DISSOLVED ORGANIC MATTER FLUXES AT THE IBERIAN MARGIN

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1 BACKGROUND

Dissolved organic carbon (DOC) is the largest oceanic reservoir of organic carbon, calculated to have a carbon load equivalent to atmospheric CO_2 (Hedges, 1992). In addition to its important role in global carbon cycling, DOC is inextricably linked to the marine biogeochemical cycling of nitrogen and phosphorous (Mantoura *et al.*, 1991). Traditional analytical methods have typically determined attenuated oceanic DOC concentration profiles, with mean apparent ages between 1300 and >6250 years (Williams and Druffel, 1987), even though DOC fluxes through estuaries may be conservative (Mantoura and Woodward, 1983; Miller and Alvarez-Salgado, 1997b), contributing up to 50% global oceanic DOC inputs. Subsequently, the first reported studies using novel high temperature catalytic oxidation (HTCO) technologies in ocean margins (Suzuki and Tanoue, 1991) and estuaries (Sharp *et al.*, 1988 & 1993; Miller *et al.*, 1993) indicated non-conservative removal of riverine and shelf produced DOC, with minimal export to the ocean. And further, molecular structure studies of oceanic DOC revealed only traces of terrestrial material (Meyers-Shulte & Hedges, 1986), implying a major contribution from *in situ* sources coupled with significant and rapid removal in the transitional zones leading from land to the open ocean. However, in the most recently published study, DOC and suspended particulate organic carbon (POC) inputs from ocean margins to the open ocean were over an order of magnitude greater than inputs through primary productivity (Bauer *et al.*, 1998).

Through recent developments, HTCO has become the favoured analytical method for the determination of DOC. At the UK centre for Coastal and Marine Sciences' Plymouth Marine Laboratory, we have developed a rapid, high-precision system for the simultaneous determination of DOC and total dissolved nitrogen (TDN), from which dissolved organic nitrogen (DON) may be simply derived (Alvarez-Salgado and Miller, in press). Investigations into DOC/DON in coastal and shelf environments are few and there is no published DOM data for the NW Iberian margin. Our previous studies in ocean margin environments (Miller *et al.*, 1997a; 1997c) have illustrated spatially and seasonally variable distributions of dissolved organic matter (DOM) within the water column. Preliminary data from the OMEX I Celtic Sea study (Miller *et al.*, 1997c), however, suggested that DOC concentration is not coupled to phytoplankton production through simple linear function, but supported a broader framework of determination through a complexity of hydrodynamic and biogeochemical processes.

This project contributes to *Work Package II* and *Work Package IV*. Dissolved organic matter (DOM) studies at PML will be focussed on Task 2, to track the upwelling and downwelling seasonal distribution of DOC/DON throughout the water column across the NW Iberian shelf into oceanic waters. Prior to the fieldwork phase, it will be essential to intercalibrate analytical systems between PML and IIM (responsible for DOC measurements in Task I), through analysis of common samples, while further collaboration will be required to synthesise the DOC/DON results from Tasks I and II. We shall also provide accurate DOC data for algorithm development of SeaWifs remotely sensed data to enable basin scale mapping of DOC distributions to be undertaken in collaboration with the remote sensing group (NSS).

2 SPECIFIC OBJECTIVE

There are 14 Specific Objectives for *Work Package II*, of which this work focuses on:

6. *To determine the seasonal distribution and fates of dissolved organic carbon, nitrogen, phosphorus and their stable isotopes along mixing gradients of Ria, coastal, shelf and upwelled waters across the Iberian Margin.*

3 BROAD OBJECTIVES

3.1 To investigate the fluxes of Dissolved Organic Carbon (DOC) and Dissolved Organic Nitrogen (DON) across the NW Iberian shelf and shelf-break, in order to construct a 3-D picture of Dissolved Organic Matter (DOM) delivery into the NE Atlantic.

3.2 Comparison between OMEX I (Goban Spur), LOIS SES (Hebridean Shelf) and OMEX II (Iberian Shelf) data, to provide estimates of the magnitude of spatial variability in cross-shelf DOM transport along the NE Atlantic ocean margin.

3.3 Undertake surface DOC mapping for potential ground truthing remotely sensed ocean colour satellite data for the SeaWifs programme.

