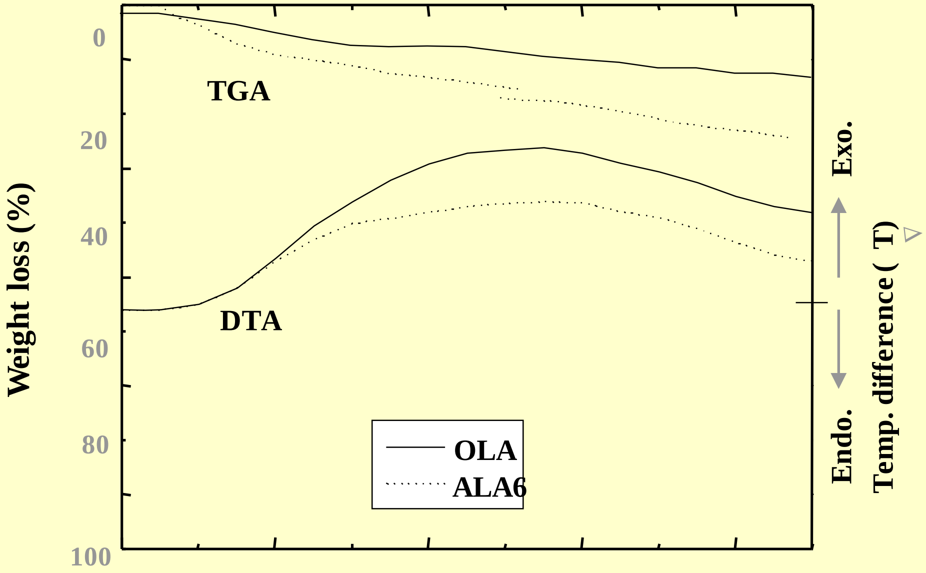
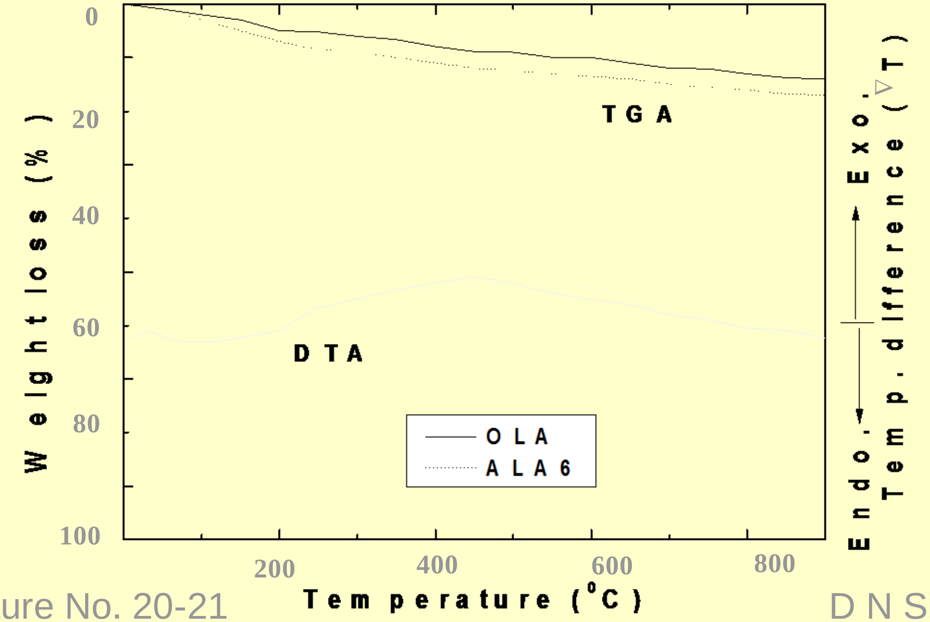
Thermo Gravimetric Analysis

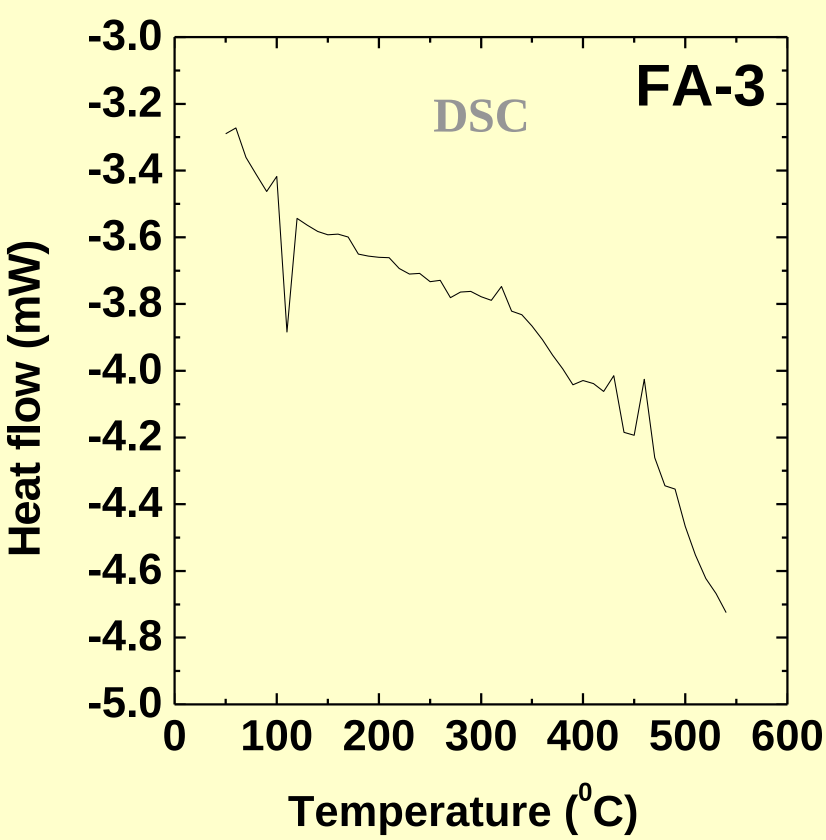
(Dry air atmosphere)

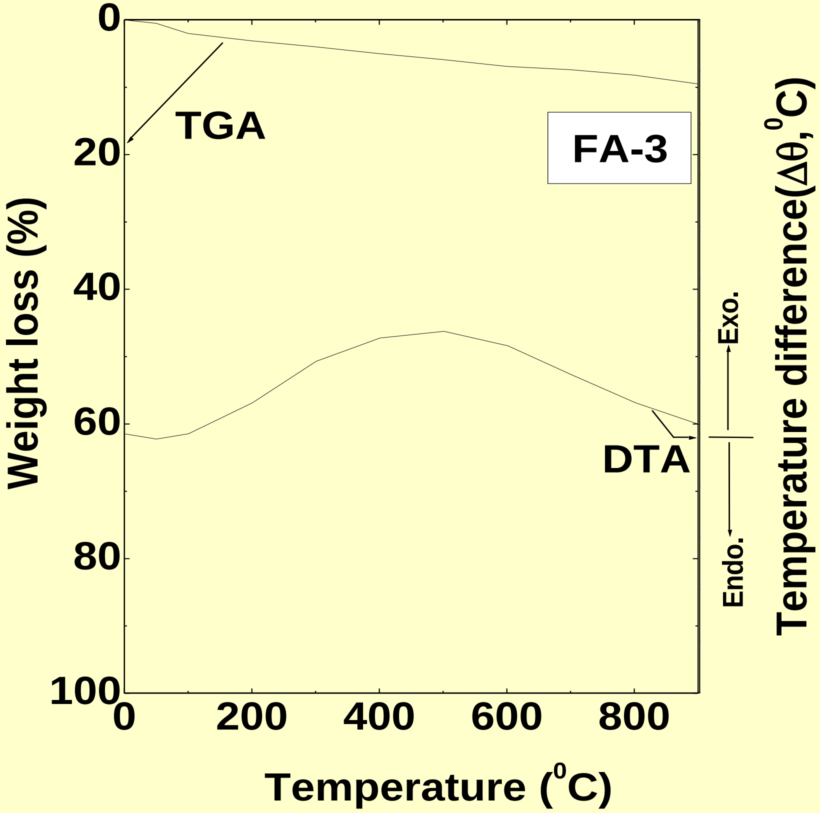


TGA and DTA curve for OLA and ALA6 samples

(Inert atmosphere)




