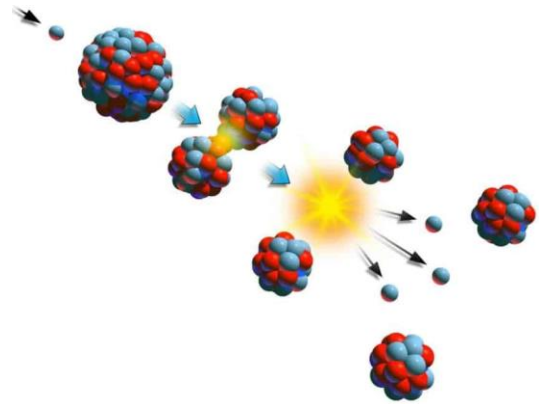
VOLGOGRAD
STATE
MEDICAL
UNIVERSITY



# Pollution of the environment with metals, nitrogen compounds, pesticides, radionuclides

*Department of General Hygiene and Ecology*
*Senior Lecturer Novikov D.S.*

# Emerging Contaminants…What they are??

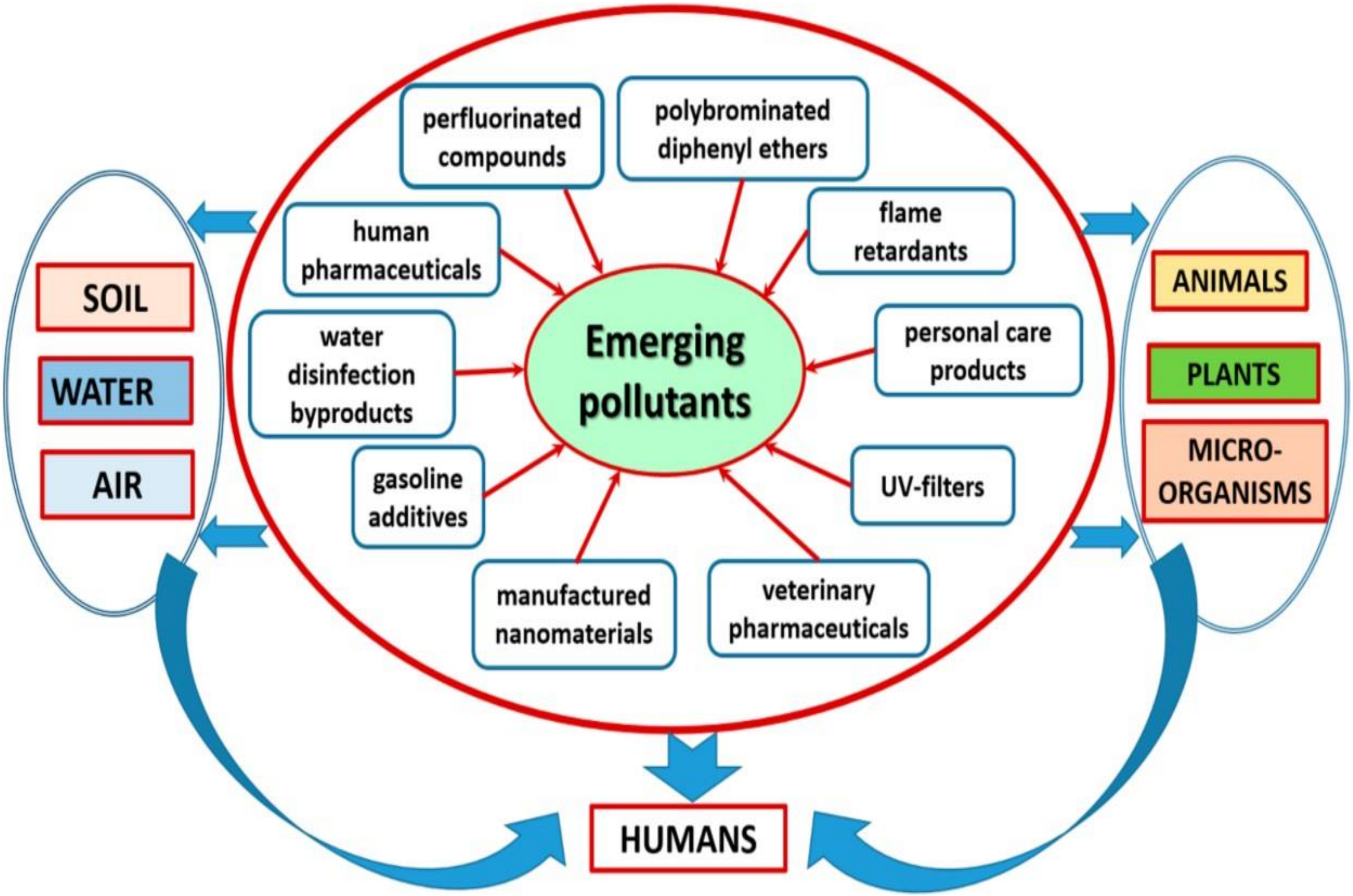
- Emerging contaminants (ECs), a class of contaminants with **low concentrations** but **significant harm**. ECs comprises of various chemicals that enter the environment every day (*VarshaP. M et al., 2021 https://doi.org/10.1016/j.chemosphere.2021.132270*)

- Contaminants of emerging concern, these are the substances that **have appeared newly** or whose presence was identified earlier **but the hazards were not known**. These could be of **natural origin or manmade**. (Sauvé and Desrosiers et al., 2014)

- Emerging pollutants, "as pollutants that are currently **not included in routine monitoring programmes**, which may be candidates for **future regulation**, depending on research on their (eco) **toxicity**, potential health effects and public perception and on monitoring data regarding their **occurrence** in the various **environmental compartments**" (NORMON groups cited in Yadav, D., et al (2021). *Chemosphere*, *272*, 129492)

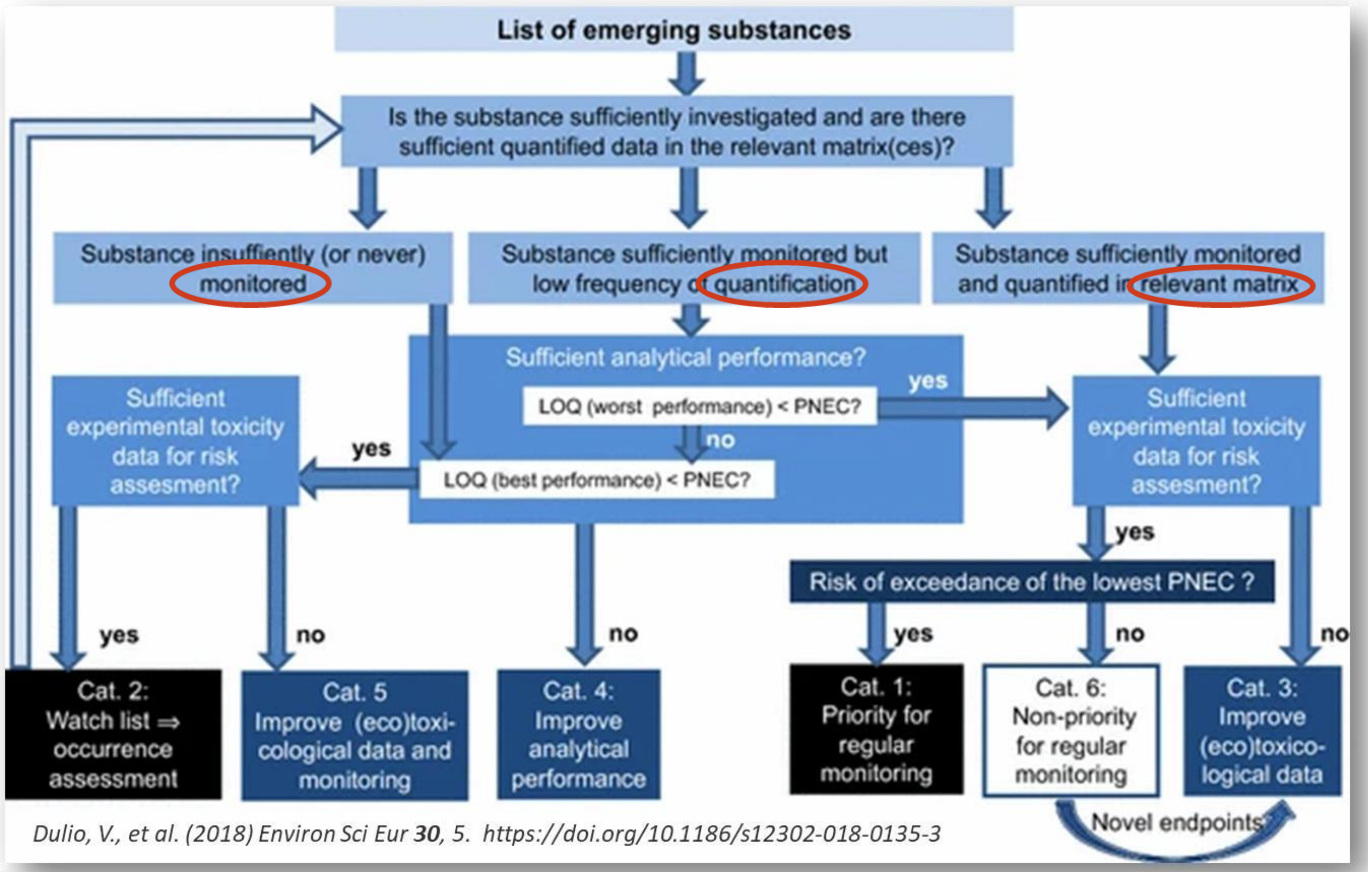
- Sauvé et al. (2018), defined Contaminants of Emerging Concern (CECs) as 'naturally occurring, manufactured or manmade chemicals or materials which have now been discovered or are suspected [to be] present in various environmental compartments and whose toxicity or persistence is likely to alter the metabolism of a living being significantly.' CECs show **high resistance to degradation** due to its **complex structure** and other factors.

# Emerging Contaminants in soils. Sources



The NORMAN network enhances the exchange of information on emerging environmental substances, and encourages the validation and harmonization of common measurement methods and monitoring tools so that the requirements of risk assessors and risk managers can be better met.

- Metals
- Radionuclides
- Pharmaceuticals
- PAHs
- Plastics
- Fertilizers




*Dulio, V., et al. (2018) Environ Sci Eur* ***30****, 5. https://doi.org/10.1186/s12302-018-0135-3*

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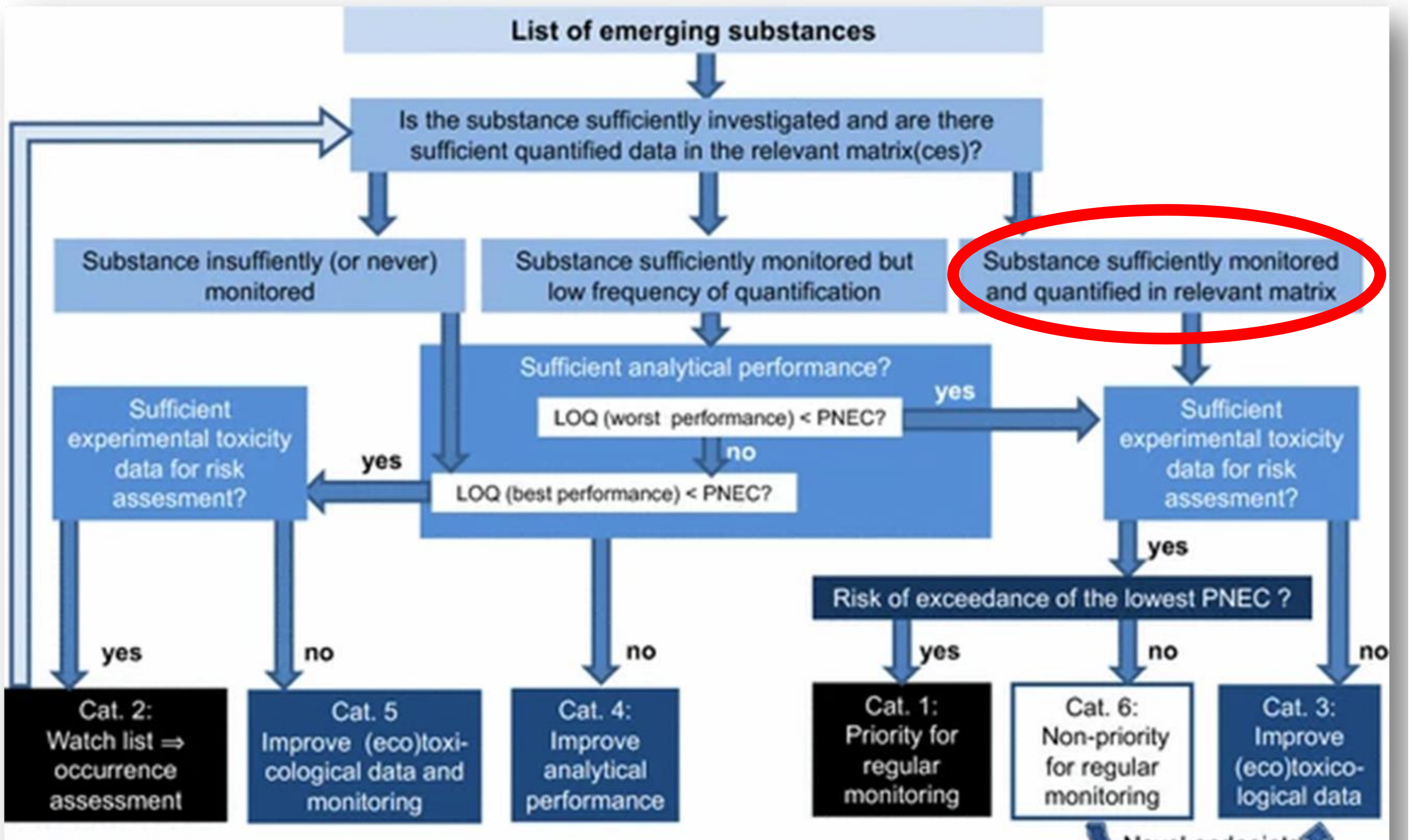
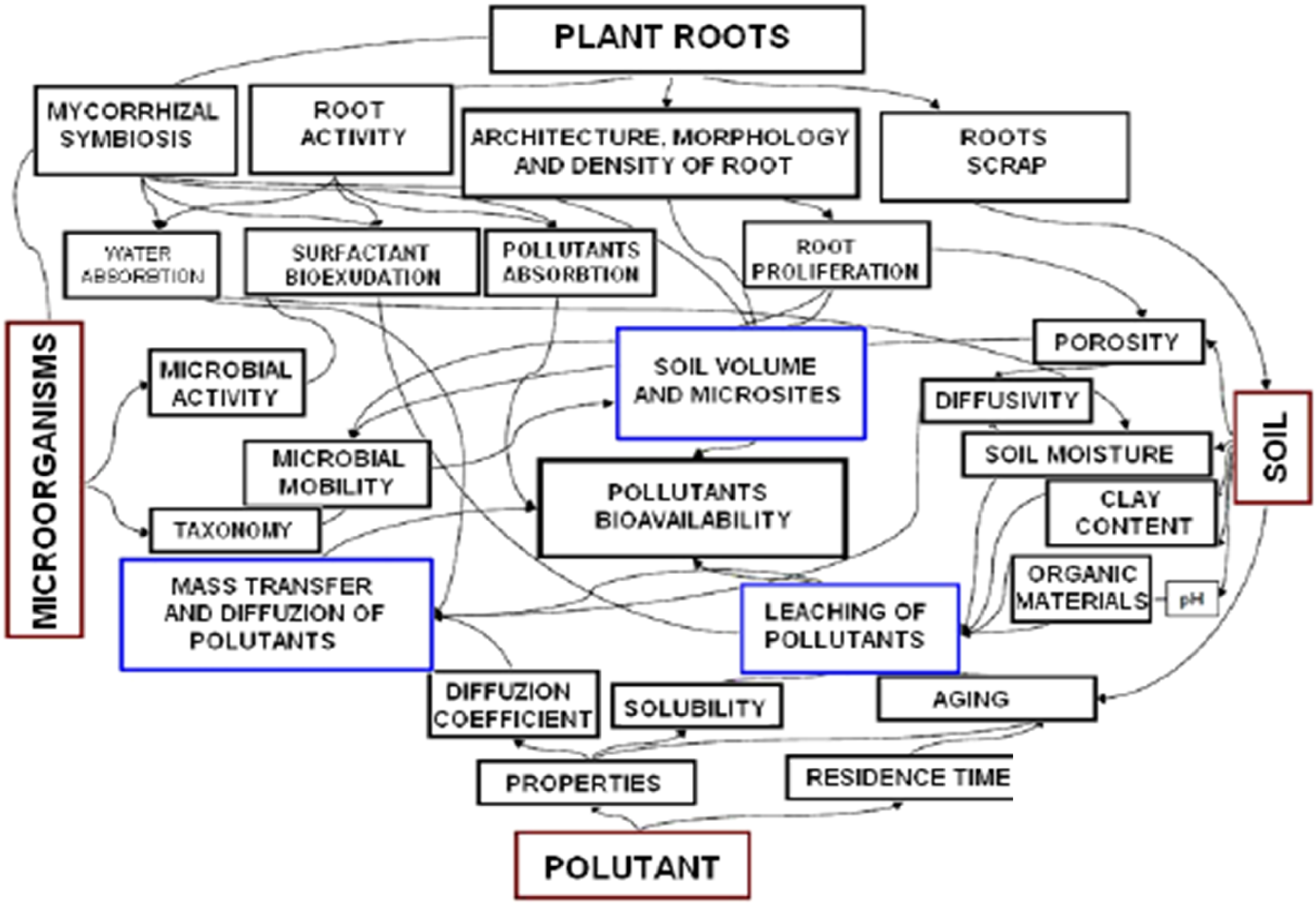