4 TASK-SPECIFIC PROGRESS

Below are listed the WPII Tasks (with lead partner in bold), for which the *DOM fluxes* project is a contributory scientific component. Detailed descriptions of relevant components, and the progress so far, shall be addressed by *Technical Annex subtask deliverables* thereafter. Reference will only be made to those subtasks on which progress has been made.

Task II.4 ***Nutrient distribution, speciation, upwelling & fluxes***
(Partners: ULB-b, PML-a, PML-c, NIOZ-b, UCG, NSS, IST, ***IIM****, NIOO-a, ULg, VUB,)*

Task II.6 ***Dissolved organic carbon***
(Partners: ***PML-a****, NSS, IIM, UAL-a, UOv, UVi,)*

Task II.12 ***Remote Sensing and Biogeochemical algorithms***
(Partners: PML-a, PML-c, UWB-a, ***NSS****, RISO, IIM, IfM, ULg, VUB)*

4.1 Nutrient Distribution, Speciation, Upwelling & Fluxes

Subtask II.4.1 Nutrient oceanography

Objective: To determine the underway and vertical distribution of DON on WPII cruises.

Methodology: DON will be determined (PML-*a*) by a specially adapted HTCO-DOC system fitted with a chemiluminescence N detector and a 0.5% Pt/Al_2O_3 catalyst, will be used for ship board determination of DOC/N. Since DOC/TDN will be routinely measured by PML-*a* and IIM, particular attention will be paid to the intercalibration of analytical systems and methodologies to ensure consistency between data for WPI and WP II.

4.1.1 Nutrient Intercalibration on preserved samples taken during OMEX cruises

DON (actually TDN) distributions will only be measured by PML-*a* (WPII). Therefore, intercalibration is not required to demonstrate consistency between data sets. However, a number of measures have been and are continuing to be taken as a matter of course, to ensure consistency between the analytical facilities at IIM and PML:

(i) A revised manuscript: "Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in sea water by high temperature catalytic oxidation: conditions for precise shipboard measurements", by Xosé A. Álvarez-Salgado (IIM) & Axel E.J. Miller (PML-*a*), has been accepted by *Marine Chemistry* for publication. This details work carried out by the authors during the period of OMEX I; which has resulted in much valuable collaboration and common experience in the analytical methodologies that will be employed during OMEX II-II.

(ii) Xosé A. Álvarez-Salgado (IIM) has collected samples from two shallow profiles (a total of 9 samples) in the Ria de Vigo, during September, 1997. Replicates of these samples have been passed to PML-*a* , for subsequent analysis. Results from this exercise are not yet available.

(iii) Representatives from PML-*a* and IIM both participated in the Charles Darwin cruise CD110-LegB, from 6th-19th January 1998. This provided another opportunity for collection of samples for intercalibration. Samples were analysed on-board and in the laboratory (PML-*a*), and further preserved aliquots will be subsequently analysed in the home laboratories of PML-*a* and IIM.

The combined results from these activities will result in repeatedly intercalibrated TDN analysis methods, producing data sets WPII.

4.1.2 DON distributions

Representatives from PML-*a* participated in the UK Centre for Marine and Coastal Sciences (CCMS) Charles Darwin cruise CD110-LegB, from 6th-19th January, 1998. Investigations were designed to track the winter distribution of DON through the water column, along transects across the NW Iberian shelf and shelf break into deep oceanic water. During the cruise, we observed *Navidad* conditions characterised by the incident northward warm and saline current off the Iberian margin. This hinders shelf ocean exchange and evokes trapping of colder, fresh water from the rias that is enhanced in nutrients, potentially increasing biological production near the coast.

Prevailing weather conditions were largely unfavourable for CTD sampling, but full depth profiles for a number of stations were possible. These comprised three along *Line V*, marking the southerly extent of the *OMEX Box*; and six on Line P, the main *OMEX Reference Line*, along which sediment traps and current meters have been moored. In addition, a surface survey was implemented, using *OMEX Grid* stations as way-points. When the ship passed through a station, surface water samples were collected from the ship's non-toxic supply. Shipboard HTCO-TDN measurements were made on the first four CTD casts, and a selection of the underway samples. Aliquots of all samples collected were preserved and archived for analysis at PML, where previously unmeasured samples were allocated analytical priority. Representative data are presented in Tables 1&2 and Figure 1. Investigations will eventually allow the fluxes of DON across the NW Iberian shelf to be determined, in order to construct a 3-D picture of dissolved organic matter (DOM) delivery into the NE Atlantic.

