



Off-line-pyrolysis–gas chromatography–mass spectrometry analyses of drilling fluids and drill cuttings – Identification of potential environmental marker substances



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ABSTRACT

Three different synthetic polymers commonly used in drilling fluids (carboxymethyl cellulose – CMC, hydroxyethyl cellulose – HEC and polyacrylamide – PAA) were analysed by off-line-pyrolysis–gas chromatography–mass spectrometry (off-line-Py–GC–MS). The aim of this study was to determine specific environmental marker compounds for the identification of contamination due to drilling activities. In a first step, reference materials of the main constituents of commonly applied water-based drilling fluids were purchased and analysed to identify potential indicator substances. For each polymer a set of two to three specific pyrolysis products was determined. Afterwards, four CMC, one HEC and two PAA based drilling fluids were pyrolysed in order to retrieve the previously identified compounds in drilling fluid mixtures. All indicator compounds were identified. In a third step, spiking experiments on drill cutting samples of various depths of one well proved the traceability of the applied polymers and verified the applicability of the indicator systems in terms of sensitivity and specificity.

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1. Introduction

The amount of drilling in the context of petroleum exploration and production increased rapidly within the last decades and is still growing. Oil and gas fields in areas difficult to reach, e.g. the Arctic regions, are now seen as potential resources. Furthermore, production from so-called unconventional hydrocarbon reservoirs (e.g. gas shales, coalbed methane) requires more drilling operations as compared to conventional reservoirs (Jarvie, 2012a,b). Such drilling operations affect the surrounding environment due to the use and discharge of certain chemical substances. Drill cuttings (crushed rock fragments) and drilling fluids (Bakke et al., 2012) represent the greatest amount of discharges from petroleum related drilling operations besides produced water. The application of drilling fluids is essential for the success of rotary drilling operations (Donaldson and Chernoglazov, 1987). These water- or oil-based fluids consist of clay minerals, weight materials (e.g. barium sulfate) and other, mostly artificial, additives. These different constituents, when added to the drilling systems, modify the borehole

properties, e.g. stabilise the well pressure and the well walls, lubricate drill pipes and support transport of the drill cutting material from the bottom of the borehole to the surface. Since 2001, offshore drilling operators in the UK are committed to collecting all drill cuttings containing oil-based muds (>1% hydrocarbons/dry weight drill cutting) (Oil and Gas UK, 2009) and drilling mud waste and to transporting it onshore to clean and recycle or to dispose this material to landfills. If a suitable formation is present re-injection is another established technique for processing cuttings offshore (Backwell et al., 2000). Drill cuttings containing solely water-based fluids are allowed to be discharged into the sea. Today, the current amount of cuttings is estimated to comprise approx. 700,000 m³ of in situ cuttings in the central North Sea and 500,000 m³ in the northern North Sea due to earlier discharges containing drill cuttings contaminated with oil- and water-based fluids (Oil and Gas UK, 2009). Cutting piles containing water-based fluids are large and persistent (Bakke et al., 2012). Such piles have different negative effects on the aquatic environment, e.g. stimulation of microbial growth, toxic impacts on reproduction and physical stress due to burial. Schaanning et al. (2008) and Trannum (2011) showed that cuttings placed on sediments in thin layers increased the consumption of oxygen and nitrate in the sediments, indicating that the drill cuttings contained easily

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biodegradable organic matter. This effect persisted in some cases for more than 6 months. Furthermore, Trannum (2011) showed that cuttings also had an effects on benthic fauna, e.g. decrease in species richness and abundance. This effect is strongly influenced by the thickness of the cuttings layer due to the reduced oxygen availability. Thus, not only chemical reactions but also physical stress due to burial may play a role whereby a critical amount of cuttings leading to this effect is normally limited to areas closer than approx. 250 m to the pile centre. Furthermore, Dijkstra et al. (2013), Terzaghi et al. (1998) and Strømgren et al. (1993) reported negative effects of drill cutting material on aquatic organisms (e.g. severe decline in abundance of benthic foraminifera, crustaceans). Other studies showed that water-based drilling fluid in a suspended state is able to cause damage to gills and influence nutrition physiology among filtering mussels (Bechmann et al., 2006), blue mussels and scallops (Bakke et al., 2012).

Further environmental effects can occur due to interactions of the drilling mud with the surrounding borehole sediments that may lead to a significant loss of the fluid which may be pressed into the rock. Especially highly porous and permeable formations are affected in which mud fluid invasion may range up to 3 m (Donaldson and Chernoglazov, 1987). These fluids may change the physicochemical properties of the sediment due to displacement of the formation fluids (Donaldson and Chernoglazov, 1987) and impact the ecosystem due to contamination with synthetic polymers. Even if most of the drilling fluid components are primarily so-called 'green and yellow' chemicals that, in principal, do not have inherent environmentally harmful properties, the emissions of any synthetic substances do affect the ecosystem (Fabbri, 2001).