*Dulio, V., et al. (2018) Environ Sci Eur* **30**, 5. *https://doi.org/10.1186/s12302-018-0135-3*

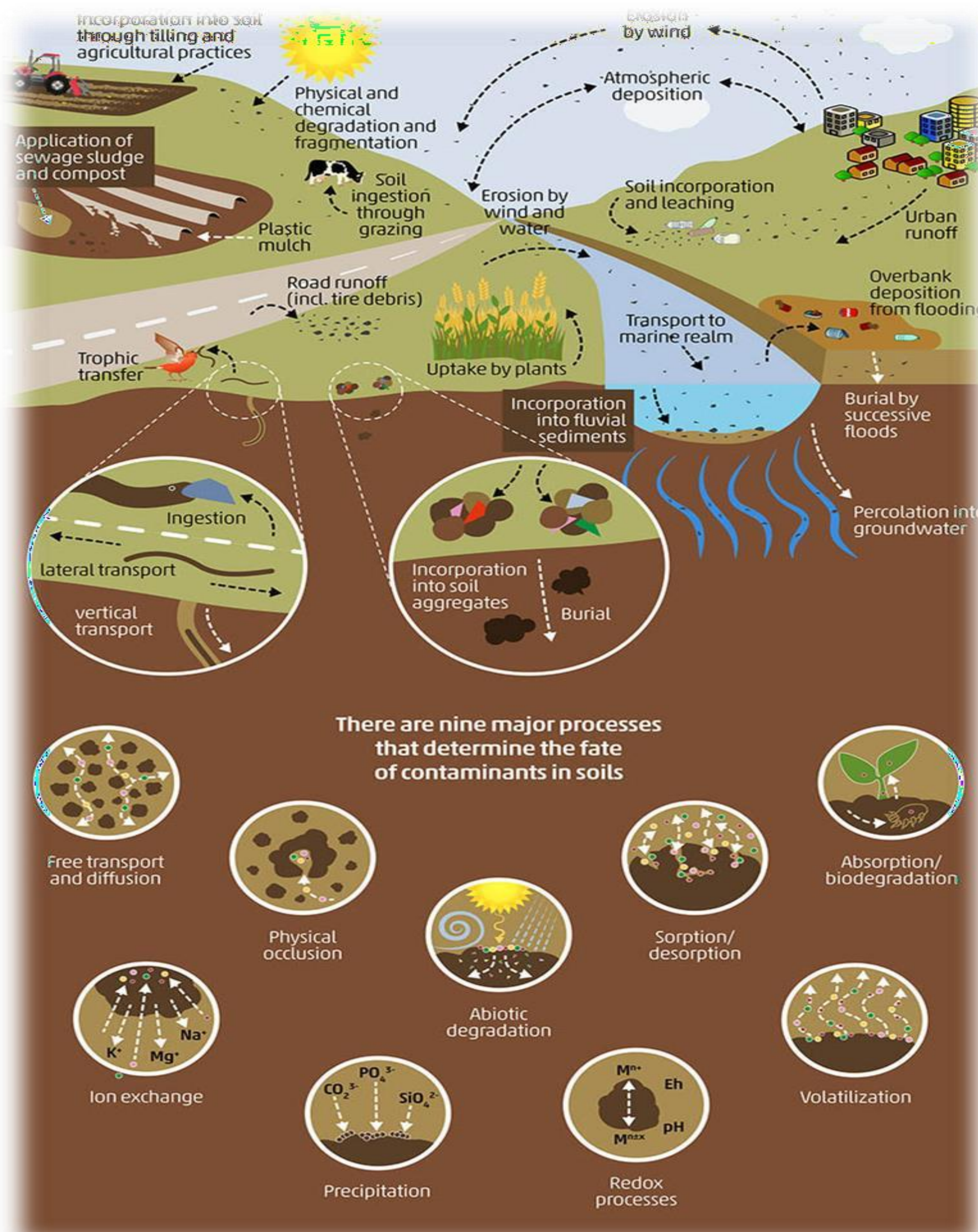
# Metals



PLANT ROOTS
MYCORRHIZAL SYMBIOSIS
ROOT ACTIVITY
ARCHITECTURE, MORPHOLOGY AND DENSITY OF ROOT
ROOTS SCRAP
WATER ABSORBTION
SURFACTANT BIOEXUDATION
POLLUTANTS ABSORBTION
ROOT PROLIFERATION
MICROORGANISMS
POROSITY
MICROBIAL ACTIVITY
SOIL VOLUME AND MICROSITES
DIFFUSIVITY
SOIL
MICROBIAL MOBILITY
SOIL MOISTURE
POLLUTANTS BIOAVAILABILITY
CLAY CONTENT
TAXONOMY
ORGANIC MATERIALS
pH
MASS TRANSFER AND DIFFUZION OF POLUTANTS
LEACHING OF POLLUTANTS
DIFFUZION COEFFICIENT
SOLUBILITY
AGING
PROPERTIES
RESIDENCE TIME
POLUTANT

# Metals

Symbiosis in
the environment
biomanagement
of soils
contaminated



# Risk assessment of rare **Earth elements**, **Antimony**, **Barium**, **Boron**, **Lithium**, **Tellurium**, **Thallium** and **Vanadium** in teas

Kowalczyk E, et a. (2022). EFSA Journal 2022;20(S1):e200410, 12 pp.
https://doi.org/10.2903/j.efsa.2022.e200410

**Boron**

Symptoms related to B intoxication includes gastrointestinal disturbances, granular degeneration of tubular cells, exfoliatedermatitis, epilepsy, cardio-circulatory collapse. Congestion of the brain, hair loss, lethargy, anorexiaand mental confusion were other identified effects (EFSA, 2006). The most sensitive endpoint of toxicity of B was, however, a developmental toxicity (Murray and Schlekat, 2004). A tolerable upper intake level (UL) was based on the decreased fetal body weight in rats resulting from maternal boron intake during pregnancy. variability) to givean UL of 0.16 mg/kg bw per day (EFSA, 2004a).

**Rare Earth Elements**

(La, Ce, Pr, Nd,Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Gd, Tb, Dy, Tm, Yb, Y, Sc). A key toxicological characteristic of the REEs is their common ability to displace calcium from calcium-binding sites in living systems, resulting in enzyme inhibition or other biochemical dysfunctions (Palasz and Czekaj, 2000)

**Lithium**

The element has been identified as having an adverse renal effect, with the most common being nephrogenic diabetesinsipidus. Some adverse effects on thyroid function, primarily asymptomatic hypothyroidism have been observed in patients treated with Li (McKnight et al., 2012).

**Thallium**

In the case of thallium, it is known that its salts can cause a wide spectrum of adverseeffects in humans and animals, and thallium is considered a cumulative poison (EPA, 2009). Acutethallium poisoning is usually accompanied by gastrointestinal symptoms, while neurologicalfindings(sensory and motor changes) predominate in chronic exposure. Other symptoms include polyneuritis,encephalopathy, tachycardia and degenerative changes of the heart, liver and kidneys (Cvjetko et al.,2010).

**Barium**

Human and animal high-dose exposure to soluble Ba compounds results in a number ofeffects including electrocardiogram abnormalities, ventricular tachycardia, hypertension and/or and hypotension, muscle weakness and paralysis (SCHER, 2012). Kidney effects are considered the most sensitive health effect associated with long-term ingestion of Ba (Kravchenko et al., 2014).

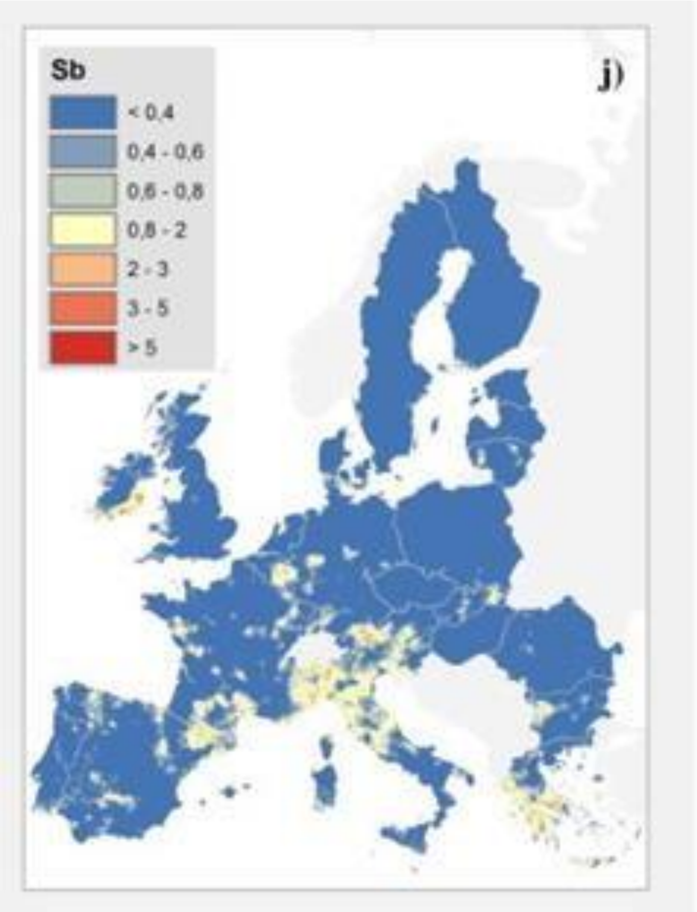
**Vanadium**

High concentrations of V may cause irreversible damage to the kidneys (EFSA, 2004b). Vanadium in mammalian species can accumulate in the liver, kidneys, bones, lungs and spleen (Rodr□guez-Mercado et al., 2011; Crebelliand Leopardi, 2012). Vanadium compounds may initiate some gastrointestinal problems such as diarrhoea, vomiting, general dehydration with weight reduction, intestinal inflammation and acharacteristic green tongue (Wilk et al. 2017)

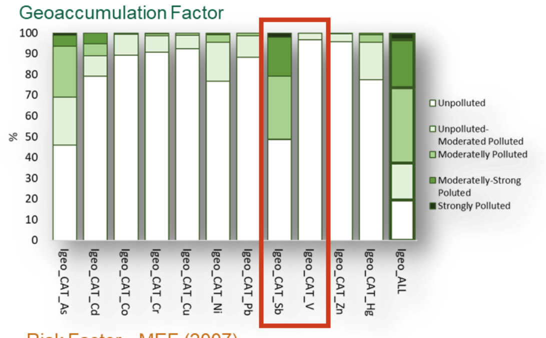
**Antimony**

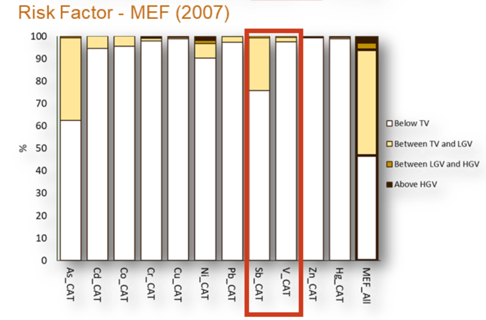
In the case of Sb, oral exposure predominantly affects the gastrointestinal systemresulting with burning stomach pains, colic, nausea and vomiting (Sundar and Chakravarty, 2010)

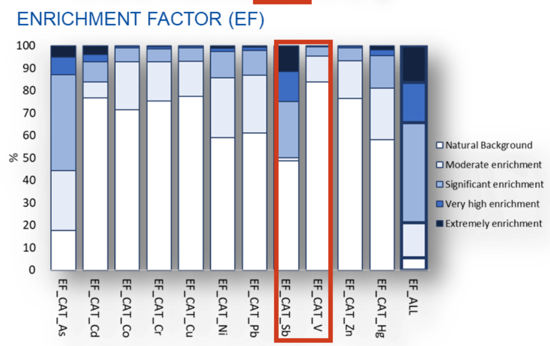
# Antimony and Vanadium from LUCAS 2009 database

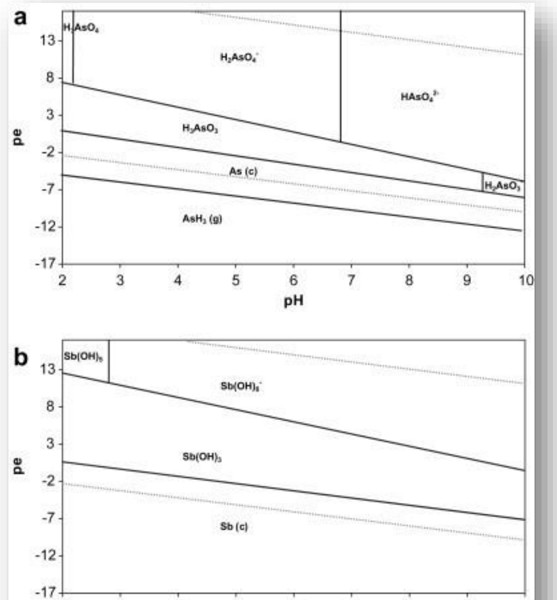



*Tóth et al. (2016) Environment International, 88, 299-309, https://doi.org/10.1016/j.envint.2015.12.017.*

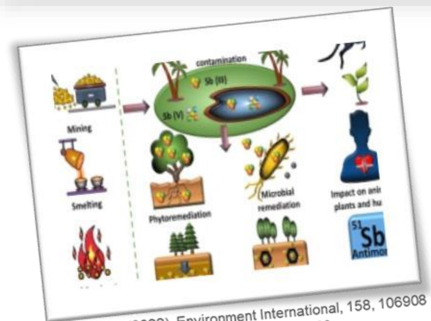


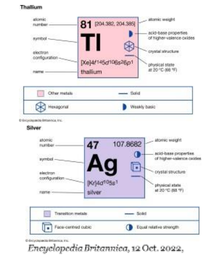




Susan C. et al. (2010) Environmental Pollution, 158, 5,1169-1181
https://doi.org/10.1016/j.envpol.2009.10.045



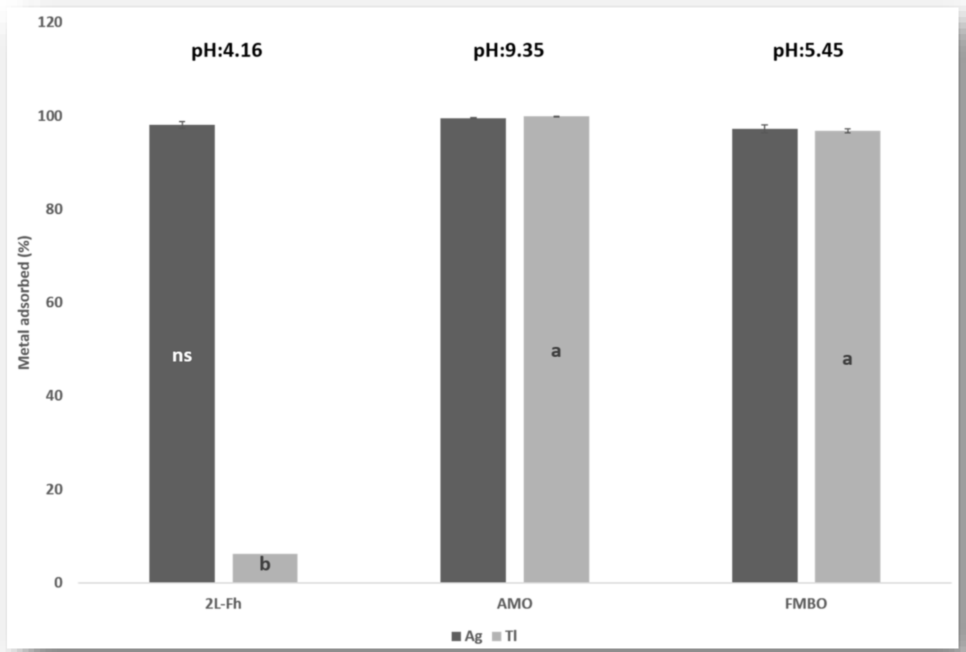

Nanthi et al.(2022). Environment International, 158, 106908
https://doi.org/10.1016/j.envint.2021.106908.

# Use of Natural Sorbents for Thallium and Silver sorption




- Four nano-metal (hydr)oxides (amorphous Mn oxide (AMO), Fe-Mn binary oxide (FMBO), two-line ferrihydrite (2L-Fh) and goethite) were successfully synthesized and fully characterized

- AMO and FMBO not only demonstrated their efficiency as Ag and Tl sorbents, but also displayed they would be promising nanomaterials as micronutrient fertilizers.


