



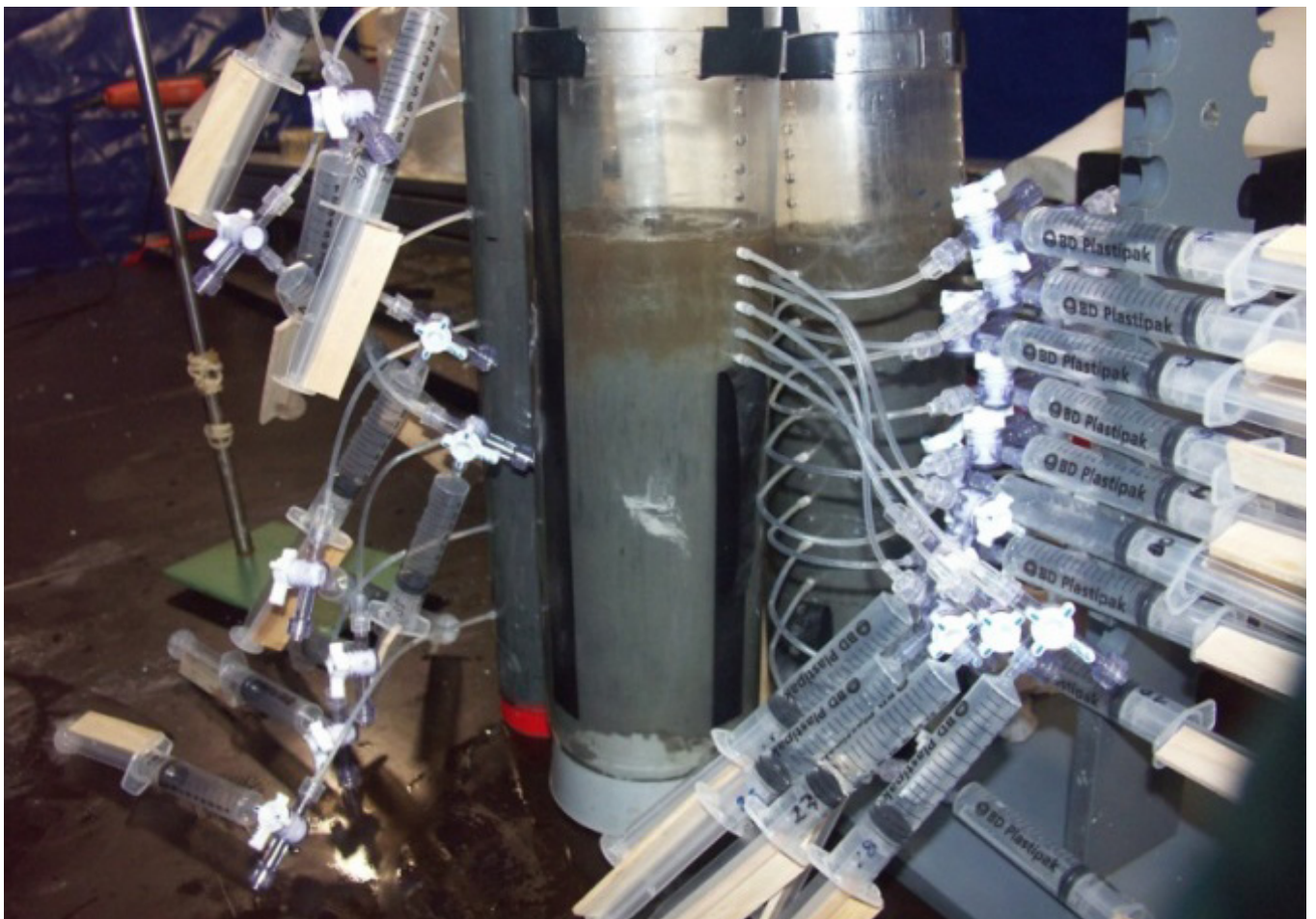
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Bachelor Thesis

Degree Project in
Geochemistry 30 hp

Pore water concentrations in Laptev Sea sediment: measurements and modelling

Mikaela Holm



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Department of Geological Sciences
Stockholm University
SE-106 91 Stockholm

Abstract

The carbon cycle is tightly connected to the climate, and plays a central role in the problematics of global warming. To achieve a comprehensive understanding of the fate of organic carbon (OC) and carbon cycle in the Arctic Ocean, it is important to investigate all parts involved, such as processes in sediment linked to mineralization of OC on the East Siberian Arctic Shelf (ESAS). Large continental areas surrounding, and parts of the ESAS, consist of permafrost. Permafrost areas are great carbon reservoirs and a big concern considering the ongoing global temperature increase, which is expected to have an even greater impact on polar regions. Remobilization of OC by increased runoff and release of methane, due to thawing permafrost and changes in the hydrological cycle is believed to occur. Model calculations of dissolved inorganic carbon (DIC) and sulfate concentrations have shown that mineralization of OC by sulfate reduction is proceeding in the ESAS sediment, with low upward fluxes of DIC. Based on stable carbon isotope analysis of DIC in the pore water the OC source is believed to be mainly terrestrial, suggesting that the terrestrial OC behaves non-conservative. High DIC production, sulfate consumption and fluxes observed in a methane seep area at station 14, together with $\delta^{13}\text{C} < -40$ indicates that oxidation of methane is taking place within the sediment. Two ongoing processes, degradation of OM and oxidation of methane, contributing to upward DIC fluxes are identified in the sediment on the ESAS, Laptev Sea.

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1 Introduction

Coastal areas and shelf environments have an important role in the global carbon cycle (Krumins et al., 2013), due to the large input of organic matter (OM) and nutrients from the continent (McClelland et al., 2014) and due to upwelling systems (Brüchert et al., 2003). The sediment at continental margins are therefore usually regions of high degradation of organic OM, contributing to a production of dissolved inorganic carbon (DIC) and upward carbon fluxes to the water column and the atmosphere. Hence, investigations of such areas are very important to gain an understanding of the carbon cycle and the climate response.

1.1 Arctic Ocean and the East Siberian Arctic Shelf

The Arctic Ocean covers a large area and stands for 4.3 % of the total ocean area, with a relative small volume of 1.4 % of the world's ocean volume, due to its very large and shallow continental shelf (Jakobsson 2002). The East Siberian Arctic Shelf (ESAS) is considered to be the largest and shallowest continental shelf, with a mean depth ~50 m (Jakobsson 2002). The ESAS includes the Laptev Sea, the East Siberian Sea and parts of the Chukchi Sea.

During Holocene climate warming, the sea level rose by more than 100 m. As a consequence, large permafrost areas became submerged and are today parts of the ESAS. Permafrost is defined as any earth material with a 2 year average temperature below freezing point (Shakhova et al., 2010), and permafrost areas are great natural carbon reservoirs. A global temperature increase has been identified and is expected to continue to rise. Polar regions are believed to have a more rapid temperature increase, resulting in permafrost thaw (IPCC, 2014) and changes the hydrological regime (Alling et al., 2010; Shakhova et al., 2010). As a consequence of the changing climate, increased release and remobilization of organic carbon (OC) is expected. Increased release and transportation of OC from escalation of continental runoff and coastal erosion, but also from release of shallow permafrost related hydrocarbon, such as methane (CH₄). High methane concentrations in the water column and gas bubbles rising from the seafloor have been observed in the ESAS area (Shakhova et al., 2010).

River transported OM is believed to be an important source of OC to the ESAS. The annual continental runoff to the Arctic Ocean is estimated to stand for 10% of the total global runoff (McClelland et al., 2008). For the Laptev Sea and the East Siberian Sea, Lena River is the main river discharge, estimated to contribute with 5.9×10^{12} gC yr⁻¹ (Cooper et al., 2008). Estimations made by Raymond et al. (2007) suggesting that 60-90% of this riverine carbon discharge is added by the spring flood, during May-June. The watershed of the Lena River covers 2.46×10^6 km² area consisting of up to 90% of permafrost (both continuous and discontinuous permafrost)(Holmes et al., 2011), which makes this a very sensitive area to climate change.

Whether the riverine terrestrial OM is degraded over the ESAS, or if it behaves conservatively to a greater extent, is an important and debated question (Alling et al., 2010). More recent studies made by Alling et al. (2010; 2014) have suggested that the terrestrial OM is more labile and behaves less conservative than suggested by previous research.

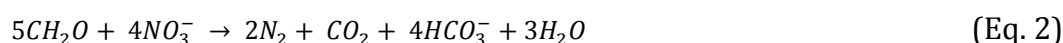
1.2 Pore water chemistry

A large fraction of the OM in the ocean is degraded in the water column, thus never reaches the seafloor. However, the OM that does reach the sediment continues to be degraded after deposition and burial. There are 6 major processes that contributes to the decomposition of organic matter in the sediment, see the reactions in Equation 1-6 (Berner and Berner, 1996, p. 325). The reactions are simplified and the OM is accounted for as CH_2O . The reactions succeed in the following order, most likely after depletion of the electron acceptor in the reaction above.

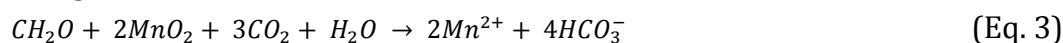
Oxygenation



Nitrate reduction



Manganese oxide reduction



Ferric oxide reduction



Sulfate reduction



Methane formation



The dominant degradation process in near shore environments, such as continental shelves is commonly sulfate reduction (Berner and Berner, 1996, p. 325). The oxygen penetration is limited in sediment. The ESAS sediment is assumed to undergo oxygen depletion within the top mm (Karlsson et al., 2015). Mineralisation of OM by sulfate reduction has a stoichiometric ratio, $r_{C:S}$ with a value of 2. Two moles of DIC is produced by every mole of sulfate being reduced.

Five of six reactions (Eq. 1-5) are producing DIC (here as HCO_3^-) and one reaction (Equation 6) is producing methane by the degradation of OM. However, microbial processes in the sediment can also oxidize methane, for instance by sulfate reduction.

All these processes play an important role for the global carbon cycle and the climate, since both CO₂ and methane are important greenhouse gases. As mentioned before, permafrost areas are large carbon reservoirs. The ESAS subsea permafrost together with the gas hydrates trapped underneath have been estimated to hold around 1400 Gt carbon (Shakhova et al., 2010), major parts are believed to consist of CH₄ as gas hydrates and free gas.

1.3 Study area

This project investigates geochemical parameters in the sediment, within a depth transect at the ESAS in the Laptev Sea (Figure 1). The depth transect consists of 7 stations, some with multiple coring casts. The stations start in the lower part of the shelf slope, in a water depth of ~3000 meters, and continues up to the ~50 m shallow shelf (Figure 1 and Table 1). Station 13, 14 cast 3 and 14 cast 4 are localities where CH₄ seeping have been observed, so called hot spots (Brüchert, 2015).

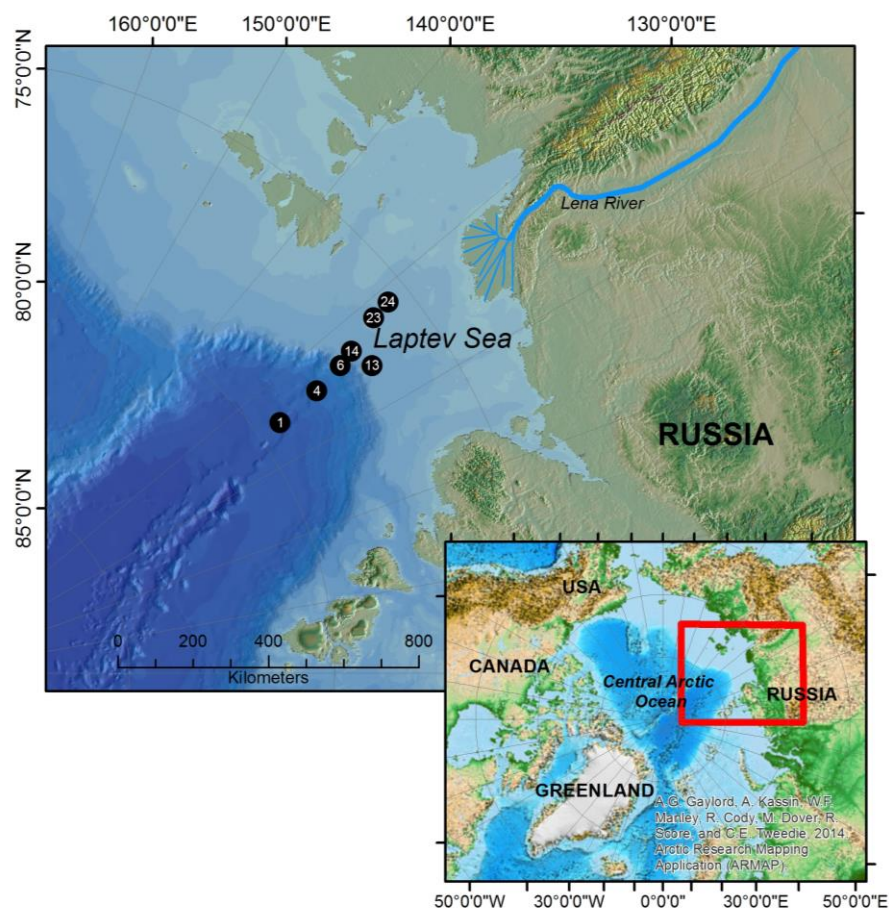


Figure 1. Overview of the study area on the East Siberian Arctic Shelf in the Laptev Sea, Arctic Ocean. The stations are shown as black points with the corresponding station ID. The map was produced in ArcMap 10.2.2. All geographic data have WGS 1984 Arctic Polar Stereographic projection. The geographic data source is the Arctic Research Mapping Application (ARMAP), station map (Johnson et al., 2009) and reference map (Gaylord et al., 2014).

Table 1. Station coordinates, water depth and type of coring method used.

| Station ID | Coordinates | | Water depth (m) | Type of core |
|---------------------------|-------------|-----------|-----------------|--------------|
| | Latitude | Longitude | | |
| Station 1 | 78.942 | 125.243 | 3000 | MUC |
| Station 4 | 77.855 | 126.664 | 2000 | MUC |
| Station 6 | 77.142 | 127.378 | 100 | MUC |
| Station 13 | 76.778 | 125.830 | 60 | MUC |
| Station 14 (cast 3 and 4) | 76.894 | 127.799 | 50 | MUC |
| Station 23 (two cores) | 76.171 | 129.333 | 54 | MUC+RUM |
| Station 24 | 75.599 | 129.558 | 44 | RUM |

2 Aim

The aim for this report is to acquire more knowledge and a better understanding of the mineralization of organic matter and carbon fluxes in the sediment on the ESAS in the Laptev Sea. By investigating sediment pore water concentrations of DIC and sulfate, degradation of OM can be detected. A one-dimension modelling approach, using the DIC and sulfate concentration depth profiles is used to understand the production and consumption rates and the fluxes. Stable carbon isotope analysis is used to trace processes and sources of OC. By tracing the OC undergoing mineralization in the sediment, the hypothesis is that terrestrial OM is degraded and behaves non-conservatively on the ESAS.

As methane is believed to have an important impact on the carbon fluxes in the ESAS, concentration profiles of methane were used in addition to the DIC, sulfate and $\delta^{13}\text{C}_{\text{DIC}}$ data. Thereby, the appearance of methane and processes involved could be investigated and identified.

3 Methods

All samples analysed and used for this study were collected during the SWERUS-C3 leg 1 expedition, summer 2014. The cores from station 1, 4, 6, 13, 14 cast 3, 14 cast 4, 23 MUC, 23 Rum and 24 were analysed for chloride, sulfate, DIC, methane, porosity and stable carbon isotopes using a variety of methods (see station location in Figure 1 and Table 1).

3.1 Sampling and preservation

According to SWERUS-C3 leg 1 Cruise Report (Gustafsson et al., 2014) sediment cores were collected with a multicorer (MUC) and a Rumohr corer (RUM). The MUC consisted of 8 polycarbonate core liners, 60 cm long and 10 cm in diameter. The 500 kg MUC, made by the German brand Oktopus GmbH, was lowered towards the seabed at a speed of 0.5 m/s and left in the sediment for one minute before extraction. This sampling

method was used to recover sediment cores with an undisturbed sediment-water interface. The RUM corer consisted of one 180 cm long and 6 cm in diameter polycarbonate core liner, with a total weight of about 100 kg.

The polycarbonate core liners were prepared with drill holes sealed with electric tape. Holes with a diameter of 0.9 cm in 2 cm interval were predrilled for the methane analysis. Syringes (3 ml) with the top cut off was used to extract 2.5 ml of sediment and bottom water samples. The sampling was done within 20 minutes and the preservation (Table 2) of the subsamples had to be done quickly when handling samples being analysed for gases.

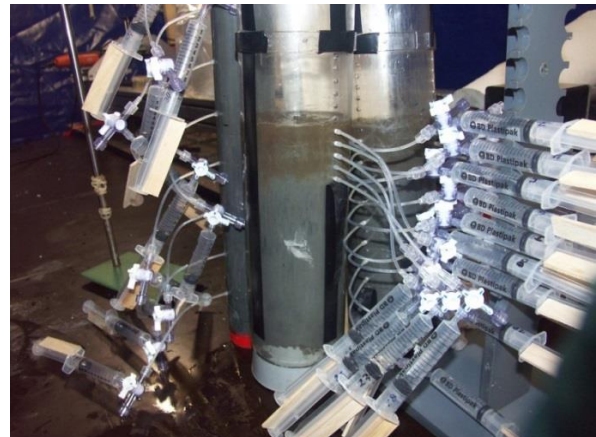


Figure 2. Extraction of pore water, using Rhizone sampling method on-board Oden 2014 (Gustafsson et al., 2014).

The core liners used for the pore water sampling was predrilled with two rows of 4 mm holes with 1 cm intervals. The rows had a 90-degree angle to each other. Samples of 10 ml pore water were extracted from the sediment core using Rhizone (0.2 μm pore filter) sampling approach described in Seeberg-Elverfelt et al. (2005) (Figure 2). First a sample was taken from the sediment-water interface with a Rhizone inserted just above the sediment surface and drawn out with a syringe (10 ml). The remaining bottom water was removed before the same approach was repeated with a 1 cm resolution in the top 5 cm and every 2 cm for the rest of the core. A lower depth resolution was used for the RUM cores, samples was taken every 5 cm. A three-way stopcock was used between the Rhizone and the syringe. After the pore water was extracted with the syringe, through the Rhizone, the state of the stopcock was changed to open between the syringe and the third (middle) outlet. This third outlet was connected to a syringe tip, from which a precise volume of pore water was pipetted (Brüchert, 2015). The pore water had to be preserved. Depending on the following analysis, different preservation methods were used (Table 2). The sampling syringes and stopcocks were acid washed with HCL and reused (Brüchert, 2015).

Table 2. Subsample preservation methods.

| Type of analysis | Preservation |
|-------------------------------|--|
| Metals | 1000 μl pore water with 50 μl 10% HCL, stored cool. |
| DIC | 1800 μl pore water without headspace, stored cool. |
| SO ₄ ²⁻ | 1000 μl pore water with 200 μl 5% Zink Acetate, stored frozen. |
| Methane | 2.5 ml sediment or bottom water with 5 ml 5 M NaCl in 20 ml serum vials sealed with rubber stoppers. |

3.2 Sulfate and chloride quantification by Ion-Chromatography

The samples were first diluted 50 times (Eq. 7).

$$100 \mu\text{l (sample)} + 4900 \mu\text{l (MQwater)} = 650 \mu\text{l (sample with df * 50)} \quad (\text{Eq. 7})$$

The sample with a dilution factor (df) * 50 was diluted additional 10 times (Equation 8) in the polypropylene vial designed for the auto sampler used, resulting in a total dilution factor of 500.

$$65 \mu\text{l (sample df * 50)} + 585 \mu\text{l (MQwater)} = 650 \mu\text{l (sample df * 500)} \quad (\text{Eq. 8})$$

The sample and the MQ-water were thoroughly mixed after each dilution step. The vials were sealed with filter caps. The pore water samples were analysed with an IC20 from Dionex (connected to an autosampler) in January and February 2015, at the Department of Environmental Science and Analytical Chemistry, Stockholm University.

The filter cap was pressed down in the vial prior to the sampling to filter out particles. Some of the sample was used to rinse the system before 10 μl was injected through the loop. The sample and the eluent (4.5 mM Na_2CO_3 /1.4 mM NaHCO_3) had a flow rate of 1.2 ml/minute. First the sample reaches the pre column where it is “cleansed” before entering the IonPac AS22, 4 \times 250 mm column. An AERS 500 Suppressor was used to remove background signal and noise, thereby improve the detection (Thermo Scientific, 2013). The ions were measured with a conductivity detector. The conductivity quantifies the ions and the retention time define the elements. The detection limit for sulfate was 0.25 mg/l = 0.0026 mM for the analysis. Note that the samples had a dilution factor of 500. A standard curve was made, according to the Swedish Standard Institute (2009), for this analysis specifically (Appendix 1). The peak areas were integrated in Dionex Chromeleon software and calibrated with the standard curve. During the analyses of the pore water samples, standard controls were made in the beginning and in the end of each analysis, approximately every 20th sample. The statistics from the method based on the standard controls are presented in Table 3.

