2 nd International Conference

Strategies toward Green Deal Implementation

Humic Substances and their Role in Waste Management

Inovatīva atkritumu stabilizācija - vides ietekmju mazināšana un resursu potenciāls aprites ekonomikā
Projekta numurs 1.1.1.2/16/I/001
Pētniecības pieteikuma numurs 1.1.1.2/VIAA/3/19/531

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Prof Maris Klavins

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LATVIJAS UNIVERSITĀTE ANNO 1919
NACIONĀLAIS ATTĪSTĪBAS PLĀNS 2020
EIROPAS SAVIENĪBA
Eiropas Reģionālās attīstības fonds
IEGULDĪJUMS TAVĀ NĀKOTNĒ

Properties and structure of peat humic acids

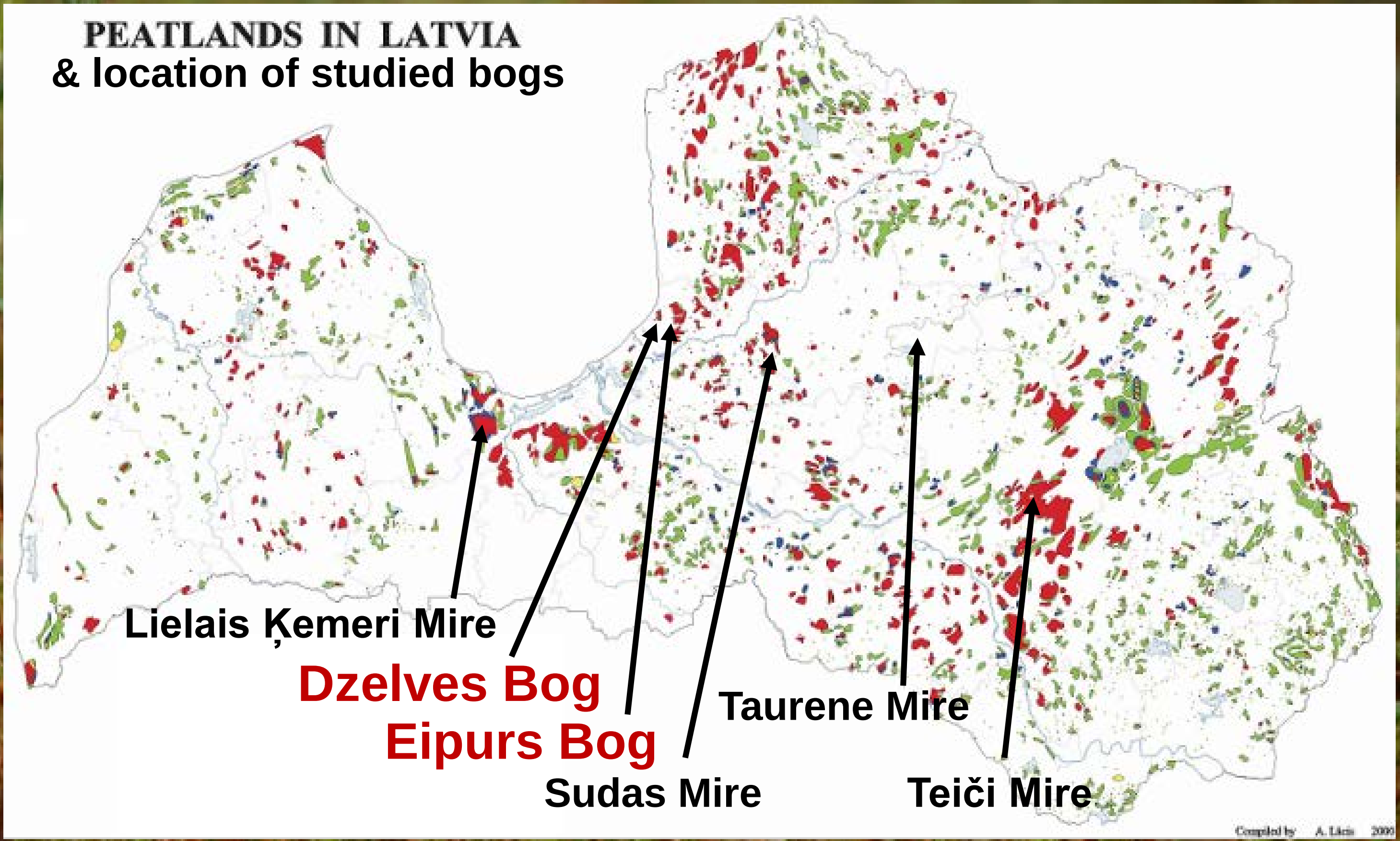
In peat the transformation and decay process of living organic matter (humification) is taking place in acidic and anaerobic environment

