



# Emergentne supstance i istraživanja 2020.



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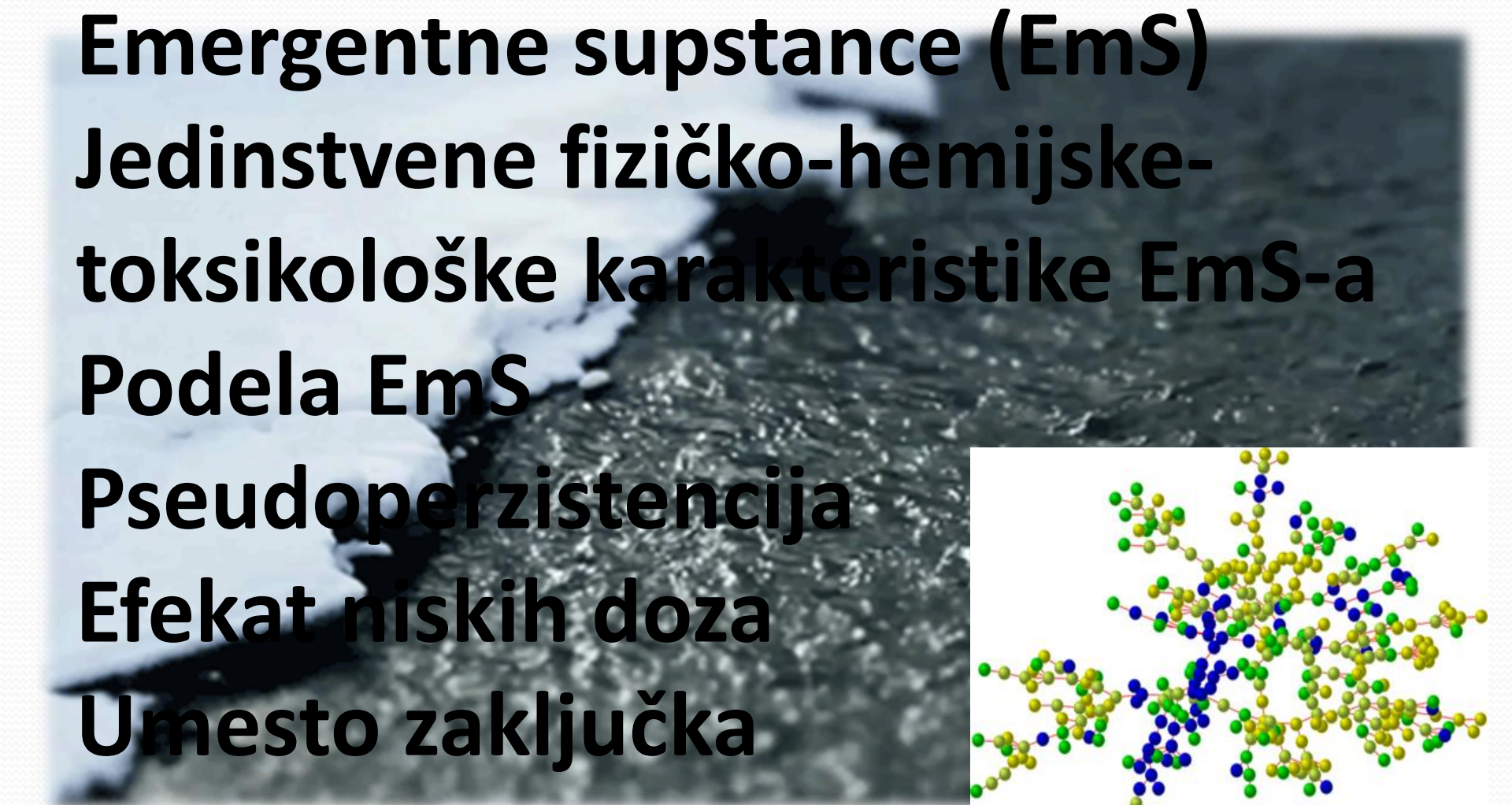
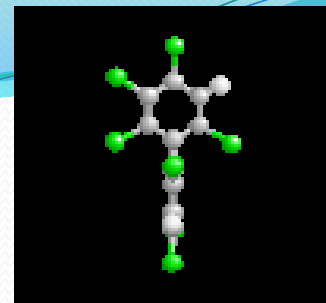
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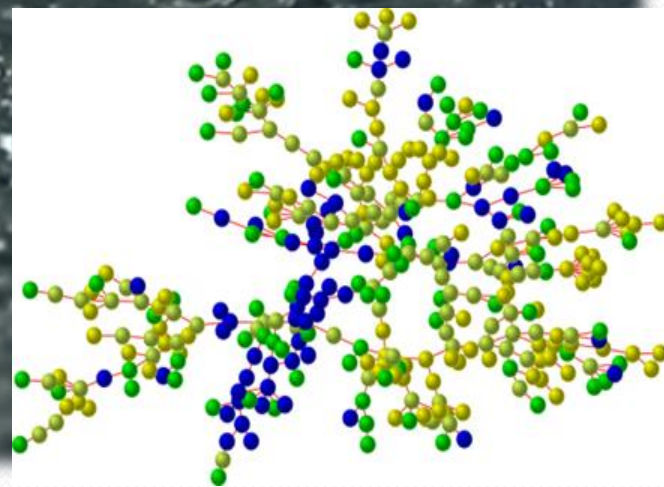
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Univerzitet u Bratislavi, SK



# Sadržaj izlaganja

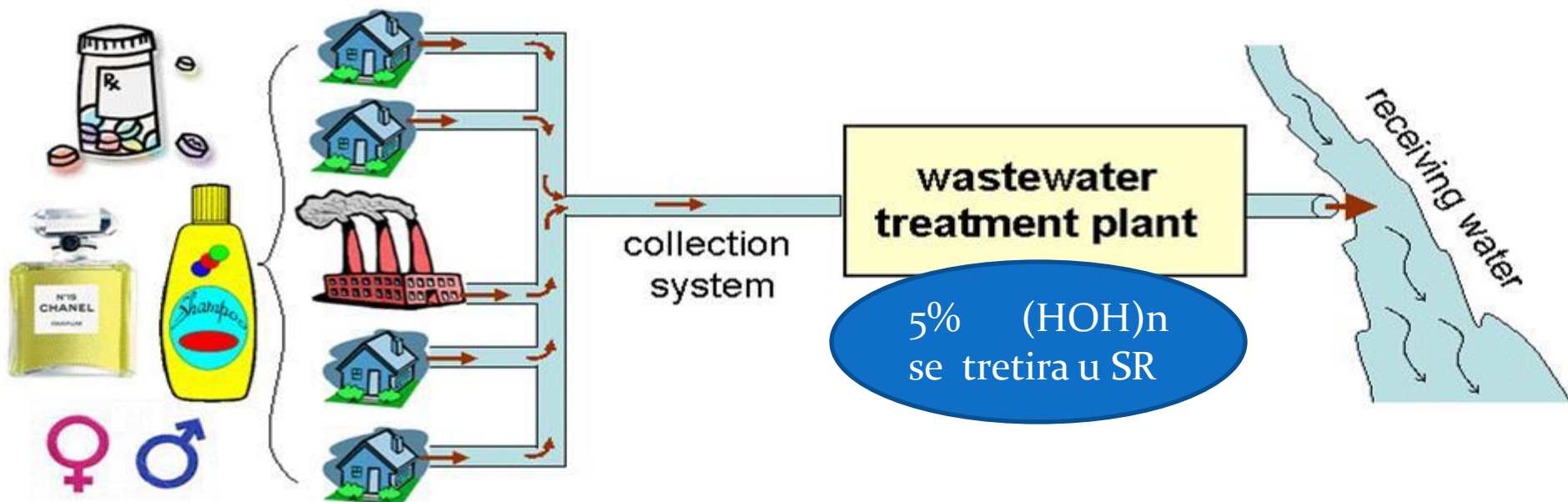


**Emergentne supstance (EmS)**  
**Jedinstvene fizičko-hemijske-**  
**toksikološke karakteristike EmS-a**  
**Podela EmS**  
**Pseudoperzistencija**  
**Efekat niskih doza**  
**Umesto zaključka**



