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Assessing hydraulic oil spills

Measuring techniques for the investigation of the spreading properties of environmentally-acceptable hydraulic oils in the ground

Along with technical and economical aspects regarding the use of environmentally-acceptable hydraulic oils produced from regenerative raw materials there are also ecological arguments to consider. For users, sanitation firms, insurance companies and law makers, it still remains to be clarified which appropriate actions should be taken in the case of damage. Presented here are investigated measuring methods for analysing the spreading properties of oils in the ground.

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Because of their good biological degradability, hydraulic oils based on rape oil are more suitable than mineral oils for use in ecologically delicate situations. In the case of an oil accident, the properties of the oil as well as the properties of the ground influence spreading behaviour. Seepage and penetration trials offer a basis for first model-based evaluations of the body of oil to be cleared-up. For exact information on the volume of contaminated ground following an accident, suitable measurement techniques are required. For analysis giving fast and simple initial judgement on seepage depth of the oil one has to decide between fine definition with sample taking and in-situ definition.

Alongside the consideration and variation of the ground parameters, the investigations into spreading behaviour were carried out with different oils. Three oils of a vegetable basis and two mineral oils were used for comparisons in the trial programme. The oils differed through the basic oil and additives used in the various formulations. Additionally, each trial was carried out with both fresh and used oils.

Ageing of oils and their suitability for use

The chosen test oils were put under pressure in a hydraulic test station. The change of physical-chemical properties in the oils during their use gave, first of all, information on the working properties of the oils. With such information it is thus possible to compare the appropriate technical properties of the oils with the behaviour of the individual oils in the ground which is now to be researched. Additionally, several oil parameters change through use and such alterations can be critical for spreading behaviour and biological degradation of the oil in the ground. For instance, the viscosity of the oil rises in general through use (the oil becomes thicker-flowing) and the content of metal particles increases. The oxidation stability of the oil decreases with increasing working hours. This is caused by the reduction in additive effectiveness (table 1). The onset temperature, which is determined by pressure differential scanning calorimetry (pressure-DSC), is a measurement of oxidation stability. The higher the onset temperature lies, the higher is the oxidation stability. The biological degradability which is determined by the CEC test is not influenced by reducing oxidation stability. Care must be taken because the CEC test appraises only the primary degradation of the oil. According to this test, an oil can be regarded as easily biologically degradable when, after 21 days under defined predetermined conditions, a degradation rate of 80% is achieved.

Seepage behaviour

Trials on the spread of oil were carried out in lysimeters with naturally-grown ground cores or artificial fillings. For simulation of environmental conditions such as wind, rain and temperature a model system was available with which the lysimeters could be integrated.

Seepage behaviour was defined through seepage speed and depth. First results emphasised that seepage speed decreases with increasing length of seepage routes. Further, both the spreading phases (saturated and unsaturated zones) are easily recognised in the ground. An enormous difference in the speed of seepage is also apparent between absorption-strong and absorption-weak soils. The times for the establishment of a quasi stationary condition (no noticeable further advancement of the oil) between sand, sandy loam

Table 1: Oxidation stability from the non-isotherm pressure measuring (Differencial Scanning Calorimetry) and biological degradability according to the CEC L-33-A94 test for fresh and used oil

Oil	Working-hours	Oxidation stability [°C]	Biological degradation rate [%]
Triglyceride/ rape oil	0	184	91
(HETG)	1000	158	90
Ester oil/ rape oil	0	204	98
(HEES)	1000	173	94
Mineral oil	0	242	41
	1000	215	55

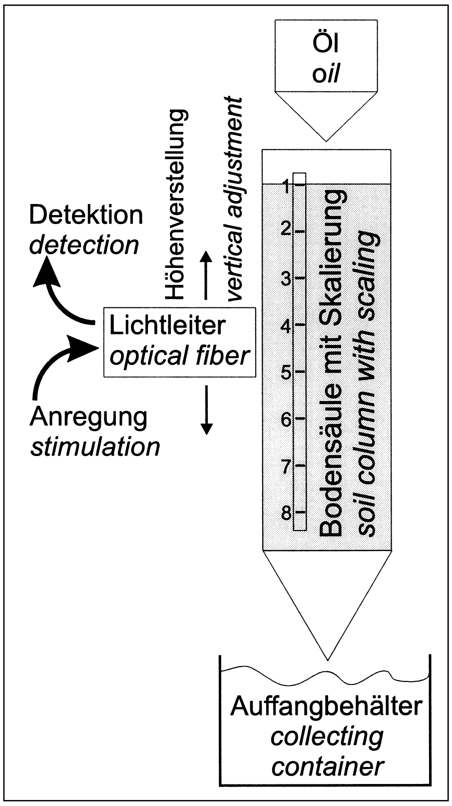

Fig. 1: Design of a test lysimeter for examining oil spreading with a laser induced fluorescence spectroscopy

and brick clay are between 5, 70 and 150 hours. The eventual depths reached by the oil fronts of all the investigated oils lay, however, within small limits. The penetration depth did not, therefore, differ markedly. There was a noticeable tendency for all ground types to set a penetration limit.

