DANMARKS OG GRØNLANDS GEOLOGISKE UNDERSØGELSE RAPPORT 2012/88

Review of selected non-seismic methods for onshore hydrocarbon exploration in Denmark

ALTKUL Project Report Part 1

T. M. Rasmussen & L. Thorning

GEOLOGICAL SURVEY OF DENMARK AND GREENLAND
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1. Executive summary

Project ALTKUL was commissioned by DONG E&P A/S and Nordsøfonden; the Danish Energy Agency followed the project closely.

The starting point of the study was the need in Danish onshore areas for more knowledge on alternative methods that could be used for hydrocarbon exploration, as an alternative to seismic investigations. DONG E&P A/S and Nordsøfonden approached GEUS, suggesting a study of seven different methods. The Danish Energy Agency was interested in the subject and requested that an actual test of a method be carried out as a part of the project. The agreement was signed in March 2011; the ALTKUL Project Report Part 1 (this report) was released mid-August 2012 for preview; the ALTKUL Project Report Part 2 is scheduled for release in November 2012. Both reports will become public domain reports at their release. A special ALTKUL Digital Archive (ADA) will become available for the participating companies and organisations only.

The seven methods considered are listed below with the most important remarks and conclusions:

Method 1: Surface geochemistry

This is almost an established field in the oil and gas industry, and a number of techniques - related to actual content of selected hydrocarbons or to the microbial effect of them - are used for different purposes, including exploration. There are many methods used to observe hydrocarbons at the surface. Although there are gaps in our understanding of how they actually migrated to the surface from deeply buried accumulations of hydrocarbons, there is agreement that this happens continuously. Often but not always their presence at surface is indicative of hydrocarbons at depth vertically below the micro seepage anomalies, whereas there is greater uncertainty in the case of macro seepage. The method has been used in Denmark, a few examples are described. The methods have a place in greenfield exploration in the Danish region; care should be taken in the design of the survey layout and multi-parameter solutions are recommended.

A review of geochemical surveying for hydrocarbons in Denmark 1972–2002 is enclosed as an appendix.

Method 2: Gravimetric modelling

The key to a proper use of gravity data in exploration is the integration with other types of geophysical data. Traditionally this has involved joint modeling of gravity and seismic data. Examples involving integration with electromagnetic and magnetic data are also reported.

The existing gravity data set from onshore Denmark is of high quality. Surveying with airborne systems used extensively offshore is not going to improve this data set.

Method 3: Magnetotellurics (MT, AMT and ZTEM)

The MT method is based on induction of time varying current in the subsurface from natural sources in the ionosphere, and involves measurements of the electromagnetic field variations at the surface. The method has undergone significant improvements with respect to acquisition of high quality data and subsequent 2D and 3D modelling of the data. Artificial sources may be utilised to improve the signal to noise ratio for high frequencies.

The advantage of the MT method is the large depth range covered and the simplicity of the field work, if no artificial sources are involved. The disadvantage of the method in relation to hydrocarbon exploration is that thin resistive layers such as hydrocarbon reservoirs or small high resistive structures are transparent. Basically the MT method is capable of mapping conductive structures, and MT has therefore been utilised in a search for conductive zones associated with pyritization above or in the surrounding of a hydrocarbon reservoir. Frequencies in the audio range (AMT) is utilised in shallow investigations. The ZTEM method is a recent airborne implementation of the AMT method and builds on an older AFMAG system that never became widely used. The various hydrocarbon plays in Denmark are concerned with deep targets and high degree of pyritization is therefore also expected to be at large depth (>1 km). A required depth of investigation deeper than 1 km excludes the audio frequency range. Nevertheless, knowledge of near surface conductivity variations are valuable in a modelling of MT data. The dense data coverage obtained with airborne systems (ZTEM or any controlled source airborne method) may improve the interpretations.

Recently interpretations of induced polarization in MT data have been reported from field studies in China. The induced polarization is linked to the occurrence of pyritization associated with hydrocarbon reservoirs. High quality data are required in order to be able to map induced polarization effects. A case study from China with known occurrences of gas reservoirs showed a good correlation between interpreted induced polarization and reservoirs.

Although MT data are unable to map resistive structures in any detail, the method has been used for structural interpretations of salt structures, where the contrast in resistivity between salt and surrounding clastic sediments or carbonates is high. MT has also been used for sub-salt/sub-basalt interpretations.

Method 4: High-Moment Electromagnetics (HMEM)

Controlled source electromagnetic methods have during the last decade received considerable attention in offshore hydrocarbon exploration. Several case studies are available that demonstrate the possibility of mapping resistive hydrocarbon reservoirs. The key to this ability of mapping (thin) resistive structures offshore is the use of a galvanic source, whereby low frequent alternating currents are injected into the seabed from high moment electromagnetic (HMEM) dipoles. Onshore applications of controlled source methods have been reported, but HMEM methods have not been used extensively. The Long Offset Transient Electromagnetic (LOTEM) system developed at the University of Cologne has been in use for about three decades and the system was commercialised by KMS Technologies Inc. This LOTEM system is, however, no longer available for routine turnkey projects onshore. Another system referred as MTEM (multi transient EM) was promoted fairly recently for onshore applications, but the development of this system is now entirely related to offshore work. A focussed source system (FSEM) has been developed recently at the Institute of Innovative Methods of Geophysics, Moscow, Russia, and the advantage of this system compared to conventional HMEM system has been described. Land application for FSEM is mentioned as a possibility, but no onshore case studies are reported. The FSEM method builds on a long tradition of using electromagnetic methods for hydrocarbon exploration in Russia and in the Soviet Union. This experience has also inspired a significant amount of work with onshore electromagnetic methods in China.

The workload involved in HMEM measurements is fairly high and this has impacted the applicability of the systems developed. Cultural electromagnetic disturbances have impacted the applicability of the methods, but a recent application of HMEM to a CO_2 injection test site in the Ketzin area near Potzdam showed that it is possible to obtain data of high quality in this high-noise area of Germany. The data may, however, be distorted by coupling to cables and pipelines, if these are present in a survey area.

The workload involved in HMEM prevents to some extent commercial application of these methods as a cost-effective exploration tool. De-risking in the evaluation of hydrocarbon prospects should be considered.

Method 5: High-Powered Spectral Induced Polarization (HPSIP)

Case studies from China with application of high-powered spectral induced polarization (HPSIP) report good correlation between hydrocarbon occurrences and induced polarization anomalies. The spectral induced polarization (SIP) method, or alternatively the complex resistivity (CR) method, was developed for mineral exploration in the early 1950'ies. In particular, the methods respond to occurrences of pyrite and this is what qualifies the method as a candidate in onshore hydrocarbon exploration. Several case studies in relation to hydrocarbon exploration from the United States are reported by Zonge – a major provider of EM instrumentation. They also provide statistics showing a good correlation between IP anomalies and occurrences of hydrocarbon. Investigations of IP are also referred in relation to the focused source EM technique referred in method 4; i.e. mapping of resistors as well as polarization. The most recent developments in China involve co-located measurements of spectral/frequency domain induced polarization and time-domain IP.

The workload involved in HPSIP measurements is similar to HMEM and thereby fairly high. This has therefore also impacted on the amount of applications reported. Cultural electromagnetic disturbances have also a negative effect on the applicability of HPSIP and IP in general.

Method 6: Electron Para-magnetic Resonance (EPR)

Application of electron para-magnetic resonance was included among the evaluated methods because it was promoted to us as a tool by TST Technology Inc. We conclude that the claims by TST Technology Inc. are not valid.

Method 7: Airborne Transient Pulse Surveys

The airborne transient pulse survey system advertised by Pinemont Technologies Inc. is essentially airborne AMT. In contrast to the ZTEM system, this system measures the time varying electric field. The frequency range is only suitable for shallow investigations.

Getting a test of one of the methods based on electromagnetic theory organised caused some difficulties. An experiment with a galvanic controlled source was considered to be the optimum choice. However, based on various contacts and failed attempts to organise a test, a contract was entered into with Uppsala University for some initial tests of the MT method. The test is to be carried out in August 2012 and will be reported in a separate report (ALTKUL Project Report Part 2).

2. Authors' Foreword

As geophysicists not normally working with seismic data acquisition, we have often noted the total reliance on seismic data in the oil and gas industry, even when other types of geophysical data seemed helpful and useful to us. We are aware that nothing can compete with e.g. modern 3D seismic surveys, and we applaud the detail, accuracy and understanding that can come out of such data. On the other hand, working mostly in the mineral sector, we often have to do with far less.

Perhaps therefore, our interest was piqued at once we were approached with the wish for a look at alternative methods for onshore exploration after hydrocarbons in Denmark. In National Parks, near vulnerable buildings etc., it is often not possible to get the necessary permissions for seismic work – are there then other methods that can help, providing sufficient data to make a decision without access to seismic data? At conferences and over coffee we hear about these alternative methods, we know some of them should work, but often claims are made that seem unreasonable. In short, we decided to take on the study, with the hope that we could learn something new from those cases, where alternative methods had been used, and perhaps suggest some approaches for non-seismic exploration in onshore Denmark.

Some of the results are laid out in this report. We were asked by the client to concentrate on seven techniques or methods, including some methods that are familiar but also some that seem farfetched. Furthermore, some sorting would have to be carried out, focussing on matters especially relevant for the Danish area. It has been a very interesting undertaking, and we have been far around. Our review can hopefully serve as a starting point for interested readers, and we hope that it will help clarify some issues for the non-experts in non-seismic methods. Can data be generated that will allow an exploration manager to make a go/no go decision for drilling a possible target without access to seismic data? Well, that question probably cannot be answered in general. It will depend very much on the precise scenario.

We have kept this report as non-technical as we could for an easy read. In Part 2 of the project report, released November 2012, the detailed results of a realistic test of magnetotellurics at Tønder will be presented.

Thorkild M. Rasmussen and Leif Thorning

September 2012

3. Introduction

This report presents the results of a study of selected alternative non-seismic, non-invasive methods for onshore exploration for hydrocarbons commissioned by DONG E&P A/S and Nordsøfonden and carried out by the authors in GEUS project no 11927, April 2011 to August 2012. This report (*Review of selected non-seismic methods for onshore hydrocarbon exploration in Denmark. ALTKUL Project Report Part 1*) presents the result of the review of seven different methods, with an underlying emphasis on the Danish onshore scenario; a second report (*ALTKUL Project Report Part 2*) will present the results of the test of one selected method and will be released to the public November 2012.

A further product is the ALTKUL Digital Archive (ADA), a collection of digital copies of papers, notes, presentations, web sites, etc. used by the authors in the project; for reasons having to do with copyrights, the ALTKUL Digital Archive can only be released in a few copies for use by those involved in the project. The ADA will <u>not</u> be released to the general public.

3.1 Project ALTKUL

Early in 2010, the authors were approached by DONG E&P A/S and Nordsøfonden, suggesting a study of possible non-seismic methods for hydrocarbon exploration in onshore Denmark. In the industry, seismic methods are still preferred; other methods are looked upon with considerable scepticism and perhaps undeserved distrust. There are claims about the success of some methods, but the documentation often is not published. A closer look seems warranted.

During the weeks leading up to the start of the project, the objectives of the projects were determined. The contract was signed late in March 2011 and the work was initiated soon thereafter. All parties to the agreement as well as the observer, the Danish Energy Agency, felt that the reports from the project should be made available in the public domain at the conclusion of the project.

A Project Steering Committee was formed at the beginning of the project, with representatives from DONG E&P A/S, Nordsøfonden and GEUS; The Danish Energy Agency took part in all meetings as an observer. Meetings were held approximately every two to three months. At fairly regular intervals, progress reports have informed the committee members of the on-goings in the project.

The draft of *ALTKUL Project Report Part 1* was released in digital form as a preview to the members and observers of the Project Steering Committee 13 August 2012, and released to the general public September 2012. The selected partner (Uppsala University) in the test of a method is obliged under contract to finish their work and input in time for the *ALTKUL Project Report Part 2* to be finished by November 2012.

With an outset from this project, further activity was initiated in two subject areas outside ALTKUL activities and without further cost to the two external financers of the project: (1) GEUS will prepare a more complete GEUS report summarizing the industry's use of near-surface geochemical surveys for hydrocarbons in Denmark. This is expected to be published in 2012 or 2013. Preview of part of the coming GEUS report can be seen in the appendix; (2) further scientific co-operation with GEUS' partner in the test of certain aspects of the use of EM for hydrocarbon exploration is expected.

3.2 **Project objective and goals**

The objectives of the project were defined in the contract as follows, here separated in part 1 and part 2 of the project, corresponding to the two reports:

Part 1: A review of seven methods

- The following non-seismic methods were to be included in the assessment:
    - Geochemistry,
    - 3D gravimetric modelling (including airborne gravity),
    - MT (magnetotellurics) and ZTEM (airborne magnetotellurics),
    - HMEM (High-Moment Electromagnetics),
    - HPSIP (High-Powered Spectral Induced Polarization)
    - TST Technology Inc. method (Electron Para-magnetic Resonance),
    - Airborne Transient Pulse Surveys.
- a digital archived library of sources to the review shall be compiled; this should include all referenced work, list of Url's, and brochures that have been accessed in the review process; the library will not be in the public domain, it is only intended for use among participants in the project.

Part 2: Results of the test of one selected method

- GEUS shall arrange a realistic test of one selected (EM-) method in the field over an area in Denmark.

From the outset it was made clear that given the nature of this project, GEUS could not guarantee any conclusive results of the research into the various methods, and not all methods could be given the same attention.

4. General description of methods

In this chapter all methods are described - and illustrated when possible.

4.1 Method 1: Surface Geochemistry

This method is based on seeps of hydrocarbons reaching the surface and becoming detectable there. It has been used for many years and there is by now a great many different methods to apply, and many that will give good results and have a significant influence on the interpretation in relation to exploration for hydrocarbons.

4.1.1 Introduction

It is an accepted fact that oil and gas seeps happen. Probably, it gave rise to the first exploration method for oil and gas employed by man. Many historical cases are known and thinking back to the start of the oil age in places like Texas, images of soiled and bubbling lakes or water-holes are indisputably related to high hopes of the explorers. Even today there are places with burning rocks proving beyond any doubt that hydrocarbons reach the surface. For many years, man’s need for hydrocarbons could be satisfied from such sources. The geochemistry was simple: if it smelled and tasted abominably and could burn, it was hydrocarbons. Today more sophisticated methods are needed, but the macro and less conspicuous micro seeps are still abundant, and we have learned to use them intelligently for exploration purposes. After all, it should strike a note of optimism that the literature seem to indicate a very good chance that the oil or gas field, you are exploring for, most likely already now signals its presence by leaking hydrocarbons for you to detect, even if you cannot see them or smell them. Based on empirical evidence, this can probably be taken as the rule rather than the exception.

In today’s exploration campaigns, the reliance on seismic data is so complete that other types of data quite often are neglected or overseen. This is still true even if modern exploration philosophy calls for multiple-discipline approaches and interpretation. Integration of many methods is always wise. Even in regions, where seismic data can be acquired, it may often be a good idea to add a geochemical survey to the repertoire. When seismic data cannot be acquired, it is very definitely a good idea to look for several other data types.

Geochemical surveys are today offered on a commercial industrial basis. There are many types to use depending on circumstances and on the surface expression of the presence of hydrocarbons in the underlying strata; many users of geochemical methods will claim that the signs of hydrocarbons will reach the surface vertically above the accumulation, even if this is several thousands of meters below, but it may be a problem pin-pointing specific reservoirs, e.g. in case of a stacked reservoir scenario. Many worry about the risk of lateral transportation of the escaping hydrocarbons. In this chapter we will briefly describe the phenomena related to especially micro seepage and how they can be utilized for hydrocarbon exploration – with emphasis on onshore exploration scenarios.

4.1.2 A simple model to set the stage

Today, foremost thanks to seismic techniques we are used to study reservoirs in considerable details; when production begins from the reservoir, we learn more from production drill holes and can develop a very detailed understanding of the reservoir and its working, and we can target specific places in the structure for further study or for production. If seismic data cannot be acquired because of special needs for environmental protection as e.g. in a national park, other methods are called for, even if they are not as accurate in pinpointing the hydrocarbon accumulations to specific structures. Especially, during the exploration phase in greenfield areas like onshore Denmark the explorer does not have the comforting knowledge of many producing wells in the vicinity and the limited task of finding a few more. In environmentally protected parks and tracts in Denmark, there are places where both the information that can be obtained from e.g. geochemical surveys and other non-invasive techniques must replace seismic data in the decision process, to drill or not to drill.

Figure 1 is from Schumacher *et al.* (2011a) and illustrates in a simple drawing, what are actually very complex systems and processes, not all perfectly understood. The processes illustrated on the figure play a role in all seeps and the resultant products are the basis for both geochemical and geophysical methods.

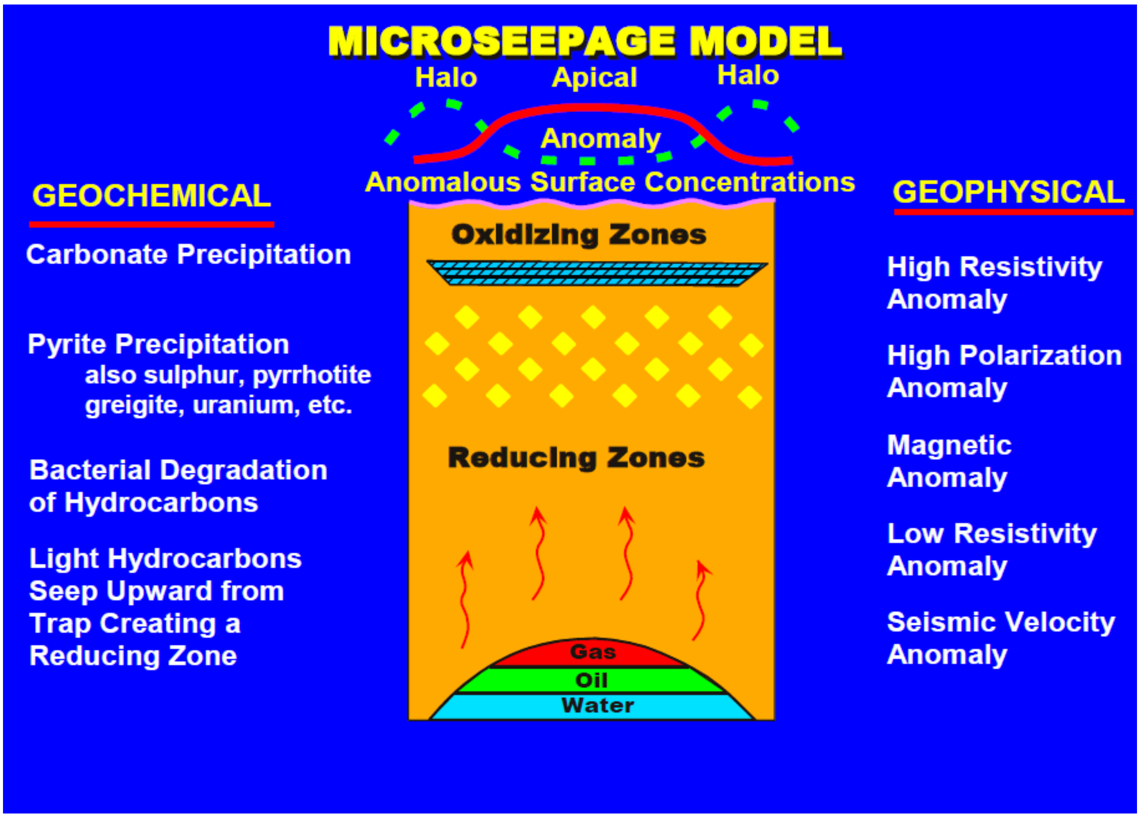


Figure 1. *Examples of the micro seepage processes taking place over a hydrocarbon accumulation. From Schumacher et al (2011a).*

According to this model, the hydrocarbons need to escape to the immediate surroundings of the accumulations, move considerable distances through the different rock types under various physical conditions, cross formation- and rock boundaries, interact physically and chemically with the rocks and soil and organisms living in them, and somehow reach the surface, where they can be detected directly or through the effects they have on the soil or bacteria living in the soil.

4.1.3 Hydrocarbons moving through the ground

It should be emphasised that there are significant differences in why, how and with what effect different hydrocarbons, gas or oil, move through the ground. They are in a sense sorted by the process, they affect the formations they move through, and each has a story to tell. Within the framework of this report, there is no room for a discussion of this, just a warning to be well aware of this, when interpreting surface geochemical data.

Understanding how the hydrocarbons move through the rock above accumulations has been the focus of much study over the last c. eighty years, although Tóth (1996) in a review of groundwater effects for seepage complains: *“Near-surface exploration for petroleum is really a problem of hydrocarbon migration from deep-seated accumulations to the land surface or the sea floor. Nevertheless, there is virtually no sign of serious and credible attempts in the otherwise extensive literature of near-surface exploration … to understand the various migration mechanisms, let alone quantify their relative importance and employ this understanding in exploration strategies”.* Many different mechanisms are at play; an overview of the different ways of hydrocarbon migration can be found in e.g. Matthews (1996) in an AAPG Memoir nevertheless containing much information (but of course few “proofs”) on this subject and thus to some extent opposing the pessimistic view of Tóth (1996). On this background, this report is in no manner intended to be a full treatise on migration of hydrocarbons; a few often discussed factors will be mentioned, because they are critical for the faith one can put into the method as an exploration tool, but otherwise this report must accept what apparently is commonly accepted: reliance on the usefulness of empirical results rather that insistence on a precise understanding of the process details.

Matthews (1996) finds that although many hydrocarbon migrating mechanisms are active in micro seepage, the dominant one is as free phase elements, rising on forces of buoyancy in the carrier and reservoir rocks. Capillary imbibition (replacement of a liquid by another immiscible liquid) is important for the movement in the transition from source and seal and into the different surrounding pore systems. The pathway taken by the hydrocarbons is determined by the heterogeneity at all scales. Underway the hydrocarbons are modified and the dominant process for this is phase partitioning.

There is ample evidence for how in the case of macro seepage, some hydrocarbons mostly follow faults and other natural paths to the surface and thus surface distribution of anomalies cannot be taken to reflect the situation directly below the seeps, but must be understood in terms of blocks with no seepage separated by faults as conduits for migrating hydrocarbons. For the occurrence of hydrocarbons (or effects created by their presence) at the surface to be taken as indicative of hydrocarbon accumulations at depth, it is required that the composite migration process is mostly vertical, when it comes to micro seepage. Any tendency for the hydrocarbons to be moved sideways any appreciable distances would severely limit the potential and accuracy of the near-surface geochemical methods. Most of the commercial companies will exhibit a tendency to put trust in the anomalies to be situated more or less vertically over the source for the leaking hydrocarbons, and rely on the safety offered by similar empirical data from surveys in different regions in general. Some studies have demonstrated that the accuracy of this assumption depends on the various seepage models related to different geologies. Thrasher *et al.* (1996) examine several different offshore sedimentary basins (the deep Gulf of Mexico, salt diapers in the North Sea, North Viking Graben, the Haltenbanken area, etc.) and convincingly show how many geological parameters must be brought into play to understand the observations. In the case of Haltenbanken, they show that hydrocarbons leaking vertically from Jurassic reservoirs at depth displaced laterally up dipping tertiary formations to be found in Paleocene sediments at the surface up to 50 kilometres away. Seepage *is* present at depth in all basins they consider in areas near the accumulations, but can apparently still in some cases be absent or minor at surface, because of complications leading to significant components of lateral transport also being involved. Klusman & Saeed (1996) discuss three different mechanisms (diffusion, by water and by buoyancy of microbubbles) and find the latter the most satisfactory model for proven vertical micro seepage.

Macro seepage and micro seepage can happen from the same accumulation simultaneously. The general tendency is to consider macro seepage of hydrocarbons mostly related to structures such as faults or crush zones; hydrocarbons moving this way can sometimes be ‘lead astray’ or stopped completely from reaching the surface, whereas micro seepage processes find ways to allow especially lighter hydrocarbons to move through contacts between different rocks and the rocks themselves more or less directly to the surface over the accumulated hydrocarbons. If nothing else, this is the sometimes untold assumption for most uses of near-surface geochemistry.

Still, it is for many a worry and a complication that horizontal transport of hydrocarbons in ground water is thought to be considerable in some cases, though it is often ignored in the interpretation. Holysh &Tóth (1996) show how otherwise expected vertical movement can be influenced by flow of formation water according to the potentiometric patterns created by glacial drift accumulations or the underlying Cretaceous units with a downward flow. Tóth (1996) emphasises how hydrological conditions may not only prevent hydrocarbon indications from reaching the surface at all but also are influencing the intensity and nature of anomalies that are detected, including their lateral position with respect to the subsurface accumulations of hydrocarbons.

Migration processes are often dynamic: variations can be seen to correlate with both natural e.g. barometric and meteorological variations and with anthropogenic seeps; e.g. gas leaked on purpose from an underground coal gasification reactor at 180 m depth were detected at the surface 2 – 15 days later (Jones III & Burtell, 1996).

4.1.4 Detection of hydrocarbons at the surface

The content of different hydrocarbons and isotopes in soil or water can be measured in many different ways and with great accuracy. The different hydrocarbons, certain isotopes and all the usual parameters used for characterization of hydrocarbons react differently to various types of seepage, and results in different possible measuring techniques being applied at the surface.

There are many radically different ways of detecting the presence of hydrocarbons in the soil. Some methods directly measure the content in a physical sample of the soil through different laboratory techniques; see e.g. Abrams & Dahdah (2010). The most common method to use is perhaps to measure the amount of hydrocarbons absorbed in the soil of the sample, others measure the microbial activity related to different hydrocarbons. Samples are usually obtained in a regular pattern representative for the expectations to underlying geology and other pre-survey information available.

As Schumacher (2011a) describes, the detection of the hydrocarbons at surface can also happen through various alterations in the soils and sediments near the surface: diagenetic alterations of carbonates, generation of sulphides, bleaching of red beds and clay mineral alterations are such processes with effects that can sometimes be seen with the naked eye, but more commonly just give rise to physical changes substantial enough to serve as the basis for geochemical or geophysical measurements.

Table 1. *Table courtesy **Gore Surveys** listing the many possible targets for the analytical package; this is in agreement with the philosophy held by the company to exploit as many parameters as possible in the use of geochemical surveys for characterisation of oil and gas and for their localisation.*

Typical Petroleum Constituents *Carbon number in ( )*			
Normal Alkane	**Iso-alkane**	**Cyclic Alkane**	**Aromatic and PAH***
Ethane (2)	2-Methylbutane (5)	Cyclopentane (5)	Benzene (6)
Propane (3)	2-Methylpentane (6)	Methylcyclopentane (6)	Toluene (7)
Butane (4)	3-Methylpentane (6)	Cyclohexane (6)	Ethylbenzene (8)
Pentane (5)	2,4-Dimethylpentane (7)	cis-1,3-Dimethylcyclopentane (7)	m,p-Xylenes (8)
Hexane (6)	2-Methylhexane (7)	trans-1,3-Dimethylcyclopentane (7)	o-Xylene (8)
Heptane (7)	3-Methylhexane (7)	trans-1,2-Dimethylcyclopentane (7)	Propylbenzene (9)
Octane (8)	2,5-Dimethylhexane (8)	Methylcyclohexane (7)	1-Ethyl-2/3-methylbenzene (9)
Nonane (9)	3-Methylheptane (8)	Cycloheptane (7)	1,3,5-Trimethylbenzene (9)
Decane (10)	2,6-Dimethylheptane (9)	cis-1,3/1,4-Dimethylcyclohexane (8)	1-Ethyl-4-methylbenzene (9)
Undecane (11)	Pristane (19)	cis-1,2-Dimethylcyclohexane (8)	1,2,4-Trimethylbenzene (9)
Dodecane (12)	Phytane (20)	trans-1,3/1,4-Dimethylcyclohexane (8)	Indane (9)
Tridecane (13)		trans-1,2-Dimethylcyclohexane (8)	Indene (9)
Tetradecane (14)		Ethylcyclohexane (8)	Butylbenzene (10)
Pentadecane (15)		Cyclooctane (8)	1,2,4,5-Tetramethylbenzene (10)
Hexadecane (16)		Propylcyclohexane (9)	Naphthalene (10)
Heptadecane (17)			2-Methylnaphthalene (11)
Octadecane (18)			

Byproduct and Alteration Compounds *Included in this method to provide a substantial inventory of the geochemical system in the surface soil zone*			
Alkene	**Alteration/Byproduct**	**Biogenic**	**NSOs***
Ethene (2)	Octanal (8)	alpha-Pinene	Furan
Propene (3)	Nonanal (9)	Camphene	2-Methylfuran
1-Butene (4)	Decanal (10)	beta-Pinene	Iodomethane
1-Pentene (5)		Limonene	Carbon Disulfide
1-Hexene (6)		Camphor	Styrene
1-Heptene (7)		Caryophyllene	Benzofuran
1-Octene (8)			Benzothiazole
1-Nonene (9)			Acenaphthylene
1-Decene (10)			Carbazole
1-Undecene (11)			

Mainly over the last 10–15 years increasing attention has been given to microbial activity in the near surface soils caused by the fundamental role these microbes have for the oxidising of the migrating hydrocarbons. The microbes are getting better and better known, even to the point at which microbes are specific to the alteration of which hydrocarbons, but still their roles are not fully understood, and neither is their influence on the amounts of hydrocarbons being left for normal measurements, which can raise some questions of accuracy. Microbial activity is today the basis for several commercial service providers' estimates of hydrocarbon abundance; see e.g. Hubert & Judd (2010) and web-pages for companies working with microbial methods.

Other providers insist on measuring the hydrocarbons themselves, together with other parameters, believing this to be the most accurate. It is also a common trend that more and more parameters or targets for the analyses are being involved; see Table 1, and that more and more complex models/methods are being used for interpreting the geochemical anomalies in terms of indications of hydrocarbons at depth; e.g. Anderson (2006).

Especially when uses of multi-parameter statistical estimations are intended but really in general, the sampling pattern should be thought out carefully and with a view towards strict sampling theorems' demands for representative sampling.

4.1.5 Discussion of near-surface geochemistry

In the Preface to the AAPG Memoir 66 (Schumacher & Abrams, eds, 1996), the two editors felt justified stating that at the conference. *"… there was general agreement on the following conclusions.*

- ✓ *Hydrocarbon accumulations are dynamic; seals are imperfect.*
- ✓ *All petroleum basins have some type of near-surface hydrocarbon leakage.*
- ✓ *Surface expression of leakage is not always detectable by conventional means.*
- ✓ *Hydrocarbon seepage can be active or passive, and it can be visible (macroseepage) or only chemically detectable (microseepage)*
- ✓ *Seepage expression, whether active or passive, is a function of many factors other than the mere presence or absence of active hydrocarbon generation and migration.*
- ✓ *Migration occurs mainly vertically, but it can also occur over long distances laterally.*
- ✓ *Hydrocarbons can move vertically through thousands of meters of strata without observable faults or fractures in a relatively short time (weeks to years).*
- ✓ *Relationships between surface geochemical anomalies and subsurface accumulation can be complex; proper interpretation requires integration of seepage data with geological, geophysical and geochemical data.*
- ✓ *Hydrocarbon migration mechanisms are still poorly understood. Present evidence favors effusion as the process of macro seepage and buoyancy of microbubles as the mechanism for micro seepage."*

The research reported in the AAPG Memoir 66 and since, very much supports these conclusions, though in many cases no final answers have been provided. Integration of data has been a dominant trend over the last fifteen years. As in all other methods used in exploration, it is certainly also true for surface geochemical survey data that as many different data as are obtainable should be used in the interpretation. Empirical results from geochemical survey data should always be used together with other types of data. So when we talk of using geochemical data for onshore hydrocarbon exploration, it is not the idea to replace e.g. 3 D seismic data with geochemical data, but rather to use the geochemical data to add extra information to the overall interpretation. In relation to the focus of this report of early phase exploration, the question then becomes: Can near-surface geochemical data compensate for the lack of seismic data to the extent that e.g. a decision to drill can be made at a reasonable level of risk *without* access to seismic data? If a situation could be achieved that would allow the answer yes to this question, it could be said that a viable alternative to seismic surveying had been found. Unfortunately, this will not generally be true.

