# Soil-Water Partitioning of a Fluorotelomer Intermediate used to Manufacture Fluorotelomer-based Polymers

**Telomer Research Program – TRP:**
**Asahi Glass Co.**
**Clariant GmbH**
**Daikin Industries**
**DuPont Co.**

W.R. Berti, R.C. Buck,
B. Szostek, N. Wang - DuPont Co

H. Iwai - Daikin Industries, Ltd.

V. Koch - Clariant GmbH

S. Shinya - Asahi Glass Co

# Abstract

Fluorotelomer intermediates are used to manufacture fluorotelomer-based polymer products, which provide unique properties to a wide variety of consumer products. Four telomer manufacturers that are collectively sponsoring research on telomer compounds jointly sponsor the Telomer Research Program (TRP). The TRP program includes investigations on the environmental fate and effects properties of fluorotelomer intermediates. A soil-water partitioning study using a batch equilibrium method is being conducted on the fluorotelomer intermediate 8-2 Telomer B Alcohol [8-2 TBA; $CF_3(CF_2)_7CH_2CH_2OH$, CAS# 678-39-7]. Results of the study demonstrated that greater than 90% of $^{14}C$-labeled 8-2 TBA initially added to the test system partitioned to soil and sediment within three hours. The 8-2 TBA partitioned to activated sludge within one hour. Less than 2% remained in the aqueous phase at a 1:1 soil:solution ratio after 3 hours at 4°C; total recovery of the compound was 95% and greater under these conditions. In one soil after a 24 h equilibration time and at room temperature, 50% or more of the $^{14}C$ label added as 8-2 TBA was bound to the residual fraction, which was determined by combusting the soil after three washings with acetone, air-drying, and grinding. Freundlich adsorption constants characterize 8-2 TBA as a non-mobile (Koc > 4000) to slightly mobile (Koc 500 to 4000) substance under these conditions.

# Fluorotelomer intermediates

Used to manufacture fluorotelomer-based polymers

- Provide unique properties in a wide variety of consumer products.

8-2 Telomer B Alcohol (8-2 TBA) focus of studies

- Primary fluorotelomeric intermediate
- $F(CF_2CF_2)_nCH_2CH_2OH$, where n = 4

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# 8-2 Telomer B Alcohol : Adsorption-Desorption

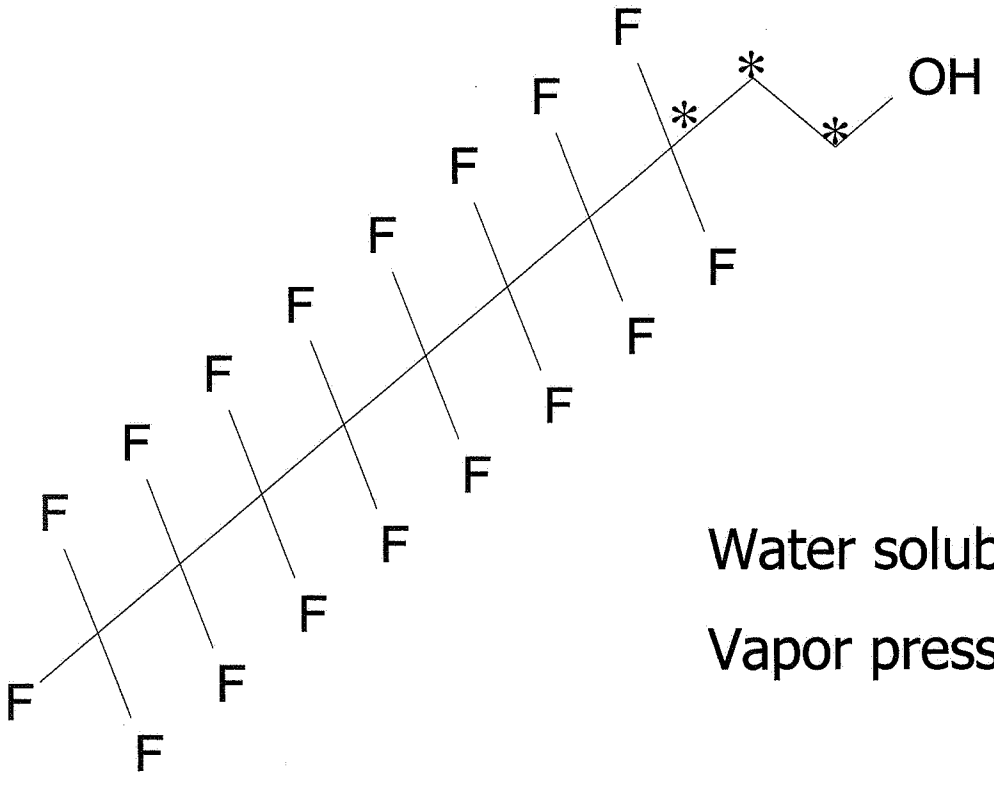
Study Objective:

- Evaluation the mobility of the test substance in soil and sediment
- Determine the Freundlich adsorption constants

# 8-2 Telomer B Alcohol : Adsorption-Desorption

- Preliminary studies with 2 soils using "cold" 8-2 TBA
- Detailed studies based on:
  - OECD 106: Adsorption - Desorption using a Batch Equilibrium Method
    - Radiolabeled [1,2-$^{14}$C] 8-2 Telomer B Alcohol
  - OPPTS 835.1110: Activated Sludge Sorption Isotherm
    - Radiolabeled [3-$^{14}$C] 8-2 Telomer B Alcohol
- Work supported by the Telomer Research Program
  - Asahi Glass Co., Ltd. (Japan), Clariant GmbH (Germany), Daikin Industries, Ltd. (Japan), DuPont Co. (USA)

# 8-2 Telomer B Alcohol: 8-2 TBA




Water solubility 150 µg $L^{-1}$ (ppb)

Vapor pressure 3 Pa at 25 °C

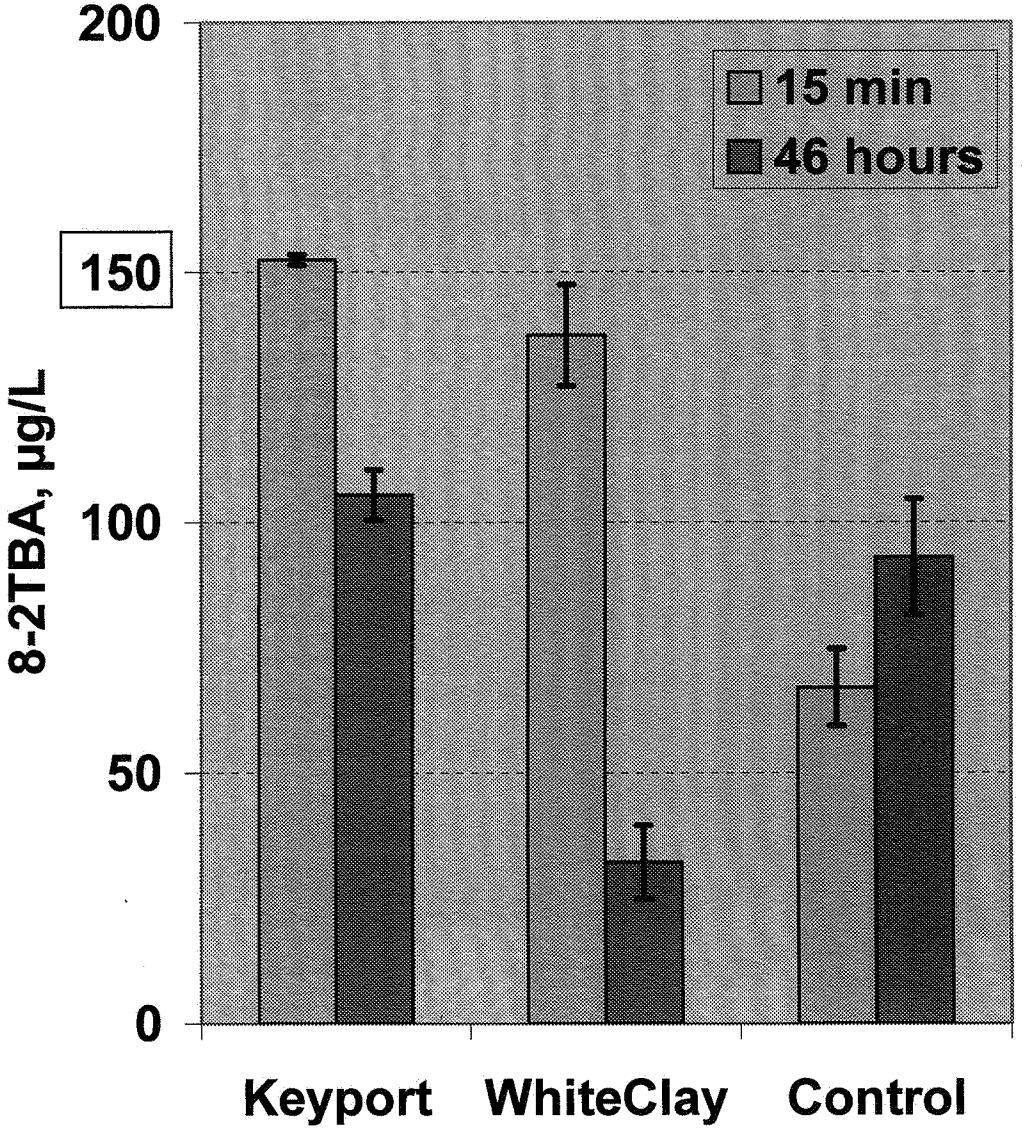
– Radiolabeled [1,2-$^{14}$C*] 8-2 Telomer B Alcohol