Cieschi, M.T. Yunta, F. *Agronomy* **2021**, *11*, 1876. https://doi.org/10.3390/agronomy11091876

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Metals

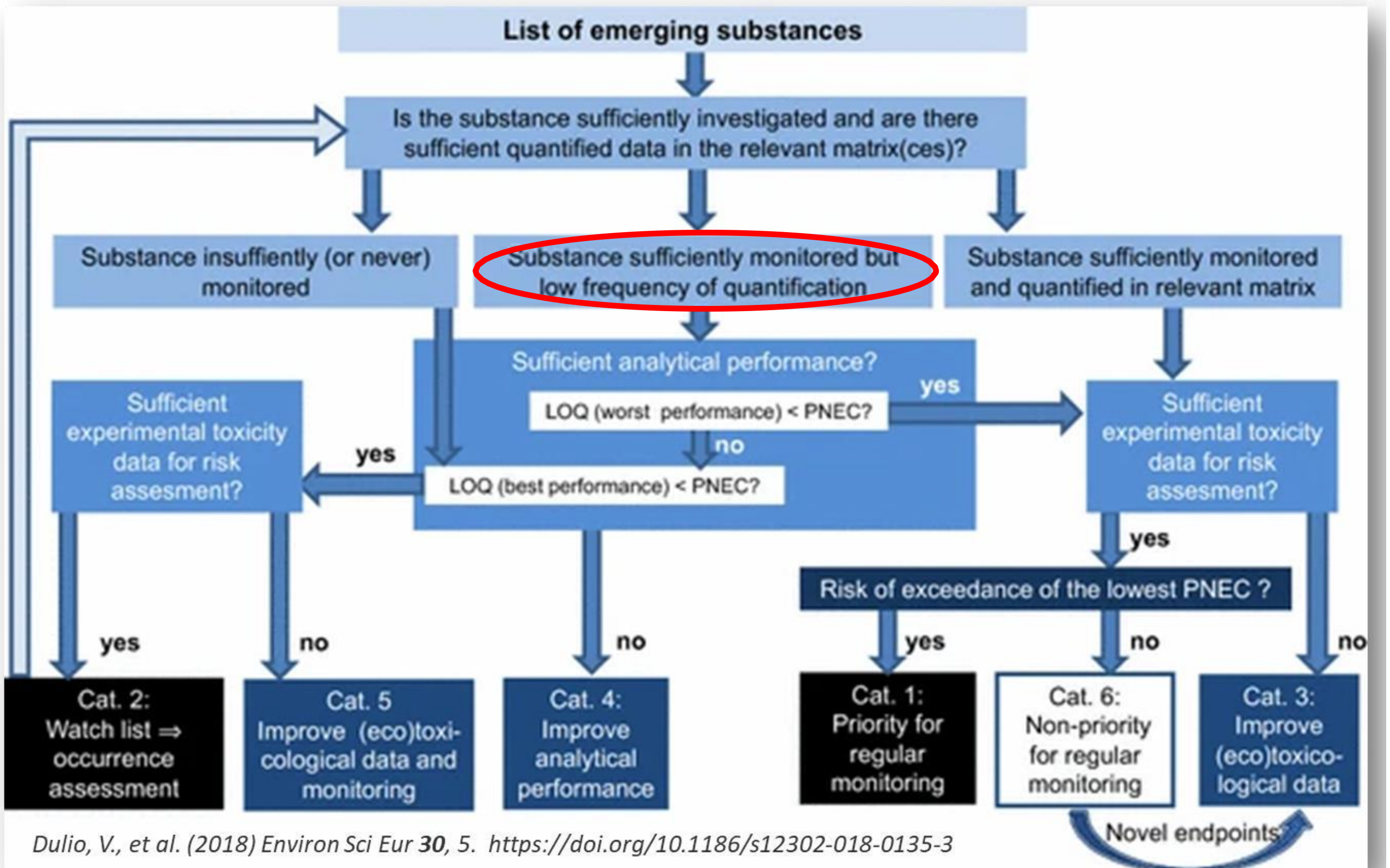
Radionuclides

Pharmaceuticals

PAHs

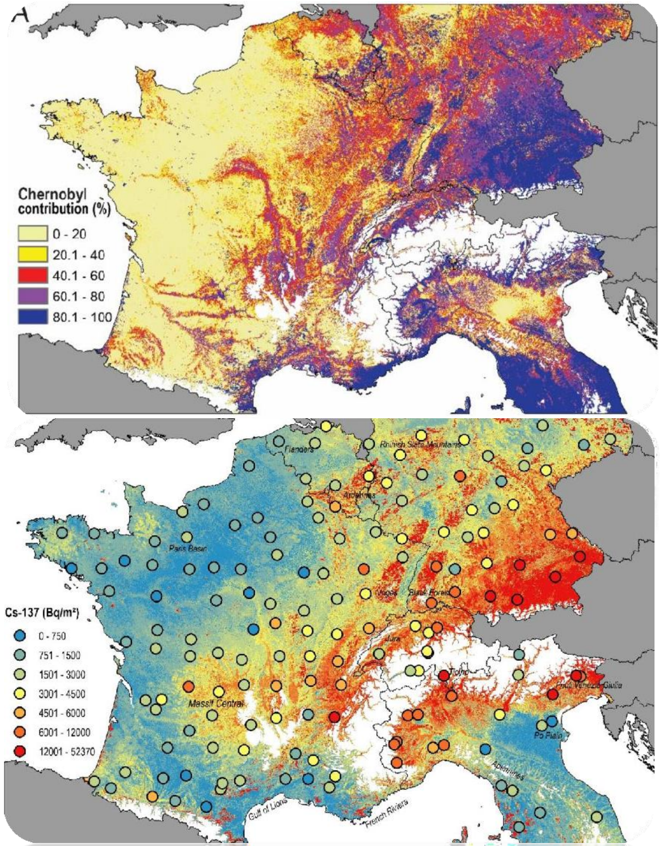
Plastics

Fertilizers

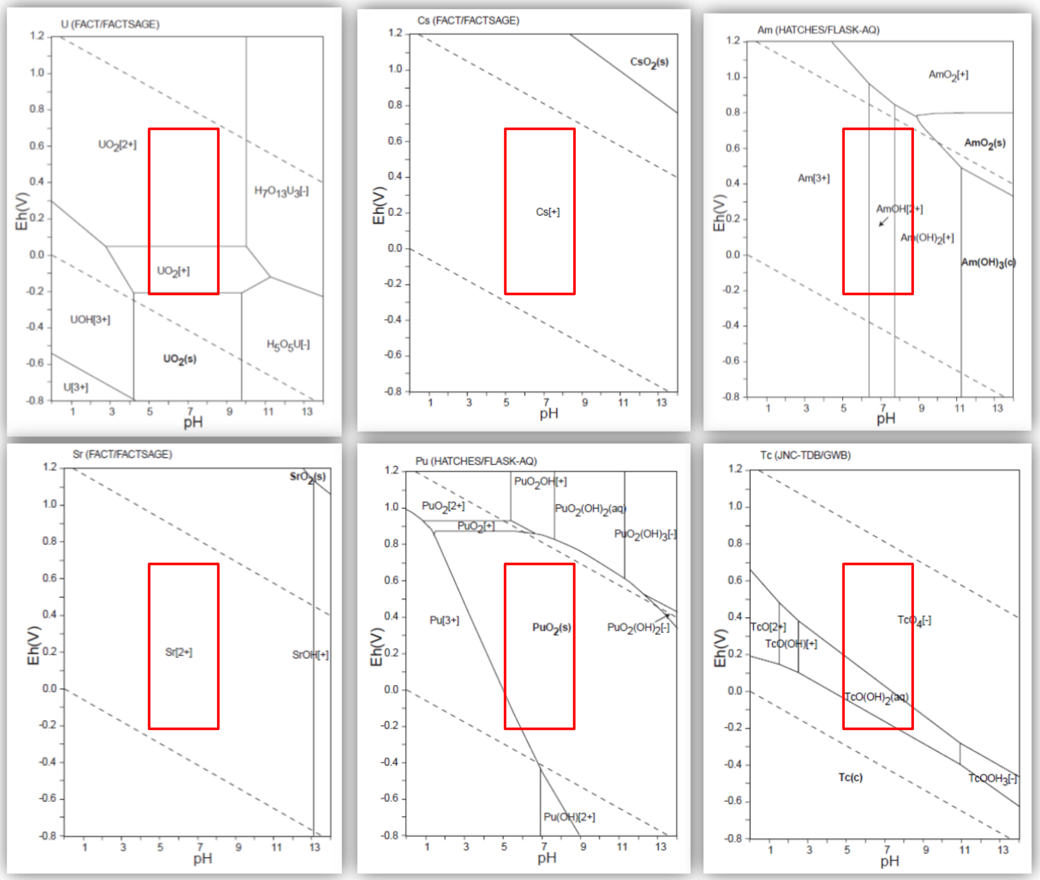


*Dulio, V., et al. (2018) Environ Sci Eur* ***30****, 5. https://doi.org/10.1186/s12302-018-0135-3*

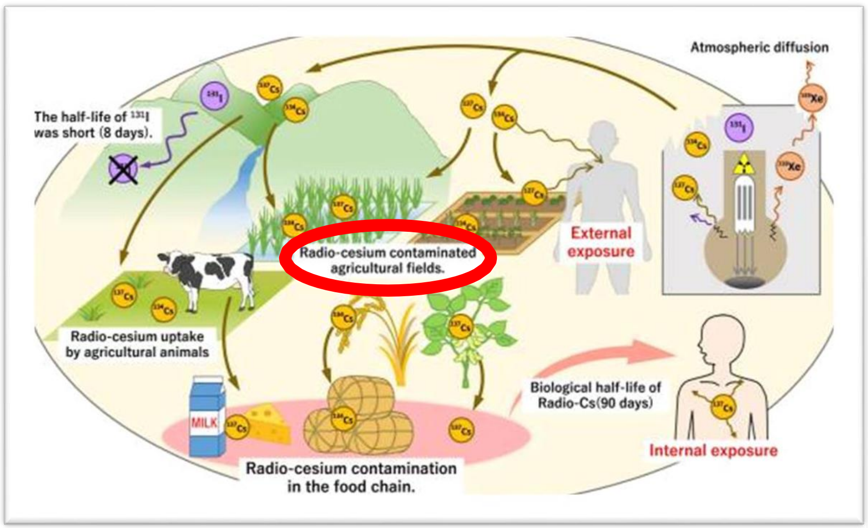
# Radionuclides

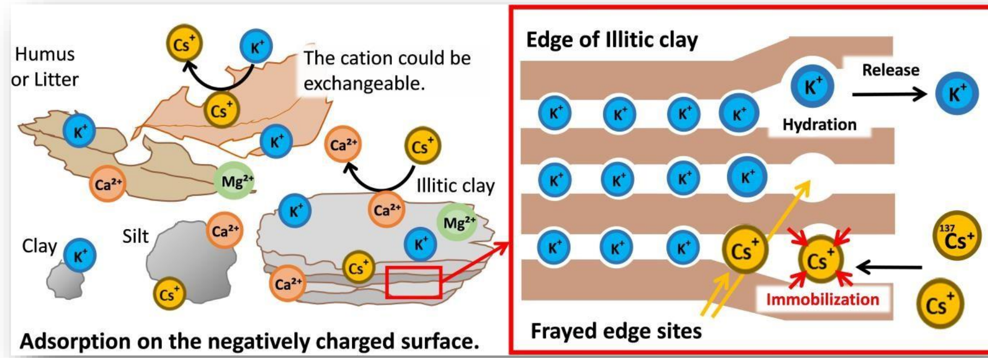


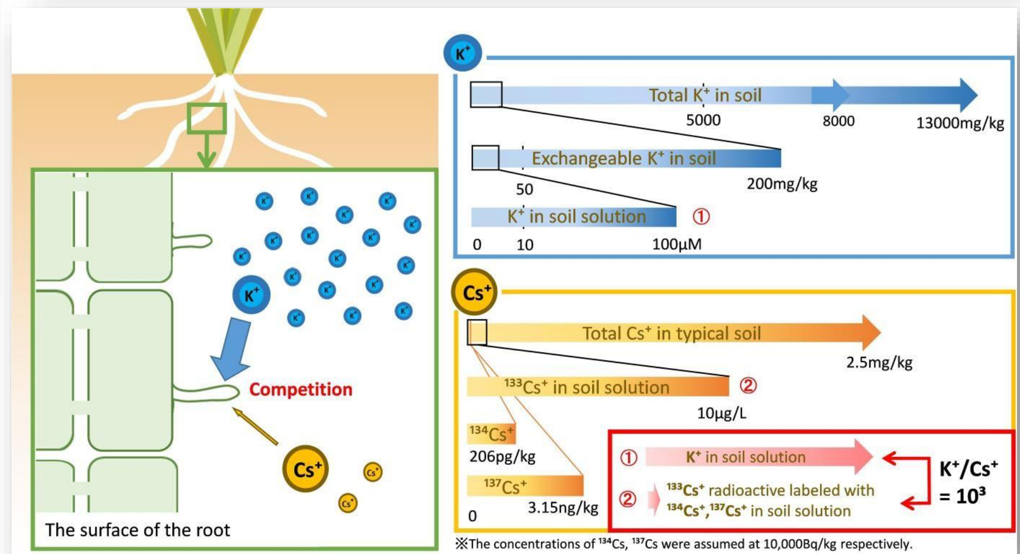

Meusburger, K., et al.. 2020.. Scientific Reports 10: 11858.
https://doi.org/10.1038/s41598-020-68736-2



# Radionuclides. Cesium vs Potassium




[Front Plant Sci. 2020; 11: 528.]

# Types of Radiation

- Non-ionizing radiations
- Ionizing radiations
- Non-ionizing radiations: Electromagnetic waves of a longer wavelength which are near ultraviolet rays to radio waves are known as non-ionizing radiations. These radiations have enough amount of energy to excite molecules and atoms of the medium via which they travel. They make atoms to vibrate faster and but does not have enough amount of energy to ionize them.

# What is Radioactive Pollution?

- Addition of radiation to environment by using radioactive elements.
- Radioactive pollution, like any other kind of pollution, is the release of something Unwanted into the environment and, in this case, the unwanted thing is radioactive material.

- **Radioactive contamination , also called radiological contamination , is the deposition of, or presence of radioactive substances on surfaces or within solids, liquids or Gases (including the human body), where their presence is unintended or undesirable .**
- **Such contamination presents a hazard because of the radioactive decay of the contaminants, which emit Harmful ionizing Radiation such as alpha or beta particles, gamma rays or neutrons . The degree of hazard is Determined by the concentration of the contaminants, the energy of the radiation being emitted, the type of radiation, And the proximity of the contamination to organs of the body . It is important to be clear that the contamination gives rise to the Radiation hazard, and the terms "radiation“ and "contamination“ are not interchangeable .**
- **Contamination may affect a person, a place, an animal, or an object such as clothing**

**Ionizing radiations**: These radiations are electromagnetic radiations that have high energy like gamma rays, x-rays, and short wavelength ultraviolet radiations. These rays of energy like alpha, beta, and gamma are generated in radioactive decay have the ability to ionize molecules and atoms via which they travel. They also have ability to change molecules and atoms into charged ions. Radioactive decay is a process from which alpha, beta, and gamma radiations are generated.

Natural sources of radiation: Natural sources of radiation are mentioned below:

In natural sources of radioactive pollution, atomic radioactive minerals are one among them.

Cosmic rays possess high energy ionizing electromagnetic radiation.

Another source of radioactive radiation is naturally occurring radioisotopes. Radioisotopes are found in soil in small quantity.

Radioactive elements like radium, thorium, uranium, isotopes of potassium and carbon occur in lithosphere

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# Effects of Radioactive Pollution

The impact of radioactive pollution on human beings can vary from mild to fatal; the magnitude of the adverse effects largely depends on the level and duration of exposure to radioactivity. Low levels of localized exposure may only have a superficial effect and cause mild skin irritation. Long-term exposure or exposure to high amounts of radiation can have far more serious health effects. Radioactive rays can cause irreparable damage to DNA molecules and can lead to a life-threatening condition.

