

# **Gas Chromatographic Determination of Organotin Compounds with Atomic Emission Detection for Geological Studies**

**Dr. Marion Hoch**

University of Erlangen-Nurnberg  
Institute of Geology and Mineralogy

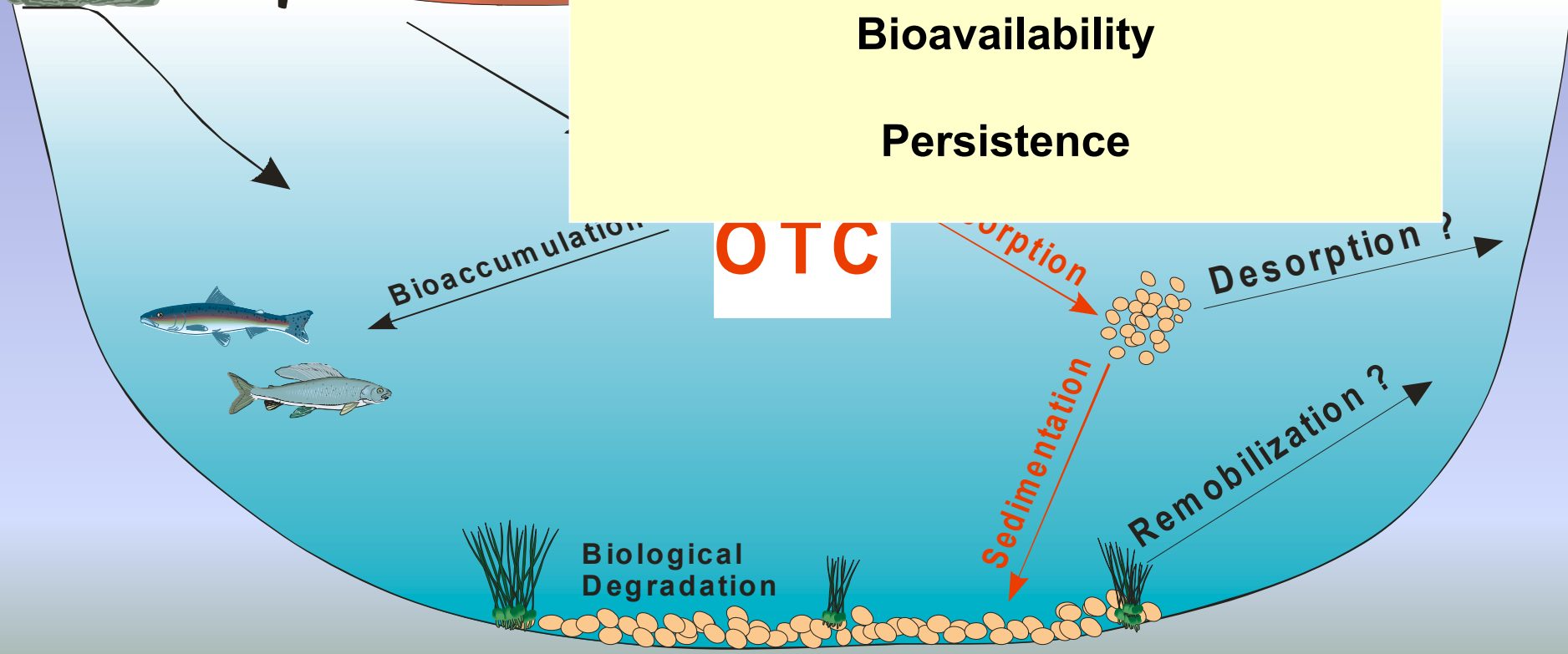
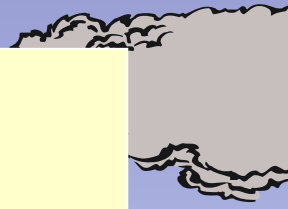


Municipal wastewater  
Sewage sludge  
Landfill leachates  
Runoffs

Industrial wastewater

Antif

**Transport and distribution**  
**Bioavailability**  
**Persistence**



Bioaccumulation

**OTC**

Absorption

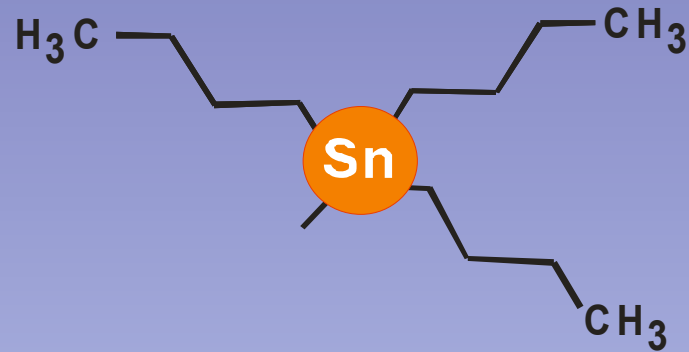
Desorption?

Sedimentation

Remobilization?

