119 Animine Academy

September 2nd, 2023, Lyon

Trace minerals added to **soils** by **animal effluents**: an **ecotoxicological** issue?

Matthieu N. Bravin, matthieu.bravin@cirad.fr

S. Legros, E. Clément, M. Tella, A. Avadí, and E. Doelsch

cirad

UR Recycling and Risk

Sustainable use of trace minerals from the feed to the food

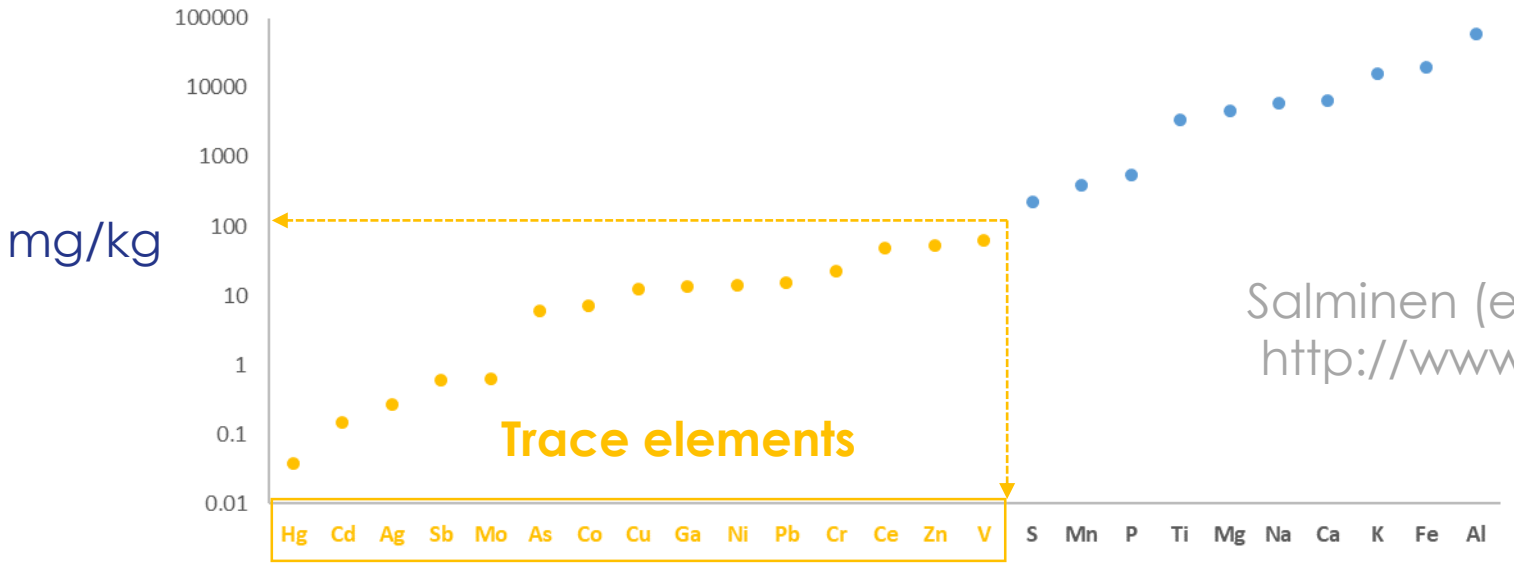
Introduction

From **trace minerals** in animal nutrition
to **trace elements** in animal effluents and agricultural soils

Soil background concentrations

- Mineral elements naturally and ubiquitously occurring at trace levels (< 100 mg/kg) in soils (Hooda, ed., 2010)
  - Awkward synonyms: heavy metals, potentially toxic elements