Humification is a three step process of:

1. degradation of components of living organic matter;
2. reassembly of the degradation products into humic substances;
3. the degradation of the humic substances formed in step 2.

The components of plant tissues during humification process can undergo three possible types of degradation reactions:

1) biotic (enzymatically catalyzed) reactions;
2) pyrolytic reactions,


PEATLANDS IN LATVIA
& location of studied bogs
Lielais Ķemeri Mire
Dzelves Bog
Eipurs Bog
Sudas Mire
Taurene Mire
Teiči Mire
Compiled by A. Lācis 2000


LEGEND
raised bog
mixed mire
transition mire
fens and wet forests on peat
mire > 100 ha
mire from 31 ha to 99 ha
peat extraction site
protected mires

Isolation of peat humic and fulvic acids

Isolation of humic acids

Humic acids

Methods

Element composition (C, H, N, S, O)

O/C, H/C, N/C

Ratio E_4/E_6 and E_2/E_3

Hydrophobicity

Carboxylic groups

Total acidity

UV, Fluorescence, ESR, FTIR spectra

^1H, ^{13}C NMR spectra

Micro- and macroelement concentration

- Despite major differences in precursor biological composition, the properties of peat humic acids are relatively similar, thus stressing significance of microbial decay process as a major group of factors affecting humification process
- Humification process within a bog body occur differently in acrotelm (upper aerobic layer), catotelm (middle anaerobic layer, and bog bottom layer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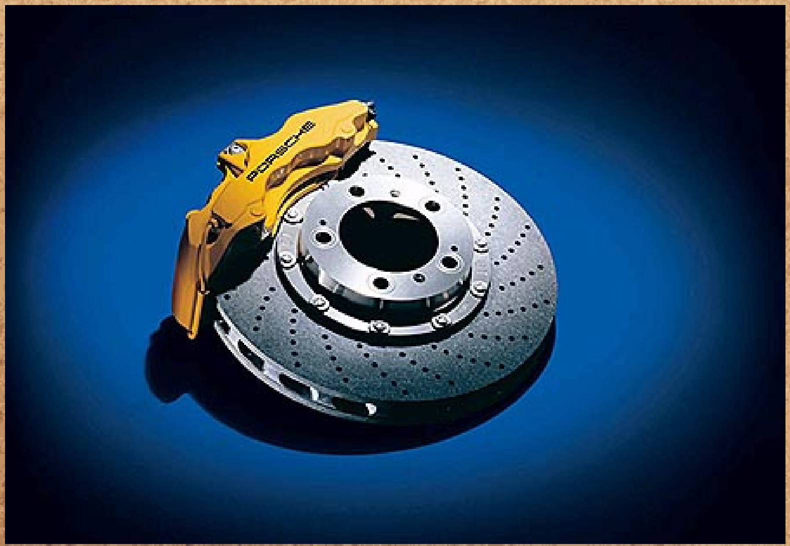
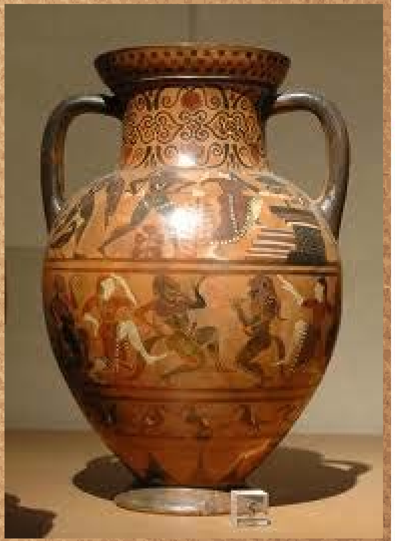
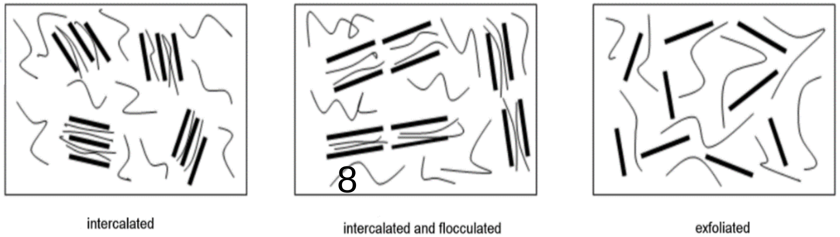