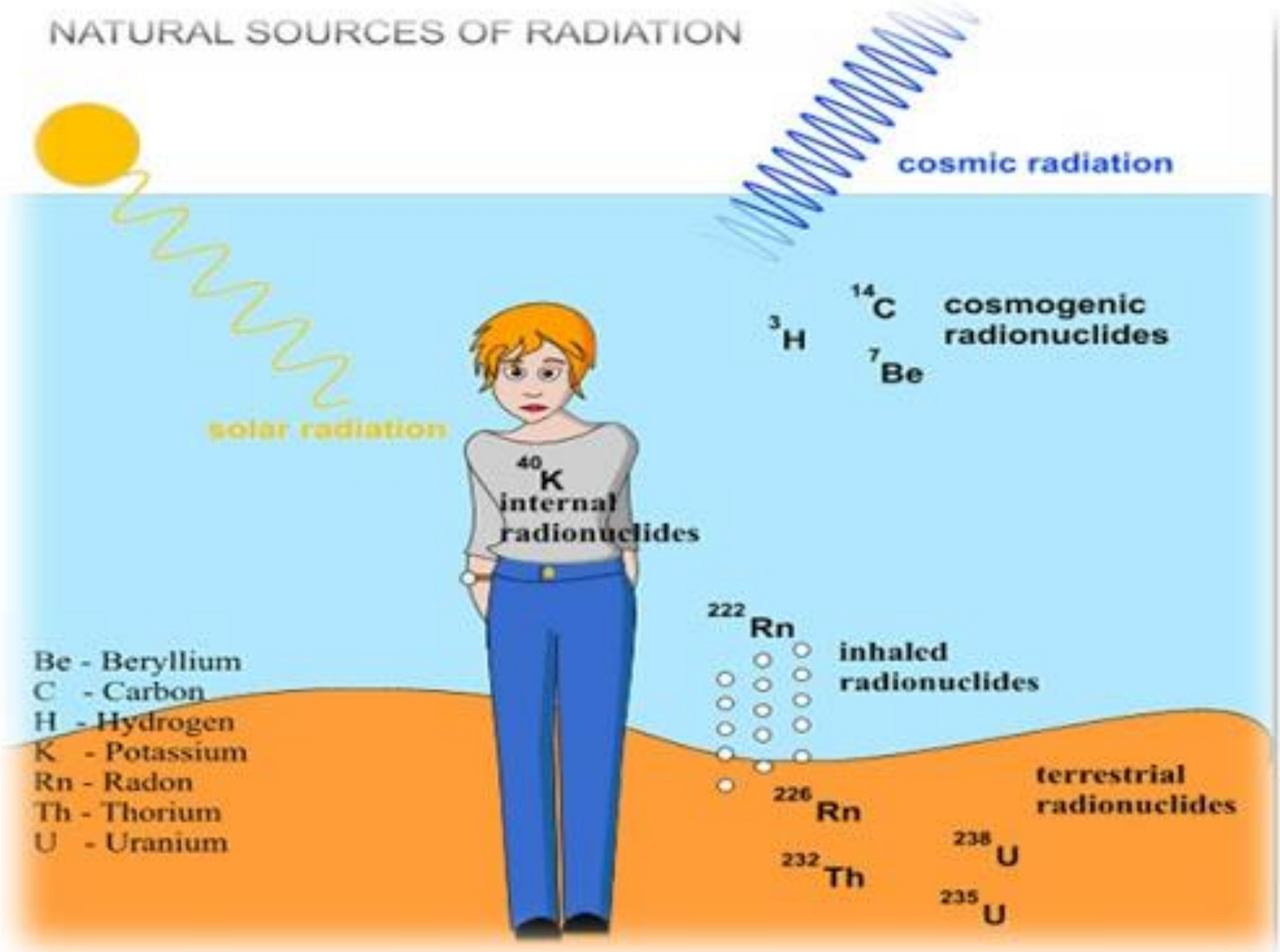
# Effects of Radioactive Pollution

- The rapidly growing/dividing cells, like those of the skin, bone marrow, are more sensitive towards radioactive emissions.

- On the other hand, cells that do not undergo rapid cell division, such as bone cells and nervous cells, aren't damaged so easily.

- Skin cancer, lung cancer and thyroid cancer are some of the common types of cancers caused by radiation effect.

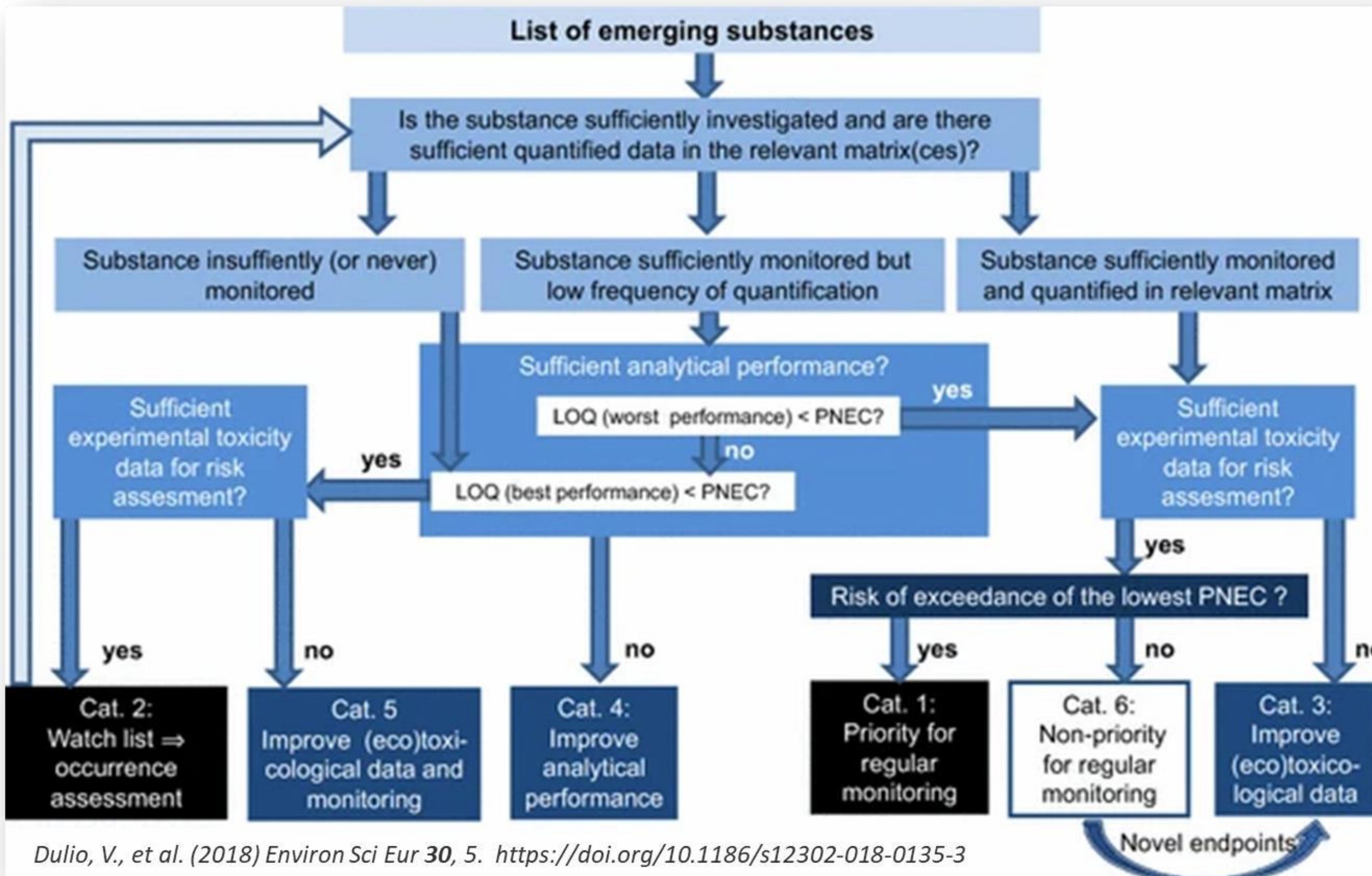
- **Effect on Human body**



# Prevention

- Nuclear devices should be exploded under ground.
- Contaminants may be employed to decrease the radioactive emissions.
- Production of radio isotopes should be minimised.
- Extreme care should be exercised in the disposal of industrial wastes contained with radionuclide's.
- Use of high chimney and ventilations at the working
- place where radioactive contamination is high.
- In nuclear reactors, closed cycle coolant system with gaseous coolants of very high purity may be used to prevent extraneous activation products.
- Fission reactions should be minimised.
- In nuclear mines, wet drilling may be employed along with underground drainage.
- Nuclear medicines and radiation therapy should be applied when absolutely necessary and earth minimum doses.

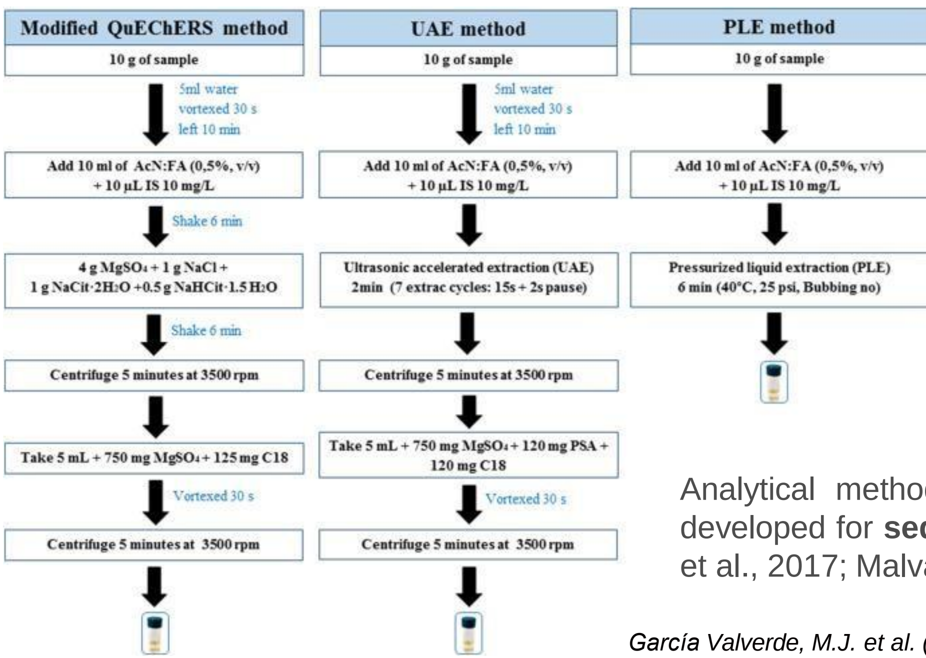
- Metals
- Radionuclides
- **Pharmaceuticals**
- PAHs
- Plastics
- Fertilizers

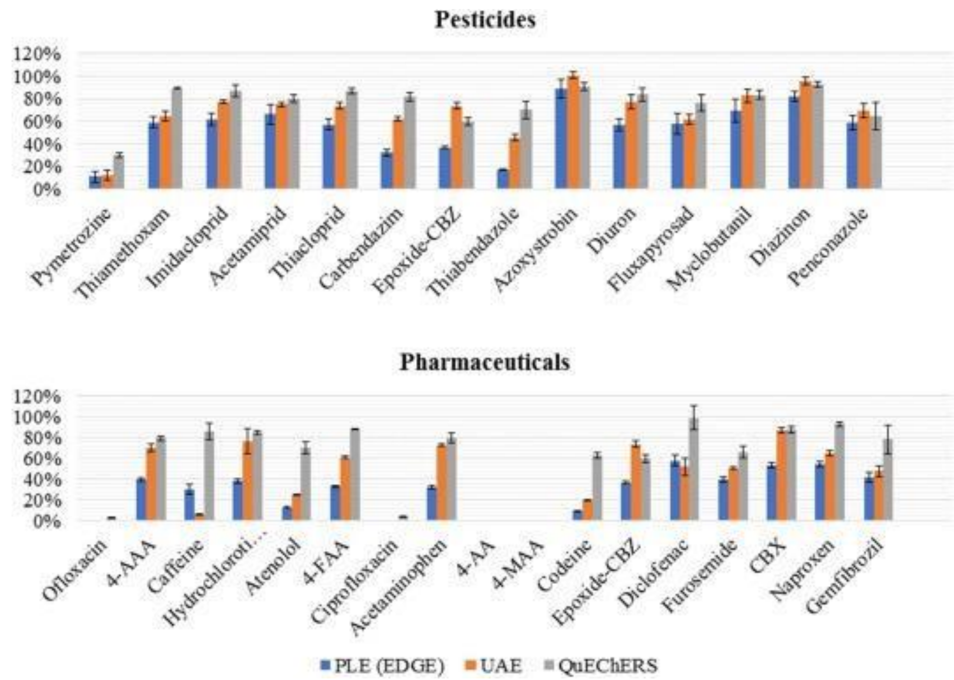



*Dulio, V., et al. (2018) Environ Sci Eur* ***30****, 5. https://doi.org/10.1186/s12302-018-0135-3*

# Pharmaceuticals

- 13 pesticides
- 12 pharmaceuticals
- 5 transformation products (4-methylamino-antipyrine, 4-amino-antipyrine, 4-formylamino-antipyrine, 4,4-acetylamino-antipyrine and carbamazepine-10,11-epoxi)



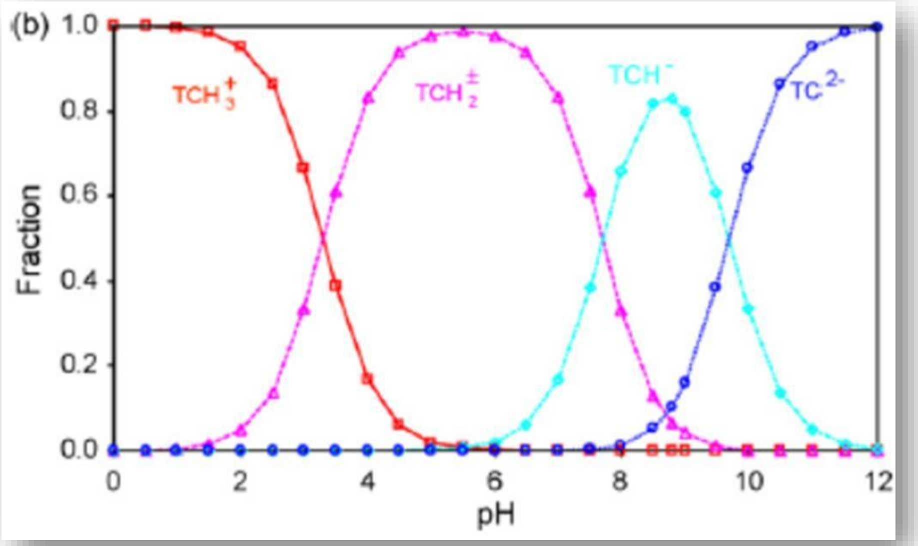




Analytical methods for the determination of EC in soil are scarce and mainly developed for **sediments** and **sewage sludge** (Benedetti et al., 2020; Luque-Munoz et al., 2017; Malvar et al., 2020; Martin-Pozo et al., 2019; Ponce-Robles et al., 2017)

*García Valverde, M.J. et al. (2021) Science of The Total Environment, 782.*
*https://doi.org/10.1016/j.scitotenv.2021.146759.*

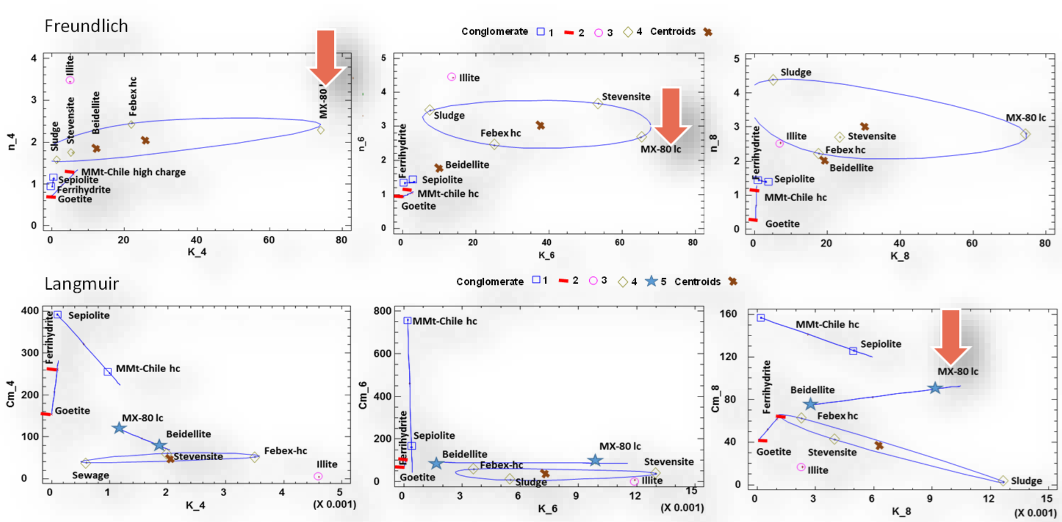
# Pharmaceuticals. Antibiotics. Tetracyclines

- Tetracyclines (TC) **are the most used antimicrobials for animal feedstock** in the EU accounting 1/3 of sales in 2014 (European Medicines Agency, 2016). 9 tones of antibiotics are used in Scottland for beef production
- The risk associated with this persistence is the development of **antibiotic resistance microbiota** which can affect ecosystems and human beings
- Acid-base aqueous chemistry of the TC molecule make its **adsorption potentially favourable at acidic pH (<4)** by means of 2:1 sheet silicates interlayer cation exchange mechanisms (Wang et al., 2008)

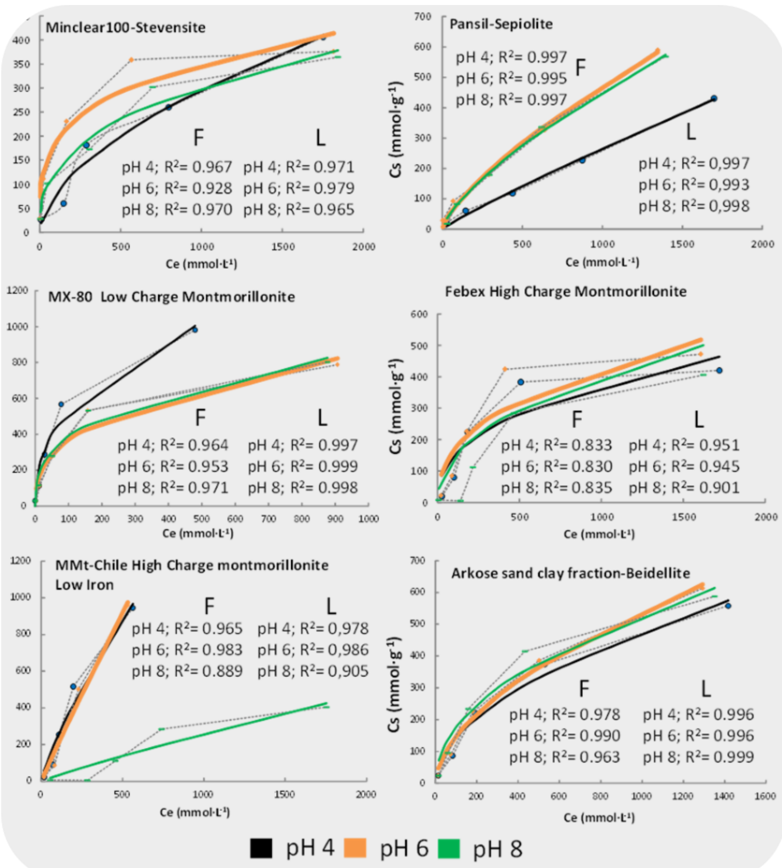


# Tetracyclines in soils

- TC adsorption rate was studied through batch experiments.
- Adsorption capacity was assessed using **different TC aqueous concentrations** (33, 132, 322, 625 and 1,176) mg/L on solid geosorbents (2.5 g for clays and calcined sewage sludge, and 4.0 g for iron oxides) **at pH 4, 6 and 8**.
- Adsorbed TC was quantified by **UV spectrophotometry at 254 nm**.
- Langmuir and Freundlich adsorption isotherms were calculated and their constants were determined (Cm and n).