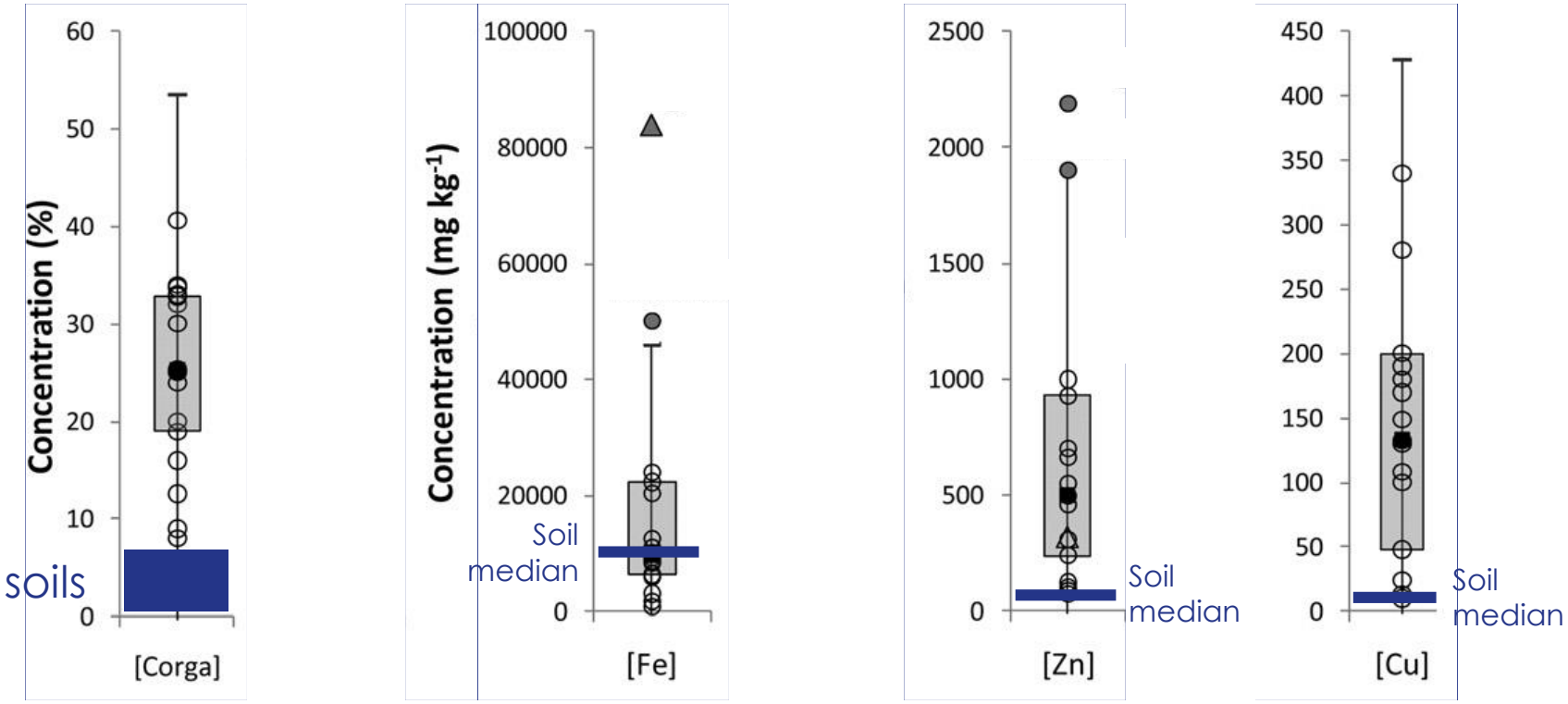
- Median concentrations



Salminen (ed.) 2005
http://www.gtk.fi/publ/foregsatlas/

Concentrations in animal effluents

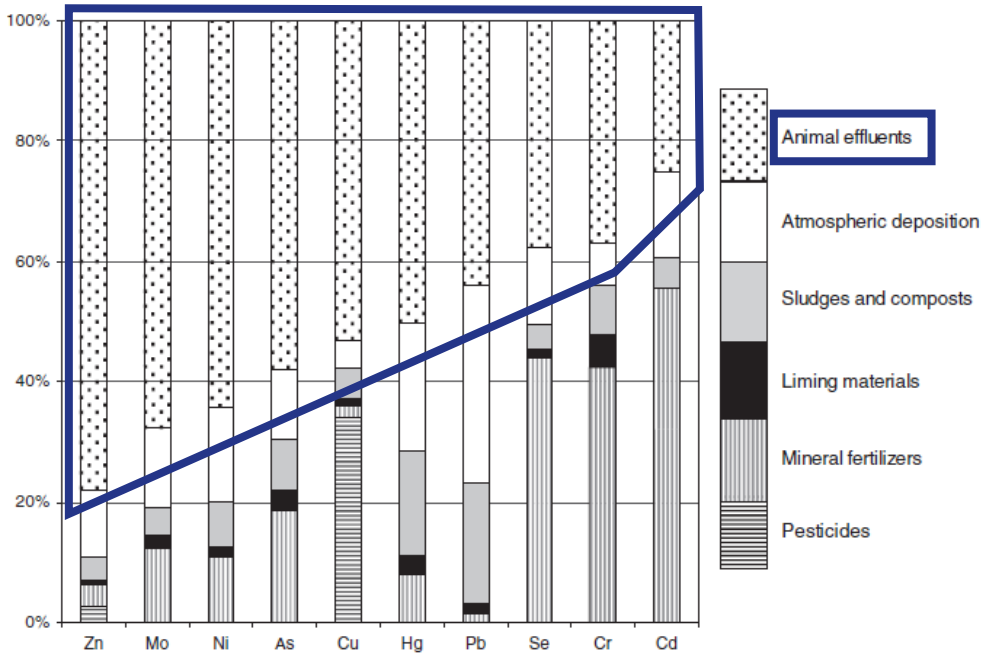
- Animal urine and feces raw, combined (with plant residues) and/or processed (aerobic and/or anaerobic digestion)
  - Animal residues usually rich in organic matter



Tella et al. (2013) Waste Manag. 33

Input to agricultural soils

- Mean flux to French soils



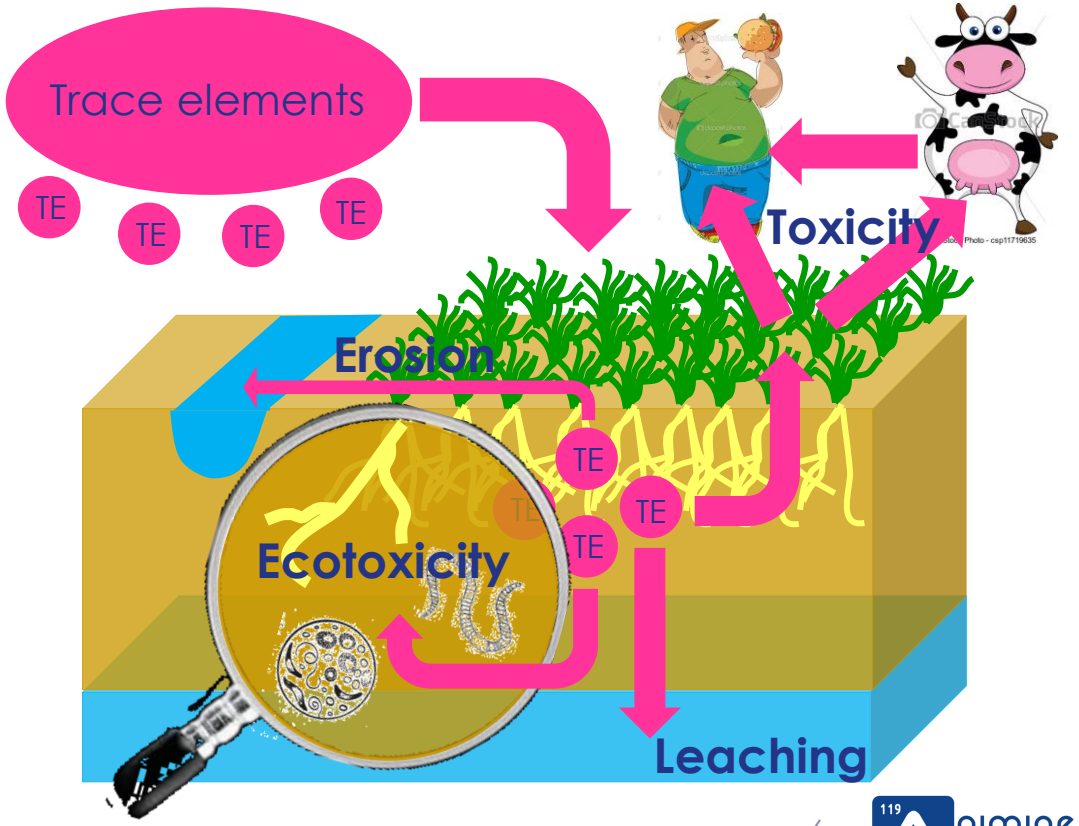
Zn >> Cu >> Cr > Pb > Ni > As >> Mo > Se > Cd > Hg

15 200 ←----------→ 12

Mg y^{-1}

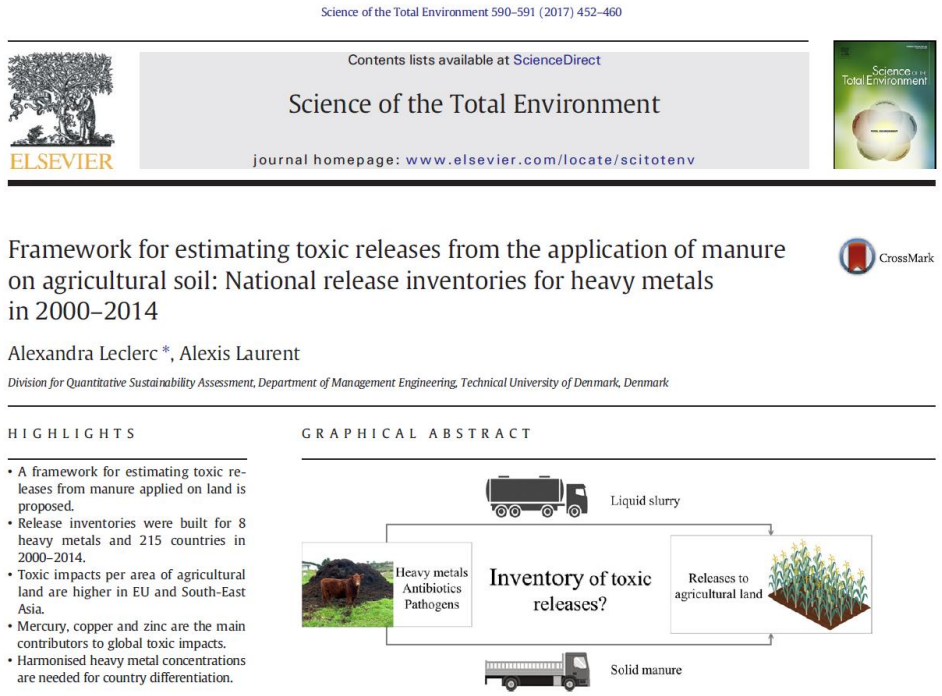
Belon et al. (2012) Sci. Tot. Environ. 439

- Potential health and environmental impacts



Global (eco)toxicity assessment

Life Cycle Assessment



Science of the Total Environment 590–591 (2017) 452–460

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Framework for estimating toxic releases from the application of manure on agricultural soil: National release inventories for heavy metals in 2000–2014

Alexandra Leclerc *, Alexis Laurent

Division for Quantitative Sustainability Assessment, Department of Management Engineering, Technical University of Denmark, Denmark

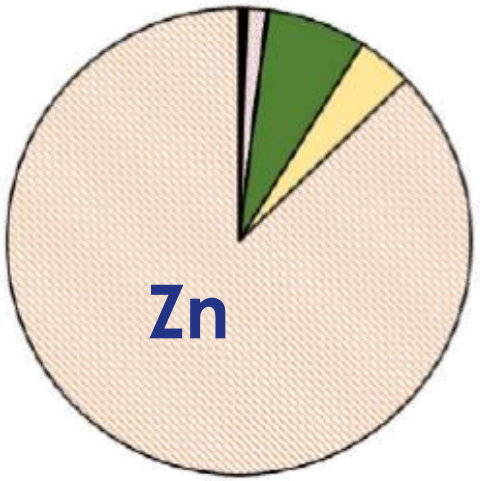
HIGHLIGHTS

- A framework for estimating toxic releases from manure applied on land is proposed.
- Release inventories were built for 8 heavy metals and 215 countries in 2000–2014.
- Toxic impacts per area of agricultural land are higher in EU and South-East Asia.
- Mercury, copper and zinc are the main contributors to global toxic impacts.
- Harmonised heavy metal concentrations are needed for country differentiation.