FA-3
DSC
Heat flow (mW)
-3.0
-3.2
-3.4
-3.6
-3.8
-4.0
-4.2
-4.4
-4.6
-4.8
-5.0
0
100
200
300
400
500
600
Temperature (⁰C)


0
20
40
60
80
100
Weight loss (%)
TGA
FA-3
DTA
Exo.
Endo.
Temperature difference(Δθ,⁰C)
0
200
400
600
800
Temperature (⁰C)

CHEMICAL CHARACTERIZATION

- X-Ray Fluorescence (XRF)
- Inductively Coupled Plasma (ICP)
- pH value
- Cation Exchange Capacity (CEC)
- Pore solution analysis

XRF Pallets

Inductively Coupled Plasma Unit

AAS

Calibration of XRF- Setup

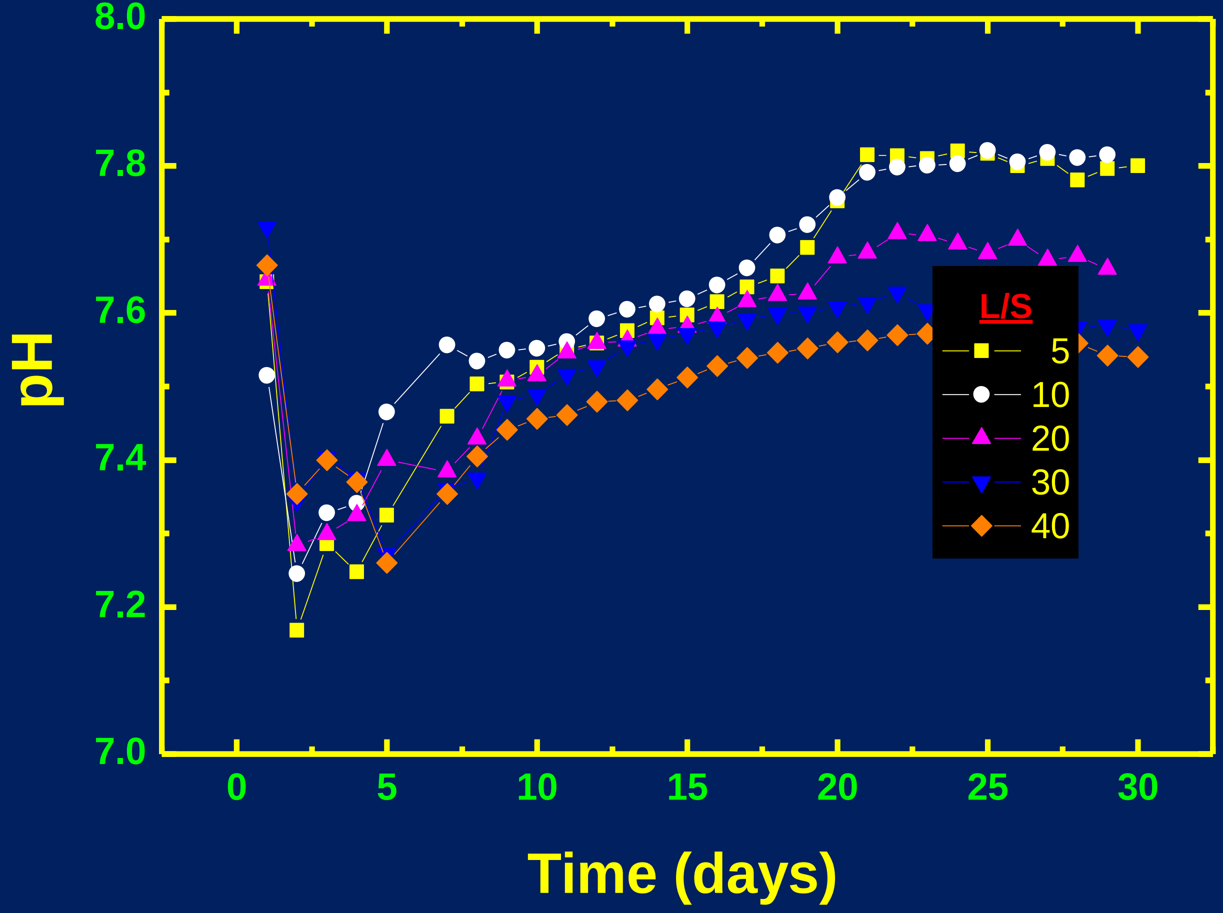
XRF Studies

- ➢Physical Calibartion
- ➢Chemical Calibration

Elemental Composition (% by weight) of Materials

	Material									
Element	**CS**	**WC**	**IC**	**RSS**	**BSS**	**FA-I**	**FA-II**	**C-I**	**C-II**	**GGBFS**
Si	15.78	20.32	11.52	39.21	40.71	25.53	28.30	24.65	23.62	15.56
Al	5.75	17.77	1.67	2.65	3.29	15.95	15.92	20.70	21.92	8.59
Fe	8.23	1.09	1.19	0.50	0.94	2.51	2.31	1.38	1.81	0.25
Ti	1.53	2.88	0.03	0.22	0.14	2.12	1.45	1.15	1.02	0.37
S	-	-	0.1	-	-	0.01	0.23	0.11	0.03	0.39
Ca	4.58	0.27	**38.9**	001	0.01	3.20	0.11	0.06	0.10	26.50
K	0.54	0.06	0.13	2.42	1.49	0.77	0.55	1.07	1.14	0.19
Mg	0.99	0.45	0.48	0.09	0.19	0.33	0.24	0.41	0.24	5.52
P	0.07	0.02	5.0	0.01	0.02	0.18	0.25	0.12	0.06	0.02
Sr	0.02	0.00	0.14	-	-	0.06	0.07	0.08	0.05	0.08
Ba	-	-	-	-	-	0.66	0.07	0.11	0.12	0.06
Na	1.49	0.13	-	0.04	-	0.09	0.04	0.08	0.02	0.05
Mn	0.12	0.04	0.01	-	0.04	0.03	0.01	0.01	0.01	0.01
Si +Al+Fe	29.76	39.18	14.39	42.35	44.94	43.98	46.54	46.74	47.35	24.41

pH variation of the OLA sample



Cation-exchange Capacity

$$CEC = \left(\frac{\text{Concentration of } Ca^{2+}\ (\mu g/ml) \times 100 \times \text{Vol. of extract (ml)}}{\text{Equivalent weight of the cation} \times 1000 \times \text{wt. of sample (g)}} \right)$$

IS:2720

Material	CEC(meq./100g)
CS	18.6
WC	5.0
IC	12.6
RSS	3.5
BSS	3.4
FA-I	4.5
FA-II	5.2
C-I	3.9
C-II	4.1
GGBFS	Not applicable

23.10.2015 **Lecture No. 22** **Lecture Name: Geomaterial Characterization**

Sub-topics

- Specific Surface Area determination
- Chemical characterization
    - Pore-solution sampling
    - Corrosion potential
    - Sorption-Desorption
- Thermal Characterization
- Electrical Characterization

Specific-surface Area (SSA)

Soil-water-contaminant interaction is strongly dependent on SSA

SSA is indicative of activity (reactivity) of fine-grained soils

A classification scheme based on SSA would help to establish:

- Swelling and shrinkage characteristics
- Frost heave
- Collapse and compressibility
- Cation-exchange capacity
- Water retention characteristics
- Sorption and desorption characteristics

These characteristics mainly depend on the grain-size distribution of the soil (i.e., the clay-size fraction) and its mineralogical composition.

SSA can capture the combined effect of these factors and hence, can be used for predicting engineering behavior of fine-grained soils.

