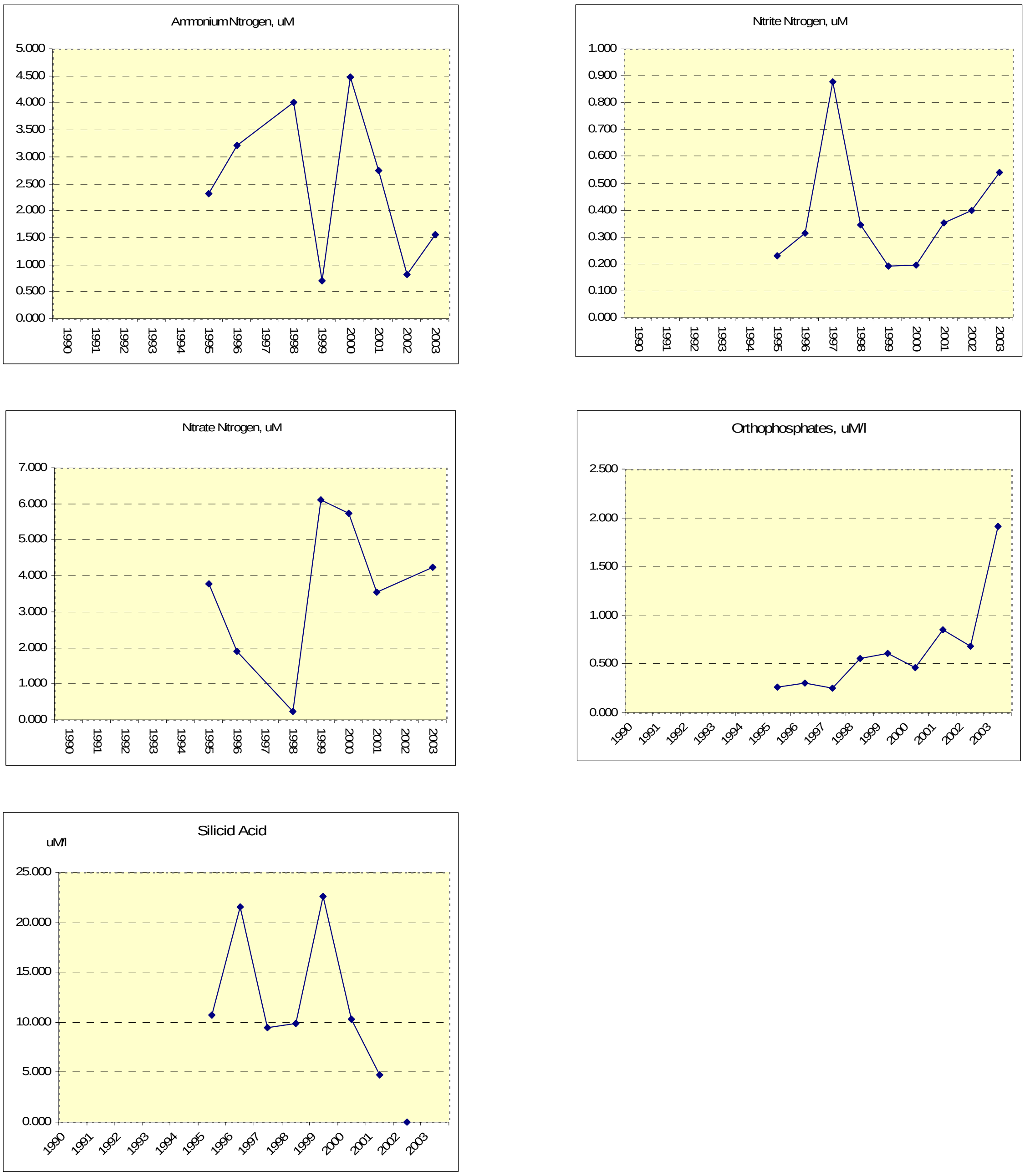


Table B.3 Annual mean dissolved oxygen and nutrient concentrations in areas of the North-Western Shelf of the Black Sea (1990-2003)

	Parameters	Years/Mean Concentrations													
		1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Ukraine (1)	NH4, μM/l	-	-	-	-	-	2.318	3.216	-	4.011	0.693	4.481	2.742	0.818	1.561
	NO2, μM/l	-	-	-	-	-	0.229	0.314	0.878	0.345	0.193	0.197	0.354	0.397	0.542
	NO3, μM/l	-	-	-	-	-	3.775	1.907	-	0.232	6.106	5.719	3.540	-	4.241
	PO4, μM/l	-	-	-	-	-	0.267	0.301	0.252	0.562	0.613	0.458	0.849	0.686	1.911
	SI, μM/l	-	-	-	-	-	10.71	21.52	9.48	9.88	22.54	10.29	4.73	-	-
Romania (2)	DOW, μM/l	314.64	334.64	315.32	345.20	323.20	324.83	-	-	-	-	-	-	-	-
	NH4, μM/l	6.240	3.832	3.465	1.780	1.758	5.297	9.560	4.088	3.717	5.552	5.573	6.988	4.531	3.076
	NO2, μM/l	0.320	0.387	0.419	0.650	0.723	0.894	1.119	0.804	0.829	0.769	0.506	0.847	0.898	0.565
	NO3, μM/l	3.195	2.836	3.877	5.988	5.089	7.854	3.767	3.349	4.213	8.896	5.303	7.215	7.736	4.643
	PO4, μM/l	0.288	0.214	0.350	1.324	1.995	1.671	1.360	0.653	0.457	0.415	0.293	0.395	0.228	0.200
	SI, μM/l	6.758	4.986	6.110	4.421	6.750	19.502	4.814	10.237	30.138	18.856	7.778	11.125	11.833	11.756
Bulgaria (3)	NH4, μM/l	-	3.434	2.549	1.708	0.925	2.767	-	13.041	5.405	11.750	27.280	4.093	3.356	2.781
	NO2, μM/l	-	0.366	1.575	1.555	1.697	0.754	-	0.687	1.664	0.587	1.899	0.326	1.205	0.655
	NO3, μM/l	-	2.196	3.716	10.838	6.872	6.519	-	-	-	-	-	42.857	-	24.286
	PO4, μM/l	-	0.282	0.349	0.822	0.381	0.578	-	2.462	1.603	2.839	1.009	0.591	1.028	2.613
	SI, μM/l	-	3.995	7.697	5.302	7.000	9.933	-	-	-	-	-	-	-	0.568

Figure B.3 Dynamics of nutrient and oxygen concentrations in North-Western Shelf waters of the Black Sea during 1990-2003. Romania (Area 2)

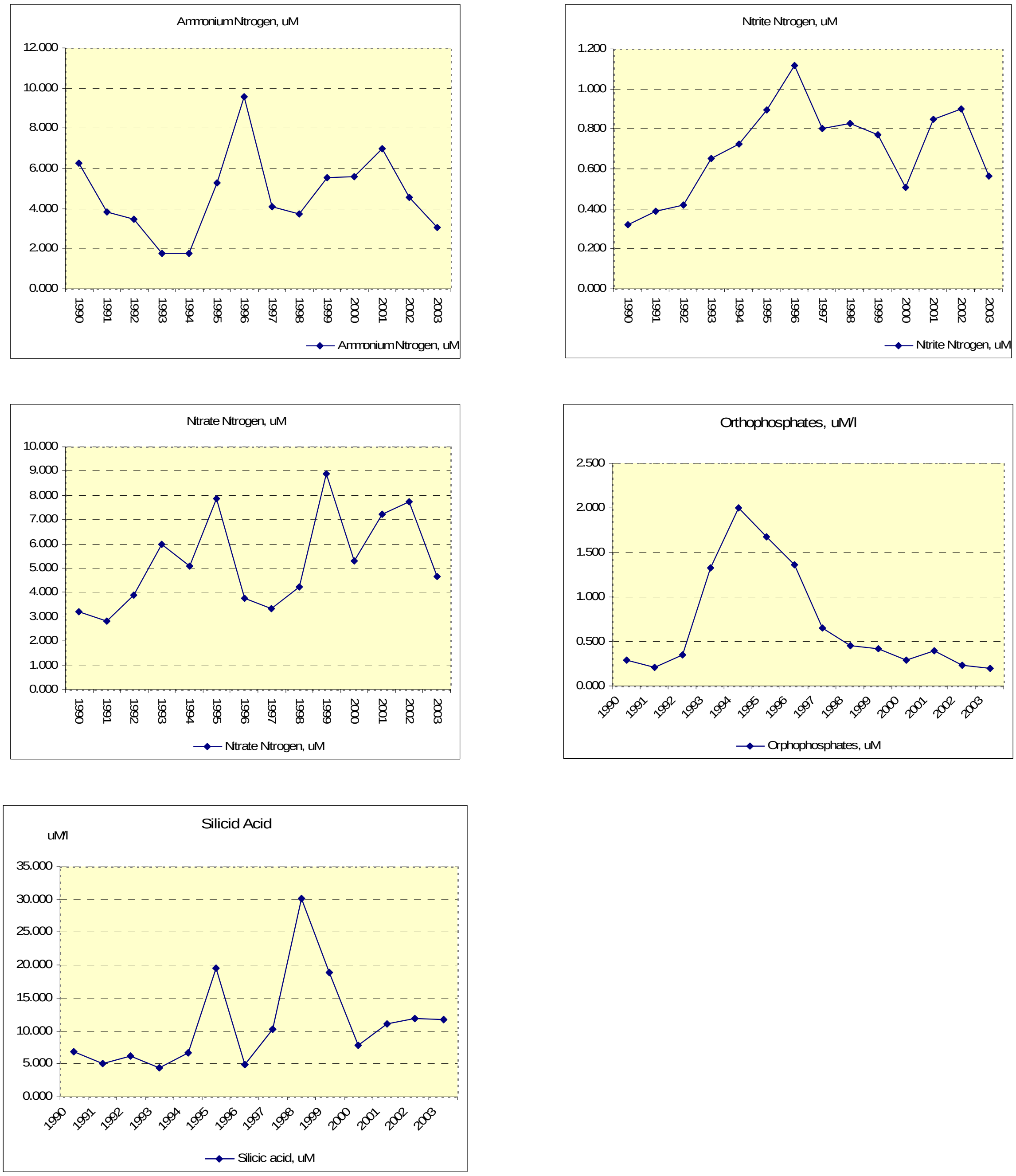
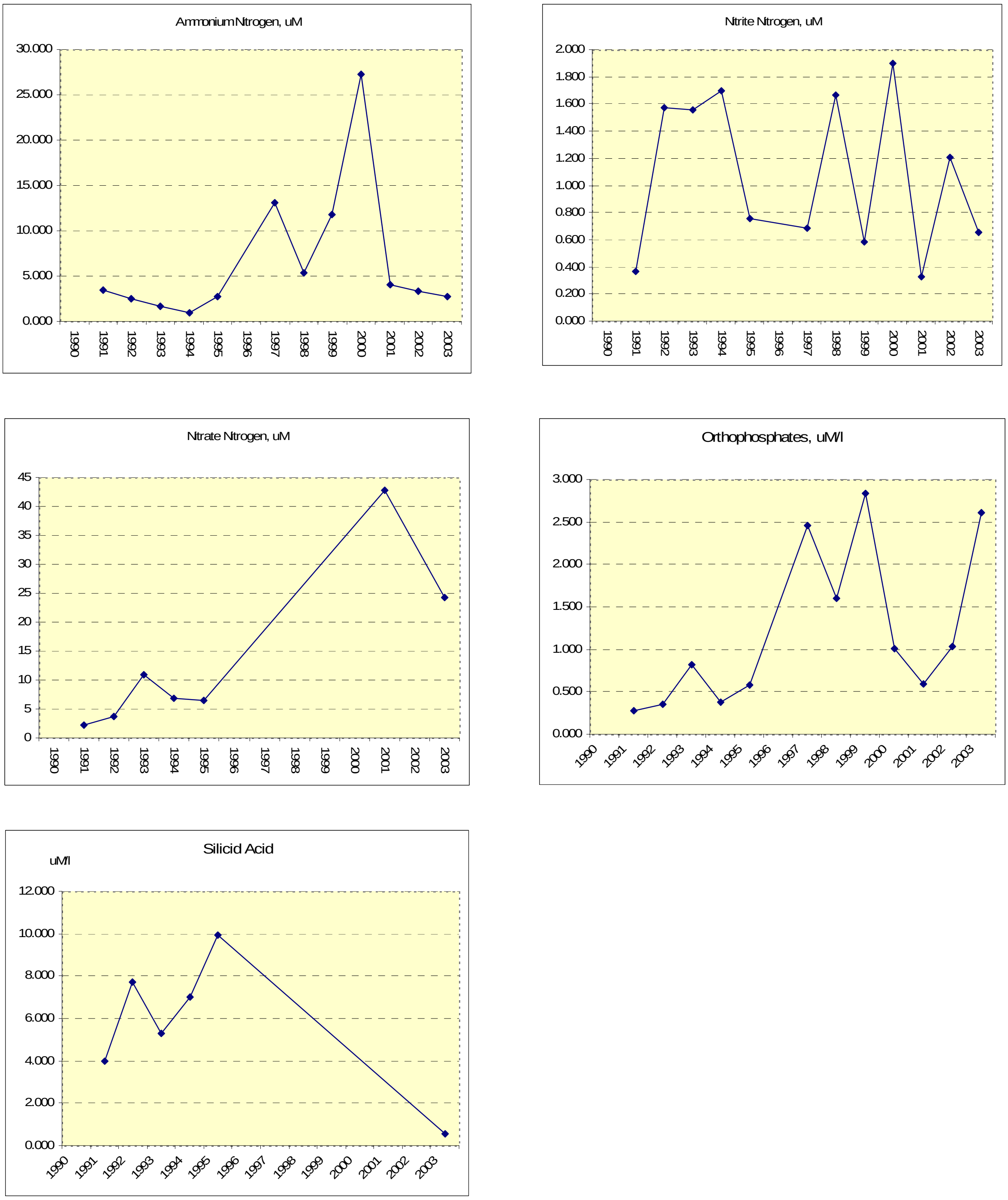


Figure B.4 Dynamics of nutrient and oxygen concentrations in North-Western Shelf waters of the Black Sea during 1990-2003. Bulgaria (Area 3)



B.2.5 Number of samples collected in different months and seasons

Very often seasonality detected within a time-series is caused by the irregularity of measurements. For instance, in a cold season of year some sampling locations are not accessible. As a result the time-series is biased towards summer concentrations. For certain parameters (e.g. water temperature and oxygen concentration) summer and winter concentrations are quite different. Thus, available time-series have been checked for the number of samples in all months/seasons (Table B.4 and B.5).

Table B.4 Number of water quality samples collected from the North-Western Shelf of the Black Sea

	Determinand											
Month	DOW	%	NH_4	%	NO_2	%	NO_3	%	PO_4	%	SiO_4	%
Jan	-	0%	1	0%	1	0%	1	0%	1	0%	1	0%
Feb	8	4%	23	8%	28	6%	16	5%	27	6%	18	6%
Mar	62	31%	57	20%	70	16%	63	21%	71	16%	65	23%
Apr	62	31%	19	7%	71	16%	63	21%	71	16%	63	22%
May	16	8%	27	10%	50	12%	26	9%	52	12%	27	9%
Jun	12	6%	27	10%	33	8%	23	8%	35	8%	21	7%
Jul	15	7%	28	10%	42	10%	22	7%	41	9%	24	8%
Aug	7	3%	23	8%	32	7%	24	8%	39	9%	14	5%
Sep	11	5%	33	12%	49	11%	26	9%	49	11%	20	7%
Oct	5	2%	12	4%	15	3%	13	4%	17	4%	12	4%
Nov	1	0%	18	6%	20	5%	8	3%	24	5%	4	1%
Dec	2	1%	16	6%	22	5%	13	4%	23	5%	17	6%
Total	**201**		**284**		**433**		**298**		**450**		**286**	

As shown in Table B.4 the number of samples taken in the Black Sea varied greatly from month to month. There was, therefore, a need to adjust the data seasonally prior to the processing of data. In contrast to this, the number of samples for the Danube River is evenly spread throughout the year (see Table B.5).

Table B.5 Number of water quality samples collected from selected Danube River sites

Month	Determinands					
	NH_4	%	NO_3	%	BOD_5	%
Jan	22	7%	22	7%	22	7%
Feb	22	7%	24	7%	24	7%
Mar	25	8%	27	8%	27	8%
Apr	25	8%	26	8%	26	8%
May	28	9%	32	10%	32	10%
Jun	23	8%	27	8%	27	8%
Jul	23	8%	27	8%	28	9%
Aug	23	8%	28	9%	28	9%
Sep	25	8%	28	9%	27	8%
Oct	27	9%	29	9%	28	9%
Nov	27	9%	28	9%	28	9%
Dec	28	9%	29	9%	29	9%
Total	**298**		**327**		**326**	

B.2.6 Seasonality

One of the most important statistical phenomena to consider with environmental data is those results, which routinely change with time (usually on a seasonal basis, but this can also occur over other time scales, e.g. the lunar tidal cycle causes large fluctuations in turbidity in some estuaries and dissolved oxygen concentrations in surface waters fluctuate on a diurnal basis). This can cause substantial overall dispersion within individual time series datasets, whereas within the same periods of year, this variability is much smaller. This is called seasonality (or periodicity), and for the most part of the water quality variables it is related to the growing season (e.g. nutrients) or meteorological season (e.g. water temperature, chloride, BOD, COD). In this report periods of high and low concentrations are reported when significant seasonality is observed.

The variability added by any repeated cycle (e.g. seasonality or periodicity) makes it more difficult to detect long-term trends. Prior to undertaking temporal regression analysis, two statistical tests were used to detect seasonality within the datasets for the Black Sea North-Western Shelf and locations on the Danube River. These tests are the Kruskal-Wallis test and one-factor ANOVA (Gilbert 1987, Helsel and Hirsch 1997).

Detected seasonality patterns are summarised in Table B.6 and presented in detail in Appendix E.

Table B.6 Detected seasonality in dissolved oxygen and nutrient concentrations in Black Sea North Western Shelf and Danube River locations

Area or site	Dissolved Oxygen (DOW)	Ammonium Nitrogen (NH_4)	Nitrite Nitrogen (NO_2)	Nitrate Nitrogen (NO_3)	Ortho-phosphates (PO_4)	Silicate (Si)
Ukraine	+				+	
Romania	+	+	+	+		+
Bulgaria	+	+		+	+	+
L1330				+		
L1390		+		+		
L1290				+		
L0430				+		

B.2.7 Linear trend analysis

For those parameters for which strong periodical cycles were detected account was taken of seasonality effects - either seasonally weighted or seasonal aggregated means/medians were used in the linear trend analyses.

A trend is a gradual increase or decrease of the annual averages of a water quality variable over a substantial number of years (at least 3 or 4 years, but preferably more). Within the framework of this report, trends are presented as a percentage related to the long-term average, corrected for seasonal influences (Gilbert, 1987; Helsel and Hirsch, 1997; Blind 1998). All trends were calculated with the significance level of 5%. The results are also presented graphically in Figs. B.5 and B.6 for Black Sea waters and the Danube River, respectively.

In Table B.7 the gradient of the linear regression line is given in column “Overall Trends”. If the likelihood of the trend is less than 95%, but more than 90%, only the direction of the trend is given, i.e. positive (concentrations increase with time) or negative (concentrations decrease with time).