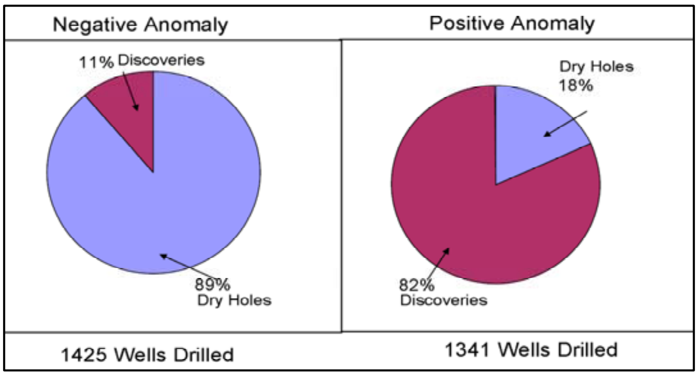


Figure 2. *From Schumacher (2011b). Summary including various geochemical methods, 2766 wells from various companies and various basins. Positive and negative geochemical anomalies and the chance of a discovery.*

On the other hand it should be emphasised that surface geochemical surveys make sense! Considering Figure 2 it is evident that non-seismic, <u>geochemical methods can be used to get meaningful information about hydrocarbon prospects</u> – and improve the odds; the simple statistics taken from Schumacher (2011b) seems convincing. However, what these figures say is that when drilling prospects identified by e.g. seismic methods and having a positive geochemical anomaly associated with them, then 82% of the 1341 wells drilled turned out to be discoveries, and only 18% dry holes. If only those with a negative geochemical anomaly had been drilled, then reversely the figures would have been less attractive with only 11% discoveries and 82% dry holes. On the face of it this is convincing. Schumacher (2011b) 'guesstimates' that probably there is generally a four to six times greater chance of hitting a commercial well, if the drilling of a defined target is done over positive geochemical anomalies.

Such statistics is always encouraging, but in the case of greenfield exploration the situation is different; the prospects have not been identified beforehand, rather the geochemical data could well have been collected to point out candidates in the first place. It is very much the question, whether or not the exploration manager can make a decision on the geochemical data alone; the odds above cannot be expected to hold – the risks will be far greater.

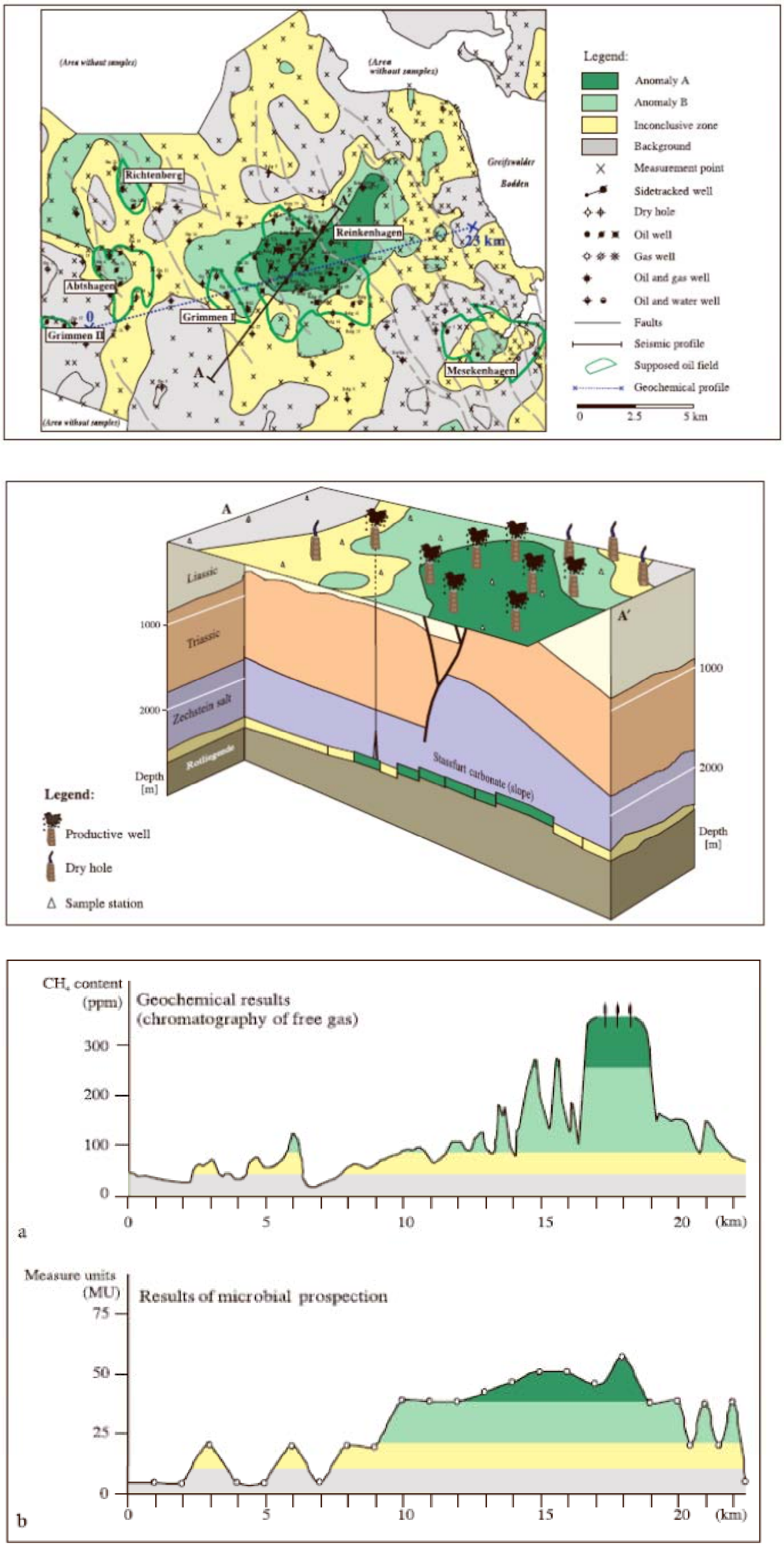


Figure 3. *Figs 12 (top), 13 & 14 from Wagner et al. (2002).The microbial survey (MPOG: microbial Prospection for Oil and Gas) gave good results at the Grimmen Oil Field. The faulting does not affect the results significantly, and the anomalies fit the producing wells. The lower panel compares the results from microbial prospection with a previous (1964) geochemical survey along the profile at the location shown in the top panel.*

In the German area, near Denmark, the microbial method has been used with success. Wagner *et al.* (2002) describe several interesting case stories, among them one from Grimmen near the Baltic Sea and Denmark. They show that the microbial prospecting method does not depend on faults; the work in Germany also provides a suitable background for the geochemical survey by Danica Resources shown later in the report.

Some commercial companies suggest measuring as many parameters as possible, which then allow multi-dimensional statistics to be used for better exploitation of the knowledge contained in many parameters, measured “simultaneously” on each sample.

Potter II *et al.* (1996) presents an independent evaluation of a gas geochemical exploration undertaken by Santa Fe Minerals, discussing many of the issues briefly mentioned in this report and explaining the choices and actions of a company faced with these. Subsequently 43 wells were drilled in prospects with negative geochemical anomalies revealing only two showing hydrocarbons; 92 wells were drilled in positive geochemical anomalies and 37 were commercial successes: the geochemical survey accurately predicted hydrocarbons in 92% of the cases.

In Monson (2003) a very detailed account is given of partly experimental, partly practical and real investigation on the Fort Peck Reservation, Northeast Montana. This report goes through a great many alternative methods and gives good descriptions of the relationship between the geology and the results.

4.1.6 Overview of geochemical surveys in Denmark

Through the years, there has been some geochemical survey activity in Denmark by the industry, though so far without a really convincing breakthrough onshore. In relation to this project report, it was reasonable to have a look at previous attempts of exploration in Danish regions for hydrocarbons by geochemical means, and to look for examples to use as directly relevant case histories. This section of the report therefore presents two items:

1. A brief pointer (4.1.6.1) to an overview included in appendix. This has been put together in a preliminary fashion by *senior adviser Troels Laier,* who has been involved in several such activities over the years. The appendix can be considered a preview of a future GEUS report to be released later this year describing geochemical surveys more fully.
2. A copy of a report concerning a recent geochemical survey on southern Denmark (4.1.6.2).

4.1.6.1 Overview: offshore and onshore surface geochemical projects in Denmark 1972-2002

Most surface geochemical surveys were carried out after 1983, when more oil companies became active in hydrocarbon exploration in Denmark. Prior to 1983 only one geochemical survey, including high methane in groundwater, had been carried out by Gulf Oil in 1972.

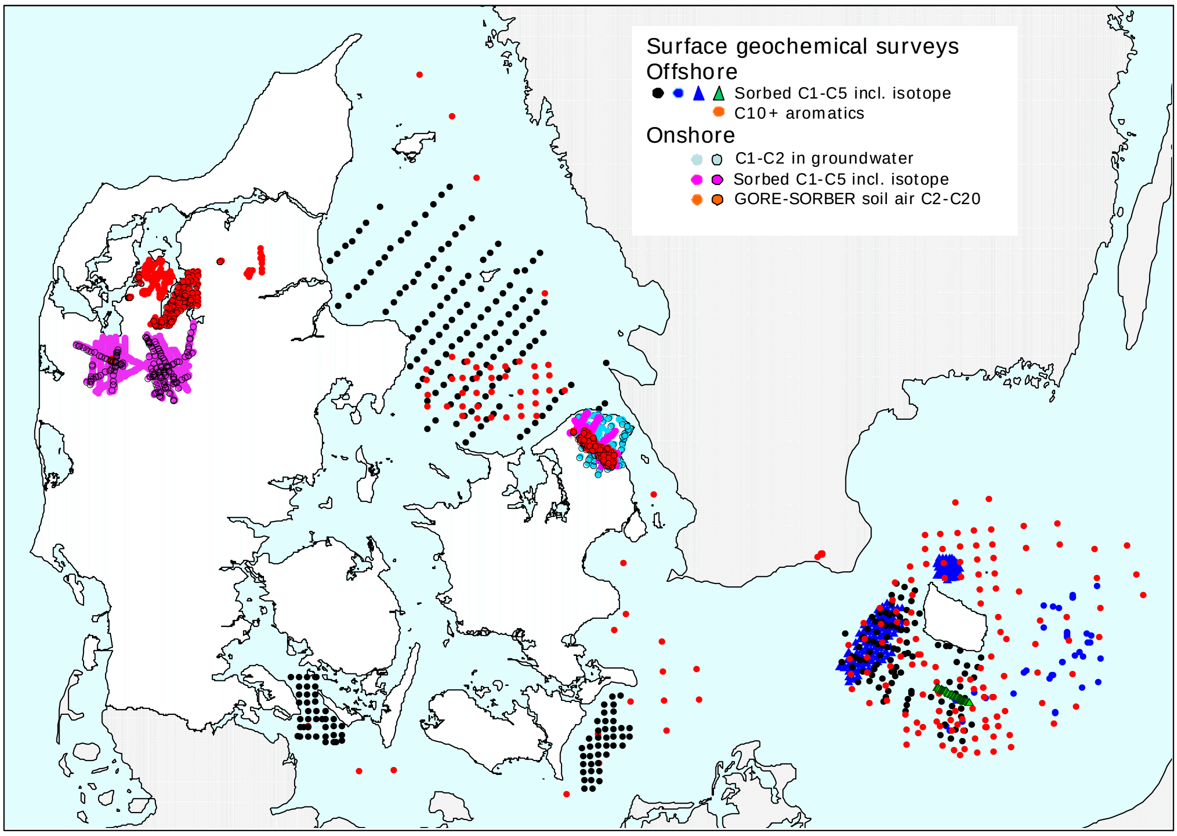


Figure 4. *Sample sites for surface geochemical surveys, see appendix for further explanation.*

Early surveys were mainly based on hydrocarbon (C1-C5) concentration in shallow samples, either soil or groundwater. Later when more sophisticated analytical techniques became available, isotopic analyses enabled discrimination of bacterial and thermogenic hydrocarbon gases. The increased sensitivity of modern analytical techniques, e.g. UV fluorescence of aromatic compounds and GC-MS analysis, made it possible to focus on higher hydrocarbons, thereby avoiding interference from hydrocarbon gases generated by bacteria. Though, in regions without any obvious hydrocarbon seepage it was still a challenge to localize subsurface hydrocarbon accumulation based on low levels of hydrocarbons in shallow samples, since traces of hydrocarbons appear to be present ubiquitously.

Apart from high methane in groundwater in a few areas only traces of hydrocarbons have been observed at shallow levels in Denmark from the various surveys performed. The high methane concentrations in areas like Nordsjælland and Vendsyssel was generated by bacteria as was shown by isotopic analyses ($\delta^{13}C$: -60 to -90 ‰). This is also true for the shallow gas (*c*.100m) that was exploited in the Frederikshavn area during the 1930'ies and 1940'ies.

License holders are obliged to deliver copies of all data and reports produced during their exploration activities to the Danish authorities. This includes data obtained from surface geochemical surveys as well. GEUS holds the national archive of all such data and in connection with the work on this report, a list of all the surface geochemical surveys within the

Danish area, except the North Sea has been prepared (appendix). The data exist in different forms, mostly in printed reports, some with maps and some with geo-coordinates of sample locations. Therefore in order to present an overview of the various surveys data, sample locations have been digitised and compiled into a GIS ArcMap project, Figure 4. The ArcMap project will allow comparison of the data of different surveys in overlapping areas. Furthermore, other information relevant for interpretation of the hydrocarbon data, e.g. soil maps etc. may easily be applied.

4.1.6.2 Danica Resources: A recent surface geochemical survey in Denmark

The most recent uses of geochemical techniques are surveys in southern Denmark in license area 1/08 carried out by Danica Resources in 2010/2011. The data have been handed in to the Danish authorities as required by Danish law and are still confidential. However, the report presented in this section has been released by for the purpose of inclusion in this report (Holland, B., personal communication, 2012). The survey was done to assist Danica Resources with the decision concerning the positioning of subsequent detailed 3D seismics (not yet acquired). For the reader of our report, it is an interesting exercise to think a little about the suitability of the data for this decision, or look at it from another angle: if seismic work is not allowed in these parts of Denmark, would it be feasible to point to a drilling site based on the geochemical survey instead?

The entire report received by Danica Resources is reproduced on the following pages in blue colour to provide an example of a realistic case story from Denmark.

Here follows a copy of original report: "DANICA RESOURCES RESULTS OF THE 2010-2011 GEOCHEMICAL SURVEY, LICENSE 1/08". With permission from the partnership in license 1/8

4.1.6.2.1 Introduction to Danica Resources Report

This report describes the analytical results obtained by the laboratory Vista Geoscience for soil samples collected in 2010 and 2011 across the onshore part of license 1/08 by license operator, Danica Resources (DR). The 2011 samples have been analyzed for oil only as the focus of the survey is to delineate lead areas of the Zechstein carbonate oil play. This play is the main focus of exploration in the license.

Samples collected in 2010 were analyzed for both oil and gas, and these results have previously been submitted. The results reported here include oil analyses for 2010 and 2011 samples and comparison to medium gravity oil (Michigan Basin oil), the Zechstein sourced oil found in the Løgumkloster-1 well (southern Jutland) and the Carboniferous sourced condensate from the Svane-1 well (Danish North Sea).

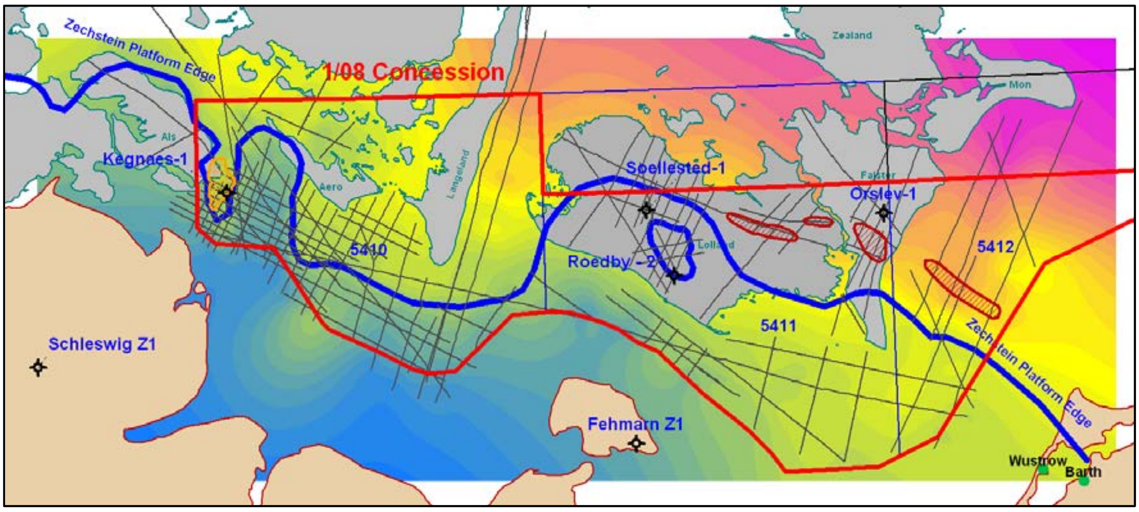


Figure DANICA 1. *The Zechstein carbonate platform margin trend in license 1/08*

The 2011 samples were taken along the Zechstein carbonate platform margin trend (Figure Danica 1) on Falster, Lolland and Ærø. The Zechstein trend and a Zechstein offshore topographic high on Lolland were mapped by Danica Resources on the basis of seismic data.

In the 2010 geochemical survey, samples were collected above seismically defined structures (leads) on eastern Als (a combined Rotliegend and Zechstein lead extending onshore) and on southern Langeland (a Bunter lead extending onshore) and above seismically defined Zechstein carbonate buildups/shoals leads on Falster and Lolland.

The follow-up geochemical survey in 2011 was conducted on a grid laid out over the seismically defined Zechstein platform margin on the islands Falster, Lolland and Ærø. The area on eastern Als was regarded as sufficiently sampled in 2010. The grid was comprised of lines 5-6 km long, oriented roughly perpendicular to the platform margin trend and spaced 3 km apart. The lines extend approximately equally across the platform (landward) and seaward off the platform margin into the slope environment. Soil samples were collected by hand auger at approximately 1 km spacing along the lines at a depth of 50 cm to 80 cm. Fluorescence analysis was carried out on organic extracts of oils found in these samples by Vista Geoscience, Denver, Colorado using a Varian spectrophotometer.

The aim of the geochemical survey was to search for hydrocarbon (oil) anomalies on the prospective Zechstein platform, its margin and the seaward slope where no seismic data has been acquired, and above seismically defined Zechstein leads along the trend. The presence of surface hydrocarbon anomalies would allow DR to focus seismic data acquisition on specific areas. Economic hydrocarbon deposits of Zechstein (Z2) age have been found in adjacent countries in these Zechstein depositional environments as:

1. Irregular “amoeboid” shaped carbonate build-ups in the platform interior
2. Oolitic shoals and carbonate build-ups on the platform margin
3. Re-sedimented carbonates (turbidites, debris flows and slumps) on the platform slope

4.1.6.2.2 Data Plots

Sample numbers, UTM coordinates and analytical results are provided in Attachment 1 (not included in this copy). Data plots are presented as Attachments 2, 3, 4 and 5 on the following pages. These plots include fluorescence intensity and similarity ranking to known oils and condensates. The data plots are posted on GoogleEarth images of the license area. The plots include:

Attachment 2. Løgumkloster oil rank and oil seep intensity

Attachment 3. Løgumkloster oil rank

Attachment 4. Svane condensate rank

Attachment 5. Løgumkloster and Michigan oil rank (an example of a medium gravity oil)

4.1.6.2.3 The known oils used in similarity ranking

All crude oils contain variable amounts of aromatic hydrocarbons, and when organic extracts of oil are exposed to ultraviolet radiation, they fluoresce radiation at diagnostic wavelengths which is detected by a Varian spectrophotometer. The intensity of these diagnostic wavelengths represents the amount of one- to six-ring aromatic hydrocarbons in oil and oil seep samples. Since these relatively small aromatic molecules are very soluble in formation waters (>1,000 ppm), they can be carried vertically to surface along micro-fractures that are too small to transport in-phase oil. These aromatic ring-type hydrocarbons are less susceptible to microbial degradation than are single-chain alkane hydrocarbons, and consequently a live seep at surface will have a similar aromatic composition to its source.

In order to quantify compositional similarity of known oils to surface seeps, the fluorescence intensity data are first normalized and then compared using an algorithm developed by Vista Geoscience. The algorithm compares the relative intensity of the diagnostic wavelengths to derive a numerical “rank” (score out of 100) of how compositionally similar the surface seep is to the known oil standard.

Fluorescence spectra of hydrocarbons found in the survey samples were compared to the fluorescence spectra of three different oils after and ranked in similarity. The known oils are:

1. The oil from the Løgumkloster-1 well drilled in southern Jutland. This oil is known to be derived from a Zechstein source rock (H. Petersen, GEUS, personal communication).

2. Condensate recovered from the Svane-1 well (Danish North Sea) derived from a Carboniferous source Based on its heavy Carbon isotope (ð13 C =-26.2) this condensate is derived from a Carboniferous source (Petersen et al, 2003, page 40; Ohm et al, 2006, page 8).

3. Oil (medium gravity) from the Albion-Scipio field in Michigan Basin, USA. This oil is derived from an Ordovician source rock. It is used in this report as an example of a type of oil that is lighter than the Løgumkloster oil. The sample was provided by Vista Geoscience from its large collection of crude oil samples. This oil was selected for comparison because some oil detected in the samples

did not rank high in similarity with either the Zechstein Løgumkloster oil or with the Svane condensate but appeared to be from a different medium gravity oil.

4.1.6.2.4 Results

The analytical results reveal the presence of surface hydrocarbon (oil) anomalies on the Zechstein carbonate platform interior, along the platform margin, and on the slope seaward of the platform margin. There are also hydrocarbon (oil) anomalies on the west and north-east flanks of the postulated Zechstein offshore topographic high (situated north of Rødby, see Attachment 1), and on southernmost Langeland and on eastern Als where they are associated with Triassic and Zechstein-Rotliegend leads respectively.

The Zechstein Løgumkloster oil rank highest has the highest rank similarity score to samples and is widely distributed across the sampled part of the license area (Attachments 2 and 3).

The medium gravity oil (typified by the Michigan Basin Albion-Scipio field oil) ranks high in similarity to samples on eastern Als, western Ærø and an area on western Lolland (Attachment 5). All three areas lie on the seismically defined Zechstein platform margin and slope.

Hydrocarbons in soils show relatively modest rankings to the Svane condensate, although a medium rank similarity to this condensate is found in samples above the seismically defined Zechstein-Rotliegend lead on eastern Als, the seismically Triassic lead on southernmost Langeland, southeastern Lolland and the seismically defined Zechstein leads on central and southern Falster (Attachment 4).

Of the three hydrocarbon ranks, samples ranking in similarity to the Svane condensate occur least, while both the Michigan Basin type oil and the heavier Løgumkloster oil occur more frequently.

4.1.6.2.5 Potential sources of the oils

Stinkdolomit

The oils found in the geochemical survey samples are likely derived from different source rock sequences. The Z2 Stinkdolomit is recognized as an oil source rock for Zechstein reservoirs throughout the Southern Permian Basin (see comprehensive discussion of the Z2 source potential in Peryt et al, 2010). The presence of a Zechstein age oil producing source rock in the license area is shown by the 34 meter thick section of the Z2 Stinkdolomit sequence penetrated in the Søllested-1 well (drilled on Lolland) at a depth of 2585 m to 2619 m. The Søllested-1 Well Completion Report describes this Z2 sequence from 2585 m – 2619 m as comprised of “Dolomite – mudstone, finely laminated, black to dark gray”. The section has several thin carbonate grain beds which have been interpreted as turbidites deposited on the Zechstein platform margin slope. In the Completion Report oil shows were described in this Stinkdolomit section as “petroliferous odor, milky white slow streaming cut”, and in sidewall cores as “spotty fluorescence with instant yellow streaming cut”.

´

Carboniferous

The other potential source rock in this license area is the lower Carboniferous. Vitrinite reflectance of samples collected from the 506 m thick Namurian section penetrated in the Ørslev-1 well over the interval 2117 m- 2516 m range from 0.57 to 0.65 (10 samples). The data show the organic material in the samples is in the early oil window (Thomsen et al, 1982). These Namurian sediments, especially the marine pyritic, carbonaceous, black to grey shales and the pyritic brown to grey marine limestone sections are comparable to the descriptions of Namurian sedimentary rocks from north Wales which have been shown to be the source rocks for the medium gravity and light oils and condensate found in the Douglas and Lennox fields in the Irish Sea (Armstrong et al, 1997).

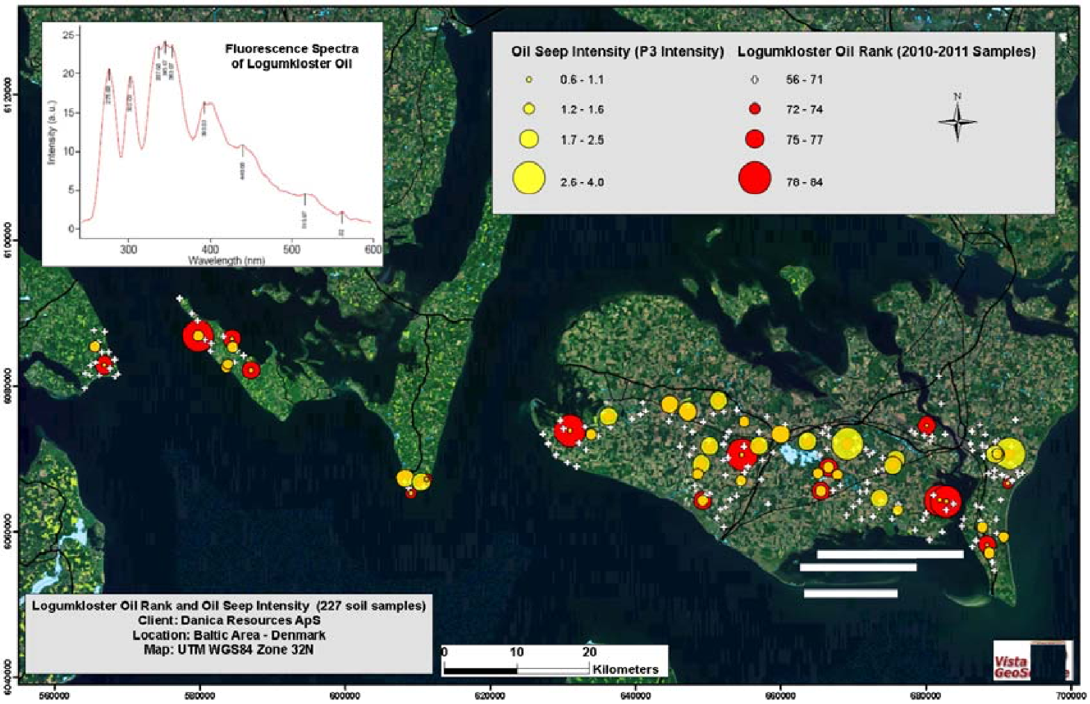
4.1.6.2.6 Conclusions

The onshore surface geochemical survey 2010-2011 in license 1/08 was conducted along the Zechstein platform, platform margin and platform slope. The survey detected hydrocarbon (oil) anomalies over this Zechstein trend on eastern Als, western Aerø, southern Langeland, and across Lolland and Falster. The hydrocarbons rank high in similarity to oil derived from a Zechstein source (Løgumkloster-1 well) and to a medium gravity oil (Michigan Basin type oil) and, to a lesser degree and less frequently, the condensate from the Svane-1 well (derived from Carboniferous source rocks). Some of the anomalies occur above Zechstein features mapped on seismic data interpreted to be stratigraphic traps composed of carbonate buildups/shoals.

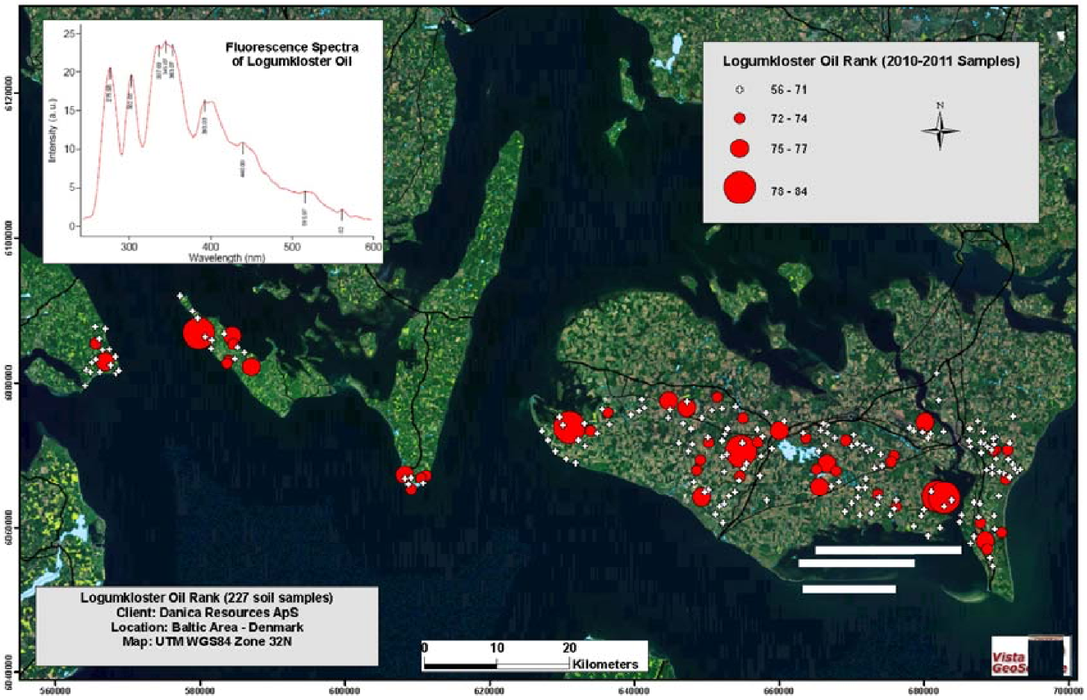
The hydrocarbon (oil) anomalies can be related to microseepage from either

1. Mature source rocks sequences along faults, fracture zones and other conduits, or from
2. Traps containing hydrocarbons.