Biological Degradation

# Tributyltin (TBT)



**Biocidal component in antifouling paints,  
wood preservations and agents for material protection**

**Even at low concentrations of 1-2 ng/L tributyltin has  
a high toxicity towards sensitive aquatic organisms  
(snails, mussels and the larval stage of some fish)**



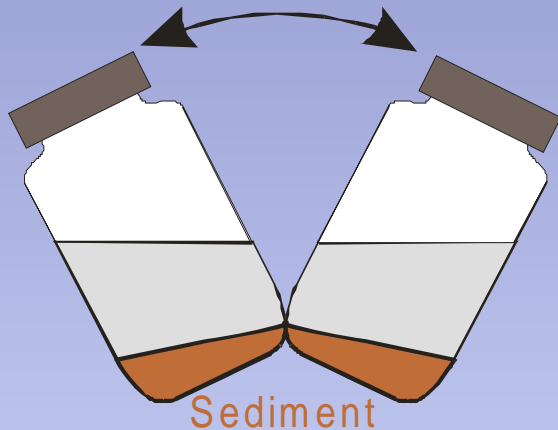
**restricted application of biocidal TBT**



**contamination of fish, mammals and birds**

# Batch technique for adsorption experiments

---



**1 gram sorbent material in teflon tubes**  
**50 mL deion. water or artificial seawater**  
**TBT (100 to 1000 ng(Sn)/mL)**  
**Buffer solution to adjust pH**

**The suspension was:**

- **shaken for a period of 24 hours at  $21 \pm 1^\circ\text{C}$**
- **centrifugated at 2500 rpm**
- **supernatant was analyzed for TBT**