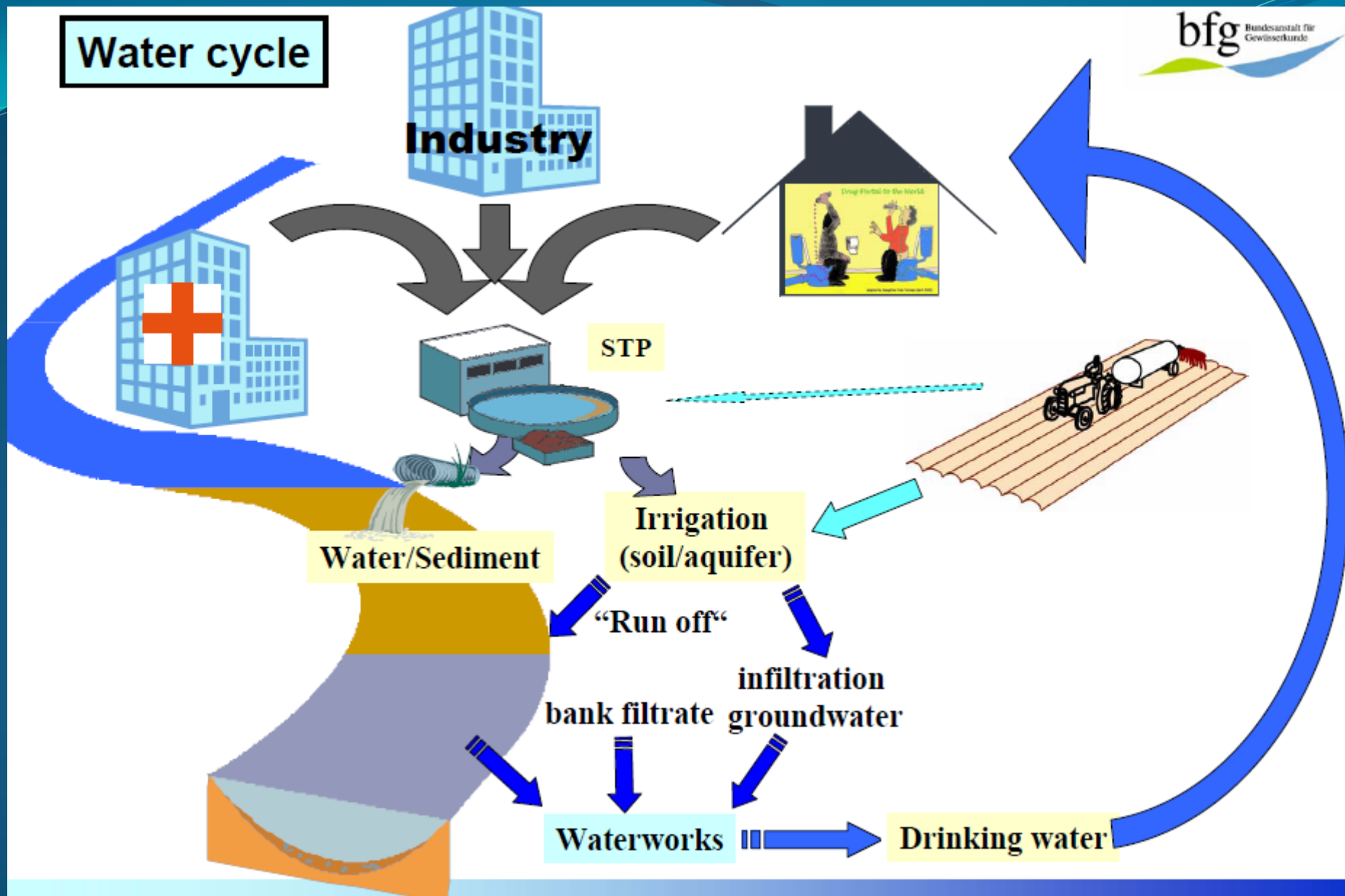
## Šta su emergentne supstance, EmS

- Sve prisutne, pseudo perzistentne, biološki aktivne hemikalije, polutanti, - rezultat su prirodnih, industrijskih i ljudskih aktivnosti...
- se nalaze u industrijskim, farmaceutskim, bolničkim, komunalnim, poljoprivrednim - otpadnim vodama, OV
- Novoprepoznati kontaminanti - promenu i pomeraju tradicionalnom pristupu Z-ŽS/istraživanja 2020
- Kako dospevaju u ŽS ? - U prirodne recipijente - netretiranim ali i tretiranim OV. EmEKOSTRESORI

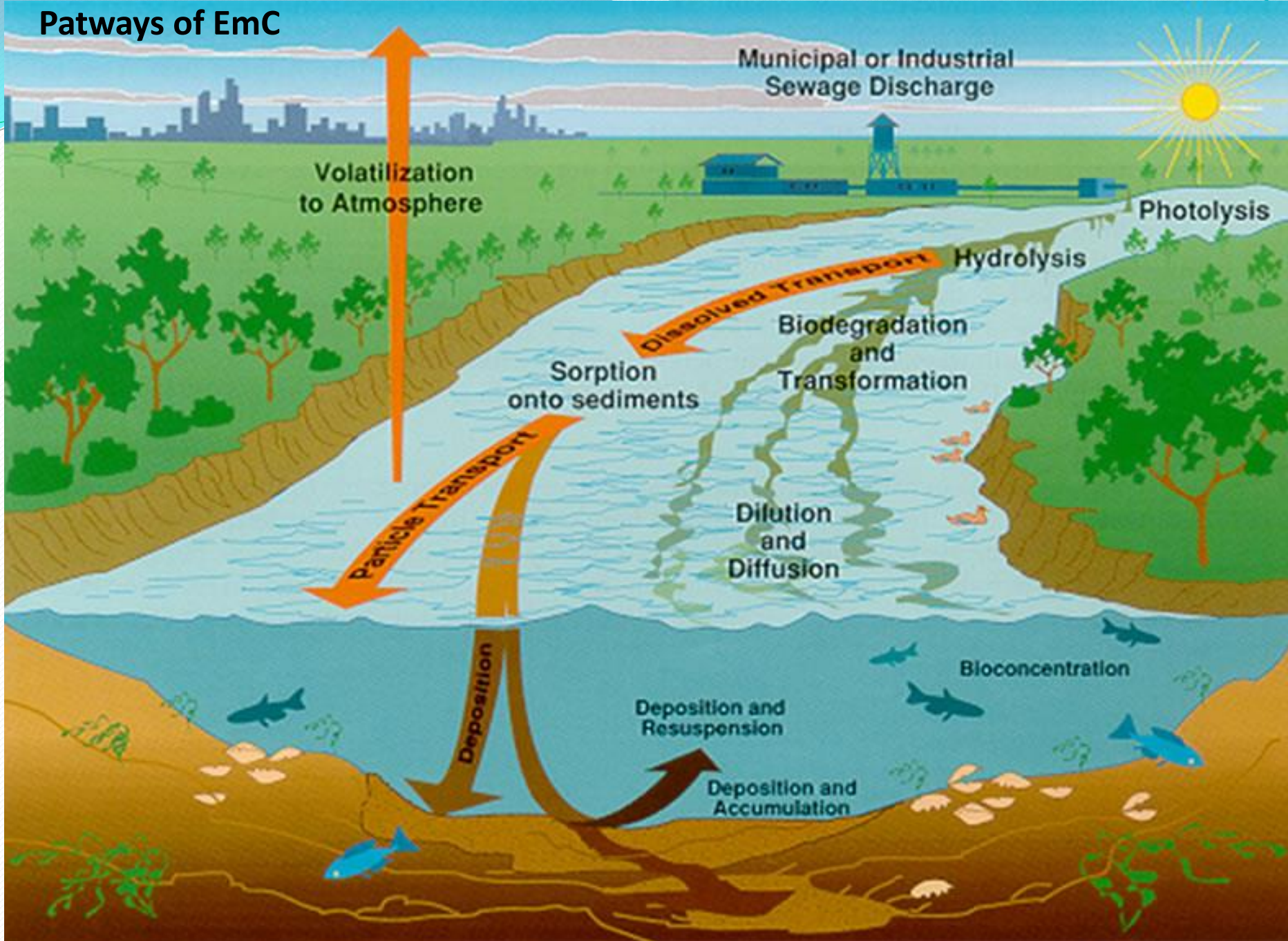




# Water cycle



# Pathways of EmC





# Prema NORMAN - u

(Network of reference laboratories for monitoring of emerging environmental pollutants)



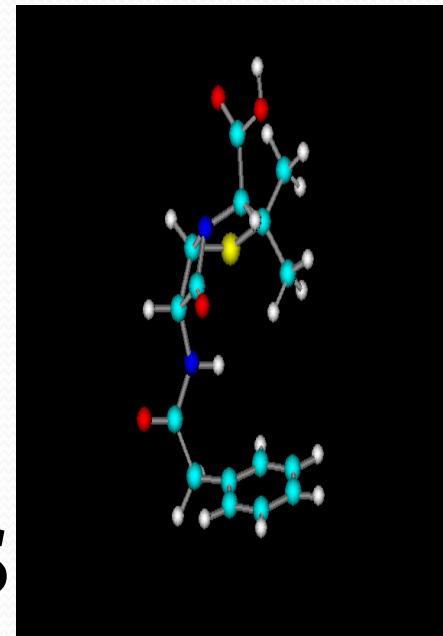
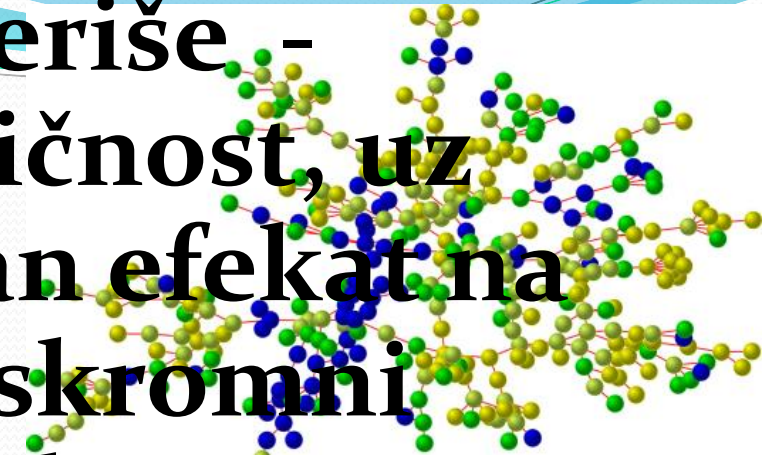
➤ EmS – ZS/K/P detektovani u ŽS, ali trenutno nisu uključene u rutinski monitoring na nivou EU !