Table 3. Statistic data from the IC analysis method, based on standard controls. Concentrations are presented in two ways to easier relate to the results.

| Standard | Chloride | | | | Sulfate | | | |
|--|---------------|-------------|-----------------|---------------|----------------------------|--------------------------|------------------------------|----------------------------|
| | IKH Cl (mg/l) | IKH Cl (mM) | IKH/4 Cl (mg/l) | IKH/4 Cl (mM) | IKH SO ₄ (mg/l) | IKH SO ₄ (mM) | IKH/4 SO ₄ (mg/l) | IKH/4 SO ₄ (mM) |
| True concentration | 12 | 0.338 | 3 | 0.085 | 12 | 0.125 | 3 | 0.031 |
| Mean | 12.23 | 0.345 | 3.31 | 0.093 | 12.43 | 0.129 | 3.09 | 0.032 |
| Standard deviation | 0.17 | 0.005 | 0.09 | 0.003 | 0.27 | 0.003 | 0.10 | 0.001 |
| Absolute error (Mean - True concentration) | 0.23 | 0.007 | 0.31 | 0.009 | 0.43 | 0.004 | 0.09 | 0.001 |
| Error % (Standard dev./Mean \times 100) | 1.42 % | | 2.70 % | | 2.19 % | | 3.29 % | |

3.3 DIC quantification by flow injection analysis

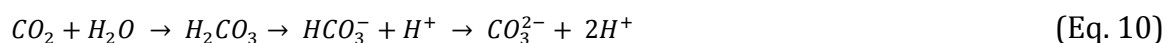


Figure 3. Flow injection analysis (FIA) instruments.

Flow injection analysis (FIA) quantifies dissolved inorganic carbon in water samples by measuring conductivity (Figure 3). The FIA was performed at Stockholm University in February-March. The acidic HCl carrier liquid changes the equilibrium and transforms all DIC to CO_2 , see Equation 9.



In the gas exchange cell, the CO_2 can diffuse through a porous Teflon membrane. On the other side of the membrane the gas is being transferred towards the conductivity detector by the receiving carrier NaOH liquid. The strong base changes the equilibrium in the opposite direction, compared to the strong acid and CO_2 forms carbonate ions (Equation 10). Neutralization of the carrier base follows which leads to a net removal of 2OH^- , resulting in a decrease in conductivity according to Equation 10 and 11.



All samples were analysed twice, 300 μl was injected per analysis. A 100 μl injection loop was used for the analyses of station 1 and 4 and a 50 μl loop was used for the analyses on the remaining stations. The loop volume was decreased to improve the calibration for high concentrations (up to 10 mM). Samples estimated to have concentrations over 10 mM were diluted with MQ-water, which only concerned station 14, cast 3 and 14 cast 4.

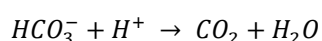
For all analyses made, 20 mM HCl was used as carrier liquid and 5 mM NaOH was used as receiver liquid. The two liquids entered the gas exchange cell (Figure 3) at the same end, and flowed in the same direction through the cell. A flow of approximately 0.6 ml/min of respective liquid was created with a tubing pump by LABINETT. A 0.075 mm Teflon membrane was used in the gas exchange cell.

A COND-158BL conductivity detector, by LAZAR, was connected to a JENCO 3101 amplifier. The signal was digitalized with a 6230N pH/mV/TEMP METER and registered with Demo6230M software on a PC. The peak height was used to calculate the concentration. The NaHCO₃ standards were analysed every day, and new calibration curve was used for the analyses made each day (see Appendix 2-10). Internal standards were analysed every fifth sample, see the statistics in Table 4.

| Flow injection Analyses | |
|---|-----------------------------|
| Standard | NaHCO ₃ 2.5 (mM) |
| True concentration | 2.5 |
| Mean | 2.62 |
| Standard deviation | 0.29 |
| Absolute error (Mean – True concentration) | 0.12 |
| Error % (Standard dev/Mean × 100) | 11.22 % |

3.4 DIC Stable carbon isotope analyses by mass spectrometry

The analysis vials was prepared with 100 µl 85% phosphoric acid (H₃PO₄), sealed with a septum cap and flushed with helium gas (100 ml/min) for five minutes. About 1 ml of pore water was injected to the vial through the septum. The acid moved the equilibrium so all DIC became CO₂ (Equation 12).



(Eq. 12)

The pore water was analysed with a Gasbench II coupled to a MAT 253 mass spectrometer in mars 2015, at the Department of Geological Sciences, Stockholm University. The analyses were performed with an autosampler (Figure 4). The measurement needle entered the vial through the septum. Helium gas, which worked as carrier gas, was injected and sample from the headspace was collected and transported it to the Gasbench II. The sample

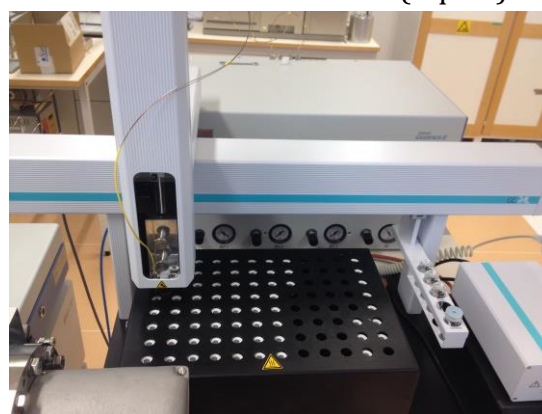


Figure 4. Autosampler used for the stable isotope analyses.

reached the first water trap before the 100 µl loop transferred the sample to the GC column. The sample got heated to 70 ° C by the GC oven and the GC column separates the different gas compounds. The sample goes through the second water trap before reaching the IRMS (Isotope-ratio mass spectrometer). The result is presented in $\delta^{13}\text{C}_{\text{DIC}}$ (‰). The reproducibility for these measurements had a precision higher than 0.1‰ for $\delta^{13}\text{C}$. Three reference gases was used for the calibration; IAEA CO1, IAEA CO8 and NBS 18. Standards were measured twice before the analysis, after every 10th sample and four times in the end. Referencing versus PDB was done according to Equation 13.

$$\delta^{13}\text{C} (\text{‰}) = \left(\frac{R_{\text{Sample}}(^{13}\text{C}/^{12}\text{C})}{R_{\text{Standard}}(^{13}\text{C}/^{12}\text{C})} - 1 \right) \times 1000 \quad (\text{Eq. 13})$$

3.5 Methane quantification by Gas Chromatography

The methane samples were provided by Joanna Sawicka, on-board Oden 2015 using a SRI GC with FID detector (Gustafsson et al., 2014). The vials containing NaCl and sample were homogenized by shaking. 3 ml of NaCl solution was injected through the rubber stopper and 3 ml of the headspace was extracted. The sample was injected into a 1 ml loop. N₂ was used as carrier gas in the GC where a 3 m Hayes Sep N column was used. The measurements were calibrated to the peak area of standards; 100 ppm, 1000 ppm and 1 %.

3.6 Porosity analysis

The porosity calculations were based on the bulk density of the sediment cores for each station. Measurements with a MSCL (Multi-Sensor Core Logger produced by Geotek, UK) were performed by Tommaso Tesi, on-board Oden 2014 (Brüchert, 2015). The core was placed horizontally in the MSCL-racks, to achieve a position that is centred in relation to the sensor. A Cesium¹³⁷ source emitted a gamma ray beam with energy at 0.662 MeV (Gustafsson et al., 2014). A detector receives the photon beam on the opposite side of the core. The photon scatter and energy loss is directly related to the core thickness and the electron density. The porosity in subsea sediment is equal to the water content and calculated according to Equation 14. Bulk density was based on the measured number of transmitted gamma photons that passes through a core with a known thickness, using a MSCL. The water density of 1.027 g/cm³, was based on the salinity and temperature and the sediment density of 2.5 g/cm³, was based on the grain size (Brüchert, 2015).

$$\text{Water content} = \frac{\text{Bulk density} - \text{Sediment density}}{\text{Water density} - \text{Sediment density}} \quad (\text{Eq. 14})$$

3.7 Production rate and flux modelling

3.7.1 PROFILE modelling

The sulfate reduction and DIC production was calculated using PROFILE, a one-dimensional numerical modelling software presented by Berg et al. (1998). The production and flux interpretations assumes steady state conditions and account for the effects of molecular diffusion, bioturbation and irrigation (Equation 15).

$$\frac{d}{dx} \left(\varphi(D_S + D_B) \frac{dC}{dx} \right) + \varphi\alpha(C_0 - C) + R = 0 \quad (\text{Eq. 15})$$

| | |
|----------------|--|
| C | = pore water concentration |
| C ₀ | = bottom water concentration |
| x | = depth |
| φ | = porosity |
| D _S | = molecular diffusion in the sediment (corrected for tortuosity) |
| D _B | = biodiffusivity |
| α | = irrigation coefficient |
| R | = production (or consumption if negative value) |

For this modelling experiment the bioturbation and irrigation was neglected due to lack of significant data. Therefore, the vertical transport was based on molecular diffusion only. The production is based on finding the least square fit of the concentration profile. The model divides the depth profile into equally shared zones with a constant production in each zone. The numbers of zones are based on F-statistics to find the simplest production profile. The statistical valuation is done in two steps. First the lowest number of equally spaced zones is identified. Then the zones may be combined, if possible without reducing the quality of the fit. See Table 5 for the parameters used for the modelling. For additional settings, such as depth, porosity and concentrations see Appendix 11-33.

| | |
|---------------------------|--|
| Boundary condition | First BC: concentration at top, concentration at bottom |
| D ₀ | D _{Sulfate} : 4,64 × 10 ⁻⁶ cm ² s ⁻¹ D _{DIC} : 5.00 × 10 ⁻⁶ cm ² s ⁻¹ |
| D _S definition | $D_S = D_0 / (1 + 3(1 - \varphi))$ |

The D_{sulfate} was based on calculations performed by Boudreau (1997) cited in Schulz and Zabel (2000) and accounts for in situ temperatures of 0 °C (Gustafsson et al., 2014). The D_{DIC} was achieved by carbonate-equilibrium calculation (Table 6) using excel scheme based on in situ pH 7,5, temperature around 0°C and salinity 34.9‰ (Brüchert, 2015).

Table 6. Diffusion factors and molar fraction used for the calculation of DIC diffusion factor.

| | Diffusion factor at 0°C | Molar fraction at pH 7.5 |
|-------------------------------|-------------------------|--------------------------|
| HCO ₃ ⁻ | 4,81E-06 | 0,95 |
| CO ₂ | 8,38E-06 | 0,05 |
| CO ₃ ²⁻ | 4,12E-06 | 0,00 |
| Total DIC | 5,00E-06 | 1,00 |

3.7.2 Fluxes determined by Fick's first law of diffusion

The sulfate and DIC fluxes were calculated using a second approach, Fick's first law of diffusion (Equation 16). Diffusion only occur within the pore space and tortuosity (θ) must be accounted for (Equation 17-19). The ϕ used is the mean porosity for each station. The dC/dx gradient was calculated by linear regression, least squared fit of the concentration depth profile. D_0 for sulfate and DIC was the same value that was used for the PROFILE modelling (Table 5 and 6).

$$J = -D_0 \frac{dC}{dx} \quad (\text{Eq. 16})$$

$$J_{sed} = -\phi D_{sed} \frac{dC}{dx} \quad (\text{Eq. 17})$$

$$D_{sed} = D_0 / \theta^2 \quad (\text{Eq. 18})$$

$$\theta^2 = 1 - \ln(\phi^2) \quad (\text{Eq. 19})$$

Rework and summarized equation used for the fluxes in sediment, see Equation 20.

$$J_{sed} = -\phi_{mean} \left(\frac{D_0}{\theta^2} \right) \left(\frac{dC}{dx} \right) \quad (\text{Eq. 20})$$

4 Results

4.1 Pore water profiles

The results from the pore water and methane analyses are shown in depth profiles for each station in Figure 5-13. DIC are presented as a concentration and as stable carbon isotope data, $\delta^{13}\text{C}_{\text{DIC}}$. Sulfate concentrations are presented in two ways; the measured concentration and the concentration compensated for sampling and dilution errors by normalizing with the mean chloride concentration. Note that the methane values are lower compared to the DIC and sulfate concentrations and thus displayed in nM with varied intervals.

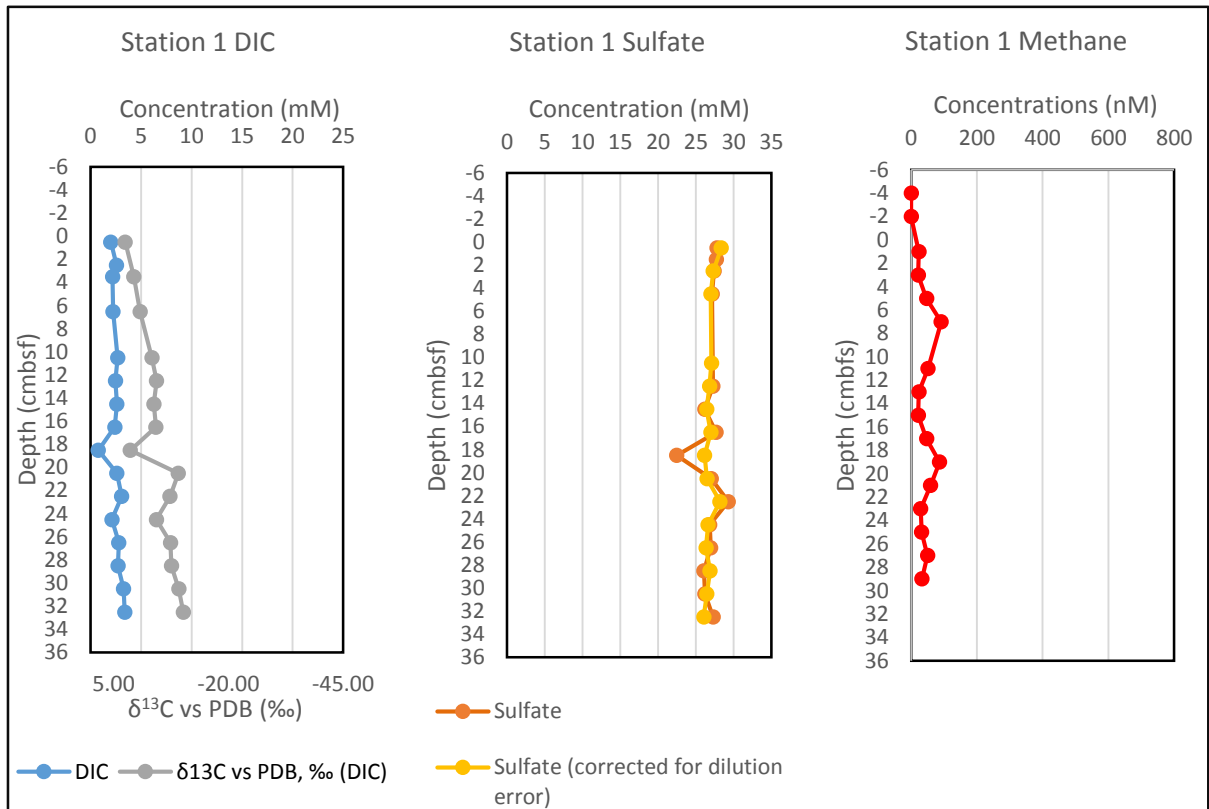


Figure 6. Pore water; DIC concentration, $\delta^{13}\text{C}_{\text{DIC}}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

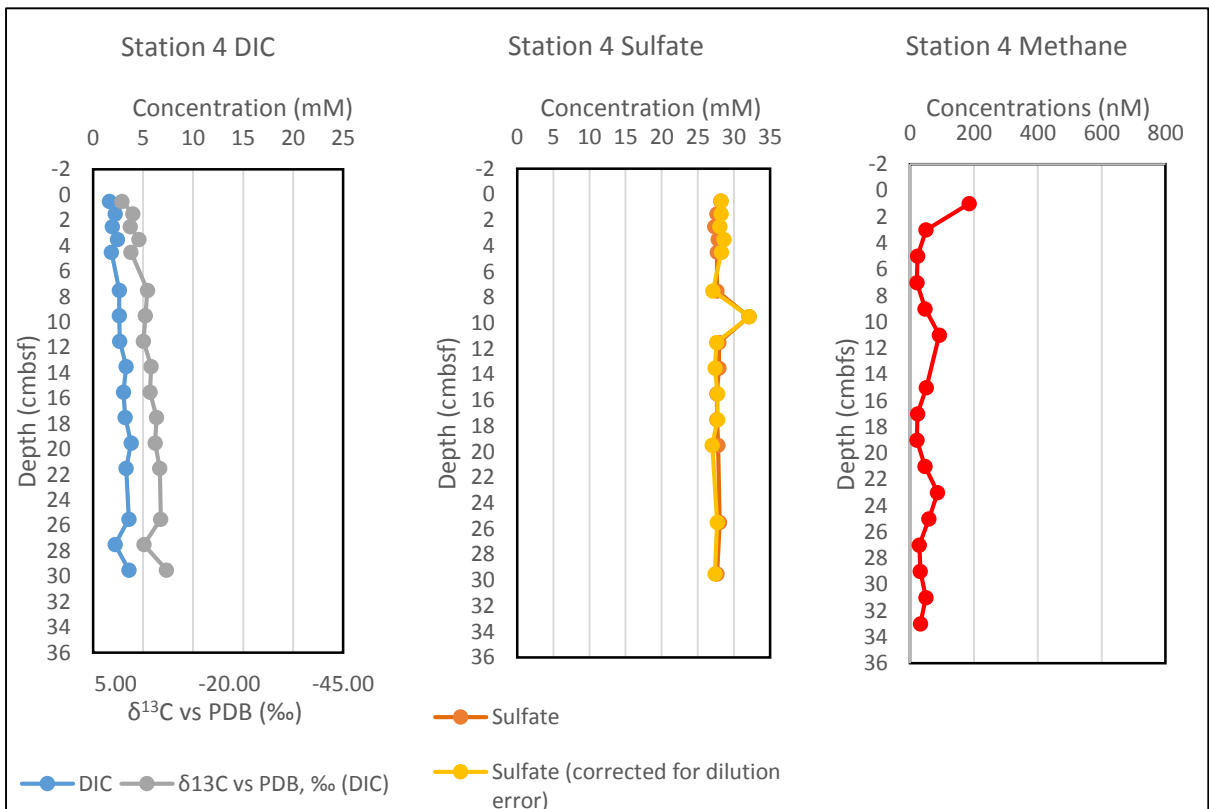


Figure 5. Pore water; DIC concentration, $\delta^{13}\text{C}_{\text{DIC}}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

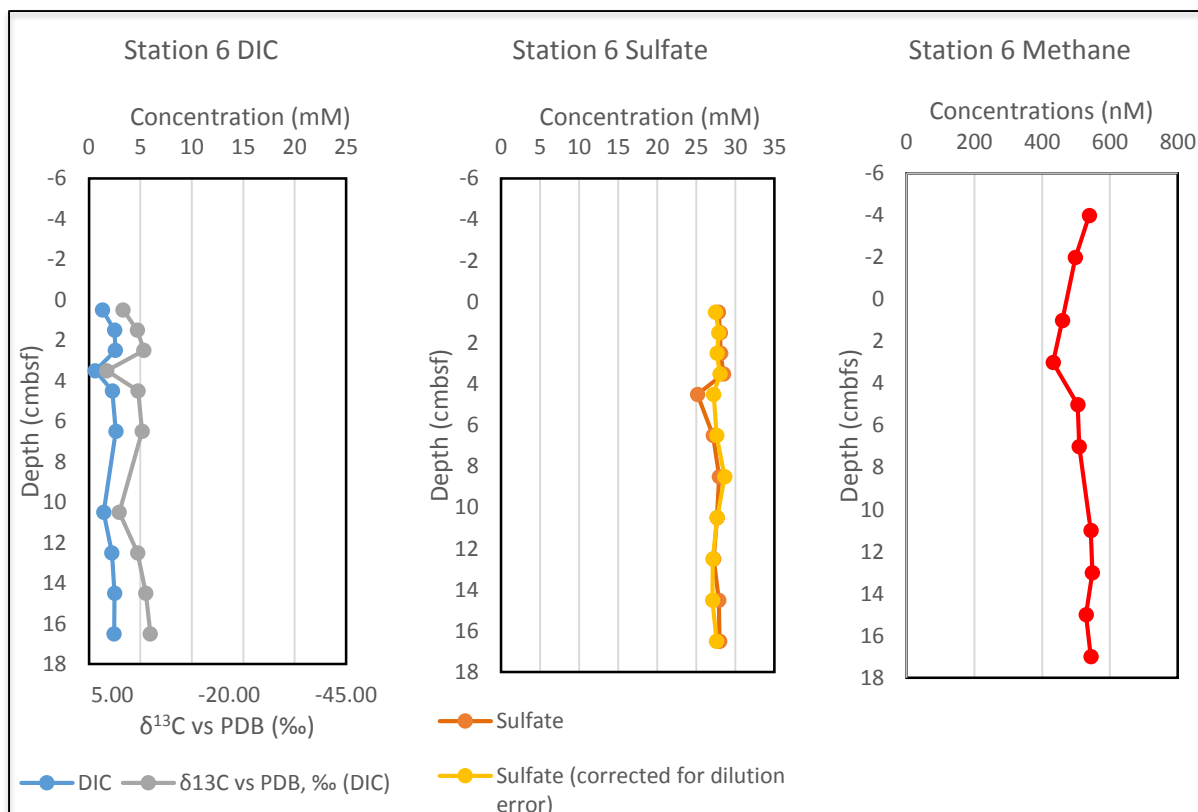


Figure 8. Pore water; DIC concentration, $\delta^{13}C_{DIC}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

