



Institut für Chemie und Dynamik der Geosphäre
Institut IV: Agrosphäre

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Institute for Chemistry and Dynamics of the Geosphere IV (Agrosphere)

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Abbreviations:

ACN	Acetonitrile
amu	atomic mass unit
AR	applied radioactivity
BTEX	Benzen, Toluene, Ethylbenzen und Xylen -aromatics
Δ	Difference
fl.	liquid
FZJ	Forschungszentrum Jülich GmbH
GOK	Geländeoberkante
GL	Groundwaterlevel
GPC	Gelpermeationschromatography
h	hour
HPLC	High Performance Liquid Chromatography
IARC	International Association of Research on Cancer
ID	Inner diameter
LSC	Liquid Scintillation Counter (Flüssigkeits-Szintillationsspektrometer)
Lsg.	solution
Lsm.	solvent
min	Minute (s)
MON	Motor octane number
NAPL	Non aqueous phase liquid
NIR	Non identified Radioactivity
NIST	National Institute of Standards and Technology
n.d.	Not detected (< Bestimmungsgrenze)
p.a.	Pro analysis (zur Analyse)
PE	Polyethylen
ppb	1 Teilchen pro 10 ⁹ Teilchen [$\mu\text{g L}^{-1}$]
ppm	1 Teilchen pro 10 ⁶ Teilchen [mg L^{-1}]
ppt	1 Teilchen pro 10 ¹² Teilchen [ng L^{-1}]
‰	Promille
RA	Radioactivity [Bq]
RBCA	risk based corrective action
rH	relative humidity [%]
RON	Reserach octane number
SCAN	full scan
SIM	selected ion monitoring
s.a.	See also
s.u.	See below
T	temperature [°C]
TB	Contaminated alluvial loam
TBA	t-Butylalcohol
TBF	t-Butyl format
TDR	Time domain reflectometry
TDS	Thermal desorption
TM	Dry mass
USGS	U.S. Geological Survey
UV	ultra violete light
VOC	Volatile organic compounds
% v/v	percent Volume = Vol %
% w/w	percent Masses
WT	Wind tunnel
WHC _{max}	Maximum water holding capacity

Movement of MTBE Through Soil After Groundwater Contamination

Volker Linnemann

Since the late seventies, methyl-tert-butyl ether (MTBE) has become one of the most widely produced chemicals in Europe and the USA due to its use as a fuel additive. MTBE was first used as a substitute for the environmental poison tetraethyl lead because of its anti-knock properties. Statutory requirements for minimum volumes of oxygen-containing additives in motor fuels, to protect the atmosphere against the climate-relevant trace gases carbon monoxide (CO) and ozone (O₃), greatly increased the demand for MTBE in the USA. One consequence was an increasing number of groundwater and soil contaminations as well as complaints of damage to health associated with MTBE. Since the air had been kept clean at the expense of the groundwater and the soil, the use of MTBE is prohibited in the USA after 2003. In Europe increased numbers of MTBE-contaminations in the groundwater and surface waters have been reported.

Goal of this project was the investigation of the MTBE mass transport into the atmosphere after a contamination of the groundwater. For this studies a tripartite experimental concept was selected:

First of all, a soil column experimental set-up for studying mass transport in undisturbed soil monoliths was designed, constructed and validated. With this facility it was possible to create under defined and reproducible experimental conditions an aquifer below the soilcore, variable in height, in which a contamination with MTBE had been simulated in a real concentration range of 100 to 200 mg L⁻¹. A stream of air flowed over the soil surface through the artificial atmosphere, and was collected and analysed with respect to the composition of volatile organic chemicals.

Adsorption onto multibed solid adsorbent material with subsequent thermal desorption GC/MS analysis was developed for air collection and displayed good sampling performance with excellent detection limits. The groundwater samples were analysed by radioactivity-HPLC, -GPC or a new direct injection-GC/MS analytical technique. For this liquid-injection-methods the detection limit still has to be improved.

In the first experiment, up to 47 ppb (170 ng m⁻³) of MTBE was detected in the air. MTBE was not continuously recovered in the air but only occurred in pulses. Maximum values were measured, in particular, in the first few days. The mass transfer rates through the soil into the atmosphere were in the region of $1.94 \pm 1.88 \mu\text{g m}^{-2} \text{h}^{-1}$ in the first experiment with an equilibrium value of approx. $0.45 \pm 0.02 \mu\text{g m}^{-2} \text{h}^{-1}$. In the second experiment with [α,α' -¹⁴C] MTBE, only low volatilisation was measurable. At the same time, the water balance in the experimental system was also recorded, which enabled a qualitative relation to the MTBE loss to be established.

The simulated aquifer was redesigned for a scale-up experiment and also the air sampler adapted for volatile hydrocarbons at the field like wind tunnel with a lysimeter. The new sampling unit was validated in several preliminary experiments and displayed good collecting efficiency for the high volume flows applied. Analogously to the second column experiment, over an experimental period of 4 weeks hardly any mass transport of MTBE through the soil was determined. The recovery rate in both experiments with ¹⁴C-MTBE was in the region of 83 to 102 % of the applied radioactivity (AR). As described in the literature only slight adsorption to the soil particles was found for MTBE.

Since the soil columns and the lysimeter represented a compartment of the ecosystem with functioning microflora, the microbial aerobic degradation in the soil was determined in laboratory studies. A maximum mineralisation of 1.6 % AR was detected as a function of the previous contaminations of the soil and the soil type. Moreover, rapid volatilisation of the MTBE from the surface took place perceptibly reducing the bioavailability. The results obtained were readily applicable to the transport studies.

Transport von MTBE durch den Boden nach einer Grundwasserkontamination

Volker Linnemann

MTBE gehört seit der weltweiten Einführung als Kraftstoffkomponente (Antiklopffmittel) zu den wichtigsten Massenchemikalien in den USA und Europa. Nach dem verstärkten Einsatz als Kraftstoffzusatz als Ersatz für Bleitetraethyl wurde MTBE als Schadstoff auch in der Umwelt detektiert. Da so auf Kosten des Wassers und des Bodens die Luft reingehalten wurde, ist der MTBE-Einsatz ab dem Jahr 2003 in den USA verboten, während in Europa der MTBE Einsatz weiter verstärkt wird.

Ziel dieses Projektes war die Untersuchung des Stofftransports von MTBE in die Atmosphäre nach einer Kontamination des Grundwassers. Es wurde ein dreistufiges Versuchskonzept gewählt: Zunächst wurde eine Bodensäulenanlage für Stofftransportuntersuchungen in ungestörten Bodenkörpern konzipiert, aufgebaut und validiert. Mit dieser Anlage konnte unter definierten und reproduzierbaren Versuchsbedingungen ein Grundwasseranstaup am Boden eingestellt werden, in dem eine Kontamination mit MTBE in einem realen Konzentrationsbereich simuliert wurde. Konditionierte Luft wurde dabei durch den nach außen abgeschlossenen Säulenkopf nahe der Bodenoberfläche gesaugt, gesammelt und im GC/MS analysiert. Für die Luftsammlung wurde eine Adsorption auf einem Multibett-Feststoffadsorbens mit anschließender Thermodesorptions-GC/MS-Analytik neu entwickelt (hohe Sammelleistung, sehr gute Nachweisgrenzen). MTBE wurde nicht kontinuierlich in der Luft wiedergefunden, sondern trat nur pulswise auf. Maximalwerte bis zu 47 ppb (170 ng m^{-3}) wurden gerade in den ersten Tagen gemessen. Die Stoffdurchgangsraten durch den Boden in die Atmosphäre lagen bei $1,94 \pm 1,88 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$ im ersten Experiment mit einem Gleichgewichtswert von ca. $0,45 \pm 0,02 \text{ } \mu\text{g m}^{-2} \text{ h}^{-1}$. Im zweiten Experiment mit $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE war nur eine geringe Verflüchtigung messbar. Gleichzeitig erfolgte eine Erfassung des Wasserhaushaltes im Versuchssystem. Hierbei konnte ein qualitativer Zusammenhang zwischen den Grundwasser- und den MTBE-Verlusten gefunden werden.

Für einen „Scale-up“-Versuch erfolgte die Neukonzeption eines Grundwasseranstaups und die Umrüstung der Luftsammeleinheit für flüchtige Kohlenwasserstoffe am Freiland-Windkanal mit Lysimeter. Die neue Probenahmeeinheit wurde in mehreren Vorversuchen validiert und zeigte eine gute Sammeleffizienz. In einem Versuchszeitraum von 4 Wochen wurde analog dem 2. Säulenversuch kaum ein Stoffdurchgang von MTBE durch das 1,10 m Bodenprofil der sauren Braunerde festgestellt. Die Wiederfindung lag in den beiden Versuchen mit ^{14}C -MTBE bei 83 bzw. 102 % der applizierten Radioaktivität (AR). Wie in der Literatur beschrieben, wurde nur eine geringe Adsorption an Bodenpartikel gefunden.

Da es sich bei den Bodensäulen und dem Lysimeter um Ökosystemausschnitte mit funktionierender Mikroflora handelt, wurde in zwei Laborstudien der mikrobielle aerobe Abbau im verwendeten Boden bestimmt. Hierbei konnte in Abhängigkeit von der Vorbelastung mit Schadstoffen und des Bodentyps eine Mineralisierung von maximal 1,6 % AR in 101 Tagen nachgewiesen werden. Die Ergebnisse aller drei Versuchsansätze konnten gut auf die Transportbeschreibungen angewendet werden.

1 Introduction and Objectives

Increasing mobility also means rising volumes of traffic. In particular, the number of passenger cars is increasing over proportionately. In spite of state-of-the-art exhaust gas technologies, progressive pollution of the air cannot be prevented. In order to reconcile a high standard of living, a clean environment and climate protection, many countries have enacted laws laying down maximum emissions of noxious substances from motor vehicles. In the United States of America, the Clean Air Act was introduced in 1992 to reduce the quantities of climate-relevant trace gases, especially carbon monoxide and ozone in urban areas and later the Reformulated Gasoline Program was also launched (ZOGORSKI ET AL., 1997). In Europe as well, changes in the composition of gasoline replaced the environmental poison, like the plumbiferous fuel additive as an anti-knocking agent (RÖSSLER, 1999). The reduction of aromatic compounds, especially benzene emissions, is planned from the year 2001 (BARRETT & POLLITT, 1993). In this connection, the most important oxygen-containing fuel additive is methyl-tert-butyl ether (MTBE). Through the oxygen in this molecule MTBE chemically promotes the combustion process in the engine and as an anti-knocking agent with a high octane number it is present in large quantities, above all in premium-grade gasolines (up to 15 % by volume). In the late seventies, MTBE began way as the most frequently used fuel additive and in 1998 took fourth place in the USA among the mass chemicals produced (JOHNSEN ET AL., 2000). Today, various constituent amounts of MTBE are contained in about one third of all fuels in Europe and America.

Nevertheless, the use of MTBE also has its drawbacks, since, especially in the USA, the air in the cities was kept clean at the expense of the groundwater quality (MÜLLER-JUNG, 1999). The increased use of MTBE as a fuel additive led to a rise in the reported MTBE groundwater contaminations. In the USA alone, more than 250,000 spillages at filling stations are known leading to MTBE being introduced into the environment. MTBE has also been found in rainwater, snow, lakes and rivers as well as in the atmosphere. Due to its physicochemical properties, MTBE can be distributed ubiquitously throughout the world with the hydrological cycle, irrespective of the fact of whether it has been released from accidents, diffuse or point sources. MTBE is no longer a problem for the USA alone. It has been found in rainwater and rivers in Germany, too, as well as considerable concentrations in the groundwater (EFFENBERGER ET AL., 2001; ACHTEN & PÜTTMANN, 2000). Another problem is the poor microbial degradation of MTBE, in comparison to the other fuel constituents, in groundwater and contaminated soils. In order to reduce environmental contamination by MTBE, it will no longer be permitted as a fuel additive in the USA after 2003.

As a consequence of this groundwater pollution, risk assessments were performed concerning health risks, possible MTBE sources and sinks, and various remediation procedures such as that using the risk-based corrective action (RBCA) approach. This advanced and efficient methodology provides those responsible for remediating a case of damage involving mineral oil contamination with a multistage procedure, taking exposure and risk assessments

into consideration. The aim is to ensure a suitable and inexpensive remediation plan according to uniform standards. In contrast to earlier conservative procedures, such as excavating and dumping the contaminated soil, the RBCA provides the user with modern remediation procedures such as bioremediation.

In this multistage risk management concept, the first stage of risk assessment ("Tier 1") contains conservative model calculations on the dispersal of MTBE after groundwater contamination (ASTM, 1999; ASTM, 1996; DEVAULL ET AL., 1994). Due to the large number of parameters it is difficult to mathematically describe the transport of mineral oil hydrocarbons out of the groundwater into the outside air or into buildings. One problem in the exposure calculations is ensuring comparability between reality and the model without having to use complex, non-user-friendly models. If, however, simplified screening methods are used for possible exposure of humans to pollutants, such as in the transport processes from the groundwater into the atmosphere in RBCA, then the correctness of the simplifications selected in the models must be verified. The transport equations used should therefore be compared with data sets from experiments performed under defined conditions simulating the field situation. The present contribution provides the first experimental data for this purpose (see **6.4**).

The central issue of this study concerned the transport paths of MTBE after groundwater contamination through the soil into the atmosphere as well as the biological degradation in the soil used. The question to be answered was whether after a contamination of the groundwater MTBE migrates along a defined soil body and can be detected in the atmosphere, and what concentration ranges are to be expected. A detailed survey of the literature on the environmental behaviour of mineral hydrocarbons, microbial degradation and health hazards of MTBE serves for an understanding of the problems involved and as a basis for planning the experiments. At that time, there were no studies in the literature concerning transport processes of MTBE from the aquifer through the natural soil into the atmosphere. The aim of this 2nd cooperation project was therefore the design and construction of a standardized experimental set-up for determining transport out of the groundwater through an undisturbed soil core under simple, defined and reproducible environmental conditions. The functionality of the system was examined in validation experiments.

A further objective was the development of a new sampling unit at the wind tunnel of the Institute of Radioagronomy (now Agrosphere: ICG- IV) for measuring the emission of volatile hydrocarbons from a soil after groundwater contamination under field-like conditions. To this end, the lysimeter concept was reversed with an accumulation of groundwater, including MTBE contamination, at a 1.1 m soil monolith (FÜHR ET AL., 1998).

In order to detect volatile organic compounds in soil, water and air, a new analytical measuring method for the structural analysis and quantification of MTBE and its degradation pro-

ducts had to be found and established at the Institute since the methods available there were not suitable for this problem.

2 Survey of the Literature

This literature survey gives an overview of the current state of the art concerning the fuel additive methyl-tert-butyl ether – abbreviated to MTBE in the following. In addition to the general properties (2.1.2.1) and the use of MTBE (2.1.1), its environmental behaviour will in particular be examined with the aid of several case studies (2.1.2, 2.1.3). Possible hazards to health are discussed in (2.1.4) in order to examine the significance with respect to a risk analysis. A new analytical technique was introduced at the Institute of Chemistry and Dynamics of the Geosphere 5 (now Agrosphere: ICG-IV) for the investigations of the transport behaviour of MTBE in soil performed for this study. A brief review of the state of the art in analytical techniques for determining volatile hydrocarbons (VOCs) in environmental samples is therefore also included.

2.1 The Model Substance MTBE

Methyl-tert-butyl ether (MTBE) is an oxygen-containing C₅ hydrocarbon with characteristic physicochemical features (**Fig. 1**). The oxygen content in the molecule is in the region of 18.2 % (w/w). The molecule is very sterically inhibited and the ether bonds are very stable with respect to biotic and abiotic reactions (SEVILLA ET AL., 1997).

On an industrial scale, MTBE is produced catalytically from the raw materials isobutylene and methanol or methane at low cost and in large quantities (NIKOLOPOLOUS ET AL., 1996; VAN GRIEKEN ET AL., 1996).

MTBE is easily volatilised, readily soluble in water and miscible with almost all organic solvents. Furthermore, MTBE is a low-boiling, high-octane fuel component. The addition of MTBE to the gasoline mixture increases the miscibility of the individual fuel additives and perceptibly reduces the overall vapour pressure of the fuel (RÖSSLER, 1999).

Further physicochemical data are discussed in detail in 2.1.2.1.

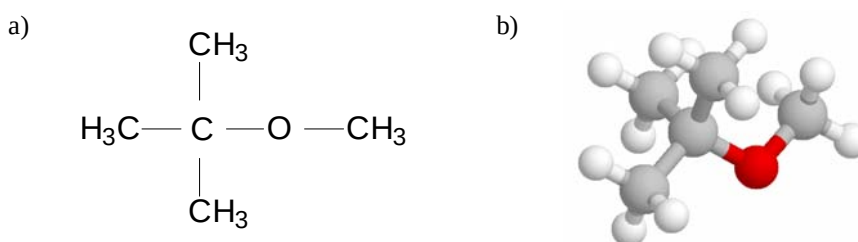


Fig. 1: Chemical structural formula of a) methyl-tert-butyl ether, b) 3D arrangement of the atoms in the MTBE molecule

2.1.1 Significance of the MTBE Fuel Additive

Since its worldwide introduction as a fuel component, MTBE has become one of the most important mass chemicals (relative to production volumes) in the USA and Europe. Modern fuels are a well-defined mixture of various hydrocarbons, which after a refining process are blended from the individual components depending on the quality required.

In order to improve the combustion quality of fuel mixtures, in addition to the mechanical input oxygen should also reach the engine along chemical paths, which is reached by combustion of oxygenated compounds (RADEMACHER, 1999).

MTBE is the most widely used oxygen-containing gasoline additive. Other oxygenated gasoline components, which are, however, not used in anything like the same quantities as MTBE are ethanol, ethyl-tert-butyl ether (ETBE), tert-amyl-methyl ether (TAME), diisopropyl ether (DIPE) and tert-butyl-alcohol (TBA) (JOHNSON ET AL., 2000). Only ethanol is of any appreciable significance, namely in South America where it is obtained from sugar cane and thus avoids expensive imports of mineral oil (GROSJEAN ET AL., 1998).

MTBE is added to gasoline to improve its anti-knock properties and has almost as high an octane number (RON = 116-120) as the proven tetraethyl-lead ($\text{Pb}(\text{C}_2\text{H}_5)_4$), which is now prohibited for reasons of environmental protection (RÖSSLER, 1999). The anti-knock properties are determined pursuant to DIN standard 51756. A differentiation is made between the RON (research method) and the MON (motor method). In Germany, the DIN standard EN 228 specifies the RON for unleaded gasoline as at least 91, for premium unleaded at least 95 and for super unleaded at least 98 (DIN, 1993b; EN, 1993b).

However, after its increasing use as a fuel component, amongst other aspects in order to prevent air pollution, MTBE was also found to be an environmental pollutant, especially in groundwater (**2.1.2.**; MÜLLER-JUNG; 1999; RADEMACHER, 1999). The danger to human health originating from MTBE cannot currently be assessed (**2.1.4**) and is a matter of controversy in the literature. The assessments range from possibly carcinogenic (SQUILLACE ET AL., 1998) to a classification as a noncarcinogenic substance (IARC, 1999). Due to the now ubiquitous occurrence of MTBE in the environment, in the near future it will no longer be used as a fuel component in the USA (RADEMACHER, 1999). Further reasons for this are the lack of success in reducing volatile organic compounds (VOC) and the ozone (O_3) content in the air by the application of MTBE in comparison to improvements brought about by a new engine generation. However, these estimates do not find support in Europe (MRASEK, 1999).

2.1.1.1 Data on MTBE use

MTBE began to be used in Europe and the USA in the late seventies and early eighties to replace the environmentally hazardous alkyl-lead compounds which had been added to gasoline as anti-knocking agents since the sixties. In 1969, TBA was added to gasoline as the first oxygen-containing fuel component. At the same time, the application of tetra-alkyl lead compounds reached its zenith with maximum concentrations. This gave the green light for the use of unleaded fuel in the United States (STOUT ET AL., 1998). When lead additives ceased to be used in gasoline, ethanol was first introduced as an oxygenated fuel component before MTBE came on the market.

In Europe, Italy was the first to add MTBE to gasoline in the late seventies. The use of crude oils from North Africa which were low in aromatics, meant that the octane number had to be perceptibly increased and a substitute found for tetraethyl lead. In the mid-eighties, the other European countries then followed suit with the introduction of MTBE and reduction of the lead content.

Only with the "Clean Air Act Amendment" (CAAA) of 1990 to reduce air pollution did the application of MTBE rise dramatically in the USA from 1992 onwards (ZOGORSKI ET AL., 1997). In these oxyfuel programmes, the use of gasoline containing a minimum volume of oxygen was laid down for the winter months (2.7 weight percent) if a carbon monoxide (CO) limit was exceeded. This corresponds to a percentage of about 14 vol. percent in the gasoline mixture. In 1995, this temporary regulation was extended to the whole year in the USA. Furthermore, the "Reformulated Gasoline Program" (RFG) entered into force, meaning that at least 2.0 % by weight had to be used throughout the year if the CO limit were exceeded. In addition to a reduction of CO₂, the aim of this programme was also to produce less ozone (O₃) in the atmosphere. The benzene and aromatics content in reformulated gasoline was perceptibly reduced. Hydrocarbons enter the atmosphere due to incomplete fuel combustion and they are regarded as the precursors of O₃. In Europe, on the other hand, there is no minimum value for oxygen in gasoline, but rather only a maximum oxygen content (2.7 weight percent).

Today, about one third of the fuels sold in the USA contain MTBE (NADIM ET AL., 2001; SQUILLACE ET AL., 1997). In Germany, the fraction of MTBE in Super Plus (RON=98) reaches values of 14 % (BREUM, 1998). By the end of nineties, the demand for fuels with an RON of 98 and thus also requirements for MTBE were reduced by the introduction of new engine technologies (MORGENROTH & ARVIN, 1999). The new EU guidelines on reducing the content of aromatics in fuels then led to a rapid rise in the MTBE quantities used in Europe to adjust the octane number (BARRETT & POLLITT, 1993). These regulations intend to reduce the previous benzene content in fuels from a maximum of 5 % to less than 1 % after the year 2000

and also to cut the total aromatics content (from 42 % to 35 %). In Europe, averaged over all fuel types and all EU countries, there was an average oxygen content of 2.1 % in gasoline although there were considerable differences in the use of MTBE between the individual countries (MORGENROTH & ARVIN, 1999). Only in France and Portugal no MTBE was used. The countries using the highest quantities of MTBE in 1998 included Austria, Switzerland, Finland, Hungary, Germany and Spain.

Although the application of oxygenated compounds considerably reduced CO₂ emissions, nevertheless no significant positive effect on O₃ reduction was established (RADEMACHER, 1999). After these findings and the occurrence of groundwater contaminations, for example, in Santa Monica near Los Angeles, California decided to abandon the MTBE programme leading to a prohibition on MTBE from 2003 (RADEMACHER, 1999; NAKAMURA, 1998). In March 2000, on the recommendation of the Blue Ribbon Panel (U.S. EPA, 1999), the American Government resolved that the use of MTBE should be phased out in all states of the Union at the earliest possible point in favour of ethanol (U.S. EPA, 2000; ANONYMOUS, 2000; HOGUE, 2000; KANASKIE, 2000). One reason for this decision was that although MTBE improves the air quality it is found ubiquitously and above all in the groundwater. Furthermore, with improved engines the limits can be complied with today without the addition of MTBE. However, the use of ethanol is not without controversy. Ethanol does not have such good blending properties as MTBE and its production is much more cost-intensive, which will lead to increased gasoline prices. In the case of spillages, ethanol is degraded very readily in the subsoil, but the effect of this property on the co-metabolisms of benzene, toluene, ethyl-benzene and xylene aromatics (BTX aromatics) and hydrocarbons still remains unclear (POWERS et al., 2001). An increased use of ethanol as a fuel additive will require a greater acreage of monocultures to cover requirements.

2.1.1.2 Production and sales

After the entry into force of the oxyfuel programmes in the eighties, the consumption of MTBE increased dramatically, from 1992 onwards at an annual rate of about 12 % (EFOA, 2000). In the USA, MTBE occupied fourth place among the mass chemicals produced, after ethylene, propylene and 1,2-dichloroethane with almost 10 million t a⁻¹ in 1998 (JOHNSON ET AL., 2000). In 1992, about 9 million tonnes of MTBE were consumed worldwide per year. This consumption doubled by 1998 to more than 19 million t a⁻¹. Forecasts for the year 2000 indicated a slight rise to 20 million t a⁻¹. Growth was perceptibly retarded by the decline in the USA due to the phase-out programmes, e.g. in California (1998: 4.2 million t a⁻¹). In other countries, mainly in Europe, the consumption of MTBE continued to rise. In 1997, 3.03 million t of MTBE was produced in Europe, 0.187 million t imported, 0.9 million t exported and 2.313 million t consumed (EFOA, 2000). The major fraction (98.5 %) of MTBE was used as a fuel additive. The remaining 1.5 % was used for the production of isobutene (1.2 %) and as a solvent (0.3 %) (EFOA, 2000). In Europe, a distinct increase in MTBE consumption is

expected in the year 2000 with the coming into force of the EU fuel quality directive (98/70/EC). Italy, Germany and Spain are the main consumers accounting for 55 % of the total MTBE used in Europe. Although the highest volumes of MTBE in gasoline are used in Finland (> 8.5 % averaged over all fuels; Germany 1.2 %) due to the low population this hardly has any effect on the overall balance.

2.1.2 MTBE in the environment: input, transport and persistence

Gasoline additives enter into the environment along various paths (Fig. 2). A differentiation is made between point and nonpoint sources. Point sources represent the main source of pollution, especially leaks from fuel depots and pipelines (SQUILLACE ET AL., 1998). The MTBE concentrations found here reach maximum values (2.1.2.2). In the literature, a very large number of incidents (approx. 300,000) are described with leaking underground storage tanks (LUST) (U.S. EPA, 1999; ZOGORSKI ET AL., 1997). In the past, these tanks were not protected in the United States so that contaminated water was able to enter directly into the groundwater where concentrations reached values of up to 230 mg MTBE L⁻¹ in wells close to LUST. Today, this water is processed together with the surface runoff before it can enter the groundwater (U.S. EPA, 1999).

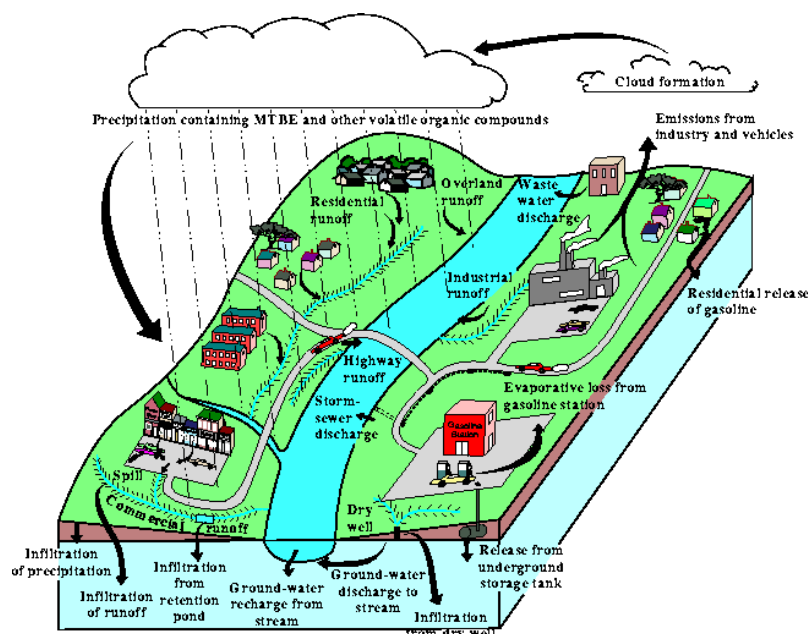


Fig. 2: Possible sources of MTBE input into the environment and transport with the hydrological cycle.

However, storage tanks above ground also represent a significant source of MTBE inputs into the environment. ZOGORSKI ET AL. (1997) report concentrations of up to 9000 mg L⁻¹ (280 – 9000 mg L⁻¹) in surface waters. Other point sources are spillages during refuelling and transportation as well as defective production plants.

Diffuse or nonpoint sources include incomplete combustion processes in motor vehicles or outboard motors as well as emissions during production (U.S. EPA, 1999). For surface

waters and groundwater close to the surface, rain and surface runoff after heavy precipitation events may represent a diffuse source (2.1.2.5).

Oxygen-containing compounds such as MTBE, ethanol, ETBE and TAME accumulate in water due to their polarity and their high solubility in water (**Tab. 1**) (2.1.2.1). They are transported to the various compartments by the hydrological cycle (**Fig. 2**, ZOGORSKI ET AL., 1997). However, due to the high vapour pressure they evaporate very rapidly from surface waters. In the following, the various distribution and transport processes in and between the atmosphere (2.1.2.5), surface waters (2.1.2.3), soils (2.1.2.4) and groundwater (2.1.2.2) will be described in detail.

2.1.2.1 Physicochemical data

Knowledge of the physicochemical properties of MTBE enables a risk assessment of its environmental behaviour to be performed before extensive studies are implemented at the polluted site, thus saving expense and enabling a rapid response to be made to minimize damage (DEVAULL ET AL., 1994).

MTBE is a clear, colourless, low-viscous, low-molecular, combustible liquid with a strong smell of ether. MTBE is liquid up to a temperature of $-109\text{ }^{\circ}\text{C}$ and has a boiling temperature of $55.3\text{ }^{\circ}\text{C}$ (EFOA, 2000) so that the compound is very suitable for use as a fuel additive. MTBE remains liquid over a wide temperature range and does not freeze in winter. With a density of 0.745 g cm^{-3} , MTBE is lighter than water and in high concentrations (greater than 54.3 g L^{-1} , see solubility in water, **Tab. 1**) it floats on the water as a non-aqueous phase liquid (NAPL).

MTBE has a high water solubility of $23.2 - 54.3\text{ g L}^{-1}$ depending on temperature and measuring method (SQUILLACE ET AL., 1997; MACKAY ET AL., 1993). All substances with a water solubility $> 1.0\text{ g L}^{-1}$ are classified as readily soluble in water (JEFFREY, 1997). This high water solubility is to be expected since MTBE is a polar low-molecular substance. One consequence of this property is the increased occurrence of MTBE in surface waters, groundwater and atmospheric water, as well as transport into the environment via the earth's natural hydrological cycle (see above).

Depending on the test procedure, the octane numbers of pure MTBE are in the region of 100 – 120 (RON = 116 – 120 and MON = 100 – 104) and display good blending properties for fuels.

Another important physicochemical parameter is the vapour pressure of a substance, which is responsible for the volatilisation of MTBE from surfaces. BUDVARI ET AL. (1989) and MACKAY ET AL. (1993) found values of 3.2659×10^5 and $3.3545 \times 10^5\text{ Pa}$ at $25\text{ }^{\circ}\text{C}$. JEFFREY

(1997) regards these values as extremely high, although typical of low-molecular compounds with a weakly polar function group (in this case ether bridges). Taking this parameter into consideration, after a spillage MTBE should evaporate into the atmosphere spontaneously and rapidly. Volatile organic compounds are often classified according to their vapour pressure. However, according to MACKAY ET AL. (1993) this does not make sense since there are also organic molecules, such as ether, which have a high vapour pressure and at the same time display high water solubility.

Tab. 1: Selected chemical and physicochemical properties of MTBE.

Parameter	Data	Reference
CAS no.	1634-04-4	
trivial names	MTBE; methyl-tert-butyl ether; 2-methoxy-2-methyl-propane	SIGMA ,1999 MERCK, 2001
molecular formula	C ₅ H ₁₂ O	
molecular weight	88.15 g Mol ⁻¹	SIGMA, 1999
physical state	Colourless liquid	OXENO 1996
melting point	-109°C	BUDAVARI ET AL., 1989
boiling point	55.2°C	BUDAVARI ET AL., 1989
water solubility	51.26 g L ⁻¹ at 25°C 43,0 - 54,3 g L ⁻¹ 23,1 - 54,3 g L ⁻¹	U.S. EPA, 1993 SQUILLACE ET AL., 1997 MACKAY ET AL., 1993
density	0.7404 g mL ⁻¹	BUDAVARI ET AL., 1989
K _{OC}	12.3 11.0 calculated	U.S. EPA, 1993 ZOGORSKI ET AL., 1997
log K _{OW}	0,94 - 1,30	MACKAY ET AL., 1993
vapour pressure	3,2659 x 10 ⁵ Pa at 25°C 3,3545 x 10 ⁵ Pa at 25°C	BUDAVARI ET AL., 1989 MACKAY ET AL., 1993
HENRY- Coefficient [H]	55.7 Pa m ³ mol ⁻¹ at 25°C 59,46 - 304,96 Pa m ³ mol ⁻¹ at 25°C	U.S. EPA, 1993 MACKAY ET AL., 1993
dimensionless [H R ⁻¹ T ⁻¹]	0,02 - 0,12	SQUILLACE ET AL., 1997

The HENRY coefficient permits an improved assessment. It specifies the distribution of a substance between the gas and aqueous phase. The HENRY coefficient is a particularly decisive parameter for environmental behaviour since there is an aqueous and gas phase in all environmental compartments. According to a classification with the HENRY coefficient, MTBE is to be regarded as a medium to highly volatile substance with values of 59.46 – 304.96 Pa m³ mol⁻¹ at 25 °C. This differs significantly from the vapour pressure estimate.

The octanol/water coefficient (K_{OW}) can be used to estimate the distribution of MTBE in the soil. This value is generally used as a decadic logarithm in order to ensure the comparability of different substances with K_{OW} values covering several orders of magnitude. As described in **2.1.2.4**, a calculation via K_{OC} is possible. Due to the low log K_{OW} value, strong sorption to the soil matrix is not expected (log K_{OW} = 0.94 – 1.24; MACKAY ET AL., 1993), and it is rapidly washed out of the soil in the case of rain or together with the groundwater.

An analysis of the chemical structure of MTBE (**Fig. 1**) assists in assessing its degradability in soil, water and the atmosphere. Apart from water solubility and polarity, caused by a weak net dipole moment due to the C-O δ^- -C bond (bond angle 110 °), reactivities can also be estimated. MTBE is more reactive than saturated hydrocarbons, and less reactive than alcohols. The ether bridge is relatively stable with respect to bases, oxidation and reduction mechanisms (OXENO, 1996). Only in the case of halogen hydroxides does the formation of a halogen alkane and an alcohol result due to the splitting of ether (SEVILLA ET AL., 1997). The cosolvency effects of MTBE for the other fuel additives make a final judgement difficult (JEFFREY, 1997; SYMINGTON, 1993).

2.1.2.2 MTBE in groundwater

In the United States, it is assumed that about 356,000 cases of leaking underground fuel tanks (LUFT) have occurred where mineral oil has entered the groundwater. In 250,000 of these cases it must be expected that MTBE has entered the surrounding soil or groundwater (JOHNSON ET AL., 2000). Of the 32,409 LUFTs in California alone it is expected that 10,000 involve MTBE (WENTZLAU, 1998). In spite of high safety standards, an accumulation of spillages involving groundwater contamination has recently been found in Europe as well (Germany, Italy, Finland, UK, Denmark and Switzerland (EFFENBERGER ET AL., 2001; PIAZZA ET AL., 2001; PAHLKE ET AL., 2000; MORGENROTH & ARVIN, 1999). In Germany, for example, spillages with in part high inputs of MTBE in the range of several ten thousand micrograms per litre of groundwater have been reported in Mecklenburg-Western Pomerania, Bavaria, Baden-Württemberg, Saxony and Thuringia (EFFENBERGER ET AL., 2001).

MTBE usually enters the groundwater as a fuel additive and not as a pure substance. However, in order to assess the hazards, it is important to know the quantity of MTBE which has been released into the environment after an accident (c_s). SQUILLACE ET AL. (1997) give an approximation procedure for this purpose:

$$c_s = \gamma \cdot x_m \cdot c_s^0 \quad (\text{Eq. 1})$$

The solubility of pure MTBE (c_s^0) is reduced by its mass fraction in the gasoline (x_m e.g. 0.1) and a substance-dependent correction factor (γ). The latter describes the difference in the chemical properties of the individual component from those of the gasoline mixture.

Possible sources of input into the groundwater are, on the one hand, the above-mentioned point sources, and, on the other hand, also diffuse sources. The most important point sources include leaks at filling stations, fuel stores, production plants and pipelines. Spillages and handling losses during refuelling are also important input paths for MTBE into the surrounding soil and subsequent into the groundwater. Although modern German filling stations have good safety measures, nevertheless accidents do occur. In particular, waste

water treatment (leaching via rainwater runoff) causes problems since the light-liquid separators used cannot separate MTBE from the aqueous phase (EFFENBERGER ET AL., 2001).

MTBE can also enter the soil and groundwater via the atmosphere (GRADY, 1997; SQUILLACE ET AL., 1997). The concentrations found in this connection are significantly lower than the point sources, which can reach values of up to several hundred milligrams per litre of groundwater (MORGENROTH & ARVIN, 1999; SCHIRMER ET AL., 1997; DAVIDSON, 1995; GARRET ET AL., 1989). Contaminations have also been found along previously unknown paths such as via heating oil. Both in the USA and Europe, MTBE is only permitted as an additive in fuels but not in heating oils (DIN, 1993a, b; EN, 1993a, b). Nevertheless, ROBBINS ET AL. (1999) found up to $4100 \mu\text{g L}^{-1}$ of MTBE in groundwater after a leakage from some heating oil tanks in Milford, USA.

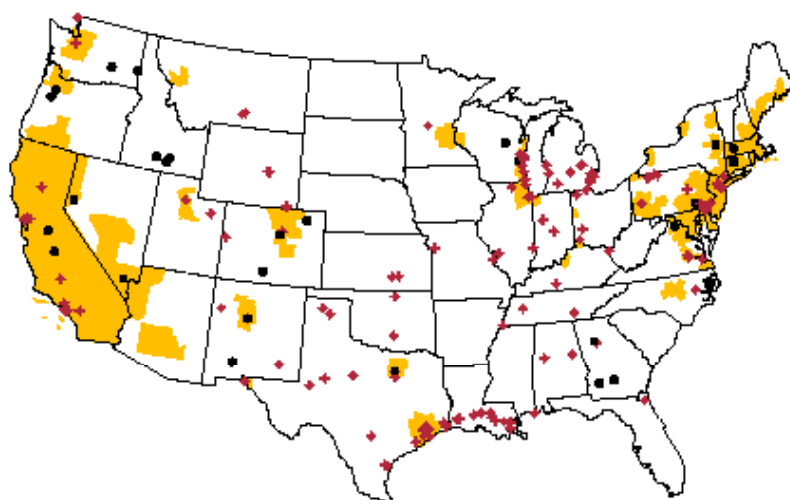


Fig. 3: Use of MTBE and MTBE releases detected in the USA, and also USGS "National Water Quality Assessment" in 1992 (SQUILLACE ET AL., 1995c).

(Yellow areas = regions where MTBE is used; ◆ = USGS NWQA measuring campaigns; ◆ = reported MTBE releases)

Due to its good water solubility (2.1.2.1), low retardation in the aquifer (HUBBARD ET AL., 1994; 2.1.2.4) and its resistance to natural degradation by microorganisms in the groundwater (2.1.3.2), MTBE is extremely mobile in the aquifer, becomes separated from the main hydrocarbon cloud and can propagate rapidly in all directions (NICHOLS ET AL., 2000). After a point contamination, e.g. by a LUFT, an MTBE pollutant cloud several kilometres in length can propagate very rapidly (WEAVER ET AL., 1996). The self-purifying capacity of a damaged site by metabolites ($16 - 9500 \mu\text{g L}^{-1}$; LANDMEYER ET AL., 1997) cannot be assessed since, for example, the source of the TBA metabolite cannot be unambiguously identified. TBA itself was added to fuels as an octane booster and could thus originate from older pollution. However, even if the quantity of MTBE added cannot be detected (SCHIRMER ET AL., 1997 &

1998) this is not proof of biological degradation since the collecting networks around a spillage cannot cover the entire aquifer.

In order to protect and monitor drinking water catchment areas, wide-area studies were performed in the United States in the nineties (1991 – 1995) by the USGS (Fig. 3). In these studies, the influence of the level of urbanization on the detection frequency and pollutant concentration of VOCs was studied by subdividing the sampling of various groundwater wells into rural (524 wells) and urban areas (211 wells) (DAVIDSON, 1995, SQUILLACE ET AL., 1995a-c). There is a significant relationship between population density and frequency of MTBE spillages (GRADY, 1994; LINDSEY ET AL., 1997).

High concentrations (15 vol.%) of MTBE were not used in all regions of the USA, but in some large cities these levels were only used temporarily for climate protection. Nevertheless, in 1992 a large number of spillages were found in federal states which had only used low concentrations of MTBE as an antiknock agent. The National Water Quality Assessment (NWQA) programmes primarily covered areas of preferential MTBE use so that it was not possible to make an area-wide assessment of the drinking water situation. Nevertheless, DAVIDSON (1995) performed some calculations on risk assessment and discovered that 0.011 % of the population were exposed to a quantity of MTBE exceeding $200 \mu\text{g L}^{-1}$, the then upper limit of the health advisory (SQUILLACE ET AL., 1995c). 1.3 % of the groundwater wells examined in rural regions displayed MTBE finds in the concentration range of $0.2 - 1.3 \mu\text{g L}^{-1}$ (mean = $0.5 \mu\text{g L}^{-1}$) (DAVIDSON, 1995). Much higher MTBE contents were found in urban regions at $0.2 - 23000 \mu\text{g L}^{-1}$, although only 3 % of all measured concentrations were above the health advisory value of the U.S. EPA (SQUILLACE ET AL., 1995c). This becomes clear due to the low mean of all measurements (mean = 0.6). Averaged over the total number of samplings, no MTBE was found in 91.4 % of all measurements, which does not support a ubiquitous occurrence (DAVIDSON, 1995).

In addition to these studies, various authors found concentrations of up to $236,000 \mu\text{g L}^{-1}$ of MTBE in Maine (USA) (GARRET ET AL., 1986). Maximum concentrations are principally detected close to the source of damage, those in the public and private drinking water catchment areas were, however, lower by a factor of $10 - 10^3$ (U.S. EPA, 1999). Reports on similarly high concentrations can be found for Maine (max. $230,000 \mu\text{g L}^{-1}$, U.S. EPA, 1999), Missouri ($510 - 17,000 \mu\text{g L}^{-1}$, ZOGORSKI ET AL., 1997), South Carolina ($5 - 31,600 \mu\text{g L}^{-1}$, LANDMEYER ET AL., 1997), Germany (Leuna, $10,000 - 185,000 \mu\text{g L}^{-1}$, CHEMTEC, 1998 and EFFENBERGER ET AL., 2001) and also Denmark (Århus, $22,000 - 55,000 \mu\text{g L}^{-1}$, MORGENROTH & ARVIN, 1999).

ZOGORSKI ET AL. (1997) report on about 90 studies concerning VOCs in groundwater in the USA. They found MTBE in groundwater and drinking water in 14 states, with contents of $10 \mu\text{g L}^{-1}$ in more than 14 % of the analyses. The major fraction of the values measured in the above-mentioned drinking water wells (92 %) were greater than $20 \mu\text{g L}^{-1}$. However, in Illinois

up to $770 \mu\text{g L}^{-1}$ was found. The lack of routine monitoring for MTBE in drinking water was regarded by the authors as a great problem. Furthermore, they reported cases of private wells in Missouri and Indiana where a maximum of 1900 and $5400 \mu\text{g L}^{-1}$, respectively, was found. Many cases of groundwater and drinking water contaminations were not detected. This is due, on the one hand, to the fact that as in Germany, there is no obligation for monitoring on the part of the government (PAHLKE ET AL., 2000; MRASEK, 1999) and, on the other hand, because the limit above which incidents must be reported is too high at $5 - 10 \mu\text{g L}^{-1}$ as in some states of the USA (STACKELBERG ET AL., 1997).

Even after several years MTBE was still detected in measurable concentrations in the groundwater. ZOGORSKI ET AL. (1997) reported, for example, that three years after contamination of an aquifer in Missouri measurable MTBE contents were still being detected. In Germany, 50 years after the end of the Second World War MTBE concentrations of up to $2000 \mu\text{g L}^{-1}$ were found at a former military site, last used by the Soviet Army (PAHLKE ET AL., 1999; EFFENBERGER ET AL., 2001). In the same way as in HUBBARD ET AL. (1994) and SCHIRMER & BARKER (1998), it was found that there was a lack of sufficient long-term data sets to estimate the risks and self-purifying capacity of the damaged aquifer (2.1.2).

On the whole, the values measured in Europe are significantly below the quantities of MTBE found in groundwater in the USA (PAHLKE ET AL., 2000).

2.1.2.3 MTBE in surface waters and rivers

As described in 2.1.2 and 2.1.2.5, MTBE has also been detected in surface waters (SQUILLACE ET AL., 1997 & 1998). Surface waters include lakes, ponds as well as rivers and streams. At Donner Lake (3.9 km^2 , California, USA), REUTER ET AL. (1998) found MTBE quantities of $< 0.1 \mu\text{g L}^{-1}$ up to $12 \mu\text{g L}^{-1}$. An extensive investigation program on possible sources and sinks, as well as the annual MTBE concentration profiles, enabled the authors to make a good assessment of the environmental behavior of MTBE in a lake, which led to transferability to other systems in the USA. Particularly in the summer months, the total amount of MTBE in the lake increased to 365 kg (estimated total water volume: $1.26 \times 10^8 \text{ m}^3$). In winter, the authors observed a significant drop in the pollution in January to 15 kg. A correlation between leisure craft traffic and the MTBE quantity found displayed a significant relation (86 % of all values). In contrast, precipitation and surface inflow did not present an attributable source.

In two studies on Long Island, New York, and in Hackensack River, New Jersey, STACKELBERG ET AL. (1997) found a maximum MTBE concentration of 20 and $30 \mu\text{g L}^{-1}$, respectively. In Suffolk County, Long Island, samples were taken regularly from 39 rivers for this purpose and on an annual average MTBE concentrations ranging from 0.5 to $47 \mu\text{g L}^{-1}$ were detected in 29 % of all analyses. In the winter months, the positive analytical frequency was higher than in the summer. The mean concentration was $0.24 \mu\text{g L}^{-1}$. This low average

value points to an input of MTBE via deposition or precipitation events into surface waters. The area around the Hackensack River is densely populated with an accumulation of Industries. This is also reflected in an average annual concentration in water of $7.75 \mu\text{g L}^{-1}$. Such a high value clearly indicates inputs from point sources. This theory is supported by LOPES & BENDER (1998) with their statistical analyses of MTBE inputs in surface waters in regions of varying population density, even if no qualitatively significant but rather only a qualitative relationship was found. In addition to MTBE, BTEX was also almost always detected. The statistical evaluation indicated a clearly significant relation between BTEX finds (factor 2 – 5) and MTBE analyses.

Tab. 2: MTBE concentrations found in river water and rainwater in Germany in the years 1998 – 2000 (modified after Achten & Püttmann, 2000, and Effenberger et al., 2001).

Fluss	Ort	Date	MTBE [ng L^{-1}]
Rhine	Mainz	21.3.99	160
Rhine	Nierstein	21.3.99	136
Elbe	Dresden	28.3.99	123
Elbe	Hamburg	22.4.99	21
Elbe	Oberrathen	15.3.00	199
Elbe	Gauernitz	15.3.00	83
Saale	Bad Dürrenberg	21.3.00	24
Saale	Kröllwitz	21.3.00	18
Saale	Hektometer 121	21.3.00	57
Saale	Leuna/Waldbad	21.3.00	150
Main	Frankfurt a.M.	14.1.99	10
Main	Frankfurt a.M.	21.1.99	13
Oder	Frankfurt a.O.	10.3.99	7
rain	Frankfurt a.M.	15.12.98	70
rain	Frankfurt a.M.	22.3.99	n.d.
rain	Frankfurt a.M.	20.4.99	9
lake	Ammelshain	15.3.00	< 10
lake	Cospuden	16.3.00	< 10
lake	Goitsche	13.3.00	18

In a large USGS study on the fate of VOC in rainwater and surface runoffs after heavy precipitation events in eleven federal states in the USA, DELZER ET AL. (1996) found MTBE as one of the major pollutants. In all positively determined samples (6.9 % of all analyses), however, the concentrations were significantly below the health advisory limit (**2.1.4**) of the US EPA (1998). Especially in towns with legally prescribed application of MTBE (e.g., CAAA or RFG programme, **2.1.1.1**), high quantities of MTBE were measured in the winter months. However, significant traces of MTBE were also found in federal states where MTBE had only been used as an anti-knocking agent.

MTBE was also detected in surface waters in Europe, even if the concentrations found were always perceptibly below those in the USA (**Tab. 2**, EFFENBERGER ET AL., 2001; PIAZZA ET AL., 2001; ACHTEN & PÜTTMANN, 2000). Maximum values of up to 199 ng L^{-1} (< 270 ppt) were found in the Rhine, Elbe and Saale. In addition to rivers and rainwater (2.1.2.5),

investigations were also made of ponds, lakes and recultivated areas after open-cast mining. A relationship between increasing MTBE concentration and infiltration with contaminated groundwater was established, in particular, in the Saale near Leuna (EFFENBERGER ET AL. (2001). In Leipzig low quantities of MTBE were even found in some urban ponds. Particularly these low concentration in lakes point to an input of pollutants via washing out of the air by rain. In Italy, PIAZZA ET AL. (2001) found similar quantities in surface waters to those identified by their German colleagues (100-150 ppt and 74-111 ng L⁻¹). The authors also studied 12 commercial mineral waters and did not find any traces of MTBE (detection limit 10 ng L⁻¹ or 14 ppt). On the whole, lower quantities of MTBE were found in water than was the case in the USA, which may be due to the lower level of application and also to the shorter period of use in Europe.

MTBE can be transported by rivers over considerable distances (up to 900 km), which results in an extensive distribution of this pollutant (SQUILLACE ET AL., 1997).

Volatilisation from surfaces represents the main source of MTBE discharge from deep surface waters. In addition to rain and surface runoff from urban land use, SQUILLACE ET AL. (1997) also mention direct input of a possible source of gasoline additives in surface waters. By this they mean, amongst other aspects, industrial discharges into rivers and standing waters. The authors describe the temperature dependence of MTBE volatilisation as well as the material transport processes in the waters themselves. In slowly flowing or deep standing waters (lakes) the loss of MTBE due to material transfer in water up to the water/air interface is the rate-determining step. Vice versa, in shallow waters the removal of MTBE from the interface into the air is the limiting factor. In this connection, wind speed and air temperature are of significance. The HENRY coefficient (**Tab. 1**) also influences volatilisation from these systems.

PANKOW ET AL. (1996) performed some model calculations on the volatilisation of MTBE and BTEX from rivers and lakes. They determined that it is not permissible to define a uniform half-life ($t_{1/2}$) for MTBE or other VOCs for all surface waters as is possible in the atmosphere. In addition to MTBE, TBA was also studied. Hardly any volatilisation was determined so that TBA made a good marker molecule for MTBE in surface waters. The authors define the half-life $t_{1/2}$ as follows:

$$\frac{C_w}{C_w^0} = e^{-K_{OL} \cdot t / z_{Wasser}} \quad C_w = \frac{1}{2} C_w^0 \quad \Rightarrow \quad t_{1/2} = \frac{\ln 2}{K_{OL} / z_{Wasser}} \quad (\text{Eq. 2})$$

K_{OL} is the mass transfer coefficient for the complete mass transfer of the system via the water depth z , which includes the mass transfer rates K_L (liquid) and K_G (gas phase) as well as the HENRY coefficient (H). C_w^0 is the initial concentration of the pollutant in water.

$$\frac{1}{K_{OL}} = \frac{1}{K_L} + \frac{1}{K_G \cdot H / RT} \quad (\text{Eq. 3})$$

At low temperatures (5 °C), the authors calculated a half-life of > 85 days for MTBE. In an extremely slowly flowing body of water (0.032 m s⁻¹, depth = 10 m). At summer temperatures of (25 °C) and otherwise identical conditions, this period is reduced to 28 days.

2.1.2.4 MTBE in soil

Various characteristics can be calculated in order to assess the transport behaviour of volatile organic compounds in the soil. Due to its good water solubility (or rather the low HENRY coefficient (H), substances such as MTBE or BTEX aromatics are mainly distributed in the aqueous phase of the soil (NICHOLS ET AL., 2000). Mass transfer in the drier, unsaturated zone is much faster than in the saturated soil zone. In the unsaturated soil zone, gas diffusion processes dominate, which are faster than diffusion in the aqueous phase by a factor of 10⁴ (DEVAULL ET AL., 1998). Transport in a soil layer can be described by the following transport equation:

$$\frac{K_i}{H_i} \cdot \frac{\partial C_{a,i}}{\partial t} + \underbrace{\frac{\partial}{\partial z} \left(\overbrace{\left(\xi_v \cdot D_{Luft,i} + \xi_w \cdot \frac{D_{Wasser,i}}{H_i} \right)}^{\text{effektiver Diffusionskoeffizient}} \cdot \frac{\partial C_{a,i}}{\partial z} \right)}_{\text{Diffusionsterm}} + \underbrace{\left(U_a + \frac{U_w}{H_i} \right) \cdot \frac{\partial C_{a,i}}{\partial z}}_{\text{Konvektionsterm}} - \underbrace{R_{T,i}}_{\text{Reaktionsterm}} = 0 \quad (\text{Eq. 4})$$

The index i in **(Eq. 4)** stands for a component i in the gasoline mixture which has entered the environment. C_{a,i} is the soil gas concentration of i and K_i the distribution coefficient of the substance i in the soil and the aqueous phase present there. The change of concentration is observed with time t and soil depth z.

For MTBE, the reaction term R_{T,i} can be neglected for the saturated zone. As an approximation, the degradation rate can be assumed to be equal to zero for the aerobic unsaturated soil zone since there are often long "lag" phases in the degradation of MTBE by microorganisms (2.1.2). Mainly diffusion-controlled mass transfer processes are assumed for the unsaturated phase, so that the convection term can be set equal to zero. The equation can then be simplified for a homogeneous layer to give the following expression:

$$\frac{\partial C_{a,i}}{\partial t} \cdot \frac{1}{(H_i / K_i) \cdot D_{eff}} + \frac{\partial^2 C_{a,i}}{\partial z^2} = 0 \quad (\text{Eq. 5})$$

This expression is easy to solve in analytical terms for various boundary conditions. Taking several components of a pollutant mixture into consideration, and also including all transport terms, various numerical approaches can be taken to solve the transport equation (DEVAULL ET AL., 1998; LAHVIS & BAEHR, 1997). If the soil-type-specific effective diffusion coefficient (D_{eff}) is known, then very good agreement can be achieved between the model and experiment (DEVAULL ET AL., 1997).

In a field study in Beaufort, South Carolina, BAEHR ET AL. 1997) performed studies on the gas phase above an aquifer and discovered up to $5237 \mu\text{g L}^{-1}$ MTBE. After 16 months, only $26 \mu\text{g L}^{-1}$ was measured at this location. Thanks to precise knowledge of the effective diffusion coefficient, the concentrations and material flows found were in good agreement with the theory.

NICHOLS ET AL. (2000) only gave a qualitative description of the transport processes. The gas phase transport of MTBE in the unsaturated zone was greatly dependent on water content. The transport rate increased with decreasing soil moisture. The reason for this was that the distribution tended to take place in the aqueous phase thus resulting in retarded transport through diffusion (see above).

ARTHURS ET AL. (1995) investigated the volatilisation of artificial gasoline mixtures from soil and soil surfaces. They discovered a perceptible dependence of volatilisation on soil type and on the vapour pressure of the gasoline constituents. Sandy soils displayed higher and more rapid losses of contaminants than soils with a greater proportion of loam. Gasoline volatilised more rapidly from these soils than from very clayey soils. In particular, the C_{org} content and the soil density (see also: (Eq. 9)) in the soil type were decisive for the degree of vaporization or retardation.

Using (Eq. 6) and (Eq. 7), SQUILLACE ET AL. (1997) calculated a potential absorption of 8 % of the total MTBE at the organic constituents of soil in the saturated zone for a sandy soil (C_{org} content = 0.1 % w/w). The sorption at the soil matrix cannot therefore be neglected although the distribution coefficient of MTBE between the organic soil matrix and the aqueous phase ($K_{OC} \cong 11$) is very low in comparison to the aromatics. In the saturated zone, it is possible to simplify the distribution of non-ionic substances, polar substances such as MTBE between the soil and water (K_d) to a distribution between the organic fraction in soil and the aqueous phase (K_{OC}) (NICHOLS ET AL., 2000; SQUILLACE ET AL., 1997). The distribution coefficient K_d is normally smaller than K_{OC} :

$$K_d = \frac{C_s}{C_l} \quad (\text{Eq. 6})$$

C_s is the concentration of contaminants, sorbed on soil particles (g g^{-1}) and C_l is the concentration of the same substance dissolved in water (g mL^{-1}). After simplification, the following formula for K_d then results with the molar fraction of organic material in the soil (f_{OC}):

$$K_d = f_{OC} K_{OC} \quad (\text{Eq. 7})$$

In addition to sorption, the retardation also plays a significant role in the transport of contaminants in the aquifer. The retardation factor R in the aquifer is defined as the ratio of groundwater velocity to the velocity of the dissolved pollutant:

$$R = 1 + \left(\frac{\rho_b K_d}{n} \right) \quad (\text{Eq. 8})$$

The retention capacity of the soil for dissolved organic substances is determined by the soil density (ρ_b), the distribution coefficient (K_d) and the porosity (n) in the soil of the aquifer. If $R > 1$, the pollutant moves more slowly than the groundwater. In a field experiment, HUBBARD ET AL. (1994) did not determine any retardation in the aquifer for MTBE ($R = 1$). This is typical of most aquifer systems with a low organic fraction and proves that MTBE is not retained in the saturated soil zone.