– Radiolabeled [3-$^{14}$C*] 8-2 Telomer B Alcohol

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

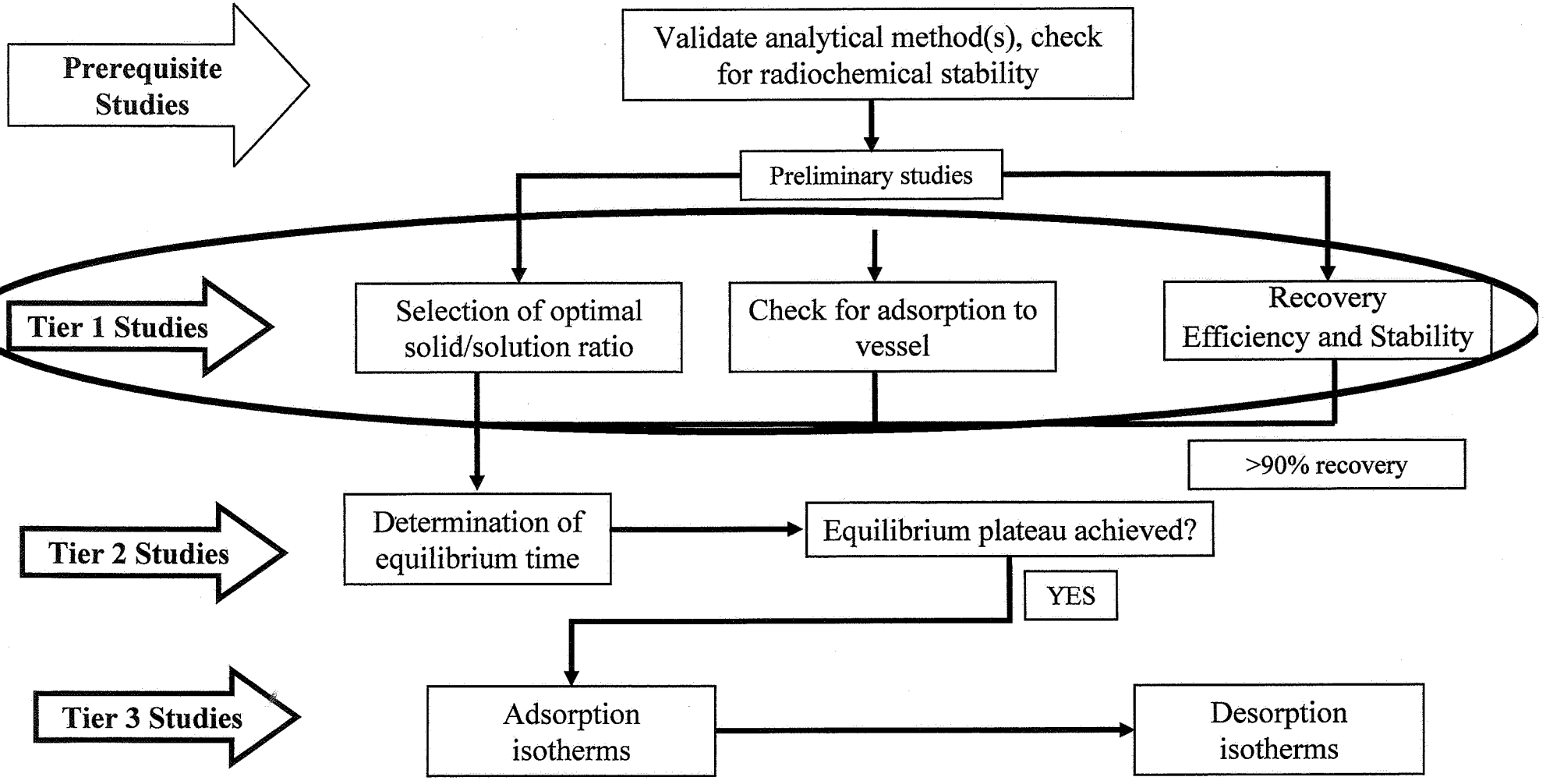
# Soil/Water Partitioning Studies: 8-2 TBA [$F(CF_2CF_2)_4CH_2CH_2OH$]

- 8-2 TBA added at ~ 0.150 ug/mL
- Keyport silt loam: Sand 17%, Silt 62%, Clay 21%, pH 5.3, OM 4.0%
- White Clay Creek sand: Sand 98%, Silt 2%, pH 7.2, OM 0.4%
- Control: 0.01M $CaCl_2$ + 8-2 TBA only; no soil




**TRP:** Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.

# OECD 106: Adsorption/Desorption using a Batch Equilibrium Method




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Study soils and characteristics

- Soils used in studies represent a broad range of characteristics

| Soil name | OECD 106 soil type | pH (0.01 M $CaCl_2$) | Organic carbon content (%) | Organic matter content (%) | Clay content (%) | Soil Texture (USDA) |
|---|---|---|---|---|---|---|
| SK961089 | 2 | 7.6 | 4.6 | 7.9 | 34 | Clay loam |
| SK566696 | 5 | 4.2 | 0.8 | 1.4 | 11 | Sandy loam |
| Emperor Son's Lake | 3 | 6 | 1.2 | 2.1 | 17 | Sandy loam |
| SK179618 | 4 | 5.6 | 3.8 | 6.6 | 20 | Clay loam |
| EUROSOIL 5 | - | 3.1 | 6.7 | 11.6 | 5 | Loamy sand |

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Recovery of $^{14}C$ 8-2 TBA from Sealed Glass Vials: 4 Soils

$^{14}C$ 8-2 TBA applied through septum to attain 25 µg $L^{-1}$

Samples centrifuged to separate phases

- 0.01M $CaCl_2$ solution removed using syringe with SS piston through PTFE-coated rubber septum
- Cap removed, supernatant decanted, $^{14}C$ by LSC