Data from analyses performed during cruise CD110 and subsequently in the laboratory at PML have been worked up and are currently undergoing control. A small number of samples are awaiting analysis, which is scheduled for early June. After final quality control of the results, the complete data set should be submitted to BODC in July 1998.

4.1.3 Plans for Year 2

(i) Analysis of OMEX-area intercomparison samples (PML-a, IIM).

(ii) Participation in summer WPII cruise (August 1998) fronted by Prof. Antonio Bode (IEO). The survey will focus on *OMEX Reference Lines N, P and S*. This will allow replication of a number of stations sampled during the CD110 winter cruise, thus providing a seasonally comparative data set.

(iii) Participation in winter WPIII cruise aboard (January 1999) fronted by Laurenz Thomsen (GEOMAR). Opportunistic WPII sampling over the whole *OMEX Box* will allow comparison between the two winter surveys, giving an estimate of inter-annual variability. A significant number of berths will be allocated to water column studies, including the essential inorganic nutrient determinations.

4.2 Dissolved Organic Carbon

Subtasks **II.6.1 Seasonal and spatial distribution of DOC**
II.6.2 Planktonic production of DOC
II.6.3 Bacterial utilisation of DOC

Objectives: To determine cross shelf concentration and seasonal gradients and fluxes of DOC/N in the Iberian Margin. [In subtasks II.6.2 & II.6.3 DOC analyses will be performed by collaboration with IIM (WPI) and PML-a (WPII).]

Methodology: A specially adapted HTCO-DOC system fitted with a chemiluminescence N detector and a 0.5% Pt/Al_2O_3 catalyst, will be used for ship board determination of DOC/N or split samples from the CTD rosette casts, to allow vertical on-shelf sections to be derived. Since DOC will be routinely measured by PML and IIM, particular attention will be paid to the intercalibration of analytical systems and methodologies to ensure consistency between data for WPI and WPII.

4.2.1 Intercalibration and optimisation of HTCO-DOC

Under '*Methodology*' it is stated that intercalibrations for DOC will be carried out by PML-*a*, UOviedo and UVI. This is not quite correct, as the only partners responsible for measurements of DOC using comparable techniques are actually IIM (WP1) and PML-*a* (WPII). UVI are measuring DOC production using radiochemical counting techniques: intercomparison of results is not possible for reasons of safety and instrument sensitivity.

A number of measures have been and continue to be taken as a matter of course, to ensure consistency between the analytical facilities at IIM and PML:

(i) A revised manuscript: "Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in sea water by high temperature catalytic oxidation: conditions for precise shipboard measurements", by Xosé A. Álvarez-Salgado (IIM) & Axel E.J. Miller (PML-*a*), has been accepted by *Marine Chemistry* for publication. This details work carried out by the authors during the period of OMEX I; which has resulted in much valuable collaboration and common experience in the analytical methodologies that will be employed during OMEX II-II.

(ii) Both PML-a and IIM groups are part of an on-going international DOC intercomparison programme, organised by Jonathan Sharp (Univ. Delaware) and Dennis Hansell (Bermuda BSR). This programme collects and circulates ampoules of deep Sargasso Sea water, of known DOC concentration, to all registered members of the international community, with formal analytical and reporting protocols. This is an extremely important move towards wide-scale analytical consistency, and will be included at all stages of the PML-*a* and IIM OMEX DOC measurement programmes.

(iii) Xosé A. Álvarez-Salgado (IIM) has collected samples from two shallow profiles (a total of 9 samples) in the Ria de Vigo, during September, 1997. Replicates of these samples have been passed to PML-*a* (and to ULB - for opportunistic participation in the intercalibration exercise), for subsequent analysis. Results from this exercise are not yet available.

(iv) Representatives from PML-*a* and IIM both participated in the Charles Darwin cruise CD110-LegB, from 6th-19th January 1998. This provided another opportunity for collection of samples for intercalibration. Samples were analysed on-board and in the laboratory (PML-*a*), and further preserved aliquots will be subsequently analysed in the home laboratories of PML-*a* and IIM; with further opportunity for participation by ULB.

The combined results from these activities will result in repeatedly intercalibrated DOC analysis methods, producing consistent data sets for both WP1 (IIM) and WPII (PML-a).