Ponašanje, particija, sorpcija/degradacija, sudbina, MDK, transport, rasprostiranje, ekotoksikološki efekti nisu dovoljno poznati i objašnjeni.



● Horizont 2020 /istraživanja

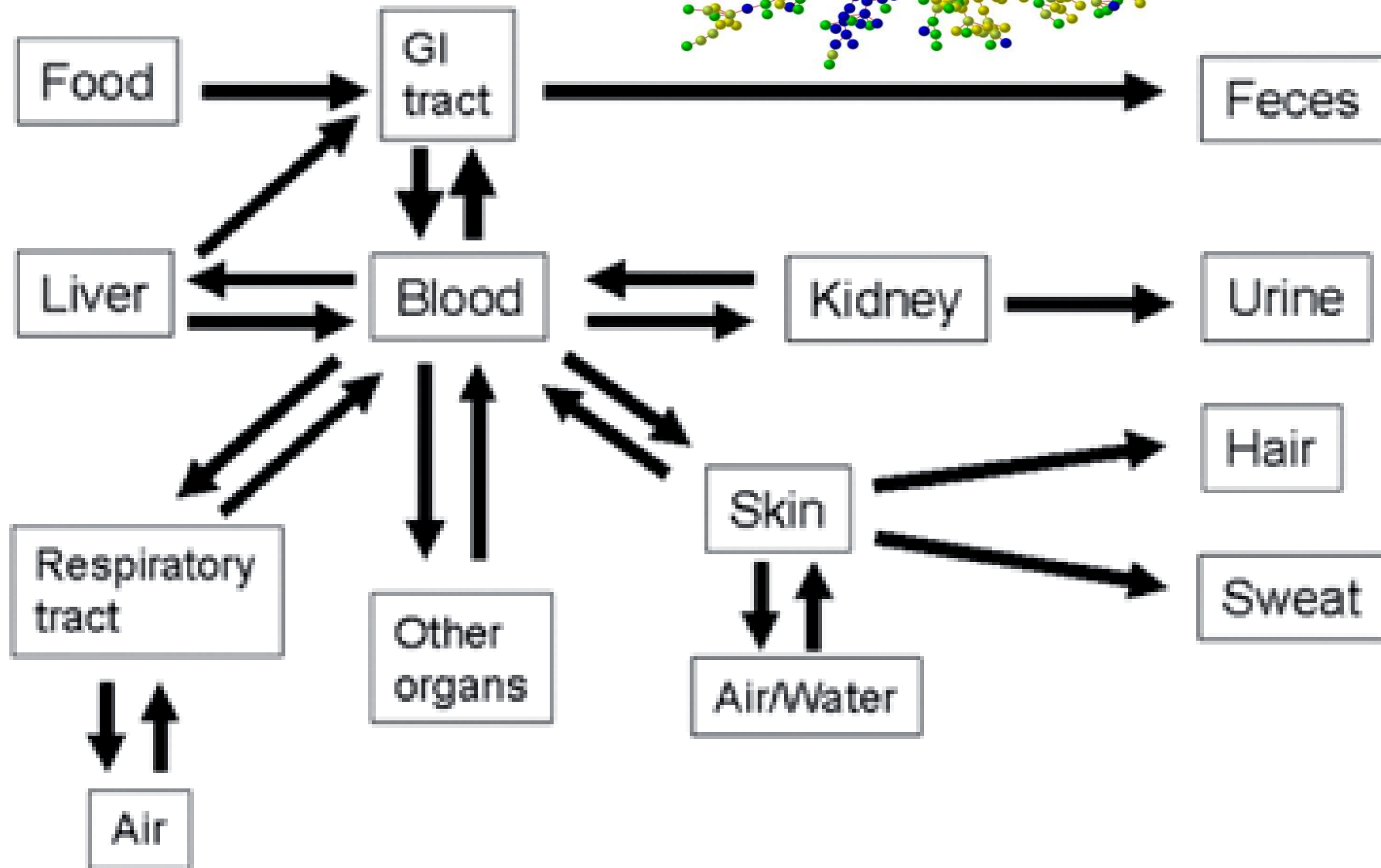
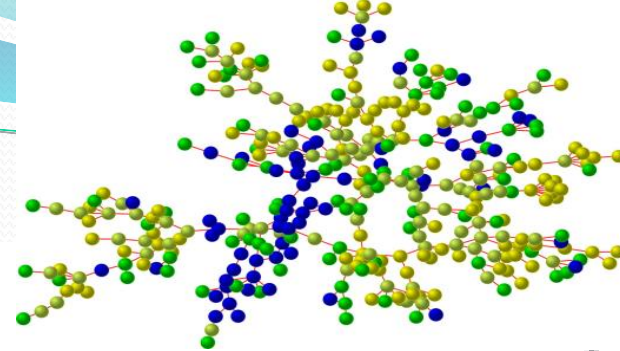
- Em polutante karakteriše - nepoznata (eko)toksičnost, uz potencialni negativen efekat na ŽS, nova percepcija, skromni podaci monitoringa ali prisustvo u svim kompartmentima ŽS – voda, zemljište, vazduh, biota.
- EmS imperativno-moraju biti
- zakonski regulisani – zbog
- ekotoksičnih i hazardnih
- efekata na zdravlje čoveka i ŽS



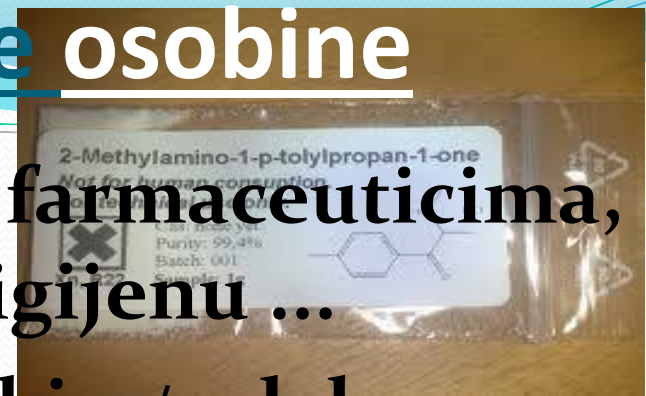
- **Oko 98% komercijalno dostupnih supstanci nije regulisano zakonskim direktivama !**
- **Prisustvo Ems-a u humanim uzorcima**
- **ekskrecija**







# Specifične fizičko hemijske osobine

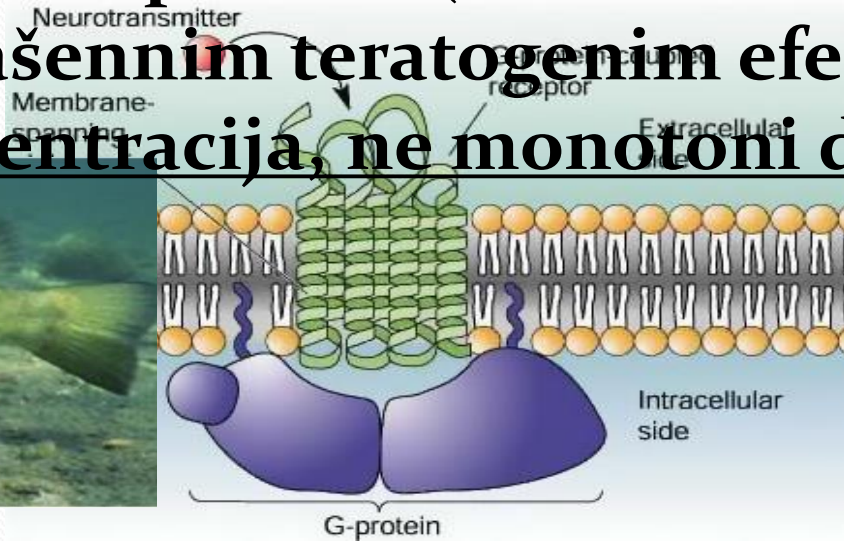


- Biološki aktivne supstance - u farmaceuticima, produktima za ličnu i kućnu higijenu ...  
EmS – prisutne su u veoma niskim/sub konc. - ppm, ppb i ppt i nižim - u otpadnim, površinskim, podzemnim vodama ...
- EmS se detektuju i u sedimentu, zemljištu, vazduhu - abiotskom ali i biotskom matriksu.
- Hazardni, kancerogeni, mutageni, teratogeni  
EmS su naša realnost - kontroverza- današnjeg modernog, industrijalizovanog života i kontaminirane ŽS.