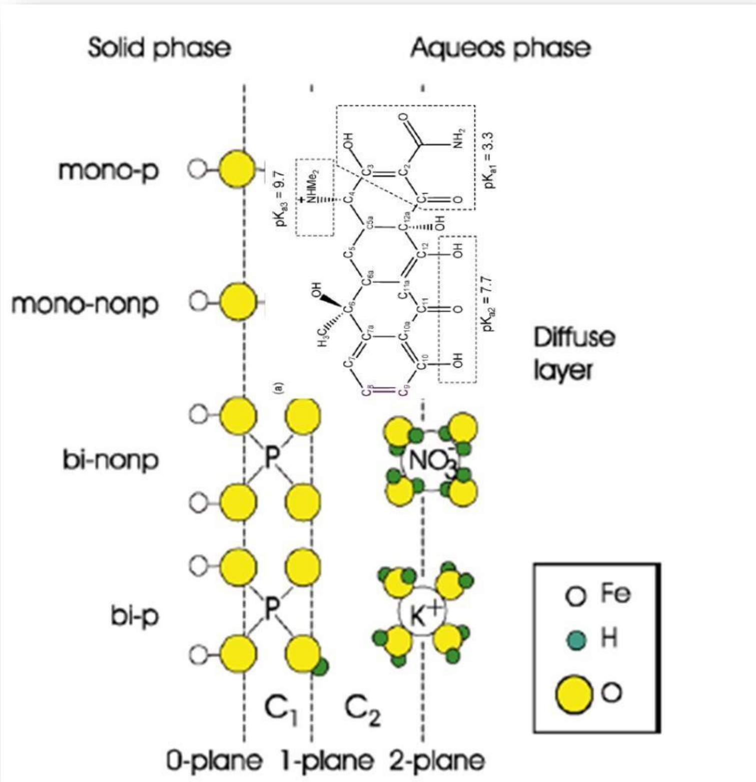


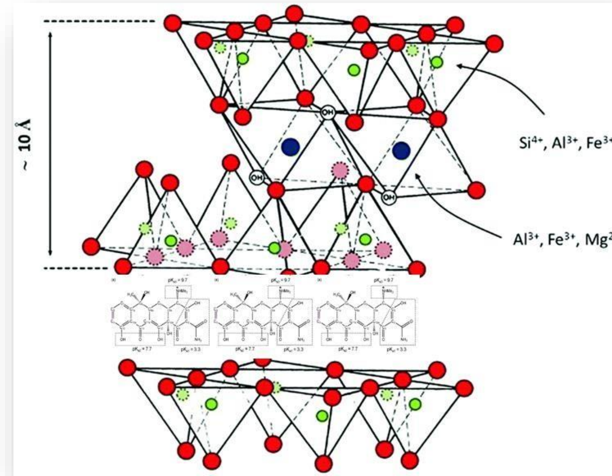

Low-charge montmorillonite shows the highest maximum adsorption capacity (Cm or K) and large adsorption intensity (n)

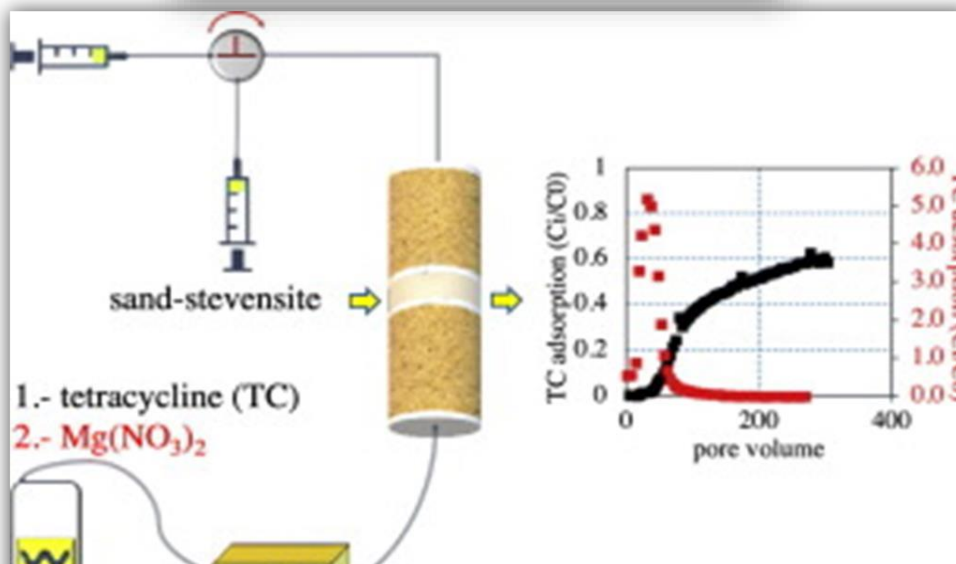



Cuevas, J.(2019) *Minerals* **2019**, *9*, 453. https://doi.org/10.3390/min9070453

# Tetracyclines in soils




Fernández et al. (2018). Science
https:/

# Antibiotics Resistance Genes from LUCAS 2018

- Abundance of antimicrobial resistance (AMR) genes is being tested on 630 soil samples from LUCAS 2018 topsoil survey

Preliminary results show as AMR abundance is affected by soil properties …TO BE CONTINUED

Metals

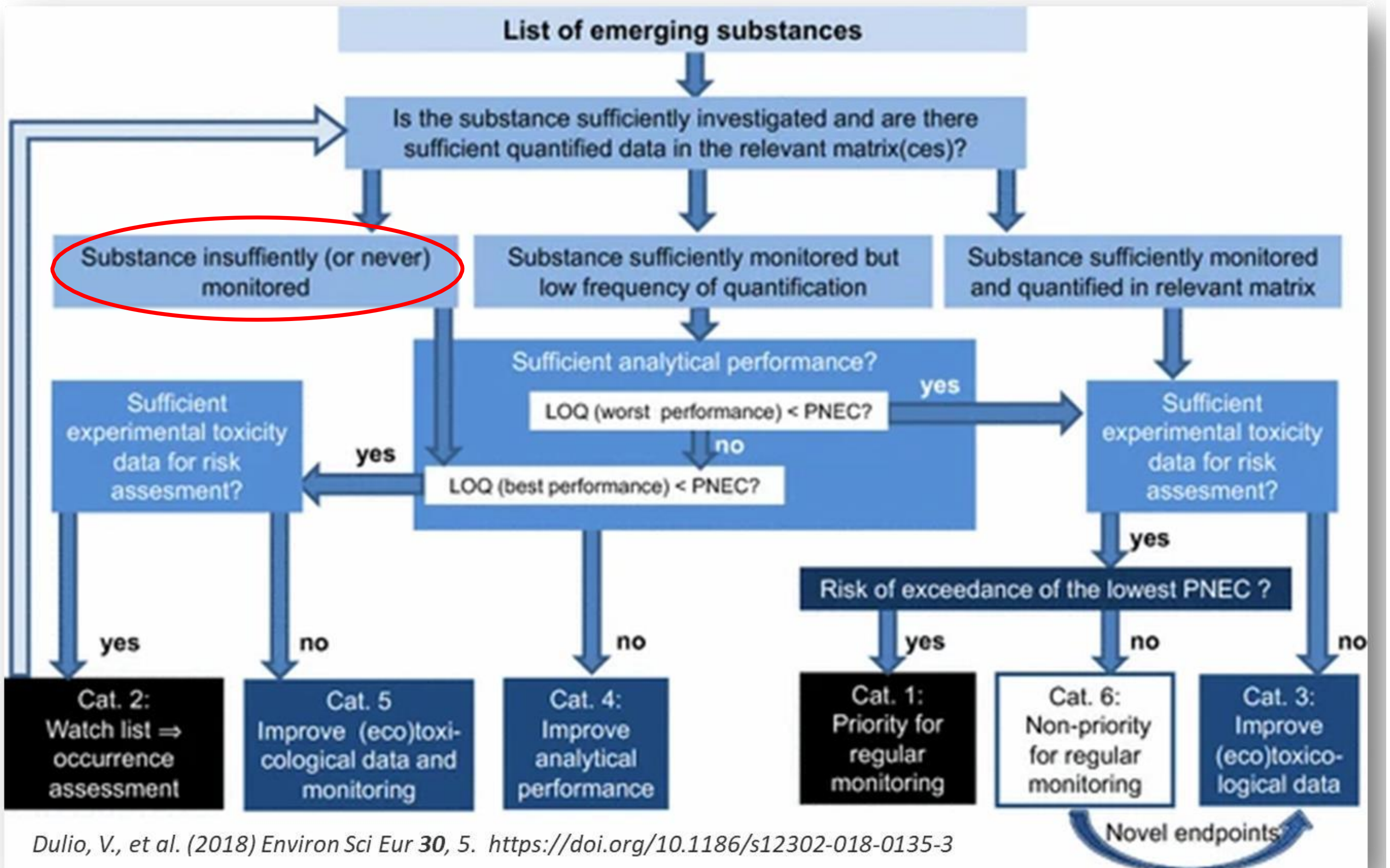
Radionuclides

Pharmaceuticals

PAHs

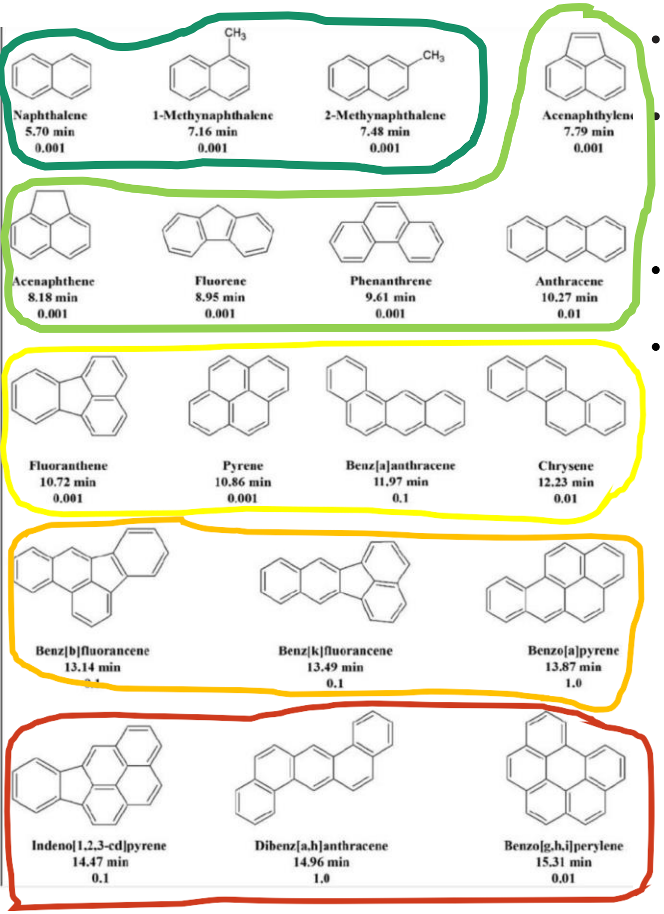
Plastics

Fertilizers



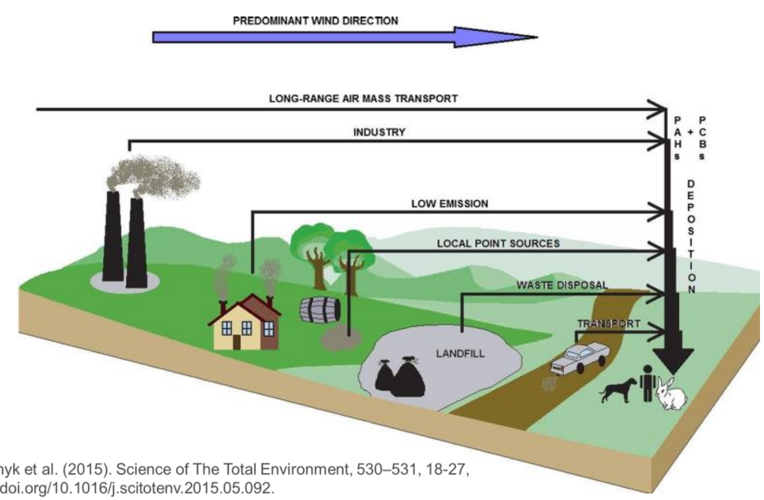

Dulio, V., et al. (2018) *Environ Sci Eur* **30**, 5. https://doi.org/10.1186/s12302-018-0135-3

# Polycyclic Aromatic Hydrocarbons (PAHs)




García-Delgado, C., Yunta, F., & Eymar, E. (2016). *International Journal of Environmental Analytical Chemistry*, *96*(1), 87-100.

- Polycyclic aromatic hydrocarbons (PAH) are a family of aromatic hydrocarbons with **<u>two or more condensed benzene</u>** rings formed during incomplete combustions.
- The PAH are persistent organic pollutants with **<u>toxic, mutagenic, and carcinogenic properties</u>** (IARC 2010) and consequently their presence in soil is hazardous for the environment and human health. These compounds are deposited on soils because of their low vapor pressure and water solubility. Garcia-Delgado, et al. (2015)
- PAHs are solid at room temperature and **are generally lipophilic**; binding potential is strong to organic material, soil organic matter and fatty tissue, or dust particles.
- The properties of the individual PAH homologues depend on the **number of hydrocarbon rings**: the smaller the molecule, the smaller the lipophilicity and the higher the volatility. Consequently, PAHs partition in nature (FAO and UNEP 2021).




A. Melnyk et al. (2015). Science of The Total Environment, 530–531, 18-27, https://doi.org/10.1016/j.scitotenv.2015.05.092.

# PAHs in soils. Quantification

### *The PAH Extraction Procedures in Soil CRM141*

Two ultrasonic and orbital shaking extraction methods were tested with four solvents, acetone/dichloromethane (1:1), acetone/hexane (1:1), methanol, and acetone. Three replicates per tested solvent were performed.

Ultrasonic extraction procedure was as follows: 0.5 g of sample plus 10 mL of each tested solvent were immersed in an ultrasonic bath for 30 min with occasional manual shaking to avoid sample caking.

Orbital shaking extraction procedure was as follows: 5 g of sample plus 25 mL of each tested solvent were shaken for 2 h at 200 rpm. The solution was left for 30 min before decanting.

After the extraction step, solutions were filtered through nylon syringe filters with a 0.45-µm pore size (Whatman International, Maidstone, UK). One mL of each resultant solution was dried by $N_2$ flow. Residue was redissolved in 1 mL of acetonitrile solvent. The PAH detection and quantification from the resultant extract were performed by HPLC-PDA.

