Politechnica University
Timisoara, Romania

The II Workshop - IPA Project
Unique physico-chemical properties of Emerging substances as the hazardous polutant in aquatic environment

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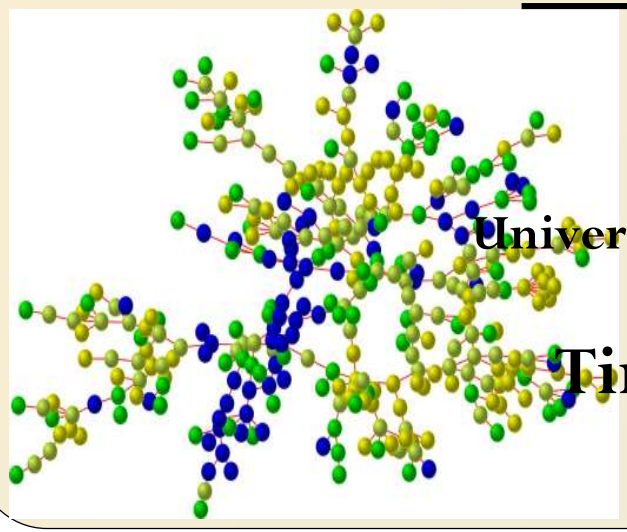
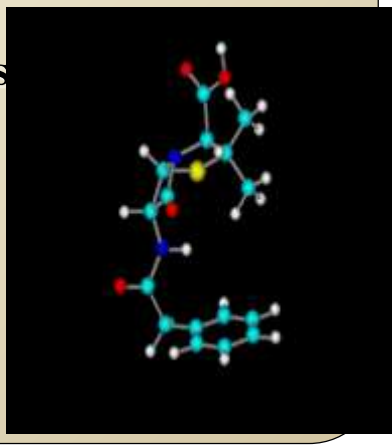
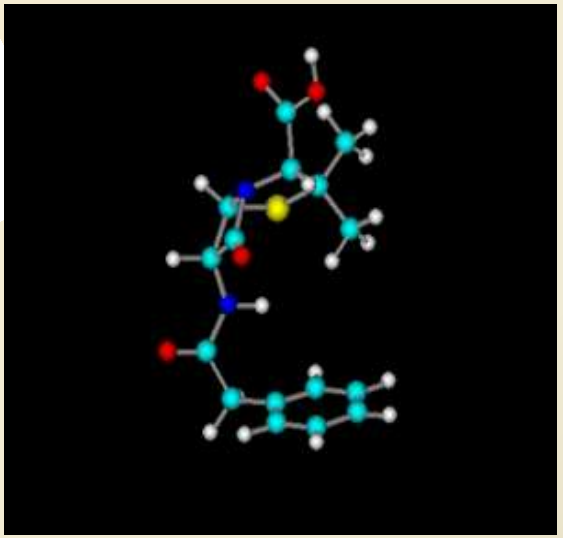


UNS, Faculty of Technical Sciences

University of Technology, Bratislava, SK

Timisoara, 29 May, 2014





CONTENT

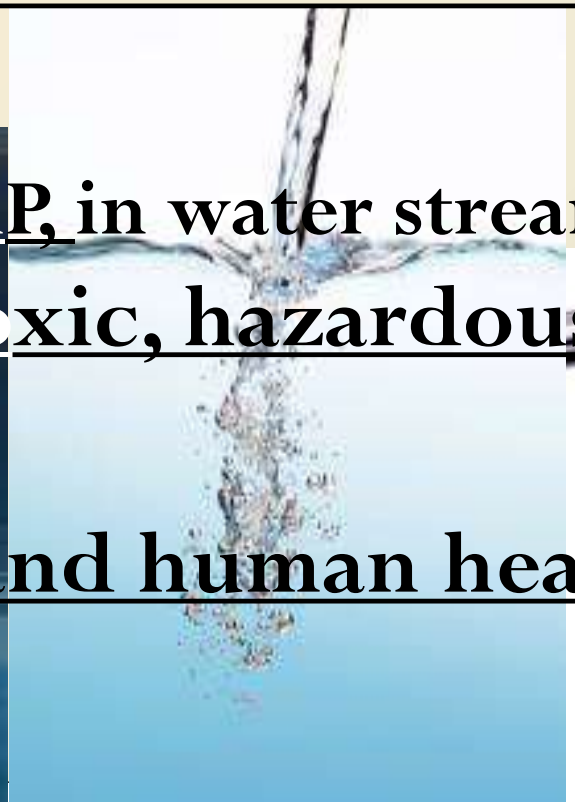
Unique physical-chemical properties in woter bodys

