Lyon, 30 March 2006

# SIMULTANEOUS DETERMINATION OF MTBE, ITS DEGRADATION PRODUCTS AND OTHER GASOLINE ADDITIVES IN SELECTED SOIL AND GROUNDWATER SAMPLES FROM SPAIN AND GERMANY


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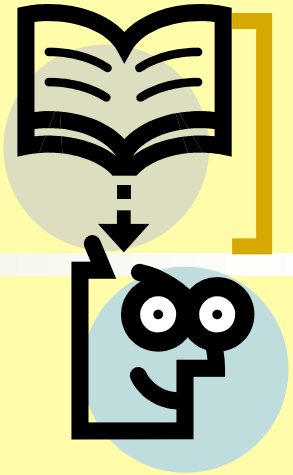
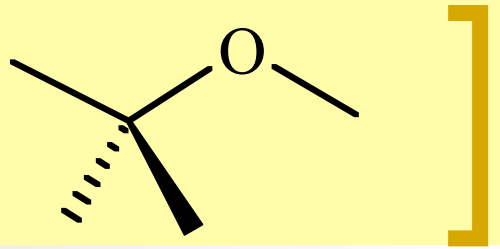
WATCH

# Outline



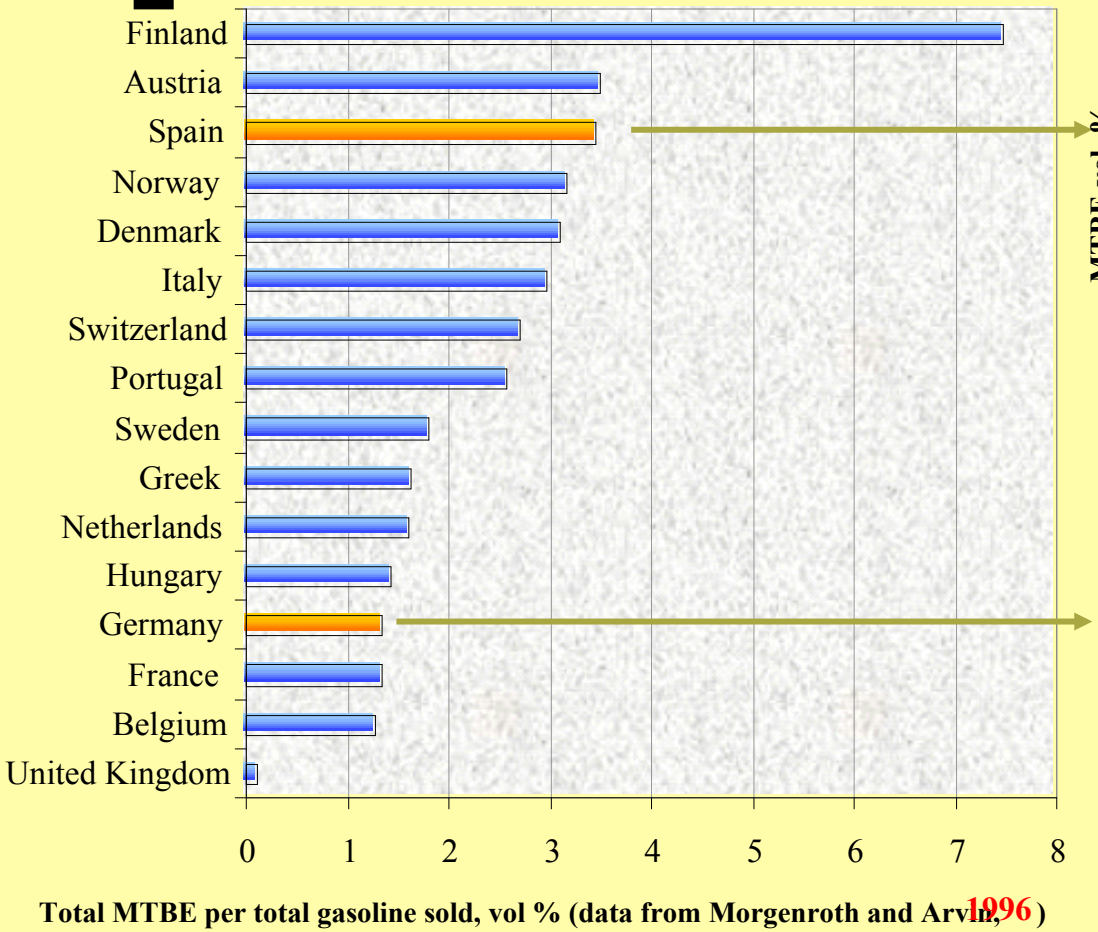
- MTBE: an EU problem
- Objectives
  - Method for analysis in groundwater samples
  - Examples: Spain and Germany GW levels
  - Method for analysis in soils and sediments
    - Sampling and storage conditions study
- Future work: application in real soil samples

# MTBE in Europe



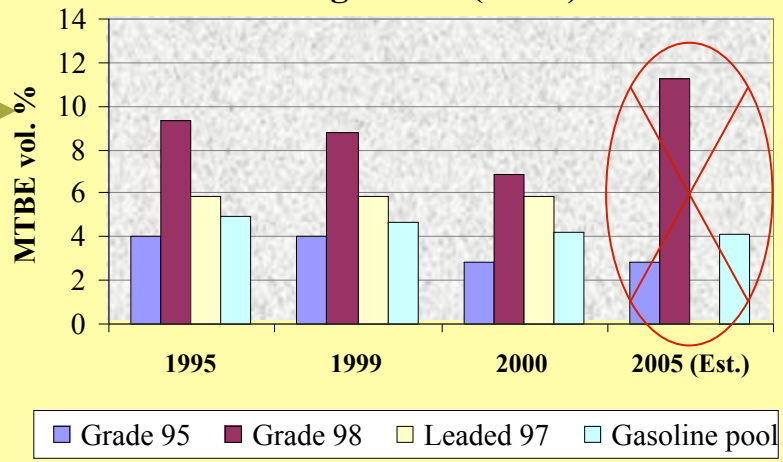

- Since 1970s, FUEL OXYGENATES (ethers and alcohols) are commonly added to gasoline to increase combustion efficiency and to reduce air pollution.
- Since the ban of lead toxic additives, Methyl tertiary-butyl ether (MTBE) became the most commonly used octane enhancer.
- In Europe, large amounts of MTBE (2-3 Mt) are produced each year (into category 'High Production Volume Chemicals').
- In European gasoline, MTBE average content around 2% vol. (up to 15%, Directive 98/70/CE).

# MTBE in EU gasoline

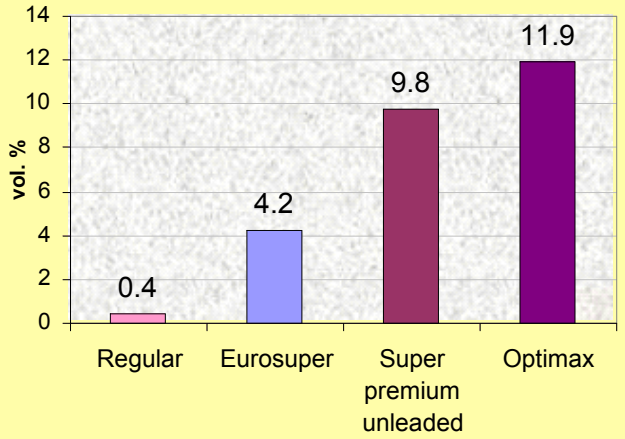



**Total MTBE per total gasoline sold, vol % (data from Morgenroth and Arvin, 1996)**

**CEPSA gasoline (2001)**




**FROM Achten et al. (2001)**




**NOW ETBE preferred alternative to MTBE: biomass-derived ethanol tax incentives!!!**

# The MTBE problem

- Accidental spills, leaking underground storage tanks (LUST): highest MTBE pollution events (from 120 µg/L up to 830 mg/L).
- MTBE become a groundwater pollutant due to its:
  - high water solubility from gasoline
  - high mobility
  - slow degradation
  - strong odour and taste (20 – 40 µg/L)

- MTBE and BTEX adsorption on subsurface solids.
- MTBE's relatively low Koc = 41 **(vs. Benzene Koc= 191)**
- Sand aquifer (0.1% organic carbon), only 8% of total mass of MTBE will be sorbed **(vs. 72% of ethylbenzene)** (Squillace et al. 1997)