**Table 1**

Soil CRM 141 certified values and average recoveries (%) of acetone/dichloromethane, acetone/hexane, methanol, and acetone with ultrasonic and orbital shaking extraction (RSD is in parentheses)

| | CRM 141 | Acetone/dichloromethane | | Acetone/hexane | | Methanol | | Acetone | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | (µg kg$^{-1}$) | Ultrasonic | Shaking | Ultrasonic | Shaking | Ultrasonic | Shaking | Ultrasonic | Shaking |
| Naph | 188 ± 40.3 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Acy | 176 ± 45.5 | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ace | 693 ± 174 | 106$^a$ (21) | 91$^a$ (27) | 297 (22) | 51$^a$ (84) | 70$^a$ (87) | 157 (17) | 117$^a$ (20) | 37 (140) |
| Flu | 338 ± 111 | 96$^a$ (10) | 99$^a$ (11) | 86$^a$ (25) | 68$^a$ (53) | 71$^a$ (31) | 136 (2) | 88$^a$ (26) | 69$^a$ (33) |
| Phe | 719 ± 221 | 116$^a$ (9) | 120$^a$ (3) | 107$^a$ (11) | 108$^a$ (9) | 109$^a$ (4) | 134 (3) | 117$^a$ (14) | 108$^a$ (7) |
| Ant | 393 ± 130 | 63 (27) | 100$^a$ (2) | 69$^a$ (11) | 91$^a$ (9) | 66 (4) | 105$^a$ (1) | 72$^a$ (17) | 75$^a$ (11) |
| Fla | 176 ± 40.3 | 168 (24) | 109$^a$ (12) | 78$^a$ (9) | 103$^a$ (9) | 101$^a$ (22) | 123 (3) | 117$^a$ (20) | 83$^a$ (8) |
| Py | 331 ± 62.0 | 112$^a$ (14) | 110$^a$ (12) | 93$^a$ (7) | 101$^a$ (14) | 82 (6) | 107$^a$ (29) | 96$^a$ (25) | 93$^a$ (5) |
| BaA | 409 ± 83.0 | 103$^a$ (10) | 116$^a$ (3) | 106$^a$ (4) | 118$^a$ (16) | 107$^a$ (8) | 116$^a$ (3) | 110$^a$ (13) | 111$^a$ (3) |
| Chr | 316 ± 52.0 | 133 (11) | 129 (4) | 136 (7) | 128$^a$ (14) | 123 (4) | 129 (0) | 134 (16) | 122 (2) |
| BbF | 364 ± 48.6 | 89$^a$ (4) | 117 (2) | 88$^a$ (10) | 117$^a$ (17) | 79 (18) | 113$^a$ (5) | 89$^a$ (16) | 112$^a$ (4) |
| BkF | 253 ± 43.9 | 94$^a$ (22) | 112$^a$ (5) | 103$^a$ (5) | 113$^a$ (16) | 97$^a$ (9) | 106$^a$ (1) | 110$^a$ (12) | 108$^a$ (5) |
| BaP | 198 ± 25.8 | 33 (87) | 102$^a$ (11) | 71 (4) | 102$^a$ (14) | 51 (15) | 85 (9) | 55 (16) | 82 (10) |
| DBhaA | 451 ± 70.4 | 97$^a$ (8) | 113$^a$ (7) | 111$^a$ (6) | 116$^a$ (17) | 81$^a$ (17) | 94$^a$ (5) | 110$^a$ (11) | 111$^a$ (6) |
| BghiP | 618 ± 109 | 82$^a$ (37) | 109$^a$ (6) | 96$^a$ (6) | 110$^a$ (19) | 79 (14) | 88$^a$ (1) | 101$^a$ (10) | 108$^a$ (2) |
| IcdP | 394 ± 52.0 | 100$^a$ (13) | 115 (4) | 105$^a$ (5) | 115$^a$ (16) | 80 (15) | 91$^a$ (5) | 107$^a$ (10) | 112$^a$ (3) |
| Mean recovery | | 99ns | 110ns | 110ns | 103ns | 85b | 113a | 102ns | 95ns |
| Mean RSD | | 16a | 8b | 9ns | 22ns | 18a | 4b | 16a | 8b |

*Notes*. n.d. indicates no detection of the compound in HPLC analysis; ns indicates no significant differences. Different letters indicate significant differences at $P \leq 0.05$; $n = 3$.

[a]Recovery validated according IRMM (2010) criteria.

The same behaviour was observed when the four solvents were compared using ultrasonic extraction. However, when orbital shaking extraction was entered as a factor, significant differences were found between acetone/hexane (14 validated PAH) and methanol (eight validated PAH)

García-Delgado C, Yunta F & Eymar E (2013).
*Commun in Soil Sci and Plant Anal, 44:1-4, 817-825*

# PAHs in soils. Remediation

Bioremediation of multi-polluted soil by spent mushroom (*Agaricus bisporus*) substrate: Polycyclic aromatic hydrocarbons degradation and Pb availability

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Department of Agricultural Chemistry and Food Sciences, University Autónoma of Madrid, 28049 Madrid, Spain

Journal of Hazardous Materials

**Table 1**
Characteristics of the multi-polluted soil and spent *Agaricus bisporus* substrate (SAS). (mean ± standard deviation, $n = 3$).

| Parameter | Soil | SAS |
|---|---|---|
| pH | 8.13 ± 0.04 | 6.28 ± 0.03 |
| Electric conductivity (dS m$^{-1}$) | 0.41 ± 0.09 | 6.52 ± 0.23 |
| Organic matter (%) | 3.3 ± 0.2 | 63.9 ± 1.5 |
| N Kjeldahl (%) | 0.14 ± 0.01 | 1.99 ± 0.05 |
| Carbonates (%) | 2.2 ± 0.1 | n.d. |
| Sand (%) | 71 ± 1 | n.p. |
| Silt (%) | 15 ± 1 | n.p. |
| Clay (%) | 14 ± 1 | n.p. |
| Pseudo-total Pb (mg kg$^{-1}$) | 1429 ± 26 | 1.20 ± 0.20 |
| Pseudo-total Mn (mg kg$^{-1}$) | 226 ± 20 | 541 ± 27 |
| Pseudo-total Cu (mg kg$^{-1}$) | 19.6 ± 3.4 | 60.1 ± 5.5 |
| Pseudo-total Zn (mg kg$^{-1}$) | 66.0 ± 6.8 | 307 ± 21 |
| Pseudo-total Cd (mg kg$^{-1}$) | 0.13 ± 0.23 | n.d. |

n.d.: not detected, n.p.: not performed.

- Natural attenuation: the preparation of the soil microcosm (SM) simply involved the adjustment of the soil moisture content prior to the beginning of the incubation.
- Biostimulation: the polluted soil was amended with sterilized SAS (121 °C, 30 min) to yield the SSAS microcosm. this approach was intended to assess the stimulatory effect of a sterilized organic waste on the resident soil microbiota and the effect of the SAS material on Pb availability, without SAS microorganism.
- Bioaugmentation SAS: the polluted soil was amended with SAS without previous treatment to yield the SAS microcosm. This approach was aimed at assessing the combined effect of both *A. bisporus* and the inherent SAS microbiota on PAH degradation and Pb availability.
- Bioaugmentation Abisp: to prepare this microcosm, sterilized SAS was re-inoculated with *A. bisporus* as described above. The colonized matrix was mixed with the contaminated soil. This bioaugmentation approach, termed the Abisp microcosm, was aimed at determining the effect of *A. bisporus* on PAH biodegradation and Pb availability.

**Table 2**
Initial PAH concentration (mean ± standard deviation), biodegradation rates at 63d incubation respect to initial concentration and reduction in carcinogenic risk assessment (RCRA) for each microcosm: non amendment soil (SM), amendment with sterilized spent *A. bisporus* substrate (SSAS), spent *A. bisporus* substrate (SAS) and sterilized spent *A. bisporus* substrate reinoculated with the fungus (Abisp). Different letters indicates significant differences between microcosms ($p < 0.05$) $n = 3$.

| | Initial soil (mg kg$^{-1}$) | PAH degradation rate (%) SM | SSAS | SAS | Abisp | Carcinogenic classification[1] | TEF[2] |
|---|---|---|---|---|---|---|---|
| Ace | 49.9 ± 0.4 | 36$^{c}$ | 20$^{ab}$ | 16$^{a}$ | 24$^{b}$ | 3 | 0.001 |
| Flu | 0.82 ± 0.05 | 79$^{c}$ | 6$^{a}$ | 44$^{b}$ | 100$^{d}$ | 3 | 0.001 |
| Phe | 28.9 ± 0.6 | 14$^{ab}$ | 0$^{a}$ | 22$^{bc}$ | 35$^{c}$ | 3 | 0.001 |
| Ant | 7.40 ± 0.13 | 13$^{ab}$ | 2$^{a}$ | 20$^{ab}$ | 32$^{b}$ | 3 | 0.01 |
| Fla | 71.0 ± 1.0 | 8$^{a}$ | 0$^{a}$ | 22$^{b}$ | 31$^{b}$ | 3 | 0.001 |
| Py | 95.8 ± 2.3 | 7$^{a}$ | 0$^{a}$ | 20$^{b}$ | 30$^{b}$ | 3 | 0.001 |
| BaA | 56.8 ± 1.3 | 5$^{a}$ | 0$^{a}$ | 17$^{b}$ | 28$^{c}$ | 2B | 0.1 |
| Chr | 76.4 ± 1.9 | 4$^{a}$ | 0$^{a}$ | 17$^{b}$ | 27$^{c}$ | 2B | 0.01 |
| BbF | 112 ± 2 | 2$^{a}$ | 0$^{a}$ | 10$^{ab}$ | 28$^{b}$ | 2B | 0.1 |
| BkF | 32.3 ± 1.7 | 3$^{a}$ | 0$^{a}$ | 9$^{ab}$ | 22$^{b}$ | 2B | 0.1 |
| BaP | 93.1 ± 0.1 | 3$^{a}$ | 0$^{a}$ | 29$^{b}$ | 39$^{b}$ | 1 | 1 |
| DBhaA | 8.47 ± 0.035 | 0$^{a}$ | 3$^{a}$ | 5$^{a}$ | 21$^{b}$ | 2A | 5 |
| BghiP | 74.1 ± 1.8 | 2$^{a}$ | 0$^{a}$ | 8$^{a}$ | 28$^{b}$ | 3 | 0.01 |
| IcdP | 49.5 ± 0.2 | 4$^{a}$ | 0$^{a}$ | 12$^{ab}$ | 30$^{b}$ | 2B | 0.1 |
| Σ3rings | 87.0 ± 0.7 | 27$^{b}$ | 11$^{a}$ | 19$^{ab}$ | 30$^{b}$ | | |
| Σ4rings | 300 ± 6 | 6$^{a}$ | 0$^{a}$ | 19$^{b}$ | 29$^{c}$ | | |
| Σ5-6rings | 370 ± 5 | 2$^{a}$ | 0$^{a}$ | 15$^{b}$ | 29$^{c}$ | | |
| ΣPAH | 757 ± 10 | 7$^{a}$ | 1$^{a}$ | 17$^{b}$ | 29$^{c}$ | | |
| RCRA | | 1.5$^{a}$ | 0.7$^{a}$ | 20.5$^{b}$ | 30.5$^{c}$ | | |

[1] IARC 2010: 1 carcinogenic, 2A probable carcinogenic, 2B possible carcinogenic, 3 not classifiable as carcinogenic.
[2] TEF: Toxic equivalence factor.

The microcosms bioaugmented with A. bisporus (SAS and Abisp) were the most efficient remediation treatments for PAH degradation and, especially for HMW-PAH, the most abundant PAH in this soil. However, the degradation rate for 4-rings, 5,6-rings and PAH was significantly higher in the Abisp than in the SAS microcosms.

| | Incubation days 0 | 28 | 63 |
|---|---|---|---|
| pH-$H_2O$ | | | |
| SM | 8.17 ± 0.08$^{Ca}$ | 8.31 ± 0.12$^{Ca}$ | 7.96 ± 0.01$^{Ba}$ |
| SSAS | 7.38 ± 0.17$^{Ba}$ | 7.76 ± 0.06$^{Bb}$ | 7.55 ± 0.08$^{Aab}$ |
| SAS | 7.96 ± 0.07$^{Cb}$ | 7.70 ± 0.07$^{Bab}$ | 7.51 ± 0.17$^{Aa}$ |
| Abisp | 6.92 ± 0.02$^{Ab}$ | 6.67 ± 0.06$^{Aa}$ | 8.61 ± 0.03$^{Cc}$ |
| pH-$CaCl_2$ | | | |
| SM | 7.13 ± 0.03$^{Ba}$ | 7.42 ± 0.11$^{Bb}$ | 7.15 ± 0.05$^{Aa}$ |
| SSAS | 7.31 ± 0.16$^{Ba}$ | 7.64 ± 0.07$^{Bb}$ | 7.38 ± 0.11$^{Aa}$ |
| SAS | 7.90 ± 0.06$^{Cb}$ | 7.59 ± 0.09$^{Ba}$ | 7.32 ± 0.22$^{Aa}$ |
| Abisp | 6.76 ± 0.10$^{Ab}$ | 6.44 ± 0.06$^{Aa}$ | 8.46 ± 0.04$^{Bc}$ |
| Available Pb (‰) | | | |
| SM | 0.003$^{Aa}$ | n.d.$^{Aa}$ | 0.004$^{Aa}$ |
| SSAS | 0.980$^{Bb}$ | 0.266$^{Ba}$ | 0.108$^{Ba}$ |
| SAS | 0.584$^{Bb}$ | 0.191$^{Ba}$ | 0.156$^{Ba}$ |
| Abisp | 1.06$^{Bb}$ | 2.52$^{Cc}$ | 0.443$^{Ba}$ |

n.d.: not detected.

No significant changes and clear differences were observed for any treatment when Pb availability was monitored along experiment.