The story about EmS

Instead of conclusion

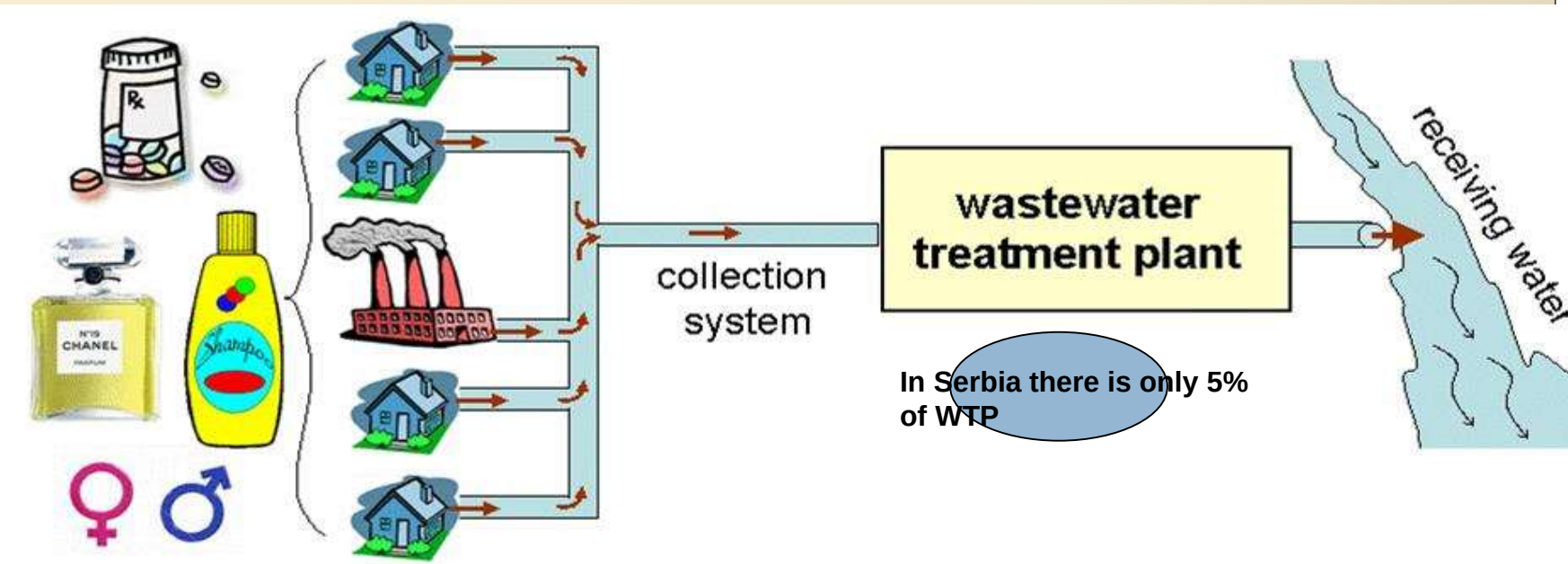
WATER IS ESSENTIAL FOR LIFE

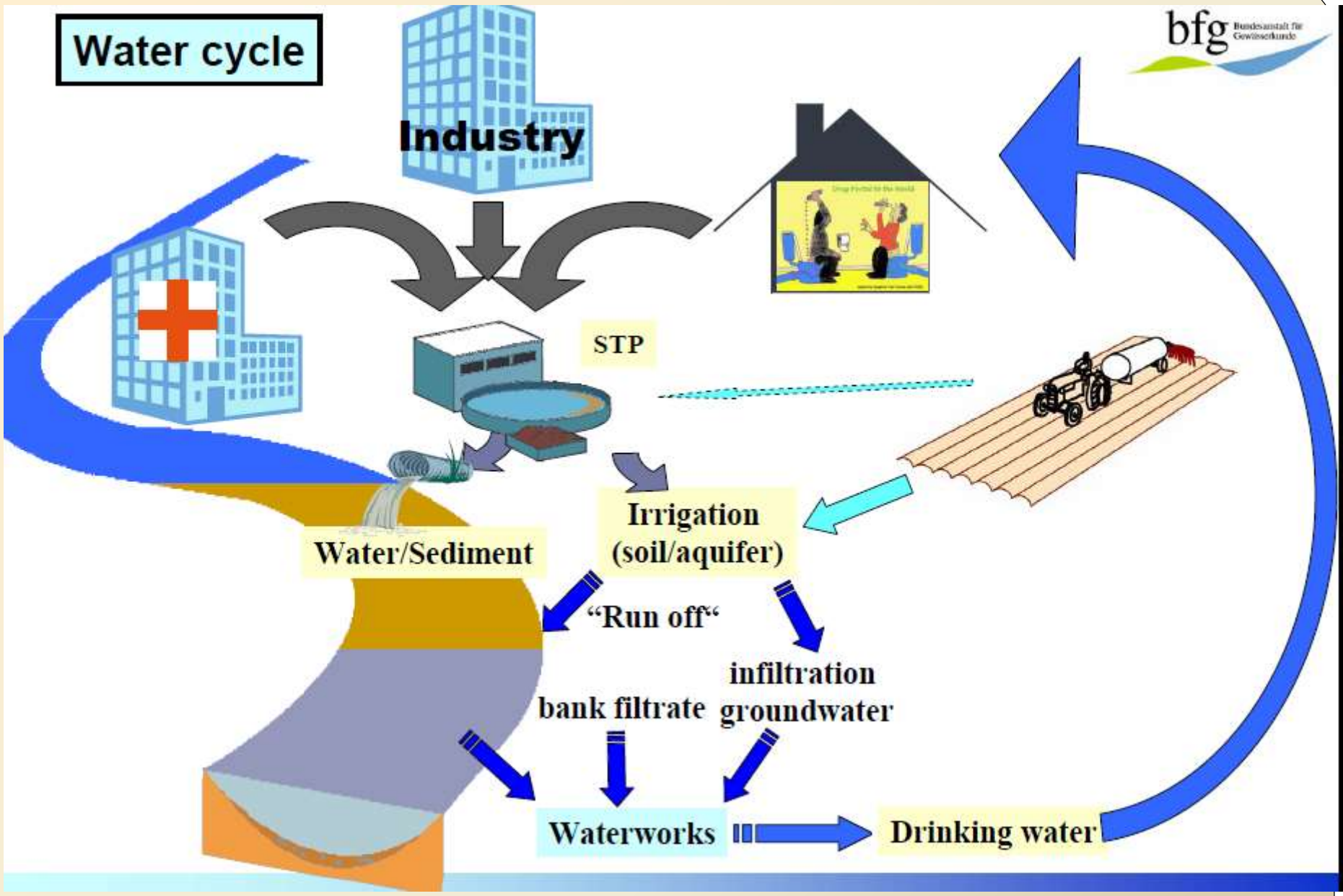
- **Strategic resource for every country and population.**
- **Its availability and sanitary safety is highly connected with the health and economy status.**
- **Many pollutants, EmP, in water streams have been identified as very toxic, hazardous and harmful to**
- **the environment and human health.**