More decisive than the type of ground proved to be the soil moisture content. The speed of seepage decreased markedly in line with increased water content.

Measuring techniques with sample taking: GC and FTIR analytic

Trustworthy qualitative and quantitative evidence of the smallest traces of oil in the ground were possible through the gas chromatography (GC) technique. An assured specific identification of individual oils is also possible. This enables the investigation of, in particular, oil traces diluted in water or of seepage processes which have taken water-soluble components into deeper ground layers following, for instance, conditions of heavy rain.

It is also possible to decide between qualitative and quantitative readings with the Fourier transformation infrared spectroscopy (FTIR-spectroscopy). Through a process differing from the DIN-norm (study of an enlarged spectrum of wave numbers between 3700 and 1400 cm-1), an absolute identification between mineral and biogenic oil is possible. The method has proved itself as suitable for following the seepage of oil through the ground. FTIR measurements, as a method involving sample taking, are relatively simple and trustworthy.

In-situ measuring techniques: fluorescence and permeability

As an in-situ measuring technique, laser-induced fluorescence spectroscopy (LIF-spectroscopy, LFS) is in the position to trace advanced spreading of oil in the ground without the necessity of invasive actions within the observed medium. Thus, LIF-spectroscopy is suitable for the monitoring of bio-oil spread regarding fresh and used oil, and especially for the recording of penetration curves. The method is based on the ability of many oil formulations to emit longer wave length light following radiation from activating light in the ultraviolet or visible spectral regions. At the Institute for Physical and Theoretical Chemistry at Erlangen University trials were carried out on ground-filling within test lysimeters consisting of glass pillars, and adjustable light conducting techniques (*fig. 1*). Four from five oils used in the project showed sufficient fluorescence ability to be suitable for direct investigation. A rape oil product could, after addition of a fluorescent tracer, also be spectroscoped. The testing of measuring points through the glass wall of the lysimeter, inclusive of measuring times and position change, was possible in all trials in times of under a minute. In general, the LIF spectroscopy proved itself as a practical and flexible method for the monitoring of the spreadage of bio-oil. The site disbandment of the LIF spectroscopy lay markedly under a square centimetre.

Also able to prove itself was a new sensor for measuring permittivity with which the water front, which precedes the oil front, can be efficiently identified. It could be proved that the measurements via electronic permittivity sensor of the advanced spreading condition could compare with exact FTIR measuring techniques.

Table 2: Overview of measuring techniques used

	Equipment type	Measuring parameters	Measuring method	Cost/time outlay	Remarks
Oriented fast procedure on the spot	electronic permittivity sensor	water content ≥ depth as oil front	injecting sensor in-situ	minimal/ minimal	The water front preceding the oilfront is measured
	LIF	fluorescence intensity	measuring sensor in-situ	high/ moderate	
Quantitive material identification by sample taking	FTIR	Light adsorption	extraction method through sample taking	medium/ medium	determination total hydrocarbon, differentiating mineral oil/ vegetable oil
	GC (detection with FID)	ion development from substances with C-C and C-H bonds	extraction method	high/ high	measuring of individual components

Conclusions and outlook

The determination of vertical oil spread after oil accidents, and therefore the clean-up actions to be taken, has been addressed within the framework of this project by using selected soil types and sorts of oil. The results up until now indicate starting points for the formalisation of rules regarding seepage speed and depth. Improved forecasts are to be expected, especially with regard to the physical-chemical properties of the ground matrix, which have extremely differing influences on spreading behaviour. Used oils from test station trials were also investigated in more detail for possible deviations in ecological behaviour. At the same time, the various in-situ measurement techniques (permittivity sensors and LIF), as well as the extractive analytical procedures (FTIR and GC), were brought together for comparative investigations.

In *table 2* is presented a complete overview of the advised measurement techniques. Available are the two methods featuring sample taking (fine investigations) and the in-situ investigation on site (orientation investigation).

Through the interaction of these different measurement techniques, a extensive data bank is created which makes it possible to give more dependable forecasts over the ecologically-relevant behaviour of oil in the ground. The models thus developed will then be available for a first assessment following an oil accident. The tested measurement techniques will allow an exact assessment of necessary sanitising actions. Further results and information on the project can be requested from the authors.