**Sodium tetraethylborate (NaBEt<sub>4</sub>) as derivatization agent**



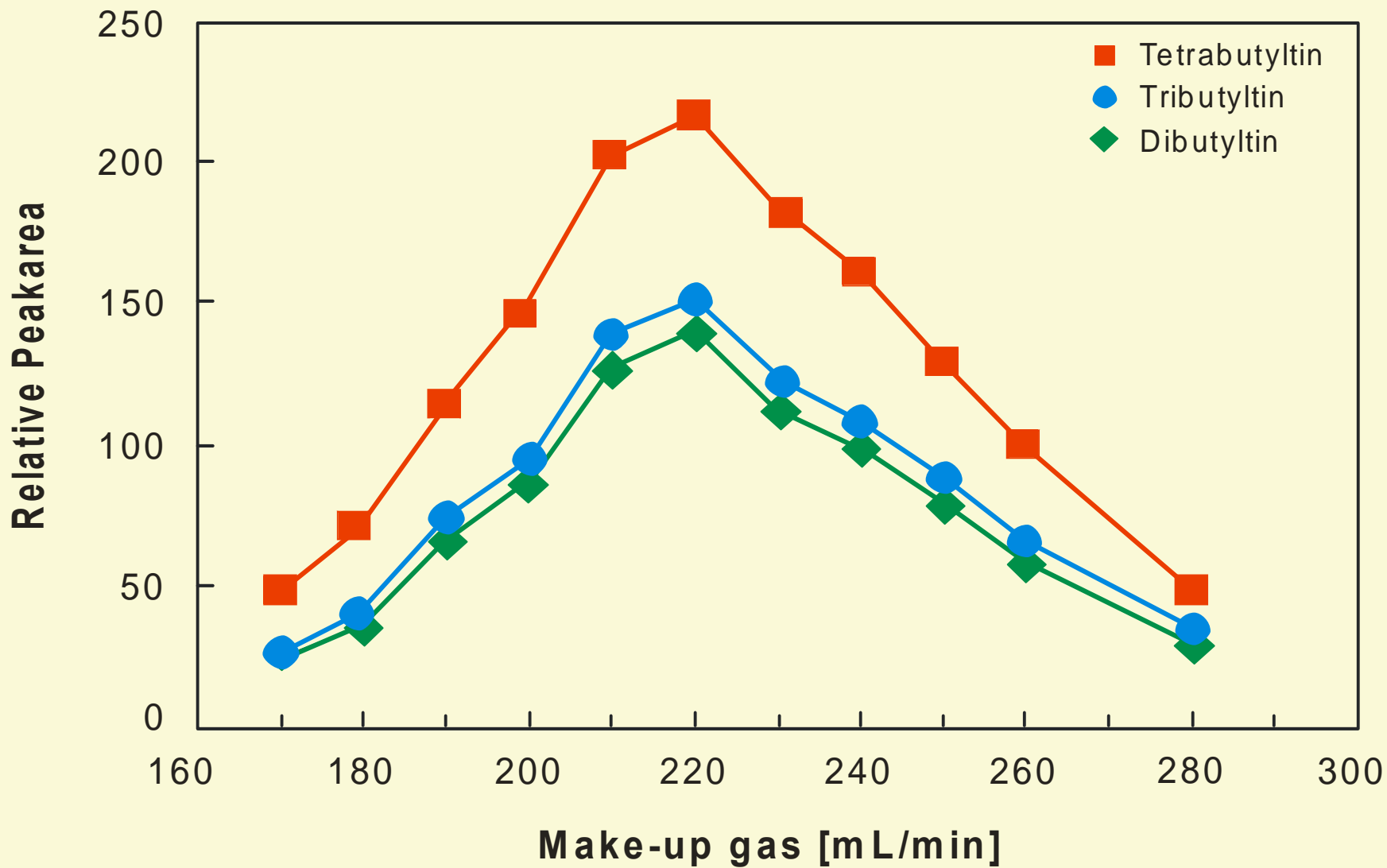
**Hexane extraction**



**Gas chromatograph**  
**HP 5890 Series II**

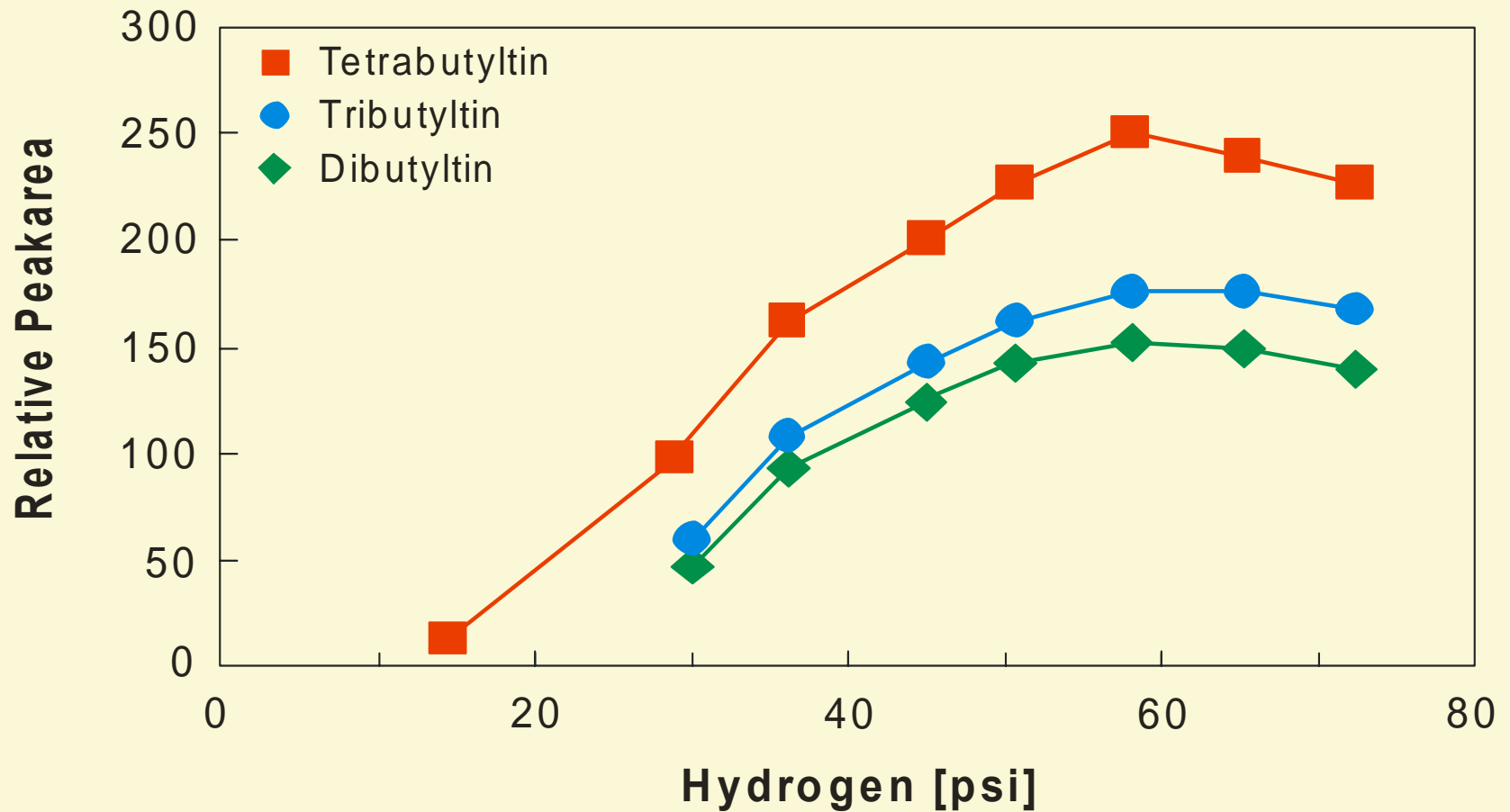
**Atomic emission detector**  
**HP 5921 A**