Determination of SSA of fine-grained soils

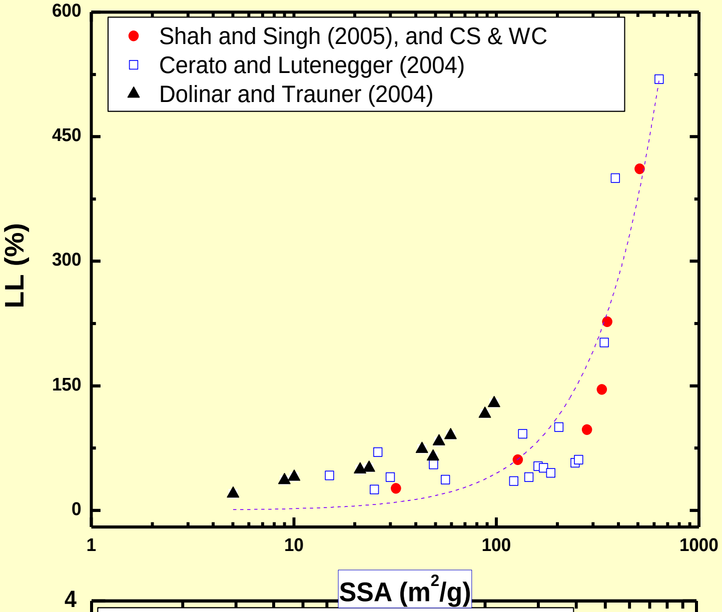
A. gas or vapor adsorption techniques
   - BET nitrogen adsorption
   - water-vapor adsorption

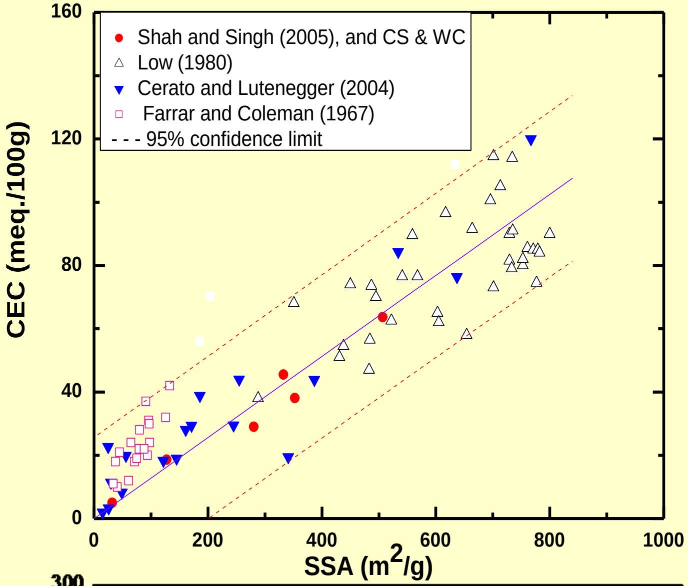
B. absorption of the polar liquids and dyes on the soil surface
   - Ethylene glycol (EG) method
   - Ethylene Glycol Monoethyle Ether (EGME) method
   - p-Nitrophenol method
   - Methylene blue (MB) dye method

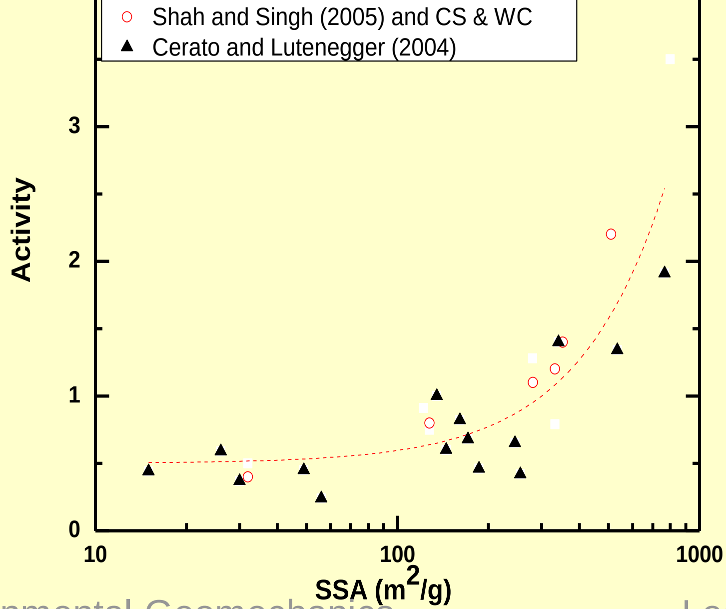
C. application of the state-of-the-art instruments
   - Mercury intrusion porosimetry (MIP)
   - Internal reflectance spectroscopy
   - X-ray diffraction
   - Gas pycnometer

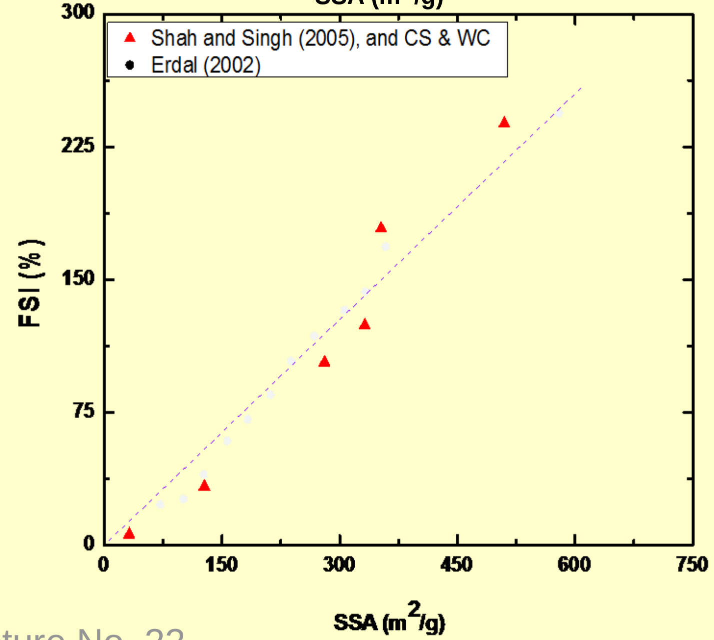
Some Relationships

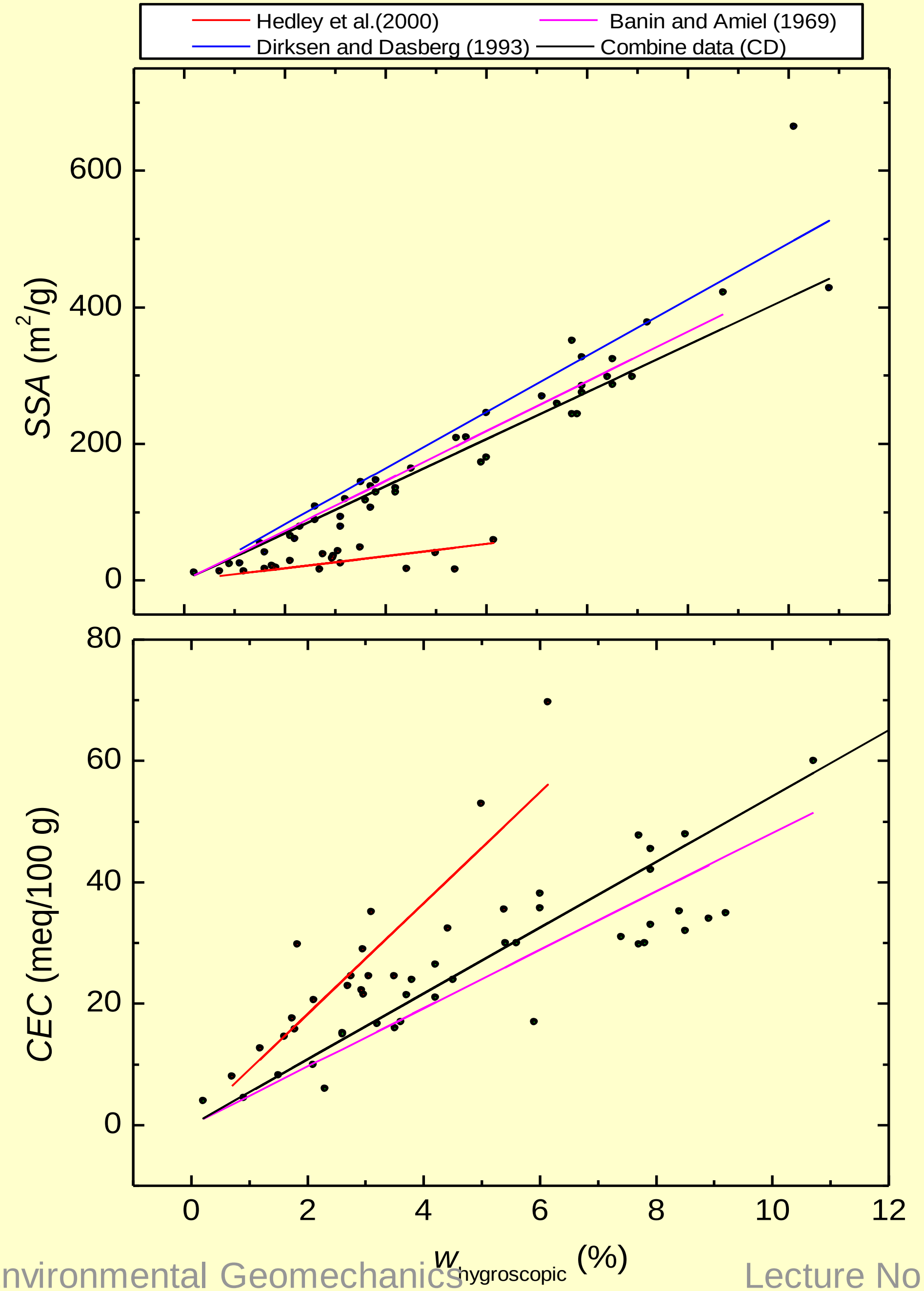
Arnepalli, D.N., Shanthakumar, S., Rao, H.B. and Singh, D.N., “Comparison of Methods for Determining Specific Surface Area of Fine-grained Soils", **Geotechnical and Geological Engineering**, 2008, 26(2), 121-137.