PORSCHE


Bentonite for Drilling

www.zahana.org ©2006 Ihanta

intercalated
intercalated and flocculated
exfoliated

What is Clays and Clay Minerals

Clays are:

Size: less than 2 um in general

Chemistry: phyllosicates with different cations

Crystal structure: monoclinic, triclinic

Morphology: various, depend on the species of clay

Common clay minerals: kaolinite, smectite (montmorillonite), and illite.

Other clay minerals: Halloysite, chlorite, vermiculite, attapulgite, sepiorlite, palygorsite, miexed-layer clays, and allophane.

Prior to 1923, clays were thought to be amorphous (Hadding, 1923)

Reference: Clay mineralogy: Grim, 1968

Very small particles – provide very large surface area
Negatively charged surface – provide very active surface for chemical interaction

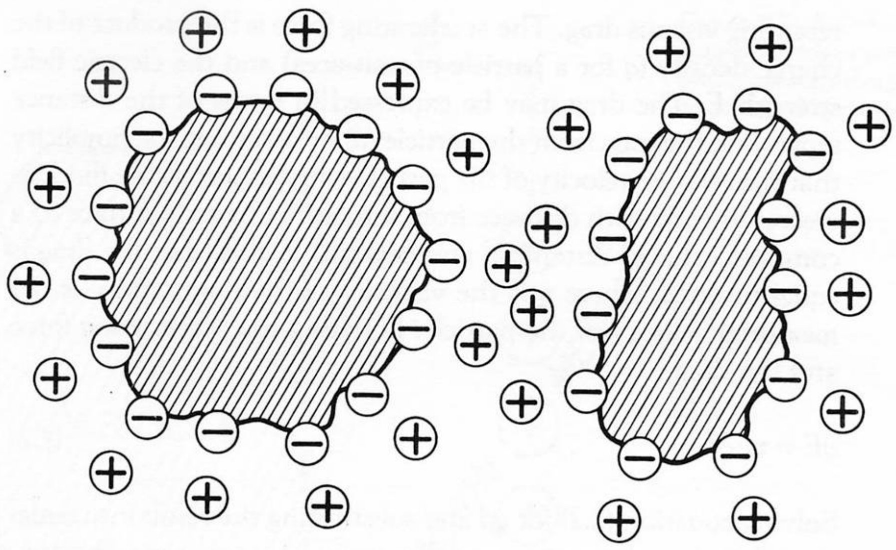


Figure 2.8 *Electrostatic repulsion between the like-charged ion layers tends to prevent coalescence of particles in suspension.* (From Bennett and Hulbert, 1986)

- Zeolites contain void space that can host cations, water, or other molecules
- Molecular sieves
  - Do not allow molecules larger than 8 to 10 nm to enter lattice
- Zeolites:
  - 40 known natural zeolites
  - > 140 synthetic zeolites

"Green Chemistry with Zeolite Catalysts." *Chemical Engineering, The Chemical Engineers'Resource Page, Distillation, Heat Transer, Design, Spreadsheet Solutions, Departments, Chemistry*. Web. 22 Apr. 2010.