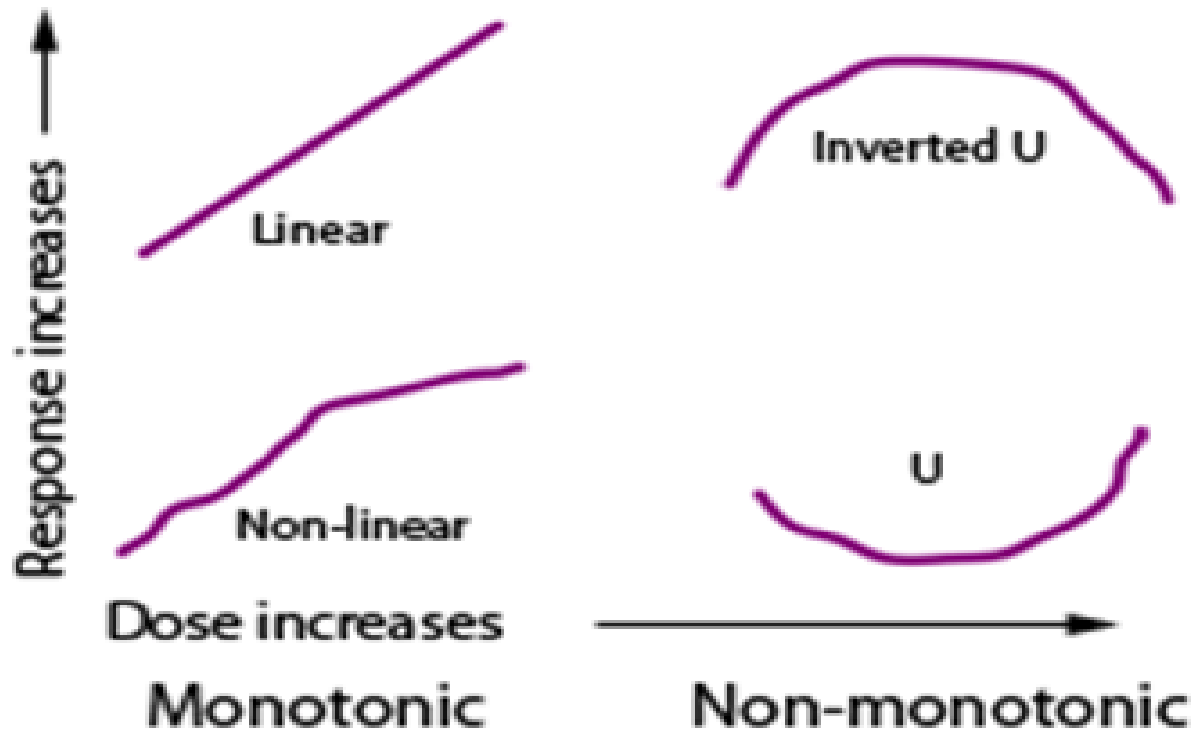
# Jedinstvene osobine i ekološki efekti

- Bioakumulacija/biokoncentracija, biomagnifikacija, snažna reakcija sa G proteinima lipo/hidrofilnost, Kow (-4,2 do 9,6), polarnost, u obliku jona, netralne molekule, bazni/kiseli oblik stabilnost, pseudoperzistencija, hemijski koktel, aditivnost, sinergija ali i antagonistički efekat...
- Hormonski aktivne supstance (ometivači HA), mimikrija-sa naglašenim teratogenim efektima, efekat niskih koncentracija, ne monotoni dozni odgovor





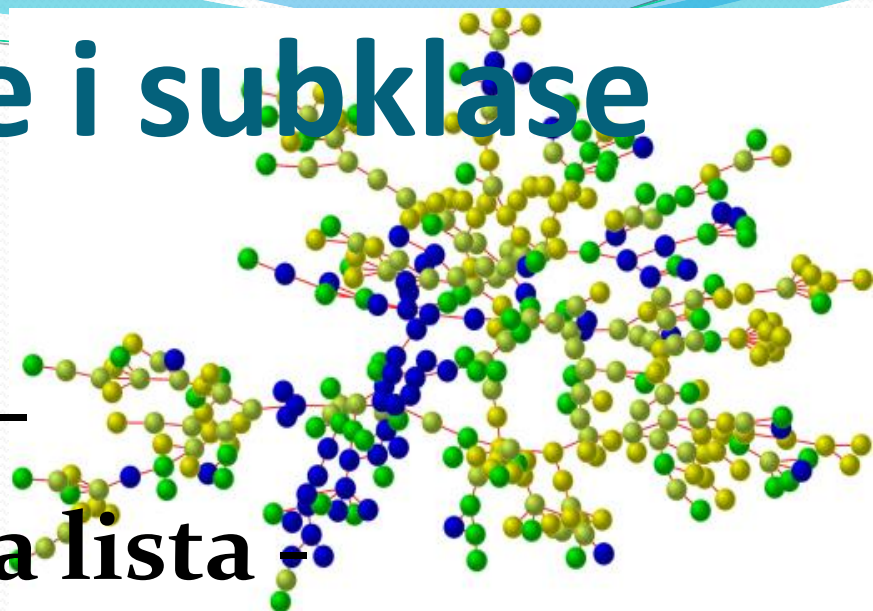
# Non monotonic response



Low dose effects cannot be predicted from high dose testing,

# Kategorije/klasse i subklase EmS

- Prema NORMANU –  
otvorena dinamična lista –
- 23 kategorije / klase EmS
- Preko 300 subklasa EmS i 750 Em  
supstanci



Category / class	Sub-class
<b>Algal toxins</b>	Cyanotoxins
<b>Antifoaming agents</b>	Antifoaming agents
<b>Antioxidants</b>	Antioxidants
<b>Antifouling compounds</b>	Antifouling compounds, Organotin compounds
<b>Bio-terrorism/ sabotage agents</b>	Bio-terrorism/ sabotage agents
<b>Complexing agents</b>	Complexing agents
<b>Detergents</b>	Aromatic sulphonates, Alcohol ethoxylates (AEs), Alkanol amides, Alkyl glucamides (AGs), Alkyl polyglucosides (APGs), Alkyl sulfates (AS), Alkylether sulfates (AES), Alkylphenol ethoxylates (APEOs), alpha-Olefin sulfonates (AOS), Amine ethoxylates, Cocamidopropyl betaine, Fatty acid diethanolamides (FADAs), Organosilicones, Polyethylene glycols, Secondary alkane sulfonates (LAS), Linear alkylbenzene sulfonates (LAS), Ethoxylates/carboxylates of octyl/nonyl phenols

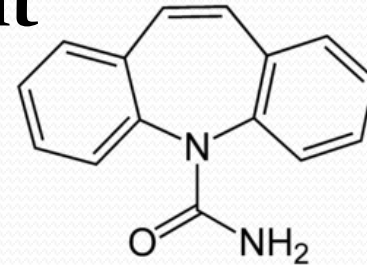


Category / class	Sub-class
<b>Disinfection by-products (drinking water)</b>	Iodo-trihalomethanes, Bromoacids, Bromoacetonitriles, Bromoaldehydes, Haloacetic acids (chloro-, bromo-, iodo-), Other disinfection by-products
<b>Plasticizers</b>	Phthalates, Benzophenone derivatives
<b>Flame retardants</b>	Brominated flame retardants, Polybrominated diphenylethers, Organophosphates, Chlorinated paraffins
<b>Fragrances</b>	Fragrances, Nitro musks, Macrocyclic musks, Polycyclic musks
<b>Gasoline additives</b>	Dialkyl ethers
<b>Industrial chemicals</b>	Industrial chemicals
<b>Nanoparticles</b>	Carbon fullerenes, Carbon nanotubes, Carbon black, Silicon-based, Titanium dioxide, Aluminium Oxide
<b>Perfluoroalkylated substances and their transformation products</b>	Perfluoroalkylated substances, Fluorotelomer alcohols, Perfluorosulfonamido alcohols
<b>Personal care products</b>	Sun-screen agents, Insect repellents, Carriers, Parabens