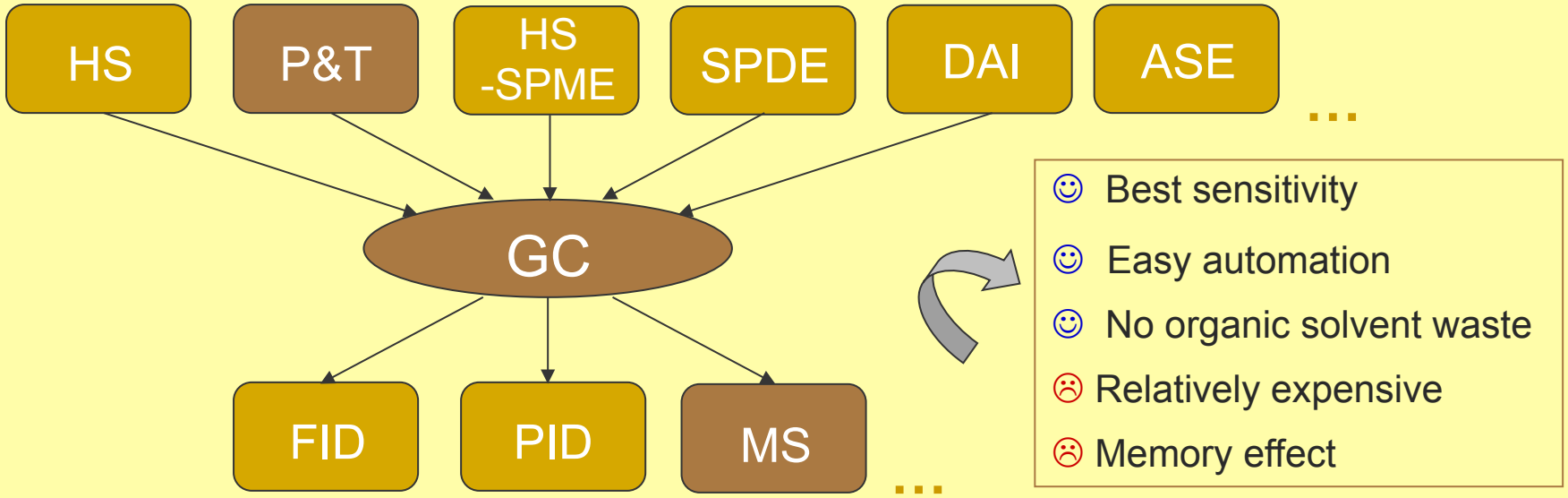
# EU legislation

- To date, there are neither regulations for MTBE in Europe no country implements any MTBE drinking water standard.
- In 1993, MTBE was put on a priority list of chemicals for risk assessment.
- Finally not included in EU Water Framework Directive (2000/60/EEC) only a Commission Recommendation 2001/838/EC.
- New forthcoming EU directive for Registration, Evaluation and Authorisation of CHemicals (REACH) when > 1 tonne per year, proposed on 29 October 2003.
- Precautionary principle: improving technology, such as use of doubled-sided tanks at petrol stations.
- Other guide values: USEPA Drinking water advisory (taste & odour): 20-40 µg/L
  - Denmark suggested toxicity level: 350 µg/L in water
  - MTBE soil action and cleanup levels (both from 5 µg/Kg) in USA

Looking for low MTBE concentrations (ppb levels)

# VOCs analytical methods

Development of sensitive methods that permit unequivocal identification of target compounds and minimization of VOCs losses during the analytical process




**EPA method 524.2**
**(Revision 4.0)**

Purgeable Organic Compounds in **Water**

**> 200 µg/Kg**

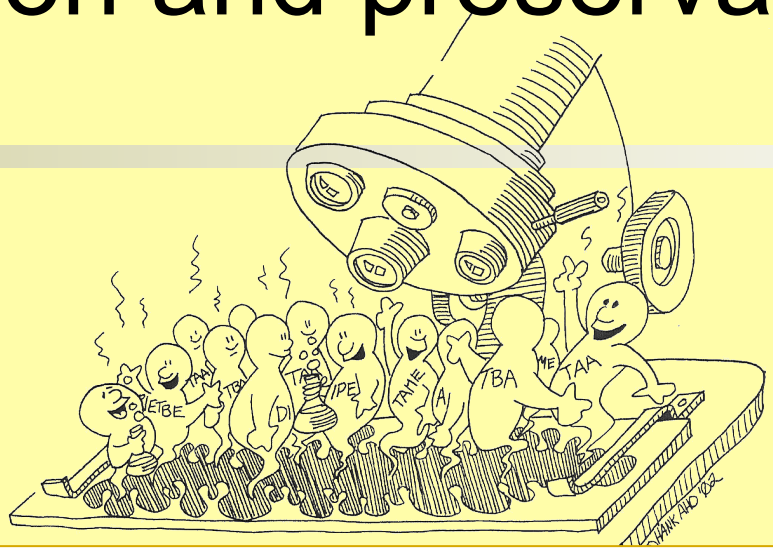
**MeOH extraction**

**+ EPA method 5030**

**EPA method 5035**

Closed-system P&T and extraction for low levels of VOCs in soil and waste samples

# Collection and preservation of VOCs




Minimization of uncontrolled losses due to VOLATILIZATION and BIODEGRADATION processes by the combination of:

## Modification of pH

pH<2

$H_2SO_4$

HCl

$NaHSO_4$

pH>10

$Na_3PO_4$

## Low storage temperatures

+ 4ºC

< -7ºC (but not below -20ºC)

## Reducing holding times

From 14 days

to 48 h

# Objectives

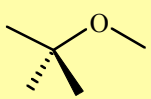
In the framework of the EU-project WATCH: *Water Catchment Areas: Tools For Management And Control Of Hazardous Compounds,* the goals were:

- The development of a fully automated purge and trap coupled to gas chromatography – mass spectrometry (P&T-GC/MS) method for the simultaneous determination of gasoline additives at trace concentrations in water and soil samples.
- The optimization of the analytical protocols included:
  - Instrumental parameters (purge time, temperature…)
  - Quality control and quality assurance studies
  - Evaluation of sample handling (preservation alternatives, storage conditions…)
- Monitoring of contaminated sites, which permits to know the presence and behaviour of MTBE and related compounds at the European aquatic environment.

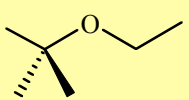
# Target compounds

**Degradation products**

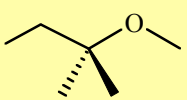
**Fuel Oxygenates**



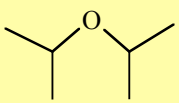

**MTBE**



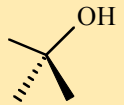

**ETBE**



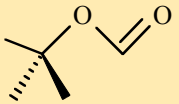

**TAME**



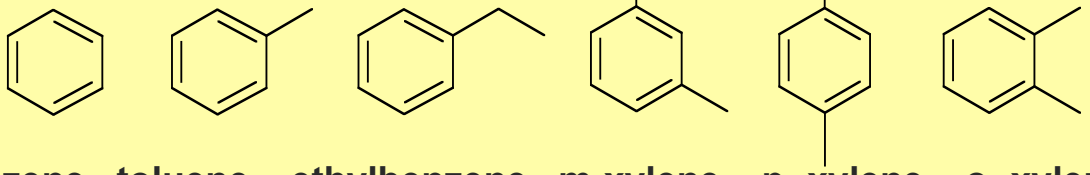

**DIPE**




**TBA**




**TBF**

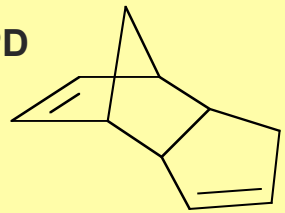


**benzene** **toluene** **ethylbenzene** **m-xylene** **p- xylene** **o- xylene**

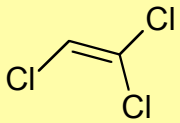
**Aromatic Hydrocarbons (BTEX)**

**Other VOCs causing odour events in GW**

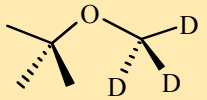
**DCPD**

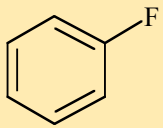


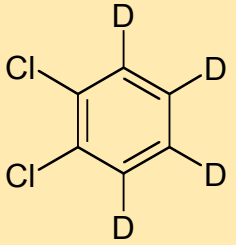
**TCE**




**MTBE-$d_3$** **Fluorobenzene** **1,2 – Dichlorobenzene – $d_4$**




**Internal Standards (IS)**

# Method for analysis in groundwater samples

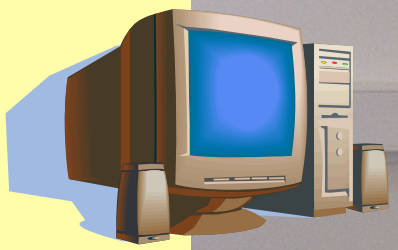
# P&T-GC/MS instrumentation

Trace GC / Voyager MS
ThermoQuest Finnigan

Purge and Trap
Concentrator Tekmar 3100

SOLATek 72 Multi-Matrix
Vial Autosampler

Automated *XCalibur Quantitative Analysis*



# P&T-GC/MS conditions

| | | |
|---|---|---|
| **P&T** | Purged sample volume | 10 mL (water) or 15 mL (solid) |
| | Purge time | 13 min. at room temperature |
| | Trap | Tenax® - Silica gel - Charcoal |
| | Desorption time | 4 min. at 225ºC |
| **GC** | Column | DB-624 (75 m x 0.53 mm ID x 3 mm) |
| | Drying gas flow | Helium from 5 mL/min. (1 min.) to 3.5 mL/min. |
| | Temperature oven program (total run time: 50 min) | 35ºC (5 min.) to 70ºC at a rate of 3ºC/min<br>70ºC (5 min.) to 210ºC at 6ºC/min<br>210ºC (5 min.) |
| **MS** | Ionisation mode | Electron impact (EI) 70 eV |
| | Source temperature | 200ºC |
| | Interface temperature | 270ºC |
| | Detector voltage | 350 - 400 V |
| | SELECTED ION MONITORING (SIM) PROGRAM | |