4.2.2 Seasonal DOC distribution

Representatives from PML-*a* participated in the UK Centre for Marine and Coastal Sciences (CCMS) Charles Darwin cruise CD110-LegB, from 6th-19th January, 1998. Investigations were designed to track the winter distribution of DOC through the water column, along transects across the NW Iberian shelf and shelf break into deep oceanic water. During the cruise, we observed *Navidad* conditions characterised by the incident northward warm and saline current off the Iberian margin. This hinders shelf ocean exchange and evokes trapping of colder, fresh water from the rias that is enhanced in nutrients, potentially increasing biological production near the coast.

Prevailing weather conditions were largely unfavourable for CTD sampling, but full depth profiles for a number of stations were possible. These comprised three along *Line V*, marking the southerly extent of the *OMEX Box*; and six on Line P, the main *OMEX Reference Line*, along which sediment traps and current meters have been moored. In addition, a surface survey was implemented, using *OMEX Grid* stations as way-points. When the ship passed through a station, surface water samples were collected from the ship's non-toxic supply. Shipboard HTCO-DOC measurements were made on the first four CTD casts, and a selection of the underway samples. Aliquots of all samples collected were preserved and archived for analysis at PML, where previously unmeasured samples were allocated analytical priority. Representative data are presented in Tables 1&2 and Figure 2. Investigations will eventually allow the fluxes of DOC across the NW Iberian shelf to be determined, in order to construct a 3-D picture of dissolved organic matter (DOM) delivery into the NE Atlantic.

In addition to samples taken to investigate the seasonal distribution of DOC, a total of four vertical profiles were taken in collaboration with *planktonic DOC production* experiments (UVI). Data will be used to estimate the relative contribution of phytoplankton production to the DOC reservoir over the course of shipboard incubations.

We shall also provide accurate DOC measurements for algorithm development of SeaWifs remotely sensed data to enable basin scale mapping of DOC distributions to be undertaken in collaboration with the remote sensing group (NSS).

Data from analyses performed during cruise CD110 and subsequently in the laboratory at PML have been worked up and are currently undergoing control. A small number of samples are awaiting analysis, which is scheduled for early June. After final quality control of the results, the complete data set should be submitted to BODC in July 1998.

4.2.3 Plans for Year 2

(i) Continued participation in the international DOC intercomparison programme, with IIM.

(ii) Analysis of OMEX-area intercomparison samples, with IIM and ULB (opportunistically).

(iii) Participation in the summer WP II cruise (August 1998) fronted by Prof. Antonio Bode (IEO). The survey will focus on *OMEX Reference Lines N, P and S*. This will allow replication of a number of stations sampled during the CD110 winter cruise, thus providing a seasonally comparative data set. In addition to the *Seasonal DOC Distribution* programme, analyses will be performed in collaboration with the *Phytoplanktonic Production of DOC* and *Bacterial Utilisation of DOC* work programmes, in an attempt to close the loop of biological DOC cycling during summer upwelling conditions.

(iv) Participation in the winter WPIII cruise aboard (January 1999) fronted by Laurenz Thomsen (GEOMAR). Opportunistic WPII sampling over the whole *OMEX Box* will allow comparison between the two winter surveys, giving an estimate of inter-annual variability. A significant number of berths will be allocated to water column studies, including the essential inorganic nutrient determinations.

4.3 Charles Darwin Cruise CD110 – Leg B

From 6th –19th January 1998, we participated in the CCMS cruise CD110B, with AEJM acting as Principal Scientist for the duration. A summary of the cruise is presented here: details from the complete cruise report (Miller, 1998) may be accessed through BODC.

RRS *Charles Darwin* cruise 110 was one of several planned at intervals of six months or less for the EU MAST project Ocean Margin Exchange (OMEX II-II) focusing on the NW Iberian continental shelf and slope. This cruise forms a contribution to Work Package II, whose purpose is to measure and model the mesoscale spatial and seasonal variability in the sources of water, particles, carbon and nutrient elements in contrasting shelf-influenced waters.