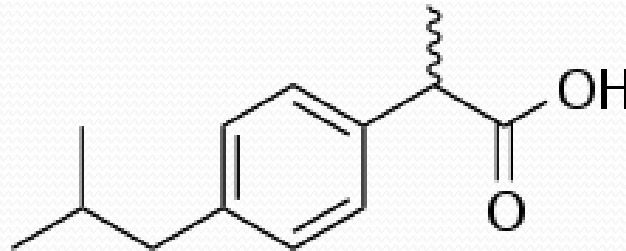
Category / class	Sub-class
<b>Pesticides</b>	Polar pesticides and their degradation products, Other pesticides, New pesticides, Degradation products of pesticides, Antimicrobial agents
<b>Biocides</b>	Biocides
<b>Pharmaceuticals</b>	Analgesic, Anorexic, Anthelmintic, Antibacterial, Anticonvulsant, Antidepressant, Antidiabetic, Antiemetic, Antihistaminic, Antihypertensive, Anti-inflammatory, Antimicrobial agent, Antineoplastic, Antiulcerative, Antiviral, Anxiolytic, Beta-Blockers, Blood viscosity agents, Bronchodilators, Diuretic, Lipid regulators, Sedatives, hypnotics, Steroids and hormones, Psychiatric drugs, X-ray contrast media
<b>Trace metals and their compounds</b>	Trace metals and their compounds
<b>Anticorrosives</b>	Benzotriazoles, Methylbenzotriazoles (MBT), Tolyltriazoles (TT)
<b>Wood preservatives</b>	Phenols
<b>Other</b>	Drugs of abuse, Benzothiazoles (BT), Nicotine metabolite

# Univerzum i svemir Ems-a – Em hemikalija-Polutanata

- Carbamazepine – antikonvulzant



- Ibuprofen – nesteroidni antiinflamatorni lek

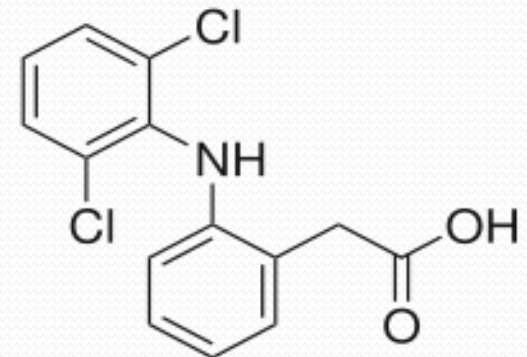


- Diclofenac- nesteroidni antiinflamatorni lek

- Mi smo detektovali...

- NATO Projekat – krajnji korisnik

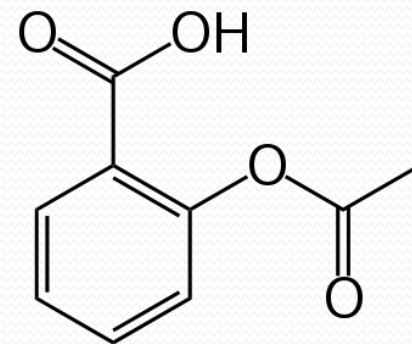
- Vodovod i kanalizacija



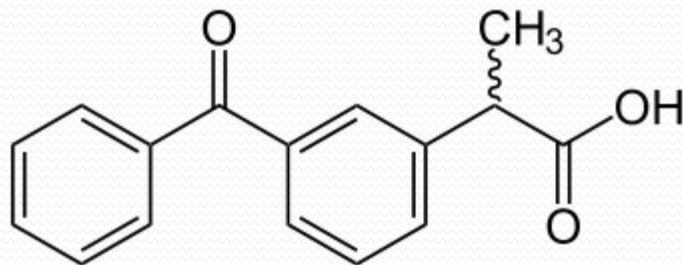


# Univerzum hemijskih polutanata

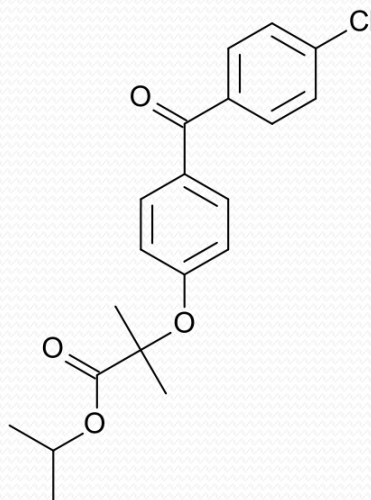
- Aspirin – analgetik i antipiretik



- Ketoprofen

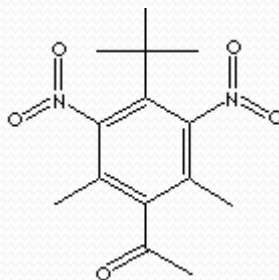


- Fenofibrate

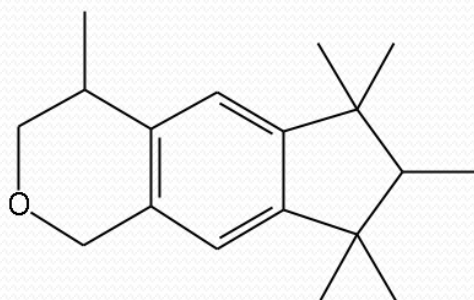


# EmS iz grupe proizvoda svakodnevne upotrebe

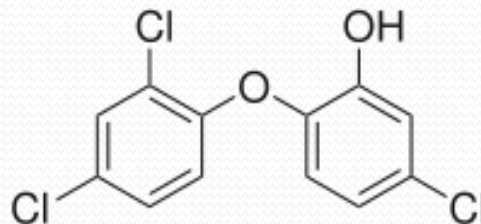
- Musk ketone



- Galaxolide

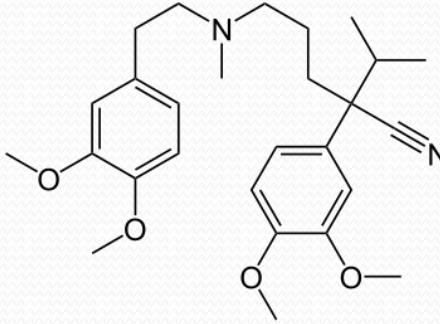


- Triclosan

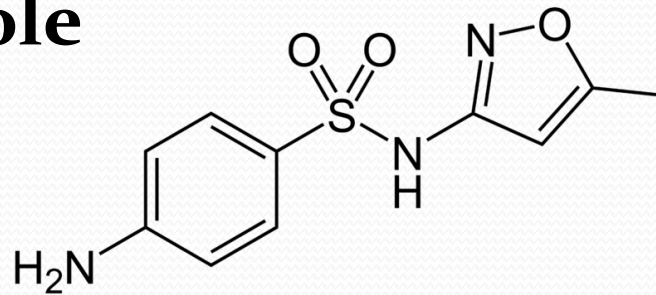


# Bogata raznovrsnost Em- polutanata

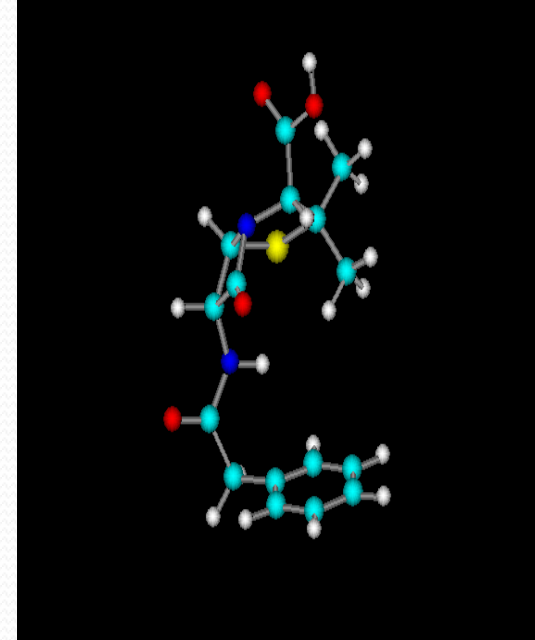
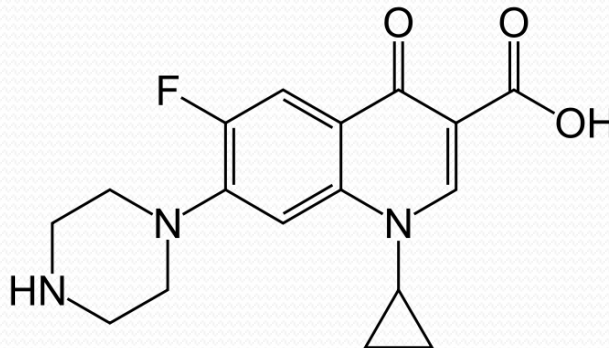
- Verapamil