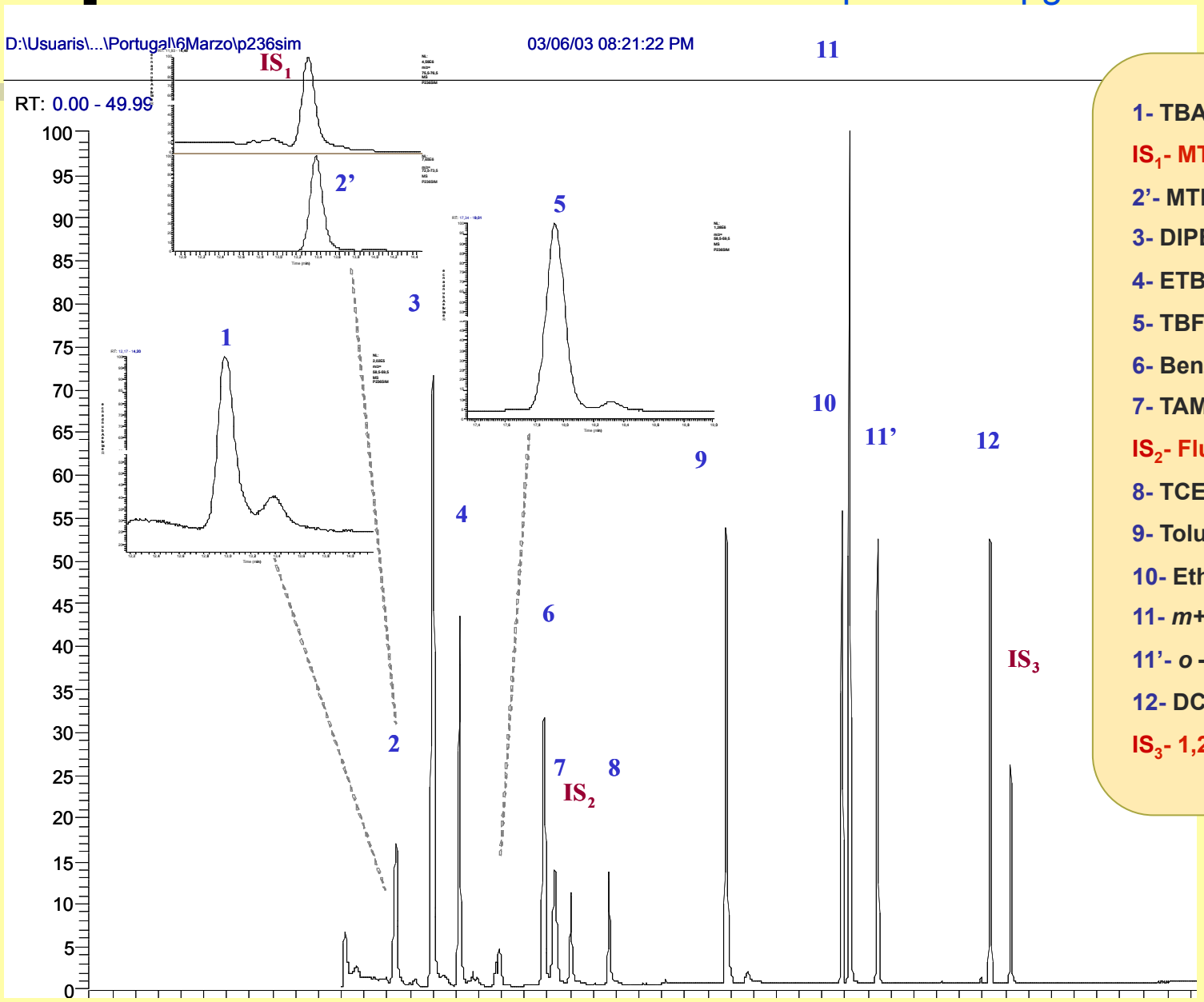
(Rosell, M.; Lacorte, S.; Ginebreda, A.; Barcelo, D. *J. Chromatogr. A* **2003**, *995*, 171-184.)

# GC-MS in time scheduled SIM acquisition program

| Compound | Rt (min) | MW (*m/z*) | Selected ions (*m/z*) | | |
|---|---|---|---|---|---|
| | | | Quantitation | Secondary | Tertiary |
| TBA | 13.11 | 74 | 59 | | |
| MTBE-$d_3$ | 13.43 | 91 | 76 | 57 | 43 |
| MTBE | 13.51 | 88 | 73 | 57 | 43 |
| DIPE | 15.11 | 102 | 45 | 87 | 59 |
| ETBE | 16.30 | 102 | 59 | 87 | 57 |
| TBF | 18.10 | 102 | 59 | 56 | 57 |
| benzene | 20.02 | 78 | 78 | 77 | 52 |
| TAME | 20.52 | 102 | 73 | 55 | 87 |
| fluorobenzene | 21.25 | 96 | 96 | 70 | 50 |
| TCE | 22.88 | 130 | 130 | 132 | 95 |
| toluene | 27.97 | 92 | 91 | 92 | 65 |
| ethylbenzene | 32.96 | 106 | 91 | 106 | 77 |
| *m*+*p*-xylene | 33.32 | 106 | 91 | 106 | 77 |
| *o*-xylene | 34.51 | 106 | 91 | 106 | 77 |
| DCPD | 39.43 | 132 | 66 | 132 | 39 |
| 1,2-dichlorobenzene-$d_4$ | 40.35 | 150 | 150 | 152 | 115 |

# Total ion chromatogram

## GW spiked at 1 µg/L in SIM mode




1- TBA

$IS_1$- MTBE-$d_3$

2'- MTBE

3- DIPE

4- ETBE

5- TBF

6- Benzene

7- TAME

$IS_2$- Fluorobenzene

8- TCE

9- Toluene

10- Ethylbenzene

11- *m*+*p* – xylene

11'- *o* – xylene

12- DCPD

$IS_3$- 1,2-dichlorobenzene-$d_4$

# Water quality parameters

| | IDLs (µg/L) | Repeatability RSD% (n=4) | Reproducibility RSD% (n=15) | Recoveries ± SD (n=3) |
|---|---|---|---|---|
| **FUEL OXYGENATES** | | | | |
| MTBE | 0.001 | 2 | 10 | 101 ±6 |
| ETBE | 0.009 | 2 | 15 | 102 ±5 |
| TAME | 0.013 | 1 | 14 | 106 ±5 |
| DIPE | 0.008 | 3 | 9 | 98 ±4 |
| **DEGRADATION PRODUCTS** | | | | |
| TBA | 0.110 | 6 | 16 | 103 ±7 |
| TBF | 0.034 | 5 | 14 | 104 ±7 |
| **AROMATIC HYDROCARBONS** | | | | |
| Benzene | 0.002 | 4 | 8 | 99 ±5 |
| Toluene | 0.001 | 3 | 7 | 97 ±4 |
| Ethylbenzene | 0.001 | 4 | 8 | 95 ±6 |
| *m*+*p*-Xylene | 0.001 | 3 | 8 | 95 ±6 |
| *o*-Xylene | 0.002 | 3 | 7 | 96 ±6 |

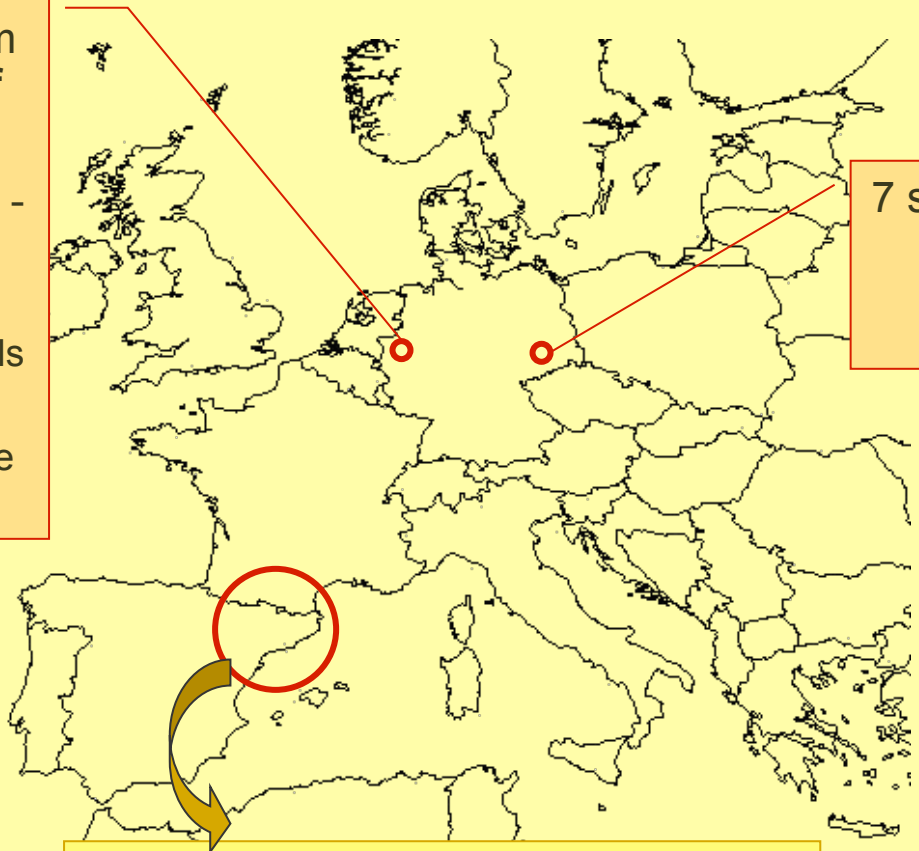
# Monitoring of contaminated sites

# GW study sites

17 wells from **Düsseldorf** (Germany)

9 campaigns - 2 years

- Petrol station (MTBE) 14 wells
- Former Gasification site (BTEX) 3 wells



7 samples from **Dresden** (Germany)

2 campaigns

- Refinery

21 wells from **Catalonia** (Spain)