Therefore, the detection and identification of emissions occurring from drilling activities due to the application of drilling fluids is vitally important. Chemical analyses of drill cuttings to keep track of their distribution have not been developed so far (MacMillan et al., 1997; Reddy et al., 2007). For this purpose, we focussed on the systematic analysis of various artificial polymers that are used as main components in technical fluids by off-line-pyrolysis–gas chromatography–mass spectrometry (off-line-Py–GC–MS). The aim of this study is to identify specific molecular indicators that can be applied as potential marker substances for drilling activities.

Analytical pyrolysis, combined with GC–MS is a well established, quick and reproducible method for the analysis of natural and artificial polymers (e.g. Wang, 1999; Bart, 2001; Fabbri,

2001; Kronimus and Schwarzbauer, 2007; Sobeih et al., 2008; Antic et al., 2011).

In the present study three different polymers that are commonly used as components in drilling fluids (carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC) and polyacrylamide (PAA)) were analysed to evaluate their potential to act as environmental marker for contamination due to drilling operations. In a first step, reference substances were analysed by means of off-line-Py–GC–MS to identify specific low molecular weight products which provide chemical markers for individual polymers. Secondly, drilling fluids containing these polymers as main constituents were pyrolysed to confirm the presence of the previously identified compounds and to confirm their potential to indicate drilling fluids. Lastly, spiking experiments with drill cutting samples were performed to verify whether the proposed markers can be identified in a complex matrix, as well as to determine sensitivity and specificity. The analysed samples included 3 polymer standards, 6 drilling fluids and 15 drill cuttings samples.

2. Material and methods

2.1. Sample material

Twenty-four samples of different materials, i.e. 3 polymer standards (carboxymethyl cellulose (CMC), hydroxyethyl cellulose (HEC), polyacrylamide (PAA)); 6 commercial drilling fluids and 15 drill cuttings samples taken before the shale shaker from various depths of one single well drilled in the Barents Sea were used in this study. An overview is given in Table 1. The compound structures of the polymers applied are shown in Fig. 1. All samples were dried at 105 °C for at least 12 h before pyrolysis.

2.2. Off-line-pyrolysis–gas chromatography–mass spectrometry

Off-line-Py–GC–MS experiments were performed using a Carbolite tube furnace model MTF 10/15/130, expanded with a quartz tube. The technical data of the furnace were as follows: maximum temperature = 1000 °C, tube length = 150 mm, tube ID = 15 mm. The quartz tube was situated within the furnace. The glass joint ends of the tube were outside the furnace. The tube was connected with the nitrogen supply at the one side, while the other was connected with a trap (cooled to –70 °C), filled with 10 ml of acetone (for CMC and HEC experiments) or dichloromethane (for PAA experiments) to which the pyrolysis products were transferred

Table 1
Sample characteristics: (A) polymer standard materials; (B) drilling fluids and their main compounds; (C) drill cuttings. (TOC: total organic carbon; TIC: total inorganic carbon. Both values were obtained using a liquiTOCII instrument). Drill cuttings were provided by Eni Norge and were taken at various depths from one single well.

Polymer	Abbreviation	Supplier
A. Standards		
Hydroxyethyl cellulose	HEC	Merck KGaA
Carboxymethyl cellulose sodium salt	CMC	Sigma–Aldrich, Inc.
Polyacrylamide	PAA	Carl Roth GmbH
Drilling fluid		
	Abbreviation	Supplier
B. Drilling fluids		
Viscopol® T (Sodium-carboxymethyl cellulose)	DF1	GWE pumpenboese
Viscopol TLV (Sodium-carboxymethyl cellulose)	DF2	GWE pumpenboese
Antisol® FL30 000 (Polyanionic cellulose/CMC)	DF3	GWE pumpenboese
CMC-HV (Carboxymethyl cellulose)	DF4	Unknown
Viscopol HEC (Hydroxyethyl cellulose)	DF5	GWE pumpenboese
Poly-Plus RD (Polyacrylamide)	DF6	Miswaco
Poly-Plus liquid (Polyacrylamide)	DF7	MGS Europe GmbH
Depth (m)	mg TOC/g rock	TIC (mg TIC/g rock)
C. 15 Drill cuttings		
1174–2026	1.98–4.41	0.07–1.67

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