Table B.7 Annual trends detected in nutrient concentrations in the North-Western Shelf of the Black Sea

Parameter	Trends				
	Overall	1990-1996	1996-2003	Winter	Summer
Ukraine					
Ammonium nitrogen	Negative	-4%	-15%	-3.1%	-1.9%
Nitrite nitrogen	Positive	0.6%	-1.4%	2.0%	3.7%
Nitrate nitrogen	Positive	0.5%	-6.9%	6.6%	10.5%
Orthophosphate	4.2%	3.1%	0.7%	4.5%	5.0%
Romania					
Ammonium nitrogen	Positive	8.7%	-5.3%	3.8%	1.5%
Nitrite nitrogen	5.1%	2.2%	13.7%	4.3%	5.8%
Nitrate nitrogen	3.1%	3.6%	8.7%	4.2%	5.7%
Orthophosphate	Negative	-2.1%	10.6%	-1.7%	-0.6%
Silica	Positive	5.7%	6.3%	4.1%	2.0%
Bulgaria					
Nitrate nitrogen	Positive	16.2%	63.9%	13.8%	10.1%
Orthophosphate*	-19.3%	-	-19.3%	19.1%	-13.6%

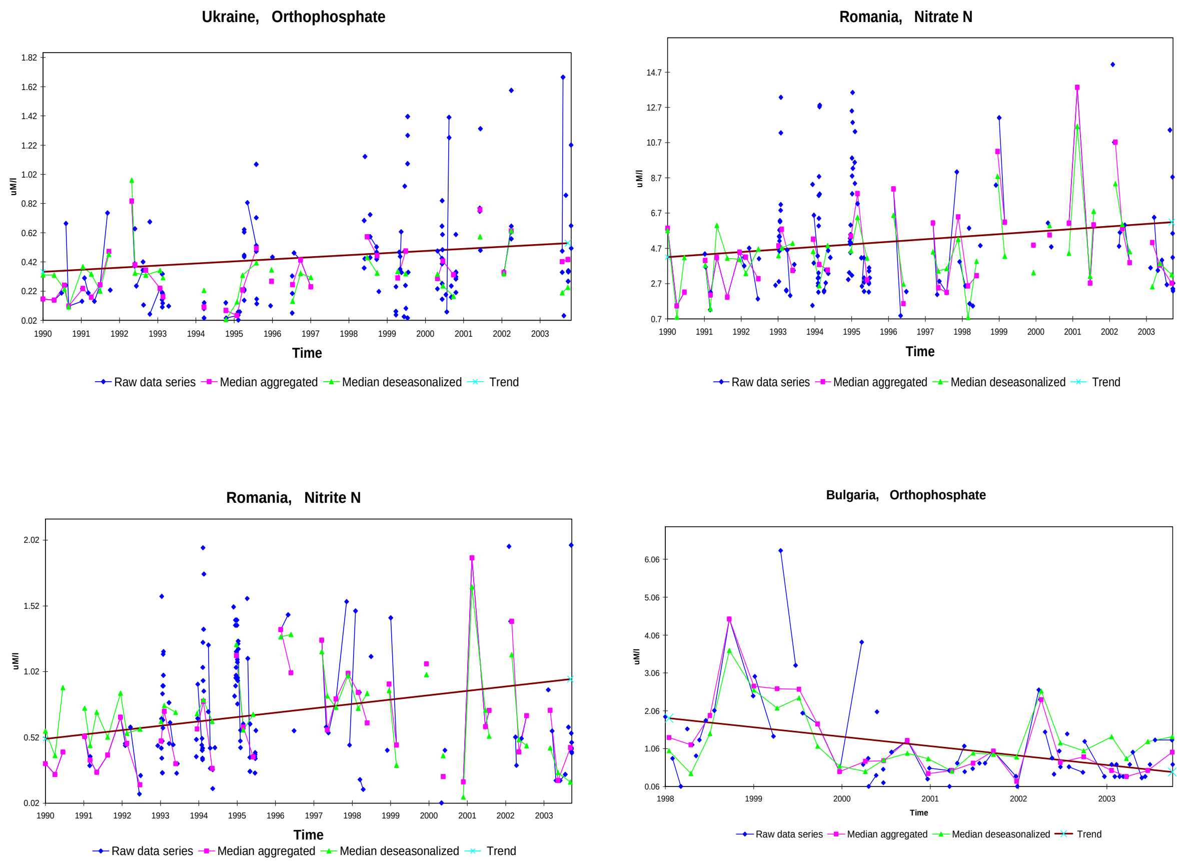
*Note: Sine the pattern of orthophosphate dynamics clearly indicated 2 periods: 1990-1998 with nearly "no trend" and 1998 onwards with a clear negative trend.

Table B.8 Annual trends detected in nutrient and BOD_5 concentrations in the Danube River

Parameter	Trends				
	Overall	1996-1998	1998-2000	Winter	Summer
Danube: L1330					
Ammonium nitrogen	-31.9%	-17.7%	-64.7%	-22.9%	-23.2%
Danube: L1390					
Ammonium nitrogen	Negative	-2.8%	0.0%	-3.3%	-4.8%
BOD_5	-35.4%	-21.6%	-61.7%	-32.2%	-40.5%
Danube: L1290					
BOD_5	Negative	-7.3%	9.8%	-3.7%	-4.7%
Ammonium nitrogen	-32.6%	-32.2%	-11.7%	-28.4%	-29.0%
Nitrate nitrogen	-12.8%	-12.5%	-37.1%	-10.2%	-12.5%

From Fig. B.7, it is apparent that changes in ammonium concentrations within the Danube River should not be regarded as trends, but rather are step changes, occurring towards the end of 1997. These results could reflect the upgrading of sewage treatment processes or closure of point source discharge upstream of the sampling points; but they could also be indicative of changes in sample collection/storage/analytical methodologies.

Figure B.5 Trends detected in nutrient concentrations in North-Western Shelf waters of the Black Sea (1990-2003)



In addition to the data presented above, plots are also provided for nutrient concentrations monitored during 1974-2004 on most working days at a single site (Constanta) along the Romanian coast (Fig. B.6, data provided by the Romanian Institute for Marine Research and Development). These results show a massive decrease in orthophosphate levels during this period, albeit that while the trend is still decreasing, since 1998 improvements have been much less dramatic. For nitrate improvements over the same period have been much less dramatic, and since 2000 the trend appears to be positive, i.e. the situation in recent years has been worsening. These conclusions are supported by the agglomerated Romanian data trend analysis results for the overall period 1990-2003, but contradict the agglomerated orthophosphate data for 1996-2003, which show a worsening trend over this period (Table B.7). During the 1970s and early 1980s, silicate levels dropped extremely rapidly, a result which can be explained by the construction of the two Iron Gate dams across the Danube and retention of silicate in these reservoirs. (The same is also true of phosphorus and, to a lesser extent, nitrate.) However, factors underlying the increase in silicate levels since the mid 1990s remain unclear.

Figure B.6 Trends detected in Black Sea nutrient concentrations at Constanta monitoring station (1974-2004)

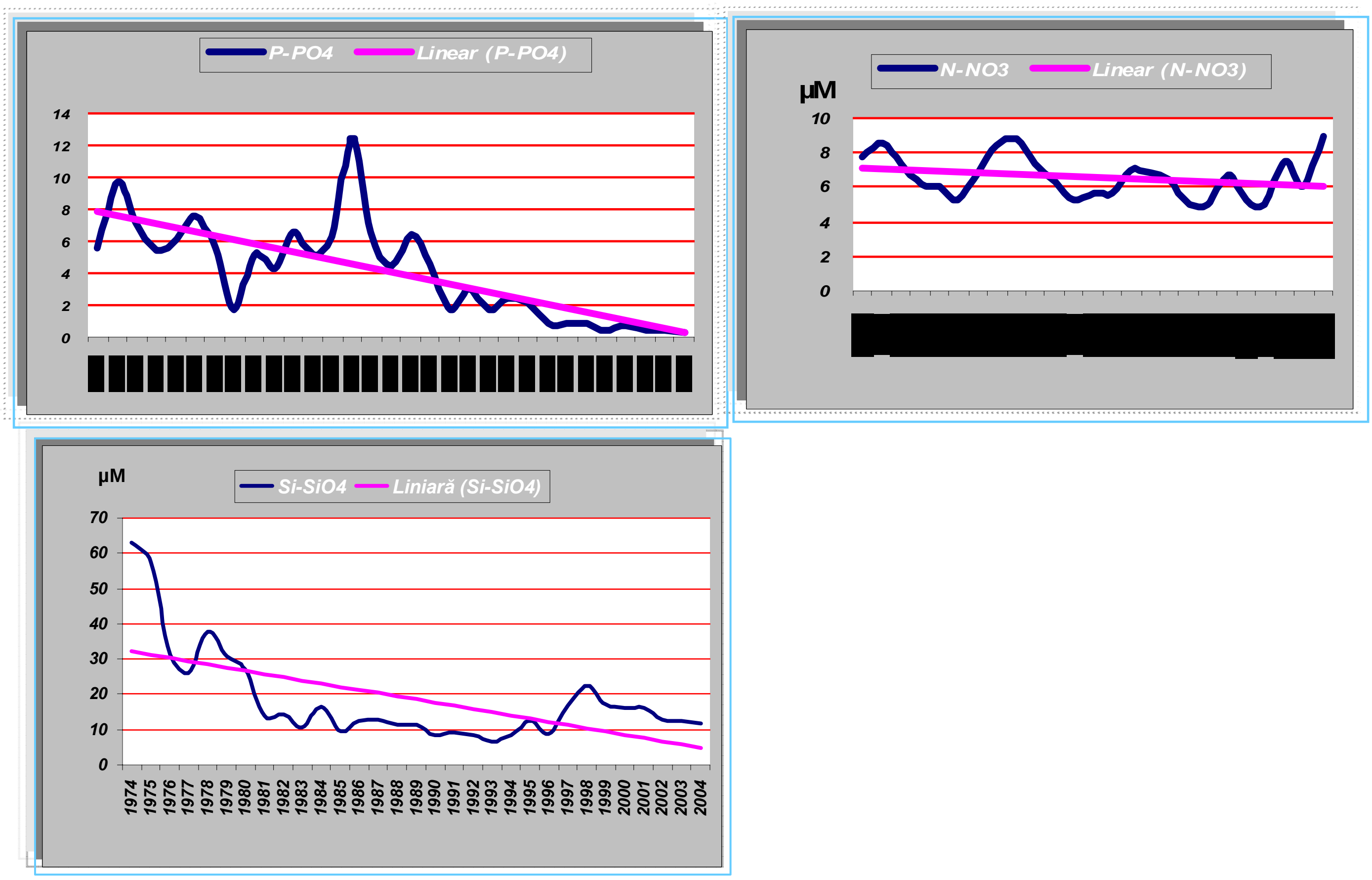


Figure B.7 Trends in nutrient and BOD_5 concentrations in the Danube River (1996-2003)

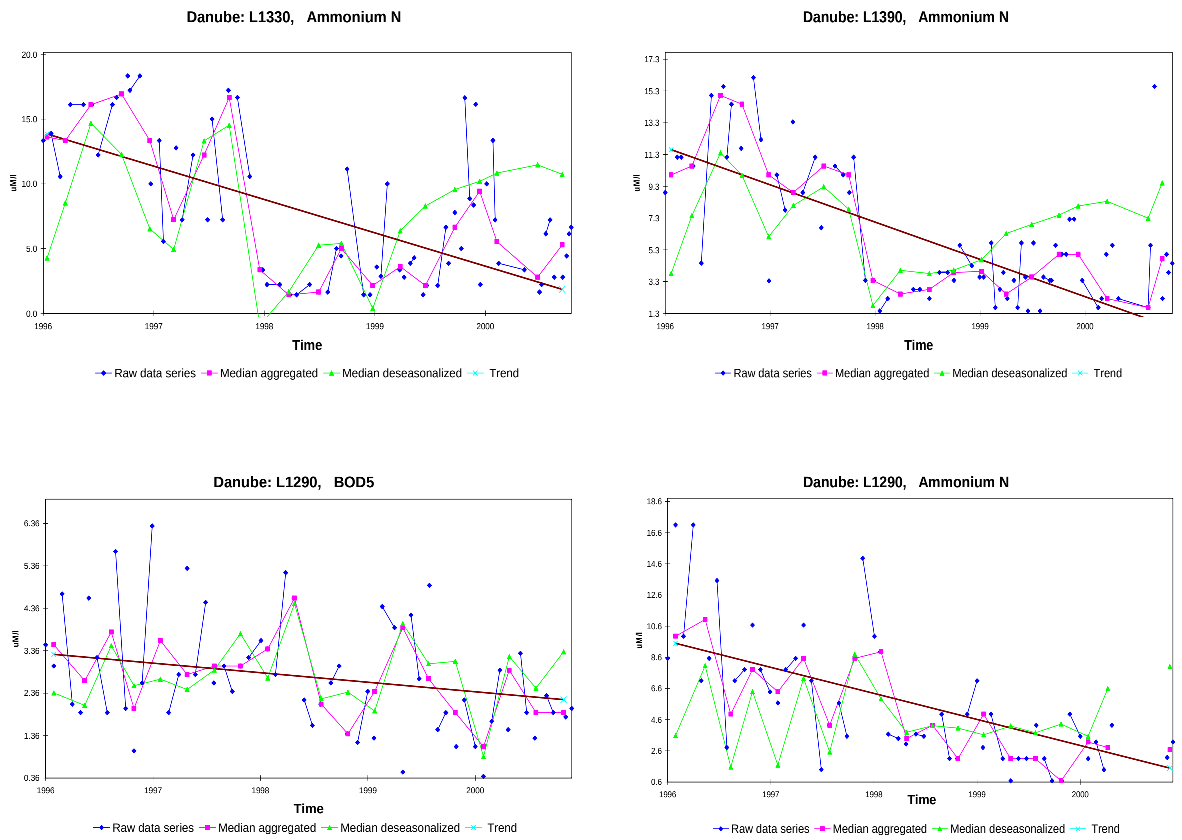
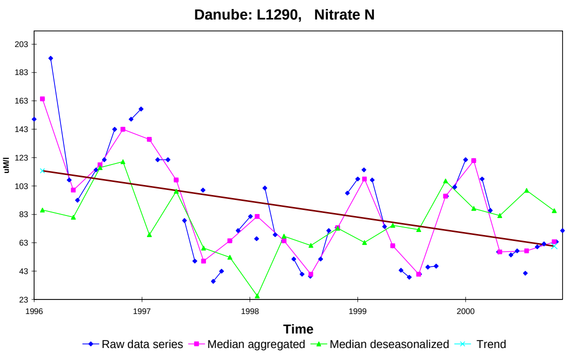


Figure B.7 Trends in nutrient and BOD_5 concentrations in the Danube River (1996-2003) (cont'd)



B.3 Chlorophyll

Despite a compelling evidence of eutrophication and degradation of marine habitats and communities observed in the 1980s, limited system-wide regional studies of this problem have been carried out in the Black Sea area. The evidence has been pieced together from fragmentary studies, but there are still huge gaps and uncertainties. Joint studies conducted under the GEF-UNDP Black Sea Ecosystems Recovery Programme have been undertaken to better define subsequent monitoring needs (ULRMC, 2004).

Chlorophylls (chl) are a group pigments present in all photosynthetically active algae and higher plants, whose concentration in suspension is used as a surrogate of phytoplankton standing crop (total phytoplankton biomass). This parameter, measured by remote sensing techniques, is a widely-acknowledged, and cost-effective indicator of the trophic status of huge areas of marine and fresh waters, albeit one for which oceanographic factors other than nutrient concentrations are required to assess and explain results (see below and Section 3.2.4).

B.3.1 Meteorological and oceanographic factors affecting seasonal and annual chlorophyll dynamics

According to published sources, typical chl-a dynamics of the Black Sea deep-water regions are characterized by a summer minimum and prolonged winter-spring maximum, declining during April-May (Beserneva, 1993; Vedermikov and Dermidov, 1993; Berseneva *et al*, 2004). Elevated values during the winter-spring period are thought to be due to upwelling of deeper nutrient-enriched water into the euphotic zone (Krivenko and Kirikova, 2002; Churilova and Georgieva, 1998). A seasonal (spring) halt to this upwelling reduces nutrient availability for phytoplankton growth. This results in a switch from deep water supply to recycling of nutrients within the upper mixed water layer as the major nutrient source for phytoplankton growth (Krivenko and Kirikova, 2002). Seasonal thermal stratification then limits transportation of nutrients from the pycnocline to the mixed surface layer above the thermocline (the epilimnion).

In North-Western Shelf surface waters nutrients are derived principally by recycling from sediment and the local influence of river run-off. The latter represents a "new" source of nutrients, which determines phytoplankton biomass and chl-a concentration, in contrast to the deep-water areas described above. Nutrient supply on the North-Western Shelf depends on both the intensity of river run-off and the direction of river water distribution within the Sea. Maximum Danube and Dnipro rivers discharges to the Sea occur during May, and for the Dniester and Southern Bug - in March-April (Ivanov and Ilyin 1995).

The area of influence of river water on the Black Sea is strongly dependent upon wind direction. This is predominantly North-Eastern during winter, promoting a southerly flow in this area of the Sea. However, during summer, a predominant Western wind promotes the distribution of river waters in an Easterly direction towards the Crimean Peninsula, where they are subsequently re-directed by an anticyclone towards the central areas of the Sea. Consequently, minima in winter, and maxima in spring characterise the seasonal dynamics of chlorophyll/chl-a concentrations in the North-Western Shelf.

Overall, SeaWiFS data correspond to the patterns of water flow discussed above, with the range of predicted chlorophyll concentrations being close to *in-situ* chl-a observations recorded earlier. However, the seasonal and inter-annual variability of meteorological conditions influence the intensity of river run-off and the characteristics of its distribution (i.e. the Danube 'plume'), which is reflected in seasonal and inter-annual dynamics of chl-a concentration in this area. Consequently, continuous *in situ* monitoring of chl-a concentrations in the North-Western Shelf area is necessary for the correct validation and adaptation of SeaWiFS algorithms for chlorophyll estimation.

B.3.2 Remote data used and approach

Two types of remote sensing data, both originating from the SeaWiFS satellite were used in this assessment:

- Level 0 format data with spatial resolution of 1.1 km, obtained using a High Resolution Picture Transmission (HRPT) station of the Ukrainian Land and Resource Management Center (ULRMC),
- Level 1 format data from archives of the Goddard Space Flight Center Distributed Active Archive Center (GSFC DAAC).

The SeaDAS program system was applied to estimate chlorophyll levels use two NASA-recommended algorithms:

- The OC4 empirical algorithm (O'Reilly *et al*, 1998).
- The GSM01 improved multispectral algorithm (Siegel *et al*, 2002).

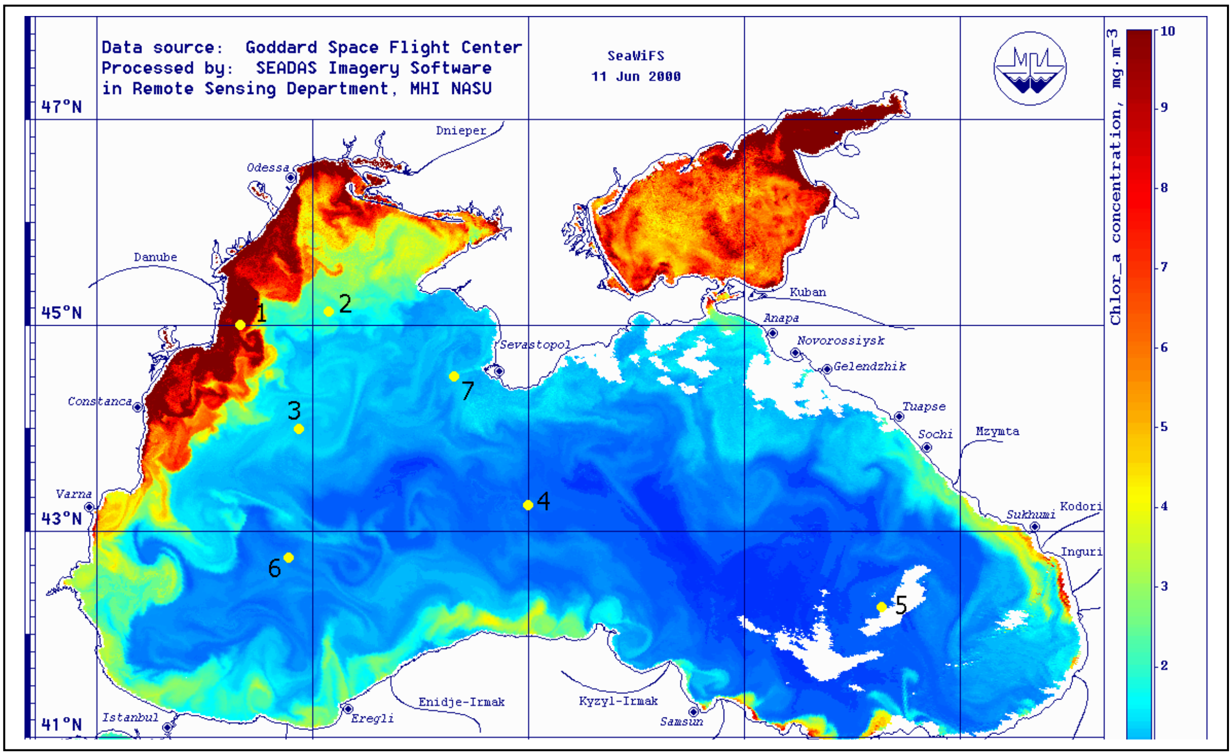
Which algorithm provides the better estimate of chlorophyll concentrations in the Black Sea is a moot point, and one which it is not necessary to discuss here. Values of chlorophyll concentrations obtained using SeaWiFS data differed from *in situ* chl-a measurements taken in the same deep water area during 1998-2000. To illustrate this point, in summer, the satellite results overestimated *in situ* chl-a concentrations by a factor of two, and during the spring (March) diatom bloom actual chl-a concentrations were underestimated by 30 %. Whilst this casts some doubt on the quantitative use of SeaWiFS data, qualitative spatial and temporal trends are considered much more trustworthy.

B.3.3 Chlorophyll concentrations in the Black Sea (SeaWiFS satellite data)

For studying the spatial and temporal variability of chlorophyll-a concentration in the Black Sea, weekly maps of chlorophyll concentrations were calculated using information derived from the SeaWiFS remote sensing scanner, with 4-km resolution. The SEADAS program and OC4 algorithm were used for data processing.