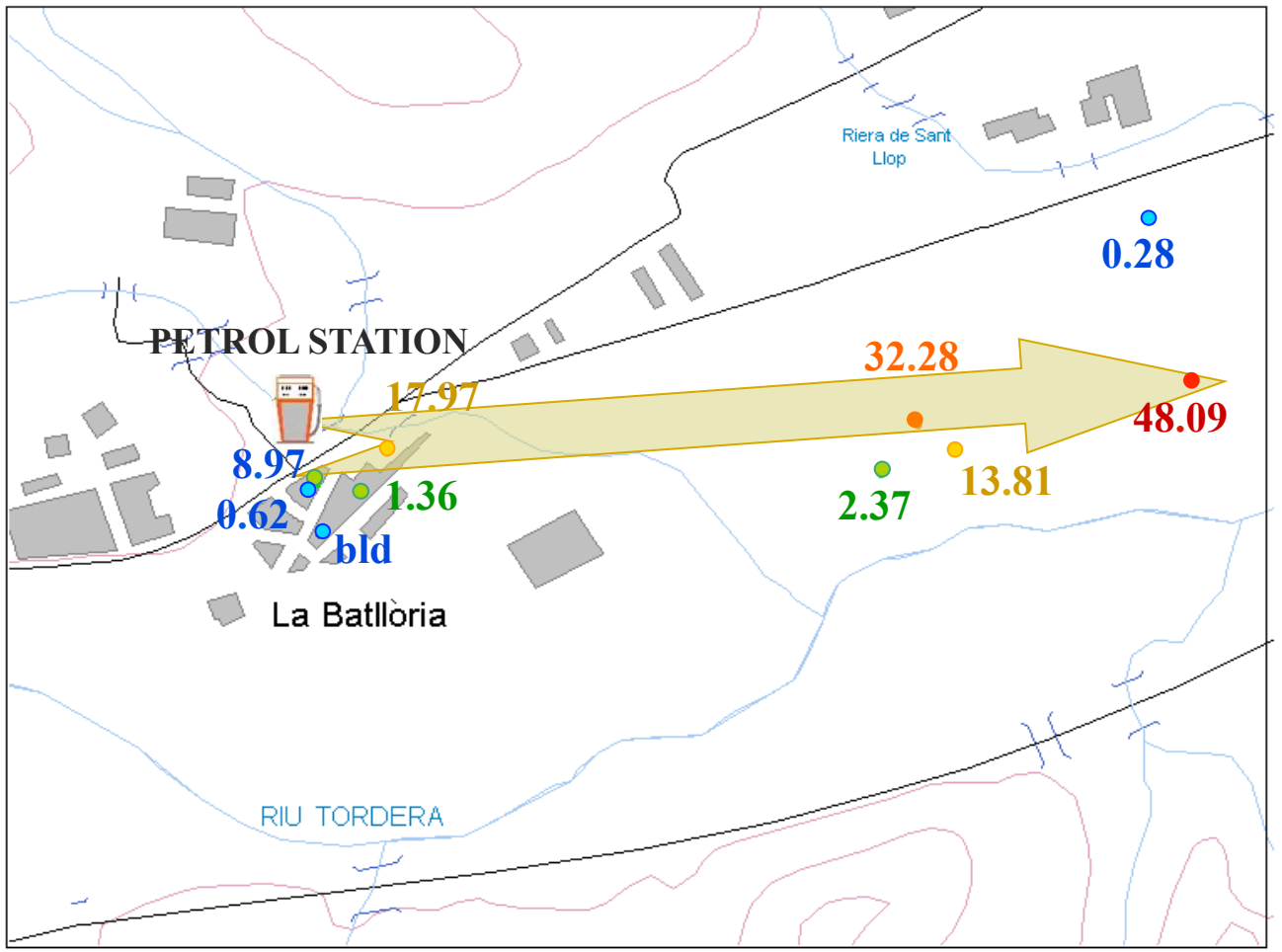
- Leaking storage tanks in a refinery
- Accidental spill in a petrol station

# Maximum detected levels (µg/L) in European GW and sludge

| | Catalonia (Spain) | | Düsseldorf (Germany) | | Dresden refinery site (Germany) | | |
|---|---|---|---|---|---|---|---|
| **Compound** | Petrol station | Refinery | Petrol station | Former Gasification | GW | Inflow | Activated sludge |
| **Fuel Oxygenates** | | | | | | | |
| **MTBE** | **48** | **666** | **645** | **0.14** | **45,100** | **12,800** | **4,312** |
| ETBE | nd | 0.68 | nd | nd | nd | nd | nd |
| TAME | nd | nd | 0.08 | nd | nd | nd | nd |
| DIPE | 0.03 | 1.53 | 0.17 | <0.01 | nd | nd | nd |
| **Degradation products** | | | | | | | |
| **TBA** | **8.86** | **62** | **440** | **<0.1** | **37,000** | **22,000** | **nd** |
| TBF | nd | <0.06 | 3.34 | nd | nd | nd | nd |
| **Aromatic hydrocarbons** | | | | | | | |
| **BTEX** | **1.43** | **4,121** | **0.2** | **4,820** | **920** | **39,000** | **3,343** |
| **Other VOCs** | | | | | | | |
| TCE | na | na | 0.04 | na | nd | nd | nd |
| DCPD | na | na | nd | na | nd | nd | nd |

nd: not detected, na: not analysed

# Catalonia: After 4 years of an accidental gasoline spill a typical MTBE plume was still observed

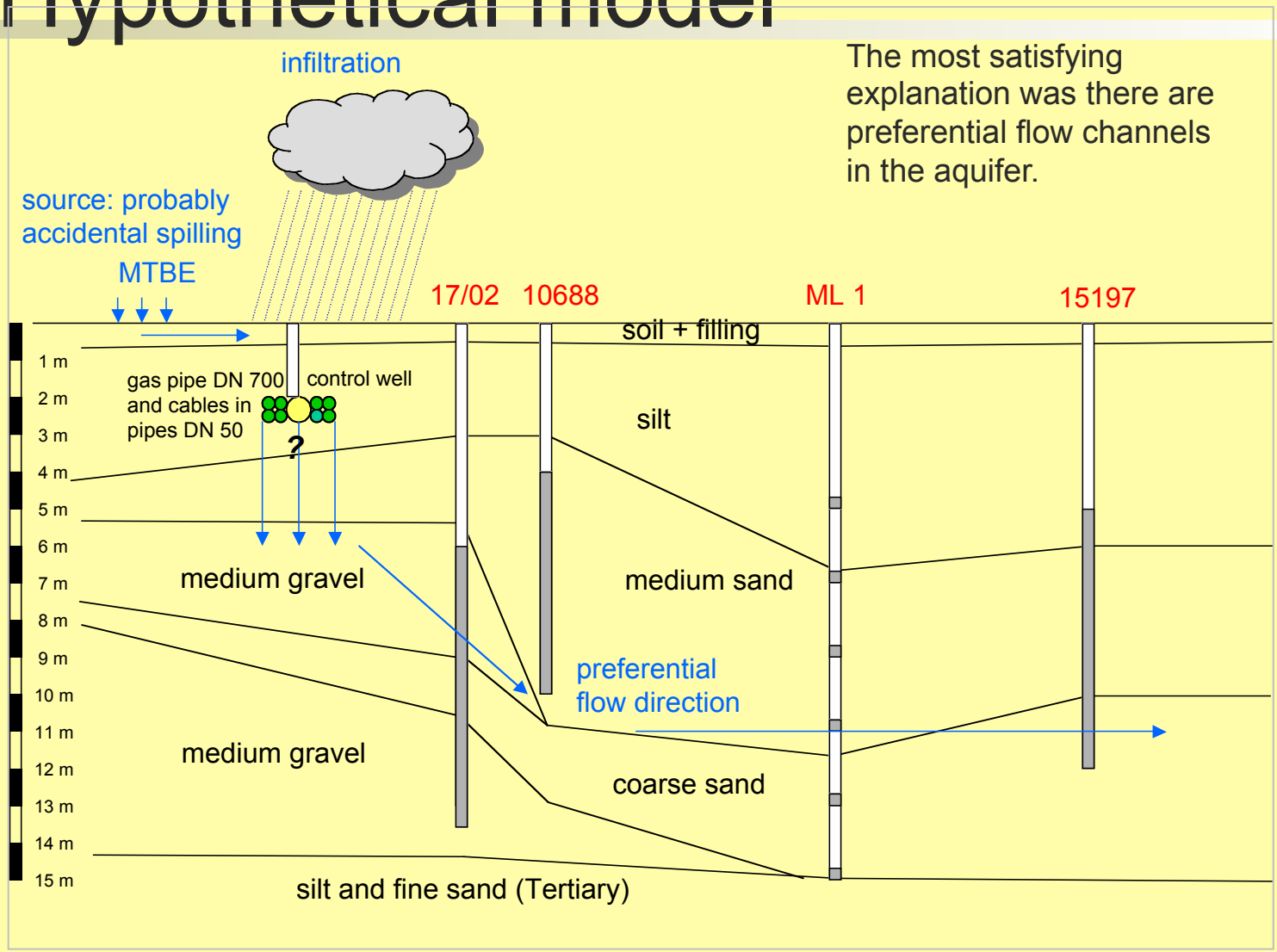



M. Rosell, S. Lacorte, A. Ginebreda, D. Barceló, Journal of Chromatography A 995 (2003) 171-184

# Hypothetical model

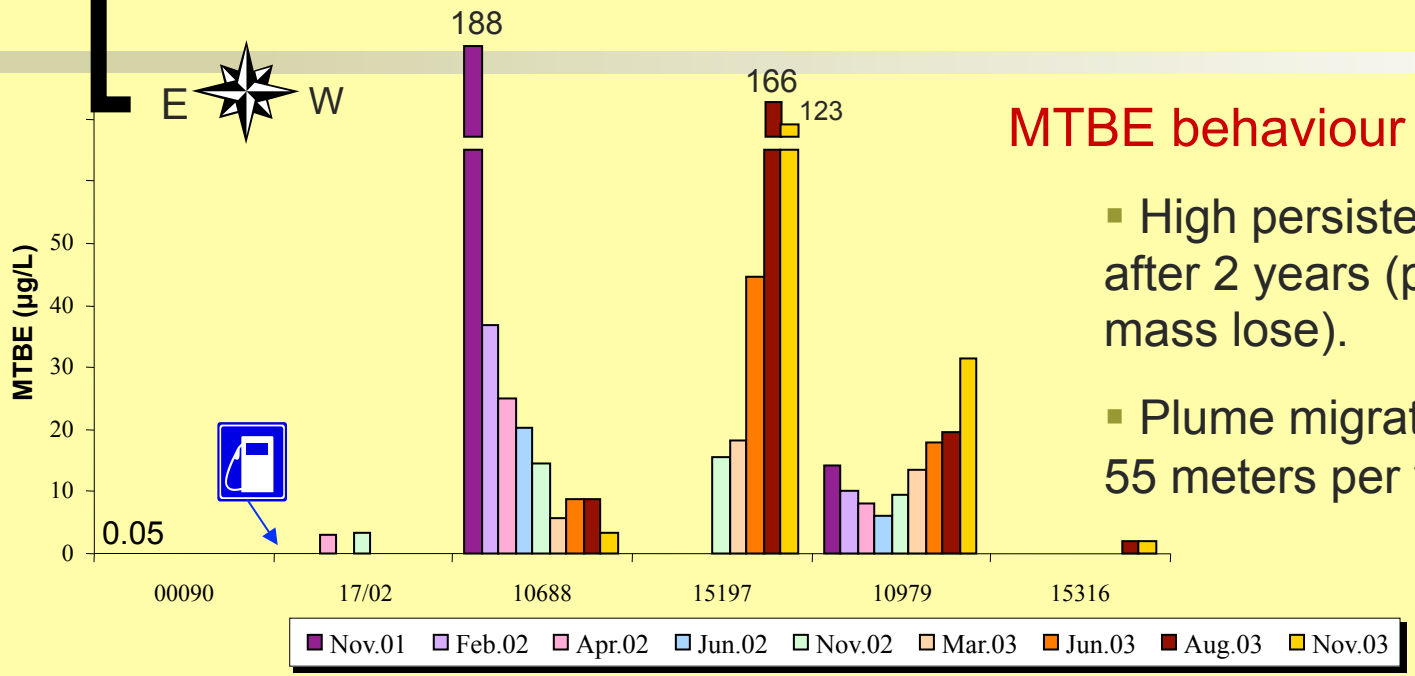
The conductivity of the different layers cannot be correlated with the MTBE vertical profile.