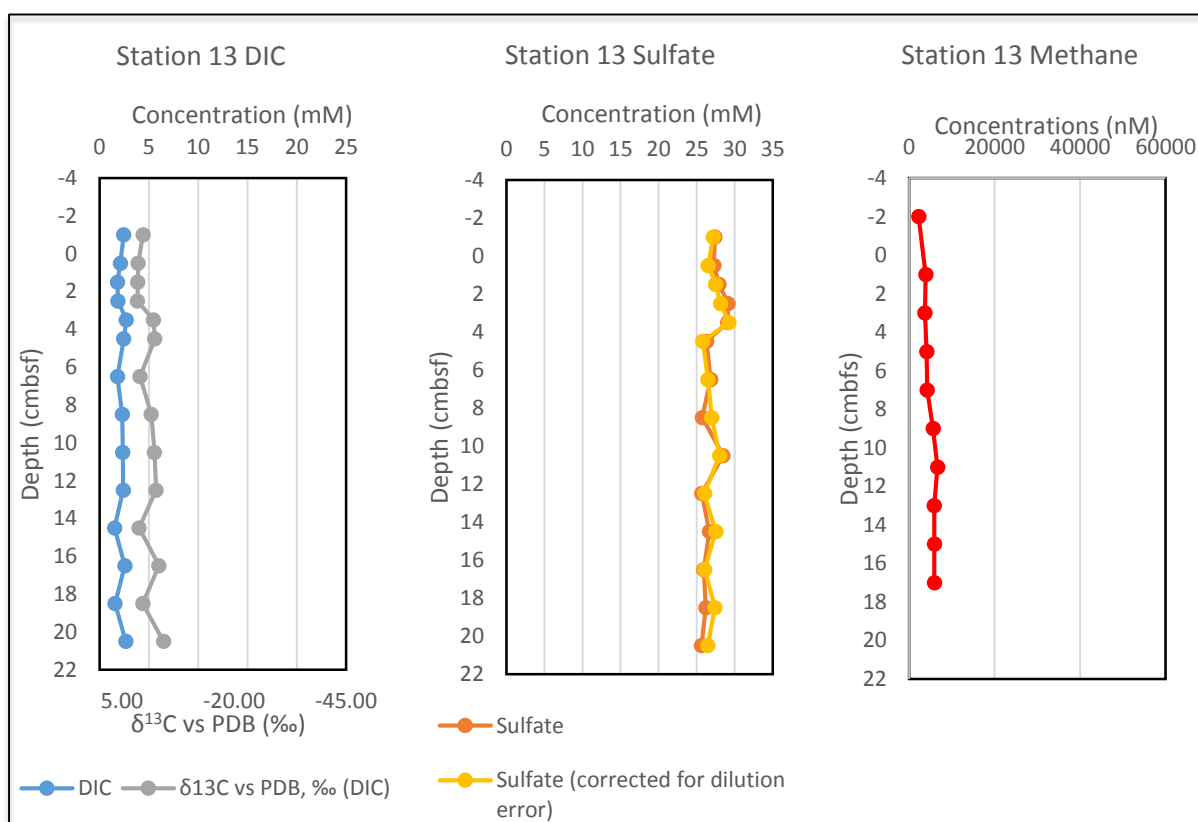


Figure 7. Pore water; DIC concentration, $\delta^{13}C_{DIC}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

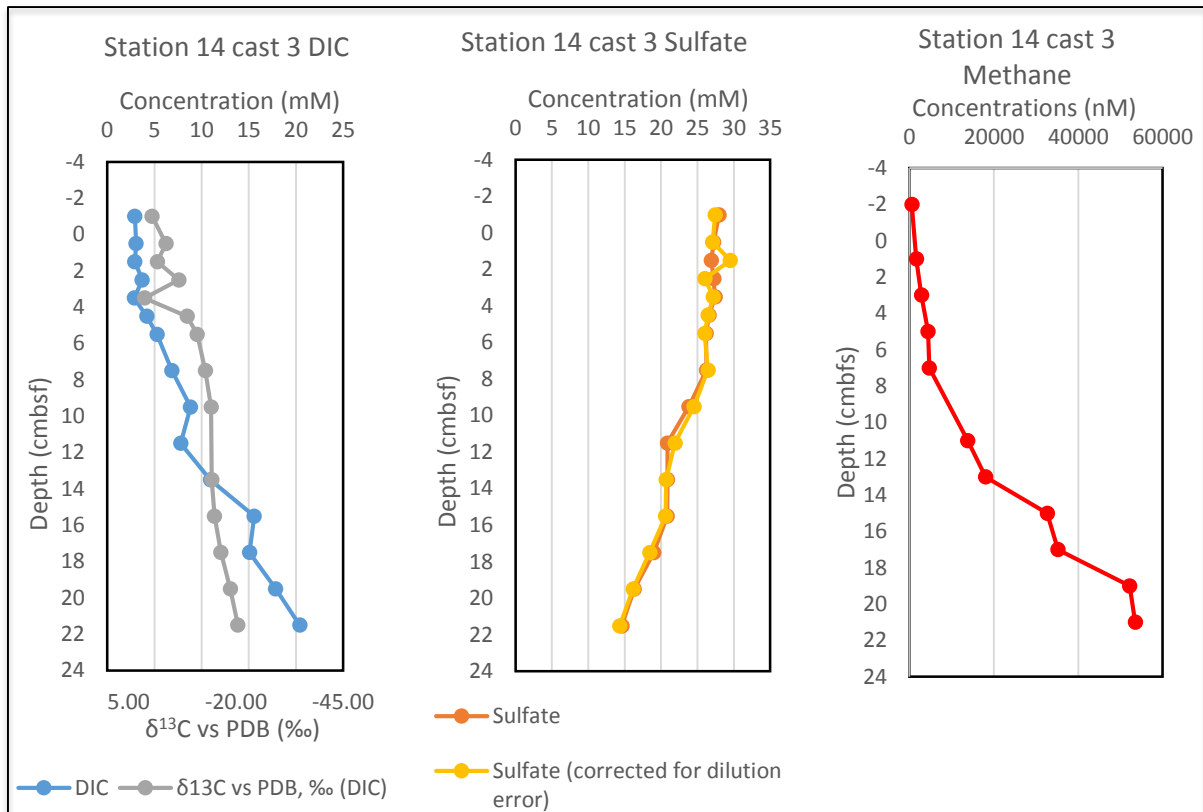


Figure 10. Pore water; DIC concentration, $\delta^{13}\text{C}_{\text{DIC}}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

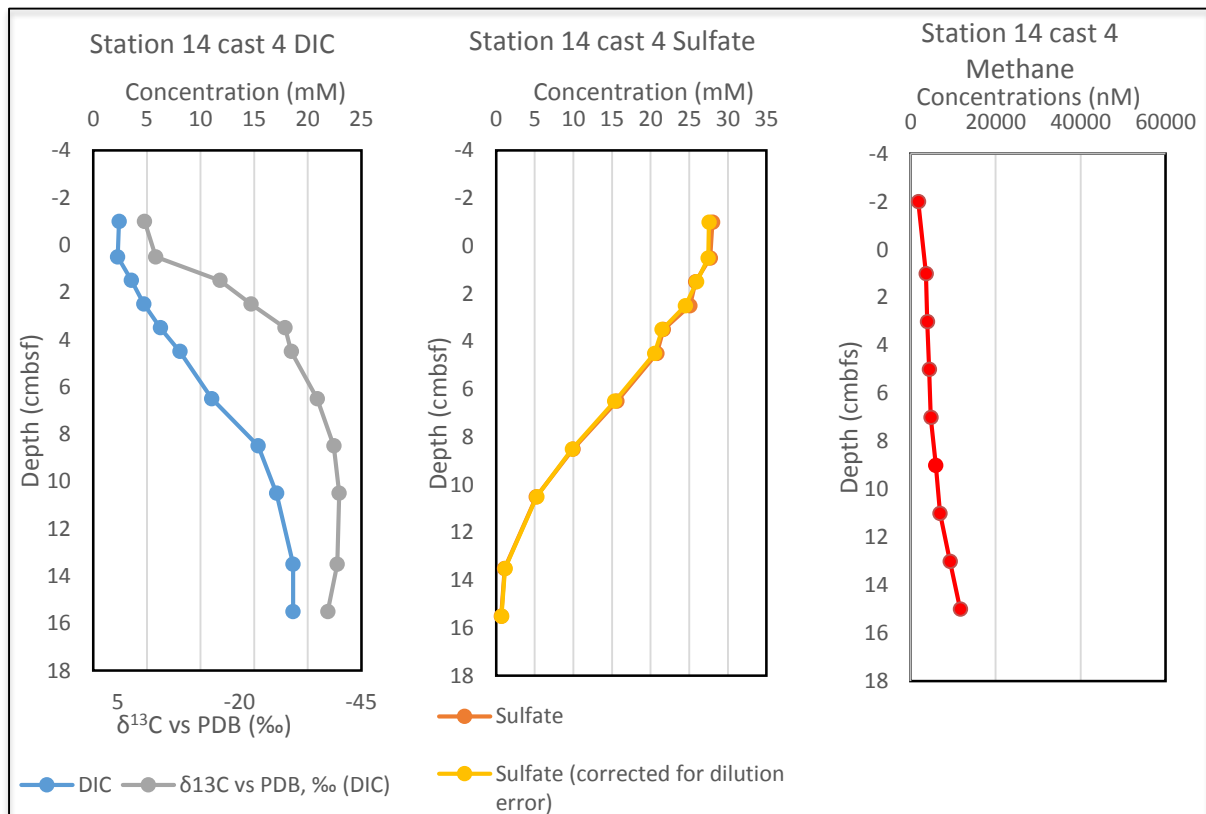


Figure 9. Pore water; DIC concentration, $\delta^{13}\text{C}_{\text{DIC}}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

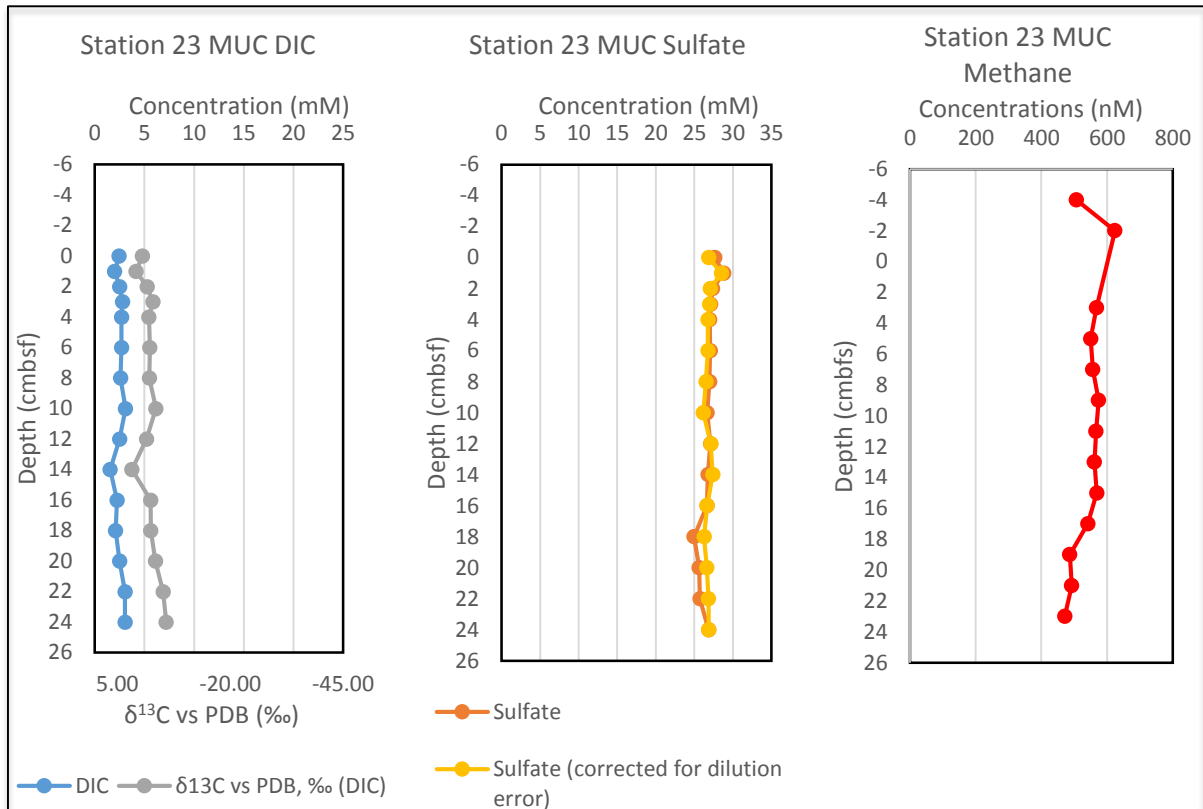


Figure 12. Pore water; DIC concentration, $\delta^{13}C_{DIC}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

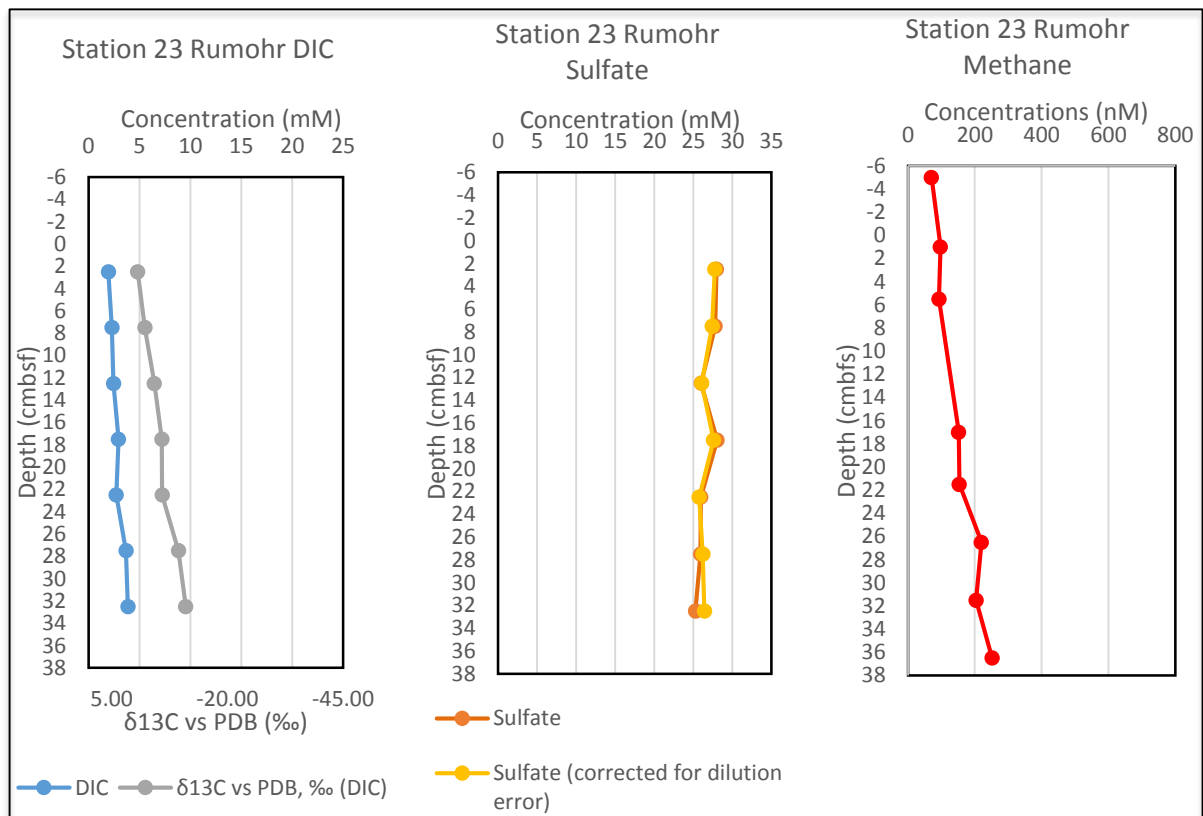


Figure 11. Pore water; DIC concentration, $\delta^{13}C_{DIC}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

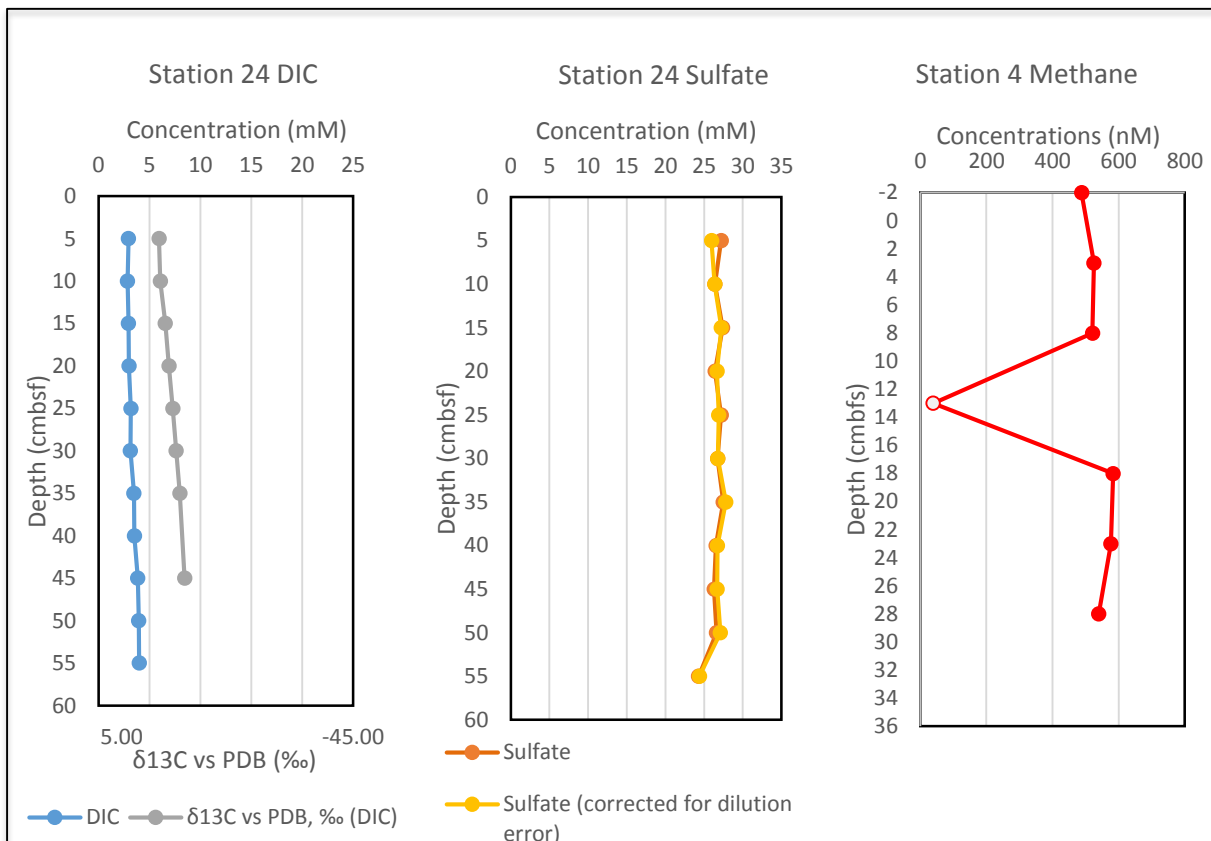


Figure 13. Pore water; DIC concentration, $\delta^{13}C_{DIC}$, sulfate concentration (shown in two ways, one with measured values and one with values corrected with chloride concentrations to avoid sampling and dilution errors) and methane concentration.

In all stations, except 14 cast 3 and 14 cast 4, a similar trend and change in concentrations and in DIC $\delta^{13}C$ value can be seen. There is a weak decrease of sulfate and a weak increase of DIC with depth. From concentrations around 2-2.3 mM, at the sediment surface, there is an increase of approximately 0.5-2 mM within the first 15-30 cm of the sediment. The sulfate concentrations decrease 0-2 mM within the same sediment interval, from around 28 mM at the sediment top. The DIC $\delta^{13}C$ value decreased with 4-11 ‰ from approximately 2.7 – -11 ‰ at the sediment top or sediment water interface.