Em C /S /P

- are derived (produced, generated, used), from industrial, pharmaceutical, domestic, municipal and agricultural **wastewater sources** and pathways, and **dispersed to the environment**
- **These newly recognized EmP represent a shift in traditional thinking -**



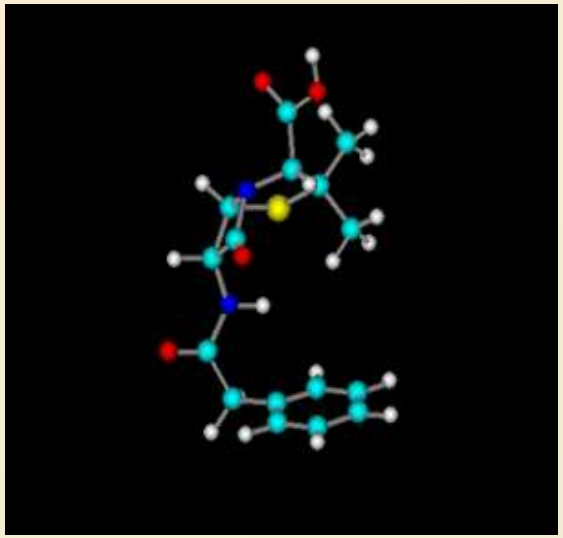

Water cycle
bfg Bundesanstalt für Gewässerkunde
Industry
STP
Irrigation
(soil/aquifer)
Water/Sediment
“Run off“
infiltration
groundwater
bank filtrate
Waterworks
Drinking water

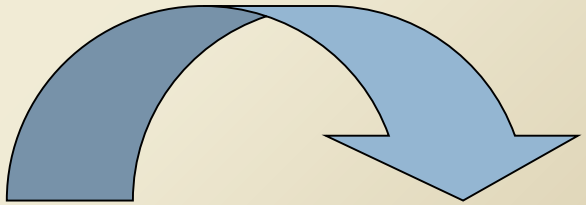
EmS

- Are substances/chemicals that have been detected in environment, in very low conc. – ppb, ppt, and lower
- but - are currently not included in routine monitoring programs at EU level and normally national !
- and whose fate, behavior and (eco) toxicological effects are not well understood.

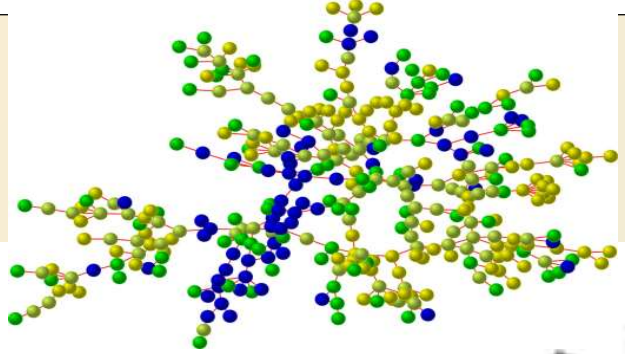
- **Around 98% of the commercially available compounds are NOT inventoried and are unregulated substances,**
- **their environmental fate, transport, ecotoxicological negativ effects on all compartiments of environment are unknown!!!**