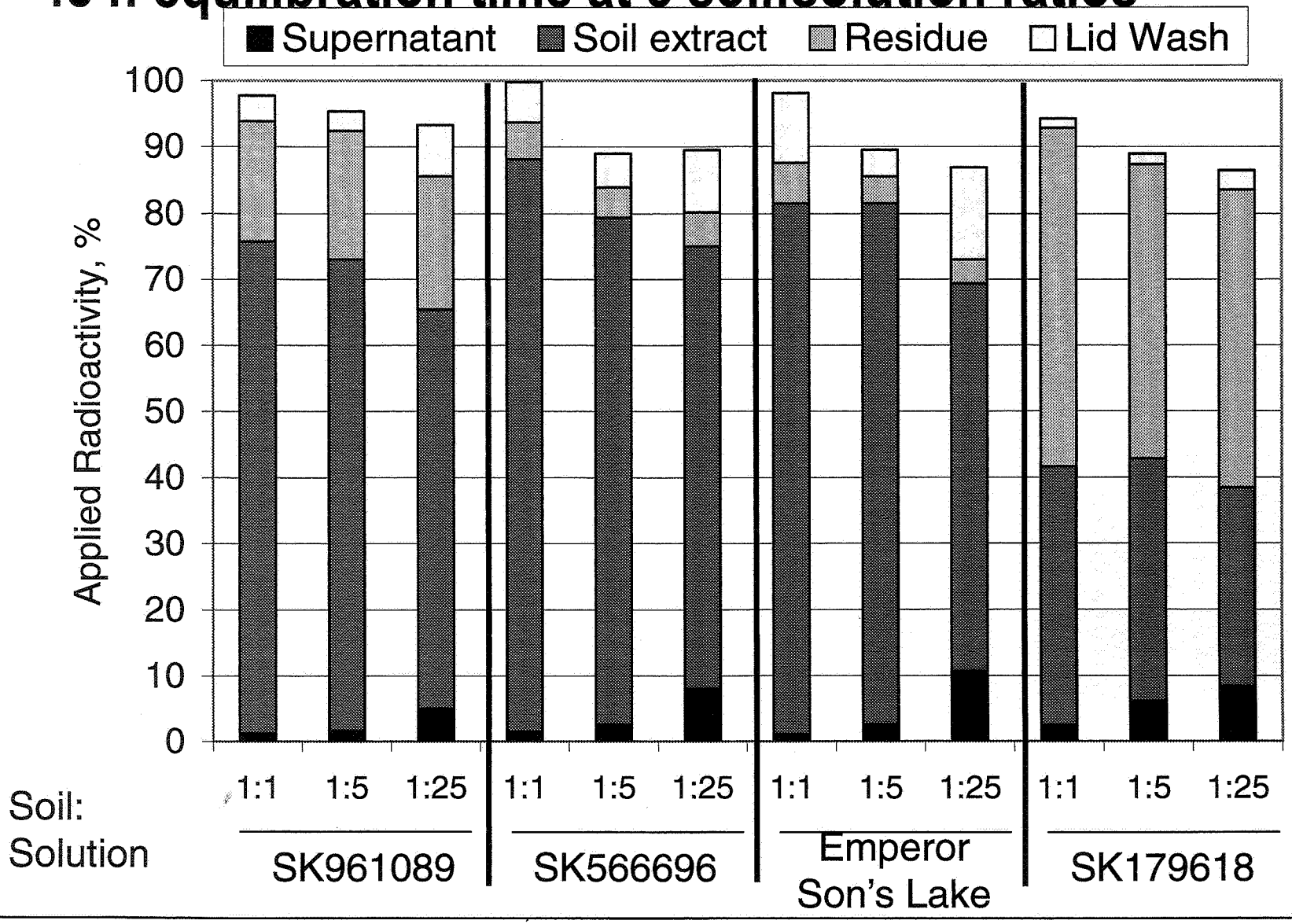
Soil extracted 3 times with acetone

- Soil extracts analyzed separately by LSC and results combined

Soil residue combusted

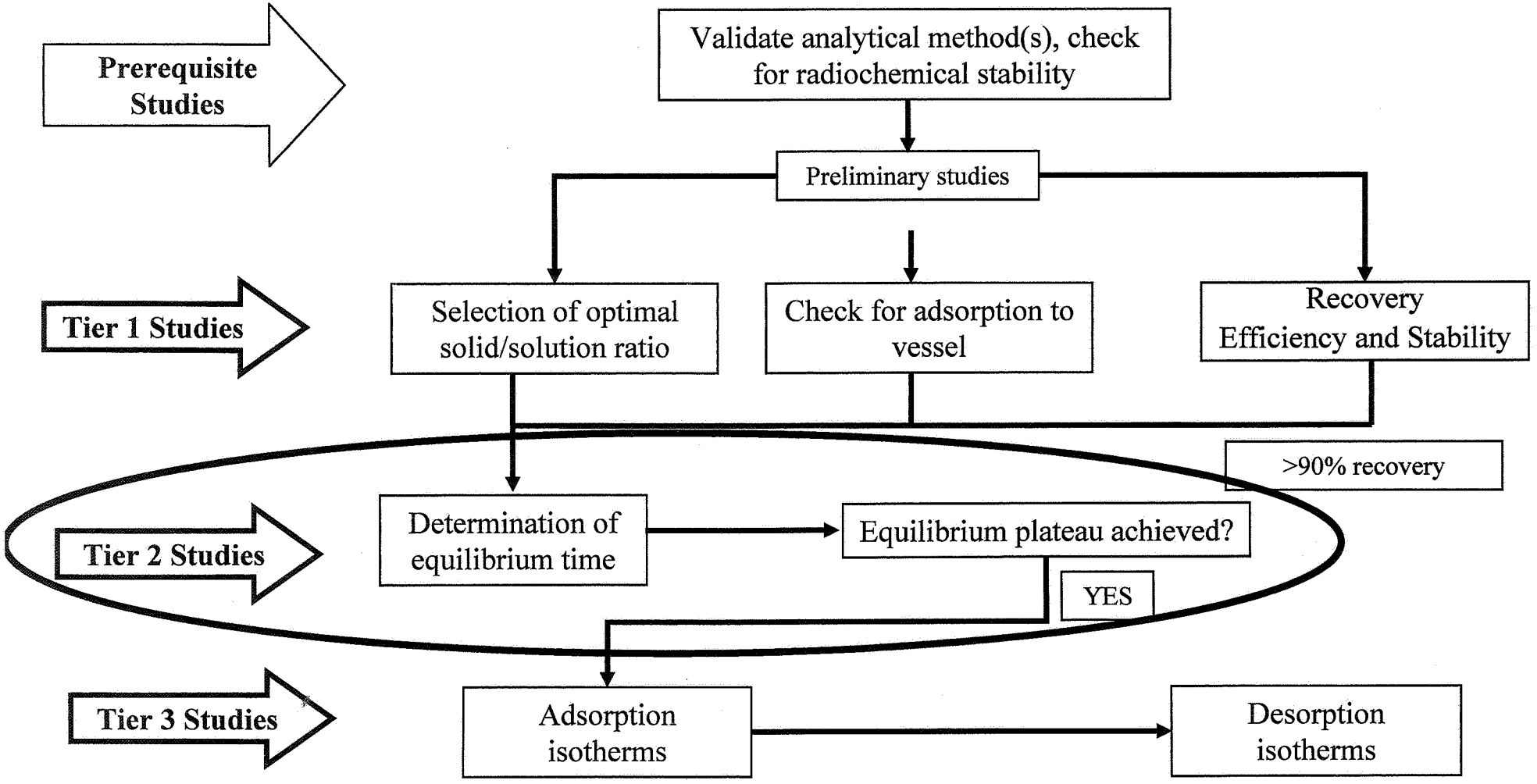
- Extracted soils dried, ground, combusted, $^{14}CO_2$ by LSC

# Recoveries of applied radioactivity of $^{14}C$ 8-2 TBA after 48 h equilibration time at 3 soil:solution ratios




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# OECD 106: Adsorption/Desorption using a Batch Equilibrium Method




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

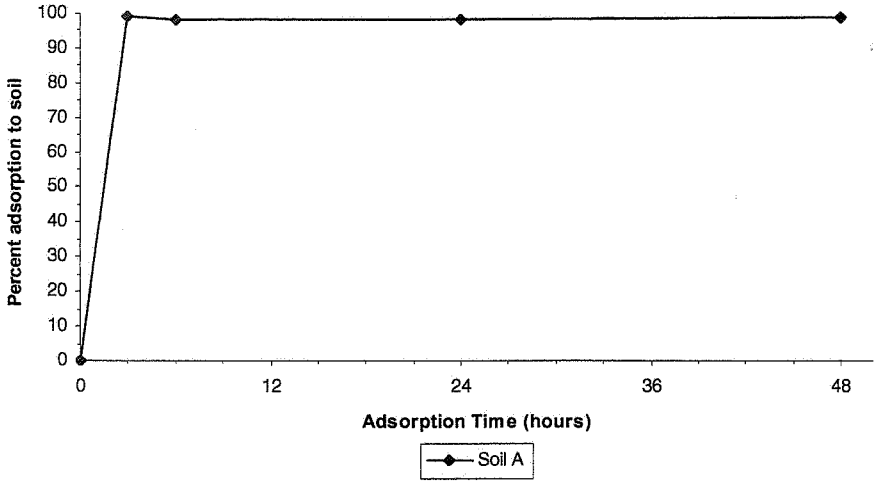
# Equilibration Time of $^{14}C$ 8-2 TBA at 1:1 Soil:Solution ratio, 25 µg 8-2 TBA $L^{-1}$

Equilibration time of 3, 6, 24 and 48 h

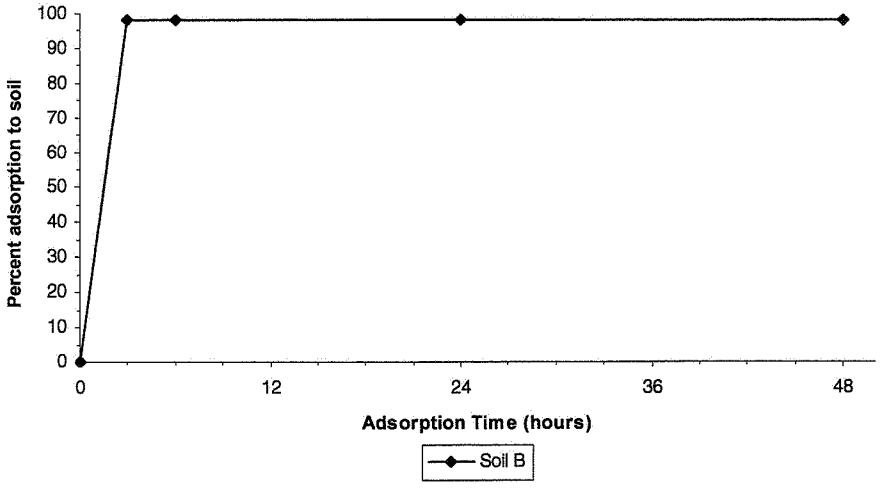
- $^{14}C$ 8-2 TBA applied through septum
- Samples centrifuged to separate phases
  - 0.01M $CaCl_2$ solution removed using syringe with SS piston through PTFE-coated rubber septum
  - Cap removed, supernatant decanted, $^{14}C$ by LSC
- Soil extracted 3 times with acetone
  - Soil extracts analyzed separately by LSC and results combined
- Soil residue combusted
  - Extracted soils dried, ground, combusted, $^{14}CO_2$ by LSC

Equilibration achieved within 3 hours

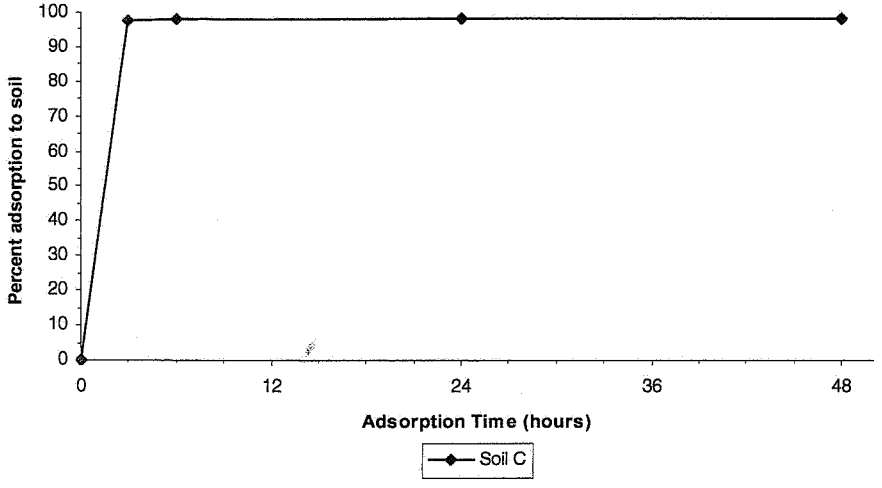
## Adsorption graph for Soil A (SK961089)