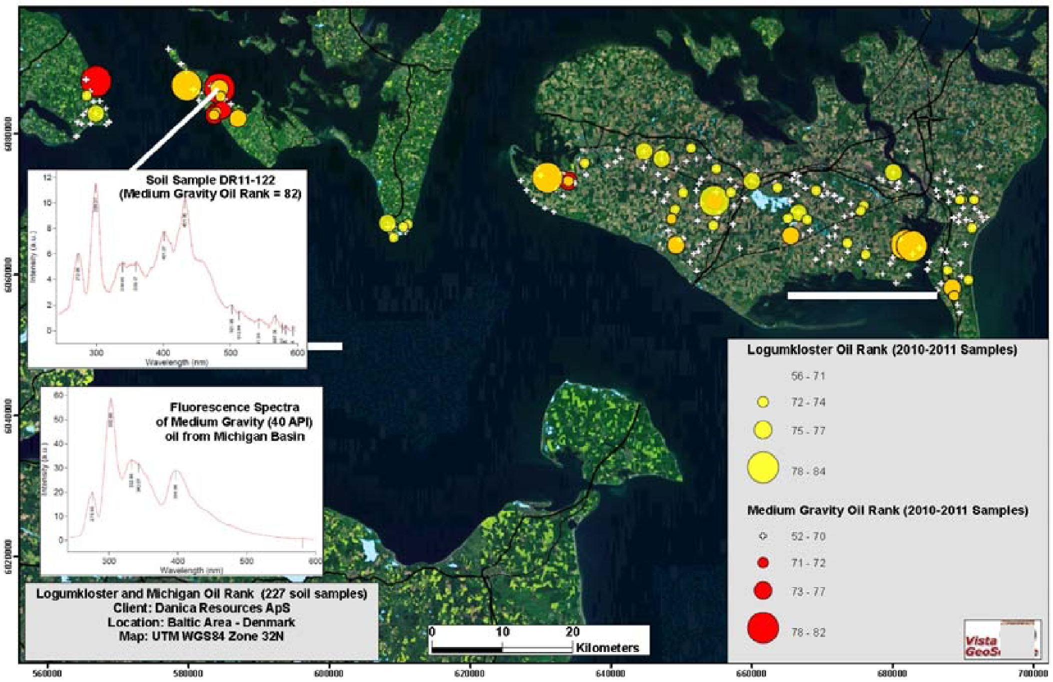
The presence and location of discrete oil anomalies will allow DR to design a focused, phased seismic program to further explore the onshore Zechstein carbonate play across the 1/08 license area.



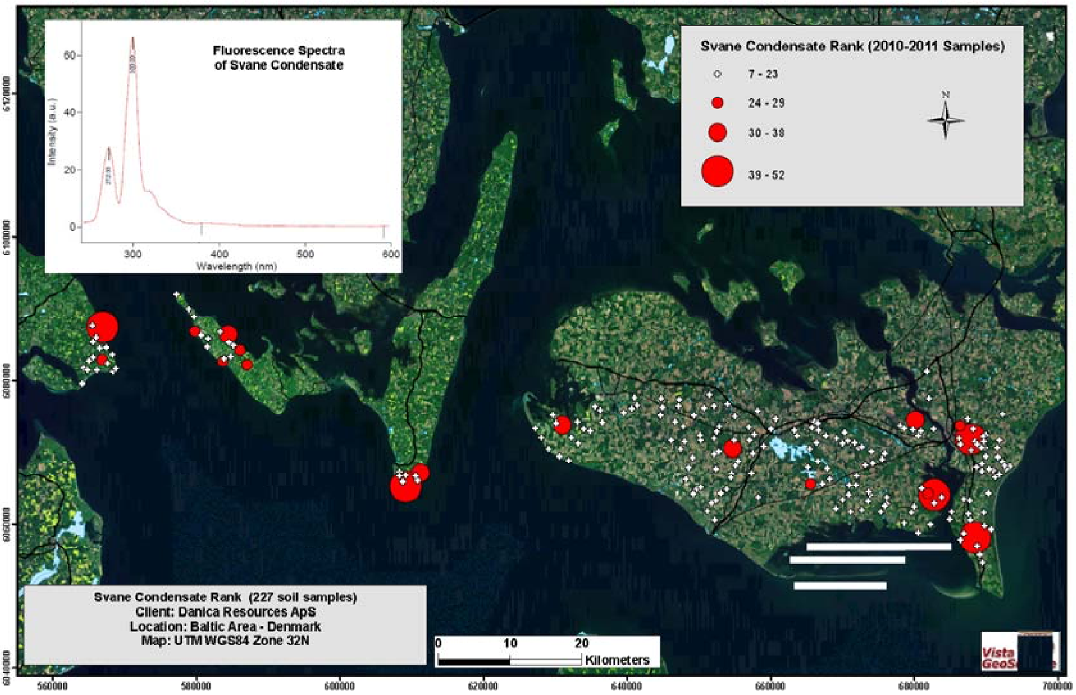
Attachment 2



Attachment 3



Attachment 4



Attachment 5

4.1.6.2.7 References

Armstrong, J. P., Smith, J. D'Elia, V. A. A. and Trueblood, S. P. 1997. The occurrence and correlation of oils and Namurian source rocks in the Liverpool Bay-North Wales. Geological Society of London Special Publications V. 124, p 195-211.

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Peryt, T. M., Geluk, M. Mathiesen, A., Paul, J. 2010. Zechstein. In: Doornebal, J. C. and Stevenson, A. G. (editors) Petroleum Geological Atlas of the Southern Permian Basin Area. EAGE Publications. Pages 123-147.

Ohm, S. E., Karlsen, D. A., Roberts, A., Johannessen, E. and Højlund, O. 2006. The Paleocene sandy Siri fairway: an efficient "pipeline" draining the prolific Central Graben? Journal of Petroleum Geology. Vol. 29 (1).

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4.1.7 Further reading

The references for this - and all other sections on methods - are gathered in Appendix (chapter 8) and collectively give a good overview of the relevant subjects for surface geochemistry. For a historically planned read-through of the literature, a suitable place would be to start with the review of Philip & Crisp (1982), which give a good account of most previous experiences all over the world in sedimentary basins with near surface geochemical surveying, going all the way back to the 1930'ties. Next, the AAPG Memoir 66 from 1996 contains many excellent papers and overviews and tries to elucidate many of the difficult subjects related to the migration of hydrocarbons.

For an illustrative review of several case histories using microbial prospection, Wagner *et al.* (2002) can be recommended. Munneche (2011) describes a typical service provider in this field.

The Texas Archival Resources Online provides access to many relevant selections of papers etc. created by researchers at Southern Methodist University, e.g. Saunders & Davidson (2007).

The multiparameter approach based on sorbed data favoured by e.g. Gore Surveys can be seen in some detail in Anderson (2006).

Monson (2003) gives a very good insight into the details of geochemical surveying for different methods and is also an example of an attempt to compare the usefulness of different methods, including magnetics and more.

A new collection of important papers will be coming out in 2013 in a SEG book (Schumacher & Warren, editors, personnel communication); this has not been available to the authors of this report, but should be sought out by potential future users of alternative methods.

Although not included among the seven methods, remote sensing is worth some attention. Several remote sensing techniques are promising and can in some cases be used to detect the signs of hydrocarbon presence already mentioned alterations, see e.g. Wettle *et al.* (2009) and Leifer *et al* (2012).

The ALTKUL Digital Archive contains more papers, web pages and company presentations relevant for near surface geochemical surveying.

4.2 Method 2: 3D Gravimetric modelling

The key to a proper use of gravity data in exploration is the integration with other types of geophysical data. Traditionally this has involved joint modeling of gravity and seismic data, but examples involving integration with electromagnetic and magnetic data are reported. In particular the experience of using of electromagnetic data in hydrocarbon exploration offshore jointly with gravity and seismic data seems promising.

The historical development of the gravity method in exploration is described in a review by Nabighian *et al.* (2005).They include a case study from the Mexican Gulf to illustrate the capability when using modern high quality gravity data in the modelling of salt tectonics.

Gravity data have also been used extensively in the study of salt structures in Denmark, and builds on a dense net of gravity stations.

The status of the Danish gravity data is described in a publication in January 2012 by Kort & Matrikelstyrelsen: “Referencenet for Danmark - Status, strategi og udvikling”. In total more than 50 000 measurements have been made. The majority of these measurements are ground based measurements. On average a sample for each km^2 is found onshore. Measurements offshore carried out from aircraft and ships are also available. The gravity network is continuously being improved and new absolute gravity measurements are used for calibration and evaluation of the gravity database. Most of this work is carried out at DTU. In general the accuracy and data density of the Danish gravity data is not a limiting factor in modelling. Møller *et al.* (2006) compare a densely sampled data profile across a buried quaternary valley on Lolland with the regional data set, and conclude that the regional data contain a reasonably representation of the gravity response from this near surface structure. The comparison is done after applying a method described by Strykowski (1998) which involves stripping off responses from deeper structures defined by seismic data and by applying simple high-pass filtering to the gravity data. In general, the presence of near surface responses in the regional data may therefore also need to be considered in modeling of deeper structures in order to fully utilize the high data quality.

Airborne gravity gradiometer measurement systems have become widely used in exploration. These systems typical measure several elements in the gravity gradient tensor $\boldsymbol{\Gamma}$ defined by

$$\boldsymbol{\Gamma} = \begin{Bmatrix} \partial g_x/\partial x & \partial g_x/\partial y & \partial g_x/\partial z \\ \partial g_y/\partial x & \partial g_y/\partial y & \partial g_y/\partial z \\ \partial g_z/\partial x & \partial g_z/\partial y & \partial g_z/\partial z \end{Bmatrix}$$

where x, y, z refer to axis of a coordinate system and g_i is the component of the gravity field in direction *i*. Component z is down with respect to a geodetic coordinate system and this direction differs slightly from vertical which by definition is the direction of the local gravity vector with magnitude g_T (total field) measured in standard gravity surveys. From knowledge of the gradient tensor it is possible to calculate the actual gravity vector by proper levelling to ground based reference data. Advantages of airborne gravity gradient measurements over measurements of the gravity field are debated, but this discussion is not of relevance to onshore gravity work in Denmark. The ground gravity station density and quality of the Danish gravity network is better in comparison to the data quality that can be achieved by modern airborne surveys. Airborne gravity is first of all applicable to rugged or remote areas that are difficult to access and for offshore work.

Despite the comment above on the applicability of gravity gradient measurements for onshore work in Denmark, a few comments on the use of gravity gradient tensor data are required. The gravity gradients, whether horizontal or vertical, has a higher ratio of the short wavelength amplitudes to the longer wavelength. Basically differentiation enhance shorter wavelength and the gradient data will emphasize the gravity response from local structures. The gravity gradient data therefore appear to resolve anomalies from local structures better that the gravity field, but this is only an apparent improvement in resolution. The three components of the gravity field and all derivatives can be calculated from measured gravity g_T provided that this is sampled properly and with a sufficient surface coverage. Measuring errors, data correction errors and insufficient sampling on g_T obviously influence the ability to calculate the gravity gradient tensor data, but any measurements of the gradient tensor elements are also subject to errors. Zhu (2007) provides a detailed comparison of measured and calculated gradient data for two areas in the United States. Another comparison is presented by Hinks *et al.* (2004) in which g_T is calculated from gravity gradient data from two airborne gravity gradient systems. Discrepancies between measured and calculated values are reported for both studies and conclusions regarding the cause of these are not straightforward. The Danish gravity network has data with a higher accuracy than the ground gravity data used in the referred study from the Unites States. Errors due to incorrect topographic corrections are considerably smaller in the case of data from the Danish area.

In a discussion on resolution it is important to make the distinction if this refers to sampling of anomalies or to resolution related to data inversion. The fact that the gravity gradient tensor can be calculated from g_T implies that all problems in terms of non-uniqueness or equivalence in interpretation of standard gravity data are also applicable to gravity gradient tensor data. Thus, the severe lack of resolution in a discussion on inversion and modelling of gravity data is also the case for gravity gradient data. Li (2011) compares standard gravity data with gradiometer data and discusses their use in modeling. A case study from the Mexican Gulf on the use of gradiometer data is presented by O'Brien *et al.* (2005) where they integrate reflection seismic prestack depth imaging data with full tensor gravity gradiometry data in the modeling of a salt structure. O'Brien *et al.* (2005) argue that full tensor gravity gradiometry data are better suited than standard gravity data for interpretation.

Figure 5 shows a map of the Bouguer gravity field published by Wybraniec *et al.* (1998). The gravity data used are from a grid with 2 km node separation; i.e. a slightly causer grid compared to the average sample distance of approximately 1 km. The anomalies caused by structures below 1 km are however reasonably well represented by the 2 km grid. The upper half of the gravity gradient tensor calculated from the data in Figure 5 is displayed in Figure 6 together with some rotational invariants (independent of coordinate system) of the tensor. The invariants are described in Pedersen & Rasmussen (1990). The invariants are useful in structural interpretations of gravity data and they serve as structural dimensionality indicators. In particular they are useful in edge detection algorithms as described in Beiki (2010) and Beiki & Pedersen (2010, 2011). Two examples in relation to hydrocarbon exploration onshore and offshore Brazil are provided in Murphy & Brewster (2007). The invariants are furthermore useful in a space domain classification of the gravity field and thereby classification of the subsurface structures.

Lyngsie *et al.* (2007) presented an integrated gravity, magnetic and seismic modelling of the Brande Graben as a case study of rift dynamics in northern Europe. The gravity data used are from a compilation described in Wybraniec *et al.* (1998). The paper by Lyngsie *et al*. (2007) serves as an excellent illustration of how to use gravity data in regional tectonic interpretations. Modelling of gravity data from the Glückstadt Graben of the North-German Basin by Yegorova *et al.* (2008) was able to reveal differences in the degree of salt saturation in salt-rich bodies and elucidate the proportion of Rotliegend salt.

Zhou & Thybo (1996, 1997) discuss the possibility of utilizing the gravity data for mapping pre-Zechstein sediments in the Danish area. Strykowski (1998) presents a method for stripping off responses from overlying layers in a study of deeper structures and apply this to gravity data from Denmark. This paper involves estimation of responses from structures in the basement, but the principles of the method are applicable also in a modelling of sedimentary structures.

An example with joint interpretation of gravity and electromagnetic data onshore are provided by Buehneman *et al.* (2002) in a modeling of the Wedehof salt dome, located in the Northern Germany.

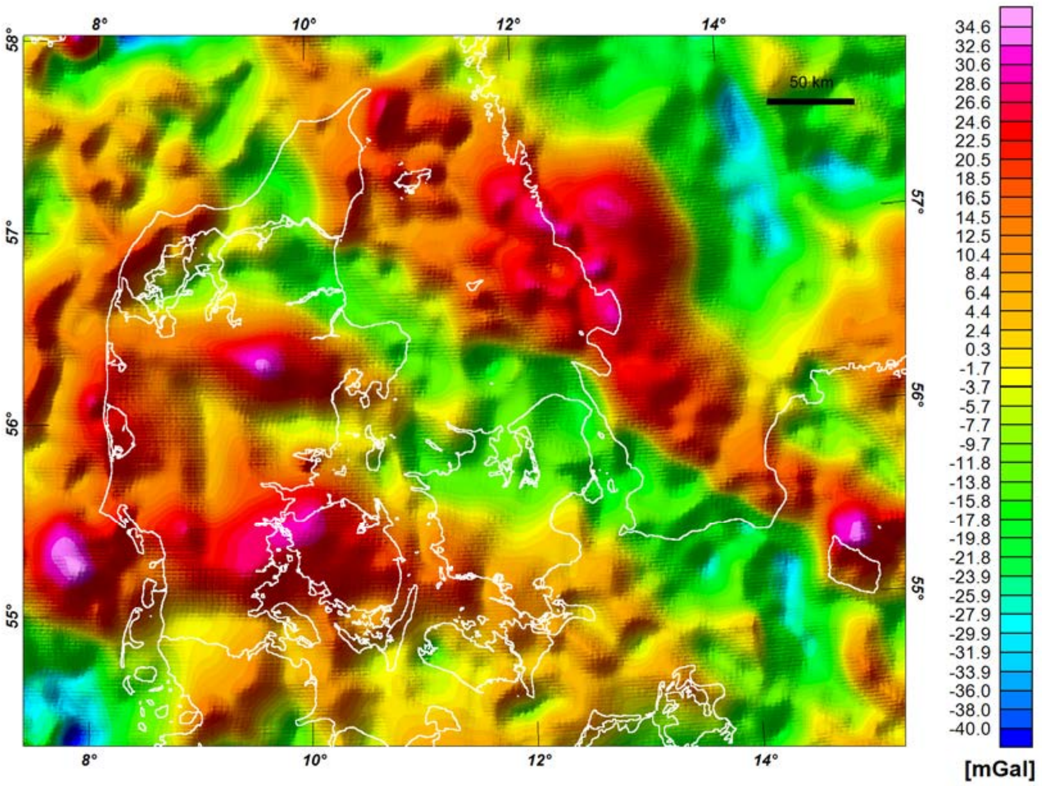


Figure 5. *Map of the Bouguer gravity field. After Wybraniec et al. 1998.*

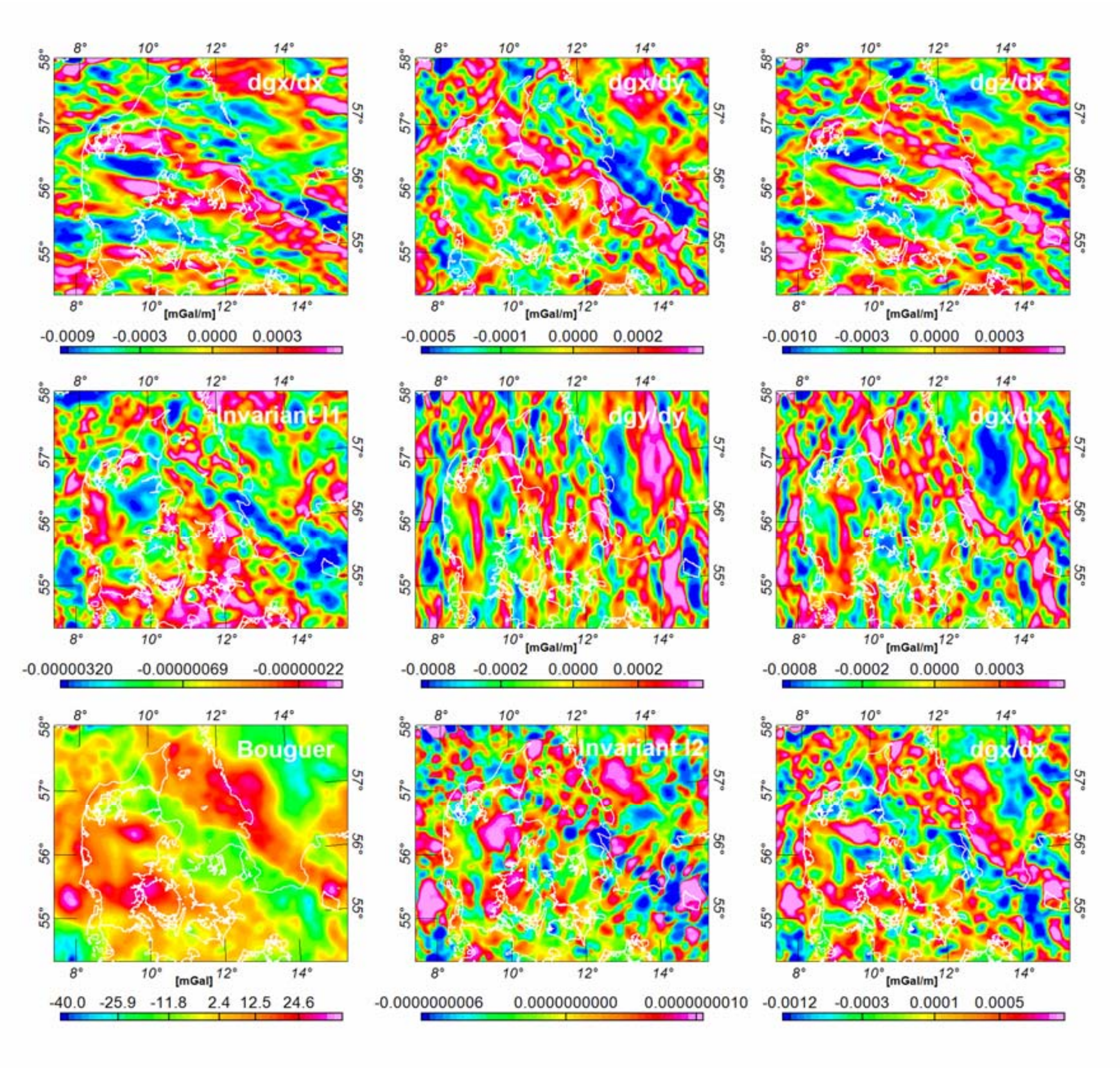


Figure 6. *Map of the gravity gradient tensor derived from the data in Figure 5. The upper triangle of the gravity gradient tensor is displayed together with images of the Bouguer field and invariants I1 and I2 of the gravity gradient tensor.*

4.3 **EM induction methods – general remarks and introduction**

4.3.1 Classification of EM methods

Electromagnetic induction methods can be classified according to a number of criteria. The most important criteria used for the classification relate to the type of energy source (**transmitter**) used for inducing electromagnetic fields into the ground and the measuring device (**receiver**) used for measuring the electromagnetic **responses** from the ground as well as the electromagnetic field propagating directly to the receiver through the air half space. Other criteria in common use are based on the effective frequency range or content covered by the recorded data, distance between electromagnetic source and electromagnetic receiver locations, field-type measured, onshore or offshore environment. Whatever classification used, the fundamental description of the methods relies on Maxwell equations and the different classes or methods therefore share a common base for their implementation and associated interpretation of data. Dependant on the above mentioned criteria, simplifications to Maxwell equations describing the methods is applied.

The physical properties of relevance for electromagnetic induction are the electrical resistivity ρ_E in units of ohm·m [Ωm], the electrical conductivity $\sigma_E = \rho_E^{-1}$ in units of Siemens [S] the magnetic permeability μ [Henry/m] and the dielectric permittivity ε [C/(Vm)].

The electrical resistivity is often, but not always, treated as a real frequency independent property. In some cases, a complex resistivity is used to describe the physical properties and inclusion of frequency dependency known as dispersion may be necessary.

In most applications, the magnetic permeability is approximated by the permeability of vacuum $\mu_0 = 4 \cdot \pi \cdot 10^{-7} H/m$.

For frequencies of relevance for hydrocarbon exploration, terms of the Maxwell equations containing the dielectrical permittivity are often neglected, when describing the behaviour of the electromagnetic fields within the electrically good conductive ground. Nevertheless, in some applications, a description of the propagation of the electromagnetic field needs to be considered and the dielectric permittivity needs to be included in the calculations. When the dielectrical permittivity can be neglected, the spatial propagation of electromagnetic fields within the earth is characterised mainly as a diffusion process instead of wave propagation; i.e. the field is attenuated by $2 \cdot \pi$ within the distance of one wavelength. The attenuation of amplitude away from the source is caused by energy loss related to heating, when currents pass through the rocks and the more simple attenuation related to the geometric spreading. In the resistive airspace, the propagation of electromagnetic field is described as wave propagation and the decay of amplitude away from the source is mainly due to the geometric spreading. The diffusive nature in the ground of EM fields used for hydrocarbon exploration has the implication that the spatial resolution is degraded when compared to cases, e.g. georadar, where wave propagation occurs.

An exception to the comments above on fully neglecting the dielectric permittivity is in relation to the method referred to as induced polarization (IP), where the rocks act as electrical capacitors. Wait & Debroux (1984) in their description of induced polarization introduce the polarizability p of the medium as the ratio between the imaginary and real parts of the complex frequency dependant conductivity; i.e. $p(\omega) = \sigma_E^i(\omega) / \sigma_E^r(\omega)$. In an ideal lossy dielectric medium, σ_E^r is the actual real conductivity and $\sigma_E^i = \omega\varepsilon$ is the imaginary part. Wait & Debroux introduce the effective permittivity for the combined effect of induced polarization and the dispersion model as defined by the ordinary permittivity of the medium. Thus, the polarization parameter of the medium implicitly includes the dispersion and the IP. The theory of induced polarization methods is described in Luo & Zhang (1998) which also includes a reprint of a paper by Wait (1959) on the theory of complex resistivity methods.

A comprehensive description of EM theory in general and examples on application of most EM methods can be found in Nabighian (1988, 1991). A single paper among this collection of papers deals with hydrocarbon exploration. In this report we shall not repeat or provide another presentation of EM theory. However, we include below a description of the most fundamental concepts and we highlight important topics that are of relevance for the use of the EM methods in hydrocarbon exploration. Table 2 serves as reference for the discussion below on classification of EM methods.

Table 2: *Various terms used in classification of EM methods. The terms in relation to transmitter type, source waveform and receiver type can be paired in various combinations with one exception: Discrete frequencies always imply ontime recordings (highlighted in blue) and the absence of offtime data. The receiver may involve any combination of the terms listed; i.e. both on and offtime and simultaneous measurements of electric and magnetic fields. As an example of combining the different terms, an electric dipole/bipole source paired with a discrete frequency transmission and measured with an electric dipole and magnetometer corresponds to CSEM data displayed in Figure 17. The waveforms in MT are essentially a superposition of a large number of transient signals. Methods based on measurements of self potential differ significantly from other methods and does not involve EM induction phenomena.*

Natural source
ionospheric currents (MT)
lightning (AMT, AFMAG, ZTEM, Airborne Transient Pulse Surveys)
self potential (chemical reactions)

Artificial source/transmitter type
grounded dipole/bipole
inducion coil/loop

source waveform
discrete frequencies
transients

Reciever type
B-field recording; e.g. squid magnetometer and fluxgate
induction coil
electric dipole/bipole
ontime recording
offtime recording

4.3.1.1 EM sources and receiver types

The sources that are utilised in EM methods are of natural origin as well as man-made (controlled source). The transmitted electromagnetic field from the source is denoted the **primary field** (the field that would exist in free space without interference with any conductors), and the electromagnetic field generated due to the interaction with the electrically conductive ground is referred as the **secondary field**.

The sources of natural origin are mainly the electrical current system in the ionosphere and electromagnetic fields associated with distant lightning phenomena. The two types differ with respect to frequency range involved. The ionosphere sources produce electromagnetic fields with frequencies mainly below 1 Hz, whereas the electromagnetic field caused by lightning has frequencies above 1 Hz. Figure 7 shows the characteristic variation in the energy spectrum produced by these natural sources. Some peaks can be observed in the spectrum and they are attributed to various favourable conditions with respect to transmission of energy above the ground. These two types of sources are utilised in magnetotellurics (MT) and audio-magnetotellurics (AMT), where simultaneous measurements of the time varying electric and magnetic fields are utilised. The distinction between the two methods is essentially a matter of differences in frequency content, whereas the data collection, processing and interpretation techniques are basically identical. Other methods utilising these natural sources are the airborne AFMAG technique and the more recent ZTEM technique, which share many similarities to (A)MT. In most applications the assumption is made of distant sources, where distant is referred relative to the depth of penetration into the Earth. Although the lightning phenomena are associated with electrical charge exchange (galvanic source) between the atmosphere and the earth locally, the energy utilised in the AMT methods is fully based on inductively generated current in the ground, where the electromagnetic wave has travelled - often several thousands of kilometres from mainly tropical regions - through the airspace before penetration into the ground. The primary electromagnetic field penetrating the ground is then approximately a plan wave with similar phases within an area of investigation. When the air wave hits the air-Earth interface, the direction of propagation becomes vertical in accordance with Snell’s law for propagation of waves due to the very large difference between conductivity of the air and Earth. The fact that non galvanic sources are involved for the above mentioned methods puts some limitations to their use for hydrocarbon exploration. Inductive source are not very suitable for mapping resistive formations typical for hydrocarbon reservoirs.

Insufficient power of the natural electromagnetic field may prevent recordings of high quality MT/AMT/ZTEM/AFMAG data. In these cases, an artificial source connected to a generator may be used to generate sufficiently high field strength and thereby ensure data of good quality. The source is typical one or several grounded wires ejecting alternating currents into the ground (**galvanic source**) or a current loop isolated from the ground. Currents in the isolated wires between grounded electrodes or in an isolated loop on the ground emits energy into the air and the ground (**inductive source**). MT data of high quality can usually be obtained without the use of a distant artificial source, whereas high quality data in the AMT frequency band are more difficult to achieve in some areas. CSAMT is often used as acronym for controlled source AMT. Apart from the above mentioned problems with respect to signal/noise ratio; the MT/AMT method has the advantage of providing a very broad depth range, basically from the upper few tens of metres to hundreds of kilometres. The depth of penetration is approximately equal to the skin depth defined as the depth (in a homogenous half space), where the electrical signal strength has decayed by a factor e=2.718282 from the strength at the surface.

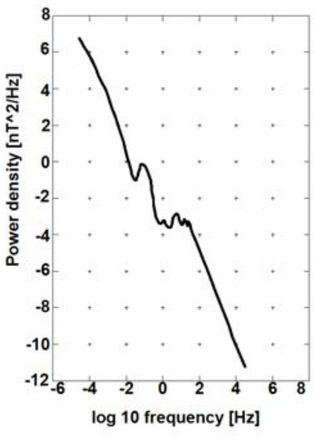


Figure 7. *Geomagnetic spectrum. Frequencies below 1 Hz is the MT frequency band and frequency above 1 Hz is the AMT frequency band.*

MT/AMT data are processed such that the final response functions used in interpretations are completely independent of the actual source; i.e. the responses are only dependent on the earth structure. Elimination of the source dependency is done by introduction of the frequency dependant magnetotellurics impedance tensor and tipper function. For a one-dimensional earth structure, the elimination is basically a matter of forming the ratio between the electric field and the magnetic field. In the case of utilising an artificial source in relation to the AMT technique, a classification of the data is often done in terms of whether data are obtained in the far-field, transition zone or near-field. In the far-field zone, the impingent electromagnetic wave fulfils the plane wave approximation mentioned above and the data are fully equivalent to natural source MT. In contrary, data obtained in the transition zone and near field zone requires that interpretations take the source-receiver geometry into account in any modelling.

Artificial man-made sources are in almost all cases constructed by transmitting electrical current into a system of wires that are either separated fully from the ground or have some galvanic contact to the ground, or to the water in case of marine methods. In general, artificial man made source for EM can be classified as being purely inductive, galvanic or they can be a combination of these two types. In addition, the classification involves how the electric currents in the wires vary with time. The classical Schlumberger sounding method makes use of two grounded electrodes connected to a current generator (battery) and a constant voltage is established between the electrodes, and a potential difference is measured simultaneously between two other grounded electrodes. The current injected into the ground is constant in time (during the measurements) and described as direct current (DC). Schlumberger soundings do not involve induction phenomena. One Schlumberger sounding includes measurements for different current electrode separations. The depth penetration increases with increased electrode separation. Induction methods are based on time varying or alternating (AC) currents being transmitted during a particular measurement. In some cases the time variation is described by a mono chromatic signal or single frequency, whereas other methods make use of more complex shaped current waveforms. Figures 8 and 9 show examples of waveforms. The waveforms are often approximations to some ideal shape such as a square (step) or triangular waveform with alternating polarity. Some sources transmit energy continuously and others have alternating periods with current on- and off-times. Ravenhurst (2001) provides an excellent description of waveform types, the implications of deviations from the ideal shape of e.g. current steps and current impulses and the relationship between data from one type with data from another type.

Various types of receivers are being used. Measurements of electric fields are typical done by measuring voltage differences between two electrodes and then dividing by the distance between the electrodes. Magnetic fields and field variations are measured by e.g. fluxgate and squid magnetometers, caesium vapour magnetometers and induction coils. Often a recording consists of sampling a voltage between electrodes or voltage output from an induction coil at regular time intervals. The time series are afterwards then processed to provide the information of relevance. The processing may involve transformation of the recorded time series or time domain data to the frequency domain for extracting the field dependency with frequency. A method in which responses are presented as a function of frequency is often referred as **frequency domain electromagnetic** method even if the actual measurements involve registration of data from the receivers as time series. A method where response data are presented as function of time where time is referenced to a specific instant of the source waveform transmission is referred as **time domain electromagnetic** method. The two domains correspond to the common time-frequency domains used in standard Fourier theory, and the data in the two domains are, in case of perfect data, fully equivalent provided that data are properly sampled. The equivalence is utilised in model response calculations, but actual measured data are seldom available with sufficient dense sampling to allow transformation from one domain to the other. Acronyms FEM and TEM are used for the two domains. However, the acronym TEM for **transient electromagnetic** method is often used with reference to a transient behaviour of the source waveform. Fortunately transient EM is also a time domain method. The term "transient electromagnetic" is compared to the term "time domain" a better description, because it emphasises the transient character of the source signal as opposed to the periodic source signal in frequency domain EM with a finite number of frequencies. Averaging in time (stacking) of responses from repeated energy transmissions is almost always performed for both frequency and time domain methods in order to improve the signal to noise ratio of the data.