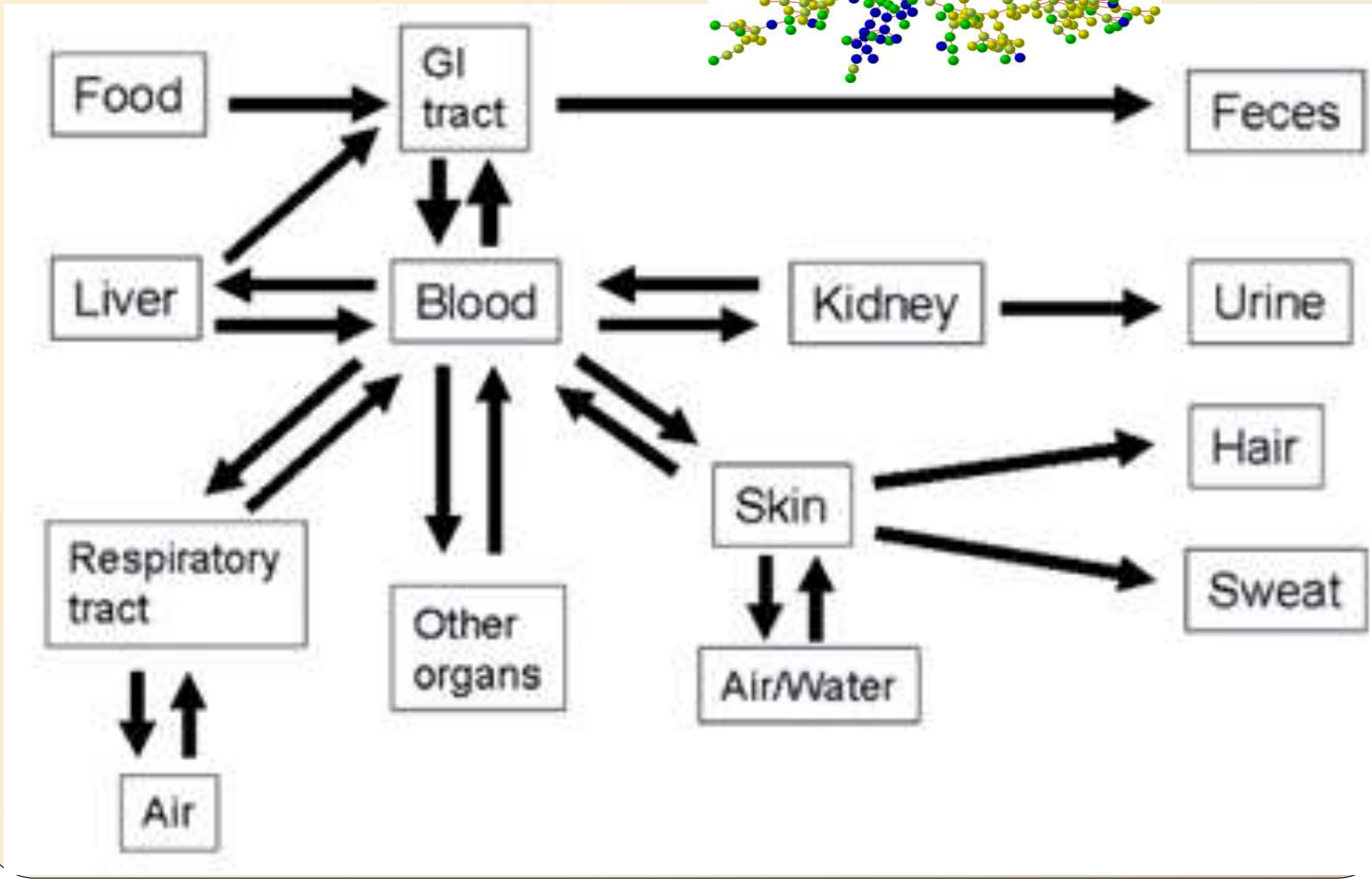
- **EmC are detected in**





Excretation




Food
GI tract
Feces
Liver
Blood
Kidney
Urine
Hair
Skin
Respiratory tract
Other organs
Sweat
Air/Water
Air

EmS are very toxic

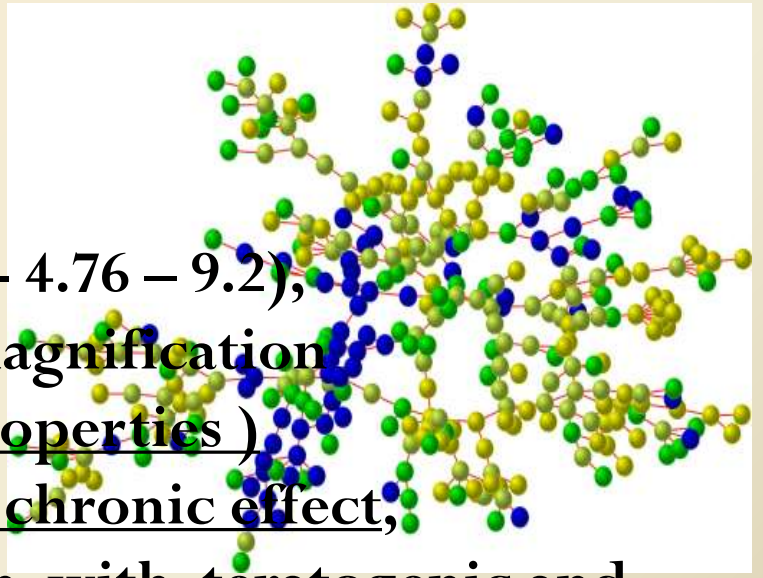
- found in a wide array of consumer goods, including pharmaceuticals, FR,
- personal care products-PPCP…
- EmS may - low concentrations between ppm, ppb and ppt in surface/ ground water, domestic/industrial wastewater, agricultural runoff, reclaimed water, drinking HOH (Danube)...
- Many of EmS also may be found in soils & in air.
- They are a fact of modern, industrialized living.
- Hazardous, carcinogenous… (TER., MUT.)

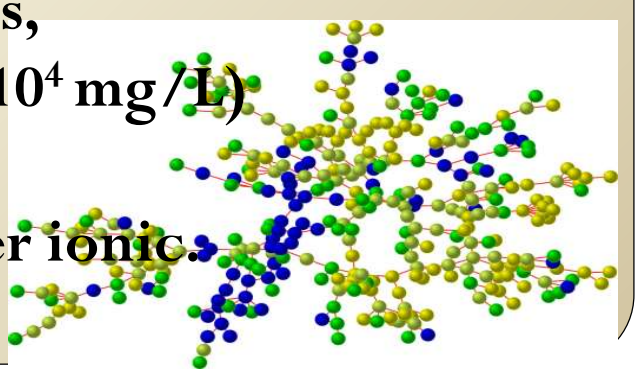
According to NORMAN

- More then 750 diferent EmS/C/P
- 23 class & 79 sub-slasses
- Emerging research, monitoring, effect, philosophy...
- List is open and dynamic ....

The unique physico-chemical characteristic of EmS

- Low doses occurrence and effects - ppm, ppb, ppt and lower
- Non monotonic dose response
- Pseudo - persistency / persistency,
- Stability low/non degradability,
- Hydro/lipo philicity - (Log K_{ow} = - 4.76 – 9.2),
- Bioconcentration/accumulation/magnification
- Binding to proteins – (biological properties)
- Toxicity with hazardous and rather chronic effect,
- Endocrine modelulating/disruption, with teratogenic and carcinogenic consequences within low / sublow doses,
- Chemical coktail,
- Volatile, non - or semivolatile compounds,
- water/lipid soluble molecules (0.06-3.1 10^4 mg/L) polar/nonpolar molecules,
- Neutral, acidic, basic, and ionic or zwitter ionic.