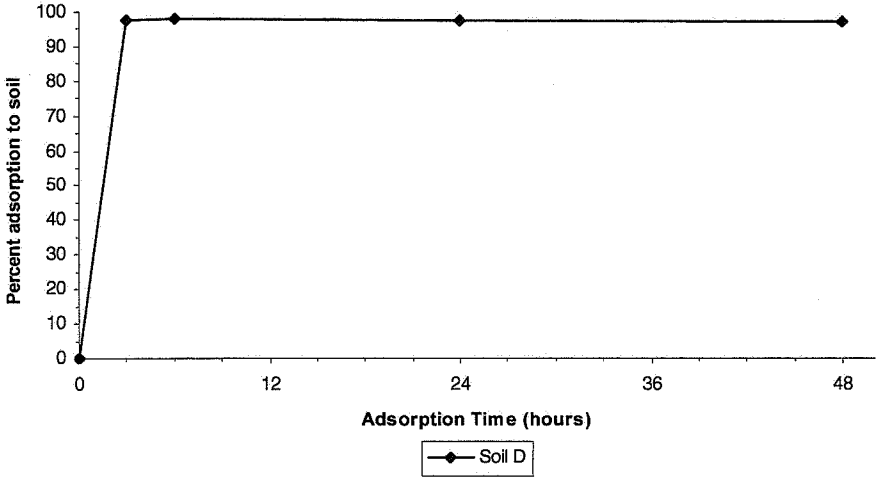

## Adsorption graph for Soil B (SK566696)




## Adsorption graph for Soil C (Emperor Son's Lake)

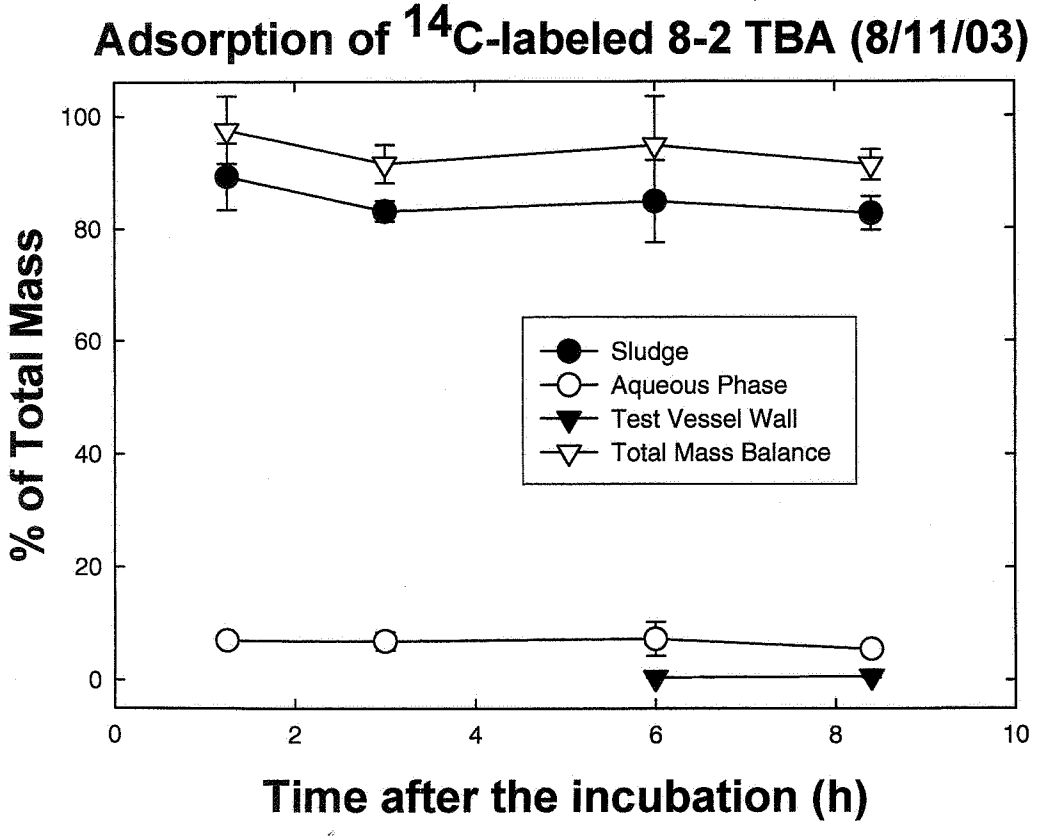



## Adsorption graph for Soil D (SK179618)




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption of $^{14}C$ 8-2 TBA by Activated Sludge




Sludge:

- POTW (Wilmington, DE), lyophilized and sterilized

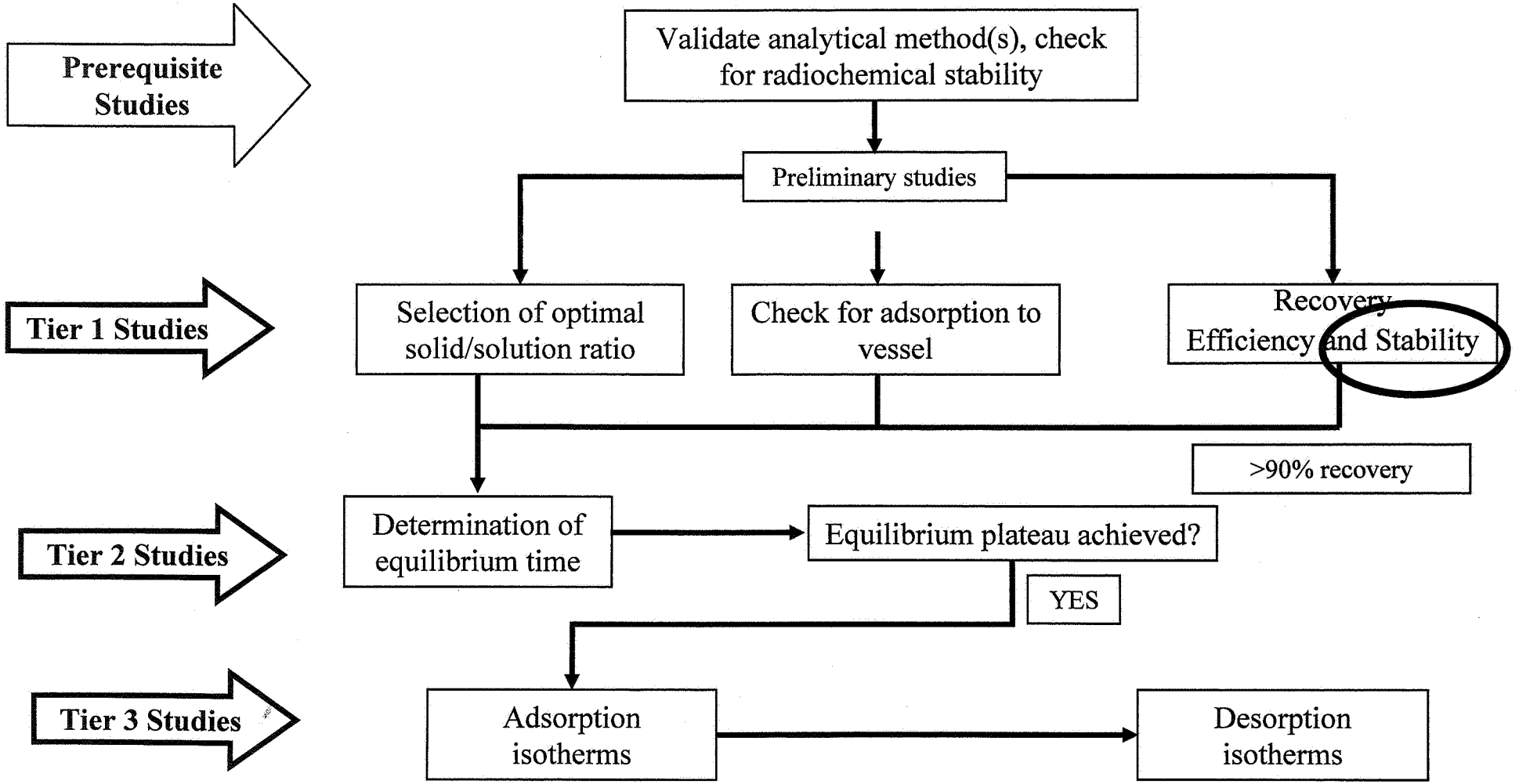
Test system:

- 4.5 g dry sludge $L^{-1}$ plus 87 µg $^{14}C$ 8-2 TBA $L^{-1}$;
- Glass vial with aluminum-lined cap

$^{14}C$ 8-2 TBA extracted and determined by LSC

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# OECD 106: Adsorption/Desorption using a Batch Equilibrium Method




