Third seminar of European PhD students working on various subjects in the field of Water & Health

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The emerging pollutants and individual wastewater treatment system: What about the role of soil in purifying the treated wastewater?

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Emerging pollutants:

are defined as compounds that are not currently covered by existing water-quality regulations, have not been studied before, and are thought to be potential threats to environmental ecosystems and human health and safety. Among these compounds are found parabens (**La Faré et al., 2008**)**.**

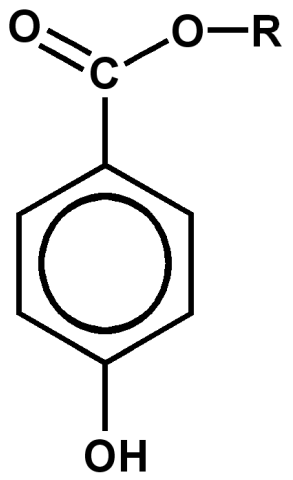
The PARABEN term:

• refers to a group of chemicals consisted of hydroxybenzoic acid esters (esters of methyl, ethyl, propyl, butyl or benzyl).

"Several forms of parabens are used in the daily life"

As <u>antimicrobial preservatives</u>

- in household products,
- cosmetics,
- pharmaceuticals,
- and food and beverage processing.



Searching for the effects of parabens?

- Estrogenic activity
  - adverse effects on male reproduction in **animal** studies
  - a factor of breast cancer development in **human** studies

(Human exposure to parabens is by dermal penetration or by ingestion)

- Toxicity activity
- Lateral effects
  - Irritation in organs

Now, let’s go into a Literature review…

A1) Human exposure to parabens

- **Ye XY et al. (2006)** assessed human exposure to parabens by measuring the conjugated or free species of parabens or their metabolites in urine. The results suggest that such conjugated parabens could be used as exposure biomarkers and finally this fact that conjugates appear to be the main urinary products of parabens and may be important for risk assessment.

A2) Human exposure to parabens

- **Janjua NR. et al. (2008)** examined the dermal adsorption of parabens. In conclusion it was revealed that BP is systemically absorbed, metabolized and excreted in urine following application on the skin in a cream preparation.
- **Calafat et al. (2010)** have assessed exposure to methyl, ethyl, propyl, and butyl parabens in urine samples of 2548 persons being more than 6 years old. After analysing the samples they detected different percents of paraben in samples.

B1) Affect of parabens on human health

- **Harvey P.W. and Darbre P. (2004, 2008 and 2010)** examined this hypothesis that if parabens affecting breast cancer incidence in women.

  They measured the intact esters of p-hydroxybenzoic acid (parabens) in human breast cancer tissues.

  They concluded that updated incidence figures show a continued incidence of breast cancer in Britain in the upper outer quadrant of the breast which is also the region to which multiple cosmetic chemicals are applied.

B2) Affect of parabens on human health

- **Paugazhendhi D. et al. (2005)** addressed the question of whether p-hydroxybenzoic acid, the common metabolite of parabens, possesses oestrogenic activity in human breast cancer cell lines. It has reported that this metabolite possesses oestrogenic activity in a panel of assays in human breast cancer cell lines. They concluded that removal of the ester group from parabens does not abrogate its oestrogenic activity.

C) Affect of parabens on animals

- **Yoshio N et al. (1998)** studied the relationship between the metabolism and the cytotoxic effects of the parabens in rats. Their results indicate that parent propyl-paraben induces cytotoxicity signs in rats.

- The oestrogenic activity of parabens was investigated by A. **Hosseini et al. (2000)** in mouse and rat. Considering the dose of paraben used in body, significant increase in the uterus weight was considered an oestrogenic effect.

- **S. Oishi (2002)** showed that propylparaben adversely affects the hormonal secretion and the male reproductive functions by a weak estrogenic activity in rat.