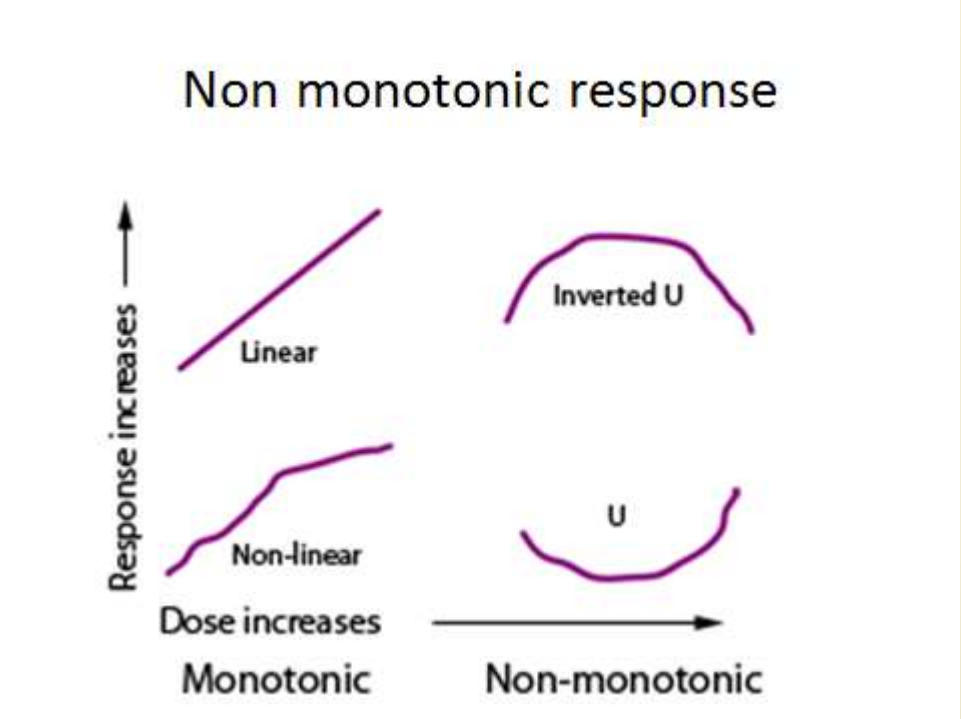
Some very specific and unique propertis of EmS

- **Non monotonic dose response**
- **Pseudo - persistency / persistency,**
- **Binding to proteins – (biological properties)**
- **Chemical coktail**

Non monotonic dose response

- **The old paradigm focused on acute toxicity with high concentration level of Chemicals/ the new paradigma -chronic negative effects and low doses of EmS.**
- **Traditional toxicology - dose-response curves are monotonic - higher doses have a greater effect than lower doses.**
- **Non monotonic response - in mathematical terms, the slope of the dose response curve changes sign.**

Non monotonic dose response



Low dose effects cannot be predicted from high dose testing

Pseudo - persistency / persistency,

Persistency, P, is one of the most important criteria in the environmental assessment of chemicals.

- **P- is determined by the rates of the removal by physical, biological and/or chemical processes**

Pseudo-persistency

- **Persistency is one of the most important criteria in the environmental assessment of chemicals.**
- **Even if there is some degree of degradation of EmS, the parent compounds will nevertheless be present at constant levels in the environment if the input rate is higher than their rate of degradation or mineralization.**
- **This can be called second order persistency or pseudo persistency – $V_{input} > V_{degradation}$.**

Binding to G proteins

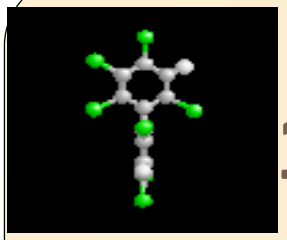
- A drug/EmS in blood exists **in two forms: bound and unbound** (depending on a specific drug's affinity for plasma protein).
- **If the protein binding is reversible, then a chemical equilibrium will exist between the bound and unbound states, such that:**
- **Protein + EmS ⇌ Protein-EmS complex**
- **G proteins are important - transducing molecules in cells.**

Chemical coktail

- Standard lab analysis and field study, examine the effects of one chemical .
- BUT, Chemical cocktails are reality- multiple chemicals mixture is typical in the enviroment and the negative effects of these coctails mixture are unknown!
- The negative effects of Chemical could not be predicted from the effect of single chemicals alone !

Screening and target analyses

- **Within NATO Project**
- **By Screening analyses we detected more than 150 Organic and inorganic chemicals in the samples of the surface water of the Danube River, in the vicinity of Novi Sad.**
- **Target Analyses – quantitatively - more than 30 organic toxic chemicals**



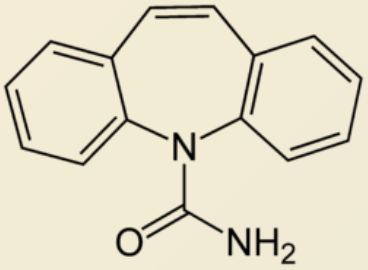
150 organic Em compounds

- **It was detected more than 150 different emerging organic compounds -phthalates, indeno derivatives, alkyl substituted benzenes, naphthalene and phenol derivatives, PAHs, hormones, triphenyl phosphate), caffeine and others EmS are found in the Danube-NS SW in very low concentartions, ppb/ppt !!!**

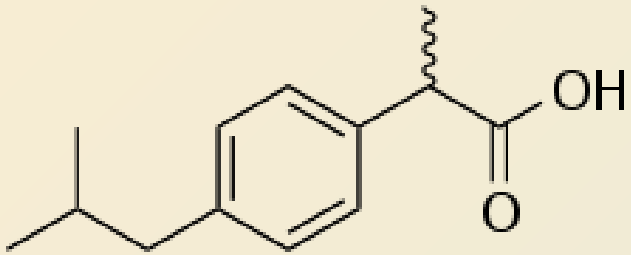

IMPORTED

The Universe of Chemical Pollutants

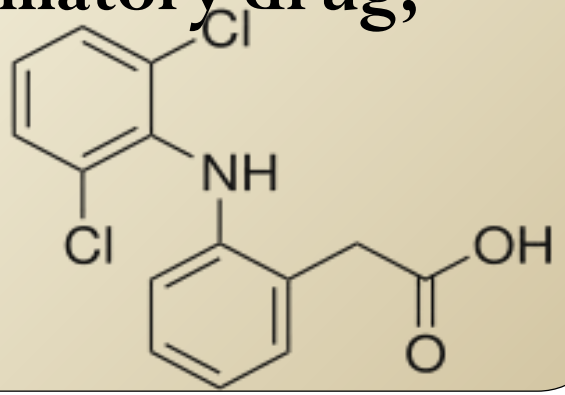
- Carbamazepine – anticonvulsant
- Log Kow= 2,25