**Column:**  
**HP-5 (30 m x 320  $\mu$ m x 0.25 mm)**

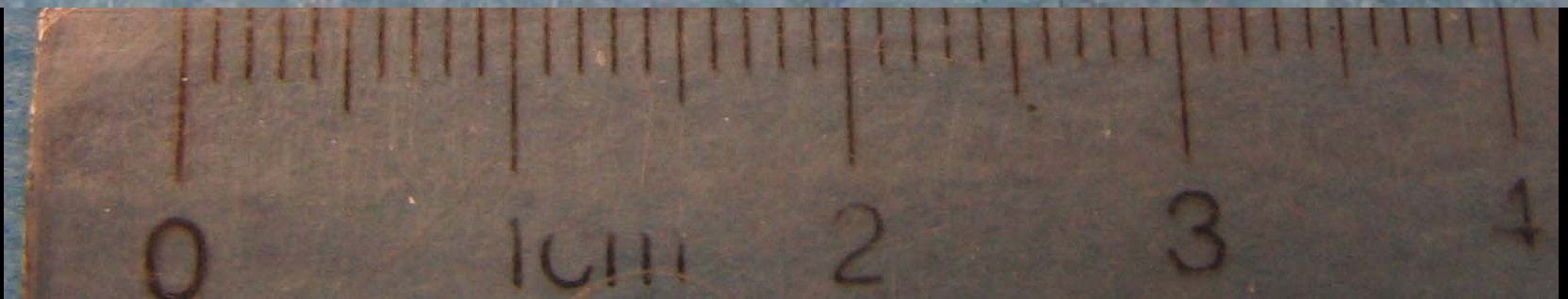


O<sub>2</sub> pressure = 23 psi, H<sub>2</sub> pressure = 60 psi

# Scavenger gases



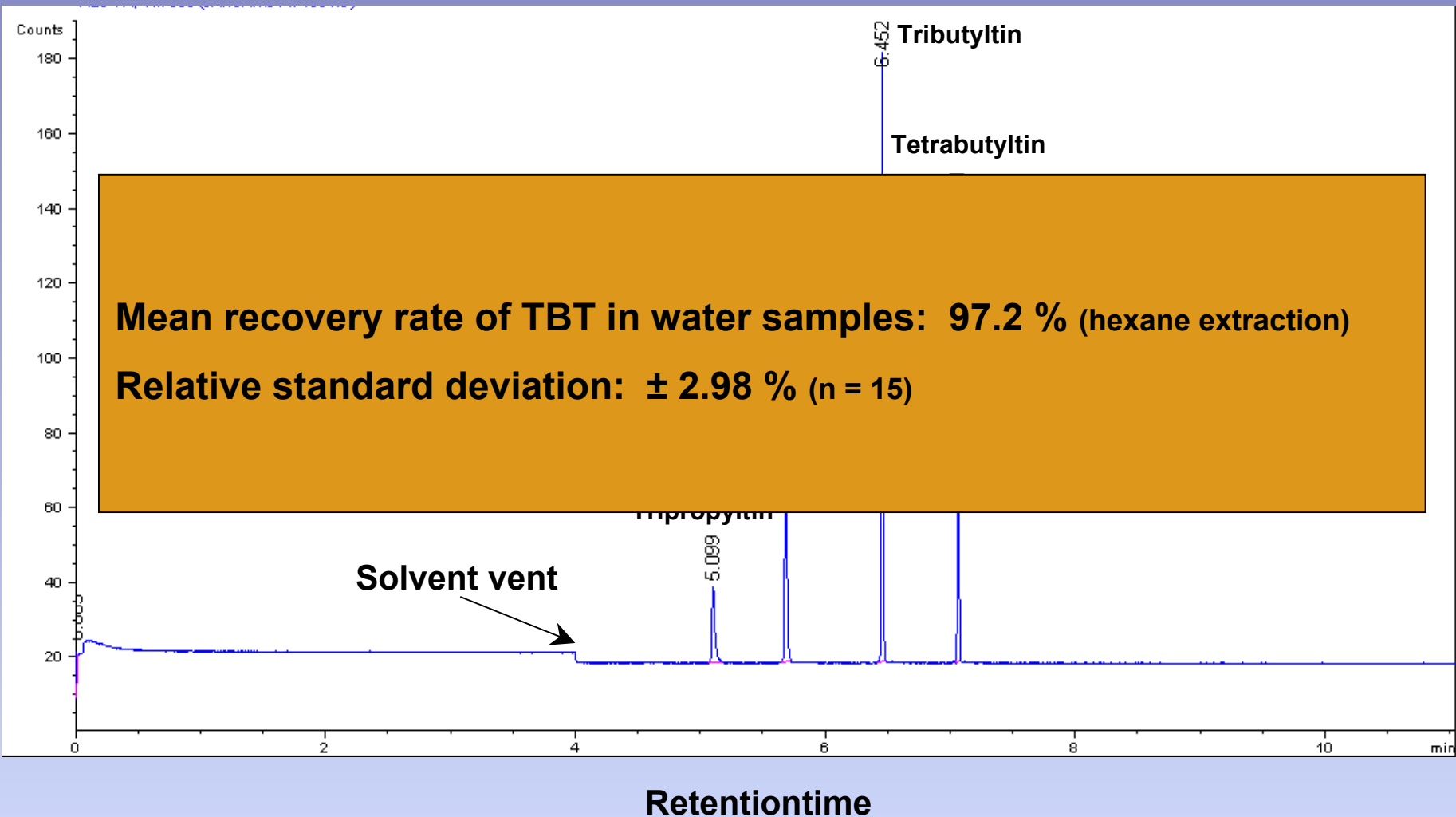
Make-up gas flow 220 mL/min, O<sub>2</sub> pressure = 23 psi



# Measuring procedure

---

- ↪ **Detection line for tin:  $\lambda = 303.419$  nm**
- ↪ **Injection 1  $\mu$ L, splitless**
- ↪ **Inlet, transfer line and cavity temperature were set to 280 °C**
- ↪ **Make-up gas (He) = 220 mL/min**
- ↪ **Scavenger gas: Hydrogen (60 psi), Oxygen (23 psi)**
- ↪ **Solvent vent off after 4 min**