$$SSA=0.0012\cdot(\sigma_h/\sigma_{dry})+16.6$$

$$SSA=1.88k_{diff}+9.4$$

SSA (in m^2/g)

σ_h, σ_{dry} : Hygroscopic and dry soil electrical conductivity, respectively

k_{diff} ($=k_h-k_{dry}$)

Shah, Paresh H. and Singh, D. N., "**Methodology for Determination of Hygroscopic Moisture Content of Soils**", Journal of ASTM International. 3(2), (2006), 14 Pages.

pH determination

Glass calomel electrode is used

Soil solutions with different Liquid to solid ratios

pH
Temperature
Total Dissolved Solids
Electrical Conductivity
Chemical Oxygen demand
Biological Oxygen Demand

Chloride and Sulphite contents determination

The chloride and sulphite contents of the soils can be obtained on an extract of 2:1 Liquid to solid ratio.

Indion Easy test kit (Ion Exchange, India Ltd.), an ion exchange resin, is employed

A sort of a titration

Change in color of the solution due to addition of chemicals

Determination of Cation exchange capacity (CEC)

Is the amount of cations a soil can hold.

Summation of exchangeable cations (Na^+, K^+, Ca^{+2} and Fe^{+3})

Factors affecting CEC are: charge carrying capacity of the soil, pH, ionic strength of the pore-solution and presence of salts.

Guidelines presented by IS 2720 (part XXIV, 1976) and (EPA SW-846) are followed for the determination of CEC of the soil sample.

IS 2720 (Part XXIV 1976):

The sample is first treated with hydrogen peroxide (H_2O_2), and boiled thoroughly for 1 h to remove organic contents.

The treated sample is oven-dried and its 5 g is mixed with 50 ml 1N Sodium acetate (CH_3COONa) solution with pH=5.

This mixture is digested in a boiling water bath for 30 min., with intermittent stirring, and later centrifuged at a speed of 5000 to 6000 rpm, for 15 min.

The supernatant liquid is discarded and the sample, settled at the bottom of the centrifuge tube is again treated with 50 ml of 1N CH_3COONa solution (pH=5) and centrifuged. Repeat this process thrice, so as to ensure exchange of Ca^{2+} in the soil by Na^+, completely.

This sample is treated with 1N Calcium chloride ($CaCl_2$) solution and is again digested and centrifuged. This process is repeated thrice, so as to ensure exchange of Na^+ by Ca^{2+}.

The sample is treated again with 50 ml 1N CH_3COONa solution (pH=7) and again digested and centrifuged. This operation is performed thrice.

The resulting supernatant from the last three steps is collected in a 250 ml volumetric flask, and the concentration of Ca^{2+} present in the solution is determined using the Atomic Absorption Spectrometer, AAS.

$$\text{CEC (meq./100g)} = \left(\frac{\text{Concentration of } Ca^{2+} \text{ or } Na^{+} \ (\mu g/ml) \times 100 \times \text{Vol. of extract (ml)} \times \text{dilution}}{\text{Equivalent weight of the cation} \times 1000 \times \text{wt. of soil (g)}} \right)$$

Minerals Present in soils(XRD)	CEC (meq./100g)
Montmorillonite	**18.6**
Kaolinite, Illite	**4.989**

Pore-solution Sampling

The pore-solution sampling is identical to blood sampling

A Prerequisite to Soil-Water-Contaminant Interaction Studies

To predict transport/fate of contaminants in the soil mass

Design of suitable containment/Barrier system

Assessment of safe waste disposal limits: Quantity & Concentration

Leaching/Attenuation characteristics of soils

Intrusion of pollutants in ground water resources

Prediction of the loss of nutrients from the root zone

Detection of the microbial activity in soils

Validation of solute transport models

Sampling Techniques

In-situ (Field)

- Lysimeter
    - Zero-tension Lysimeter
    - Tension Lysimeter
- Soil Salinity Sensors

- Absorption Techniques

Laboratory

- Centrifugation
- Pressure-membrane extractor (PME)

In-situ studies

Objective:

To simulate disposal facility in a Control Volume

based on moisture movement

concentration of contaminant(s)

Using a Lysimeter

A device which collects and senses percolating water through soil mass and helps in determining the Concentration of water soluble contaminant(s)

As a function of time and space

Lysimeter Studies

- Simulate the effect of percolating rainfall on the release of contaminants from waste froms

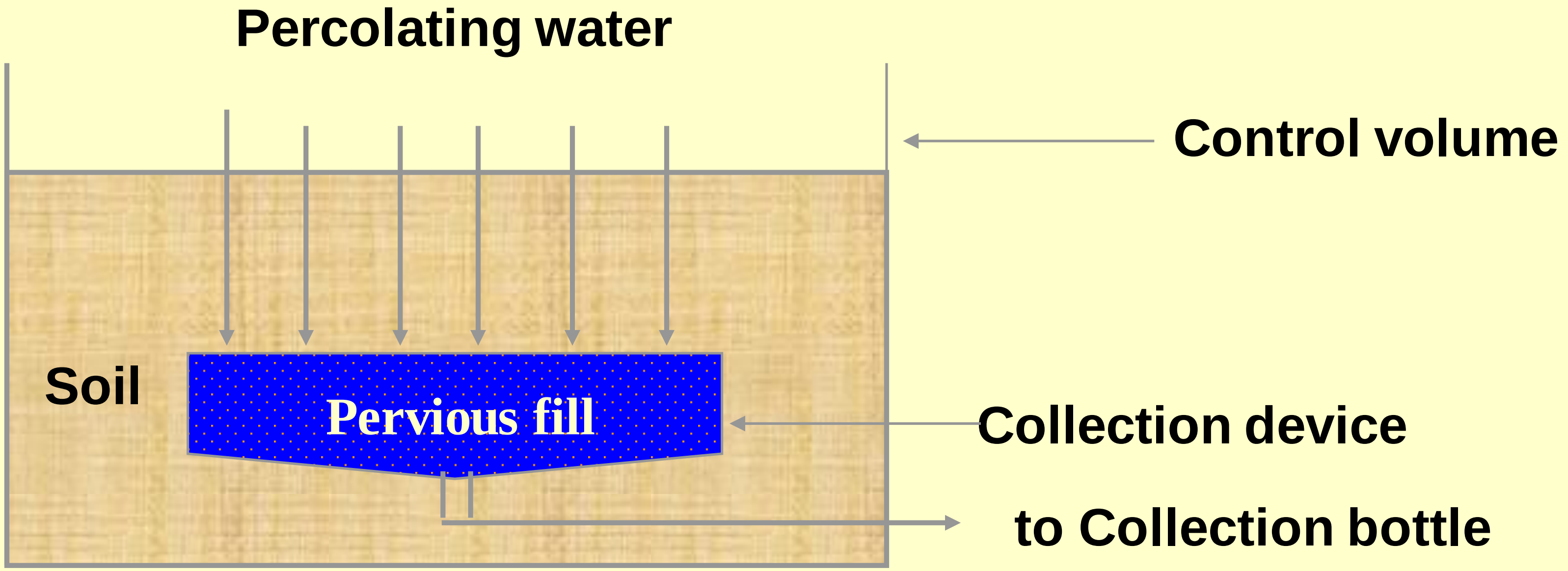
- Provide insight in understanding the site as well as validating water balance studies and radionuclide migration in the unsaturated zone