For analysis of the time-series, seven areas of the Black Sea were selected (Fig. B.8), which clearly shows that the depth of water plays a significant role in chlorophyll distribution. Since the geographical scope of this report covers only the North-Western Shelf of the Black Sea, results from Areas 4-7 are excluded from this assessment. The chlorophyll concentration values shown (Figs. B.9-B.11), are average concentrations recorded in a 28x28 km square at each of the Areas. The areas were selected on the basis of having different hydrological conditions known to influence phytoplankton standing crop/productivity:

Figure B.8 Areas of investigation of chlorophyll concentration temporal variability (SeaWiFS OC4 chlorophyll map for 11/06/2000)

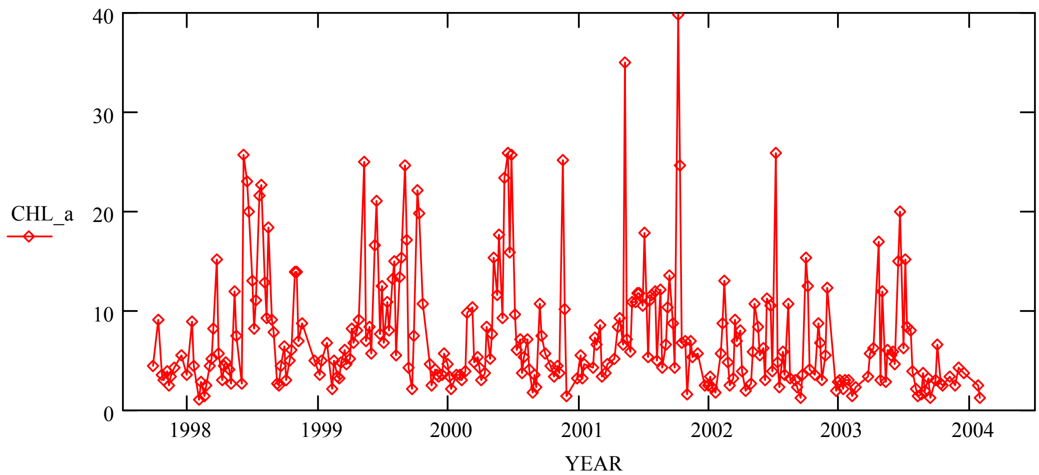


- Area 1 is close to the Danube Delta and strongly impacted by the river run-off effect (freshwater phytoplankton carry-over).
- Area 2 is at the centre of the North-Western Shelf and strongly subject to the impacts of both the Danube and Dnipro rivers.
- Area 3 is influenced by the Black Sea Main Stream (BSMS) and anticyclonic activity; it is subject to both shelf and central sea waters effects.

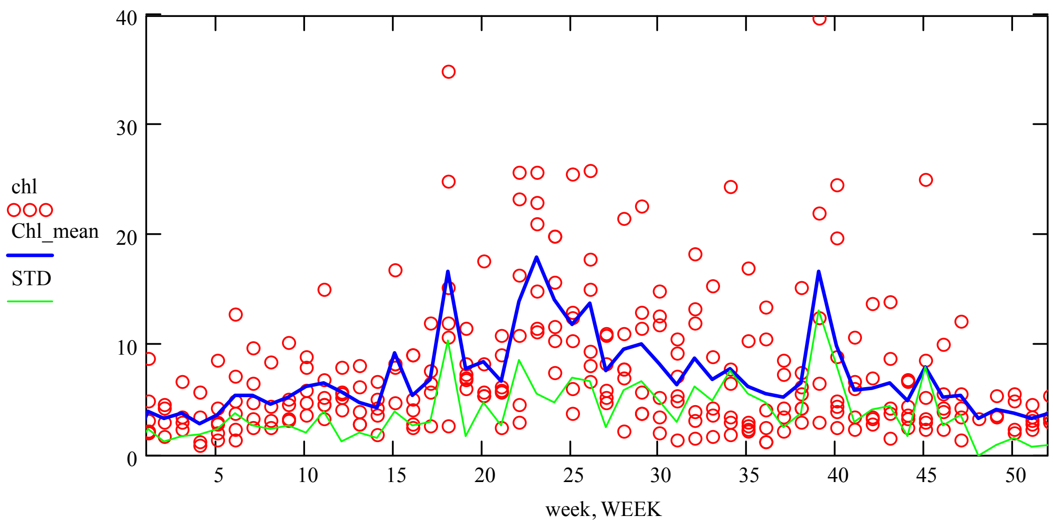
Area 1 – the Danube River Delta

Fig. B.9 illustrates temporal variability of chlorophyll concentration for the period from 1997 to 2004 (the upper diagram), as well as the annual course, average and average quadratic deviation (the lower diagram). Note the relatively high chlorophyll concentrations compared to other areas of the Black Sea (*cf*. Figs. B.8, B.10 and B.11) and the pronounced inter-annual variability, as well as an overall increase in concentration for the considered period (0.453 mg/m^3 per year). This dataset clearly illustrates summer maxima and winter minima values, as influenced by river discharges.

Figure B.9 **Chlorophyll time series (1997 –2004), Area 1.** Yearly variation (red), weekly mean (blue) and standard deviation (green)



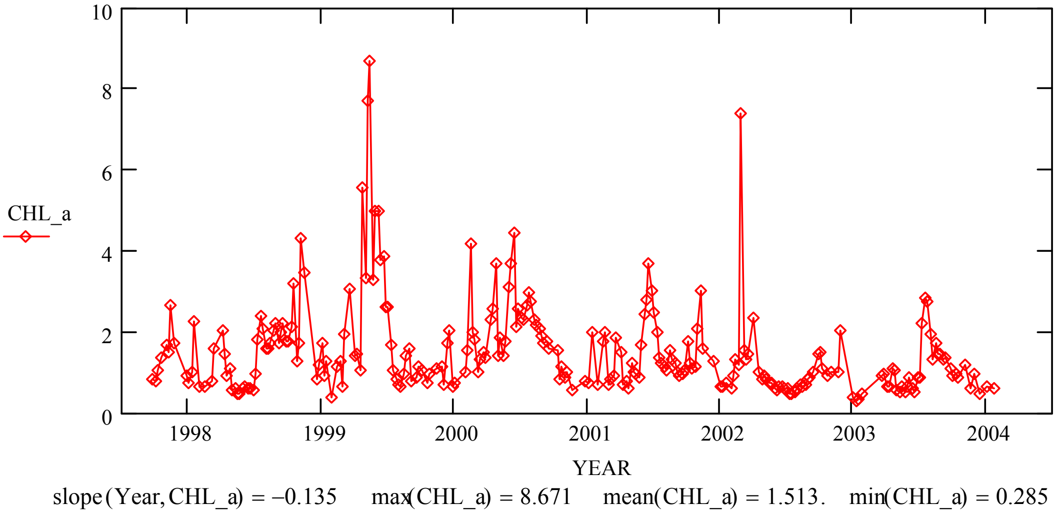
slope(Year, CHL_a) = −0.452 max(CHL_a) = 39.72 mean(CHL_a) = 7.5 . min(CHL_a) = 0.945

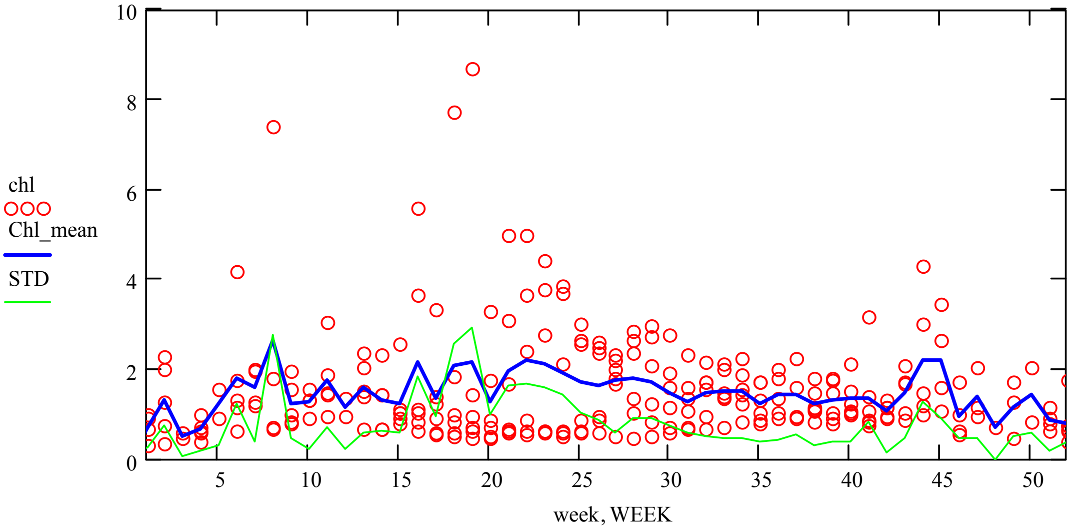


Area 2 – Ukraine

Fig. B.10 illustrates chlorophyll dynamics that are strongly influenced by both Danube river run-off and mixing with less nutrient–enriched rich Shelf waters. Maximum annual concentrations can be observed at almost any time between weeks 7 and 45, illustrating considerably less pronounced seasonality than that observed for Area 1 (Fig B.9). Winter minima could be recoded at almost any time between weeks 46 and 6. During the period of data collation, unlike Area 1, a trend of reducing chlorophyll concentrations occurred (a decrease of 0.135 mg/m^3 per year).

Figure B.10 Chlorophyll time series (1997 –2004), Area 2. Yearly variation (red), weekly mean (blue) and standard deviation (green)

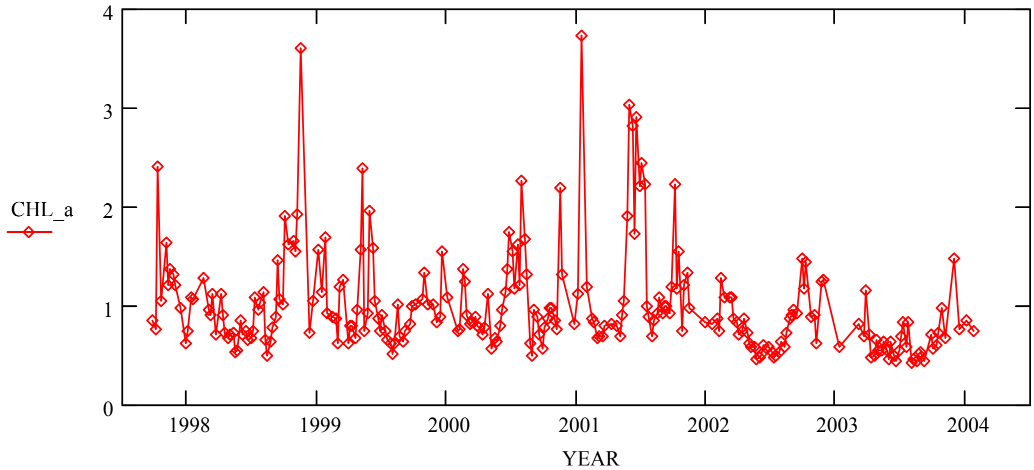


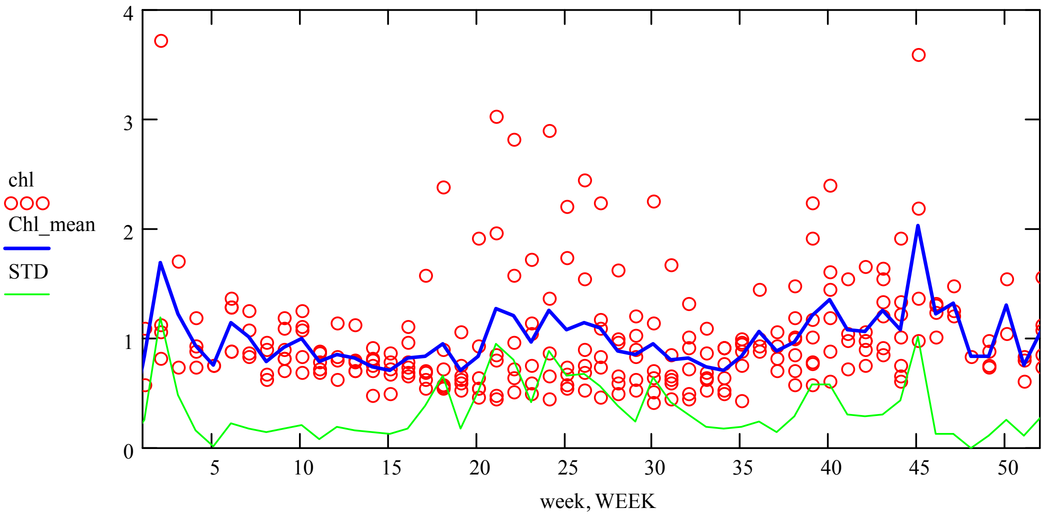


Area 3 – Romania

Intensive mixing of heavily river-influenced Shelf waters (containing relatively high concentrations of chlorophyll) with central Sea waters (less nutrient-enriched, with lower chlorophyll levels) occurs in this area. This mixing has a major influence on chlorophyll concentrations (Fig. B.11), resulting in lower overall levels that those exhibited in Area 2 (Fig. B.10) and much lower than those in Area 1 (Fig. B.9). The year-on-rear plot shows autumn-winter maxima with a secondary increase in chlorophyll concentrations during summer. This pattern occurred most notably during the 1999-2001 period. Throughout the entire 6-year monitoring period chlorophyll concentrations reduced by 0.06 mg/m^3 per year.

Figure B.11 Chlorophyll time series (1997 –2004), Area 2. Yearly variation (red), weekly mean (blue) and standard deviation (green)



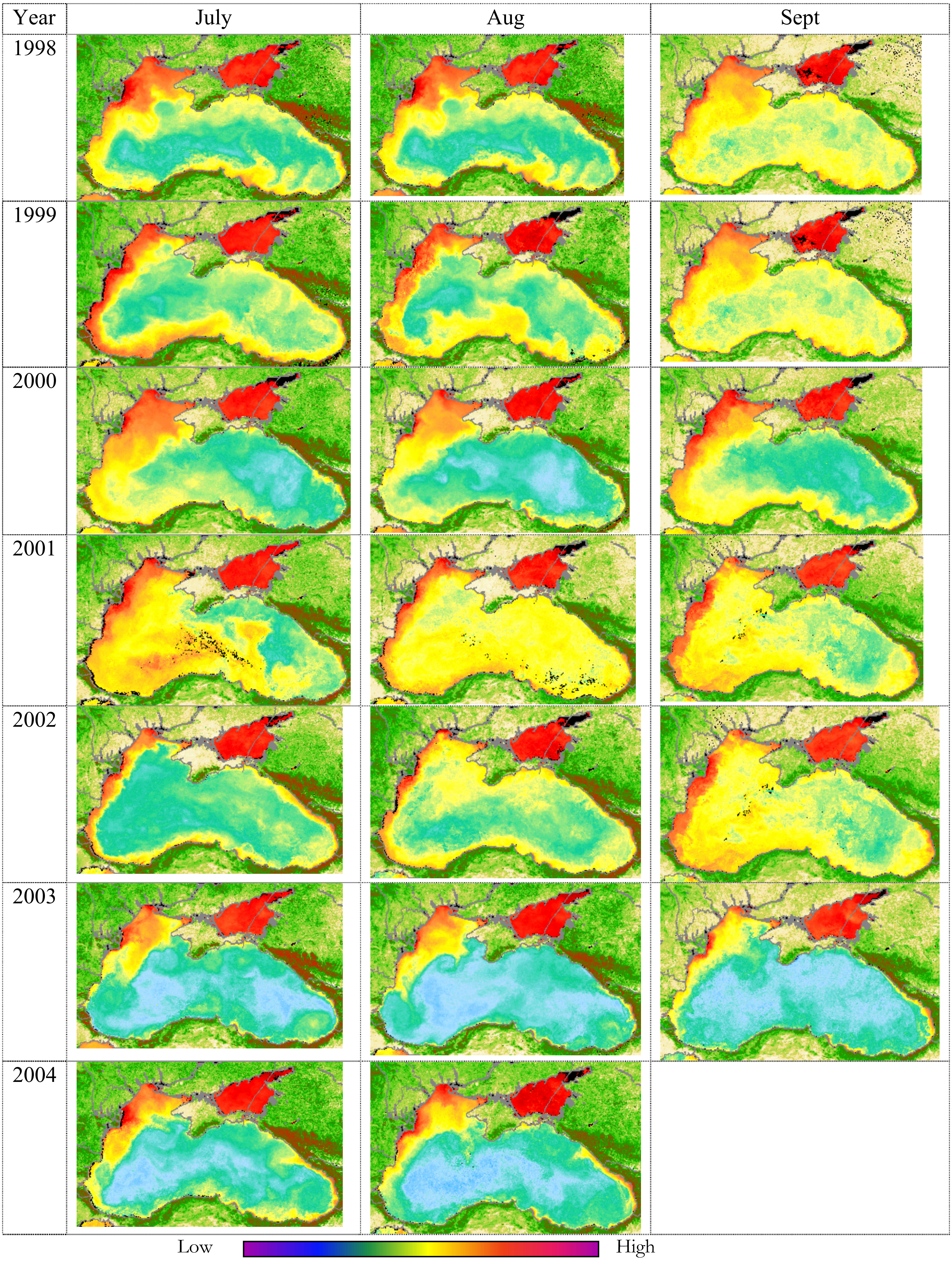


B.3.4 Overview of chlorophyll dynamics (1998-2004)

The maps presented in Fig. B12 were provided to the Black Sea Commission by the Joint Research Center of the European Commission, Ispra, Italy. They are produced from SeaWiFS satellite images showing July, August, and September (1998 – 2004) mean concentrations of chlorophyll-like pigments in the Black Sea. Annual averages, monthly averages, as well as weekly averages vary significantly from year to year and between different areas of the Sea (see Section B.3.3). Throughout all the years the North-Western parts of the Black Sea (with the Danube, Dniester and Dnepr river mouths) show higher values in chlorophyll concentration compared to other Black Sea coastal areas and the 'open' Black Sea.

In general, there is a tendency of reducing chlorophyll concentrations in the worst months throughout the period from 1998 to 2004. The latest years (2003 and 2004) are characterised by low chlorophyll concentrations, coincident with small or absent areas of hypoxia on the North-Western Shelf.

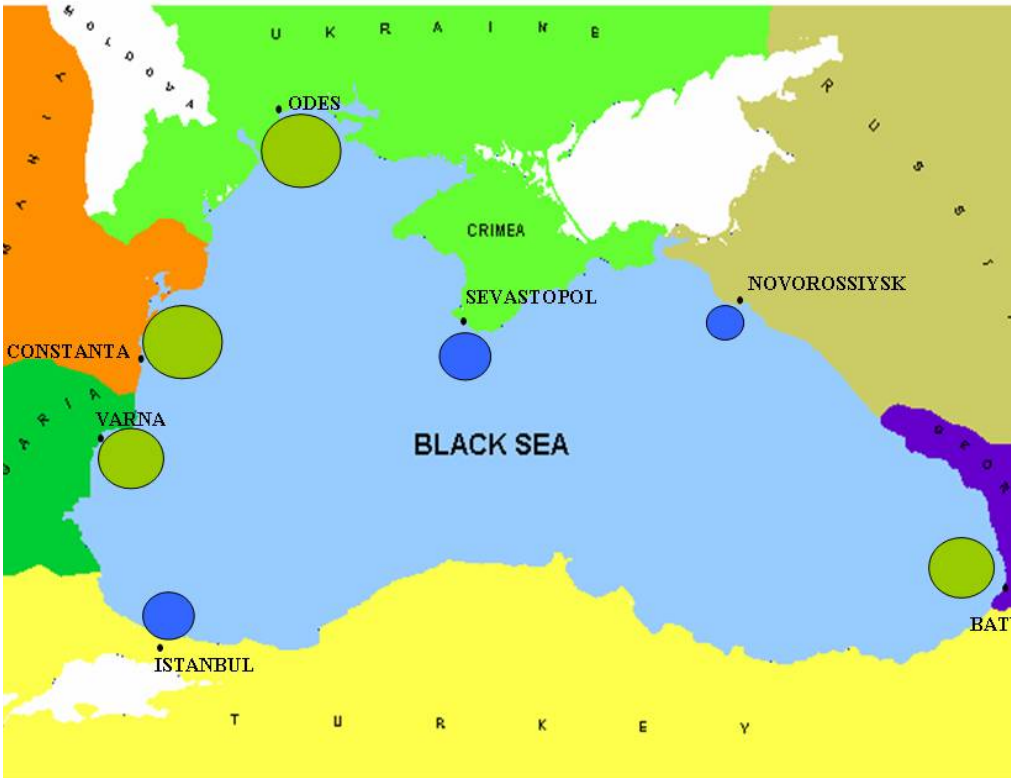
Figure B.12 Remote sensing chlorophyll images (mean values) for July, Aug, and Sept (1998-2004)



B.4 Aquatic vegetation

A methodology using rocky shore macroalgae morpho-functional indices to monitor trophic status has been developed and tested at seven transects in the Sea. The results of this assessment (See Fig B.13) demonstrate a higher trophic status of rocky shores close to the Danube delta than those further away. Coastal waters at Sevastopol and Istanbul (regarded as being at the outer edge of influence of the Danube in this assessment) are define as mesotrophic ("clean enough") according to this methodology, while Odessa, Constanta and Varna are all described as eutrophic (moderately polluted). However, the results from Batumi, where the macroalgal community is also described as eutrophic, illustrate how this methodology is more prone to local influences (e.g. relatively small local discharges) than further offshore methodologies (e.g. zoobenthos assessments) when investigating the impact of the Danube.

Figure B.13 Trophic status of Black Sea coastal waters as determined by macro-algal morphological indices (Minicheva 2004)



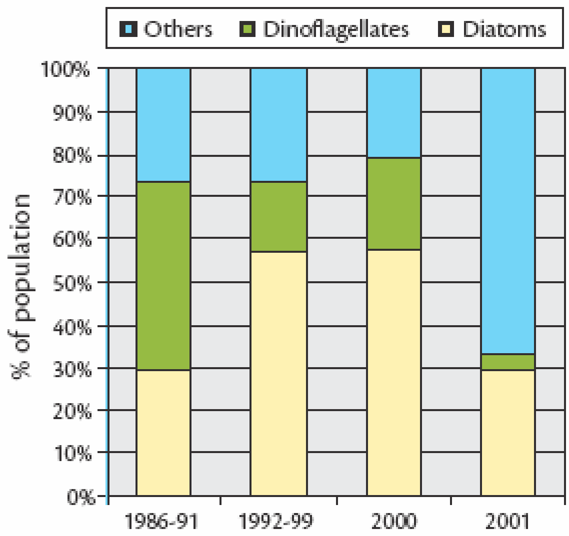
Mesotrophic	Novorossiysk	
	Sevastopol, Istanbul	
Eutrophic	Varna, Batumi	
	Odessa, Constanta	

B.5 Phytoplankton

Because of sampling and analytical methodology differences, data from Bulgaria, Romania and Ukraine have not been comparable. However, at a recent workshop in Odessa (15-19August 2005) a first Black Sea Regional phytoplankton intercalibration exercise was undertaken to facilitate comparison of historical data, and agreement was reached over the use of standardised sampling/processing equipment. No formalised lists of key taxa or other phytoplankton trophic status metrics have yet been made, but these are expected as a reported output of the Odessa workshop.