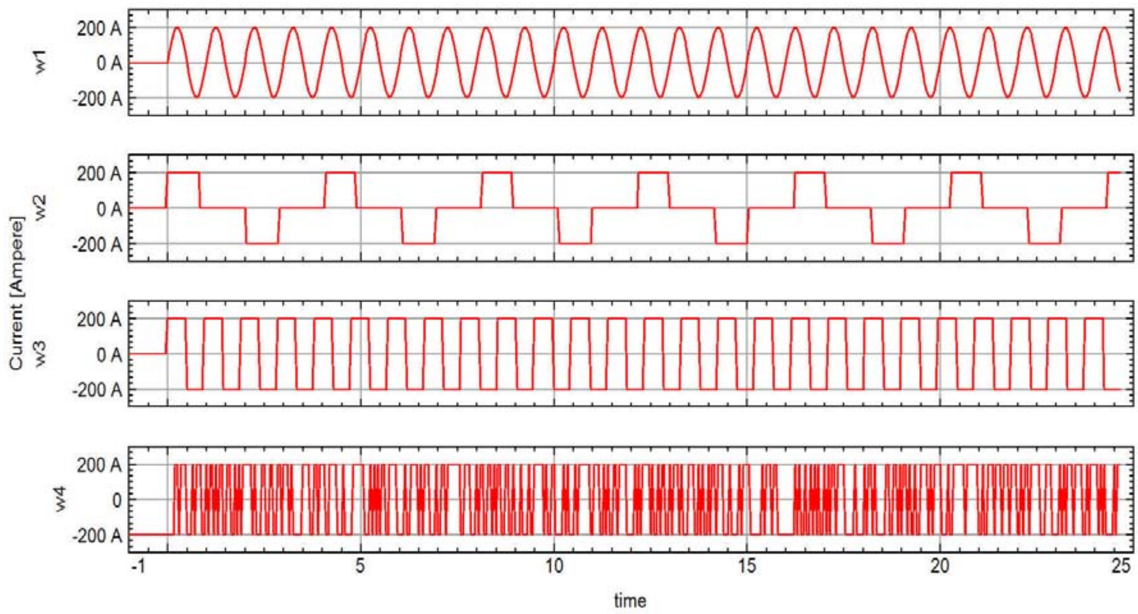
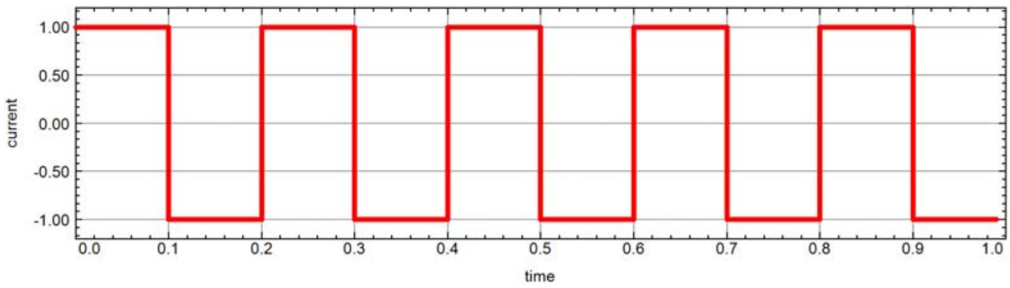


Figure 8. *Examples of waveforms used in controlled source methods. Upper panel is a monochromatic signal used in frequency domain methods, second panel is a waveform used in transient methods that includes both ontime and offtime data. The third panel is a square waveform without offtime data (see further explanation in Figure 9). The lower panel is a pseudo random binary sequence (PRBS).*

(a)



(b)

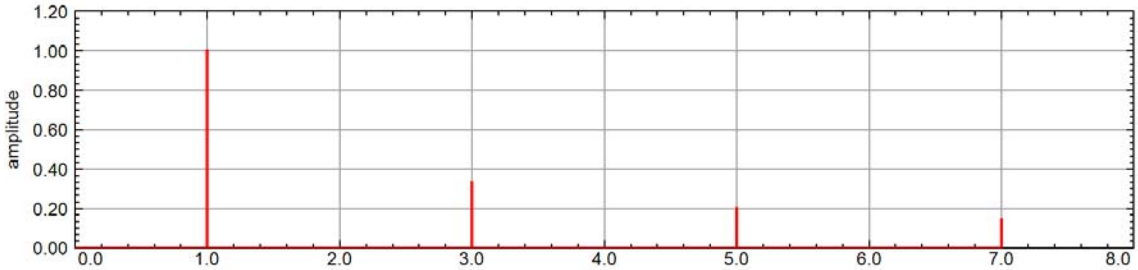


Figure 9. *The square waveform in **(a)** is equivalent to the frequency spectrum shown in **(b).** The spectrum has peaks at all odd harmonics of the repetition frequency. Arbitrary units are used. Although the spectrum contains an infinite number of frequencies, all practical applications are limited to a finite number since the amplitude decays with increased frequency. Signals at high frequencies are therefore masked by noise in the recordings.*

4.3.1.2 Primary and secondary fields and the airwave problem

EM methods have during the last decade become a recognised tool in offshore hydrocarbon exploration and are gaining a lot of attention today. Both natural source MT and controlled source methods are in use and often combined in joined data interpretations. A phenomenon referred as the “airwave problem” has obtained a lot of attention when surveying in shallow water with controlled sources towed close to the seabed. In short, the airwave here refers to signal propagating from the transmitter through the conductive water column into the air and back again through the water to receivers at the sea bottom. The signal recorded may involve propagation back and forth through the water columns several times. This signal is superimposed onto the secondary response carrying information from the ground. The signal propagating to the sea-air interface and back to the receivers can be very strong compared to the secondary field of interest and thereby lower the signal to noise ratio in the recordings. In deep water surveys, the signal travelling to the water-air interface is attenuated to very low amplitude and does therefore not create any problems. The term “airwave” in this context of an “airwave problem” is misleading because the problem essentially is due to induction effects in the water column. Onshore controlled source methods also involve energy transmitted into the airspace, but this is not necessarily a problem. This airwave or primary field propagates at the speed of light, whereas the secondary response from the ground in comparison to the arrival of the primary field is significantly delayed in time before arriving at the receivers. Thus, the airwave/primary field and secondary fields are clearly separated in time for time-domain data and in phase for frequency domain data, and it is in general possible to extract the secondary field. It should be noted that time-domain methods with off-time data recordings (the time with zero current in transmitter) directly measure the secondary field, whereas frequency domain measurements with continuous transmission of energy involve simultaneous recording of the primary and secondary fields. Thus, despite the equivalence between time and frequency domain data, the time domain method has an advantage over the frequency domain method because the secondary signal is not embedded in a strong primary field. The reason for the advantage is that the limited dynamic range of the recording equipment may become insufficient for obtaining a high signal to noise ratio for the secondary field if a strong primary signal is present at the same time.

4.3.2 EM methods and hydrocarbon exploration in a historical perspective

In 1983, Larry Hughes of Environmental and Safety Engineering (EnSafe) of Memphis, Tennessee published a report entitled "Case Histories of an Electromagnetic Method for Petroleum Exploration". The report was produced during Zonge Engineering's 1983 speculative "groupshoot" project named as described by the title of the report. In a chapter entitled "A Short History of Electrical Techniques in Petroleum Exploration" he wrote that "*The utilization of electrical techniques in oil and gas exploration has always been a subject of great interest to geophysicists, largely because of the hope that the application of such techniques would eventually lead to the direct detection of hydrocarbons through their insulating properties. However, 60 years of constant and at times frenzied debate over direct detection has failed to produce clear evidence of success, and wildly unrealistic claims by competitive service companies have done much to discredit the use of all electrical methods in petroleum exploration.*" Another statement is that "*The petroleum industry is bombarded with a large number of exploration proposals, some of which are aggressively marketed by persons with minimal technical understanding of the processes they claim to measure. As a result, most if not all electrical methods have quietly been filed in the bottom drawer of "unconventional methods" by the petroleum industry, despite their widespread acceptance and extensive utilization by the mining industry over the past 30 years*."

The report by Hughes (1983) serves as an excellent key reference on the use of electrical methods onshore for hydrocarbon exploration. The report also contains description of methods in general. Most of the surveys discussed are from the United States. Another important review from the eighties was presented by Spies (1983), which covers electromagnetic methods used at that time in the Soviet Union for hydrocarbon exploration. The role of geoelectrical methods in hydrocarbon and deep structural investigations in Russia is furthermore described in Berdichevsky (1994). Standard MT as well as both frequency and time domain IP recordings were reported to be in use. Experiments involving very high power transmitters are mentioned. The studies show many similarities to those reported from the United States. Most of the Soviet Union studies are with a focus on structural mapping but also direct hydrocarbon detection is mentioned. Application of electromagnetic methods for hydrocarbon exploration in China today (He *et al.* 2010, 2012; Luo & Zhang, 1998) builds heavily on the experience gained in the Soviet Union.

The report by Hughes (1983) contains a thorough discussion and critical evaluation of the techniques applied. The evaluation presented is both in respect to direct hydrocarbon detection (mapping of resistors) and to indirect detection (mapping conductors, IP and self potentials associated with pyritisation (see Figure 1) caused by hydrocarbon seepage and occurrences). Also structural mapping with geophysical techniques is covered. Most of the electrical and electromagnetic techniques in use today in other types of exploration work (minerals, water, general geological mapping) appear to have been considered and tested in relation to hydrocarbon exploration:

1) Direct Detection of Hydrocarbons
    i) Resistivity methods
    ii) Transient methods
2) Indirect Detection of Hydrocarbons (electrochemical alteration)
    i) Induced polarization / resistivity methods
    ii) Self-potential methods (oxidation/reduction cells)
3) Structure Delineation
    i) Magnetotelluric methods
    ii) Induced polarization methods

The case studies on detection of alteration zones reported by Hughes (1983) are mainly concerned with shallow investigation and the experience is therefore not directly applicable for investigation onshore Denmark, when taking into account that any hydrocarbon reservoirs are expected to be deep. We shall not repeat the content of the referred report, but it is worthwhile to cite some of the conclusions made:

"The key to the future seems to be in lowering our expectations of what electrical techniques can provide to an exploration program. They will not provide the answers to all exploration problems by themselves, as some have claimed in the past. As those of us who look at geophysical data on a daily basis know all too well, no geophysical interpretation is totally unique; it must be used sensibly in the context of geologic, geophysical, and other data. If we approach the future in this context, we may well find electrical techniques to be the valuable prospecting tool we have been hoping for.

Two exploration approaches show promise during the next decade: the detection of electrochemical alteration over oilfields and the direct detection of hydrocarbons at depth. The detection of alteration has already been demonstrated to be a viable technique, but a great deal of work remains to be done in distinguishing electrochemical anomalies from structural and cultural anomalies, and in providing more quantitative information to the exploration geologist. It is important to realize that anomalies can often be subtle, and the mechanisms which cause them can be very complex. Hence, a full understanding of these mechanisms must surely be gained in order to utilize the technique fully in oil exploration. The second approach, direct detection, should also be considered, despite its unsavoury reputation in the past. Some of the evidence that direct detection of hydrocarbons can be achieved, at least over shallow fields in geologically simple environments, appears to be substantiated.

However, a complete revolution in instrumentation sensitivity and data processing techniques will be necessary in order to use direct detection as a viable exploration technique for deep fields. Such a revolution is not imminent, but the incentive for it is certainly there."

In retro-perspective, the statement on the most promising exploration approaches as the detection of electrochemical detection of alteration zones and the direct detection of hydrocarbons at depth was correct. In particular, the direct detection of hydrocarbons at depth in offshore environments must be viewed as a major breakthrough. However, direct detection onshore is only reported for a very limited number of case studies. Some of the recent Russian and Chinese case histories involve exploration depth of several km and they are therefore of interest in a discussion of deep onshore exploration in Denmark. Some of these case studies are discussed in separate sections below, where the various methods used are discussed in some detail.

An important theoretical study was published by Passalacqua (1983) on the direct detection of resistive layers using a grounded dipole as source. Both frequency domain and time domain data were discussed for onshore work. The conclusion from this work was that this type of source had a potential for direct hydrocarbon detection. The ability to map resistive layers at large depth is linked to the presence of a galvanic source. The statement is valid for both onshore and offshore EM. Weidelt (2007) and Chave (2009) provide detailed discussion on the physics involved in controlled source methods. Development of equipment and subsequent applications of a grounded dipole source was later used onshore by Vozoff *et al*. (1985, 1989) in Australia. Much of this work was done in collaboration with the University of Cologne in the development of the LOTEM system (Strack, 1984, Strack 2010).

The detection of alteration zones has not become a generally accepted standard exploration tool onshore, even though case studies are reported from North America, China and Russia. The more recent North American studies are mainly concerning shallow investigations. In particular mapping of tar-sands is done using both airborne and ground EM techniques. Shallow investigations in relation to shale gas have also been reported. Structural mapping using airborne EM techniques are gaining more interest. The increased interest in using airborne EM is linked to recent developments with respect to both data acquisition and capabilities for modelling of very large data sets. The penetration depth for the airborne EM systems is however not sufficient for deep investigations in sedimentary environments.

4.4 **Method 3: Magnetotellurics (MT and ZTEM)**

The MT method, which is based on induction of time varying current in the subsurface from natural sources in the ionosphere was introduced in the 1950'ties by Cagniard (1953) and Tikhonov (1950, 1965). The method has undergone very significant improvements in terms of data quality of the measurements as well as possibilities for 2D and 3D inversion of the derived impedance tensor and tipper function. Chave & Jones (2012) provide a comprehensive treatment of theory and practice of the MT method. They mention that over 500 broad band MT systems from one manufacturer alone are in continuous use in China for oil and gas exploration onshore.

The method involves measurements of the electromagnetic field variations at the surface of the earth along two horizontal orthogonal directions. The vertical magnetic field component may also be recorded. Processing of the recorded data with time variations of the electromagnetic field involves transformation into the frequency domain and calculation of the magnetotellurics impedance tensor Z and magnetic tipper function T=[A B] defined as follows:

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = Z \cdot \begin{bmatrix} H_x \\ H_y \end{bmatrix} = \begin{bmatrix} Z_{xx} & Z_{xy} \\ Z_{yx} & Z_{yy} \end{bmatrix} \cdot \begin{bmatrix} H_x \\ H_y \end{bmatrix}$$

$$H_z = \begin{bmatrix} A & B \end{bmatrix} \cdot \begin{bmatrix} H_x \\ H_y \end{bmatrix}$$

where E_i is the electric field component in direction i and H_i is the magnetic field component in direction i. Subscripts i=x,y and z refer to a right angle coordinate system with z down

The transformation of the measured time series into the impedance tensor and tipper function remove the information about the inducing primary field in the measured data and the tensor and tipper are solely dependent on the electrical structure of the earth. The source independency of the tensor and tipper is valid for the far-field approximation if artificial or controlled sources are used as described in Li & Pedersen (1984) and Hughes & Carlson (1987). The application of data in the transition zone is treated in the chapter of HMEM.

An important limitation for the MT method is that it is based on induction alone and therefore is not very sensitive to the presence of resistive structures such as hydrocarbon reservoirs. The application of MT in hydrocarbon exploration is directed towards mapping of conductive alteration zones surrounding reservoirs. The increase in conductivity is mainly a result of disseminated pyrite. The presence of pyrite may also imply that induced polarization phenomena are associated with the presence of reservoirs.

An example of mapping induced polarisation phenomena with the MT method is presented by He *et al.* (2010) from the Qaidam Basin, China. The Qaidam MT survey was performed in an area with known gas reservoirs at a depth of about 1.5 km. Despite the limitations of mapping resistors with MT, the authors state that a known gas-bearing formation had a high-resistivity anomaly. The gas bearing formation was also associated with a high IP anomaly. They furthermore identified two similar anomalous regions outside the known gas-bearing formations. As a result, two new prospects were determined as targets. High quality data are required in order to be able to map induced polarization with the MT method.

Another example involving use of the MT method in hydrocarbon exploration is presented in David *et al.* (2002). They emphasise mapping of structural features in a complex geological environment. Western Geco has reported a successful application of MT in Greece (Figure 10), in an area where seismic data obtained and processed with modern techniques gave almost no useful results. The objective was to map the 3D structure of multiple-thrusted carbonate and anhydrite units and the underlying autochthon. This region is an active petroleum exploration area where carbonates can represent both source and reservoir rocks.

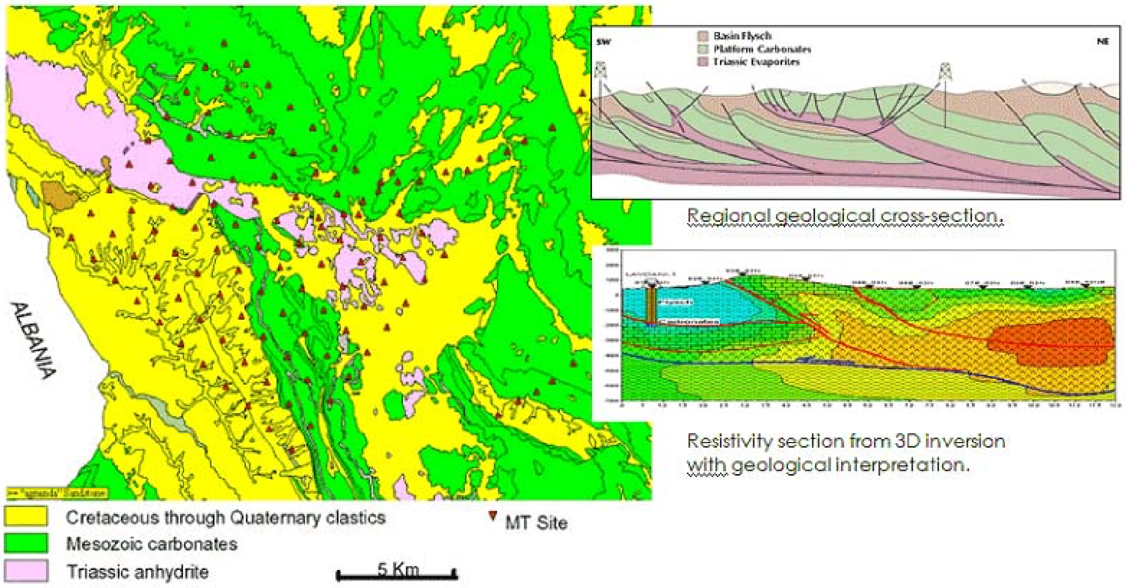


Figure 10. *Results of MT measurements in Greece reported by Western Geco.*

Although MT data are unable to map resistive structures in any detail, the method has been used for structural interpretations of salt structures, where the contrast in resistivity between salt and surrounding clastic sediments or carbonates is high.

The MT method has been used extensively in northern Germany (see Figure 11) for mapping of sedimentary structures. Hoffman *et al*. (2001,2005) utilised MT and geochemical data for mapping the distribution of deep potential source rocks in the Emsland area (Figure 12) and the Glückstadt Graben (Figure 13). In the Emsland survey the conductive structures at depths of 6-7 km in the southern part of the profile are interpreted as Lower Carboniferous black shales. Similarly, a conductor mapped at a depth of 8 km in the northern part of the Emsland profile is interpreted as potential source rocks. A conductor at a depth of 9-10 km was mapped in the Glückstadt Graben.

MT measurements from Denmark are reported in two M.Sc. theses from Aarhus University. Nissen (1982) interpreted data from a N-S profile in western Jutland and Thomsen (1989) interpreted data from a NE-SW profile running approximately from Nissum Fjord to Skagen, a second profile running N-S in the eastern part of Jutland and a third profile above and along the Ringkøbing-Fyn High (see Figure 14) . The existence of clastic sediments below the Zechstein salt is indicated in the data, but no details concerning thickness of these are revealed in the data. The thesis by Thomsen(1989) contains a comparison of estimated conductance values for post-Zechstein sediments obtained from MT data and from electrical logs in deep boreholes. In general, good agreements between the two types of data are observed. A paper by Thomsen *et al.* (1990) summarises the results presented by Thomsen (1989). Interpretation of an MT profile across the Sorgenfrei-Tornquist zone in southern Sweden and Denmark is presented by Smirnov & Pedersen (2009).

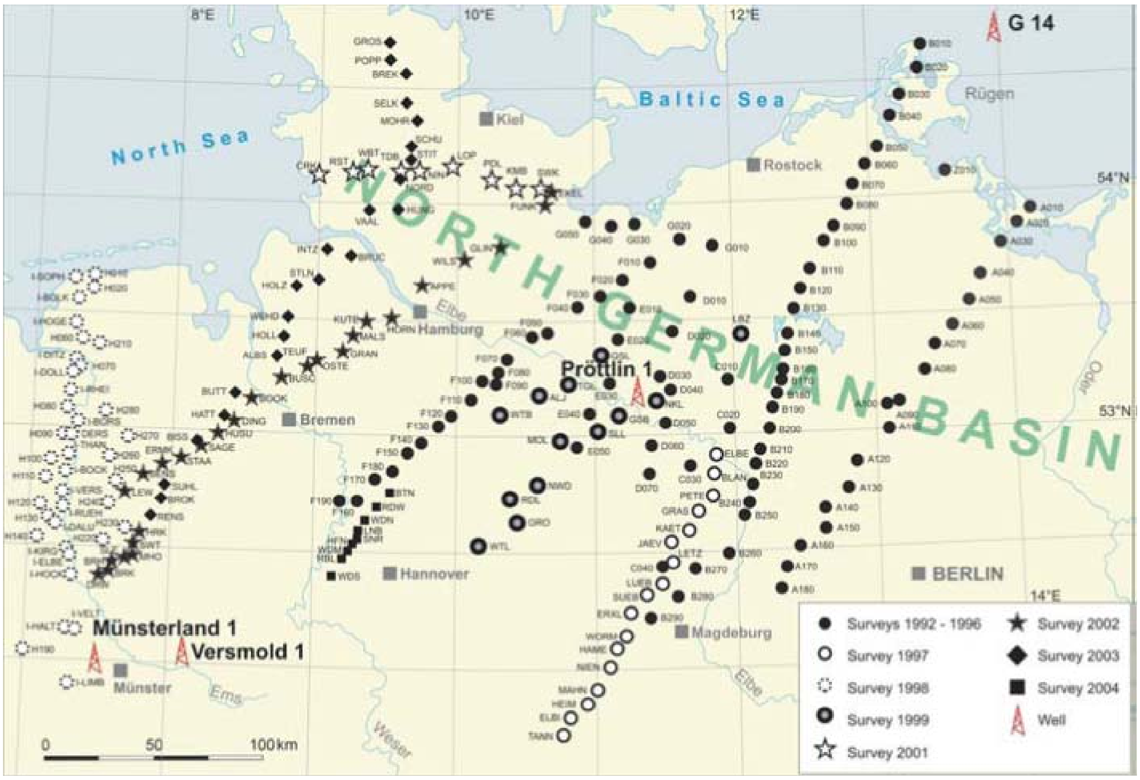


Figure 11. *Map of North German MT stations. From Hoffman et al. (2001,2005).*

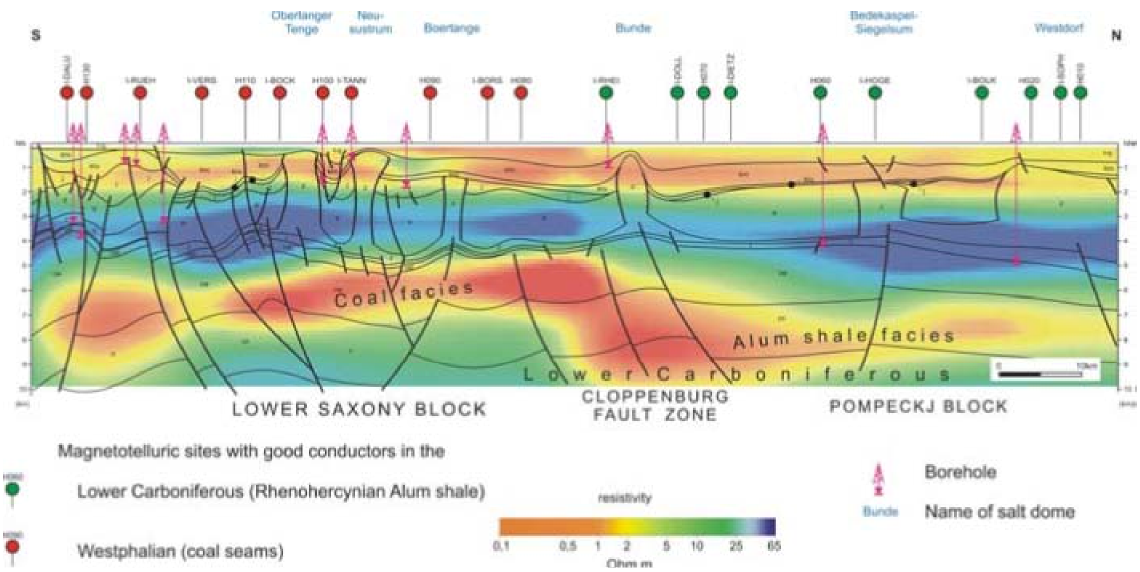


Figure 12. *Resistivity section derived from MT measurements in the Emsland survey. From Hoffman et al. (2001, 2005).*

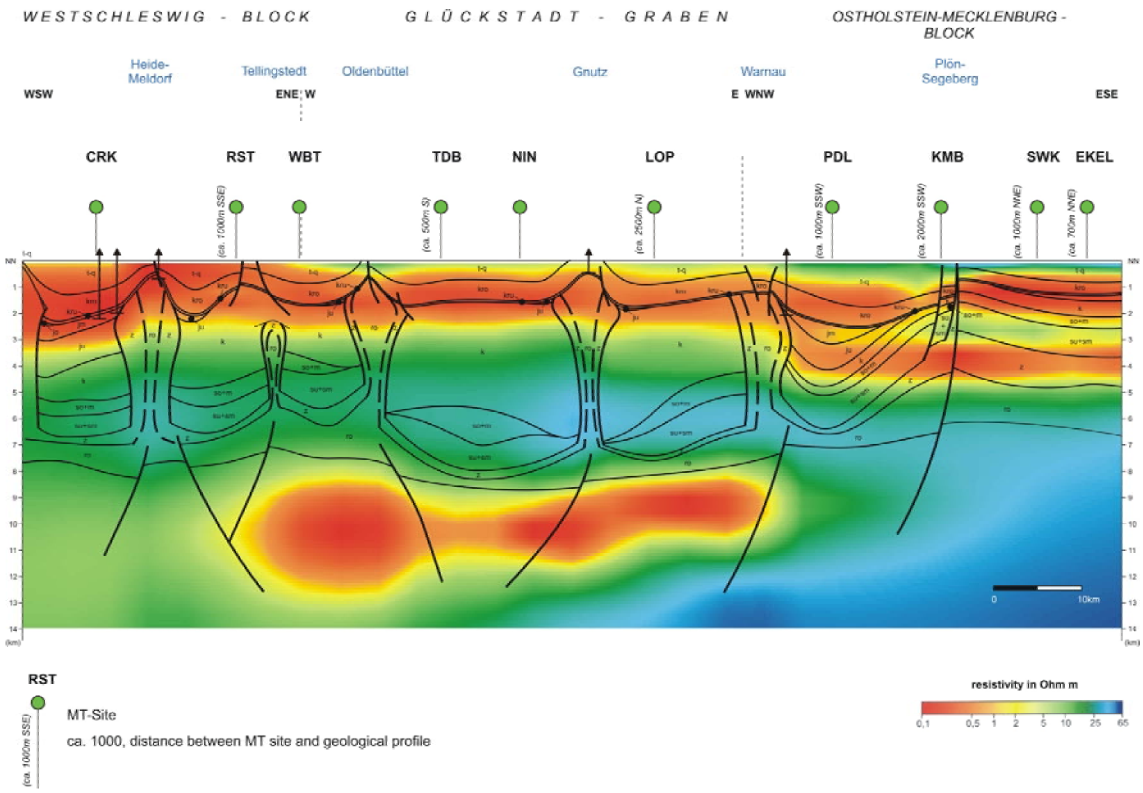


Figure 13. *Resistivity section derived from MT measurements in the Glückstadt survey*

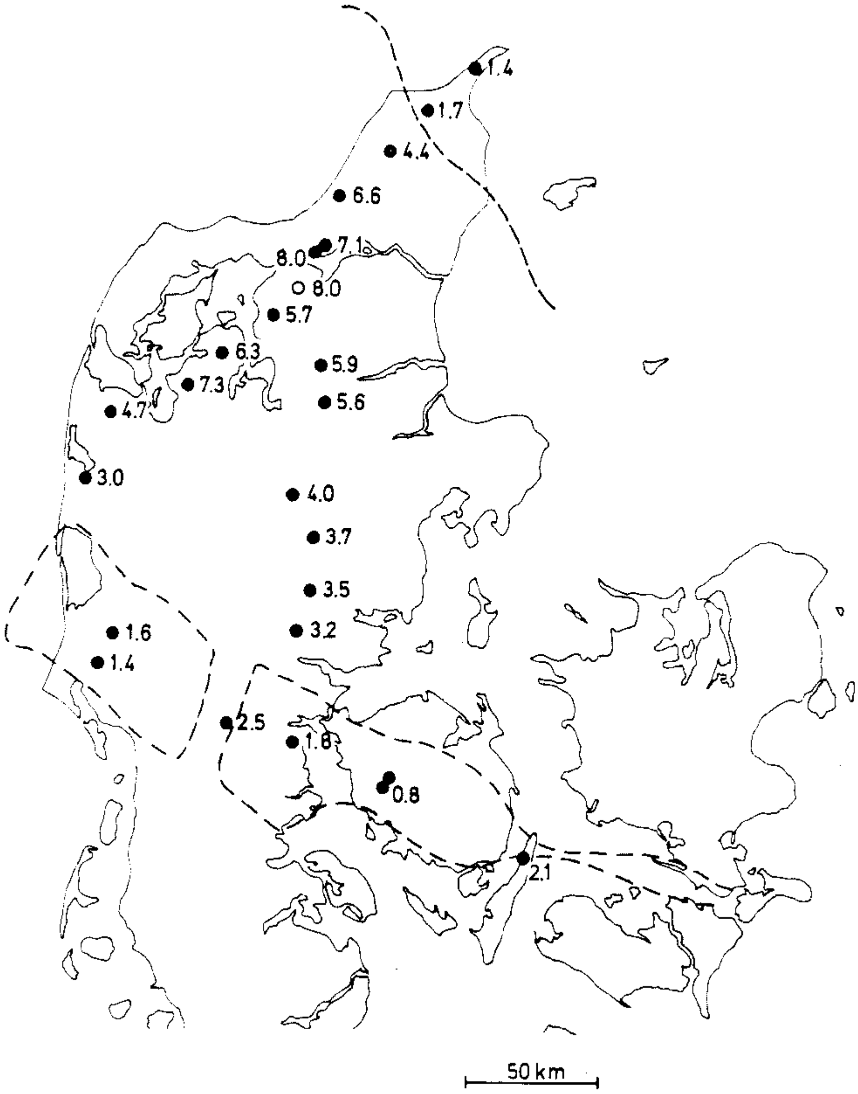


Figure 14. *Depth to top-Zechstein/basement from MT measurements by Thomsen (1989).*

A review paper by Unsworth (2005) on EM for hydrocarbon exploration refers to an interpretation of MT data from Alberta by Xiao & Unsworth (2004), which demonstrates consistency with electrical logs from a 5 km deep well.