D1) Fate and metabolite of parabens in environment

- **P. Canosa et al. (2006)** investigated chemical transformations of four parabens, in chlorinated water samples. They noticed that chlorinated parabens were produced by chlorination and an hydroxyl group. They also detected bromo- and bromochloro-parabens, formed due to the existence of traces of bromide in tap water sources. In addition, the presence of the di-chlorinated forms of methyl and propyl paraben has been detected in raw sewage water samples.
- Clorination

D2) Fate and metabolite of parabens in environment

- **Kheng Soo Tay et al. (2010)** investigated the reaction kinetics and degradation mechanism of parabens during ozonation. Hydroxylation has been found to be the major reaction for the formation of the identified compounds. Through the hydroxylation reaction a variety of hydroxylated parabens was formed.
- Ozonation

- **Johnson TA et al. (1999)** examined the effects of bioavailability on degradation of 14C-p-hydroxybenzoate using sterile soil inoculated with Arthrobacter sp. The results showed that arthrobacter sp. accessed 94% of p-hydroxybenzoate in soil.
- Bacteria

E1) Paraben in wastewaters

- In France within the framework of Amperes project (2006-2009) 21 French wastewater treatment plants were studied in order to measure the composition of raw and treated wastewaters regarding pharmaceutical substances but in the list of analysed substances there are not parabens. They noticed that compounds like antibiotics and betablokers are not efficiently removed unless specific tertiary treatments are used, such as activated carbon filtration, reverse osmosis and ozonation.

- **Yamamoto et al. (2007)** in Japan, **Jonkor N. (2009)** in Switzerland, reported the removal efficiency for parabens of batch-activated sludge treatment and chlorination as a tertiary treatment in WWTPs are to 99% and 72% respectively.

E2) Paraben in wastewaters

- **Eva Eriksson et al. (2009)** measured the concentraion of parabens in influant and effluant of Small on-site greywater treatment and reuse plants in Denmark. They noticed that paraben degradation was proven to occur in the rotating biological contactor (RBC) by the biofilm which contains microorganisms. In the greywater samples which had not passed by RBC, all the parabens were present until the end of the experiment, illustrating that any bacteria suspended in the greywater did not degrade parabens.

- **Metaclafe C. (2010)** classified the parabens as “NOT Well Studied” microcontaminant in wastewater treatment plants in Canada.

Now, what is to retain from the Literature review ?

Important viewpoints 1

- Human and animals expose to parabens by dermal penetration and/or by ingestion.
- Parabens have been considered harmful (estrogenic and toxically activity) for health and environment by several individual researches but there are not epidemiologic evidences.
- In human body, free parabens are absorbed, metabolised (Hydrolysed and conjugated) and finally excreted in urine. Conjugates are the main urinary product of parabens.
- Parabens existing in household products void in free and/or hydrolysed state in environment.

Important viewpoints 2

- So paraben as an emerging pollutant is found in domestic wastewaters.
- Degradation of parabens in wastewater by chlorination, ozonation and biological methods (adding the bacteria) is done in WWTPs as tertiary treatment (Artificial).
- The fate and transfer of Parabens by individual domestic wastewater treatment systems and its impact on soil have not been studied (lack of research) : What to do?

ANCRES

- Proposition of ANCRES project

Fouché O. et al. (2010-2013) - Ministre of Ecology, France

- Assainissement Non Collectif – Rétention, Epuration par les Sols

Objective:

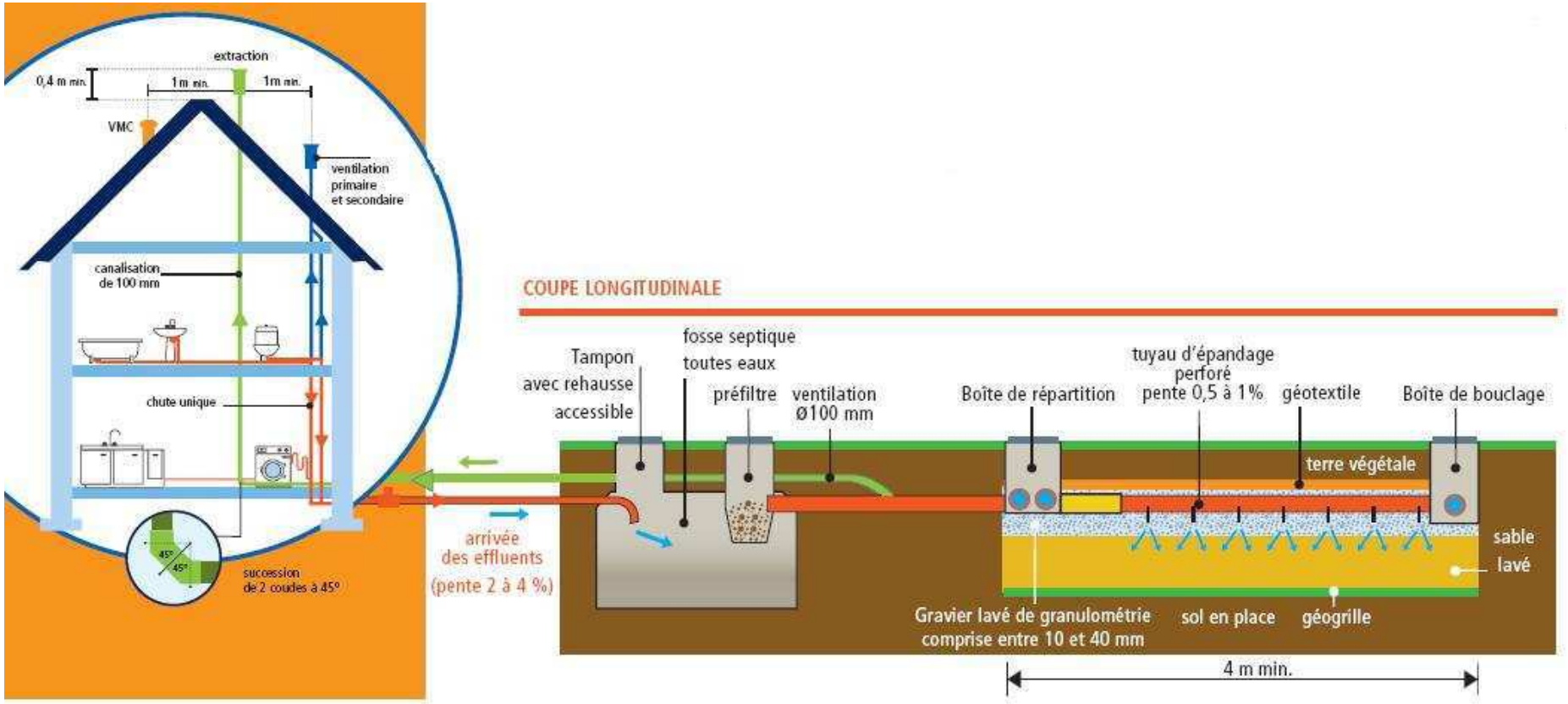
- Integrated study of subsoil in Individual Sanitation systems

Partners:

- Ecole de Ponts ParisTech (Coordinator Establishment)
- Le Cnam of Paris (Geotechnical analysis)
- ….

Individual wastewater treatment systems

Individual Sanitation = IS



Individual Sanitation

- Individual Sanitation (septic tank and soil infiltration) is the most efficient method available to treat domestic wastewater in the case that it is not possible to join it to a WWTP.
- In France 5-6 millions homes (20% of French population) use this system. (majority in rural media)
- Septic tank collects and provides primary treatment of wastewater by separating solids from the wastewater.
- From the septic tank, the pretreated wastewater passes through the outlet of the tank and enters the soil infiltration field.