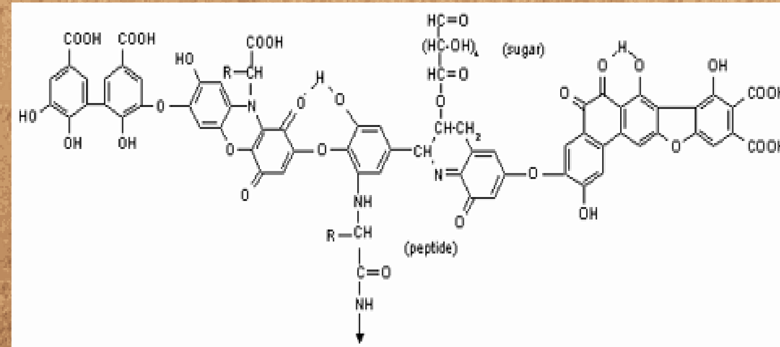
http://www.freefoto.com/images/13/53/13_53_21---Sunset--Teesside-

Environment

[Picture: http://www.cerpa.appstate.edu/images/environment.jpg](http://www.cerpa.appstate.edu/images/environment.jpg)

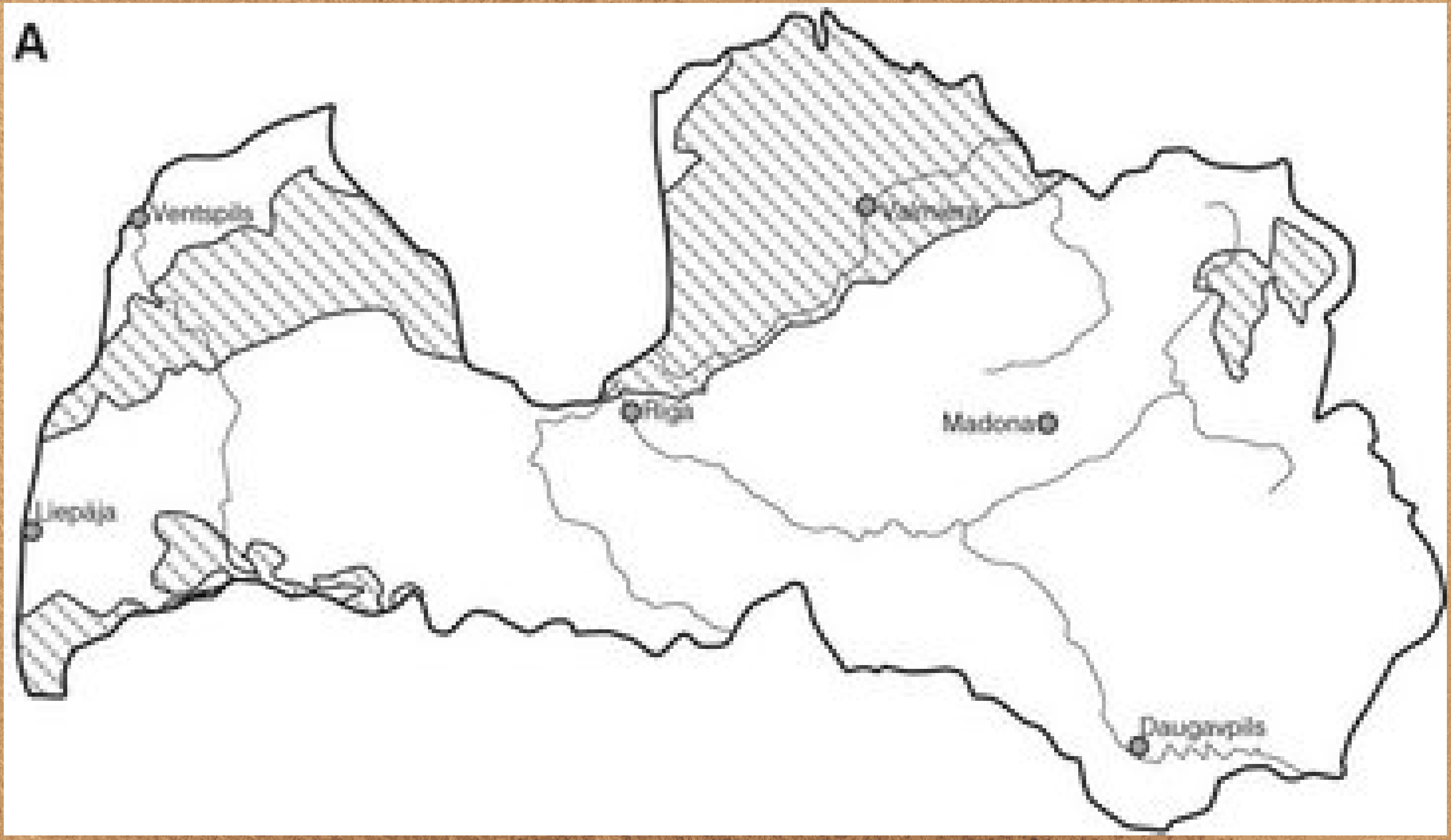
- Contribute to a cleaner, safer environment
- In powder detergents, zeolites replaced harmful phosphate builders
- Solid acids, zeolites reduce the need for corrosive liquid acids
- Redox catalysts and sorbents
  - Remove atmospheric pollutants, such as engine exhaust gases and ozone-depleting CFCs.
- Zeolites can also be used to separate harmful organics from water
  - Heavy metals and NH_4^+