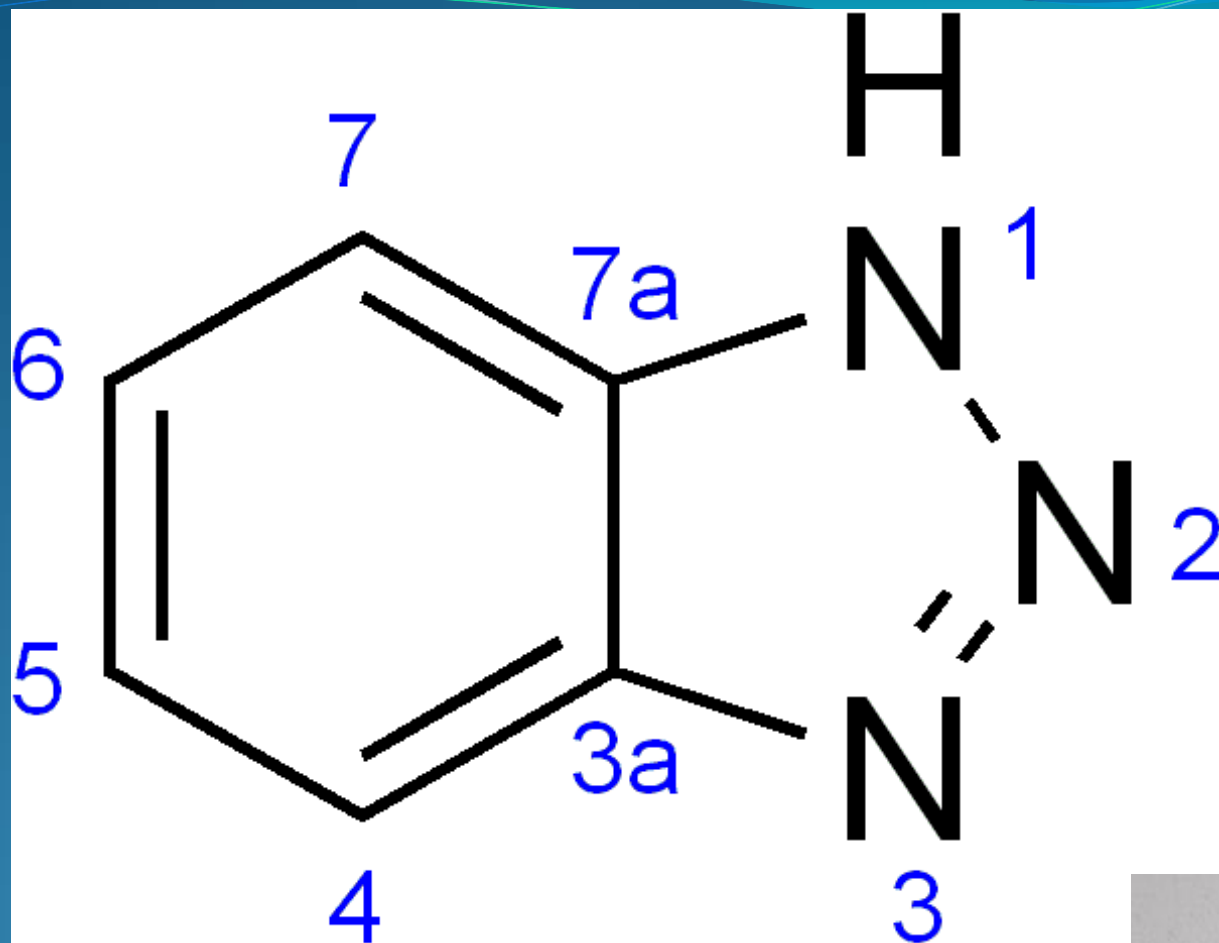
- Sulfamethoxazole



- Ciprofloxacin







**BENZOTRIAZOL**



# EmS su razvrstane u 6 osnovnih klasa

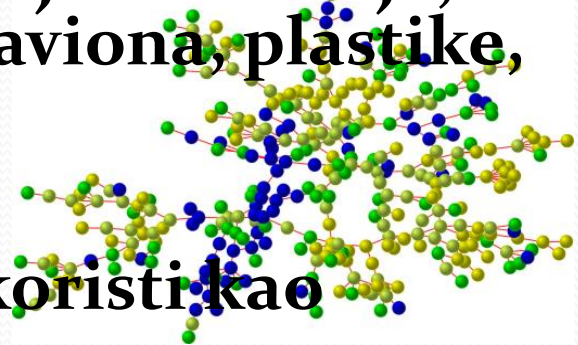
- Globalni organski polutanti: PBDEs, HBCDs, PFOS, PFOA i siloksani (vazduh-saobraćaj...
- Farmaceutici i produkti za ličnu higijenu uključuju sve lekove koji se prodaju sa i bez recepta, dijagnostički agensi, suplementi ishrani, parfemi, sapuni, omekšivači, kreme za sunčanje, kozmetika, kofein i nikotin...
- Supstance koje regulišu rad endokrinog sistema uključuju prirodne i sintetičke hormone, surfaktante, pesticide, tributilin (TBTO), PCB i dioksini/furani.

# Globalni organski kontaminanti

- Polibromovani difenil etri - PBDEs, organobromne supstance - se koriste kao usporivači gorenja, u građevinarstvu, elektronici, proizvodnji nameštaja, tekstilnih prevlaka, motornih vozila, aviona, plastike, poliuretanske pene, tekstila...

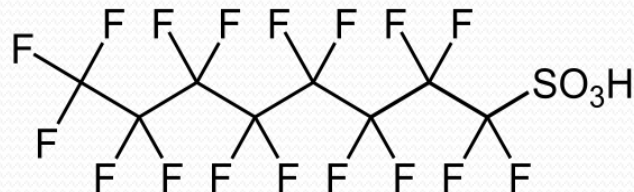
## Heksahlorobutadien – HBCDs,

# hlorirani alifatični dien - najčešće se koristi kao rastvarači za ostale hlorovane supstance



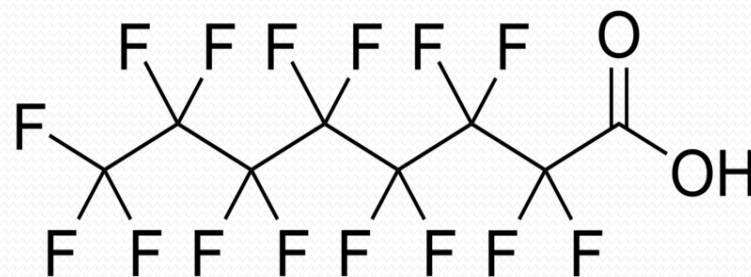
- Perfluorooctanosumporna kiselina - PFOS,

**fluorosurfaktant – sintetski - globalni polutant – dodat  
u Aneks B STOKHOLMSKE KONVENCIJE .**



# PFOA and Siloksani

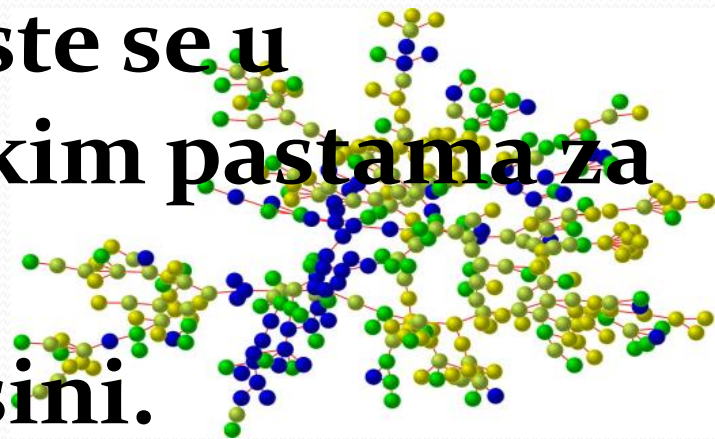
- Perfluorooktanska kiselina -PFOA, sintetička hemikalija, perzistentna u životnoj sredini, ima negativne efekte na razvoj laboratorijskih životinja



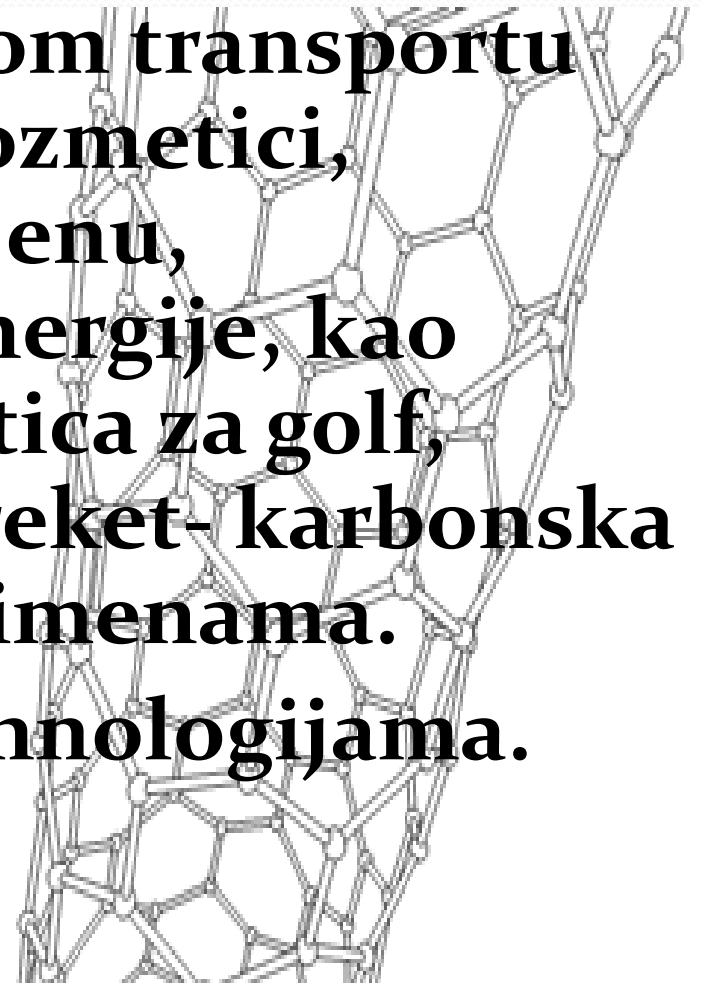
- Siloksani – empirijske hemijske formule,  $R_2SiO$ , R atom vodonika ili ugljenohidratna grupa. Pripadaju široj grupi organosilikonskih supstanci.
- Dopuniti --:\_?