- Data obtained from the study provide a link between the laboratory and field conditions and thus aid in predicting radionuclide migration from shallow land disposal facility

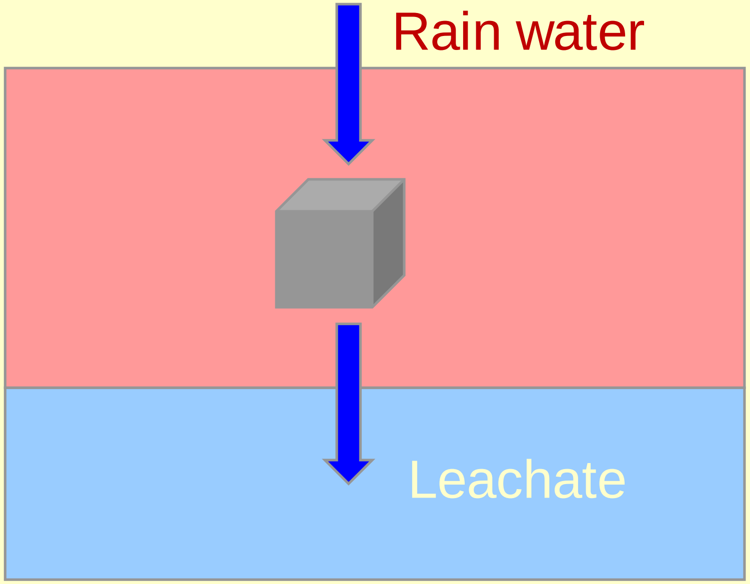
Lysimeter (Pore Solution Collection Device)

Zero Tension Lysimeter

Collects Pore Solution From Saturated Soils



Basic Philosophy



Upper compartment with fill material, sensors and moisture extraction cups

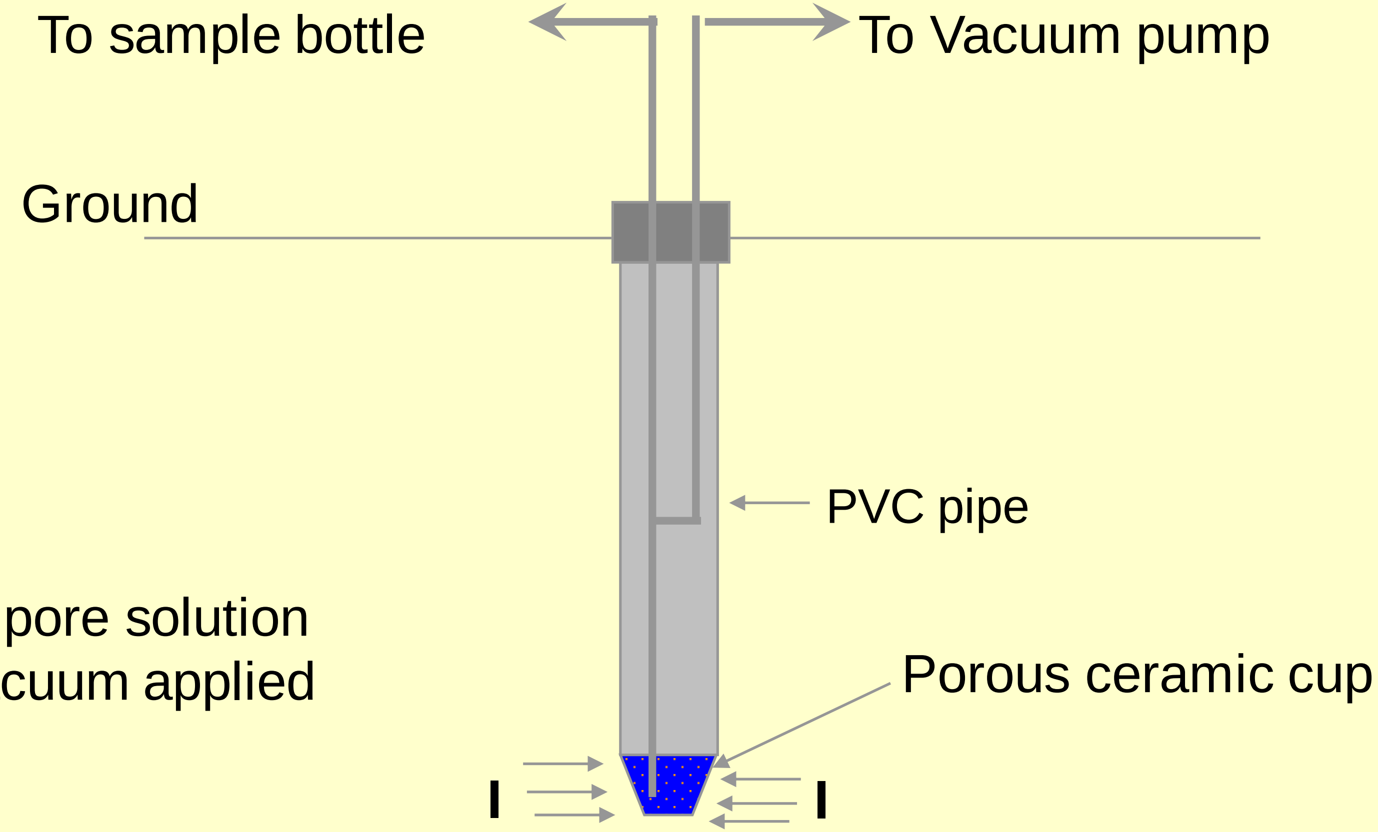
Lower compartment for leachate collection

- Performance assessment of solidified radioactive waste
- Attenuation properties of soils

Validation of theoretical model by fitting
Mathematical model to Lysimeter data

Tension Lysimeter

Collects pore-solution from “Unsaturated Soils”