"Green Chemistry with Zeolite Catalysts." *Chemical Engineering, The Chemical Engineers'Resource Page, Distillation, Heat Transer, Design, Spreadsheet Solutions, Departments, Chemistry*. Web. 22 Apr. 2010. <http://www.cheresources.com/zeolitezz.shtml>

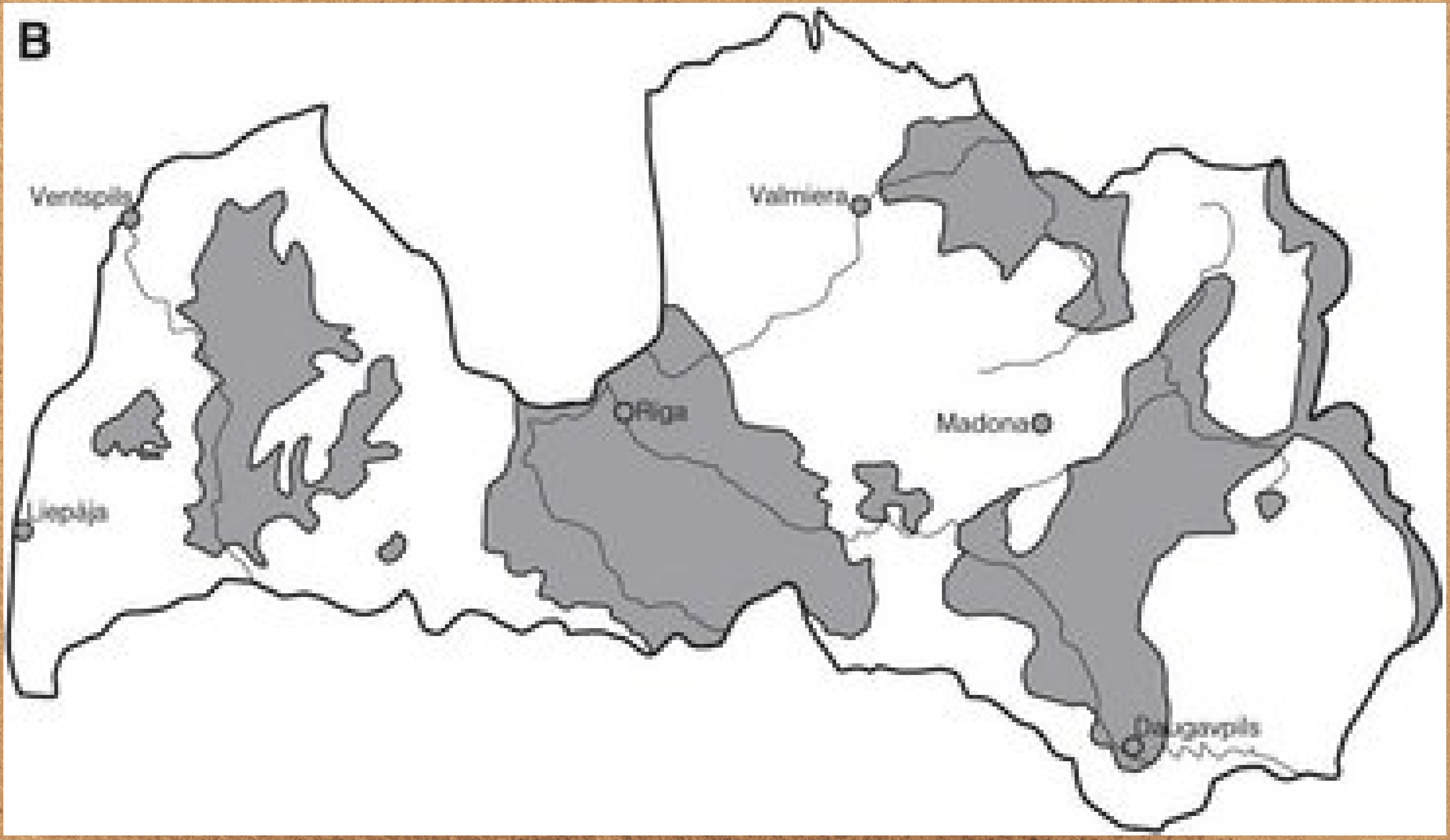


Model structure of humic acid

DEVONIAN and TRIASSIC CLAY IN LATVIA



QUATERNARY CLAY IN LATVIA



SCOPE OF THE STUDIES

The aim of the work is to provide alternative solution for landfill closure by giving theoretical considerations from multidisciplinary knowledge of environmental engineering, chemistry and waste management