Nevertheless, data are shown for phytoplankton populations off the Romanian coast during periods of severe eutrophication (1986-1991), recovery (1992-2000), and during the unexpected return of eutrophic conditions in late summer 2001 (Fig. B.14). This plot illustrates the sudden change that occurred in 2001 as eutrophic conditions returned, but also casts doubt on use of the diatoms:dinoflagellates cell count ratio as an indicator of marine trophic status, illustrating that individual indicators should not be used in isolation. No data were available to make a comparison against use of the diatoms:dinoflagellates biomass ratio as an indicator of trophic status.

Figure B.14 Phytoplankton populations off the Romanian coast (Bodeanu *et al*, 2002, Mee *et al*, 2005)



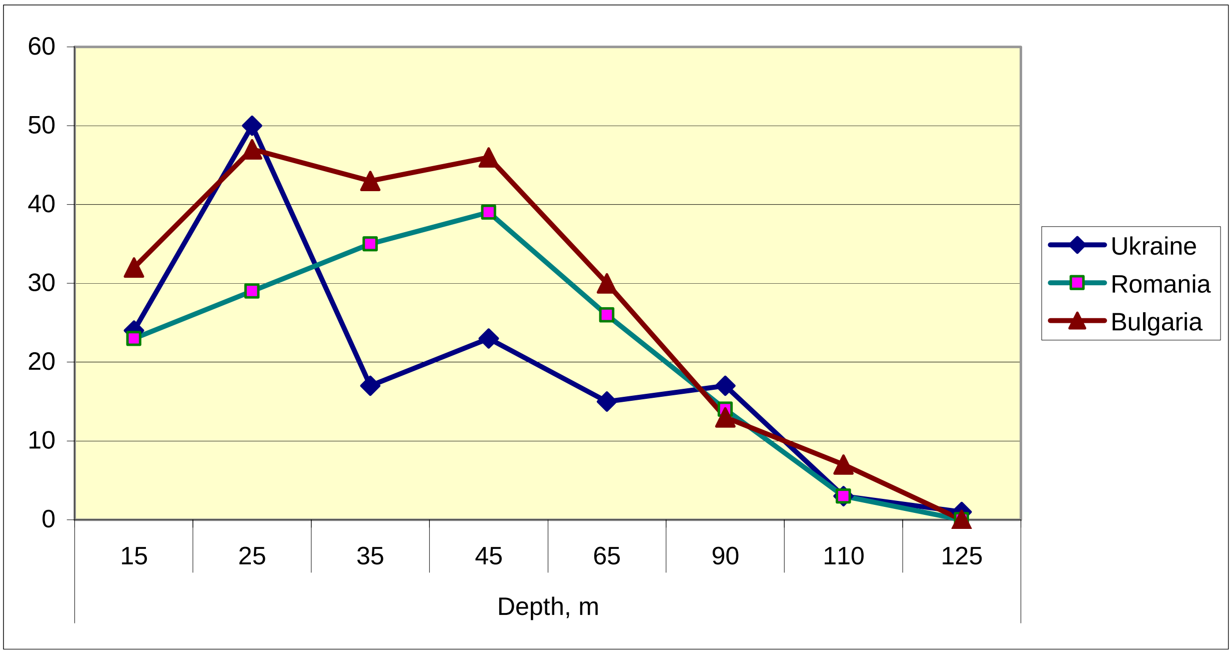
B.6 Zoobenthos

B.6.1 Assessment of macrozoobenthic community status in the North-Western Shelf of the Black Sea (Oct 2003)

Assessment of macrozoobenthic communities in the North-Western Shelf of the Black Sea followed the first BSERP scientific cruise in October 2003. This section (B.6.1) contains the main conclusions. Details can be found in Sinegub (2004) and Todorova *et al* (2004).

Fig. B.15 illustrates the apparent importance of depth on the number of zoobenthic taxa present. The reasons for this represent a combination of factors, such as light limitation of phytobenthos (both larger plants - macrophytes and macroalgae - and benthic microalgae) and changes in wave and current-influenced sediment type (as determined by particle size analysis), as well as the degree of gross organic and pollutant enrichment from land-based sources. This is a clear demonstration of the importance of depth as a key consideration in the selection of BSIMAP sites for macrozoobenthos sampling.

Figure B.15 Numbers of macrozoobenthos taxa at different depths on the shelf of Ukraine, Romania and Bulgaria (R/V Akademik. 23.09.2003 – 13.10.2003; Sinegub, 2004)



Data on the number of taxa, density and biomass of macrozoobenthic communities are presented in Figs. B.16 and B.17 on the basis of major taxonomic groups and functional feeding groups, respectively. The results presented are averages from numerous sites at 15-45 metres depth (4 depths, 13 samples for Bulgarian stations; 4 depths 12 samples for Romanian stations; 4 depths 13 samples for Ukrainian stations).

According to a series indicator taxa, structural and diversity criteria, results from 60 macrozoobenthos samples were used to divide the North Western shelf of the Black Sea into areas of differing ecological health, ranked in the following order:

1. The worst ecological status is evident at Odessa area manifested by: low diversity indices, low average abundance and biomass of molluscs, scarce development of crustaceans (most sensitive to hypoxia group), overabundant development of oligochaetes (first-order opportunistic species, pioneer colonizers after benthic mortality, tolerant to hypoxia) indicating highest level of community disturbance. Lowest average concentration and saturation of dissolved oxygen among upper circalittoral areas explain well the community disturbance. Hypoxic conditions observed at relatively shallow depth are not associated with the natural depth gradient but with the anthropogenic pressure on the North-Western Black Sea shelf– eutrophication and pollution.
2. Second worst ecological status is assigned to the Danube Delta as evidenced by low species diversity, excessive abundance of deposit feeding first order opportunistic polychaetes and oligochaetes - indicators of organic enrichment of the sediments, decreased abundance of the crustaceans, mass development of hypoxia tolerant bivalves and high variation in species composition, abundance, biomass and diversity indices implying ecological instability. Decreased oxygen saturation at shallow depths is associated with the Danube impact on the area, with the river identified as the major source of nutrients, BOD_5 and TSS to the Black Sea (Mee and Topping 1999).
3. The “Southern shallow” area and Dniester area rank higher in ecological “health” compared to the previous areas. Both of the areas manifest generally good ecological quality but still some signs of disturbance.

4. The ecological status of the "southern" circalittoral area can be described as slightly unbalanced. The signs of community disturbance are: over-stimulation of the biota manifested in high total average abundance, high abundance of opportunistic polychaetes and decreased evenness in the abundance structure. However, there are also signs of good ecological quality: highest number of species and species richness and second highest community diversity index, highest abundance and/or exclusive presence of crustaceans sensitive to hypoxia, high abundance of polychaetes sensitive to disturbance. Oxygen saturation is highest among upper circalittoral despite greater average depth which is in good correlation with the increased species richness and high crustaceans abundance.
5. Good ecological status of benthic communities is manifested by Dniester area evident in: the highest evenness of the abundance distribution, highest community diversity index, high average number of species and species richness, high abundance of crustacean sensitive to hypoxia. Increased zoobenthic diversity is associated with the heterogeneity of the sediment. The coarse sediments, shallow depth and probably the hydrographic conditions result in favourable oxygen regime in this area, despite inputs from the Dniester River.
6. The "deep" area is characterised by a naturally deteriorated environment in terms of oxygen saturation reflected in decreased species diversity. However, the community structure is undisturbed. In general, the community status is recognizes as normal under the specific Black Sea conditions at greater depth of the lower circalittoral.

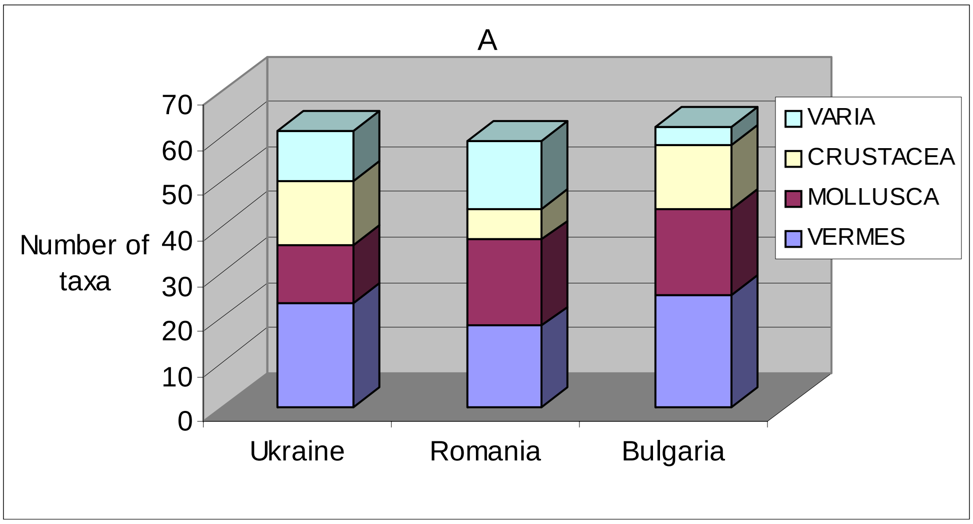
Macrozoobenthic community status in different areas of the North-Western Black Sea reflects environmental gradients manifested in two directions:

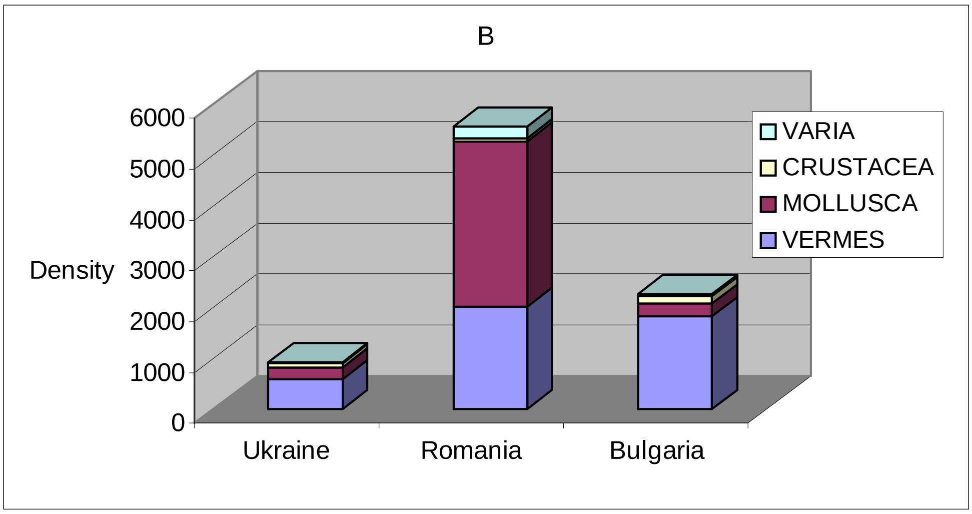
- The first direction of increasing environmental stress is coincident with the depth gradient and is natural for the Black Sea in relation to the basin's specific hydrophysical and hydrochemical characteristics. These promote stagnancy hypoxia/anoxia at greater depths. Decreased benthic diversity is evident in the lower circalittoral of the entire North-Western Shelf, however the community is mature and typical of a late ecological succession stage, due to a stable and predictable environment.

- The second gradient of increasing stress is evident in south - north direction on the upper circalittoral and is associated with the anthropogenic pressure (eutrophication, pollution) from the major rivers (Danube, Dniester, Dnipro) and other land-based sources of contamination. This gradient is clearly reflected in the decreasing oxygen saturation and respectively increasing disturbance of benthic communities from south to west. Coarse heterogeneous sediments and probably the hydrographical conditions (intensive water circulation) mitigate the anthropogenic impact in the Dniester area preventing hypoxia and thus benefiting the bottom community.

Thus, while there are still some signs of the impact of the Danube, the situation has improved substantially from that in the mid-late 1990s (Fig. B.18), albeit that full zoobenthos recovery is probably some way off, particularly in the north of the North-Western Shelf (Fig. B.19). This latter plot illustrates that while the area off Constanta has the greatest biodiversity, sites closer to where the Danube enters the Black Sea are in a considerably worse state. (Note that species diversity results in Figs. B.18 and B.19 are not directly comparable, since the data shown represent different populations (macrozoobenthos and meiobenthos) at different monitoring stations.)

Figure B.16 Number of zoobenthos taxa (A), average density (ind/m^2) (B) and biomass, g/m^2) (C) on the Black Sea North-Western Shelf at 15 – 45 m depth. Autumn 2003 (Sinegub 2004). Results expressed in terms of major taxonomic groups





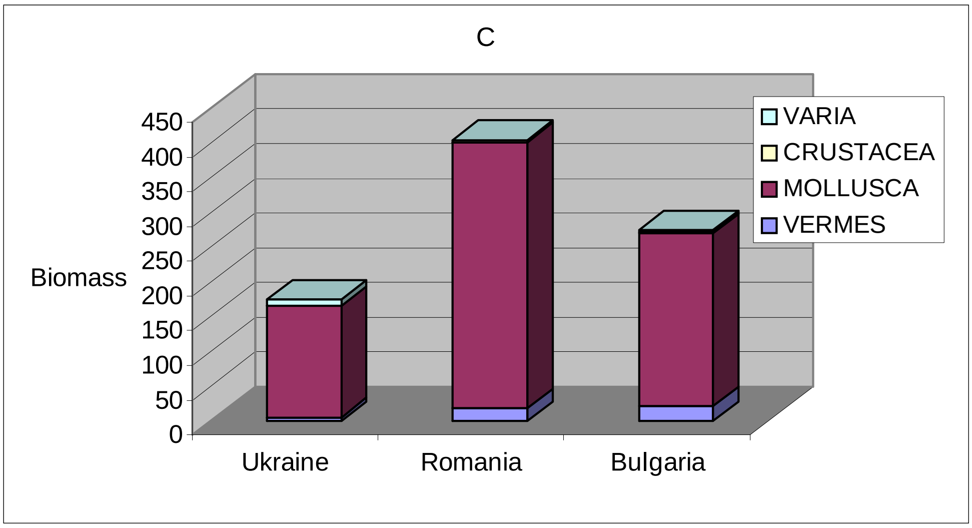


Figure B.17 Number of zoobenthos taxa (A), average density (ind/m^2) (B) and biomass, g/m^2) (C) on the Black Sea North-Western Shelf at 15 – 45 m depth. Autumn 2003 (Sinegub 2004). Results expressed in terms of functional feeding groups

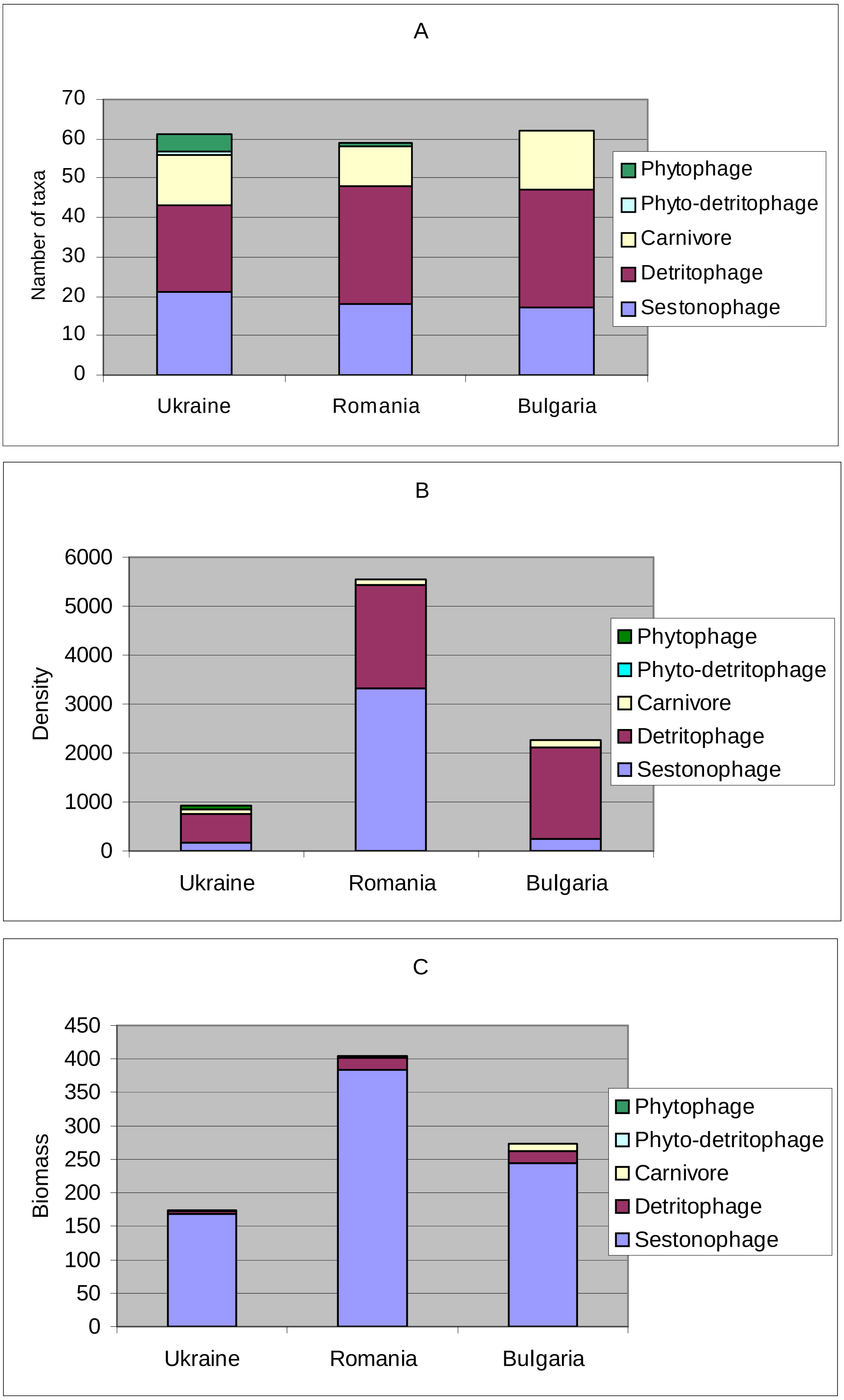


Figure B.18 Number of macrozoobenthic taxa in front of the Danube Delta (10 stations on three transects off Constanta (data from C. Dumitrache, IRCM Constanta; ICPDR, 2005**)**