The most satisfying explanation was there are preferential flow channels in the aquifer.



# Düsseldorf: Gasoline spill

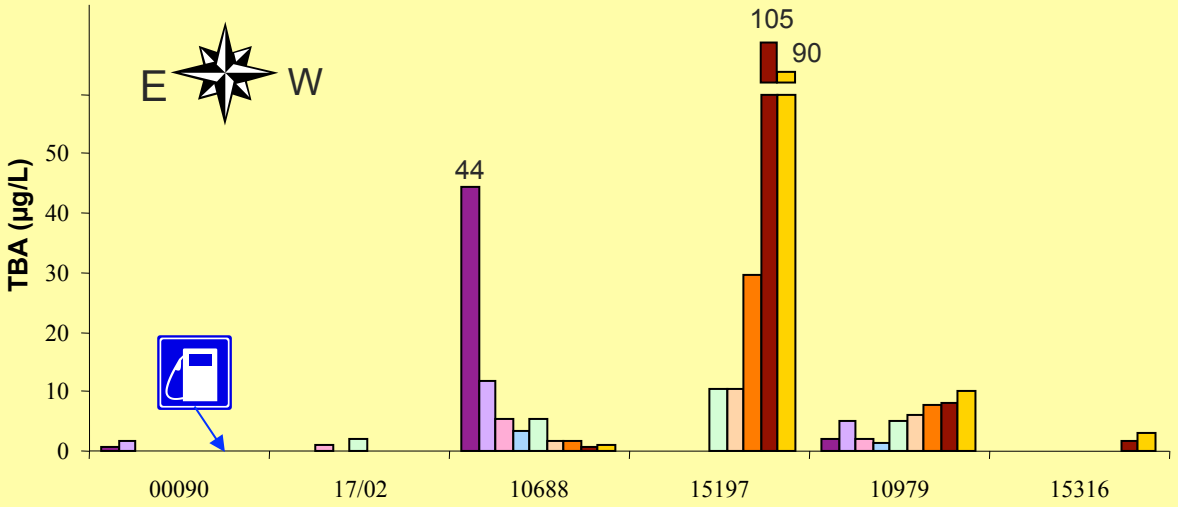
## Plume horizontal movement (From Nov.01 to Nov.03)




## MTBE behaviour

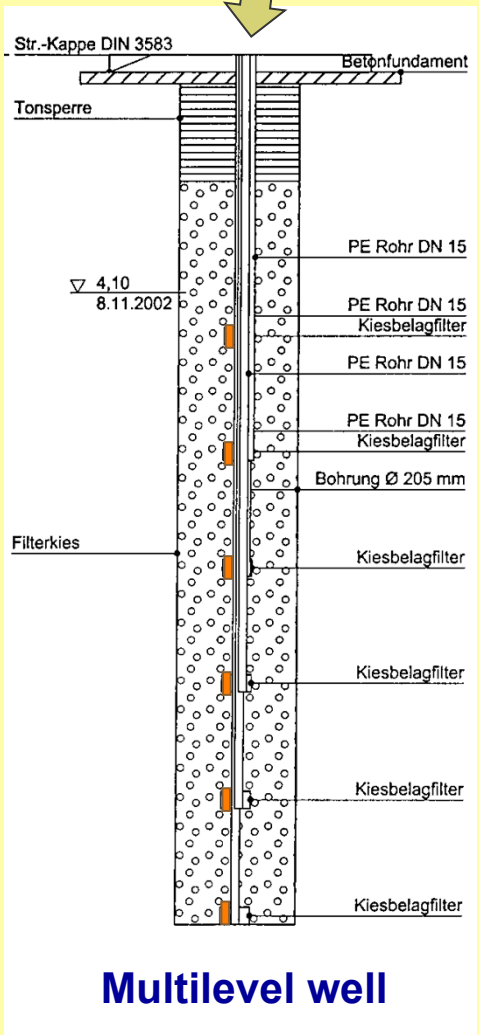
- High persistence in the aquifer after 2 years (practically no mass lose).
- Plume migration rate around 55 meters per year

- TBA plume similar profile
- But seems to be increased after 2 years.
- Hypothesis:
  - TBA was present in the contamination source?
  - Other sources: TBA widely used solvent and intermediate in industrial processes

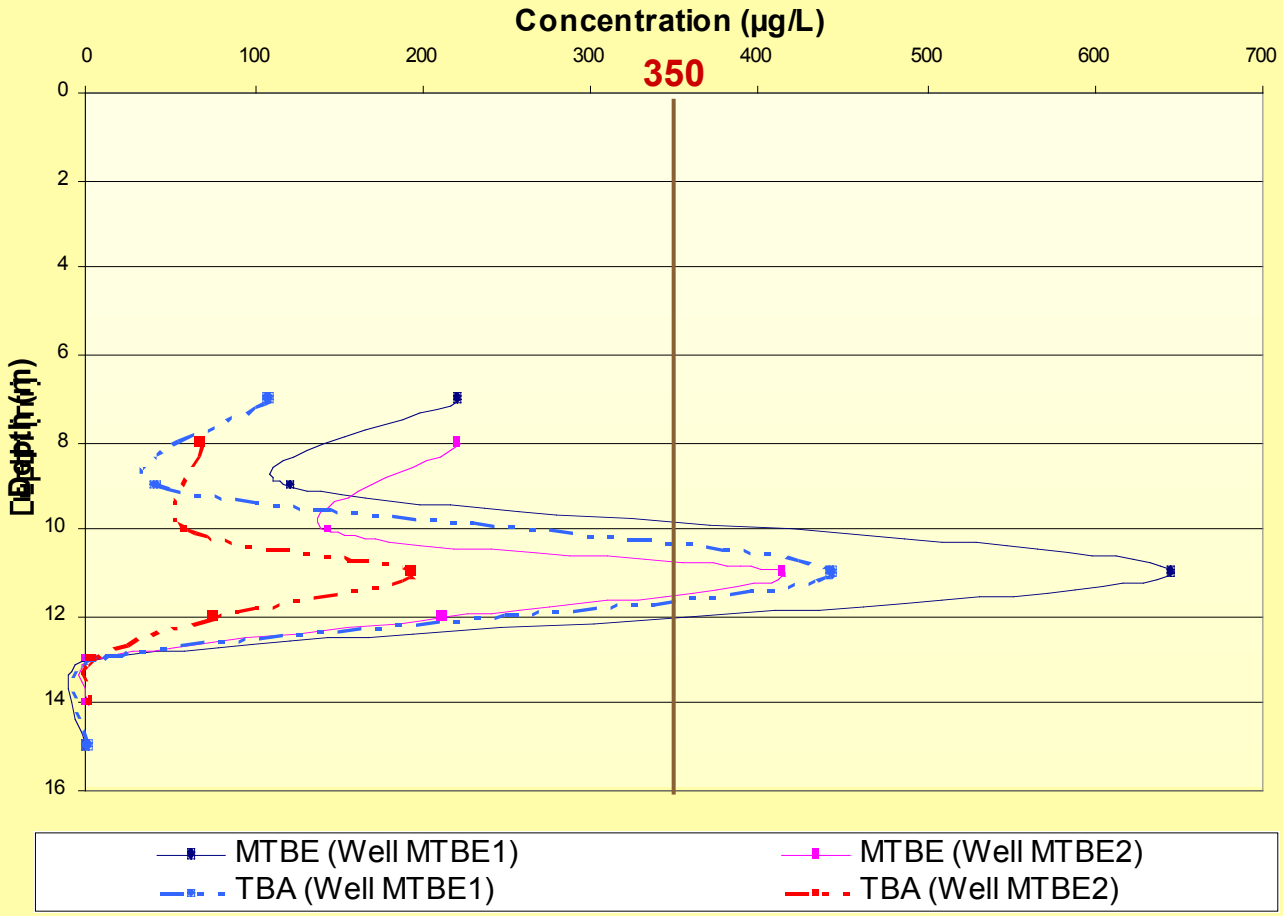


# Düsseldorf:
# Plume vertical profile

**Multilevel Wells permitted to investigate the distribution and evolution of the pollutants in depth giving more information than the average value obtained from conventional wells**




**Multilevel well**



# Toxicity

To date, there are neither regulations for MTBE in Europe nor Germany implements any MTBE drinking water standard. However, some other guide values can be used for comparison although they are not enforced not recognized in this country:

- In view of MTBE values,
  - 5 monitoring wells = hot spots that exceeded the USEPA maximum permissible levels of taste and odour in water (20 – 40 µg/L)
  - Maximum detected level practically doubled Danish suggested toxicity level of 350 µg/L in water.
  - Stricter measures: Swiss guideline value (2 µg/L) based on precautionary principle or California primary and secondary action levels (13 and 5 µg/L).

- In view of TBA values,
  - TBA is known animal carcinogen.
  - California provisional drinking water action level of 12 µg/L has recently been set because of its anticipated human toxicity.

# Conclusions I

- Significant concentrations of MTBE up to 645 μg/L reached the local groundwater, and the narrow contamination plume is currently over 400 meters long (MTBE migration rate was around 55 m/y).
- Similar behaviour of MTBE and TBA was observed in the present study (horizontal movement and vertical profile).
- Low BTEX levels in contrast to higher MTBE concentrations could be explained by their lower solubility and higher degradation rates. For this reason a single spill event was considered as the most probable source of MTBE contamination. Moreover, it was confirmed the suitability of MTBE as a tracer or indicator of long-term gasoline contamination than the historically used BTEX.
- An hypothetical model of the study site was developed presenting probable preferential channels.