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

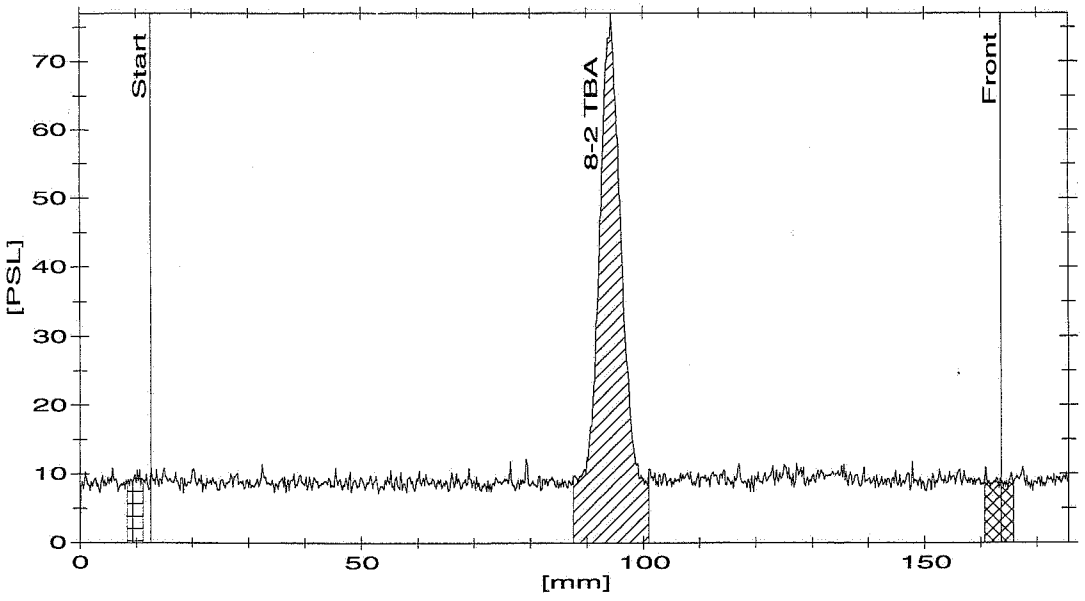
# $^{14}C$ 8-2 TBA Stability Studies

3 h equilibration time at 4°C

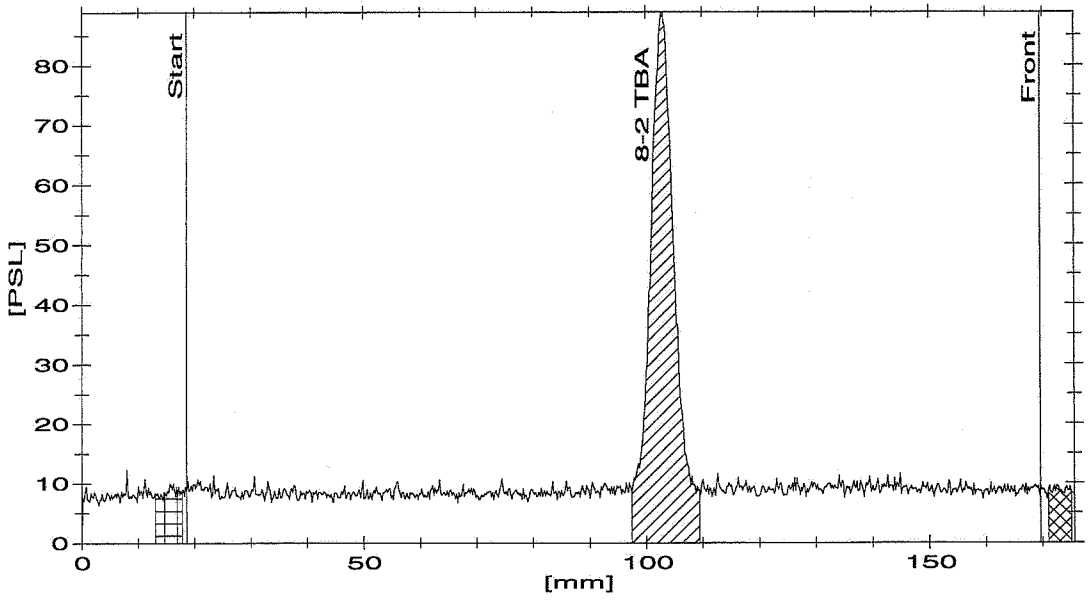
- Soils sterilized by gamma irradiation
- TLC/LSC method used to determine $^{14}C$, 8-2 TBA
  - 50:50 toluene: ethyl acetate mobile phase