In the unsaturated zone, the retention factor (R_{vp}) depends on other factors such as the volumetric water fraction in the soil θ_w , the volumetric air void fraction (θ_a) and the dimensionless HENRY coefficient:

$$R_{vp} = 1 + \left(\frac{\rho_b K_d + \theta_w}{\theta_a K_H} \right) \quad (\text{Eq. 9})$$

2.1.2.5 MTBE in the atmosphere

MTBE was used to protect the population in regions where the atmosphere was extremely polluted, in particular to reduce the CO and O₃ concentration (2.1.1.1). Although these substances have indeed been reduced, as a consequence MTBE and its degradation products can now be measured in the atmosphere (GROSJEAN ET AL., 1998). Although the introduction of the Clear Air Act Amendments (CAAA) stipulates that the air should be monitored for various pollutants, MTBE was not covered on a regular basis (ZOGORSKI et al., 1997).

MTBE enters the atmosphere by various paths and does not remain there long. PIQUET ET AL. (1998) investigated the reaction kinetics of MTBE with OH radicals and calculated a lifetime of MTBE in the atmosphere of 4 days. The main reaction product is tert-butyl formate (TBF). According to data in the literature, the lifetime of MTBE in the atmosphere is between

4 days and 2 weeks at an OH concentration of 10^6 radicals cm^{-3} (WALLINGTON ET AL., 1988, SQUILLACE ET AL., 1997). Most authors regard photolysis and other chemical reaction processes as negligible, although in their studies MIYAKE & SHIBAMOTO (1999) discovered significant quantity of formaldehyde, butanal and 2-butanone as photolysis products of MTBE.

In the case of point-source inputs due to spillages of gasoline, the atmospheric pollution can be very high. With a lifetime of several days in air, high concentrations of MTBE can be transported by advection processes in rural regions and are, for example, washed out there together with the rain (see below; SQUILLACE ET AL., 1997).

Production processes in an eight-hour shift led to less than 3 mg m^{-3} entering the air (ECETOC, 1997). Values of about 9.5 mg m^{-3} resulted in a refinery or from industrial emissions. In the short term, up to 120 mg m^{-3} was detected in the ambient air during the loading of road tankers and trains. In particular, high short-term pollution resulted during the top loading of road tankers and during delivery at filling stations.

BORGHOFF ET AL. (1996) estimated the exposure of the population resulting from incomplete combustion and refuelling their cars to be more or less negligible, even for car mechanics and filling station attendants, since only short-term emissions are involved. One source of MTBE and ethanol which cannot be neglected is motor vehicles. The oxygen-containing fuel additives are released into the environment by incomplete combustion. In Porto Alegre, Brazil, GROSJEAN ET AL. (1998) measured samples for more than a year and discovered a mean air concentration for MTBE of $6.6 \pm 4.3 \text{ ppb}$ ($23.8 \pm 15.5 \text{ } \mu\text{g m}^{-3}$) with maximum values of 17.1 ppb ($61.6 \text{ } \mu\text{g m}^{-3}$). Calculations by the authors of the concentrations found yielded MTBE emissions from motor vehicles in Brazil of $1668 \pm 193 \text{ t a}^{-1}$. The ethanol emissions in the same period represented a much higher strain on the atmosphere with $2338 \pm 393 \text{ t a}^{-1}$. The authors only reported a small number of other measurements in North and South America. MIYAKE & SHIBAMOTO (1999) made an estimate of the total MTBE losses into the atmosphere for the United States. A total of 1427 t MTBE escaped per year, the vast majority from refineries (1360 t a^{-1} ; BROWN, 1997). The concentrations measured after the introduction of MBTE as a fuel additive in California were in the same orders of magnitude as the above-mentioned results (GROSJEAN ET AL., 1998; PANKOW ET AL., 1997). An estimate of the atmospheric pollution with MTBE can be made according to the population density and volume of traffic in a region. In addition to 85 VOCs, in several analyses of various regions in New Jersey (NJ, USA), PANKOW ET AL. (1998) also found various concentrations of MTBE. In a rural region (Coles Farm, NJ) the data were below the calibration values and were estimated to be 0.14 ppb ($0.5 \text{ } \mu\text{g m}^{-3}$). In Rowan College (NJ), a moderately urbanized region, 0.37 ppb ($1.3 \text{ } \mu\text{g m}^{-3}$) was detected, and in Turnersville (NJ), a small town with a high volume of traffic, as much as 0.52 ppb ($1.9 \text{ } \mu\text{g m}^{-3}$) was detected. Furthermore, MTBE was detected in all samples, although they had been collected on different dates and at different times of day. This points to a permanent pollution of the ambient air with MTBE.

The investigations by PIQUET ET AL. (1998) also found a constant reaction rate of MTBE with hydroxy radicals, which supports this theory. After the introduction of the CAAA, an MTBE concentration in the outside air of 0.13 - 4.6 ppb (0.5-16.6 µg m⁻³) was found in 6 towns in California (ZOGORSKI ET AL., 1997).

The atmosphere can be regarded as a diffuse source of MTBE on surfaces and in rainwater. Several authors have made estimates (**Eq. 10**) and model calculations (PANKOW ET AL., 1997) on input into rainwater and thus washout from the atmosphere with rain events (EFOA, 2000; LOPES ET AL., 1998; SQUILLACE ET AL., 1997; ZOGORSKI, 1997; DAVIDSON, 1995). As already described in 2.1.2.1, MTBE is mainly distributed in the atmospheric aqueous phase and is then washed out during rain events. This washing out only makes a small contribution to eliminating MTBE from the air (0.14 % with 25 mm precipitation; SQUILLACE ET AL., 1997). The major fraction of MTBE is photochemically degraded in the atmosphere or transported together with the various atmospheric layers to more distant regions. In rural areas, however, inputs via rainout frequently represent the solar source of MTBE in surface waters (**2.1.2.3**).

$$\frac{m_{Luft}}{m_{Wasser}} = \frac{H}{RT} \frac{V_{Luft}}{V_{Wasser}} \quad (\text{Eq. 10})$$

The volume of washout is temperature-dependent through the HENRY coefficient (**Eq. 10**). SQUILLACE ET AL. (1996) describe the temperature dependence of the HENRY coefficient as follows:

$$K_H = \frac{H}{RT} = 1000 \cdot e^{18,4 - \frac{7666}{T}} \quad (\text{Eq. 11})$$

The K_H changes by a factor of 2 for each 10 °C of temperature difference. This means a change in the atmospheric concentration by precisely this factor and results in the quantity of MTBE potentially available for washout together with the precipitation.

At 20 °C only 0.2 µg L⁻¹ of MTBE is recovered in surface water, but 1.5 µg L⁻¹ at 0 °C. MTBE is frequently only used in the winter months in towns so that both low temperatures and a higher atmospheric pollution mutually reinforce their effects with respect to washout (LOPES ET AL., 1998). The maximum concentration in rain is 1-2 µg L⁻¹ (EFOA, 2000; DAVIDSON, 1995). This is also the maximum concentration in surface water, if MTBE has not been introduced along other paths. In reality, however, this concentration is reduced further in surface water by evaporation and seasonal use (PANKOW ET AL., 1997).

MTBE traces in the air and in rain or snow have not only been measured in the USA, but also in Europe. There are no direct air monitoring values for MTBE. Nevertheless, the air concentration can be determined indirectly from (**Eq. 10**) via rain. In Germany, up to 70 ng L⁻¹

MTBE was measured in rain in the vicinity of Frankfurt am Main in December 1998 (**Tab. 2**; ACHTEN & PÜTTMANN, 2000). The concentration was hardly measurable in the warmer months. Samples were measured in Italy from a busy road in Bologna. In order to obtain a more realistic estimate of the concentrations in the atmosphere, the authors did not collect and analyse rain, but rather samples of snow at various heights along the road (PIAZZA ET AL., 2001). With increasing height above the ground (0.30 and 60 cm), the quantity of MTBE found decreased from 7.03 to 0.72 ppb (5.20 to 0.53 $\mu\text{g L}^{-1}$). MTBE was also detected in snow in Denver, Colorado, USA (SQUILLACE ET AL., 1995 c).

2.1.3 Microbiological degradation of MTBE in the environment

As already described in **2.1.1**, MTBE enters the environment through a large number of spillages, incomplete combustion processes and losses during production. The pollutant is distributed through all compartments of the environment: water, soil and atmosphere (**2.1.2**). The ubiquitous occurrence of MTBE in whole regions of a country represents a serious problem for the people living there since MTBE can damage health and makes drinking water unfit to drink.

In the atmosphere, MTBE is only stable for a brief period and is eliminated by the self-purifying capacity of the air ($h\nu$, OH radicals) (**2.1.2.5**). In contrast, the residence time in the soil and groundwater is greater by several orders of magnitude. Little has been reported in the literature so far concerning natural degradation ("bioremediation") from the corresponding compartment (LINNEMANN & JAGETSBERGER, 2000; LINNEMANN ET AL., 2000; PRINCE, 2000). Laboratory studies on the biological degradation behavior were only performed by FUJIWARA ET AL. (1984) more than 14 years after the first application of MTBE as a fuel additive. Until 1993 because of its chemical structure (stable ether bonding, sterically bulky structure due to tert.-butyl groups) MTBE was regarded as not biodegradable under aerobic or anaerobic conditions (ODENCRANTZ, 1998; SEVILLA ET AL., 1997; SQUILLACE ET AL., 1997; HUBBARD ET AL., 1994; SYMINGTON, 1993). Many environmental authorities adhered to this assessment as the state of the art for a considerable period (CAL-EPA, 1998; COONEY, 1997; U.S. EPA, 1994). However, this opinion has changed amongst experts due to the findings of more recent studies. In comparison to other compounds from reformulated fuels, such as BTEX aromatics and alkanes, MTBE is still regarded as not readily biodegradable, although degradation is possible (PRINCE, 2000; DEEB ET AL., 2000). An aerobic experimental procedure has proved optimal for the degradation of MTBE and some of its metabolites (e.g. TBA) (**2.1.3.1**). Only a few studies have been able to demonstrate appreciable degradation under anaerobic conditions (**2.1.3.2**). These findings on the microbial degradation of MTBE in the soil and groundwater can be used in practice in order to deal with cases of damage by mineral oil hydrocarbons by applying various methods.

Three different methods are differentiated:

- the natural degradation of a contamination within a reasonable period to a minimal concentration of the pollutant in the ecosystem, e.g. drinking water limit (natural attenuation) (PAVNE ET AL., 1997).
- the biological and biotechnological remediation of an ecosystem (bioremediation).
- digging out or pumping off of the contaminated material followed by dumping.

Biological and biotechnological remediation has today proved to be very promising for processing the many cases of fuel contamination (BORDEN, 1997; JAVANMARDIAN & GLASSER, 1997; MOSTELLER ET AL., 1997). This type of remediation ensures environmentally friendly, cost-effective handling of cases of pollution according to the standards of a risk management approach such as RBCA (Risk Based Corrective Action; ASTM, 1999; ASTM, 1996; DEVAULL ET AL., 1994). Inoculation with active MTBE-degrading microorganisms, previously taken from the contaminated system and cultivated, accelerates pollutant elimination (PRINCE, 2000). Irrespective of the experimental procedure, many experiments only displayed low cell growth of about $0.18 \text{ mg}_{\text{cell mass}} \text{ mg}_{\text{MTBE}}^{-1}$ on an average of all experiments, which points to a possibly toxic metabolite formation or to MTBE itself as a poor nutrient source. In comparison to other compounds in a biotechnological remediation measure, this growth rate is very low. DEEP ET AL. (2000, 2001) were, furthermore, able to show that BTEX reduced or even inhibited MTBE degradation. The reverse case, however, did not arise.

Not only MTBE but also ethanol, methanol, TBA, ETBE and TAME are used as fuel additives and may enter the environment after spillages. Ethanol is regarded as very rapidly degradable and is indeed often used as an initiator for microorganisms in order to metabolize more complex systems (PRINCE, 2000). After release into the environment, methanol has a somewhat poorer degradation potential than ethanol. If the ethers MTBE, ETBE and TAME are compared it can be shown that, after ETBE and TAME, MTBE is the most difficult compound to metabolise (PRINCE, 2000). TBA is not only a fuel additive and a impureness in MTBE, but also an intermediate product of MTBE degradation (HICKMAN & NOWVAK, 1989). In some experiments, DEEB ET AL. (2000) were able to show that TBA can apparently be oxidized in the start reaction by the same proteins as MTBE. Conversely, however, a metabolism of MTBE with the monooxygenase from TBA degradation was not possible.

2.1.3.1 Aerobic microbial degradation

The most effective way of degrading MTBE in the soil or in solution is an experimental approach under aerobic conditions. For this reason, the majority of publications on the topic of microbial degradation of MTBE also take this approach (DEEB ET AL., 2000; SALANITRO, 1994). To this end, during remediation oxygen or oxygen-donating chemicals are frequently supplied to the ecosystem (SALANITRO ET AL., 2000).

PARK & COWAN (1997) demonstrated that the kinetics of the aerobic degradation of MTBE are dependent on the temperature and oxygen quantity. As expected, a lower level of elimination was determined with decreasing temperature. It was only possible to qualitatively demonstrate the influence of the oxygen content. In the lower oxygen ranges, lower degradation of MTBE was also recorded.

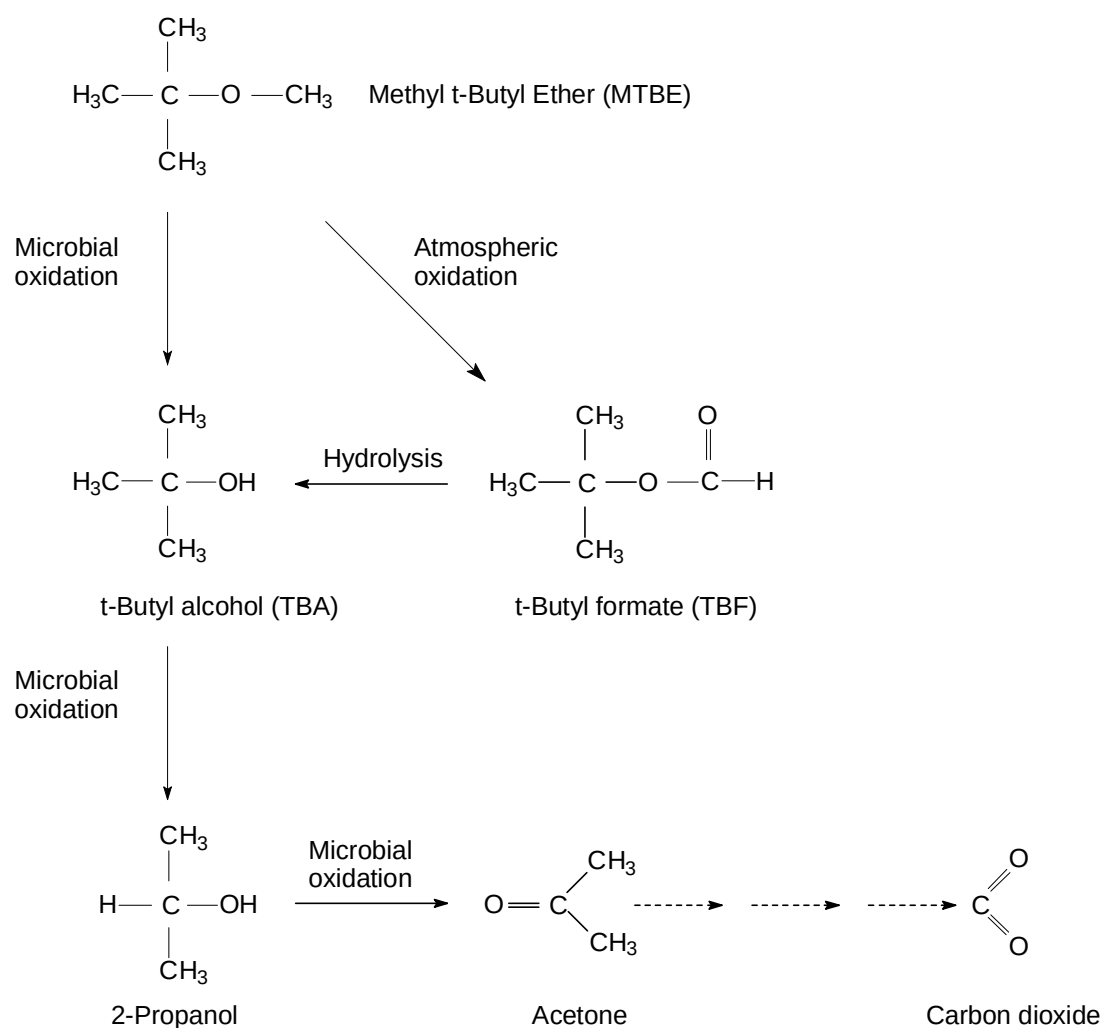


Fig. 4: Possible metabolites and degradation pathways of MTBE in the environment after CHURCH ET AL. (1997); DEEB ET AL. (2000) and STEFFAN ET AL. (1997).

SALANITRO ET AL. (1994) were the first to isolate microorganisms from industrial sewage sludge (BC-1), which quite clearly used MTBE as the carbon and energy source and thus degraded the former. The growth of a sufficient quantity of MTBE-degrading microorganisms required an incubation time of 80-90 days until these microorganisms demonstrated a constant degradation performance and could then be used in the degradation experiment. This mixed culture was capable of metabolising high concentrations ($120\text{--}200\text{ mg L}^{-1}$), as measured in the vicinity of contamination sources (DAVIDSON, 1995), at a maximum rate of $34\text{ mg g}_{\text{cell mass}}^{-1}\text{ h}^{-1}$, in the course of which TBA was identified as a metabolite (Fig. 4). This maximum degradation rate was only reached at a concentration $< 5\text{ mg L}^{-1}$. The mineralisation was also concentration-dependent and had its maximum (40 % AR) at $20\text{ mg}_{\text{MTBE}}^{-1}$. A further 40 % of the applied radioactivity was recovered in the biomass at the end of the experiment. At $0.21\text{--}0.28\text{ mg}_{\text{cell mass}}\text{ mg}_{\text{MTBE}}^{-1}$ over the experimental period and a growth rate of 0.01 d^{-1} , the cell growth was very low in comparison to other fuel additives. From this culture the scientists developed further mixed cultures (BC-4; MC-100), which were later used in field experiments (SALANITRO ET AL., 2000; DEEB ET AL., 2000).

Many authors selected industrial waste water or sewage sludges from refineries and MTBE production types as the basis for their isolations of MTBE-degrading microorganisms in order to be able to exploit the greatest possible degradation potential for MTBE in the cultures by natural selection and specialization. MO ET AL. (1997) used cultures from three species which they isolated from refinery effluents, the fruit of a ginkgo tree and the soil surrounding it. The ginkgo is one of the few plants in whose fruits molecules with tert-butyl groups occur as functional groups. The researchers succeeded in identifying the species as *Methylobacterium mesophilicum* (ATCC 700107), *Rhodococcus* sp. (ATCC 700108) and *Arthrobacter ilicis* (ATCC 700109). According to ALEF (1993) all these species are capable of degrading mineral oil hydrocarbons (alkanes and alkenes) and in part also (PAHs) and thus of reducing fuel contaminations in the environment. However, since MTBE displays a different chemical structure than alkanes, an equally good degradation capacity of these organisms for MTBE does not necessarily follow. The above-mentioned microorganisms degraded 29 % of the applied MTBE in a contaminated microcosmos (200 mg L^{-1}) within 2 weeks, in the course of which 8 % of the applied radioactivity was released in the form of $^{14}\text{CO}_2$ per week. The cell growth was perceptibly reduced when the nutrient medium was converted to MTBE as the carbon and energy source. LIU ET AL. (2001) confirmed the good degradation behaviour of MTBE with arthrobacters (ATCC 27778), but in a different concentration range ($600\text{ }\mu\text{g L}^{-1}$) and formulated MONOD kinetics for the degradation of MTBE.

In addition to the above-mentioned direct metabolism mechanisms a number of co-metabolism studies had been performed. STEFFAN ET AL. (1997) carried out one of the most comprehensive studies on the co-metabolism of MTBE with propane in pure cultures. They made a decisive contribution to the development of possible biological degradation pathways of MTBE in the environment (Fig. 4). The scientists discovered different degradation rates for MTBE and TBA. The bacteria were only able to metabolise TBA at $4.4\text{--}5.9\text{ mg g}_{\text{cell mass}}^{-1}\text{ h}^{-1}$,

but MTBE in contrast at $26.7 \text{ mg g}_{\text{cell mass}}^{-1} \text{ h}^{-1}$. In this way it was first possible to identify TBA as a metabolite. They moreover found that the oxidation of MTBE to TBA is initiated by a monooxygenase enzyme (in this case cytochrome P-450). This was also confirmed by SALANITRO ET AL. (2000) and HARDISON ET AL. (1997) for other cultures. TBA degradation only took place after the complete metabolisation of MTBE. A possible intermediate stage in the degradation of MTBE to TBA is TBF, which, however, has not been identified as an intermediate (HARDISON ET AL., 1997).

In contrast to STEFFAN ET AL. (1997), GARNIER ET AL. (1999) were able to demonstrate a co-metabolism with alkanes (in this case pentane) with a mixed culture. The degradation rates were in the region of $2.3 \text{ mg g}_{\text{cell mass}}^{-1} \text{ h}^{-1}$. In addition, they used *Pseudomonas aeruginosa* as a pure culture and were thus able to demonstrate a metabolisation of MTBE to TBA after cultivation on pentane with up to $900 \text{ mg}_{\text{MTBE}} \text{ L}^{-1}$ at a degradation rate of $10.2 \text{ mg g}_{\text{cell mass}}^{-1} \text{ h}^{-1}$.

In addition to the bacterial degradation studies, a metabolism of MTBE to TBA with fungi was also shown. The fungal culture *Graphium sp.* (ATCC 58400) used by HARDISON ET AL. (1997) was able to convert a maximum of $18 \text{ mg}_{\text{MTBE}} \text{ L}^{-1}$ with $0.92 \text{ mg g}_{\text{cell mass}}^{-1} \text{ h}^{-1}$ to TBA via TBF with propane or butane as the carbon and energy source. In the same way the fungus studied was able to metabolise diisopropyl ether.

Other studies were performed with bacteria isolated from biofilters, in which both pure cultures (HANSON ET AL., 1999) and also mixed cultures were used (PRINCE, 2000; DEEB ET AL., 2000). Aquifer materials contaminated with fuels were, furthermore, also used as a good source of bacteria for MTBE degradation. The authors measured a mineralisation of up to 70 % AR (BRADLEY ET AL., 1999).

In addition to the microcosms studies described above, experiments were also performed in bioreactors (DEEB ET AL., 2000; FORTIN & DESHUSSES; 1999b). After a 6-month acclimatization phase with $5\text{-}10 \text{ mg g}_{\text{cell mass}}^{-1} \text{ h}^{-1}$, very high MTBE concentrations of $560\text{-}800 \text{ mg L}^{-1}$ were converted in the reaction system. The good mineralisation of 97 % of the quantity applied is comparable to that of benzene. No other metabolites were detected.

In contrast to previous opinion, the large number of studies indicate that MTBE can be regarded as a substance that is degraded in the environment. Nevertheless, it cannot be said that there is an appreciable elimination from the soil or groundwater using solely biotechnological processes, since the natural degradation potential without human intervention is extremely limited. SCHIRMER ET AL. (1998) reported on a long-time field experiment on the release of oxygenated gasoline at the "Canadian Forces Base" in Borden, Ontario. Samples were collected here for 6 years and analysed with respect to their content of MTBE and BTEX. During this period there was hardly any reduction in MTBE concentration whereas the BTEX content was significantly reduced. However, at the end of the experiment only 3 % of

the applied MTBE was recovered. This led the authors to indirectly conclude that natural degradation had taken place since sorption, abiotic degradation, plant uptake and volatilisation in laboratory experiments could be ruled out.

At the US National Environmental Test Site at Port Hueneme, California, USA, SALANITRO ET AL. (2000) detected a considerable degradation of MTBE in the aquifer after inoculation with a bacterial culture and the addition of supplementary oxygen (BETTS, 1998). In 261 days, the groundwater concentration of initially $2\text{--}9\text{ mg}_{\text{MTBE}}\text{ L}^{-1}$ was reduced to $\leq 0.001\text{--}0.01\text{ mg L}^{-1}$ by this procedure. The MC-100 species used is a further development of the above-mentioned BC-1 culture for the degradation of MTBE by extending the microorganism spectrum (SALANITRO ET AL., 1994).

2.1.3.2 Anaerobic microbial degradation

Mainly anaerobic conditions prevail in the groundwater and the saturated zone above the aquifer. Some of the experiments performed cannot therefore be used to estimate the natural degradation potential of an ecosystem for MTBE and other fuel additives. Until 1994, MTBE was regarded as a non degradable compound under anaerobic conditions and was therefore classified as a persistent compound in groundwater and surface water (PRINCE, 2000; YEH & NOVAK, 1994; MORMILE ET AL., 1994; MØLLER JENSEN & ARVIN, 1990). ETBE is also regarded as difficult to degrade under anaerobic conditions. However, a good degradation rate of $0.05\text{--}2\text{ mg L}^{-1}\text{ d}^{-1}\text{ g}_{\text{dry soil}}^{-1}$ for TBA was found under denitrifying experimental conditions (YEH & NOVAK, 1994).

MORMILE ET AL. (1994) were the first to report an MTBE degradation under methanogenic conditions, although this was not significant and only began after 152 days (only one of 3 parallel samples). BRADLEY ET AL. (2001) and FINNERAN & LOVLEY (2001) showed that under denitrifying conditions MTBE was mineralised to a considerable extent and did not, as in YEH & NOVAK (1994), form a toxic metabolite (TBA). The constant NO_3 concentrations enabled the degradation of MTBE to be initiated by terminal electron acceptor processes (4.6 mmol L^{-1}). River sediments of different origins (Charleston, South Carolina; Pensacola, Florida) and with different levels of exposure with respect to MTBE were studied. At constant NO_3 concentrations, about 25 % AR was metabolised to $^{14}\text{CO}_2$ on both soils in 71 days, although the authors did not find any bioaccumulation of TBA in the system. However, with a non-constant NO_3 content up to 10 % TBA was identified, as under methanogenic conditions (BRADLEY ET AL., 2001).

In addition to the river bed sediments contaminated with fuel (Beaufort, South Carolina), FINNERAN & LOVLEY (2001) additionally used crystalline Fe(III) as an electron acceptor ($40\text{--}100\text{ mmol kg}_{\text{sediment}}^{-1}$) and humic acids as electron transfer molecules ($100\text{ }\mu\text{mol L}^{-1}$) to degrade MTBE and TBA. No degradation of MTBE was observed in the untreated soil

variants. After a starting phase of 250-300 days, MTBE was degraded to 80 % AR, as was TBA, but without an initiation phase.

2.1.4 Toxicology of MTBE and its metabolites

After the introduction of fuels containing MTBE in the seventies, a rise in complaints about their health from people living in regions where MTBE was used as a fuel additive began to be heard with the increasing use of oxygenated fuels (fuels with additives containing oxygen). In order to identify impacts on health (see below) research programmes and literature reviews of possible health risks were commissioned by environmental authorities (OSTP 1996; U.S. EPA 1994), political bodies (FROINES ET AL., 1998) and industry (NICHOLS ET AL., 2000; McKEE ET AL., 1997). Such studies were also performed in Europe with the increasing application of MTBE, although with a slight time lag (TESSERAUX & KOSS, 1999; ECOTOC, 1997). The most important studies will be discussed in detail in the following.

In all these assessments of health risks, it must always be remembered that the data are mainly derived from animal experiments. Only a few readily assessable experiments with humans and case studies are described in the literature. The transferability of findings from animal experiments to humans is only possible to a limited extent and is also controversial (STELLJES, 1997; MENNEAR, 1997). In addition to studies of possible dangers to health, investigations were also performed on the unpleasant smell and taste of MTBE in drinking water. In addition to identifying possible risks to health, these studies were also of significance in laying down limits for MTBE (U.S. EPA, 1999; TESSERAUX & KOSS, 1999) and dispensing with it as a fuel additive (U.S. EPA, 2000). The alternative oxygenated compounds such as TAME, ETBE and to a limited extent ethanol have still not been adequately tested with respect to their toxicology under environmental conditions. It is therefore not possible to forecast whether a substitute does not involve a much higher toxicological potential. For example, acetaldehyde and peroxyacetyl nitrate (PAN), both combustion or reaction products of ethanol, the preferred renewable additive after MTBE, are both much more toxic than the parent substance. Acetaldehyde is classified as carcinogenic. PAN is genotoxic and can lead to lung damage. Studies have related ethanol vapours to DNA damage (FROINES ET AL., 1998).

With respect to the above-mentioned health hazards, a differentiation must be made between the acute, chronic, neurotoxic and genotoxic potential of a pollutant (**2.1.4.3, 2.1.4.4, 2.1.4.5**). None of these classes of health risk consider the carcinogenic behaviour of a substance, although special attention must be paid to precisely this point. For this reason, the carcinogenic potential of MTBE and its metabolites, above all formaldehyde and tert-butyl alcohol (TBA), is dealt with separately (**2.1.4.6**). A brief overview is given for MTBE in **2.1.4.2** in order to obtain both a qualitative and also quantitative understanding of the toxicology of the pollutant in the living organism.

The highest short-term pollution with concentrations of up to 120 mg m^{-3} was measured during the loading of MTBE from the production process (ECETOC, 1997) in various case studies and from the manufacturers' data sets (McKEE ET AL., 1997). Up to 200 mg L^{-1} of MTBE has been recorded in the groundwater (DAVIDSON, 1995). The responsible supervisory authorities reacted to the reports of health hazards discussed in detail below with limit values at which there is no danger to human health. KLAN & CARPENTER (1994) performed the first calculations for a health advisory for drinking water for MTBE eliminating dangers to human health. Using the reference dose from toxicological studies they calculated a value of $200 \text{ } \mu\text{g L}^{-1}$. The U.S. EPA has recently prescribed a drinking water limit for the USA of 20-40 $\mu\text{g L}^{-1}$, whereas the Californian EPA laid down 35 ppb ($26 \text{ } \mu\text{g L}^{-1}$) for drinking water quality. A reduction to 14 ppb ($10 \text{ } \mu\text{g L}^{-1}$) is recommended (SCHWARTZ, 1999). These prescribed limits are lower than the concentrations at which an increased incidence of cancer arose in animal experiments by a factor of 20,000-100,000.

Depending on the nation, there are different limits for the concentration of MTBE in the air. In Europe, only Sweden, Germany and Finland have a legally binding threshold limit value (TLV) of 180 mg m^{-3} air (50 ppm). None of the other countries have any restrictions on this value. In the USA, an even lower value of 40 ppm is prescribed (144 mg m^{-3} ; TESSERAUX & KOSS, 1999; ATSDR, 1997).

2.1.4.1 Taste and odour nuisance

Apart from its health hazards, MTBE is characterized by an unpleasant smell and taste. People's ability to perceive MTBE in the air is far below the previously studied toxic limit (3.4-1000 ppb) and is sex- and person-specific (NICHOLS ET AL., 2000; TESSERAUX & KOSS, 1999; STELLJES, 1997; KLAN & CARPENTER, 1994). This low odour threshold protects the population against taking up toxic quantities of MTBE. The great difference in values is influenced by the temperature, the chlorine content in water and the test conditions. The odour thresholds for fuels with and without an addition of MTBE are higher by roughly a factor of 10 than for pure MTBE.

The taste threshold for MTBE in water has been tested as 39 ppb $\mu\text{g L}^{-1}$ (KLAN & CARPENTER, 1994). In order to maintain drinking water quality, a secondary maximum contaminant level (MCL) has been recommended by the Californian Office of Environmental Health Hazard Assessments (OEHHA) of 5 ppb ($3.7 \text{ } \mu\text{g L}^{-1}$) and a health-related primary MCL of 17 ppm ($13 \text{ } \mu\text{g L}^{-1}$) (SCHWARTZ, 1999; NICHOLS ET AL., 2000).

2.1.4.2 Toxicokinetics and metabolism

Toxicokinetics is taken to mean quantitative studies of how a substance (in this case MTBE) is taken up in the body of a living organism, distributed in its individual internal organs, metabolized there or eliminated from the body. Many authors have concerned themselves with the toxicokinetics of MTBE in animal experiments, especially with rats (FROINES ET AL., 1998; MILLER ET AL., 1997) and mice (FROINES ET AL., 1998; ECETOC, 1997; BORGHOFF ET AL., 1996). MTBE can enter the organism along various paths. The most important uptake paths are oral uptake, e.g. with contaminated groundwater, and inhalation uptake from polluted air (BROWN, 1997). Different distributions are also observed in the animal organism depending on the uptake path. Only after the oral uptake did recovery was equal to 100 % of the applied radioactivity (% AR). More MTBE is thus taken up into the human organism with the drinking water than by other paths so that this uptake path represents a special risk (ECETOC, 1997). The net uptake after inhalation amounts to 38-40 % of the MTBE supplied. These studies indicate that after a rapid flooding into the blood with subsequent distribution among the internal organs, MTBE and its metabolites do not accumulate in the lipid-rich tissue in the long term. When high doses of MTBE are to be metabolized, the metabolization capacity is rapidly exceeded and MTBE is excreted unchanged out of the body (TESSERAUX & KOSS, 1999).

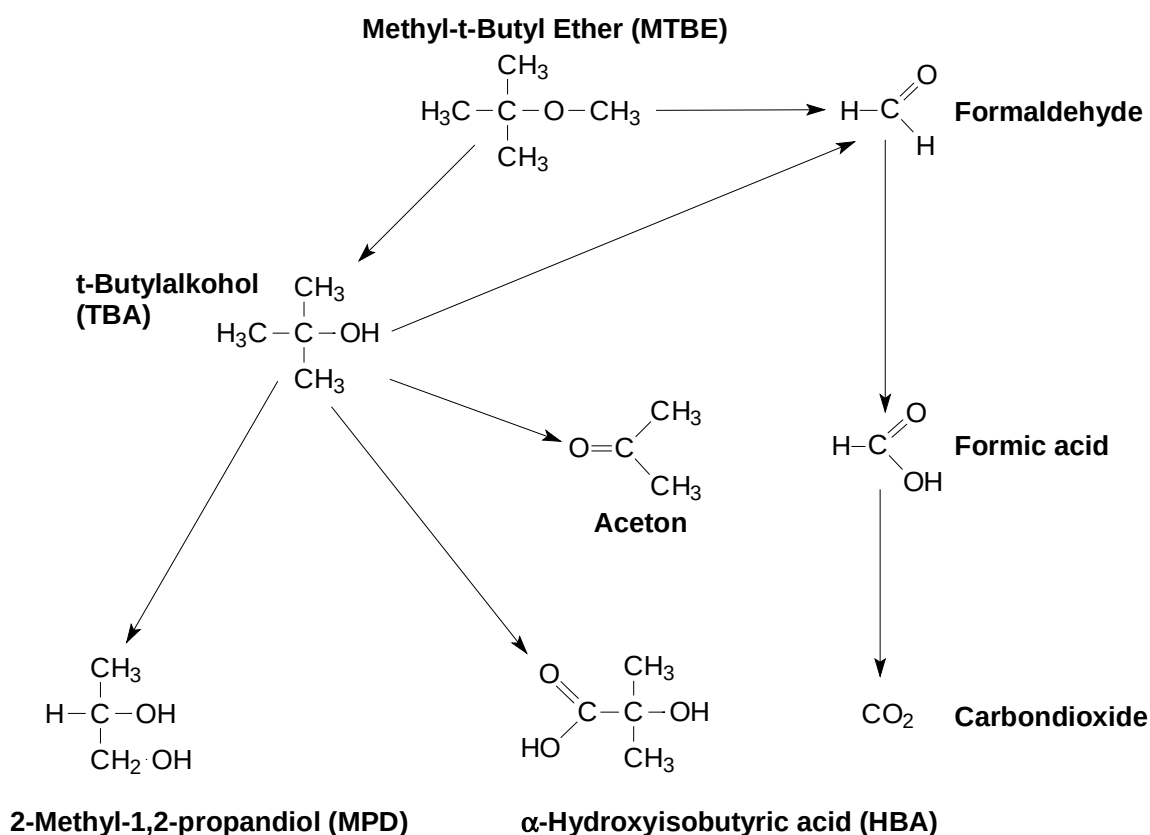


Fig. 5 Scheme of the possible metabolism of MTBE in animals (rat, mouse, rabbit) modified after TESSERAUX & KOSS (1999) and MILLER ET AL. (1997).

Possible metabolites are TBA, formaldehyde, α -hydroxyisobutyric acid (HIBA), 2-methyl-1,2-propanediol (MPD) and CO_2 (**Fig. 5**). The blood/fat distribution is in equilibrium at 1:10. Elimination is mainly performed via the kidneys (urine 65 % AR) and by exhalation through the lungs (21 % AR). Other excretion paths, such as via the faeces and skin, are only of minor significance. The elimination half-life for MTBE is < 1.0 h, and < 10 h for TBA (FROINES ET AL., 1998; MILLER ET AL., 1997). In a short-time tolerance study on healthy test subjects, NIHLIN ET AL. (1998a) found an exhalation rate of 32-47 % of the pollutant quantity taken up via the respiration (42-49 % of the available MTBE), which is roughly the same as found by MILLER ET AL. (1997) in an animal experiment. Due to its short biological half-life, they propose TBA as a marker molecule for MTBE in the body.

2.1.4.3 Acute toxicity

The acute risks to health of MTBE and its metabolites have also been studied on humans in some studies. In inhalation chamber experiments with various doses (5, 25, 50 ppm), NIHLIN ET AL. (1998b) did not find any concentration-dependent damage to health. They merely observed in all cases a slight irritation of the mucous membrane of the nasal cavity, which was, however, not concentration-dependent. After discontinuing MTBE pollution, the acute non-lethal health effects can mainly be classified as reversible.

In case studies, various symptoms were described by patients living in regions with increased use of oxygenated fuel additives. These symptoms include shortness of breath, hyperactivity, irritation of the mucous membranes, slight skin irritations as well as a reduced sensation of fright and pain (TESSERAUX & KOSS, 1999; OSTP, 1996; U.S. EPA, 1994). MTBE is one of the ethers and some of this group are used as anaesthetics. Various authors also report patients with anaesthesia and reversible disturbances of the central nervous system, even including coma, after an overdose (ECETOC, 1997). The latter effects mainly occurred with patients who had had gallstones dissolved using MTBE (**2.1.1**).

For oral uptake a "No Observed Adverse Effect Level" (NOAEL) of $40\text{-}100\text{ mg kg}^{-1}\text{ d}^{-1}$ was determined for acute toxicity (STELLJES, 1997; KLAN & CARPENTER, 1994). The "Lowest Observed Adverse Effect Level" (LOAEL) was established at $100\text{ mg kg}^{-1}\text{ d}^{-1}$. In some studies, the lethal dose (LD_{50}) after oral uptake was found to be in a range of $1600\text{-}3900\text{ mg kg}^{-1}\text{ d}^{-1}$ (TESSERAUX, 1999; ECETOC, 1997; STELLJES, 1997; U.S. EPA, 1994). The values determined for inhalation uptake for NOAEL, LOAEL and LC_{50} were 1440, 3600 and $65,000\text{-}649,000\text{ mg m}^{-3}$, respectively (TESSERAUX & KOSS, 1999; ECETOC, 1997; STELLJES, 1997).

For uptake via the skin, there is only an LD_{50} value for rabbits ($>10,200\text{ mg kg}^{-1}$, WHO, 1998). BROWN (1996) calculated possible uptake doses on the basis of environmental analyses and population data in order to compare them with the critical data. For this estimation, the author differentiated between various exposure scenarios - occasional uptake (0.1 mg kg^{-1}

¹ d⁻¹), exposure during working hours (0.4-6.0 µg kg⁻¹ d⁻¹) and a lifetime dose (0.01-0.1 mg kg⁻¹ d⁻¹). All theoretical exposure values were several orders of magnitude below the limits regarded as an acute danger to health. In addition to these theoretical estimates, there are also data from industry on measured concentrations in handling MTBE. Concentrations caused by production are less than 10 mg m⁻³, whereas values of up to 200 mg m⁻³ were measured while loading road tankers and up to 7.6 mg m⁻³ at filling stations (consumers) (ECETOC, 1997).

MEDLIN (2000) reports on a study in progress with various groups of test subjects, including a group of persons who state that they have been sensitised for MTBE, under environmentally relevant short-term pollutant exposure (e.g. filling up with gasoline). The sensitised group of test subjects reported significantly more acute complaints than the other persons and the control group. However, no psycho-physiological or neural changes were diagnosed. The study reinforces the findings of other working groups, according to which in the concentration ranges observed in handling MTBE, there is no dose-dependent effect relationship for the substance. Studies have also been performed that clearly relate the frequency of the reported complaints with the level of information of the persons concerned, and the media interest (ECOTOC, 1997; OSTP, 1996).

Taking into consideration the EU criteria for the classification of hazardous substances (EU 67/548 EWG), MTBE was not classified, so it is therefore not even regarded as "harmful". In general, MTBE can be regarded as having low toxicity for humans (KLAN & CARPENTER, 1994).

2.1.4.4 Chronic toxicity and asthma

The long-term use of MTBE as a fuel additive and its in part high persistence in the environment can lead to a long-term exposure of humans. The possible health hazards involved in such exposure will be described in detail in the following. The LOAEL and NOAEL are roughly in the same order as that of acute toxicity. Chronic and subchronic health complaints that have been found are diarrhoea and in some cases anaesthesia in the case of high doses (100-1200 mg kg⁻¹ d⁻¹). A reduction of body weight and that of some internal organs with an associated exhaustion of the experimental animals was observed with increasing duration of exposure (TESSERAUX & KOSS, 1999; GESTIS, 2001). It was not possible to establish a clear relation between the use of fuels blended with MTBE and an increase in the incidence of asthma in comparison to conventional gasoline. However, for its metabolites and combustion products, mainly formaldehyde, there is an increased risk of asthma in regions with heavy traffic (FROINES ET AL., 1998).

2.1.4.5 Neurotoxicity, mutagenicity and reproduction toxicity

As already described in **2.1.4.3**, high doses of MTBE can lead to reversible disturbances of the central nervous system. However, no permanent damage to the central nervous system has been described in the literature. However, temporary ataxia, lack of concentration and hyperactivity have been recorded for doses of 1200 mg kg^{-1} (U.S. EPA, 1994). However, as yet, a case study on the neurotoxicity of MTBE has only been performed in Finland. However, due to a lack of blood values this study is difficult to evaluate (FROINES ET AL., 1998).

In in-vivo and in-vitro experiments, MTBE has usually proved to be mutagenic (GESTIS, 2001, ECETOC, 1997; KLAN & CARPENTER, 1994), although its metabolite TBA is suspected of being mutagenic and the mutagenic potential of formaldehyde has been confirmed (OSTP, 1996).

At present, insufficient data are available for the assessment of the risk of reproductive toxicity of MTBE in man (OSTP, 1996). In animal experiments, only a slight reduction of the uterus weight and an increase in the oestrogen metabolism with increasing MTBE contamination ($28,800 \text{ mg m}^{-3}$) has been determined (GESTIS, 2001; TESSERAUX & KOSS, 1999; WHO, 1998). For formaldehyde, on the other hand, contradictory findings have been obtained with respect to the reproductive ability of the experimental animals. In some cases spontaneous abortions took place and anomalies were found in the offspring of the experimental animals (FROINES ET AL., 1998).

MTBE is not genotoxic (ECETOC, 1997).

2.1.4.6 Carcinogenicity

As yet, there have been no studies of MTBE and its metabolites on humans that was able to establish a relation between MTBE exposure and an increased risk of cancer. Many animal experiments have been performed with various uptake paths and doses of different levels. A carcinogenic potential has been established both for MTBE and also its metabolites and gasoline containing MTBE in animal experiments (OSTP, 1996). The elevated benzene fraction is probably responsible for the latter, which, regarded separately, has a higher cancer potential than MTBE. In all studies, the carcinogenic properties of MTBE were only determined in the medium- to high- dose groups (e.g. $10,800\text{-}28,800 \text{ mg m}^{-3}$) (STELLJES, 1997). After an inhalation uptake of 3000 ppm of MTBE over a period of two years, BORGHOFF ET AL. (1996) found renal carcinomas in male rats (FISCHER 344) and carcinomas of the liver in female mice (CD-1). The authors related these types of cancer to the protein α -2- μ -globulin, which, however, only exists in male rats. TESSERAUX & KOSS (1999) report lymphomas and leukaemia in female rats, which can probably be attributed to formaldehyde as the metabolite of MTBE.

A type of cancer frequently diagnosed in animal experiments with rats is the Leydig interstitial-cell tumour. Such tumours mainly occur in male rats and only at a high exposure level (34 % of the experimental animals, dose: $1000 \text{ mg kg}^{-1} \text{ d}^{-1}$) whereas in the female animals merely an increase in the number of leukaemia cases was found in the same dose group (25 % of the female experimental animals) (BELPOGGI ET AL., 1997). Many authors only indirectly related these leukaemia cases to MTBE, linking them instead to formaldehyde as the metabolite (Fig. 5) (TESSERAUX & KOSS, 1999; WHO, 1998). According to the IARC criteria, formaldehyde should be classified in the group of substances potentially suspected of being carcinogenic in man (2A).

The antiestrogenic effects of MTBE may be responsible for the formation of non-malignant liver tumours in mice ($\text{NOEL} = 10,800 \text{ mg m}^{-3}$). However, this concentration is far above the previously effective doses for acute and chronic effects (TESSERAUX & KOSS, 1999).

Doubt has been cast on the transferability of findings from animal experiments to humans and in some cases these results are not transparent (FROINES ET AL., 1998; OSTP, 1996). The mechanism of the origin of many types of cancer is not yet understood and thus makes transferability difficult. This is also true of formaldehyde. In the inhalation uptake of MTBE and the cancer potential resulting from it, the physiognomy of the organ of smell in humans and rats differs too greatly for reliable reactions in man to be concluded from the findings (FROINES ET AL., 1998).

On the basis of the different findings without any definitely positive or negative evidence for the carcinogenic potential of MTBE, the National Toxicological Program (NTP) in the latest version of its report on carcinogens has classified MTBE as a substance reasonably anticipated to be a human carcinogen (NTP 2001). The search for concentrations and mechanisms of action should not distract attention from the possible cancer risk emanating from MTBE but should rather protect consumers until MTBE is prohibited on the basis of an unambiguously positive classification (MEHLMANN, 2000). The International Association of Research on Cancer (OARC) has now corrected the cancer risk classification (Group 2b) of 1996 and only classed MTBE as a substance which cannot be classified as a carcinogen for humans (Group 3). The reasons for this were the lack of evidence for the cancer potential in humans and the limited data from animal experiments (IARC, 1999). In Germany, MTBE is classified in category 3B for carcinogenic substances ("Substances which due to a demonstrated or possible carcinogenic effect in man give rise to concern. There are indications of a carcinogenic effects, but these are not sufficient for classification in a different category. If the substances do not display any genotoxic effects than a TLV value can be laid down.", GESTIS, 2001). According to the EU Directive on Dangerous Substances (67/548/EEC), MTBE is to be classified in the group of non-carcinogenic substances (ECETOC, 1997).

2.1.4.7 Toxicity for terrestrial and aquatic organisms

In addition to studies on determining the toxicology of MTBE for humans, particularly with an environmental contaminant, the impacts on terrestrial and aquatic organisms must also be investigated. STUBBLEFIELD ET AL. (1997) only found slight toxicity for the invertebrate water organisms and fishes tested. Depending on species, the lethal concentration (LC_{50}) where 50 % of all experimental animals die, was on average about 250-550 mg L⁻¹. These concentrations are several orders of magnitude higher than those previously found in surface waters and rivers (2.1.2.3).

A further measuring parameter for the toxicity of a substance is the concentration of this substance in the environment at which a 25 % inhibition of the experimental organisms' activity is to be observed (IC_{25}). In the above-mentioned study this value was about 200 mg L⁻¹. Similar values were found by WERNER ET AL. (2001), WHO (1998) and ROWE ET AL. (1997), nevertheless in this case the fluctuations were much greater (invertebrate fresh water organisms: 57-1000 mg L⁻¹; aquatic vertebrates: 388-2600 mg L⁻¹). The values found for lethal doses to rodents such as rats, mice and rabbits can be taken from the toxicological studies on man (2.1.4.3, 2.1.4.4). No bioaccumulation was determined in fish since MTBE is completely exhaled or metabolised (WERNER ET AL., 2001; MANCINI, 1997). No other toxicological studies with different species of experimental animals have been described in the literature (U.S. EPA, 1994).

2.2 Analysis and sampling

Various already established methods can be used for the sampling and analysis of organic pollutants in the environment. Consideration must be given to the following points before selecting a suitable method:

- Concentration range in which the xenobiotics are expected in the environment (e.g. trace, ultratrace range).
- Matrix in which the pollutant is to be detected.
- Sample preparation (e.g. extraction, solid phase extraction (SPE), clean-up).
- Sampling technique (e.g. adsorption on solid phases).
- Qualitative or quantitative analysis.
- Pollutant and degradation products.
- Separation problem (various analytes and degradation products).

There are a number of publications on the detection of MTBE and other VOCs in the environmental compartments of water, soil and air, especially after the introduction of MTBE as a fuel component and its ubiquitous occurrence in the environment. However, only in the past few years it has been possible to perform inexpensive environmental analysis in the ppt range by the routine application of modern analytical techniques. A major focus of this literature survey is the detection of MTBE in groundwater and surface water, above all since more and more incidents of groundwater pollution are also becoming known in Europe and MTBE can be distributed over a wide area through the hydrological cycle (2.1.2). Nevertheless, it is not only important to identify the damage but also to localize the sources, such as atmospheric MTBE pollution as a diffuse source for the near-surface groundwater (PANKOW ET AL., 1997).

MTBE is a volatile semi-polar hydrocarbon (VOC), which can largely be readily separated from other organic substances by gas chromatography in one analytical scheme and can be determined by a suitable detector (e.g. flame ionisation detector (FID), electron capture detector (ECD) and the mass-selective detector (MSD)).

Other analytical methods for MTBE have been described in the literature by various authors: Fourier-transform infrared spectroscopy (FTIR) (IOB ET AL., 1998), microwave spectroscopy (SUENRAM ET AL., 1997) and nuclear magnetic resonance spectroscopy (MEUSINGER, 1999). A disadvantage of these methods is the lack of a separation of substance mixture or a matrix separation, which makes it difficult to use them for unknown mixtures of substances in environmental analysis.

Due to the wide range of techniques, in the following only analytical methods based on gas chromatography (GC) will be discussed in detail.

2.2.1 VOC and MTBE analysis in aqueous samples

A classical chromatographic method for the analysis of organic substances in aqueous medium is high-performance liquid chromatography (HPLC) with a diode array detector (DAAD) or coupled to a mass spectrometer (LC-MSⁿ). For MTBE the detection limit in groundwater without sample preparation is perceptibly above the ppm range (mg L^{-1}) using HPLC-DAAD due to weak absorption in the UV region.

The ppm concentration range (mg L^{-1} to $\mu\text{g L}^{-1}$) can be achieved with a simple GC/FID system. As yet, no analytical method has been developed which operates linearly with highly contaminated samples (mg L^{-1}) as well as in the trace range. The U.S. EPA has not laid down any method for MTBE analysis (POPP ET AL., 2001).

A robust and low-cost analytical method with detection limits in the ppm to ppb concentration range is static headspace-GC/FID. This headspace analysis can be used for aqueous and also solid matrices such as soil (LACY ET AL., 1995; MANURA, 1995). POPP ET AL. (2001) demonstrated that the headspace method displays a linearity for MTBE over a wide concentration range of 2-1500 $\mu\text{g L}^{-1}$ and can thus be used for the initial screening of a polluted site.

MTBE often occurs in the groundwater together with other hydrocarbons from the gasoline mixture. Due to their different physicochemical properties, particularly the HENRY coefficient, the composition of the headspace varies so that co-elutions may occur in the subsequent analysis. LACY ET AL. (1995) describe how a sequential flushing of the headspace can be used to separate MTBE from its co-eluent such as n-pentane, n-hexane and cyclopentene.

A somewhat lower detection limit can be achieved by the purge and trap (P&T) GC/FID method ($\text{DL} = 200 \text{ ng L}^{-1}$, sub-ppb concentration range; POPP ET AL., 2001). The P&T method is the standard method used by the U.S. EPA and USGS to detect volatile organic hydrocarbons in water. As yet, MTBE has not been included as a component to be detected in the U.S. EPA methods 602, 610 and 625 (THOMAS & DELFINO, 1991), nor was MTBE included in the P&T-GC/MS multimethod of the USGS up to 1995 (ROSE & SCHROEDER, 1995). For this reason, RAESE ET AL. (1995) expanded an analytical technique for MTBE and other oxygen-containing gasoline compounds from water samples on the basis of this method. They determined a detection limit for MTBE of 60 ng L^{-1} (80 ppt) and discovered a linearity in a range from 0.05 to 20 $\mu\text{g L}^{-1}$. MTBE can be unambiguously identified by a mass-selective detector and a co-elution with other compounds can be ruled out.

In 1995, the USGS then published an expanded P&T method for 86 VOCs which included MTBE. Although at 0.072 $\mu\text{g L}^{-1}$ the detection limit was somewhat poorer, nevertheless several substances could be detected simultaneously. Today the P&T analytical technique is

not only used in environmental monitoring, but also in industrial medicine, e.g. detection of MTBE in blood and urine after exposure (LEE & WEISEL, 1998; BONIN ET AL., 1995).

A simple and yet just as sensitive method as the headspace or P&T technique is direct injection (DAI) into a GC/MS system (CHURCH ET AL., 1997), in which a small quantity of aqueous sample (1-5 μl) is directly injected into the injection system of a gas chromatograph where it vaporizes and is separated into its components via the capillary column. Since during vaporization water is subject to a much greater expansion than other organic solvents (BRODACZ, 1998), a larger inlet must be installed in order to ensure the reproducibility of the measurement. In contrast to many other authors, CHURCH ET AL. (1997) used a polar capillary column so that polar components could also be better separated. With their method, they determined a detection limit of $0.1 \mu\text{g L}^{-1}$ for a wide spectrum of analytes. Using a combined GC/MS-FID, HONG ET AL. (1999) detected a minimum of $30 \mu\text{g L}^{-1}$ or 1 mg L^{-1} by FID. However, the direct injection method does not only involve advantages, such as simplicity and speed since there is no sample preparation (POTTER, 1996), but also leads to a reduction of separation column life (GROB, 1984) and in part a perceptible retention time shift during the injection of water onto the separation column (POTTER, 1996). If a suitable separation column and furnace programme were selected, all the above-mentioned methods were capable of separating MTBE and its metabolites from other gasoline additives.

Detecting MTBE in the ultratrace range requires somewhat greater sample preparation and measurement efforts. Solid phase microextraction (SPME), coupled with a GC/MS analysis, has proved to be very sensitive (ppt range) for MTBE and other gasoline components (e.g. BTEX) (POPP ET AL., 2001).

ACHTEN & PÜTTMANN (1999) detected MTBE in the ppt concentration range (ng L^{-1}) in surface waters. To this end, they used a cooled carboxene/polydimethylsiloxane (PDMS) fibre (5°C) for the extraction. This loaded fibre was then thermally desorbed, and separated and analysed by means of GC/MS. In order to improve the extraction yield, salting out with sodium chloride and an optimum sample temperature of approx. 18°C was additionally selected.

In the same way, CASSADA ET AL. (2000) and PIAZZA ET AL. (2001) used SPME to extract MTBE and other oxygenated components from water. They also optimised the extraction yield by salting out, but they used a divinyl benzene/carboxene/PMDS fibre for the SPME. After an analysis with the GC/MS system, they achieved a detection limit of 8 and 14 ng L^{-1} respectively (8 and 14 ppt).

Using a carboxene/PMDS fibre and coupled to a GC/MS system, POPP ET AL. (2001) achieved a detection limit of less than 37 ng L^{-1} (50 ppt) even without salting out and reducing the sample temperature.

2.2.2 Sampling, VOC and MTBE analysis in air

Three procedures are differentiated for the sampling of VOCs in air:

1. Sampling in evacuated, polished steel vessels
2. Active sampling on solid adsorbent materials
3. Passive sampling on solid adsorbent materials

In the same way as with the analysis of VOCs in the aqueous phase, before taking samples in air the spectrum of analytes and the concentrations to be expected must be estimated. Before sampling can begin, the stability of the collected substance in the sampling system must first be investigated in the evacuated steel vessels and on the adsorbent material. KELLY ET AL. (1993) tested this in some preliminary experiments and then also performed field experiments which demonstrated the performance of this collecting technique. The authors found a detection sensitivity $< 0.2 \mu\text{g m}^{-3}$ (< 54 ppb). In Germany, there is a VDI (Verein Deutscher Ingenieure e.V.) guideline which describes the performance and evaluation of such analyses with sampling in stainless-steel vessels (VDI, 1986a-c). The American environmental protection authority (U.S. EPA) has also issued a guide for measuring VOCs with sampling in passivated stainless-steel canisters (U.S. EPA, 1997).

With a solid adsorbent material, the breakthrough volume of the components to be analysed must be additionally determined (3.4.1.1.2; BROWN & PURNELL, 1979). There is a suitable adsorbent material for almost all VOCs (FIGGE ET AL., 1987). Sampling is followed by desorption with subsequent analysis. This procedure is often performed today by coupling thermodesorption to GC/MS. Thermodesorption cannot be applied if activated charcoal is used as the adsorbent material. Carbon disulphide (CS_2) has proved to be the best solvent for eluting adsorbed hydrocarbons on activated charcoal (VDI, 1984d-e). However, this method is only rarely used for reasons of health due to the high toxicity of CS_2 . Furthermore, in the case of a solvent elution the sample is diluted and detection sensitivity reduced.