The sulfate and DIC concentrations and the $\delta^{13}C$ value at station 14 cast 3 and 14 cast 4 change with a stronger gradient. At station 14 cast 3 the sulfate concentrations decrease by approximately 13 mM within the top 21.5 cm, from 27.4 mM at the sediment water interface. The DIC concentration at station 14 cast 3 increases by approximately 17 mM from 2.9 mM at the sediment water interface. The $\delta^{13}C_{DIC}$ value decreased by 20 ‰ from -0.45 ‰ at the sediment water interface. At station 14 cast 4 the sulfate almost gets depleted (0.7 mM at the deepest pore water sample) within the top 15.5 cm from 27.6 mM at the sediment water interface. The DIC concentration at station 14 cast 4 increases with approximately 16 mM from 2.4 mM at the sediment water interface. At station 14 cast 4 the $\delta^{13}C_{DIC}$ values decrease by approximately 37.5 ‰ from 0.4 ‰ at the sediment water interface, which is the largest decrease seen in the pore water analysed from all stations.

The methane concentrations were low, $< 1 \mu\text{M}$, in most of the stations excluding station 13, 14 cast 3 and 14 cast 4. No significant change in methane concentration with depth can be seen in station 2, 4, 6, 23 MUC and 24. Station 23 Rumohr shows a very weak increase of methane with depth, from 70 nM to 252 nM. Station 13 shows a weak methane increase with depth, from approximately 2000 nM to 5000 nM. At station 14 cast 4 the methane concentration change from 1800 nM to 11700 nM with depth. Station 14 cast 3 shows the highest methane concentrations and also the greatest change, which increases from 600 nM to 53500 nM with depth.

4.2 Stoichiometric ratio, $r_{c:s}$

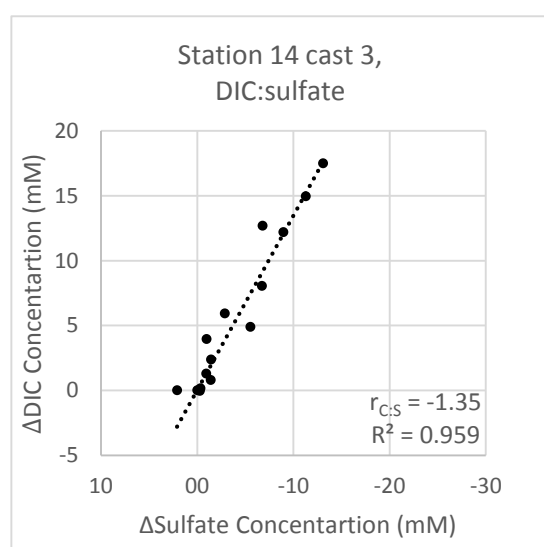


Figure 14. Station 14 cast 3 pore water property-property plots of Δ sulfate concentrations and Δ DIC concentrations, both relative to the bottom water concentration. A best linear fit is used to calculate the stoichiometric DIC:sulfate ration ($r_{c:s}$).

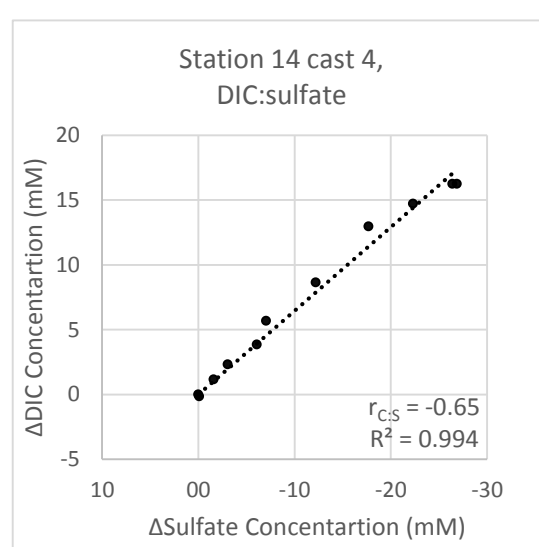


Figure 15. Station 14 cast 4 pore water property-property plots of Δ sulfate concentrations and Δ DIC concentrations, both relative to the bottom water concentration. A best linear fit is used to calculate the stoichiometric DIC:sulfate ration ($r_{c:s}$).

The relation between the change in sulfate concentration and the change in DIC concentration is shown in a scatter property-property plot, see Figure 14 for station 14 cast 3 and Figure 15 for 14 cast 4. The Δ concentration values were calculated relative to the bottom water concentrations. A best linear fit was used to calculate the $r_{c:s}$ value, which represents the DIC:sulfate stoichiometric ratio. For station 14 cast 3 the $r_{c:s}$ is 1.35 and the $r_{c:s}$ for station 14 cast 4 is 0.65. Both stations have $r_{c:s}$ values < 2 . The gradient of the change in concentration were too low to determine a statistically significant linear relation of the Δ concentrations for the remaining stations.

4.3 Fluxes determined by Fick's law of diffusion

The fluxes calculated with Fick's first law of diffusion are shown in table 7. The DIC results show upward fluxes between $-0.03 - 0.16 \text{ mmol m}^{-2} \text{ day}^{-1}$ for station 1, 4, 6, 13, 23 RUM and 24. The sulfate fluxes at the same stations vary from -0.02 to $0.14 \text{ mmol m}^{-2} \text{ day}^{-1}$. Station 23 MUC fluxes were slightly higher, $-0.35 \text{ mmol m}^{-2} \text{ day}^{-1}$ for DIC and 0.23 for sulfate. The highest fluxes were determined at station 14 cast 3 with DIC flux of $-1.65 \text{ mmol m}^{-2} \text{ day}^{-1}$ and sulfate flux of $1.12 \text{ mmol m}^{-2} \text{ day}^{-1}$ and at station 14 cast 4 with a DIC flux of $-1.75 \text{ mmol m}^{-2} \text{ day}^{-1}$ and sulfate flux of $3.06 \text{ mmol m}^{-2} \text{ day}^{-1}$. $rc:s$ ratios were calculated from these fluxes, compensating for differences in diffusion coefficient. All stations except station 6 had $rc:s$ values less than 2. Station 14 cast 4 had the lowest $rc:s$ value, 0.62.

Table 7. DIC and sulfate fluxes in sediment for all stations, calculated with Fick's first law of diffusion and the DIC sulfate ratio based on the fluxes are presented in this table. The porosity and gradient used for the calculation is shown.

| Station | Porosity (ϕ) | Gradient nmolcm ⁻⁴ | Flux | | Ratio |
|---------------|---------------------|----------------------------------|--|--|-------------|
| | | | DIC | Sulfate | DIC:Sulfate |
| | | | mmol m ⁻² day ⁻¹ | mmol m ⁻² day ⁻¹ | |
| 1 | 0.66 | -56.06 | -0.08 | 0.08 | -1.10 |
| 4 | 0.72 | -80.49 | -0.15 | 0.14 | -1.18 |
| 6 | 0.48 | -90.13 | -0.16 | 0.07 | -2.51 |
| 13 | 0.65 | -32.91 | -0.05 | 0.05 | -1.15 |
| 14.3 | 0.5 | -1333.39 | -1.65 | 1.12 | -1.58 |
| 14.4 | 0.54 | -3155.78 | -1.75 | 3.06 | -0.62 |
| 23 muc | 0.49 | -282.58 | -0.35 | 0.23 | -1.64 |
| 23 rum | 0.55 | -90.00 | -0.07 | 0.09 | -0.88 |
| 24 | 0.56 | 18.08 | -0.03 | -0.02 | 1.88 |

4.4 PROFILE modelling results

The result derived from the production and fluxes model calculations of DIC and sulfate using PROFILE, according to the method approach of Berg et al. (1998), are shown in figure 16-24 and summarized in table 8. Negative production rate values are consumption rates. Positive fluxes have a downward direction and negative fluxes have an upward direction. For input files and log files for all stations see Appendix 11-33.

Table 8. DIC and sulfate production and fluxes in the ESAS sediment, Laptev Sea. The production is integrated with depth and shown for all zones and each zone separate, for all station. Negative production represent a consumption. Positive fluxes are downward and negative fluxes in upward.

| Station | DIC | | | | | | Sulfate | | | | | |
|----------------------|--|--------|---|--------|--------|----------------|--|--------|---|--------|--------|----------------|
| | Flux (mmol m ⁻² day ⁻¹) | | Depth integrated Production (mmol m ⁻² day ⁻¹) | | | R ² | Flux (mmol m ⁻² day ⁻¹) | | Depth integrated Production (mmol m ⁻² day ⁻¹) | | | R ² |
| | Top | Bottom | All Zones | Zone 1 | Zone 2 | | Top | Bottom | All Zones | Zone 1 | Zone 2 | |
| 1 (a) | -0.05 | -0.07 | -0.02 | -0.02 | | 0.63 | 0.50 | 0.24 | -0.25 | -0.66 | 0.41 | 0.34 |
| 1 (b) | | | | | | | 0.17 | 0.03 | -0.13 | -0.13 | | -0.20 |
| 4 | -0.23 | 0.02 | 0.25 | 0.25 | | 0.89 | 0.12 | -0.02 | -0.15 | -0.15 | | 0.52 |
| 6 (a) | -0.16 | 0.07 | 0.23 | 0.23 | | -0.99 | -0.09 | 0.09 | 0.19 | 0.19 | | 0.07 |
| 6 (b) | 0.02 | -0.01 | -0.03 | -0.03 | | 0.10 | | | | | | |
| 13 | -0.04 | -0.03 | 0.01 | 0.01 | | 0.63 | -0.20 | 0.16 | 0.36 | 0.36 | | -0.15 |
| 14 cast 3 (a) | -0.44 | -0.80 | -0.36 | -0.36 | | 0.97 | 0.22 | 0.60 | 0.38 | 0.38 | | 0.96 |
| 14 cast 3 (b) | | | | | | | 0.40 | 0.40 | 0.00 | 0.00 | | 0.92 |
| 14 cast 4 (a) | -1.46 | 0.43 | 1.88 | -0.40 | 2.29 | 1.00 | 1.45 | -0.29 | -1.75 | 0.17 | -1.92 | 1.00 |
| 14 cast 4 (b) | -1.63 | 0.51 | 2.14 | 0.01 | 2.12 | 1.00 | 2.17 | -0.05 | -2.22 | 0.00 | -2.22 | 1.00 |
| 23 MUC | -0.01 | -0.03 | -0.03 | -0.03 | | 0.42 | 0.02 | -0.02 | -0.04 | -0.04 | | 0.00 |
| 23 RUM | -0.05 | -0.05 | 0.00 | 0.00 | | 0.92 | 0.11 | -0.03 | -0.15 | -0.15 | | 0.48 |
| 24 | 0.01 | -0.01 | -0.03 | -0.05 | 0.02 | 0.97 | 0.03 | -0.02 | -0.05 | -0.05 | | -0.14 |

For station 1 the PROFILE modelling results show a constant DIC consumption rate of 0.066 nmol cm⁻³ day⁻¹ in the sediment (Figure 16). The flux at the top sediment was calculated to be -0.05 mmol m⁻² day⁻¹. The results of the simulated sulfate production and flux for station 1 (Figure 16) shows a production profile divided in two equally shared zones, with respect to the depth. The first zone is interpreted to have a consumption rate of -4.15 nmol cm⁻³ day⁻¹ and the second zone a production rate of 2.57 nmol cm⁻³ day⁻¹ and a top sediment flux of 0.50 mmol m⁻² day⁻¹. However, a net production of sulfate is not likely to be an interpretation reflecting the system (see discussion). To avoid this high net production an experiment was made where the maximum production was limited to 0, see sulfate b in Figure 16. The second simulation calculated only one zone, based on the F-statistics, with a consumption of -0.42 nmol cm⁻³ day⁻¹ and a top sediment flux of 0.17 mmol m⁻² day⁻¹.

The PROFILE model calculations made for station 4 are shown in figure 17. The DIC depth profile was calculated to have one zone with a production rate of 0.86 nmol cm⁻³

day⁻¹ and a top sediment flux of -0.23 mmol m⁻² day⁻¹. For the sulfate depth profile one zone of consumption was calculated, with a rate of 0.51 nmol cm⁻³ day⁻¹ and a top sediment flux of 0.12 mmol m⁻² day⁻¹.

The results from station 6 show one zone of DIC production with a rate of 1.42 nmol cm⁻³ day⁻¹ and a top sediment flux of -0.16 mmol m⁻² day⁻¹ (Figure 18). The DIC profile was recalculated without the top concentration value included, since that value was lower than the concentrations for seawater with a salinity of 35‰. The sulfate was calculated to have one zone with a production of 0.72 nmol cm⁻³ day⁻¹ and a top sediment flux of -0.09 mmol m⁻² day⁻¹.

Modelling of the data from station 13 gave a calculated DIC consumption rate of -0.007 nmol cm⁻³ day⁻¹ within one zone and a top sediment flux of -0.04 mmol m⁻² day⁻¹ (Figure 19). The sulfate at station 13 was calculated to have one zone with a production of 0.44 nmol cm⁻³ day⁻¹ and a top sediment flux of -0.20 mmol m⁻² day⁻¹ (Figure 19).

The model results for station 14 cast 3 are shown in figure 20. The DIC depth profile was calculated to have one zone with a consumption rate of -1.70 nmol cm⁻³ day⁻¹ and a top sediment flux of -0.44 mmol m⁻² day⁻¹. The sulfate was calculated to have one zone with a production rate of 1.8 nmol cm⁻³ day⁻¹ and a top sediment flux of 0.22 mmol m⁻² day⁻¹. An experimental sulfate simulation was done with the production limit set to 0, the same approach as used with station 1 (Figure 16). The result in the second sulfate simulation for station 14 cast 3 have one zone with a very low consumption rate close to 0 cm⁻³ day⁻¹ and a top sediment flux of 0.40 mmol m⁻² day⁻¹.

Station 14 cast 4 shows the highest production/consumption rates and fluxes of all the stations analysed. For the model simulation of the DIC, there was no statistical suggestion for the number of zones, therefore two simulations were done. The first one was based on two zones and was calculated to have a consumption rate at -6.67 cm⁻³ day⁻¹ within the first zone, a production of 25.39 cm⁻³ day⁻¹, a within the second zone top sediment flux of -1.46 mmol m⁻² day⁻¹. The second simulation was based on five and then combined to two zones and was calculated to have a production rate at 0.17 cm⁻³ day⁻¹ within the first zone, a production of 28.3 cm⁻³ day⁻¹ a within the second zone top sediment flux of -1.63 mmol m⁻² day⁻¹. The sulfate was calculated to have two zones with a production rate of 2,26 nmol cm⁻³ day⁻¹ within the first zone, a consumption rate of 25.56 nmol cm⁻³ day⁻¹ in the second zone and a top sediment flux of 0.45 mmol m⁻² day⁻¹. Due to high production rate within the first zone an experimental sulfate simulation was done with the production limit set to 0, the same approach as used with station 1 and 14 cast 3 (Figure 21). The result in the second sulfate simulation for station 14 cast 4 have two zones with a consumption rate of -5.85 cm⁻³ day⁻¹ within the first zone, a consumption rate of -29.57 within the second zone and a top sediment flux of 2.17 mmol m⁻² day⁻¹.

The results from station 23 MUC show one zone of DIC consumption with a rate of $-0.12 \text{ nmol cm}^{-3} \text{ day}^{-1}$ and a top sediment flux of $-0.01 \text{ mmol m}^{-2} \text{ day}^{-1}$ (Figure 22). The sulfate concentration profile calculated to have one zone with a consumption rate of $-0.15 \text{ nmol cm}^{-3} \text{ day}^{-1}$ and a top sediment flux of $0.02 \text{ mmol m}^{-2} \text{ day}^{-1}$.

Station 23 RUM showed one calculated DIC production zone with a rate of $0.01 \text{ nmol cm}^{-3} \text{ day}^{-1}$ and a top sediment flux of $-0.05 \text{ mmol m}^{-2} \text{ day}^{-1}$ (Figure 23). The sulfate consumption rate at station 23 RUM was calculated to be $-0.49 \text{ nmol cm}^{-3} \text{ day}^{-1}$ and a top sediment flux of $0.11 \text{ mmol m}^{-2} \text{ day}^{-1}$ (Figure 23).

The PROFILE modelling calculations from the DIC profile at station 24 resulted in two zones (Figure 24). The first zone shows a consumption rate $-0.20 \text{ nmol cm}^{-3} \text{ day}^{-1}$, the second zone show a production rate of $0.09 \text{ nmol cm}^{-3} \text{ day}^{-1}$ and a top sediment flux of $0.01 \text{ mmol m}^{-2} \text{ day}^{-1}$. The sulfate was calculated to have one zone with a consumption rate of $-0.10 \text{ nmol cm}^{-3} \text{ day}^{-1}$ and a top sediment flux of $0.03 \text{ mmol m}^{-2} \text{ day}^{-1}$ (Figure 24).

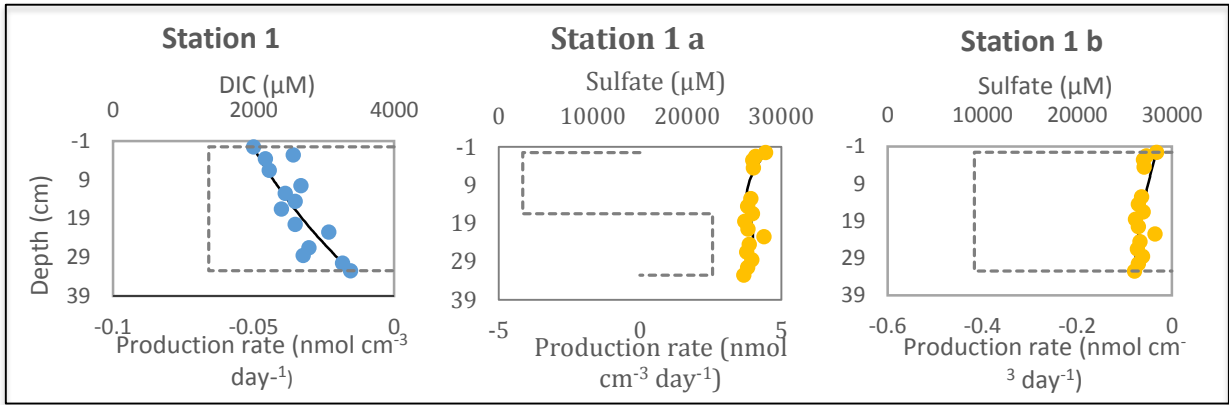


Figure 16. PROFILE modelling results for station 1, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

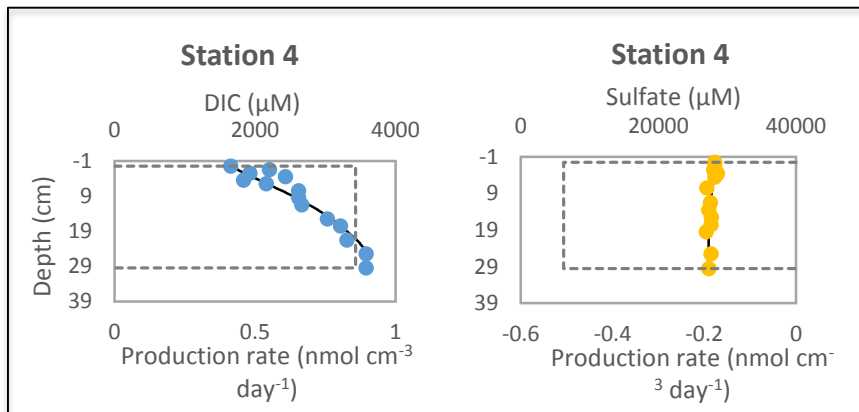


Figure 17. PROFILE modelling results for station 4, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

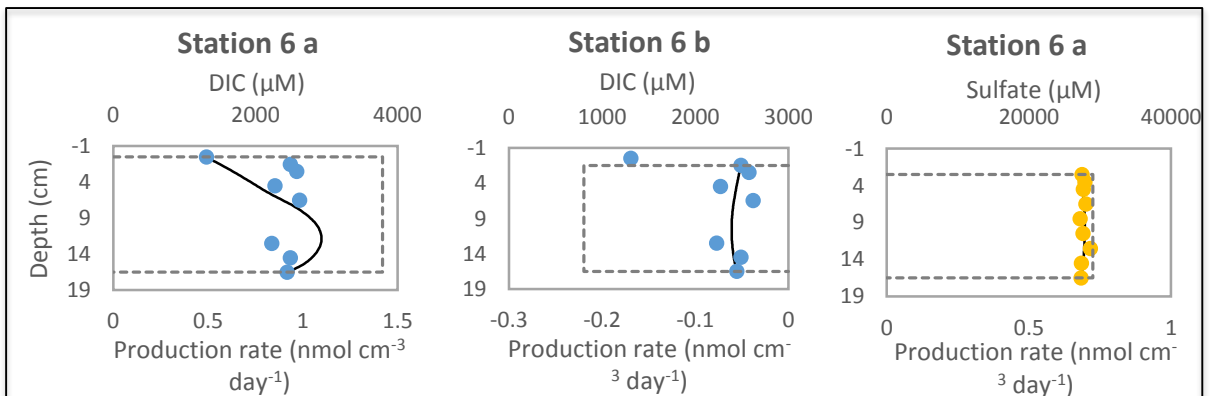


Figure 18. PROFILE modelling results for station 6, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