Metals

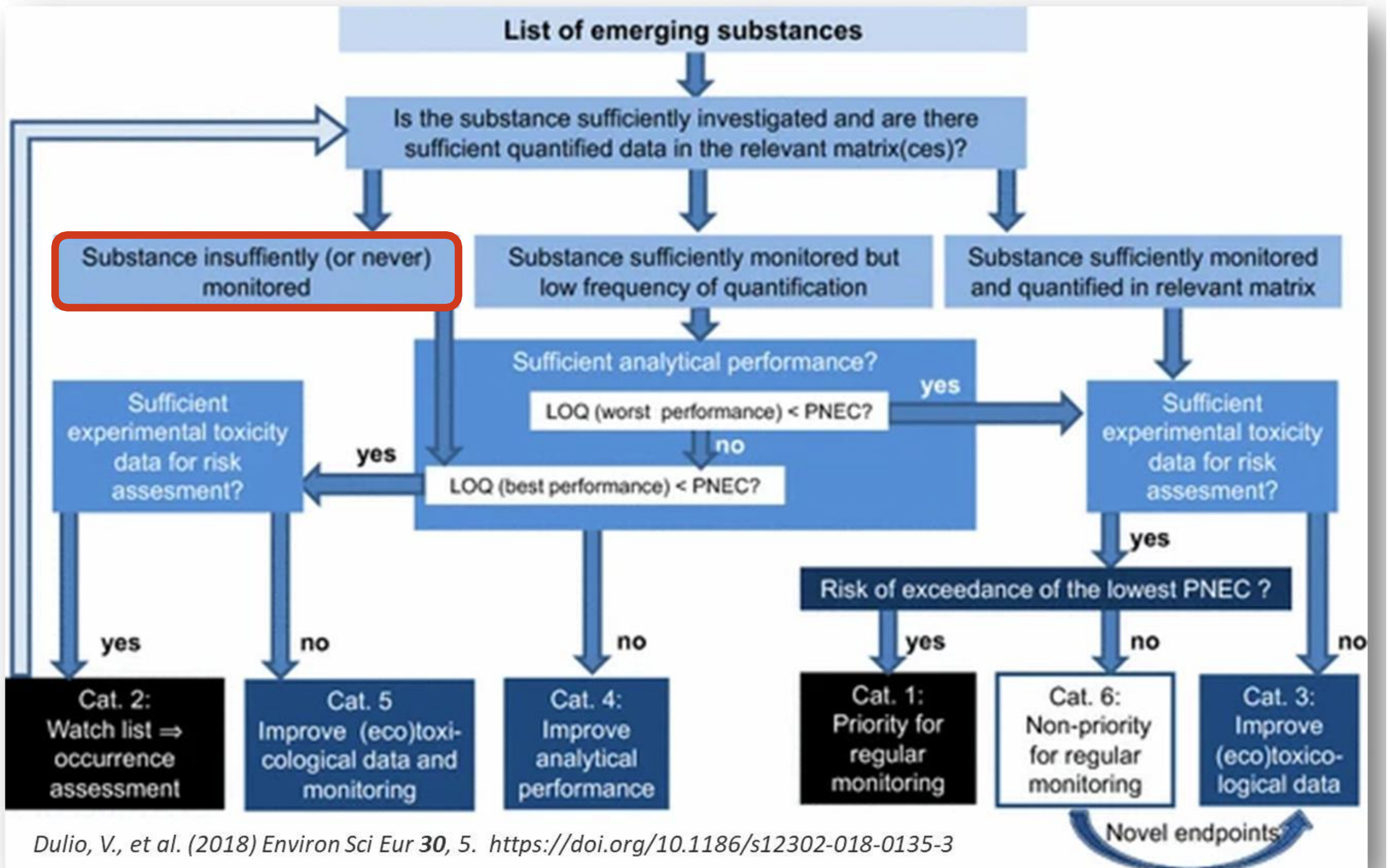
Radionuclides

Pharmaceuticals

PAHs

Plastics

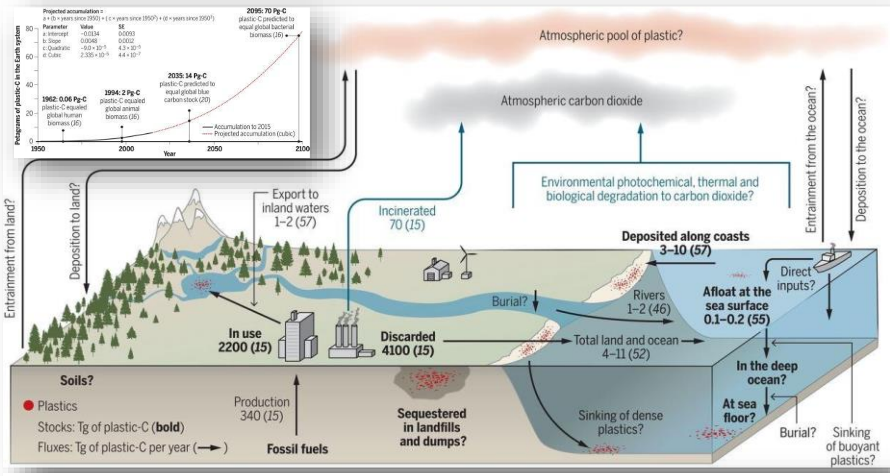
Fertilizers

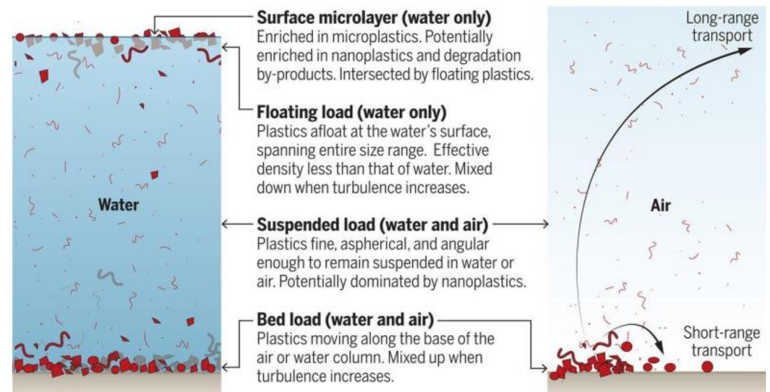


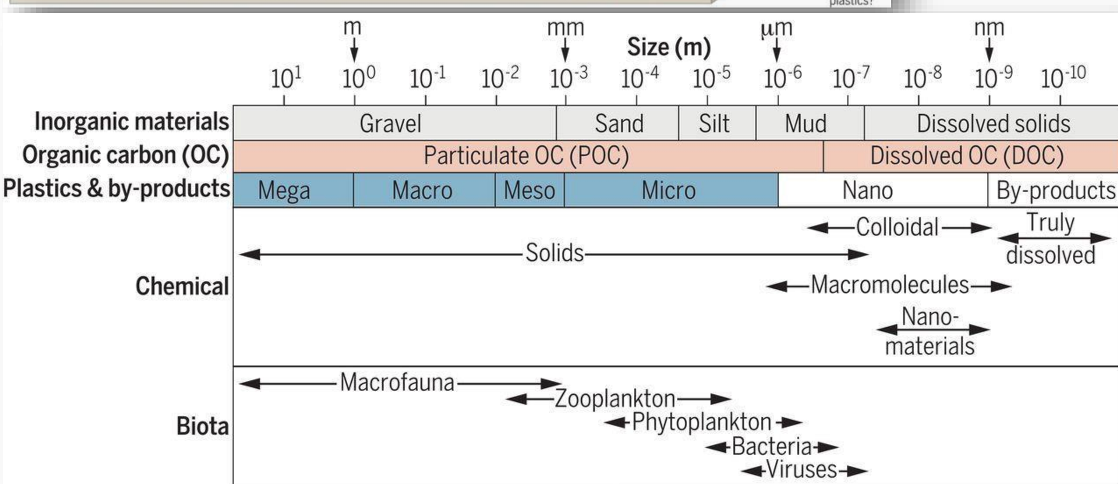

*Dulio, V., et al. (2018) Environ Sci Eur* ***30****, 5.* *https://doi.org/10.1186/s12302-018-0135-3*

# Plastics in the Earth System

Science, 373 (6550), • DOI: 10.1126/science.abb0354



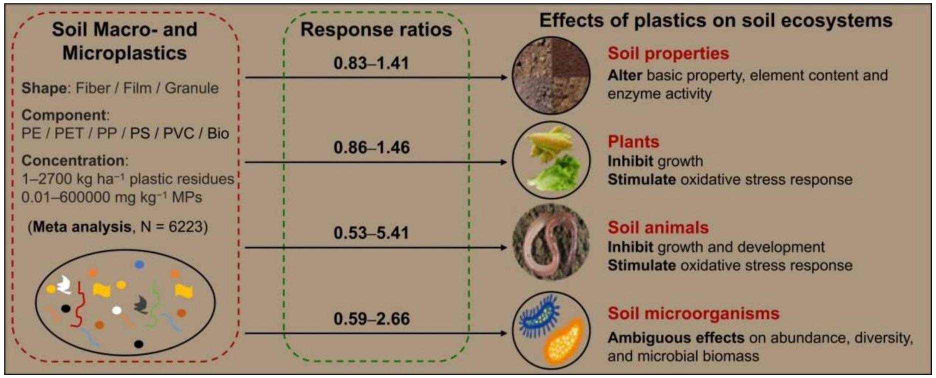



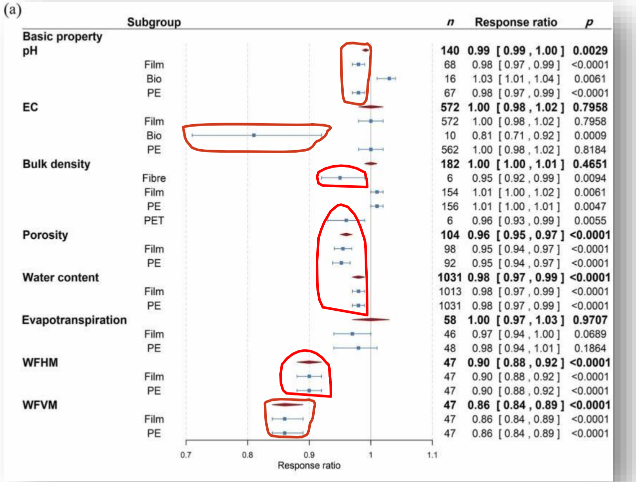

Soil ???

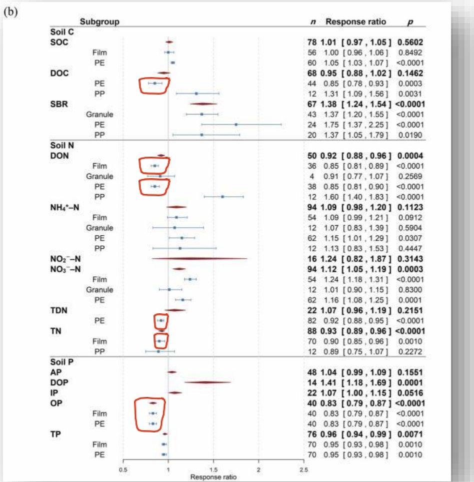
# Microplastics in soils

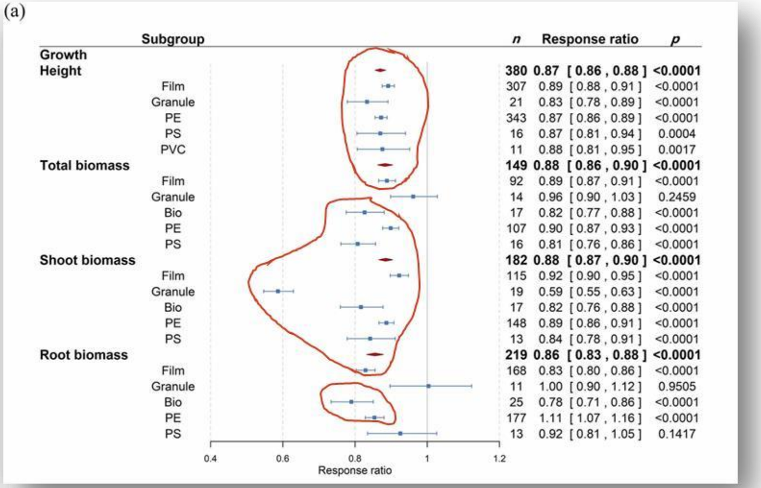
*Jinrui Zhang et al. (2022). Journal of Hazardous Materials, 435*
*https://doi.org/10.1016/j.jhazmat.2022.129065.*

- ❑ Plastic residue and MPs can alter soil physicochemical properties.
- ❑ Plastic residue and MPs inhibit growth and development of plant and soil animal.
- ❑ Effect of plastic residue and MPs on soil microorganism is uncertain.

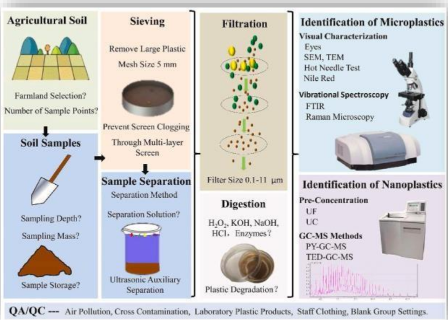


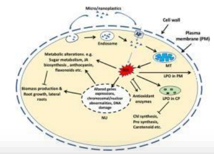
# Nanoplastics in soils




Extraction and identification methods of MPs in soil do not accurately extract and identify NPs, and the content and typeof NPs in soil are unknown.

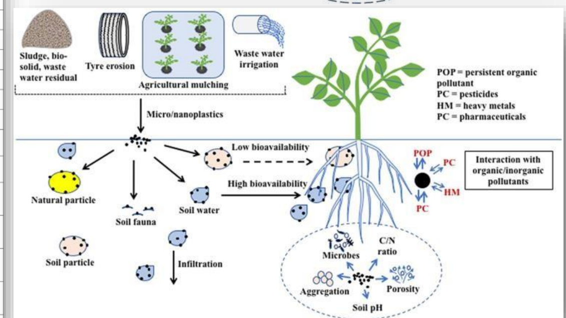
| Group | Method | Advantages | Limitations | Reference |
|---|---|---|---|---|
| Sample purification | Density separation | •High separation efficiency •Simple operation •Inexpensive •Handling large sample numbers | •Low-density solution cannot separate high-density plastics •High-density solutions are expensive or toxic •Time-consuming | Nuelle et al. (2014) Ruggero et al. (2020) |
| | Electrostatic separation | •High separation efficiency •Simple operation •Fast •Simple sample handling | •Difficult to separate small-sized MPs •Samples need to be dispersed and dried | Felsing et al. (2018) |
| | Oil separation | •High separation efficiency •Simple operation •Inexpensive •Fast | •Identification of interference MPs | Crichton et al. (2017) |
| | Froth flotation | •Separation of large quantities of samples •Simple sample handling | •Time-consuming •Low separation efficiency •Complex procedures | Fraunholcz (2004) Jiang et al. (2020) |
| | Magnetic extraction | •Separate small-sized MPs •Inexpensive | •Time-consuming •Complex procedures •Sample damage | Grbic et al. (2019) |
| Digestion | $H_2O_2$ | •Inexpensive •Can be used in complex environments | •Destructive to MPs •Time-consuming •Produce high temperature | He et al. (2018b) Kumar et al. (2020) Hurley et al. (2018) |
| | Alkaline | •Inexpensive •Suitable for biological samples •Strong digestion ability | •Destructive to MPs •Removal efficiency varies with the types of MPs | Cole et al. (2014) Foekema et al. (2013) Dehaut et al. (2016) |
| | Acid | •Effective removal of organic matter •Inexpensive | •Destructive to MPs •Carbon black cannot be removed | Blaesing and Amelung, (2018) Avio et al. (2015) Kappenberg et al. (2016) |
| | Enzyme | •Does not degrade plastic •Suitable for biological samples •Relatively gentle | •Expensive •The removal efficiency of soil organic matter is unclear | Karlsson et al. (2017) Nguyen et al. (2019) |
| Identification and quantification | Visual characterization | •Fast, easy, and quick •Inexpensive •Identifies shape, size, and colors •Non-destructive | •Judging by people's subjective consciousness •Lack of information on plastic composition •Large size | Munno et al. (2018) Nguyen et al. (2019) |
| | FTIR | •Non-destructive •Fast, simple •Identifies the composition of plastic •Automated | •Expensive •Difficult to analyze NPs •Strong interference from water | Elert et al. (2017) Löeder and Gerdts (2015) Hufnagl et al. (2019) |
| | Raman | •Identifies the composition of plastic •Generates high-resolution images •NPs can be analyzed •Non-destructive •Easy sample preparation | •Expensive •Time-consuming •Samples require refinements •Small area | Kaeppler et al. (2015) Cabernard et al. (2018) |
| | UF | •Inexpensive •Easily available •Large volumes •Mild •Little sample damage | •Membrane with small pores •No separation from the particulate matrix •Low flow rates | Schwaferts et al. (2019) Pitt et al. (2018) Pansare et al. (2017) |
| | UC | •Simple •Easily available •Inexpensive | •Small volumes •Slow •Harsh conditions •No separation from the particulate matrix •Sample damage | Laborda et al. (2016) |
| | Py-GC-MS | •Quick sample preparation •Easy and reliable •Identifies MPs of any size •Quantification of MPs •Identify any plastic additives present | •Expensive •Small sample masses •Destructive to MPs •Dry sample needed •Pre-concentration | Fischer and Scholz-Boettcher (2017) Fries et al. (2013) Kaeppler et al. (2018) |
| | TED-GC–MS | •Higher sample masses •Quantification of MPs •Identifies MPs of any size •Fast | •Expensive •Destructive to MPs •Dry sample needed •Pre-concentration | Duemichen et al. (2017) Duemichen et al. (2015) Duemichen et al. (2014) |


Cao Junhao, et al. (2021). Journal of Environmental Management, 294, 202
https://doi.org/10.1016/j.jenvman.2021.112997.

Toxicological effects in plants such as: biomass production, reduction in chlorophyll content

Remote Sensing




| Soil type | M/NP | Polymer type | Size range | Abundance | Reference |
|---|---|---|---|---|---|
| Floodplain | MP | PE, PS, SBR, PVC | 125–500 mm | 5–55.5 mg/kg. Mean: 5–mg/kg | Scheurer and Bigalke (2018) |
| Agricultural | MP | PE | >100 μm | <0.54 mg/kg | S. Zhang et al. (2018) |
| | | PE, PP | <1–5 mm | 664 pieces/kg | Choi et al. (2021) |
| | | PP, polyester, rayon, acrylic and polyamide (PA). | 1–3 mm | 571 pieces/kg (for mulching soil) & 263 pieces/kg (for non-mulching soil) | Zhu et al. (2019) |
| Farmland | MP | PP, PE | 0.03–16 mm | 78.00 items/kg of shallow soil and 62.50 items/kg of deep soils | M. Liu et al. (2018) |
| | | PP, PA | <0.2 mm | 320–12 560 items/kg DW | Chen et al. (2020) |
| Beach soil | MP | PE, PP, PS, polyether urethane | 60% <1 mm | 1.3–14 712.5 number/kg | Q. Zhou et al. (2018) |
| | | | 0.3–4.75 mm | From 3 to 7 items/kg dw to upto 17 items/kg dw | Pérez-Alvelo et al. (2021) |
| Industrial | MP | PVC (>80%), PE, PS | <1 mm | 300–67 500 mg/kg. Mean 4191 mg/kg | Fuller and Gautam (2016) |
| Tree-planted | MP | - | <1 mm | 7100–42 960 items/kg. Mean: 26 410 items/kg (for Estuary of the Cha river), 48 960 items/kg (for Dagoujian), 27 310 (for Dunshang), 53 090 (for Anle) and 22 610 (for Shangsuan). | Zhang and Liu (2018) |
| | | - | 10–50 μm | 0.87 ± 1.9 particles/g of home garden soil | Lwanga et al. (2017) |


Plant Cell & Environment (2022), 45, (4), 1011-1028, DOI: (10.1111/pce.14248)


The adsorption of micro/nanoplastic onto the surface of soil particles is mediated by hydrophobic and electrostatic interaction

- Fast, convenient, and practical standard procedure for MPs/NPs extraction and identification in agricultural soil should to be designed
- There are few extraction and identification processes for MPs/NPs in agricultural soil, relative to those available in water.
- Only a few studies have estimated the concentrations of microplastics in soils with a large knowledge gap in the understanding of nanoplastic abundance