Frequencies in the audio range (AMT) is utilised in shallow investigations. The ZTEM method is a recent airborne implementation of the AMT method and builds on an older AFMAG system that never became widely used. The ZTEM system records only magnetic data, and therefore only the tipper function is estimated. The various hydrocarbon plays in Denmark are concerned with deep targets and any high degree of pyritization is therefore also expected to be situated at large depth (>1 km). A required depth of investigation deeper than 1 km excludes the audio frequency range. Nevertheless, knowledge of near surface conductivity variations are valuable in a modelling of low frequency MT data. The dense data coverage obtained with airborne systems (ZTEM or any controlled source airborne method) may improve the interpretations of standard MT data when modelled jointly with the high-frequency data from the same area (Holtham & Oldenburg, 2010). The ZTEM system and other airborne system with deep penetration may be valuable tools in other environments, where hydrocarbons are found at shallow depth. An example is provided by Pfaffling *et al*. (2009) from a survey in Mozambique.

4.5 **Method 4: High-Moment Electromagnetics (HMEM)**

We use the term High-Moment Electromagnetics (HMEM) as a collective term to cover all electromagnetic methods, where a controlled source is used to map resistivity variations at depth of relevance for hydrocarbon exploration in Denmark. Mapping of induced polarization with a controlled source is treated in a separate chapter. This section includes a review of published case studies and a discussion of sensitivity of controlled source methods to the presence of resistive hydrocarbon reservoir layers. Evaluation of EM in relation to mapping of underground storage of CO_2 shares many similarities to mapping of resistive hydrocarbon reservoirs, and the conclusions published with respect to sensitivity are therefore applicable to both types of mapping. In particular, we refer to the Ketzin survey near Potsdam described in Streich *et al.* (2011). Investigations in relation to hydrocarbon reservoir monitoring during production are also applicable in an evaluation.

Figure 15 shows frequency domain responses from a model often referred at the canonical 1D model in marine CSEM. The software used for the calculations is described in Key (2009). The model consists of 1000 m seawater, a sedimentary layer with thickness 1000 m and resistivity 1 Ωm. The second layer below sea bottom is a 100 m thick reservoir with resistivity 100 Ωm followed by 2900 m of sediments with 1 Ωm resistivity. The basement layer has a resistivity of 10 Ωm. The response shown is the inline electric field along a 15 km long profile, where the transmitter (inline configuration) is placed at 0.0 and transmitting at a frequency of 0.1 Hz. The transmitter and receiver are located 50 m above sea bottom. The corresponding CSEM (controlled source EM) response for an onshore model with the same resistivity distribution except for the seawater is shown for comparison. The response calculations for the onshore and offshore models are normalized by the source current. We note that the onshore response is about one order of magnitude larger than the offshore response. A similar comparison is presented in Figure 16, where the reservoir is placed 2000 m below sea bottom and ground surface. Also in this case an order of magnitude difference is noted in amplitude. A current of approximately 1000 A are common in present day offshore applications, which is about 25 times higher than used in the onshore Ketzin survey. Thus, when normalising by typical values for currents, the onshore responses will be comparable to or slightly lower than the offshore responses. The magnetotellurics signal and any artificial sources such as transformers in wind-mills etc. will act as noise in controlled source data. Offshore, these signals are attenuated due to the seawater, and the number of cultural noise sources offshore is furthermore in general much lower than onshore. Longer recording time onshore for data stacking are, therefore, expected to be required to obtain data of similar quality as obtained offshore. Remote reference MT measurements may be used to the remove electromagnetic fields caused by the geomagnetic field variations if the MT impedance tensors are estimated at the site of the controlled source receivers (see eg. Couliares & Rasmussen, 1987). The Ketzin survey shows that it is possible in high noise areas to improve the signal to noise ratio by stacking and obtain data of high quality. Distortion of the data caused by electromagnetic coupling to cables and pipelines in and above the ground may however distort the data (Nelson 1977, Carlson

& Zonge, 1996) and prevent reliable interpretation of the data. These distortions may be difficult to identify and erroneous interpretations are likely to occur.

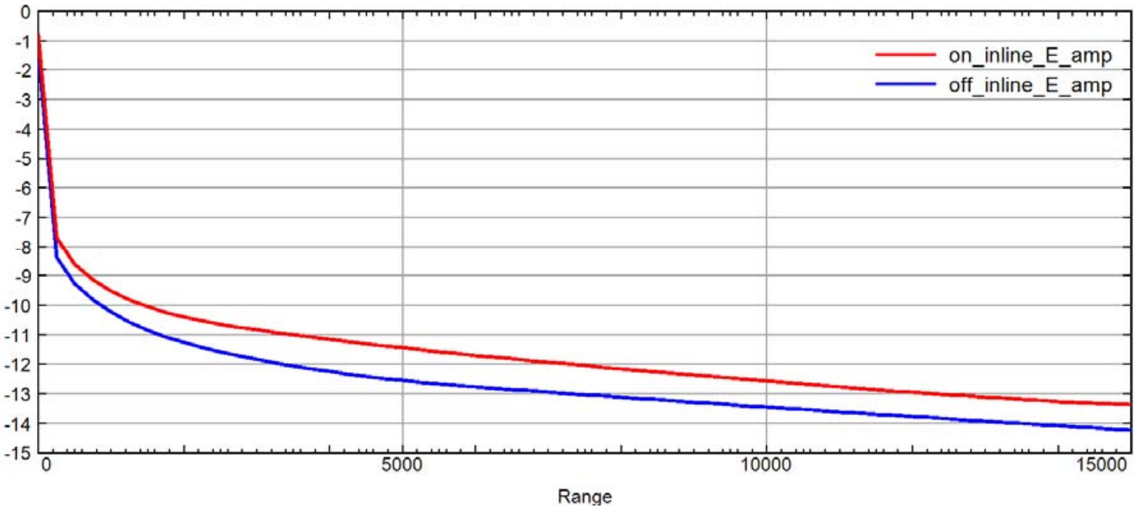


Figure 15. *Inline electric fields responses along a 15 km profile for an inline oriented transmitting electrical dipole with frequency 0.1 Hz. The curve in red colour is for onshore measurement and the curve in blue colour is for offshore measurements, where the transmitter and receivers are 50 m above the sea floor. Thickness and resistivity values are from top to bottom 1: [1000 m; 1 Ωm]; 2: [100 m; 100 Ωm]; 3: [2900 m; 1 Ωm]; 4: [∞; 10 Ωm]. The resistivity of seawater is 0.3 Ωm and the water depth is 1000 m.*

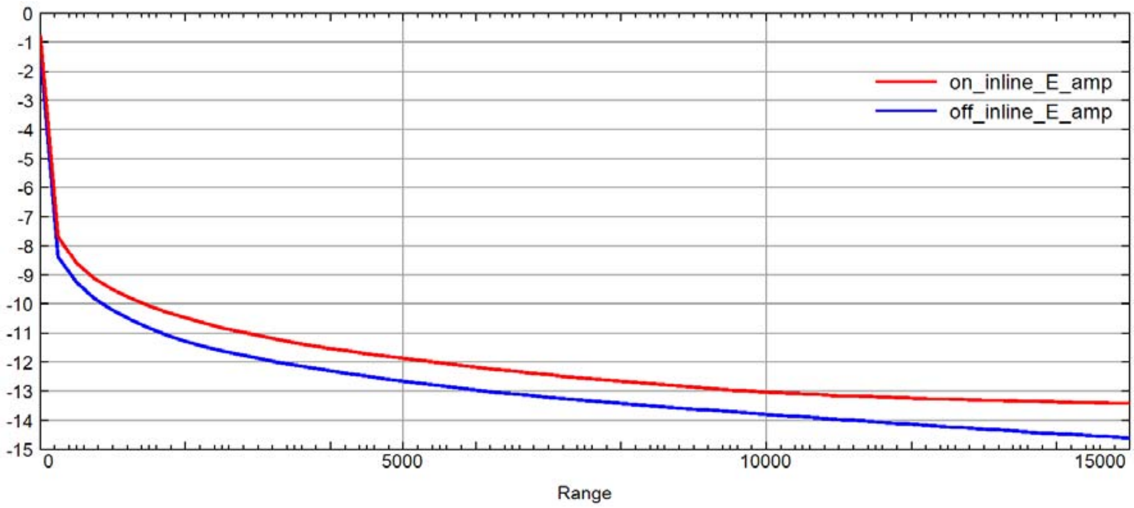


Figure 16. *Inline electric field responses along a 15 km profile for an inline oriented transmitting electrical dipole with frequency 0.1 Hz. The curve in red colour is for onshore measurement and the curve in blue colour is for offshore measurements, where the transmitter and receivers are 50 m above the sea floor. Thickness and resistivity values are from top to bottom 1: [2000 m; 1 Ωm]; 2: [100 m; 100 Ωm]; 3: [2900 m; 1 Ωm]; 4: [∞; 10 Ωm]. The resistivity of seawater is 0.3 Ωm and the water depth is 1000 m.*

Figures 17–19 contain a comparison similar to those in Figure 16 between onshore and offshore field strength, but with inclusion of all possible transmitter and receiver combinations; i.e. inline, crossline (=broadside), vertical electric dipole sources and inline, crossline and vertical electric and magnetic receivers. Responses are calculated in the range from 1 Hz to 0.01 Hz. The models are identical to those used for the responses in Figure 16; i.e. a reservoir 2000 m below ground surface or seafloor. Deviations between onshore and offshore responses are approximately one order of magnitude. It should be noted that measurements of the vertical E-field is very difficult onshore and vertical transmitters are only possible, if drill holes are available in the survey area. Despite that the source current amplitudes for onshore systems is more than an order of magnitude smaller than for sources used offshore, the field strength onshore will in general be comparable to those measured offshore. The responses are within a measurable range and the major problem in obtaining a good signal to noise ratio will be due to the presence of external noise.

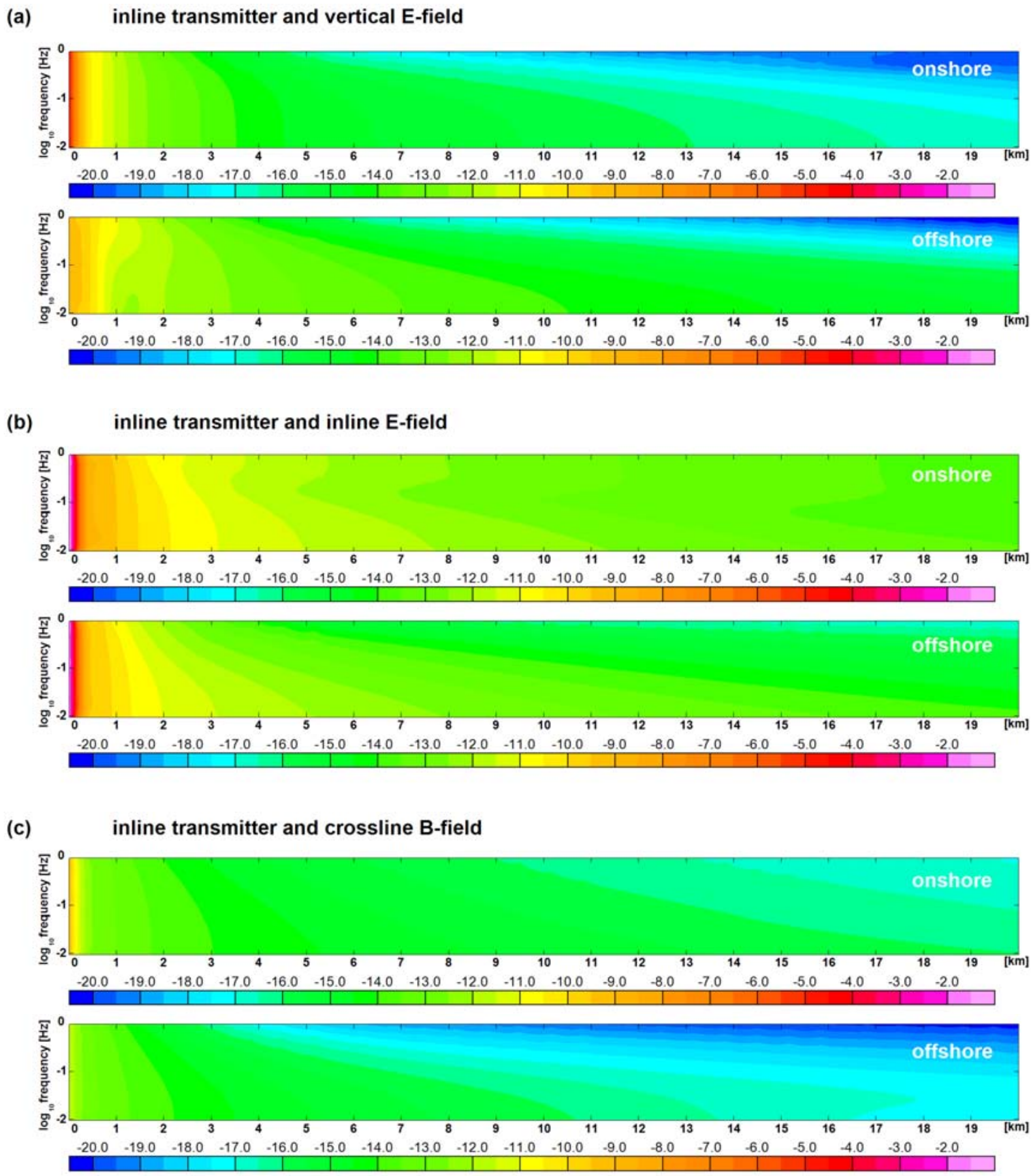


Figure 17. *Log_{10} values of amplitude for responses from a model with a reservoir and a model without a reservoir. The source is an inline electric dipole placed at 0.0 km and receivers are placed along a 20 km profile with (a) vertical electric field; (b) inline electric field and (c) crossline magnetic field.*

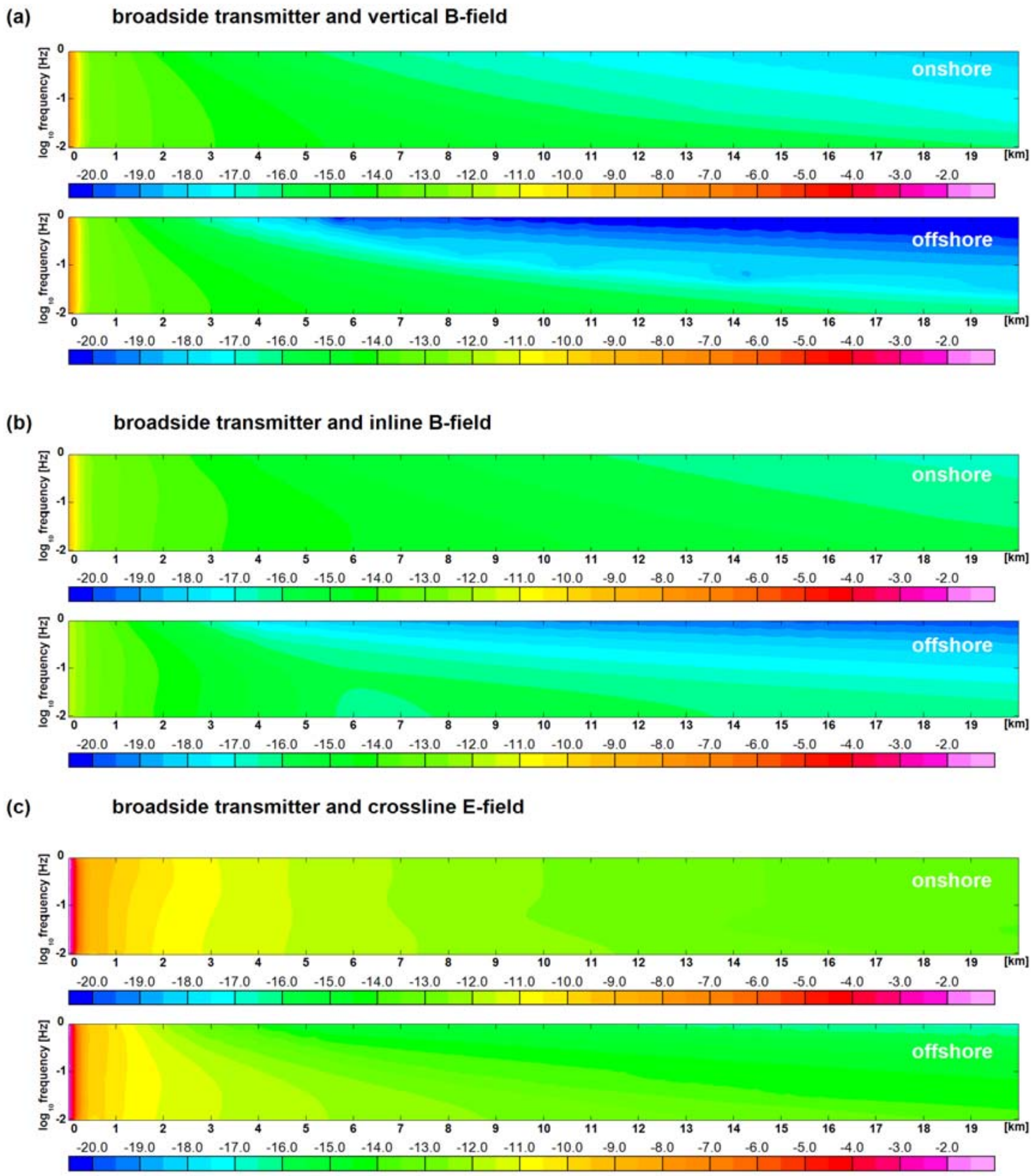


Figure 18. *Log_{10} values of amplitude for responses from a model with a reservoir and a model without a reservoir. The source is a crossline/broadside electric dipole placed at 0.0 km and receivers are placed along a 20 km profile with (a) vertical magnetic field; (b) inline magnetic field and (c) crossline electric field.*

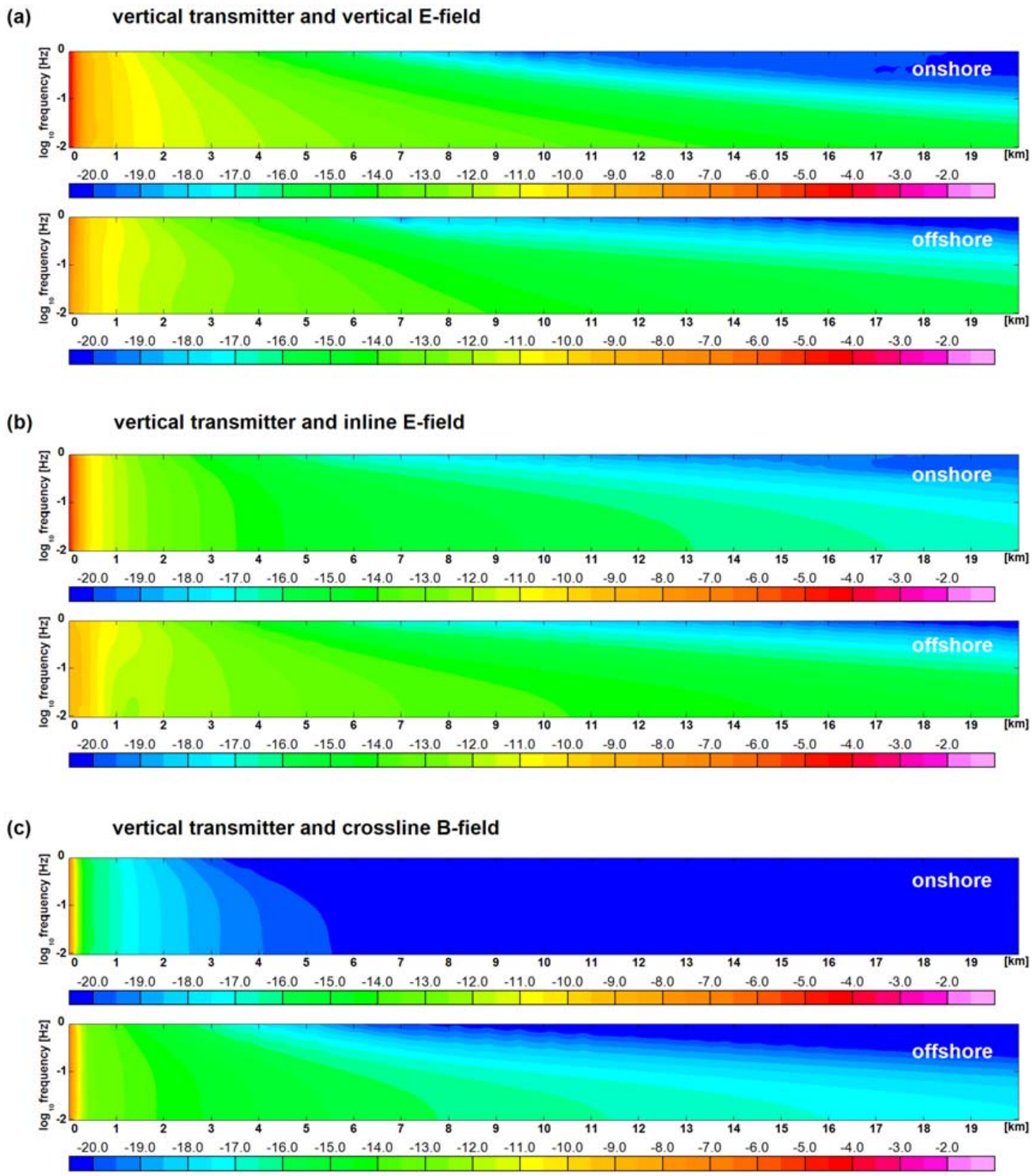


Figure 19. *Log_{10} values of amplitude for responses from a model with a reservoir and a model without a reservoir. The source is a vertical electric dipole placed at 0.0 km and receivers are placed along a 20 km profile with (a) vertical electric field; (b) inline electric field and (c) crossline magnetic field.*

It is common practice to evaluate the sensitivity of the CSEM method to the presence of a resistive reservoir by comparing the responses from a model without the resistivity layer. This comparison is illustrated in Figures 20–22, where the ratio ($Ampl_{reservoir}/Ampl_{no\_reservoir}$) in $\log_{10}$ units between the response amplitudes are displayed. The model is similar to the one used for the amplitude calculations in Figure 16, i.e. a 100 m thick reservoir at a depth of 2000 m with resistivity 100 Ωm. The reference model has a resistivity of 1 Ωm. In general we notice that the ratios for the offshore responses are higher than for the onshore responses. It is evident that the inline transmitter combined with inline E-field and vertical E-field measurements provide the best option for detection of the resistive reservoir. A vertical transmitter and crossline magnetic field recordings are also indicative of the reservoir. These results are consistent with the results presented by Streich & Becken (2011), who presented analytical expression for the sensitivities (Fréchet derivatives) in CSEM and exemplified their derivations using a model describing the Ketzin CO_2 storage area. The smaller response ratios for onshore responses compared to offshore imply that it is not straightforward to conclude that the experience gained in offshore exploration can be transferred with little modification to the onshore environment. Nevertheless, the frequency domain CSEM method responds to the reservoir layer and the methods do have a potential in relation in hydrocarbon exploration.

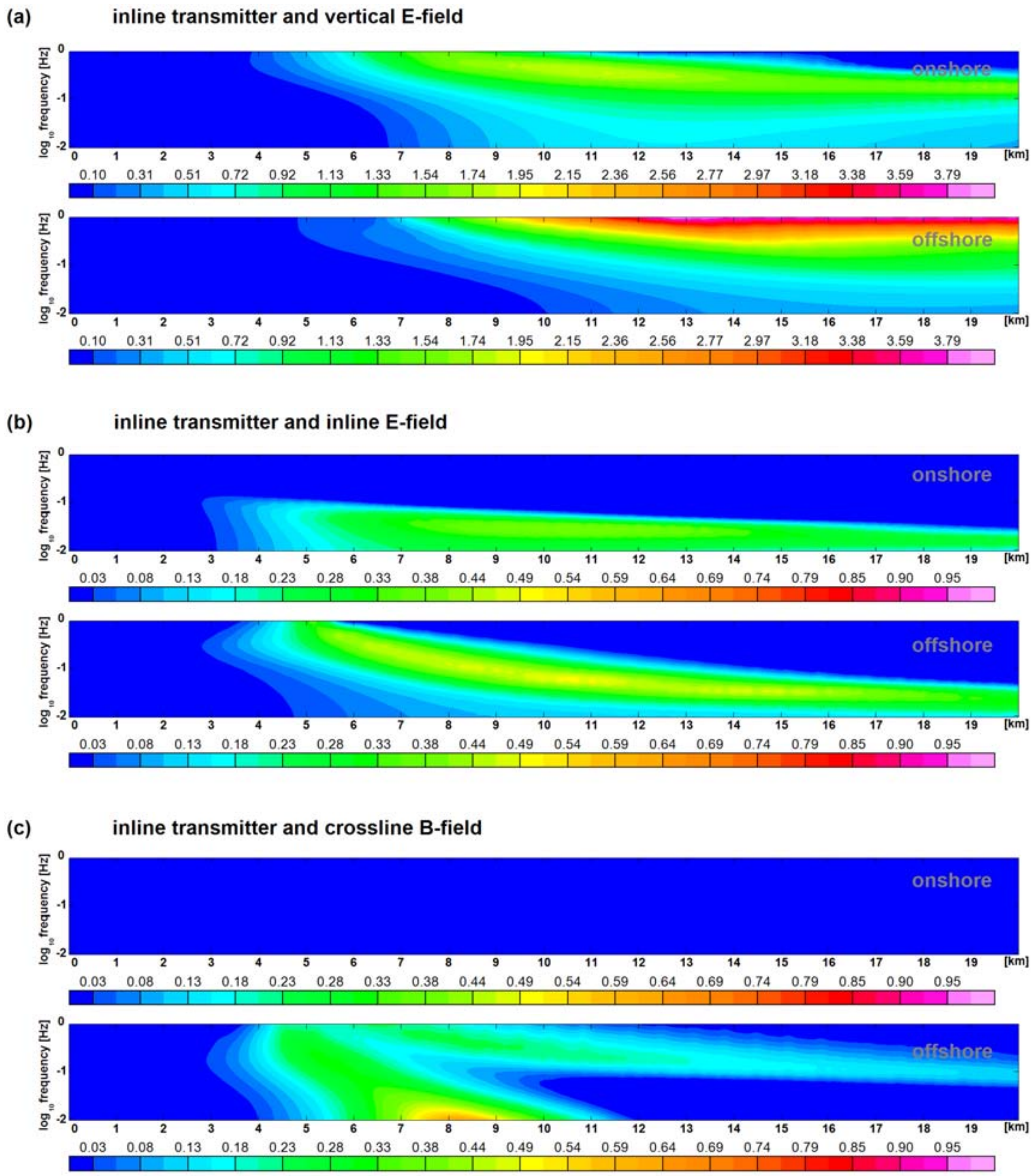


Figure 20. *Log_{10} values of amplitude ratios for responses from a model with a reservoir and a model without a reservoir. The source is an inline electric dipole placed at 0.0 km and receivers are placed along a 20 km profile with (a) vertical electric field; (b) inline electric field and (c) crossline magnetic field.*

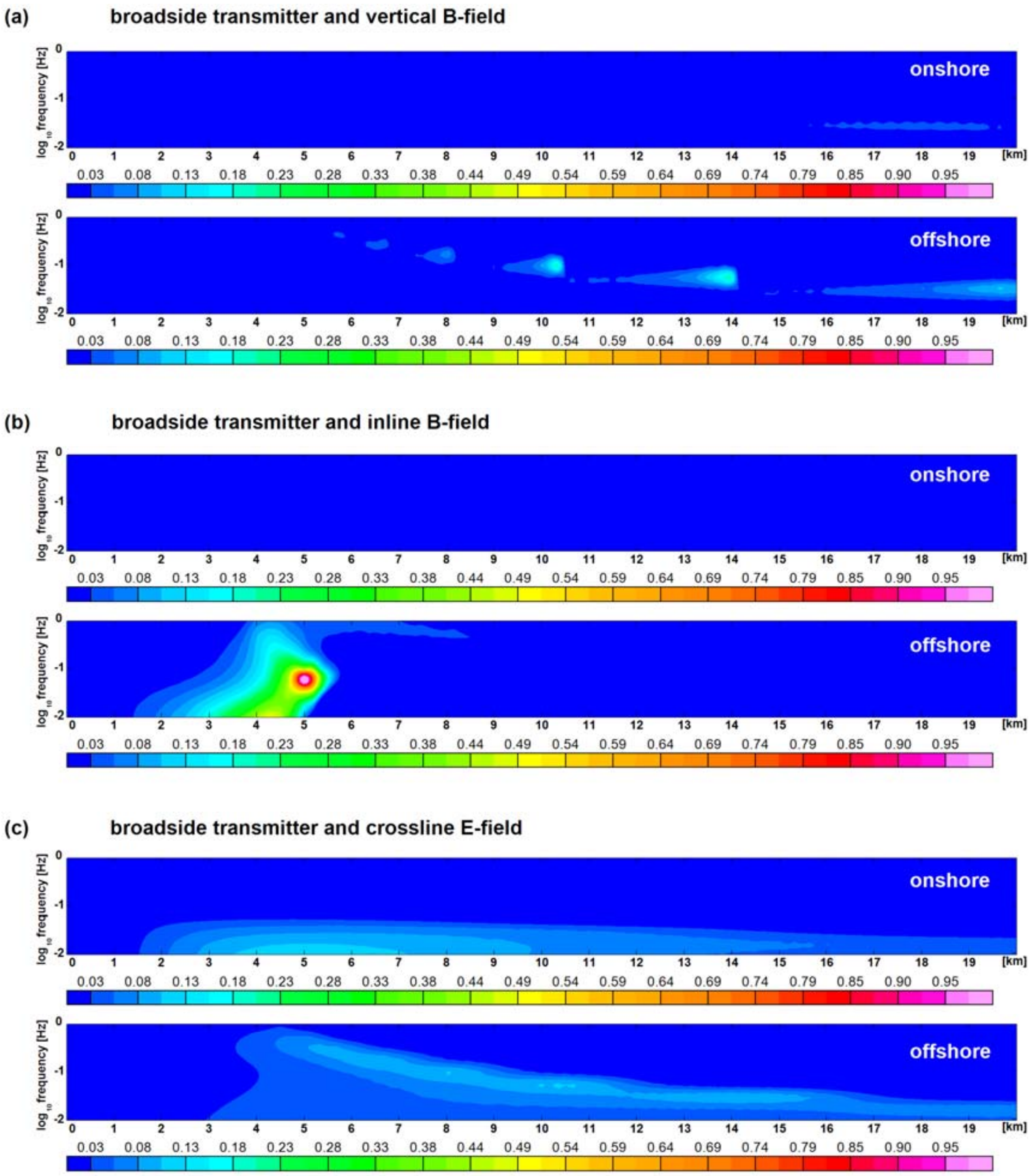


Figure 21. *Log_{10} values of amplitude ratios for responses from a model with a reservoir and a model without a reservoir. The source is a crossline/broadside electric dipole placed at 0.0 km and receivers are placed along a 20 km profile with (a) vertical magnetic field; (b) inline magnetic field and (c) crossline electric field.*

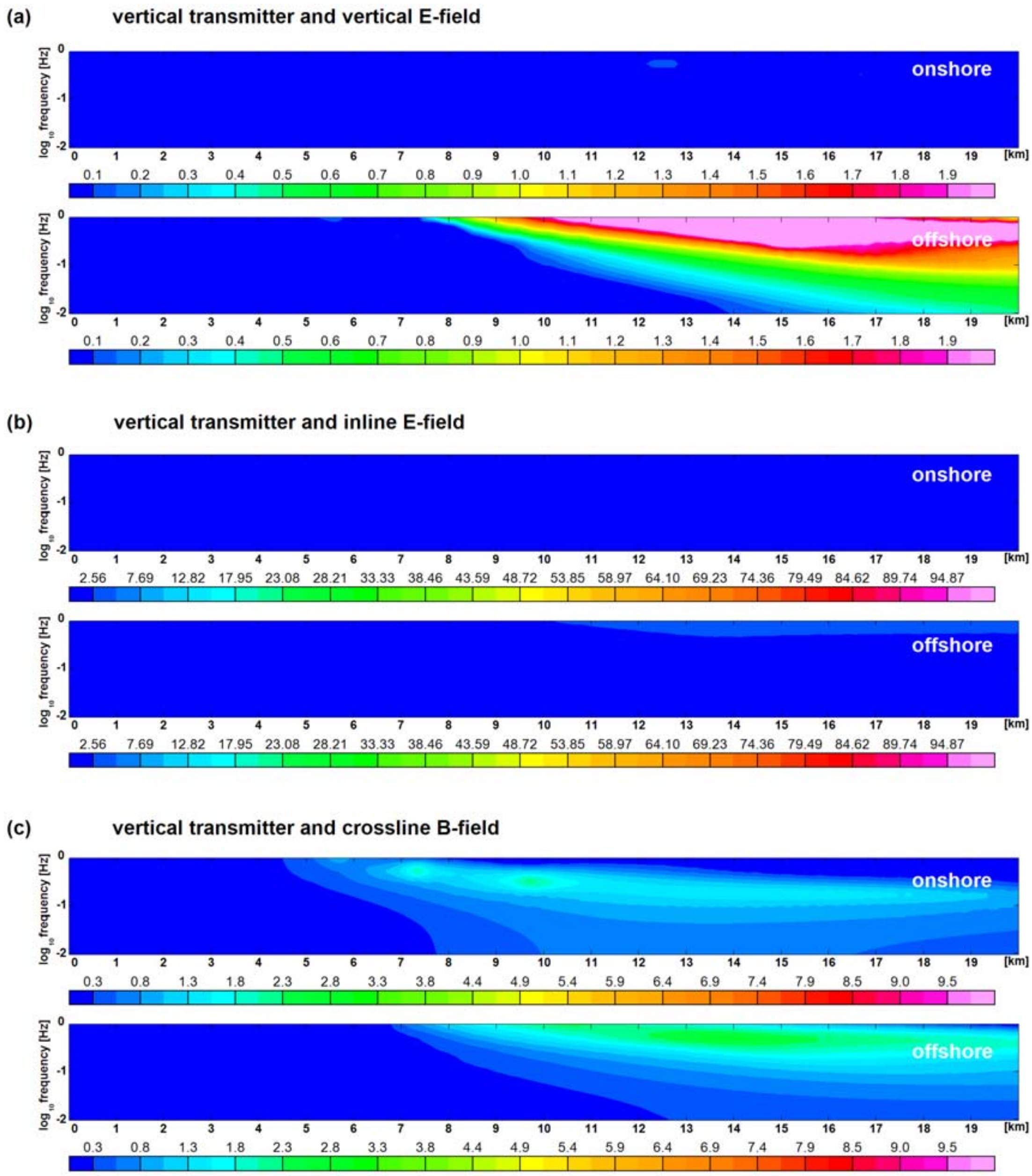


Figure 22. Log_{10} values of amplitude ratios for responses from a model with a reservoir and a model without a reservoir. The source is a vertical electric dipole placed at 0.0 km and receivers are placed along a 20 km profile with (a) vertical electric field; (b) inline electric field and (c) crossline magnetic field.