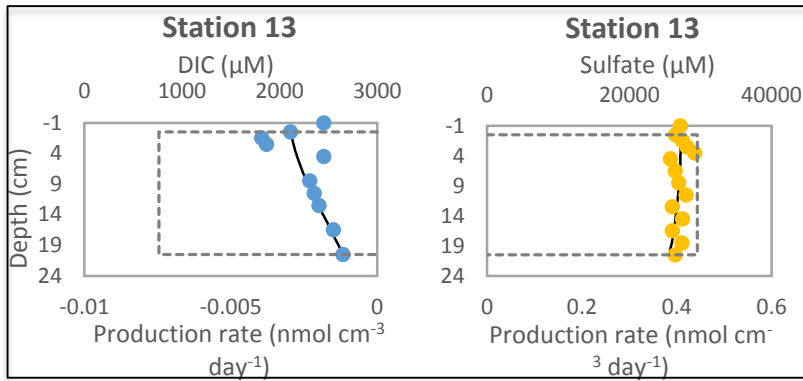


Figure 19. PROFILE modelling results for station 13, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

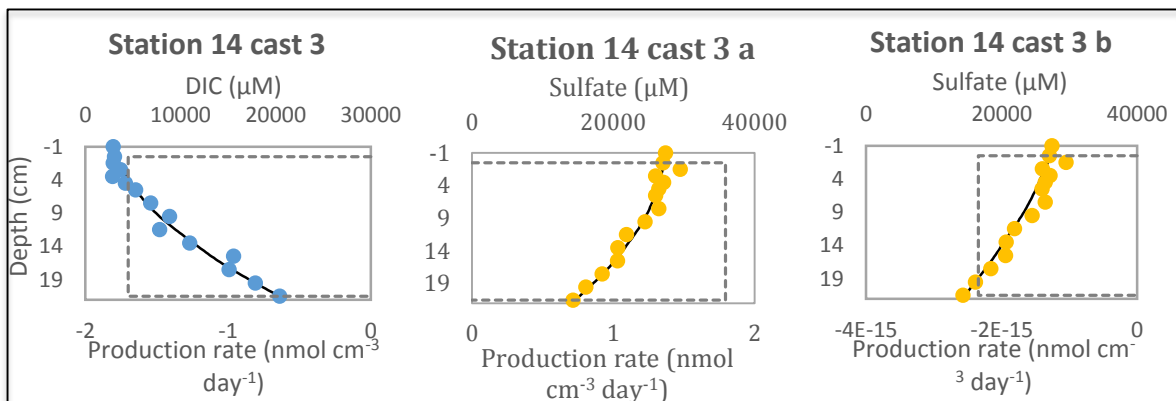


Figure 20. PROFILE modelling results for station 14 cast 3, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

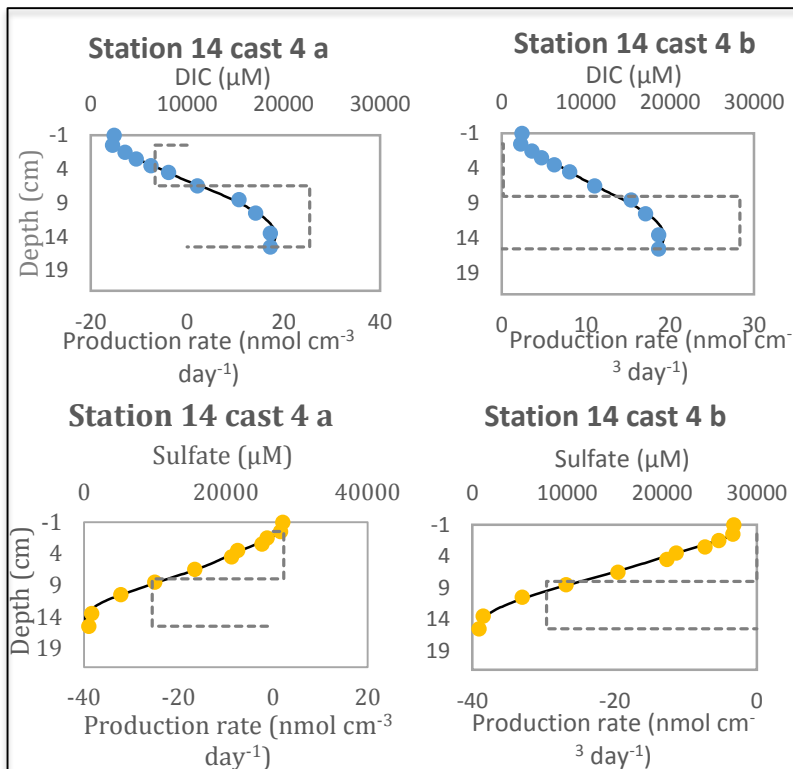


Figure 21. PROFILE modelling results for station 14 cast 4, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

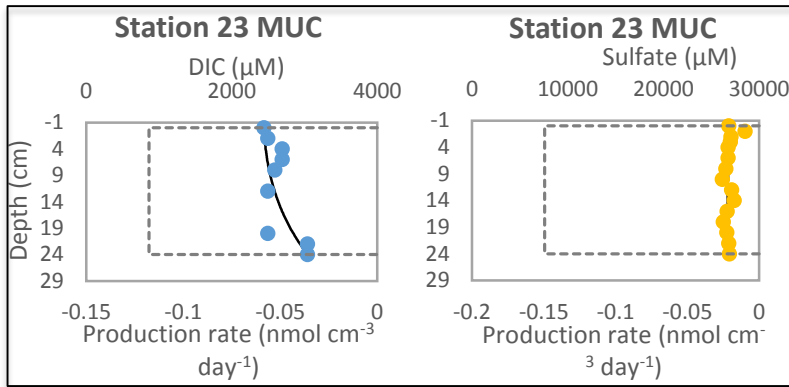


Figure 22 PROFILE modelling results for station 23 MUC, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

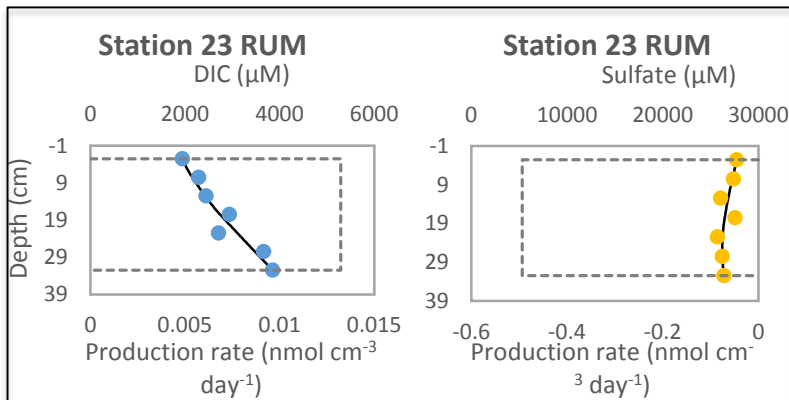


Figure 23. PROFILE modelling results for station 23 RUM, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

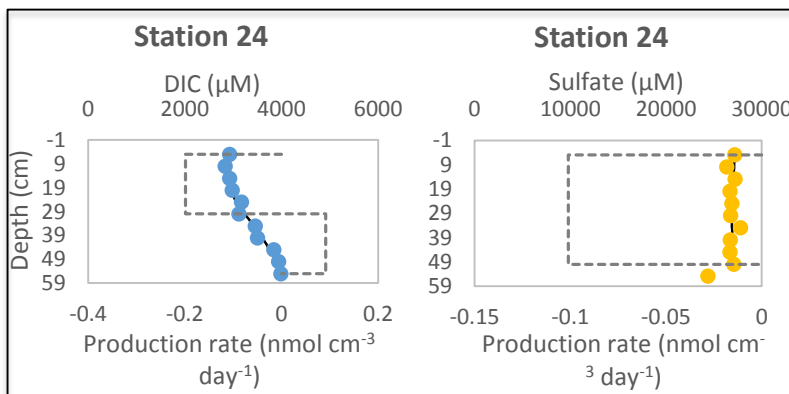


Figure 224. PROFILE modelling results for station 24, based on pore water concentrations. The points are measured concentrations (μM). The dashed line is the production rate, based on the best-fit production profile (black line). Negative production represent consumption of the constituents.

5 Discussion

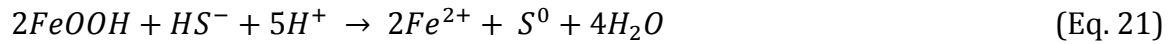
5.1 Pore water analysis

The pore water analyses gave concentration profiles with only a few anomalies. The DIC concentrations at the sediment-water interface correspond well to the concentration in the bottom water at the study area (Alling et al., 2012), which indicates accuracy of the results from the FIA. The same can be done with the sulfate concentrations. When comparing the sulfate concentrations at the sediment-water interface with the salinity of 35‰ in the bottom water at ESAS, it corresponds well. All together this suggests that the results are accurate within the analytical uncertainty of the methods. Concentration anomalies could be due to error during sampling, preservation, dilution, integration and/or contamination. Time of storage could also have affected the quality. Some of the DIC pore water samples were not filled completely and air was trapped inside the vial. This may have resulted in a loss of CO₂ from the pore water to the headspace due to equilibrium, affecting both the concentration and the $\delta^{13}\text{C}$. However, no anomalies could be seen in the results for the specific samples identified as not filled completely. The CO₂ concentration was estimated to be 5% and would only lead to a small error. No precipitation of carbonate minerals was observed in the vials, which also would result in a loss of DIC. FIA of marine pore water samples may lead to a small loss of conductivity response due to the ionic background. According to Hall and Aller (1992) the salinity is not expected to have a major effect.

5.2 PROFILE modelling, production rates and fluxes

Most of the concentration profiles used in the PROFILE modelling had a gradient change that was too low for the PROFILE model to successfully interpret the production and fluxes. Consequently, there are high uncertainties in the results from station 1, 4, 6, 13, 23 and 24. Overall, the model results indicate low fluxes, of both DIC and sulfate. Even though the gradient was higher at station 14 cast 3, the model had problems interpreting the concentration profile. Since the model calculates the net production or consumption based on the concentration depth profile, it does not calculate the gross sulfate reduction or gross DIC production. The model interpretation reflects all processes contributing to changes in concentration, not a specific reaction.

The model interpretation for station 14 cast 3 gave a net production of sulfate, just as for stations 1, 6, 13 and 14 cast 4. It is unlikely to have been a net production of sulfate in the sediment, even though there may have been sulfate producing processes proceeding under anoxic conditions, such as oxidation of hydrogen sulfide by the use of Mn(IV)oxides and Fe(III)oxide as electron donors (Zopfi et al., 2004). However, iron is usually more abundant in marine sediment, see Equation 21 and 22.



These are all re-oxidation processes, of sulfide, which would have been produced from sulfate reduction. The cycling of sulfur in the sediment may also lead to reduced change in sulfate concentration with depth. Due to sulfide oxidation the concentrations remain constant with depth. Net sulfate reduction can therefore not be detected from observations based on concentration depth profiles. After forcing the model to calculate production lower than 0, the production rate at station 14 cast 3 was calculated to be close to 0, but negative, and the downward sulfate flux increased. This could indicate that the main sulfate reduction and DIC production is taking place deeper down in the core, below the core recovery depth.

Diffusion was assumed to be the only transport, which may be incorrect. There are no specific data achieved for the bioturbation or irrigation for the different stations investigated. However, macro benthic fauna were found during the expedition, indicating that bioturbation and irrigation most likely influence the geochemical transportation in the sediment. Because there were no data to constrain bioturbation or irrigation, or how deep in the sediment it was significant and how efficient it was, it was neglected here. It is therefore important to understand that the production and fluxes probably could have been underestimated. The model uses the total transport to calculate the production (Equation 15). If processes contributing to the net transport is ignored, it will result in underestimated production and fluxes. This is a problem for all the stations, not only the ones resulting in high production of sulfate. Forcing the model to calculate a sulfate production <0 does not solve the problem with neglected bioturbation and irrigation. If the bioturbation and irrigation was contributing with significant transport, it must be accounted for.

Negative DIC production, representing consumption, can be interpreted in two ways. First, a consumption of DIC can proceed in sediments due to precipitation of carbonate minerals. Precipitation of calcium carbonate was found at station 14 (Brüchert, 2015). The fact that calcium carbonate was found only proves that it was precipitated at one point. It does not say when, or at what rate it was precipitated. Therefore it does not prove that it has, or to what degree it has contributed to the consumption of DIC. The stoichiometric r_{c:s} <2 values seen at station 14 cast 3 and station 14 cast 4 could also

have been caused by precipitation of carbonate minerals. Additional data of calcium and magnesium concentrations could give a better understanding of the effects of precipitation of carbonate minerals. The second interpretation can be that the transport defined was too low due to neglected bioturbation and irrigation. To model a production curve that fits the concentration depth profile and the transport defined, the system had to remove DIC to stay balanced.

To avoid problems with underestimated production and fluxes, complementary data is needed of bioturbation and irrigation transportation rates. Another possible way could be to use sulfate reduction rates from radioactive ^{35}S -sulfate incubations to do a two-step modelling. The bioturbation rate could be adapted to fit the sulfate reduction rate. It might also be useful to investigate the precipitation of carbonate minerals. If precipitation could be revealed not to have an effect on the DIC concentration, the modelling could be done by adapting the bioturbation transport to fit a curve where no consumption of DIC occur.

The flux trend calculated by PROFILE modelling can be compared with the calculations made with Fick's law of diffusion. The two methods revealed results that correspond well, with slightly higher fluxes from the Fick's law calculations. The $r_{c:s}$ values from the Fick's law calculations can be compared with the property-property plot $r_{c:s}$ of station 14, both casts. The stoichiometric ratio for the remaining stations is based on low fluxes with high uncertainties, too high to be used for interpretations.

Based on modelling calculations the ESAS, in the Laptev Sea, has relatively low sulfate reduction and DIC production rates in the marine sediment, compared to other shelf areas. The global mean sulfate reduction rate estimation of coastal environments made by Canfield et al. (2005, p. 323) are shown in table 9. The DIC fluxes have been calculated based on the sulfate reduction and assuming a stoichiometric 2:1 DIC:sulfate ratio.

Table 9. Global average of depth integrated sulfate reduction and DIC production rates in sediment in coastal environments. The sulfate reduction and DIC production for the stations investigated along the depth transect in the Laptev Sea is also shown.

| Marine environment | DIC depth integrated production rate $\text{mmol m}^{-2}\text{day}^{-1}$ | | Sulfate depth integrated reduction rate $\text{mmol m}^{-2}\text{day}^{-1}$ | |
|---------------------------|--|---------------------------------|---|--------------------------------|
| | Global average* | Laptev Sea | Global average* | Laptev Sea |
| Depositional shelf | 9.32 | - | 4.65 | - |
| Non depositional shelf | 2.18 | 0-0.44 1.88-2.14 (14 cast 4) | 1.09 | 0-0.22 1.75-2.22(14 cast 4) |
| Upper slope (200-1000 m) | 2.06 | - | 2.03 | - |
| Lower slope (1000-2000 m) | 0.82 | 0-0.25 | 0.41 | 0.13-0.66 |

*Data from Canfield et al. (2005)

The sulfate reduction and DIC production in the sediment on the ESAS in the Laptev Sea have shown production/consumption rates lower than the global average. Negative

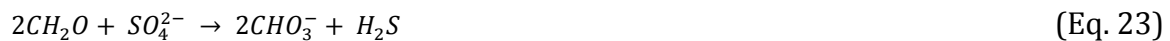
values are not shown. Based on the stations investigated in this study, no significant variation in the production and flux, depending on water depth or distance to the shore, could be seen.

5.3 Mineralization of organic carbon in the sediment

Even though there are uncertainties in both the production and the fluxes calculated with the PROFILE model and Fick's law of diffusion, important information is revealed. All stations except station 14 cast 3 and 14 cast 4 show low production rates and low fluxes. However, the weak increase in DIC concentration with depth together with decrease of sulfate indicates that mineralization of organic matter is proceeding, by sulfate reduction. As mentioned before, the degradation rate is most likely underestimated. Fresh OM is in general more labile and exists in the top sediment, resulting in higher sulfate reduction and DIC production. If there is a significant transport effect due to bioturbation and irrigation, the signal of degradation of OM in pore water concentrations might not be preserved in the top centimetres.

5.4 Stoichiometric ratio, $r_{c:s}$

The property-property plots were used to understand the stoichiometric relationship between DIC production and sulfate reduction. The DIC:sulfate ratio expected for oxidation of OM is 2, according to Equation 23.



In both station 14 cast 3 and 14 cast 4 the $r_{c:s} < 2$. The $r_{c:s}$ is related to the oxidation state of the organic material being oxidized according to Equation 24 (Burdige and Komada, 2011).

$$r_{c:s} = 8 / (4 - \text{oxidation state of organic matter}) \quad (\text{Eq. 24})$$

If the OC undergoing oxidation is methane, with an oxidation state of -4, the $r_{c:s} = 1$ (Equation 25).



The $r_{c:s}$ at station 14 cast 3 was 1.35 to 1.58 (two methods used). The stoichiometric ratio is too low to be explained by degradation of OM only, and too high to be explained by oxidation of methane. A combination of many processes might be the cause. For instance, processes such as precipitation and dissolution of carbonate minerals can also affect the concentration, thus also the $r_{c:s}$ value (Burdige and Komada, 2011). Mineralization of methane and OM could together create $r_{c:s}$ between 1 and 2. It could also be explained by mineralization of OM together with precipitation of carbonate minerals.

At station 14 cast 4 the stoichiometric ratio had a $r_{C:S}$ value 0.62 to 0.65. Methane oxidation together with precipitation of calcium carbonate could be an explanation. Stoichiometric ratio cannot be explained based on the concentrations and fluxes only, hence, this $r_{C:S}$ value can only be used as an indication of the stoichiometric relation. With additional data of calcium and magnesium concentration depth profiles, the possible precipitation and dissolution of carbonate minerals can be better understood. Methane concentration profiles matching the pore water concentrations could have been used to understand the sulfate methane relation. Unfortunately the methane concentrations were too low to balance DIC and sulfate for the corresponding stations, likely because of significant lateral heterogeneity.

The methane concentrations show a strong heterogeneity of the geographic distribution of light hydrocarbons within the sediment. All pore water subsamples for each station were taken from the same core and the methane samples were taken from another core, collected during the same multicoring cast or from two different Rumhor cores collected at the same station. This may indicate that the methane distribution is heterogeneous on less than a 0.5m scale. Due to the fact that the methane concentrations supposedly does not correspond to the DIC and sulfate concentrations from the pore water samples, no methane production and flux modelling results were included in this report. The great heterogeneity makes it difficult to extrapolate and generalize the data.

5.5 Source of organic carbon

The $\delta^{13}C$ data can be used to understand the source of the OC being oxidized and the processes involved. The stable carbon isotope fractionation during degradation of OM is minor (Alling et al., 2012). Therefore, the $\delta^{13}C_{DIC\ added}$ (DIC added to the pore water) is used as a proxy for the $\delta^{13}C$ value of the OC being mineralised. Equation 26 was used to calculate the $\delta^{13}C_{DIC\ added}$.

$$\delta^{13}C_{total\ DIC} = x\delta^{13}C_{DIC\ added} - y\delta^{13}C_{Bottom\ water} \quad (\text{Eq. 26})$$

x= mass fractionation of DIC concentration added to the pore water in relation to the total DIC concentration.

y= mass fractionation of DIC concentration in the bottom water compared to the total DIC concentration.

All stations except 2 and 14 cast 4 have values in the range of $\delta^{13}\text{C}$ -26 - -31‰. Station 2 showed slightly higher values of $\delta^{13}\text{C}$, \sim -24‰. Station 14 cast 4 showed values more negative, $\delta^{13}\text{C} \sim$ -46‰, which indicate that the OC have another source, compared with the other stations. The small anomaly seen at station 2, might as well indicate a different source. However, small errors within the concentration profile may affect the $\delta^{13}\text{C}_{\text{DIC added}}$ value. The $\delta^{13}\text{C}_{\text{DIC added}}$ for each station is an average, all mass fractionations values >1 or negative values were ignored.

Previous investigations have shown that one of the main inputs of OM to the Laptev Sea is terrestrial material from the Lena River (Holmes et al., 2011; Alling et al., 2010; 2012). The $\delta^{13}\text{C}$ value of terrestrial OC discharge from the Lena River have been estimated to around -27‰ with even lower values during spring flood (Raymond, et al., 2007; Alling et al., 2012). The $\delta^{13}\text{C}$ value of marine OC is higher, \sim -21‰, and methane have a $\delta^{13}\text{C}$ of -65‰ up to -40‰ (Alling, et al., 2012; Grant and Whiticar, 2002). When comparing the calculations of $\delta^{13}\text{C}_{\text{DIC added}}$ to previous research, the OM being mineralized had most likely a terrestrial origin. According to Alling et al. (2012), marine OM in the Laptev Sea have shown $\delta^{13}\text{C}$ values more negative than what is common. This is believed to be a result of primary production using the low $\delta^{13}\text{C}_{\text{DIC}}$ produced by the degradation of terrestrial OM. It could therefore be hard to distinguish between the DIC produced by mineralization of marine and terrestrial OM by using the $\delta^{13}\text{C}$ value. However, the low $\delta^{13}\text{C}_{\text{DIC}}$ value is, either way, most likely caused due to significant degradation of terrestrial OM. This strengthens the hypothesis of that the terrestrial OM input to the Laptev Sea behaves non-conservative. Most likely, the mineralization of terrestrial material in the sediment at the ESAS contributes to upward carbon fluxes.