# Method for analysis in soils and sediments

# Preparation of performance samples

Native soil samples from 4 meters below surface

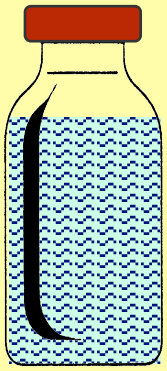
- Big particles removed
- Fractions and TOC
- Lyophilisation

**Homogeneous sample**

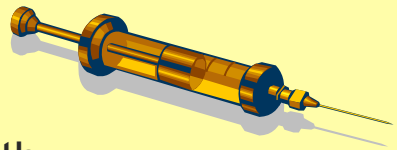
- 54% clay
- 46% silt
- 0.1% organic carbon

5 g of soil

Teflon® - faced silicone septa



Working solution with target compounds at 1 mg/L in ultra pure MeOH

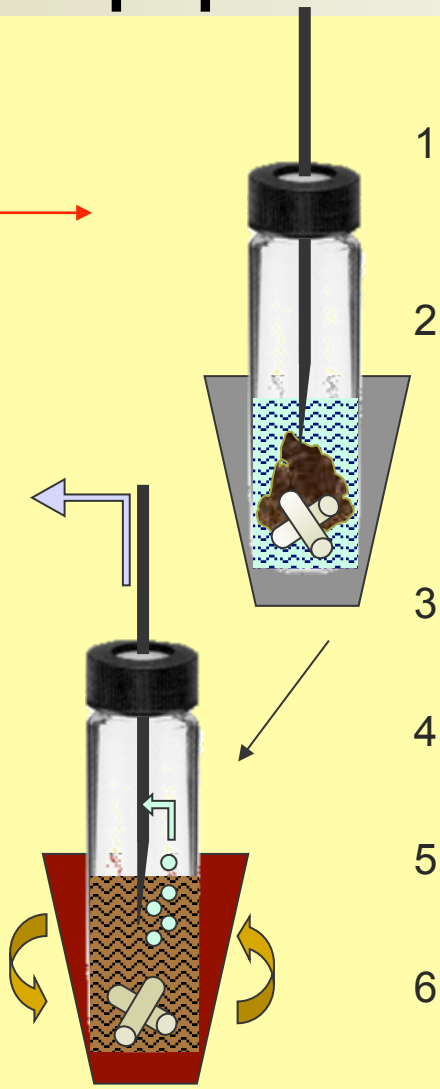


25 µL

40 mL glass vial

Clean magnetic stirring bar –cross shape

# Purge and Trap process

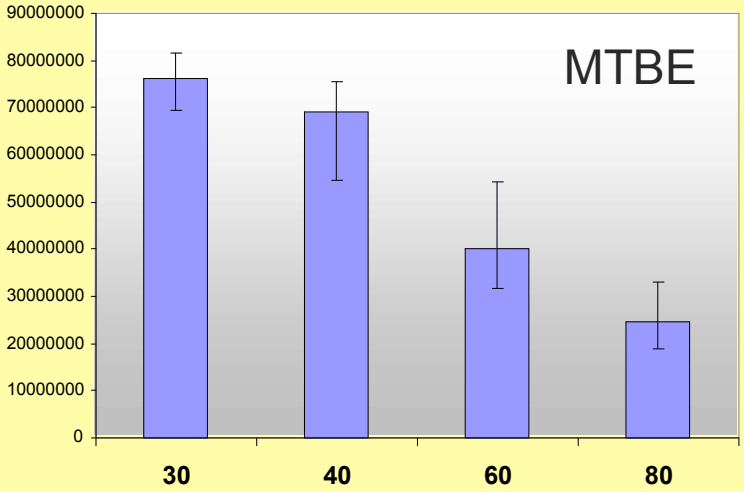
1) 15 mL of HPLC water from a pressurized tank with 5 µL of IS (final conc. of 1 µg/Kg)
2) Sample preheat 1 min. to reach the temperature
3) Heated and magnetically stirred
4) Purge with He at 40 mL/min during 13 min.
5) VOCs absorbed onto Tenax®-Silica gel-Charcoal Trap
6) Thermal desorption at 225ºC during 4 min.

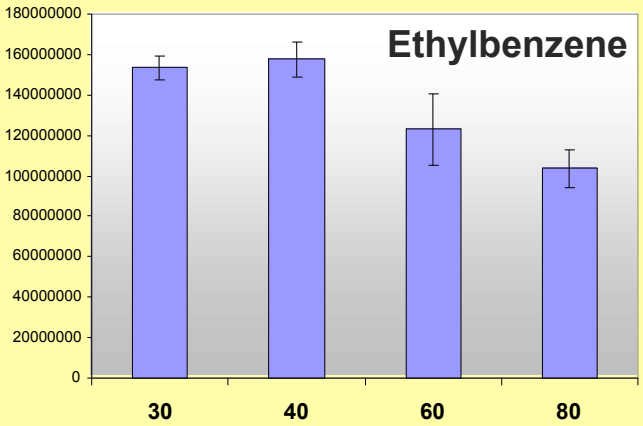
**EPA Method 5035A**

Purging efficiency can be improved for water soluble analytes when purging at an elevated temperature of 80ºC as compared to 20ºC or 40ºC

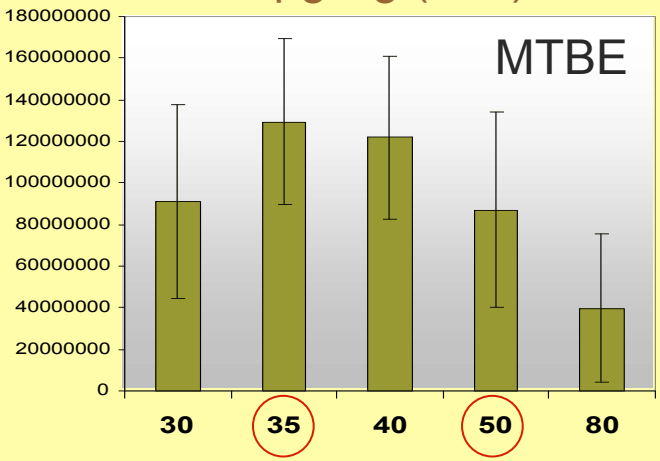
# Purge temperature selection

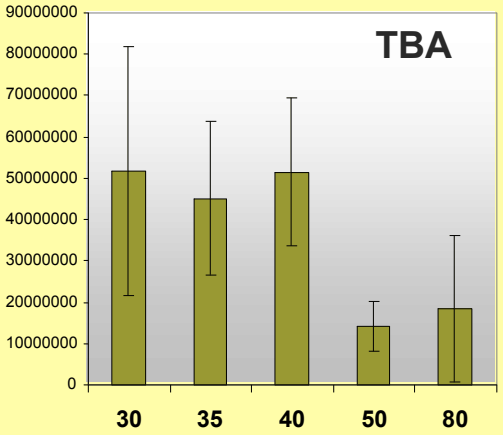
1st experiment (n=2) in water

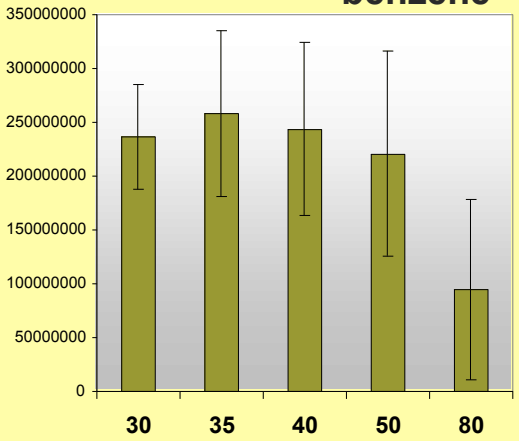



2nd Lyophilised Ebro river basin sediments at 5 µg/Kg (n=5)