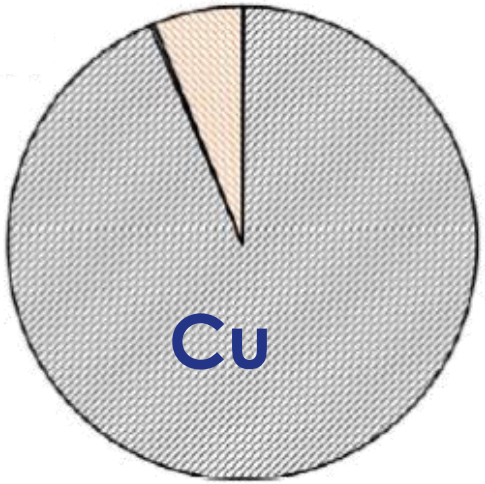
GRAPHICAL ABSTRACT

Leclerc et al. (2017) Sci. Tot. Environ. 590-591

- Human toxicity



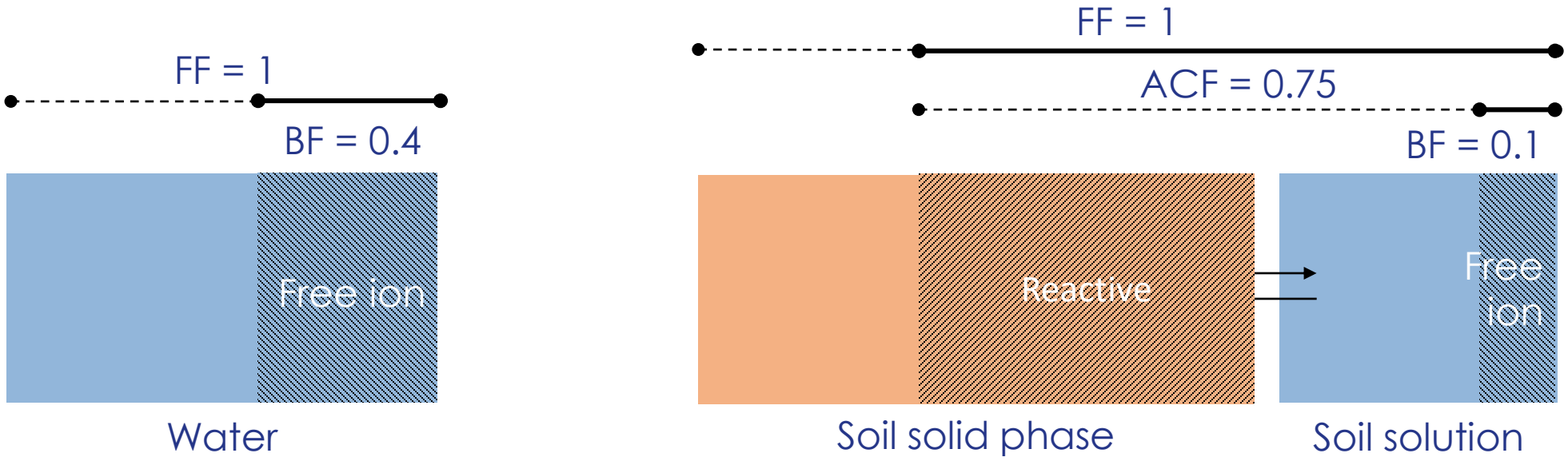
- Freshwater ecotoxicity



Assessing soil ecotoxicity

- **Impact** = **Emission** × **C**omparative **T**oxicity **P**otential
  - $\mathbf{CTP_{water}}$ = FF × BF × EF

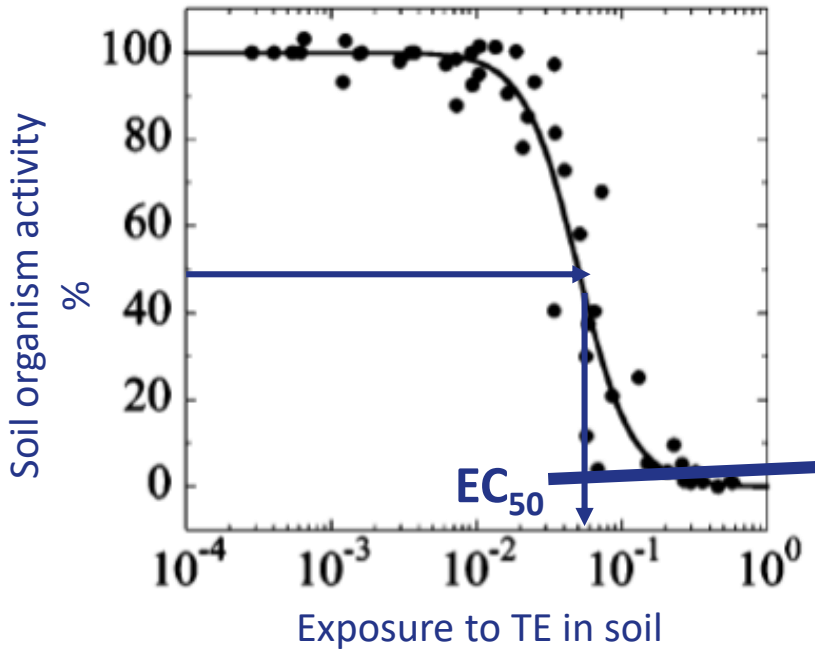
$\Rightarrow$ $\mathbf{CTP_{soil} = FF \times ACF \times BF \times EF}$