A decrease of $\delta^{13}\text{C}_{\text{DIC added}}$ values could be explained by oxidation of methane or dissolution of carbonate minerals. Carbonate minerals have $\delta^{13}\text{C}$ values of \sim 0-4‰ (Hu and Burdige, 2007) and cannot be the reason for such negative $\delta^{13}\text{C}_{\text{DIC}}$ values of $<$ -40‰ seen in station 14 cast 4. Oxidation of methane is more likely the process taking place to explain the depleted carbon isotope composition. The $\delta^{13}\text{C}_{\text{DIC added}}$ value at station 14 cast 3 was too high to have been from oxidation of methane only. However, the sulfate reduction and DIC production rates were significant higher than at the other stations. It is therefore likely to have been two DIC producing process, degradation of OM and oxidation of methane, at the station 14 cast 3.

6 Conclusions

Even though the Laptev Sea receives great amounts of riverine terrestrial OC, the degradation in the shelf sediment is low. In this study, the sulfate reduction rates have been modelled to be low, for most stations on the ESAS in the Laptev Sea. The modelled DIC production and upward fluxes from the sediment, to the water column was also low, ~ 0.01 to $0.35 \text{ mmol m}^{-2} \text{ day}^{-1}$. The OC that was mineralized is believed to origin from terrestrial OM, based on $\delta^{13}\text{C}_{\text{DIC}}$ values ~ -26 to -31‰ . The fate of terrestrial OC is therefore suggested to degrade over the ESAS to a larger extent, and not behave conservatively as was believed before. Station 14, showed stronger sulfate reduction and upward DIC fluxes of ~ 0.44 to $3.06 \text{ mmol m}^{-2} \text{ day}^{-1}$. Station 14 cast 4, also showed a significant depletion of DIC $\delta^{13}\text{C}_{\text{DIC}}$ and DIC:sulfate ratio < 2 , both indicate oxidation of methane. This anaerobic oxidation of methane might have an important role for upward methane fluxes from marine sediment. The result of this study in combination with previous research is suggesting that two processes, mineralization of terrestrial OC and methane, contributing to upward DIC fluxes are taking place in the sediment on the ESAS in the Laptev Sea.

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Appendix

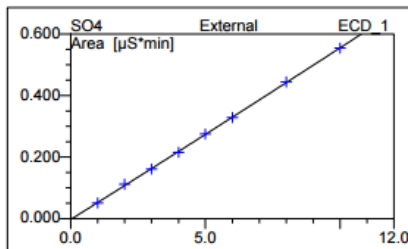
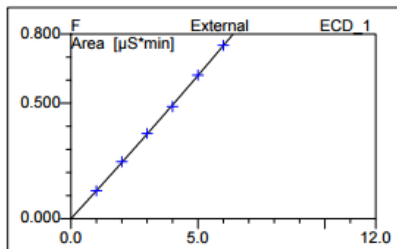
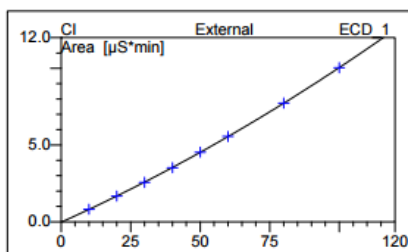
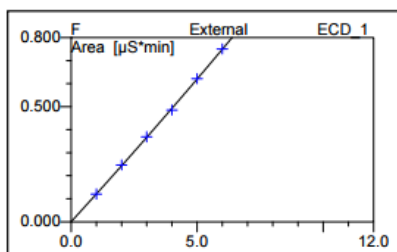
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Page 1-1
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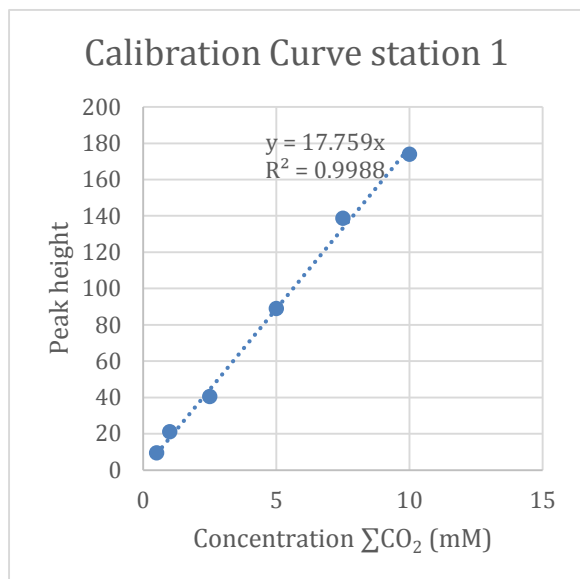
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| n.a. | n.a. | Cl | QOff | 8 | 99.8685 | -0.0303 | 0.0814 | 0.0002 |
| n.a. | n.a. | SO4 | QOff | 8 | 99.9886 | -0.0024 | 0.0547 | 0.0001 |
| Average: | | | | | 99.9448 | -0.0109 | 0.0853 | 0.0004 |

Calibration/Calibration

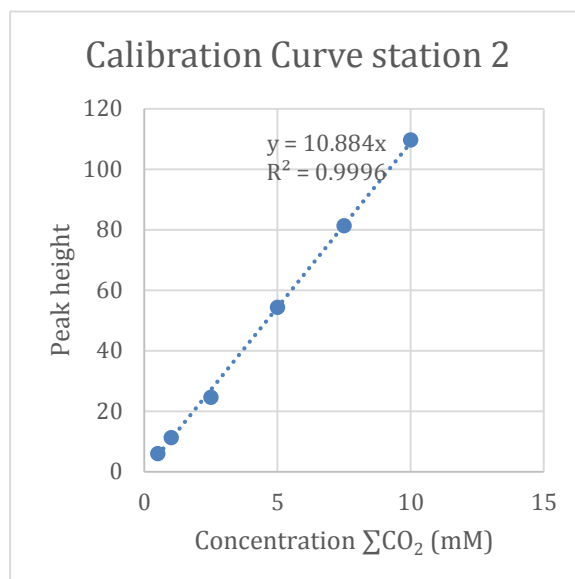
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Appendix 1.

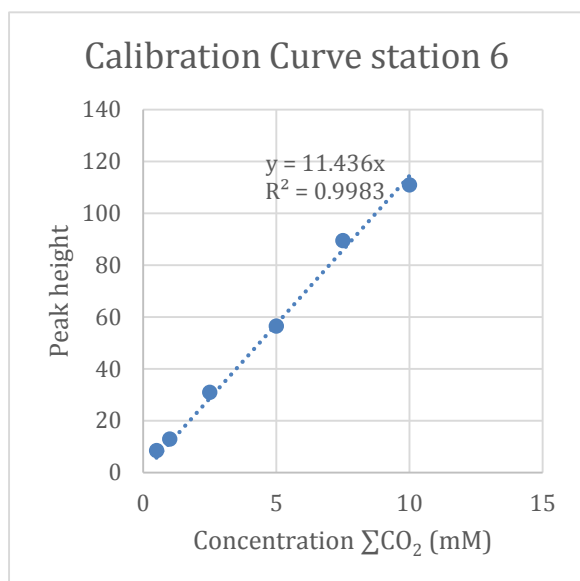
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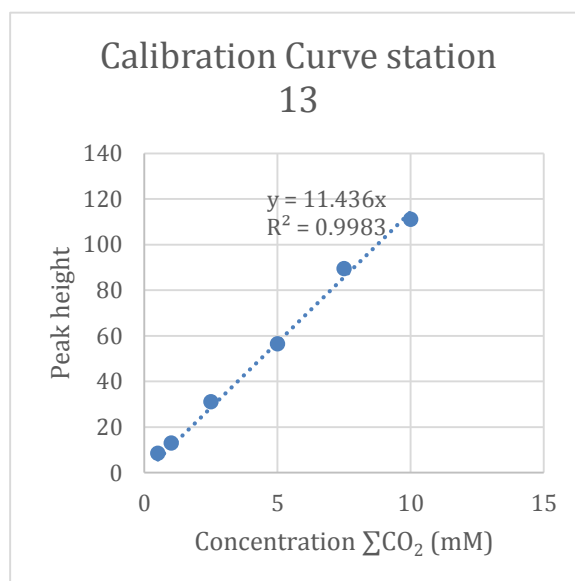
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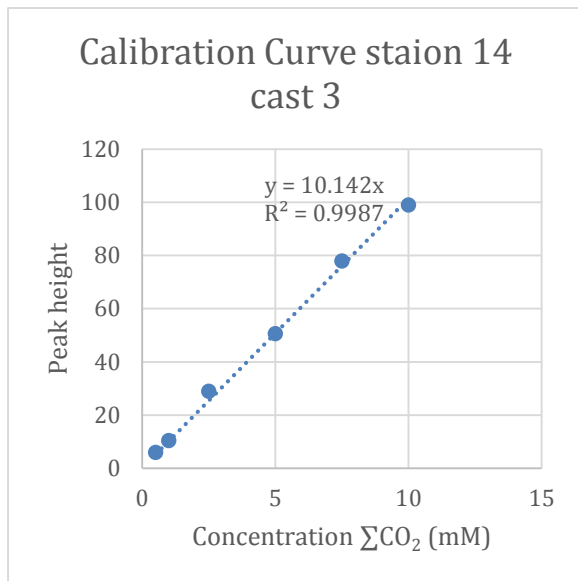
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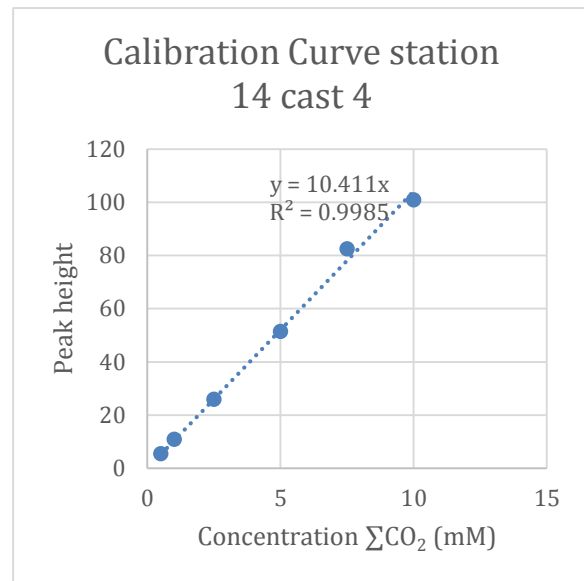
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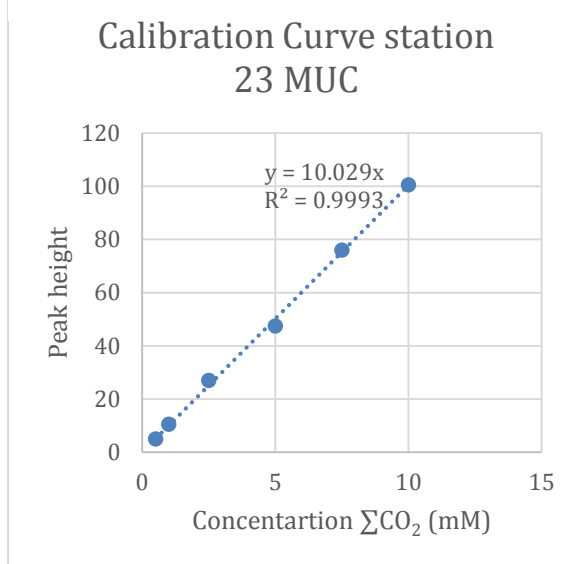
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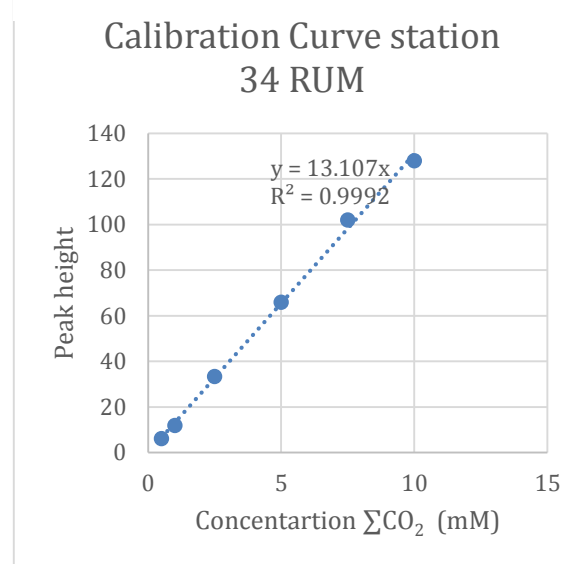
Appendix 6



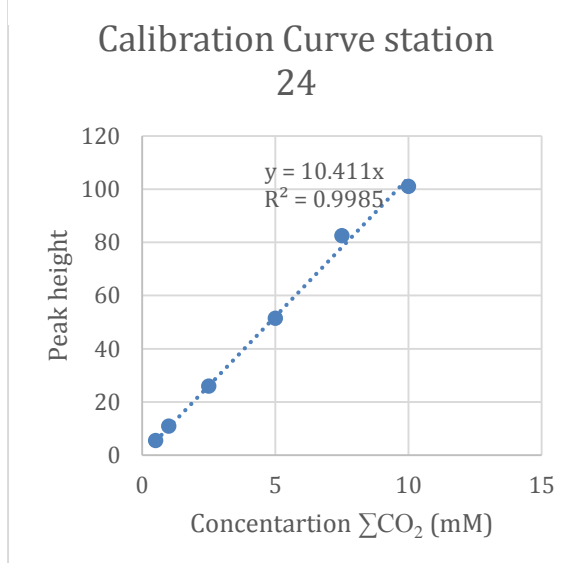
Appendix 7.



Appendix 8.



Appendix 9.



Appendix 10.

PROFILE input and log files

| X | FI | DB | ALFA | C |
|------|------|----|------|----------|
| 0.5 | 0.73 | 0 | 0 | 1998.986 |
| 2.5 | 0.72 | 0 | 0 | 2562.081 |
| 3.5 | 0.71 | 0 | 0 | 2167.915 |
| 6.5 | 0.68 | 0 | 0 | 2224.224 |
| 10.5 | 0.67 | 0 | 0 | 2674.7 |
| 12.5 | 0.67 | 0 | 0 | 2449.462 |
| 14.5 | 0.66 | 0 | 0 | 2590.236 |
| 16.5 | 0.66 | 0 | 0 | 2393.153 |
| 20.5 | 0.65 | 0 | 0 | 2590.236 |
| 22.5 | 0.64 | 0 | 0 | 3068.866 |
| 26.5 | 0.63 | 0 | 0 | 2787.319 |
| 28.5 | 0.63 | 0 | 0 | 2702.855 |
| 30.5 | 0.62 | 0 | 0 | 3265.95 |
| 32.5 | 0.62 | 0 | 0 | 3378.569 |

Name of input file : c:\modelling\st1DIC.txt
 Name of output file: c:\modelling\st1DIC.out

Input read from file - the calculation begins.

| Zones | SSE | R**2 | Zones: 2 | 3 | 4 | 5 | 6 |
|-------|-----------|-------|----------|-------|------|------|-----------|
| 1 | .7738E+06 | .6248 | ---- | .044 | .106 | .155 | .153 .293 |
| 2 | .5434E+06 | .7365 | ----- | .446 | .478 | .382 | .607 |
| 3 | .5143E+06 | .7506 | ----- | .348 | .299 | .550 | |
| 4 | .4688E+06 | .7727 | ----- | .221 | .535 | | |
| 5 | .3932E+06 | .8093 | ----- | 1.000 | | | |
| 6 | .4008E+06 | .8056 | | | | | |

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

| Zones | SSE | R**2 | Zones: |
|-------|-----------|-------|--------|
| 1 | .7738E+06 | .6248 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 38028 steady state profiles are tested.

Calculated concentration at top : .1999E+04
 Calculated concentration at bottom: .3379E+04
 Calculated flux at top : -.5750E-04
 Calculated flux at bottom : -.8192E-04
 Depth integration of production : -.2442E-04
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| Zones | Production | Irrigation |
|-------|------------|------------|
| 1 | -.2442E-04 | .0000E+00 |

```

St 1
Sulfate a
  0.5
 32.5
  6
  1
28355.184
26035.999
 4.64E-06
  3
28355.184
-1.00E+20
 1.00E+20
  0.001
  0.01
X      FI    DB  ALFA  C
  0.5  0.73   0    0  28355.18
  1.5  0.72   0    0  27301.12
  2.5  0.71   0    0  26979.93
  4.5  0.68   0    0  27053.53
 12.5  0.67   0    0  26795.98
 14.5  0.67   0    0  26431.1
 16.5  0.66   0    0  26967.74
 18.5  0.66   0    0  26143.72
 20.5  0.65   0    0  26458.7
 22.5  0.65   0    0  28188.96
 24.5  0.64   0    0  26608.98
 26.5  0.64   0    0  26328.73
 28.5  0.63   0    0  26872.43
 30.5  0.63   0    0  26451.15
 32.5  0.62   0    0   26036

```

Name of input file : c:\modelling\st1sulfatea.txt
Name of output file: c:\modelling\st.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2   3   4   5
6
  1 .7579E+07 -.2005 ---- .006 .011 .028 .034
.071
  2 .4179E+07 .3380 ----- .180 .338 .286
.425
  3 .3575E+07 .4337 ----- .511 .359
.530
  4 .3431E+07 .4565 ----- .211
.421
  5 .2912E+07 .5387 -----
.624
  6 .2831E+07 .5516

```

The F statistics suggest 2 zones. Choose the number of zones for further calculations: 2

```

Zones  SSE  R**2
Zones:  1
  2 .4179E+07 .3380 ----
.006
  1 .7579E+07 -.2005

```

The F statistics suggest 2 zones. Choose the number of zones in final result: 2

The calculation is done - 59878 steady state profiles are tested.