8-2 TBA Stable under study conditions

## Soil SK961089

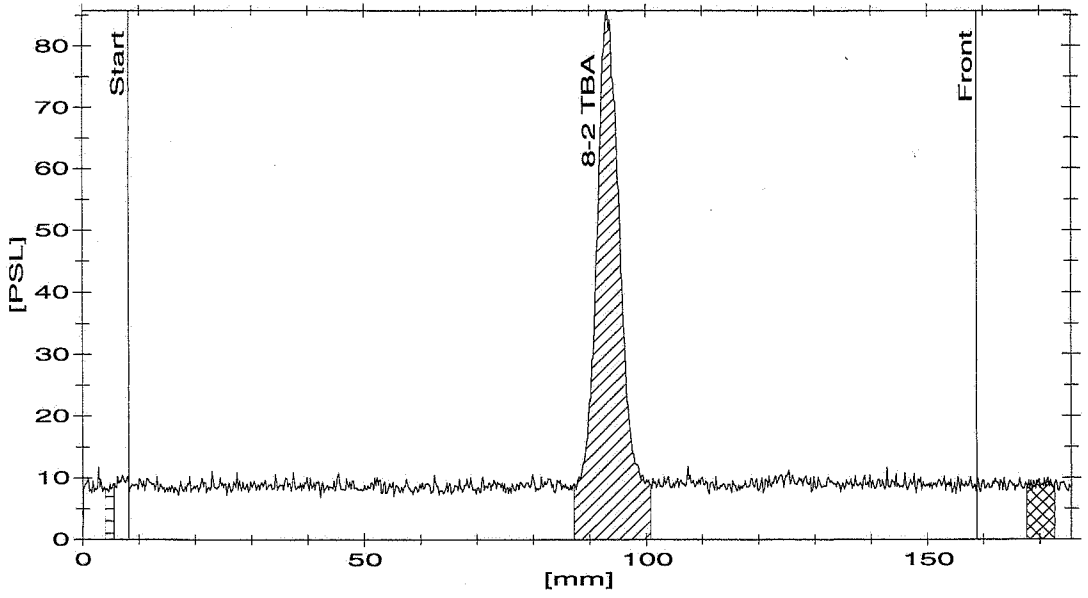



## Soil SK566696

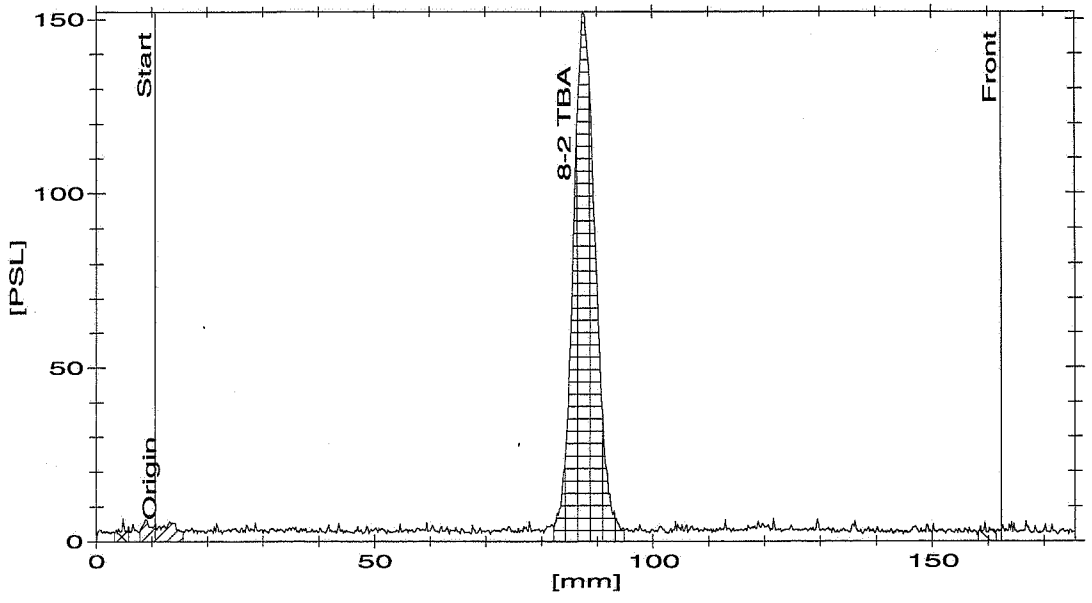



**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Emperor Son's Lake Sediment

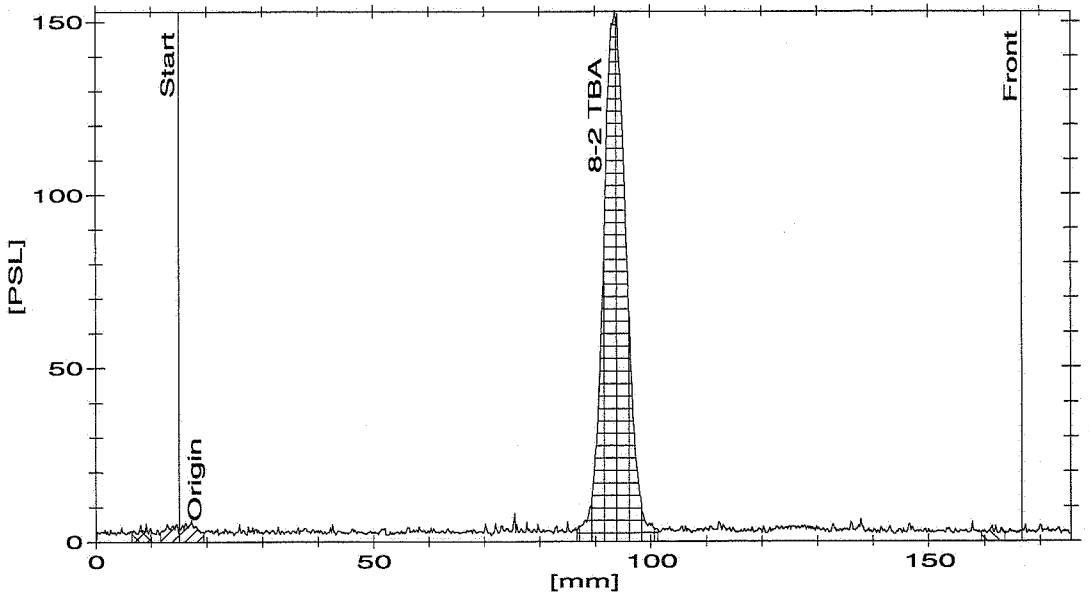



Soil SK179618



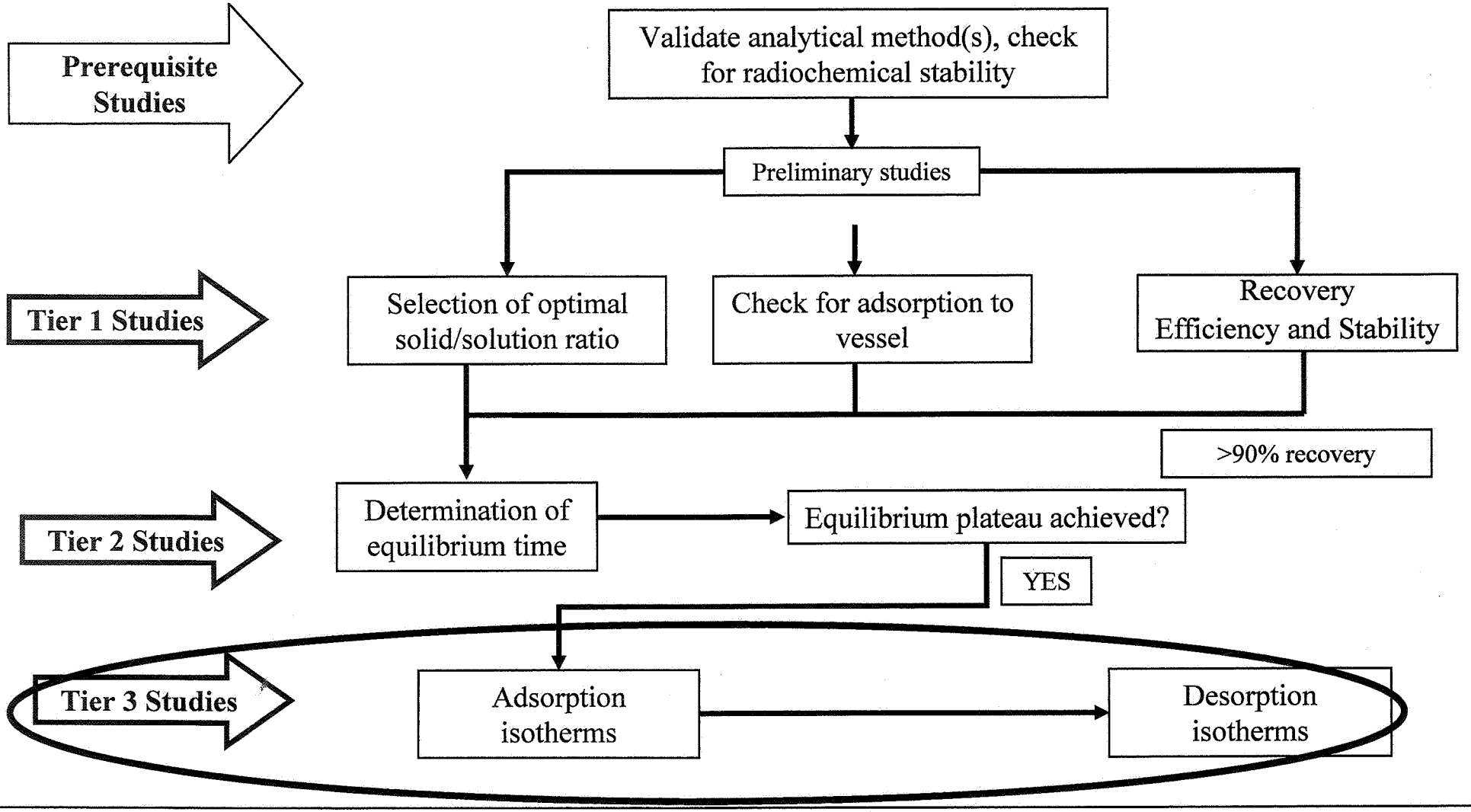

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

EUROSOIL 5




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# OECD 106: Adsorption/Desorption using a Batch Equilibrium Method




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption and Desorption Studies

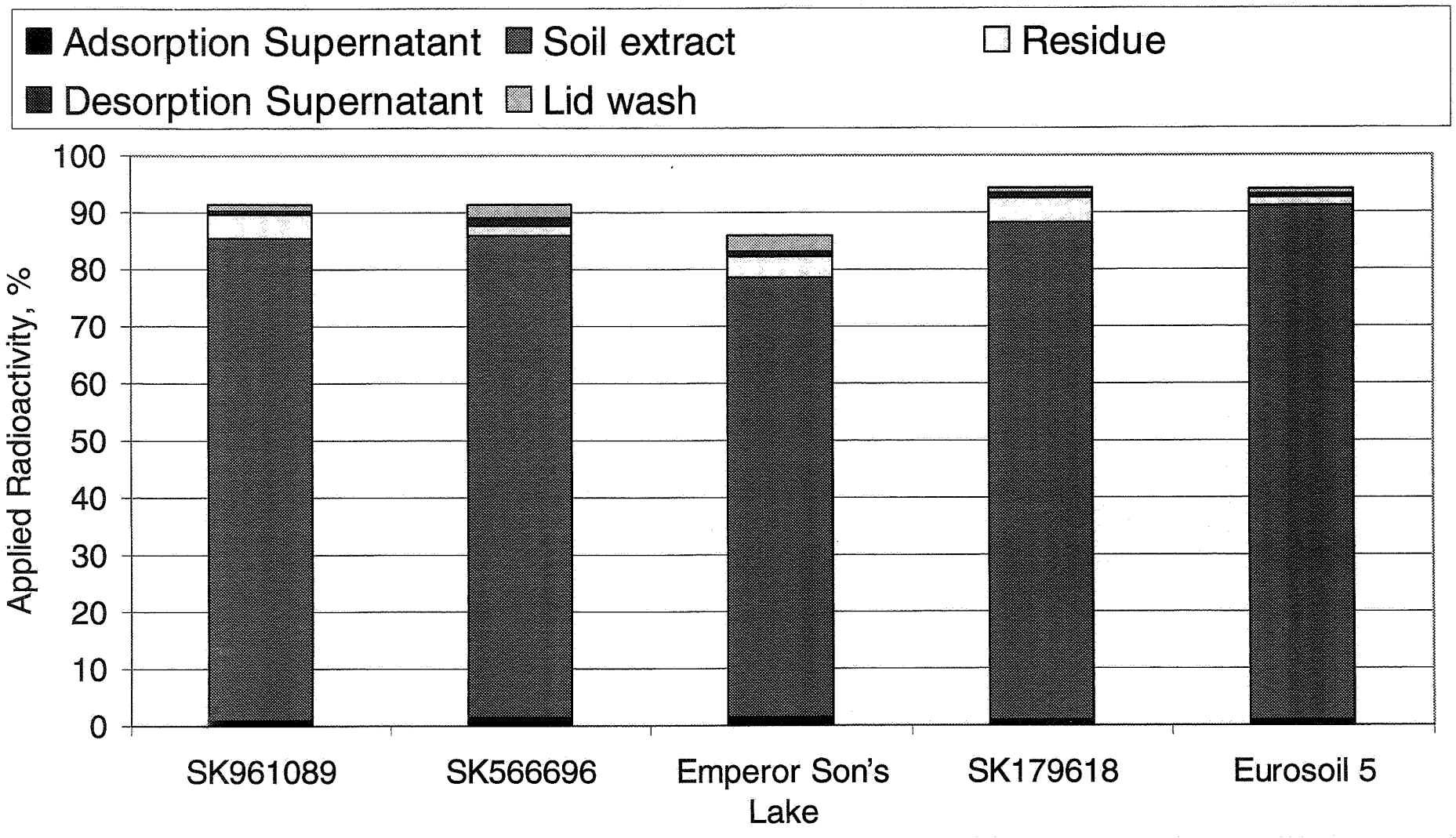
Adsorption step

- 8-2 TBA at 5 concentrations in duplicate
  - 0.125, 0.100, 0.075, 0.050, 0.0125 µg 8-2 TBA/mL
- 1:1 soil:solution ratio, 3 hours, 4 C as used previously
- Samples centrifuged, liquid and soil phases separated, supernatant analyzed by LSC

Desorption step

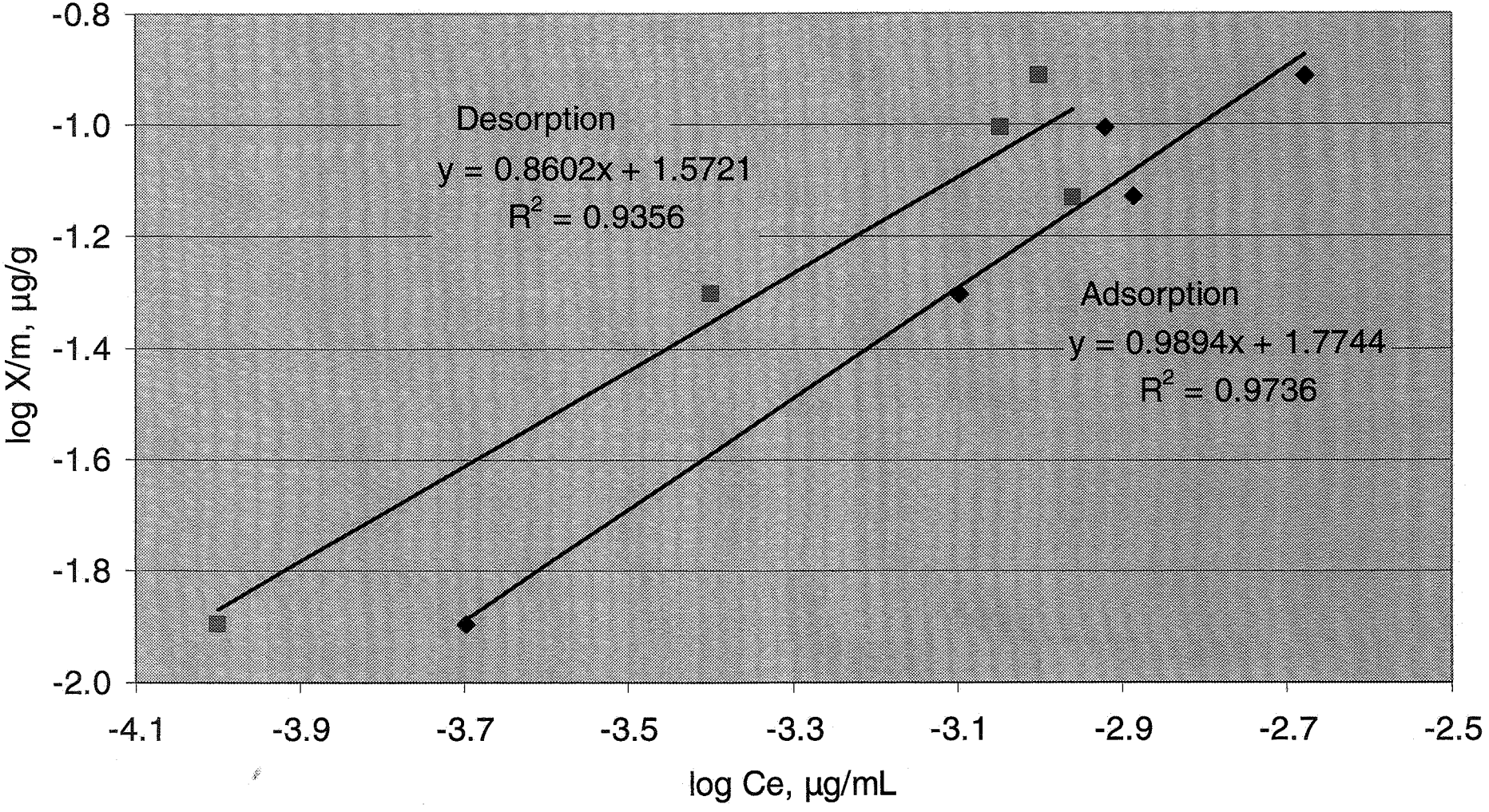
- Adsorption supernatant replaced by fresh 0.01M CaCl2
- Mixed for 3 h, centrifuged, supernatant analyzed by LSC
- 0.125 µg 8-2 TBA/mL samples extracted 3 times with acetone, samples pooled, and analyzed by LSC
- Soil samples air-dried, ground, combusted and analyzed by LCS