Various adsorbents on a polymer basis (HAIDER & MALISSA, 1999; MOSKOPP, 1998; BROWN & PURNELL, 1979) and on a carbon basis (BROWN, 1996; STEIN & NARANG, 1996; PANKOW ET AL., 1998; FIGGE ET AL., 1987) are available for sampling VOCs in air. The selection of suitable sorbents, sampling volumes and methods is laid down in a number of regulations. The Verband Deutscher Ingenieure (VDI - Association of German Engineers) presented a guideline for air accumulation on adsorbents for thermal desorption (VDI, 1988).

For this purpose, Tenax TA, a polymer adsorbent, is suggested to be suitable for the accumulation of C6-C26 hydrocarbons for environmental sampling. In addition to the wide range of substance classes, Tenax also displays an extremely low affinity for atmospheric water which increases collecting efficiency. Another spectrum of analytes and adsorbents is described in the draft of the European standard (prEN ISO 16017-1) (EN, 1998)..

The NIOSH Guidelines for Air Sampling (KENNEDY ET AL., 1996) represent a current world-wide standard. During sampling on adsorbent test tubes, air is pumped over the adsorbent at a low volumetric flow rate of 10-200 mL min⁻¹. The sampling duration depends on the air concentration and breakthrough volume of the substances (EN, 1998). A sampling volume of 1-10 L and an enrichment duration of 4-8 h are usually applied.

PANKOW ET AL. (1998) developed a method for enriching MTBE and 86 other analytes in the outside air with a detection limit (< 0.06 ppb (0.21 µg m⁻³). No breakthrough was measured for any of the 87 analytes using Carbotrap B/Carboxen 1000 multibed at a sampling volume of 1.5-5 L of outside air.

Diffusion collectors are used today for workplace monitoring and job-related estimates of health risks. The systems used have, for example, a recovery rate of 100 % for MTBE (HARPER ET AL., 1996).

3 Materials and Methods

The present dissertation investigates the transport behaviour of the fuel additive MTBE from the aquifer through a soil layer into the atmosphere. Transport through the soil is of special significance in this process. This involves a complex system consisting of the soil structure, soil gas, soil water and a variety of microorganisms in which strong interactions between MTBE and its environment can take place.

In order to understand details of the transport processes, a three-stage experimental approach was selected:

1. Degradation studies in the soil type used (3.1)
2. Column experiments under defined conditions (3.2)
3. Wind-tunnel lysimeter study (3.3)

An appropriate sampling and analysis technique first had to be developed and established for these experiments (3.4).

3.1 Degradation studies

3.1.1 Experimental concept

Two studies were performed on the degradation and volatilisation behaviour of [α , α' -¹⁴C]-MTBE in a soil which had not been previously petrochemically contaminated (A_p horizon). A modified experiment approach was chosen based on the BBA guideline (Biologische Bundesanstalt für Land- und Forstwirtschaft, 1986) after ANDERSON (1975) and ANDERSON & DOMSCH (1975) (3.1.2). In a preliminary experiment, the influence of various environmental

parameters on degradation and variation over time (Study 1: JAGETTSBERGER, 2000). This also included the influence of soil moisture and soil type. A detailed investigation was subsequently started, taking into consideration the findings of Study 1 (Study 2). Only the most efficient variants from Study 1 were selected and investigated in detail. **Tab. 3** gives an overview of the different variants from the two studies.

Tab. 3: Variants in degradation study 1 and 2 on the degradation behaviour of [α , α' - ^{14}C]-MTBE in soil

Variants	Abbreviation		Parallels		Sampling Dates	
	Study 1	Study 2	Study 1	Study 2	Study 1	Study 2
control, sterile, 80 % WHC _{max}	KSF	KSF	3	3	5	8
control, sterile, 40 %WHC _{max}	KST	-	-	-	5	8
untreated, 80 % WHC _{max}	FF	FF	3	3	5	8
untreated, 40 % WHC _{max}	FT	-	-	-	5	8
alluvial loam, 40 % WHC _{max}	DS	-	-	-	5	8

3.1.2 Experimental procedure

The experimental system consisted of a 250 mL Erlenmeyer flask, with a trap for gaseous organic molecules such as CO₂, and a sealable aeration nozzle (**Fig. 1**). 100 g air-dried soil sieved to a grain size of 2 mm from the Ap horizon of a gleyic cambisol (Kaldenkirchen-Hülst) was weighed into the 250 mL Erlenmeyer flask, or in the case of Study 1 also from the fAhGo horizon of an alluvial loam (Research Centre Jülich). A more comprehensive list of the soil parameters and a brief profile analysis of the soils used are described in Chapter 3.5).

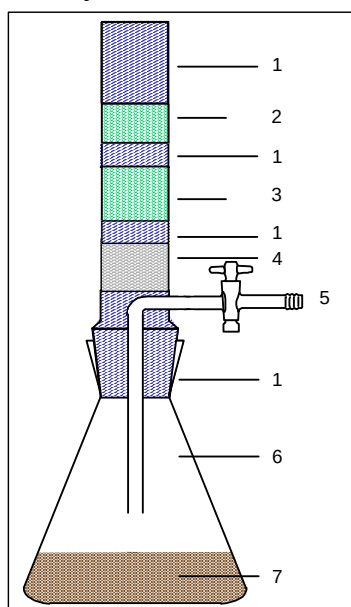


Fig. 6: Cultivation system for investigating the degradation, evaporation and soil fixation of [α , α' - ^{14}C] MTBE in soil (modified after ANDERSON, 1975):

1 = glass wool, 2 = soda lime pellets for CO₂-absorption, 3 = soda lime pellets for $^{14}\text{CO}_2$ absorption, 4 = activated charcoal, 5 = air inlet, 6 = Erlenmeyer flask, 7 = soil

After having been weighed into the flask, the soil was partially moistened with CaCl₂ solution (10 mM), the flask was covered with aluminum foil as a protection against contamination and stored in the incubation cupboard at 20 °C until the experiment began. The degree of moistening varied depending on the variant (**Tab.3**). The initial addition of CaCl₂ solution was 5 mL less than necessary for adjusting the WHC_{max} values since this was added later with the application solution. The water content of the soil in the experimental pots was determined gravimetrically at regular intervals and if necessary the original value was adjusted again.

For the sterile variants, some of the flasks were sterilized three to five times in the autoclave (**Tab. 4**). Between sterilizations, these reaction vessels were placed in the incubation cabinet for one to two days to germinate. Some of the traps were also subjected to heat stabilization for the sterile experimental variants.

Tab. 4: Sterilization parameters for soil, instruments, solutions and traps in the degradation studies

	Sterilization Type		
	moist	dry	dry
target	CaCl ₂ -Lsg, bidist, soil	instruments	traps
instrument	GLA40/3 ^①	GLA40/3 ^①	VT 5042 ^②
pressure	2 bar	2 bar	1 bar
duration	60 min	60 min	4 h
temp.	121 °C	121 °C	180 °C

1 Goessner, Hamburg

2 Heraeus, Hanau

The traps were filled with layers of different absorbents. On the one hand, with activated charcoal (1.5 mm grain size, Merck, Darmstadt) to adsorb volatile organic compounds such as MTBE and its metabolites and, on the other hand, with two layers of soda lime pellets with an indicator (Fa. Merck, Darmstadt). The upper layer of soda lime serves to take up atmospheric CO₂ and the middle soda lime filling serves for the sorption of ¹⁴CO₂ as a mineralization product of ¹⁴C-labeled MTBE as well as CO₂ from the soil respiration.

The first samples were taken directly after application (**3.1.2.1**) in order to obtain the original degradation values. Depending on the study, further sampling was performed on different days. In accordance with the experimental approach, some of the flasks were sampled in Study 1 after 0; 3; 8; 10 and 18 days after application, and in Study 2 after 0; 0.3; 1; 2; 3; 4; 8 and 101 d. To this end, in each case three flasks of the individual variants were taken from the experiment as parallels on the day in question. In doing so, the experiments were investigated with respect to the distribution of MTBE (**3.1.2.3**), volatilised and mineralised MTBE (**3.1.2.2**) remaining in the soil/soil water.

3.1.2.1 Application

The application consisted of a CaCl_2 solution (10 mM), MTBE for spectroscopy (Merck, Darmstadt) and radioactive $[\alpha, \alpha'\text{-}^{14}\text{C}]$ - MTBE (Sigma Chemical Company, St. Louis, USA). Since MTBE is a very volatile substance at room temperature, the radioactive MTBE was supplied in a glass break-seal ampoule (**Fig. 7**). In order to avoid gaseous losses in preparing the stock solution, a special gastight application container was attached to this ampoule. This container has a reservoir for the CaCl_2 solution, a double-safety system consisting of a Teflon/glass tap with a subsequent silicone septum and a magnetic agitator.

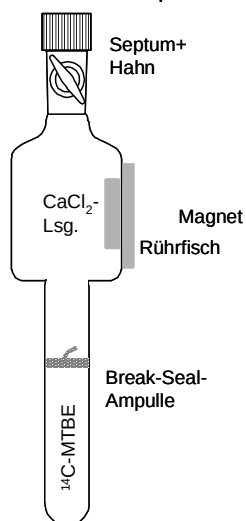


Fig. 7: Arrangement of the application container for the degradation studies.

First of all, 227.6 ml of CaCl_2 solution (10 mM) was placed in the container, 240 μL of MTBE was then added and the application container sealed. In order to add the radioactive MTBE to this solution, the predetermined breaking point of the break-seal ampoule was broken by the magnetic agitator and an external magnet. The solution was then shaken several times to ensure complete mixing.

Using a 20 cm hollow stainless-steel needle and a gastight glass syringe, 5 mL of this solution was removed through the septum and the plug and added dropwise to the Erlenmeyer flask, in the course of which the tip of the needle was inserted into the soil at various locations in order to achieve the most uniform distribution possible in the moist soil. For the sterile variants, the syringe and hollow needle were replaced by sterilised instruments. After the application solution had been mixed in, the gas trap was mounted directly on the cultivation system (**Fig. 6**).

3.1.2.2 Trap preparation

On each sampling day, the traps and the corresponding Erlenmeyer flasks were first separated, the flask being flushed for 3 min with a nitrogen flow (N_2) of 100 mL min^{-1} via the

aeration nozzle so that the molecules present in the gas phase were adsorbed in the trap. The trap was subsequently removed and the individual fractions separated. The activated charcoal (7 g) was ground and homogenized by a ball mill (Retsch) before the 3 x 100 mg aliquots mixed with microcrystalline cellulose were combusted in the incinerator (Oxidizer, **3.4.2.1**).

The remaining activated charcoal was then extracted with 20 mL acetonitrile p.a. (Merck, Darmstadt) for 30 min at 1750 U min^{-1} by means of a mechanical shaker (type SM 25A, Bühler, Tübingen). This mixture was then centrifuged (type GPKR, Beckmann, Munich) at 2000 U min^{-1} to sediment the activated charcoal. The supernatant was decanted and centrifuged again in an ultracentrifuge (type Mikro Rapid, Hettich, Tuttlingen) at $10,000 \text{ U min}^{-1}$ in order to sediment all the remaining suspending matter. The supernatant was subsequently examined in the liquid scintillation counter (LSC) (**3.4.2.1**) with respect to its radioactivity content. In this way it was possible to determine the quantity of volatilized substance and the extraction yield in comparison to the ashing values. The extract was examined for possible metabolites using radio-HPLC (**3.4.2.3**).

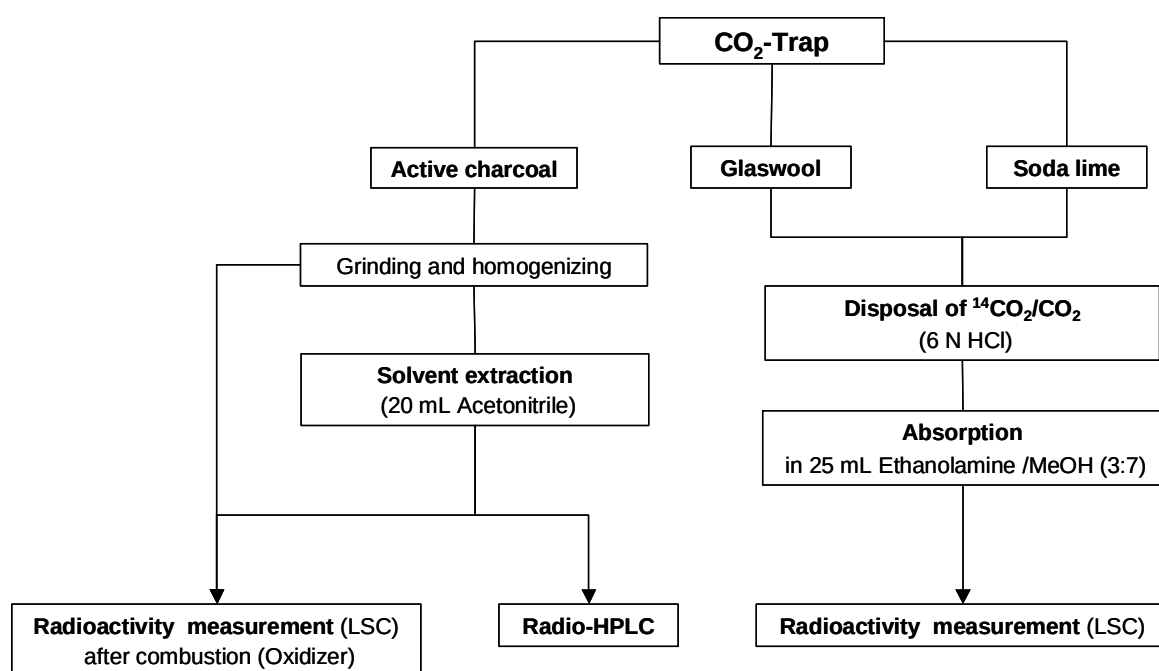


Fig. 8: Block diagram of trap workup in the degradation studies with [α,α'-14C]- MTBE on the individual sampling days.

The glass wool and the soda lime were recombined and the adsorbed ¹⁴CO₂ was released with 6 N hydrochloric acid (HCl) in an apparatus modified after ANDERSON (1975). The resulting ¹⁴CO₂/CO₂ was sorbed in an ethanolamine-methanol solution (v/v 30:70) and the quantity of mineralized MTBE determined by ashing the radioactivity in the LSC.

3.1.2.3 Soil samples preparation

After the trap had been removed, approx. 10-14 g of moist soil was removed from each Erlenmeyer flask and transferred to a special Duran flask to determine the biological activity (DMSO/DMS reductase rate (ALEF, 1990) (3.4.2.4)). The remaining soil was covered with 50 mL CaCl_2 solution (10 mM), sealed with a glass plug and extracted for 30 min on the mechanical shaker at 1750 U/min^{-1} . The soil/ CaCl_2 solution suspension was subsequently transferred into a centrifuge glass and centrifuged for 30 min 2000 U min^{-1} . In order to minimize gaseous losses, the centrifuge glasses were sealed with silicone plugs. The supernatant was decanted and the extraction yield directly determined in the LSC (3.4.2.1). Furthermore, the extract was examined for possible metabolites by radio-HPLC (3.4.2.3). The unextracted radioactivity was determined by ashing the previously air-dried and homogenized soil in the oxidizer (3.4.2.1).

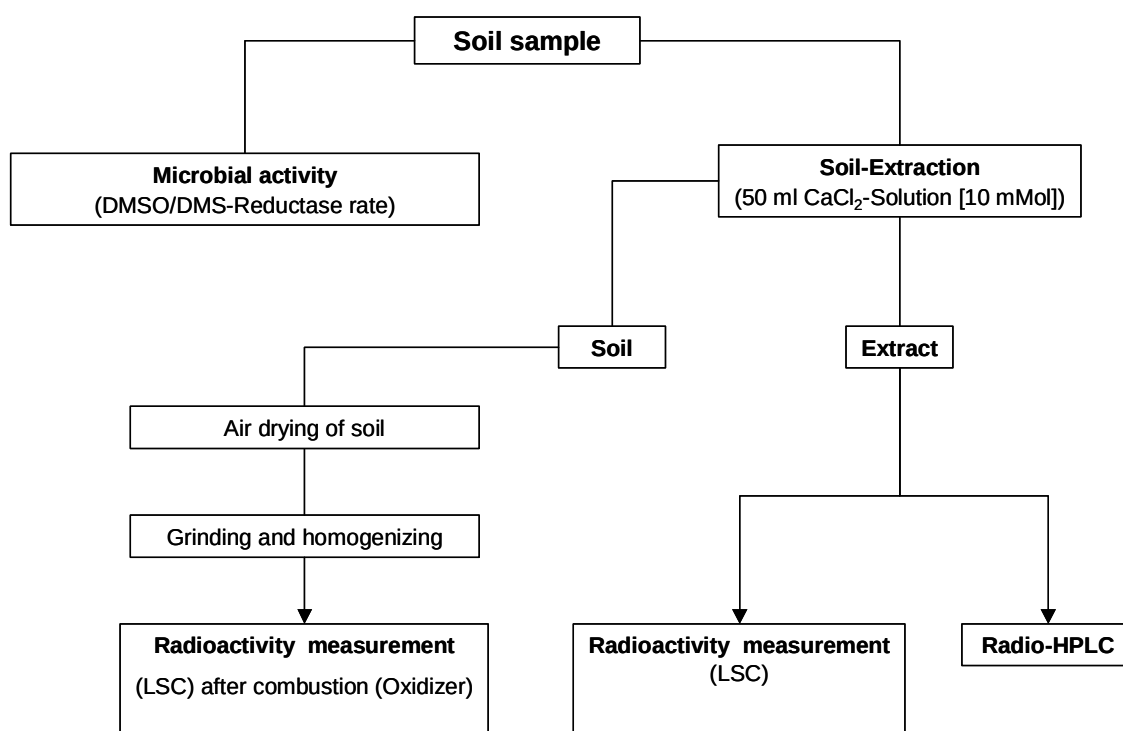


Fig. 9 Block diagram of soil workup in the degradation studies with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ - MTBE on the individual sampling days.

3.2 Column experiments

The transport studies were performed under defined conditions in an undisturbed soil core with the aid of column experiments. The apparatus required was not as sophisticated as for the lysimeter experiments in the wind tunnel (3.3). However, it differed considerably from simple laboratory experiments and represented an intermediate stage between the simplified laboratory experiment (3.1) and the wind-tunnel experiment under field-like conditions (3.3). First of all, a column experiment was designed and constructed as a undisturbed ecosystem section with the three environmental compartments of groundwater, soil and atmosphere. Two column experiments were then performed with this facility. The first experiment was performed with inactive MTBE without the application of the radioactively labeled model substance. In the second experiment, ^{14}C labeled MTBE was additionally used for detection reasons.

3.2.1 Conception/environmental compartments

An experimental facility for transport studies on gaseous substances was first designed on the basis of undisturbed soil columns previously used at the Institute of Radioagronomy (20 cm Ø, 60 cm column length) (BRANDT, 1997) (**Fig. 10**). This facility consisted of an aquifer (3.2.1.3, GW), an undisturbed soil core (3.2.1.2, SC) and an atmospheric chamber (3.2.1.1, GT). Furthermore, the facility enabled all the necessary parameters such as temperature, air humidity and the selected volumetric flows, to be recorded and the experiments to be run by PC-controlled sampling (3.2.1.4) without investing a great deal of manpower. **Fig. 11** gives a diagrammatic overview of the experimental column facility with continuous implementation of the experiment with respect to air sampling. The facility was set up in an air-conditioned room in the restricted area of the Institute of Radioagronomy (ICG-5) in order to create isothermal conditions for the respective experiments. During the experiments, the room temperature was kept at $22.4 \pm 0.9^\circ\text{C}$ and $21.2 \pm 1^\circ\text{C}$ during the day and night, respectively. Neither the illumination nor the humidity of the room air had any influence on the experiments. The glass dome was shielded from the illumination and the initial moisture of the experimental facility was almost constant since there was an air-conditioning system at the air inlet of the column.

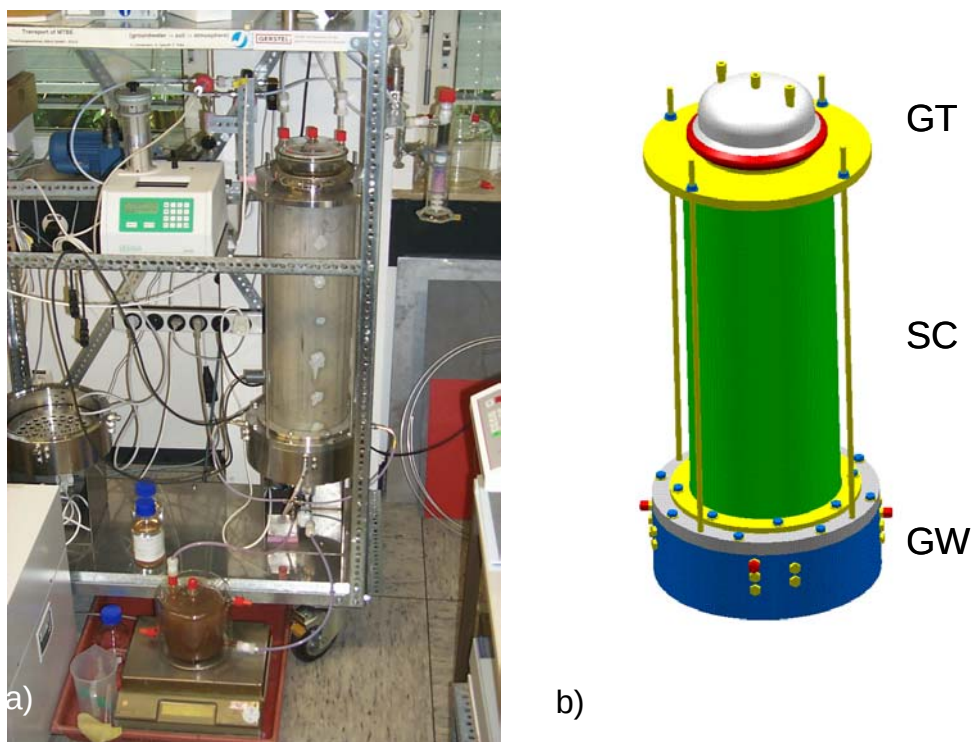


Fig. 10: (a) Experimental column facility at the Institute of Radioagronomy for measuring the transport of volatile organic compounds after groundwater contamination, (b) 3-D view of the undisturbed soil column (SC) including the groundwater vessel (GW) and column head (GT).

3.2.1.1 Atmosphere

In the stainless-steel column used, there was an airspace 10 cm in height above the soil, which together with the glass dome and the column head formed the atmospheric chamber. On the top, the glass dome had three openings with screwed connection caps GL 14 (**Fig. 10**) and on the lower surface a standard flat flange (DN 150), by means of which it could be connected gastight to the column head by a quick-release lock. The two outer screwed joints served as the inlet and outlet for the air flow over the soil surface through the artificial atmosphere (GT). To this end, two crescent-shaped blower rods perforated on the lower side and adapted to the inside of the column were fixed at a height of 1 cm above the soil by means of a silicone seal with PTFE sleeves (Schott, Mainz) and the GL 14 screwed joint in the glass dome. This arrangement is intended to generate a laminar flow profile over the soil by drawing in the air from the atmosphere at the inlet. The only access to the gas chamber (atmosphere) was provided via the second blower rod and the air conditioning connected in front of it (**Fig. 11**, AF). Air conditioning was provided by intensive washing bottles (250 mL) filled with layers of silica gel (Merck, Darmstadt), Sikapent (Merck, Darmstadt) and activated charcoal. In the first experiment a flow meter was connected in the air flow at the column inlet, but due to a very high flow resistance this was replaced in the second experiment by a

flow meter at the air conditioning inlet. The atmospheric humidity and the temperature were determined in the air flow (100 mL min^{-1}) drawn in from the column atmosphere, and controlled via various solenoid valves (**Fig. 11**, VM_x), before adsorption of the organic components of the air on the thermal desorption tube (**Fig. 11**, TDT). In the second experiment, an air dehumidifier (**Fig. 11**, C) was installed and, connected in series, another temperature/air humidity sensor (**Fig. 11**, RH/T). The resulting condensate was collected at the end of the dehumidifier and examined with respect to possible dissolved organic components. A second pump (**Fig. 11**, P) was integrated into the system for the continuous sampling of the atmosphere, also during measurement of the external air. Air analysis and also the total air flow was undertaken by a Desaga gas sampler (Ttype GS 301, Desaga GmbH, Wiesloch). This consisted of a pump with flow controller and sample revolver for 10 thermodesorption tubes. Each thermodesorption tube can be programmed and sampled separately with respect to time and either volume or volumetric flow. The total volumetric flow was passed through the thermodesorption tubes in order to achieve the highest possible detection sensitivity. The air temperature above the soil column was recorded continuously by temperature sensors (Pt-100).

3.2.1.2 Soil

As described in **3.1**, a gleyic cambisol from the Kaldenkirchen-Hülst site (for soil parameters see **3.5**) was used as the experimental soil. Removal of the soil columns and their preparation is described in **3.2.2.1**. The soil cores were 60 cm in length with a diameter of 20 cm. In the experimental facility, the soil column was positioned about 62 mm in the gastight groundwater vessel fixed by the column foot and the lid of the groundwater vessel with a pinch seal. The soil moisture was read off manually once a day at two heights (20 and 40 cm below the soil surface) by means of time-domain reflectometry (TDR) sensors (type Trime FM, IMKO Mikromodultechnik GmbH, Ettlingen). The TDR method is based on a measurement of the dielectric constants of the soil and the resulting moisture content (per cent by volume = vol%). The soil temperature was assumed to be constant and the same as the room temperature since before starting the experiment the soil column had been in the temperature-controlled environment for a sufficient time. However, the soil temperature in the topmost centimeter of the soil surface was measured in order to record any possible temperature differences due to evaporation (**Fig. 11**, T). In addition to these parameters, the column was also prepared for the withdrawal of soil gas.

The steel case was provided with small boreholes ($\varnothing 2 \text{ mm}$) at intervals of 10 cm, which were sealed with fungicide-free silicone (Sista F109 Silikon seam sealant, Henkel KGaA, Düsseldorf). These septa were pierced by a 20-cm-long stainless-steel needle for gas sampling, the hollow space of the needle being protected against clogging with soil particles by a stainless-steel core. This core was carefully removed after the injection. Gas from the soil was sampled by a gas tracer pump (type accuro, Dräger Sicherheitstechnik GmbH, Lübeck).

and an adsorbent test tube (**3.4.1.1.2**) between the hand pump and the stainless-steel needle. All other soil parameters were only determined after the experiment.

3.2.1.3 Groundwater

The simulated aquifer consisted of a cylindrical stainless-steel vessel which could be sealed gastight (**Fig. 10b**, GT). The soil column was centred in this vessel and sealed gastight with the column foot, cover of the groundwater vessel and the pinch ring. O-ring seals of acrylonitrile-butadiene rubber (Perbunan N, NBR) were positioned between the components to seal the individual metallic components. A CaCl_2 solution flow (10 mM) flowed through the groundwater vessel from bottom to top. To this end, a $\frac{1}{2}$ " opening with a regulator valve was incorporated as a central inlet under the soil column in the bottom of the vessel. In this way, groundwater was pumped into the groundwater tank from a storage tank. The overflow returned to the temperature-controlled groundwater reservoir (**Fig. 11**, WT) through four $\frac{1}{4}$ " overflow outlets arranged at a 90° angle. This design enabled the level of the groundwater level at the soil column to be freely selected by varying the height of the over-flow in the groundwater container. By installing a baffle plate above the inlet opening and by using a fine-meshed stainless-steel gaze, it was possible to prevent the soil being washed out by the water jet. This ensured that the contaminated groundwater in contact with the soil body at all times. The water temperature was determined directly at the column by using a temperature sensor (Pt-100). This temperature was adjusted by varying the temperature of the cooling jacket at the groundwater storage vessel. The cooling jacket and the air dehumidifier for the gas chamber were operated at a temperature of 7.3°C via a water circulator (type FE 1100, Julabo, Seelbach). This corresponds to a water temperature of $11.4^\circ\text{C} \pm 0.8^\circ\text{C}$ or $9.4^\circ\text{C} \pm 0.4^\circ\text{C}$ inside the groundwater reservoir.¹ In order to keep the cold losses low and to avoid condensation problems, the storage tank and all the hose connection to the groundwater vessel were fitted with insulated jackets (type Armaflex AF, Armcell, Leutkirch). In order to indirectly record the evaporation, the groundwater reservoir was placed on a balance and, moreover, in the second experiment was equipped with a volumetric scale via a riser pipe. In addition to this equipment, it was also possible to take samples and, if required, to supplement the substance to be studied at the groundwater reservoir. For this purpose, a stainless-steel needle with a Luer seal and a 3-way cock with a T-hole of PTFE (CS-Chromatographie, Langerwehe) attached to it was passed through a septum in the middle of the reservoir and was sealed with silicone. In this way it was possible to sample the groundwater without losing any substance to the outside air.

¹ There was a higher groundwater change rate in the second experiment, which resulted in a lower groundwater temperature in the groundwater reservoir.

3.2.1.4 Data acquisition and control unit

Data acquisition and sampling control was performed via a computer-assisted data acquisition system (type PCI-20,000, Intelligent Instrumentation, Leinfelden), as already described in STORK (1995). Various parameters such as air humidity, air temperature, soil temperature and groundwater temperature were recorded (**Fig. 11**). The first time the data acquisition was also used for process control. In the column experiment, air sampling was controlled via a PC plug-in (type PCI-20,048 with 48 I/O channels). The data recorded were stored on the computer every 24 hours in the form of an AFD file (ASCII format) and were subsequently imported in Microsoft® Excel and further processed. All data were recorded every 5 min and stored together with the date and time.

3.2.2 Experimental

The column experimental facility described in **3.2.1** was used to perform two experiments with continuous air sampling. MTBE was used in the first experiment, and in the second experiment [α,α - ^{14}C]-MTBE and MTBE. First of all, in November 1997 soil columns were removed (**3.2.2.1**), conditioned and installed in the facility before the experiment.

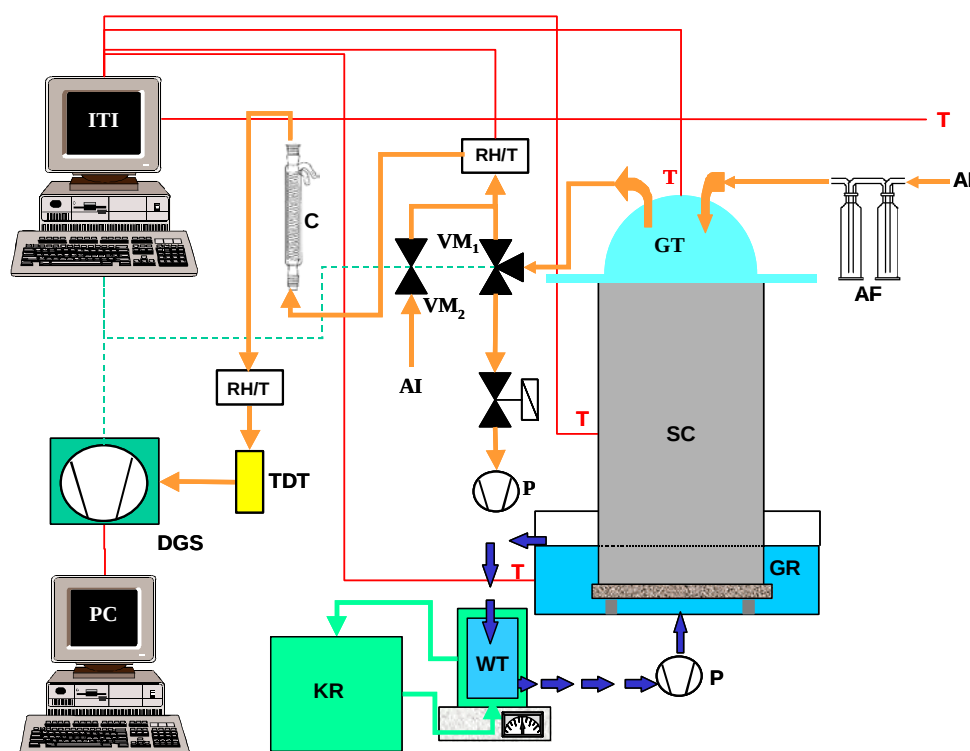


Fig. 11: Schematic diagram of the experimental set-up of the new column facility for continuous sampling of the volumetric air flow over an undisturbed soil column with simulated groundwater accumulation.

(AF = activated charcoal and dryer unit, AI = air inlet, C = air dehumidifier, DGS = Desaga gas sampler, GR = groundwater reservoir, GT = column head, ITI = data acquisition, KR = water circulator, P = pump, PC = data storage, SC = soil column, RH/T = moisture/temperature sensor, T = Pt-100, TDT = thermodesorption tube, VM_x = solenoid valve, WT = groundwater tank.

After a period of 14 days, the experiment was concluded and the final samples taken (3.2.2.4). **Fig. 11** shows the mode of operation of the experimental facility. The control lines from the PC system (ITI) are shown by dotted lines, the recorded parameters by solid lines, and the material flows by arrows (air flows; groundwater flow; coolant).

3.2.2.1 Taking the soil columns

In November 1997, four soil columns were removed at the Kaldenkirchen-Hülst site (3.5) by means of a hand-held hydraulic ram and an abutment fixed by ground anchors. To this end, two 3-m long ground anchors were screwed into the ground to a depth of 1 m at a distance of 1.9 m from each other. These anchors fixed a double-T steel girder which served as an abutment for the hydraulic ram. The empty stainless-steel columns were arranged uniformly and perpendicularly below the steel girder. The stainless-steel cylinders were driven vertically into the ground by a pressure plate and the hydraulic ram.

After the first steel cylinder had been almost completely sunk into the ground, the procedure continued analogously for the other cylinders. Subsequently, all the soil columns obtained in this way were then excavated by hand and the sub-soil removed from the bottom. The columns were transported to the open-air site (restricted area) of the Institute of Radioagronomy and prepared for the column experiments by being stored and conditioned for several weeks before beginning the experiment. The sub-soil was carefully leveled off to ensure safe positioning in the experimental facility, low soil leaching in the simulated groundwater accumulation and the necessary capillary connection of the soil monoliths.



Fig. 12: Getting the undisturbed soil columns with a hand-held hydraulic ram and a T-girder abutment fixed by ground anchors in Kaldenkirchen-Hülst on 26 Nov., 1997.

The column prepared in this way was placed on a base plate with a stainless-steel gaze (mesh width 40 μm , Kaldenbach, Berlin) covered with quartz sand (height 2-5 mm, $\varnothing$ 40-70 μm , SiLibeads type S, Lindner, Warmensteinach). During column conditioning, the columns were irrigated with 3 mm d⁻¹ CaCl₂ solution (10 mM) to saturate the soil with water and stabilize the colloids. This procedure was repeated several times until a constant percolate volume had been established per unit time so that it could be assumed that the soil had been saturated with moisture.

3.2.2.2 Experimental preparations

One week before the first experiment at the latest, the conditioned soil column was installed in the facility and directly exposed to an accumulation of groundwater, initially without contamination. Due to material defect at the foot of the column and the resulting corrosion, in the second experiment the soil column was only installed two days before beginning the experiment. Furthermore, the column foot was sealed with silicone (type Sista F109) at the transition to the soil column, and all components in contact with water were inertized with a Teflon spray (Klinger flon, Klinger, Idstein) after scrubbing with steel-wool. Using a special carrying device, the columns were placed manually in the groundwater containers and screwed to the other components. All joints were sealed once again with silicone from the outside. The TDR sensors were then installed and also pasted over with silicone. Immediately after the facility had been set up, the groundwater accumulation began, in the course of which the system was flooded with 3.6 L or 3.75 L CaCl₂ solution (10 mM) via the storage tank (**Fig. 11**, WT) until the first solution flowed back from the overflow.

3.2.2.3 Experimental procedure

After the experimental facility had been set up, the experiment was first performed for 1-2 d without the groundwater being contaminated. This enabled the blind values of the air samples to be obtained and the system checked with respect to correct functioning and tightness. In the first experiment, 970 μL of unlabelled MTBE was applied with a glass syringe via the 2/3 way-cock to the groundwater reservoir and the syringe flushed several times with the groundwater ($C_{\text{MTBE}} = 198 \text{ mg L}^{-1}$).

In the second experiment, initially 20 mL of the application solution from 555 μL of non-radioactive MTBE and [α,α' -¹⁴C]- MTBE (34.7 kBq mL⁻¹) was prepared in 10 mM CaCl₂ solution in a graduated flask ($C_{\text{MTBE}} = 110 \text{ mg L}^{-1}$). The content of the flask was injected into the groundwater reservoir by a glass syringe. Both the flask and also the syringe were rinsed several times with the groundwater in order to ensure that the MTBE was transferred as completely as possible. The quantity of MTBE remaining in the syringe and in the decontamination solutions was measured in the LSC to ascertain its radioactivity and the net quantity of MTBE

/ [α,α' - ^{14}C]- MTBE applied was determined. 24 h after application, the first groundwater sample was taken. All groundwater samples were measured in the LSC and the loss of MTBE determined (3.4.2.1). The samples were separated and analyzed by the gas chromatograph /mass spectrometer (GC/MSD) (HP 6890/HP5973, Hewlett Packard, Ratingen) (3.4.2.2) and radio-HPLC (3.4.2.3).

The air was sampled by a PC controlled Desaga gas sampler, which had a sample unit with 10 thermodesorption tubes each (3.4.1.1.2). Sampling was performed in such a way that an air flow of 100 mL min^{-1} continuously flowed through the gas chamber above the soil column. However, sampling only took place for 21.6 h (90 %) of a day; 2.4 h (10 %) of the day was used to take a reference sample of the outside air via the solenoid valves VM_{1+2} . The air flow passed over each thermodesorption tube for 2 h 20 min. The sample unit was then replaced every 24 h and the data on volumetric flows and sampling periods of each adsorbent tube were transferred to a PC and stored. The adsorbent tubes were subsequently examined by thermal desorption with the GC/MS (3.4.2.2.3) with respect to the composition of the artificial atmosphere. If necessary, the air conditioning was replaced minimum every three days. In the second experiment, the condensate was additionally drained off from the air dehumidifier (Fig. 11, C) in front of the adsorption unit (TDT) every day and measured in the LSC. Subsequently, the experimental program was restarted via the data acquisition system. This was changed once again every 24 h.

3.2.2.4 End of the experiment

After the final sample exchange, the groundwater circulation was immediately interrupted, the remaining solution drained off and the radioactivity determined in the LSC. The glass dome was then removed with all the connections and the column facility dismantled until the soil column with the column foot was left standing free in the groundwater tank. The column was removed from the experimental facility using the carrying device. Three soil cores were immediately taken by a hand-drill probe ($\varnothing$ 50 mm, length 30 cm, Humax, Lucerne) and frozen in liquid nitrogen (N_2) to prevent gaseous losses of MTBE during processing. In order to sample a total length of 60 cm, the remainder of the 60 cm soil monolith was sampled through the existing boreholes using a $\varnothing$ 35 mm hand-drill probe and also frozen in liquid N_2 . The remaining soil of the soil column was dried for several days on the open-air site at the Institute of Radioagronomy and then disposed of.

The soil cores were cut up in the frozen state into 10 cm segments using a right angle grinder with a stone-separator sheet (type EW7115S, Metabo, Nürtingen, with Klingspor C24, stone cutting-off wheel). The segments were then coated in the frozen state with CaCl_2 solution (10 mM) and extracted (3.4.1.4.3).

3.3 Lysimeter experiment with wind tunnel

After the degradation studies and the column experiments, a scale-up experiment was performed on the transport of [^{14}C] -U-MTBE after groundwater contamination under field-like conditions in the wind-tunnel system at the Institute of Chemistry and Dynamics of the Geosphere 5: Radioagronomy. Findings from the previous studies were used for the implementation of this study under unique, non-reproducible conditions. In particular, the duration of the experiment was estimated in this way. The overall design and the performance characteristics of the wind tunnel are described in **3.3.2**.

The wind tunnel was previously used for volatilization studies of higher-molecular compounds such as pesticides or polycyclic aromatic hydrocarbons (PAHs) in the agroecosystem after application to plants or soil (STORK, 1995; STORK ET AL., 1998; OPHOFF ET AL., 1996; OPHOFF, 1998). In order to study highly volatile, low-molecular hydrocarbon compounds, the high-volume sampler (HVS) at the exit of the wind tunnel had to be modified (**3.3.1.1**). For soil gas measurements and an accumulation of groundwater, the lysimeter concept (FÜHR & HANCE, 1992; FÜHR ET AL., 1998) had to be reversed and an accessible outer container with a gastight lysimeter tank had to be manufactured (**3.3.1.2**).

3.3.1 New design

3.3.1.1 Air sampling

The air in the wind tunnel was sampled by various sensors, whose dimensions were based on the DIN standards for measuring emissions in industrial stacks (VDI, 1981). Before the actual collection of air in the outgoing air tower of the wind tunnel (**Fig. 16**), the air was intensively mixed with internal vortexing bodies, which was necessary for representative air sampling (STORK, 1995). It was possible to perform air sampling in two different modes: on the one hand, an isokinetic air collection with automatic air-speed control and, on the other hand, constant aliquot sampling.

3.3.1.1.1 Extending the high-volume sampler

The high-volume sampler (HVS) designed by STORK (1995) on the basis of the guidelines of the Verband Deutscher Ingenieure (VDI - Association of German Engineers) for continuous representative air sampling was used for the quantitative separation of volatile organic environmental chemicals and their metabolites from the agroecosystem making use of the ^{14}C - tracer technique. The adsorber unit had to be replaced for the determination of volatile organic compounds (VOCs). A rotary vane pump (Rietschle, Schopfheim) was used to collect a total sample volume of $319.2 \pm 87.1 \text{ m}^3$ at 24 h collection intervals with a volumetric flow of $13.3 \pm 3.6 \text{ m}^3 \text{ h}^{-1}$ and analysed in the laboratory. The total volumetric flow of the wind tunnel was $283.7 \pm 17.1 \text{ m}^3 \text{ h}^{-1}$ so that an aliquot of 3.5 - 8.1 % was removed from the main

air flow using the HVS. Since no particle-bound residues were expected in the outgoing air in this study, there was no need to use the isokinetic sensors for controlling the sample volume. In order to reduce contamination losses, very short sampling paths were chosen and only stainless steel and glass used as materials.

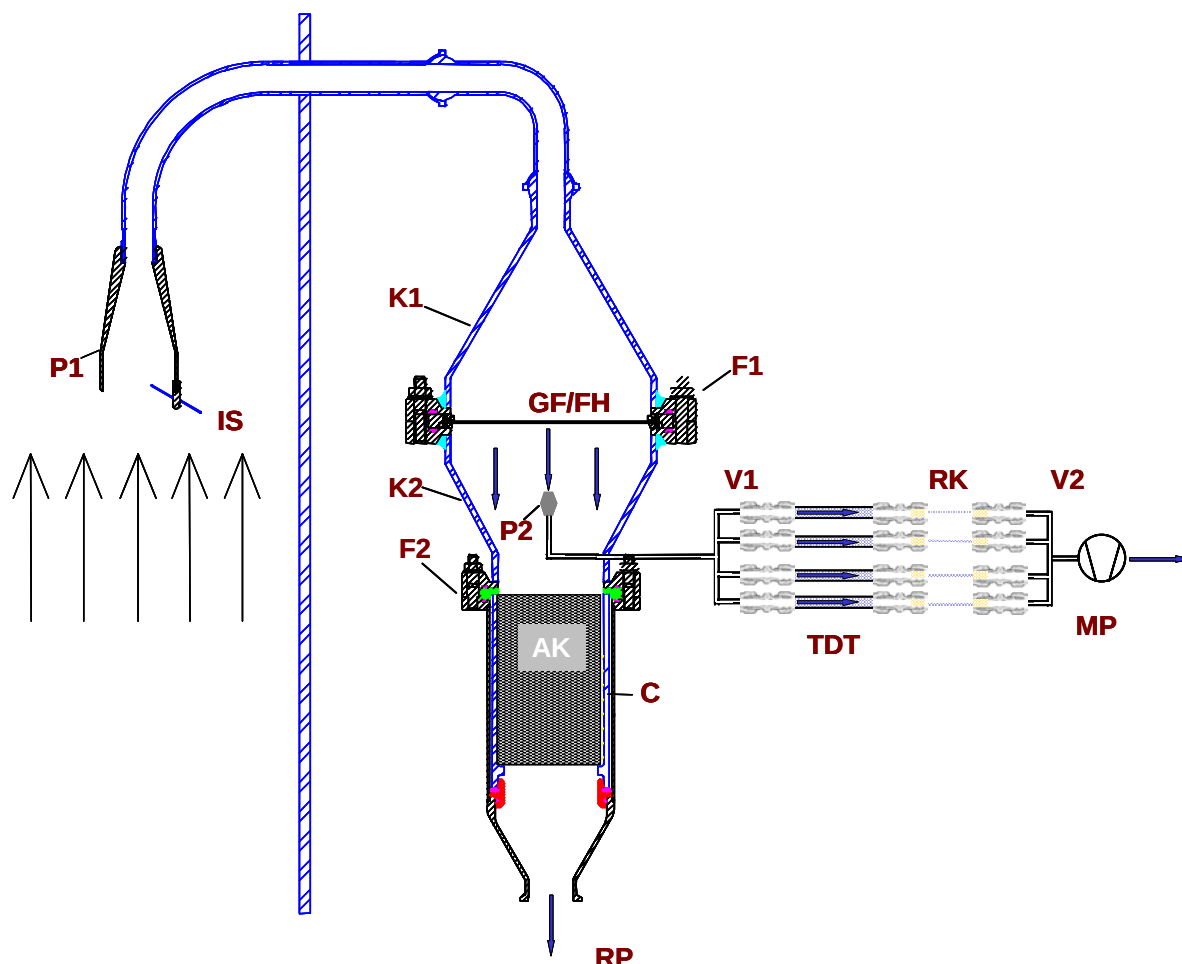


Fig. 13: Arrangement of the extended high-volume sampler in the outgoing air tower of the wind tunnel (modified after STORK (1995)).

AC = activated charcoal; C = glass cartridge; F1/F2 = flange; FH = filter holder; GF = glass-fibre filter; C1/2 = cone; IS = isokinetic sensor; MP = membrane pump; P1/2 = sensor; RC = restriction capillary; RP = rotary vane pump; TDT = thermodesorption tubes; V1/2 = distributor

In order to avoid contamination of the activated charcoal with soil dust, a glass-fiber filter with a high deposition capacity (**Fig. 13** GF, type MN GF5, Ø 185, Macherey & Nagel, Düren) was connected in front of the adsorber unit. The adsorber unit itself consisted of a glass cartridge (C, Ø 95 mm, h = 15.7 mm), filled with 400 g activated charcoal (2.5 mm grain size, Merck, Darmstadt). The bottom of the glass cartridge was covered by a glass-fibre filter which was then coated by activated charcoal to prevent the loaded fine activated charcoal dust being removed at the high volumetric flows. An additional sampling unit (TDT, **Fig. 13**) was added to detect volatile MTBE and its metabolites without further sample preparation and the

associated HVS losses. To this end, a sensor, leading to the outside via a stainless-steel line, was mounted centrally above the adsorber cartridge. The dimensions of this sensor were based closely on the VDI guidelines. The four thermal desorption tubes were loaded with a maximum air flow of 400 mL min^{-1} over the distributor (V1, **Fig. 13**). These test tubes were loaded by a membrane pump (MP, type 200, WISA) via another distributor (V2). The volumetric flow was limited to 12.1 mL min^{-1} per tube (0.06 ‰ of the HVS air flow) by restriction capillaries (RC, $\varnothing_{\text{ID}} = 100 \text{ }\mu\text{m}$, $L = 80 \text{ mm}$). The air-collecting interval was also 24 h. The analysis was then performed by thermodesorption-gas chromatography-mass spectrometry (**3.4.2.2.3**). The collecting efficiency of this new adsorber unit was verified in four validation experiments (**3.3.1.1.2**).

3.3.1.1.2 Validating the high-volume sampler

On the basis of experiments by WITTE (1993) and STORK (1995) on validating the vapour separation performance, four experiments were performed with ^{14}C -labeled MTBE on the new activated charcoal cartridges. ^{14}C -labeled MTBE was volatilized in an evaporation system consisting of a heating unit for the secondary air flow, a glass evaporator with an inlet, a T-connecting piece to the HVS at a temperature of $60 \text{ }^{\circ}\text{C}$.

In the validation studies, the sampling conditions were the same as those in the lysimeter experiment, but the HVS inlet was not coupled to the wind tunnel but rather directly to the evaporator system. This system was used to feed ^{14}C -labeled MTBE into the main air flow, along a short path with a secondary air flow. The air temperatures at the HVS and the evaporator were noted and recorded on the data acquisition system. In order to determine the effectiveness of the new HVS, $100 \text{ }\mu\text{L}$ of a CaCl_2 solution (10 mM) with dissolved ^{14}C -labeled MTBE (approx. 500 kBq) was applied with an active air flow through a septum at the evaporator inlet using a Hamilton syringe. After the application, the syringe was sealed with a septum at the needle tip and decontaminated in the laboratory with CaCl_2 solution (10 mM) followed by methanol. The experiment was discontinued after 24 h. All the components of the HVS and the evaporator were separated and decontaminated with methanol. All decontamination solutions were examined with respect to their radioactivity content (LSC). The activated charcoal from the HVS was crushed by hand in a mortar, 5 aliquots of 250 mg each were taken, pressed to a pellet with cellulose and combusted in the oxidizer. The same procedure was applied to the glass-fibre filter, cut into pieces (approx. 70 mg each). Furthermore, in addition to the activated charcoal cartridge, four thermodesorption tubes were also sampled in parallel via the installed sensor. Three of these tubes were analysed by thermodesorption GC/MS (**3.4.2.2.3**), the fourth tube was separated and the adsorbent material also combusted. The balances of the experiment are described in **4.3**.

3.3.1.1.3 Medium volume sampler

In addition to the continuous detection of volatilized MTBE in the HVS, it was also possible to directly determine the biomineralization rate of the applied [^{14}C -U]-MTBE in the medium volume sampler (MVS) with the wind-tunnel system (STORK, 1995). This effective air-collecting system (STORK, patent No. 4319914, German Patent Office, Munich) represents an efficient tool operating with high detection sensitivity and simple sample preparation for the selective determination of $^{14}\text{CO}_2$ in the outside air. On the basis of ASTM (1986), an aliquot was withdrawn from the main air flow with a maximum collection rate of 3.5 L min^{-1} (approx. 0.04 %) using a hook sensor the exhaust air tower. In order to exclusively determine $^{14}\text{CO}_2$, the air flow first had to be purified with two stainless-steel XAD-4-cartridges (polymer adsorber resin for a broad spectrum of organic compounds, Amberlite Sigma, Deisenhofen) of ^{14}C -labeled organic compounds. Due to the very high volumetric flow, in comparison to other methods, a special, cooled intensive gas-washing bottle filled with 2-methoxy-propylamine (60 mL, CarboSorb E, Canberra Packard, Frankfurt) had to be used for the quantitative absorption of $^{14}\text{CO}_2$ in the form of Carbamat. The intensive cooling prevents the loss of the readily volatile amine, which is heated by the outside temperature and the reaction heat. In order to prevent the water in the sintering plate of the gas-washing bottle from freezing at low temperatures (-40°C) the air was first thoroughly dried over silica gel and then over phosphorus pentoxide (Sicapent, Merck, Darmstadt) before entering the washing bottle. The maximum collection period was 48 h. Since a very low biomineralization was expected, the absorbers were initially replaced every 24 h and towards the end of the experiment every 48 h. A twofold arrangement of the MVS unit ensured continuous sampling by simply turning a three-way cock. In order to determine the biomineralization, the absorber solution was drained off from the washing bottle and rinsed with 5 mL CarboSorb E. For measurements in the LSC, the remaining quantity of absorber was gravimetrically determined, mixed with scintillator cocktail (Permafluor E⁺, Canberra Packard, Frankfurt) in a ratio of 1:1 and analyzed completely. The dry units were replaced as required (displayed by indicator change-over), however, every 7 d at the latest. The XAD-4 cartridges were extracted for 4 h with 270 mL methanol in a special Soxhlet apparatus. The radioactivity of the extract was determined in the LSC. Before reusing the cartridges, the adsorber resin was first pre-dried in the air flow and then dried for 24 h in the drying oven at approx. 50°C .

3.3.1.2 Lysimeter set-up

In order to simulate an accumulation of groundwater at the wind tunnel lysimeter and to ensure that the sensors installed in the lysimeter remained accessible, the outer container of the lysimeter was redesigned and extended. To this end, a container was fabricated for the 0.5 m^2 lysimeter so that it could be installed gastight in the outer container. Furthermore, a closed extension approx. 1 m^3 in size was attached to the side of the actual outer container of the lysimeter. The new outer container design (AL **Fig. 14**, Wolff, Schevenhütte) was x-

rayed in the area of accumulated water (GW, LW **Fig. 14**) with respect to its tightness in order to detect hair cracks. The lysimeter container had a vertically adjustable outlet and an inlet installed on the opposite side. The connection to the outer container was sealed with a 15 mm wide, self-sealing PTFE strip seal (Seybold, Düren) and Atmosit sealing compound (Teroson, Heidelberg). The lysimeter was placed in the gastight container which had been prepared by stainless-steel gauze and quartz sand. In order to ensure the gastightness of this system, a PTFE sealing strip was placed between the lower edge of the lysimeter and the container and the joints were additionally filled with silicone. The lysimeter was pressed onto the seal in the container by four tensioning screws. The required level of the rised water in the saturated soil zone (10 cm in the 0-14.5 cm zone) was adjusted via the outlet level. Groundwater was continuously extracted via a PTFE hose line to the groundwater reservoir (**Fig. 15**) so that the water level was maintained. The expected evaporation of soil water from the saturated lysimeter meant that groundwater was consumed via the capillary connection. This groundwater was replenished from the reservoir by a pump. The daily water loss was read off from a graduated riser pipe.

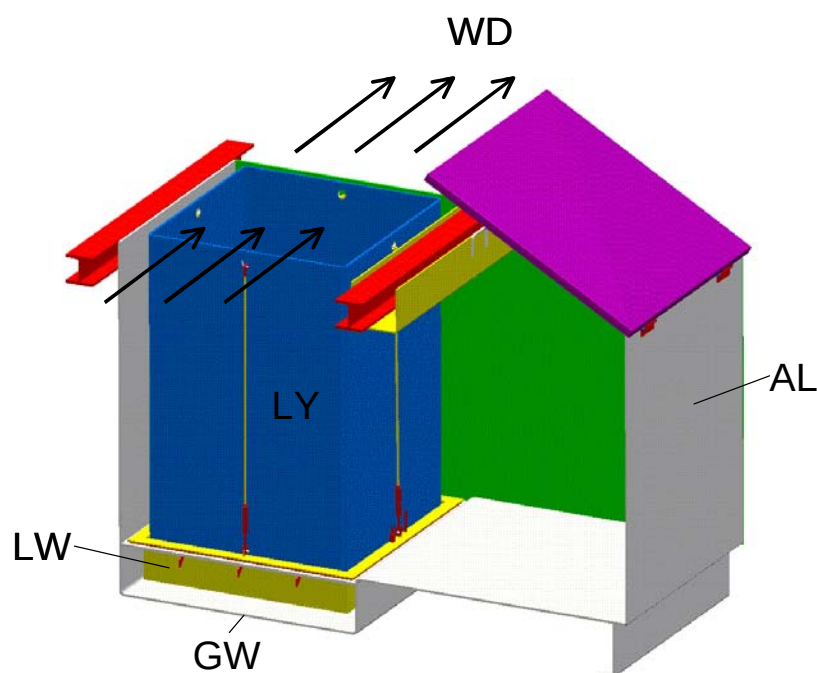


Fig. 14: Schematic diagram of the new lysimeter set-up (0.5 m² lysimeter) under the wind-tunnel system to measure the persistence of organic substances in the groundwater/soil/(plant)/atmosphere system under field-like conditions.

AL = accessible outer container; GW = groundwater reservoir; LW = gastight lysimeter vessel; LY = lysimeter; WD = wind direction in the wind

The groundwater temperature was kept at approx. 10 °C via the cooling jacket of the storage tank with a water circulator (type FE 1100, Julabo, Seelbach). It was possible to replenish the groundwater and withdraw samples via a PTFE 3-way cock with a T-hole, i.e. without any loss of gaseous ¹⁴C-labelled MTBE. The temperature in the outer container and thus the soil

temperature was read off daily. The container was insulated with Armaflex sheets (Armcell, Leutkirch), which ensured a constant temperature of the experimental system.

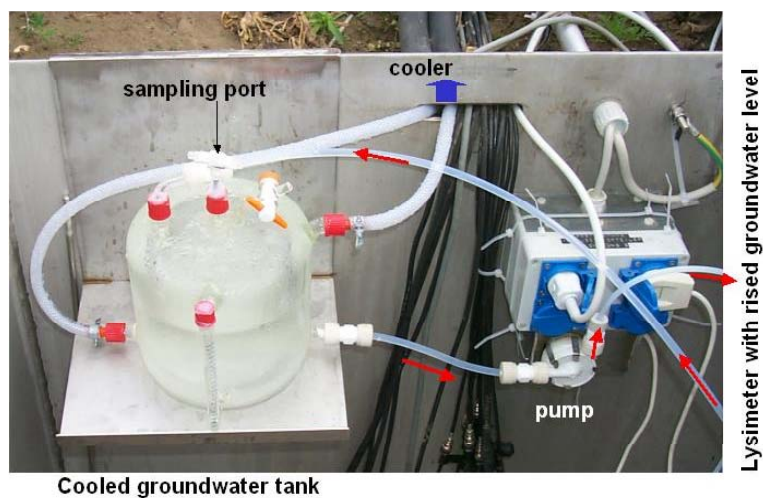


Fig. 15: Illustration of the circulating groundwater reservoir in the new lysimeter design for the wind tunnel.