```

Calculated concentration at top : .2836E+05
Calculated concentration at bottom: .2604E+05
Calculated flux at top          :
.5742E-03
Calculated flux at bottom       : .2810E-03
Depth integration of production : -.2932E-03
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1    -.7687E-03  .0000E+00
  2     .4755E-03  .0000E+00

```

| |
|------------------------|
| St 1 |
| Sulfate b |
| 0.5 |
| 32.5 |
| 6 |
| 1 |
| 28355.184 |
| 26035.999 |
| 4.64E-06 |
| 3 |
| 28355.184 |
| -1.00E+20 |
| 0.00E+00 |
| 0.001 |
| 0.01 |
| X |
| FI |
| DB |
| ALFA |
| C |
| 0.5 0.73 0 0 28355.18 |
| 1.5 0.72 0 0 27301.12 |
| 2.5 0.71 0 0 26979.93 |
| 4.5 0.68 0 0 27053.53 |
| 12.5 0.67 0 0 26795.98 |
| 14.5 0.67 0 0 26431.1 |
| 16.5 0.66 0 0 26967.74 |
| 18.5 0.66 0 0 26143.72 |
| 20.5 0.65 0 0 26458.7 |
| 22.5 0.65 0 0 28188.96 |
| 24.5 0.64 0 0 26608.98 |
| 26.5 0.64 0 0 26328.73 |
| 28.5 0.63 0 0 26872.43 |
| 30.5 0.63 0 0 26451.15 |
| 32.5 0.62 0 0 26036 |

Name of input file : c:\modelling\st1sulfateb.txt
 Name of output file: c:\modelling\st1sulfate.out

Input read from file - the calculation begins.

| | | | | | | | | |
|-------|-----------|--------|--------|------|------|------|------|------|
| Zones | SSE | R**2 | Zones: | 2 | 3 | 4 | 5 | 6 |
| 1 | .7579E+07 | -.2005 | ---- | .179 | .235 | .301 | .386 | .488 |
| 2 | .6560E+07 | -.0391 | ----- | .291 | .383 | .481 | .589 | |
| 3 | .5954E+07 | .0568 | ----- | .366 | .499 | .621 | | |
| 4 | .5509E+07 | .1273 | ----- | .445 | .612 | | | |
| 5 | .5181E+07 | .1793 | ----- | .523 | | | | |
| 6 | .4939E+07 | .2177 | | | | | | |

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

| | | | |
|-------|-----------|--------|--------|
| Zones | SSE | R**2 | Zones: |
| 1 | .7579E+07 | -.2005 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 3805 steady state profiles are tested.

Calculated concentration at top : .2836E+05
 Calculated concentration at bottom: .2604E+05
 Calculated flux at top : .1906E-03
 Calculated flux at bottom : .3611E-04
 Depth integration of production : -.1545E-03
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | -.1545E-03 | .0000E+00 |

```

St 4 DIC
  0.5
 29.5
   6
   1
1653.8037
3583.2415
 5.00E-06
   3
1653.8037
-1.00E+20
 1.00E+20
  0.001
  0.01
X      FI    DB  ALFA  C
  0.5  0.83   0     0 1653.804
  1.5  0.80   0     0 2205.072
  2.5  0.78   0     0 1929.438
  3.5  0.77   0     0 2434.767
  4.5  0.76   0     0 1837.56
  5.5  0.75   0     0 2159.133
  7.5  0.71   0     0 2618.523
  9.5  0.73   0     0 2618.523
 11.5  0.71   0     0 2664.462
 15.5  0.70   0     0 3031.974
 17.5  0.70   0     0 3215.73
 21.5  0.61   0     0 3307.607
 25.5  0.64   0     0 3583.241
 29.5  0.61   0     0 3583.241

```

Name of input file : c:\modell\st4DIC.txt
 Name of output file: c:\modell\st4DIC.out

Input read from file - the calculation begins.

| Zones | SSE | R**2 | Zones: 2 | 3 | 4 | 5 | 6 | |
|-------|-----------|-------|----------|------|------|------|------|------|
| 1 | .5780E+06 | .8908 | --- | .326 | .433 | .588 | .746 | .810 |
| 2 | .5316E+06 | .8996 | ----- | .397 | .606 | .786 | .841 | |
| 3 | .4965E+06 | .9062 | ----- | .582 | .821 | .858 | | |
| 4 | .4810E+06 | .9092 | ----- | .750 | .792 | | | |
| 5 | .4753E+06 | .9102 | ----- | .554 | | | | |
| 6 | .4537E+06 | .9143 | | | | | | |

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

| Zones | SSE | R**2 | Zones: |
|-------|-----------|-------|--------|
| 1 | .5780E+06 | .8908 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 13964 steady state profiles are tested.

Calculated concentration at top : .1654E+04
 Calculated concentration at bottom: .3583E+04
 Calculated flux at top : -.2690E-03
 Calculated flux at bottom : .1868E-04
 Depth integration of production : .2877E-03
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| Zones | Production | Irrigation |
|-------|------------|------------|
| 1 | .2877E-03 | .0000E+00 |

Appendix 14.

| | | | | | |
|--------------|-----------|------|------|---|----------|
| St 4 Sulfate | | | | | |
| | 0.5 | | | | |
| | 29.5 | | | | |
| | 6 | | | | |
| | 1 | | | | |
| | 28229.478 | | | | |
| | 27367.778 | | | | |
| | 4.64E-06 | | | | |
| | 3 | | | | |
| | 28229.478 | | | | |
| | -1.00E+20 | | | | |
| | 1.00E+20 | | | | |
| | 0.001 | | | | |
| | 0.01 | | | | |
| X | FI | DB | ALFA | C | |
| | 0.5 | 0.83 | 0 | 0 | 28229.48 |
| | 1.5 | 0.80 | 0 | 0 | 28222.03 |
| | 2.5 | 0.78 | 0 | 0 | 28061.59 |
| | 3.5 | 0.77 | 0 | 0 | 28599.92 |
| | 4.5 | 0.76 | 0 | 0 | 28253.15 |
| | 7.5 | 0.71 | 0 | 0 | 27086.16 |
| | 11.5 | 0.71 | 0 | 0 | 27594.14 |
| | 13.5 | 0.71 | 0 | 0 | 27380.53 |
| | 15.5 | 0.70 | 0 | 0 | 27735.72 |
| | 17.5 | 0.70 | 0 | 0 | 27715.59 |
| | 19.5 | 0.69 | 0 | 0 | 26984.6 |
| | 25.5 | 0.64 | 0 | 0 | 27672.93 |
| | 29.5 | 0.61 | 0 | 0 | 27367.78 |

Name of input file : c:\modelling\st4sulfate.txt
 Name of output file: c:\modelling\st4sulfate.out

Input read from file - the calculation begins.

```
Zones  SSE  R**2  Zones:  2  3  4  5  6
1 .1373E+07 .5207 ---- .533 .803 .810 .069 .052
2 .1323E+07 .5381 ----- .798 .747 .046 .038
3 .1314E+07 .5412 ----- .482 .023 .023
4 .1240E+07 .5671 ----- .010 .014
5 .5138E+06 .8206 ----- .132
6 .3629E+06 .8733
```

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

```
Zones  SSE  R**2  Zones:
1 .1373E+07 .5207
```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 75490 steady state profiles are tested.

```
Calculated concentration at top : .2823E+05
Calculated concentration at bottom: .2737E+05
Calculated flux at top : .1420E-03
Calculated flux at bottom : -.2797E-04
Depth integration of production : -.1700E-03
Depth integration of irrigation : .0000E+00
```

Depth integration of production and irrigation in each zone:

```
Zones  Production  Irrigation
1      -.1700E-03 .0000E+00
```

Appendix 15.

```

St 6 DIC a
  0.5
 16.5
   6
   1
 1311.65
2448.4085
5.00E-06
   2
 1311.65
-1.00E+20
 1.00E+20
 0.001
 0.01
X      FI    DB  ALFA  C
  0.5  0.6   0    0   1311.65
  1.5  0.56  0    0   2492.13
  2.5  0.56  0    0  2579.573
  4.5  0.53  0    0  2273.522
  6.5  0.44  0    0  2623.295
 12.5  0.44  0    0  2229.801
 14.5  0.44  0    0   2492.13
 16.5  0.39  0    0  2448.409

```

Name of input file : c:\modell\st6DICa.txt
Name of output file: c:\modell\st6DICa.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2   3   4   5   6
1  .2503E+07 -.9856 ---- .038 .047 .077 .015 .054
2  .1149E+07 .0885 ----- .157 .210 .033 .094
3  .7394E+06 .4135 ----- .272 .038 .110
4  .5263E+06 .5825 ----- .029 .105
5  .8422E+05 .9332 ----- .412
6  .5508E+05 .9563

```

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

```

Zones  SSE  R**2  Zones:
1  .2503E+07 -.9856

```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 45160 steady state profiles are tested.

```

Calculated concentration at top : .1312E+04
Calculated concentration at bottom: .2448E+04
Calculated flux at top          : -.1866E-03
Calculated flux at bottom       : .7664E-04
Depth integration of production : .2632E-03
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
1      .2632E-03 .0000E+00

```

Appendix 16.

```

St 6 DIC b
  1.5
  16.5
  6
  1
2492.1301
2448.4085
  5.00E-06
  3
2492.1301
-1.00E+20
  1.00E+20
  0.001
  0.01
X      FI    DB  ALFA  C
  0.5  0.6   0    0   1311.65
  1.5  0.56  0    0   2492.13
  2.5  0.56  0    0  2579.573
  4.5  0.53  0    0  2273.522
  6.5  0.44  0    0  2623.295
 12.5  0.44  0    0  2229.801
 14.5  0.44  0    0   2492.13
 16.5  0.39  0    0  2448.409

```

Name of input file : c:\modelling\st6DICb.txt
Name of output file: c:\modelling\st6DICb.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2  3  4  5  6
1  1.165E+06 .1038 ---- .530 .752 .417 .000 .000
2  1.068E+06 .1787 ----- .659 .327 .000 .000
3  1.010E+06 .2228 ----- .182 .000 .000
4  5.064E+05 .6104 ----- .000 .000
5  4.577E-03 1.0000 ----- .089
6  8.908E-05 1.0000

```

The F statistics suggest 5 zones. Choose the number of zones for further calculations: 5

```

Zones  SSE  R**2  Zones:  4  3  2  1
5  4.577E-03 1.0000 ---- .000
4  9.328E+05 .2824 ----- .927
3  9.359E+05 .2800 ----- .388
2  1.155E+06 .1111 ----- .848
1  1.165E+06 .1038

```

The F statistics suggest 5 zones. Choose the number of zones in final result: 1

The calculation is done - 816882 steady state profiles are tested.

```

Calculated concentration at top : .2492E+04
Calculated concentration at bottom: .2448E+04
Calculated flux at top : .2303E-04
Calculated flux at bottom : -.1509E-04
Depth integration of production : -.3812E-04
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
1      -.3812E-04 .0000E+00

```

Appendix 17.

Name of input file : c:\modelling\st6sulfate.txt
 Name of output file: c:\modelling\st6sulfate.out

Input read from file - the calculation begins.

| X | FI | DB | ALFA | C |
|------|------|----|------|----------|
| 2.5 | 0.56 | 0 | 0 | 27467.6 |
| 3.5 | 0.5 | 0 | 0 | 27867.47 |
| 4.5 | 0.53 | 0 | 0 | 27643.52 |
| 6.5 | 0.44 | 0 | 0 | 28013.69 |
| 8.5 | 0.47 | 0 | 0 | 27208 |
| 10.5 | 0.44 | 0 | 0 | 27606.66 |
| 12.5 | 0.44 | 0 | 0 | 28625.23 |
| 14.5 | 0.44 | 0 | 0 | 27397.39 |
| 16.5 | 0.39 | 0 | 0 | 27332.94 |

| Zones | SSE | R**2 | Zones: 2 | 3 | 4 | 5 | 6 |
|-------|-----------|-------|----------|-------|------|------|-----------|
| 1 | .1404E+07 | .0731 | ---- | .543 | .340 | .482 | .010 .065 |
| 2 | .1326E+07 | .1243 | ----- | .195 | .372 | .007 | .053 |
| 3 | .9797E+06 | .3532 | ----- | .518 | .007 | .058 | |
| 4 | .8933E+06 | .4103 | ----- | .003 | .041 | | |
| 5 | .8223E+05 | .9457 | ----- | 1.000 | | | |
| 6 | .1054E+06 | .9304 | | | | | |

The F statistics suggest 5 zones. Choose the number of zones for further calculations: 1

| Zones | SSE | R**2 | Zones: |
|-------|-----------|-------|--------|
| 1 | .1404E+07 | .0731 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 41526 steady state profiles are tested.

Calculated concentration at top : .2747E+05
 Calculated concentration at bottom: .2733E+05
 Calculated flux at top : -.1056E-03
 Calculated flux at bottom : .1087E-03
 Depth integration of production : .2143E-03
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| Zones | Production | Irrigation |
|-------|------------|------------|
| 1 | .2143E-03 | .0000E+00 |

Appendix 18.

| | | | | | |
|-----------|------|-----|------|---|----------|
| St 13 | DIC | | | | |
| | 0.5 | | | | |
| | 20.5 | | | | |
| | 6 | | | | |
| | 1 | | | | |
| 2110.1188 | | | | | |
| 2649.9166 | | | | | |
| 5.00E-06 | | | | | |
| 3 | | | | | |
| 2110.1188 | | | | | |
| -1.00E+20 | | | | | |
| 1.00E+20 | | | | | |
| 0.001 | | | | | |
| 0.01 | | | | | |
| X | FI | DB | ALFA | C | |
| | -1 | 1.0 | 0 | 0 | 2453.626 |
| | 0.5 | 0.8 | 0 | 0 | 2110.119 |
| | 1.5 | 0.8 | 0 | 0 | 1815.684 |
| | 2.5 | 0.8 | 0 | 0 | 1864.756 |
| | 4.5 | 0.7 | 0 | 0 | 2453.626 |
| | 8.5 | 0.6 | 0 | 0 | 2306.409 |
| | 10.5 | 0.6 | 0 | 0 | 2355.481 |
| | 12.5 | 0.6 | 0 | 0 | 2404.554 |
| | 16.5 | 0.6 | 0 | 0 | 2551.772 |
| | 20.5 | 0.6 | 0 | 0 | 2649.917 |

Name of input file : c:\modelling\st13DIC.txt
Name of output file: c:\modelling\st13DIC.out

Input read from file - the calculation begins.

| | | | | | | | | |
|-------|-----------|-------|--------|------|------|------|------|------|
| Zones | SSE | R**2 | Zones: | 2 | 3 | 4 | 5 | 6 |
| 1 | .2483E+06 | .6346 | --- | .985 | .983 | .934 | .503 | .005 |
| 2 | .2483E+06 | .6346 | ----- | .859 | .821 | .384 | .003 | |
| 3 | .2469E+06 | .6367 | ----- | .565 | .255 | .002 | | |
| 4 | .2295E+06 | .6624 | ----- | .141 | .002 | | | |
| 5 | .1247E+06 | .8165 | ----- | .002 | | | | |
| 6 | .3100E+04 | .9954 | | | | | | |

The F statistics have no suggestion. Choose the number of zones for further calculations: 1

| | | | |
|-------|-----------|-------|--------|
| Zones | SSE | R**2 | Zones: |
| 1 | .2483E+06 | .6346 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 612296 steady state profiles are tested.

Calculated concentration at top : .2110E+04
Calculated concentration at bottom: .2650E+04
Calculated flux at top : -.4763E-04
Calculated flux at bottom : -.3622E-04
Depth integration of production : .1141E-04
Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | .1141E-04 | .0000E+00 |

Appendix 19.

| |
|---------------|
| St 13 Sulfate |
| 0.5 |
| 20.5 |
| 6 |
| 1 |
| 26524.352 |
| 26449.894 |
| 4.64E-06 |
| 3 |
| 26524.352 |
| -1.00E+20 |
| 1.00E+20 |
| 0.001 |
| 0.01 |
| X |
| -1 |
| 0.5 |
| 1.5 |
| 2.5 |
| 3.5 |
| 4.5 |
| 6.5 |
| 8.5 |
| 10.5 |
| 12.5 |
| 14.5 |
| 16.5 |
| 18.5 |
| 20.5 |
| FI |
| 1.0 |
| 0.8 |
| 0.8 |
| 0.8 |
| 0.8 |
| 0.7 |
| 0.7 |
| 0.6 |
| 0.6 |
| 0.6 |
| 0.6 |
| 0.6 |
| 0.6 |
| 0.6 |
| 0.5 |
| 0.6 |
| DB |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| ALFA |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| C |
| 27157.55 |
| 26524.35 |
| 27485.68 |
| 28126.95 |
| 29225.42 |
| 25797.21 |
| 26470.86 |
| 26968.36 |
| 27999.92 |
| 26034.11 |
| 27495.62 |
| 26058.92 |
| 27404.74 |
| 26449.89 |



Name of input file : c:\modelling\st13sulfatea.txt
 Name of output file: c:\modelling\st13sulfatea.out

Input read from file - the calculation begins.

| | | | | | | | |
|-------|-----------|--------|----------|------|------|------|-----------|
| Zones | SSE | R**2 | Zones: 2 | 3 | 4 | 5 | 6 |
| 1 | .1359E+08 | -.1461 | ---- | .440 | .562 | .544 | .238 .189 |
| 2 | .1284E+08 | -.0828 | ----- | .456 | .467 | .189 | .157 |
| 3 | .1211E+08 | -.0213 | ----- | .332 | .132 | .120 | |
| 4 | .1084E+08 | .0856 | ----- | .084 | .095 | | |
| 5 | .7304E+07 | .3841 | ----- | .177 | | | |
| 6 | .5528E+07 | .5338 | | | | | |

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

| | | | |
|-------|-----------|--------|--------|
| Zones | SSE | R**2 | Zones: |
| 1 | .1359E+08 | -.1461 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 39396 steady state profiles are tested.

Calculated concentration at top : .2652E+05
 Calculated concentration at bottom: .2645E+05
 Calculated flux at top : -.2287E-03
 Calculated flux at bottom : .1863E-03
 Depth integration of production : .4151E-03
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | .4151E-03 | .0000E+00 |

```

St 14 cast 3 DIC
  0.5
 21.5
   6
   1
3056.596332
20410.17551
  5.00E-06
   3
3056.596332
-1.00E+20
  1.00E+20
   0.001
   0.01
X      FI    DB  ALFA  C
  -1     1    0     0  2908.70
   0.5  0.65  0     0  3056.60
   1.5  0.6  0     0  2908.70
   2.5  0.56  0     0  3697.50
   3.5  0.55  0     0  2859.40
   4.5  0.6  0     0  4190.49
   5.5  0.54  0     0  5275.09
   7.5  0.52  0     0  6852.69
   9.5  0.46  0     0  8824.69
  11.5  0.43  0     0  7789.39
  13.5  0.44  0     0  10944.59
  15.5  0.44  0     0  15578.78
  17.5  0.4  0     0  15085.78
  19.5  0.4  0     0  17846.58
  21.5  0.4  0     0  20410.18

```

Name of input file : c:\modelling\st13cast 3DIC.txt
Name of output file: c:\modelling\st.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2   3   4   5   6
  1 .1251E+08 .9736 ---- .409 .606 .658 .179
.195
  2 .1179E+08 .9751 ----- .564 .625 .142
.164
  3 .1142E+08 .9759 ----- .441 .086 .116
  4 .1073E+08 .9774 ----- .043 .078
  5 .6630E+07 .9860 ----- .278
  6 .5668E+07 .9880

```

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

```

Zones  SSE  R**2  Zones:
  1 .1251E+08 .9736

```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 36814 steady state profiles are tested.

```

Calculated concentration at top : .3057E+04
Calculated concentration at bottom: .2041E+05
Calculated flux at top      : -.5128E-03
Calculated flux at bottom   : -.9257E-03
Depth integration of production : -.4130E-03
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1     -.4130E-03  .0000E+00

```

```

St 14 cast 3
Sulfate a
  0.5
 21.5
   6
   1
27202.238
14600.329
 4.64E-06
   3
27202.238
-1.00E+20
 1.00E+20
  0.001
  0.01
X      FI    DB  ALFA  C
  -1     1    0     0 27418.19
  0.5  0.65  0     0 27070.28
  1.5   0.6  0     0 29499.62
  2.5  0.56  0     0  26012.7
  3.5  0.55  0     0 27152.12
  4.5   0.6  0     0 26457.88
  5.5  0.54  0     0  25988.1
  7.5  0.52  0     0  26444.1
  9.5  0.46  0     0 24532.52
 11.5  0.43  0     0 21895.78
 13.5  0.44  0     0  20684.7
 15.5  0.44  0     0 20609.47
 17.5  0.4  0     0  18439.6
 19.5  0.4  0     0 16136.74
 21.5  0.4  0     0  14314.11

```

Name of input file : c:\modelling\st14cast3sulfatea.txt
Name of output file: c:\modelling\st.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones: 2  3  4  5
6
  1 .1175E+08 .9573 ---- .192 .339 .544 .598
.490
  2 .1014E+08 .9631 ----- .474 .754 .744
.574
  3 .9656E+07 .9649 ----- .786 .692
.504
  4 .9581E+07 .9652 ----- .427
.341
  5 .8898E+07 .9677 ----- .226
  6 .7320E+07 .9734

```

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

```

Zones  SSE  R**2
Zones:
  1 .1175E+08 .9573

```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 33530 steady state profiles are tested.

```

Calculated concentration at top : .2720E+05
Calculated concentration at bottom: .1460E+05
Calculated flux at top          :
.2572E-03
Calculated flux at bottom       : .6936E-03
Depth integration of production : .4364E-03
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1     .4364E-03  .0000E+00

```

```

St 14 cast 3 b
Sulfate
  0.5
 21.5
   6
   1
27202.238
14600.329
 4.64E-06
   3
27202.238
-1.00E+20
 0.00E+00
 0.001
 0.01
X      FI    DB  ALFA  C
-1     1     0     0    27418.19
0.5    0.65  0     0    27070.28
1.5    0.6   0     0    29499.62
2.5    0.56  0     0    26012.7
3.5    0.55  0     0    27152.12
4.5    0.6   0     0    26457.88
5.5    0.54  0     0    25988.1
7.5    0.52  0     0    26444.1
9.5    0.46  0     0    24532.52
11.5   0.43  0     0    21895.78
13.5   0.44  0     0    20684.7
15.5   0.44  0     0    20609.47
17.5   0.4   0     0    18439.6
19.5   0.4   0     0    16136.74
21.5   0.4   0     0    14314.11

```

Name of input file : c:\modelling\st14cast3sulfateb.txt
Name of output file: c:\modelling\st.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2   3   4   5
6
  1 .2161E+08 .9214 ---- 1.000 .994 1.000 1.000 1.000
  2 .2161E+08 .9214 ----- .915 1.000 1.000
1.000
  3 .2159E+08 .9215 ----- 1.000 1.000
1.000
  4 .2161E+08 .9214 ----- 1.000
.990
  5 .2161E+08 .9214 ----- .892
  6 .2156E+08 .9216

```

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

```

Zones  SSE  R**2
Zones:
  1 .2161E+08 .9214

```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 2576 steady state profiles are tested.

```

Calculated concentration at top : .2720E+05
Calculated concentration at bottom: .1460E+05
Calculated flux at top          :
.5011E-03
Calculated flux at bottom       : .5011E-03
Depth integration of production  : -.5692E-18
Depth integration of irrigation  : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1    -.5692E-18  .0000E+00

```

Appendix 23.