# Radioactivity Recovery from 5 soils treated with 0.125 µg 8-2 TBA/mL



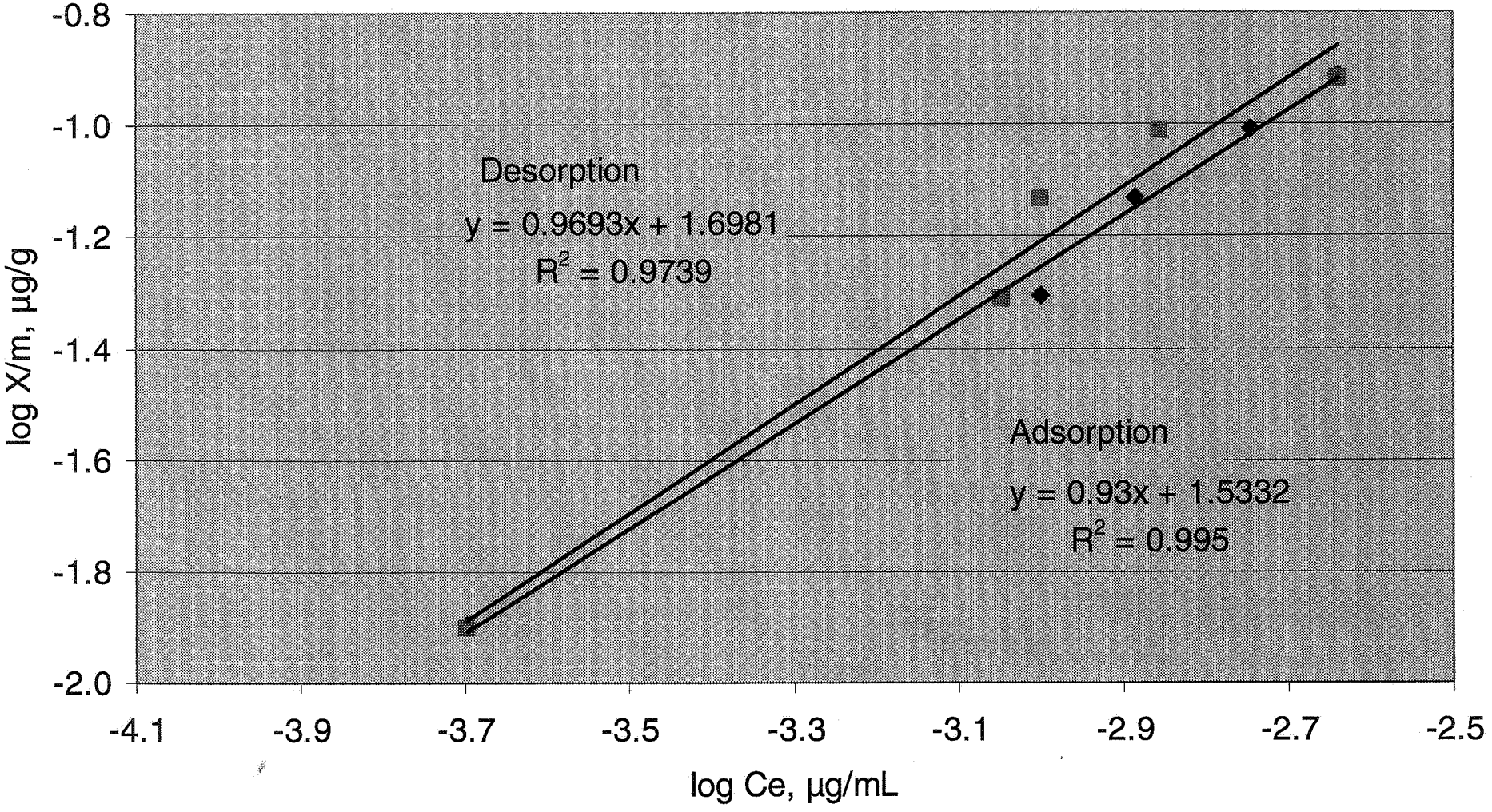

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption and desorption chart for 8-2 TBA on Soil SK961089



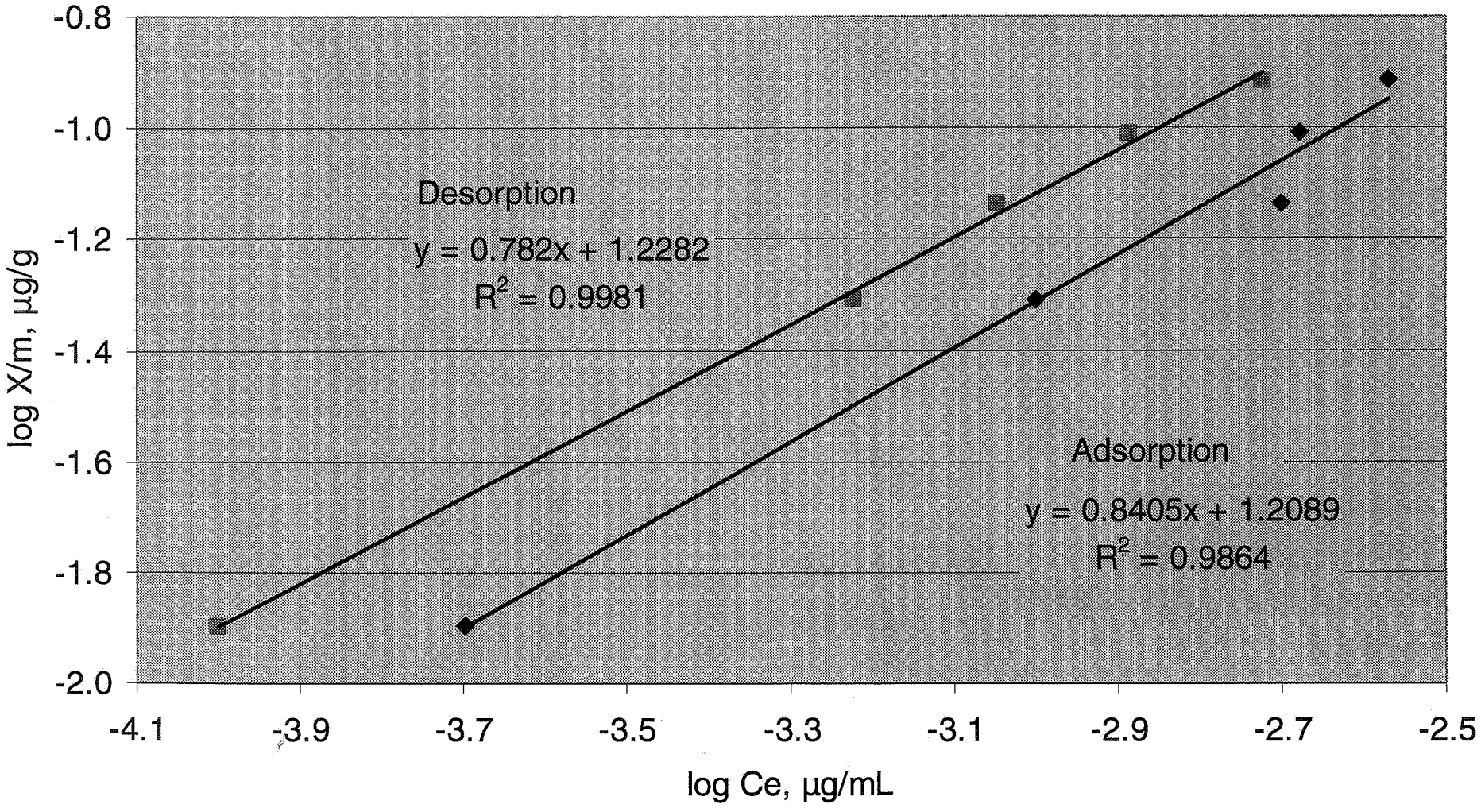

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption and desorption chart for 8-2 TBA on Soil SK566696