The modelling results above were done for a frequency domain system. This was initially the most used transmitter type in offshore applications, but transient systems are getting considerable interest (Weiss, 2007, Strack *et al.* 2008). The MTEM system was initially developed for onshore applications (Wright *et al*. 2002) and is based on a transient source signal generated as a pseudo random binary sequence (PRBS). The recorded response data are afterwards processed by de-convolution with the transmitter waveform data, whereby an input-response function is calculated (see Figure 23). The PRBS signal does not have a well-defined ontime and offtime sequence common to most airborne transient systems used for mineral exploration. The advantage of using a PRBS is described in Ziolkowski *et al.* (2011). The Ketzin survey mentioned above involved both application of PRBS signal and a square pulse. The square pulse is equivalent to simultaneous transmissions of discrete frequencies at the odd harmonics of the base frequency (see Figure 9). Hydrocarbon exploration based on the onshore MTEM system is mentioned in the publications describing the development of the MTEM system, but no onshore case studies are included. Result from a demonstration survey in France is provided in Ziolkowski *et al.* (2007). This survey mapped an underground gas storage reservoir in south-western France. Figure 24 displays a resistivity section obtained by inversion of the data. The resistive gas reservoir is clearly mapped at a depth below 500 m. The results from the demonstration survey in France are encouraging. The lack of case stories from hydrocarbon exploration onshore makes it difficult to make prediction of future application of this system

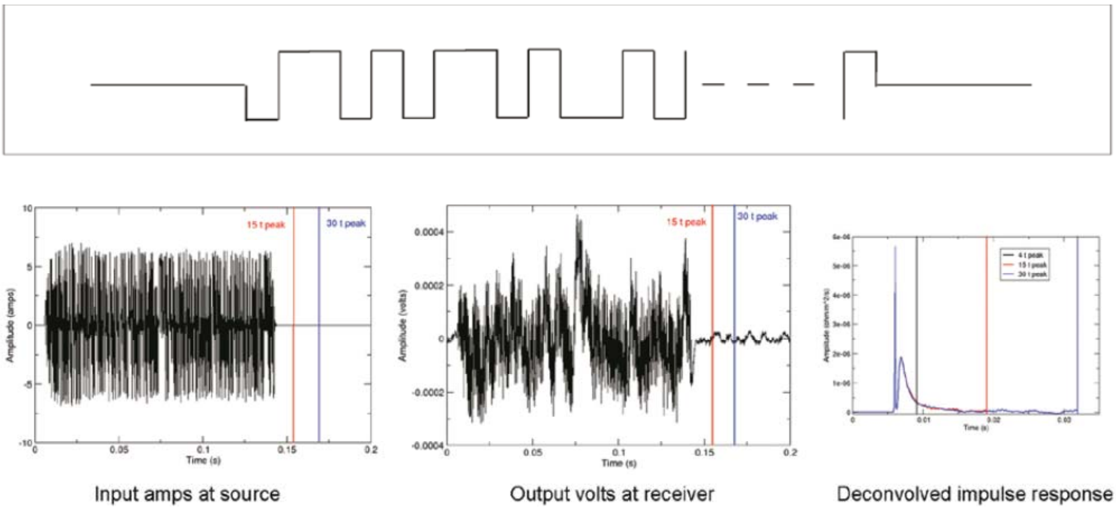


Figure 23. *Waveform of the MTEM system. The upper panel shows a small section of the waveform in the lower left panel. The measured response at the receiver is shown together with the processed response.*

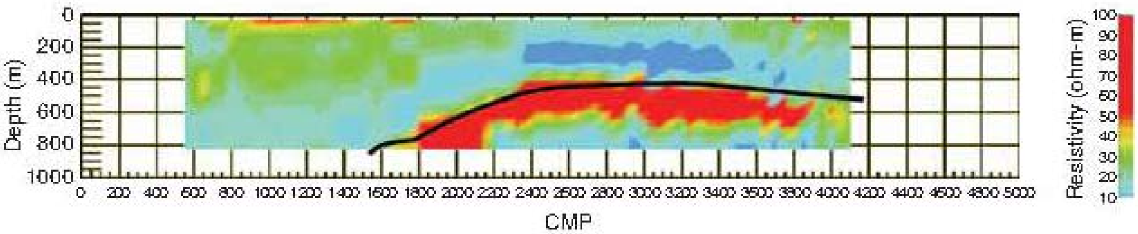
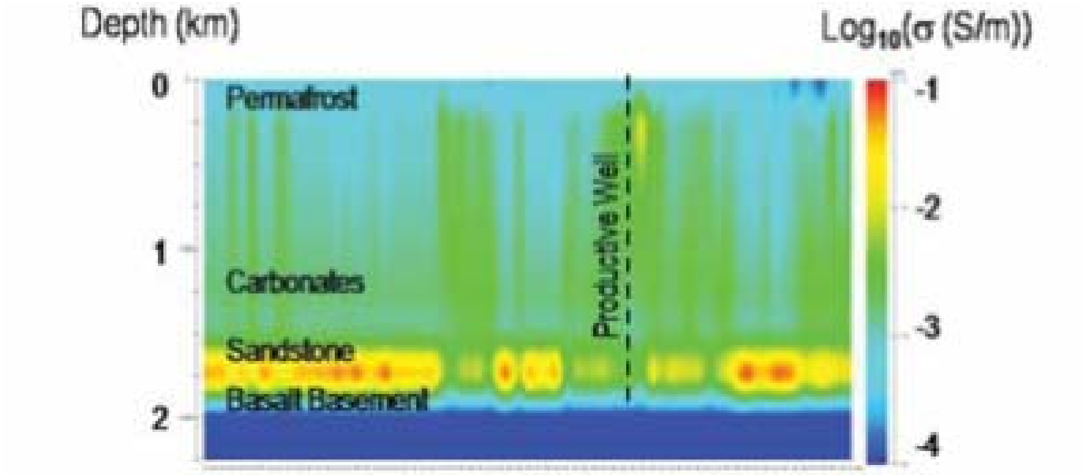


Figure 24. *Collated 1D full-waveform inversions of CMP gathers of the MTEM step-response data. The black curve shows the top of the reservoir.*

Tasci *et al.* (2007) present case stories from the United States where HMEM has been used successfully in hydrocarbon exploration. They used a square wave transmitter to map reservoirs at a depth of about 2 km.

Davydycheva *et al.* (2009) and Davydycheva & Rykhlinski (2011) present a focused-source electromagnetic method (FSEM) with an improved depth penetration and resolution. Figure 25 shows a resistivity section from the Tympuchikan Gas-condensate deposit in Siberia. The deposit is mapped as a resistive section with the sandstone at a depth of 1800 m.

(a)



(b)

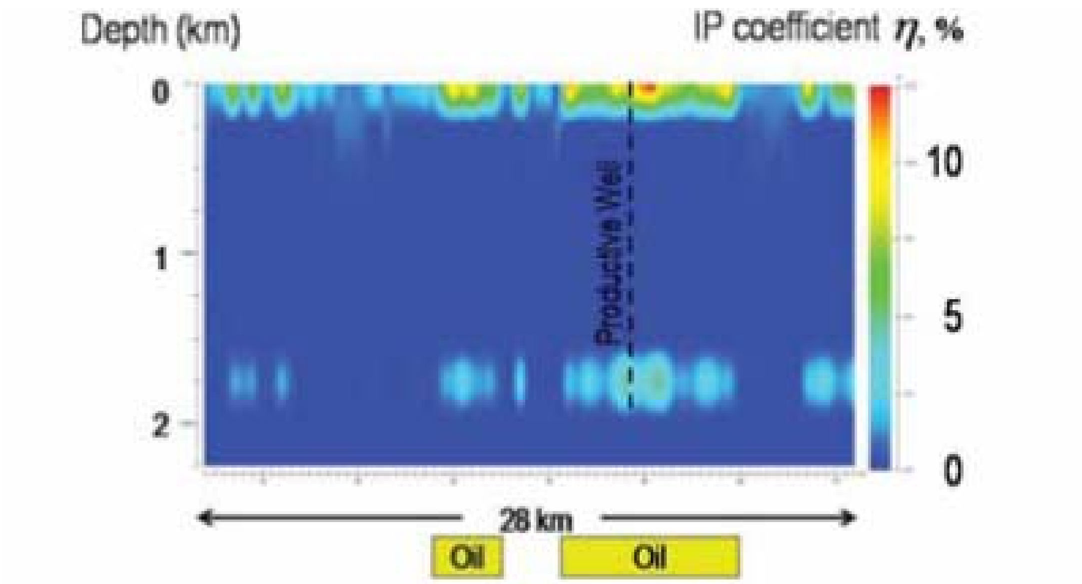


Figure 25. *Tympuchikan Gas-condensate Deposit: 1D inversion results for the electric conductivity (a) and the IP coefficient η (b). Figure reproduced from Davydycheva et al. (2009).*

Published case histories with application of HMEM for hydrocarbon exploration are somewhat limited. The reason is most likely a result of the logistic difficulties in performing controlled source surveys onshore.

4.6 Method 5: High-Powered Spectral Induced Polarization (HPSIP)

Burtman *et al.* (2009, 2012) present laboratory studies on hydrocarbon bearing rocks and it is concluded that induced polarization is a general feature when hydrocarbons are present.

Two case studies from China in which spectral induced polarisation (SIP) have been used with success in hydrocarbon exploration were presented by He *et al.* (2005). They used a high-power transmitter and were able to model resistivity and induced polarization to a depth of about 5 km in a sedimentary environment. High-powered spectral induced polarization (HPSIP) was therefore selected for this report. We include in this section also a discussion on time-domain induced polarization methods. The distinction between spectral/frequency domain and time domain induced polarization is primarily in relation to instrumentation, whereas the interpretation of polarization parameters obtained from the two domains are equivalent. He *et al.* (2012) describe applications with joint interpretation of frequency and time domain IP data (TFEM) from the Tarim Basin.

The field work involved in induced polarization method is basically similar to controlled source surveys such as the Ketzin survey reported by Streich *et al.* (2011). He *et al.* (2005) and He *et al.* (2010) mention injected currents of about 100 A. In order to achieve such high currents it is necessary to have a very low (10 Ωm) grounding resistance for the current electrodes. Drilling to the ground water table is therefore often required. Figure 26 shows transmitter and receiver set-up for the TFEM system used in China. Transmitter dipole lengths of 3–12 km are used. Efficiency of the methods is obviously proportional to the number of receivers available when transmitting currents. Judging from the illustration of the survey setup in Figure 26, the workload involved is comparable to seismic data acquisition. The heavy work-load is also mentioned by He *et al.* (2005) as a limiting factor in IP surveys.

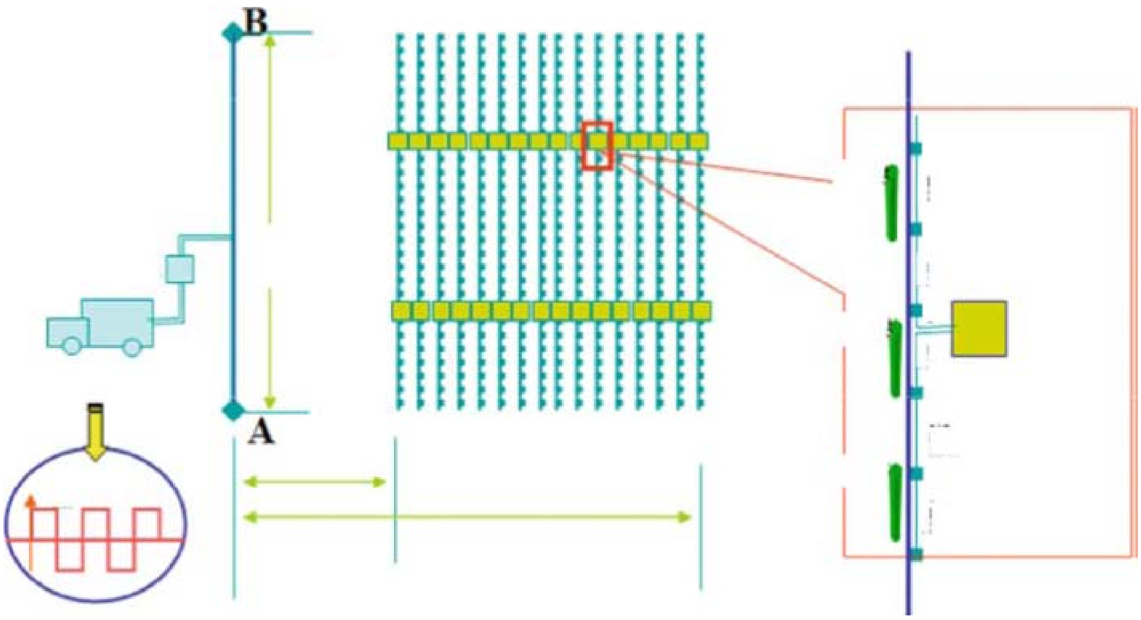


Figure 26. *Outline of FTEM system setup as described by He et al. (2010)*

Electromagnetic noise from cultural activity and currents induced by the geomagnetic variations are clearly of concern in IP, and may prevent acquisition of high quality data. Electromagnetic coupling to cables, fences and pipelines are expected in cultivated areas like Denmark. In particular is capacitive coupling to partly isolated cables likely to produce responses with similarity to induced polarisation responses from the ground. Nelson (1977) and Carlson & Zonge (1996) describe the influence of cultural disturbances on IP measurements.

Certain types of clay minerals are known to be polarisable. However, according to Luo & Zhang (1998) are both the decay constant and the frequency constant for hydrocarbon significantly different from the corresponding values of clay minerals. Luo & Zhang (1998) provide a detailed description of the data inversion and interpretation technique used in China. The principal model used for describing the induced polarization and electromagnetic responses in the measured data is a double Cole-Cole model, with one Cole-Cole model describing the IP effect and the other is used to describe the electromagnetic induction. Figures 27 and 28 show examples with interpretation of IP from the Tarim Basin.

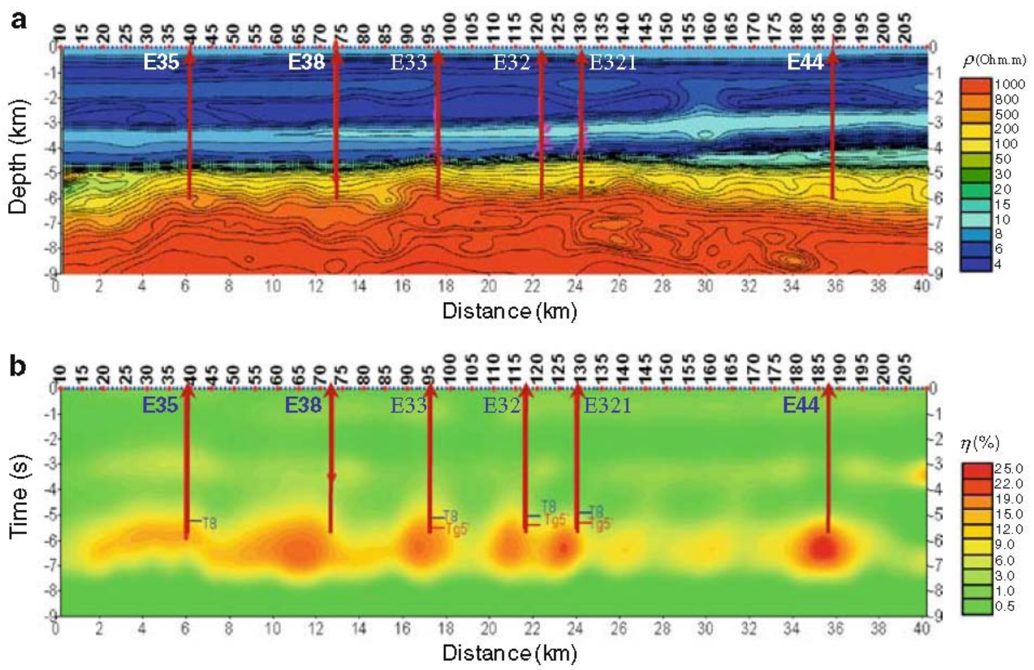
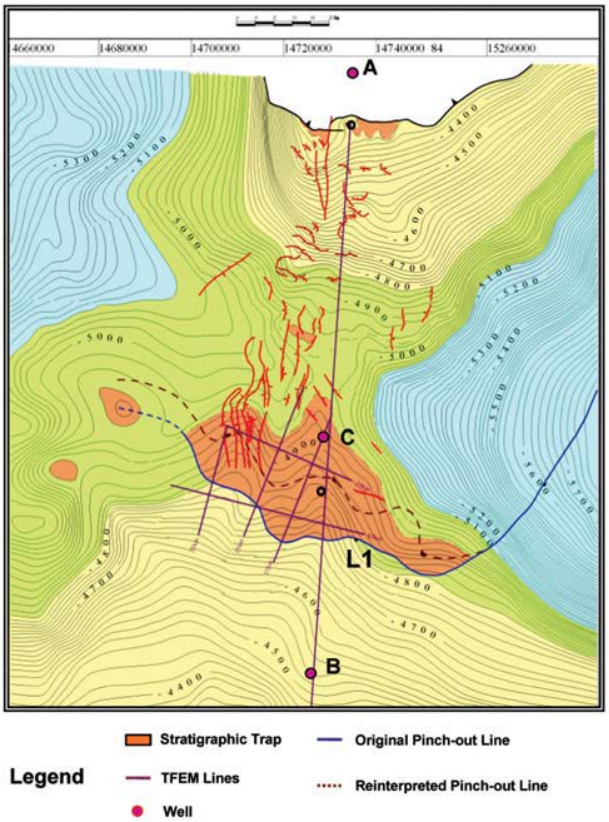


Figure 27. *TFEM survey presented by He et al. (2010) with (a) resistivity and (b) polarization*

(a)



(b)

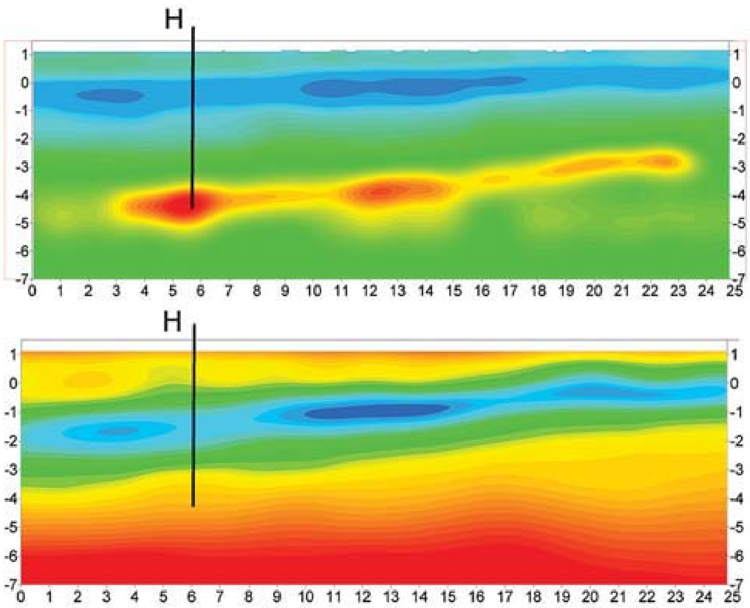


Figure 28. *TFEM survey presented by He et al. (2012) with (a) location of TFEM profile and (b) inverted sections of polarisation (top) and resistivity (bottom). No colour legend bars were provided in the referenced paper. Red colours represent high values and blue represents low values.*

Davydycheva *et al.* (2006,2009) and Davydycheva & Rykhlinski (2011) present a method for IP measurements and case histories are included from Siberia. An example was presented in the previous section (Figure 25) with a joint inversion for IP parameter and resistivity.

Veeken *et al.* (2009) show a case history from the mid-Volga basin where they demonstrate the applicability of IP in hydrocarbon exploration.

4.7 Method 6: Electron Para-magnetic Resonance

Prior to the onset of project ALTKUL, a technique for hydrocarbon prospecting based on the physics of electron para-magnetic resonance was promoted to us by a private company TST Technology Inc through its associates. EPR was therefore included among the methods to be investigated. Some documents that describe the company's technology and claims were provided for the project. The evaluation given here of EPR is divided into three sections. Section 4.7.1 describes the basic principles of EPR, section 4.7.2 includes a review of publications referring to EPR in relation to hydrocarbon exploration and section 4.7.3 contains an evaluation of the claims of TST Technology Inc. It is evident from the discussion below that the claims by TST Technology Inc are not valid.

4.7.1 Basic principles of EPR

A comprehensive treatment of EPR is provided in a text book by Weil & Bolton (2007). The physical phenomenon is linked to the absorption of microwave electromagnetic energy in matter in the presence of spin angular magnetic momentum of unpaired electrons as well as in the presence of a magnetic dipole momentum caused by the electron orbital motion. The spin magnetic angular momentum is significantly larger than the momentum associated with the orbital motion. Therefore, the term electron spin resonance (ESP) is often used instead of the more general term EPR. Nevertheless, the orbital spin is important as explained below.

The electron possesses a magnetic vector moment $\boldsymbol{\mu_e}$ due to its spin vector described by the quantum number $\boldsymbol{S} = \pm½$

$$\boldsymbol{\mu_e} = -g_e \cdot \beta_e \cdot \boldsymbol{S}$$

where the g-factor or Landé-factor is given by $g_e = 2.0023$ and the electron Bohr magneton $\beta_e = 9.42 \cdot 10^{-24} J$. Two energy levels $E = \pm g_e \cdot \beta_e \cdot B_0$ exist in the presence of an external magnetic field B_0 (either the Earth natural magnetic field or any artificially made magnetic field) corresponding to the two oppositely directed spin vectors. This is known as the Zeeman interaction. The two states are almost equally populated. Utilisation of the spin electromagnetic properties is done by imposing an alternating electromagnetic magnetic field with frequency ϑ propagating in the direction orthogonal to B_0. A necessary condition for energy absorption is that the frequency ϑ is given by the resonance frequency:

$$\vartheta = \frac{g_e \cdot \beta_e \cdot B_0}{h}$$

where h is Planck's constant. The condition above is modified in the presence of interaction with the magnetic field of the orbital motion as well as between the orbital motion and the magnetic field. Therefore, the g-factor is not given by the value $g_e = 2.0023$ but has to be replaced by a value that differs from 2.0023. The g-factor (g is in fact no longer a scalar but needs to be replaced by a tensor) depends on the molecular structure and is thereby an indicator of the actual type of matter. In addition to the above mentioned couplings, the existence of non-zero nuclear spin also interacts with the electron spin. This coupling is known as hyperfine interaction.

A requirement for energy absorption is that the electromagnetic field has well-defined frequencies (the Larmor frequency) with a value that depends on both the composition of the matter and the external magnetic field. The absorbed energy is released subsequently as electromagnetic waves with the same frequency as the external electromagnetic field used to energize the matter. EPR is used as a spectroscopic method to analyse small samples (cm size) of material in laboratory work. Weckhuysen *et al.* (2004) provides a good description of various laboratory techniques based on EPR. A significant difference exists between EPR in laboratory work where the magnetic field can be controlled, compared to any application in the natural Earth magnetic field. In laboratory work a common procedure is to keep the frequency (usually a value in the 3–95 GHz range) of the transmitted electromagnetic field constant and then simply vary or sweep the magnetic field strength within a certain range, where absorption is expected. In this manner an absorption "spectrum" is obtained as function of the external magnetic field strength for the particular frequency of the electromagnetic field selected for the measurements. In nature, the Earth magnetic field determines for which frequencies it is possible to observe the resonance phenomenon. This has a limitting effect for the use of this phenomenon in geophysical field

The mathematical description of EPR shares some similarities to Nuclear magnetic resonance (NMR), where the spin properties of protons are utilised. NMR utilises frequencies in the range of radio waves. Magnetic resonance sounding (MRS) is a well-established surface geophysical method based on NMR for estimation of water content in rocks and sediments by utilising the spin properties of the protons in water molecules (Plata & Rubio 2007, Kirsch, 2006). In MRS a monochromatic electromagnetic signal produced by a horizontal loop lying on the ground (for example a 40 m by 40 m loop) is used to energize the protons in the water molecules, or in any hydrocarbons present. The frequency used depends on the strength of the static magnetic field in the survey area and needs to be tuned accordingly to obtain resonance. In Denmark this frequency is in the order of 1000 Hz. The maximum penetration depth of MRS is determined primarily by the attenuation of electromagnetic signals in the ground. A typical depth of penetration in Denmark for MRS is about 50–100 m. EPR occurs at frequencies an order of magnitude larger than for NMR, and this implies that the depth of penetration is much smaller. In case of an analogue sounding technique based on EPR instead of NMR, a penetration depth less than 10 m would be the case. An estimate of which frequencies are required for obtaining electron spin resonance under natural conditions in Denmark can be obtained by converting the result reported by Di Mauro *et al*. (2005) from laboratory EPR on crude oil (see Figure 29). Table 3 contains the conversion for three frequencies used in the laboratory to the corresponding frequencies in the case of field work in Denmark, where the external magnetic field is approximately 49000 nT =0.000049 Tesla = 0.49 Gauss. Frequencies above 100 kHz are required in order to obtain resonance. In comparison to MRS used for water prospecting where resonance is obtained around 1000 Hz, the depth of penetration is therefore approximately 10 times smaller. Thus, in Denmark a penetration depth less than 10 m would be the case.

In addition to the differences in frequency, and associated penetration depth, between MRS and EPR, another difference is of importance. The protons involved in MRS are almost entirely linked to the occurrence in water molecules, but EPR are likely to occur for many different substances in the ground. Therefore, provided that a similar type of equipment used for MRS is applied with a frequency adjusted to EPR under natural conditions, responses from several substances may occur. It is highly unlikely that it will be possible to make any discrimination in terms of determining which type of substance is responding. The reason for this statement is that the g-factor does only differ slightly from $g_e = 2.0023$ and that the static magnetic field is never known with any high degree of certainty. The static field is inhomogeneous spatially and the local static magnetic field is furthermore superimposed with a time varying magnetic field due to induction from currents in the ionosphere and local artificial disturbances. In MRS it is possible, but not always easy, to tune the frequency and obtain resonance.

Table 3. *Conversion table with calculation of resonance frequency if the measurements in Figure 29 should be done in an area with a magnetic field strength of 49000 nT, which approximately equals the geomagnetic field in Denmark.*

Magnetic field in laboratory [Gauss]	Magnetic field in laboratory [Tesla]	Frequency in laboratory [Hz]	Frequency fieldwork Denmark [Hz]
3200	0.32	900000000	125284
12160	1.216	3400000000	137007
33450	3.345	9500000000	139163

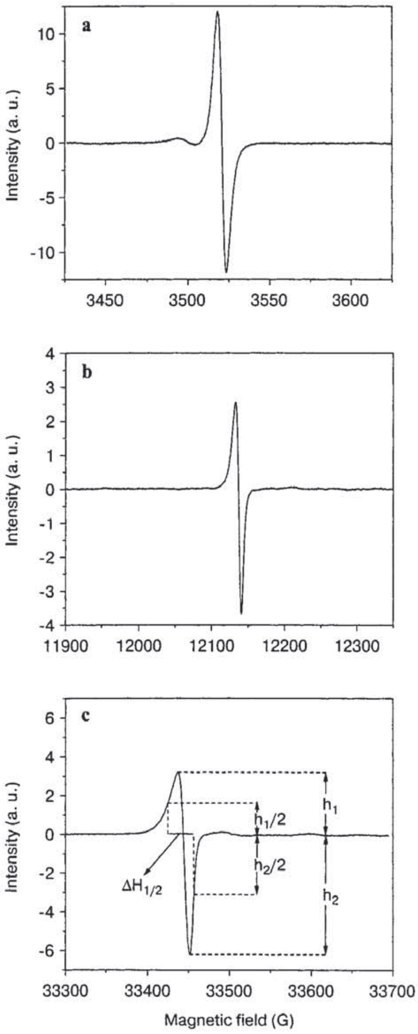


Figure 29. *EPR/ESP spectra of Arabian petroleum at room temperature obtained with 1 Gauss modulation amplitude and microwave power X-band (a); 2 mW (Q-band, 1 mW (b); W-band, 50 microW (c). Figure reproduced from Di Mauro et al. (2005)*

4.7.2 Publications on ESP and hydrocarbon

A search on applications of ESP for hydrocarbon exploration resulted in a very limited number of publications. One patent application by Nicksic & Starke (1985) with respect to well-logging was found, but no references to this patent were noted. Almost all other publications on EPR and hydrocarbon are in relation to laboratory work. It is interesting to note that the use of NMR in well-logging is well established, whereas EPR is not despite the mathematical similarities between the two physical phenomena.