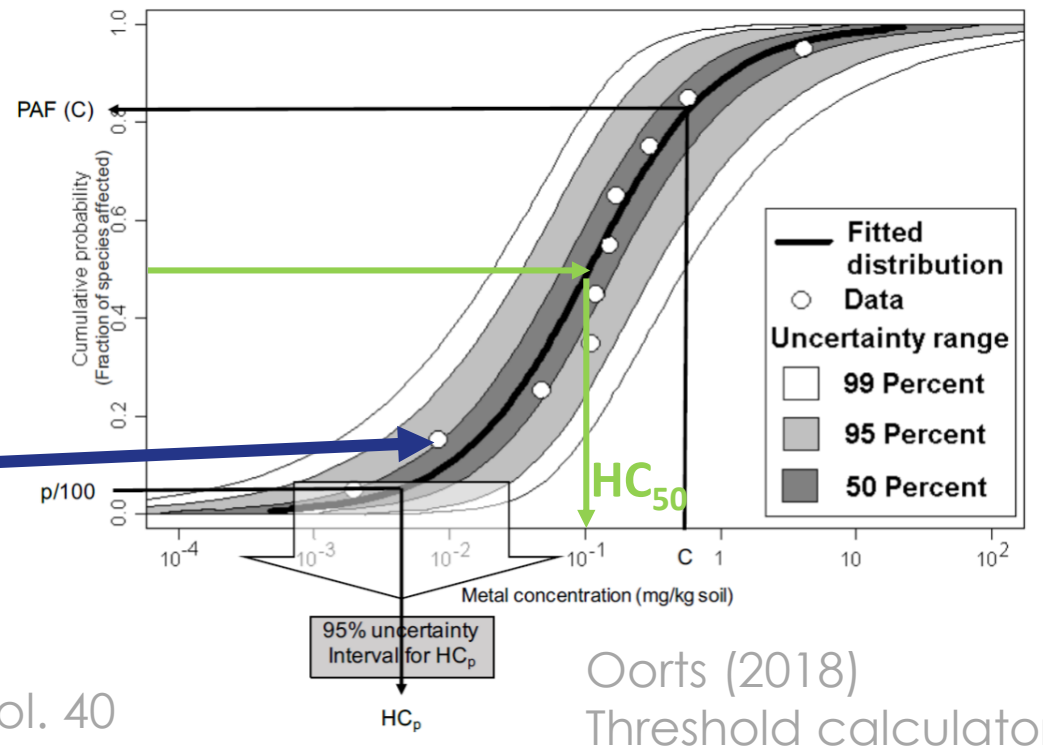


Owsianiak et al. (2013) Environ. Sci. Technol. 47

Assessing soil ecotoxicity

- USEtox: Comparative Toxicity Potential
  - $CTP_{soil} = FF \times ACF \times BF \times EF$
  - CFs = f {soil physical-chemical properties}



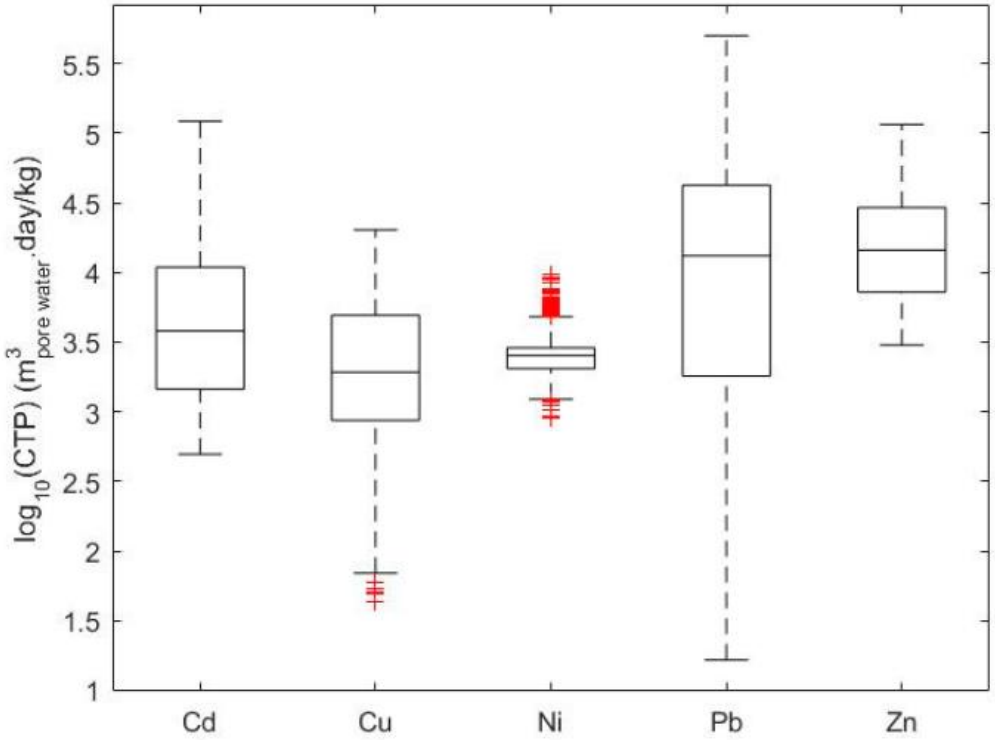


Thakali et al. (2006) Environ. Sci. Technol. 40

Oorts (2018)
Threshold calculator v 2.0

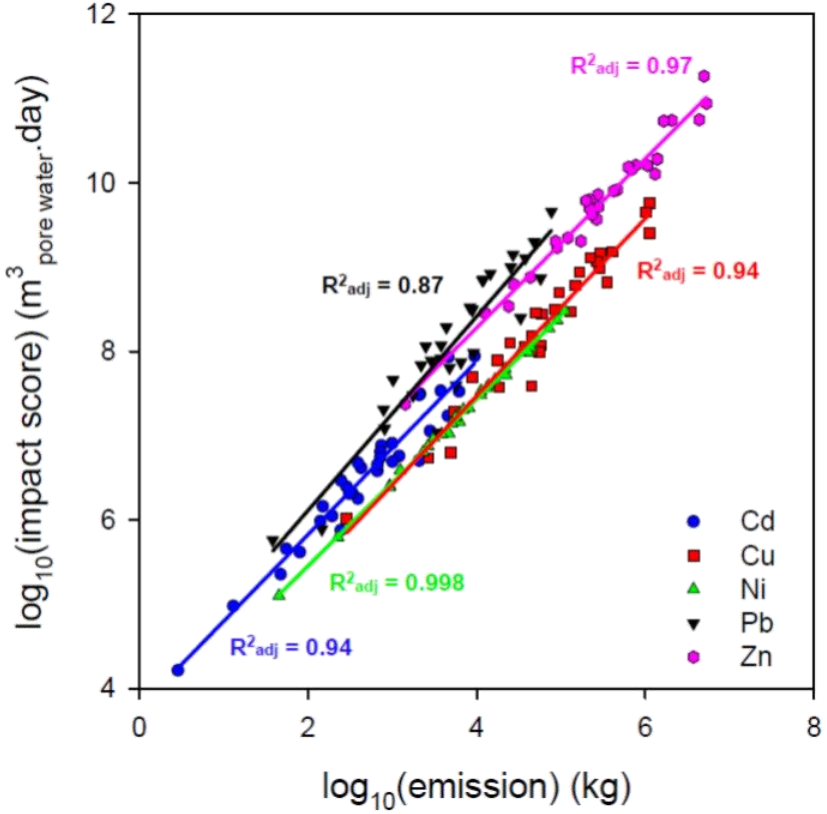
Ecotoxicity in amended soils

- CTP ranges within Europe



Sydow et al. (2018) Sustain. 10

- Impact at the country level
  - **Impact** = CTP × **emission**



Ecotoxicity: only a matter of quantity?

- According to LCA, animal effluent application to soils could be (eco)toxic: mainly Cu and Zn

- (eco)Toxicity would only depend on the amount of TE applied with animal effluents