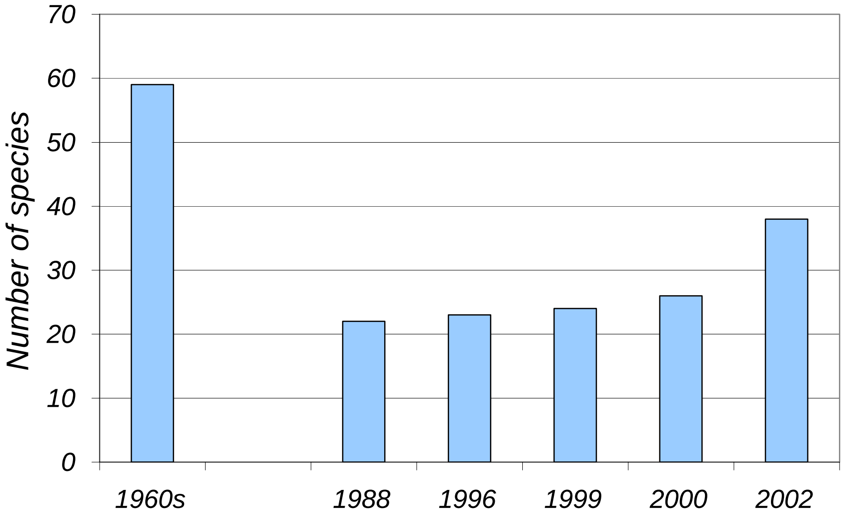
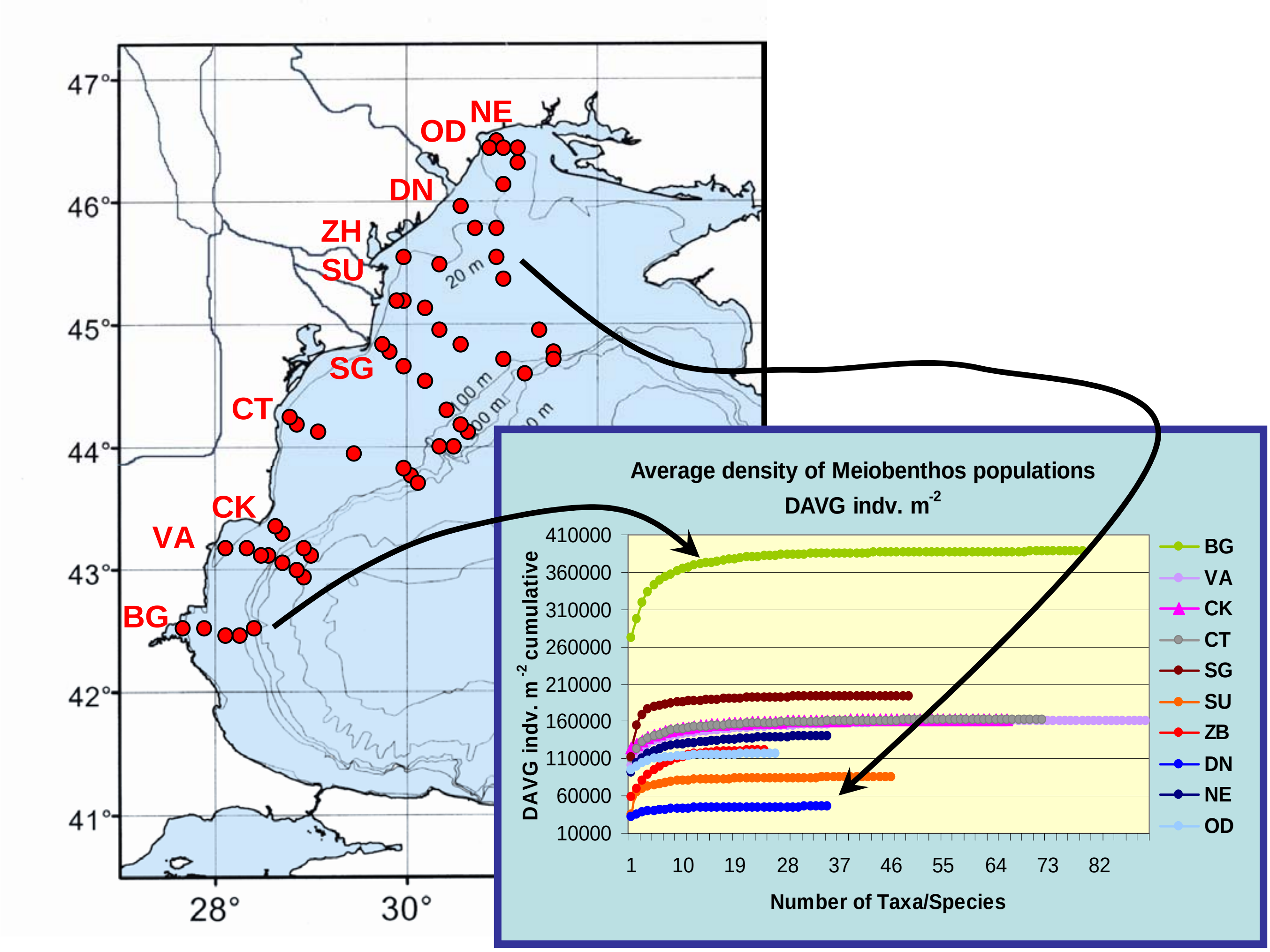


Figure B.19 Meiobenthos biodiversity, Autumn 2003 (Mee *et al* 2005)



B.6.2 Evidence for recovery of mussel beds on the North-Western Shelf of the Black Sea (Mee 2005)

Background

The mussel *Mytilus galloprovincialis* is widespread in the Black Sea. Benthic settlements of this species occur on silt, sand and all types of hard substrates. Numerous settlements of this mollusk are suitable substratum for various invertebrate species. This commercial mollusk is also an important subject of marine aquaculture in the Black Sea. The mussels are organisms which active filtrate waters and very quickly react to changes in the environmental conditions. Therefore some characteristics of mussel settlements may be regarded as sensible indexes of marine water quality. On the basis of analysis of the mussel population state negative influences of environmental changes can be revealed at early stages.

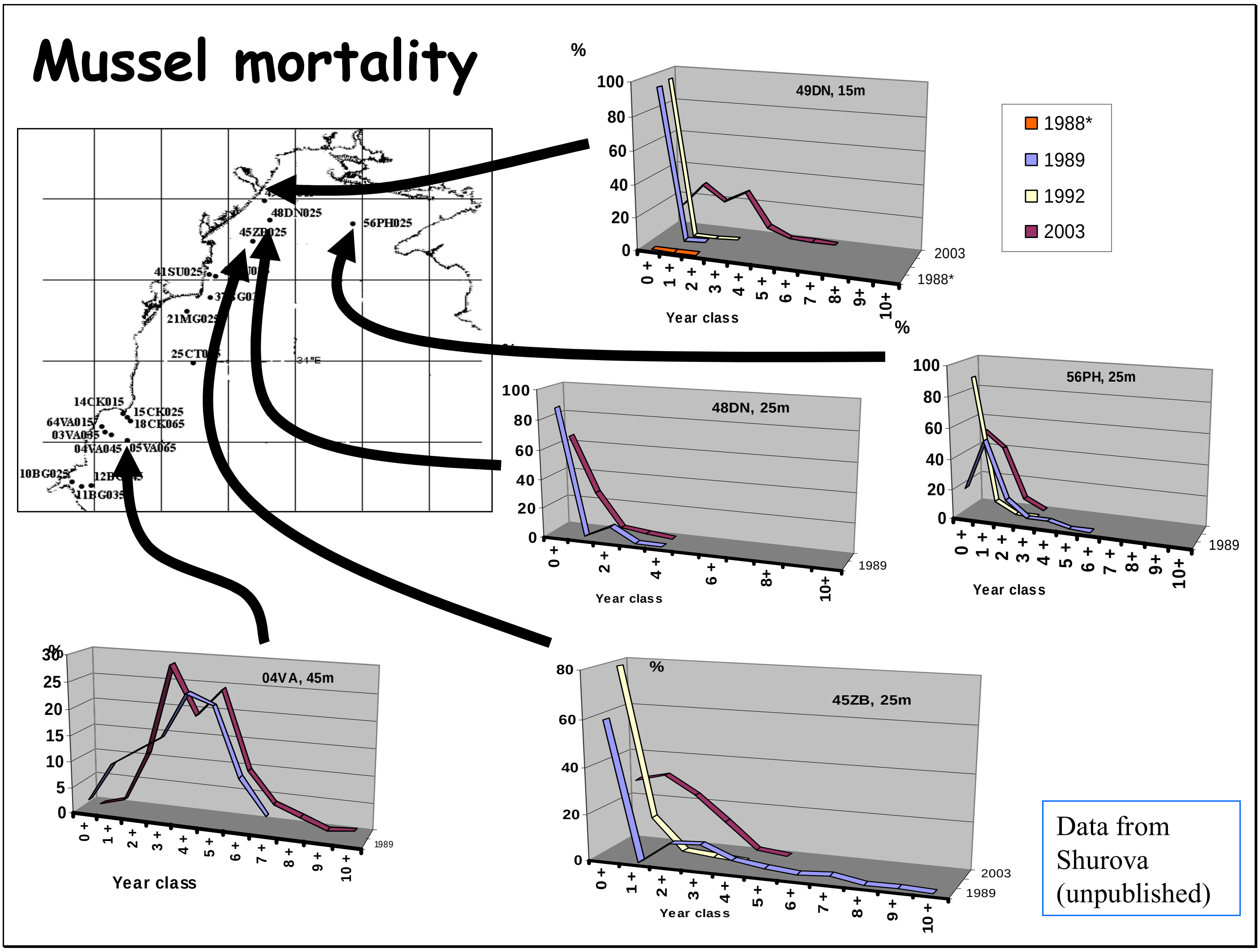
During the early 1960s mussels formed numerous, dense, extended settlements on the North-Western Shelf of the Black Sea. From 1970 to 1984 decrease of the mussel biomass and changes in the size structure of this mollusc occurred in the Romanian shelf (Gomoiu, 1984). In 1970–1990 anoxia, which served as the reason for mass death of bottom invertebrates including mussels, was observed practically annually in Ukrainian shelf of the Black Sea. This phenomenon has negatively affected on structure of the mussel settlements. Higher mortality of the larger mollusks in during prolonged anoxia is a cause for constant rejuvenation of the mussel settlements (Shurova 2000). From 1984 to 1992 the average age of mussels from Ukrainian shelf of the Black Sea decreased over two-fold, from 28 to 10 years. A decrease in the amount of molluscs of older age groups, whose fecundity is markedly higher than that of younger mussels, was a reason for lowering the reproduction coefficient in the mussel populations. When compared with 1985 results, this parameter was reduced more than ten-fold. The relationship between the size (surface area) of hypoxic zones, the mean age of mussels and their reproduction coefficient was negative (Shurova and Studnichenko, 2003). In 1993–2003 population parameters of Black Sea mussels were not analyzed.

The status of mussel settlements on the North-Western Shelf of the Black Sea

An extensive survey conducted in summer 2003 has provided a unique picture of animal communities in the Black Sea. The research team was able to repeat earlier surveys of mussel beds carried out during the worst periods of eutrophication. Mussel shells have ‘growth rings’ that enable their age to be calculated, in a similar manner to the rings on trees. This allows the age distribution of individuals at various stations on the NW shelf (Sinegub, 2004). Fig. B.20 shows the age distribution at stations that were surveyed in 1989, 1990 and 1992. The vertical axis shows the percentage of any particular ‘age class’ in the total population. The horizontal axis shows the age class (e.g. 2+ means mussels between two and three years old).

Stations in the far south of the region had a wide range of age classes in all surveys; these were not seriously affected by hypoxia. Those in the north of the region previously showed only very low age classes (0-1 years old). Most of the mussels that settled there were killed by hypoxia the previous summers. Now this range has been extended as the events are less frequent. This can be interpreted as a clear sign of slowly starting recovery of the benthic ecosystems on the North-Western Shelf of the Black Sea.

Figure B.20 **Evidence of recovery of mussel beds on the North-Western Shelf of the Black Sea** (Mee 2005)



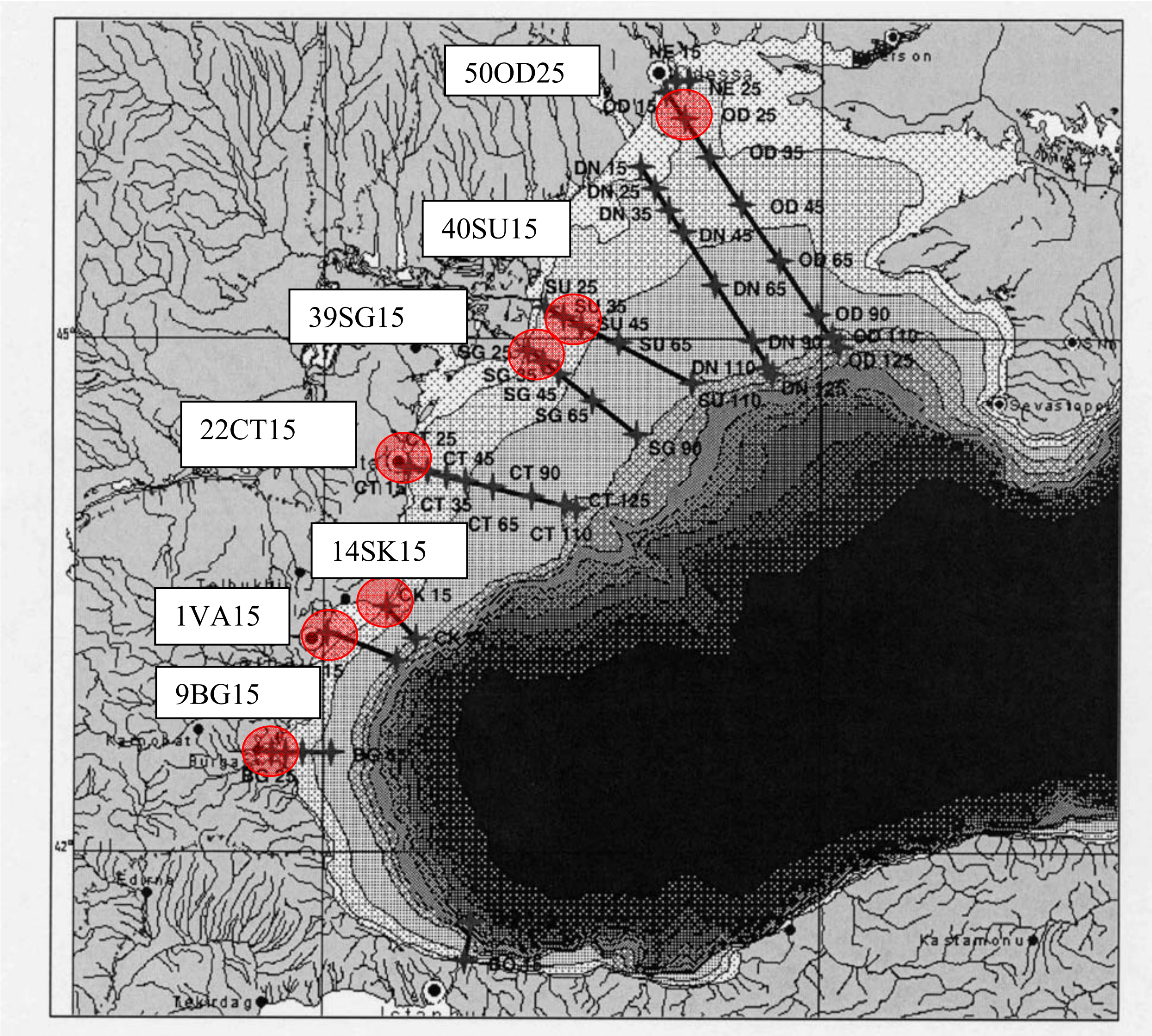
B.7 Pollutants in sediments

B.7.1 Overview of data used

A special activity was included in the research programme of the benthic BSERP cruise (Oct 2003) on request of the BSC/PS - to screen for pollutants on the North-Western Shelf of the Black Sea. The sediment cores analysed were selected from 7 locations out of the 55 stations which were sampled (Fig. B.21). The cores were sliced to produce 0-1, 1-2, 2-4, 4-6, 9-11, 14-16, 19-21, 24-26, 29-31, 34-36, 39-41, and 44-46 centimeter layers. In this report only the data for the surface layer (0-1 cm) of sediments are presented, with the exception of Fig. B23.

Seven sediment cores were collected and analysed of chlorinated pesticides and PCBs. Six of these cores (not 39SG15) were also analysed for heavy metals. All analyses were undertaken by the Marine Environmental Studies Laboratory of the International Atomic and Energy Agency (IAEA). A detailed description of the methodologies/analytical procedures and results is presented in de Mora (2004).

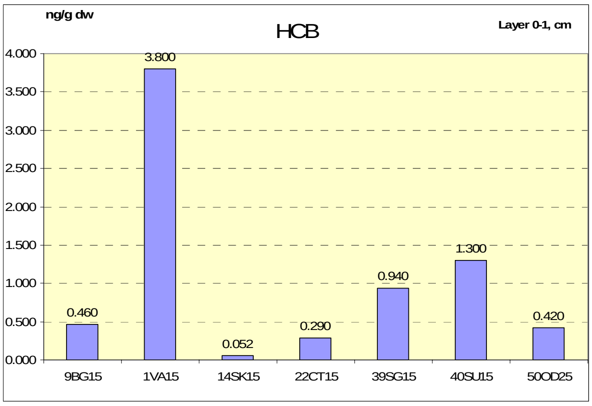
Figure B.21 Sediment pollutant screening locations on the North-Western Shelf of the Black Sea

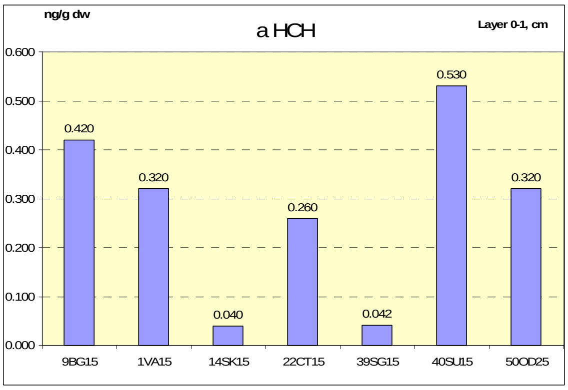


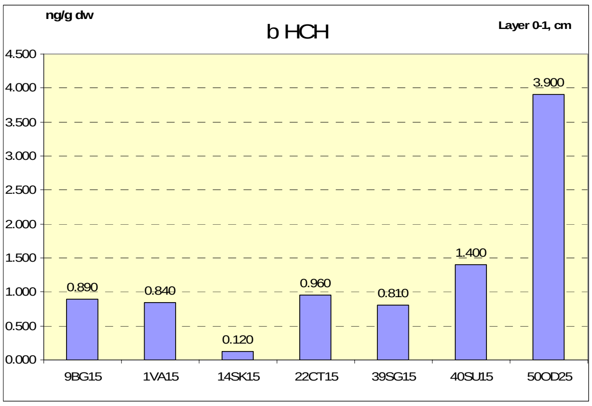
B.7.2 Chlorinated pesticides

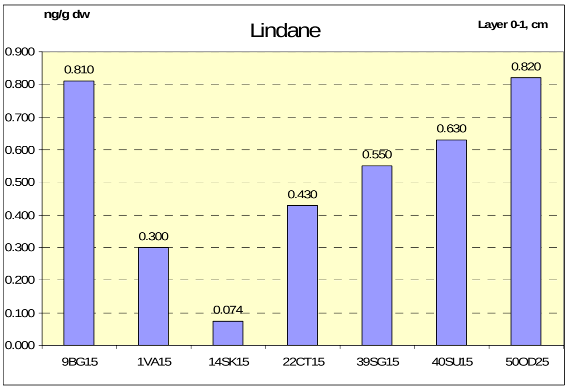
The seven surface sediment sample were analysed for the following pesticides: HCB, α HCH, β HCH, , Lindane, δ HCH, pp'DDE, pp'DDD, pp'DDT, DDMU, op DDE, op DDD, op DDT, cis chlordane, trans chlordane, trans nonachlor, heptachlor, aldrin, dieldrin, endrin, α endosulfan, β endosulfan and endosulfan sulfate. Chlorinated pesticide concentration profiles from south to north (left to right - Bulgarian-Romanian-Ukrainian coastal sediments; see Fig. B.21) are shown in Fig. B.22.

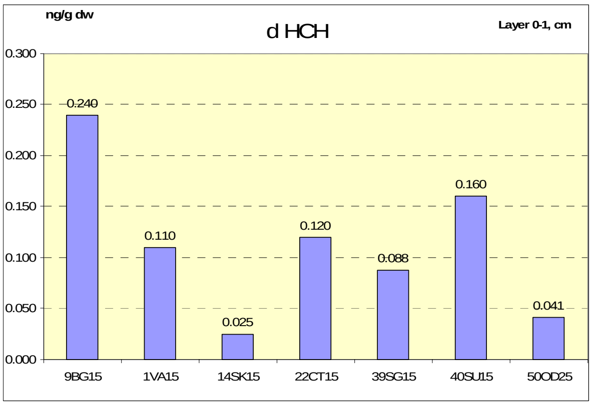
Figure B.22 Chlorinated pesticide concentrations in surface sediment of the North-Western Shelf of the Black Sea, October 2003

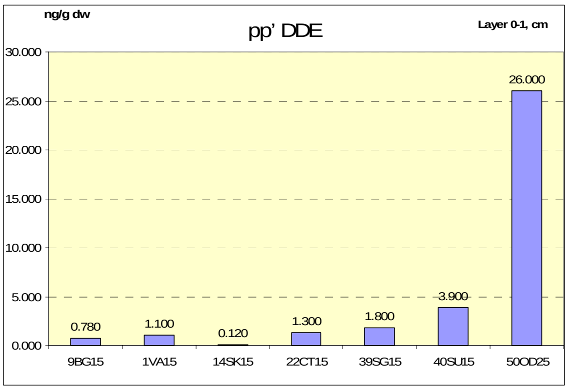


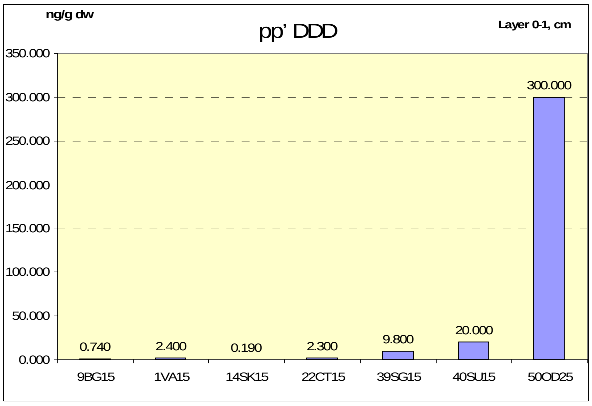












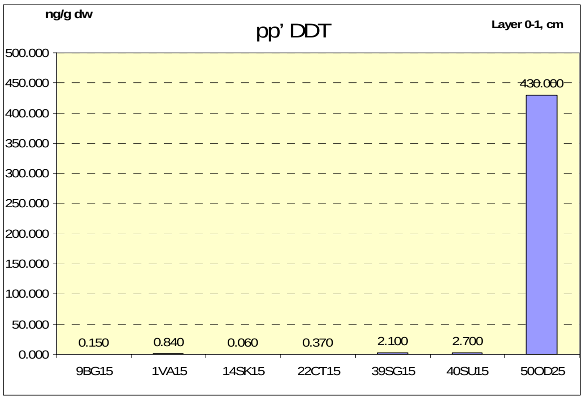
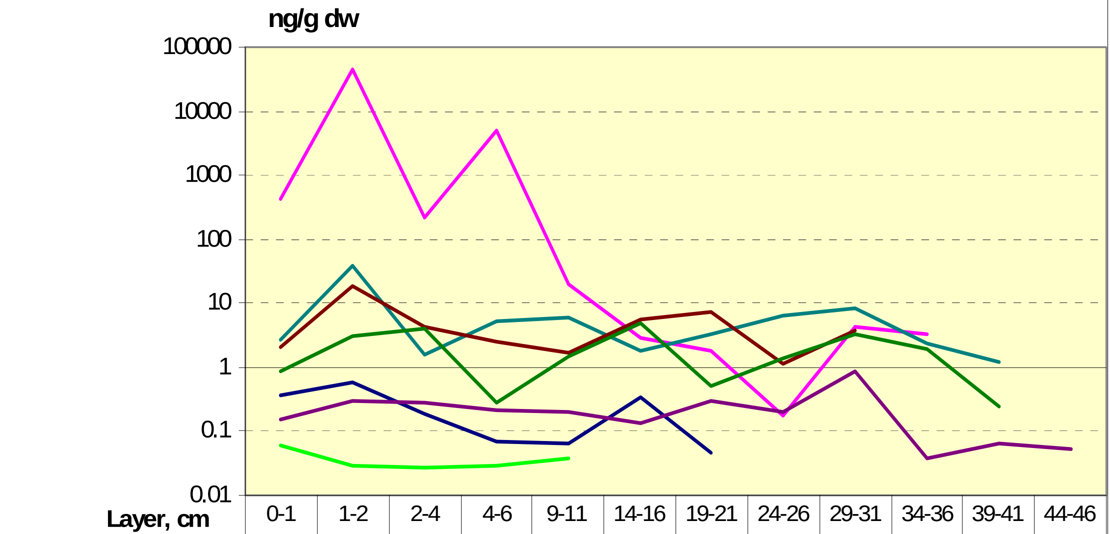


Figure B.22 Chlorinated pesticide concentrations in surface sediment of the North-Western Shelf of the Black Sea, October 2003 (cont'd)

Figure B.22 Chlorinated pesticide concentrations in surface sediment of the North-Western Shelf of the Black Sea, October 2003 (cont‘d)

As shown in Fig. B.22, above, heptachlor was only found at concentrations above the limit of detection at Bulgarian site 1VA15. Massive DDT (and its derivatives) contamination was recorded in surface sediment at Ukrainian site 50OD25 (see Figure B.23).