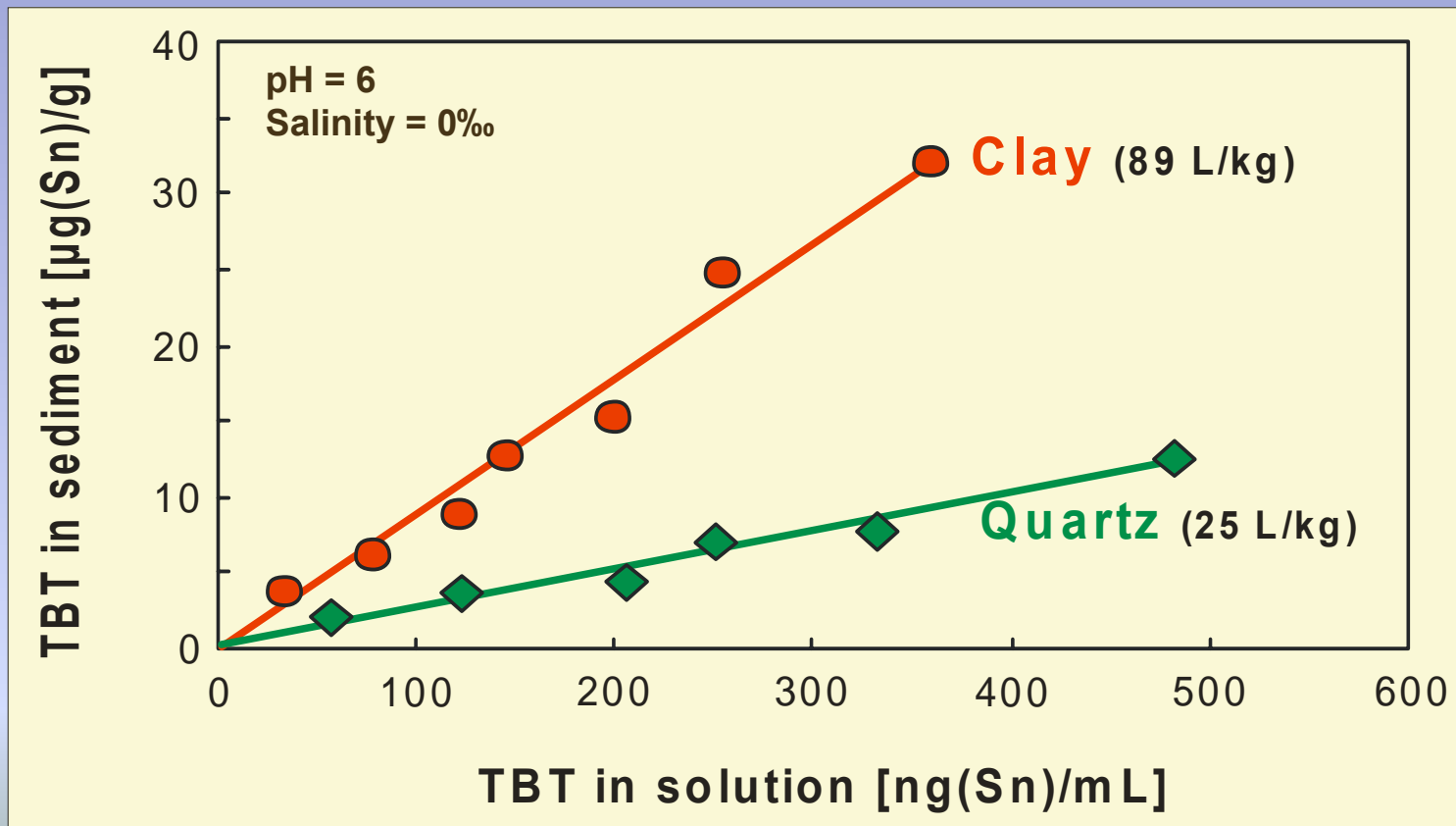


### GC temperature program:

Initial temperature 80 °C for 1 min, heated to 120 °C at 8 °C/min, heated at 28 °C/min to the final temperature of 280 °C, final temperature for 3 min

# Adsorption isotherm of TBT for pure phased minerals

Adsorption coefficient ( $K_d$ ) =  $C_{\text{solid}} [\mu\text{g}/\text{kg}] / C_{\text{fluid}} [\mu\text{g}/\text{L}]$  in L/kg