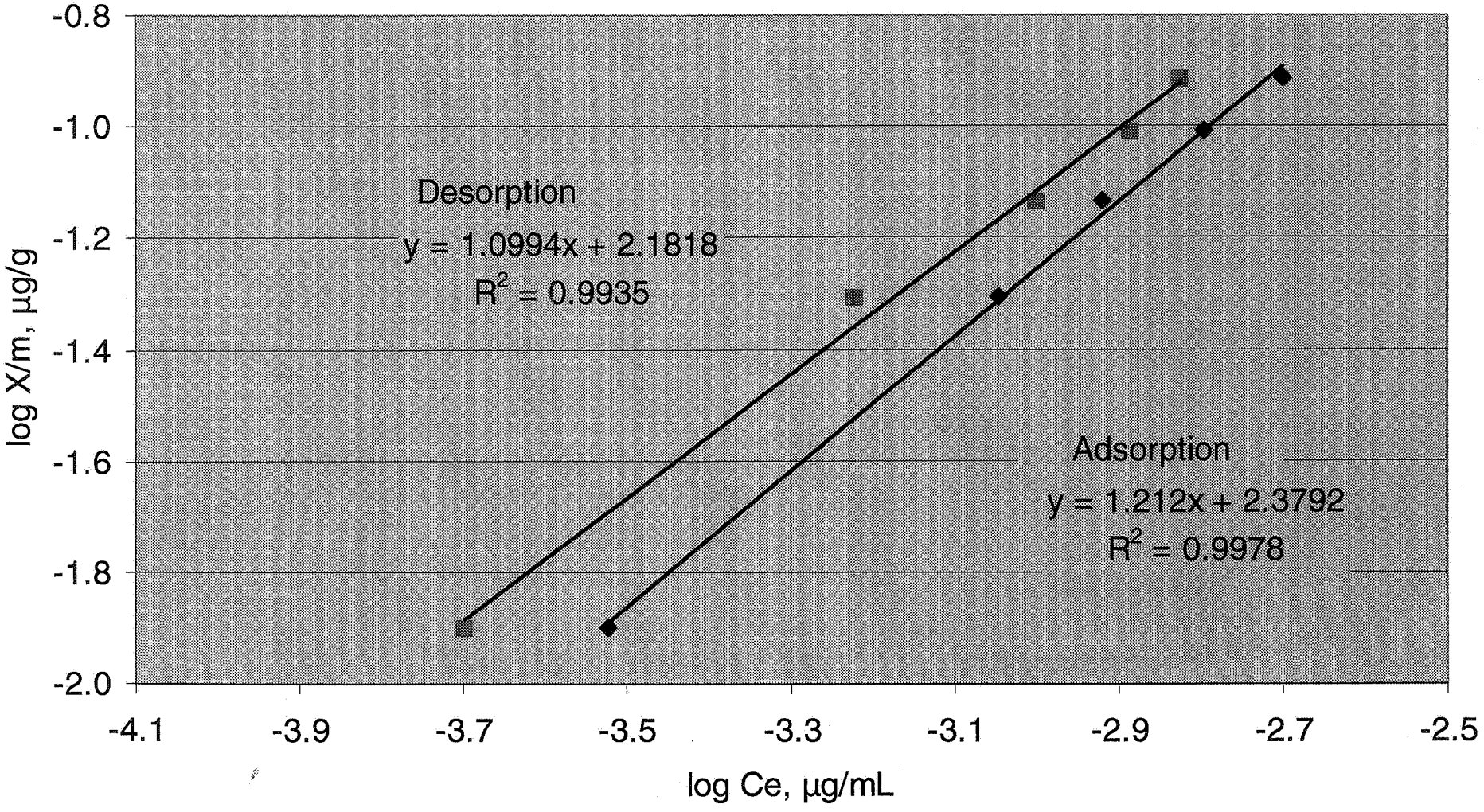

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption and desorption chart for 8-2 TBA on Emperor Son's Lake Sediment



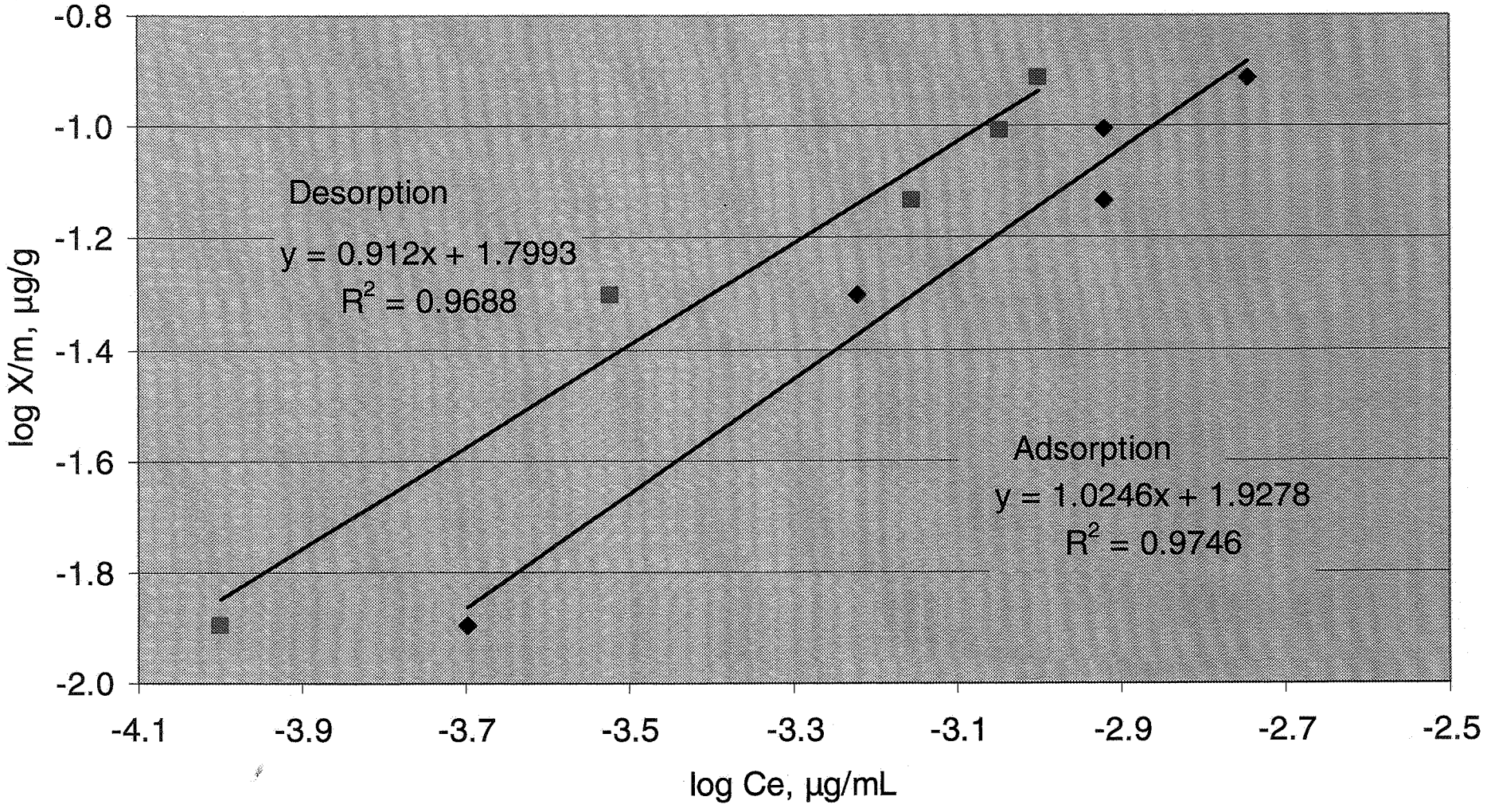

**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption and desorption chart for 8-2 TBA on Soil SK179618




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Adsorption and desorption chart for 8-2 TBA on Eurosoil 5




**TRP: Asahi Glass Co., Clariant GmbH, Daikin Industries, DuPont Co.**

# Freundlich adsorption and desorption constants and regression analysis for 8-2 TBA

| Soil | Experimental Stage | Adsorption constants | | | 1/n | $R^2$ |
|---|---|---|---|---|---|---|
| | | K | Koc | Kom | | |
| SK961089 | Adsorption Step | 59 | 1293 | 753 | 0.9894 | 0.9736 |
| | Desorption Step | 37 | 812 | 473 | 0.8602 | 0.9356 |
| SK566696 | Adsorption Step | 34 | 4266 | 2438 | 0.9300 | 0.9950 |
| | Desorption Step | 50 | 6238 | 3564 | 0.9693 | 0.9739 |
| Emperor Son's Lake Sediment | Adsorption Step | 16 | 1348 | 770 | 0.8405 | 0.9864 |
| | Desorption Step | 17 | 1409 | 805 | 0.7820 | 0.9981 |
| SK179618 | Adsorption Step | 239 | 6302 | 3628 | 1.2120 | 0.9978 |
| | Desorption Step | 152 | 4000 | 2303 | 1.0994 | 0.9935 |
| EUROSOIL 5 | Adsorption Step | 85 | 1264 | 730 | 1.0246 | 0.9746 |
| | Desorption Step | 63 | 940 | 543 | 0.9120 | 0.9688 |

# Summary

>90% radiolabel recoveries in 4 of 5 soils at 1:1 ratio

- Fifth soil 86% recovery

Predominately recovered from soil extracts and residue

- Recovered 88 to 99% sorbed to soil at 1:1 soil:solution ratio

8-2 TBA reaches equilibrium in less that 3 hours

- Less than 1 h in freeze-dried, activated sludge

Freundlich adsorption constants characterize 8-2 TBA as non-mobile (Koc > 4000) to slightly mobile (Koc 500 to 4000)

- Based on classification by Hollis 1991

Hollis, J M (1991). Mapping the vulnerability of aquifers and surface water to pesticide contamination at the national/regional scale. Pesticides in Soil and Water: Current Perspectives (A Walker Ed), BCPC Monograph 47, pp 169 to 174

# Acknowledgements

Pat Folsom

Mark Starr

Lisa Sulecki

Sharon Swales