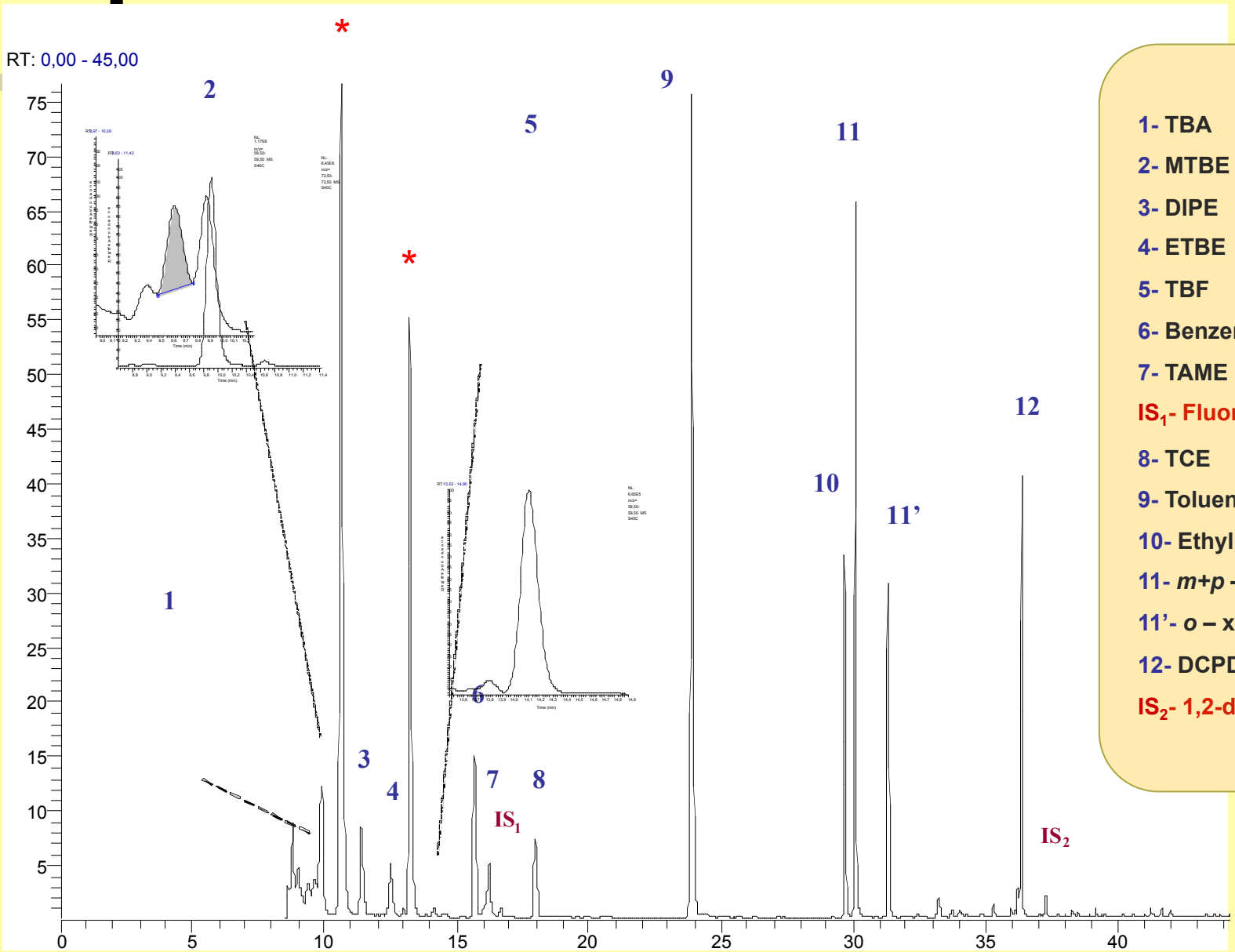




**Purge efficiency was found to be better at 40ºC**

# Total ion chromatogram

## Lyophilised urban soil spiked at 10 µg/Kg in SIM mode

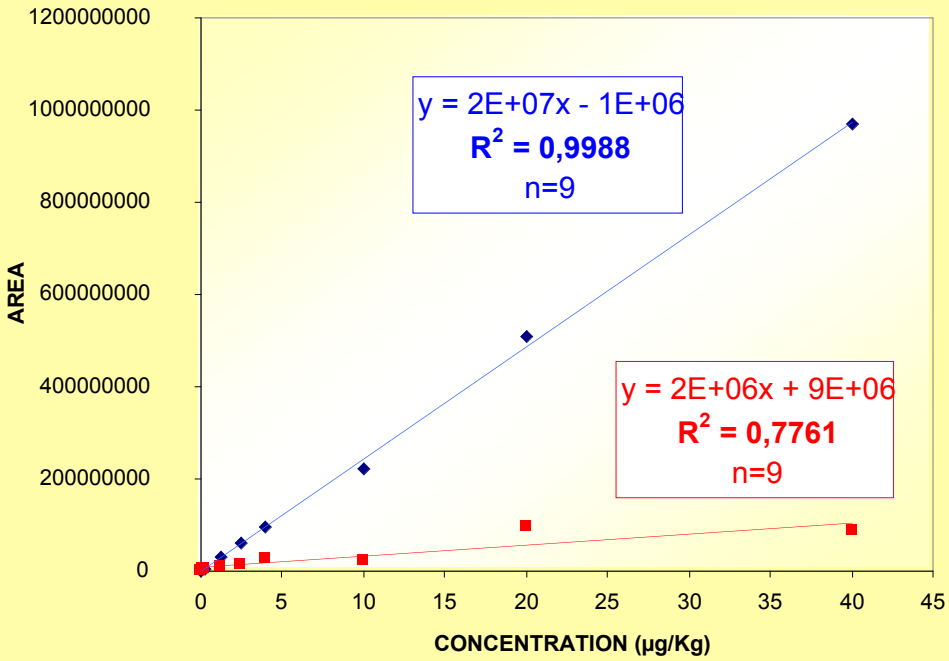



1- TBA
2- MTBE
3- DIPE
4- ETBE
5- TBF
6- Benzene
7- TAME
$IS_1$- Fluorobenzene
8- TCE
9- Toluene
10- Ethylbenzene
11- *m+p* – xylene
11'- *o* – xylene
12- DCPD
$IS_2$- 1,2-dichlorobenzene-$d_4$

# Matrix effects

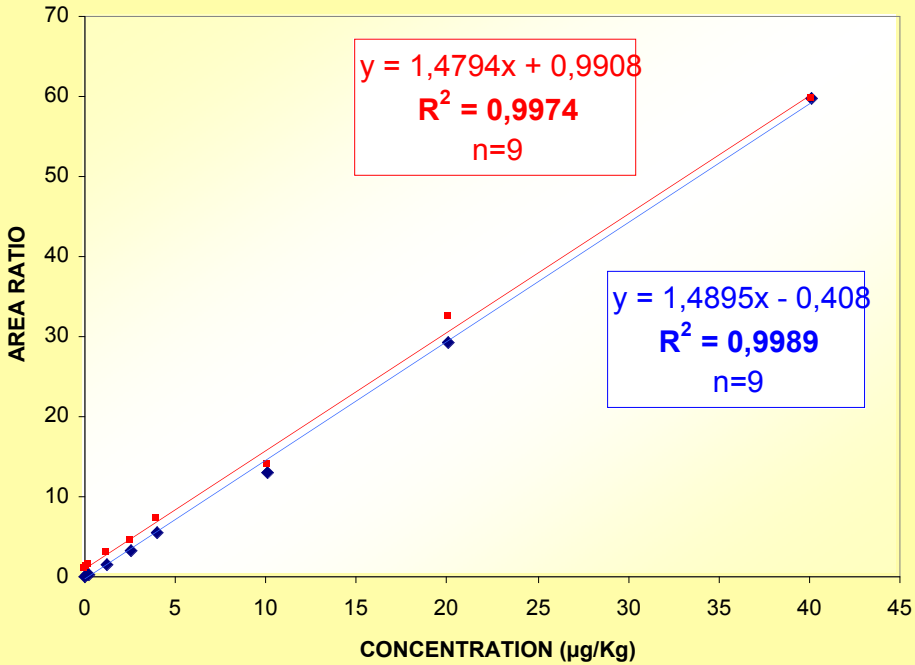
EPA Method 5035 suggests that the calibration curves can be obtained by analysing blank water samples spiked with target compounds, but…

**Benzene EXTERNAL STD. CALIBRATION**

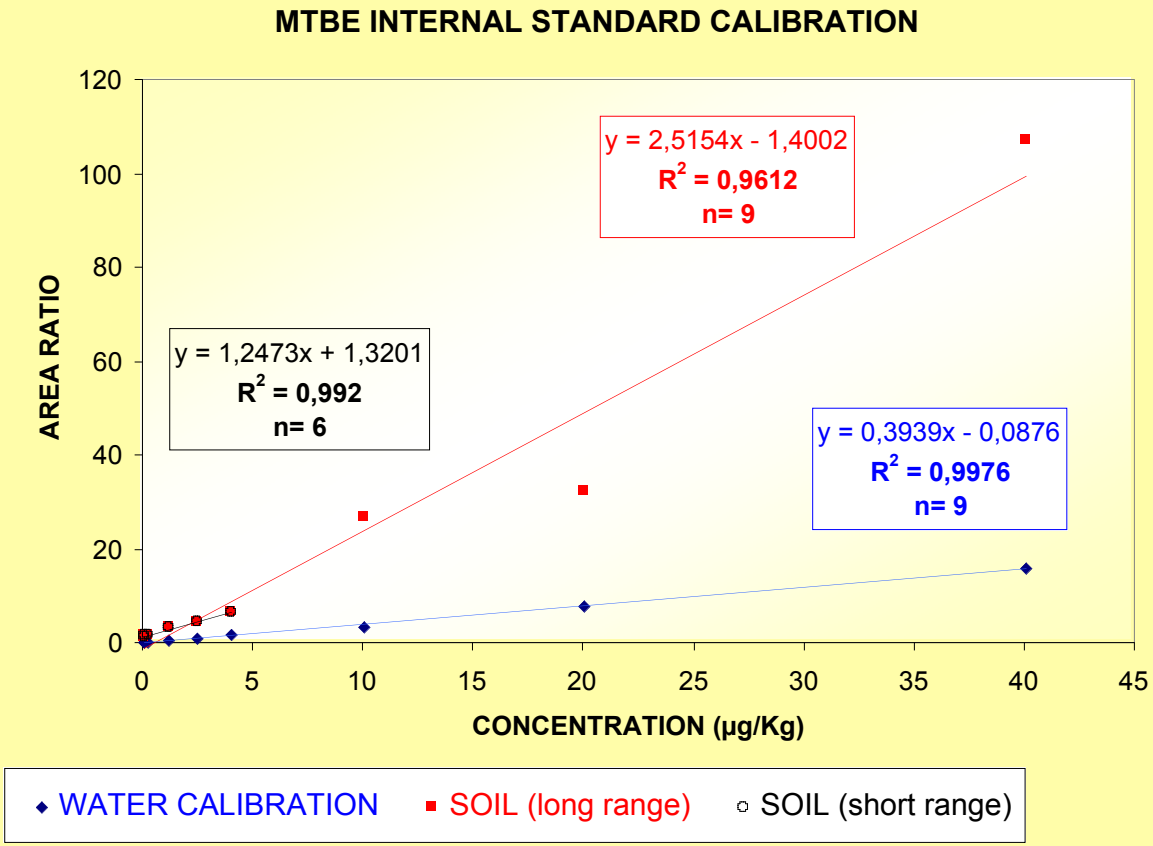



**Fluorobenzene as IS**

**Benzene INTERNAL STD. CALIBRATION**



# Matrix effects




COMPOUND dependency

- Use of the same matrix as the sample is recommended
- Reduction of the linear range

<u>Possible solution:</u>

- Use of more specific IS (such as Isotope labeled target compound)
- More expensive