Leg B aimed to systematically map water properties from coastal to oceanic environments, along cross-shelf surface transects and throughout the water column. Due to persistent, extremely poor weather conditions, the scientific objectives were severely curtailed. Of the 74 stations along the nine latitudinal OMEX lines, only six stations were occupied, resulting in a total of 12 CTD casts. Attached to the CTD frame were two transmissometers, an optical back-scatter sensor (for investigations of pelagic nepheloid layers), a fluorometer, a dissolved oxygen probe, and an upwelling PAR sensor. Due to the high water-volume demands, a number of replicate CTD casts were undertaken at most stations. Casts were designated ‘Biogeochemistry’ (typically dissolved and particulate organic matter, five nutrients, pigments, bacterioplankton, phytoplankton and microzooplankton), ‘Incubations’ (focussed on primary production and dissolved organic carbon production) and ‘Radionuclides’ (radionuclides and suspended particulate matter), according to the range of parameters being sampled. In addition to the standard programme, a number of samples were collected for OMEX-community DOM and nutrients intercomparison exercises. Where weather conditions prevented deployment of the CTD, and where casts had not been accomplished during Leg A, XBT probes were launched (17 profiles).

Three water downwelling light field profiles were collected using a data-logging spectroradiometer rig. At two stations, one at the shelf edge and one in deeper water, particulate material samples were collected using the stand alone pumps (SAPs). The FLY (free-falling light yo-yo) turbulence probe was successfully deployed over 300m on seven occasions, from inshore to intermediate depth (~2800m) oceanic stations. A repeat series at one station within five hours provides a measure of short time-scale variability the shelf edge. A total of 17 WPII and drifting (25m) zooplankton net hauls were completed (day and night). These provided integrated sampling over the surface 200m at stations from inshore to the oceanic (~3100 m), and complementary collection of live copepods for egg production experiments.

Surface mapping of pCO_2 and pH were an integral component of the cruise programme, using 'continuous' computerised logging system to collect data every minute. To provide complementary measurements over the broader OMEX grid area, a near-surface sampling regime was instigated. This entailed collection of samples for determination of a suite of biogeochemical parameters (including dissolved and particulate organic matter, five nutrients, pigments, radionuclides, SPM, bacterioplankton, phytoplankton and microzooplankton) from the non-toxic supply at each way-point on the OMEX grid. Continuous recording of the standard underway parameters utilised the ship-borne ADCP, thermosalinograph (temperature, salinity), on-deck transmissometer, fluorometer and PAR sensors.

The cruise was continuously hampered by the poor weather conditions. Scheduled over-the-side work with the CTD, FLY and SAPS was only possible on three days out of 11 in the working area. The only mooring work consisted of the collection of STABLE. In addition, an ADCP (presumed lost) which had been picked up by the Spanish Maritime Authorities was recovered in Vigo, but a current meter line mooring which had been located during Leg A was not recovered.

ACKNOWLEDGEMENTS

I should like to express my thanks to the ship's company of RRS *Charles Darwin* for their help and co-operation during the cruise; to RVS for its unerring support; and to the patience of the scientific party; for producing valuable observations, under the 'somewhat testing' winter conditions over the Galician shelf. I raise a toast to your memory, ladies and gentlemen.