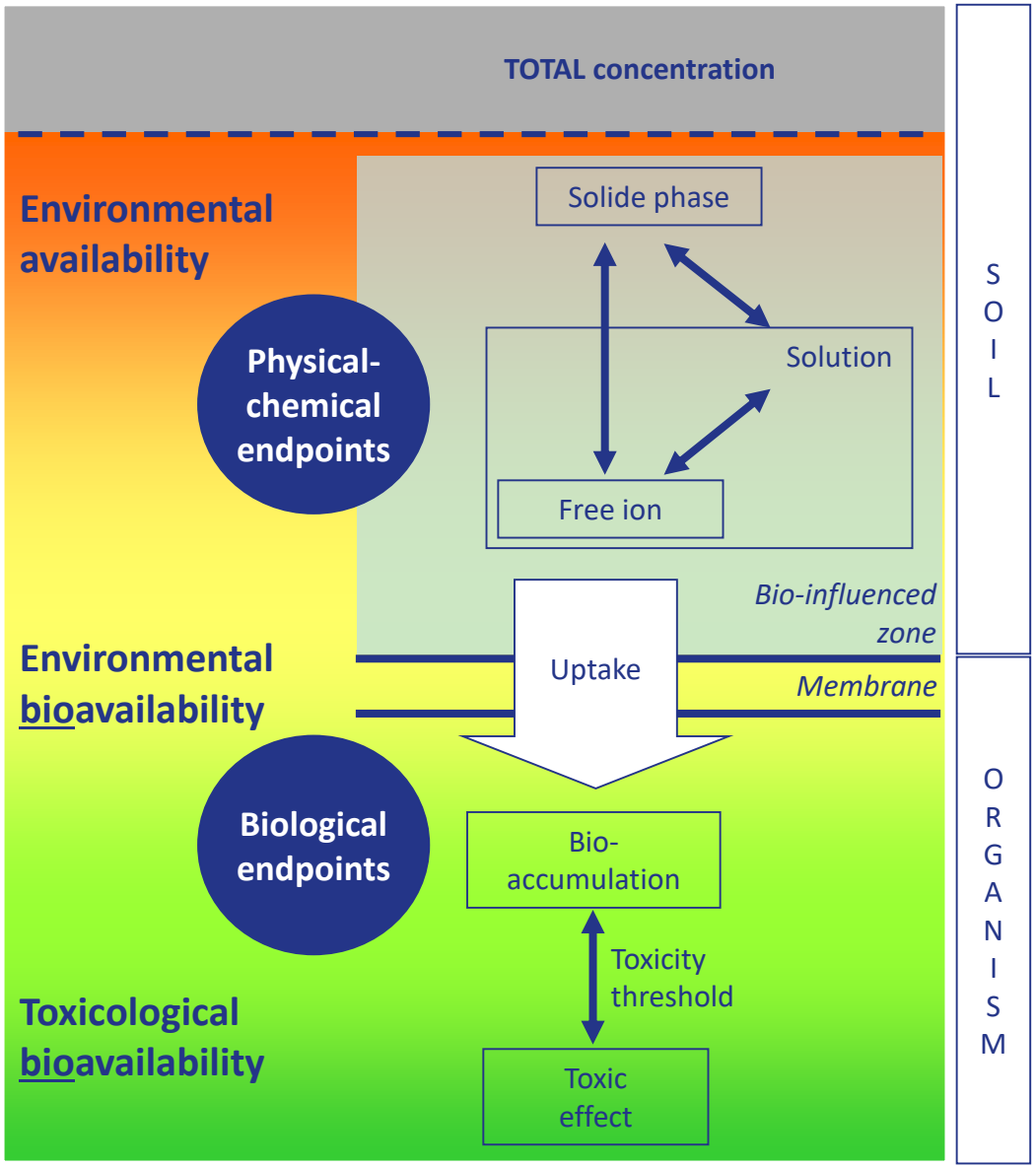
⇒ Confront with the **bioavailability theory** and the **empirical knowledge**

From TE-contaminated soils to ecotoxicity

A (hist)story of bioavailability

Bioavailability: the consensus

CTP = FF × ACF × BF × EF



- Fraction of total soil TE made available by **physical-chemically-driven desorption processes** that can be **potentially taken up by soil organisms**

- Fraction of available TE **effectively taken up by a soil organism** under the control of **physiologically-driven processes**

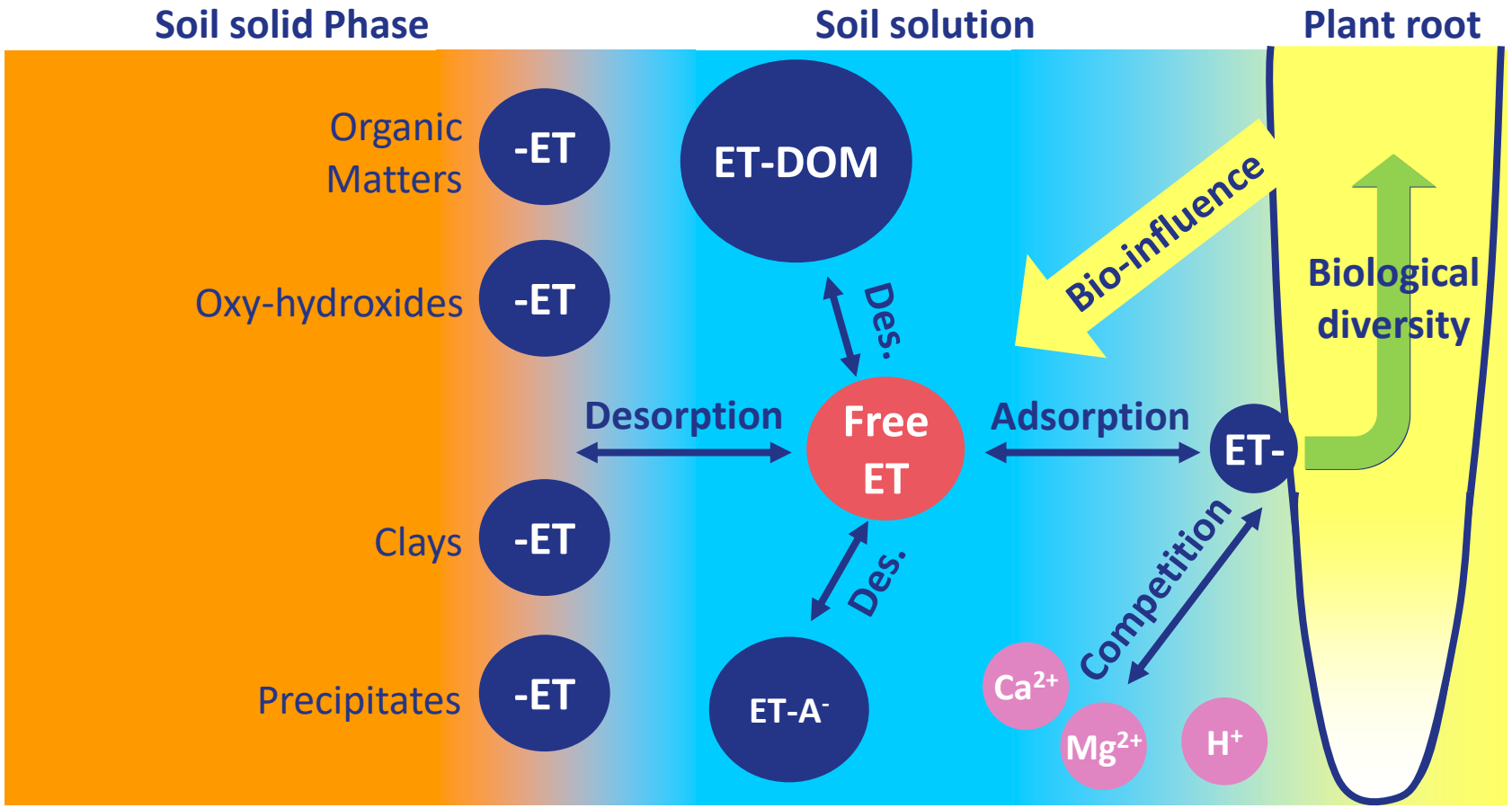
⇒ Specific of each target organism

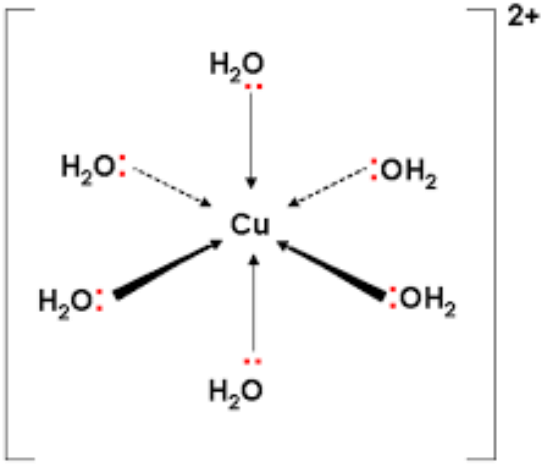
- **Bio-accumulated fraction** of bioavailable TE that **may induce a toxic effect**