- Ibuprofen - nonsteroidal anti-inflammatory drug

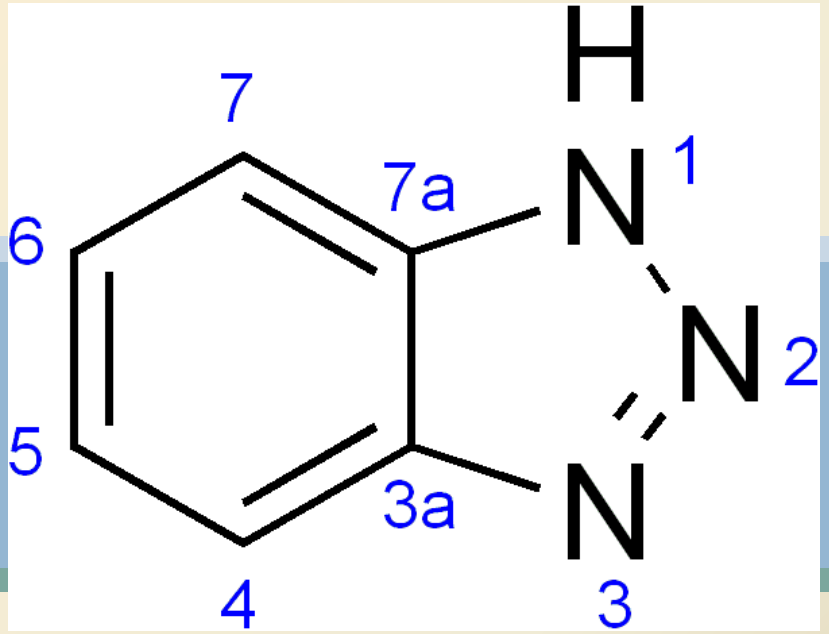


- 3,5
- 4,51
- Diclofenac- nonsteroidal anti-inflammatory drug,



- **We detected: caffeine**
- **Benzotriasole (Danube, sw)**
- **The international Project**

We detected



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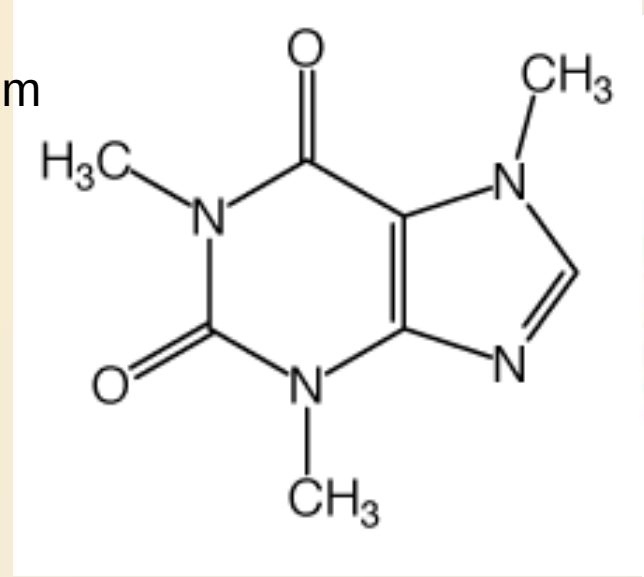
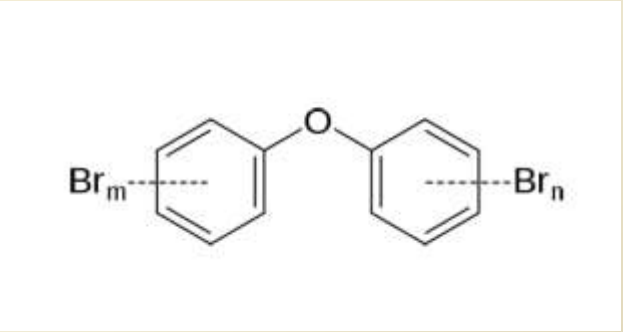
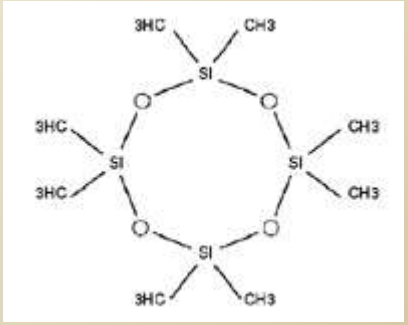


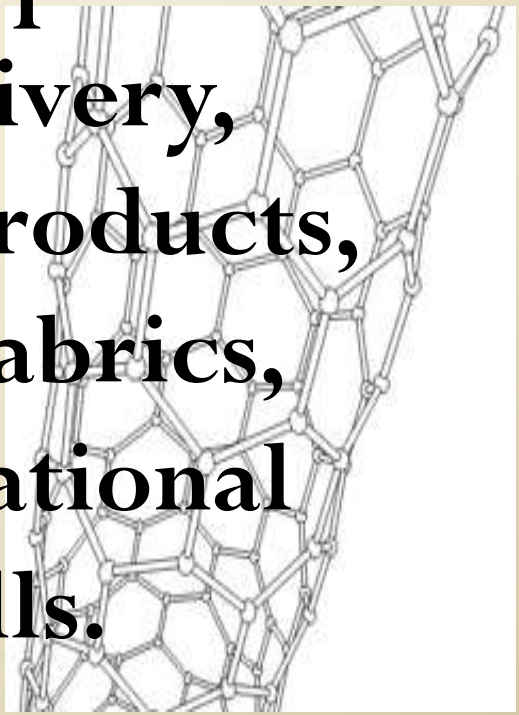
Global organic Emcontaminants:

- **Pharmaceuticals and personal care products**
- **Endocrine-modulating compounds**
- **Polybrominated diphenyl ethers - PBDEs,**
- **Hexachlorobutadiene – HBCDs,**
- **Perfluorooctanesulfonic acid – PFOS.**
- **Perfluorooctanoic acid -PFOA,**
- **Siloxanes**



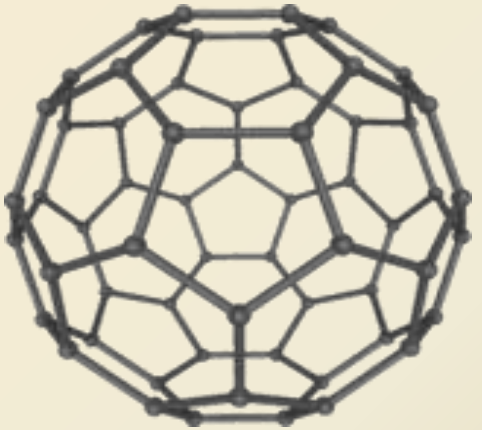


- **Nanomaterials - are natural and man-made structures, ranging in size from 1 nanometer (nm) to 100 nm,**
- **widely used in nano-therapeutic - pharmaceuticals, drug delivery, cosmetics, personal care products, energy storage products, fabrics, lubricants, and even recreational equipment such as golf balls.**

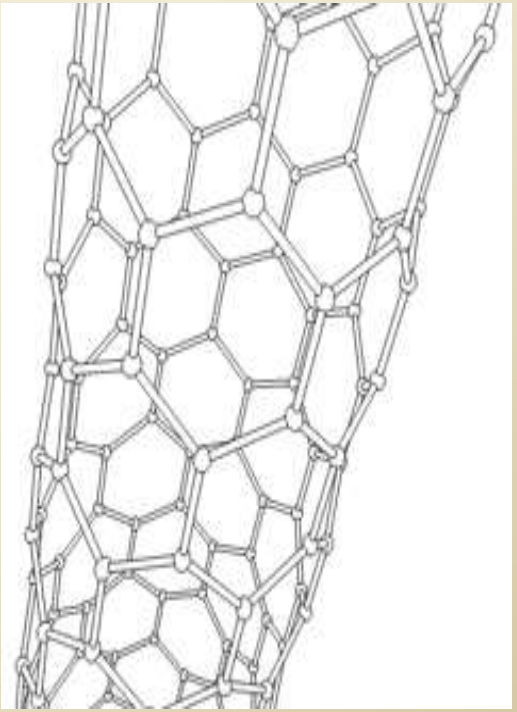


Nanoparticles

NanoMats

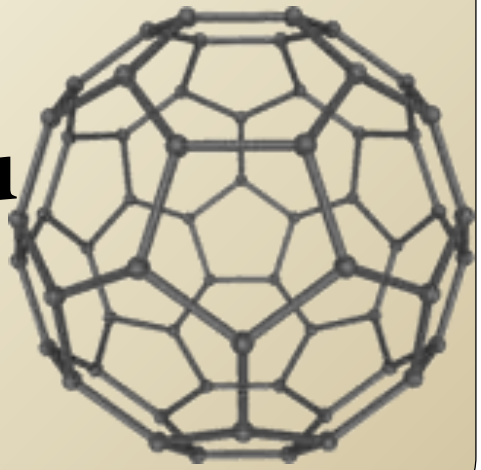


- **Fullerenes (a.k.a. buckyballs)**
- **Nanotubes**
- **Quantum dots**
- **Nanopowders (metal oxides)**
- **Natural particles (e.g., soot)**



Nanoparticles

- Chemical and physical properties change at nano scale -
- Magnetization, charge capacity, melting point, hardness
  - Matter may now act as a catalyst or semiconductor
  - Non-ferrous metals like Au
  - and silver
  - can become magnetic



Toxicity

- Toxicity of most nano
- products has not been determined
  - Different toxicological properties from parent compound
  - Cross biological membranes and blood-brain barrier

What is new?

Old Pollutant – New Concern
Newly identified -Unregulated

due to improved analytical techniques-

UPHC(TOF)MS/MS – EmS detected

- **Highest Propensity for Adverse Effects**

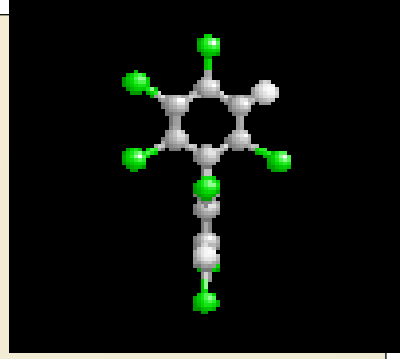
  Possess structural stability, short ½-life)