EPR has been used in the analysis of cuttings from hydrocarbon exploration wells drilled in Venezuela (Dias *et al.* 2000, Constanzo-Alvarez *et al.* 2006, Aldano *et al.* 2011). They include investigations of correlation between magnetic properties related to hydrocarbon deposits and occurrences of peaks of the organic matter free radical concentration (OMFRC), which are identified by ESP in laboratory measurements. These papers refer to magnetic anomalies above oilfields and analysis of magnetic properties by laboratory investigations on drill cuttings.

Another application of EPR is in relation to the laboratory study of degradation of kerogen as function of temperature (Dalal *et al.* 1984). EPR is a non-destructive method and is therefore useful in the study of alteration in the samples caused by an exposure to a physical phenomenon such as varying temperature or exposure to sunlight (Guedes *et al.* 2006) in environmental applications.

4.7.3 Evaluation of claims by TST Technology Inc

Below are some citations from the documents provided by TST Technology Inc associates. Statements that are underlined will be commented below.

> ***"General:*** *TST is a long-range, substance-discriminating detection system whereby an electromagnetic signal emitted at a precise frequency and amplitude and possessing a certain wave-form results in a targeted substance radiating <u>a return signal which can be picked up and measured to locate and identify this substance regardless of its position on, above or under the ground and above or under the seabed regardless of what other materials or substances may shield it.</u>*
>
> ***Description:*** *TST consists of two separate but field-coupled units: an Emitter and a Receiver. The Emitter radiates an omni-directional electromagnetic signal at a precise low frequency and amplitude and with a specific waveform. Frequencies for over 150 substances have now been identified including explosives, hydrocarbons, minerals and narcotics. This Emitter signal causes the targeted substance to radiate a return signal. The targeted-substance radiated signal is of a different format and band to that of the emitter signal. It is a narrow and precise directional beam that can be detected and measured to locate and identify the target substance. A carrier wave is used to detect range.*
>
> *It can detect any substance, whether organic or mineral, natural or synthetic, simple or complex, for which the target substance's resonance frequency is known. <u>The targeted substance may be on, above, or under the ground or seabed. No materials or substances can shield the target substance.</u>*
>
> ***Stated Performance.*** *TST detects substances out to five plus kilometers. It works from vehicles moving up to 30 miles per hour on smooth roads or water borne craft on relatively calm water, It has also been tried from aircraft in Australia and submersibles in Florida with considerable success. It can detect any substance, whether organic or mineral, natural or synthetic, simple or complex, for which the target substance's resonance frequency is known. <u>The targeted substance may be on, above, or under the ground or seabed. No materials or substances can shield the target substance.</u>*
>
> ***Specific, Quoted Performance Claims of the TST System Include:***
>
> *1. The ability to detect and differentiate with great accuracy between closely, structurally/chemically related substances.*
>
> *2. The ability to detect and locate a substance at ranges from several kilometres or greater depending on target mass.*

3. The absence of shielding - as far as current knowledge goes- by any intervening materials (and therefore the ability to detect and locate a substance at virtually any depth or behind any physical obstacle)

4. The TST system can be operated on land (from a ground vehicle or on foot, indoors or outdoors), at sea (on the surface or underwater) and from an aircraft."

The underlined statements above relate to distance between instrumentation and target. As mentioned in the previous section on the basic principles of EPR, a resonance frequency for crude oil is slightly above 100 kHz. The penetration depth in typical soil (resistivity less than about 10 ohmm) for such a signal is less than 5 m, and there is no way that any useful signal can be obtained at the depth claimed by TST. In seawater the penetration depth will be above an order of magnitude lower.

In conclusion the statements by TST Technology Inc. do not make sense, and we cannot on basis of the material available to us recommend the use of this method for hydrocarbon exploration onshore.

4.8 **Method 7: Airborne Transient Pulse Surveys**

The airborne transient pulse survey system advertised by Pinemont Technologies Inc. is essentially airborne AMT. The frequency range is only suitable for shallow investigations and the method is therefore not considered relevant for applications in Denmark.

5. Discussion and conclusions

The hydrocarbon seepage model has a significant role in several of the methods proposed for hydrocarbon exploration. In summary these are with typical depth range of investigations listed in parenthesis:

- Hyperspectral imagery [0 m]
- Gamma-spectrometry [0 –½ m]
- Geochemistry [0 – 1 m]
- Electron Para-magnetic resonance [0 – 5 m]
- Induced polarization [1 m – 2 km]
- Controlled source EM [5 m – 5 km]
- Magnetotellurics [5 m – 10+ km]

The list is ordered with respected to increasing depth of investigation or sampling. The values are approximate, and the actual values in a survey depend on various choices made in the design of a survey. In geochemistry, although the depth of investigation is small, the implications can reach depths of thousands of meters. Note that no convincing evidence for application of electron para-magnetic resonance in the field has been published. Table 4 summarises the applicability of the methods reviewed.

Table 4. *Overview of applicability of methods.*

Methodology general	Method - specific	Depth of investigation	Direct hydrocarbon detection	Indirect hydrocarbon detection	Structural mapping
Geochemistry		no depth resolution	No	Yes	No
Inductive source EM	MT	deep	No	Yes	Yes
	AMT, CSAMT, ZTEM, Pulsed EM	shallow	No	Yes	Yes
Galvanic source EM	CSEM, FSEM, TFEM, MTEM, LOTEM	shallow & deep	Yes	Yes	Yes
Induced polarization	HPSIP, TFEM, FSEM, MT, AMT	shallow & deep	No	Yes	Yes
Gravity	standard gravity and tensor gravity gradiometry	shallow & deep	No	No	Yes
Electron para-magnetic resonance (EPR)	TST	shallow	No	No	No

The methods listed respond to different properties described by the seepage model. The applicability of the methods is linked to local conditions, which in addition to the actual geology also may involve present and past climate, cultural activity that may distort the measurements etc. The seepage model encompasses a very broad range of geological processes that furthermore are influenced by boundary conditions specific to the actual geology. This complexity makes it extremely difficult to transfer the experience gained from one location to another. In particular, these difficulties apply to greenfield exploration. The fact that several methods respond to the same conceptual seepage model may be utilised in setting up a viable strategy for hydrocarbon exploration onshore.

In general, integration of data is the key to an optimum exploration strategy, but cost in performing the measurements is obviously a limiting factor. Magnetotellurics is in comparison with controlled source EM methods and induced polarization methods with artificial sources a fairly simple method, but problems may occur due to local electromagnetic noise. Magnetotellurics is used intensively in China for hydrocarbon exploration and induced polarization responses in MT data have recently been interpreted from a survey with dense station spacing. The structural information on electrical resistivity variations from the MT measurements is furthermore valuable for the general interpretation of the geology. The optimum approach if costs are of no concern is to combine MT data with controlled source EM data (induced polarisation and/or resistivity mapping) obtained from application of a galvanic source. However, a controlled source survey with sufficient depth of penetration in a Danish environment is going to be very costly. In particular, coverage of a larger area is not considered feasible unless hydrocarbon occurrences are considered highly likely in the area.

Airborne radiometric measurements and airborne EM may be used for reconnaissance in certain geological environments, but we do not expect these methods to be applicable in Denmark for hydrocarbon exploration, when considering the expected large depth of any hydrocarbon reservoirs. Hyperspectral data are likely not useful in a Danish environment where vegetation and humidity prevents signal from the soil. Furthermore, experiences from application of hyperspectral data are in general fairly limited in relation to hydrocarbon.

Geochemistry has a potential to be used for both reconnaissance work and for more detailed surveys in relation to seepage from reservoirs. It was shown earlier (see 4.1.6.2 and appendix) that traces of hydrocarbons appear to be present ubiquitously in the Danish region, and furthermore that different sources can be identified and recognised (see the Danica Resources case story in 4.1.6.2): Useful information can no doubt be gained from the Danish strata. Probably most if not all the geochemical methods mentioned above will give meaningful data. The critical issue then becomes the interpretation of the data, and here we can only support the modern trend of (i) interpreting together with all other types of data available – and thus the EM methods described in this report could be considered complementary methods, not conflicting methods, and (ii) using multi-parameter approach, when interpreting the geochemical data. Inherently in this approach is a need to be very careful of sampling methods and patterns. Fairly close sampling is recommended, if the hope is to get vectors to success out of the data.

It is not really feasible to recommend one geochemical method over another. Microbial geochemistry has proven its worth and so have methods based on the content in soil of hydrocarbons. Several companies offering geochemical services are easy to find on Internet; we recommend a very clear description of the anticipated model, any pre-history and drilling information, geology and other data types as the foundation for a fruitful discussion with the professional service companies for the geochemical survey you need. Most companies have an element of 'black box' in their preferred procedures!

Whether or not any geochemical survey can ever replace detailed seismic mapping of a possible prospect is impossible to say. In the greenfield conditions of most of onshore Denmark, no assemblage of producing wells are present, so we cannot use existence of positive geochemical anomalies over prospects as an additional qualifier. Pointing out new drill positions solely based on the non-seismic data will always be riskier; that is why integrated interpretation and multivariate statistics should be used to minimize the risk. And then the final decision is the explorer's!

Mapping of resistive layers as direct hydrocarbon indicators by using galvanic high moment EM sources has a potential in hydrocarbon exploration. The experiences gained from offshore work are going to be useful in a continued development of EM systems for onshore applications: However, we expect that this development will be slow due to the workload involved to carry out this type of measurements. Security issues in relation to the use of long cables for injecting strong currents into the ground may impact in a negative way the possibility of using these methods in a densely populated environment such as in Denmark. High moment EM has been used in the past, but the number of surveys reported to have led to discoveries is fairly limited. Exception to this is the work reported from China and Russia. The use of high moment EM as a de-risking method in the evaluation of prospects defined from other types of data may be considered.

Gravity data and to some extent also magnetic data are expected to be an integral part of any evaluation of the prospectively of an area. The structural information that can be gained from these data is valuable on both a regional scale and in more detailed studies. Gravity gradient tensor data are acquired in some airborne systems. The properties of the gravity gradient tensor are useful in structural interpretations, but it is important to emphasise that the non-uniqueness in interpretation of standard gravity data also apply to tensor data.

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8. Appendix: Preview of upcoming GEUS report on surface geochemical surveys

By Troels Laier, senior adviser, GEUS

Overview of surface geochemical surveys in Denmark 1972–2002

8.1 Abstract

The results of 16 surface geochemical surveys covering the Danish area, excluding the North Sea area, have been summarized. The number of surveys was equally distributed between onshore and offshore, showing up to 2,500 ppb of light hydrocarbons mostly methane in soils and sediments. The analytical methods applied included dissolved hydrocarbons in groundwater, desorption of light hydrocarbons from soils and sediments by acid, one air-borne sniffer survey and measurements of heavier hydrocarbons by total scanning fluorescence and thermal desorption mass spectrometry (Gore sorber method). Locally over 25,000 ppb of methane in groundwater has been observed (Nordsjælland and Vendsyssel), but stable carbon isotopic analyses ($\delta^{13}C$: -60 to -90 ‰) showed the gas to be entirely bacterial in origin.

The geochemical surveys showed that low levels of hydrocarbons, particularly light hydrocarbon gases, appear to be present ubiquitously in soil and shallow sediments. The main problem in identifying subsurface hydrocarbon accumulations using surface geochemical methods appear to be lack of proper sampling strategy combined with appropriate statistical analysis of data.

8.2 Introduction

Most surface geochemical surveys were carried after 1983, when revision in Danish legislation allowed more oil companies to become active in hydrocarbon exploration in Denmark. Prior to 1983 only one geochemical survey, including high methane in groundwater, had been carried out by Gulf Oil in 1972. Early surveys were mainly based on hydrocarbon (C1-C5) concentration in shallow samples, either soil or groundwater. Later when more sophisticated analytical techniques became available, isotopic analyses enabled discrimination of bacterial and thermogenic hydrocarbon gases. The increased sensitivity of modern analytical techniques, e.g. UV fluorescence of aromatic compounds and GC-MS analysis made it possible to focus on higher hydrocarbons, thereby avoiding interference from hydrocarbon gases generated by bacteria. Though, in regions without any obvious hydrocarbon seepage it was still a challenge to localize subsurface hydrocarbon accumulation based on low levels of hydrocarbons in shallow samples, since traces of hydrocarbons appeared to be present ubiquitously.

Apart from high methane in groundwater in a few areas only traces of hydrocarbons, up to 2500 ppb have been observed at shallow levels in Denmark from the various surveys performed. The high methane in areas like Nordsjælland and Vendsyssel was generated by bacteria as was shown by isotopic analyses ($\delta^{13}C$: -60 to -90 ‰). This is also true for the shallow gas (*c*.100m) that was exploited in the Frederikshavn area during the 1930'ies and 1940'ies.

Information on surface geochemical surveys has been gathered from company reports, Table A1, delivered to GEUS as part of the License holders' obligations. Additionally, information has been obtained from direct contact by the author to the companies. A laboratory for shallow hydrocarbon surveys establish at GEUS in 1985, has been involved in a few surveys and data thus obtained are also included in the summary, Table A1. No particular guidelines concerning the form of the surface geochemical data to be delivered to GEUS by the companies exist. Therefore, the data in the GEUS archive appear in different forms, mostly printed reports, some with maps and some with geo-coordinates of sample locations. In order to be able to present an overview of the various data from all the surveys, the data have been compiled into an ArcMap project, Figure A1. The ArcMap project will allow comparison of the data of different surveys in overlapping areas. Furthermore, other information relevant for interpretation of the hydrocarbon data, e.g. soil maps etc. may easily be applied.

Table A1. *Surface geochemical surveys 1972–2002*

Date	Area	Method	Operator	Laboratory	Samples	Constituents analyzed	Isotope, δ13C	Soil/ sediment	Interpretation
Nov. 1972	North Sjælland / Møn	Hydrocarbons in groundwater	Gulf Oil	Gulf R&D Company	> 100	C1-C2	none		C1 contour plot
Nov. 1972	North Sjælland / Møn	Sorbed hydrocarbons in soil	Gulf Oil	Gulf R&D Company	30	C1-C3	none		C3 contour plot
Nov. 1984	North Sjælland	Hydrocarbons in groundwater	Amin Oil/ Phillips Petroleum	GEUS	59	C1-C2	C1 (25)		C1 contour plot
spring 1985	North Sjælland	Sorbed hydrocarbons in soil	Phillips	Phillips	850	C1-C5	none	six classes	
1984 - 1985	Viborg	Sorbed hydrocarbons in soil	Phillips	Phillips/GEUS	2391	C1-C5	none	six classes	Oil/gas contour plots
May 1985	Baltic Sea, Bornholm W	Sorbed hydrocarbons in sediment	Texas-Eastern/ IKU	M. Schmidt Hannover/IKU	224	C1-C5	C1-C3	TOC, CaCO3	
June 1985	Baltic Sea, Bornholm W	Sorbed hydrocarbons in sediment	Danpec	GEUS	80	C1-C5	C1-C2	TOC, CaCO3	
Aug. 1985	Kattegat	Sorbed hydrocarbons in	Danpec	GEUS	80	C1-C5	C1-C2	TOC, CaCO3	

		sediment							
Sept. 85	Baltic Sea, Bornholm E	Sorbed hydrocarbons in sediment	Geophys, Sopot	GEUS	39	C1-C5	C1-C2	TOC, CaCO3	
1988	Hjelm Bugt/Lille Bælt	Free gas N2; hydrocarbons. Sorbed hydrocarbons	Danpec/ COWI	GEUS/ Risø/ Hedeselskabet	80	N2, CO2, C1-C5	C1, CO2	CEC	
1988	Baltic Sea	Sniffer survey	Amoco/ Barringer	Barringer	11500 km2				Contour map
1989	Kattegat-Baltic Sea	C10+ hydrocar. fluorescence, GC	HIOST	GERG	190	C10+, fluorescence, GC-FID			Ranking
1992	Baltic Sea, Bornholm S	Sorbed hydrocarbons in sediment	DANOP	GEUS	50	C1-C5, δ13C, TOC, sediment incl. CaCO3	C1-C2		
1999	Salling	Collection of C2-C20 from soil gas		Gore & Associates Inc.	164	C2-C20; GC-MS			Contour map
2000	North Sjælland	Collection of C2-C20 from soil gas	Sterling Resources LTD	Gore & Associates Inc.	126	C2-C20; GC-MS			Contour map
2002	Salling	Collection of C2-C20 from soil gas	Sterling Resources LTD	Gore & Associates Inc.	172	C2-C20; GC-MS			Contour map

8.3 ArcMap project

Data from a number of surveys already existed in spread sheet files, other data had to be digitized from printed reports, mostly using scanning and optical character recognition (OCR). In a few cases sample locations had to be digitized from printed maps. Sample locations were converted to UTM zone 32 coordinates, WGS84 datum.

Table A2. *List of files created for ArcMap presentation*

Date	Area	GEUS Archive File No.	shapefile	content in dbf file
Nov. 1972	North Sjælland / Møn	none	gulf1972	station; UTM; depth; Litho; CH4 mg/l; C2H6*E-4
Nov. 1972	North Sjælland / Møn	none	none	
Nov. 1984	North Sjælland	none	aminoil1984	DGU well No, UTM, depth-Litho, CH4 mg/l, C1/C2 ratio, DelC13-isotope

spring 1985	North Sjælland	none	frbrg1985	UTM; soil code; CH4 ppm; C1/(C+C3), C5plus
1984-1985	Viborg	none	vibeorg85-86	UTM; soil code; CH4 ppm; C1/(C+C3), C5plus
1987	Viborg	none	Vibeorg85-86dgu	station, UTM; CH4 ml/kg; C1/(C+C3); del13C1
May 1985	Baltic Sea, Bornholm W	5192	tx-east1985	station; UTM; CH4 ppb; del13C1; del13C2; del13C3; CaCO3; C1/(C2+C3);
June 1985	Baltic Sea, Bornholm W	none	danpec1985	station; UTM;CH4 ppb; C1/(C2+C3); CaCO3; del13C1
Aug. 1985	Kattegat	none	dankat1985	station; UTM
Sept. 85	Baltic Sea, Bornholm E	none	polsk-dgu	station; UTM;CH4 ppb; del13C1; drymatter; CaCO3; C1/(C2+C3)
1988	Hjelm Bugt/Lille Bælt	none	hjelmb	station; UTM
1988	Baltic Sea	????	none	
1989	Kattegat-Baltic Sea	4813-4821	hiost-gerg	station, UTM, core-section; int-rank, R1-rank; GC-rank; fluor-int; fluor-R1
1992	Baltic Sea, Bornholm S	6130-6131	danop92	station, UTM; CH4 ml/kg; C1/(C+C3); del13C1; CaCO3
1999	Salling	18051	gore-sorber1999	UTM
2000	North Sjælland	18897	gore-sorber2000	station; UTM; cluster
2002	Salling	19547	goresoerber2002	UTM

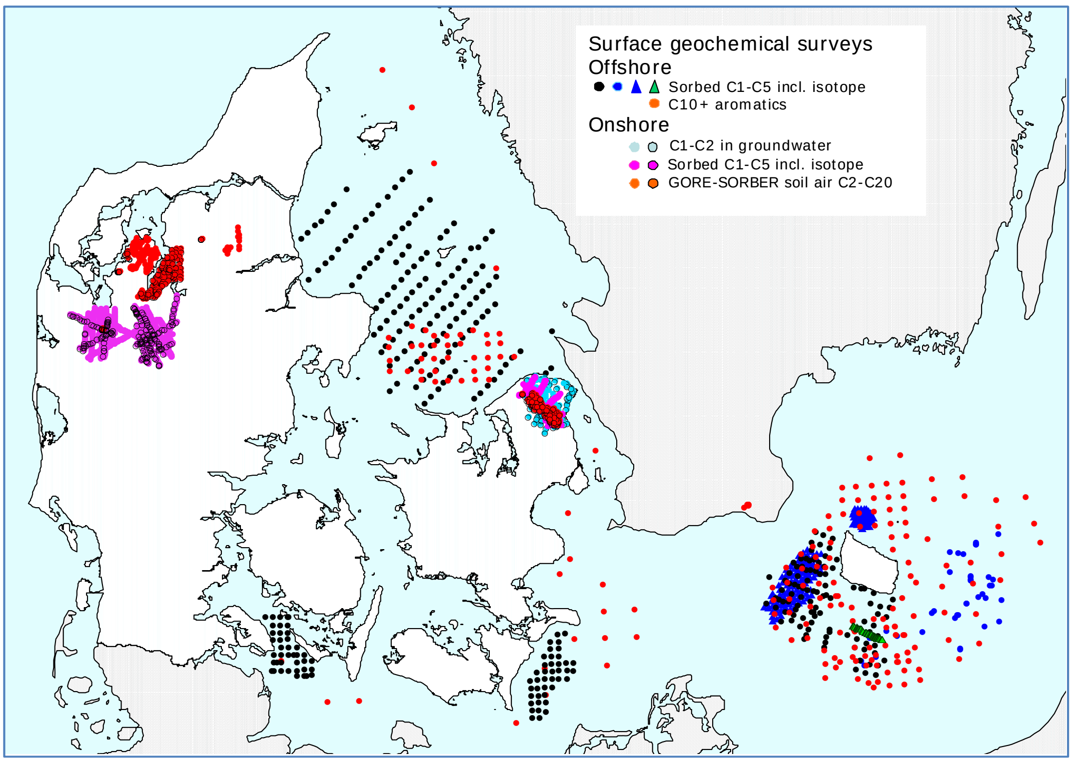

Figure A1. *Overview of surface geochemical exploration surveys for oil and gas performed 1972–2002*

The geochemical parameters considered to most essential were extracted into DBASE files and shape files were created using ESRI ArcView3.2a, Table A2. These files are stored on a CD-ROM together with coast lines and shape files containing information on available soil maps and sediment maps of the Danish area to form an ArcMap project.

8.4 **Brief account of most important surveys**

A brief account of the surveys and their results, including information obtained during active GEUS participation in some of the projects, will be presented below. The data are all in the public domain.

8.4.1 Gulf Oil survey 1972

The Gulf Oil report presents a brief account of the field and laboratory work, but contains no information on sample locations. A summary of methane in groundwater is presented as contour map (Fig. A2.) Sample locations were later obtained from old hand written DGU lists and methane data were plotted using ArcMap, see Fig. A3.

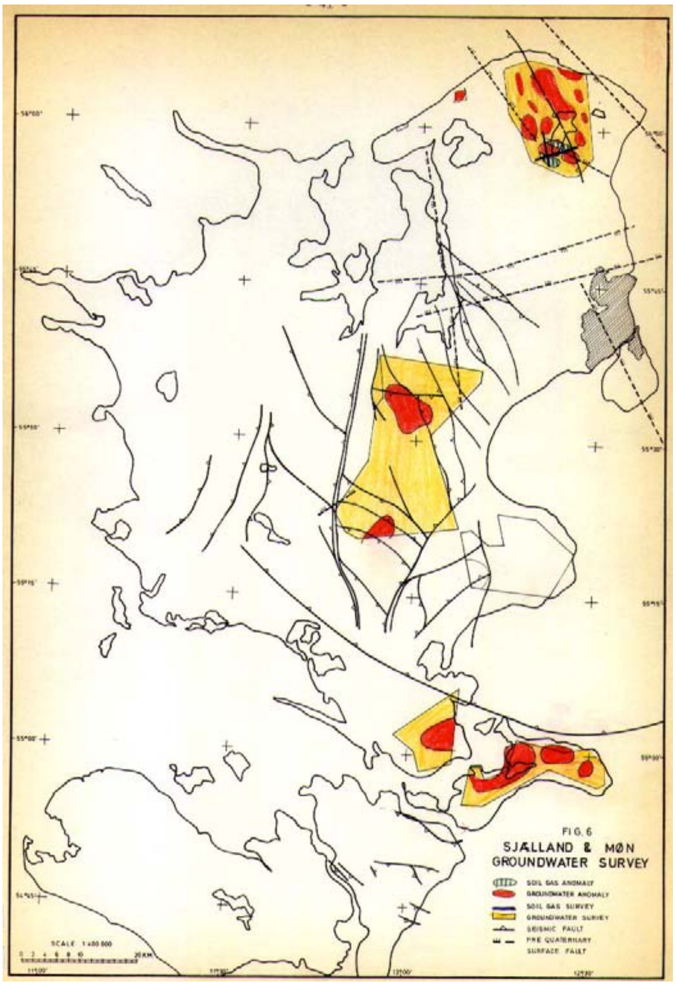

Figure A2. *Contour plot of CH4 in groundwater (Gulf report 1973)*

8.4.2 Amin Oil and Phillips Petroleum North Sjælland surveys 1984-1985

Groundwater methane data obtained by the Amin Oil survey more or less confirmed the data obtained by Gulf Oil in 1972, see Fig. A3.

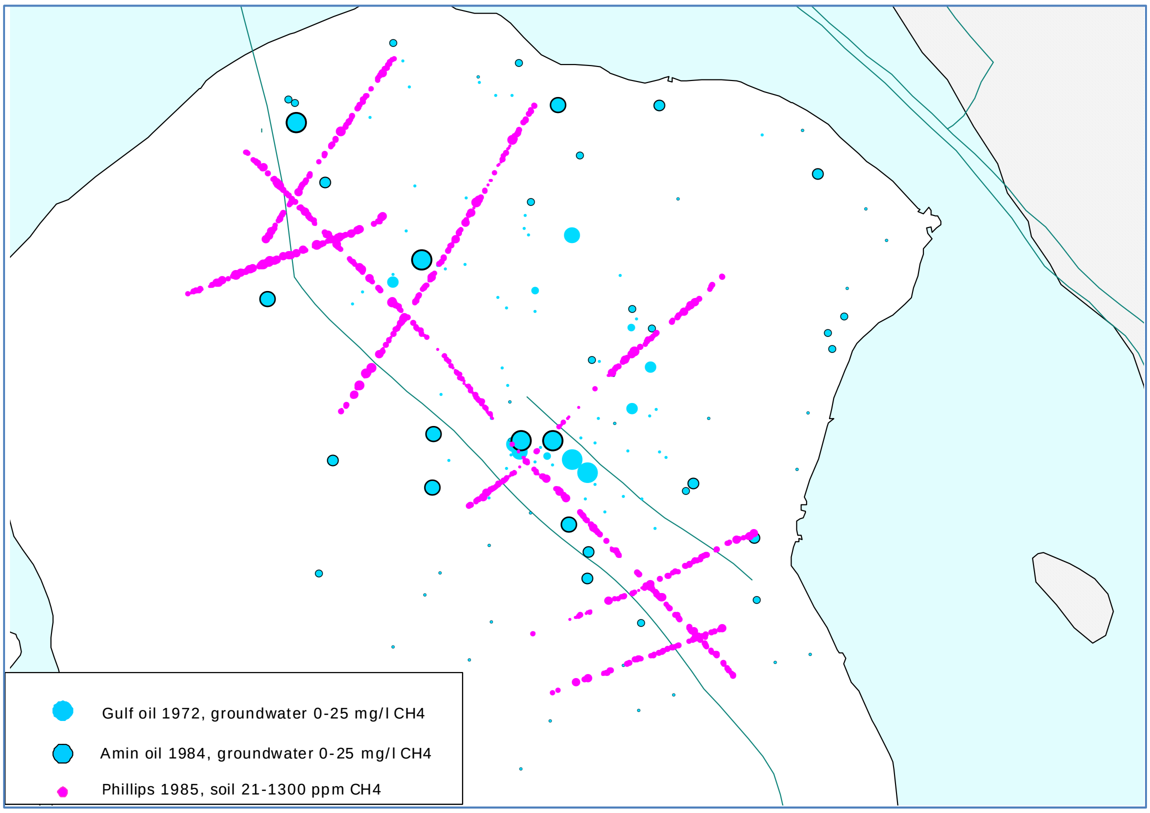

Figure A3. *ArcMap plot of methane content in groundwater, and sorbed methane in soil, North Sjælland.*

Stable carbon isotopic data (unpublished) on dissolved methane from some of the same localities obtained during a GEUS research project showed the methane to be essentially bacterial in origin, Fig. A4.

The Amin Oil licence area was taken over by Phillips Petroleum, who performed a soil geochemical hydrocarbon survey using samples collected from drilled shot holes, using the method described for the Viborg license area below.

An illustration on the use of other relevant data for the interpretation of geochemical data is presented in Fig. A5, where sample locations have been plotted on a soil map of North Sjælland.