AL = accessible outer container; GW = groundwater reservoir; LW = gastight lysimeter vessel; LY = lysimeter; WD = wind direction in the wind

3.3.2 Experimental concept

The wind tunnel for recording organic substances in the environment was built up in 1994 and represents an extension of the lysimeter concept (STORK, 1995). This experimental set-up made it possible for the first time to achieve a complete radioactivity and mass balance using radioactively labeled environmental chemicals in a lysimeter experiment. The glass wind tunnel was set up above a 0.5 m² lysimeter, which is a standard tool for studying pesticides in the environment (FÜHR ET AL., 1998). Direct air sampling made it possible to investigate volatilization and biomineralization processes under field-like conditions. Detailed descriptions of the conception, design, set-up and validation can be found in STORK (1995) and OPHOFF (1998) including data from extensive experiments with various active ingredients and scenarios. In a combined field and wind-tunnel application, OPHOFF ET AL. (1998) demonstrated that the wind-tunnel experiments can be transferred to a field situation.

A particular advantage of this experimental system, which is unique in Europe, is the semi-continuous, direct sampling of volatilized model substances and their metabolites as well as the recording of biomineralization (¹⁴CO₂), which was designed on the basis of various VDI guidelines (VDI 175, VDI 1981). **Fig. 16** gives a schematic overview of the wind tunnel and the electronically recorded parameters.

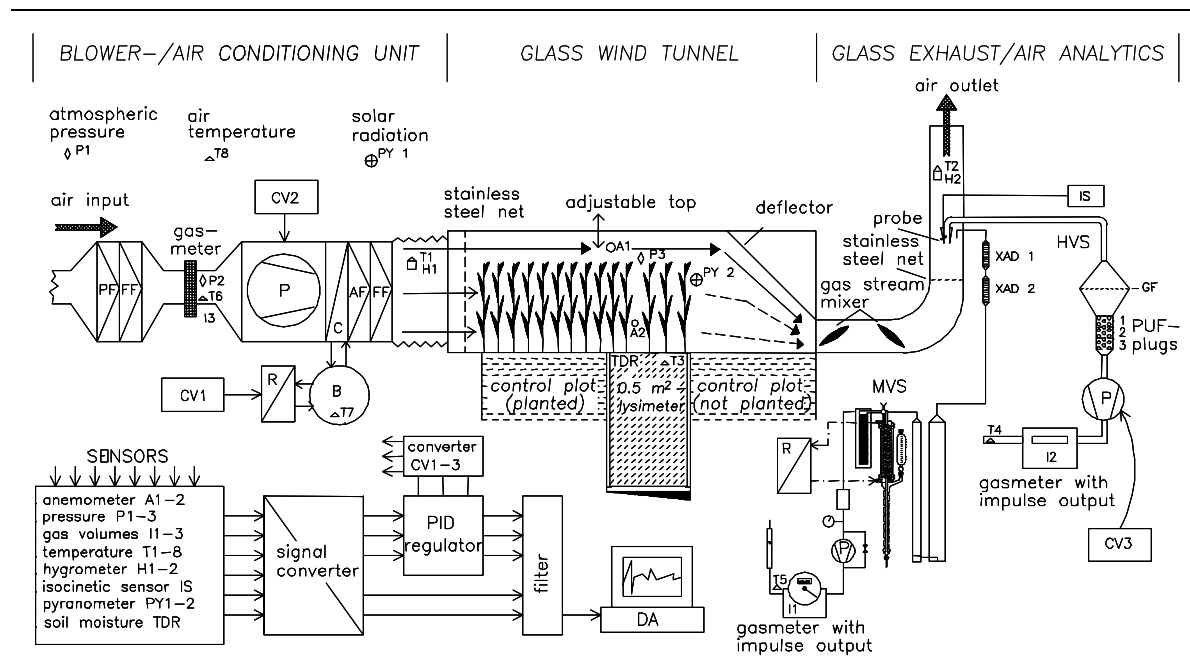


Fig. 16: Schematic diagram of the wind tunnel system above a 0.5 m² lysimeter for measuring the persistence of organic substances in the groundwater/soil/(plant)/atmosphere system under field-like conditions (STORK, 1995).

(Dimensions of the glass wind tunnel: H = 1.1 m; W (width) = 0.7 m; D (depth) = 2.7 m)

AF = active charcoal filter, B = brine tank, C = cooler, CV = converter, DA = data acquisition, FF = fine filter, GF = glass fibre filter, HVS = high volume sampler (¹⁴C-labelled organics), MVS = medium volume sampler (¹⁴C-labelled carbon dioxide), P = pump/blower, PF = prefilter, PUF = polyurethane foam, R = refrigeration, TDR = time domain reflectometry, XAD = adsorbing resins (Amberlite XAD-4).

The wind-tunnel system consists of three main components: the blower/air conditioning unit, the glass wind tunnel above a 0.5 m² lysimeter and the exhaust air system with the air sampling apparatus.

The blower/air conditioning unit generates a laminar flow in the wind tunnel, via various types of filters and vortexing bodies, which increases with increasing height above the soil (logarithmic wind profile) (STORK, 1995; OPHOFF, 1998). This flow is adapted to natural conditions in the field, and is discussed in detail by STORK (1995). Both the wind speed and the air temperature can be controlled and operated in the wind tunnel system in various ways. The wind speed can be optionally controlled by a preset value (internal regulation in % of blower power) or a fixed wind speed (0.3 - 3.5 ms⁻¹) or by an external control. In the case of external control, a set value can be selected from an anemometer (type Kleinwindgeber 4.3400.10.000, Thies GmbH, Göttingen) on the open-air site of the Institute or via a modem line (Telelink AG, Cham, CH) from an anemometer (type A100, Vector Instruments, Hilversum, NL) at the climatological station on the reference field in Merzenhausen near Jülich. The function is controlled by a PID controller by comparing the preset value with that of the actual wind speed measured by an anemometer (type 4.3311.20.000, Thies, Göttingen) at a height of approx. 30 cm above the ground and the blower power then being automatically adjusted.

In addition to the wind speed, the air temperature in the wind tunnel was also automatically adjusted to the temperature of the outside air by a second control loop. In the same way as with the wind speed, a comparison was made between the actual temperature (mean value from the temperature at the inlet and outlet of the wind tunnel) and a set value. This value was either directly input as a preset value or permanently updated as an external reference value. Either the temperature at the open-air grounds of the Institute was taken as the external value or that of the reference field in Merzenhausen near Jülich. The incoming air was cooled down to the required reference value by a very powerful heat exchanger and a cooling unit. It was not necessary to heat the incoming air since in comparison to the outer air drawn into the set-up the air flow was in any case heated by the waste heat of the blower unit and the greenhouse effect in the glass wind tunnel.

There was no need to regulate the atmospheric humidity in climate control so that the atmospheric moisture of the incoming air of up to 90 vol.% in the outside air remained uninfluenced (STORK, 1995).

As indicated in **Fig. 14**, various temperatures, atmospheric humidities, pressures, levels of solar radiation, wind speeds and volumetric flows were continuously recorded and stored on the computer-assisted data acquisition (type PCI-20.000, Intelligent Instrumentation, Leinfelden, STORK (1995)).

Tab. 5: Technical data of the wind tunnel system for the experiment with [^{14}C -U]-MTBE after an accumulation of groundwater in a lysimeter with gleyic cambisol (modified after OPHOFF, 1998).

Technical Variables:	Parameters
soil surface:	approx. 0.5 m ²
height of lid:	30-110 cm above soil surface, height used = 30 cm
vegetation height:	max. 90 cm
blower unit:	5.5 kW, corresponding to max. 2100 m ³ h ⁻¹
volumetric air flow:	approx. 284 m ³ h ⁻¹ in a range from 250-1500 m ³ h ⁻¹
air exchange:	max. 500 up to >2000 h ⁻¹ , depending on position of tunnel roof
wind speed:	0.5 m s ⁻¹ ; constant or variable, depending on present rate and height of tunnel roof: 0.3-3.5 m s ⁻¹ above the target surface
air temperature:	as a function of the outside temperature, at least approx. +3 °C
filters:	EU 6 and S-class filter and activated charcoal
irrigation:	with 2 solid-cone nozzles
transparency:	tunnel roof: UV-B-transparent Plexiglas side walls: UV-B-transparent Borofloat glass
detection of organic substances in the air:	continuous, non-isokinetic (optional) high-volume sampler (HVS), max. 50 m ³ h ⁻¹ with binder-free glass-fibre filter (185 mm Ø) and activated charcoal absorption bed (400 g), detection sensitivity [#] : approx. 0.02 % AR h ⁻¹
detection of $^{14}\text{CO}_2$ in the air:	continuous, non-isokinetic, medium-volume sampler (MVS), max. 3.5 L min ⁻¹ , absorption of 10 m ³ air in approx. 55 mL 2-methoxy-propylamine, detection sensitivity [#] : approx. 0.002 % AR d ⁻¹

[#]Relative to a net quantity of applied radioactivity of 98.3 MBq.

The interface parameters (soil/air) important for transport studies, such as the surface temperature, were continuously measured by an infrared thermometer (type R22, Ultrakust, Gottesszell). The sensor had a measuring ellipse diameter of 0.45 m and covered the major part of the experimental surface.

The radiation situation in the wind tunnel was adapted to the outside situation by several modifications and the light situation verified by a diode array spectrophotometer (OPHOFF, 1998). This involved replacing the glass lid by a UV-transparent Plexiglas lid and replacing the glass walls by UV-transparent Borofloat glass. These modifications were particularly important for photochemical reactions on the soil or plant surfaces. However, due to the short residence time of the molecules in the glass structure, the wind tunnel is not suitable for photochemical investigations of the gas phase. Due to weather damage, a new Plexiglas cover was fabricated as part of work for this project according to the specifications in STORK (1995) (Plexiglas XT 24370, Cadillac Plastic, Cologne).

The soil moisture was measured semi continuously by a TDR measuring system (type Trase, Soilmoisture Equipment Corp., Santa Barbara, CA, USA) in the soil core at a depth of 10, 30, 50, 70, 90 cm. At each of these depths two three-rod TDR sensors (buriable coated type, Soilmoisture Equipment Corp., Santa Barbara, CA, USA) were installed. Measurements were made every 30 min and stored on the Trase-system via a multiplexer. The stored soil moisture, K_a values (apparent relative permeativity constant) and associated time data were read out every 3 d by a serial interface cable on a standard PC. The data were then imported in Microsoft® Excel and processed.

3.3.3 Experimental

3.3.3.1 Experimental preparations

The soil monolith was removed in 1994 at Kaldenkirchen/Hülst according to a recognized method developed by the Institute (STEFFENS ET AL., 1992). After having been used agriculturally for five years at the lysimeter station of the Institute, the lysimeter was prepared in autumn 1999, as described in **3.3.1.2**, and placed in the new outer container of the wind tunnel. The 10 TDR sensors were installed in the soil through the prepared longitudinal boreholes and sealed gastight with silicone. Two weeks before the start of the experiment, the glass structure of the wind tunnel was placed over the lysimeter and connected gastight by means of stainless-steel sheets 1 mm in thickness sealed by silicone. Three days before starting the experiment, the Plexiglas cover was installed in the wind tunnel and the transition elements fitted from the blower/air conditioning unit to the wind tunnel and from the wind tunnel to the exhaust air tower (**Fig. 16**). After testing for leaktightness, all the sensors were connected, the wind tunnel was put into operation and the data acquisition system activated. In order to saturate the soil with water and ensure the necessary capillary connection, the lysimeter was irrigated nine times in 14 days with 10 mm of tap water via a solid-cone nozzle (Fulljet 1/8G-SS2.8W, Spraying Systems, Hamburg). The collected percolate was regularly pumped off. One day before application, the groundwater container and reservoir were flooded with CaCl_2 solution (10 mM), the circulation activated and the groundwater cooling put into operation in order to determine the blind values of the individual sampling procedures.

3.3.3.1.1 Experimental procedure

For the application on 11 May 2000, the glass ampoule with the ^{14}C -U-MTBE was opened at a room temperature of -20°C and the liquid MTBE taken up by two Hamilton syringes. 56 μL (98.3 MBq) was injected into the groundwater reservoir via a septum and the syringe rinsed several times. The syringe and ampoule were decontaminated with distilled water and methanol, and measured to ascertain the remaining radioactivity. 12.53 mL of unlabelled MTBE was applied to the groundwater at the sampling point and the sampling point was then

flushed ($c_{\text{GW}} = 192.4 \text{ g L}^{-1}$). After 6 h 25 min, the first groundwater sample was taken and the radioactivity determined. The meter readings of the HVS and MVS, the temperature in the outer container, the level of the groundwater reservoir were recorded every 24h. Furthermore, the HVS was replaced every 24 h and the MVS switched over every 48 h. When changing the HVS, it was necessary to turn off the blower and the rotary vane pump for a short period, but this downtime was negligible in relation to the 24 h sampling period. The sealed outer container was also checked daily for radioactivity in the outside air by using a hand monitor in order to discover any possible losses of MTBE from the groundwater vessel due to untightness.

3.3.3.2 End of the experiment

After 27 days, on 7 June 2000, the experiment was discontinued by switching off the blower and sampling systems. The wind tunnel was removed from the lysimeter in order to sample the lysimeter soil. Samples were subsequently taken from the lysimeter using a sampling system from Bayer AG. Details of the equipment and its mode of operation can be found in HAGEMANN (2000) and KAISER (2002). With a system operating on the WACKER hammer drill principle (**Fig. 17-1**), seven cores (PVC cartridge, $\varnothing$ 50 mm, L=100 cm, **Fig. 17-2, Fig. 17-3**) were taken at various points in the lysimeter within a few minutes and halved. These cores were then frozen in liquid N_2 and stored in liquid N_2 before being segmented and extracted (**Fig. 17-4**). The sampling locations were selected, including the area which could not be sampled, by the installed TDR sensors so that the sampling locations were mainly situated in the front and central part of the lysimeter since only undisturbed soil was to be sampled.



Fig. 17: Termination of the lysimeter experiment with wind tunnel: Taking soil cores with the WACKER hammer drill sampling system from Bayer, AG, Monheim, at a 0.5 m² lysimeter, the samples being frozen in liquid

After all samples had been taken, the frozen soil cores were divided into 10-cm segments with a circular-cross cut saw (Einhell AG, Landau). Approx. 60 g of soil was covered with CaCl_2 solution (10 mM) in the frozen state and extracted for 24 h by shaking gastight on a mechanical shaker (1750 rpm^{-1}), type SM 25A, Bühler, Tübingen). After the samples had

been left to settle, they were decanted and centrifuged gastight. The supernatant was then examined for extracted radioactivity. In addition to a determination in the LSC, the solution was also examined for possible metabolites of MTBE by radio-HPLC (**3.4.2.3**). One soil core was not frozen but was directly segmented in order to determine the microbial activity in the different soil layers (**3.4.2.4**).

3.4 Analysis

3.4.1 Sampling and sample preparation

As described in **2.2.2**, the adsorption of volatile organic compounds on solid adsorbents with subsequent thermodesorption or solvent extraction is an efficient method of collecting and analyzing atmospheric pollutants. The sampling method in the various experiments was therefore developed on the basis of this technique. In the degradation studies activated charcoal was used, in the column experiments multibed adsorption tubes, and in the lysimeter experiment both types of adsorbent material. First of all, suitable adsorbents had to be found for MTBE and its major metabolites, and the breakthrough volumes of the individual substances determined.

3.4.1.1 Gas samples

3.4.1.1.1 Activated charcoal

In the literature, activated charcoal is described as the standard adsorbent for airborne organic compounds. However, activated charcoal is not suitable for thermodesorption. For this reason, the activated charcoal was cobusted in the oxidizer (**3.4.2.1**) or extracted with organic solvents in the experiments performed. CS₂ is known as an extracting agent in this respect. Due to its very high toxicity and the principles of safety at work, acetonitrile was selected as a substitute solvent. In JAGETSBERGER (2000), various solvents were examined with respect to their extraction performance for MTBE from activated charcoal. Different grain sizes of activated charcoal were used in the experiments. In the degradation studies, activated charcoal with a grain size of Ø 1.5 mm was used for the adsorption of MTBE and its metabolites in the traps, whereas in the wind tunnel experiment, activated charcoal with a grain size of Ø 2.5 mm was used in the HVS.

3.4.1.1.2 Multibed adsorption tube

Various adsorbents were tested in selecting a suitable adsorbent material for MTBE. The adsorbents were selected according to the following criteria (FIGGE ET AL., 1987; SIS, 1997a).

- High adsorption capacity for the substances to be determined (large breakthrough volume).
- Quantitative adsorption (under the selected air collection conditions).
- High selectivity for the organic substances sought in the air.
- Low sorption capacity for H_2O (for the collection of samples of outside air).
- Complete desorption of the collected substances (solvent or thermally).
- Physical and chemical stability of the adsorbent.

Bearing these criteria in mind, porous polymers (Tenax TA, Chromosorb 106) and adsorbents on a carbon basis (activated charcoal, Carbosieve SIII, Carbotrap, Carboxen 1000) were selected and determinations of the breakthrough volume performed with these adsorbents. A simple method after MANURA (1997) was used for this purpose. A glass tube ($\varnothing_{\text{ID}} = 4 \text{ mm}$, $L = 177 \text{ mm}$), filled with one of the above mentioned adsorbents, was installed in a commercial gas chromatograph (type GC 8A, Shimadzu, Duisburg) by means of Swagelok fittings between the injector and the flame ionization detector. This glass tube was enclosed by a glass jacket connected to a thermostat (**Fig. 18**) to ensure temperature control. In order to determine the breakthrough volume, a defined quantity of MTBE, methanol or TBA was injected and their retention time (RT) on the adsorbent in the glass tube determined. The breakthrough volume and thus the capacity of the adsorbent for a certain substance was calculated (eq. 12) using the analytical parameters such as volumetric flow (F) and adsorbent quantity (W_A). Since the retention time of a substance on a separation column is temperature-dependent, the breakthrough volume is also a temperature-dependent variable so that this investigation had to be performed at different temperatures. In order to keep the apparatus required for sampling as simple as possible, the attempt was made to discover an adsorbent displaying acceptable behaviour at room temperature.

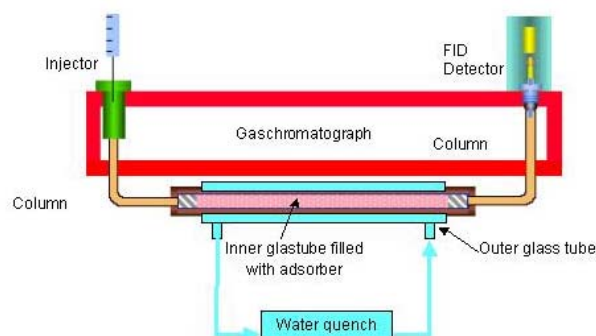


Fig. 18: Experimental set-up for determining the breakthrough volume of volatile organic compounds on different solid adsorbents at varying temperatures.

The experiments were performed in cooperation with CS-Chromatographie in Langerwehe. It was possible to estimate the maximum samples volumes with the breakthrough volumes of the individual substances (MANURA, 1997). In this connection, an ideal peak shape was used by chromatographic separation without tailing or fronting (Gaussian distribution). $V_B = B_V \times 0.5$ was assumed as a rule of sum for estimating the sampling volume.

$$B_V = \frac{RT \times \text{Flowrate}}{W_A} \quad (\text{Eq. 12})$$

B_V =breakthrough volume [L g^{-1} (adsorbent)]

RT =retention time [min]

flow rate=flow of carrier gas through the adsorption unit [L min^{-1}]

W_A =quantity of adsorbent in glass tube [g]

In estimating the minimum elution volume, $V_E = B_V \times 2$ was assumed in order to ensure complete desorption of the loaded adsorbent tubes with thermodesorption. The influence of negative air pressure on sampling was not determined. The maximum flow for the $\varnothing$ 4 mm (ID) tube used was 250 mL min^{-1} so that at the selected volumetric flow of 100 mL min^{-1} the influence of back pressure on sampling was negligible.

3.4.1.2 Soil gas

The sampling of soil gas was planned for the column experiments and the lysimeter study. For this purpose, the stainless-steel vessels (soil column, lysimeter) were equipped at various depths with $\varnothing$ 2 mm boreholes which were sealed with silicone. It was possible to sample the soil gas compartment through these septa using hollow stainless-steel needles. In order to prevent the hollow needles from becoming clogged with grains of soil, this cavity was occupied by a wire while the needle was inserted into the soil. This wire was then removed and the hollow needle connected to the sampling device. In the column experiment, this device was a hand pump, and in the lysimeter study the Desaga gas sampler. However, due to the fine sandy soil the hollow needle became clogged with soil particles or in the more saturated zones with soil suspension after a sample volume of a few milliliters, which made it impossible to take samples from the soil gas compartment. The hollow needles were removed and it was not possible to perform further gas sampling.

3.4.1.3 Accumulated water

The accumulated water contaminated with MTBE was sampled in all studies by a 10 mL glass metal syringe. From this syringe 3-4 aliquots were directly withdrawn during sampling in glass vials (1.5 mL) with PTFE silicone flanged caps for HPLC and GC/MS analysis. The

volume withdrawn varied in each sampling procedure due to infiltrated air entering the glass-metal syringe. Furthermore, a corresponding sample volume was withdrawn for the LSC analysis and 20 mL was taken as a reference sample in a glass Packard vial.

3.4.1.4 Soil

3.4.1.4.1 pH value

Before measuring the pH value in the soil used, the latter was first air-dried for a few days. The procedure after SCHEFFER & SCHACHTSCHABEL (1989) was applied. For this purpose 10 g of dry soil was weighed into a beaker, covered with 25 mL CaCl₂ solution (10 mM) and the suspension then homogenized several times within 1 h by stirring. For the measurements, the temperature-corrected pH electrode (Mettler Toledo, Schwerzenbach, CH) was immersed in a suspension and the pH read off at a constant measuring value.

3.4.1.4.2 Water holding capacity (WHC_{max})

The air-dried soil was sieved to a grain size of Ø 2 mm. A glass funnel was attached to a support and lined with a moistened filter paper. 100 g of dry soil (m_{TB}) was placed in the filter and moistened with drops of 100 ml of distilled water from a tap funnel. The excess water from the soil (V_{H_2O}) was collected under the funnel in a 100 mL measuring cylinder. The determination was performed in five replicates (V_{H_2O}). The maximum water-holding capacity (WHC_{max}) was calculated according to **(Eq. 13)**:

$$Wk_{max} = \left(\frac{(100 \text{ mL}) - \bar{V}_{H_2O}}{m_{TB}} \right) \quad (\text{Eq. 13})$$

3.4.1.4.3 Soil extraction

Various solvents for extracting MTBE from soil were tested in JAGETSBERGER (2000) and the recovery rate determined. A 10 mM CaCl₂ solution with 76 % recovery proved to be the most effective extraction medium. Our own studies on a gleyic cambisol (80 % WHC_{max}) displayed a recovery relative to the theoretically applied radioactivity of between 95 - 112 %.

In the column experiments, extraction was performed by covering 43 - 49 g of soil frozen in liquid N₂ with 50 mL of 10 mM CaCl₂ solution in a sealable centrifuge tube and extracting it for 24 h on a mechanical shaker (type SM 25A, Bühler, Tübingen) at 1750 rpm⁻¹. In the lysimeter experiment, approx. 60 g of soil frozen in liquid N₂ was covered with 50 mL 10 mM

CaCl₂ solution and shaken. The soil/ CaCl₂ solution suspension was then transferred to a centrifuge tube, sealed with a silicone plug and centrifuged gastight at 2000 U min⁻¹ for 30 min (type GPKR, Beckmann, Munich). The supernatant was decanted and the quantity of extractable radioactivity directly determined in the LSC (**3.4.2.1**). In parallel, MTBE was detected in the soil extracts by radio-HPLC.

3.4.1.4.4 Calibration of the soil moisture sensors

The soil moisture measurements in the various experimental systems described in **3.2.1.2** and **3.3.2** were first performed after the sensors had been calibrated appropriately. A calibration kit was available for the Trime system (column experiment) consisting of a calibration dongle and quartz beads. After activating the calibration mode in the measuring instrument with the dongle, a two-point calibration was performed in dry quartz beads and in quartz beads saturated with distilled water.

No calibration was necessary for the Trase system (lysimeter experiment) since a standard calibration curve was stored in the system. For this system, the entire system, its multiplexer and sensor cables was verified by the defined calibration kit of the Trime system. Particular attention was paid here to examining the influence of cable length (> 20 m). The results and the influence of the multiplexer card are described in **4.3**.

3.4.1.4.5 Other soil parameters

As one of the important variables for the binding characteristics, the carbon content was determined at the Central Department of Analytical Chemistry at Research Centre Jülich. The samples were incinerated in a radio-frequency induction furnace in an oxygen flow and the CO₂ quantity determined by non-dispersive infrared absorption detectors (type RC-412, LECO, Mönchengladbach) (BIRKELBACH, 2000).

The grain-size distribution in the various layers of the soil column (0.60 cm) was determined by the Institute of Soil Science at the University of Bonn (**Tab.11**)

3.4.2 Measuring methods

3.4.2.1 Radioactivity measurements

Determination of the radioactivity in various matrices was used to draw indirect conclusions about the quantity (concentration) of the substance sought since in addition to the radioactively labelled compounds, unlabelled material was also always present. The measuring instrument for ¹⁴C-radioactivity was the liquid scintillation counter (LSC, Tri-Carb 2500 TR,

Canberra Packard, Frankfurt). The solid radioactive samples first had to be transformed into a form that could be measured by the LSC. To this end, they were combusted with subsequent $^{14}\text{CO}_2$ sorption and afterwards measurement in the LSC.

3.4.2.1.1 Solid samples

In the experiments, various solid materials such as soil (3.1.2.3, 3.2.1.2, 3.3.3), activated charcoal (3.1.2.2, 3.3.2) and glass-fibre filters (3.3.2) were investigated for ^{14}C activity. Depending on the composition of the sample, a certain quantity of material was weighed (Tab. 6), mixed with approx. 600 mg of microcrystalline cellulose (Merck Avicel®) to improve the incineration process and pressed into a solid pellet.

Tab. 6: Weighed quantities for radioactivity determination from solid matrices

	activated charcoal ^①	soil	glass-fibre filter
weighed quantity	100-250 mg	500 mg	70 mg
cellulose	600 mg	600 mg	600 mg
time	3 min	2 min	2-3 min

^① 100 mg degradation study, 250 mg wind-tunnel experiment

Each sample was weighed in triplicate and incinerated in the oxidizer (type Oxidizer 306 D, Canberra-Packard GmbH, Frankfurt). The $^{14}\text{CO}_2/\text{CO}_2$ resulting from incineration was absorbed in CarboSorb E (Canberra Packard, Frankfurt) and automatically mixed with a scintillator cocktail (Permafluor E⁺) (Canberra Packard, Frankfurt). This mixture was then measured in LSC.

3.4.2.1.2 Liquids

Depending on the constitution of the liquid matrix in which the radioactive sample is dissolved, a corresponding quench curve has to be created at the LSC in order to correct the measured value for the detector efficiency. On the other hand, various scintillator cocktails are used to measure the samples. In the experiments, samples were characterized in aqueous and organic solvents.

As calculated by STORK (1995), on the basis of TSCHURLOVITS (1977), the detection limit was 0.5 Bq (15 min). For aqueous samples such as CaCl_2 solution or condensate water, Ultima-Gold XR (Canberra Packard, Frankfurt) or Instagel (Canberra Packard, Frankfurt) was used. Samples with up to 10 mL aliquots and 10 mL scintillator were characterized. For the organic samples, toluene scintillator (Canberra Packard, Frankfurt) or Instagel was used as the scintillator. In contrast to Instagel, however, the former can only be used with a maximum 2 mL aliquot from the sample. Since Instagel is suitable for both organic and aqueous

matrices, it was also used for multicomponent solutions (e.g. activated charcoal extract: acetonitrile with condensate water).

The CarboSorb E solution from the MVS was mixed with Permafluor E⁺ in a ratio of 1:1 and then exhaustively characterized in the LSC.

3.4.2.2 GC/MS

Within the framework of this project, a gas chromatograph with a mass-selective detector (type 6890 with MSD 5973, Hewlett Packard, Ratingen) and an automated thermodesorption unit (type TDS A on TDS2 with KAS 4, Gerstel GmbH, Mühlheim a.d. Ruhr) were introduced at the Institute to analyse volatile organic compounds in environmental samples. This coupled system offered a wide range of analytical possibilities, with mass spectrometry making it possible to identify organic compounds and metabolites even in difficult matrices such as soil extract. The mode of operation and instrument parameters for thermodesorption are described in detail in **3.4.2.2.3**. Liquid samples were analysed by an automatic sample dispenser (HP 7683, Hewlett Packard, Ratingen) (**3.4.2.2.2**).

Tab. 7: Components and parameters of the gas chromatograph with mass-selective detector

component	parameters
gas chromatograph GC 6890 Plus	2 x FS-OV-1-CB-1 column (60 m x 0.25 mm Ø, film thickness 1.2 µm) (CS-Chromatographie Service GmbH, Langerwehe) oven program: starting temperature: 30 °C, 6 min 1st ramp: 10 °C min ⁻¹ to 80 °C, 4 min 2nd ramp: 25 °C min ⁻¹ to 175 °C, 1 min volumetric flow: 1 ml min ⁻¹ (active column) carrier gas: He transfer line temperature: 280 °C
retention times	MeOH = 4.90 min acetone = 6.89 min isopropanol = 7.31 min TBA = 8.28 min MTBE = 10.04 min TBF = 12.03 min
automated injection system HP 7683	8 sample positions with two additional solvent phials 10 µl syringe injection volume 1 µL
mass selective detector MSD 5973	ionization: electron impact ionization (EI) at 70 eV mass range SCAN mode: 1-350 amu MTBE 73, 57, 43 amu TBA 59, 41, 29 amu MeOH 31, 15 amu
software	Control, data analysis, : HP Chemstation G1701BA, version B.00.00, 1997 database: NIST, version 98, 1998

The gas-chromatography system is equipped with a dual-column interface so that the gas and liquid injection unit can be used without further modification. The separation columns from the liquid injector and the cold application system simultaneously enter the MSD through a Y-shaped component. The additional gas flow leads to a slight increase in the detection limit during the analysis (dilution effect). Depending on the injection mode, the volumetric flow of the non-active separation column is reduced to a minimum (0.3 ml min^{-1}) in order to prevent a reflux of the separated substances from the active to the non-active separation column in the interface.

The MSD is a quadrupole mass spectrometer with a maximum measuring range of 0-850 amu (atomic mass unit) and a resolution of 1 amu. The substance mixture is first separated on the gas-chromatograph column. Every separately eluted substance enters the ionization chamber via a transfer line and is ionised in the chamber by an electron impact (approx. 70 eV) via a filament. These ions are guided through a quadrupole magnetic field under a high vacuum (10^{-5} - 10^{-8} Pa). By varying the mass filter voltage, the molecular ion or the molecular fragments are deflected in the radiofrequency magnetic field in such a way that only molecules of one size reach the detector. In the case of singly positively charged ions, the voltage applied then corresponds to a certain molecular mass. In order to protect the filaments, the detector is only activated after the solvent has been eluted (5-9 min). This means that only the compounds eluted after this time are detected.

3.4.2.2.1 SCAN and SIM mode

A choice between two mass-spectrometer operating modes can be made for the analysis. On the one hand, the SCAN mode and on the other hand the SIM mode. In SCAN operation, every sample is scanned with one mass range, which is especially advantageous for unknown samples. In this process, molecular fragments are also included, which is absolutely necessary for comparing the spectra in the database (NIST 98) in order to obtain the most accurate agreement possible between the spectra. However, a disadvantage is the lower detection sensitivity. The SIM mode is used for the quantitative analysis. Quantification is performed via a target mass ($m = 73$ for MTBE) and identification is additionally carried out via the qualifier ($m = 57$ and 43 for MTBE). A calibration curve was recorded for each substance before the experiments and after the integration of the target mass a substance quantity of, for example, MTBE was calculated from this calibration function. The other molecules (TBA, MeOH) were quantified analogously.

3.4.2.2.2 Liquid samples

Normally samples dissolved in organic solvents are used for analysis with gas chromatography. As already described in TRATNYEK ET AL. (1997), POTTER (1996) and LEMLEY (1999) it is, however, also possible to apply aqueous samples directly to the separation column. In order to prevent overloading of the separation column, on the one hand with soil matrix and on the other hand by an increased salt load, the inlet of the injector was filled with silanised glass wool. A major fraction of the interfering components remained in the inlet (Hewlett Packard, Ratingen) during the evaporation process and thus did not clog the inlet to the capillary separation column. Replacing the inlet before each experiment prevented the separation column from becoming overloaded.

The injections (1 μL) were performed by the automatic sample unit. Before each injection, the injector syringe was rinsed four times with the sample. After the injection, the syringe was rinsed twice with distilled water to avoid the samples being carried over.

3.4.2.2.3 Thermodesorption

The gaseous samples were desorbed from the multibed adsorption tubes by an automated thermodesorption unit. According to the selected method (parameters **Tab. 8**), the sample tube was automatically inserted into the desorption unit and first purified of oxygen at $-10\text{ }^{\circ}\text{C}$ for 1 min in a helium flow in order to prevent oxidation processes during the subsequent thermal desorption. Desorption took place for approx. 13 min at up to $250\text{ }^{\circ}\text{C}$. All the organic compounds collected were eluted from the adsorbent material without splitting and cryo-focused at $-120\text{ }^{\circ}\text{C}$ in the cold application system. After complete desorption, the injector was rapidly heated ($12\text{ }^{\circ}\text{C s}^{-1}$) to permit a pulse-shaped injection of the collected substance mixture onto the separation column without splitting. This procedure was of great significance for the chromatographic separation efficiency in order to obtain a satisfactory peak shape and a baseline-resolved chromatogram. Transferring the substances from the adsorbent to the separation column without splitting ensured a low detection limit. Stored water was also desorbed with the substances which resulted in a crystallization of ice in the injector. In addition to the low adsorption capacity, this caused a shift in the retention time of the chromatogram and a reduced separation performance of the column. For this reason, before adsorption the air in the inlet of the column experiment was partly dehumidified (**3.2.1.1**).

Tab. 8: Components and instrument parameters of the coupled automatic thermodesorption-cold application unit at the GC/MS system for MTBE studies

Component	Parameters
automated thermodesorption	maximum number of thermodesorption tubes 20
TDSA	programmable positions
thermodesorption system TDS2	starting temperature/time: -10 °C for 1 min heating rate: 30 °C min ⁻¹ final temperature: 250 °C for 3 min transfer temperature: 280 °C
cold injection system KAS 4	starting temperature/time: -120 °C for 0.2 min heating rate: 12 °C s ⁻¹ final temperature: 250 °C for 0.5 min
software	Gerstel Master Software version 1.75, 1998

3.4.2.3 High-performance liquid chromatography (HPLC) and gel-permeation chromatography (GPC)

In the various experiments both organic and also aqueous extracts were obtained. The radioactivity was first determined in the LSC. In searching for metabolites by distribution chromatography, a minimum volume of radioactivity of 0.2 Bq µL⁻¹ had to be present in the samples in order to ensure an unambiguous characterization of the peak in the ¹⁴C-through-detector. Since a clear integration of the peaks in the GPC was not possible, the individual fractions were collected in previously determined time windows, mixed with scintillator cocktail and measured in the LSC. Depending on the radioactivity content, the injection volume varied from 50 - 200 µL. In addition to the ¹⁴C flow-through detector, a UV detector was also available in parallel. MTBE and its metabolites did not have sufficient adsorption capacity in the UV range so that no selective detection was possible given the sensitivity of the instrument. The UV detector was therefore only used if the time range was established by high-purity substances. **Tab. 9** gives an overview of the HPLC system used in the analyses of the degradation experiments.

$$A = \left(\frac{I \times F}{E \times V} \right) \times 0,0166 \frac{Bq}{dpm} \quad (\text{Eq. 14})$$

E=detection probability [= 0.82, YG-150 cell]

A=radioactivity [Bq]

I=pulses [cts]

F=total flow rate through the measuring cell [mL min⁻¹]

V=cell volume [mL]

It was only possible to quantify integrated peaks the HPLC by calculating the radioactivity from the raw data (**Eq. 14**) or if the total radioactivity injected was known.

A selection of HPLC spectra from the degradation studies is given in the appendix (**Fig. A-57** - **Fig. A-66**).

Tab. 9: Components and instrument parameters of HPLC application for [α,α' - ^{14}C]-MTBE and metabolites in the degradation studies

Instrument	Type	Data
pump	Merck Hitachi, type L6200	flow rate: 0.5 mL min ⁻¹
injector	Gynkotek Injektionsautomat Gina 50	injection volume: 50-100 μL ^② ; or 100-200 μL ^① in the range of 1-250 μL
detectors	Gynkotek UV - detector UVD 160 S	1 x 10 ⁻⁵ AU noise signal at 250 nm
^{14}C Detector	Berthold Wildbad LB 506 C1	wavelength range: 190-360 nm yttrium glass solid cell, type YG 150U 4D; cell volume 0.15 mL
RT value	MTBE	7.30 ^① min; 4.2 ^② min
	TBA	5.22 ^① min; 3.2 ^② min
	MeOH	4.52 ^① min; 3.12 ^② min
	TBF	3.4 ^② min
software	Berthold	version 1.51
column thermostat	STH 585 Gynkotek	temperature: 35 °C
pre-columns	Merck LiChrospher Si 60 RP-select B (50 μm)	$\varnothing$ = 5 μm ; length 4mm; i.d. 4mm
columns	Merck LiChrosorb RP-60 ^①	$\varnothing$ =5 μm ; length 250mm; i.d. 4mm
	Multopher ^②	$\varnothing$ =5 μm length 250mm; i.d. 4mm
eluent	75 % acetonitril	Riedel-de-Haën Chromasolv®
	25 % H ₂ O (bidest.)	Millipore Milli-Q 145 Plus

① soil extractions with CaCl₂ solution (10 mM)

② activated charcoal extractions with acetonitrile (ACN)

Following SIGMA (1999), gel permeation chromatography of the aqueous samples was performed in the lysimeter study. In general, substances were only separated according to their molecular size in the GPC and not according to substance properties (e.g. polarity). However, if the molecular sizes could not be clearly separated, substance properties may also influence the elution series. In the GPC, the peak widths were significantly greater than in the HPLC which led to problems in peak recognition due to the relatively high detection limit of the ^{14}C detector.

Quantification was therefore not performed by the peak integration method, but by measuring the eluate in the LSC. **Tab. 10** gives an overview of the instrument parameters for the GPS method. A clear separation of MTBE and its metabolites was achieved on the GPC column used. Some model chromatograms are shown in the appendix (**Fig. 57**).

Tab. 10: Components and instruments specification of GPC application for [¹⁴C-U]-MTBE and metabolites in the lysimeter study with wind tunnel

Instrument	Type	Data
pump	Gynkotek IP 850	flow rate: 0.5 ml min ⁻¹
injector	Gynkotek automated injection Gina 160	injection volume: 200 µL
detectors	Gynkotek UV - detector DAD	1x10 ⁻⁵ AU noise signal at 255 nm wavelength range: 200-595 nm
¹⁴ C detector	Berthold, Wildbad LB 507A	yttrium glass - solid cell type YG 150U 4D; cell volume 0.15 ml
column thermostat	column thermostat STH 585A	temperature range: 25 °C
RT range	TBF	10-20 min and 66-86 min
	MeoH	20-25 min
	TBA	25-32 min
	MTBE	44-61 min
software	Softron Chromeleon®	version 4.21
columns	Promochem Hema-Bio Linear	Ø=5µm; length 300mm; i.d. 8mm
eluent	100 % H ₂ O (bidistilled) isocratic	Millipore Milli-Q 145 plus

3.4.2.4 Microbial activity

An important soil parameter is the microbial activity and biomass. It was determined following the method of ALEF(1990) and ALEF & KLEINER (1989), who were able to demonstrate that a large number of microorganisms could be determined in this way. In the degradation studies, various layers of the soil were examined with respect to microbial activity on every sampling day, and in the column experiments and the lysimeter study after terminating the experiment.

Following ALEF (1990), the sample quantity was increased here to compensate for interferences due to inhomogeneities in undisturbed soils. The procedure described here is based on the microbial reduction of dimethylsulphoxide (DMSO) to dimethyl sulphide (DMS). The determination was performed in three replicates. Approx. 10 g of moist soil was placed into a gastight 54 mL Duran flask with a septum and then preincubated for 24 h in this vessel at room temperature. Subsequently, 2.5 mL of 10 % DMSO solution was pipetted onto the soil. The vessel was then immediately sealed and incubated for 3 h at 40 °C. After the incubation period, analogously to the head space technique, 250 µL of gas was taken from the gas space above the soil using a gastight syringe and injected into a gas chromatograph with a flame ionization detector (FID) (type HP 5890 II, GS-Q Megabore column, length 30 m, Ø 0.53 mm, Hewlett Packard, Ratingen). For quantification purposes, a calibration was performed before each measuring series by transferring 50 µL DMS into a Duran flask (55 mL), removing 250 µL after equilibration and transferring this quantity into a 57 mL Duran

flask with a gastight lid. From this sample, a calibration curve was recorded with different volumes, so that the quantity of DMS ($\text{ng DMS g(TM)}^{-1}\text{h}^{-1}$) of the individual samples could then later be calculated.

3.5 Experimental soils

In the experiments, a gleyic cambisol was used. Only for the degradation studies was an alluvial loam used additionally as a reference soil (**Tab. 12**). The gleyic cambisol was taken in Kaldenkirchen-Hülst, from the plot known as "Am Hüschesweg", and the alluvial loam from Research Centre Jülich beneath the former filling station. The sandy soil corresponds to the standard soil type in the guidelines for metabolism studies (BBA, 1986) and lysimeter studies (BBA, 1990) of pesticides from the Federal Biological Research Centre for Agriculture and Forestry (BBA). **Tab.11** gives an overview of the most important soil data from a profile evaluation after PÜTZ & KLIMSA (1991) and some recently determined parameters for the Kaldenkirchen soil.

Tab. 11: Selected soil characteristics of the Kaldenkirchen-Hülst experimental site: gleyic cambisol (PÜTZ & KLIMSA, 1991).

Horizon Depth	Ap 0-30 cm	B _{V1} 30-62 cm	B _{V2} 62-80 cm	B _{V3} 80-115 cm	II B _V >115 cm
pH-value ^①	5,35	5,49	5,61	6,49	6,47
WHC _{max} ^① [g(100g soil) ⁻¹]	32	-	-	-	-
C _{tot} [%] ^①	1,075	0,384	0,200	0,080	0,072
C _{org} [%] ^①	1,007	0,362	0,193	0,076	0,067
C _{inorg} [%] ^①	0,068	0,022	0,007	0,004	0,005
humus [%]	1,7	0,5	0,3	0,1	0,4
total N [%]	0,06	0,02	0,01	0,01	0,01
sand, total [%]	69,5 ^①	64,1 ^①	76,9	92,3	83,1
silt, total [%]	26,2 ^①	31,9 ^①	20,6	5,9	10,8
clay [%]	4,4 ^①	4,0 ^①	2,5	1,3	6,1
soil density [g cm ⁻³]	1,41	1,69	1,53	1,57	1,70
total pore volume [%]	45,2	39,2	45,9	43,3	38,1
coarse pores, wide [%]	11,3	12,5	20,4	25,2	16,3
coarse pores, fine [%]	20,6	13,2	13,4	11,4	8,6
medium pores [%]	8,8	9,7	8,9	4,6	9,1
fine pores [%]	4,5	3,8	3,2	2,1	4,1

^① Parameters determined by FZJ.

The soil data for the alluvial loam were taken from report by consulting engineers (Herbst, Herzogenrath 1999) drawn up for the remediation of the soil below the former filling station at Research Centre Jülich. The profile analysis of this soil polluted with mineral oil hydrocarbons was undertaken by BURKHARDT (1999) and SEEBERGER ET AL. (1999).

Tab. 12 summarizes the most important soil parameters:

Tab. 12: Selected soil characteristics of the experimental site at the FZJ filling station: alluvial loam

Horizon Depth	fAH 110-130 cm	fAh-fGo 130-150 cm
pH-value	5,97	5,71
WHC _{max} ^① [g(100g soil) ⁻¹]	67	
C _{tot} [%] ^①	1,6	1,7-1,8
sand, total [%]	9,4	8,5
silt, total [%]	68,2	68,2
clay [%]	22,4	23,3

① Parameters determined by FZJ.

3.6 MTBE and possible metabolites

3.6.1 Model substance

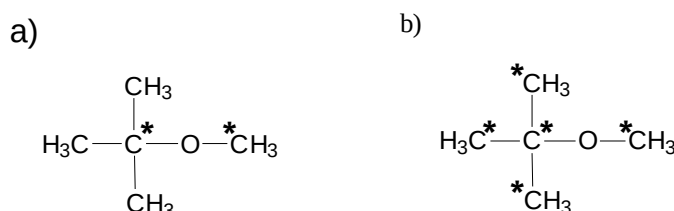


Fig. 19: Chemical structural formula of a) [α,α' -¹⁴C]-MTBE (methyl-tert-butyl ether) and b) [¹⁴C-U]-MTBE

For the experiments, MTBE was radioactively labelled at various C-atoms of the model compound (**Fig. 19**). In the degradation studies [α,α' -¹⁴C]-MTBE was used, which was labelled on the one hand at the central C position and on the other hand at the methoxy carbon (**Tab. 13**). Uniformly labelled [¹⁴C-U]-MTBE was used in the lysimeter study. Multiple labelling in one molecule permitted the persistence of the substance used to be identified with the aid of the radiotracer technique even after cleavage or biological conversion.

Tab. 13: Radiochemical data for [α,α' -¹⁴C]-MTBE (SIGMA, 1999) and [¹⁴C-U]-MTBE (NEN, 1998)

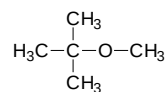
	[α,α' - ¹⁴ C]-MTBE	[¹⁴ C-U]-MTBE
molecular weight:	88,15 g Mol ⁻¹	88,15 g Mol ⁻¹
radiochemical purity:	99.2 – 100%	≥ 99,7 %
chemical purity:	> 95%	-
specific activity	37 MBq mMol ⁻¹	217 MBq mMol ⁻¹
Manufacturer	Sigma-Aldrich	NEN™ Life Science Products

3.6.2 Reference substances

The reference substances for GC/MS were used according to the literature data as major metabolites of MTBE and were all commercially available (**Fig. 4** and **Fig. 5**). An overview of

non-¹⁴C-labelled MTBE and the most important metabolites with their specifications is given in the following.

1. Tert-butylmethyl ether Uvasol®



chemical name:

Methyl-tert-butyl ether (MTBE) Fig. A-72

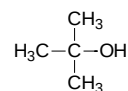
molecular weight / purity:

88,15 g Mol⁻¹ / ≥ 99,9 %

producer/supplier/ article no.:

Merck Eurolab GmbH, Darmstadt (101984)

2. Tert-butanol analytically pure



chemical name:

2-Methyl-2-propanol (TBA) Fig. A-71

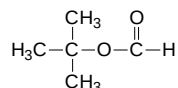
molecular weight / purity:

74,12 g Mol⁻¹ / ≥ 99,5 %

producer/supplier/ article no.:

Merck Eurolab GmbH, Darmstadt (109629)

3. Tert-butyl formate pure



chemical name:

2-Methyl-2-propanol (TBF) Fig. A-73

molecular weight / purity:

74,12 g Mol⁻¹ / ≥ 99,5 %

producer/supplier:

Merck Eurolab GmbH, Darmstadt (109629)

4. Methanol Uvasol®



chemical name:

Methyl alcohol (MeOH) Fig. A-68

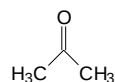
molecular weight / purity:

32,04 g Mol⁻¹ / ≥ 99,9 %

producer/supplier:

Merck Eurolab GmbH, Darmstadt (106002)

5. Acetone Uvasol®



chemical name:

2-Propanone (Aceton) Fig. A-69

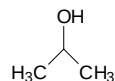
molecular weight / purity:

58,08 g Mol⁻¹ / ≥ 99,9 %

producer/supplier:

Merck Eurolab GmbH, Darmstadt (100022)

6. Isopropanol Uvasol®



chemical name:

2-Propanol (Isoprop) Fig. A-70

molecular weight / purity:

60,10 g Mol⁻¹ / ≥ 99,9 %

producer/supplier:

Merck Eurolab GmbH, Darmstadt (100993)

4 Results

4.1 Degradation Studies

In addition to transport studies in undisturbed soil monoliths with gleyic cambisol, two degradation studies (3.1) were performed under aerobic conditions as predominately existing in the unsaturated soil zone. The first study was a short-time study with different variants. In the second study, the variant from study 1 with the greatest degradation potential for MTBE was repeated with a higher time resolution. The experimental design used is not suitable for studying anaerobic microbial degradation, which is rarely described in the literature (2.1.3.2) and can therefore be neglected for the following experiments.

In the first degradation study, different variants and soil types were initially examined with respect to their degradation potential for $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ after a soil contamination. **Fig. 20** shows the total radioactivity balance (distribution between the individual compartments) in the first degradation study. A standardization to 100 % was then performed, relative to the respective sum of radioactivity found in the individual variants. In all variants, a very rapidly progressing volatilization of $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ from the soil/soil-water system became apparent. After approx. 7 h, 50.71 % AR (**Fig. 23**) and after 3 d more than 93.4 % AR (and 98.7 % AR respectively, Fig. 20) had already passed over from the soil to the gas phase. Volatilization reached its maximum up to the third (degradation study 1) and fourth day (degradation study 2) depending on the study. Subsequently, the system reached a state of quasi-equilibrium. The figures and tables in the Appendix are not numbered in the order they are described in the text, but are rather arranged according to experiments and topics.

In the moisture sterile variants of the gleyic cambisol (KSF, 80 % WHC_{max}) the volatilization was always lower than in the less moist sterile variants of the gleyic cambisol (KST, 40 % WHC_{max}). Up to the third day, the differences between the two moist variants were perceptibly higher at up to $\Delta = 6.43$ % AR than on subsequent sampling days when the Δ values were 0.5 % AR. It can thus be clearly seen that volatilization is dependent on soil moisture. With the same soil moisture (40 % WHC_{max}), the soil type (gleyic cambisol or alluvial loam) did not have any significant influence on the volatilization process. If all sampling days are considered, then the volatilization of $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ for the alluvial loam was only slightly higher than the previously unpolluted gleyic cambisol. Comparing the variants in contrast to the dependence on soil moisture, the less moist variant of the alluvial loam (TB 40 % WHC_{max}) must be compared with the less moist variant of the gleyic cambisol (FT, 40 % WHC_{max}). Both displayed roughly the same microbial activity (**Fig. 24**) and there was no sterile variant of the alluvial loam for a direct comparison.

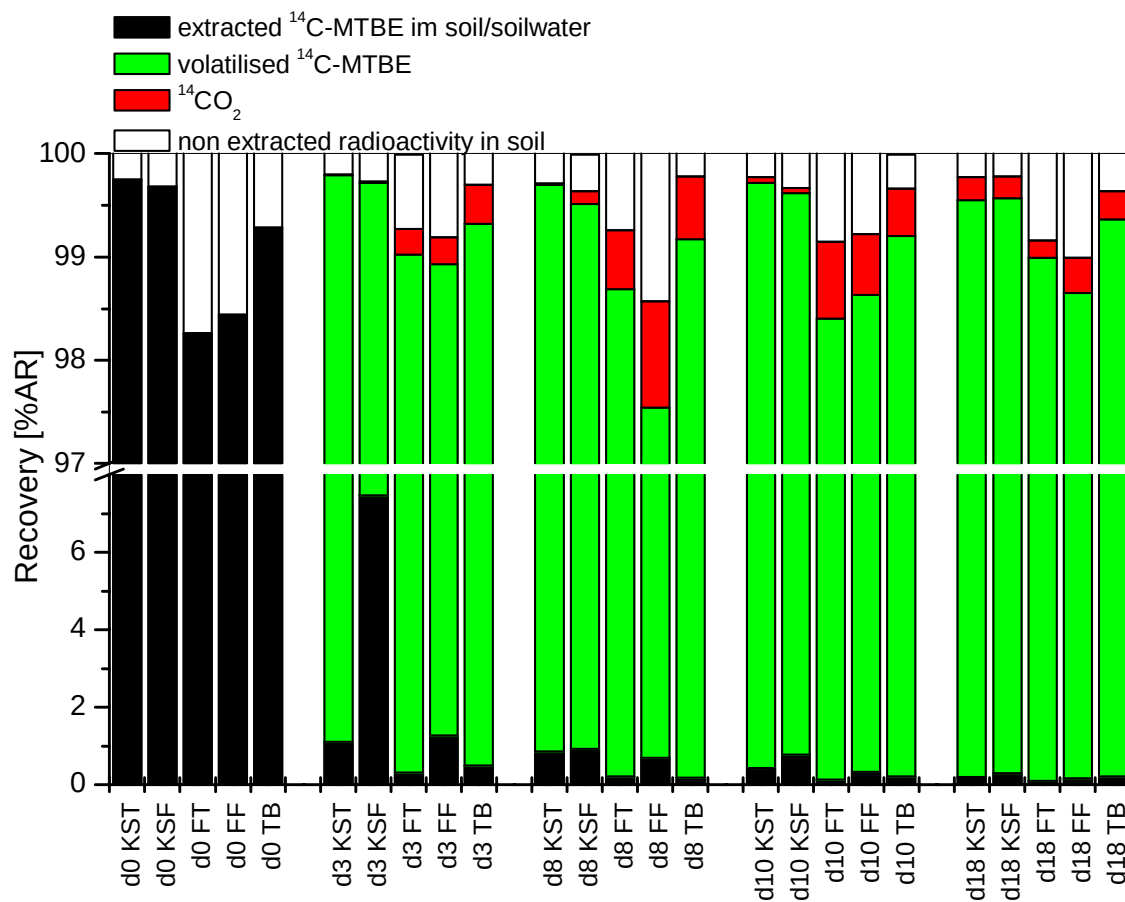


Fig. 20:1st degradation study with [α,α' - ^{14}C]-MTBE in a gleyic cambisol and an alluvial loam:
Radioactivity distribution of the different variants in the 1st degradation study on the sampling dates
 (modified after JAGETSBERGER, 2000) (applied radioactivity [AR] = 100 %).

(KST = sterile less moist control for the gleyic cambisol (40 % WHC_{max}), KSF = sterile moist control for the gleyic cambisol (80 % WHC_{max}), FT = less moist gleyic cambisol (40 % WHC_{max}), FF = most gleyic cambisol (80 % WHC_{max}), DS = less moist alluvial loam (40 % WHC_{max}))

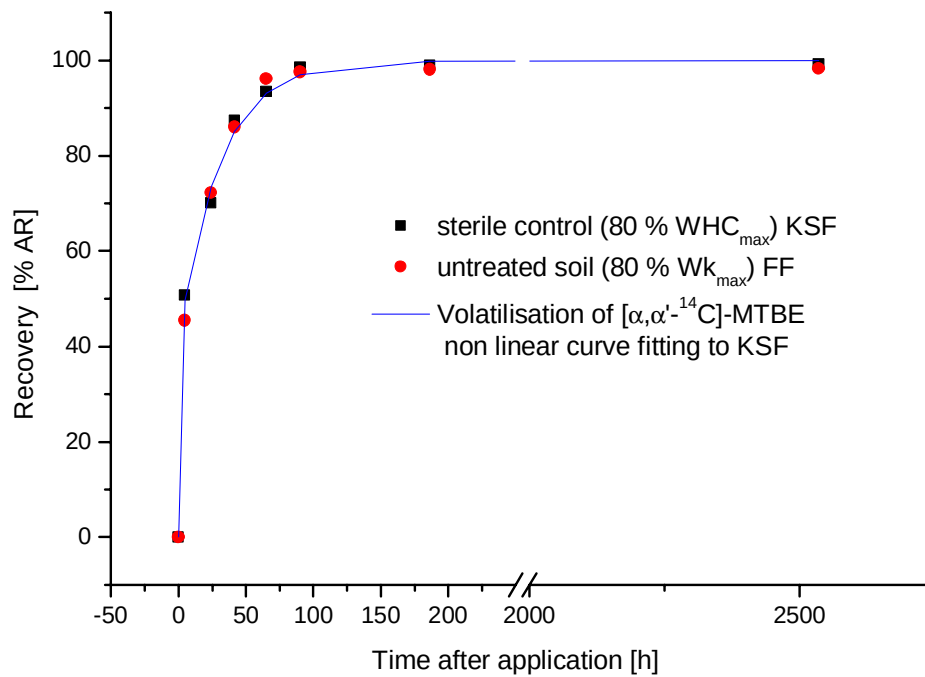


Fig. 21: 2nd degradation study with $[\alpha, \alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ in a gleyic cambisol: Degradation behaviour of $[\alpha, \alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ in the moist variants of the gleyic cambisol in the 2nd degradation study at a moisture of 80 % WHC_{max} .

Fig. 21 shows the volatilization in the course of time. The volatilization can be described by a non-linear fitting according to the least squares method with Microcal™ Origin® Version 6.0 in the following function (**Eq. 15**). A simple exponential function showed the best agreement (correlation coefficient $r^2 = 0.935$) of the measured values with the fitted function. A composite exponential function as in OPHOFF (1998) displayed a considerably better fitting curve for the data, although some parameters were over estimated so that the function was not applicable.

$$y = y_0 + A_1 \left(1 - e^{-\frac{x}{t_1}} \right) \quad (\text{Eq. 15})$$

In both the studies, the mineralization of $[\alpha, \alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ to $^{14}\text{CO}_2$ was only very slight. In the 1st and 2nd degradation study, the mineralization rate after 8 d was approx. 1 % AR. In the 2nd degradation study, a mineralization of 1.6 % AR was only detectable after 101 d. In the sterile variants of the gleyic cambisol, a weak mineralization (0.21 % AR at 80 % WHC_{max} (KSF) & 0.27 % AR at 40 % WHC_{max} (KST)) was measurable after an experimental period of 18 d in the first study. At the same time, a strong fungal mycelium formation was observed on the soil in these experimental pots.