# Plastics in soils

| | CAS6 NANOPLASTICS | ER SOLACE | ER PLASTIC-WEB |
|---|---|---|---|
| TITLE | Towards a technological platform for NANOPLASTICS detection | Understanding the links between SOiL pollution and CancEr | Tracing microPLASTICs up the EU marine food WEBs: implications for marine biodiversity and EU ecosystem services |
| START/END | 16/01/2021-15/01/2024 | 16/01/2022-15/01/2024 | 01/09/2021-31/08/2023 |
| OBJECTIVE | To provide the scientific community with novel, cost-effective analytical methods and strategies for the widespread detection and environmental monitoring of nanoplastic (NP) pollution. | To develop a methodology that moves from measures of concentrations of carcinogenic substances in soil towards the identification of hazards and risk analysis that may help explain eventual potential pathways that cause cancers (i.e. soil-plant-food, erosion by wind and water). | To develop a food-web model that includes species direct and indirect uptake of microplastic (MP). The model will be then use to assess temporal-spatial impact of MP in the marine food-webs. |
| PERFORMING UNIT | F.2 (Consumer Products Safety) | D.3 (Land Resources)<br>F.1 (Centre for the Study of Cancer) | D.2 (Water and Marine Resources) |
| PROJECT LEADER/ SCIENTIFIC CO-ORDINATOR | Miguel-Angel SERRA BELTRAN (A.5)/ Douglas GILLILAND (F.2) | Arwyn JONES (D.3)/Panos PANAGOS (D.3) | Natalia SERPETTI (D.2) |
| TEAM MEMBERS | Gabriella SCHIRINZI and Marisa PASSOS (A.5) | Joanna BARTINICKA (A.5)<br>Raquel CARVALHO (F.1)<br>Felipe YUNTA (A.5//D.3) | Elisa GARCIA GORRIZ, Svetla MILADINOVA, Chiara PIRODDI, Diego MACIAS MOY (D.2) |
| INTERNAL COLLABORATORS (JRC) | John SEGHERS (F.6 Reference Materials)<br>Natalia SERPETTI, Elisa GARCIA GORRIZ (D.2)<br>Felipe YUNTA (D.3) | F.3 (IPCHEM - the Information Platform for Chemical Monitoring)<br>D.5 (Earth Observation Systems)<br>Gabriella SCHIRINZI and Marisa PASSOS (A.5) | Gabriella SCHIRINZI and Marisa PASSOS (A.5) |
| EXTERNAL COLLABORATORS | Ulrich SCHWANEBERG (RWTH Aachen University, DE)<br>Julien GIGAULT (CNRS FR/Univ. Laval CAN)<br>Miren CAJARAVILLE (UPV/EHU Leioa/Plentzia, ES)<br>Nicoletta RICCARDI (CNR-IRSA, Pallanza, IT) | | William WALTER (Penn State University, USA) |
| WEB PAGE | https://webgate.ec.europa.eu/connected/community/jrc/directorate-a/a5/centre-for-advanced-studies/projects/nanoplastics/pages/hom<br>https://joint-research-centre.ec.europa.eu/knowledge-research/centre-advanced-studies/towards-technological-platform-nanoplastics-detection-nanoplastics_en | https://esdac.jrc.ec.europa.eu/projects/solace | https://webgate.ec.europa.eu/connected/community/jrc/directorate-d/d2/projects/plastic-web-tracing-microplastics-up-the-eu-marine-food-webs |
| CONTACT | JRC-CAS-NANOPLASTICS@ec.europa.eu<br>Miguel.SERRA-BELTRAN@ec.europa.eu<br>Douglas.GILLILAND@ec.europa.eu | Arwyn.JONES@ec.europa.eu<br>Felipe.YUNTA-MEZQUITA@ec.europa.eu | Natalia.SERPETTI@ec.europa.eu<br>Elisa.GARCIA-GORRIZ@ec.europa.eu |


- Different extraction methods tested in soils
- Full characterisation of soil samples (LUCAS surveys)
- Validation of screening analytical methodologies in soils (heavy metals, NPs)
- NPs interactions with the most important soil fractions
- Accumulation, transformation and uptake of NPs in soil via the food chain and impact on human health


**CHALLENGES**

- Preparation of environmentally realistic reference NPs
- Analytical methodologies for the reliable characterisation and quantitation of NP particles
- Novel specific methods for labelling environmental NPs
- Environmentally-relevant organisms as bioaccumulators and indicators of NP pollution

- Different extraction methods tested in soils
- Full characterisation of soil samples (LUCAS surveys)
- Validation of screening analytical methodologies in soils (heavy metals, NPs)
- NPs interactions with the most important soil fractions
- Accumulation, transformation and uptake of NPs in soil via the food chain and impact on human health

- Database of the uptake of MP by marine species
- Ecotracer and lagrangian particle tracking modelling (Black & Mediterranean Seas)
- Development of methods for model calibration
- Define MP pathways in food-web
- Running "what-if scenarios" to assess the impact of EU management measures

Development of novel approaches for the study of plastic particles pollution in the environment and assessment of their impact

Metals

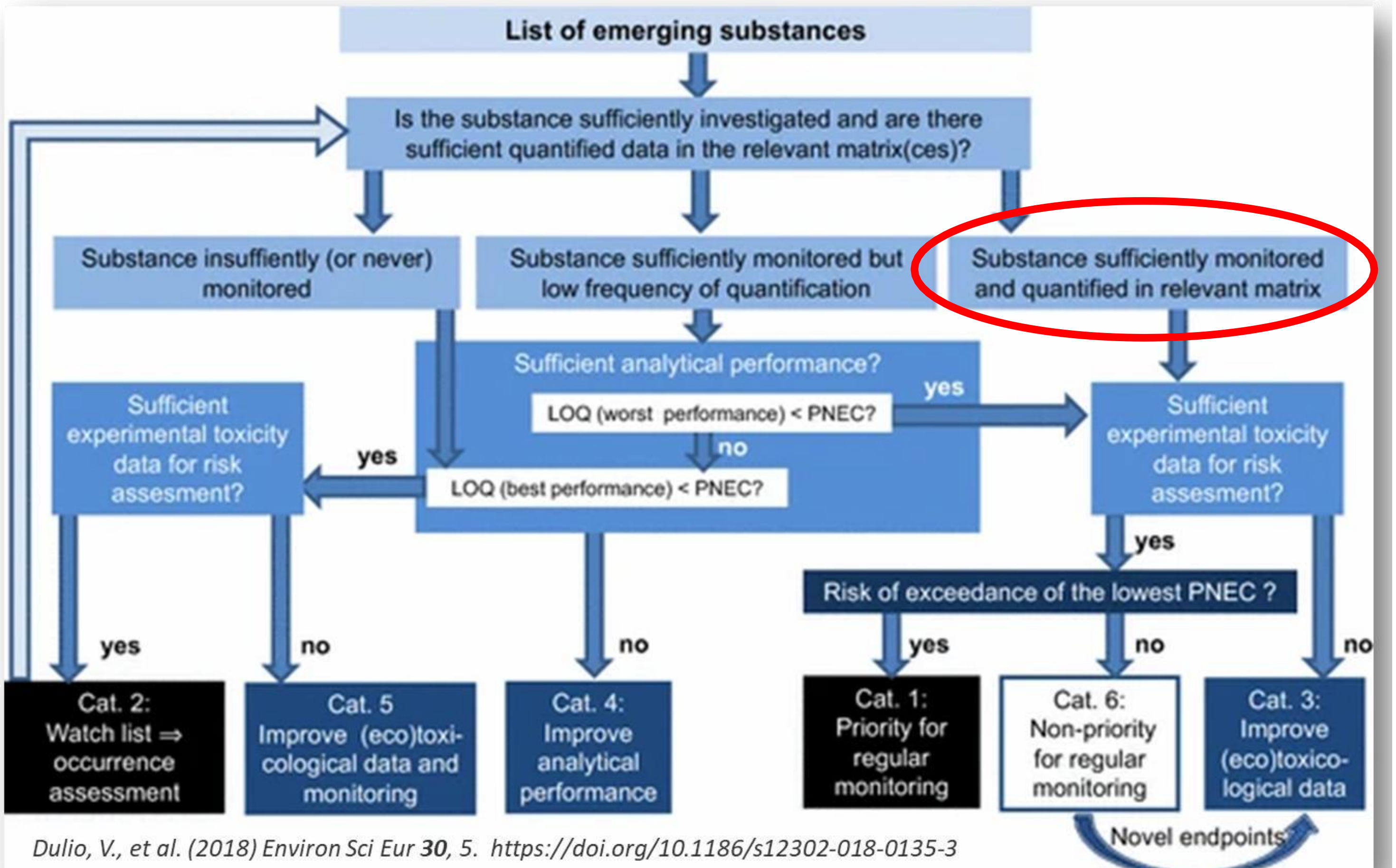
Radionuclides

Pharmaceuticals

PAHs

Plastics

Fertilizers




*Dulio, V., et al. (2018) Environ Sci Eur* ***30****, 5. https://doi.org/10.1186/s12302-018-0135-3*

# Nutrients. Trends in diffuse pollution. Nitrogen

Gross nitrogen balance decreased (in Kg N per hectare) from 72 to 46 from 2000 to 2009 but no significant reductions have been registered from 2010.

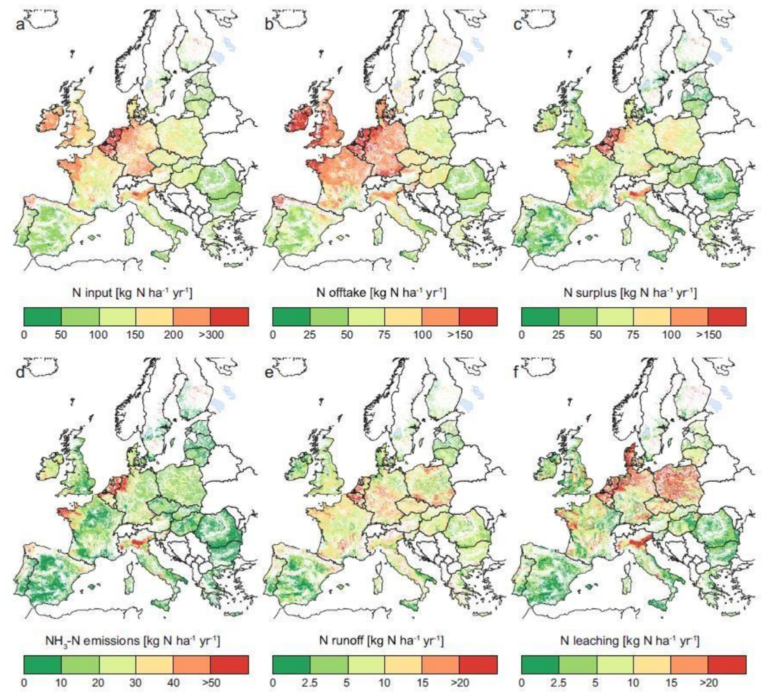
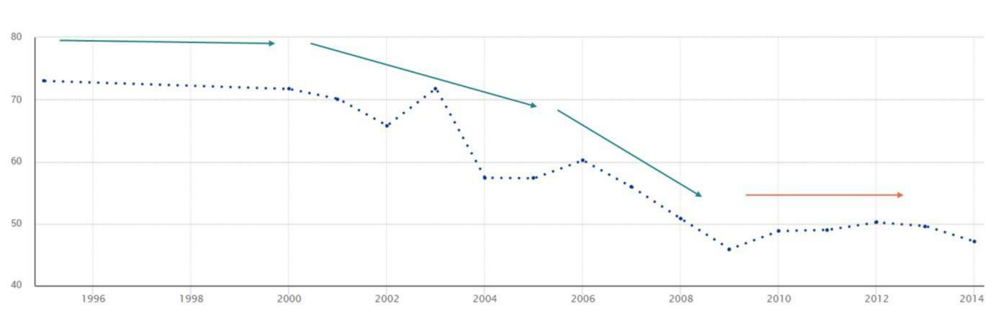



**Fig. 4.** Spatial variation in different terms of the actual (year 2010) N balance for all agricultural land in the EU at NCU level. a) Actual total N input (external N input plus net N mineralisation), b) N offtake, c) N surplus (total N input minus N offtake), d) $NH_3$-N emissions, e) N runoff to surface water and f) N leaching to groundwater.




*EUROSTAT*

On average, 145 kg N/ha are added to European soils in 2010 (N inputs)

Average crop N offtake is 92 kg N/ha

Nitrogen surplus remained around 50 Kg N/ ha from 2010 to 2014.

*W. de Vries, L. et al. (2021) Science of the Total Environment 786*

# Nitrogen in soils…should be considered as EC?

Environ Chem Lett (2006) 4: 51–61
DOI 10.1007/s10311-005-0016-z

$$NH_4^+ + 1.5\,O_2 \xrightarrow{\text{Nitrosomonas}} NO_2^- + 2H^+ + H_2O\,[\Delta G'_0 - 275\,\text{kJ/mol}] + 6e^-$$

$$NO_2^- + 0.5\,O_2 \xrightarrow{\text{Nitrobacter}} NO_3^- + [\Delta G'_0 - 75\,\text{kJ/mol}] + 2e^-$$

and overall

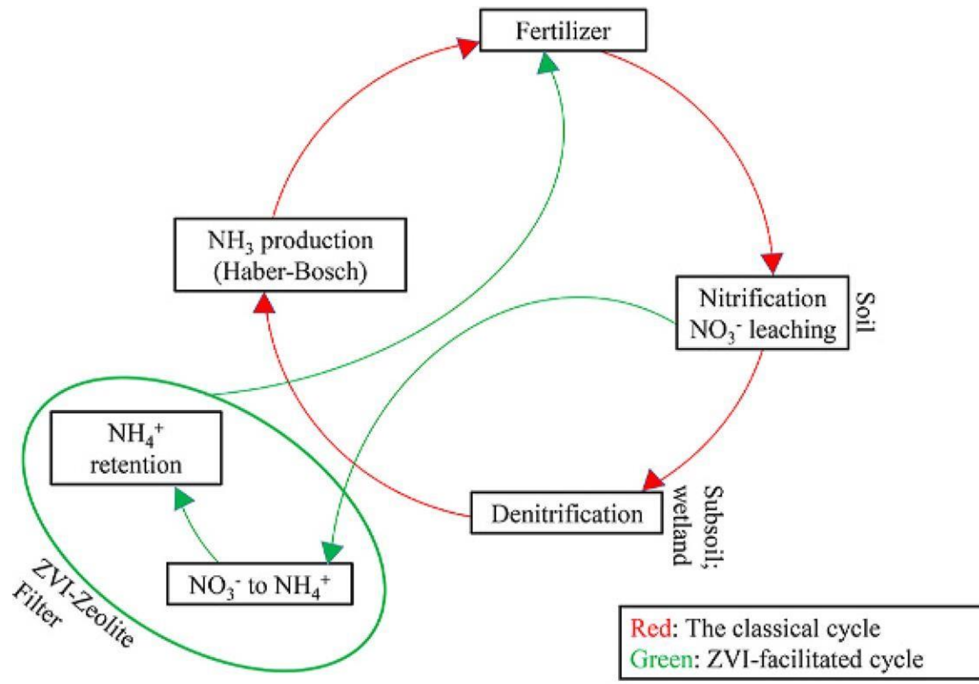
$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O + 8e^- + [\Delta G'_0 - 350\,\text{kJ/mol}]$$

$$NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O$$

$$4Fe^0 \rightarrow 4Fe^{2+} + 8e^-$$

$$NO_3^- + 4Fe^0 + 10H^+ \rightarrow NH_4^+ + 4Fe^{2+} + 3H_2O$$

- Emerging contaminants (ECs), a class of contaminants with **low concentrations** but **significant harm**. ECs comprises of various chemicals that enter the environment every day (*VarshaP. M et al., 2021 https://doi.org/10.1016/j.chemosphere.2021.132270*)
- Contaminants of emerging concern, these are the substances that **have appeared newly** or whose presence was identified earlier **but the hazards were not known**. These could be of **natural origin or manmade**. (Sauvé and Desrosiers et al., 2014)
- Emerging pollutants, "as pollutants that are currently **not included in routine monitoring programmes**, which may be candidates for **future regulation**, depending on research on their (eco) **toxicity**, potential health effects and public perception and on monitoring data regarding their **occurrence** in the various **environmental compartments**" (NORMON groups cited in Yadav, D., et al (2021). *Chemosphere*, *272*, 129492)
- Sauvé et al. (2018), defined Contaminants of Emerging Concern (CECs) as 'naturally occurring, manufactured or manmade chemicals or materials which have now been discovered or are suspected [to be] present in various environmental compartments and whose toxicity or persistence is likely to alter the metabolism of a living being significantly.' CECs show **high resistance to degradation** due to its **complex structure** and other factors.



# Conclusions

- Sources of Emerging Pollutants should be well identified
- Emerging Pollutants in soils should be monitored and quantified taking in account those specific features of soils as complex matrix. Different soil types are affecting on different way on the availability of Emerging pollutants and on their potential impact.
- Impact of Emerging Pollutants in soil phases should be well know and taken into consideration as part or the impact assessment on ecosystems and human health.
- Active Emerging Pollutant fractions should be adequately quantified to be taken into consideration in support of environmental policies and regulations

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# THANK YOU FOR ATTENTION!