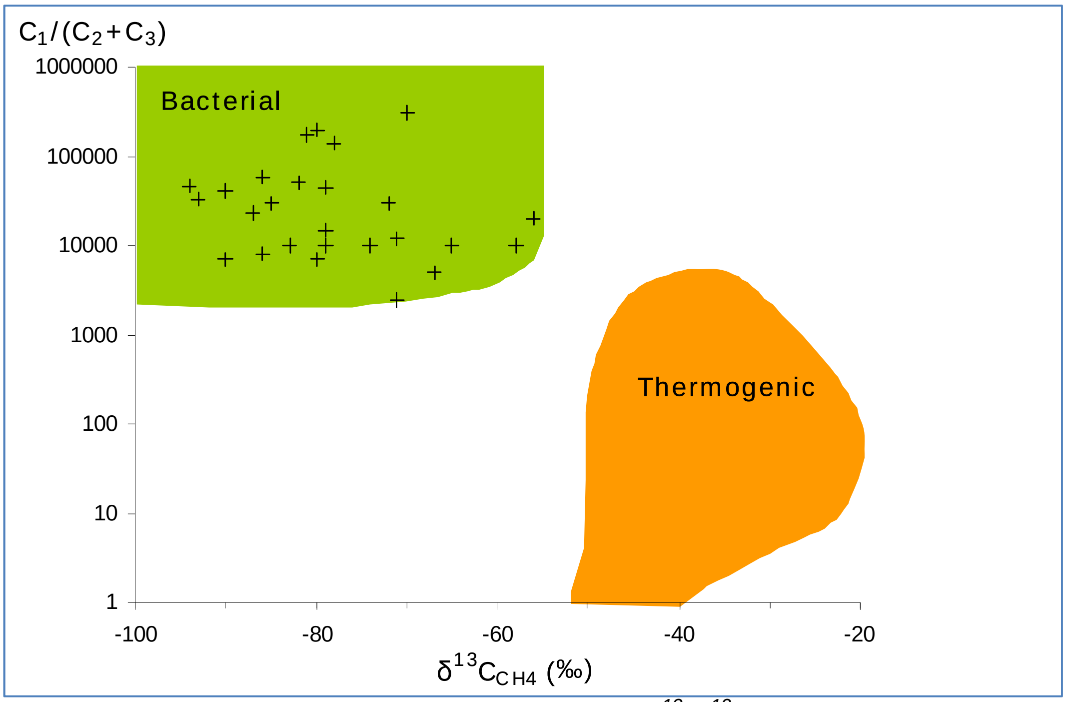

Figure A4. *Chemical composition (C1/C2+C3) vs. CH4 $^{13}C/^{12}C$ isotopic ratio for hydrocarbons in groundwater*

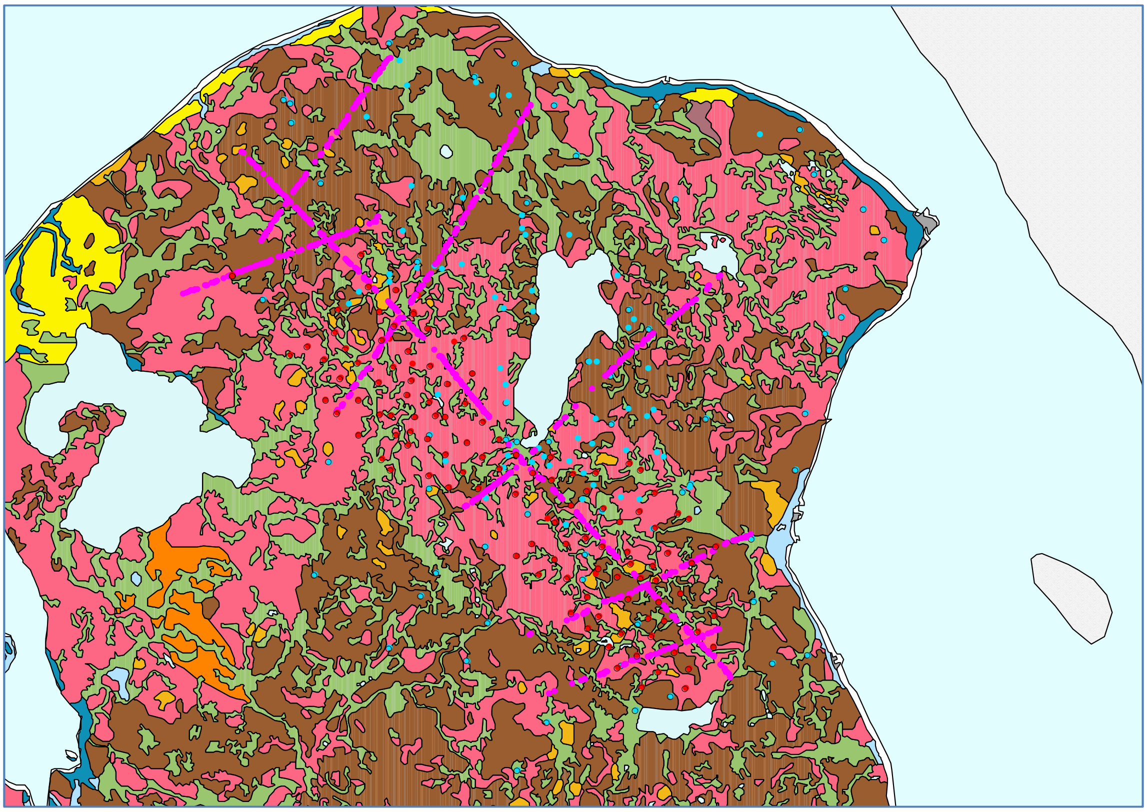

Figure A5. *ArcMap plot, soil map of North Sjælland including sample stations*

8.4.3 GORE- SORBER survey in North Sjælland, 2000

C2-C20 hydrocarbons collected using passive sampling from soil air on special absorbent material, were analyzed by mass spectrometry after thermal desorption. No information on concentration of specific compounds were given in the report, rather statistical evaluation on C2-C20 compound distribution of was performed leading to 11 clusters as illustrated in Fig. 6. Based on the distribution of the 11 clusters it was concluded that no indication on migrating thermogenic hydrocarbons could be observed.

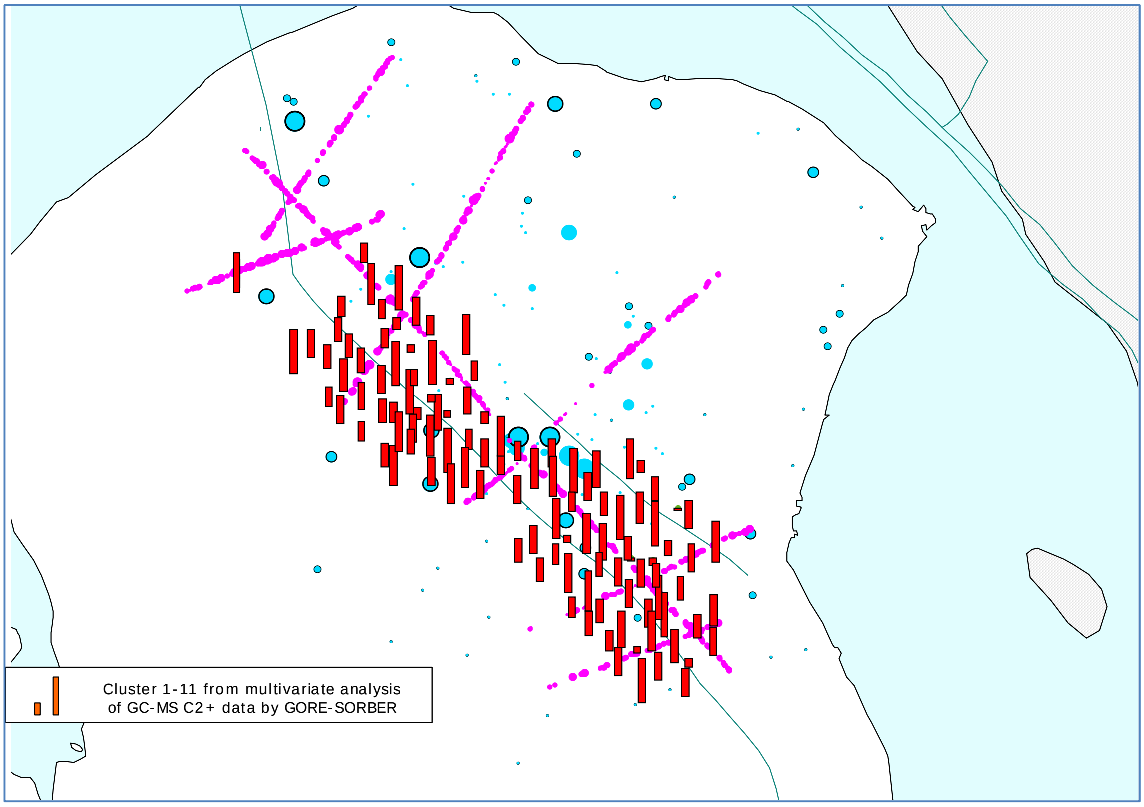

Figure A6. *ArcMap plot distribution of clusters form GORE-SORBER soil gas analysis C2-C20*

8.4.4 Sampling for geochemical survey analysis during drilling of seismic shot holes, Viborg 1984–1986, Phillips Petroleum

Data for the Viborg area obtained from laboratories of Phillips Petroleum and DGU (GEUS) are presented in Fig. A9. Hydrocarbons (C1-C5) in ppm obtained from fixed amounts of sediment (100 or 200 g) were given by the Phillips Petroleum lab, however since no information on the volume of container holding the gas was provided it was not possible to compare results of the two laboratories directly.

Figure A7. *Solids were collected from drilling fluid using a sieve, and stored in 0.5 l tin can to be sent for analysis. Replicate samples were taken for analysis by GEUS.*

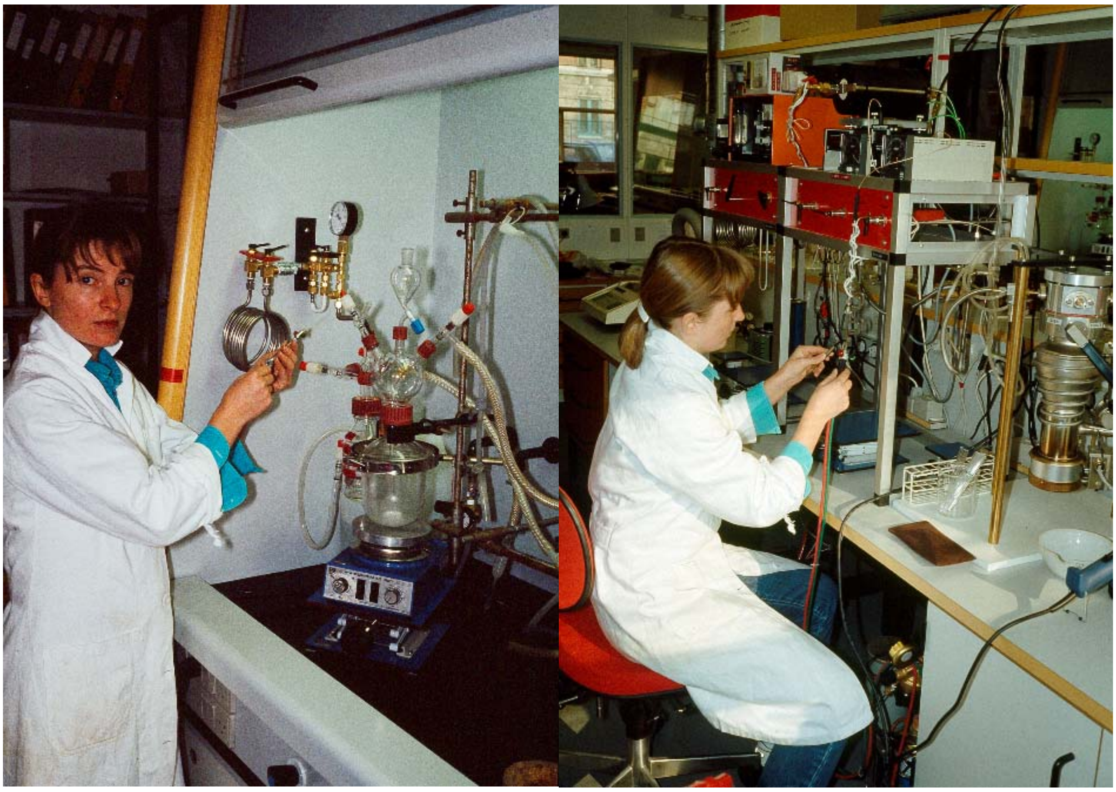

Figure A8. *(Left) DGU (GEUS) laboratory for sorbed gas analysis, established in 1985. Samples, either soil or seabed sediment, is placed in a glass container which is evacuated. Acid is added and gas is collected in the coil. CO2 liberated by the acid treatment is removed by conducting the gas through NaOH solution before being collected. 0.2 ml gas is withdrawn through a septum using a syringe and analysed. (Right) Hydrocarbon gases are converted to CO2 passing over CuO at 900 °C, CO2 is collected in a glass ampoule by cryo-focussing, and sent to a mass spectrometer lab for isotopic analysis*.

Isotopic analysis of methane (DGU only) indicated a mixture of thermogenic and bacterial gases in some samples, Fig. A10.

Interpretation of the hydrocarbon results was summarized by Phillips Petroleum in 8 areal plots, one of which is shown in Fig. A11.

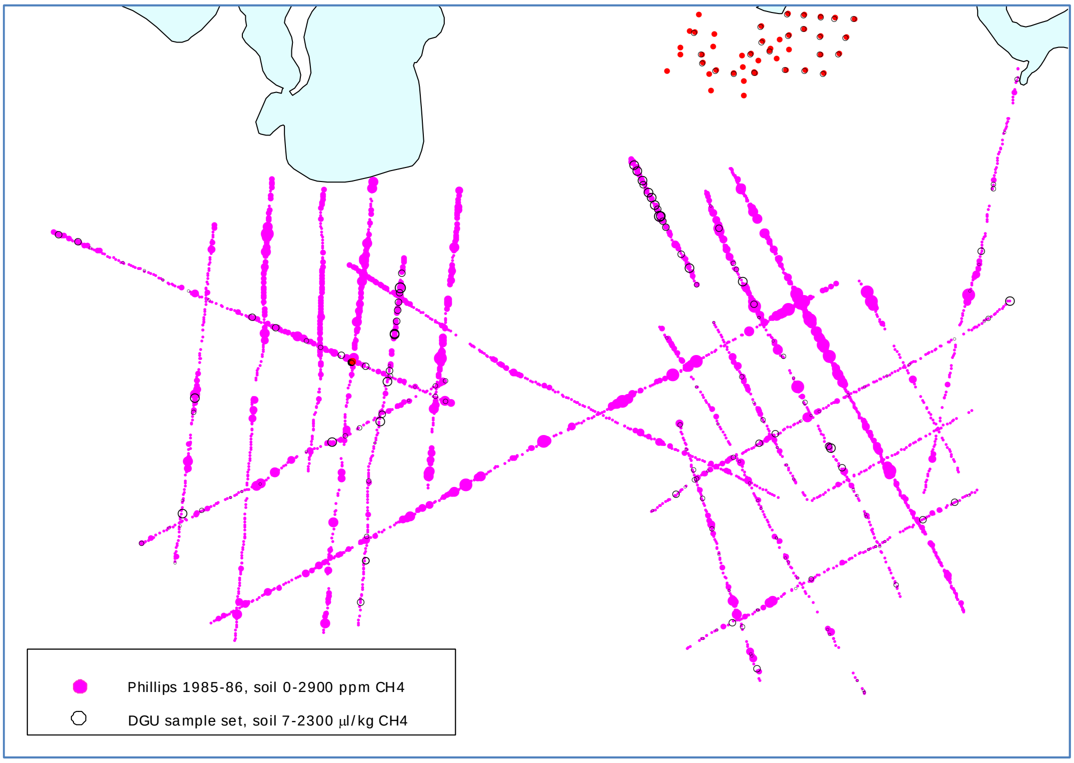

Figure A9. *ArcMap plot of sorbed methane in soil collected during drilling of seismic shot holes, Viborg*

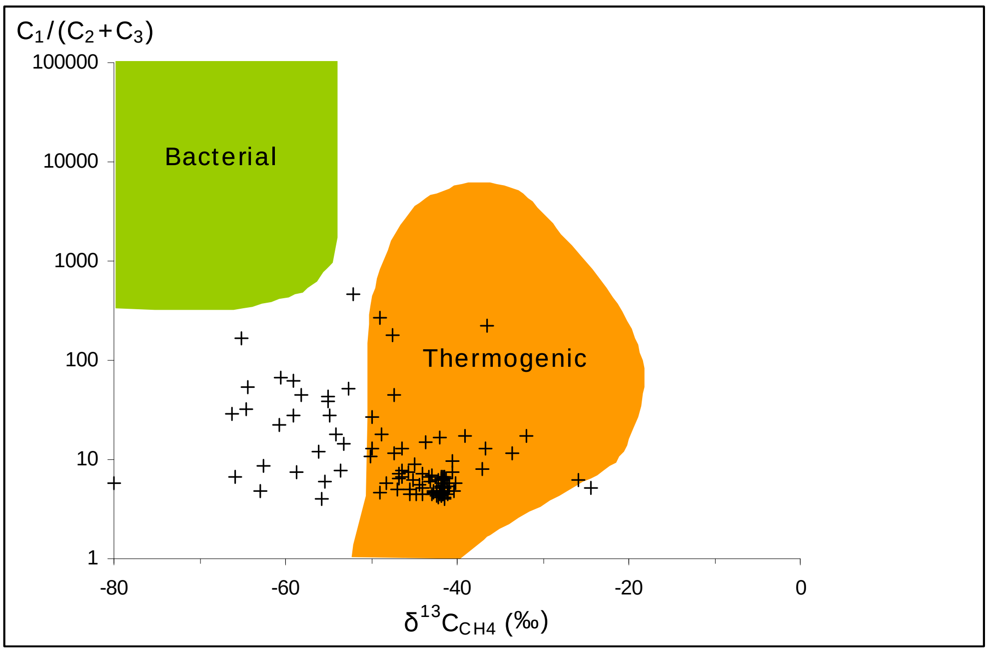

Figure A10. *Chemical composition (C1/C2+C3) vs. stable isotopic ratio of sorbed methane in soils, Viborg area*

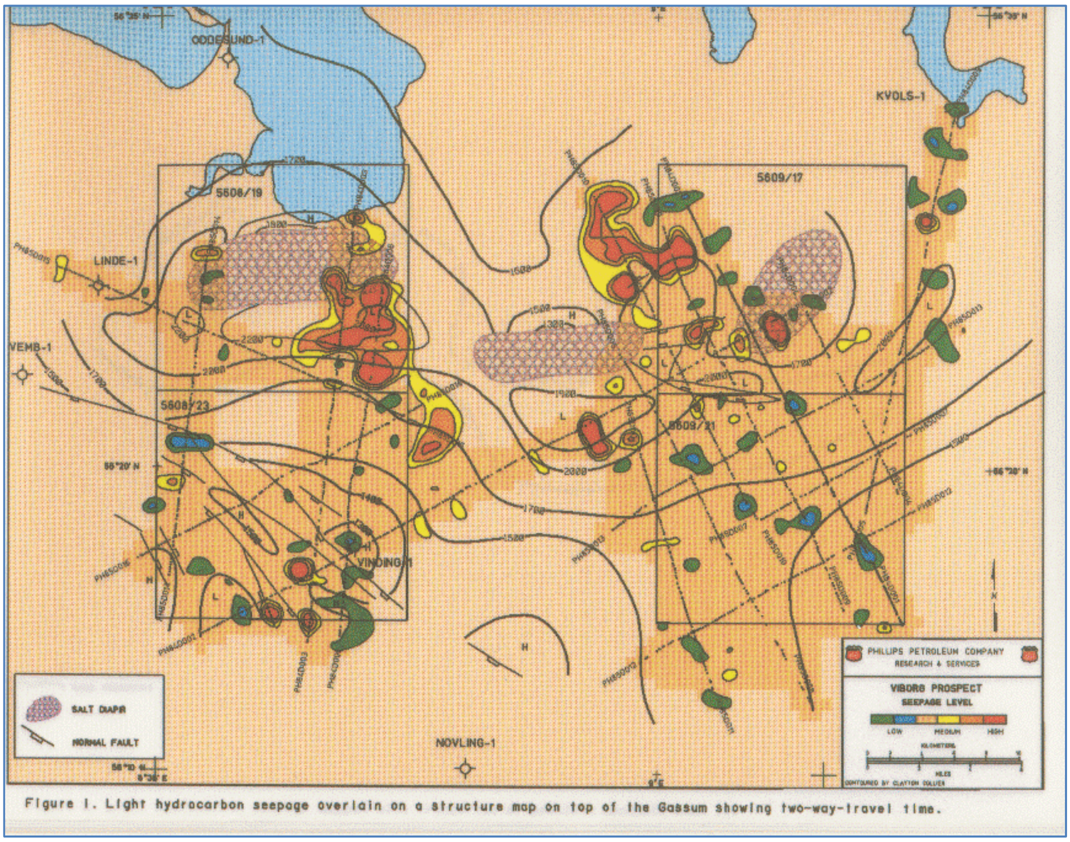

Figure A11. *One example of Phillip's interpretation of Viborg sorbed hydrocarbon data*

8.4.5 GORE-SORBER surveys, Salling, 1999 and 2002.

Passive samplers are left for 17 days ca. 60 cm below ground surface to collect C2-C20 hydrocarbons from soil air on two different absorbent materials in Teflon tubing. The absorbent is then sealed in vials and shipped to the lab for GC-MS analysis. Around 160 different compounds may be detected. Also blanks, including trip blanks, shipped back and forth, are analysed and data are grouped to help to include only meaningful data, see example in Fig. A12.

Next, likely compounds from vegetation are removed form data sets. Other compounds are weighted according their probability of being an oil/gas reservoir indicator. See example in Fig. A13.

Finally, compound data set for each set is treated by multivariate analysis to produce contour maps, for the area, Fig A14.

Fig. A15 shows the sample points, and in Fig. A16, the points are underlain by a soil map of the area. This is relevant because the sampling is done in the top meter of the soil, and this could influence the results.

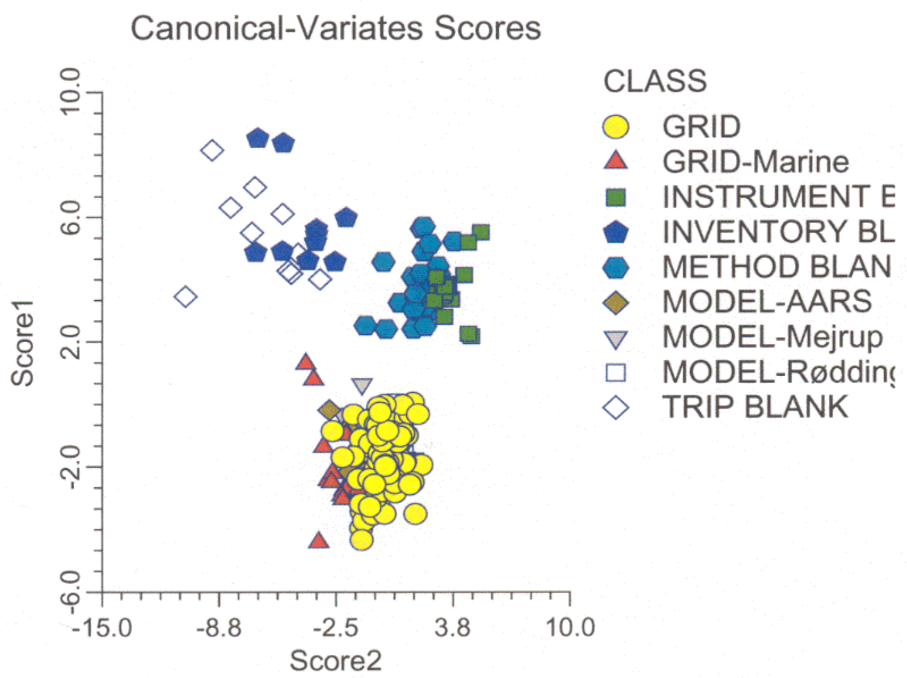

Figure 4: Canonical variates scores plot for Score 1 vs. Score 2 for all sample classes. Canonical scores relate to specific mixtures of the analytical compounds for the survey (not shown here). The separation between field sample classes and all other classes demonstrates acquisition of in-situ geochemical signatures and hence data validity.

Figure A12. *Initial statistical data analysis to include only meaningful data (GRID and GRID-Marine)*

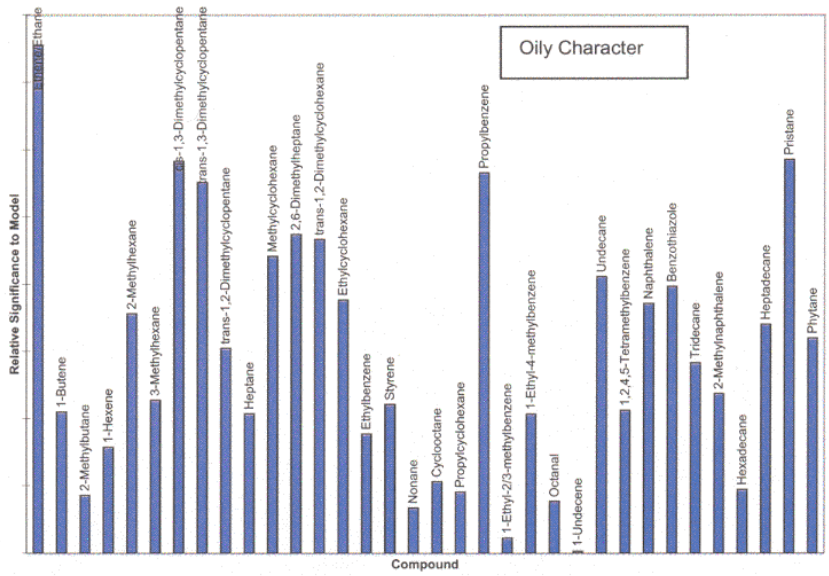

Figure 7: Plot of the specific target analytes significant to oily emanation character (as compared to background) measured at the Mejrup-1 well in 2-way Geochemical Model 1. Background end-member is Rødding-1.

Figure A13. *Weighted compound distribution*

W. L. Gore & Associates, Inc. **11th November, 2002**
GORE-SORBER® Exploration Survey – Report of Findings
STERLING RESOURCES (UK), LTD. – Salling Area, DENMARK

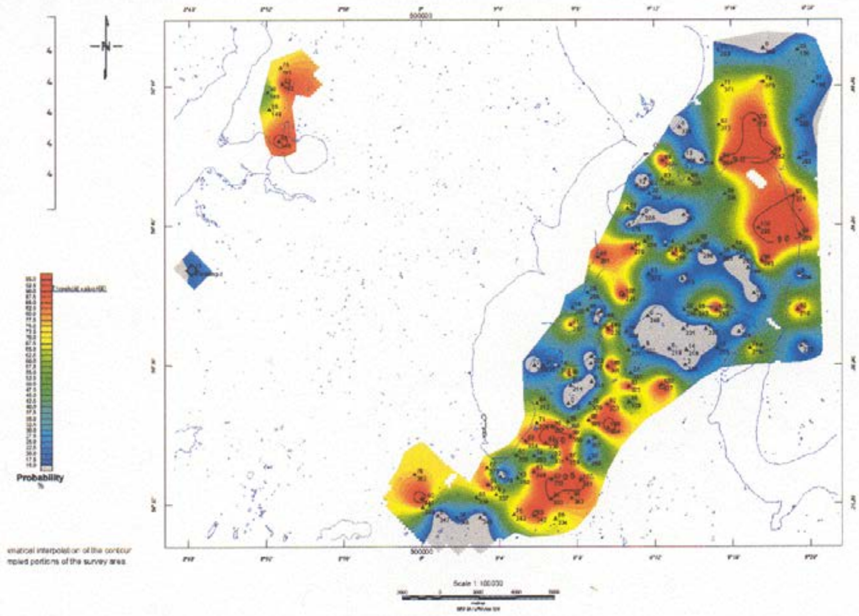

Figure 11: Model 1, Mejrup-1 vs Rødding-1 (see Plate 1)

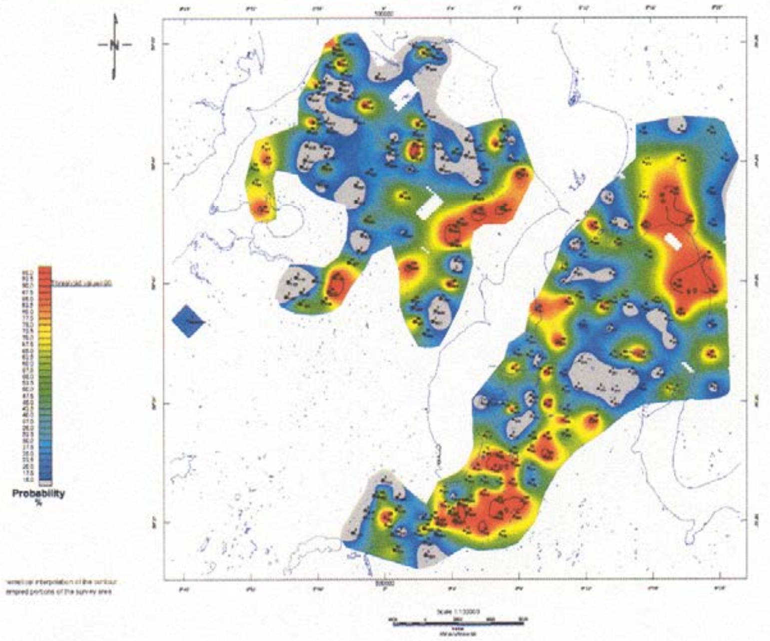

Figure 12: Combined 1999 & 2002 Mejrup-1 vs Rødding-1 model Probabilities (see Plate 2)

Figure A14. *Contour maps thermogenic hydrocarbon probabilities in the Salling area.*

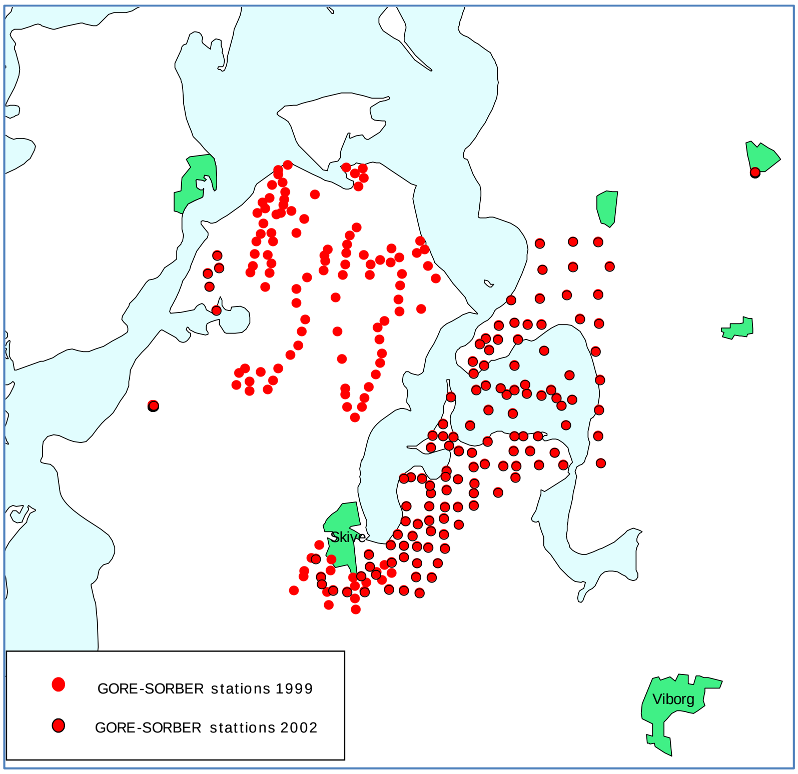

Figure A15. *Sample stations of passive GORE-SAMPLERS in the Salling area.*

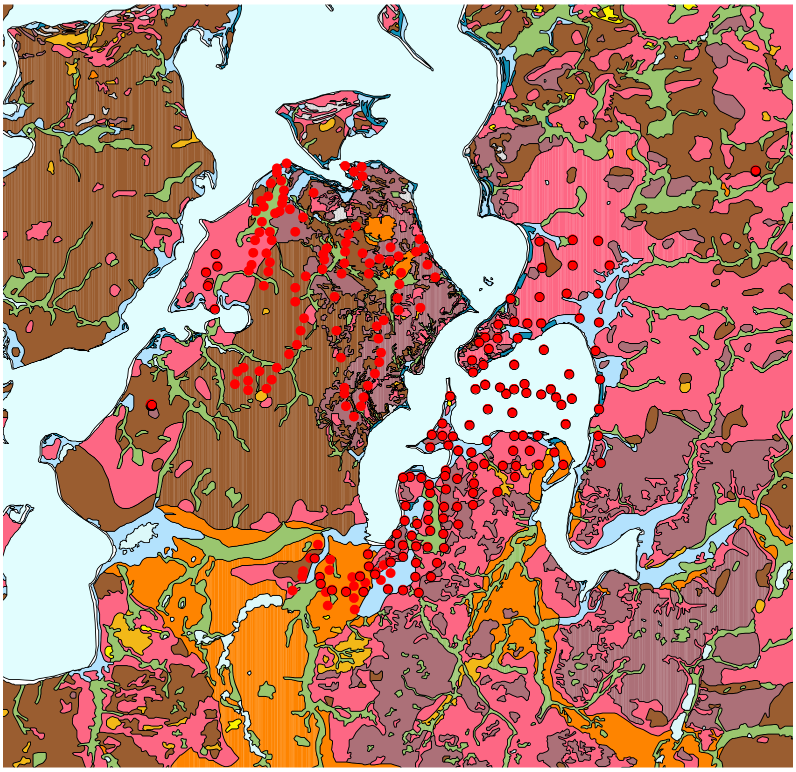

Figure A16. *Soil map of the Salling area including GORE-SAMPLER stations*

8.5 **Offshore geochemical surveys**

The GEUS report under preparation also contains an overview of the offshore geochemical surveys, see Table A1. However, these are not included in this preview of the report. The survey data (in public domain) are included in the coming report and associated CD-ROM.