Figure B.23 pp’DDT concentrations (depth profile) in sediment cores collected from site 50OD25 station (Ukraine)



Layer, cm	0-1	1-2	2-4	4-6	9-11	14-16	19-21	24-26	29-31	34-36	39-41	44-46
50OD25 UA pp’ DDT	430	45200	223	5090	20	2.9	1.8	0.17	4.3	3.2		
40SU15 RO pp’ DDT	2.7	38	1.6	5.3	5.8	1.8	3.2	6.2	8.1	2.4	1.2	
39SG15 RO pp’ DDT	2.1	19	4.4	2.5	1.7	5.7	7.1	1.1	3.8			
22CT15 RO pp’ DDT	0.370	0.580	0.190	0.067	0.066	0.350	0.046					
14CK15 BG pp’ DDT	0.06	0.03	0.027	0.029	0.039							
1VA15 BG pp’ DDT	0.84	3	3.9	0.28	1.5	5	0.51	1.4	3.2	1.9	0.25	
9BG15 BG pp’ DDT	0.15	0.3	0.28	0.21	0.2	0.13	0.3	0.2	0.86	0.038	0.064	0.052

For a number of pesticides (dieldrin, lindane, opp DDD, opp DDT, pp’DDD, pp’DDT, DDMU, op’DDE, pp’DDE and β HCHa) the highest concentrations were found at Ukrainian station 50OD25. Then the level of pollution decreased in a southerly direction from station to station. For two of these contaminants (dieldrin and op’DDE), however, there was an increase of pollution again at one of the Bulgarian locations (1VA15 or 9BG15).

For three pesticides (cis- and trans-chlordane and *a*-HCH), maximum levels were associated with the Sulina branch of the Danube, although for *a*-HCH, comparable levels were detected at a number of other sites.

Concentrations of other pesticides were low at all stations on the North-Western Shelf of the Black Sea, except at one or both Bulgarian stations. Elevated levels of HCB, δ HCH, lindane, heptachlor, aldrin and endosulfan pesticides were detected at Bulgarian sites.

Endrin was not recorded at concentrations greater than limit of detection at any site.

Reported differences in the levels of pesticide contamination at individual sites reflect both current and historical levels of pesticide usage, as well as differences in crops grown/pesticides used in different areas of land surrounding the North-Western Shelf. The level of DDT contamination at site 50OD25 is so great that it is considered much more likely to reflect illegal discharges/dumping than land run-off.

B.7.3 PCBs

The seven surface sediment samples were analysed for the following 22 PCB congeners: aroclor 1254, aroclor 1260, PCB 44, PCB 49, PCB 52, PCB 87, PCB 101, PCB 105, PCB 110, PCB 118, PCB 128, PCB 138, PCB 149, PCB 153, PCB 170, PCB 174, PCB 177, PCB 180, PCB 183, PCB 187, PCB 194, PCB 201. Concentration profiles from south to north (left to right - Bulgarian-Romanian-Ukrainian sediments; see Fig. B21) are shown in Fig. B.24.

Figure B.24 Concentrations of PCBs in surface sediment of the North-Western Shelf of the Black Sea, October 2003 (Ukraine-Romania-Bulgaria)

Figure B.24 Concentrations of PCBs in surface sediment of the North-Western Shelf of the Black Sea, October 2003 (cont'd)

Figure B.24 Concentrations of PCBs in surface sediment of the North-Western Shelf of the Black Sea, October 2003 (cont'd)

PCB concentrations were highest at more northerly sites in the North-Western Shelf. For 12 PCBs (aroclor 1254, PCBs 44, 49, 52, 87, 101, 105, 110, 118, 128, 138 and 201) maximum concentrations were recorded at Ukrainian station 50OD25' while maximum concentrations of a further 10 PCBs (aroclor 1260, PCBs 149, 153, 170, 174, 177, 180, 183, 187 and 194) were recorded at station 40SU15. Results from the Ukrainian site would have reflected inputs from land run-off, as well as inputs from the Dneister and Dnipro rivers. However, concentrations of the latter group of PCB congeners most obviously reflect inputs via the Sulina Branch of the Danube Delta.

Sediment concentrations of all PCB except one (PCB 201) were lowest at the northernmost Bulgarian site (14SK15), but for most PCBs greater contamination was detected in southerly Bulgarian sediments

B.7.4 Heavy metals

Six surface sediment samples were analysed for nine metals: Cd (µg/g), Pb (µg/g), Co (µg/g), Ni (µg/g), Cu (µg/g), Zn (µg/g), Al (mg/g), As (µg/g), Hg (µg/g). Concentration profiles from south to north (left to right - Bulgarian -Romanian-Ukrainian coastal sediments; see Fig. B.21) are shown in Fig. B.25.

Figure B.25 Concentrations of heavy metals in surface sediment of the North-Western Shelf of the Black Sea, October 2003

Figure B.25 Concentrations of heavy metals in surface sediment of the North-Western Shelf of the Black Sea, October 2003 (cont'd)

For eight of the nine metals (not cobalt), highest concentrations were recoded at Station 40SU15 and so are associated with inputs from the Sulina Branch of the Danube Delta. Elevated levels of contamination of some metals (cobalt, nickel copper and aluminium) was also noted in samples from off the coast of southern Bulgaria, and the Ukrainian sampling site also had elevated levels of arsenic. However, as stated for organic contaminants, the latter results are also likely to reflect greater influence of inputs from the Dnipro and Dneister rivers.

APPENDIX C - DESCRIPTIVE STATISTICS FOR NUTRIENT AND DISSOLVED OXYGEN CONCENTRATIONS IN NORTH-WESTERN SHELF WATERS, 1990-2003

Table C.1 Descriptive statistics for Ukrainian marine waters (1990/1995-2000/2003) (Area 1)

	N	Minimum, μM/l	Maximum, μM/l	Mean, μM/l	Std. Deviation, μM/l
DOW	29	194.808	385.413	313.508	53.320
NH_4	29	0.024	14.643	2.893	3.269
NO_2	57	0.017	1.471	0.272	0.271
NO_3	35	0.038	27.852	2.454	5.541
PO_4	64	0.025	4.205	0.356	0.584
SI	69	0.600	98.894	12.022	13.634

Table C.2 Descriptive statistics for Romanian marine waters (1990/1995-2000/2003) (Area 2)

	N	Minimum, μM/l	Maximum, μM/l	Mean, μM/l	Std. Deviation, μM/l
DOW	94	120.933	476.100	326.740	
NH_4	112	0.057	21.230	4.350	
NO_2	142	0.020	1.980	0.732	
NO_3	141	0.910	27.600	5.777	
PO_4	138	0.030	21.220	1.192	
SI	142	1.000	58.500	11.686	

Table C.3 Descriptive statistics for Bulgarian marine waters (1990/1995-2000/2003) (Area 3)

	N	Minimum, μM/l	Maximum, μM/l	Mean, μM/l	Std. Deviation, μM/l
DOW	74	237.250	491.918	332.590	49.108
NH_4	109	0.043	52.000	5.505	8.429
NO_2	157	0.029	14.786	1.108	1.700
NO_3	79	1.546	50.000	8.446	8.120
PO_4	160	0.032	20.363	1.153	2.150
SI	75	0.375	25.200	7.317	5.244

Table C.4 Descriptive statistics for Danube River site L1330 (1990/1995-2000/2003)

	N	Minimum, μM/l	Maximum, μM/l	Mean, μM/l	Std. Deviation, μM/l
NH_4	70	1.429	18.339	7.848	5.510
NO_3	81	67.500	169.500	108.258	17.928

Table C.5 Descriptive statistics for site L1390 (1990/1995-2000/2003)

	N	Minimum, µM/l	Maximum, µM/l	Mean, µM/l	Std. Deviation, µM/l
NH_4	71	1.429	16.116	6.096	4.080
NO_3	81	48.786	146.900	79.429	22.201

Table C.6 Descriptive statistics for site L1290 (1990/1995-2000/2003)

	N	Minimum, µM/l	Maximum, µM/l	Mean, µM/l	Std. Deviation, µM/l
NH_4	53	0.714	17.143	5.582	3.881
NO_3	59	35.714	228.571	89.479	41.894

Table C.7 Descriptive statistics for site L0430 (1990/1995-2000/2003)

	N	Minimum, µM/l	Maximum, µM/l	Mean, µM/l	Std. Deviation, µM/l
NH_4	67	2.857	99.524	24.639	16.557
NO_3	68	26.190	232.381	114.479	44.715

APPENDIX D - RESULTS OF ROSNER'S TEST FOR OUTLIERS

Area/Site	Determinand	Date	Value, µM/l
Ukraine	Ammonium	26-6-1991	14.643
Ukraine	Ammonium	16-12-2000	10.204
Ukraine	Nitrite	14-5-1994	1.122
Ukraine	Nitrite	9-7-1997	1.471
Ukraine	Nitrite	1-8-2001	1.093
Ukraine	Nitrite	23-9-2003	1.214
Ukraine	Nitrite	29-9-2003	1.179
Ukraine	Nitrite	24-12-2003	1.357
Ukraine	Nitrate	14-5-1994	27.852
Ukraine	Nitrate	22-5-1999	19.211
Ukraine	Nitrate	23-9-2003	28.571
Ukraine	Orthophosphate	23-8-1991	4.205
Ukraine	Orthophosphate	14-5-1994	2.306
Ukraine	Orthophosphate	10-9-1999	2.097
Ukraine	Orthophosphate	23-9-2003	2.903
Ukraine	Orthophosphate	4-11-2003	16.613
Ukraine	Si	14-5-1994	98.894
Romania	Ammonium	21-3-1995	21.23
Romania	Nitrate	29-3-1993	20.6
Romania	Nitrate	13-3-1995	22.51
Romania	Nitrate	15-3-1995	26
Romania	Nitrate	16-3-1995	27.6
Romania	Nitrate	17-3-1995	23.34
Romania	Orthophosphate	26-3-1993	9.12
Romania	Orthophosphate	20-4-1994	21.22
Romania	Orthophosphate	21-4-1994	6.08
Romania	Orthophosphate	4-5-1994	9.83
Romania	Orthophosphate	5-5-1994	4.54
Romania	Orthophosphate	23-3-1995	7.58
Romania	Orthophosphate	24-3-1995	14.62
Bulgaria	Ammonium	1-10-1997	27.857
Bulgaria	Ammonium	2-9-1999	37.071
Bulgaria	Ammonium	2-2-2000	52
Bulgaria	Ammonium	4-9-2000	43.714
Bulgaria	Ammonium	5-9-2000	31.857
Bulgaria	Nitrite	9-9-1992	4.784
Bulgaria	Nitrite	25-4-1994	4.19
Bulgaria	Nitrite	3-5-1994	8.29
Bulgaria	Nitrite	1-6-1998	9.357
Bulgaria	Nitrite	10-5-2000	14.786
Bulgaria	Nitrite	9-11-2000	4.179
Bulgaria	Nitrite	14-11-2002	5.414
Bulgaria	Nitrate	7-8-2001	50
Bulgaria	Nitrate	27-9-2001	35.714

Area/Site	Determinand	Date	Value, µM/l
Bulgaria	Orthophosphate	1-4-1993	4.97
Bulgaria	Orthophosphate	4-7-1997	9.194
Bulgaria	Orthophosphate	3-6-1999	6.29
Bulgaria	Orthophosphate	10-10-2003	20.363
Bulgaria	Orthophosphate	10-11-2003	11.091
Bulgaria	Orthophosphate	10-12-2003	6.58
L1390	BOD_5	4-12-1997	9.60
L1390	Nitrate	4-12-1997	146.9
L1290	Nitrate	8-4-1996	228.571
L0430	Ammonium	19-1-1998	99.524

APPENDIX E - RESULTS OF TESTS FOR SEASONALITY OF NUTRIENTS AND DISSOLVED OXYGEN

Location	Variable	Datatype[3]	Probability of absence of seasonality in dataset[4]	
			Kruskal-Wallis test	One-factor Anova
Ukraine	DOW	RD	0.00016	0
		SAD	0.04126	0.02095
		MDD	1	0.93873
		SDD	0.04126	0.01585
	Orthophosphate	RD	0.00224	0.00864
		SAD	0.0581	0.12511
		MDD	1	0.33417
		SDD	0.0282	0.16713
Romania	DOW	RD	0	0
		SAD	0.00618	0.00041
		MDD	1	0.99175
		SDD	0.00615	0.00088
	Ammonium	RD	0.01172	0.09514
		SAD	1	0.79143
		MDD	1	0.96155
		SDD	1	0.64345
	Nitrite	RD	0	0
		SAD	0.0286	0.0278
		MDD	1	0.74357
		SDD	0.00579	0.00727
	Nitrate	RD	0.00003	0.00012
		SAD	0.00968	0.01797
		MDD	1	0.98246
		SDD	0.00111	0.0027
	Si	RD	0.02591	0.03079
		SAD	1	0.68494
		MDD	1	0.96485
		SDD	1	0.5126
Bulgaria	DOW	RD	0.03585	0.03514
		SAD	0.02979	0.06332
		MDD	1	0.98235
		SDD	0.05597	0.06448
	Ammonium	RD	0.07406	0.12547
		SAD	1	0.5459
		MDD	1	0.54694
		SDD	1	0.56432

[3] Raw Data (RD), Seasonal Aggregated Data (SAD), Median Deseasonalised Data (MDD), Seasonal Sen Slope Detrended Data (SDD). A detailed description of different types of data for the statistical analysis is presented by Blind (1998).
[4] If the probability is close/equal to zero, cycles (of any types) are present in the dataset. If the probability is close to 1, there is no seasonality in the dataset.

Location	Variable	Datatype	Probability of Absence of Seasonality in Dataset	
			Kruskal-Wallis test	One-factor Anova
Bulgaria	Nitrite	RD	0.00007	0.005
		SAD	1	0.79512
		MDD	1	0.90562
		SDD	1	0.80069
	Orthophosphate	RD	0.00039	0.00107
		SAD	0.02648	0.10524
		MDD	1	0.88448
		SDD	0.01351	0.13931
	Si	RD	0.03662	0.07005
		SAD	1	0.16444
		MDD	1	0.97368
		SDD	1	0.11392
Danube: L1330	BOD_5	RD	0.00468	0.00312
		SAD	1	0.36861
		MDD	1	0.51077
		SDD	1	0.35071
	Nitrate	RD	0.00002	0.00006
		SAD	0.10046	0.14959
		MDD	1	0.82746
		SDD	0.10228	0.12918
Danube: L1390	BOD_5	RD	0	0
		SAD	0.00196	0.00004
		MDD	1	0.35124
		SDD	0.00188	0.00003
	Ammonium	RD	1	0.35111
		SAD	1	0.88433
		MDD	1	0.9392
		SDD	0.16603	0.13769
	Nitrate	RD	0	0
		SAD	0.00253	0
		MDD	1	0.8999
		SDD	0.00081	0
	BOD_5	RD	0.08009	0.09431
		SAD	0.16367	0.13428
		MDD	1	0.26646
		SDD	1	0.11888

Location	Variable	Datatype	Probability of Absence of Seasonality in Dataset	
			Kruskal-Wallis test	One-factor Anova
Danube: L1290	BOD_5	RD	0.08009	0.09431
		SAD	0.16367	0.13428
		MDD	1	0.26646
		SDD	1	0.11888
	Nitrate	RD	0.00003	0.00001
		SAD	0.03293	0.03775
		MDD	1	0.89684
		SDD	0.04405	0.00974
Danube: L0430	Ammonium	RD	0.03328	0.04301
		SAD	0.09793	0.14632
		MDD	1	0.83846
		SDD	0.11078	0.14194
	Nitrate	RD	0.00002	0.00001
		SAD	0.03725	0.01379
		MDD	1	0.61749
		SDD	0.0227	0.01099

APPENDIX F – PROPOSED BSIMAP MONITORING SITES, 2005

No	Waterbody type	Station name	Longitude	Latitude
Bulgaria				
1	?	Shabla	28.62833	43.53800
2	?	Varna	27.94117	43.20500
3	?	Obzor	27.90833	42.81850
4	?	Burgas	27.47517	42.47367
5	?	Ahtopol	27.95583	42.09317
Georgia				
6	Coastal Water	Batumi	41.51333	41.51333
7	Transitional Water	Kulevi	42.17667	41.51000
8	Coastal Water	Poti	42.16667	41.67000
9	Coastal Water	Supsa	42.00167	41.67833
10	Coastal Water	Kobuletti	41.78333	41.83333
Romania				
11	Transitional Water	Sulina, discharging point	29.77167	45.14667
12	Transitional Water	Mila 9, 5 m isobate	29.65000	45.01667
13	Transitional Water	Mila 9, 20 m isobate	28.90000	44.16667
14	Transitional Water	Sf. Gheorghe, 5 m isobate	29.63333	44.88333
15	Transitional Water	Sf. Gheorghe, 20 m isobate	29.67833	44.16667
16	Transitional Water	Portita, 5 m isobate	28.78333	44.16667
17	Transitional Water	Portita, 20 m isobate	29.37500	44.67667
18	Transitional Water	Buhaz , 5 m isobate	28.76000	44.40000
19	Transitional Water	Buhaz, 20 m isobate	28.84333	44.40000
20	Coastal Water	Mamaia, beach	28.58333	44.23333
21	Coastal Water	Mamaia, 5 m isobate	28.61667	44.23333
22	Coastal Water	Mamaia, 20 m isobate	28.70000	44.23333
23	Coastal Water	Constanta N, 5 m isobate	28.67833	44.21333
24	Coastal Water	Constanta N, 20 m isobate	28.70333	44.21333
25	Coastal Water	Constanta S, 5 m isobate	28.64667	44.08333
26	Coastal Water	Constanta S, 20 m isobate	28.69333	44.03333
27	Coastal Water	Constanta E, 5 nautical miles	28.78333	44.16667
28	Coastal Water	Constanta E, 10 nautical miles	28.90000	44.16667
29	Coastal Water	Constanta E, 20 nautical miles	29.13333	44.16667
30	Coastal Water	Constanta E, 30 nautical miles	28.36667	44.16667
31	Coastal Water	Eforie Sud, beach	28.65667	44.03333
32	Coastal Water	Eforie S, 5 m isobate	28.66333	44.03333
33	Coastal Water	Eforie S, 20 m isobate	28.67833	44.03333
34	Coastal Water	Costinesti, beach	28.64167	43.95000
35	Coastal Water	Costinesti, 5 m isobate	28.64333	43.95000
36	Coastal Water	Costinesti, 20 m isobate	28.68667	43.95000
37	Coastal Water	Mangalia, beach	28.59000	43.81667
38	Coastal Water	Mangalia, 5 m isobate	28.59000	43.81667
39	Coastal Water	Mangalia, 20 m isobate	28.63333	43.81667
40	Coastal Water	Vama Veche, beach	28.64000	43.75000
41	Coastal Water	Vama Veche, 5 m isobate	28.62667	43.75000
42	Coastal Water	Vama Veche, 20 m isobate	28.61667	43.75000