I – Inflow of pore solution under vacuum applied

Soil Salinity Sensors

Used for in situ measurement of soil salinity

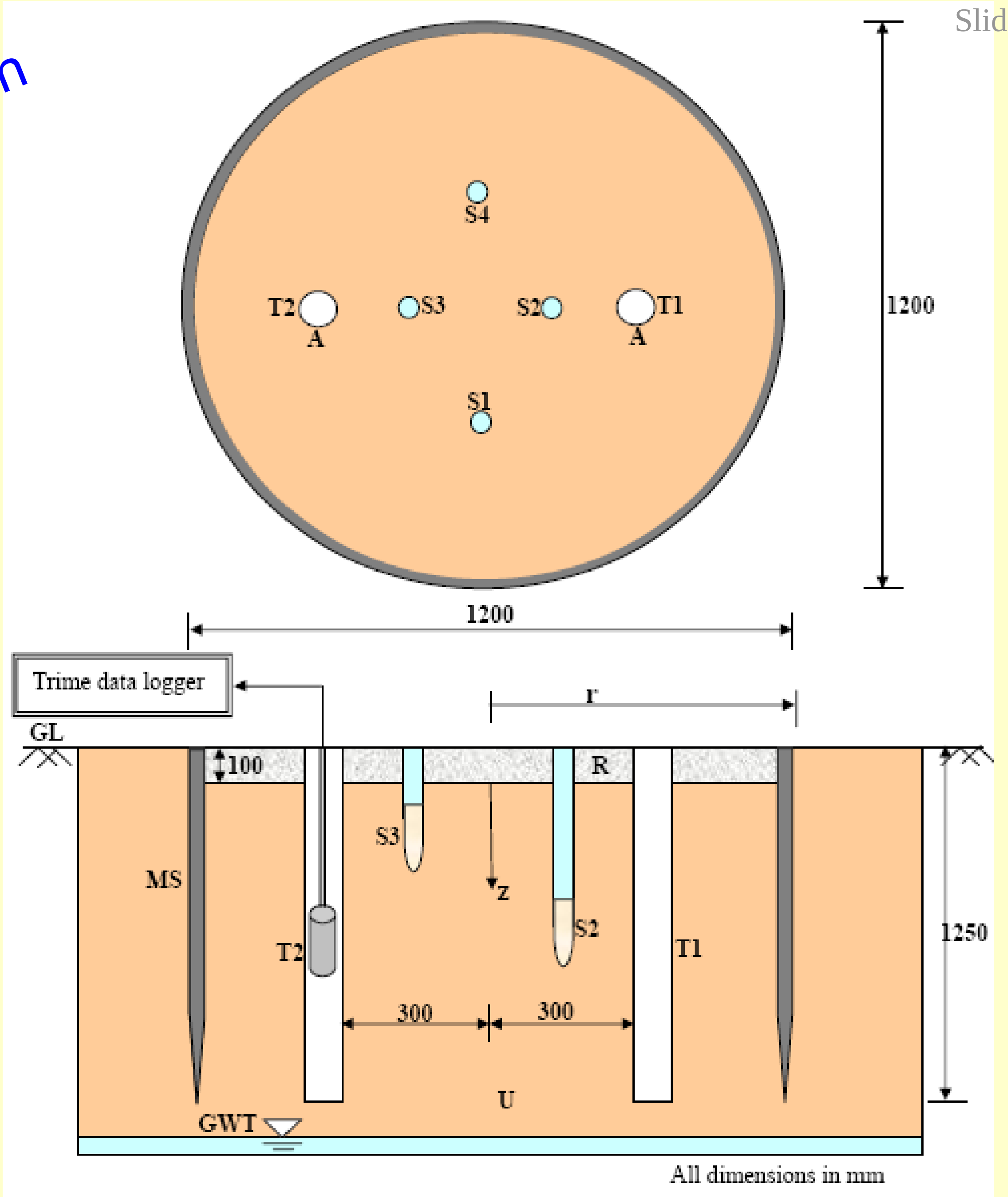
Soil salinity is an indication of soil contamination

Absorption techniques

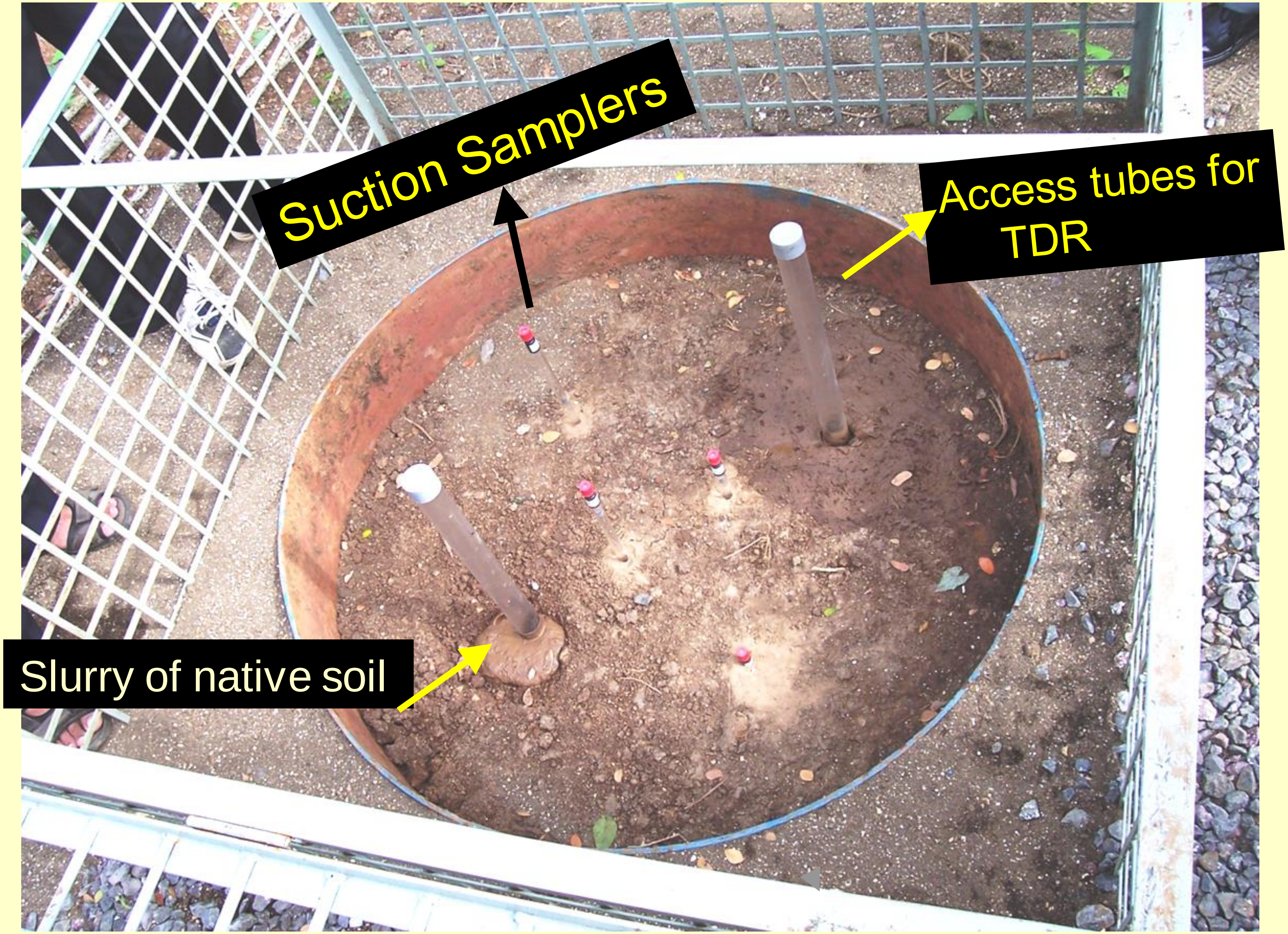
Sponge material as absorbent for sampling pore solution

- Large surface area of the sponge improves sampling efficiency
- Not a fully harnessed method

Details of Instrumentation in the lysimeter



R is the soil spiked (with Cs, Co & Tritium)