NF EN ISO 17402 (2008)

Physical-chemically-related concepts

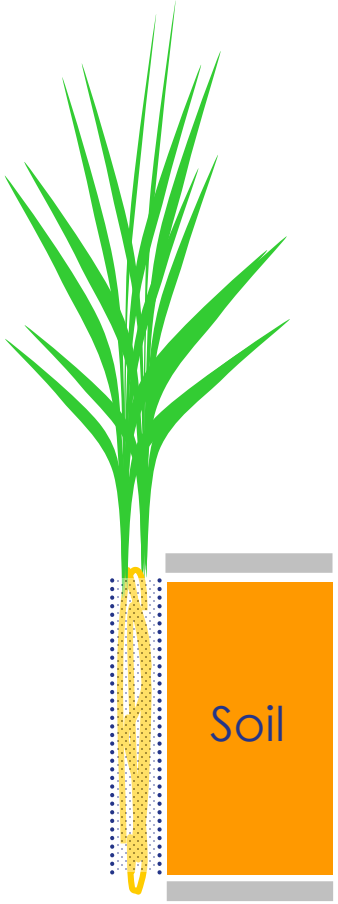
- **The free ion concept** and its consequences

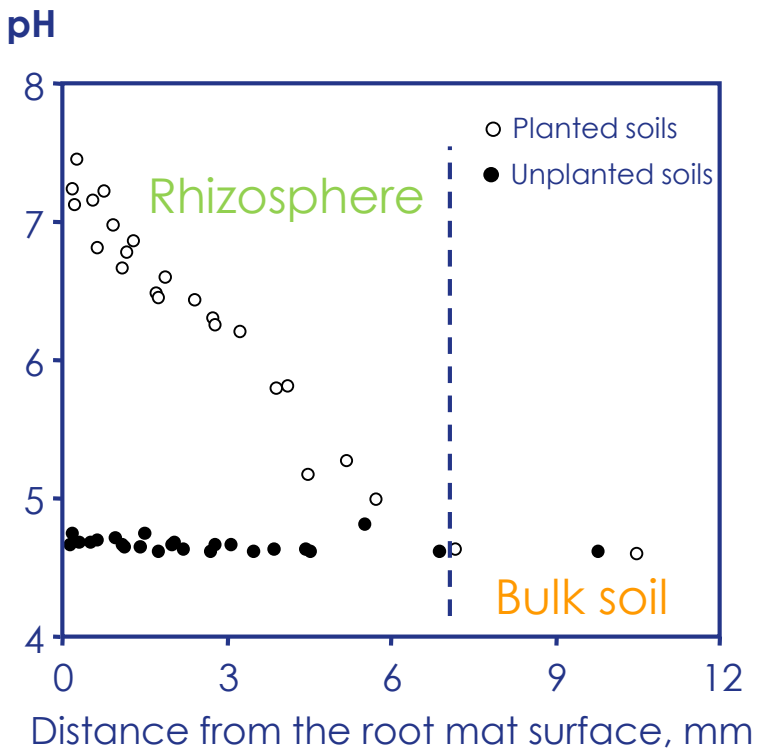


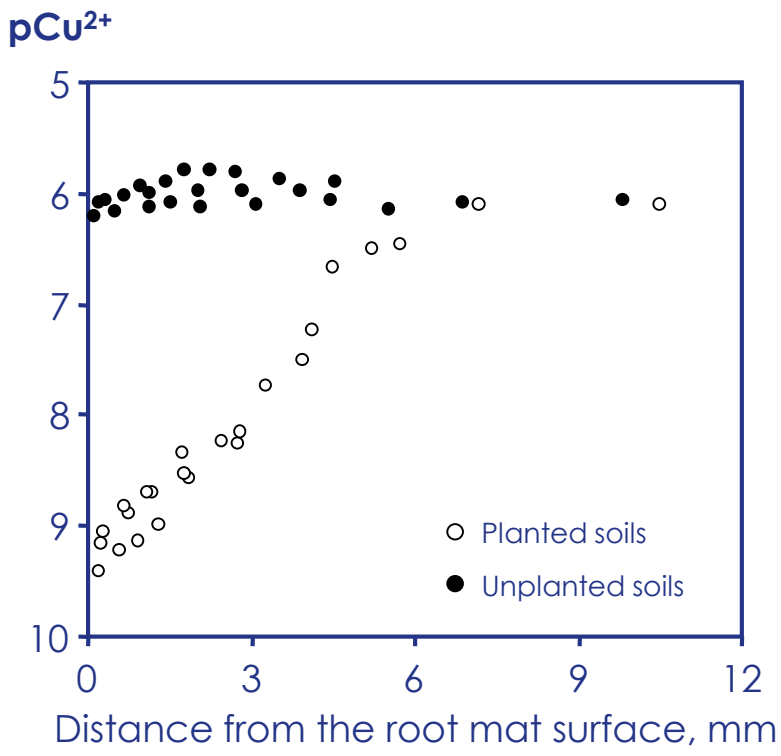


Biologically-related concepts

- Bio-influence



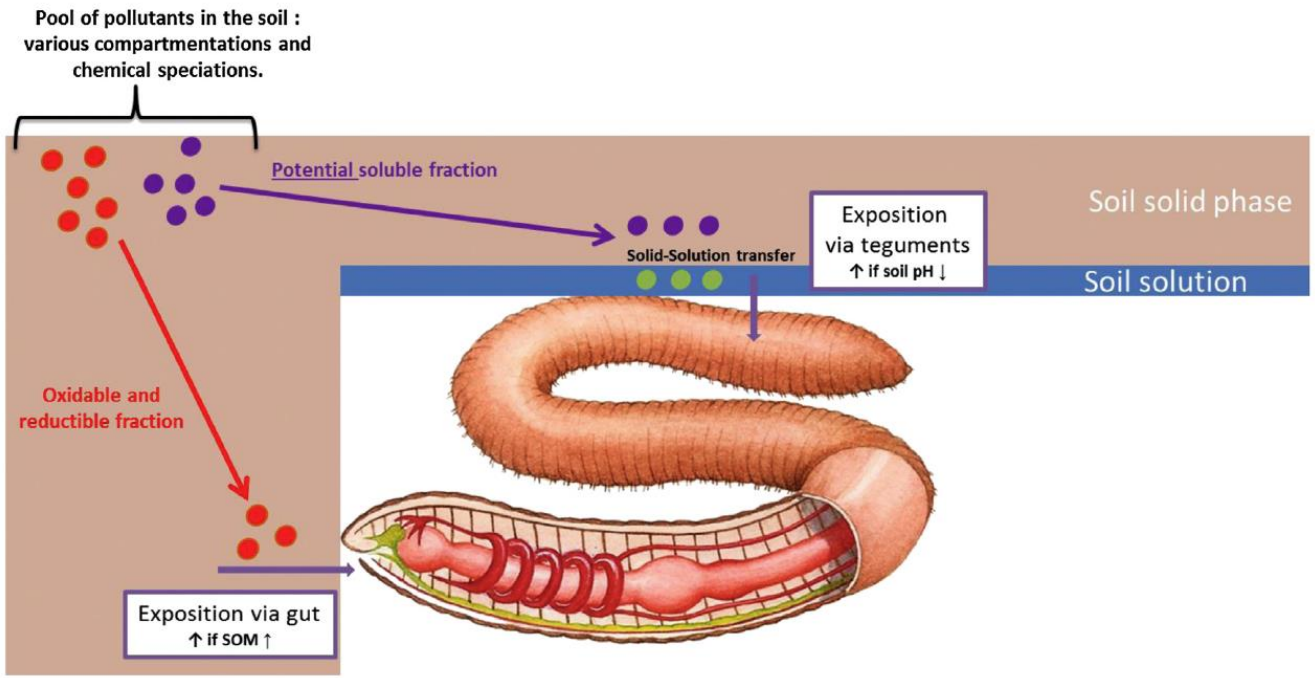




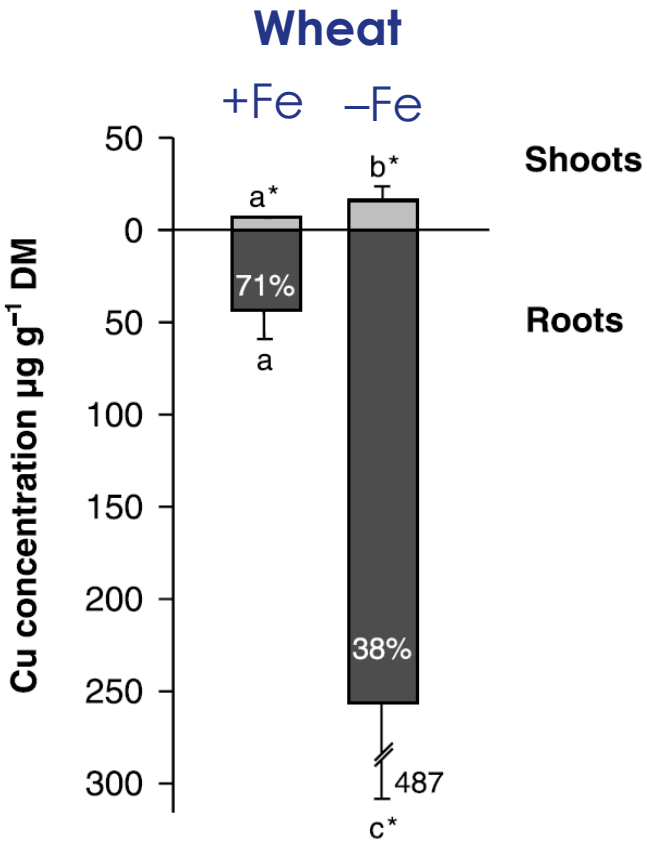
Bravin et al. (2009) Environ. Sci. Technol. 43

Biologically-related concepts

- Individual plasticity



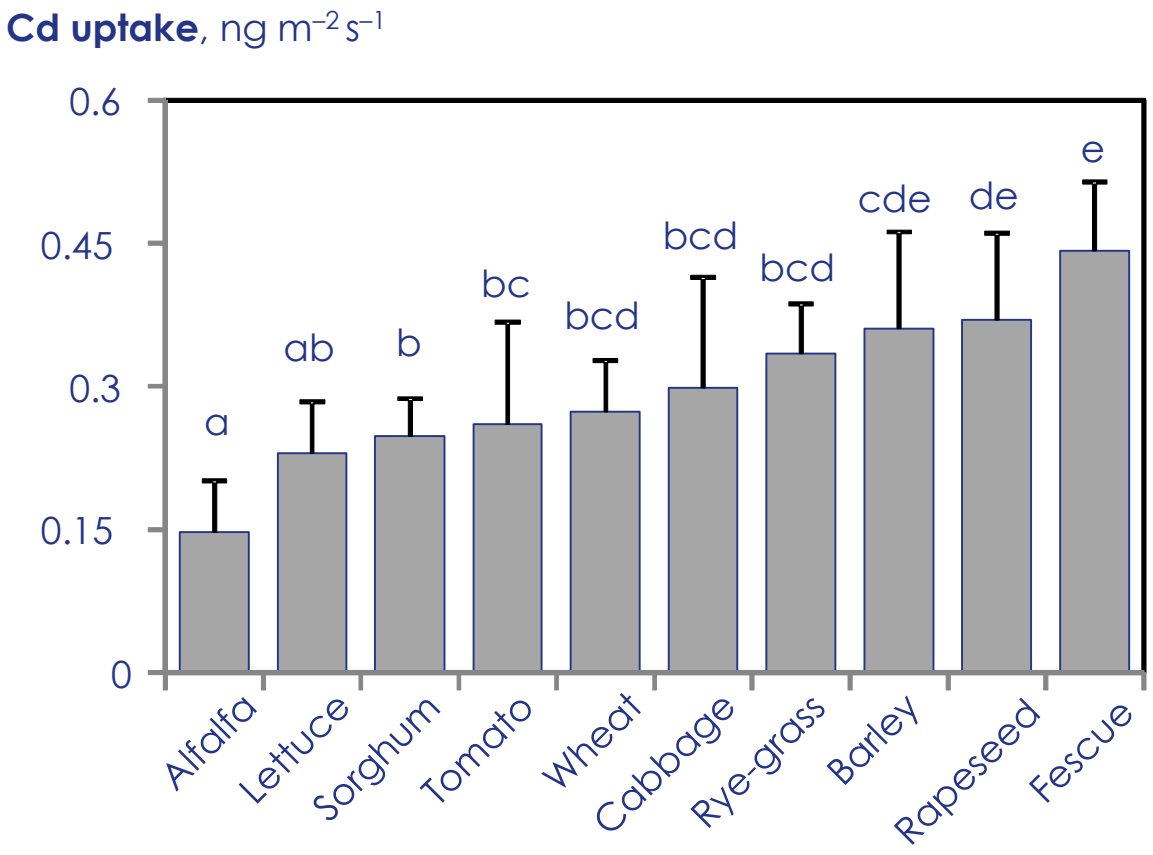
Leveque et al. (2013) Environ. Pollut. 179



Chaignon et al. (2002) New Phytol. 154