# Parameters controlling the adsorption of TBT

---



## Properties of the solid phase

Mineralogical composition

Type of clay minerals

Amount of organic matter

Solid/solution-ratio



## Properties of the water phase

pH level

Salinity

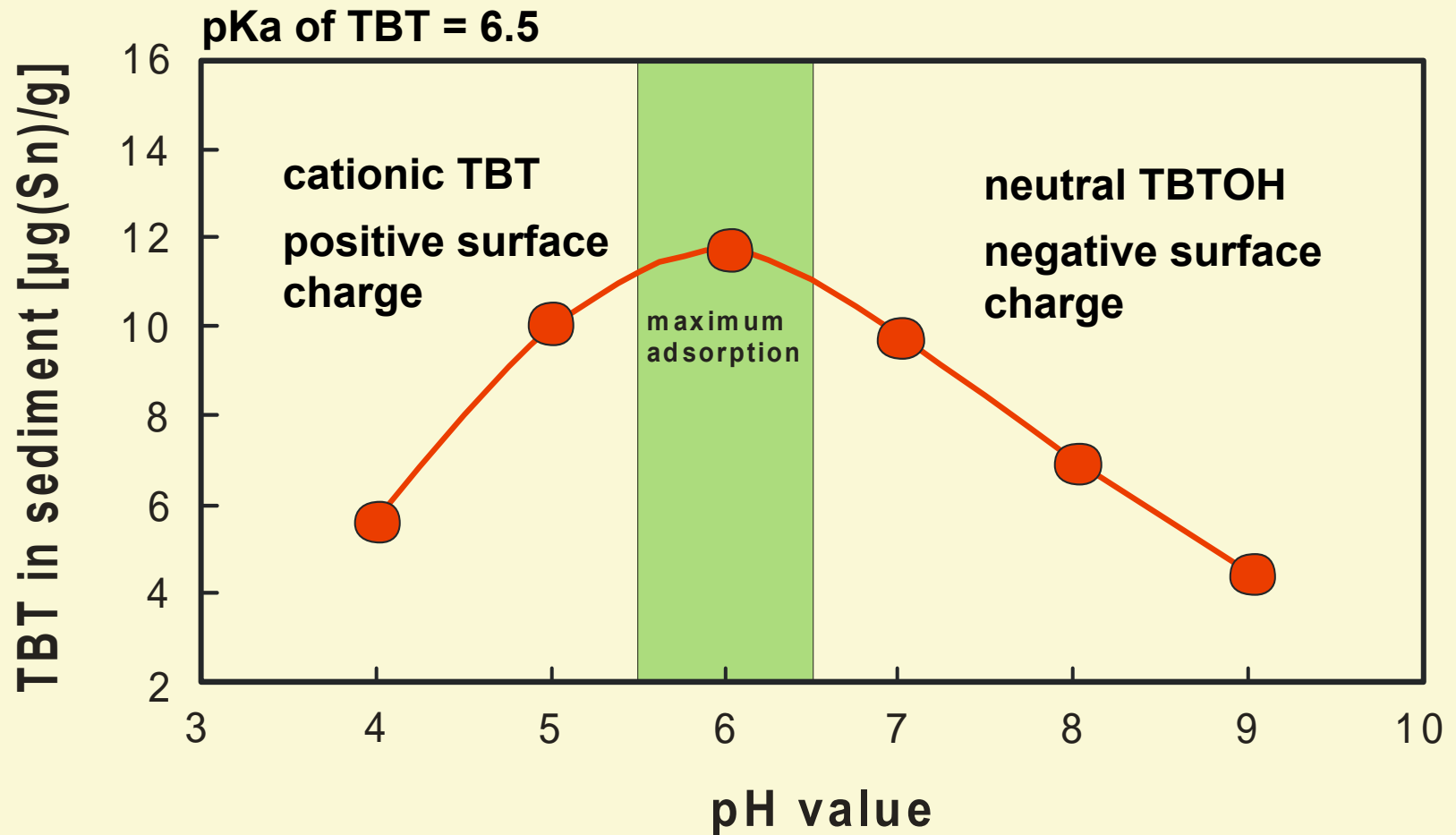


## Properties of the organotin compounds

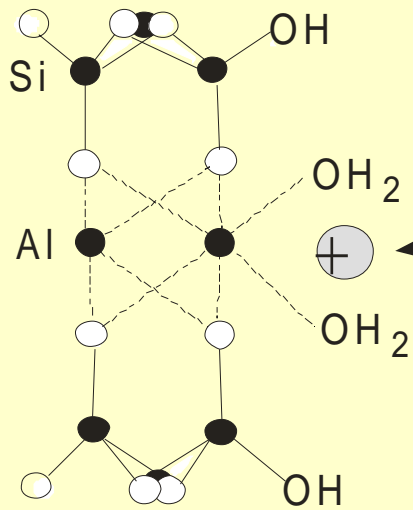
Molecular structure

Organotin species

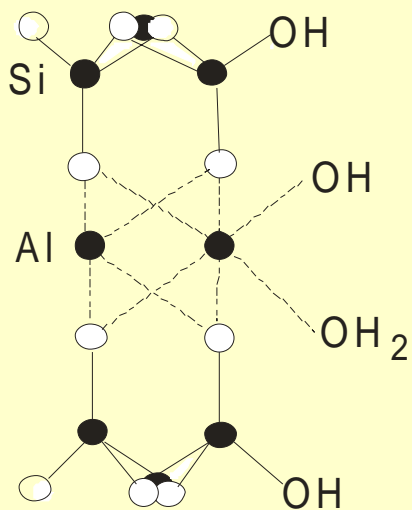
# TBT adsorption to kaolinite as a function of pH