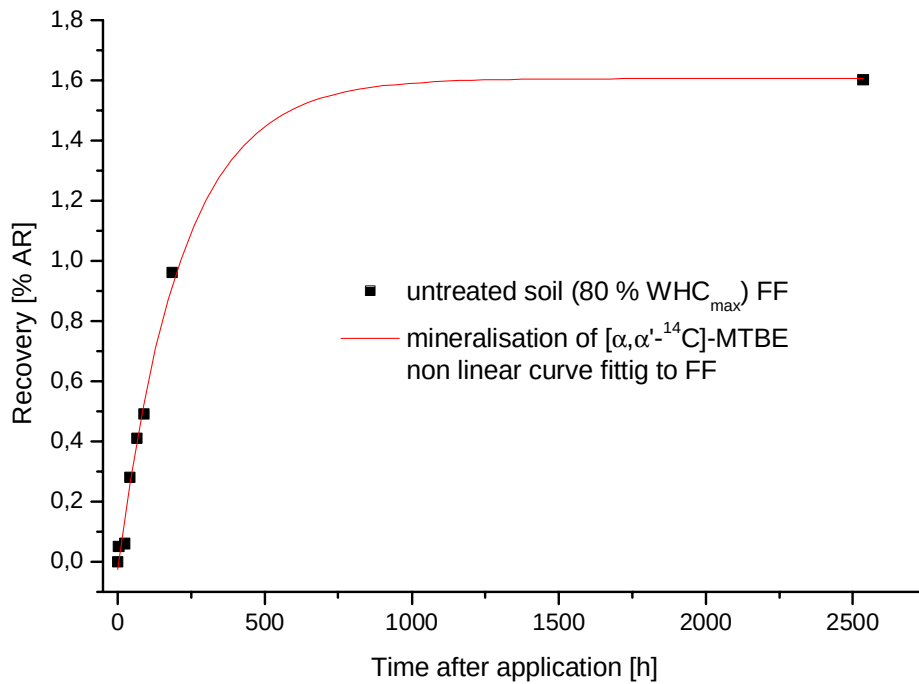


Fig. 22: 2nd degradation study with $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE in a gleyic cambisol: Mineralization of $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE in the moist untreated gleyic cambisol of the 2nd degradation study at a soil moisture of 80 % WHC_{max} .

A more rapid $^{14}\text{CO}_2$ formation was observed in the alluvial loam than in the other variants of the gleyic cambisol. In the former case, after the first measurement (3 d) 0.38 % AR was already mineralized in contrast to 0.25 % AR in the less moist gleyic cambisol (FT, 40 % WHC_{max}). Mineralization reached its maximum (0.61 % AR) in the alluvial loam on the 8th day after contamination. The mineralization rate did not increase further on the following sampling days. It was not possible to establish any maximum after contamination in the case of the gleyic cambisol previously unpolluted with MTBE in the 1st degradation study since the variation range of the individual samples on days 8 and 10 does not permit any unambiguous conclusion.

In the 2nd degradation study, a continuously increasing mineralization rate over time was obtained for the untreated (native) gleyic cambisol in the same order of magnitude as that in the 1st degradation study. The 1st order relation for the formation of $^{14}\text{CO}_2$ from $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE in the gleyic cambisol unpolluted before the contamination is described by (Eq. 16). It can be seen that the fit function is in good agreement with the data. At 0.00278 the square error sum is very low so that a first-order degradation can be assumed with respect to the formation of $^{14}\text{CO}_2$.

$$y = y_0 + A_1 \left(1 - e^{-\frac{x}{t_1}} \right) \quad (\text{Eq. 16})$$

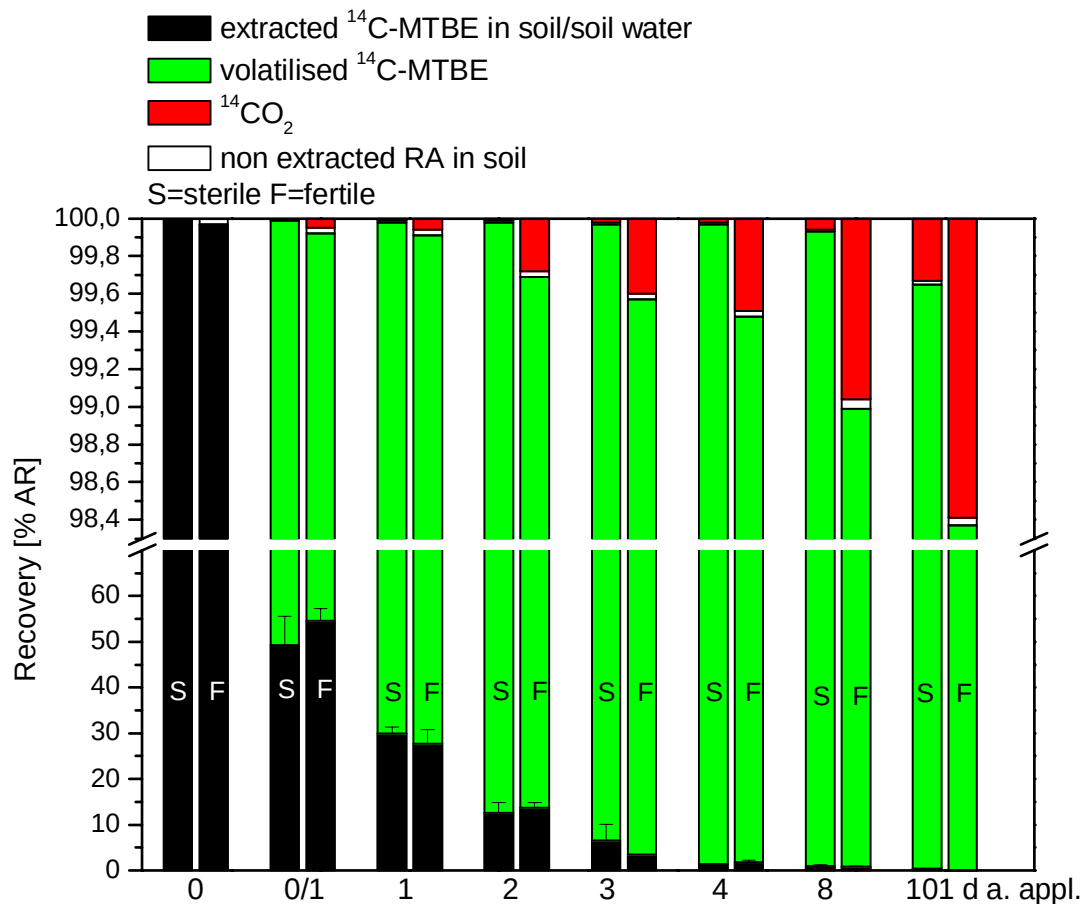


Fig. 23: 2nd degradation study with [α,α' - ^{14}C]-MTBE in a gleyic cambisol: Radioactivity distribution of the different variants in the 2nd degradation study on the individual sampling dates at a soil moisture of 80 % WHC_{max} (applied radioactivity = 100 %).

(S = sterile moist control for the gleyic cambisol (80 % WHC_{max}), F = moist native gleyic cambisol sample (80 % WHC_{max}))

Another obvious effect of the individual variants was observed in the formation of non extracted radioactivity (**Fig. 20**). A much greater formation of non-extracted residues was observed in the untreated samples (unsterilized gleyic cambisol (FT, 40 % WHC_{max}), (FF, 80 % WHC_{max}) and the alluvial loam variant (TB, 40 % WHC_{max})) with the native microflora than in the sterilized control variants of the gleyic cambisol ((KST, 40 % WHC_{max}), (KSF, 80 % WHC_{max})). At approx. 1 % AR, the recovered radioactivity was about three times that of the control variants. The gleyic cambisol sample displayed greater residue formation than the alluvial loam. Almost no formation of bound ^{14}C activity (< 0.04 % AR, **Fig. 23**) occurred in the moister samples in the 2nd degradation study (80 % WHC_{max}).

In addition to the radioactivity distributions on the individual sampling days, the microbial activity was also determined in three replicates each (**3.1.2.3**). The measurements indicate the level of activity and thus the conversion of organic substances in the soil. In the 1st degradation study it was shown that the microbial activity decreased with increasing experimental time up to 192 h ($\approx$ 8 d) after contamination with MTBE (**Fig. 24**). The effect of a minimum

value was also confirmed in the 2nd degradation study. In addition, the biological activity in an unpolluted system (control with moist soil) was examined in the 2nd study to determine the toxicity effect of MTBE on the microorganisms. After 186 h, the biological activity was somewhat higher than in the same system with MTBE. At the end of the study (101 d), a higher value was again measured for the contaminated soil sample. On the whole, on all sampling days, especially the first 3 days, a high variation range of the individual measurements (3 per sampling day and variant) was found, which made it impossible to differentiate between contaminated and uncontaminated soil (**Fig. 25**).

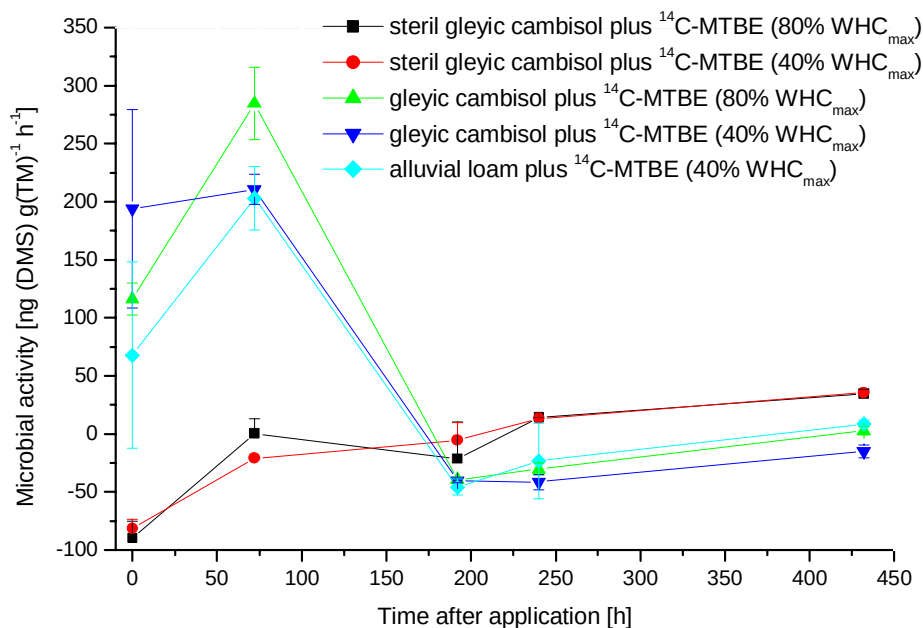


Fig. 24: 1st degradation study with [α,α' -¹⁴C]-MTBE in a gleyic cambisol and an alluvial loam: Measured biological activity (ALEF, 1990) of the variants in the first degradation study on the various sampling dates.

In the 2nd degradation study (Fig. 25), a significant increase in biological activity was measured ranging from 44 ng (DMS) g(TM)⁻¹ h⁻¹ at 186 h after contamination to 407 ng (DMS) g(TM)⁻¹ h⁻¹ after 101 d in the native moist gleyic cambisol variant (FT, 80 % WHC_{max}). The uncontaminated control similarly displayed a sharp increase from 81 to 361 ng (DMS) g(TM)⁻¹ h⁻¹ in the same period (**Fig. 25**). This slight rise after passing through a minimum was confirmed in both studies. In the first degradation study, after 192-240 h the biological activity of the sterile controls was higher than the values of the different soil variants (40, 80 % WHC_{max}). After 192 h, perceptible fungal mycelium growth was also visible on the soil surface of the sterile controls for the gleyic cambisol ((KST, 40 % WHC_{max}) (KSF, 80 % WHC_{max})).

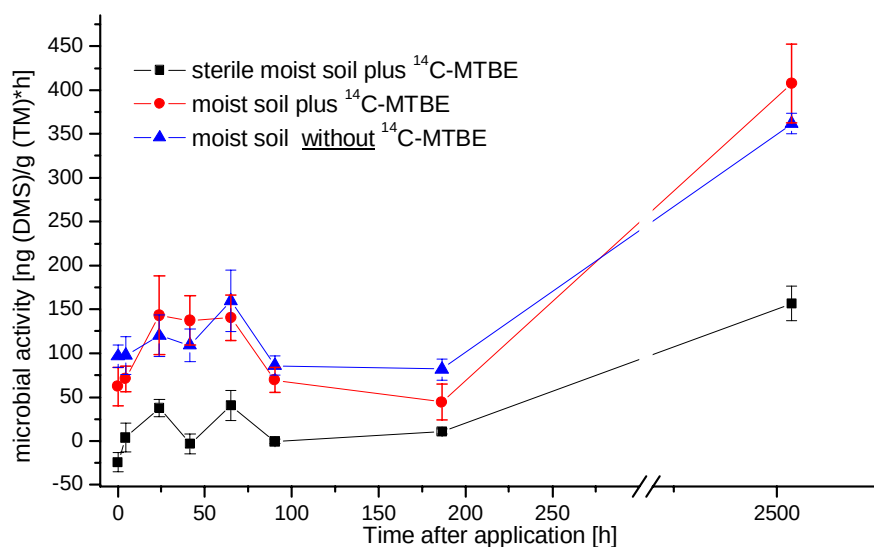


Fig. 25: 2nd degradation study with [α,α' -¹⁴C]-MTBE in a gleyic cambisol: Measured biological activity (ALEF, 1990) of the variants in the 2nd degradation study on the various sampling dates.

4.2 Column experiments

The column experimental set-up for examining the transport behaviour of volatile hydrocarbons from the soil into the atmosphere after a simulated leak (groundwater contamination) was validated in several experiments. Two experiments (MTBE-S1, MTBE-S2) were performed and evaluated.

4.2.1 First column experiment with MTBE

An important precondition for studies with climate-influenced transport processes is to record and control the temperatures, moistures and volumetric flows. As described in 3.2.2, various climatic data were continuously recorded and monitored by computer throughout the entire experimental period (3.2.1.4). **Fig. 26** shows all the measured climatic data in the first column experiment (MTBE-S1).

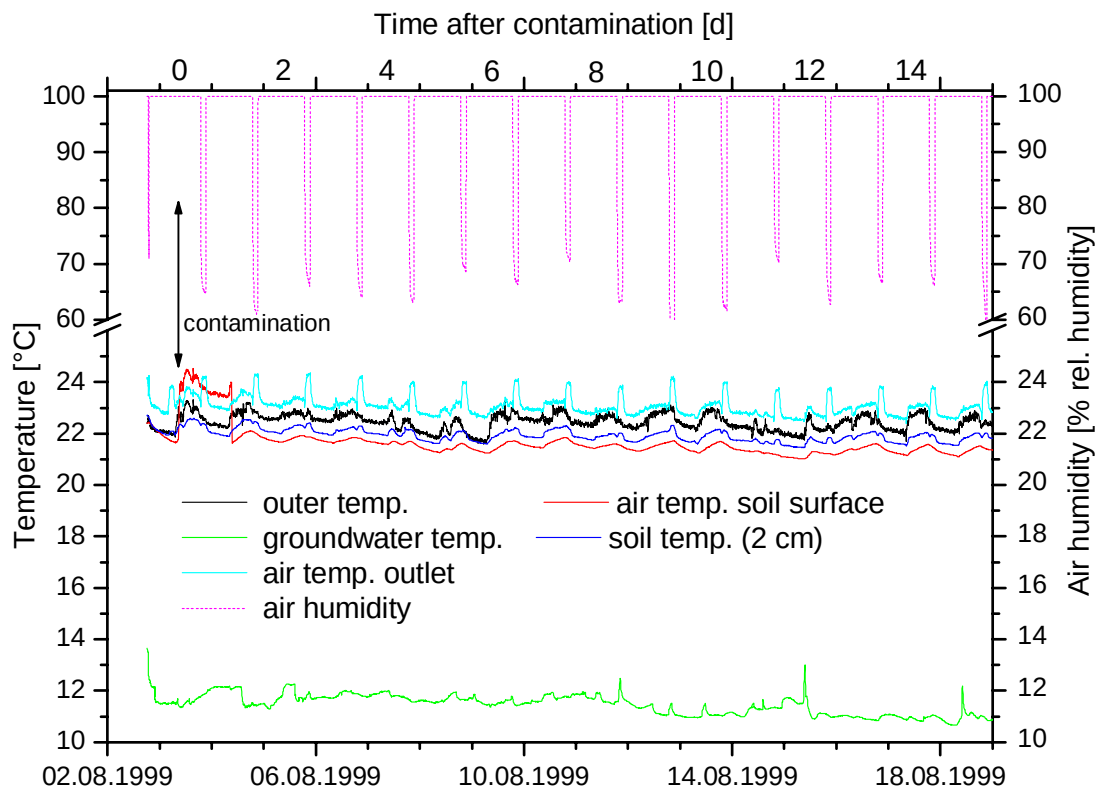


Fig. 26: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Climatic conditions of the first column experiment (MTBE-S1) during the experiment.

The temperature of the outside air was kept constant throughout the experimental period and only displayed slight deviations from the average (approx. 1 %). This was an important pre-condition for the column set-up in order to ensure constant and reproducible conditions throughout the experimental period. Temperature fluctuations of ± 0.3 °C from the daily average were measured within one experimental day.

Due to the poor heat transmission through the steel jacket and the soil body, these fluctuations only had a slight effect on the soil monoliths. The perceptible peaks in the air humidity and air temperature at the outlet were caused by sampling of the reference outside air and the associated valve connection (3.2.2.3) and were eliminated by averaging the corresponding parameters.

The groundwater temperature displayed greater variations (± 3.4 %) than the other parameters. In part, brief disturbances of the thermostat or blockages of the inlet valve by rust particles were responsible for the distinct temperature increases (11 d and 13 d after contamination) (LINNEMANN ET AL., 2000). This disturbance was also apparent in the concentration of MTBE in the groundwater. The measured concentration of 247 mg L^{-1} was

perceptibly greater than the calculated concentration resulting from the measured value on the previous days and the quantity of MTBE subsequently added (approx. 198 mg L^{-1} , **Fig. 27**).

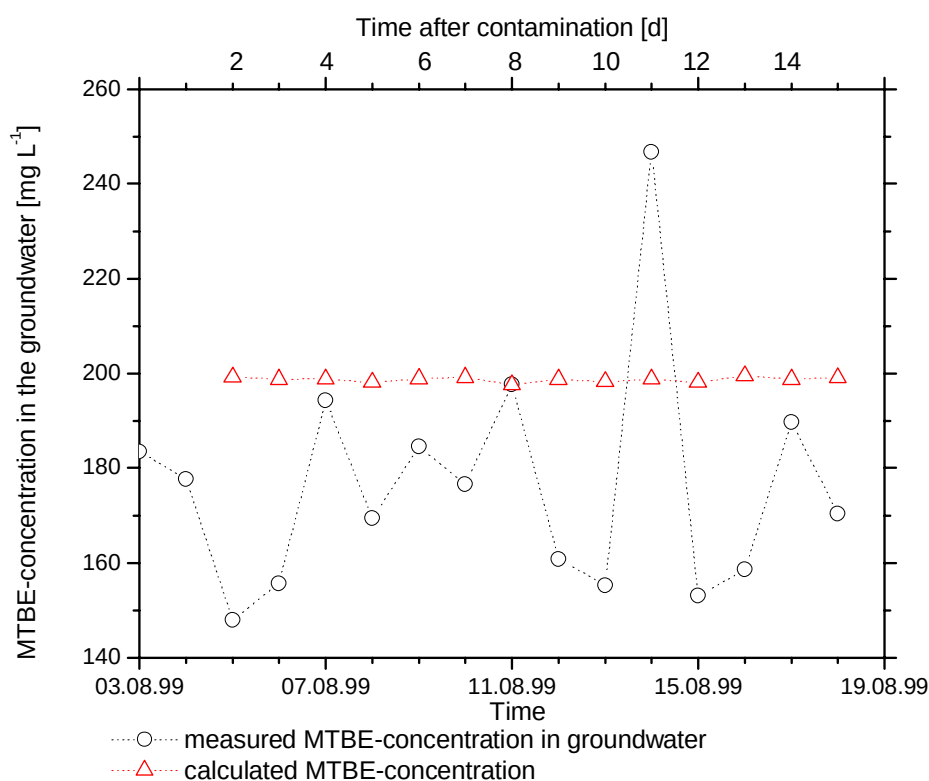


Fig. 27: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: MTBE concentration in the groundwater - measured and calculated content in the 1st column experiment (MTBE-S1) over time.

After a starting phase of 2 d, the required quantity of MTBE was added in order to reach $198 \pm 0.5 \text{ mg L}^{-1}$ in the groundwater. With the exception of the above-mentioned date, this theoretical concentration was not exceeded on any day. A perceptible loss of MTBE from the groundwater reservoir was usually found. The measured contents of MTBE were $170.3 \pm 16.9 \text{ mg L}^{-1}$. In the first two days after contamination, there was no MTBE addition. After it had been established that the losses of MTBE from the groundwater reservoir fluctuated very greatly per day ($95.1 \pm 64.4 \text{ mg d}^{-1}$) and that far more than 10 % per day of the total quantity of MTBE from the aqueous compartment entered the soil, the volume was made up to the preset value every day.

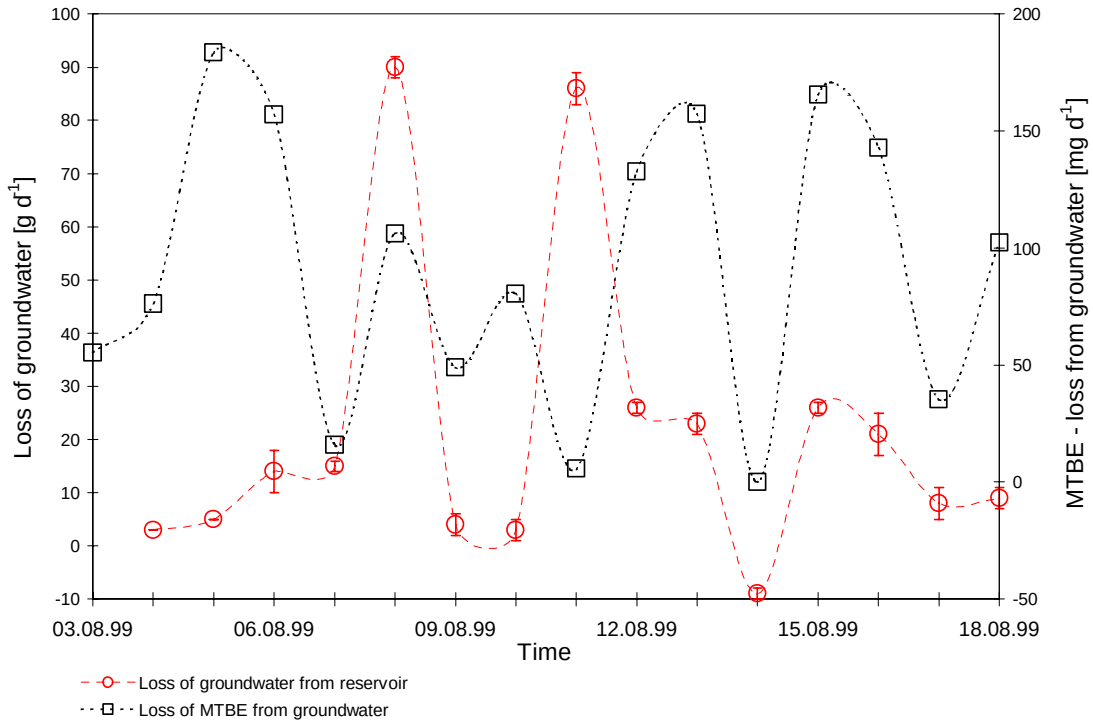


Fig. 28: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Dependence of MTBE loss on groundwater loss from the reservoir in the first column experiment (MTBE-S1).

No constant MTBE loss from the groundwater was detected during the experimental period. However, a qualitative relation between the groundwater loss and the MTBE loss became apparent in the 1st column experiment (**Fig. 28**). With one exception, an increased MTBE loss was always measured together with an intensified water consumption from the simulated perched aquifer. However, it was not possible to derive a quantitative relationship so that no simple empirical function could be found for correlating the two parameters. Failure of the groundwater circulation system meant that the loss of MTBE had to be manually set to zero on 14 August 1999. Once the system was restarted, an obvious rise in groundwater loss with the concomitant MTBE loss became apparent.

$$x_s = 0,622 \cdot \frac{p_s}{(p - p_s)} \quad (\text{Eq. 17})$$

$$p_s = 288,68 \text{ Pa} \cdot \left(1,098 + \frac{T}{100^\circ\text{C}} \right)^{8,02} \quad (\text{Eq. 18})$$

x_s =moisture content at saturation [$\text{kg}_{\text{water}} \text{ kg}_{\text{air}}^{-1}$]

p_s =saturation pressure at T[Pa]

p =total pressure [101300 Pa]

T =system temperature [22 C]

Allowing for the measuring error, the soil moisture was constant at both measured levels (20 and 40 cm GL) (**Tab. A-30**).

The evaporation can be calculated from the relative air humidity at air saturation by the formulae (**Eq. 17**) and (**Eq. 18**) (HYGROTEC, 1998). A mean moisture content of $16.67 \text{ g}_{\text{water}} \text{ kg}_{\text{air}}^{-1}$ is obtained for the experimental temperature of 22°C . If 138.4 L d^{-1} is assumed to be the total air volume per day and this is converted by the density of the dry air ($\rho_{\text{air}} = 1.2928 \text{ g dm}^{-3}$) this yields a mean evaporation rate of $2.98 \text{ g}_{\text{water}} \text{ d}^{-1} \text{ column}^{-1}$ ($\cong 0.095 \text{ mm d}^{-1}$). Arithmetically, a constant evaporation rate was expected since pressure and temperature remained constant (**Tab. A-30**). However, the measured groundwater loss is significantly higher than the calculated evaporation value (**Fig. 28**). **Tab. 14** shows the evaporation rates calculated from the groundwater loss. The maximum deviations were greater than the calculated values by an order of magnitude. In order to understand these deviations, in the 2nd column experiment an air dehumidifier was installed in the column outlet with a temperature-moisture sensor connected in series and the actual evaporation was not only calculated but also determined gravimetrically (**Tab. 16**).

Tab. 14: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Evaporation rates in the 1st column experiment calculated from the groundwater losses in the 1st column experiment.

Days after contamination	Groundwater loss [$\text{kg d}^{-1} \text{ column}^{-1}$]	Evaporation [mm d^{-1}]	Deviation from theory① [%]
	0,003	0,095	+0,67
	0,005	0,159	+67,78
	0,014	0,446	+369,78
	0,015	0,477	+403,34
	0,09	2,865	+2920,05
	0,004	0,127	+34,22
	0,003	0,095	+0,67
	0,086	2,737	+2785,82)
	0,026	0,828	+772,46
	0,023	0,732	+671,79
	-0,009	-0,286	-402,00
	0,026	0,828	+772,46
	0,021	0,668	+604,68
	0,008	0,255	+168,45
	0,009	0,286	+202,00
Mittelwert	$0,022 \pm 0,028$	$0,688 \pm 0,882$	

① Theoretical evaporation (0.098 mm d^{-1}) at air saturation (see above)

In addition to measurements in the aqueous phase, the air flow above the soil surface was collected continuously and the MTBE content in the air was determined by TDS-GC/MS analysis. For this purpose, the air was collected for 144 min on a thermodesorption tube and then analysed. Averages of the air concentration were thus recorded for 2.4 h and the daily average then calculated from these values. Two methods were used to evaluate the spectra, which only differed in the quality and reliability of the given data. Quantification was only formed via a target mass, which was identical in both methods ($m/t = 73 \text{ amu}$).

In the first method, only those analytical data were analysed that additionally displayed two other qualifier ions in the correct ratio to the target ion. In the second evaluation method, only one qualifier ion was required for a positive analytical result (RAESE ET AL., 1995). **Fig. 29** shows the concentrations (2.4 h averages) found in the gas phase over time.

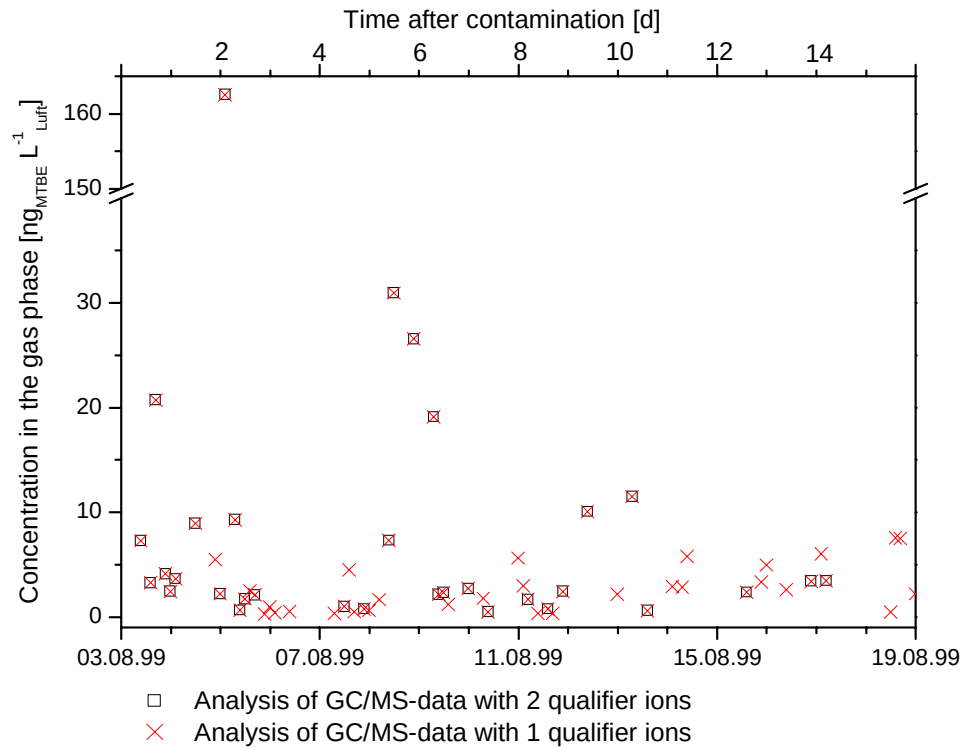


Fig. 29: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Evaluation of thermodesorption GC/MS measurements from the 1st column experiment (MTBE-S1) with evaluation methods with different levels of reliability in the form of MTBE concentration in air.

In the first sampling interval (0 - 2.4 h after contamination), 7.29 ng L⁻¹ MTBE was already detected in the gas phase above the soil. However, it was not possible to detect continuous transport out of the groundwater through the soil into the atmosphere. The concentrations found ranged between 0.3 and 168 ng L⁻¹ with an average of 15.2 ng L⁻¹ of air (9.63 ng L⁻¹ for 1 qualifier). The 2nd evaluation method identified considerably more positive results (×, **Fig. 29**) than the more reliable method (□, **Fig. 29**). These data were all in the low concentration range, where it is important to validate the analytical data in comparison to the matrix pollution from the groundwater. Finally, only 20.5 % (and 40.6 % respectively) of the samples measured were evaluated with a positive result (> 0.2 ng L⁻¹ air).

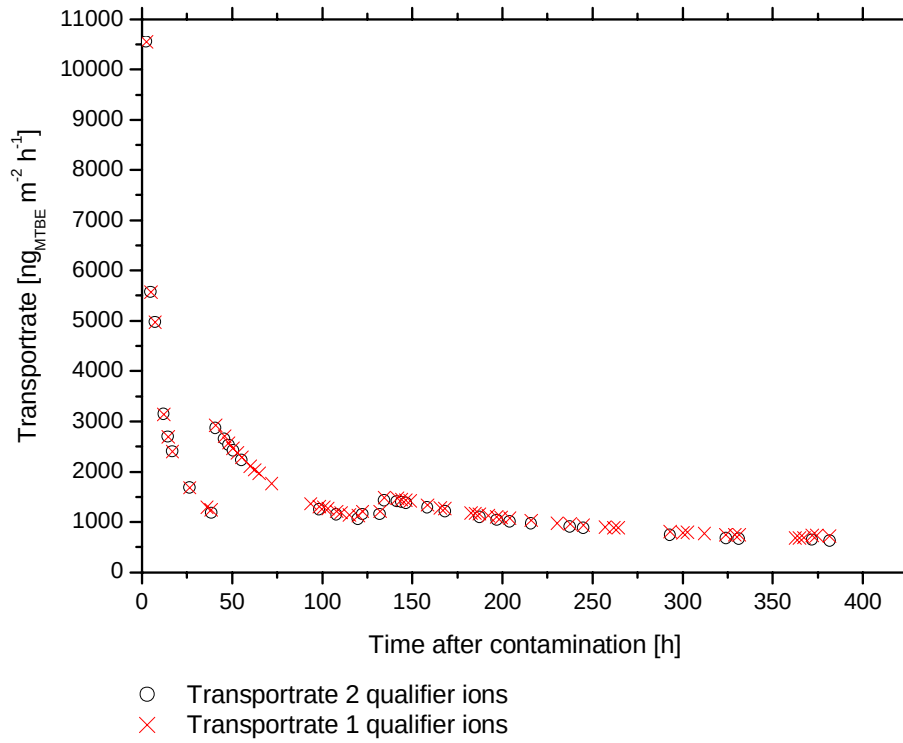


Fig. 30: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Transport rates of MTBE from the soil into the air in the 1st column experiment (MTBE-S1) over time after evaluation with various quality levels.

The transport rates were calculated from the MTBE quantities found in the air and the associated time after contamination. The rates were on average $1.94 \pm 1.88 \mu\text{g m}^{-2} \text{h}^{-1}$. The transport rates are represented as a function of time in **Fig. 30**. It became apparent that the transport rates are exponentially reduced with increasing time and approach a value of about $800 \text{ ng m}^{-2} \text{h}^{-1}$ five days after contamination. The course of the curve was only interrupted by two outliers after 40 h and 134 h respectively, which due to the very high values caused a sharp rise in the transport rates. If these outliers are neglected, a good correlation of the curve with time can be found ($R^2 = 0.97$). Even a fit to the original data still yielded an acceptable correlation (**Eq. 19**).

$$y = y_0 + A_1 \cdot e^{-\frac{x}{t_1}} + A_2 \cdot e^{-\frac{x_0}{t_2}} \quad (\text{Eq. 19})$$

$$y_0 = 451,61 \pm 22,54 \quad (471.14 \pm 249.56)$$

$$A_1 = 15952,53 \pm 2752,51 \quad (14395.59 \pm 2710.92)$$

$$t_1 = 2,61 \pm 0,46 \quad (3.79 \pm 0.73)$$

$$A_2 = 3846,92 \pm 476,61 \quad (1967.07 \pm 235.85)$$

$$t_2 = 25,34 \pm 2,82 \quad (151.65 \pm 57.54)$$

$$R^2 = 0.97631 \quad (0.910)$$

$$\text{Chi}^2 = 20.96288(69.90)$$

(Values in brackets were calculated with the original dataset without eliminating the outliers)

The cumulative volatilization is shown in **Fig. 31** together with the cumulative loss of MTBE from the groundwater. It was demonstrated that only minimal transport of MTBE occurs out of the groundwater into the atmosphere. The ratio of the MTBE measured in the gas phase to the MTBE escaping from the groundwater in the same period is $1:10^5$. A total of only 0.004 ‰ of the applied quantity of MTBE was volatilized during the experimental period. After completing the experiment, 30.34 % of the total MTBE added to the groundwater throughout the experimental period was detected (100 % = total applied MTBE) (**Tab. 16**).

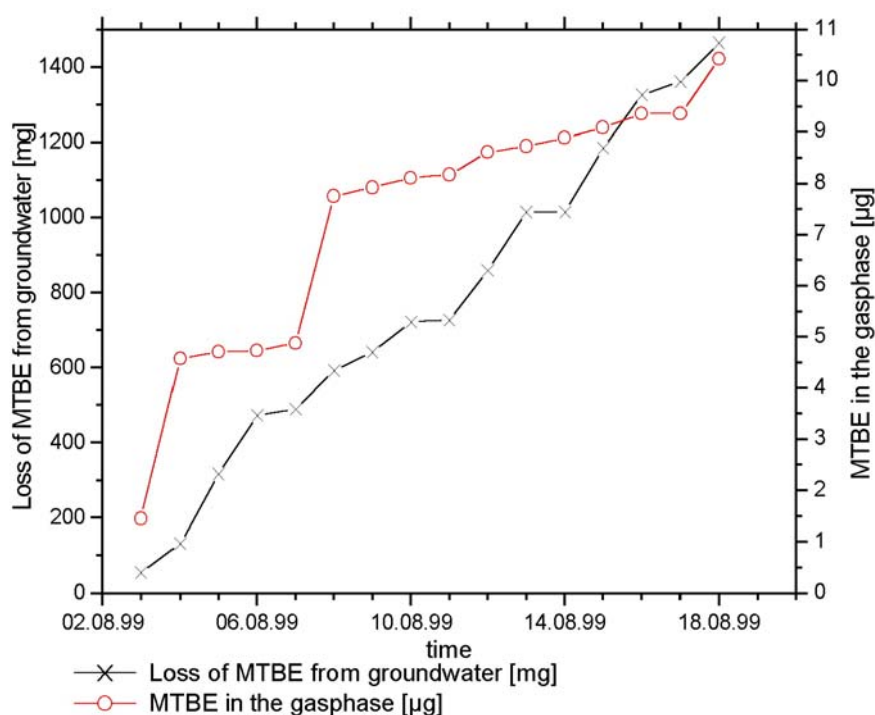


Fig. 31: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Cumulative MTBE losses from the accumulated water and the quantities of MTBE found in the gas phase in the 1st column experiment (MTBE-S1).

The quantity of MTBE determined in the gas phase increased continuously at a lower rate than the total MTBE losses from the groundwater. Only on the first two days and on the sixth day after application was volatilization measurable that was higher than the average by a factor of 10.

On three experimental days, the loss of groundwater was perceptibly lower than on the other days. As already described above for the evaporation, **Fig. 31** only permits qualitative comparisons to be made between the MTBE source (groundwater) and the possible MTBE sink (atmosphere). At the end of the experiment, the groundwater was drained off and samples immediately taken from the soil core (**3.2.2.4**). Although the soil samples were frozen in liquid N₂ immediately after sampling, the extraction of the soil samples did not provide any insights about the distribution of MTBE in the soil since all the soil extracts analysed were below the detection limit. On the whole, the balance of the experiment with 30.34 % of the applied

quantity of MTBE was very poor (**Tab.15**). For this reason, in the second experiment the radioisotope technique was applied in addition to conventional analytical methods.

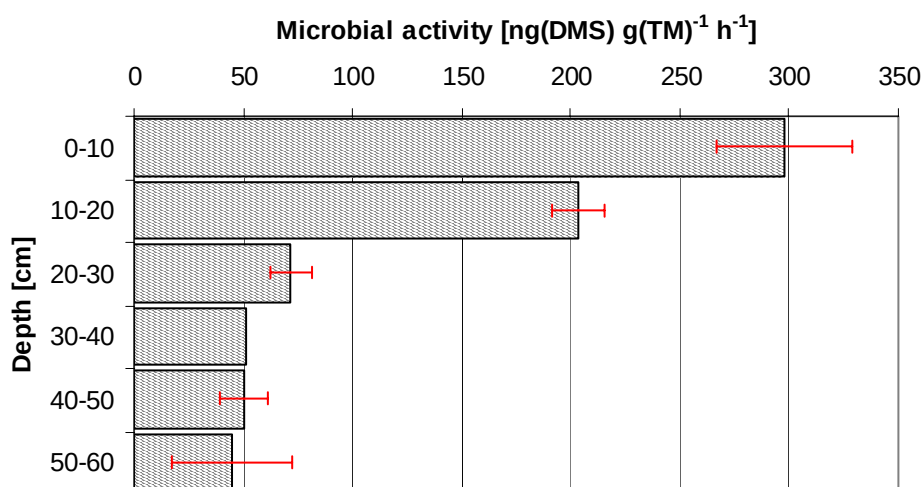


Fig. 32:1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: Microbial activity (ALEF, 1990) at the individual soil depths in the 1st column experiment (MTBE-S1) after terminating the experiment.

In addition to the pollutant analyses, at the end of the experiment analyses were performed of the microbial activity (**Fig. 32**), the carbon distribution and also other soil and groundwater analyses. Soil cores removed using a HUMAX hand-held soil coring system were examined with respect to the biological activity at various depths. With increasing soil depths, the biological activity dropped from almost 300 ng (DMS) g(TM)⁻¹ h⁻¹ to less than 50 ng (DMS) g(TM)⁻¹ h⁻¹ at a depth of 60 cm. In this segment, at least half the soil layer was saturated with groundwater (5 cm groundwater rising). Below the plough layer (= 30 cm tillage horizon), the microbial activity was almost constant.

A soil gas investigation involving the adsorption of MTBE on thermodesorption tubes could not be evaluated since the needles for gas sampling came clogged with fine sand particles in the soil and thus insufficient gas volume was collected for an analysis (**3.4.1.2**).

Tab. 15: Column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation: MTBE balance of the first column experiment (MTBE-S1) at the end of the experiment including volatilization during the experimental period of 16 d and selected climatic conditions

Net applied quantity = 2050.45 mg (1 major contamination with 12 subsidiary contaminations)

Experiment	Substance quantity (mg)	% appl. MTBE
volatilisation	0,01	0,004 ⁰ / ₀₀
groundwater	622,20	30,34
soil extraction	n. d.	0,0
Σ MTBE (mg or % AR) ^①	622,21	30,34
climatic data^②		
T _{air} above the soil	21,6 ± 0,6 °C	
T _{outside air}	22,5 ± 0,2 °C	
T _{soil} (2 cm)	21,9 ± 0,2 °C	
T _{groundwater}	11,5 ± 0,4 °C	
groundwater volume	3,611 L (start) – 3,287 L (end)	
T _{air} flow/rH _{air} flow (column outlet)	23,0 ± 0,2 °C / > 99,5 %	
T _{air} /rH _{air} (outside)	23,8 ± 0,2 °C / 69,9 ± 4,3 %	
volumetric flow (air)	0,1 L min ⁻¹	
air volume per sample	13,8 ± 0,0 L	
total air volume per day	138,4 ± 0,2 L	
total air volume in experiment	2214,4 L	

^① Deviations between the sum of the individual values and the sum specified are due to rounding errors.

^② The climate and air cumulative data are only averages/or total values (Tab. A-31).

4.2.2 Second column experiment with $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$

The 2nd column experiment (MTBE-S2) was performed under conditions similar to those of the MTBE-S1 study. $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ was additionally injected into the system together with unlabelled MTBE so that a concentration of $117 \text{ mg L}^{-1}\text{MTBE}$ was adjusted in the groundwater. In addition to the main application on 13 April 2000, a further three subsidiary contaminations (17, 19 and 20 April 2000) were applied to keep the MTBE content constant. **Fig. 33** shows the climatic data throughout the experimental period of 14 days.

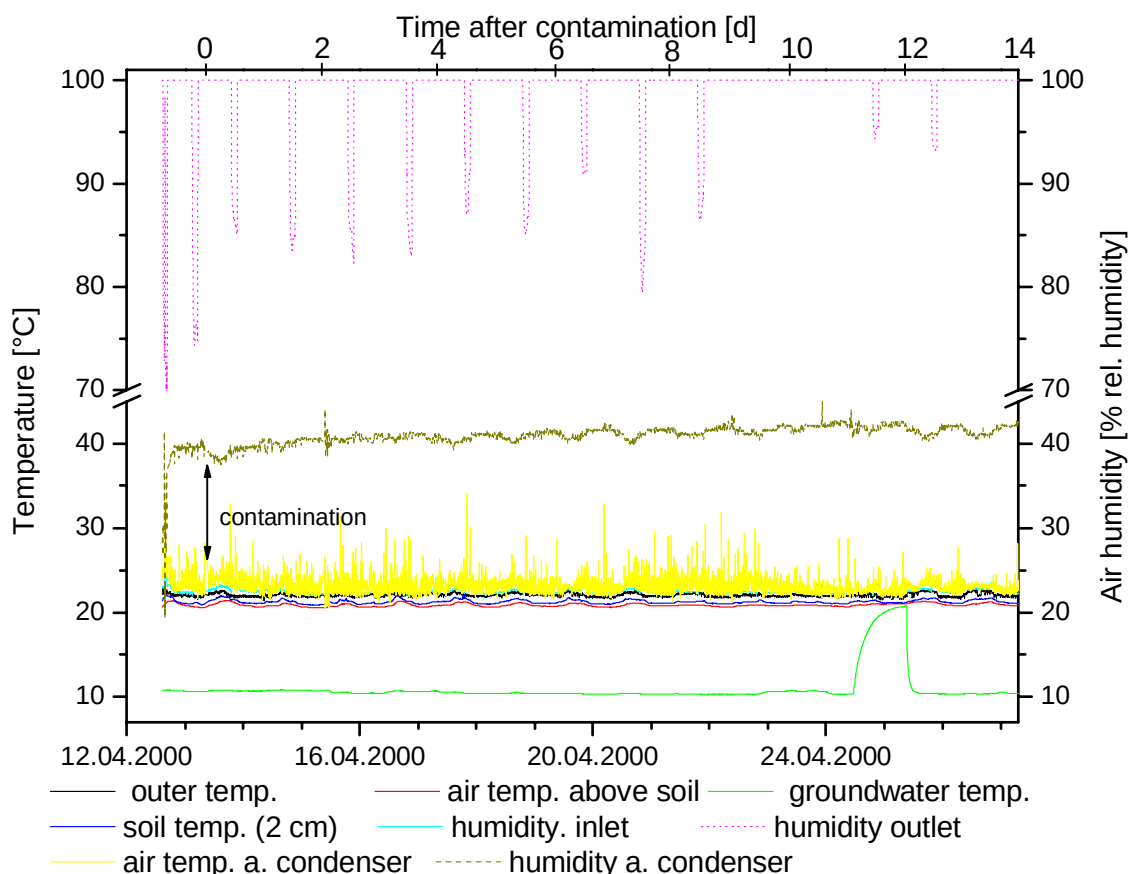


Fig. 33: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ in the simulated groundwater accumulation: Climatic conditions of the 2nd column experiment (MTBE-S2) during the experiment.

All the temperatures shown above were almost constant ($\pm 1 \%$) throughout the experimental period. The diurnal range of the outside air temperature could also be clearly seen in this experiment. At $21.2 \pm 0.2 \text{ }^{\circ}\text{C}$ the soil temperature was about $0.8 \text{ }^{\circ}\text{C}$ lower than the outside temperature. On average, the air temperature was always 1.4 and $0.5 \text{ }^{\circ}\text{C}$, respectively, lower than the soil temperature in the experiment. The air humidity outside the air dehumidifier was $40 \pm 4.7 \%$ and thus displayed a perceptibly greater variation range than the other parameters since here the deviations were more than 10% of the measured value. The associated air temperature also displayed significant fluctuations within one day due to a very sensitive air humidity sensor. However, this effect was no longer recognizable in the daily average

since the fluctuations here were $\pm 0.3 - 0.6$ % rH. Due to failure of a cooling water thermostat two days before the end of the experiment the groundwater temperature almost rose to that of the soil. In the same period, a perceptible drop in MTBE groundwater concentration was measured by the GC/MS system (Fig. 35). In parallel, the ^{14}C activity in the samples was also determined, from which the MTBE equivalents were then calculated. As shown in Fig. 35, the concentrations calculated in this way are not subject to such great fluctuations ($117.4 \pm 4.1 \text{ mg L}^{-1}$) as the concentrations measured directly ($84.7 \pm 16.6 \text{ mg L}^{-1}$). It was not possible to perform a GC/MS analysis of the groundwater on 19 April 2000.

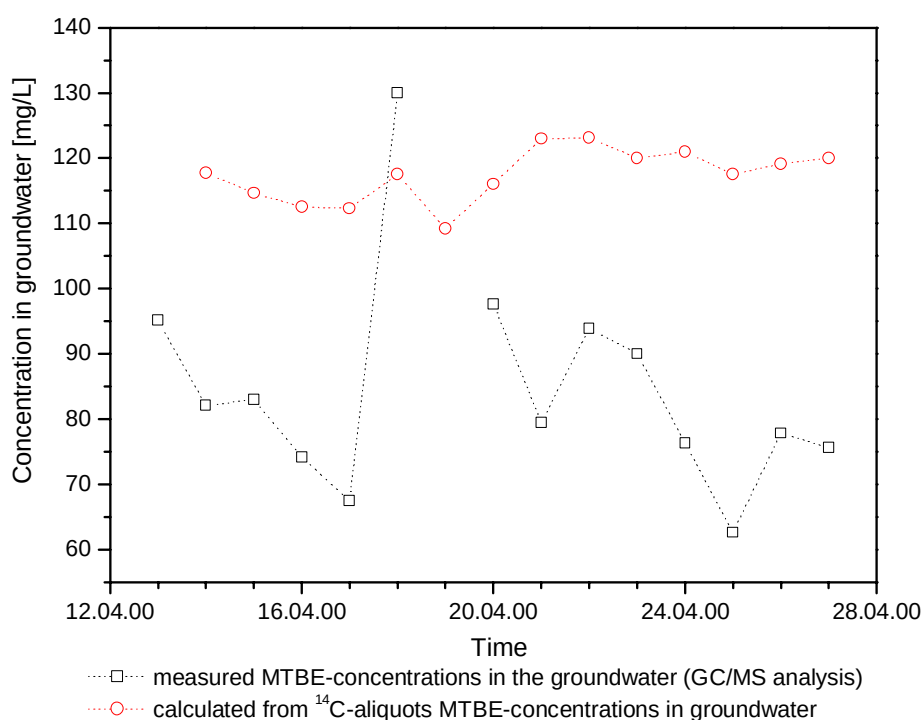


Fig. 34: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Concentration of MTBE in the groundwater in the course of the experiment (calculated by two independent analytical methods) in the 2nd column experiment (MTBE-S2).

MTBE and ^{14}C -labelled MTBE were supplemented 4, 6 and 7 d after the first contamination in order to keep the defined concentration in the groundwater approximately constant. In Fig. 35 an appreciable rise in concentration above the calculated concentration of 117 mg L^{-1} , one day after the first application (18 April 2000) can be observed. None of the other subsequent contaminations displayed this effect. After the two following applications on 19/20 April 2000, the concentration measured by GC/MS initially dropped. After every subsequent contamination, the MTBE equivalents calculated from the ^{14}C activity displayed a significant concentration increase in the groundwater. After 9 d, the content calculated by this method stagnated at a concentration of about 120 mg L^{-1} .

With respect to the cumulative loss of MTBE from the groundwater, then at the end of the experiment it was not on the same level. The total loss calculated from the ^{14}C values was about half that (64.8 mg) of the chromatographically determined value (141 mg). **Fig. 35** shows the total loss of MTBE/ $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE from the simulated water accumulation throughout the experimental period of 14 d.

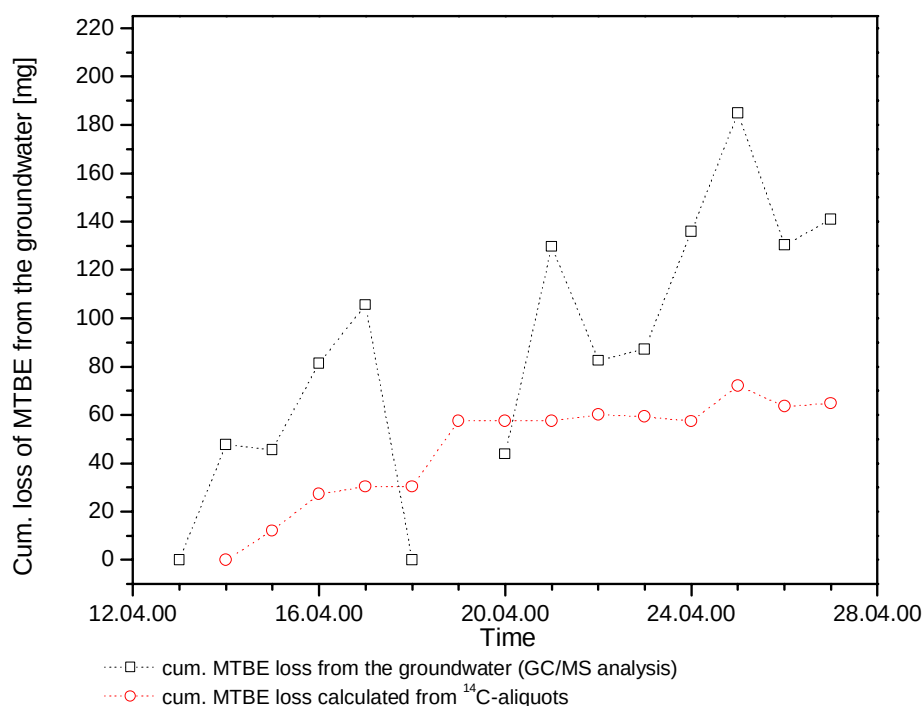


Fig. 35: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Cumulative loss of MTBE from the groundwater calculated according to two different analytical methods - GC/MS analysis with direct injection and conversion of the ^{14}C aliquots into MTBE equivalents in the second column experiment (MTBE-S2).

Tab. 16: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Comparison of groundwater losses in the 2nd column experiment and the true evaporation calculated from the quantities of condensate water at the air dehumidifier.

Days after contamination	Groundwater loss [mm d^{-1}]	True evaporation [mm d^{-1}]
0	0,00	0,000
1	0,73	0,107
2	0,35	0,068
3	2,13	0,059
4	0,70	0,071
5	0,16	0,068
6	-0,22	0,077
7	-1,18	0,065
8	0,35	0,070
9	0,80	0,068
10	-2,99	0,088
11	0,38	0,073
12	0,73	0,083
13	-0,80	0,078
14	1,15	0,059
average	$0,164 \pm 1,21$	$0,074 \pm 0,012$

This column experiment showed that the loss of groundwater, as already represented in the first column experiment (MTBE-S1, **Fig. 28**) was also in this case qualitatively related to the MTBE loss (**Fig. 36**). An exception was the 7th day after contamination where the losses were reversely proportional. In this case as well, no simple mathematical relationship could be found for this correlation. The maximum evaporation rate calculated according to (Eq. 17) was 0.093 mm d^{-1} and was thus insignificantly lower than in the first column experiment. If the actual evaporation calculated from the deposited condensate water is compared with the theoretical value than a slight deviation of $-20 \% \pm 13.4 \%$ results. In comparison, the deviation of the possible evaporation calculated from the groundwater loss from the theoretical evaporation of $+76 \% \pm 1305 \%$ is significantly greater. The gravimetric determination of the evaporation validated the equations used to estimate the maximum evaporation rate. The latter were applied to this experiment since after leaving the column the air flow was saturated ($> 99.5 \% \text{ rH}$). In this case as well, it became apparent that the groundwater loss was not suitable for estimating possible evaporation from the soil monolith.

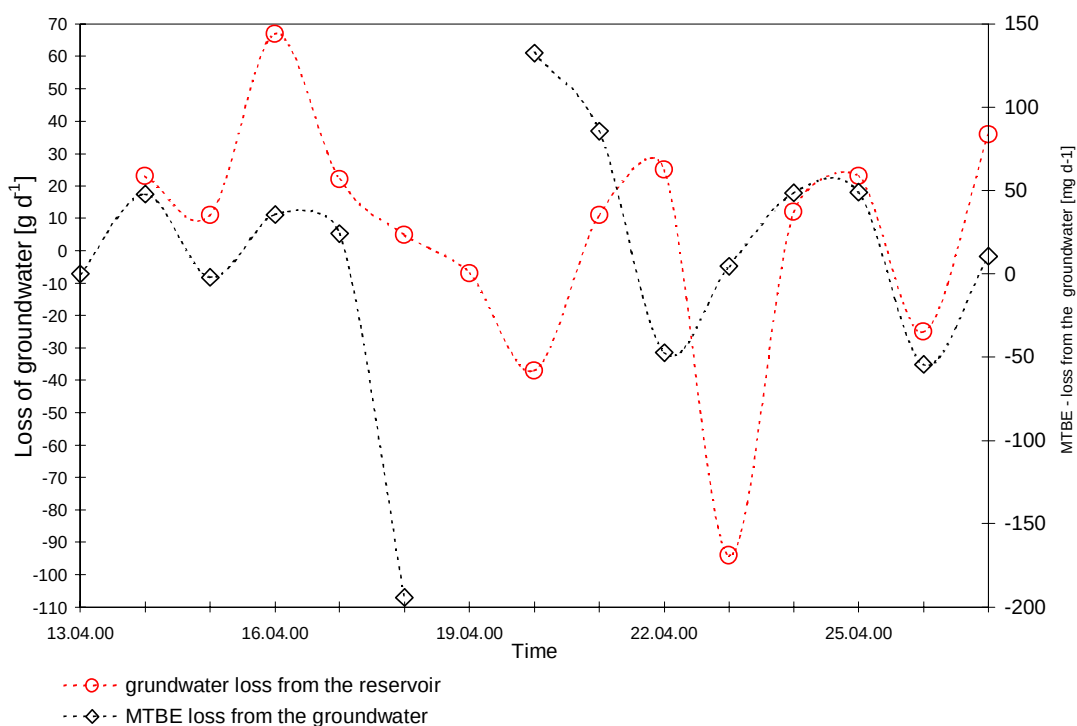


Fig. 36: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Dependence of MTBE loss on groundwater loss from the reservoir in the 2nd column experiment (MTBE-S2)

In the second column experiment, MTBE was added to the system for the 2nd time 7 d after starting the experiment. Some of the measured losses were subsequently found to be negative, i.e. more MTBE was found than could theoretically be present in the system (**Fig. 37**). In order to discuss this phenomenon, several methods for calculating the cumulative loss of ^{14}C -labelled MTBE (% AR) from the simulated aquifer are depicted in the following figure. If all negative values are excluded as impossible events, then a continual rise in MTBE content is obtained (**Fig. 37**). If exclusive use is made of the measurements as a basis, without any

other calculations, then the ^{14}C activity found decreased below its maximum of 7 d and did not reach this level again within the experimental period. The content of ^{14}C -MTBE found fluctuated by approx. 20 % AR. Another evaluation method is to assume a measuring error on the 8th day and to calculate a theoretical value for this day and the subsequent days. The possible reasons for such a course are mentioned in 5.2.