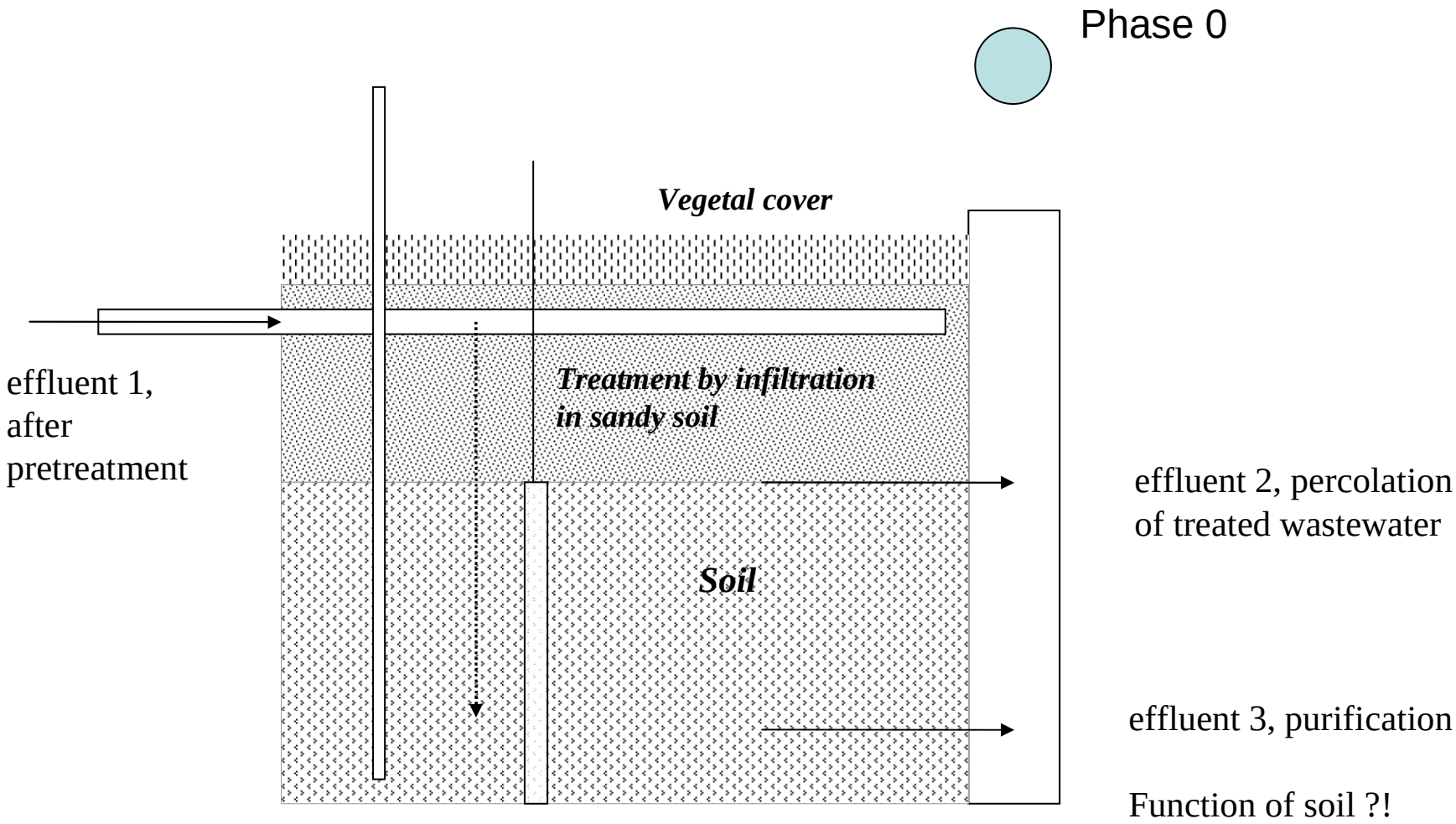
Individual Sanitation

- The soil infiltration field provides final treatment and distribution of the wastewater. The conventional system consists of perforated pipes surrounded by such media as gravel and covered with geotextile fabric in 70 cm thickness of granulated sandy soil.
- To treat wastewater, this system relies heavily on the soil, where physico-chemical and microbial activities help remove the pollutants in wastewater. So sandy soil is a media for treating the septic tank effluent by infiltration.
- The treated wastewater after passing the system, percolate directly in the natural underlying soil.
- What happens?

Impact of treated wastewater and soil functions

- The impact of treated wastewater on underlying soil and the functions of soil regarding to treated wastewater have not yet been studied. In other word the efficiency of these systems for treating the emerging pollutants especially for parabens is unknown.
- In order to evaluate soil functions faced with treated wastewater and impacts, we develop a methodology measuring the physico-chemical parameters and soil monitoring.

Sampling Scheme



Performed and predicted works

- Sociology (field study, selection of private systems)
- Take the samples of phase 0 (Yonne, France)
- Soil physical Analysis
- The tests for identifying the chemical and enzymatic properties of the samples are done in chemical laboratories of CNAM and LEESU.

We use the results of phase 0 as a witness for comparing with future samples that will be taken from soil which contains effluents level 1, 2 and 3.

Performed and predicted works

- One of the major aims of ANCRES:

Find the correlations between certain soil physico-chemical properties (as below) and the fate of emerging pollutants (retained, degraded or transferred by porous media and particles of soil).

- Soil texture (especially the type and portion of clay):