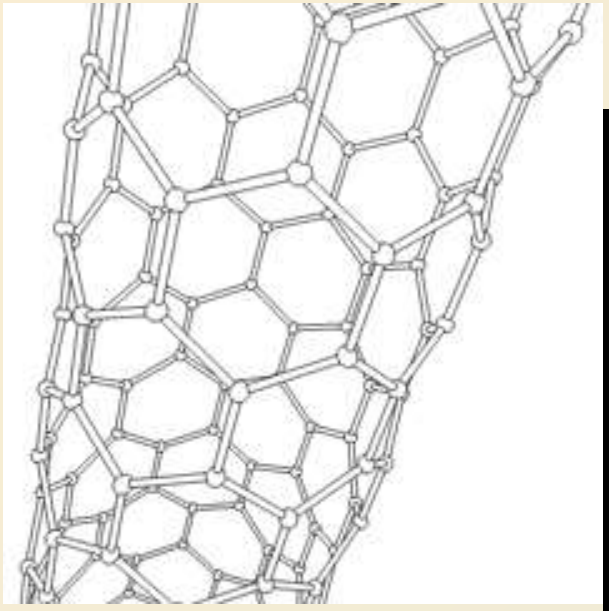
  - **Lipophilic (bioaccumulative)**
  - **Cause acute or chronic toxicity**
  - **Pseudo persistent substances**
  - **Very low concentr. - ppb, ppt or lower**

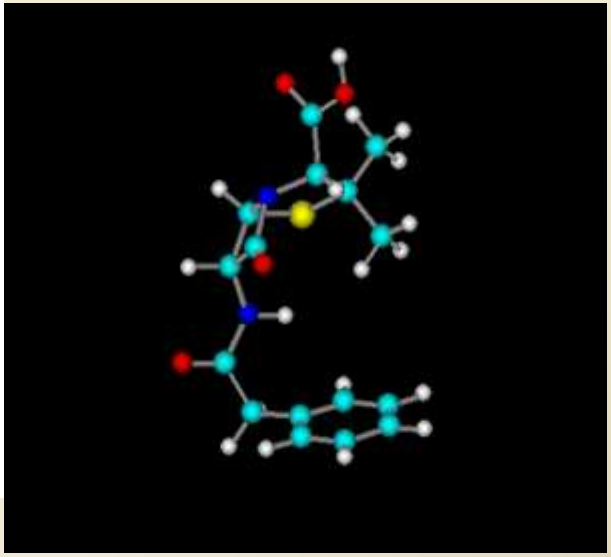
Em chemicals

- **Chemicals are a part of modern life and are present in all spheres of human life.**
- **The biggest number of organic and inorganic chemicals belongs to emerging chemicals.**
- **EmS contribute to our well being, high life expectancy and economic prosperity.**

Instead of conclusion

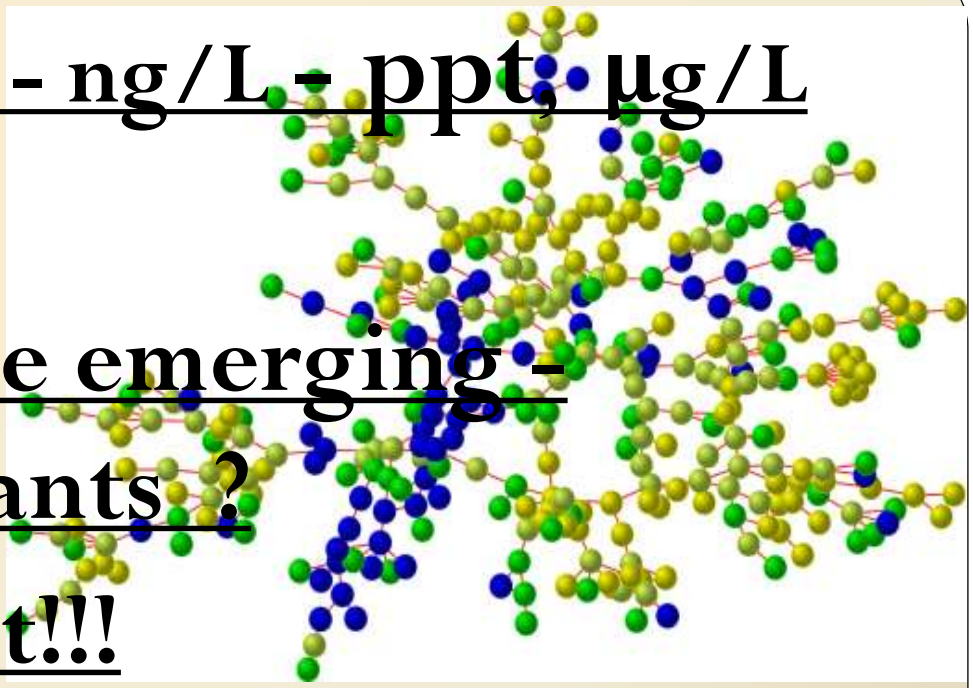






- **Millions of EmS entering the environment – every year espetially in urban areas.**
- **The most common mechanism for EmC - input into the environment - is <u>through wastewater discharges,</u> land application of sewage sludge, landfill leachate…**
- **Potential adverse effects on human health, environment, unknown fate …**

Range concentration - ng/L - ppt, µg/L - ppb.



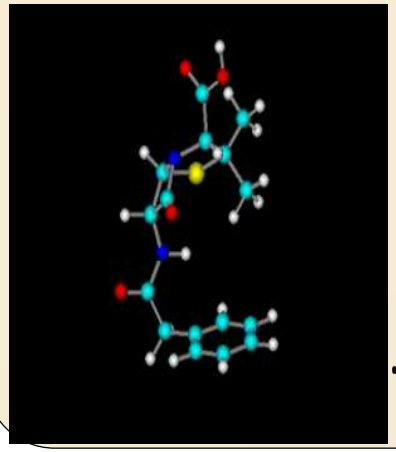
- How we can remove emerging – micro, nano pollutants ?
- We do not know yet!!!
- Our responsibility is to seek for ways to deal with the presence of EmS in the environment, urban areas – ground and drinking
- water sources.

Acknowledgment for financial support

NATO - Science for Peace Project "Drinking Water Quality Risk Assessment and Prevention in Novi Sad municipality, Serbia" (ESP.EAP.SFP 984087).

- the Projects III 46009 funded by the Ministry of Education and Science of the Republic of Serbia

- Gradska Uprava



- Bilateral Project Slovakia- Srbia