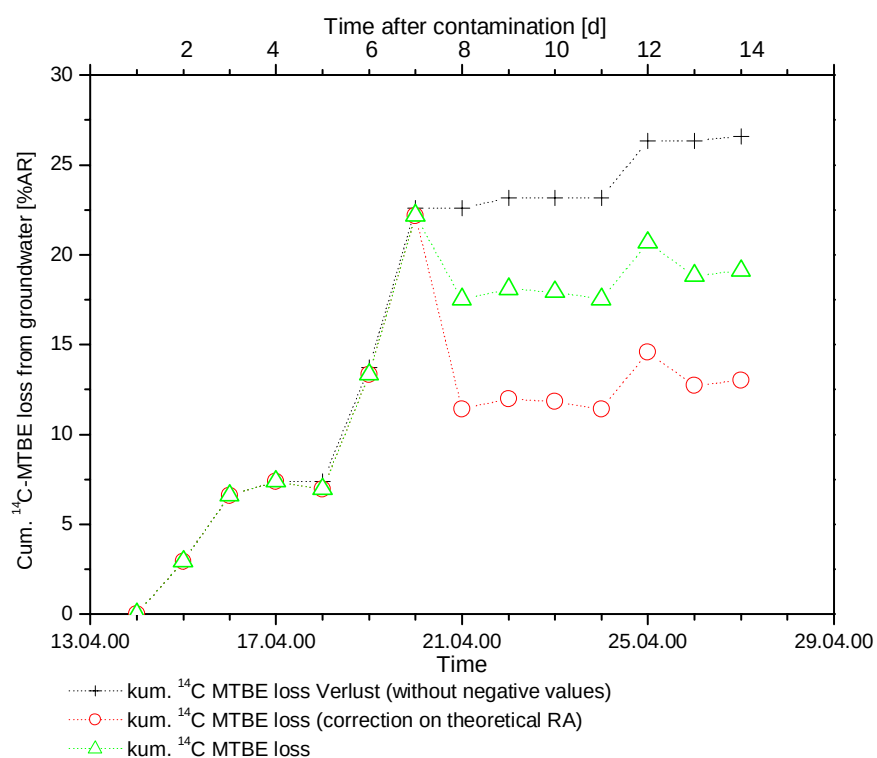


Fig. 37: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Cumulative ^{14}C -MTBE losses from the groundwater calculated according to different evaluation methods in the 2nd column experiment (MTBE-S2).

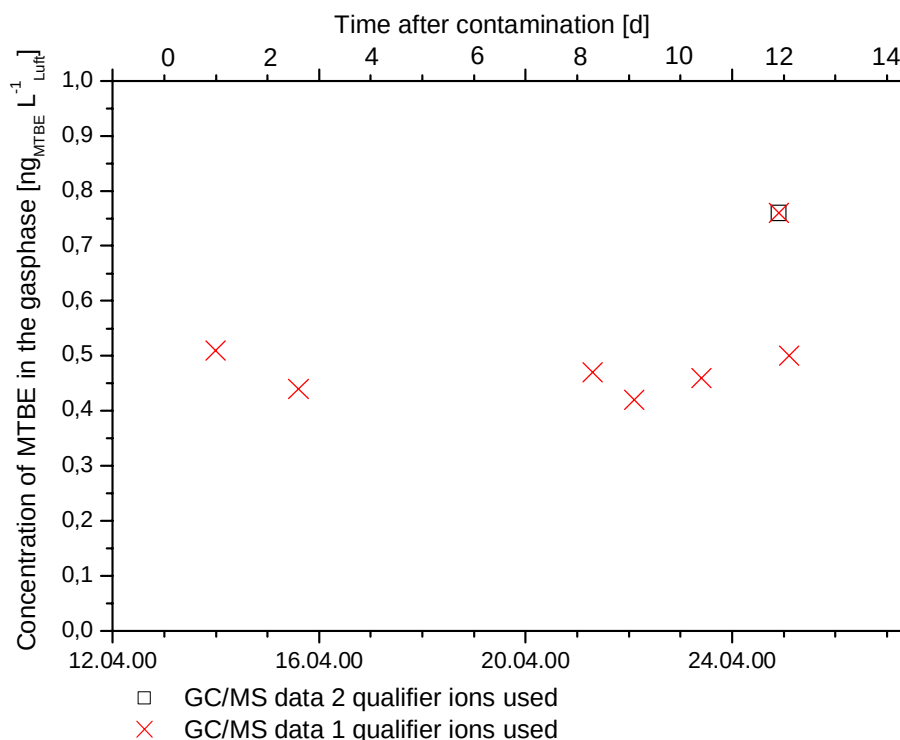


Fig. 38: 2nd column experiment in a gleyic cambisol after contamination with [α,α' -¹⁴C]-MTBE in the simulated groundwater accumulation: Evaluation of thermodesorption GC/MS measurements from the 2nd column experiment (MTBE-S2) with various reliable evaluation methods.

In addition to the groundwater analyses, as in the 1st column experiment (MTBE-S1), 100 mL of air min⁻¹ also continuously flowed through the atmosphere. This air flow was collected and analysed by TDS-GC/MS. It was only possible to quantify the inactive MTBE since the calibration curve had only been set up for unlabelled MTBE. It should be noted that an excess of unlabelled MTBE was present with respect to ¹⁴C-MTBE and its proportion only had to be corrected. It was not meaningful to compare the MTBE losses from the groundwater with the volumes of MTBE found in the atmosphere in this experiment since only slight quantities of MTBE were measured in the air. Only 4.6 % (or 0.7 % if two qualifiers were taken as a basis) of all the samples available were evaluated with a positive result. Only one measurement was unambiguously identified as MTBE (2 qualifiers). All other measurements were in the range of 0.4 -0.5 ng L⁻¹ air (**Fig. 38**). All other analyses indicated data below the determination limit of 0.2 ng L⁻¹ which could not be evaluated. A total volatilized quantity of 49.26 ng was found in the experimental period. The break-through time was 14.4 h after contamination. If the possible transport rates are calculated from the latter, then they are on average 6.49 ± 4.28 ng m⁻² h⁻¹ or 0.76 ng m⁻² h⁻¹ from the more reliable evaluation of the analytical data. **Fig. 39** shows that this does not involve continuous transport but rather a pulsed emission of MTBE as also already observed in the first experiment. In comparison to the first column experiment, no exponentially decreasing curve can be seen.

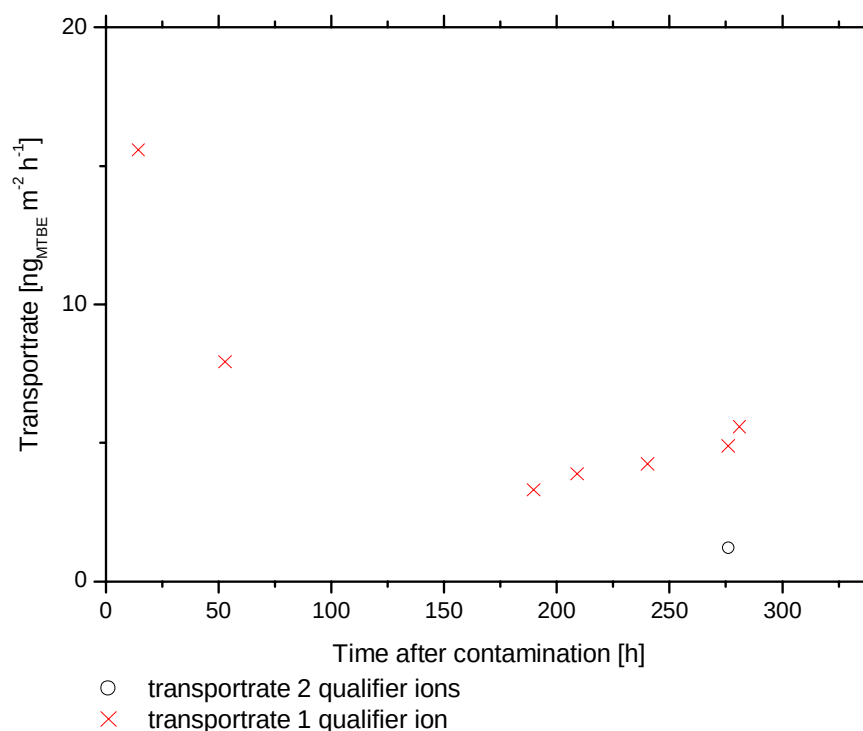


Fig. 39: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Transport rates of MTBE out of the soil into the air in the 2nd column experiment (MTBE-S2) over time after evaluation with different levels of reliability.

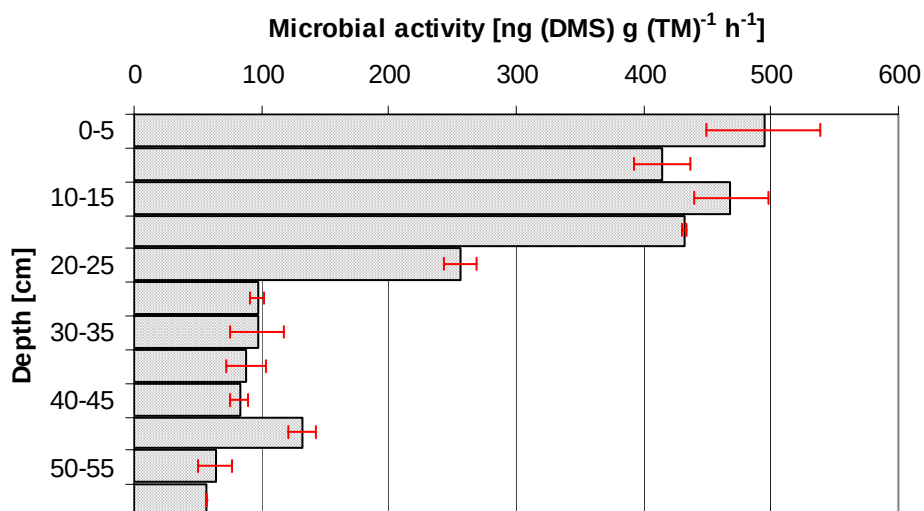


Fig. 40: 2nd column experiment in a gleyic cambisol after contamination with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE in the simulated groundwater accumulation: Biological activity (ALEF, 1990) at the individual soil depths in the 2nd column experiment at the end of the experiment (divided into 5-cm segments).

After the experiment had been terminated, the biological activity was examined in the different horizons and other soil chemical studies were also performed. Furthermore, after freezing in liquid N₂ the soil was extracted with CaCl₂ solution (10 mM). The extracted soil was air-dried and the unextracted radioactivity determined after ashing in the LSC. A continuous decrease in biological activity with soil depth was found (**Fig. 40**). In the upper 10 cm, the values were about 60 % higher than those in the first experiment (**Fig. 32**) although the two columns came from the same plot and were removed at the same time.

The application of ¹⁴C activity made it possible to draw up a balance for all compartments studied (**Tab. 16**). The recovery rate of 102.35 % AR was somewhat higher than the applied quantity of [α,α' -¹⁴C]-MTBE. At the end of the experiment, 89.05 % AR was still contained in the groundwater. The volatilization of 0.0001 o/oo AR was just as low as in the first experiment and is of no significance for the radioactivity balance in this study. In 30 min only 0.01 % AR was extracted from the soil. This ¹⁴C activity was not distributed throughout the soil, but was only detectable in the lowest layer (55 - 60 cm below GL). All other extracts display values below the detection limit of 0.3 Bq per sample. After this extraction, 13.3 % AR still remained in the soil and was distributed between three layers (15 - 20 cm, 45 - 50 cm, and 55 - 60 cm below GL). A clear graduation in the measured radioactivity with soil depth thus became apparent. Due to the poorer detection limits, the GC/MS or HPLC/GPC method was not used to analyse the soil extracts.

Tab. 17: 2nd column experiment in a gleyic cambisol after contamination with [α,α' -¹⁴C]-MTBE in the simulated groundwater accumulation: Radioactivity balance after the 2nd column experiment (MTBE-S2) at the end of the experiment in soil, groundwater and the volatilization of the [α,α' -¹⁴C]-MTBE in the undisturbed column experimental set-up.

Net applied radioactivity = 82,409.089 Bq (including unlabelled MTBE $\equiv$ 477.49 mg)

(1 main contamination with 3 subsidiary contaminations)

Test period = 14 d

Experiment	¹⁴ C activity [Bq]	% AR	Soil moisture [%]
Volatilisation	0,008	0,0001 ⁰ / ₁₀₀	-
groundwater:	73387,2	89,05	-
Soil extraction:			
Only soil layer (55-60 cm)	7,4	0,01	15,6 $\pm$ 0,4
Soil ashing (Σ , nicht extrahierte RA):	10951,5	13,29	
Soil layer (00-05 cm)	-	-	10,5 $\pm$ 0,6
Soil layer (05-10 cm)	-	-	13,9 $\pm$ 0,4
Soil layer (10-15 cm)	-	-	14,2 $\pm$ 0,8
Soil layer (15-20 cm)	1632,0	1,98	10,7 $\pm$ 0,6
Soil layer (20-25 cm)	n.b. ^③	-	9,8 $\pm$ 1,2
Soil layer (25-30 cm)	n.b. ^③	-	9,9 $\pm$ 0,3
Soil layer (30-35 cm)	n.b. ^③	-	11,3 $\pm$ 0,6
Soil layer (35-40 cm)	-	-	14,5 $\pm$ 0,7
Soil layer (40-45 cm)	-	-	13,6 $\pm$ 0,3
Soil layer (45-50 cm)	3611,2	4,38	14,9 $\pm$ 0,5
Soil layer (50-55 cm)	-	-	14,4 $\pm$ 1,2
Soil layer (55-60 cm)	5708,4	6,93	15,6 $\pm$ 0,4
Σ 14C (Bq or % AR)①	84326,4	102,35	
Climatic data②	20,7 $\pm$ 0,3 °C		
T _{air} over the soil	22,1 $\pm$ 0,1 °C		
T _{outside air}	21,2 $\pm$ 0,2 °C		
T _{soil} (2 cm)	10,5 $\pm$ 0,2 °C		
T _{groundwater}	3,512 L (Start) – 3,440 L (End)		
groundwater volume	22,5 $\pm$ 0,1 °C / > 99,5 %		
T _{air flow} /rH _{air flow} (column outlet)	23,2 $\pm$ 0,3 °C / 40,0 $\pm$ 4,7 %		
T _{air flow} /rH _{air flow} (after air dehumidifier)	23,2 $\pm$ 0,1 °C / 91,7 $\pm$ 6,2 %		
T _{air} /rH _{air} (outside)	0,1 L min ⁻¹		
volumetric flow (air)	13,9 $\pm$ 0,1 L		
air volume per sample	138,5 L		
total air volume per day	1939 L		

① Deviation between the sum of the individual values and the given sum are due to rounding errors.

② The climate and air collection data are only averages/or total values (**Tab. A-31**)

③ Determination limit of the LSC is set at 0.3 Bq per sample

If the two column experiments are compared, there is not found in an agreement in all areas. There were obvious differences in behaviour and daily losses especially in the field of the groundwater reservoir of MTBE. In the 1st column experiment, about 1 order of magnitude

more MTBE disappeared from the groundwater than in the 2nd column experiment. The daily losses calculated from the GC/MS analysis fluctuated less in the 1st column experiment than in the 2nd. Both curves showed the same trend, but on different scales. If the ¹⁴C values were used in the evaluation, then the difference relative to the curve and the final values reached was even more apparent. The quantity of MTBE found in the groundwater in the 2nd experiment was roughly twice as great as in the 1st experiment. Possible reasons for this will be discussed in 5.2.

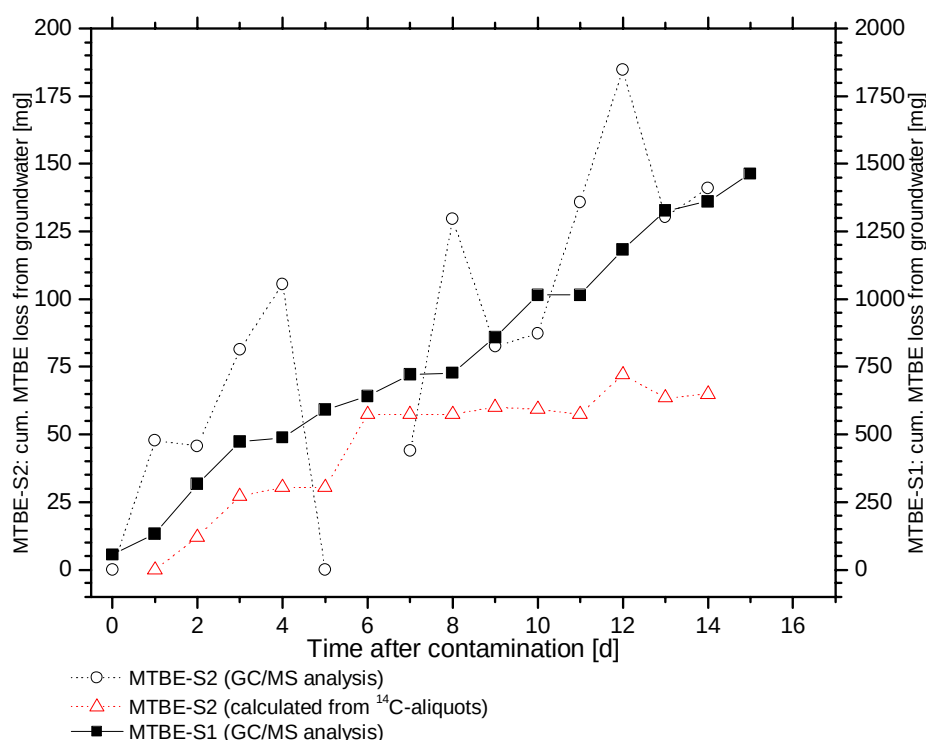


Fig. 41: Column experiments in a gleyic cambisol after contamination with $[\alpha,\alpha'\text{-}^{14}\text{C}]$ -MTBE and MTBE in the simulated groundwater accumulation: Comparison of the cumulative MTBE losses from the simulated groundwater of the two column experiments (MTBE-S1, MTBE-S2) over time.

Due to a lack of time and material (conditioned soil columns, radioactivity, etc.), it was not possible to perform any further column experiments within the framework of this study.

4.3 Lysimeter study with wind tunnel

The wind-tunnel experiment studying the transport behaviour of $[\text{}^{14}\text{C-U}]$ -MTBE from the aquifer through the soil represents a field-like scale-up of the column experiments previously performed with undisturbed soil cores (4.2). In preparation for the experiment and during its performance, the following investigations and analyses were performed: validation of the high-volume sampler (HVS) (4.3.1), soil moisture measurements (4.3.2), analyses and climatic data during the experiment (4.3.3) and drawing up a radioactivity balance (4.3.4).

4.3.1 Validation of the high-volume sampler

Apart from the reconstruction of the wind tunnel, the sampling unit at the exhaust air tower (HVS) was also modified for measuring volatile hydrocarbons. The applicability of the newly developed sampling system for volatilization experiments with MTBE from the soil was verified in four preliminary experiments. The mean quantity of radioactivity (or substance) applied per experiment was 509.31 ± 22.37 kBq (or 12.42 ± 0.55 mg) per experiment. At the end of the experiment, the apparatus was decontaminated, the loaded sampling units analysed and the ^{14}C activities determined. Three of the loaded multibed thermodesorption tubes were desorbed in the GC/MS system and analysed, and with one the sorbed ^{14}C radioactivity determined by combustion and measuring in the LSC (3.3.1.1.2).

Tab. 18: Validation experiments of the redesigned HVS at the wind tunnel with [^{14}C -U]-MTBE after application and volatilization in an evaporator with continuous volumetric flow.

Data in [% AR]; net applied radioactivity = 100 %

Experiment	V1	V2	V3	V4
net applied [kBq]	533,71	513,53	479,53	510,5
contamination HVS	0	0,02	0,04	0
contamination evaporator	0,16	0,25	0,26	0,20
Glass-fibre filter extract (HVS)	0,12	0,03	0,02	0,05
activated charcoal cartridge (HVS)	93,66	73,64	81,71	65,77
Σ ^{14}C (% AR)①	93,94	73,95	82,03	65,97
volumetric flow HVS	288,50	248,89	329,74	255,35
volumetric flow evaporator	20,48	19,91	28,22	19,93
volumetric flow in % HVS	7,1	8,0	8,6	7,8
temperature air flow evaporator	-	47	47	45
temperature evaporator	60	60	60	60
temperature air flow HVS [$^{\circ}\text{C}$] or T_{outside}	$18,0 \pm 0,1$	$18,3 \pm 0,6$	$18,5 \pm 0,2$	$14,4 \pm 0,0$
parallel measurement			($19,0 \pm 3,4$)	($16,4 \pm 2,4$)
relative air humidity	$81,5 \pm 1,5$	$81,0 \pm 2,0$	$79,0 \pm 0,0$	$84,5 \pm 3,5$
parallel measurement			($74,1 \pm 19,0$)	($82,4 \pm 16,8$)

① Deviations of 0.01 % AR between the sum of the individual values and the sum specified result from rounding errors.

The theoretically available quantity of MTBE per thermodesorption tube in the validation experiments was 186.33 ± 8.18 ng (or 7.64 ± 0.33 Bq). These values were significantly higher than the determination limits of the analytical systems used (Tab. 23). In addition to the radioactivity balances, Tab. 18 also lists the air collection conditions. In the first two experiments, no electronic data acquisition was available for temperature and moisture measurements. To ensure comparability of the air humidity and air temperature in the individual experiments, in addition to our own measurements on site (Tab. 18, values in brackets), data from the meteorological tower at the Research Centre were also used. This data always represent 2-d averages.

The validation experiments for the new HVS displayed different recovery rates in the range of 66 -94 %. The major quantity of radioactivity was recovered from the activated charcoal cartridge (> 99.5 %). The glass-fibre filter was neglected in the experiments performed since hardly any particle-bound radioactivity was to be expected as demonstrated by the values of 0.02 - 0.012 % AR. However, this collection apparatus is certainly of significance in a wind-tunnel experiment on soil with strongly sorbing organic compounds (STORK, 1995).

In addition to the desired adsorption on the activated charcoal cartridge, little radioactivity was found adhering to the walls in the HVS. After the volatilisation experiment, a measurable residue of ^{14}C activity always remained in the evaporator and was always of approximately the same level (approx. 0.2 % AR). The recovery of 65.97 % AR in V4 was distinctly lower than in the other experiments. Moreover, a higher air humidity (82 % rH) and a lower air temperature (16.4 °C) was measured than in V3. A superior recovery rate was achieved in V3 with 82.03 % AR at 74 % rH and 19 °C. These ^{14}C values are probably dependent on air humidity as can be qualitatively seen in the experiments. Climatic conditions were approximately the same in the 1st (V1) and 2nd (V2) experiment, but nevertheless different recovery rates were obtained.

No MTBE was detected on the additionally installed thermodesorption tubes in any of the experiments, irrespective of the analytical method.

4.3.2 Soil moisture measurements

As described in **3.3.2**, the soil moisture was measured semicontinuously (every 30 min) in the wind-tunnel experiment by a double determination at five different installation heights over the experimental period of four weeks (**Fig. 44**). These measurements were performed with a Trase™ soil moisture measuring device. The soil moisture was determined by 3-rod sensors. This instrument calculated the soil moisture in percent by volume (vol%) from a calibration curve and the measured dielectric constant. No calibration to the experimental soil was performed. The existing TDR system was first verified by a calibrated measuring system (Time Domain Reflectometry, type Trime FM, IMKO Micromodultechnik GmbH, Ettlingen). The following figure shows the deviations of the Trase measuring sensors from the calibrated system (**Fig. 42**).

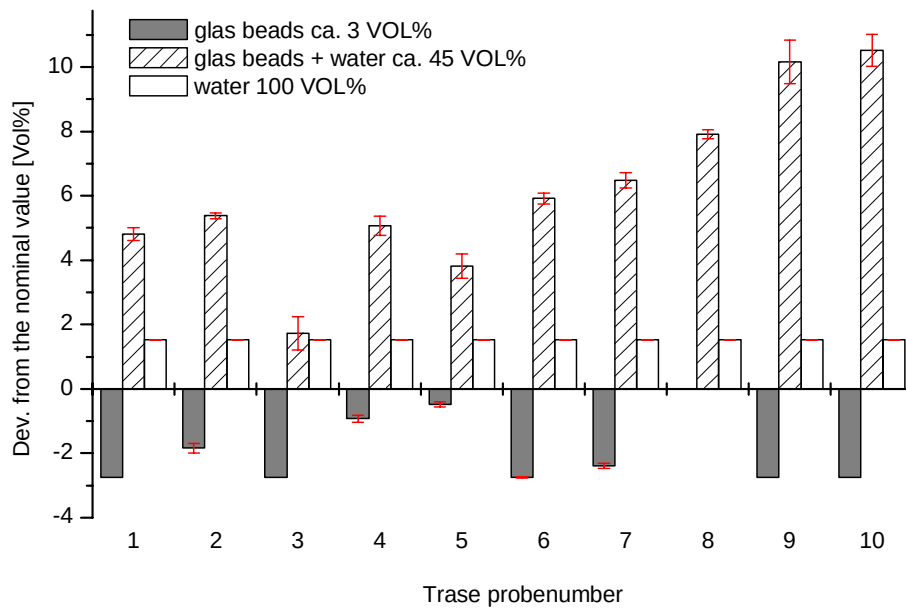


Fig. 42: Validation of the soil moisture measuring system at the wind-tunnel lysimeter: Selection of the Trase TDR sensors not within the specifications after a reference measurement with a calibrated Trime TDR system.

As becomes apparent from **Fig. 42**, some of these sensors displayed perceptible deviations from the rated value of the Trime system. After a closer optical inspection, slight damage to the cables and waveguides was discovered on sensors no. 3, 8, 9 and 10. These sensors were then replaced by new ones in the experiment. Only sensors with deviations from the rated value of $< 6\%$ were used in the experiment since they displayed the same measuring results and closer agreement with the Trime system was not to be expected due to the Trase-type waveguide. Furthermore, only relative changes in soil moisture were to be recorded in the experiment.

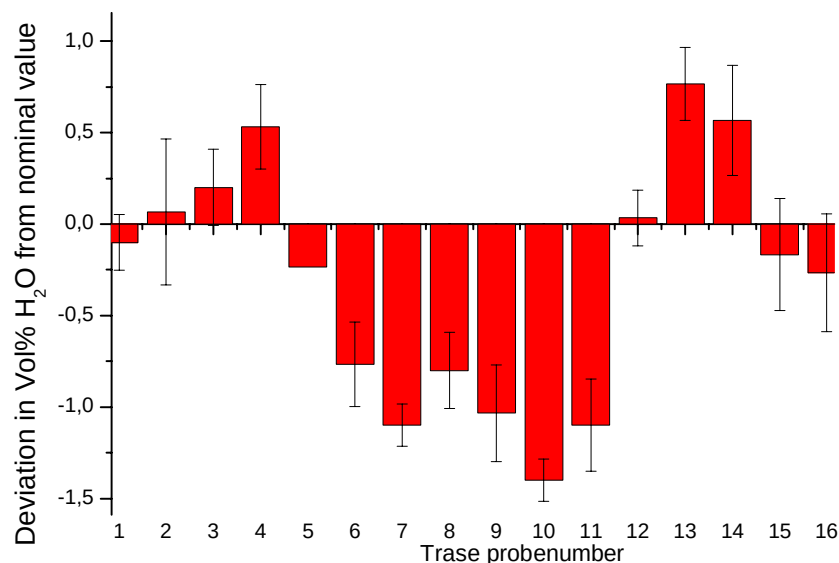


Fig. 43: Validation of the soil moisture measuring system at the wind-tunnel lysimeter: Influence of the multiplexer on the measured values for soil moisture measurements using the Trase TDR system, investigated on moist glass beads (approx. 45 vol%).

In addition to verifying the sensors, the influence of the multiplexer system and the cables on measurements of soil moisture was also investigated. Falsifications of the measured data could have occurred here due to corrosion and weathering. No deviation of the measured data from the rated value was found for the existing system, irrespective of the sensor used (error ± 2 vol% permissible).

Tab. 19: Wind-tunnel experiment with a gleyic cambisol after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation: Averages and average deviation of the TDR sensors for measuring soil moisture in the wind-tunnel lysimeter in % by volume and relative %

Installation depth [cm]	Sensor no.	Average [vol%]	Deviations [vol%]	
10	1	19,9		
10	6	15,0		
average		17,5	3,5	20
30	2	20,7		
30	7	19,4		
average		20,1	1	4,8
50	3	27,0		
50	8	24,7		
average		25,8	1,6	6,2
70	4	32,3		
70	9	28,0		
average		30,1	3,0	10,1
90	5	34,0		
90	10	34,6		
average		34,4	0,4	1

The soil moisture was continuously evaluated in the wind tunnel-experiment in order to plan and observe any irrigation that might have been necessary. **Fig. 44** shows the curve of the soil moisture at the different installation levels over time. The data shown are averages of two sensors per depth. These sensors were installed on opposite sites of the lysimeter in order to cover heterogeneities in the soil. The averages and deviations of the individual sensors are listed in **Tab. 19**. The deviations of the individual sensors of up to 3 vol% were large. Depending on the overall moisture, the relative deviation of the individual sensors was up to 20 %. This high value was found in particular for the measuring sensors in the topsoil layer. In the same way, the greatest variations in soil moisture throughout the experimental period were recorded in this soil layer. This is discussed in detail in 4.3.3. In all other soil moisture profiles, there was hardly any change in soil moisture over time ($\Delta_{\text{max}} = 0.42$ vol%). The highest average soil moisture was recorded for the lowest arrangement of measuring sensors, which was close to the saturated zone (+10 cm above the groundwater level). From 31 May to 6 June 2000 the measuring system was out of operation and so there are no TDR soil moisture data for this period.

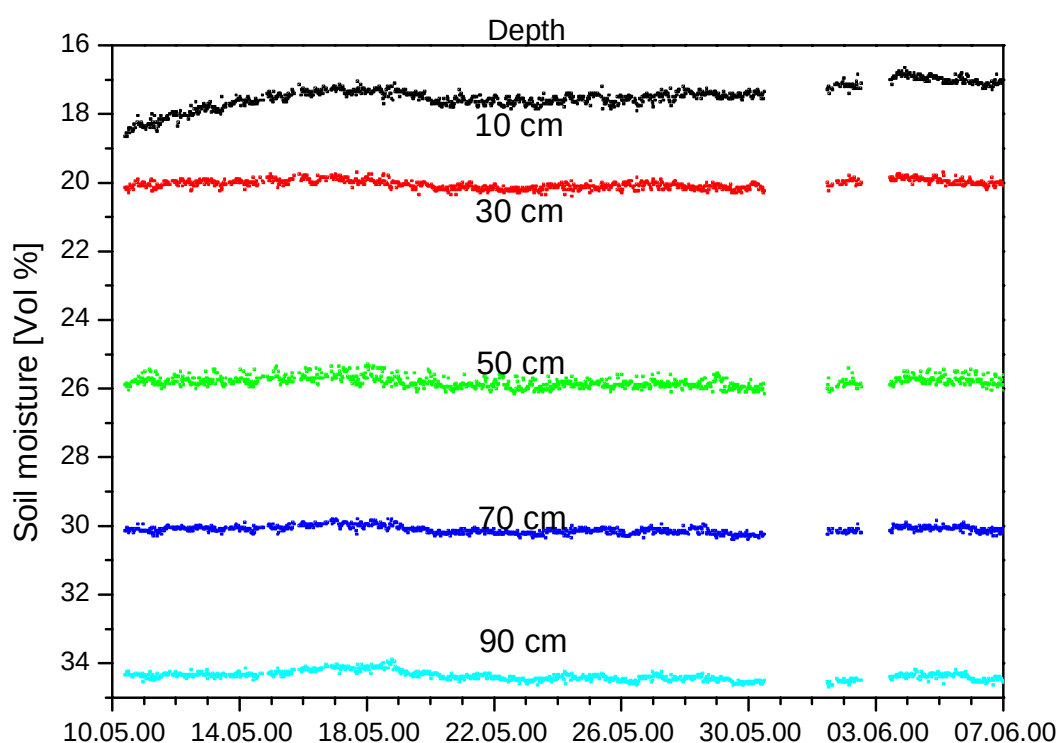


Fig. 44: Wind-tunnel experiment with a gleyic cambisol after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Representation of the soil moisture measurements in the wind-tunnel lysimeter at various installation heights (20, 40, 60, 80 and 100 cm) as averages of two sensors each per depth throughout the entire experimental period of four weeks.

4.3.3 Experimental description

As already described in 4.3.2, the greatest differences in soil moisture during the experimental period were found in the topsoil layer (10 cm installation depth). The soil moisture first dropped slightly until day seven. In the same period, the air temperatures were on average relatively high at 22 °C (Fig. 45). The soil temperature in the upper 5 cm was roughly at the same temperature, but with a slight time shift. From the 7th day onwards, the air temperature and also the soil temperature dropped perceptibly to an average of approx. 13 °C. During this period, the soil moisture also rose slightly again by approx. 1 vol%. This effect was reversed after the 20th day of the experiment. The irradiation intensity was not uniform throughout the entire experiment. Only in the starting phase and towards the end of the experiment did increase solar irradiation lead to warming. The diurnal range of temperatures and the irradiation situation can also be seen clearly in all the climatic data.

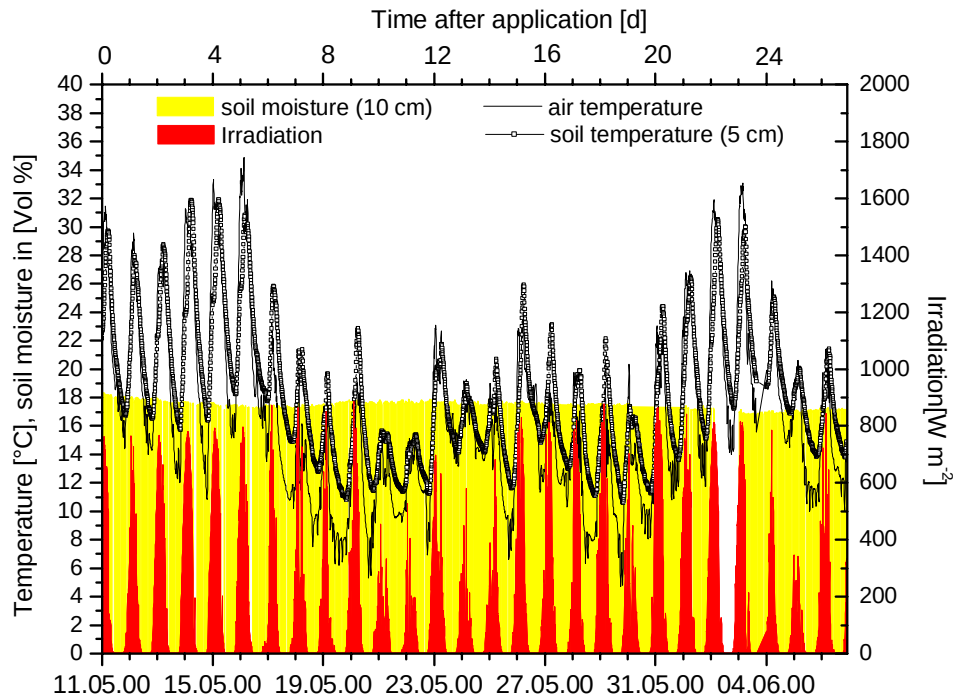


Fig. 45: Wind-tunnel experiment with a gleyic cambisol after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Climatic conditions during the lysimeter experiment (soil temperature at a depth of 5 cm, soil moisture at a depth of 10 cm, irradiation on the soil surface and average air temperature over the wind-tunnel lysimeter).

Fig. 47 shows the soil moistures both at the inlet and outlet of the wind tunnel together with the soil temperature at a depth of 5 cm. On the whole, a similar trend is seen to that already shown in Fig. 46. The air humidity rose significantly after the 8th experimental day. It was apparent that at the soil temperature peaks the air humidity at the inlet to the wind tunnel was higher than at the outlet. During this phase, the soil took up some of the humidity so that the water content in the air stream decreased. At low soil temperatures this effect was reversed. A qualitative assessment of these effects is in the following.

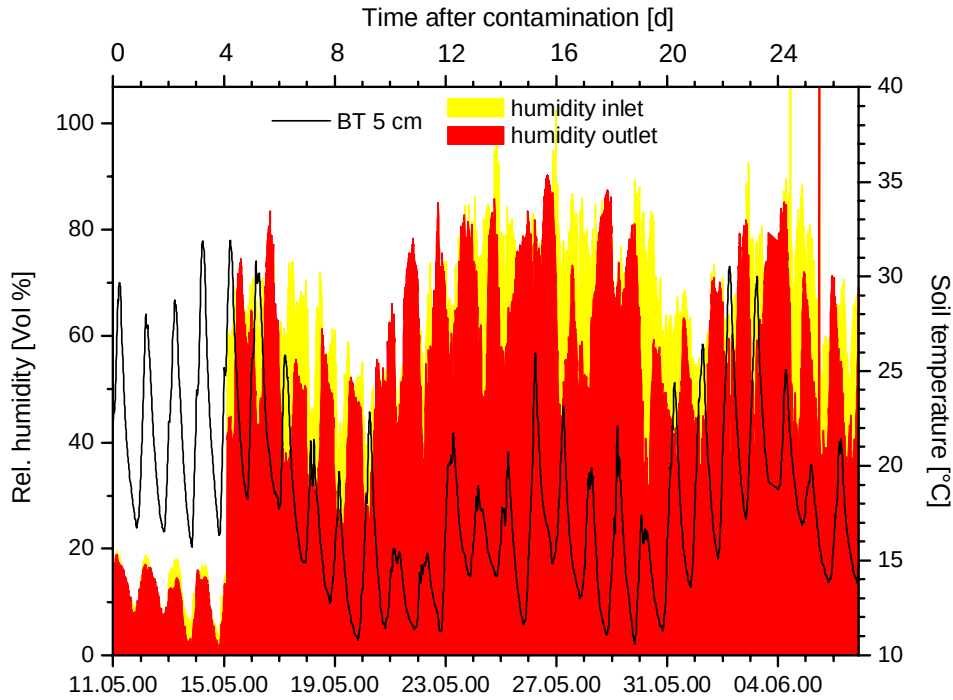


Fig. 46: Wind-tunnel experiment with a gleyic cambisol after contamination with $[^{14}\text{C-U}]$ -MTBE in the simulated groundwater accumulation: Relative air moisture at the wind-tunnel inlet and outlet, and soil temperature at a depth of 5 cm during the lysimeter experiment.

$$x = 0,622 \cdot \frac{6,108 \cdot \exp\left(\frac{17,27 \cdot \vartheta_d}{237,3 + \vartheta_d}\right)}{p - 6,108 \cdot \exp\left(\frac{17,27 \cdot \vartheta_d}{237,3 + \vartheta_d}\right)} \quad (\text{Eq. 20})$$

x =moisture content at saturation [$\text{kg}_{\text{water}} \text{ kg}_{\text{air}}^{-1}$]

p =total pressure [1013 hPa]

t =system temperature

ϑ_d =dew-point temperature

The actual evaporation can be readily estimated using (Eq. 20) from the measurement of air humidity or the dew-point temperature ϑ_d with a dew-point measurement at the inlet and outlet of the wind tunnel (ALLEN, 1998). The evaporation rates can be calculated by the mixing ratio (x , HYGROTEC, 1998) and the volumetric flows. It was possible to calculate the evaporation very accurately (mm h^{-1}) due to the high time resolution of data acquisition at the wind tunnel. In **Fig. 47** it can be seen that at high soil temperatures a higher evaporation results from the differences in air humidity. The soil temperature is only time-delayed by a few minutes in the curve with the evaporation rate. A high resolution of the evaporation rates cannot be determined at low soil temperatures. On the whole, however, it was apparent that on the average of the experiment the evaporation is negative. A total of 101 mm of air

humidity was precipitated in the wind tunnel. The mean "evaporation rate" was $-0.03 \pm 0.16 \text{ mm d}^{-1}$ with minimum and maximum values at -2.53 mm and 2.28 mm respectively. The phenomena described above are discussed in 5.3.

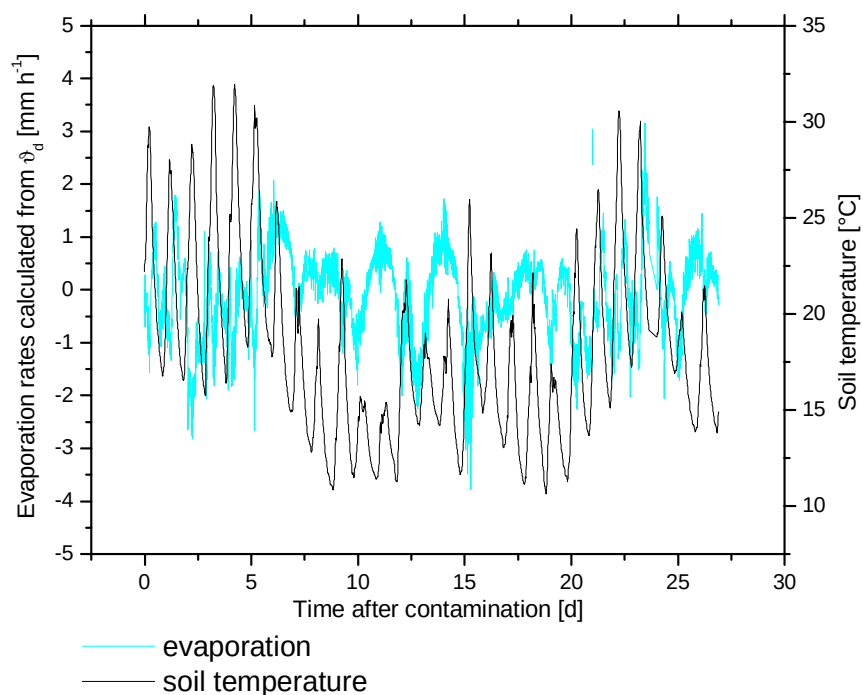


Fig. 47: Wind-tunnel experiment with a gleyic cambisol after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation: Calculated evaporation and measured soil temperature during the lysimeter experiment in the wind-tunnel system.

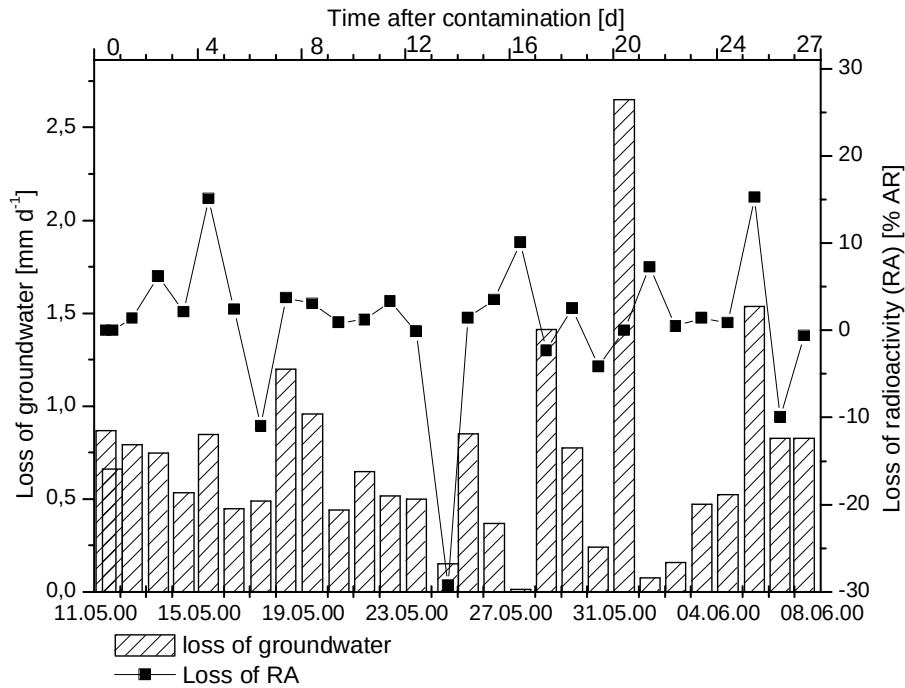


Fig. 48: Wind-tunnel experiment with a gleyic cambisol after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Decrease of groundwater and daily course of the measured radioactivity (% of applied radioactivity) over the entire experimental period.

As in the column experiments, the groundwater was also sampled daily in the wind-tunnel experiment and its radioactivity determined. In addition, the groundwater loss was detected via a riser pipe at the groundwater reservoir. **Fig. 48** shows the loss of groundwater in comparison to the loss of radioactivity ([^{14}C -U]-MTBE) during the experiment. In contrast to the column experiments, no relationship between groundwater loss and radioactivity was apparent here. On average, a loss of $0.96 \pm 8.49 \text{ \% AR d}^{-1}$ was measured from the groundwater. However, there were some strong deflections in the ^{14}C activity decrease ($\approx$ [^{14}C -U]-MTBE decrease), which were then generally compensated on the following day by the opposite behaviour. For this reason, it is more correct to speak here of fluctuations of MTBE concentration in the groundwater rather than of a loss.

On the 23rd day after contamination, 22.61 MBq of [^{14}C -U]-MTBE was added once again to keep the pollutant content (MTBE) in the groundwater approximately constant. On this day, a decline in the MTBE decrease (% AR) and also in groundwater consumption occurred. This drop can very probably be attributed to balancing at a higher total radioactivity quantity, a not yet completely homogeneous mixing and the system applied to replenish the reservoir. When the groundwater reservoir was replenished on day 7, 20 and 25, this led to a greater decrease in groundwater. Due to a short starting phase while the groundwater circulation was being restarted, the necessary vacuum in the system was not established fast enough to maintain the groundwater in the reservoir so that an increased quantity of groundwater

flowed out of the groundwater reservoir which was installed at a higher position (see **Fig. 15**) into the gastight container below the lysimeter.

An analysis of the groundwater samples by radio-GPC did not identify any MTBE metabolite formation in the groundwater during the entire experimental period (**Fig. 49**). The tert-butyl alcohol (TBA) concentration remained almost constant at 2 % AR during the entire experimental period. In the same way, on average 1.27 % AR of tert-butyl formate (TBF) was detected from day 0 until the experiment was terminated. In addition to these two major metabolites, 1-2 % AR of non-identified radioactivity (NIR) was detected between the individual peaks. According to the manufacturer's information, the MTBE used had a radiochemical purity of 99.7 % AR and was contaminated with traces of ^{14}C -TBA (**Fig. A-67**) so that this always had to be considered as the zero value for metabolization. Our own analysis using GPC chromatography indicated a much lower purity of 2.7 % AR TBA as a contamination. In **Fig. 49**, not all the metabolites listed in the legend can be recognized optically due to the in part very small fractions.

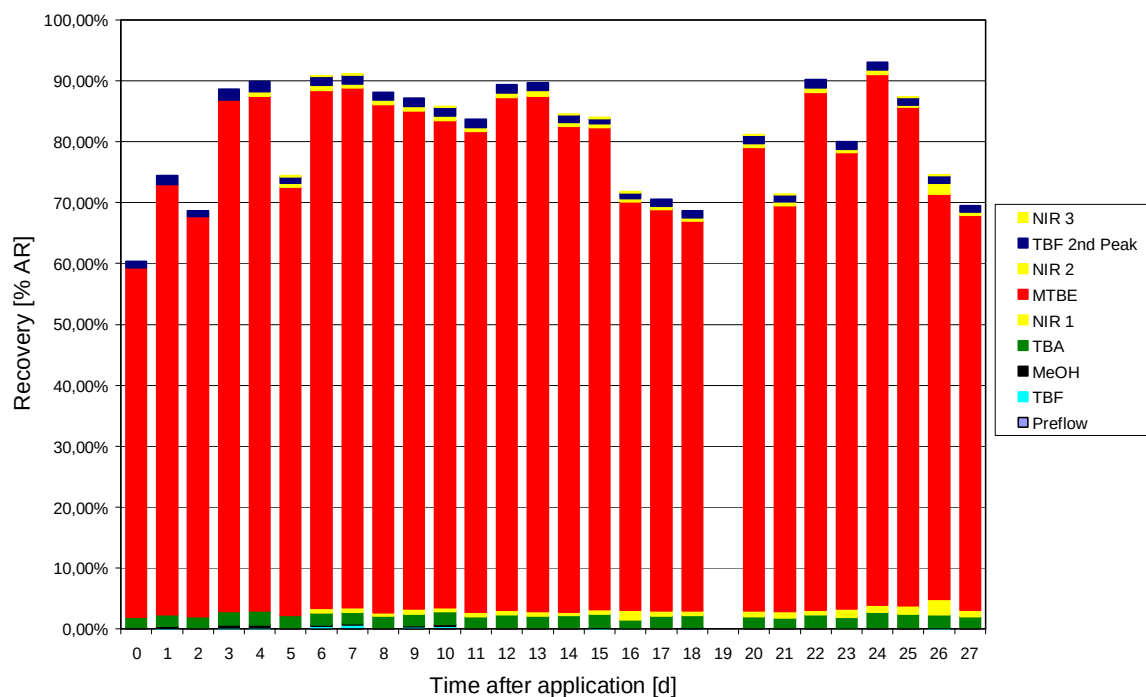


Fig. 49: Wind-tunnel experiment with a gleyic cambisol after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Composition of the groundwater samples taken daily in the wind-tunnel experiment (MTBE-L1) in % of applied radioactivity determined by gel-permeation chromatography.

In addition to the groundwater, part of the main air flow was passed through the HVS (volatilised organic compounds) and MVS ($^{14}\text{CO}_2$) each day and examined in the laboratory for radioactivity, MTBE and metabolites (**3.3.3.2**). During the experiment, measurable quantities of MTBE were only found in the HVS samples on three days (**Tab. 20**) confirming the findings of the column experiments. In the wind-tunnel experiment, MTBE in the air flowing over the soil monoliths was also measured non-continuously. It was only possible to detect

MTBE on the first two days of the experiment and once again eight days later. The total MTBE found was about 0.1 % of the applied radioactivity corresponding to 8.36 mg of MTBE equivalent in absolute terms. Apart from $^{14}\text{CO}_2$, no other metabolites were found in the air samples. This finding also confirms the degradation studies, in which apart from MTBE only $^{14}\text{CO}_2$ was detected (**4.1**). Due to the small quantities of $^{14}\text{CO}_2$, in contrast to the HVS measurement, samples were only taken from the MVS every 48 h after the 9th day in order to increase the detection sensitivity. Over the experimental period, a total of 0.07 % AR was found on six individual dates in the form of $^{14}\text{CO}_2$ (**Tab. 20**).

Tab. 20: Wind-tunnel experiment with a gleyic cambisol after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Radioactivity found in the air flow subdivided into volatilisation (HVS) and mineralisation (MVS) during the wind-tunnel experiment (MTBE-L1).

Day	MVS		HVS	
	[Bq 24 h ⁻¹]	[% AR]	[Bq 24 h ⁻¹]	[% AR]
1	- ^①	-	44858,1	0,05
2	12143,4	0,01	23054,1	0,02
3	- ^①	0,00	- ^①	-
4	20707,2	0,02	- ^①	-
5	2625,6	0,00	- ^①	-
6	15712,5	0,02	- ^①	-
7	- ^①	0,00	- ^①	-
8	7414,9	0,01	- ^①	-
9	- ^①	0,00	- ^①	-
10	-	-	20563,6	0,02
11	6419,1	0,01	- ^①	-
Σ	65022,7	0,05 ^②	88475,7	0,07 ^②

① Below the determination limit of 0.3 Bq 24 h⁻¹ maximum sample volume⁻¹

② Differences between the sum of the individual values and the total shown are due to rounding errors.

In addition to a radiochemical analysis, the air was also measured by adsorption of pollutants on the adsorbent material in the thermodesorption tubes at the HVS. These measurements did not yield any mass spectra that could be positively evaluated.

4.3.4 Final sampling and radioactivity balance

The lysimeter experiment was terminated after 27 days and, as described in **3.3.3.3**, samples were taken using a Wacker-hammer system. The sampling grid is shown in **Fig. 50**. In order to rule out any boundary effects, samples were mainly taken in the inner region of the lysimeter surface. A total of eight soil cores were taken, of which samples A - H were frozen in liquid N₂ and then extracted. Sample I was immediately divided into 20-cm segments in order to measure the microbial activity. The TDR sensors on the rear side of the wind channel were removed before sampling and the boreholes sealed to prevent any MTBE losses from

the soil. Only soil core B was situated close to such a disturbed soil segment penetrated at three levels by TDR sensors.

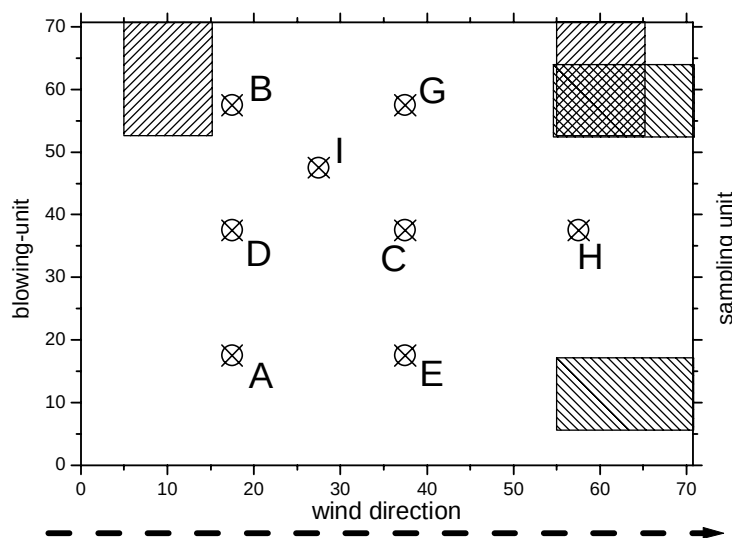


Fig. 50: Termination of the wind-tunnel experiment after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Sampling grid (A-I) for sampling the soil of the wind-tunnel experiment at the end of the experiment using the Wacker hammer system from Bayer AG.

(Shaded areas = soil disturbed by the lateral installation of TDR sensors)

The individual results of the soil extraction are shown in **Tab. A-27** in the Appendix. Only those data were evaluated where the quantity of radioactivity per soil extract was at least 0.07 Bq mL^{-1} . In the upper layers, the quantities of ^{14}C MTBE found were below this determination limit as expected. Only at depths of 20 cm below ground level was an evaluable quantity of radioactivity found in one sample. At a depth of 80-90 cm, sufficient quantities of MTBE were found in all soil cores. The lowest layer (100-110 cm below ground level) was only reached by two soil cores (A & G), in this case, the soil in the upper horizon was somewhat compressed since the sleeves of the soil cores were only 100 cm in length. A total of $9.71 \pm 2.15 \%$ AR was extracted from the soil. The values obtained in this way were entered into a data representation programme together with their coordinates. Using the "inverse distances to a power" method, a possible distribution of the radioactivity found in the respective soil layer was calculated (Surfer, version 6.04, Golden Software Inc.). Using this weighted average interpolator, it was possible to make an exact and also running calculation of the values. The power chosen determined the extent to which the weighting factors change with increasing distance from the measuring point (**Fig. 51**). A possible disadvantage of the method is the occurrence of so-called "bull's eyes" around the measuring points. In order to reduce this effect in the representation, a moving adaptation of the experimental data was selected. Below a water quantity of $0.12 \text{ g}_{\text{water}} \text{ g}_{\text{TB}}^{-1}$, no more radioactivity was extracted from the soil, which was the case in the upper 60 cm of the soil monolith.

After extraction, the soil was air-dried and in every soil core the unextracted radioactivity in the individual soil fragments was determined in the LSC after ashing (**Tab. A-28**). A radioactivity balance of the experiment is given in **Tab. 21**.

In addition to the radioactivity distribution in the individual soil layers, the soil moisture in the cores was also determined (**Tab. A-29**). As described for the radioactivity distribution, these values were used to calculate an area distribution (**Fig. 52**) in the individual soil layers. If the respective layers are compared in the diagrams in **Fig. 52** and **Fig. 51**, then no direct dependence of the radioactivity on soil moisture can be observed.