- Industrijske hemijske supstance uključuju ftalate, nonilfenol i alkilfenol etoksilate – APE (surfaktanti, supstance protiv formiranja pene, UV stabilizatori u plastici)
- bisfenol A-Ems sa naglašenom hormonskom aktivnošću, PCBs, dioksini/furani, PBDEs (usporivači gorenja), parabeni – koriste se u kozmetici i antibakterijskim pastama za zube).
- Biološki metaboliti i toksini.

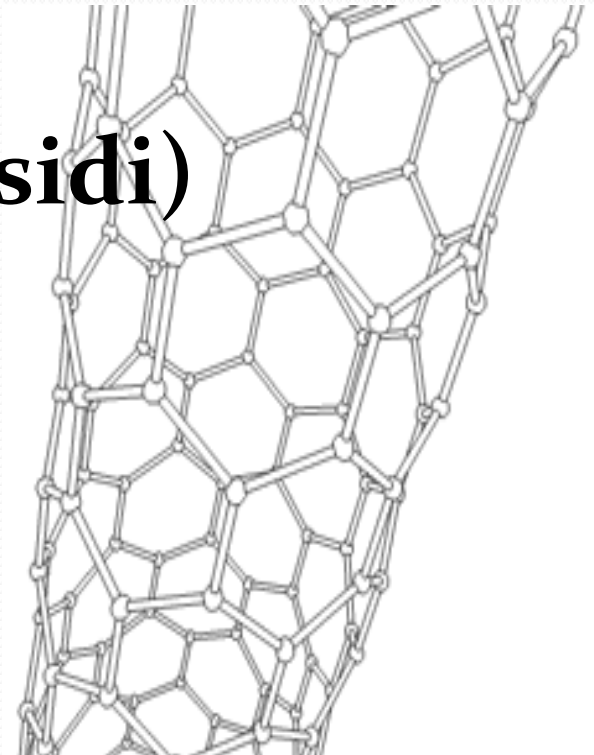
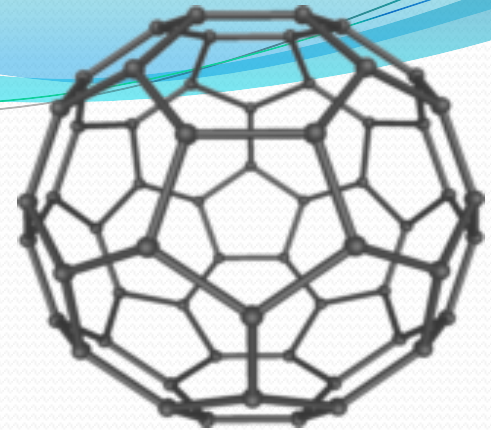


- **Nanomaterijali** - prirodne i antropogenog porekla strukture - variraju u veličini od 1 nm do 100 nm, široko se koriste u nano-terapeutskim farmaceuticima, pametnom transportu leka( ugljenične tube), kozmetici, produktima za ličnu higijenu, produktima za čuvanje energije, kao lubrikanti, u sportu (loptica za golf, tenis, savremeni teniski reket- karbonska nano vlakna) i drugim primenama.
- Svim naprednim, nanotehnologijama.
- **Izazovi 21 veka**



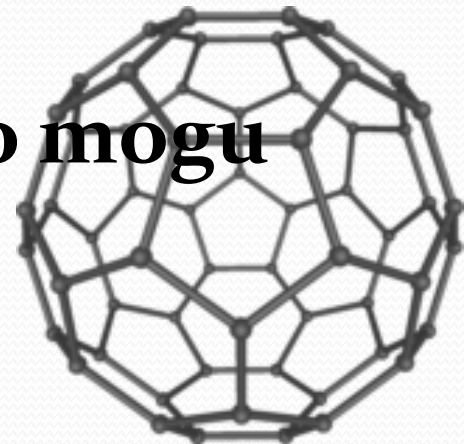
# Nanopartikule

- Fulereni (buckyballs)
- Nanotube (nosači lekova-ugljenične tube)
- Nanopuderi (metalni oksidi)
- Prirodne partikule (čad, nano prašina)



# Nanopartikule

- Hemijske i fizičke osobine se drastično menjaju zbog promene u talasnim osobinama - zbog **nano veličine partikule**
  - Magnetizam, kapacitet punjenja, tačka topljenja, tvrdoća
  - Materija može da funkcioniše kao katalizator ili poluprovodnik
  - Obojeni metali kao zlato i srebro mogu da dobiju magnetna svojstva





# Toksičnost

- Toksičnost nanotehnoloških proizvoda nije još poznata.
- prolaze kroz biološke membrane i kroz krvno – moždanu barijeru - jer je veličina pora/kanalića- nekoliko nm kao i nanopartikule.
- Preliminarni rezultati
- Ukazuju na novu vrstu
- **Nano toksičnosti**



# Scarce informations

- *For most EmS, there is currently scarce information about their potential toxicological effects in ecosystems - the fate and the transport of EmS in eco media are practically unknown !!!*
- *as well as the distribution and partitioning processes –  $K_{oc}$  ,  $K_{LW}$*
- *soil/water/atmosphere -  $K_{ow}$  ,  $K_{oA}$  ,  $K_{Aw}$*



# 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**

## P-P and kinetic equations

- P-P -the input rate of EmS is higher than their rate of degradation or mineralization.
- $V_{input} > V_{degradation}$
- This can be called second order persistency or pseudo persistency, P-P
- $\underline{v_i} \gg \underline{v_{ou}}$   $v_i$  rate of EmS input,  $v_{ou}$  - output





EmS

Umesto zaključka



EmS



EmS

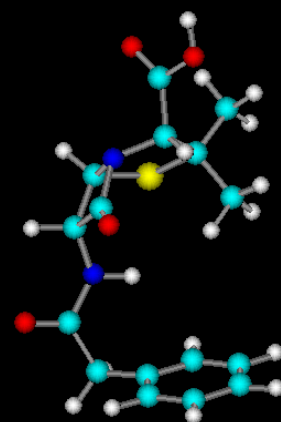
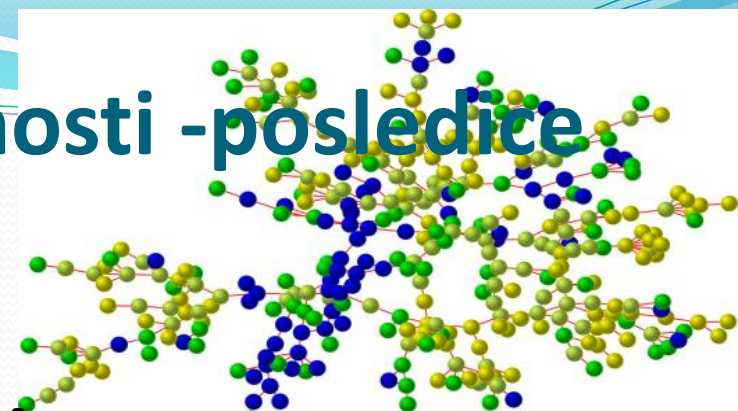
# Šta je novo-izazovi, specifičnosti -posledice

- Neregulisane hemikalije

Stari polutanti – nova zabrinutost;

EmP - novoprepoznati i detektovani u ŽS  
zahvaljujuće naprednoj-sofisticiranoj  
analitičkoj instrumentaciji UPHPLC- TOF-  
tandem MS-MS.