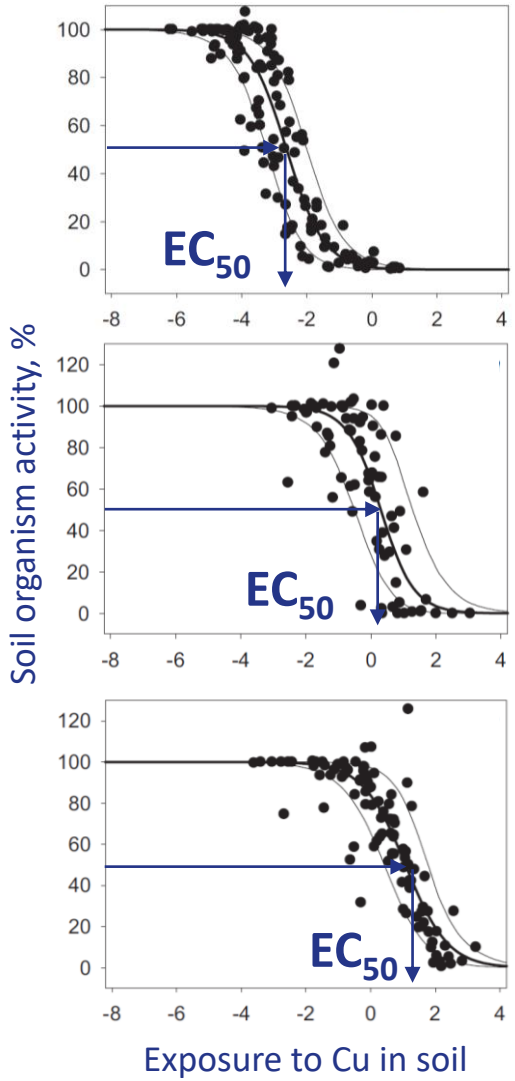
Biologically-related concepts

- Taxonomic diversity



Bravin et al. unpublished

Lofts et al. (2013) Environ. Pollut. 178



Plants

Earthworms

Microorganisms

USEtox vs Bioavailability theory

- **Bioavailability** is driven both by **physical-chemical** and **biological** processes
  - Physical-chemical endpoints are only indicators of bioavailability
  - Bioavailability is specific to each *target* organism

- **USEtox** is **in line with the bioavailability theory**

  ⇒ To which extend it accounts empirically for physical-chemical and biological drivers?