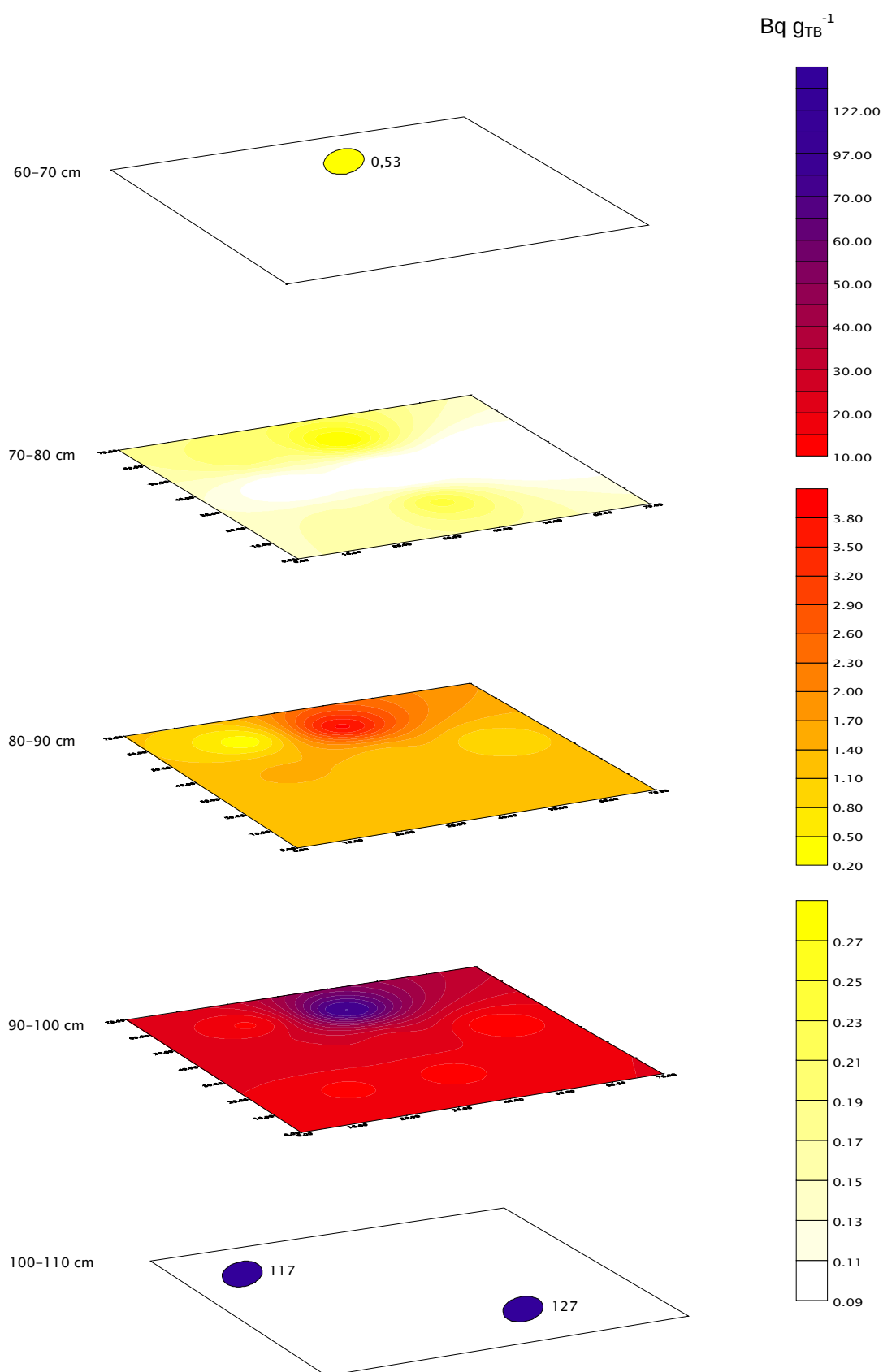


Fig. 51: Termination of the wind-tunnel experiment after contamination with [14C-U]-MTBE in the simulated groundwater accumulation: Spatial representation of the radioactivity distribution (Bq g_{dry soil}⁻¹) in the final sampling of the wind-tunnel lysimeter with seven cores for the soil layers below a depth of 60 cm after an interpolation by the inverse distance method.

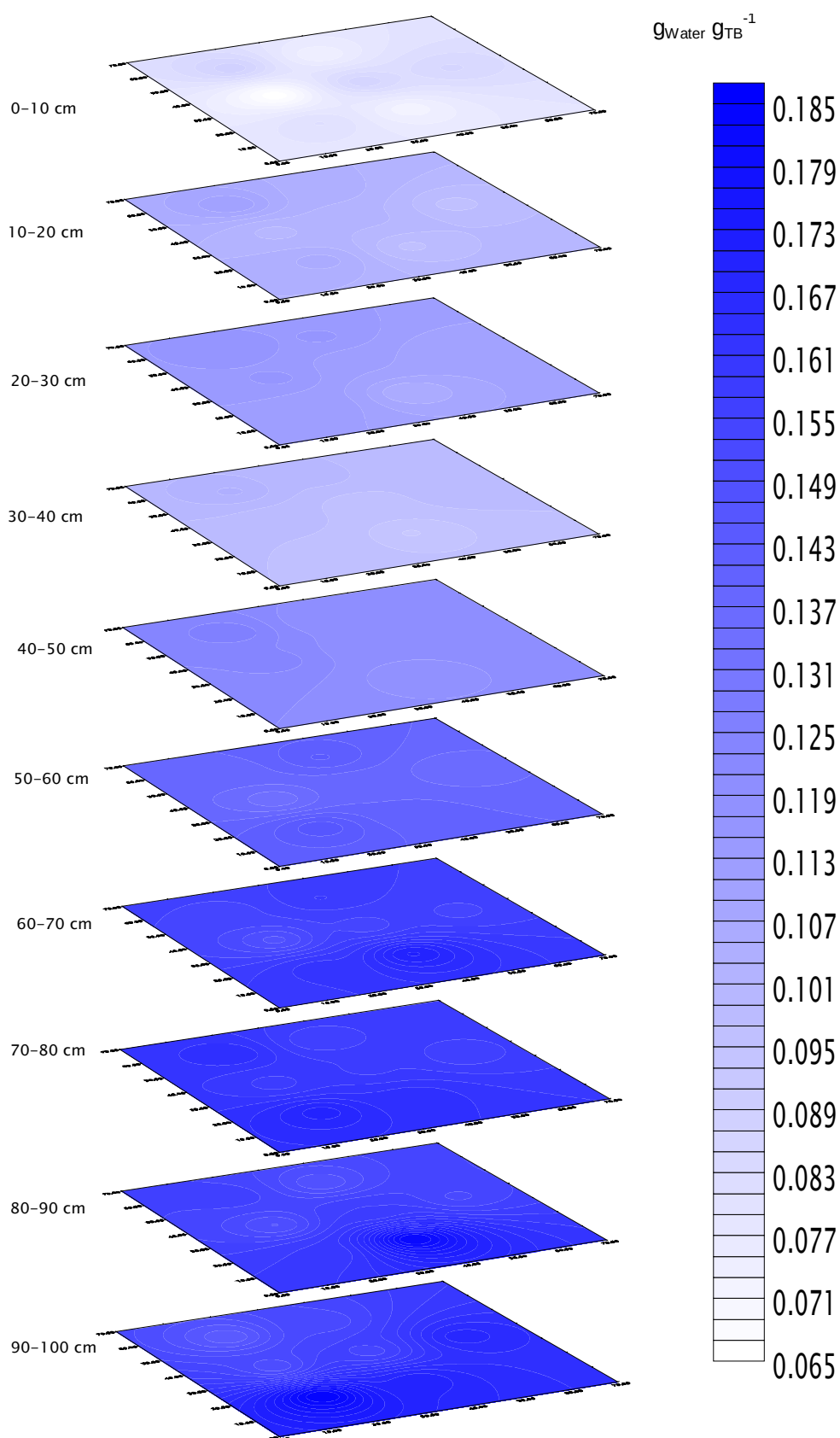


Fig. 52: Termination of the wind-tunnel experiment after contamination with $[^{14}\text{C-U}]\text{-MTBE}$ in the simulated groundwater accumulation: Spatial representation of the soil moisture distribution (mass %) in the final sampling of the wind-tunnel lysimeter in 10-cm segments with seven cores over the complete soil depth (110 cm) after an interpolation by the inverse distance method.

Tab. 21: Radioactivity balance after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation and lysimeter experiment

Net applied radioactivity = 120.864 MBq (including unlabelled MTBE ≡ 9.286 g)

(1 main contamination with 1 subsidiary contamination); experimental period = 27 d

	¹⁴ C- activity [Bq]	% AR	Soil moisture[%]
Volatilisation:	88475,7	0,07	
Mineralised MTBE (¹⁴CO₂):	65022,7	0,05	
Groundwater:	74354264,6	61,52	
Soil extraction:	11732131,5	Σ 9,71	
layer (1-10 cm)	1318± 1333	< 0,01	7,8±0,84
layer (10-20 cm)	1874± 2659	< 0,01	10,2±0,51
layer (20-30 cm)	1260± 2372	< 0,01	11,2±0,42
layer (30-40 cm)	8555± 17691	0,01	9,7±0,33
layer (40-50 cm)	11209± 18224	0,01	12,1±0,33
layer (50-60 cm)	1067± 586	< 0,01	13,9±0,44
Bodenschicht (60-70 cm)	6893± 14900	0,01	15,7±0,73
Bodenschicht (70-80 cm)	11157± 8128	0,01	16,1±0,54
layer (80-90 cm)	112667± 87623	0,09	15,7±1,19
layer (90-100 cm)	1961403±1837451	1,62	16,0±1,45
layer (100-110 cm)	9614726± 607089	7,95	16,1±0,20
Soil ashing (nicht extrahierte RA):^②	124882	Σ 0,10	
layer (10-20 cm)	39636	0,03	
layer (30-40 cm)	4635	< 0,01	
layer (40-50 cm)	63326	0,05	
layer (80-90 cm)	7737	0,01	
layer (90-100 cm)	5269	< 0,01	
layer (100-110 cm)	4278	< 0,01	
Σ ¹⁴C (Bq bzw. % AR):^①	86364777	71,46%	
Climatic data:			
Air temperature (outside) [°C]:	16,4±3,8		
average air temperature (WK) [°C]:	16,7±4,0		
soil temperature (outside) [°C]:	16,3±2,7		
soil temperature (WK) [°C]:	18,3±3,1		
soil temperature (soil surface) [°C]:	18,2±6,0		
rel. humidity (außen) [%]:	64,2±12,6		
rel. humidity (WK) [%]:	61,4±7,8		
wind speed 0,2 m s ⁻¹ :	0,5±0,0		
wind speed 0,02 m s ⁻¹ :	0,16±0,04		
irradiation (outside) [W m ⁻²]:	128,3±174,5		
irradiation (WK) [W m ⁻²]:	172,0±217		
main air flow [m ³ h ⁻¹]:	283,7±17,2		
HVS volumetric flow [m ³ h ⁻¹]:	13,3 ± 3,6 ≡ 4,7± 1,3[% HLS]		
MVS volumetric flow [L min ⁻¹]:	3,3 ± 0,2 ≡ 0,067 ± 0,015[% HLS]		

① Deviations between the sum of individual values and the given total result from rounding errors.

② Only the soil layers with measured data above the detection limit of 1 Bq g_{soil}⁻¹ are listed.

The climatic and air collection data are only averages/or total values (**Tab A25 +26**)

The evaluation of all data, both during performance of the experiment (**4.3.3**) as well as after the experiment, enabled a balance of the wind-tunnel experiment to be drawn up concerning the volatilisation of [¹⁴C-U]-MTBE from the aquifer through an undisturbed soil monolith into the atmosphere. With an experimental duration of 27 days after groundwater contamination, a total of 71.46 % of the applied radioactivity was recovered (**Tab. 21**). The major fraction of the MTBE was still in the groundwater at the end of the experiment (61.52 %). At the end of

the experiment, 9.81 % of the applied radioactivity was detected in the soil extract and the subsequent soil ashing. Volatilisation and mineralisation were of no significance in the balance due to their low values (0.07 and 0.05 % AR, respectively). In comparison to the results of the degradation studies, the mineralisation of [^{14}C -U]-MTBE was low in the wind-tunnel experiment under field-like conditions. A comparison of the microbial activity in the various experimental systems showed on the whole lower values in the soil of the wind-tunnel experiment (**Fig. 53**) than in the degradation studies (**Fig. 24** and **Fig. 25**) and column experiments (**Fig. 32** and **Fig. 40**). At the soil depth at which MTBE was also detected in measurable quantities, the biological activity was lower by about a factor of two than in the preceding studies. On the whole, a reduction in microbial activity was measurable with soil depth. However, the quantity of $^{14}\text{CO}_2$ was not recorded in the column experiment and it was thus not possible to make a comparison of this parameter between the experiments with undisturbed soil profiles.

In the lysimeter experiment, the volatilisation rates were 175- to 7000-fold higher than in the column experiments, although the different climatic conditions and air change rates in the systems must be taken into consideration. In the wind tunnel, the air flow was significantly higher than in the column experiments (47000 : 1). Moreover, the soil and air temperatures fluctuated more greatly than in the column experiments, where the incidence of light into the system had also been excluded.

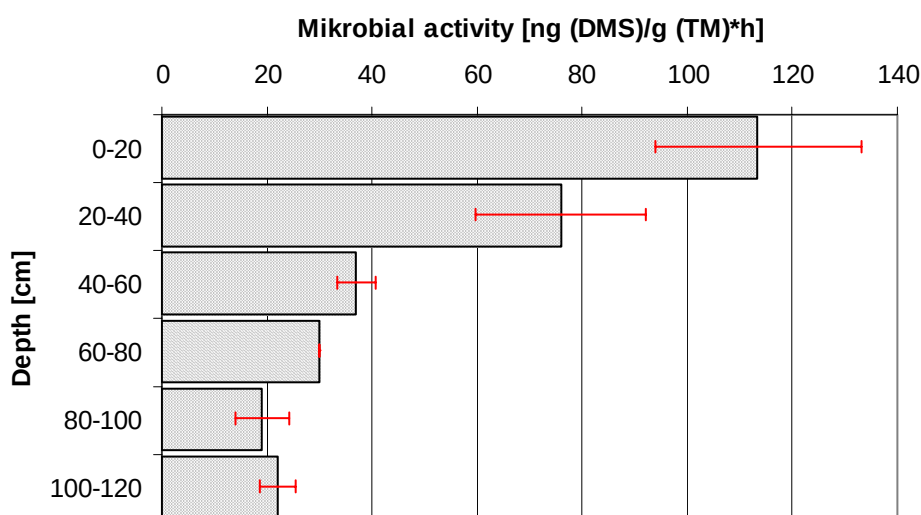


Fig. 53: Biological activity (ALEF, 1990) in the soil layers of the lysimeter profile at the end of the experiment with [^{14}C -U]-MTBE contamination in the simulated groundwater accumulation.

4.4 Analysis

4.4.1 Sampling

As described in **3.4.1.1.2**, the adsorption capacity of various solid adsorbents for MTBE, MeOH and TBA was first tested. Literature data were in part also used as the basis for the calculations in **Tab. 22**. The breakthrough volume (BV) was used as a measure of the adsorption capacity. The former was calculated with the aid of (Eq. **12**) from the experimentally determined retention time, flow rate and quantity of adsorbent (W_A). As can be seen from **Tab. 22**, all the adsorbent materials tested are suitable for fixing the compounds from air samples tested here. All the adsorbent materials display a low affinity for water vapour and thus ensure a quantitative sampling of these organic compounds even with varying air humidities. Chromosorb 106 and Tenax TA can also be used for the quantitative extraction of VOCs from water.

Tab. 22: Breakthrough volumes (B_V), sampling volumes (V_B) and elution volumes (V_E) of MTBE, MeOH, TBA and water on different adsorbents at room temperature as well as of MTBE on multibed adsorbent at different temperatures

test substance	B_V [L g _{Ads.} ⁻¹]	V_B [L g _{Ads.} ⁻¹]	V_E [L g _{Ads.} ⁻¹]	Flowrate [L min ⁻¹]	W_A [g]	Retention time [min]
Tenax TA						
MTBE	0,07	0,04	0,14	0,060	0,16	0,19±0,01
TBA	0,13	0,06	0,25	0,060	0,16	0,33±0,01
MeOH	0,29	0,14	0,58	0,060	0,16	0,76±0,02
Wasser [•]	0,06	0,03	0,12	-	-	-
Carbosieve SIII						
MTBE	7,72	3,86	15,43	0,170	0,52	23,6
MeOH [•]	7,5	3,75	15	-	-	-
Wasser [•]	0,32	0,16	0,64	-	-	-
Chromosorb 106 (60/80 mesh)						
MTBE	7,17	3,58	14,34	0,138	0,5	25,97
Wasser [•]			hydrophob			
Multibed (Carbotrap/Carboxen 1000)						
MTBE 120°C	7,93±0,23	3,97	15,86	0,047	0,25	41,84±1,34
MTBE 160°C	1,09±0,14	0,55	2,18	0,036	0,25	7,49±0,96
MTBE 200°C	0,20±0,04	0,1	0,4	0,029	0,25	1,69±0,37
MTBE 22°C [•]	21,91	10,96	43,83	-	-	-
Wasser [•]	0,05 [•]	0,02	0,1	-	-	-

[•] Breakthrough volume taken from an SIS database (1997a)

[•] WOOLFENDEN & MCCLEENY (1999)

[•] Calculated by interpolation from values at higher temperatures.

($B_V = 18,038 \times T^{-1} - 39,232$; $R^2=0,8718$)

[•] Average of the two adsorbents.

Tenax TA hardly displayed any adsorption properties for MTBE, TBA and MeOH. With increasing carbon character (Chromosorb 106) and higher porosity (Carboxen 1000) the adsorption capacity for MTBE and other low-molecular substances becomes greater. The multibed system consisting of Carbotrap and Carboxen displayed the highest breakthrough volume ($B_V = 21.91 \text{ L g}_{\text{Ads.}}^{-1}$). According to FIGGE ET AL. (1987) there should be a linear

relation between the reciprocal temperature (in kelvin [K]) and the measured retention time of a substance on the adsorbent studied. The breakthrough time can thus be measured at higher temperatures and an interpolation to the air collection temperatures subsequently performed. The higher temperatures mean that the peak form can be more readily interpreted and the retention times determined more clearly. At room temperature (air collection temperature) a perceptible peak broadening can be seen, which may even make it impossible to determine the peak (**Fig. A-74**). This interpolation could not be satisfactorily applied to the multibed adsorber. The linear regression was very poor and thus the value determined at room temperature too imprecise to estimate the sampling volume.

For this reason, a second determination method was applied, in which two multibed adsorption tubes (quantity of adsorbent = 250 mg; **Fig. 54**) were connected in series and the first loaded with 1 μL MTBE. 30 L of air was then passed through this arrangement. Even after a loading volume of 30 L, no MTBE was detected on the adsorbent downstream of the air flow. The breakthrough volume $B_v > 120 \text{ L g}_{\text{ads}}^{-1}$ and thus significantly higher than that calculated (Tab. 22; $B_v = 21.91 \text{ L g}_{\text{ads}}^{-1}$). The maximum sampling volume (V_B) per adsorber tube should therefore not be much greater than 15 L. The minimum elution volume (V_E) for conditioning the adsorber tube should be 60 L.

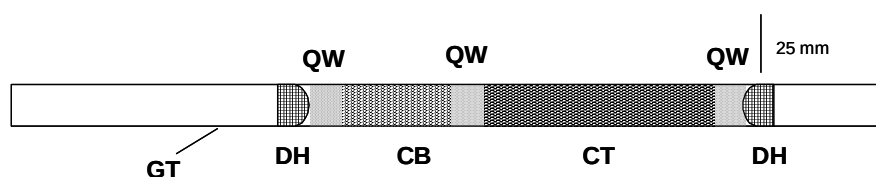


Fig. 54: Schematic representation of the multibed thermodesorption tubes developed for the column experiments and the lysimeter study with wind tunnel.

CB = Carboxen 1000; CT = Carborap; WC = wire cap; GT = glass tube; QW = quartz wool

In addition to the modified carbon adsorbents, activated charcoal was also used in the degradation studies (**3.1**) and the experiments in the wind tunnel (**3.3**) as an adsorbent material for airborne ^{14}C -labelled MTBE and its metabolites. The adsorbent properties of activated charcoal for degradation studies can be found in JAGETTSBERGER (2000). The results of the HVS activated charcoal validation are presented in **4.3.1**.

4.4.2 Measuring methods

4.4.2.1 Radioactivity measurements

The results of radioactivity measurements of solid and liquid samples are described for the individual experiments (**4.1-4.3**).

4.4.2.2 GC/MS

After a suitable chromatographic column had been found for the separation of MTBE and its metabolites (**Fig. 4; Fig. 5**), irrespective of the type of injection (thermodesorption, aqueous samples), the separation was optimised by adjusting the parameters (**Tab. 7**) to such an extent that an interval of at least 1 min was established between the elution times of the individual substances. This was performed successfully except for the separation of acetone and isopropanol (**Fig. 56**). On the non-polar column, all polar components are first eluted and then the less polar substances such as MTBE and TBF. Water is the first to elute from the separation column, although it cannot be detected by the mass spectrometer due to delayed activation of the energy in the ion source in order to protect the filament and thus the operating life of the instrument. A tailing was always apparent for the substances found, caused by the thick film of the stationary phase and residual traces of water on this separation phase (non-polar OV-1 material). Furthermore, at high concentrations overloading of the separation phase with substance can easily occur.

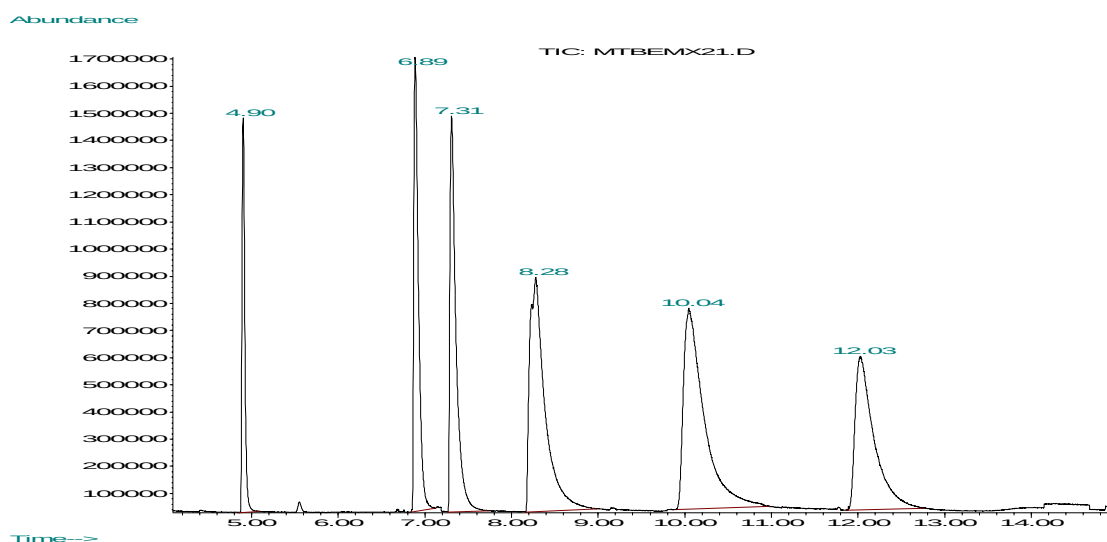


Fig. 55: GC/MS chromatogram (total ion current) of the separation of MTBE and possible metabolites on a thick-film column FS-OV-1-CB-1 column (60 m x 0.25 mm Ø, 1.2 µm film thickness, parameters **Tab. 7**, but splitting ratio 200:1 with an injection volume of 0.2 µL of cocktail).

In evaluating an analytical method, apart from the separation efficiency for the analytical problem in question, the detection and determination limits are also decisive parameters. The detection limit can be derived from the smallest measuring signal that can be reliably distinguished from the background. However, for quantification purposes, the determination limit is the decisive parameter. It is a pragmatically defined parameter and specifies the lower content limit for a maximum tolerable random error (DOERFFEL ET AL., 1994).

The detection and determination limits of the analytical procedures applied in the experiments are listed in **Tab. 23**. The limit values given for the GC/MS system are only valid for the selected ion mode (SIM) and the retention time determination of the samples to be

analysed. It was immediately apparent that GC/MS had much lower determination limits than HPLC or GPC. A lower determination limit could have been reached for the liquid injection if the samples solvents had been organic. This is possible, for example, with solid-phase extraction or solid-phase microextraction from water (2.1.4). Due to the losses in sample preparation, the direct injection method was preferred for groundwater analysis. With matrix-polluted samples such as the soil extracts or some of the groundwater samples, the application of radio-HPLC or radio-GPC was of great benefit and increased detection sensitivity for the analytes sought. A further advantage of this methodology is the high injection volume (up to 200 μL) with which the absolute quantity available in the detector for analysis can be increased by a factor of 200 in comparison to the GC/MS analysis.

Tab. 23: Overview of the detection and determination limits of the analytical methods used in the individual experiments (degradation studies [MTBE-A], column experiments [MTBE-S] and wind-tunnel experiment [MTBE-L1]).

Method	Study		Detection limit		Determination limit	
			[kBq L ⁻¹]	[mg L ⁻¹]	[kBq L ⁻¹]	[mg L ⁻¹]
HPLC	MTBE-A ^①	BE	12,5	72,4	41,7	241,3
		AKE	25	144,8	83,3	482,5
	MTBE-S2 ^②	GW	12,5	72,4	41,7	241,3
	MTBE-L1		-	-	-	-
GPC	MTBE-A		12,5	0,34	41,7	1,13
	MTBE-S2	GW	12,5	72,4	41,7	241,3
	MTBE-L1	GW	12,5	1,2	41,7	3,9
GC/MS	MTBE-S	Gas	-	0,2 ng L ⁻¹	-	0,6 ng L ⁻¹
		GW	-	1	-	3
	MTBE-L1	Gas	-	0,2 ng L ⁻¹	-	0,6 ng L ⁻¹
		GW	-	1	-	3

① Dependent on the possible injection volume BE = 200 μL AKE = 100 μL

② Theoretical value; no analyses with HPLC/GPC

ACE = activated charcoal extraction (ACN),

SE = soil extraction (CaCl₂= LSg. (10 mM));

GW = groundwater samples; gas = air analyses with thermodesorption

4.4.2.3 HPLC/GPC

In the wind-tunnel experiment, HPLC was not able to adequately separate MTBE and its metabolites. For this reason, GPC was used in the MTBE-L1 study. GPC achieved a much better separation of the analyte and its degradation products (**Fig. 56**). However, the poor recovery of the injected quantity of radioactivity was a problem in GPC. On average, the recovery of radioactivity in the sample was $81.04 \pm 9.13 \%$. Possible reasons for this will be examined in detail in the Discussion (5). The analysis of an MTBE standard yielded the following distribution: TBF (0.34 % AR), MeOH (0.08 % AR), TBA (2.74 % AR), NIR 1 (0.54 % AR), MTBE (75.32 % AR), TBF 2nd peak (1.66 % AR), NIR (1.67 % AR). The sum of these values indicates a recovery of the injected radioactivity of the standard of only 82.34 % AR. This must always be borne in mind in the discussion of the values later.

It furthermore became apparent that the MTBE supplied was not very pure. TBA (2.74 % AR), a starting product in MTBE synthesis, was always found.

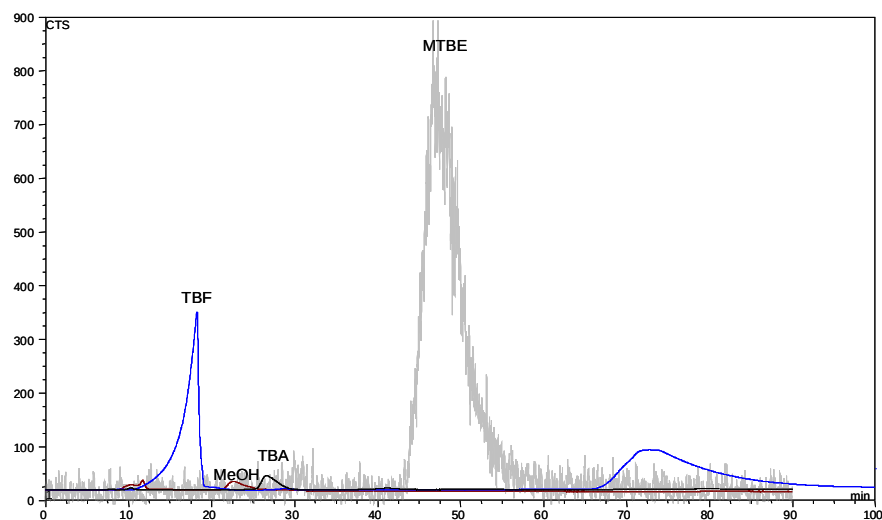


Fig. 56: GPC chromatograms of MTBE, TBA, TBF, MeOH with a Promochem Hema-Bio linear separation column on the Gynkotek P850 GPC set-up represented as a superposition of individual chromatograms.

(MTBE = ^{14}C signal [grey], TBF [blue], TBA [black], MeOH [red] = DAAD signal)

5 Discussion

The studies performed within the framework of this project served to develop a multiple-scale experimental approach to observe the transport of groundwater after contamination with MTBE through an undisturbed soil core into the atmosphere. To this end, an experimental setup with undisturbed soil cores was redesigned and constructed. Two standardised experiments in this facility were used to obtain initial insights into the transport phenomena. Due to the heterogeneity of the soil and the different results thus obtained (4.2) further column experiments were to be performed under different environmental conditions in order to obtain clearer information and to forecast the transport behaviour. In 5.2, the findings are first considered separately and then a detailed comparison is made.

A scale-up was performed to verify the transferability of the results obtained in the column experiments to the field situation under variable climatic conditions and displayed a similar trend in MTBE behaviour as in the column experiments (4.3). The findings are discussed in detail in 5.3, where, among other aspects, the modifications and new design of the wind tunnel and sampling units are assessed.

In addition to pure transport processes, the natural degradation potential of the soil micro-organisms for MTBE was also to be examined. The aerobic degradation of MTBE in the soil was demonstrated in two degradation studies (4.1). The findings are discussed exhaustively in 5.1 and the degradation kinetics determined taking into consideration the residence times and concentrations of MTBE in the soil. Furthermore, in these experiment a quantitative description was obtained of the volatilization of MTBE from the surface (soil type used: gleyic cambisol) (5.1).

The selected sampling techniques and the analytical methods (4.4) are not listed separately but discussed as part of the individual experiments in 5.1 - 5.3.

5.1 Degradation studies

As described in 3.1, two degradation studies were performed with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE with respect to various issues. No significant dependence of $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE mineralisation on soil moisture was found. The quantities of $^{14}\text{CO}_2$ on the 8th day after contamination in the native, moist variants of the gleyic cambisol (FF, 80 % WHC_{max}) were greater than for the less moist variants (FT, 40 % WHC_{max}), but this situation was reversed after 10 days (Fig. 20). Measurements of the microbial activity in the different variants did not indicate any dependence on soil moisture either (Fig. 24). In the first degradation study it was difficult to evaluate the data on the 18th day after contamination with respect to degradation since in the sterile controls $^{14}\text{CO}_2$ and increased microbial activity was also found. As already described in 4.1, at the same time a perceptible mycelium formation was also apparent in the sterile and untreated variants. In these variants, at the end of the first study, a fungal culture

had apparently asserted itself, which had not only survived the sterilization process, but had also in the unsterilized variants propagated more rapidly than the soil bacteria.

HARDISON ET AL. (1997) already demonstrated that fungi are capable of eliminating MTBE so that it is not possible to differentiate the $^{14}\text{CO}_2$ quantities found on the 18th day with respect to the microorganisms. A dependence of the mineralisation rate on the water content of the soil is only indirectly indicated in the literature for the anaerobic degradation of MTBE. With increasing soil moisture the availability of oxygen in the soil structure drops and the microorganisms function under anaerobic, generally denitrifying conditions (GISI, 1990). At constant NO_3 content under anaerobic conditions, BRADLEY ET AL. (2001) found a considerable mineralization of MTBE in 71 days with up to 25 % of the applied radioactivity. In larger experimental systems (e.g. in the lysimeter experiment) or in field experiments, this may be of significance. In spite of high soil moisture (up to 80 % WHC_{max}), anaerobic conditions cannot be assumed for the experimental set-up used in the degradation studies.

In the literature, the metabolites formed (including TBA) are described as toxic compounds for the MTBE-degrading microorganisms (YEH & NOVAK, 1994). In order to verify this for the gleyic cambisol investigated here, in parallel to the microcosms with added MTBE, a sample of gleyic cambisol without MTBE application was studied with respect to its microbial activity on the individual sampling days. However, no significant differences from the untreated, moist variant with MTBE were found. This was confirmed by the lack of TBA as a possible metabolite.

The temperature and oxygen dependence of degradation were not investigated. PARK & COWAN (1997) found a greater elimination of MTBE with rising temperature in the experimental system and also with increasing quantities of available oxygen.

In almost all studies described in the literature on the microbial degradation of MTBE it must be remembered that this involves degradation in an aqueous environment (nutrient solution or groundwater). There are only a few degradation studies on MTBE degradation in soil, preferentially under anaerobic conditions (BRADLEY ET AL, 2001). The reason for this is the high volatilisation potential of MTBE from surfaces and surface waters. No experimental approach is described in the literature for the aerobic degradation of readily volatile organic compounds, with little tendency to adsorb on soil such as MTBE. Many authors reporting on field experiments cannot differentiate between MTBE degradation in the saturated and unsaturated soil zone on the basis of their findings (SALANITRO ET AL., 2000; SCHIRMER ET AL., 1998).

A dependence of the mineralisation rate on the soil type was indicated in the first degradation study. In the gleyic cambisol previously uncontaminated with MTBE, $^{14}\text{CO}_2$ was formed more slowly than in the alluvial loam, which had been removed from a site previously contaminated with motor fuel (**Tab. 12**). Various authors report on sometimes long lag phases after

contamination with MTBE before any appreciable degradation of the pollutant begins (SALANITRO ET AL., 1994; MORMILLE ET AL., 1994). Apparently some microorganism strains specialized for the degradation of fuels were already present in the alluvial loam whereas in the gleyic cambisol a natural selection first had to take place. As described in **4.1**, mineralisation in the alluvial loam reached its maximum on the 8th day. A possible reason for this may be the experimental procedure. Since the alluvial loam had been removed from the fAh-Go horizon close to the groundwater, the microorganisms were adapted to an anaerobic degradation of organic molecules. This also explains the consistently lower microbial activity in the alluvial loam throughout the experimental period in comparison to the gleyic cambisol (**Fig. 24**). The aerobic experimental conditions were optimal for the microorganisms since aerobic conditions normally prevail in the plough layer (Ap horizon). This is also indicated by the continuously rising mineralization rate in the second degradation study (**Fig. 22**).

On the whole, in comparison to the literature, very low mineralization was found here, which only reached 1.6 % of the applied radioactivity after 101 days. However, this corresponds to the data found in the literature on natural elimination (PRINCE, 2000). It must be remembered that within a very brief period the major fraction of MTBE had volatilized out of the experimental system and was thus no longer available for degradation in the soil (see below). After 101 days, a total of just 1.73 % of the applied radioactivity was available. This is the sum of the extracted radioactivity, the not extracted radioactivity and the quantity of $^{14}\text{CO}_2$. The volatilized MTBE was no longer available for mineralisation. If the quantity of $^{14}\text{CO}_2$ found is related to the available MTBE, then a continuously rising mineralisation rate of up to 37 % is obtained (0.1 % after 0.3 d and 37 % after 101 d). MO ET AL. (1997) report a mineralisation of 8 % of the applied radioactivity in seven days, and SALANITRO ET AL. (1994) of as much as 40 % of the applied radioactivity for selected cultures. In an alluvial loam similar to that used in the present study, BRADLEY ET AL. (1999) found an MTBE mineralisation of up to 70 % of the applied radioactivity in a previously contaminated aquifer material. In bioreactors operated aerobically, the mineralisation rate was even higher (**2.1.3.1**).

As described in **4.1**, the mineralisation in the second degradation study was very well described by a first order function, relative to time (Eq. **16**). In the degradation reaction of $[\alpha, \alpha\text{-}^{14}\text{C}]\text{-MTBE}$ to $^{14}\text{CO}_2$, this points to the fact that the rate-determining step is the formation of TBA and not the mineralization of the metabolites formed. Similar curves can be found for the mineralization of MTBE in HANSEN ET AL. (1999) and LIU ET AL. (2001). The above-mentioned theory is also supported by the fact that neither in the soil nor in the activated charcoal extracts of the degradation studies were any possible metabolites (**Fig. 4**) such as TBA found (**Fig. A-57 - Fig. A-66**). In comparison, BRADLEY ET AL. (2001) and FINNERAN & LOVLEY (2001) found an in part very high mineralization for the anaerobic degradation of MTBE but no metabolite formation. In contrast, SALANITRO ET AL. (1994) and STEFFAN ET AL. (1997) unambiguously identified TBA as a metabolite in aerobic MTBE degradation. Two hypotheses can therefore be set up for the experimental design described here. The

degradation of TBA to carbon dioxide is either very fast so that TBA cannot be detected as an intermediate, or in view of the on the whole very low degradation of MTBE (approx. 1 % AR) no metabolites can be unambiguously determined due to the detection limits in radio-HPLC (**Tab. 23**). On the basis of experiments by JAGETSBERGER (2000), a breakthrough of MTBE or insufficient absorption on the activated charcoal can be ruled out.

In addition to recording the mineralisation and determining the microbial activity, the not extracted radioactivity was also quantified in the individual samples. This radioactivity was higher in all the untreated gleyic cambisol variants of the two degradation studies than in the sterile variants (**Fig. 20, Fig. 23**). This points to a partial incorporation of radiocarbon at the labelling positions of the $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE into the biomass of the microorganisms. In the bound ^{14}C -activity fraction, this may in part also involve a chemical or physical binding of MTBE or its metabolites to the soil particles (see also **2.1.2.4**) since no active biomass was present in the sterile variants (exception: study 1, sampling date 18 days after contamination, see above), and only traces of non-extracted ^{14}C activity were found here.

A further important priority in the degradation studies was the determination of volatilisation from surfaces as a function of soil type and soil moisture. This was, on the one hand, significant for understanding transport processes in the upper soil layers and also for assessing the microbial degradation. The activated charcoal packing connected in front of the CO_2 traps prevented, on the one hand, the mineralization rate being overestimated by MTBE possibly sorbed on soda lime and other volatile metabolites (**Fig. 6**), and on the other hand, it enabled the volatilised $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE to be recorded at the respective sampling time. A dependence of volatilisation on soil moisture was indicated in the first degradation study. In the moister gleyic cambisol variants (KSF, 80 % WHC_{max}), the volatilisation was lower throughout the experimental period than with the less moist sterile gleyic cambisol variants (KST, 40 % WHC_{max}). This is also described in the literature by NICHOLS ET AL. (2000) and DeVAULL ET AL. (1998). In the aqueous phase, the diffusion is reduced by a factor of 10^4 in comparison to the gas phase. With higher soil moisture in the unsaturated soil, the MTBE is distributed to a greater extent in the aqueous phase and the transport rate is thus retarded. As shown in **4.1**, the differences were greatest particularly in the first few days after contamination. After three or four days, an equilibrium was established in all variants, and the volatilisation rate was very low and almost constant. As described by JEFFREY (1997), this shows that a spontaneous volatilisation took place from the dry surface, controlled by the high vapour pressure (**Tab. 1**), followed by a slow subsequent supply from the underlying moister soil layers and the soil water (see above). In this case, the rate-determining transport mechanism is transport to the surface (SQUILLACE ET AL., 1997). Furthermore, slight sorption can be assumed due to the low K_{OW} of MTBE (**Tab. 1**) and the low organic fraction in the gleyic cambisol (**Tab. 11**, MACKAY ET AL., 1993). Irrespective of the soil moisture, this encourages the high volatilization rate found on the whole in all variants.

A dependence of volatilisation on soil type, as in ARTHURS ET AL. (1995), was not indicated since there was no sterile variant of the alluvial loam for a direct comparison with the gleyic cambisol samples (see also **4.1**) and the results obtained do not unambiguously describe volatilisation alone.

5.2 Column experiments

As described in **4.2**, two column experiments were performed with undisturbed soil columns with a contamination of MTBE (**4.2.1**) and also with $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE (**4.2.2**) in a simulated groundwater accumulation. The experimental assembly as well as the conception and design of the new experimental facility and the implementation of the experiments are described in detail in **3.2**.

As yet, no studies can be found in the literature describing the transport of MTBE out of the aquifer through the undisturbed soil core into the atmosphere. There is only one study with packed soil columns on the diffusion-based transport of MTBE and BTEX aromatics in the soil (DEVAULL ET AL., 1998). Although the authors recorded the microbial degradation of MTBE in various soils by their experimental approach, they did not investigate the mass transfer from the aqueous to the gaseous phase and the slow, diffusion-controlled transport in the water phase (e.g. groundwater) up to the phase boundary. It was thus only possible to transfer the findings of DeVAULL ET AL. (1998) to the real situation in the environment to a limited extent. Furthermore, the natural layer structure of the soil, as described in (*Eq. 4*) and (*Eq. 9*), is not taken into consideration. The study was, however, very helpful for the development of a diffusion model for the transport of organic molecules in the unsaturated phase with a biological reaction and the model calculations show good agreement with the results found.

In addition to this study, there are some field experiments on the fate of MTBE in the environment after groundwater contamination. Since not all the necessary data were recorded (heterogeneity of the soil, natural degradation potential of the soil for the pollutant, complete coverage of the aquifer flows and volatilisation) these experiments raise many new questions (SCHIRMER ET AL., 1998; BORDEN, 1997).

As already mentioned in the introduction, a new reproducible experimental concept was planned to be implemented under defined conditions in order to observe the transport of MTBE from a simulated aquifer through the soil into the atmosphere. The transferability of the findings from the column experiments (laboratory approach) to the field situation is discussed in **5.3**. In addition to the data sets obtained from the experiments, the measuring methods presented in **3.4.2** were also examined critically with the example of the column experiments (**4.4**).

In the first experiment, a groundwater contamination with approx. $198.7 \text{ mg}_{\text{MTBE equivalent}} \text{ L}^{-1}$ of MTBE was applied, and in the second experiment $117 \text{ mg}_{\text{MTBE equivalent}} \text{ L}^{-1}$ as a concentration to be kept constant (**3.2**). These values are in the same order of magnitude as the measured groundwater contamination quoted in the literature (EFFENBERGER ET AL., 2001; U.S. EPA, 1999; CHEMTEC, 1998; GARRETT ET AL., 1989). The results (**4.2**) of the column experiments can thus be applied to a real case of pollution.

As described in **2.1.2.4**, the transport of MTBE in the unsaturated soil zone depends very greatly on the soil moisture and soil properties. For this reason, the soil moisture and variation in groundwater quantity were recorded daily in both soil experiments (**Fig. 28** and **Fig. 36**). The soil moisture was constant throughout the experimental period, which, on the one hand, points to sufficient conditioning (**3.2.2.2**) and a good capillary connection of the soil to the groundwater (**3.2.1.3**). In both experiments, the temperatures (soil, groundwater) were almost identical (**Fig. 26** and **Fig. 33**). On average, the soil temperatures were 21-22 °C and the groundwater temperatures 10-11 °C. These values are comparable with field measurements of the corresponding parameters (PÜTZ, 2001; HARMS, 2001).

The changes in groundwater quantity were determined gravimetrically each day and in the second column experiment additionally by optical means. In both experiments, it was possible to derive a qualitative relation between the change in groundwater quantity and the MTBE loss from the groundwater (**Fig. 28** & **Fig. 36**). With increasing groundwater losses, more MTBE was also evaporated from the groundwater. There was one exception each in the first and second column experiments. It has not yet been possible to explain this phenomenon. No graphically evaluable correlation of the two parameters was obtained so that it was impossible to find any quantitative relation.

As described above, the soil moisture was almost constant throughout the experimental period at soil depths of 20 and 40 cm allowing for the measuring accuracy of the sensors ($\pm 2 \text{ vol\%}$). An attempt to derive the evaporation rate in the respective experiment from the groundwater losses was not successful. The values calculated from the difference in air moisture by (**Eq. 17**) and (**Eq. 18**) were lower than the groundwater losses per unit time by an order of magnitude (**Tab. 16**). In the second experiment, the equations used were additionally supported by a gravimetric determination of the condensed air moisture (C, **Fig. 11**). On an experimental average, the true evaporation for MTBE-S2 had a value of $0.074 \pm 0.012 \text{ mm d}^{-1}$. The theoretical evaporation in both experiments was approx. $0.098 \pm 0.005 \text{ mm d}^{-1}$. The low air flow (100 mL min^{-1}) over the soil surface probably meant that insufficient water was transported. The wind speed is not included in (**Eq. 17**) and an unlimited transport of water with the air is assumed, which is why the water contents determined in the air were somewhat reduced in comparison to the actual data. Due to a possible breakthrough of MTBE on the collecting tubes it was not possible to increase the air flow (**2.2.2** & **4.4.1**). The quantity of water evaporated from the surface was not dependent on the groundwater losses. However, due to the column length (60 cm) and the experimental

period (14 and 16 d, respectively) this can be reconstructed since the evaporation rates were low. It is thus not permissible to derive the evaporation rate from the groundwater losses. The evaporation can be calculated approximately using the above formulae (*Eq. 17*) and (*Eq. 18*). This demonstrates the good agreement with the data in the second column experiment.

The calculation of the theoretical evaporation is, however, very sensitive to pressure differences (p) in the atmosphere (*Eq. 17*). The volumetric flow meter at the column inlet, whose flow resistance was too high, and the extraction of air from the column at the outlet probably generated a negative pressure in the air compartment above the soil column so that the evaporation was somewhat increased. The calculation of the theoretical evaporation for the first experiment may therefore be too low. In the second experiment, the volumetric flow meter was replaced by an almost resistanceless flow meter. The results show good agreement between the theory and the measured evaporation values (*Tab. 16*). For further experiments, a pressure transducer should be installed in the system in order to record any negative pressure and initiate the necessary countermeasures so that the system can be operated at normal pressure. Another reason for the differences between groundwater losses and evaporation rates may be the inaccuracy of the balance and the fluctuating cooling-water content in the groundwater reservoir (*Fig. 11*, WT). This may have led to measuring errors and thus to incorrect conclusions about the groundwater losses. For more precise measurements, the filling level in the groundwater reservoir should be determined by an ultrasonic sensor.

As can be seen from *Fig. 27*, in the first column experiment it was attempted to keep the groundwater concentration almost constant at 198 mg L^{-1} . Nevertheless, the measured values displayed perceptible fluctuations. The sharp drop in MTBE concentration in the first few days can be explained by the accumulation of MTBE in the water-saturated region of the soil column (level of accumulated water, 5 cm). Such low MTBE contents were not subsequently measured. The MTBE loss 11 days after the start of the experiment was negative, i.e. no MTBE was consumed. Failure of the groundwater circulation system due to rust particles meant that after restarting the system values within the normal fluctuation range were found again. The elevated measured value was therefore caused by a lack of mixing in the system and thus an insufficient distribution of the subsequently added MTBE. Similar fluctuations to those in the first column experiment were also found in determining the MTBE concentration in the second column experiment. As described above, the experimental system should be in equilibrium after a few days. Nevertheless, fluctuations in the MTBE concentration in the groundwater were detected. A possible reason for this may be the lack of reproducibility for the GC/MS analyses. CHURCH ET AL. (1997) and BRODACZ (1998) also report this phenomenon for the direct injection of aqueous samples in gas chromatography as well as a possible retention time shift (POTTER, 1996) and a reduction in the lifetime of the separation column (GROB, 1984) (**2.2.1**). For this reason, a triple determination was performed for each water analysis in order to validate the measured data. At a concentration of 222 mg L^{-1} , the fluctuation range was up to 58 mg L^{-1} . It was not possible to

analyse the aqueous samples by HPLC since MTBE did not display sufficient sensitivity in the UV range and the concentrations of MTBE were below the detection limit for radio-HPLC.

In the second column experiment, the application of $[\alpha, \alpha'\text{-}^{14}\text{C}]$ -MTBE made it possible to convert the ^{14}C activity measurement to MTBE equivalents, in the course of which much weaker daily differences were established than in the GC/MS analyses (**Fig. 34**). Replenishment to the envisaged MTBE content was performed according to the MTBE losses calculated from the ^{14}C data. In the second column experiment, a state of quasi-equilibrium was reached in the system seven days after starting the experiment. From this point on, no MTBE loss could be measured from the simulated groundwater and consequently no MTBE had to be supplemented (**Fig. 35**).

Two obvious maxima are apparent in the cumulative curve of the MTBE losses. The first occurred after the first MTBE supplementation (18 April) and the second after a thermostat failure (24 April) and the resulting warming of the groundwater (**Fig. 33**). An explanation for the second rise may be as follows. The distribution of the MTBE between the aqueous phase and the air-void compartment of the soil above the accumulated groundwater depends on the HENRY coefficient (**Eq. 10**). The influence of temperature on the distribution equilibrium becomes apparent from (**Eq. 11**) (ROBBINS ET AL., 1993). If the temperature of the groundwater is increased from 11 to 20 °C the fraction of MTBE in the air-void compartment is roughly doubled. On the whole, the ratio of MTBE in the soil air to MTBE in the aqueous phase is $< 1:100$. It is only possible to approximately estimate the soil air available for the uptake of evaporated MTBE (210 cm³ soil-gas sensor⁻¹). Altogether, the soil column has a soil-air volume of approx. 5.6 L. The cumulative loss of ^{14}C activity is shown in **Fig. 37**. A perceptible increase in ^{14}C losses from the groundwater took place each time that MTBE was added to the groundwater. After the third replenishment, an oversaturation of the system was apparently reached and MTBE was returned from the soil water to the groundwater (negative MTBE loss).

If the groundwater is considered as the source of MTBE transport through the soil and release into the atmosphere, i.e. the air compartment above the soil column as a sink for the MTBE, then different quantities of MTBE can be detected in the air in the two studies performed. These quantities are not related to the somewhat lower initial concentration of MTBE in the groundwater of the second experiment. In the first column experiment, MTBE was already detected in the air after just a few hours (**Fig. 29**). The MTBE detected always only occurred as a pulse in the air and could not be continuously detected. The major fraction of measured data was 15 ng L⁻¹ air and therefore significantly above the determination limit for gaseous samples in the GC/MS instrument (**Tab. 23**). The analytical data were supported by two qualifier ions and quantification was performed via a target mass. Other authors such as RAESE ET AL. (1995) only validated their data with one qualifier ion. In the first column experiment, the average air concentration was reduced to 9.63 ng L⁻¹ air by the less reliable method (1 qualifier ion) since data with a lower concentration and a higher signal-noise ratio

were included here. In the calculation of the possible outside air concentration due to transport out of the groundwater, similar air concentrations were determined with the computer model as in RBCA Tier-1 screening (DeVAULL ET AL., 1994). If the transport rate out of the soil was calculated from the MTBE content found in the air, then on average in the first experiment this was $1.94 \pm 1.88 \mu\text{g m}^{-2} \text{h}^{-1}$. DeVAULL ET AL. (1998) found a flux of $1\text{--}15 \text{ g m}^{-2} \text{h}^{-1}$ after a direct MTBE vapour contamination at the lower end of the column. The passage of MTBE from the aqueous to the soil air phase is, however, a limiting factor for mass transport out of the groundwater into the atmosphere. The higher flow rates of MTBE through the soil known from the literature are therefore comprehensible, especially since diffusion in the gas compartment is faster than in water by a factor of 10^4 .

Fitting to the measured data yielded an exponential drop in transport rates with time. A composite exponential function was found which displayed good agreement with the calculated transport rates ($r^2 = 0.976$) (Eq. 19). Equilibrium was reached after five days, and the values approached a transport rate of approx. $800 \text{ ng m}^{-2} \text{h}^{-1}$ (at time $\rightarrow \infty$ this value is $\equiv y_0 = 450$ in (Eq. 19)). After considerable MTBE losses from the groundwater, a perceptible rise in air concentrations was recorded, also after the supplementation of MTBE into the groundwater. An explanation for this may be the occurrence of hot spots or NAPLs, i.e. high not yet dissolved or completely mixed quantities of MTBE (2.1.2.1). This phenomenon was particularly apparent after the first application (Fig. 31). In addition, the figure shows the magnitude of volatilisation. The MTBE quantities found in the air only correspond to a fraction ($1:10^5$) of the MTBE losses from the groundwater. In the second column experiment hardly any MTBE was found in the air. MTBE was only identified in 5 % of all analyses and, moreover, only with values close to the determination limit (Fig. 39). It was not possible to validate the data with two qualifier ions. The transport rates calculated from the soil into the atmosphere were $6.49 \pm 4.28 \text{ ng m}^{-2} \text{h}^{-1}$ so that a meaningful calculation is doubtful due to the sparse data. A possible explanation for the slight rise of air pollution with MTBE on 24–25 April may be failure of the thermostat maintaining the groundwater temperature (see above, Fig. 33).

At the end of the experiment, samples were immediately taken from the soil columns and the cores stored in liquid nitrogen. The soil samples were segmented and extracted (3.2.2.4). This procedure was intended to also record the MTBE residues sorbed at the soil or dissolved in the soil water in order to make a final balance. In the first experiment, the recovery was 30.3 % with the MTBE being almost exclusively found in the groundwater (Tab. 15). In total, only 0.004 ‰ of the total MTBE applied was volatilised. No MTBE was detected in the soil extracts, which may be due to the detection limit which was too high for aqueous MTBE analyses on the GC/MS (Tab. 23). Other modern analytical methods such as SPME extraction with GC/MS analysis first accumulate the pollutant and then separate it from the matrix (in this case the groundwater) (CASSADA ET AL., 2000). In this procedure, aqueous samples can be determined in the ppt range (ng L^{-1}) (ACHTEN & PÜTTMANN, 2000; PIAZZA ET AL., 2001) and thus measured more sensitively by a factor of 10^6 than in the

case of direct injection. In this way, some soil samples would perhaps have been positively determined. Another reason may be the sampling process itself. Removing the column from the groundwater reservoir and taking soil cores took more than 1 h and therefore, according to JEFFREY (1997), MTBE may volatilise spontaneously from surfaces exposed during sampling (4.1).

The quantity of MTBE adsorbed to the soil particles can be estimated by (Eq. 6) and (Eq. 7) with the aid of the distribution coefficient K_d . A K_d value of $0.045 \text{ cm}^3 \text{ g}^{-1}$ is obtained for a C_{org} content of 0.362 % at a depth of 30-60 cm (Tab. 11) and a K_{OC} value of $12.3 \text{ cm}^3 \text{ g}^{-1}$ (Tab. 1). 4.5 % of the MTBE should be adsorbed on the lower soil layers alone. This approximately corresponds to the quantities found in the soil of the second column experiment (Tab. 17). The values were considerably higher here, although in sampling and extraction the MTBE in the soil water of the corresponding soil layers was also determined. Particularly in the region of accumulated water, this soil water had a high (Eq. 7) activity corresponding to the groundwater concentration. Furthermore, a retardation of the MTBE was detected in the saturated zone for the soil used in the column experiments (55-60 cm GL). With an average soil density ρ_b of 1.69 g cm^{-3} and a total pore volume (n) of 39.2 %, the application of (Eq. 8) yields an R value of 1.19. This value is significantly greater than 1, which leads to a retardation of the MTBE. The retardation in the unsaturated soil zone was perceptibly higher, but could only be recorded very imprecisely due to the heterogeneity of the soil (soil moisture, soil density, C_{org}) as well as the various specifications concerning the HENRY coefficient and its temperature dependence. At 102.35 %, the overall balance of the second column experiment was very good. During the soil analysis (extraction and ashing), however, the overall activity in the soil may be overestimated by extrapolating the ^{14}C activities in the aliquots to the soil column.

In order to come to a conclusion about the self-purification behaviour in the soil used, at the end of each experiment the microbial activity in the soil was determined as a function of the soil depth (Fig. 32 and Fig. 40). Especially in the Ap horizon, almost constant values of 300-500 ng (DMS) $\text{g}_{\text{TM}}^{-1} \text{ h}^{-1}$ were found. In the first experiment, this value was about 60 % below that of the second column experiment. In comparison to the degradation studies, the parameters were in the same order of magnitude so that the results from the degradation studies are transferable to this case, especially since the temperature was the same. In the experimental period of two weeks, a mineralisation of approx. 1 % AR could therefore be expected. However, in the experimental design used it was not possible to record $^{14}\text{CO}_2$.

5.3 Lysimeter experiment with wind tunnel

The lysimeter experiment on the volatilisation of [^{14}C -U]-MTBE from the groundwater through the 1.1 m profile of a gleyic cambisol into the atmosphere served to validate the results of the column experiments (4.2). In previous experiments, OPHOFF ET AL. (1998) demonstrated the transferability of datasets from windtunnel experiment to the field scale. In comparison to

some field sites, the redesigned wind tunnel with a simulation of accumulated water (**3.3.1.2**) represented a well-defined, closed system in which good recovery was achieved (**Tab. 21**) by rapid sampling in contrast to field experiments (SCHIRMER ET AL., 1998; SCHIRMER ET AL., 1997).

With respect to its design, the wind tunnel is a well established large-scale device for field experiments to determine the volatilisation and mineralisation of, in particular, ^{14}C -labelled organic substances after application onto or into compartments of the agroecosystem (OPHOFF, 1998; STORK, 1995). However, sampling in the high-volume sampler (HVS) based on polyurethane foam was not suitable for volatile low-molecular hydrocarbons such as MTBE. A new adsorber therefore had to be sought for this class of materials (**3.3.1.1**). The new HVS with an activated charcoal cartridge was validated in several preliminary experiments. In spite of high volumetric flows, the experiments displayed good separation performance (**Tab. 18**). The recovery rate fluctuated between 66 and 94 % of the applied radioactivity. In the preliminary experiments, however, climatic conditions such as air moisture and temperature were also varied (**4.3.1**), both of which are decisive parameters for the breakthrough volume and consequently the separation performance of an adsorbent for the selected substance. High air humidity reduces the breakthrough volume of a substance since part of the sorption sites are occupied by water instead of the organic molecules so that the latter are no longer available for the actual separation process. The collecting temperature affects the breakthrough volume via the vapour pressure of the compound to be absorbed. A greater volume of MTBE can be sorbed at decreasing temperatures (FIGGE ET AL., 1987). Although in validation experiment V4 a lower temperature prevailed than in the other experiments, the air humidity was also perceptibly raised (**Tab. 18**). This air humidity may therefore be a reason for the poorer recovery and seems to have a stronger effect on collection performance than temperature. It is possible to make a direct comparison between the validation experiments V3 and V4 since in this case as well the air-flow temperature was determined after the HVS. In spite of the good detection limit in the GC/MS system, it was not possible to detect any MTBE with the additionally installed thermodesorption tubes (TDT, Fig. 13). A possible reason for this may be the performance of the sampling pump which in continuous operation may not have been sufficient to withdraw an aliquot against the HVS volumetric flow. In a new study of our own, a positive adsorption of various pesticides on Tenax TA® in a wind tunnel was made possible by installing a more powerful pump.