4.3 REFERENCES

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4.4 TABLES AND FIGURES

Table 1 *Range of DOC and TDN Concentrations at Stations V2200 and V110*

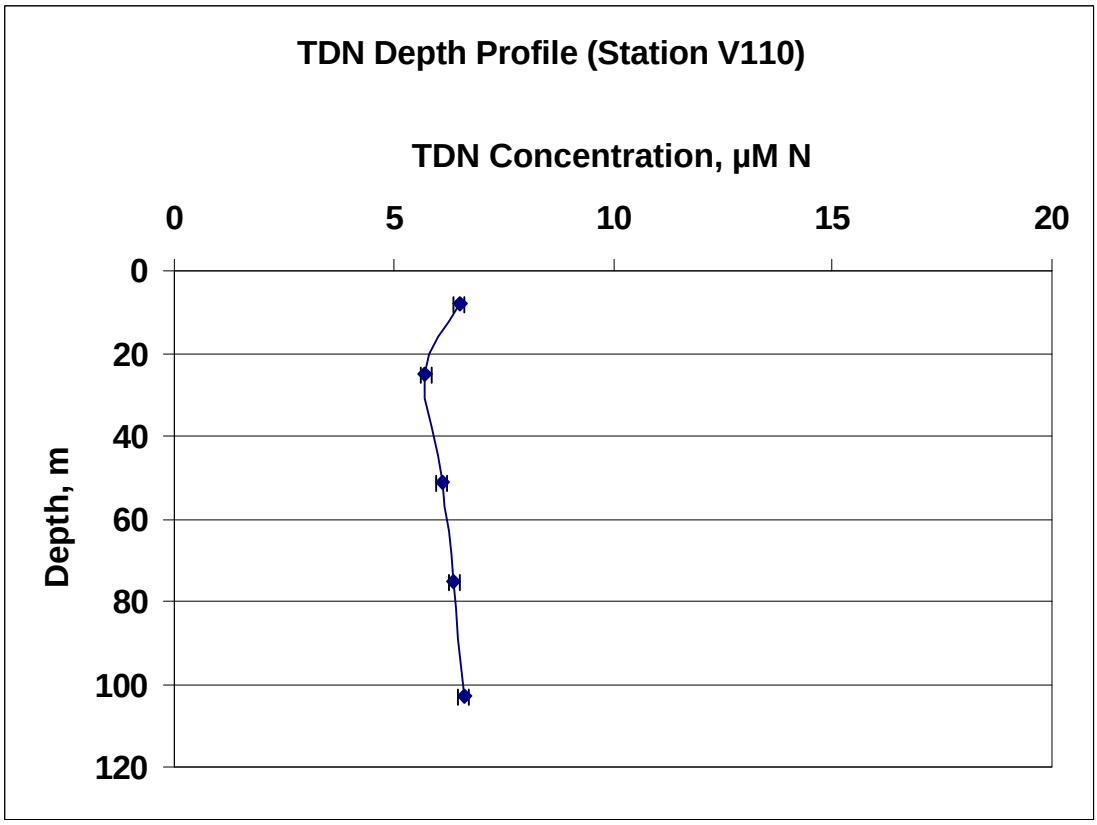
STATION	DOC, µM C	CV (%)	TDN, µM N	CV(%)
V110	63 – 78	0.7 – 1.7	5.7 – 6.6	0.0 – 3.0
V2200	48 – 72	0.3 – 2.2	6.4 – 17.3	0.1 – 2.0
P2800	48 - 66	0.1 – 2.3	5.0 – 17.0	0.1 – 1.9

Table 2 *Range of DOC and TDN Concentrations of Transects N and O and Q*

Transect	DOC, µM C	CV(%)	TDN, µM N	CV (%)
N	70 - 82	0.5 – 2.2	6.2 – 6.9	0.1 – 2.0
O	77 – 86	0.7 – 2.1	5.8 – 7.5	0.0 – 1.5
Q	63 - 76	0.5 –2.1	5.8 – 7.6	0.3 – 4.1

Figure 1 Total dissolved nitrogen profiles for (a) inshore and (b) offshore stations.

(a)



(b)