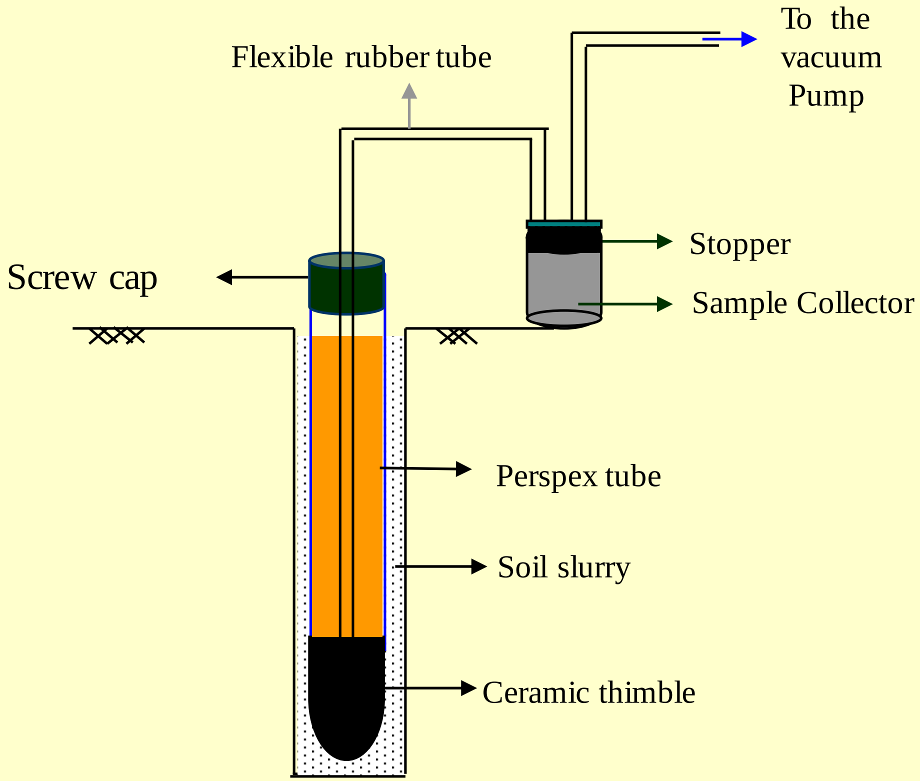


Suction Samplers

Access tubes for TDR

Slurry of native soil

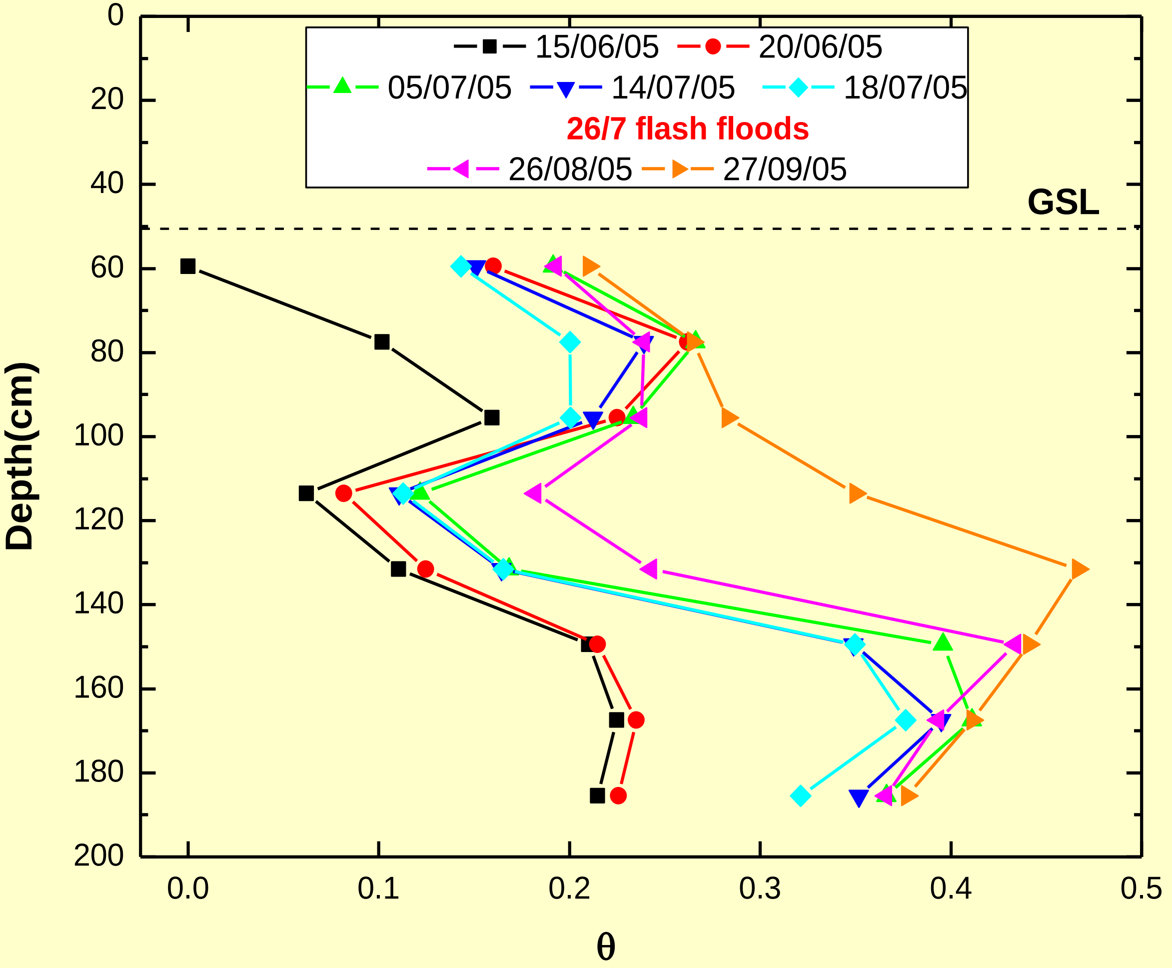

Vial for pore-solution collection



Details of the suction sampler

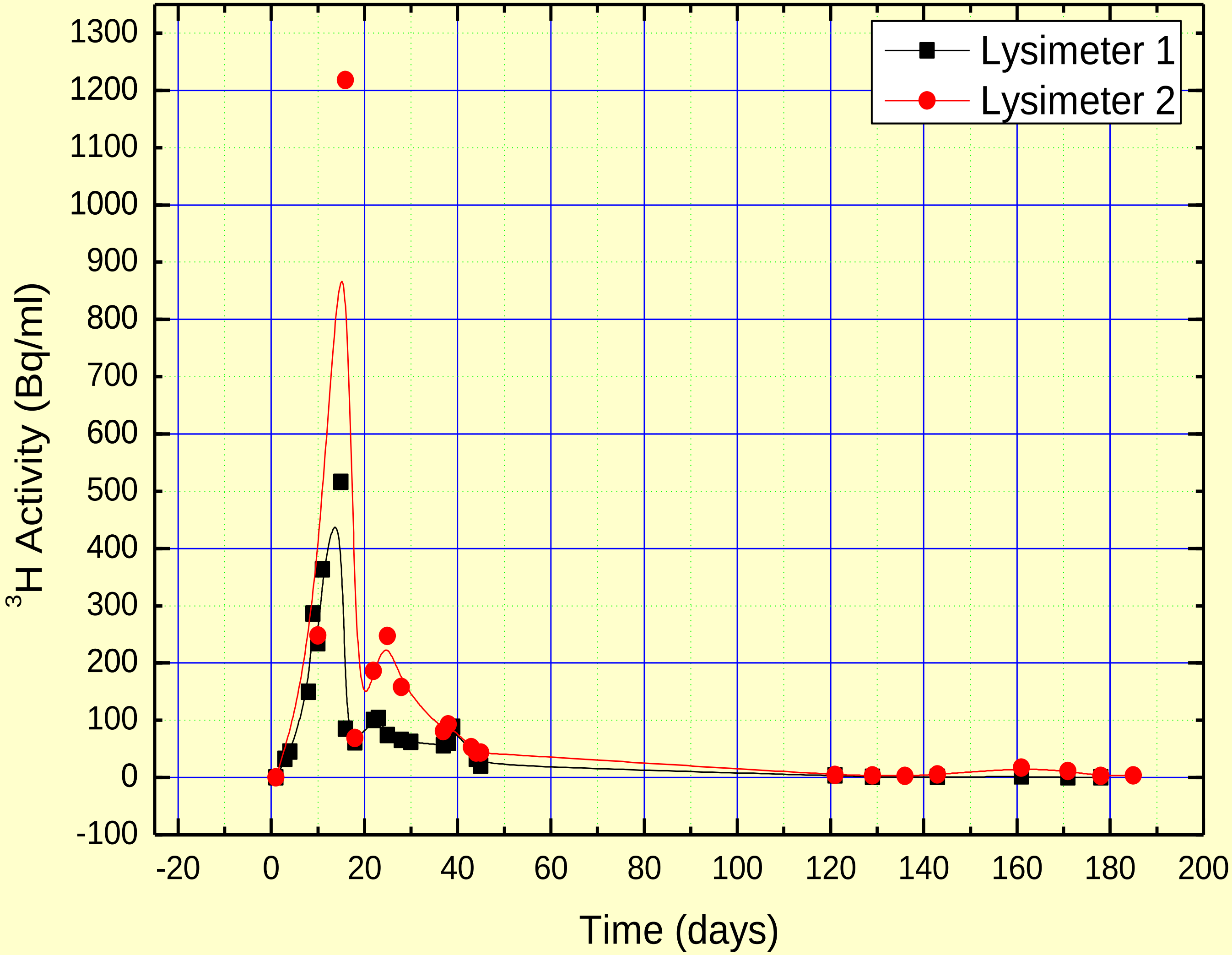
Activities at a Glance

TDR studies

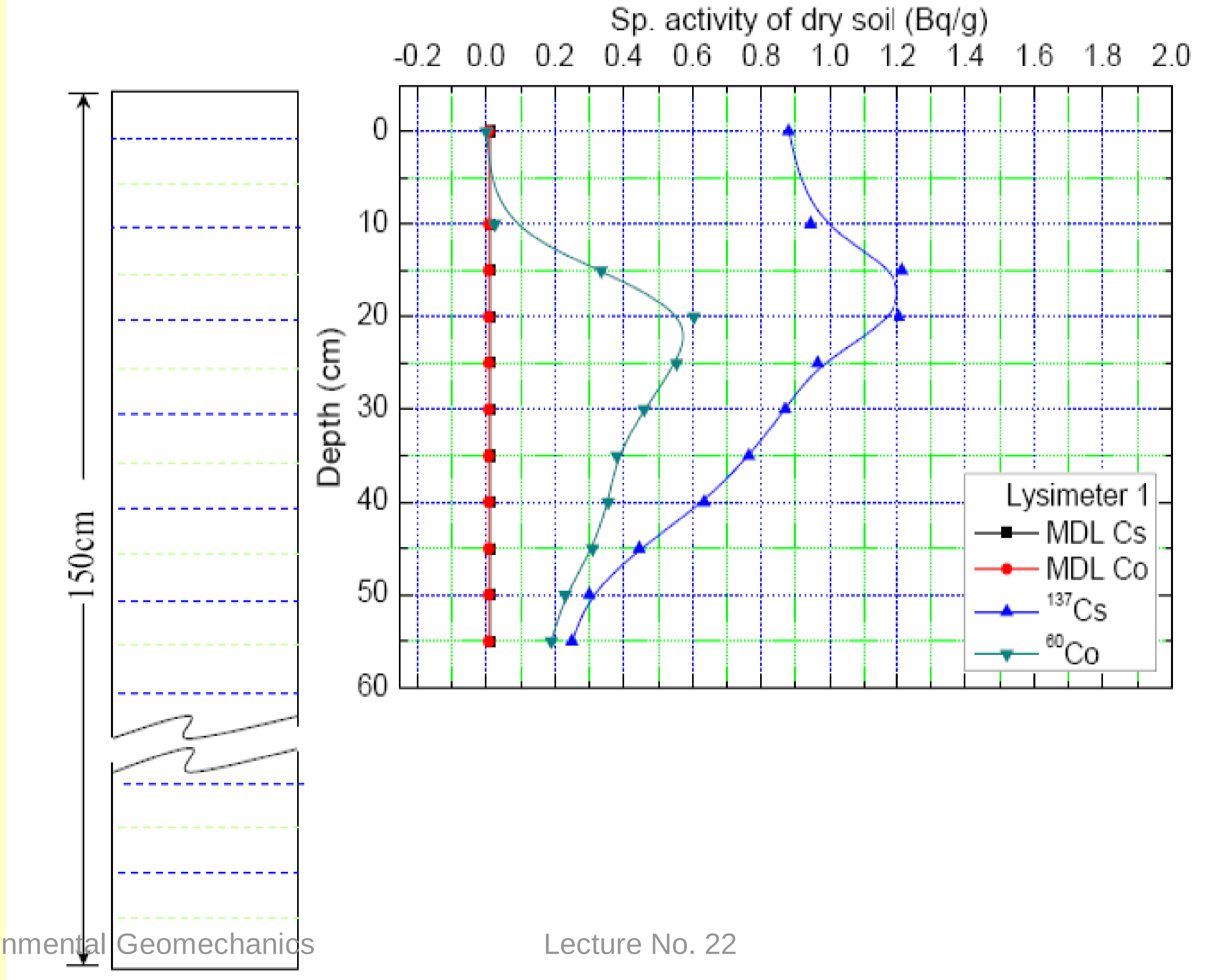


Hanumantha Rao, B, Sridhar, V., Rakesh, R.R., **Singh, D.N.**, Narayan, P.K. and Wattal, P.K., "Application of In-situ Lysimetric Studies for Determining Soil