TOPICALITY OF THE RESEARCH

- The landfills are systems with pollution and aftercare period that takes a long time
- Humic substances has own unique chemical category with distinct unique properties, and those might be isolated from the organic mass
- Clay components and humic acids treatment performed to contaminated soil with heavy metals as model contaminants has been done previously and might be a good solution
- Modified clay may also capture pharmaceuticals which is huge leachate problem at landfills

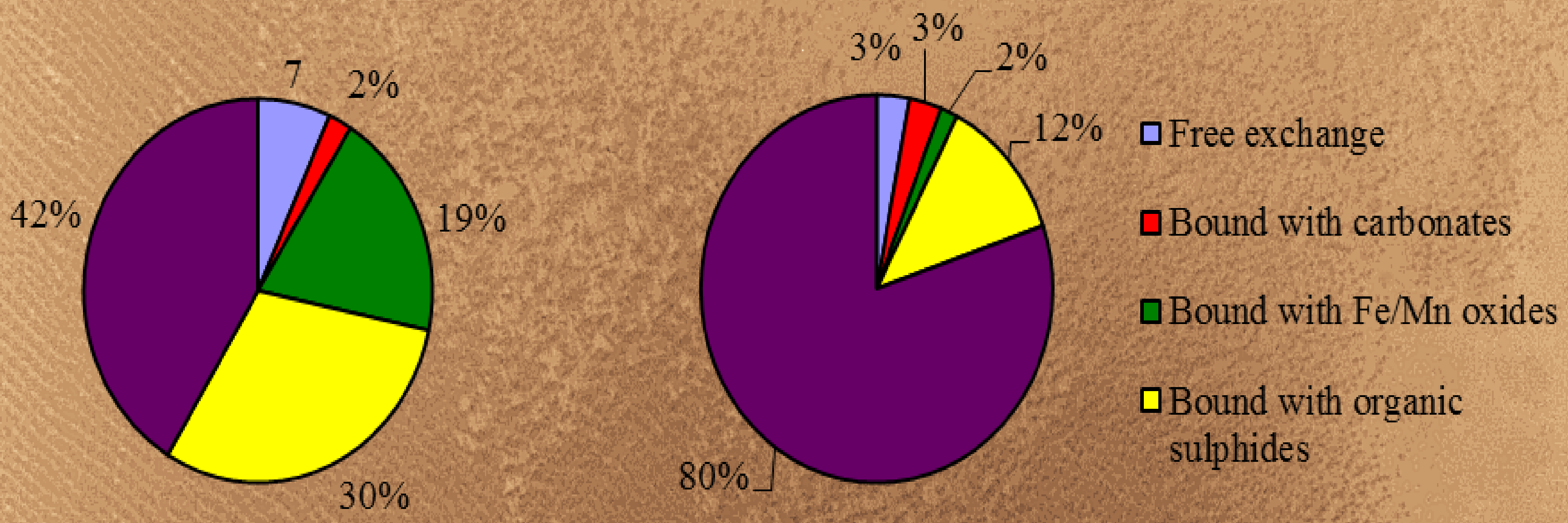
Field work	Experimental work	Analytical work	Sorption kinetics