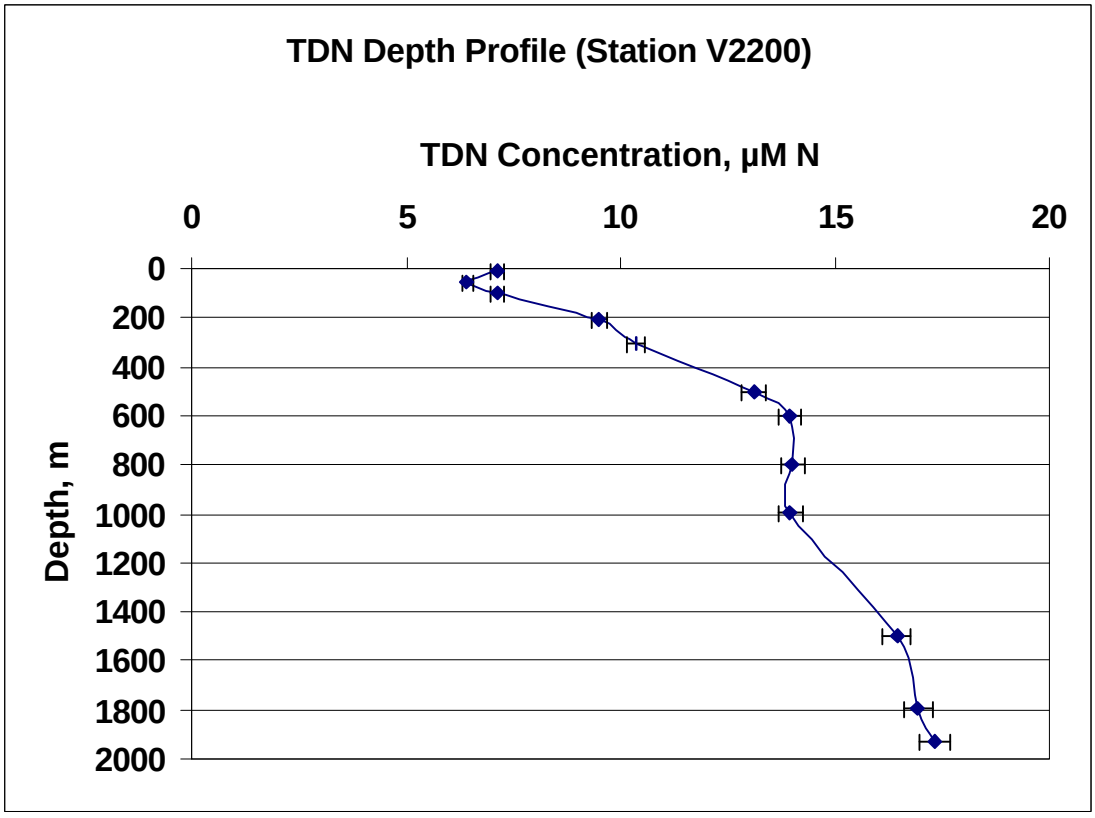
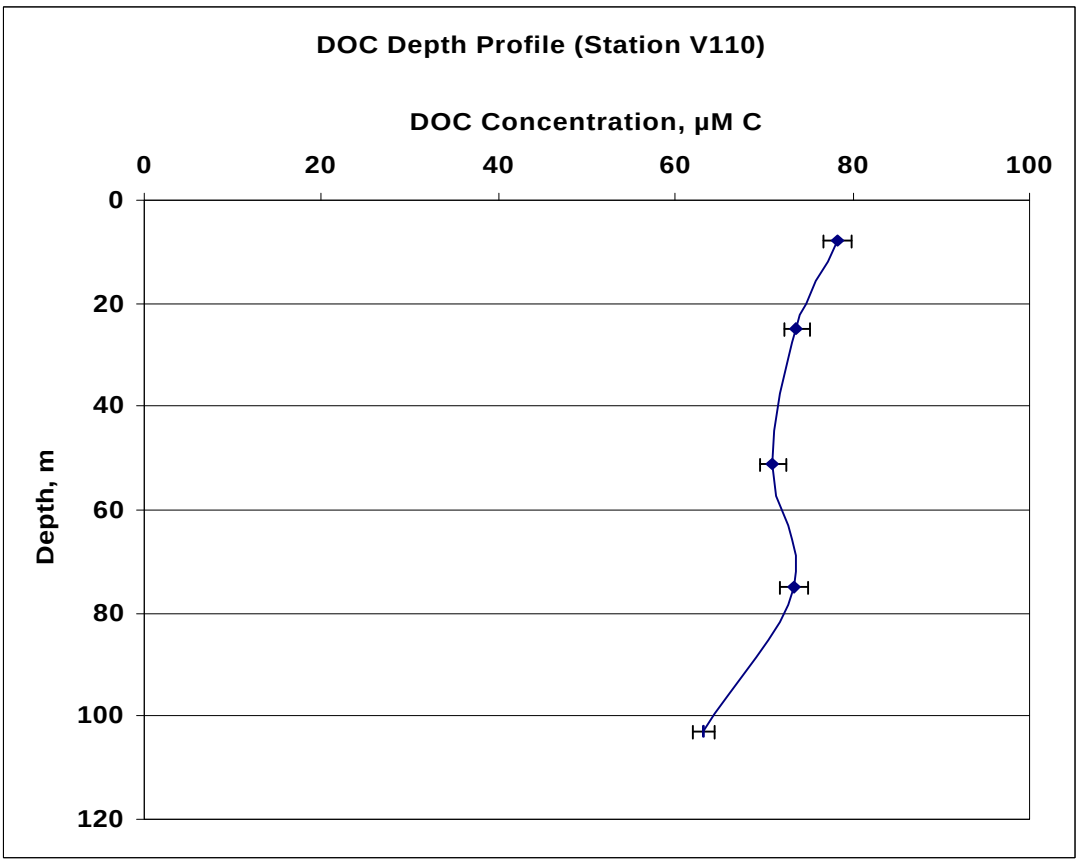


Figure 2 *Dissolved organic carbon profiles for (a) inshore and (b) offshore stations.*

(a)



(b)