Hydraulic Conductivity", **Geotechnical and Geological Engineering, 2009**, DOI 10.1007/ s10706-009-9260-5. Published Online: 13 May 2009.

Variation of ^{3}H activity concentration with time in pore solutions in different Lysimeters at approx. 40 cm depth

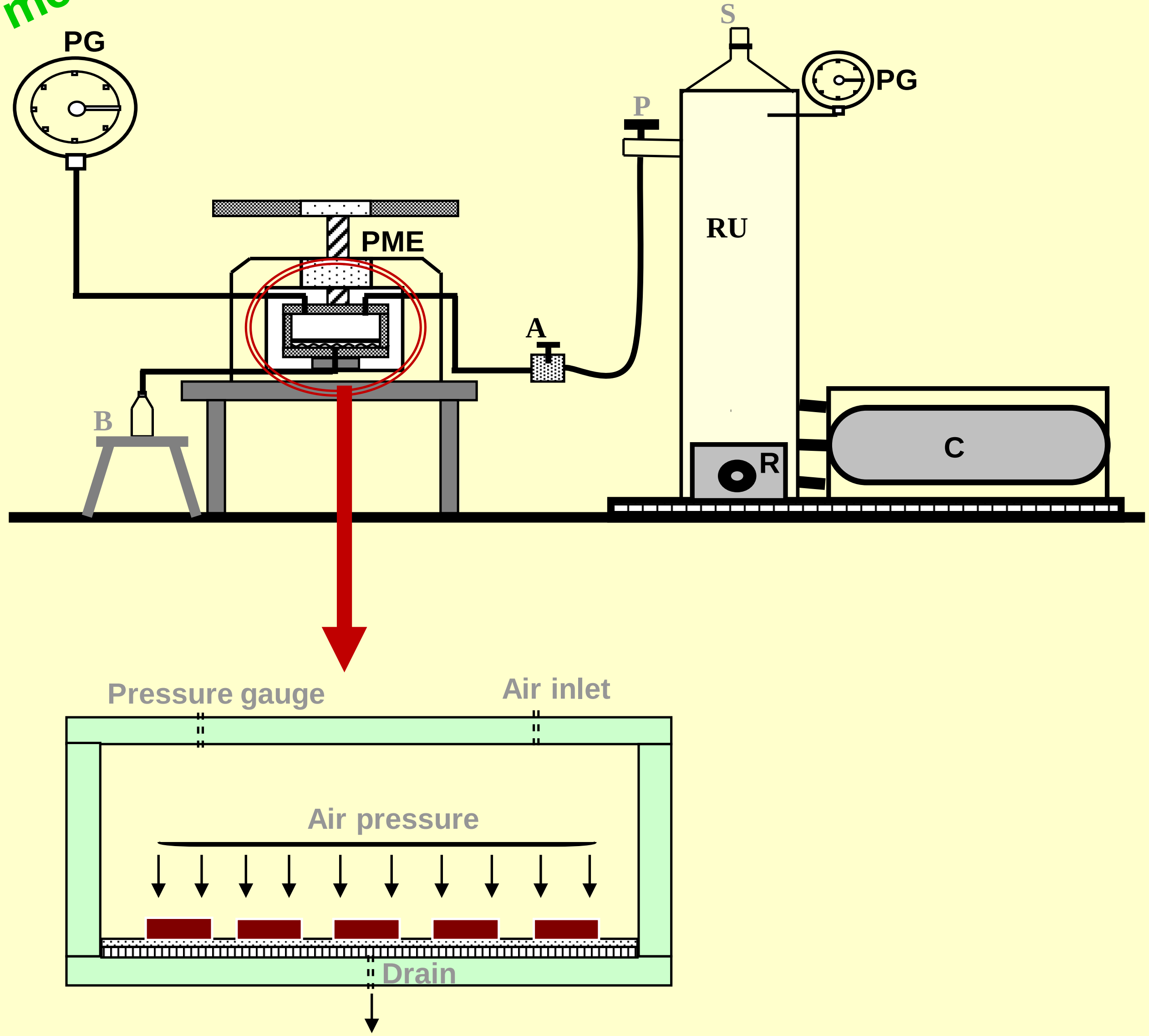


Variation of ^{137}Cs and ^{60}Co activity concentration with depth in dry soils after a period of 500 days



Pressure Membrane Extractor

Laboratory method



Expelled water to the sampling bottle