Triassic clay deposit, dominantly smectite >75%, illite 10-20%, clayey fraction (<0.005 mm) varies ~43 %, aleirolitic ~40%

Field work	Experimental work	Analytical work	Sorption kinetics

Metal ion complex formation with its natural ability of metal complexation is of unexplored potential for landfill coverage in future. The strength of the interaction among organic ligands and metals may be modeled as a function of pH and reactant concentration (Byrne *et al*., 2011) and experimentally proves usefulness of natural clays and humic substances as remediation amendment for contaminated soils in dumps

Field work	Experimental work	Analytical work	Sorption kinetics



Illustrative example of enhanced copper stability (a) copper with no humic amendment; (b) copper with humic amendment

Field work	Experimental work	Analytical work	Sorption kinetics

Metal ions in the solution as well as the ability of metals to bind with humic acids and clays are calculated according formulas (1) and (2)

Cu+HS=CuHS

where the Cu is the amount of Cu^{2+} moles in solution and HS – amount of moles of humic acid in the solution, and

$$Ko = \frac{CuHS}{[Cu]\cdot(HS - CuHS)}$$

(2),

where [Cu] – concentration of hydrated Cu^{2+} in the solution; Ko - stability constant of complex forming; CuHS – amount of moles, which are included in complexes (Bresnahan, Grant, &Weber, 1978)

Field work	Experimental work	Analytical work	Sorption kinetics

- Scanning Electron Microscopy (*SEM)*

thin layer of gold
and palladium powder
ion coater (JB-3, Eiko, Japan)

- Fourier transform infrared spectroscopy (FTIR)

Perkin Elmer Spectrum BX FT - IR System spectroscope

Field work	Experimental work	Analytical work	Sorption kinetics

- Brunauer–Emmett–Teller *(BET)* test

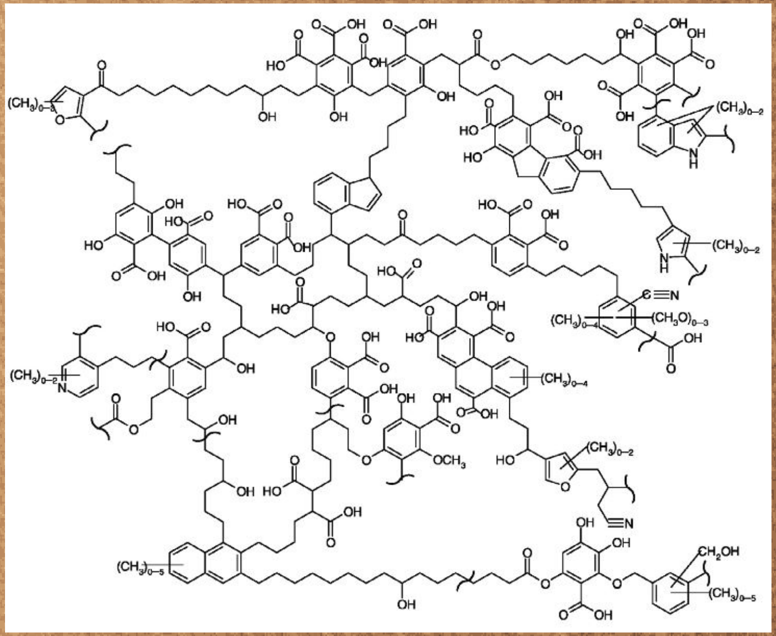
  nitrogen multilayer adsorption
  Micromeritics instrument:Gemini2360