St 14 cast 4 DIC
a

| |
|-----------|
| 0.5 |
| 15.5 |
| 6 |
| 1 |
| 2257.22 |
| 18634.13 |
| 5.00E-06 |
| 3 |
| 2257.22 |
| -1.00E+20 |
| 1.00E+20 |
| 0.001 |
| 0.01 |
| X |
| -1 |
| 0.5 |
| 1.5 |
| 2.5 |
| 3.5 |
| 4.5 |
| 6.5 |
| 8.5 |
| 10.5 |
| 13.5 |
| 15.5 |
| FI |
| 1 |
| 0.65 |
| 0.6 |
| 0.56 |
| 0.55 |
| 0.6 |
| 0.54 |
| 0.52 |
| 0.46 |
| 0.44 |
| 0.44 |
| DB |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| ALFA |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| 0 |
| C |
| 2401.3 |
| 2257.22 |
| 3553.93 |
| 4706.56 |
| 6243.39 |
| 8068.38 |
| 11046 |
| 15368.36 |
| 17097.3 |
| 18634.13 |
| 18634.13 |

Name of input file : c:\modell\st14.4DICa.txt
Name of output file: c:\modell\st14.4DICa.out

Input read from file - the calculation begins.

| | | | | | | | |
|-------|-----------|-------|----------|------|------|------|-----------|
| Zones | SSE | R**2 | Zones: 2 | 3 | 4 | 5 | 6 |
| 1 | .6374E+07 | .9829 | ---- | .001 | .000 | .001 | .002 .001 |
| 2 | .1473E+07 | .9961 | ----- | .030 | .043 | .052 | .009 |
| 3 | .7160E+06 | .9981 | ----- | .180 | .171 | .024 | |
| 4 | .5177E+06 | .9986 | ----- | .187 | .171 | .025 | |
| 5 | .3531E+06 | .9991 | ----- | .022 | | | |
| 6 | .8198E+05 | .9998 | | | | | |

The F statistics have no suggestion. Choose the number of zones for further calculations: 5

| | | | | | | |
|-------|-----------|-------|----------|------|---|---|
| Zones | SSE | R**2 | Zones: 4 | 3 | 2 | 1 |
| 5 | .3531E+06 | .9991 | ---- | .851 | | |
| 4 | .3558E+06 | .9990 | ----- | .269 | | |
| 3 | .4436E+06 | .9988 | ----- | .031 | | |
| 2 | .9061E+06 | .9976 | ----- | .000 | | |
| 1 | .6374E+07 | .9829 | | | | |

The F statistics suggest 2 zones. Choose the number of zones in final result: 2

The calculation is done - 70712 steady state profiles are tested.

Calculated concentration at top : .2257E+04
Calculated concentration at bottom: .1863E+05
Calculated flux at top : -.1685E-02
Calculated flux at bottom : .4965E-03
Depth integration of production : .2181E-02
Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | -.4634E-03 | .0000E+00 |
| 2 | .2645E-02 | .0000E+00 |

```

St 14 cast 4 DICb
0.5
15.5
6
1
2257.22
18634.13
5.00E-06
3
2257.22
-1.00E+20
1.00E+20
0.001
0.01
X      FI      DB      ALFA      C
-1      1      0      0      2401.3
0.5    0.65    0      0      2257.22
1.5    0.6     0      0      3553.93
2.5    0.56    0      0      4706.56
3.5    0.55    0      0      6243.39
4.5    0.6     0      0      8068.38
6.5    0.54    0      0      11046
8.5    0.52    0      0      15368.36
10.5   0.46    0      0      17097.3
13.5   0.44    0      0      18634.13
15.5   0.44    0      0      18634.13

```

Name of input file : c:\modell\st14.4DICb.txt
Name of output file: c:\modell\st14.4DICb.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2   3   4   5   6

1 .6374E+07 .9829 ---- .001 .000 .001 .002 .001
2 .1473E+07 .9961 ----- .030 .043 .052 .009
3 .7160E+06 .9981 ----- .180 .171 .024
4 .5177E+06 .9986 ----- .187 .025
5 .3531E+06 .9991 ----- .022
6 .8198E+05 .9998

```

The F statistics have no suggestion. Choose the number of zones for further calculations: 2

```

Zones  SSE  R**2  Zones:  1

2 .1473E+07 .9961 ---- .001
1 .6374E+07 .9829

```

The F statistics suggest 2 zones. Choose the number of zones in final result: 2

The calculation is done - 57844 steady state profiles are tested.

```

Calculated concentration at top : .2257E+04
Calculated concentration at bottom: .1863E+05
Calculated flux at top : -.1887E-02
Calculated flux at bottom : .5859E-03
Depth integration of production : .2473E-02
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
1      .1493E-04  .0000E+00
2      .2458E-02  .0000E+00

```

```

St 14 cast 4 a
Sulfate
    0.5
    15.5
    6
    1
27721.096
664.83849
4.64E-06
    2
27721.096
-1.00E+20
1.00E+20
    0
    0.01
X      FI    DB  ALFA  C
    -1     1    0     0  28022.96
    0.5   0.65  0     0  27721.1
    1.5   0.6   0     0  25815.98
    2.5   0.56  0     0  25087.18
    3.5   0.55  0     0  21661.32
    4.5   0.6   0     0  20805.64
    6.5   0.54  0     0  15637.94
    8.5   0.52  0     0  9975.498
   10.5   0.46  0     0  5196.122
   13.5   0.44  0     0  1102.568
   15.5   0.44  0     0  664.8385

```

Name of input file : c:\modell\st14cast4sulfatea.txt
Name of output file: c:\modell\st144sul.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2  3  4  5  6
1 .1531E+08 .9843 ---- .000 .001 .002 .007
.031
2 .2302E+07 .9976 ----- .243 .255 .369 .621
3 .1868E+07 .9981 ----- .242 .396 .686
4 .1459E+07 .9985 ----- .454 .841
5 .1289E+07 .9987 ----- 1.000
6 .1338E+07 .9986

```

The F statistics suggest 2 zones. Choose the number of zones for further calculations: 2

```

Zones  SSE  R**2  Zones:
1
2 .2302E+07 .9976 ----
.000
1 .1531E+08 .9843

```

The F statistics suggest 2 zones. Choose the number of zones in final result: 2

The calculation is done - 204404 steady state profiles are tested.

```

Calculated concentration at top : .2772E+05
Calculated concentration at bottom: .6648E+03
Calculated flux at top : .1682E-02
Calculated flux at bottom : -.3412E-03
Depth integration of production : -.2023E-02
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
1      .1958E-03  .0000E+00
2     -.2219E-02  .0000E+00

```

```

St 14 cast 4 b
Sulfate
  0.5
 15.5
   6
   1
27721.096
664.83849
 4.64E-06
   3
27721.096
-1.00E+20
 0.00E+00
 0.001
 0.01
X      FI      DB      ALFA      C
  -1      1      0      0      27565.36
  0.5    0.65    0      0      27459.98
  1.5    0.6     0      0      25970.54
  2.5    0.56    0      0      24515.52
  3.5    0.55    0      0      21489.74
  4.5    0.6     0      0      20519.77
  6.5    0.54    0      0      15344.35
  8.5    0.52    0      0      9869.09
 10.5    0.46    0      0      5255.033
 13.5    0.44    0      0      1150.126
 15.5    0.44    0      0      694.5271

```

Name of input file : c:\modelling\st14.4sulfateb.txt
Name of output file: c:\modelling\st14.4sulfate.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2  3  4  5  6
  1 .1467E+08 .9847 ---- .000 .003 .008 .019 .064
  2 .2476E+07 .9974 ----- 1.000 .764 .690 .859
  3 .2675E+07 .9972 ----- .337 .421 .673
  4 .2264E+07 .9976 ----- .367 .698
  5 .1893E+07 .9980 ----- .971
  6 .1892E+07 .9980

```

The F statistics suggest 2 zones. Choose the number of zones for further calculations: 2

```

Zones  SSE  R**2  Zones:  1
  2 .2476E+07 .9974 ---- .000
  1 .1467E+08 .9847

```

The F statistics suggest 2 zones. Choose the number of zones in final result: 2

The calculation is done - 10094 steady state profiles are tested.

```

Calculated concentration at top : .2772E+05
Calculated concentration at bottom: .6648E+03
Calculated flux at top : .2507E-02
Calculated flux at bottom : -.5890E-04
Depth integration of production : -.2566E-02
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1     -.5082E-18 .0000E+00
  2     -.2566E-02 .0000E+00

```

| |
|----------------------|
| St 23 Muc DIC |
| 0 |
| 24 |
| 6 |
| 1 |
| 2442.9155 |
| 3041.1806 |
| 5.00E-06 |
| 3 |
| 2442.9155 |
| -1.00E+20 |
| 1.00E+20 |
| 0.001 |
| 0.01 |
| X |
| FI |
| DB |
| ALFA |
| C |
| 0 0.73 0 0 2442.916 |
| 2 0.68 0 0 2492.771 |
| 4 0.61 0 0 2692.193 |
| 6 0.59 0 0 2692.193 |
| 8 0.55 0 0 2592.482 |
| 12 0.51 0 0 2492.771 |
| 20 0.43 0 0 2492.771 |
| 22 0.42 0 0 3041.181 |
| 24 0.41 0 0 3041.181 |

Name of input file : c:\modelling\st23mucDIC.txt
Name of output file: c:\modelling\st23mucDIC.out

Input read from file - the calculation begins.

| | | | | | | | | |
|-------|-----------|-------|--------|------|------|------|------|------|
| Zones | SSE | R**2 | Zones: | 2 | 3 | 4 | 5 | 6 |
| 1 | .2463E+06 | .4247 | ---- | .015 | .038 | .093 | .010 | .006 |
| 2 | .9901E+05 | .7687 | ----- | .325 | .503 | .037 | .016 | |
| 3 | .8310E+05 | .8059 | ----- | .502 | .029 | .014 | | |
| 4 | .7523E+05 | .8243 | ----- | .014 | .010 | | | |
| 5 | .1417E+05 | .9669 | ----- | .055 | | | | |
| 6 | .3426E+04 | .9920 | | | | | | |

The F statistics suggest 5 zones. Choose the number of zones for further calculations: 1

| | | | |
|-------|-----------|-------|--------|
| Zones | SSE | R**2 | Zones: |
| 1 | .2463E+06 | .4247 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 119420 steady state profiles are tested.

Calculated concentration at top : .2443E+04
Calculated concentration at bottom: .3041E+04
Calculated flux at top : -.7143E-05
Calculated flux at bottom : -.3986E-04
Depth integration of production : -.3272E-04
Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | -.3272E-04 | .0000E+00 |

Appendix 28.

| | | | | | |
|------------|-----------|------|------|---|----------|
| St 23 MUC] | | | | | |
| Sulfate | | | | | |
| | 0 | | | | |
| | 24 | | | | |
| | 6 | | | | |
| | 1 | | | | |
| | 26834.669 | | | | |
| | 26873.525 | | | | |
| | 4.64E-06 | | | | |
| | 3 | | | | |
| | 26834.669 | | | | |
| | -1.00E+20 | | | | |
| | 1.00E+20 | | | | |
| | 0.001 | | | | |
| | 0.01 | | | | |
| X | FI | DB | ALFA | C | |
| | 0 | 0.73 | 0 | 0 | 26834.67 |
| | 1 | 0.71 | 0 | 0 | 28521.28 |
| | 2 | 0.68 | 0 | 0 | 27060.51 |
| | 3 | 0.68 | 0 | 0 | 26976.59 |
| | 4 | 0.61 | 0 | 0 | 26757.75 |
| | 6 | 0.59 | 0 | 0 | 26766.91 |
| | 8 | 0.55 | 0 | 0 | 26510.57 |
| | 10 | 0.52 | 0 | 0 | 26153.55 |
| | 12 | 0.51 | 0 | 0 | 27131.94 |
| | 14 | 0.5 | 0 | 0 | 27383.24 |
| | 16 | 0.5 | 0 | 0 | 26664.89 |
| | 18 | 0.41 | 0 | 0 | 26256.66 |
| | 20 | 0.43 | 0 | 0 | 26616.66 |
| | 22 | 0.42 | 0 | 0 | 26818.13 |
| | 24 | 0.41 | 0 | 0 | 26873.53 |

Name of input file : c:\modell\st23mucsulfate.txt
 Name of output file: c:\modell\st23mucsulfate.out

Input read from file - the calculation begins.

| | | | | | | | | |
|-------|-----------|-------|--------|------|------|------|------|------|
| Zones | SSE | R**2 | Zones: | 2 | 3 | 4 | 5 | 6 |
| 1 | .4247E+07 | .0015 | --- | .763 | .859 | .504 | .401 | .328 |
| 2 | .4216E+07 | .0088 | ----- | .649 | .338 | .285 | .243 | |
| 3 | .4141E+07 | .0264 | ----- | | .170 | .179 | .168 | |
| 4 | .3462E+07 | .1861 | ----- | | | .210 | .203 | |
| 5 | .2935E+07 | .3099 | ----- | | | | .203 | |
| 6 | .2428E+07 | .4292 | | | | | | |

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

| | | | |
|-------|-----------|-------|--------|
| Zones | SSE | R**2 | Zones: |
| 1 | .4247E+07 | .0015 | |

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 32228 steady state profiles are tested.

Calculated concentration at top : .2683E+05
 Calculated concentration at bottom: .2687E+05
 Calculated flux at top : .2234E-04
 Calculated flux at bottom : -.1915E-04
 Depth integration of production : -.4148E-04
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | -.4148E-04 | .0000E+00 |

```

St 23 rum DIC
  2.5
 32.5
  6
  1
1945.525
3852.903
5.00E-06
  3
1945.525
-1.00E+20
1.00E+20
  0.001
  0.01
X      FI    DB  ALFA  C
  2.5  0.69   0    0  1945.525
  7.5  0.54   0    0  2288.853
 12.5  0.51   0    0  2441.444
 17.5  0.43   0    0  2937.362
 22.5  0.42   0    0  2708.476
 27.5  0.41   0    0  3662.165
 32.5  0.41   0    0  3852.903

```



Name of input file : c:\modelling\st23rumDIC.txt
Name of output file: c:\modelling\st23rumDIC.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2  3  4  5  6

  1 .2483E+06 .9170 ---- .421 .761 .507 .000 .000
  2 .2152E+06 .9280 ----- 1.000 .445 .000 .000
  3 .2166E+06 .9276 ----- .237 .000 .000
  4 .1255E+06 .9580 ----- .000 .000
  5 .2245E-05 1.0000 ----- 1.000
  6 .8597E-05 1.0000

```

The F statistics suggest 5 zones. Choose the number of zones for further calculations: 1

```

Zones  SSE  R**2  Zones:
  1 .2483E+06 .9170

```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 119388 steady state profiles are tested.

```

Calculated concentration at top : .1946E+04
Calculated concentration at bottom: .3853E+04
Calculated flux at top : -.5955E-04
Calculated flux at bottom : -.5495E-04
Depth integration of production : .4595E-05
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1      .4595E-05  .0000E+00

```



Appendix 30.

```

St 23 Rum
Sulfate
  2.5
 32.5
  6
  1
27739.809
26415.863
 4.64E-06
  3
27739.809
-1.00E+20
 1.00E+20
  0.001
  0.01
X      FI      DB      ALFA      C
  2.5  0.69    0      0      27739.81
  7.5  0.54    0      0      27408.83
 12.5  0.51    0      0      26062.69
 17.5  0.43    0      0      27576.38
 22.5  0.42    0      0      25747.07
 27.5  0.41    0      0      26219.75
 32.5  0.41    0      0      26415.86

```

Name of input file : c:\modelling\st23rumsulfate.txt
Name of output file: c:\modelling\st23rumsulfate.out

Input read from file - the calculation begins.

```

Zones  SSE  R**2  Zones:  2   3   4   5   6
  1 .2080E+07 .4756 ---- .980 .659 .980 .000 .000
  2 .2080E+07 .4757 ----- .390 .923 .000 .000
  3 .1689E+07 .5742 ----- 1.000 .000 .000
  4 .1971E+07 .5031 ----- .000 .000
  5 .4749E-04 1.0000 ----- 1.000
  6 .2143E-03 1.0000

```

The F statistics suggest 5 zones. Choose the number of zones for further calculations: 1

```

Zones  SSE  R**2  Zones:
  1 .2080E+07 .4756

```

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 119446 steady state profiles are tested.

```

Calculated concentration at top : .2774E+05
Calculated concentration at bottom: .2642E+05
Calculated flux at top : .1324E-03
Calculated flux at bottom : -.3881E-04
Depth integration of production : -.1712E-03
Depth integration of irrigation : .0000E+00

```

Depth integration of production and irrigation in each zone:

```

Zones  Production  Irrigation
  1      -.1712E-03 .0000E+00

```

Appendix 31.

| | |
|-----------|-------------------|
| St 24 | DIC |
| 5 | |
| 55 | |
| 6 | |
| 1 | |
| 2929.5937 | |
| 3986.1685 | |
| 5.00E-06 | |
| 3 | |
| 2929.5937 | |
| -1.00E+20 | |
| 1.00E+20 | |
| 0.001 | |
| 0.01 | |
| X | FI DB ALFA C |
| 5 | 0.75 0 0 2929.594 |
| 10 | 0.68 0 0 2833.541 |
| 15 | 0.64 0 0 2929.594 |
| 20 | 0.62 0 0 2977.62 |
| 25 | 0.53 0 0 3169.724 |
| 30 | 0.52 0 0 3121.698 |
| 35 | 0.51 0 0 3457.881 |
| 40 | 0.5 0 0 3505.907 |
| 45 | 0.49 0 0 3842.09 |
| 50 | 0.48 0 0 3938.142 |
| 55 | 0.47 0 0 3986.168 |

Name of input file : c:\modelling\st24DIC.txt
 Name of output file: c:\modelling\st24DIC.out

Input read from file - the calculation begins.

| | | | | | | | |
|-------|-----------|-------|----------|------|------|-------|-----------|
| Zones | SSE | R**2 | Zones: 2 | 3 | 4 | 5 | 6 |
| 1 | .1142E+06 | .9389 | ---- | .009 | .019 | .023 | .053 .154 |
| 2 | .5117E+05 | .9726 | ----- | .229 | .183 | .302 | .577 |
| 3 | .4222E+05 | .9774 | ----- | .166 | .326 | .652 | |
| 4 | .3149E+05 | .9832 | ----- | | .504 | .985 | |
| 5 | .2905E+05 | .9845 | ----- | | | 1.000 | |
| 6 | .3131E+05 | .9833 | | | | | |

The F statistics suggest 2 zones. Choose the number of zones for further calculations: 2

| | | | |
|-------|-----------|-------|-----------|
| Zones | SSE | R**2 | Zones: 1 |
| 2 | .5117E+05 | .9726 | ---- .009 |
| 1 | .1142E+06 | .9389 | |

The F statistics suggest 2 zones. Choose the number of zones in final result: 2

The calculation is done - 18868 steady state profiles are tested.

Calculated concentration at top : .2930E+04
 Calculated concentration at bottom: .3986E+04
 Calculated flux at top : .1450E-04
 Calculated flux at bottom : -.1657E-04
 Depth integration of production : -.3107E-04
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | -.5754E-04 | .0000E+00 |
| 2 | .2647E-04 | .0000E+00 |

| | | | | | |
|---------------|-----------|------|------|---|----------|
| St 24 Sulfate | | | | | |
| | 5 | | | | |
| | 50 | | | | |
| | 6 | | | | |
| | 1 | | | | |
| | 27197 | | | | |
| | 27103.643 | | | | |
| | 4.64E-06 | | | | |
| | 3 | | | | |
| | 27197 | | | | |
| | -1.00E+20 | | | | |
| | 1.00E+20 | | | | |
| | 0.001 | | | | |
| | 0.01 | | | | |
| X | FI | DB | ALFA | C | |
| | 5 | 0.75 | 0 | 0 | 27197 |
| | 10 | 0.68 | 0 | 0 | 26367.28 |
| | 15 | 0.64 | 0 | 0 | 27222.15 |
| | 20 | 0.62 | 0 | 0 | 26672.98 |
| | 25 | 0.53 | 0 | 0 | 26896.77 |
| | 30 | 0.52 | 0 | 0 | 26765.43 |
| | 35 | 0.51 | 0 | 0 | 27794.58 |
| | 40 | 0.5 | 0 | 0 | 26718.29 |
| | 45 | 0.49 | 0 | 0 | 26678.23 |
| | 50 | 0.48 | 0 | 0 | 27103.64 |
| | 55 | 0.47 | 0 | 0 | 24395.78 |

Name of input file : c:\modelling\st24sulfate.txt
 Name of output file: c:\modelling\st24sulfate.out

Input read from file - the calculation begins.

Zones SSE R**2 Zones: 2 3 4 5 6

1 .1653E+07 -.1385 ---- .491 .699 .842 .913 .958
 2 .1552E+07 -.0691 ----- .612 .822 .905 .956
 3 .1492E+07 -.0278 ----- .705 .852 .935
 4 .1454E+07 -.0014 ----- .678 .870
 5 .1400E+07 .0359 ----- .738
 6 .1356E+07 .0659

The F statistics suggest 1 zones. Choose the number of zones for further calculations: 1

Zones SSE R**2 Zones:
 1 .1653E+07 -.1385

The F statistics have no suggestion. Choose the number of zones in final result: 1

The calculation is done - 2845 steady state profiles are tested.

Calculated concentration at top : .2720E+05
 Calculated concentration at bottom: .2710E+05
 Calculated flux at top : .3190E-04
 Calculated flux at bottom : -.2076E-04
 Depth integration of production : -.5266E-04
 Depth integration of irrigation : .0000E+00

Depth integration of production and irrigation in each zone:

| | | |
|-------|------------|------------|
| Zones | Production | Irrigation |
| 1 | -.5266E-04 | .0000E+00 |

Appendix 33.