In addition to validating the HVS, moisture measurements in the soil were also verified before starting the experiment (**4.3.2**). The dependence of mass transfer in the unsaturated soil zone on soil moisture is described in (**Eq. 9**). In order to be able to make a comparative assessment of the influence of soil moisture on the transport processes in the various soil horizons, all TDR sensors should display identical measuring results if possible (**Fig. 42**). In comparison to the calibrated Trime system, the Trase TDR sensors used in the experiment overestimated the measured data at higher moisture levels. At low moisture levels the reverse was true (**4.3.2**). After this comparison, only sensors recording similar measurements

were used in the experiments. The different moisture contents of the two measuring systems are due to the design of the sensors. The multiplexer that had been subjected to severe weathering due to outside conditions and which was responsible for the simultaneous recording of measurements from up to 16 TDR sensors with one measuring instrument did not influence the experimental data [measuring accuracy ($\pm 2\text{vol}\%$) **Fig. 43**].

In the experiment, the soil moisture was almost constant in all soil layers (10, 30, 50, 70, 90 cm GL), as also in the column experiments (**4.3.2**). Increasing soil moisture with soil depth up to water saturation in the groundwater accululation was expected and also found. Two TDR sensors were used at each installation level in order to take the heterogeneities in the soil monolith into consideration. At installation depths of 70 cm and 10 cm, greater differences in soil moisture were observed within one layer. Only in the upper arrangement (10 cm) were slight fluctuations in soil moisture measured with the experimental time and changing climatic conditions. An explanation for this is the slight distance of the sensor from the surface (10 cm) and thus also a dependence of the soil moisture on solar radiation, soil temperature and air humidity (**Fig. 45**) (**4.3.3**). At the beginning of the experiment, the gleyic cambisol dried out at the surface. At a depth of 10 cm below the soil surface, a soil moisture of approx. 17 vol% was still measured (**Fig. 44**). As the outside climate (**Fig. 45**) cooled down, the upper soil layer was remoistened, which could be seen by a depletion of the water content in the air flow passing over the lysimeter in the wind tunnel.

Using (**Eq. 20**) it was possible to calculate the evaporation from these differences in air humidity at the wind tunnel inlet and outlet and from the air temperature at the measuring locations. A good qualitative relation between the evaporation and soil temperatures was found (**Fig. 47**). Increasing evaporation was calculated with rising soil and air temperature. On the whole, averaged over the experimental period, the water content of the air flow was depleted. Due to the soil structure, insufficient moisture was supplied from the groundwater to compensate that dried out by the wind so that, especially at lower temperatures, more water was precipitated in the upper soil layers. A measuring error can be ruled out since the dew-point level was calibrated daily. The measurement of the air pressure at various locations inside and outside the wind tunnel was important in order to apply (**Eq. 20**) correctly, and to give proper consideration to the dependence on air pressure.

In **Fig. 48**, the changes in groundwater volume and the MTBE loss are compared. In contrast to the column experiments, no qualitative relationship was found between the two parameters. The groundwater losses increased after the groundwater reservoir had been replenished (**Fig. 15**). On subsequent days, a below average reduction in groundwater volume was apparent. These fluctuations are design-dependent and are discussed in detail in **4.3.3**. After the groundwater reservoir had been restarted (**Fig. 15**), too much water flowed into the groundwater tank (GW, **Fig. 14**) until a stable circulation had been reached. In the following days, this excess water migrated into the soil and thus no further water was required from the

reservoir. The loss of [^{14}C -U]-MTBE from the groundwater varied at values of about 3 % of the applied radioactivity. There is still no explanation for the outliers.

The gel permeation chromatography (GPC) described in **3.4.2.3** was used to analyse the groundwater. The good separation performance (**Fig. 56**) meant that the groundwater could be examined radio chemically for MTBE and its metabolites without encountering the problems arising in a water analysis by GC/MS (**5.2**). Furthermore, it was possible to exploit the lower detection limit by an LSC measurement of the fractions. However, this analytical method only recovered approx. 90 % of the theoretically applied ^{14}C activity (**Fig. 49**). It cannot be ruled out that the collection of GTC eluent fractions in open vessels meant that part of the volatile organic components such as [^{14}C -U]-MTBE evaporated before they could be measured in the LSC. It was also found that the [^{14}C -U]-MTBE supplied no longer had its original radiochemical purity of 99.7 % of the applied radioactivity but only 97.3 %. ^{14}C -tert-butyl alcohol (^{14}C -TBA) was thus already detected in the standard and in the first analyses and its volume did not vary until the end of the experiment although with a metabolism of MTBE in the groundwater the less volatile TBA should accumulate (PANKOW ET AL., 1996). Together with the very low mineralisation (**Tab. 21**), an extremely low MTBE elimination by microbiological anaerobic degradation in the groundwater is to be assumed (0.05 % AR) since TBA does not occur as a marker molecule (BRADLEY ET AL., 2001; FINNERAN & LOVLEY, 2001).

In addition to the groundwater analyses and determination of the evaporation rates, the volatilisation and mineralisation of [^{14}C -U]-MTBE was also continuously recorded in the HVS and MVS (**Tab. 20**). However, in the four-week experimental period MTBE was only detected in the air up to the 10th day after the start of the experiment and even then on just three days (total 8.36 mg_{MTBE} in 27 days). At 0.07 % of the applied radioactivity the volatilisation was appreciably stronger than in the column experiments (factor 175-7000), but on the whole still very low. In this connection, consideration must be given to the larger volumetric flow per soil surface in comparison to the soil column (factor $3 \times 10^3:1$) (ASTM, 1996). A good correlation between the two experimental approaches was then apparent after the above-mentioned normalization. Mineralisation was only measurable up to the 11th day of the experiment and in spite of a collection period of two days, no more $^{14}\text{CO}_2$ was subsequently detected in the air flow. These irregular, pulse-shaped readings also occurred in the column experiments (**4.2.2**). A possible explanation for the lack of mineralisation after the 11th day may be the toxicity of TBA for the microorganisms in the anaerobic saturated zone of the soil (BRADLEY ET AL., 2001). This conjecture would also be supported by the values lower by a factor of 2 for the microbial activity (**Fig. 53**) in comparison to the degradation studies (**Fig. 24** and **Fig. 25**) and the column experiments (**Fig. 32** and **Fig. 40**). At approx. 1 % of the applied radioactivity, the mineralisation rates found in the degradation studies were considerably higher. Possible reasons for these differences have already been discussed above. A shorter MTBE residence time and lower volume in the aerobic soil horizons could also have influenced the low mineralisation.

Immediately after the experiment had been concluded, the soil cores were sampled by a Wacker hammer system and the cores stored in liquid nitrogen (**3.3.3.3**). Sampling down to a depth of approx. 100 cm was very rapid in comparison to sampling by hand in the soil column experiments so that the volatilisation losses were kept very low. This also becomes apparent through the ^{14}C activity distribution in the individual soil layers (**Fig. 51**). Below a depth of 80-90 cm a sufficient quantity of activity was found in all six cores from a soil layer. Due to bad planning, the PVC cartridges of the sampling system were about 5-10 cm too short so that only two of the six samples completely covered the saturated region. It was therefore not possible to establish a quantitative relationship between the soil moisture and ^{14}C activity distribution. The soil moisture tended to increase downwards in the soil body and thus also the ^{14}C found in each soil layer. No radioactivity was measured below $0.12 \text{ g}_{\text{water}} \text{ g}_{\text{TB}}^{-1}$. This trend can also be derived from (**Eq. 9**) (**Tab. 24**). The retardation in the unsaturated soil zone is dependent on the soil moisture and the soil-water distribution coefficient (K_d). **Tab. 24** shows the calculated retardation factors and K_d values in the individual horizons. These two parameters are a measure of the adsorption and retention capacity for an organic substance in the soil. In contrast to the soil column experiments, no retardation is to be expected in the saturated zone of the lysimeter experiment due to the lower C_{org} content ($R \equiv 1.0$).

Tab. 24: Wind tunnel experiment with a gleyic cambisol after contamination with [^{14}C -U]-MTBE in the simulated groundwater accumulation: Retardation factor (R) of MTBE in the saturated and unsaturated soil zones as well as the soil-water distribution coefficient (K_d) in the individual soil layers as a function of soil moisture (θ_w), air voids (θ_a) and soil density (ρ_b) after SQUILLACE ET AL. (1997).

Parameter Soil layer	C_{org} [%]	$K_d^{\bullet}$ [$\text{cm}^3 \text{ g}^{-1}$]	θ_w [$\text{cm}^3 \text{ cm}^{-3}$]	θ_a [$\text{cm}^3 \text{ cm}^{-3}$]	ρ_b [g cm^{-3}]	R
0 – 30 cm	1,007	0,124	0,175	0,277	1,41	64 ^①
30 - 62 cm	0,362	0,045	0,230	0,162	1,69	93 ^②
62 – 80 cm	0,193	0,024	0,301	0,158	1,53	107 ^③
80-100 cm	0,076	0,009	0,344	0,089	1,57	201 ^③
100 – 110 cm	0,076	0,009	0,344	0	1,57	1,033 ^③

① Calculated after (Eq. 7)

② Calculated after (Eq. 8)

③ Calculated after (Eq. 9)

A K_H of 0.02 was assumed for the calculation of R (MACKAY ET AL., 1993).

After evaluating all the data, a radioactivity balance was drawn up concerning the distribution of ^{14}C activity during and after the wind-tunnel experiment (**Tab. 21**). The recovery of 71 % of the applied radioactivity at the end of experiment pointed to some weaknesses in the experimental procedure. The major fraction of the missing ^{14}C activity probably remained in the bottom centimetres of the groundwater accumulation. Due to the insufficient length of the core sleeves it was not possible to take samples down to the bottom of the lysimeter (3-5 cm). However, high concentrations of the groundwater contaminated with [^{14}C -U]-MTBE were to be found in this region in particular. In comparison to the second column experiment (89 % AR), the [^{14}C]-MTBE quantity remaining in the groundwater was slight (61 % AR).

Another possible source of error may be the incomplete coverage of the entire groundwater since it was not completely pumped off. Slight quantities were also found in the soil in the form of unextracted ^{14}C activity (0.1 % AR, **Tab. 21**). There is as yet no explanation for the fact that the radioactivity was only detected in two soil segments in the upper soil layers. As can be seen from **Fig. 45** and **Fig. 46**, throughout the experimental period air humidity of between 60-80 % relative humidities and temperatures of up to 34 °C prevailed. The high temperatures could have caused a more rapid breakthrough of MTBE through the activated charcoal unit at the HVS thus leading to a poorer separation performance (see above).

5.4 Summarizing discussion, assessment and outlook

In the present report, the transport of MTBE through an undisturbed soil body was studied after contamination by a simulated leak or some other point source in the aquifer on various size scales (**3.1-3.3** and **4.1-4.3**). The groundwater concentrations used were in the range of the concentrations occurring at real polluted sites of up to several hundred milligrams per litre of groundwater, e.g. close to a point source (EFFENBERGER ET AL., 2001). In the following, the most important relations and findings are summarized with respect to the objectives (**1**) and a short outlook is given concerning future issues.

The following findings were obtained in the three-stage experimental concept:

- A low aerobic microbial degradation of MTBE was found in soil (max. 1.6 % of the applied radioactivity in the form of $^{14}\text{CO}_2$ in 101 days). Relative to the quantity of $[\alpha,\alpha'\text{-}^{14}\text{C}]\text{-MTBE}$ still present in the experimental setup, this rate rose continuously up to 37 % so that a good conversion of the MTBE can be assumed. The measured mineralisation was not dependent on soil moisture. As described in the literature, the microorganisms in an alluvial loam previously polluted with motor fuels achieved a more rapid mineralisation than in a previously uncontaminated gleyic cambisol.

- The theory of a spontaneous volatilisation of the substance from surfaces formulated by JEFFREY (1997) on the basis of the high vapour pressure of MTBE was confirmed in the second degradation study and very well described by a simple exponential function.

- The design of the column experiment set-up was validated into two experiments with undisturbed soil monoliths of a gleyic cambisol with groundwater rising. The experimental conditions used were constant throughout the experimental period and thus provided the basis for defined reproducible experimental conditions. Taking into consideration the sample preparation and analysis methods available, the application of ^{14}C -labelled MTBE proved indispensable to detect this substance in the soil matrix as well. Only in this way is it possible to draw up a mass and radioactivity balance. Furthermore, if plants are included in the experimental system, the radio-tracer technique is absolutely essential in order to monitor the uptake.

-After an accumulation of groundwater, the soil columns used display different transport behaviour of MTBE through the soil. As discussed above, this may be due to the structure of the experiment or heterogeneities in the soil. The concentration of MTBE in the air found in the first column experiment was in the range of 0.1-47 ppb with an average of 4.6 ppb. These values are orders of magnitude lower than the concentrations acute or chronically toxic for humans (2.1.4.3.). According to the state of the art in research, MTBE is not carcinogenic in the order of magnitude found, especially since the quantities were always only emitted in pulses. The MAC values (40-50 ppm) legally defined in Germany, Sweden, Finland and the USA are greater than the concentrations found here by a factor of 10^3 . Only the odour threshold of 3.4-1000 ppb may be reached in the MTBE content in the air detected here.

-The selected groundwater concentrations of 117-200 mg L⁻¹ are significantly above the taste threshold of 29 µg L⁻¹. The maximum permissible drinking water concentration of 20-40 µg L⁻¹ is also clearly exceeded. However, it must be remembered that with increasing distance from the point source caused by leakages the concentrations are rapidly reduced by dilution.

-The wind-tunnel experiment and also the second column experiment showed an almost analogous transport behaviour of MTBE in soil and at the soil/atmosphere transition. The scale-up has thus been successful and the reproducibility was also indicated in a large number of column experiments. In agreement with literature data, MTBE is only slightly distributed in the soil body and only low quantities were sorbed. Soil sampling still has to be optimized for volatile compounds such as MTBE in order to exclude as far as possible losses due to analytical processing.

-The analysis of groundwater sample by DAI-GC/MS still has to be optimised with respect to reproducibility and detection limits. A more sensitive detection of VOCs in water may be obtained by using Stirr Barr Sorptive Extraction GC/MS (SBSE - "Twister") or SPME-GC/MS. In contrast, the TDS-GC/MS analyses of the air samples were very sensitive and provided good results even at high air humidities. The selected collection technique on thermodesorption solid adsorbents was readily reproducible and displayed high collecting efficiency.

In further studies with the column experimental facility, an examination of MTBE transport through various soil types after leakages into the groundwater with a larger number of parallel experiments would be informative. Both the wind tunnel and also the soil columns can be used for studies with plant cover. In particular, the uptake of MTBE in plants from air, water and soil in an undisturbed compartment of the ecosystem and the effects on transport rates would be an interesting complement to previous findings (SCHROLL ET AL., 1994). However, trees which are frequently used in the phytoremediation of groundwater pollution, cannot be studied with the set-up (LARSEN ET AL., 2001). In view of the increasing application of MTBE as a fuel additive in the EU and against the background of the environmental problems occurring in the USA and now also observed in Germany, a continuation of these

studies is of current interest and can also make an important contribution to a better understanding of the problem and to possible solutions.

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8 Annex

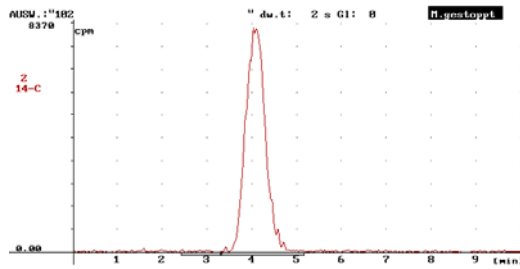


Fig. A-57: HPLC- Chromatogram of 2. degradation study – active charcoal extract, sterile Control 80% WHC_{max}(KSF), 3 d, 50µL.

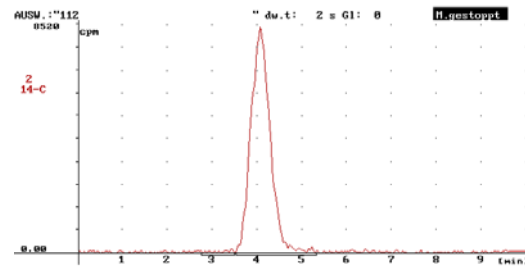


Fig. A-58: HPLC- Chromatogram of 2. degradation study – active charcoal extract, sterile Control 80% WHC_{max} (KSF), 8 d, 50µL.

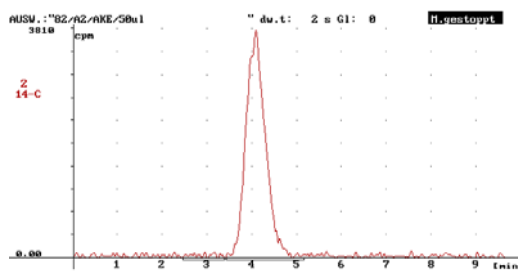


Fig. A-59: HPLC- Chromatogram of 2. degradation study – active charcoal extract, sterile Control 80% WHC_{max} KSF), 0,5 d, 50µL.

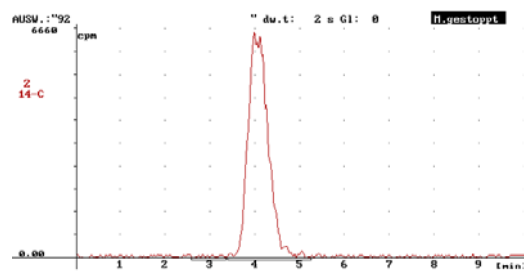


Fig. A-60: HPLC- Chromatogram of 2. degradation study – active charcoal extract, native sample 80% WHC_{max}(FF), 1 d, 50µL.

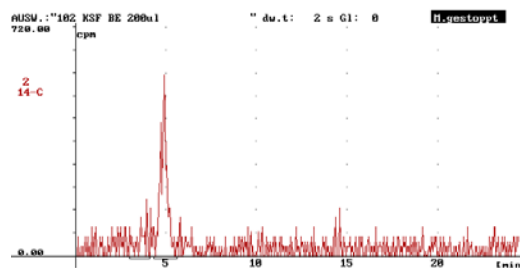


Fig. A-61: HPLC- Chromatogram of 2. degradation study – soil extract, sterile Control 80% WHC_{max}(KSF), 3 d, 200µL.

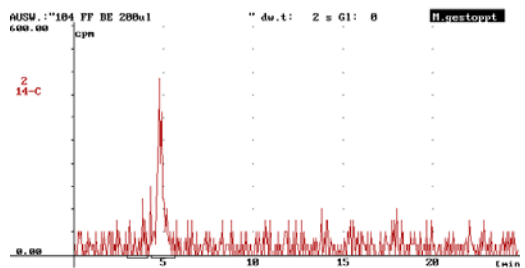


Fig. A-62: HPLC- Chromatogram of 2. degradation study – Soil extract, native Sample 80% WHC_{max}(FF), 3 d, 200µL.

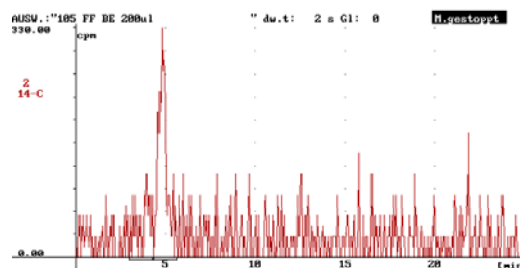


Fig. A-63: HPLC-Chromatogramm der 2. Abbau-

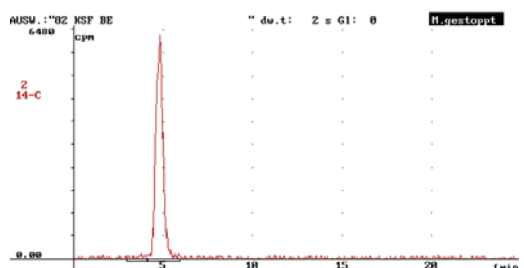


Fig. A-64: HPLC-Chromatogramm der 2. Abbau-

studie – Soil extract, native Sample 80%
WHC_{max}(FF), 3 d, 200µL.

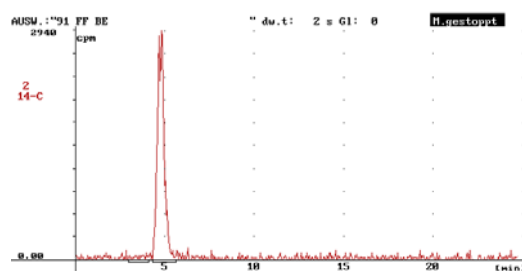


Fig. A-65: HPLC- Chromatogram of 2. degradation study – Soil extract, native Sample 80% WHC_{max}(FF), 1 d, 200µL.

studie – Soil extract, sterile Control 80%
WHC_{max}(KSF), 0,5 d, 200µL.

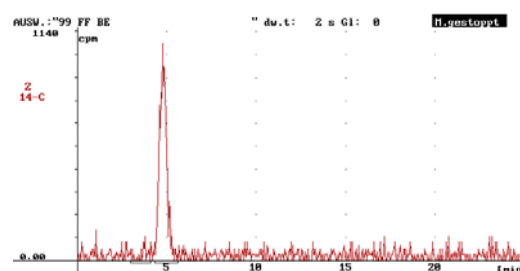
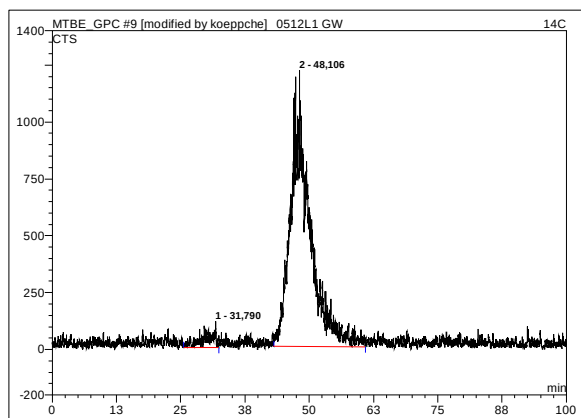
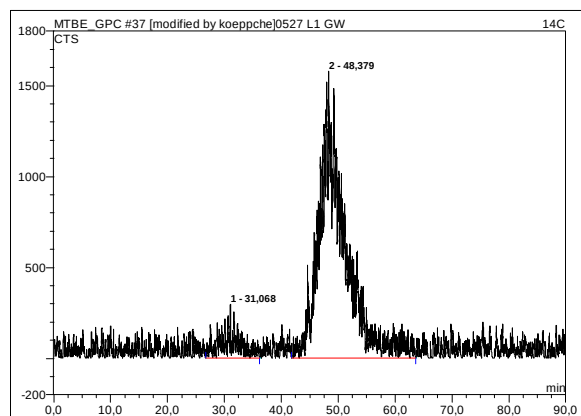


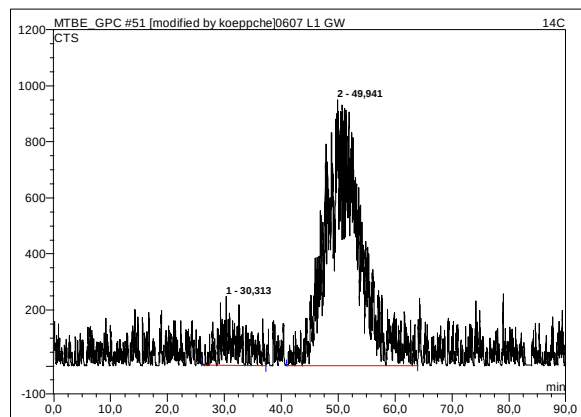
Fig. A-66: HPLC- Chromatogram of 2. degradation study – Soil extract, native Sample 80% WHC_{max}(FF), 4 d, 200µL.



Sample date at 13.05.01
Before injection
Injection volume 200 μ L
 ^{14} C-Signal



Sample date at 28.05.01
Injection volume 200 μ L
 ^{14} C-Signal



Sample date at 7.06.01
End of experiment
Injection volume 200 μ L
 ^{14} C-Signal

Fig. A-67: Examples for GPC-chromatograms of the groundwater after contamination with [^{14} C-U]-MTBE in the wind tunnel (MTBE-L1).

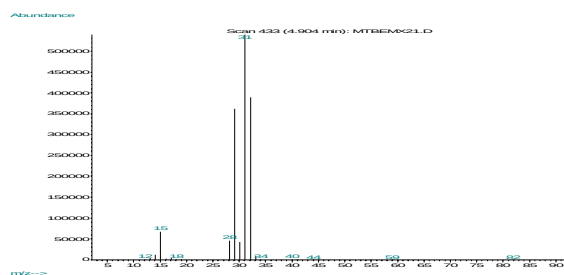


Fig. A-68: Mass spectrum of Methanol Uvasol : SCAN – Modus (15-150 AMU), HP 5973 mass spektrometer, Retention time 4,90 min Fig. 55.

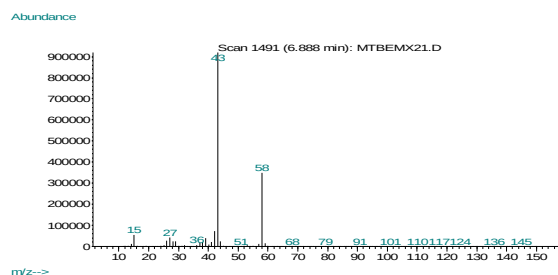


Fig. A-69: Mass spectrum of Acetone : SCAN – Modus (15-150 AMU), HP 5973 mass spektrometer, Retention time 4,90 min Fig. 55.

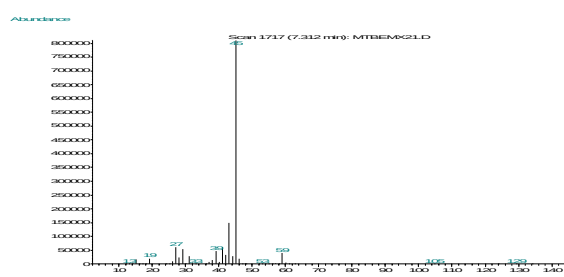


Fig. A-70: Mass spectrum of: SCAN – Modus (15-150 AMU), HP 5973 mass spektrometer, Retention time 4,90 min Fig. 55.

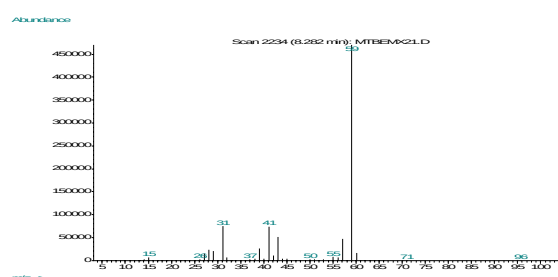


Fig. A-71: Mass spectrum of TBA): SCAN – Modus (15-150 AMU), HP 5973 mass spektrometer, Retention time 4,90 min Fig. 55.

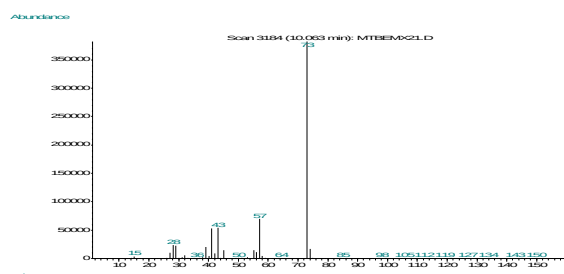


Fig. A-72: Mass spectrum of MTBE: SCAN – Modus (15-150 AMU), HP 5973 mass spektrometer, Retention time 4,90 min Fig. 55.

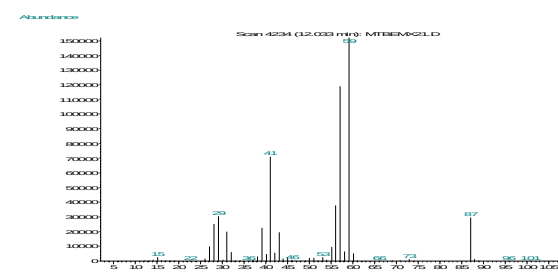
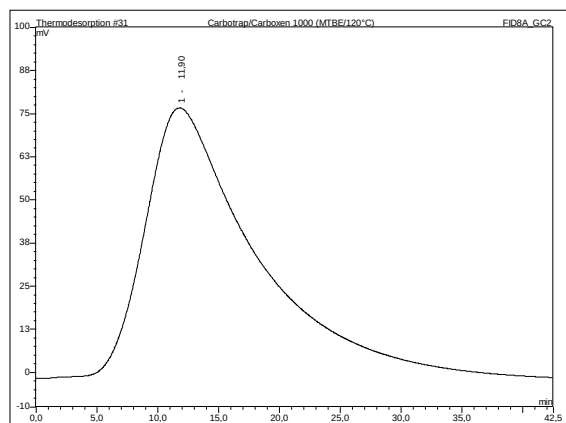
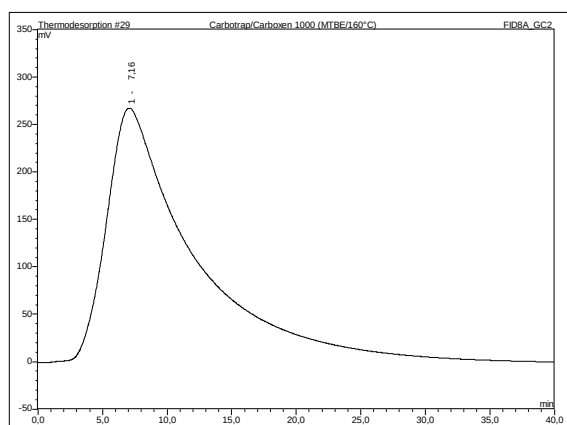


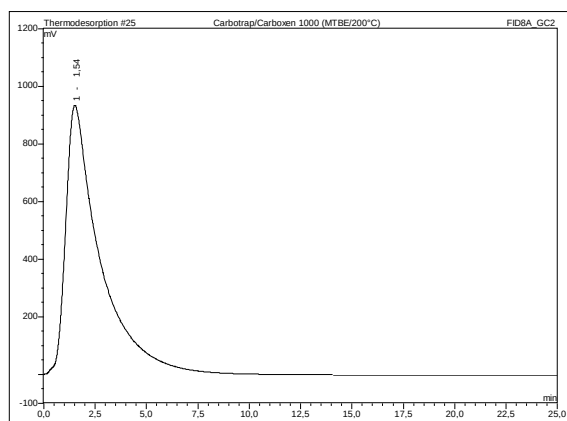
Fig. A-73: Mass spectrum of TBF : SCAN – Modus (15-150 AMU), HP 5973 mass spektrometer, Retention time 4,90 min Fig. 55. .



Temperature = 120 °C



Temperature = 160 °C



Temperature = 200 °C

Fig. A-74: Retention time detection of the multibed-adsorptionstubes (Carbotrap/Carboxen 1000) at different temperatures

Tab. A-25: Wind-tunnel experiment with a gleyic cambisol after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation: Climatic conditions during the lysimeter experiment and operating data.

Date 2000 days after application		11./12.5. 1	12./13.5. 2	13./14.5. 3	14./15.5. 4	15./16.5. 5	16./17.5. 6	17./18.5. 7	18./19.5. 8	19./20.5. 9	20./21.5. 10	21./22.5. 11	22./23.5. 12	23./24.5. 13	Average of experiments
T _{air outside}	[°C]	21,6±5,2	21,7±4,6	20,1±5,8	21,4±7,0	23,2±6,1	22,8±6,3	14,9±3,0	11,9±2,5	9,9±2,8	12,2±3,9	11,4±1,9	12,3±2,0	17,3±2,7	16,4±3,8
T _{air WT inlet}	[°C]	20,7±4,2	19,3±4,1	19,3±4,6	20,2±5,5	22,2±5,0	22,7±5,7	13,8±2,9	11,4±2,5	9,4±2,4	11,1±2,8	11,0±1,5	11,6±1,7	16,5±1,8	15,7±3,1
T _{air WT outlet}	[°C]	22,7±6,5	21,7±5,9	22,1±7,1	23,4±8,4	25,2±7,6	24,4±8,0	15,9±4,7	13,1±3,8	10,7±3,7	13,4±5,2	12,1±2,4	13,1±2,7	18,3±3,6	17,7±5,0
T _{average}	[°C]	21,7±5,3	20,5±4,9	20,7±5,8	21,8±6,8	23,7±6,2	23,5±6,8	14,8±3,8	12,3±3,0	10,1±3,0	12,2±4,0	11,6±1,9	12,4±2,1	17,4±2,6	16,7±4,0
ΔT _{air WT outside}	[K]	0,1±1,1	0,5±0,9	0,6±1,5	0,4±2,1	0,5±2,1	0,7±1,2	-0,1±1,4	0,4±0,9	0,2±0,7	0,0±1,0	0,2±0,5	0,1±0,7	0,0±0,9	0,3±1,1
T _{soil outside}	[°C]	19,9±3,1	19,1±3,2	19,3±3,8	20,9±4,8	21,8±4,4	21,8±4,2	16,9±2,8	14,2±2,4	12,3±2,0	13,3±2,8	12,1±1,2	12,2±1,0	15,1±1,7	16,3±2,7
T _{soil WT}	[°C]	22,4±2,2	21,3±3,6	21,7±4,2	23,2±4,9	24,2±4,3	23,7±4,2	19,2±3,6	16,2±2,7	13,9±2,6	15,6±3,6	13,4±1,5	13,4±1,3	17,3±2,4	18,3±3,1
ΔT _{soil WT outside}	[K]	2,1	2,2	2,4	2,3	2,4	1,3	2,3	2,0	1,6	2,3	1,3	1,2	2,2	1,9
T _{soil surface WT}	[°C]	22,6±4,4	22,9±7,9	24,7±9,7	24,7±9,6	26,4±9,2	25,0±9,1	18,4±7,2	14,7±5,5	11,8±5,0	14,6±6,6	11,8±2,9	12,6±3,0	17,9±4,6	18,2±6,0
ΔT _{soil surface T_{air} WT}	[°C]	0,9	2,4	4,0	2,9	2,7	1,5	3,6	2,4	1,7	2,4	0,2	0,2	0,5	1,6
ΔT _{soil surface T_{soil} WT}	[K]	2,3	1,6	3,0	1,5	2,2	1,3	-0,8	-1,5	-2,1	-1,0	-1,6	-0,8	0,6	0,0
rH _{outside}	[%]	62,6±15,8	63,2±14,8	55,7±18,9	49,8±19,9	43,7±17,9	60,6±20,9	59,1±8,4	66,9±8,9	77,6±10,4	66,3±13,7	75,1±5,5	82,0±5,0	58,6±11,1	64,2±12,6
rH _{WT average}	[%]	59,5±6,1	60,6±8,0	52,4±6,5	47,8±7,1	42,0±7,0	44,7±8,1	57,9±9,0	60,7±10,1	67,9±7,8	70,0±8,9	70,0±4,5	77,0±6,5	63,8±6,4	61,4±7,8
ΔrH _{WT outside}	[%]	-3,11	-2,7	-3,3	-1,94	-1,7	-15,9	-1,2	-6,2	-9,72	3,6	-5,1	-5,0	5,2	-3,0
Wind 0,2 m	[m s ⁻¹]	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0
Wind 0,05 m	[m s ⁻¹]	0,14±0,06	0,17±0,05	0,17±0,05	0,18±0,06	0,17±0,05	0,16±0,04	0,16±0,03	0,15±0,03	0,15±0,03	0,15±0,03	0,14±0,01	0,14±0,02	0,15±0,03	0,16±0,04
Rad. Außen	[W m ⁻²]	70,9±141,4	145±167,8	175±216,1	201,8±269,7	197,2±259,4	132,3±201,2	115,2±173,7	95,2±135,9	77,4±108,4	140,8±201,9	52,8±67,9	74,6±83,5	117,8±150,7	128,3±174,5
Rad. WT Mittel	[W m ⁻²]	178,7±239,9	207,6±236,5	234,4±270	259,1±207,2	261,1±301,5	184,4±259,5	161,6±237,9	148,4±208	113,3±167	171±231,7	72,2±94,8	101,8±115	173,1±184,5	172,0±217
ΔRad. WT außen	[W m ⁻²]	107,8	62,6	53,9	57,3	63,6	52,1	46,4	53,1	35,9	30,17	19,4	7,2	55,9	43,6
HLS	[m ³ h ⁻¹]	213,0	282,8	270,0	306,7	285,6	282,2	286,9	286,0	295,2	296,3	284,6	288,4	279,9	283,7±17,2
HVS	[m ³ h ⁻¹]	14,2	11,1	9,6	16,5	12,1	18,7	11,5	19,4	11,5	11,5	10,3	21,8	10,3	13,3±3,6
HVS	[% HLS]	6,7	3,9	3,6	5,4	4,2	6,6	4,0	6,8	3,9	3,9	3,6	7,6	3,7	4,7±1,3
MVS	[L min ⁻¹]	3,3	3,3	3,2	3,4	3,2	3,3	3,3	3,4		3,3	2,6	3,5	3,3	3,3±0,2
MVS	[% HLS]	0,092	0,070	0,071	0,066	0,067	0,071	0,069	0,071		0,067	0,055	0,074	0,070	0,067±0,015

T = temperature;
WT = wind tunnel;
Δ = difference;
rH = relative humidity;
Wind = wind speed;
Rad. = irradiation;
HLS = main air flow;
HVS = high-Volume Sampler;
MVS = medium-volume Sampler

Tab. A-26: Wind-tunnel experiment with a gleyic cambisol after contamination with [14C-U]-MTBE in the simulated groundwater accumulation: Climatic conditions during the lysimeter experiment and operating data.

Date 2000 days after application	24./25.5. 14	25./26.5. 15	26./27.5. 16	27./28.5. 17	28./29.5. 18	29./30.5. 19	30./31.5. 20	31.5./1.6. 21	1.6./2.6. 22	2.6./3.6. 23	3.6./4.6. 24	4.6./5.6.. 25	5.6./6.6. 26	6.6./7.6. 27	average of experiments
T _{air outside} [°C]	15,8±1,4	12,9±3,3	17,8±3,5	13,9±2,1	11,5±3,3	11,5±3,3	12,0±2,7	16,3±3,9	19,4±5,1	22,2±5,8	23,9±5,4	18,9±3,5	13,8±3,1	14,6±2,8	16,4±3,8
T _{air WT inlet} [°C]	15,4±1,4	11,9±2,6	16,8±2,8	13,1±1,2	10,6±3,0	10,7±2,6	11,5±2,1	15,1±2,6	18,4±3,9	21,4±5,0	23,2±4,8	17,9±2,7	13,6±2,9	14,0±2,0	15,7±3,1
T _{air WT outlet} [°C]	16,3±2,1	13,5±4,1	19,0±4,4	14,9±3,2	12,4±4,6	13,0±4,7	12,9±3,5	17,8±5,2	21,2±6,3	24,2±7,5	25,8±7,3	19,9±2,6	14,5±3,6	15,6±3,7	17,7±5,0
T _{average} [°C]	15,8±1,6	12,7±3,3	17,9±3,4	14,0±2,1	11,5±3,8	11,9±3,6	12,2±2,8	16,5±3,8	19,8±5,1	22,8±6,2	24,5±6,2	18,9±3,5	14,0±3,2	14,8±2,9	16,7±4,0
ΔT _{air WT outside} [K]	0,1±0,7	-0,1±0,9	0,1±1,0	0,1±0,8	0,5±1,0	0,3±1,2	0,2±0,8	0,1±1,3	0,4±1,2	0,5±1,4	0,6±1,2	-0,1±0,8	0,2±0,6	0,1±0,7	0,3±1,1
T _{soil outside} [°C]	15,0±1,2	13,2±2,4	17,8±3,5	13,7±2,4	12,0±2,6	12,6±2,6	12,8±1,5	15,9±2,7	17,3±2,7	20,4±3,5	22,5±3,3	18,4±2,2	15,4±1,9	15,4±2,0	16,3±2,7
T _{soil WT} [°C]	16,2±1,5	15,4±2,7	18,5±3,2	16,6±3,1	14,7±3,0	15,1±3,1	14,1±2,0	17,6±3,4	19,9±3,6	22,7±4,2	24,2±3,3	19,9±2,6	16,5±2,1	17,0±2,4	18,3±3,1
ΔT _{soil WT outside} [K]	1,2	2,2	0,7	2,9	2,7	2,5	1,3	1,7	2,6	2,3	1,7	1,5	1,1	1,6	1,9
T _{soil surface WT} [°C]	15,7±2,7	13,8±4,6	19,4±6,0	15,6±5,0	13,5±6,0	14,2±6,3	12,7±3,9	18,4±6,5	21,2±7,2	24,5±8,6	26,1±8,4	19,4±4,9	14,4±3,6	15,7±4,5	18,2±6,0
ΔT _{soil surface T_{air} WT} [°C]	-0,1	1,1	1,5	1,6	2,0	2,3	0,5	1,9	1,4	1,7	1,6	0,5	0,4	0,9	1,6
ΔT _{soil surface T_{soil} WT} [K]	-0,5	-1,6	0,9	-1,0	-1,2	-0,9	-1,4	0,8	1,3	1,8	1,9	-0,5	-2,1	-1,3	0,0
rH _{outside} [%]	78,9±7,0	67,6±6,3	49,3±10,3	48,9±5,7	64,8±1,1	68,9±12,4	75,2±15,4	56,6±17,1	62,1±19,7	61,8±16,5	60,4±18,2	67,5±11,5	80,1±9,4	70,7±9,3	64,2±12,6
rH _{WT average} [%]	72,6±7,5	69,3±5,5	56,3±5,9	52,8±5,9	55,8±8,8	63,5±9,9	70,3±8,3	61,2±8,7	53,0±10	56,3±7,9	55,4±8,2	71±7,5	70,8±4,8	70,6±6,2	61,2±7,4
ΔrH _{WT outside} [%]	-6,3	1,7	7,0	3,9	-9,0	-5,4	-4,9	4,6	-9,1	-5,5	-5,0	3,5	-9,3	-0,1	-3,0
Wind 0,2 m [m s ⁻¹]	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0	0,5±0,0
Wind 0,05 m [m s ⁻¹]	0,15±0,03	0,14±0,02	0,16±0,04	0,15±0,03	0,15±0,04	0,15±0,04	0,14±0,02	0,16±0,06	0,17±0,05	0,17±0,05	0,17±0,05	0,15±0,02	0,14±0,01	0,15±0,02	0,16±0,04
Rad. Außen [W m ⁻²]	60,4±84,1	97,9±133,5	174,2±251,7	130,9±196,7	124,7±173,4	148,7±206,2	87,3±132,5	183,7±236,8	169,2±198,3	204±268	203,4±253,9	108,1±151	58,4±75	116,2±172,1	128,3±174,5
Rad. WT Mittel [W m ⁻²]	80,7±110,2	121,0±149,6	208,8±268,1	160,1±218,4	170,8±226,4	193,6±248,4	112,1±154,1	234,3±281,1	227,6±260,1	258,8±302,5	278,3±310,3	128,4±171,3	79,7±104,4	144±198,7	172,0±217
ΔRad. WT außen [W m ⁻²]	20,3	23,1	34,6	29,2	46,1	44,9	24,8	50,6	58,5	54,9	74,8	20,2	21,3	27,8	-43,6
HLS [m3 h ⁻¹]	281,7	295,5	274,3	299,8	285,7	290,4	278,6	289,3	272,5	310,6	279,2	280,7	290,0	273,8	283,7±17,2
HVS [m3 h ⁻¹]	12,3	10,8	13,4	11,2	17,4	10,3	12,9	10,6	11,8	11,9	22,5	10,4	12,7	12,1	13,3±3,6
HVS [% HLS]	4,4	3,7	4,9	3,7	6,1	3,5	4,6	3,7	4,3	3,8	8,1	3,7	4,4	4,4	4,7±1,3
MVS [L min ⁻¹]	3,3	2,5	3,3	3,3	3,3	3,3	3,4	3,3	3,3	3,4	3,3	3,3	3,5		3,3±0,2
MVS [% HLS]	0,070	0,050	0,072	0,066	0,069	0,068	0,073	0,068	0,072	0,066	0,070	0,070	0,073		0,067±0,015

T = temperature; WT = wind tunnel;
Δ = difference; rH = relative humidity;
Wind = wind speed; Rad. = irradiation;
HLS = main air flow; HVS = high-Volume Sampler;
MVS = medium-volume Sampler

**Tab. A-27: Wind-tunnel experiment with a gleyic cambisol after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation:
Radioactivity in different soil layers calculated from radioactivity in the CaCl₂-extracts (10 mM).**

No.	depth	Soil core [Bq/g[TB]]								RA / layer	recovery
	[cm]	A	B	C	D	E	G	H	MW	[kBq]	[% AR]
1	0-10	0,01	0,01	0,04	0,00	0,01	0,01	0,05	0,02±0,02	1,32±1,33	0,00±0,00
2	10-20	0,00	0,01	0,00	0,10	0,01	0,01	0,02	0,03±0,04	1,87±2,66	0,00±0,00
3	20-30	0,00	0,00	0,01	0,00	0,00	0,09	0,00	0,02±0,03	1,26±2,37	0,00±0,00
4	30-40	0,03	0,06	0,01	0,01	0,01	0,01	0,57	0,10±0,21	8,56±17,69	0,01±0,01
5	40-50	0,52	0,02	0,01	0,01	0,00	0,36	0,00	0,13±0,22	11,21±18,22	0,01±0,02
6	50-60	0,02	0,00	0,01	0,02	0,01	0,01	0,01	0,01±0,01	1,07±0,59	0,00±0,00
7	60-70	0,01	0,02	0,01	0,01	0,53	0,03	0,02	0,09±0,19	6,89±14,90	0,01±0,01
8	70-80	0,21	0,16	0,03	0,07	0,29	0,24	0,03	0,15±0,11	11,16±8,13	0,01±0,01
9	80-90	0,36	1,16	1,17	1,45	3,84	1,17	0,89	1,44±1,12	11,27±87,62	0,09±0,07
10	90-100	14,36	13,92	22,30	22,98	77,04	13,19	11,11	24,99±23,41	1961,40±1837,45	1,62±1,52
11	100-110	117,01					127,95		122,49	9614,73±607,09	7,95±0,50
Sum										11732,13±2598,06	9,71±2,15

MW = average

TB = dry soil

RA = radioactivity

AR=applied radioactivity (120,86 MBq)

**Tab. A-28: Wind-tunnel experiment with a gleyic cambisol after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation:
Residual radioactivity in the different soil layers after CaCl₂-extraction (10 mM).**

No.	Depth [cm]	Soil core [dpm/500mg [TB]]								RA / layer [Bq]	recovery [% AR]
		A	B	C	D	E	G	H	MW		
1	0-10	-	-	-	-	-	-	-	-	-	0,00
2	10-20	-	-	-	-	118,1	-	-	16,9	39636,9	0,03
3	20-30	-	-	-	-	-	-	-	-	-	0,00
4	30-40	0	0	0	0	11,5	0	0	1,6	4635,1	0,00
5	40-50	0	0	0	0	157,4	0	0	22,5	63326,2	0,05
6	50-60	-	-	-	-	-	-	-	-	-	0,00
7	60-70	-	-	-	-	-	-	-	-	-	0,00
8	70-80	-	-	-	-	-	-	-	-	-	0,00
9	80-90	-	-	-	20,7	-	-	-	2,95	7737,0	0,01
10	90-100	0	14,1	0	0	0	0	0	2,01	5269,0	0,00
11	100-110	11,4	0	0	0	0	0	0	1,6	4278,1	0,00
Sum										124882,4	0,1

MW = average

TB = dry soil

RA = radioactivity

AR=applied radioactivity (120,86 MBq)

**Tab. A-29: Wind-tunnel experiment with a gleyic cambisol after contamination with [¹⁴C-U]-MTBE in the simulated groundwater accumulation:
Soil moisture partitioning in the soil layers after taking 7 soil cores at the end of the experiment.**

Nr.	Tiefe [cm]	Bohrkern [$g_{\text{Wasser}}/g_{\text{TB}}$]							average
		A	B	C	D	E	G	H	
1	0-10	0,081	0,075	0,079	0,062	0,069	0,067	0,079	0,073±0,007
2	10-20	0,100	0,096	0,092	0,091	0,095	0,088	0,088	0,093±0,004
3	20-30	0,105	0,101	0,100	0,103	0,103	0,095	0,098	0,101±0,003
4	30-40	0,094	0,088	0,087	0,090	0,090	0,085	0,090	0,089±0,003
5	40-50	0,112	-	0,107	0,110	0,107	0,105	0,107	0,108±0,002
6	50-60	0,122	0,127	0,121	0,118	0,125	0,123	0,119	0,122±0,003
7	60-70	0,134	0,139	0,133	0,129	0,137	0,146	0,134	0,136±0,005
8	70-80	0,141	0,145	0,137	0,137	0,134	0,141	0,135	0,139±0,004
9	80-90	0,135	0,137	0,136	0,130	0,128	0,155	0,132	0,136±0,008
10	90-100	0,126	0,156	0,134	0,130	0,132	0,146	0,144	0,138±0,010
11	100-110	0,138	-	-	-	-	0,140	-	0,139±0,001

MW = average

TB = dry soil

**Tab. A-30: 1st column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation:
Climatic conditions of the first column experiment (MTBE-S1) during the experiment and sampling conditions.**

date 1999		3.8/4.8.	4./5.8.	5./6.8.	6./7.8	7./8.8	8./9.8	9./10.8	10./11.8	11./12.8.	12./13.8.	13./14.8.	14./15.8.	15./16.8.	16./17.8.	17./18.8.	18./19.8.	Average of
days after application		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	experiment
T air above soil	[°C]	23,8±0,4	21,8±0,2	21,8±0,1	21,7±0,1	21,5±0,1	21,4±0,1	21,5±0,1	21,6±0,1	21,4±0,1	21,5±0,1	21,4±0,1	21,1±0,1	21,3±0,1	21,4±0,1	21,3±0,1	21,3±0,1	21,6±0,6
T outside air	[°C]	22,6±0,3	22,8±0,2	22,7±0,2	22,6±0,2	22,2±0,3	22,1±0,3	22,7±0,2	22,6±0,2	22,5±0,2	22,6±0,3	22,5±0,3	22,0±0,2	22,3±0,2	22,4±0,3	22,4±0,3	22,4±0,2	22,5±0,2
T soil (2 cm)	[°C]	22,2±0,2	22,3±0,2	22,2±0,2	22,1±0,1	21,9±0,2	21,8±0,2	22,0±0,1	22,0±0,2	21,8±0,1	21,9±0,2	21,9±0,2	21,6±0,1	21,8±0,1	21,8±0,2	21,8±0,2	21,8±0,1	21,9±0,2
T groundwater	[°C]	11,9±0,3	11,6±0,3	11,8±0,2	11,9±0,1	11,7±0,1	11,7±0,1	11,6±0,1	11,8±0,1	11,6±0,2	11,1±0,2	11,1±0,1	11,5±0,2	11,1±0,3	11,0±0,1	10,9±0,1	11,0±0,2	11,5±0,4
T outlet	[°C]	23,3±0,3	23,3±0,2	23,2±0,2	23,2±0,1	22,9±0,2	22,9±0,2	23,0±0,2	23,0±0,2	22,9±0,1	22,9±0,2	23,0±0,2	22,7±0,1	22,8±0,1	22,9±0,2	22,9±0,2	22,9±0,2	23,0±0,2
rH outlet.	[%]	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100,0±0,0
T outside air	[°C]	24,0±0,3	24,1±0,3	24,1±0,4	24,0±0,3	23,8±0,3	23,8±0,3	23,9±0,3	23,8±0,2	23,7±0,3	24,0±0,3	23,8±0,3	23,5±0,4	23,5±0,4	23,6±0,3	23,6±0,3	23,7±0,4	23,8±0,2
rH outside	[%]	69,2±8,8	66,1±9,9	71,4±8,4	69,8±9,2	68,1±9,5	72,8±7,8	71,1±8,7	74,7±7,6	67,4±9,5	58,0±11,7	66,2±9,6	76,8±9,6	71,0±12,0	72,3±10,8	73,0±10,9	70,0±12,6	69,9±4,3
Air flow	[L min ⁻¹]	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Volume per sample	[L]	13,8±0,1	13,8±0,0	13,8±0,1	13,8±0,1	13,8±0,1	13,9±0,1	13,8±0,1	13,8±0,0	13,8±0,1	13,9±0,0	13,8±0,1	13,8±0,1	13,8±0,1,0	13,9±0,1	13,8±0,1	13,9±0,1	13,8±0,0
Total volume	[L]	138,3	138,3	138,3	138,4	138,4	138,5	138,2	138,3	138,4	138,6	138,2	138,3	138,4	138,9	138,1	138,5	138,4±0,2
Soil moisture (20cm GOK) [Vol %]		20,2	20,5	20,3	20,3	20,6	20,4	20,6	20,0	20,4	20,6	20,6	19,7	20,6	19,9	20,2		
Soil moisture (40cm GOK) [Vol %]		31,2	31,6	31,6	31,1	31,4	31,2	31,5	31,4	31,2	31,2	31,7	31,5	32,0	31,5	31,4		

T = Temperature; rH = relative humidity; Vol % = Volume percent

**Tab. A-31: 2nd column experiment in a gleyic cambisol after contamination with MTBE in the simulated groundwater accumulation:
Climatic conditions of the first column experiment (MTBE-S6) during the experiment and sampling conditions.**

date 2000	13./14.4.	14./15.4.	15./16.4.	16./17.4.	17./18.4.	18./19.4.	19./20.4.	20./21.4.	21./22.4.	22./23.4.	23./24.4.	24./25.4.	25./26.4.	26./27.4.	average of
days after application	1	2	3	4	5	6	7	8	9	10	11	12	13	14	experiment
T air above soil [°C]	20,9±0,3	20,7±0,2	20,7±0,1	20,1±0,2	20,1±0,2	20,8±0,2	20,8±0,2	20,9±0,1	20,8±0,1	20,8±0,0	20,8±0,1	20,9±0,1	21,0±0,2	21,0±0,1	20,7±0,3
T outside air [°C]	22,1±0,3	22,0±0,2	22,0±0,1	22,1±0,2	22,1±0,2	22,1±0,2	22,0±0,2	22,1±0,2	22,1±0,2	22,0±0,1	22,0±0,1	22,0±0,2	22,1±0,3	22,2±0,3	22,1±0,1
T soil (2 cm) [°C]	21,4±0,3	21,2±0,2	21,2±0,2	21,3±0,3	21,3±0,3	21,3±0,2	21,2±0,2	21,3±0,2	21,2±0,1	21,2±0,1	21,2±0,1	20,4±0,1	21,4±0,2	21,4±0,2	21,2±0,2
T groundwater [°C]	10,7±0,0	10,7±0,0	10,5±0,1	10,6±0,1	10,4±0,1	10,4±0,0	10,3±0,0	10,3±0,0	10,3±0,0	10,5±0,2	10,5±0,2	18,0±3,2	10,5±0,5	10,4±0,1	10,5±0,2 ^⓪
T outlet [°C]	22,7±0,3	22,4±0,2	22,3±0,2	22,5±0,2	22,4±0,2	22,4±0,2	22,4±0,2	22,5±0,2	22,4±0,2	22,4±0,2	22,4±0,2	22,4±0,2	22,5±0,2	22,6±0,2	22,5±0,1
rH outlet. [%]	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100±0,0	100,0±0,0
T air after condenser [°C]	23,9±1,1	23,2±1,0	23,1±1,2	23,2±1,2	23,3±0,8	23,3±0,9	23,0±0,9	23,4±1,2	23,4±1,3	23,2±1,1	22,7±0,8	22,7±0,7	23,1±0,7	23,0±0,5	23,2±0,3
rH after condenser [%]	23,9±1,1	40,2±0,4	40,6±0,5	40,8±0,3	40,7±0,5	41,0±0,5	41,2±0,5	41,2±0,6	41,5±0,5	41,7±0,4	42,2±0,4	42,1±0,4	41,6±0,6	41,6±0,6	40,0±4,7
T outside air [°C]	23,3±0,3	23,1±0,4	23,0±0,1	23,1±0,3	23,2±0,3	23,2±0,3	23,1±0,3	23,3±0,3	23,2±0,4	23,3±0,4	23,1±0,4	23,1±0,4	23,5±0,4	23,4±0,3	23,2±0,1
rH outside [%]	88,1±3,4	86,1±4,1	85,9±2,7	85,2±2,2	89,9±3,4	87,6±3,8	92,5±2,7	84,0±5,3	88,8±0,4	100±0,0	100±0,0	95,9±1,7	94,6±2,2	100±0,0	91,7±6,2
Air flow [L min ⁻¹]	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1	0,1
Volume per sample [L]	13,8±0,1	13,8±0,0	13,8±0,0	13,8±0,1	13,9±0,1	13,9±0,0	13,8±0,0	13,8±0,1	13,8±0,1	13,9±0,0	13,9±0,1	13,9±0,1	13,8±0,0	13,8±0,1	13,9±0,1
Total volume [L]	138,4	138,5	138,4	138,3	138,7	138,7	138,4	138,5	138,4	138,6	138,9	138,8	138,3	138,4	138,5

T = Temperature; rH = relative humidity;

^⓪ = without the values of day 12

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