# Soil quality parameters

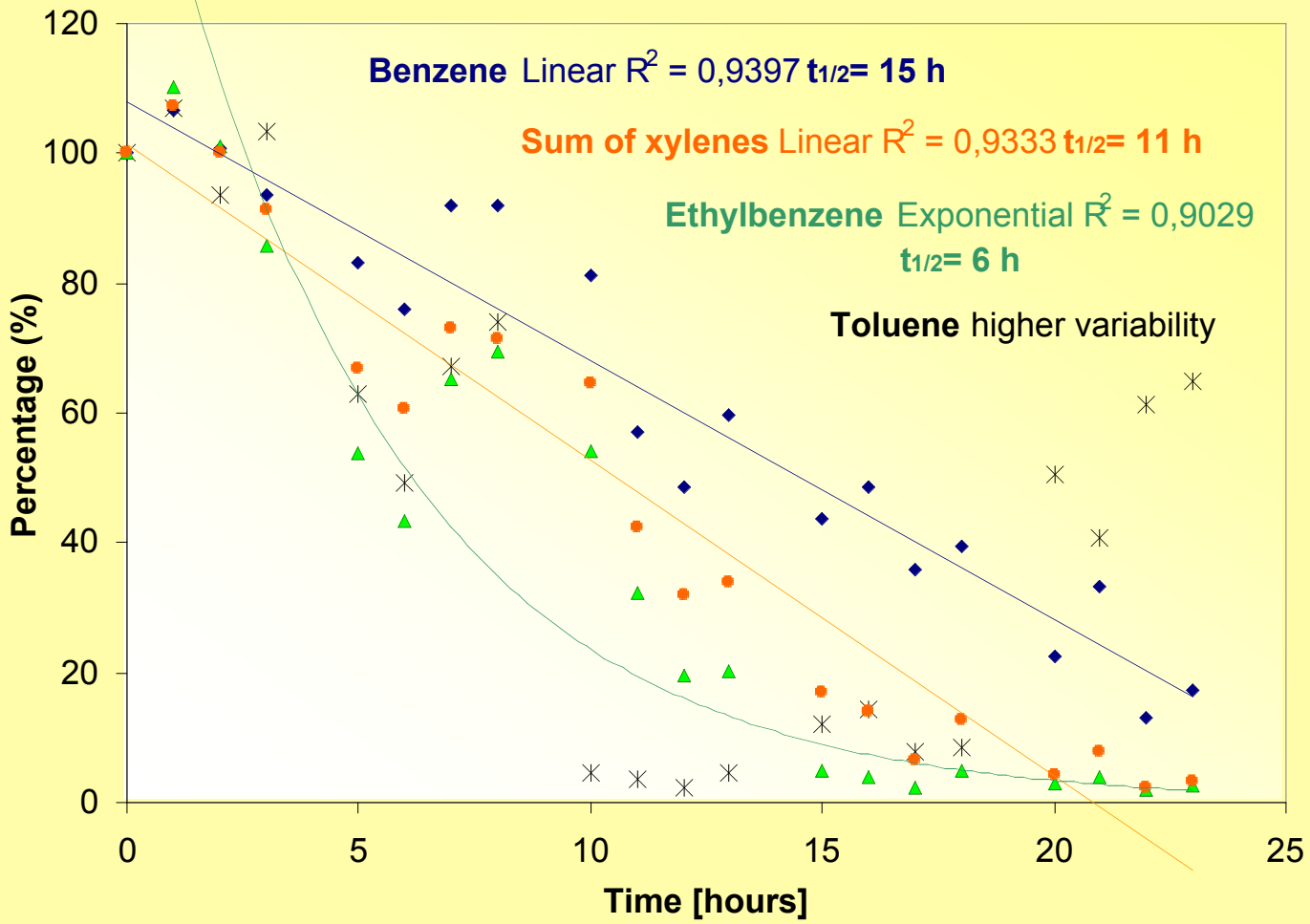
| | MDLs (µg/Kg) | Repeatability 4 µg/Kg RSD% (n=5) | Reproducibility 10 µg/Kg RSD% (n=5) |
|---|---|---|---|
| **FUEL OXYGENATES** | | | |
| MTBE | 0.13 | 8 | 6 |
| ETBE | 0.49 | 5 | 2 |
| TAME | 0.06 | 9 | 6 |
| DIPE | 0.41 | 23 | 2 |
| **DEGRADATION PRODUCTS** | | | |
| TBA | 1.36 | 10 | 24 |
| TBF | 0.17 | 7 | 13 |
| **BTEX** | 0.33 – 1.63 | 7-13 | 4-20 |
| **OTHER VOCs** | | | |
| TCE | 0.70 | 8 | 8 |
| DCPD | 0.02 | 4 | 4 |

# BTEX degradation problems

Raw Ebro river basin sediments (Spain)

33% sand, 44% clay and 22% silt, 21% water content

Storage at 4ºC and 20ºC in the autosampler




Which was the reason?

Volatile losses

or

Extremely biologically active soils?

# Stability experiment design

**3 Preservation Alternatives**

1) Empty vial without any additive
2) pH<2, $NaHSO_4$
3) pH>10, TSP ($Na_3PO_4$)

×

**At 2 Storage Temperatures**

+ 4ºC

-15ºC

×

**At 3 Holding Times**

0h

48h

7 days

14 days

×

3 replicates of each treatment

# Stability preliminary results

## EFFECT OF THE TEMPERATURE

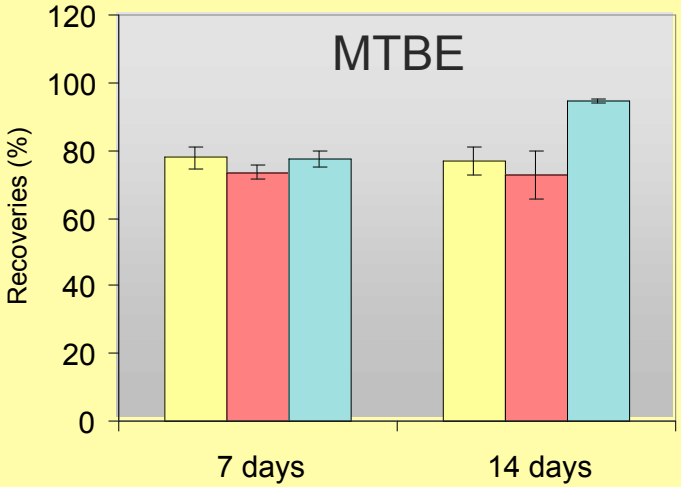
Empty vial after 7 days of storage

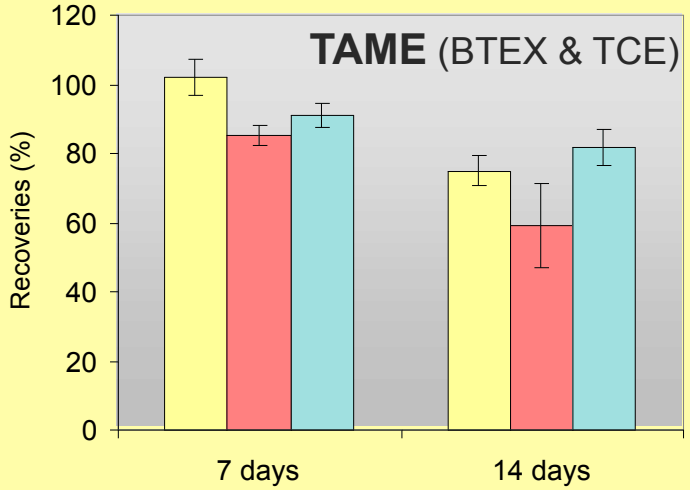
**Recoveries (%)**

| | +4ºC | -15ºC |
|---|---|---|
| **MTBE** | **88** | **78** |
| **ETBE** | **45** | **98** |
| **TAME** | 101 | 102 |
| **DIPE** | **45** | **88** |
| **TBA** | 72 | 127 |
| **TBF** | **4** | **66** |
| **BTEX** | 94 - 101 | 91 – 98 |
| **TCE** | 98 | 97 |
| **DCPD** | 102 | 104 |

## EFFECT OF TIME AND PRESERVATION

At -15ºC **Recoveries (%)**

# Stability conclusions or precautions

- In general, the concentration of target compounds decrease with time; but some of them (such as the degradation products, TBA and TBF) can increase.
- Samples not analysed at the moment should be stored in the freezer at <-7ºC until the moment of the analysis.
- Samples should be analysed as soon as possible after collection and not longer than 7 days is recommended.
- Empty vial without any additive as an agreement (when degradation products must be analysed)
- When a preservative is needed, TSP offers better results than $NaHSO_4$

# Soil sample handling

The principal purpose is to reduce the amount of disturbance when collecting solid/soil samples for the analysis of VOCs. Special cores all-in-one design eliminate the need for a field balance, separate handle or cutting off syringes.

## The Terra Core Sampler

One time use transfer tool, designed to easily take 5 gram-samples and transfer to appropriate containers in the field

**1.50 $/unit**

## The En Core Sampler

5 or 25 gram sizes for "one time" use

It can be a short-time holding vessel

But additional stainless steel T-Handles and Extrusion tools are needed

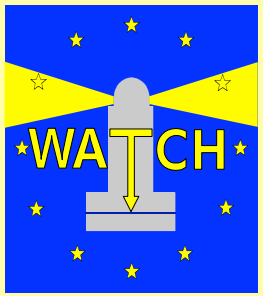
**(125 $ or 200 $)/amortization + 7.50 $/unit**

En Novative Technologies, Inc., USA

# Conclusions II

- A method for analysis of MTBE, its degradation products and other gasoline additives in soil was reported by using SOLATek coupled to a Purge and Trap concentrator Tekmar GC-MS system
- Method detection limits varied from 20 to 1000 ng/Kg (MTBE and ETBE were 130 and 490 ng/Kg)
- Future work will include soil samples from a contaminated site of a gas plant in Poland (EU project PROMOTE)

# Acknowledgements


- This research was part of the WATCH (EVK1–CT–2000–00059) EU project that was funded by the EU Environment and Sustainable Development sub-program and from the Ministerio de Ciencia y Tecnología (REN2001-5039-E).
- M. Rosell acknowledges PhD grant from Departament d'Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya (2005FIR 00348).