No	Waterbody type	Station name		Longitude	Latitude
Russian Federation					
43	Coastal Water	Anapa		44.90333	44.90333
44	Coastal Water	Novorossiysk		37.85167	44.66667
45	Coastal Water	Gelendzik		38.04667	44.56000
46	Coastal Water	Tuapse		39.07000	44.08667
47	Coastal Water	Sochi		43.58333	39.71667
Turkey					
48	Coastal Water	KO		29.13333	41.22500
49	Coastal Water	K1		29.13333	41.33333
50	Coastal Water	K3		29.21000	41.25167
51	?	TRK1	Igneada and Danube Water, Reference	41° 87.03	28° 05.86
52	?	TRK2		41° 86.42	28°11.41
53	?	TRK3		41°82.57	28°60.54
54	Coastal Water	TRK4	West Black Sea, Reference	41° 36.84	28° 62.49
55	Coastal Water	TRK5		41° 38.90	28° 64.67
56	Coastal Water	TRK6		41° 58.05	28° 84.70
57	Coastal Water	TRK7	Sile, Reference	41° 11.56	29° 35.57
58	Coastal Water	TRK8		41° 14.24	29° 36.21
59	Coastal Water	TRK9		41° 20.55	29° 38.83
60	?	TRK10	Sakarya River, Reference	41° 08.68	30° 37.76
61	?	TRK11		41° 10.06	30° 38.47
62	?	TRK12		41° 10.65	30° 38.66
63	Coastal Water	TRK13	Zonguldak, Reference	41° 27.59	31° 46.38
64	Coastal Water	TRK14		41° 28.09	31° 46.54
65	Coastal Water	TRK15		41° 30.14	31° 46.33
66	Coastal Water	TRK16	Bartın, Reference	41° 35.23	32° 02.60
67	Coastal Water	TRK17		41° 35.55	32° 02.88
68	Coastal Water	TRK18		41° 36.37	32° 02.21
69	Coastal Water	TRK19	Cide , Reference	41° 41.40	32° 13.19
70	Coastal Water	TRK20		41° 41.55	32° 13.11
71	Coastal Water	TRK21		41° 41.83	32° 13.13
72	Coastal Water	TRK22	Inebolu, Reference	41° 59.24	33° 47.17
73	Coastal Water	TRK23		41° 59.90	33° 47.12
74	Coastal Water	TRK24		42° 04.96	33° 47.19
75	Coastal Water	TRK25	Sinop 2, Reference	42° 03.85	34° 55.08
76	Coastal Water	TRK26		42° 04.92	34° 54.27
77	Coastal Water	TRK27		42° 08.34	34° 51.88
78	Coastal Water	TRK28	Sinop 1, Reference	42° 01.84	35° 09.33
79	Coastal Water	TRK29		42° 00.34	35° 09.94
80	Coastal Water	TRK30		41° 59.84	35° 18.89
81	Coastal Water	TRK31	Kızılırmak, Reference	41° 44.79	35° 57.54
82	Coastal Water	TRK32		41° 44.58	35° 57.40
83	Coastal Water	TRK33		41° 45.19	35° 56.76
84	Coastal Water	TRK35	Samsun, Reference	41° 18.09	36° 920.79
85	Coastal Water	TRK36		41° 20.80	36° 23.31
86	Coastal Water	37		41° 22.59	36° 24.73

No	Waterbody type	Station name		Longitude	Latitude
87	Coastal Water	TRK37	Yesilırmak, Reference	41 º 23.61	36 º 39.34
88	Coastal Water	TRK38		41 º 24.35	36 º 39.21
89	Coastal Water	TRK39		41 º 25.21	36 º 39.16
90	Coastal Water	TRK40	Fatsa, Reference	41 º 02.14	37 º 30.13
91	Coastal Water	TRK41		41 º 04.02	37 º 31.50
92	Coastal Water	TRK42		41 º 04.06	37 º 31.68
93	Coastal Water	TRK43	Ordu, Reference	40 º 59.75	37 º 53.04
94	Coastal Water	TRK44		41 º 01.20	37 º 54.50
95	Coastal Water	TRK45		41 º 04.22	37 º 59.98
96	Coastal Water	TRK46	Giresun, Reference	40 º 55.37	38 º 24.11
97	Coastal Water	TRK47		40 º 56.00	38 º 24.70
98	Coastal Water	TRK48		40 º 56.65	38 º 24.67
99	Coastal Water	TRK49	Akcaabat, Reference	41 º 05.16	39 º 22.22
100	Coastal Water	TRK50		41 º 05.33	39 º 22.05
101	Coastal Water	TRK51		41 º 05.83	39 º 21.67
102	Coastal Water	TRK52	Trabzon, Reference	41 º 00.39	39 º 44.52
103	Coastal Water	TRK53		41 º 00.93	39 º 44.04
104	Coastal Water	TRK54		41 º 01.85	39 º 43.52
105	Coastal Water	TRK55	Rize, Reference	41 º 02.05	40 º 32.16
106	Coastal Water	TRK56		41 º 02.78	40 º 32.12
107	Coastal Water	TRK57		41 º 03.42	40 º 31.96
108	Coastal Water	TRK58	Pazar, Reference	41 º 11.62	40 º 54.22
109	Coastal Water	TRK59		41 º 12.08	40 º 54.19
110	Coastal Water	TRK60		41 º 12.64	40 º 54.31
111	Coastal Water	TRK61	Pazar, Reference	41 º 25.39	41 º 25.77
112	Coastal Water	TRK62		41 º 25.43	41 º 25.28
113	Coastal Water	TRK63		41 º 26.10	41 º 24.17
Ukraine					
114	Coastal Water	WWTP Evpatoriya		33.43333	45.15833
115	Marine Water	Karkinitski bay		32.00000	45.66667
116	Marine Water	Tendra		31.83333	45.16000
117	Coastal Water	Odessa bay		30.77000	46.49500
118	Marine Water	Phyllophora field		31.00000	45.16667
119	Coastal Water	WWTP "Pivnichni"		30.80000	46.55000
120	Marine Water	WWTP Port "Uzhnyi"		31.10000	46.56667
121	Marine Water	Dnipro and South Bug Mouth		31.00000	45.53333
122	Marine Water	WWTP Kerch		36.50167	45.26667
123	Coastal Water	WWTP Sevastopol		33.40000	44.66667
124	Transitional Water	Dnister River Mouth		30.70000	46.00000
125	Marine Water	WWTP Port Illichivsk		30.75000	46.26667
126	Coastal Water	WWTP Pivdenni		30.76667	46.36667
127	Coastal Water	Port Odesa		30.76667	46.55000
128	Transitional Water	Danube River mouth		30.25000	45.16667
129	Transitional Water	Danube River mouth		29.85000	45.18333

APPENDIX G – DRAFT QUALITY ASSURANCE MISSION REPORT AND RECOMMENDATIONS

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G.1 Introduction

This report is based on the visits of Dr. Stephen de Mora (IAEA-MESL) and Dr. Oksana Tarasova (Black Sea Commission) to Turkey, Romania, Bulgaria, Ukraine and the Russian Federation during November (8-12 & 25-29), 2002. Laboratories are described below in chronological sequence of being visited.

The prime purpose of visits was to appraise the current state of infrastructure, equipment and staff for measuring nutrients, metals and organic contaminants in marine samples from the Black Sea. An overview of Quality Assurance and Quality Control (QA/QC) procedures was gained. On this basis, recommendations could be made regarding capacity building and training requirements. Secondly, discussions were held in each case with respect to previous and ongoing monitoring programmes, together with data reporting mechanisms. Necessarily, these consultations focused on the laboratory's own efforts in this regard, rather than on a national monitoring programme.

An important consideration is that the number of facilities visited varied from one country to another. Recommendations are made here on a country basis, as a means to present a balanced approach. It is apparent that the capacity building and training that can be provided to the region cannot be manifest at every laboratory. Also, the discussions on monitoring comprised a rather piecemeal approach that might lead to a false impression of the differing national efforts. Some countries rely on a single facility to undertake monitoring, whereas in other countries the effort is spread through several small laboratories often in different ministries. Regardless, it was apparent that no country in the region has yet formulated a national strategy for monitoring their Black Sea marine environment.

G.2 Turkey

G.2.1 Institute of Marine Sciences and Management, University of Istanbul, Istanbul

We visited the Institute of Marine Sciences and Management at the University of Istanbul on November 8. Dr. Erdogan Okus (marine biologist) was our host and we met other senior staff, namely Dr. Kasom Cemal Guven (marine organic chemist), Dr. Nuray Balkis (chemical oceanographer) and Dr. Oya Algan (marine geochemist).

This institute is a research centre rather than a monitoring centre. Staff members are clearly enthusiastic and competent. They have and have had several international collaborators, including the IAEA, and publish in the international scientific literature. Although the institute does not presently conduct monitoring, the staff could certainly perform the necessary work. They have previously undertaken sample collection and analysis on a project basis. Wider discussions revealed that there is not yet have in place a mechanism for reporting data neither to national authorities nor to the Black Sea Commission.

The institute has several laboratories, which are quite spacious and organised to separate sample work up from instrumental analysis. The institute is quite well equipped, but lacks some funds for running expenses. They have appropriate equipment for sample pre-treatment, including sieves, freeze-dryer, and Soxlet extraction glassware. The fume cupboard for acid digestions is suitable for use of perchloric acid. However, it is made of metal and is rusting badly, and should be covered with a suitable acid-resistant coating. The atomic absorption spectrometer is old and still functions, but will need replacing in the near future. They have a gas chromatograph with mass selective detector for organic contaminant analyses, but they do not analyse organochlorinated substances. The laboratory currently analyses nutrients and has recently purchased a Bran Luebbe Autoanalyser for this purpose. This is a two-channel system (*i.e.* for simultaneous determination of two nutrients) that would benefit from being upgraded to four channels. Other instruments in the institute include HPLC, fluorimeter, UV-visible spectrophotometer, FTIR spectrophotometer and metal-free Dionex ion chromatograph (but with no detector).

Other relevant facilities include a constant temperature room for cell cultures, a laboratory with microscopes for cell identification, plankton nets, Anderaa current meter, portable ADCP and diving equipment. They also operate a research vessel, but this was not visited.

The laboratory does not have adequate QA/QC procedures in hand (*i.e.* limited use of Reference Materials, no evidence of quality control charts or participation in Intercomparison Exercises).

G.2.2 Recommendations

- The laboratory requires from the Turkish Government a firm commitment and commensurate funding to implement a national monitoring programme in the Black Sea.
- The autoanalyser for nutrient analyses should be upgraded from a two- to a four-channel system.
- The institute requires training in good laboratory management practice, including the establishment of better Quality Control procedures.
- The institute needs an electron capture detector and suitable training for the analysis of organochlorinated pesticides.

G.3 Romania

G.3.1 National Institute for Marine Research and Development "Grigore Antipa", Constanta

We visited the National Institute for Marine Research and Development "Grigore Antipa" (NIMRD) in Constanta on November 10. Our host was Dr. Simeon Nicolaev, the General Director of NIMRD. Other staff members present during the tour and most discussions were Dr. Radu Mihnea (Senior Scientist), Ms. Adriana Cociaşu (nutrients), Ms. Andra Oros (metals), Ms. Victoria Pisscu (hydrocarbons) and Ms. Valentina Coatu.

This institute has a long history of monitoring dating back to 1972. Currently, NIMRD is the only competent authority in Romania for monitoring the marine environment. They also have a role in emergency response and have monitored two oil spills in recent years. They report results to the National Romanian Water Authority in the Ministry for Water and Environment Protection, but also have an active public outreach programme and provide weekly reports in the summertime on coastal water quality. They have some ongoing co-operation with NGOs. NIMRD expects to be the agency in Romania to implement marine monitoring aspects of the EU Water Framework Directive. They have had a monitoring network for some time along the length Romanian Black Sea coastline. Originally this network comprised 17 transects (now 13) from the coast with sampling sites at the beach, and 5 and 20 m depth contours, together with a reference site 30 nautical miles offshore (55 m water depth).

Although separate instrument rooms are available for nutrient, metal and organic contaminant determinations, the space for sample preparation is limited. The institute has been quite well equipped from external donors, but needs funds for running expenses. The laboratory lacks sieves, a high purity water system (*i.e.* Milli-Q) and a freeze dryer. The atomic absorption spectrometer is seven years old and still functions well. NIMRD has a gas chromatograph with mass selective detector and electron capture detector for organic contaminant analyses. The laboratory analyses nutrients by colorimetric procedures. They recently acquired a Bran Luebbe Autoanalyser for nutrient measurements. As above, this is a two-channel system that would benefit from being upgraded to four channels. However, it should be noted that staff has not received training on this instrument and so still use a manual analytical procedure for nutrient analyses. Other relevant instruments at NIMRD include a TOC analyser and an UV-visible spectrophotometer.

The use of QA/QC procedures throughout the laboratory is not consistent and needs to be improved. The staff is aware of this deficiency, particularly as the laboratory plans to become accredited by a national authority. They do use IAEA reference materials and participate in IAEA intercomparison exercises.

G.3.2 Recommendations

- The laboratory requires from the Romanian Government a firm commitment and commensurate funding to implement a national monitoring programme in the Black Sea.
- The autoanalyser for nutrient analyses should be upgraded from a two- to a four-channel system.
- The institute needs an ultrapure (*e.g.* Milli-Q) water system.
- The institute needs training in good laboratory management practice, including the establishment of better Quality Control procedures.
- NIMRD needs on-site training for setting up and using the recently acquired autoanalyser. Given that this is the same instrument that is used in the Institute of Marine Sciences and Management at the University of Istanbul, Dr. Erdogan Okus could be contracted to provide such training. This approach should also lead to interesting synergisms within the Black Sea Environment Programme.

G.4 Bulgaria

Dr. Svetoslav Cheshmedjiev, a monitoring expert from the Executive Environmental Agency, Ministry of the Environment, in Sofia, accompanied us on our visits to facilities in Bulgaria.

G.4.1 Regional Environmental Inspectorate of Varna, Varna

We visited the Regional Environmental Inspectorate of Varna (REIV) on November 11. We were welcomed to the laboratory complex by Mr. Hristo Pavlov, the Director, and given a comprehensive tour of the facilities by Dr. Darina Bangieva, the Chief of Laboratory.

The institutional framework for environmental monitoring is still evolving in Bulgaria. All monitoring currently comes under the mandate of the Regional Environmental Inspectorates. RIEV conducts routine monitoring of waters, soils and air. Marine sample collection is restricted to the coastal beach zone. They analyse only a few marine sediment samples and no biota at this time. Their region covers about half the Bulgarian Black Sea coast, the remainder being monitored by a sister REI laboratory in Burgas. The laboratories report data monthly to the Executive Environment Agency (EEA) of the Ministry of the Environment in Sofia. The EEA is responsible for data processing and database management. They produce a 3 monthly report and an annual report that includes a chapter on the Black Sea.

The REIV has spacious, clean and well-organised laboratories. They have a receiving room for samples and a wet laboratory dedicated to preparing sample bottles. One laboratory is used for the analysis of several standard water quality characteristics, including conductivity, pH, oxygen and various ions using ion-selective electrodes. Regarding facilities for sample preparation, soils and sediments are presently oven-dried and thus, the laboratory would benefit from having a freeze-dryer. They have a microwave digestion system for preparing samples for metal determinations. Gas cylinders in the laboratory are boxed and vented to comply with National Health and Safety Regulations.

They are well equipped for the analyses of nutrients, metals and organic contaminants. They have 2 atomic absorption spectrophotometers, one for flame and the other having a graphite furnace with Zeeman correction. They are also equipped for hydride generation work. They have a gas chromatograph with multiple detectors (electron capture, flame ionisation, nitrogen-phosphorus) suitable for the analysis of organochlorinated pesticides and PAHs. Although at the time of visiting the laboratory the post of organic contaminant analyst was vacant, someone was expected to start the following week. They were concerned about training for this person.

REIV has national accreditation and is starting to prepare for compliance with new ISO standards. As such, they have excellent quality management in place. This comprises documentation and clear protocols for all aspects of sample collection, handling and analysis. They have a dedicated Quality Assurance office where they keep instrument manuals, documentation on instrument maintenance, staff training, and complaints (an empty file). External personnel routinely check instruments. Written documentation with instruments includes Standard Operating Procedures, log book and quality control charts. The laboratory uses Reference Materials and participates in Intercomparison Exercises, including those run by IAEA-MEL.

G.4.2 Institute of Oceanology, Varna

We visited the Bulgarian Academy of Sciences Institute of Oceanology at Varna and were welcomed by the Director, Dr. Hristo Slabakov. We toured the chemistry laboratories with Dr. G. Andrev and Dr. G. Shtereva. Dr. Tsonka Konsulova showed us the marine biology and ecology department.

Using the *Akademik* (see below) for sample collection, the institute has a monitoring network throughout the Black Sea economic zone of Bulgaria, out to 2100 m depth. However, the institute receives no national funding for this activity. They collect waters at sites in Varna Bay and Burgas Bay monthly. A more extensive suite of stations throughout the economic zone of Bulgaria is visited seasonally. Sediments are collected only from sites <130 m. Data are disseminated through technical reports for each mission, an annual report to the Bulgarian Academy of Sciences and publications in the scientific literature. No data are provided to the Ministry for the Environment at this time.

The institute now has very limited capacity for chemical analyses, being restricted to classical wet chemistry. While they undertake nutrient analyses using colorimetric procedures, the atomic absorption spectrophotometer and two gas chromatographs were not functioning rendering it impossible to analyse metals and organic contaminants. Regarding biological monitoring, the institute has a strong and enthusiastic team. Under the leadership of Dr. Tsonka Konsulova, several young technicians identify and quantify phytoplankton, zooplankton and benthos. They have conducted projects on mussel mariculture.

The Institute of Oceanology operates a research vessel called the *Akademik.* This ship, 56 m in length, has a crew of 20 and can house up to 22 scientists. It is equipped with winches, wire, and A-frames for a wide range of sampling operations, together with a rosette sampler and CTD. It also serves as the tender vessel for a small submersible craft.

G.4.3 Recommendations

- Bulgaria should formulate a national monitoring programme. All the prerequisites are available. Samples from the entire coastal zone could be collected using staff and facilities of the Institute of Oceanology. Chemical analyses could be undertaken in RIEV, and possibly its sister laboratory (<u>not visited</u>) in Burgas. Biological measurements could be made at the Institute of Oceanology.
- A freeze-dryer suitable to be used for organic contaminant analyses should be purchased for RIEV.
- Training in the analysis of organic contaminants should be provided at RIEV.

G.5 Ukraine

On our visit to all laboratories in the Odessa region on November 25, we were accompanied by Mr. Patlatiyk Evgeni, Chief of Analytical Chemistry for the State Inspection for Protection of the Black Sea in Odessa.

G.5.1 Ukrainian Scientific Centre of the Ecology of Sea (UkrSCES), Odessa

We were welcomed at the Ukrainian Scientific Centre of the Ecology of Sea and given a tour of the facilities by Dr. Yuri Denga, Senior Researcher and Acting Head of Laboratory of Analytical Works and Methodics Developments. Dr Edward Kostylev, Head of the Hydrobiology Laboratory, showed us the Mussel Watch Laboratory.

With respect to monitoring, UkrSCES had an extensive programme in 1992 with sample collection on a seasonal basis. The extensive network investigated water, sediment and biota, together with land-based sources of pollutants. However, the programme has degraded with time and no sampling has been conducted since 2000 due to an apparent shortage of funds. The data from 1996-2000 was compiled into a State of the Environment Report. We did not visit the research vessels that the Centre operates.

UkrSCES has benefited from various donor organisations that have provided capacity building in the Black Sea region. They have good instrumentation for both organic analyses (gas chromatograph with electron capture detector and mass spectrometric detector) and metal analyses (flame and graphite furnace atomic absorption spectrophotometers). They have various spectrophotometers and fluorimeters for analyses of nutrients, *etc.* The laboratory is also equipped with a good water system, freeze-dryer, microwave digestion system and sample homogenisers.

The laboratory lacks running expenses and has very restricted space for the amount of equipment on hand. Such limitation was exacerbated by the generally untidy nature of the laboratory work place. They have a room designated as a storage and sample preparation area. This is in need of refurbishment and presently a large homogeniser rests on the floor unused.

UkrSCES also has a small Mussel Watch Laboratory equipped with various aquaria facilities. They are able to undertake various physiological and biochemical studies of benthos, including some bioassay techniques (*e.g.* lysosomal stability of membranes, spawning test). It is set up as a training facility, having a microscope with a TV system for demonstration purposes. This small laboratory seems to be entirely dependent on external funds and was dormant at the time of visiting.

UkrSCES has good AQCS procedures in place. They produce their own laboratory reference materials for routine work and have been supplied with internal standards and Reference Materials from IAEA-MESL. The laboratory is accredited nationally and maintains good documentation on staff training and instruments. An external expert performs an annual inspection of the 3 major instruments.

G.5.2 State Inspection for Protection of the Black Sea, Odessa

We visited the State Inspection for Protection of the Black Sea in Odessa and were welcomed by both the Director and First Deputy Chief. We toured the analytical laboratory with Mr. Patlatiyk Evgeni, Chief of Analytical Chemistry.

This analytical laboratory in Odessa is 1 of 4 such facilities that the State Inspection for Protection of the Black Sea operates. It has 4 staff, the others having only 1 per laboratory. The laboratory in Odessa undertakes trend and compliance monitoring at a total of 128 sites. Sampling in Odessa Bay is carried out using their vessel, the *m/v Ukraine*, and elsewhere they hire boats.

They measure 11 parameters in water, including nutrients, phenols, and oil. However, they do not analyse sediments. Total oil is determined colorimetrically following extraction into carbon tetrachloride. They have no gas chromatographic facilities and contract UkrSCES for measurements of individual organic components. Similarly, they pay the university for metal analyses on a needs basis.

The laboratory is nationally accredited and maintains rigorous AQCS procedures, including Quality Control charts, because they can be involved in litigation against polluters. They participate in intercomparison exercises organised by the Ministry for the Environment.