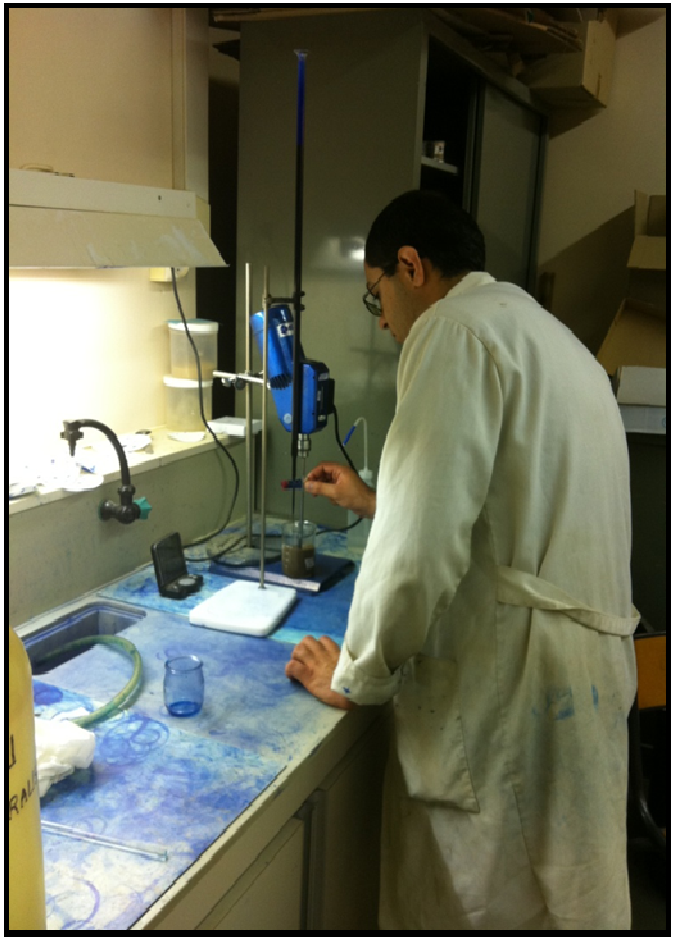
Measured by classical soil mechanics tests, adsorption tests, Scanning Electron Microscopy Imaging and microanalysis of the elements.

Performed and predicted works

- Soil Specific Surface Area (SSA) for the fine particles of soil
  Methylene blue Method (conventional / spectrophotometer methods) and Brunaur, Emmet and Edward (BET) method.
- Soil saturated and unsaturated Hydraulic Conductivity
  Guelph, Porchet and Double ring methods included with analytical interpretation methods like BEST
- Cation Exchange Capacity of soil
  Chemical parameter that will be measured in laboratory of soil chemistry

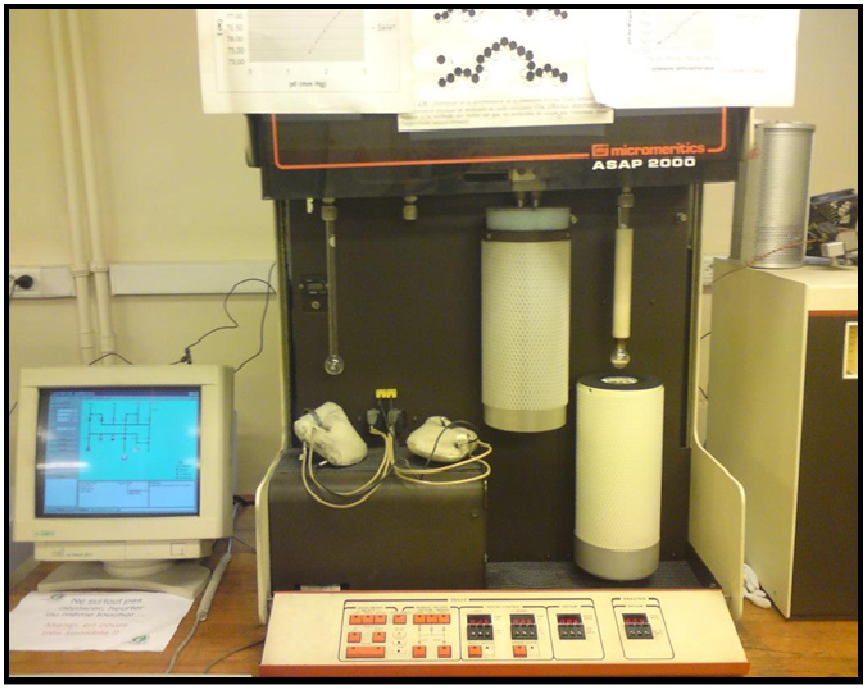
Soil profiles

Laboratory experiments



Methylene blue Method

Brunaur, Emmet and Edward (BET) method.



Questions that have to be answered

- How is the exact behaviour of parabens in water?
- Is the process of degradation of parabens reversible in water and soil?
- Are there species of bacteria which consumes parabens (naturally in soil)?
- The average content of parabens in septic tank inflow is about 1 mg per person per day. Is this quantity measurable in effluents in soil (considering the two step of treatment). Is it a good tracer?

Thank you for your attention