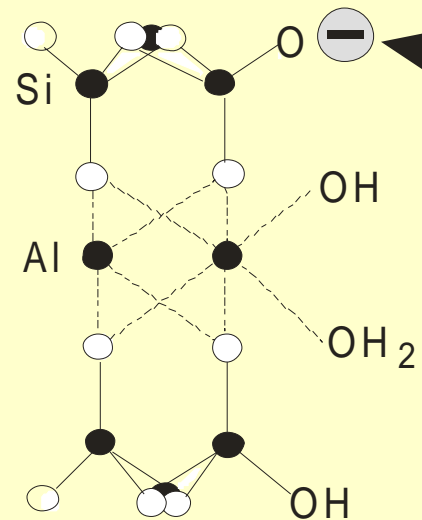
increasing pH



$A^-$

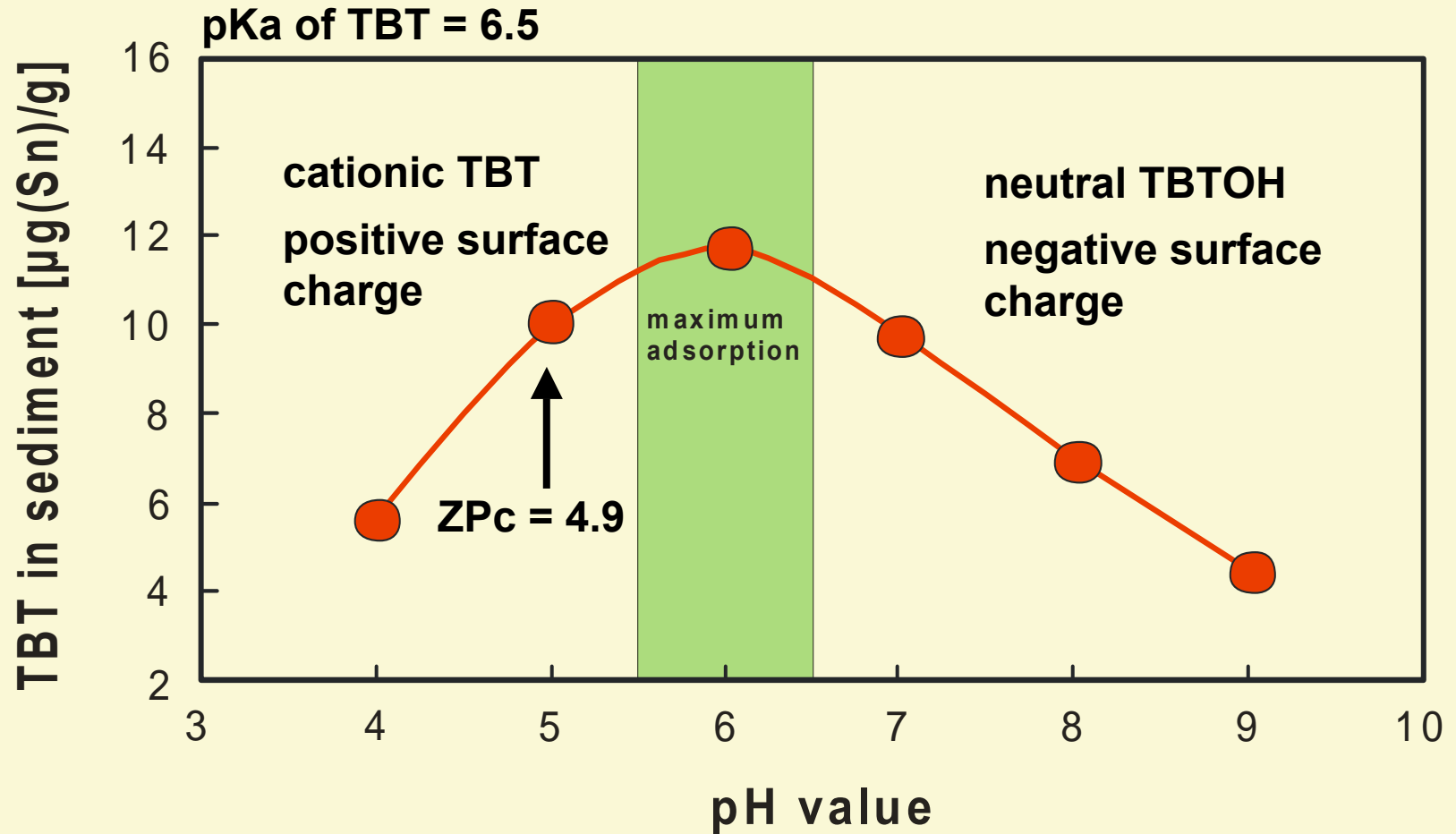


Zero point of charge

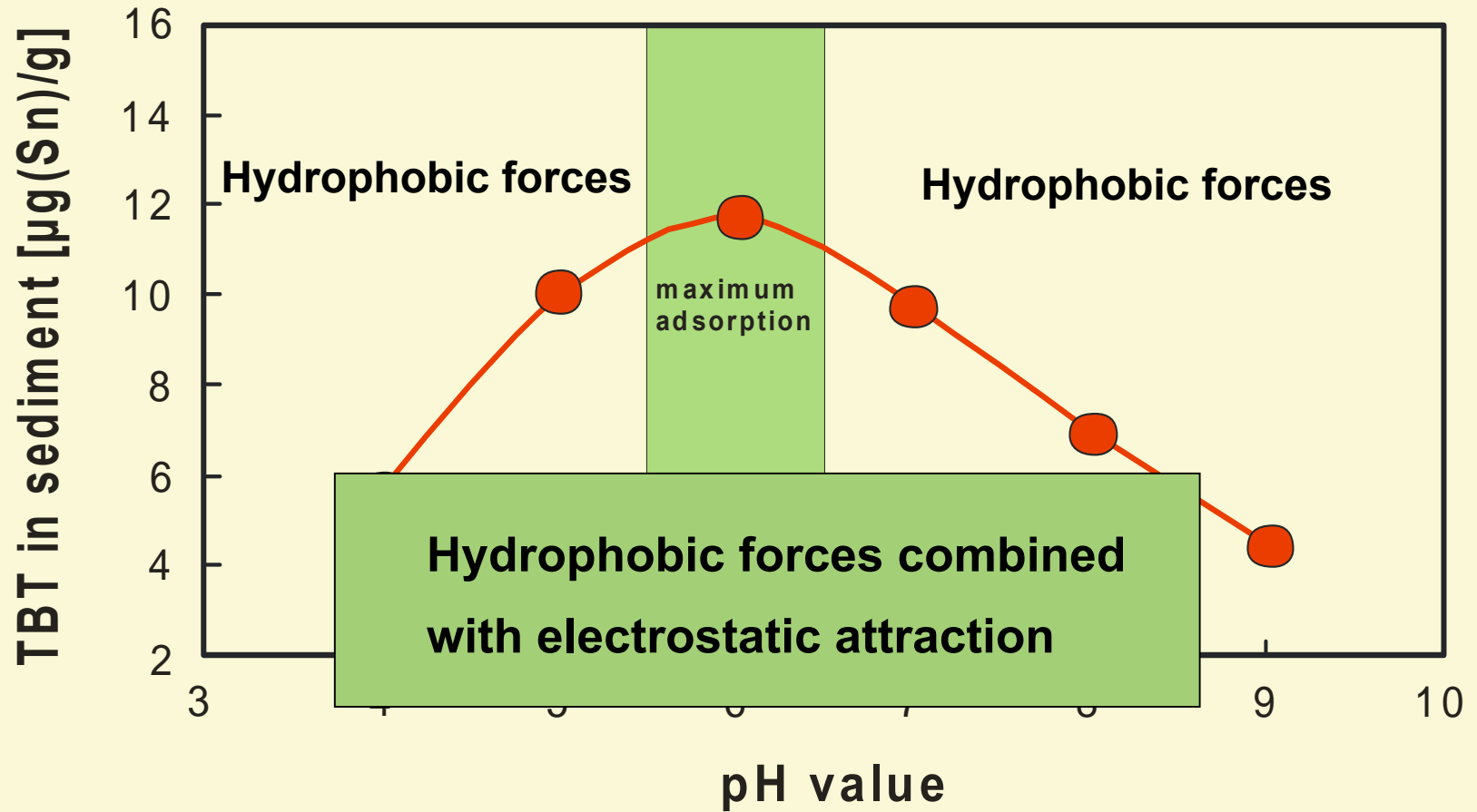


$M^+$

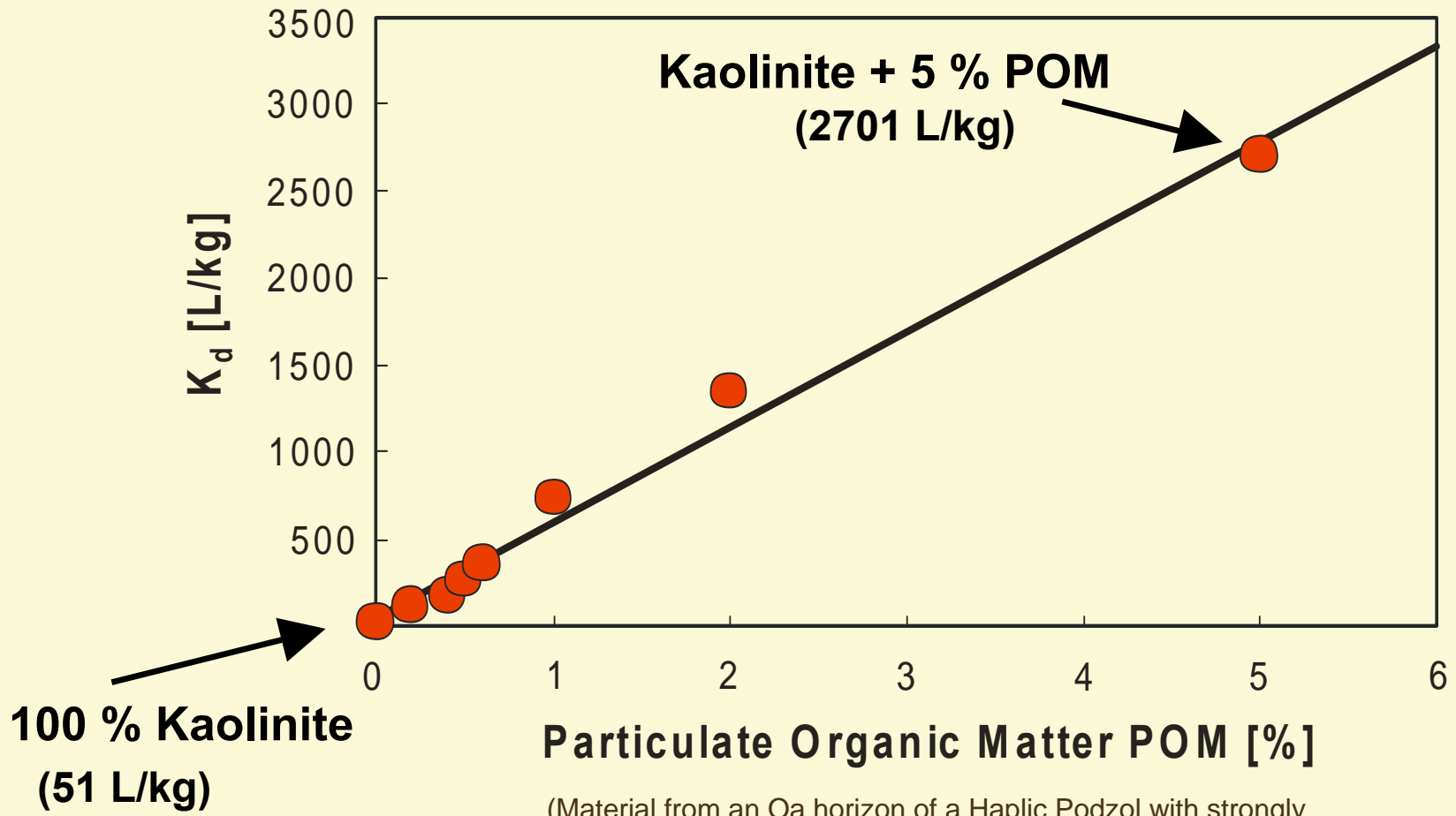
# TBT adsorption as a function of pH



# TBT adsorption as a function of pH



# Effect of Organic Matter to the Adsorption of TBT



(Material from an Oa horizon of a Haplic Podzol with strongly humified decomposition products of spruce litter)

# Conclusions

---



**GC-AED system is very suitable for organotin determination**



**Numerous parameters influence the adsorption behavior of TBT in natural systems, in particular pH and amount of organic matter**



**Detailed knowledge of adsorption behavior is necessary to develop an applicable decontamination concept and estimate the ecological risk**

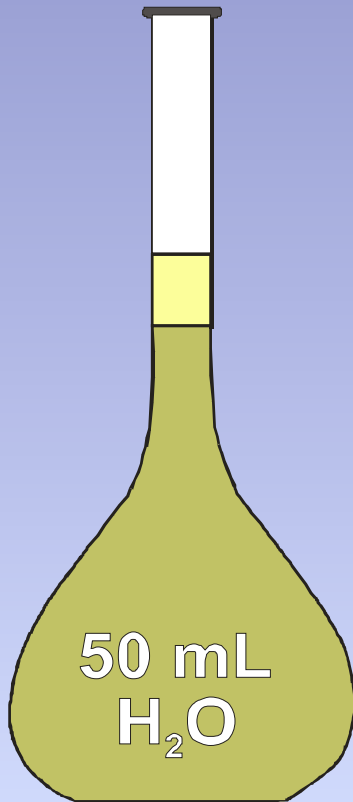


**Basic data are useful to model and predict TBT distribution in the environment**



## Sample preparation

---



- + 1 mL of the supernatant
- + 1- 2 mL sodium acetate/acetic acid buffer (to adjust pH 5)
- + 1 mL sodium tetraethylborate (NaBEt<sub>4</sub>) (1% w/v) as derivatization agent
- + TTBT and TPrT as internal standards
- + 1 mL Hexan for extraction

<b>Gas chromatograph</b>	<b>HP 5890 Series II</b>
<b>Atomic emission detector</b>	<b>HP 5921 A</b>
<b>Automatic sampler</b>	<b>HP 7673 A</b>

**Carrier gas Helium 2.6 mL/min**

**Spectrometer purge flow rate (N<sub>2</sub>) 2 L /min**

**Cavity pressure 1.5 psi**

**Column: HP-5 (30 m x 320 μm x 0.25 mm)**