- Registuju se hazardni i
- toksični efekti
- Ubikvitarnost





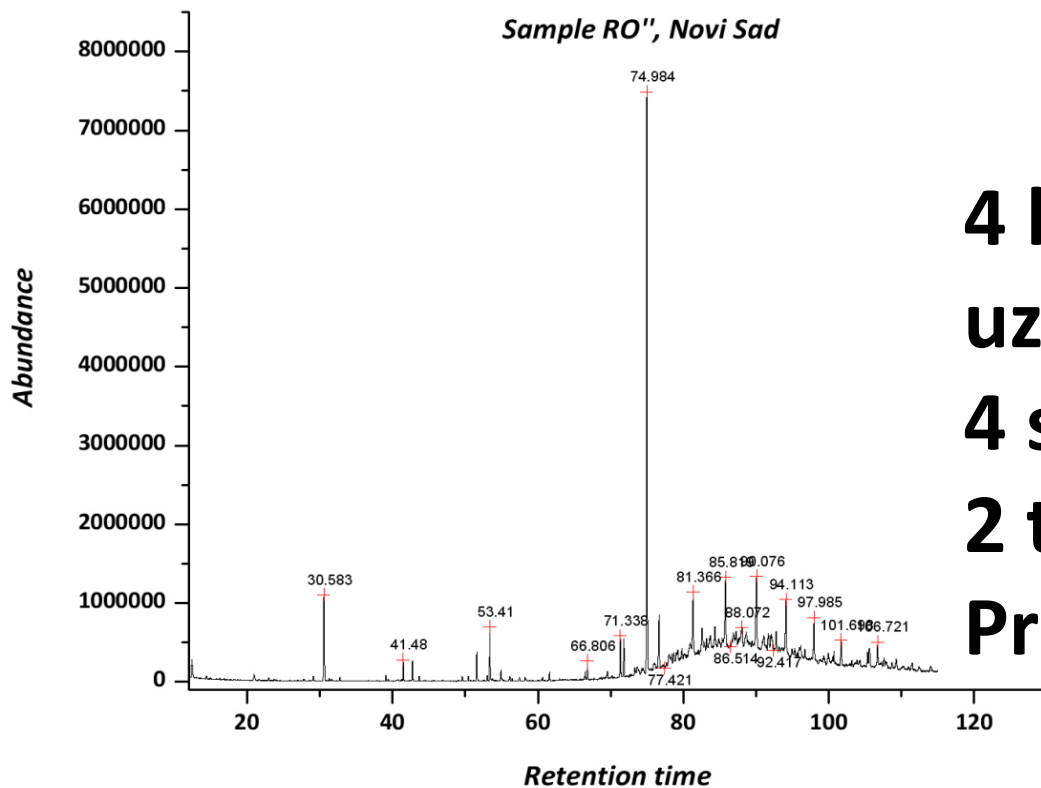


# Skrining i target analiza

- **Detektovano je više od 150 različitih prioriternih, prioritarno hazardnih i emergentnih organskih jedinjenja - ftalati, indeno derivati, alkil supstituisani benzeni, naftalen, fenolni derivati, PAH, hormoni, trifenil fosfati), kofein i druga. -NS površinska voda Dunava niskih koncentracija, ppb/ppt !!!**



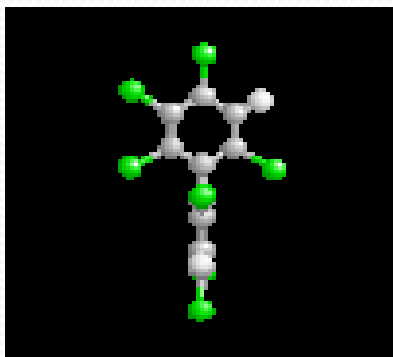
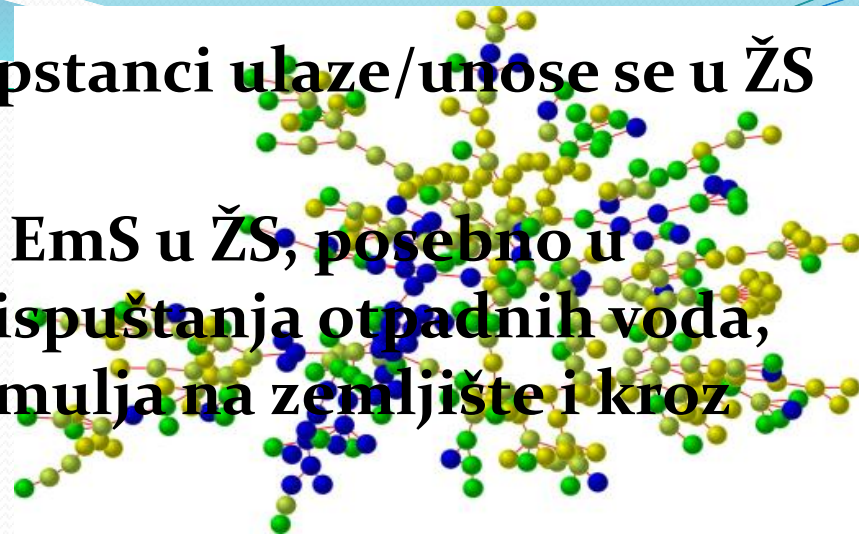
# Skrining analiza



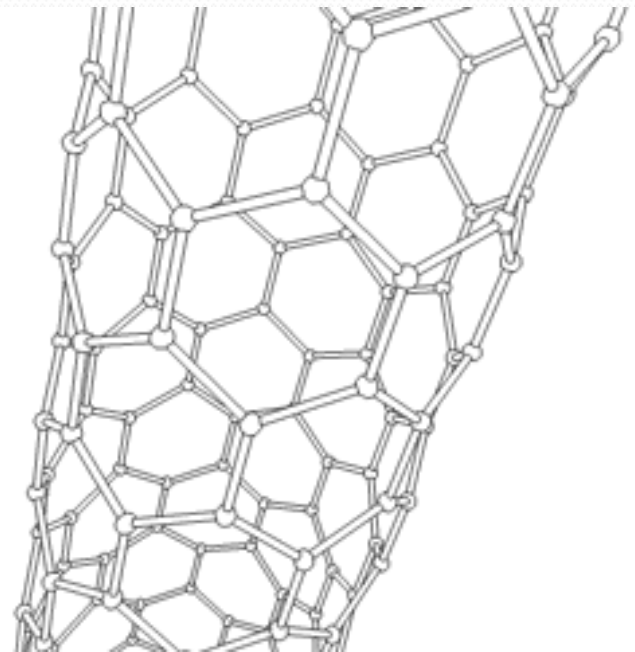
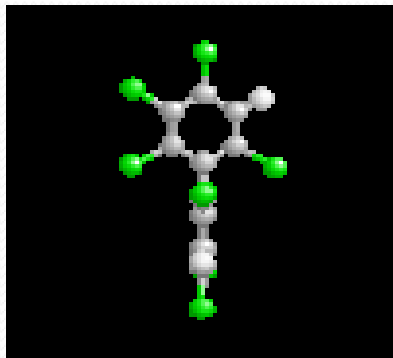
**4 kampanje  
uzorkovanja-2012/13  
4 skrining analize  
2 target analize  
Proces prioritizacije**



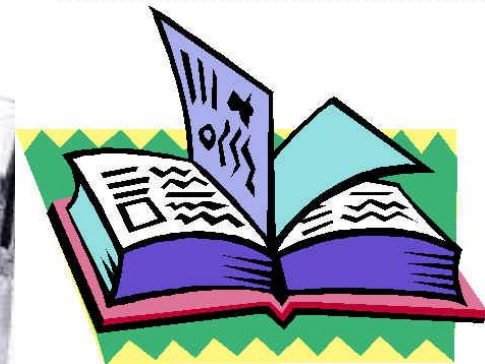
- Milioni novih hemijskih supstanci ulaze/unose se u ŽS svake godine.
- Najčešći mehanizam unosa EmS u ŽS, posebno u površinske vode, je putem ispuštanja otpadnih voda, primenom kanalizacionog mulja na zemljište i kroz procedne vode deponija.
- Za većinu EmS nema adekvatnih informacija o visini/nivoima negativnih posledica i toksičnim efektima na ljudsko zdravlje i životnu sredinu !!!



- EmS – aditivni i sinergistički efekt  
združenih hemijskih stresora
- nepoznat sumarni negativan efekt  
na ŽS i zdravlje čoveka



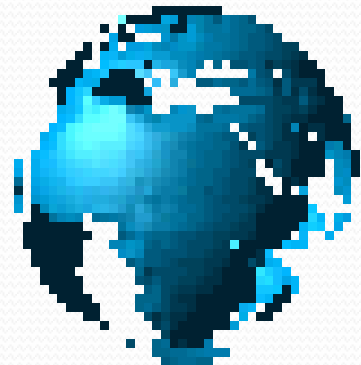
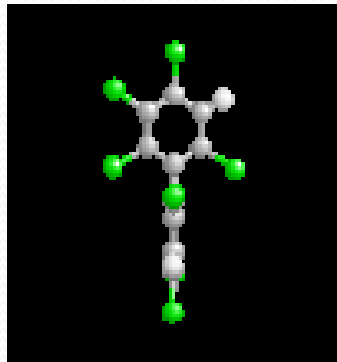
- Detektovane koncentracije EmS su u rasponu od:  
ng/L - ppt,  $\mu\text{g/L}$  – ppb čak i niže.
- Kako mogu da se uklone mikro i nano zagađujuće materije tipa EmS ? Mogu da kontaminiraju i pijaću vodu !
- Istražuje se !!!
- Istraživanja Budućnosti
- 2020 .....



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