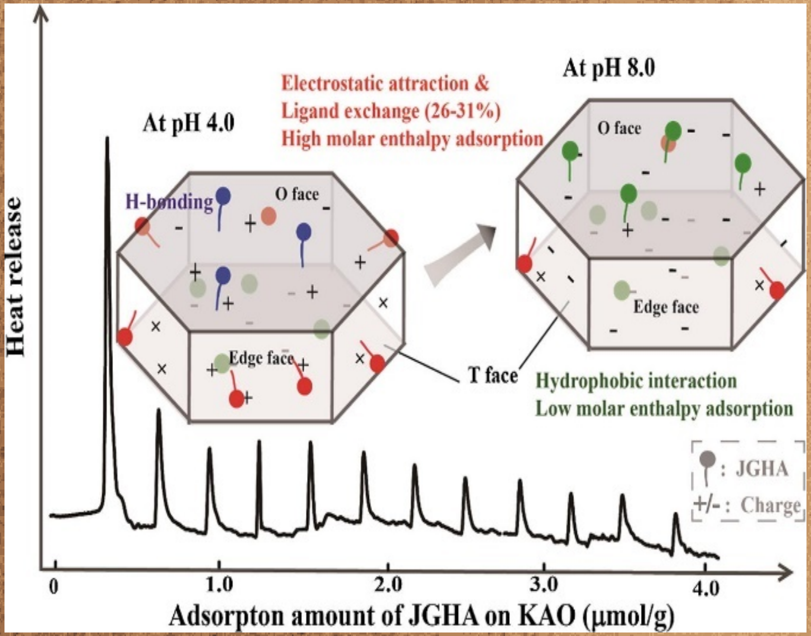
- Powder X-Ray Difractometry *(PXRD)*

Series of experiments by using humic substances have shown promising results for diminishing the content of biologically available Cu and Pb, ingredients might be of good use for using in landfill closure to stop the migration of heavy metal pollution when closed by innovative fine fraction material mixed with modified clays

NOVELTY

Innovative clay sorbents produced from local resources can be offered for applied remediation





Effective at pharmaceuticals hunting

Recent studies have shown that clay minerals and clay-humic acid composites can be natural, low cost and effective sorbents to remove various pharmaceutical products from environment

For example, montmorillonite has been used to remove pharmaceutical products such as tramadol and doxepine (Thiebault, Guegan, & Boussafir, 2015); kaolinite to remove ofloxacin (Li, Bi, & Chen, 2017); and natural clay (mainly consisting from smectite and kaolinite) to remove ibuprofen, naproxen and carbamazepine from aqueous solutions (Khazri *et al*., 2017)

Summary I

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Summary II

The landfill closure process has similarities with environmental remediation process; however, there are additional components related whether the capping of contamination includes the need of sorption, such as water of irrigation or leachate recirculation and total produced leachate treatment with innovative materials

Innovative closure of landfills by capping with landfill mined fine fraction material mixed with modified clay with humic substances is one of prospective solutions

More studies are needed and modelling elaborated in order to find the right recipe for finding the best constituents to stop leaching of pollution out of the landfill as well as mitigate greenhouse gas emissions through methane degradation

This study was supported by Project 1.1.1.2/VIAA/3/19/531 “Innovative technologies for stabilization of landfills - diminishing environmental impact and resources potential in frames of circular economy”

Dziękuję!

THANK YOU FOR ATTENTION!

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