G.5.3 Hydrometeorological Bureau Laboratory, Port of Illichivsk

We visited the Hydrometeorological Bureau's laboratory at the Port of Illichivsk in the Odessa region, Ukraine. We were welcomed by Ms. Ludmila Siboliarova, Director, and Ms. Galina Yeremeeva, Chemist.

This small, clean laboratory has old analytical equipment that has been kept in working order. They have their own small boat and conduct a monitoring programme in the Port of Illichivsk. Analysing only water, and not sediments or biota, they measure standard water parameters, including nutrients, at 19 sites in the port from 4 depths. Some sites are sampled 3 times per month. For oil in water determinations, they carry out the extraction into carbon tetrachloride and the resulting extracts are sent for analysis to the Laboratory of the State Inspection for Protection of Black Sea in Odessa. Samples for analysis by gas chromatograph are sent to the Hydrometeorological Bureau Laboratory in Yalta.

Regarding AQCS considerations, an external expert from Sevastopol visits the laboratory at 6 monthly intervals to verify calibration of instrumentation and they participate twice annually in intercomparison exercises organised within the Hydrometeorological Bureau. There are 5 other such laboratories in the Hydrometeorological Bureau's network at various ports along the Ukrainian coast.

G.5.4 Ukrainian Land and Resource Management Centre, Kiev

We visited the Ukrainian Land and Resource Management Center in Kiev on November 26. We toured the facility with Dr. Olexander Mazurkevich, the General Director, Mr. Eric Luhmann, Chief Financial Officer, and Dr. Mykola Zalogin, Senior Specialist.

This facility makes use of GIS and satellite technology for environmental management. They have access to various remote sensing platforms, including Landsat and SeaWiFS (Sea-viewing Wide Field of view Sensor). Thus, some potential uses in Black Sea studies would be temperature and chlorophyll mapping for the whole of the Black Sea.

G.5.5 Recommendations

- Ukraine should formulate a national monitoring programme for the Black Sea. The expertise and facilities for such a programme are in place, but need to be co-ordinated. Presently, two laboratory networks belonging to the Black Sea Inspectorate and the Hydrometeorological Bureau handle monitoring. While they do provide good coverage of the Black Sea environment, measurements are restricted to standard water quality parameters. Nutrient analyses are well handled by the two laboratory networks. More demanding analyses, such as metals and organic contaminants in sediments and biota, could be undertaken at the Ukrainian Scientific Centre of the Ecology of Sea.

- Not counting the Ukrainian Scientific Centre of the Ecology of Sea, nutrient analyses are currently conducted locally at 10 different laboratories belonging to the Black Sea Inspectorate and the Hydrometeorological Bureau. It is difficult to recommend capacity building with such diffuse networks. An autoanalyser for nutrient determinations could be purchased if analyses were to be centralised, possibly at the Analytical Laboratory of the State Inspection for Protection of the Black Sea in Odessa or the Hydrometeorological Bureau Laboratory in Yalta (not visited).
- The Ukrainian Scientific Centre of the Ecology of Sea needs to reinstate good housekeeping practices, and refurbish the sample storage and preparation area.

G.6 Russian Federation

Mr. Leonid Yakmak, Krasnodar Regional Deputy Director of the Environmental Protection Inspectorate, Ministry of Natural Resources, was our host in the Russian Federation and accompanied us on all laboratory visits.

G.6.1 Environmental Protection Inspectorate Laboratory, Sochi

The first laboratory we visited in Sochi on November 27 was the Environmental Protection Inspectorate Laboratory. We were shown the laboratory by Mr. Svetoslav Udintsev, Head of Analytical Inspection Department.

This laboratory undertakes compliance monitoring of discharges and waster waters along a 140 km stretch of the Black Sea coast. They analyse standard water quality parameters, including oil, suspended solids and nutrients. Samples for heavy metal analyses are sent to the Central Laboratory in Krasnodar. The laboratory is equipped with UV - visible and infrared spectrophotometers for determinations of nutrient and oil, respectively.

In terms of AQCS characteristics, the laboratory uses standard techniques and equipment that have been approved by the Ministry of Natural Resources. The laboratory is accredited nationally and is audited annually by a visiting expert from St Petersburg, at which time the performance of instruments is verified. They participate in intercomparison exercises organised by the Central Laboratory of the Environmental Protection Inspectorate in Krasnodar. There no evidence of quality control charts being kept.

The laboratory needs computers and has no gas chromatograph.

G.6.2 Hydrometeorological Laboratory, Sochi

Ms. Diana Lysak, Chief, and Yuri Yuzenko welcomed us to the Hydrometeorological Laboratory in Sochi.

Regarding monitoring, they sample seasonally the waters and sediments just around Sochi. Sample collection extends to ~3 km offshore. They want to continue their work along the length of the Black Sea coast, but currently lack a vessel for sample collection. They collaborate quite closely with the Ministry of Natural Resources and data for waters are published in a yearbook. Although data for sediments and biota are collected, the results are not published.

The laboratory is equipped to determine standard water quality parameters, including nutrients, oil, and detergents. They analyse chlorinated pesticides, but the gas chromatograph with electron capture detector currently does not work well. They also have an atomic absorption spectrophotometer.

The laboratory has national accreditation, but does not participate in intercomparison exercises. A gas chromatograph with a mass spectrometry detector that was provided in an earlier capacity building programme was considered too complicated and expensive to operate locally and so was sent to a sister laboratory in St Petersburg.

G.6.3 Environmental Protection Inspectorate Laboratory, Tuapse

Ms. Albina Kirichenko, Director of Specialised Inspectorate of Analytical Control, showed us this small laboratory in Tuapse on November 28. This is a sister laboratory to the one in Sochi and monitors water quality in and around the port city. They, too, analyse only standard water quality parameters using protocols mandated by the Ministry of Natural Resources.

G.6.4 Environmental Protection Inspectorate Central Laboratory, Krasnodar

Ms. Lidia Tarasova, Deputy Director of the Laboratory, guided us through the laboratory. This Central Laboratory controls 5 smaller laboratories in the region, including the Inspectorate laboratories visited in Sochi and Tuapse. The laboratory network involves a total of ~200 staff, of whom ~30 are based in Krasnodar.

This is a well-maintained and well-organised suite of laboratories with a competent staff that handles a diverse range of analyses in air, biota, waters, soil and sediment. They have a sample preparation room. They currently lack a microwave digestion system and air-dry samples. Acid dissolution of solid samples for metal analyses is conducted using Parr-type digestion vessels. Key instruments include infrared and UV-visible spectrophotometers, graphite furnace atomic absorption spectrophotometer, and gas chromatographs for analysis of hydrocarbons, together with organophosphorus and organochlorine pesticides. Nutrients are analysed colorimetrically. They also have an air quality laboratory and an ecotoxicology laboratory.

The Central Laboratory runs in-house Quality Assurance programmes for the regional laboratories, undertakes specialised analyses, develops methods and is responsible for regional data handling. They have developed a simple technique for oil fingerprinting and designed a surface water sampler. They participate in national and international intercomparison exercises.

They would benefit from training focusing on new techniques (*e.g.* microwave digestion procedures) and the analysis of oil sludge.

G.6.5 Recommendations

- The Russian Federation should formulate a national monitoring programme for the Black Sea. The expertise and facilities for such a programme are in place, but need to be co-ordinated, particularly with respect to sample collection. Standard water quality parameters, including nutrients, could be measured in the Hydrometeorological Laboratory in Sochi and at the various regional laboratories of the Environmental Protection Inspectorate. The more demanding analyses, such as metals and organic contaminants in sediments and biota, should be performed at the Central Laboratory of the Environmental Protection Inspectorate in Krasnodar.
- A microwave digestion system should be purchased for the Central Laboratory of the Environmental Protection Inspectorate in Krasnodar.
- The Central Laboratory of the Environmental Protection Inspectorate in Krasnodar would benefit from training on microwave digestion procedures and the analysis of oil sludge.

APPENDIX H - PROPOSED MANDATORY PARAMETERS AND ANNUAL MONITORING FREQUENCIES - BSIMAP

Table H.1 BSIMAP, 2005

Parameter	Bulgaria	Georgia	Romania	Russian Federation	Turkey	Ukraine
CHEMISTRY & PHYSICO-CHEMISTRY						
Temperature	4	4	4	4	4	4
Salinity	4	4	4	4	4	4
pH	4	4	4	4	4	4
Dissolved O_2 (% saturation and mg/l)	4	4	4	4	4	4
Suspended solids	4	4	4	4	4	4
Secchi depth	4	4	4	4	4	4
BOD_5	4	4	4	4	4	4
PO_4-P	4	4	4	4	4	4
P total	4	4	4	4	4	4
NH_4-N	4	4	4	4	4	4
NO_3-N	4	4	4	4	4	4
NO_2-N	4	4	4	4	4	4
Total N	4	4	4	4	4	4
Petroleum Hydrocarbons	4	4	4	4	4	4
SiO_4	4	4	4	4	4	4
Cd	1	1	1	1	1	1
Cu	1	1	1	1	1	1
Hg	1	1	1	1	1	1
Pb	1	1	1	1	1	1
BIOLOGY						
Phytoplankton						
Chl a[5]	4	4	4	4	4	4
Phytoplankton, total density	4	4	4	4	4	4
Phytoplankton, total biomass	4	4	4	4	4	4
Fishery data						
Annual fish catches	1	1	1	1	1	1

5 Strictly a chemical parameter, but included as a biological parameter because of its use as an indicator of phytoplankton biomass.

Table H.2 BSIMAP, 2006-2011

	Country	BG	GE	RO	RU	TR	UA	BG	GE	RO	RU	TR	UA
Parameter	**Medium**	**No of sampling sites**						**Annual monitoring frequency**					
Temperature	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Salinity	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Dissolved O_2[6] (% saturation and mg/l)	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Total suspended solids	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Secchi depth	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Ortho-PO_4	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Total P	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
NH_4-N	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
NO_3-N	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
NO_2-N	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Total-N	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
SiO_4	**Water**	5	5	21	9	63 (3)	14	7	4	4	4	2 (4)	4
Petroleum Hydrocarbons	**Water**	5	5	21	9	63 (3)	14	4	4	4	4	2 (4)	4
Cd	**Water**	5	5	21	5	66	14	1	1	1	1	1	1
Cu	**Water**	5	5	21	5	66	14	1	1	1	1	1	1
Hg	**Water**	5	5	21	5	66	14	1	1	1	1	1	1
Pb	**Water**	5	5	21	5	66	14	1	1	1	1	1	1
Chl a	**Water**	5	5	21	5	63 (3)	14	4	4	4	4	2 (4)	4
Phytoplankton	**Water**	5	5	21	5	63 (3)	14	4	4	4	4	2 (4)	4
Mesozooplankton	**Water**	5	5	21	5	63 (3)	14	4	4	4	4	2 (4)	4
Biomass of *Noctiluca*	**Water**	5	5	21	5	63 (3)	14	4	4	4	4	2 (4)	4
Aquatic vegetation	**Sediment**	5	5	21	5	66	14	1	1	1	1	1	1
Macrozoobenthos	**Sediment**	5	5	21	5	66	14	1	1	1	1	1	1
Fish landing[7]		1	1	1	1	1	1	1	1	1	1	1	1
Particle size distribution	**Surface sediment**	2	2	2	2	2	2	1	1	1	1	1	1
Cd	**Surface sediment**	2	2	2	2	2	2	1	1	1	1	1	1

[6] Hypoxic events (<30% DO) should be reported if they are found to occur, but there is no mandatory programme specifically to monitor for them.
[7] To be reported on an annual basis for landings from the whole Black Sea.

	Country	BG	GE	RO	RU	TR	UA	BG	GE	RO	RU	TR	UA
Parameter	**Medium**	**No of sampling sites**						**Annual monitoring frequency**					
Cu	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
Hg	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
Pb	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
DDT	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
DDD	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
DDE	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
Lindane	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
PCBs	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
Hydrocarbons Total	**Surface sediment**	**2**	**2**	**2**	**2**	**2**	**2**	**1**	**1**	**1**	**1**	**1**	**1**
Cd	**Biota**[8]	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Cu	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Hg	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Pb	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
DDT	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
DDD	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
DDE	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
Lindane	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**
PCBs	**Biota**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**

[8] Mussels, anchovies, sprat, horse mackerel and turbot.

APPENDIX I – REPORTED BSIMAP MONITORING FREQUENCIES, 2001 and 2003

Table I.1 Monitoring of mandatory parameters undertaken as part of the BSIMAP, 2001
Results expressed as a percentage of the minimum recommended sampling frequency. See Section 4.7 for a detailed explanation of which individual parameters are included in the calculations and how the calculations are made.

Station No.	Station name	Oxygen balance determinands (%)	Nutrient determinands (%)	Heavy metal determinands (%)	Petroleum hydrocarbons (%)	Physico-chemical determinands (%)	Chlorophyll a (%)
1	Shabla	175	175	0	0	175	0
2	Varna	175	175	0	0	175	0
3	Obzor	175	175	0	0	175	0
4	Burgas	175	175	0	0	175	0
5	Ahtopol	175	175	0	0	175	0
6	Batumi	100	75	400	100	100	0
7	Kulevi	100	75	400	100	100	0
8	Poti	100	75	400	100	100	0
9	Supsa	100	75	400	100	100	0
10	Kobuletti	100	50	300	100	100	0
11	Sulina, discharging point	0	50	0	0	0	0
12	Mila 9, 5 m isobate	0	0	0	0	0	0
13	Mila 9, 20 m isobate	0	0	0	0	0	0
14	Sf. Gheorghe, 5 m isobate	0	0	0	0	0	0
15	Sf. Gheorghe, 20 m isobate	0	0	100	25	0	0
16	Portita, 5 m isobate	0	0	0	0	0	0
17	Portita, 20 m isobate	0	0	100	25	0	0
18	Buhaz , 5 m isobate	0	0	0	0	0	0
19	Buhaz, 20 m isobate	0	0	0	0	0	0
20	Mamaia, beach	125	100	200	0	100	0
21	Mamaia, 5 m isobate	150	75	100	125	100	0
22	Mamaia, 20 m isobate	75	75	100	75	75	0
23	Constanta N, 5 m isobate	50	50	0	25	50	0
24	Constanta N, 20 m isobate	75	75	100	75	75	0
25	Constanta S, 5 m isobate	50	50	0	50	50	0
26	Constanta S, 20 m isobate	50	50	100	50	50	0
27	Constanta E, 5 nautical miles	100	100	0	0	100	0
28	Constanta E, 10 nautical miles	100	100	0	25	100	0
29	Constanta E, 20 nautical miles	100	100	0	0	100	0
30	Constanta E, 30 nautical miles	100	100	0	25	100	0
31	Eforie Sud, beach	100	75	300	50	100	0
32	Eforie S, 5 m isobate	75	50	0	50	75	0
33	Eforie S, 20 m isobate	75	50	0	50	75	0
34	Costinesti, beach	100	100	200	75	100	0

Station No.	Station name	Oxygen balance determinands (%)	Nutrient determinands (%)	Heavy metal determinands (%)	Petroleum hydrocarbons (%)	Physico-chemical determinands (%)	Chlorophyll a (%)
35	Costinesti, 5 m isobate	75	75	0	50	75	0
36	Costinesti, 20 m isobate	75	75	100	75	75	0
37	Mangalia, beach	100	100	200	75	100	0
38	Mangalia, 5 m isobate	75	75	0	50	75	0
39	Mangalia, 20 m isobate	75	75	100	75	75	0
40	Vama Veche, beach	100	100	200	75	100	0
41	Vama Veche, 5 m isobate	75	75	0	50	75	0
42	Vama Veche, 20 m isobate	75	75	100	75	75	0
43	Anapa	100	75	100	100	100	0
44	Novorossiysk	100	75	0	75	100	0
45	Gelendzik	100	100	0	100	100	0
46	Tuapse	100	100	0	100	100	0
47	Sochi	100	100	0	75	100	0
48	KO	800	800	2400	0	1600	800
49	K1	625	575	0	0	1200	575
50	K3	525	525	0	0	850	500
114	WWTP Evpatoriya	75	0	0	175	150	0
115	Karkinitski bay	0	0	0	0	0	0
116	Tendra	25	25	0	0	25	0
117	Odessa bay	275	0	0	275	275	0
118	Phyllophora field	25	25	0	0	25	0
119	WWTP "Pivnichni"	100	0	0	100	100	0
120	WWTP Port "Uzhnyi"	250	0	0	250	250	0
121	Dniepr and South Bug Mouth	25	25	0	0	25	0
122	WWTP Kerch	325	0	0	325	300	0
123	WWTP Sevastopol	300	0	0	325	300	0
124	Dnister River Mouth	0	0	0	0	0	0
125	WWTP Port Illichivsk	150	0	0	150	150	0
126	WWTP Pivdenni	200	0	0	200	175	0
127	Port Odessa	275	0	0	275	275	0
128	Danube River mouth	50	50	0	0	50	0
129	Danube River mouth	0	0	0	0	0	0

Table I.2 Monitoring of mandatory parameters undertaken as part of the BSIMAP, 2003
Results expressed as a percentage of the minimum recommended sampling frequency. See Section 4.7 for a detailed explanation of which individual parameters are included in the calculations and how the calculations are made.

Station No.	Station name	Oxygen balance determinands (%)	Nutrient determinands (%)	Heavy metal determinands (%)	Petroleum hydrocarbons (%)	Physico-chemical determinands (%)	Chlorophyll a (%)
1	Shabla	400	200	0	0	200	0
2	Varna	400	200	0	0	200	0
3	Obzor	250	175	0	0	175	0
4	Burgas	200	100	0	0	100	0
5	Ahtopol	350	175	0	0	175	0
6	Batumi	0	0	0	0	0	0
7	Kulevi	0	0	0	0	0	0
8	Poti	0	0	0	0	0	0
9	Supsa	0	0	0	0	0	0
10	Kobuletti	0	0	0	0	0	0
11	Sulina, discharging point	0	125	0	50	100	0
12	Mila 9, 5 m isobate	100	50	200	50	50	0
13	Mila 9, 20 m isobate	100	50	200	50	50	0
14	Sf. Gheorghe, 5 m isobate	50	25	100	25	25	0
15	Sf. Gheorghe, 20 m isobate	100	50	200	50	50	0
16	Portita, 5 m isobate	100	50	200	50	50	0
17	Portita, 20 m isobate	100	50	200	50	50	0
18	Buhaz , 5 m isobate	100	50	200	50	50	0
19	Buhaz, 20 m isobate	100	50	100	50	50	0
20	Mamaia, beach	200	100	100	75	100	0
21	Mamaia, 5 m isobate	150	75	100	75	75	0
22	Mamaia, 20 m isobate	200	100	400	100	100	0
23	Constanta N, 5 m isobate	150	75	100	100	75	0
24	Constanta N, 20 m isobate	200	100	200	100	100	0
25	Constanta S, 5 m isobate	200	100	200	100	100	0
26	Constanta S, 20 m isobate	200	100	200	100	100	0
27	Constanta E, 5 nautical miles	50	25	100	25	25	0
28	Constanta E, 10 nautical miles	50	25	100	25	25	0
29	Constanta E, 20 nautical miles	50	25	100	25	25	0
30	Constanta E, 30 nautical miles	50	25	100	25	25	0
31	Eforie Sud, beach	175	100	100	100	100	0
32	Eforie S, 5 m isobate	175	100	200	100	100	0
33	Eforie S, 20 m isobate	200	100	200	100	100	0
34	Costinesti, beach	200	100	100	100	100	0
35	Costinesti, 5 m isobate	200	100	200	75	100	0

Station No.	Station name	Oxygen balance determinands (%)	Nutrient determinands (%)	Heavy metal determinands (%)	Petroleum hydrocarbons (%)	Physico-chemical determinands (%)	Chlorophyll a (%)
36	Costinesti, 20 m isobate	200	100	200	100	100	0
37	Mangalia, beach	225	100	100	100	100	0
38	Mangalia, 5 m isobate	200	100	200	100	100	0
39	Mangalia, 20 m isobate	200	100	200	100	100	0
40	Vama Veche, beach	200	100	100	100	100	0
41	Vama Veche, 5 m isobate	200	100	200	100	100	0
42	Vama Veche, 20 m isobate	200	100	200	100	100	0
43	Anapa	0	0	0	0	0	0
44	Novorossiysk	0	0	0	0	0	0
45	Gelendzik	0	0	0	0	0	0
46	Tuapse	0	0	0	0	0	0
47	Sochi	0	0	0	0	0	0
48	KO	2325	1725	6000	0	2325	0
49	K1	750	550	0	0	775	0
50	K3	500	500	0	0	1075	0
114	WWTP Evpatoriya	0	0	0	0	0	0
115	Karkinitski bay	0	0	0	0	0	0
116	Tendra	0	0	0	0	0	0
117	Odessa bay	0	0	0	0	0	0
118	Phylophora field	0	0	0	0	0	0
119	WWTP "Pivnichni"	0	0	0	0	0	0
120	WWTP Port "Uzhnyi"	0	0	0	0	0	0
121	Dniepr and South Bug Mouth	0	0	0	0	0	0
122	WWTP Kerch	0	0	0	0	0	0
123	WWTP Sevastopol	0	0	0	0	0	0
124	Dnister River Mouth	0	0	0	0	0	0
125	WWTP Port Illichivsk	0	0	0	0	0	0
126	WWTP Pivdenni	0	0	0	0	0	0
127	Port Odesa	0	0	0	0	0	0
128	Danube River mouth	0	0	0	0	0	0
129	Danube River mouth	0	0	0	0	0	0

APPENDIX J - REFERENCES

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