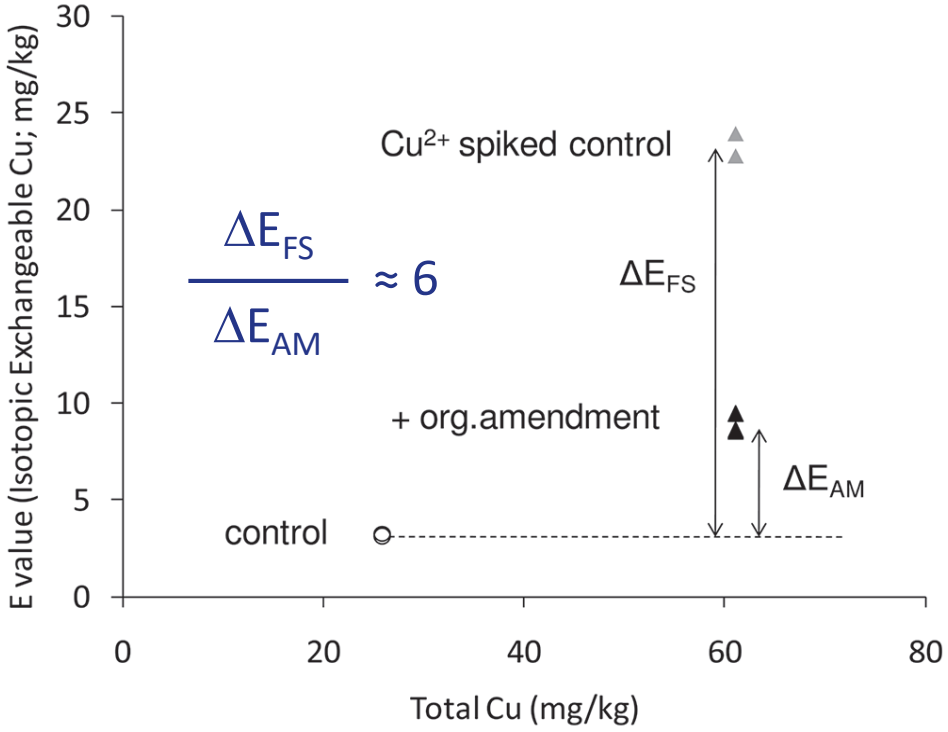
TE bioavailability and ecotoxicity in soils amended with organic residues

including animal effluents

Protective effect: Empirical evidences

- Methodology
  - **22 sites** with **control** and **amended soils** for a few years to a century
  - **Cu availability** in control soils spiked as amended soils ⇒ **Reduction factor**
  - **Plant toxicity test** with control and amended soils similarly spiked ⇒ **Protection factor**

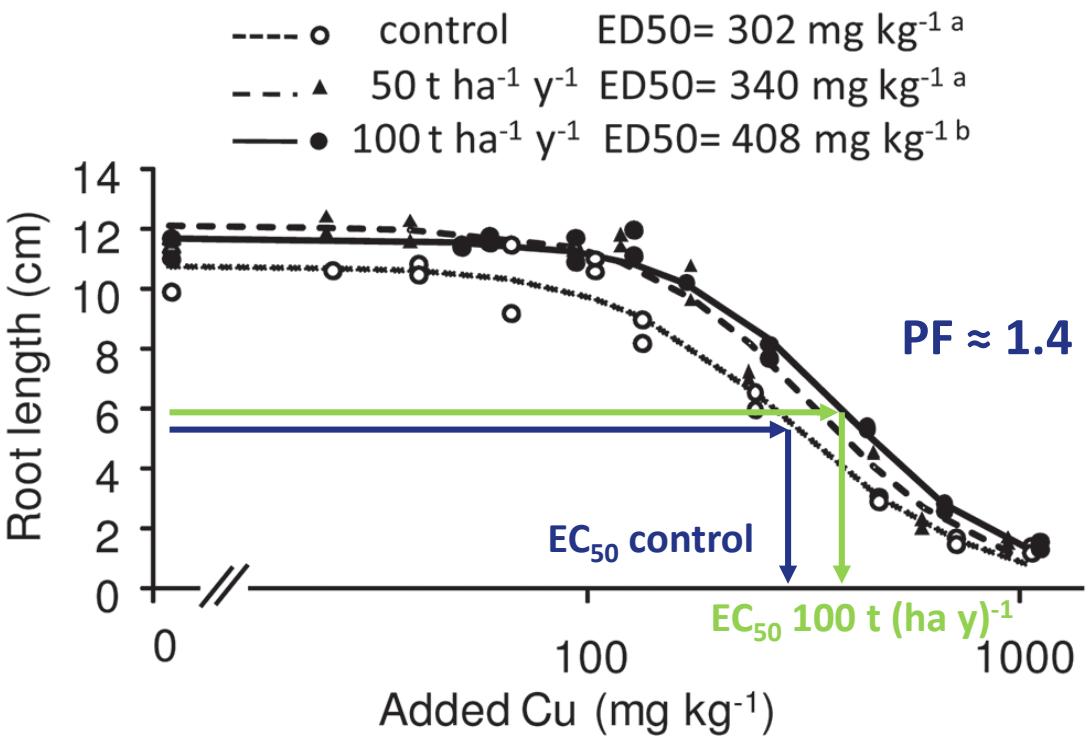
- **Reduction factor** on soil Cu availability



Smolders et al. (2012) J. Environ. Qual. 41

Protective effect: Empirical evidences

- **Protection factor** (PF) on Cu phytotoxicity



- Experimental **limits**
  - Soil pH correction
  - Protective effect compared to no soil contamination?

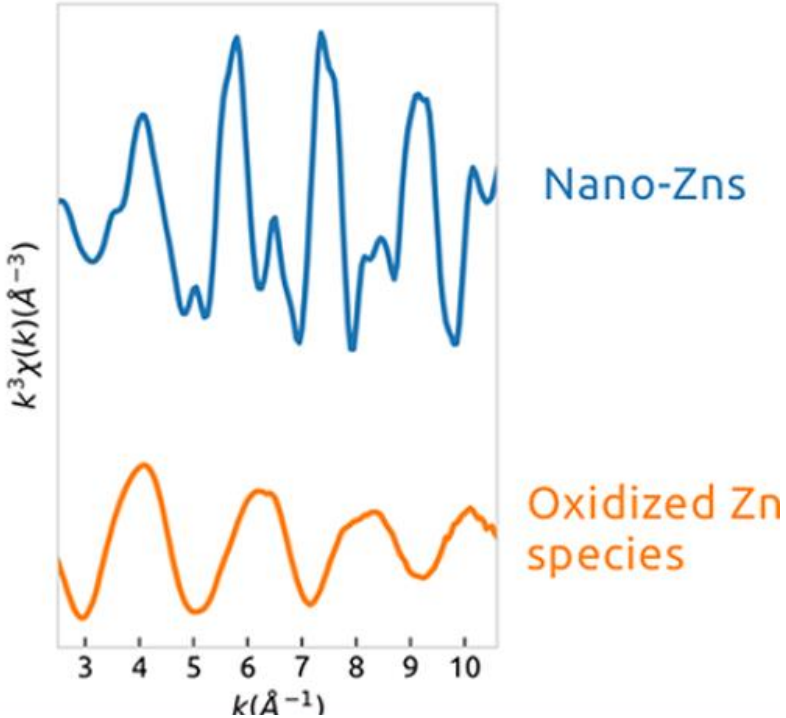
- Hypothetical **protection mechanisms**
  - Lower Cu availability in organic residues (OR)?
  - No impact of OR-induced soil properties evolution?

Smolders et al. (2012) J. Environ. Qual. 41

Mechanisms: 1. Organic residues

- Cu and Zn **speciation** in organic residues strongly **changes along the process** according to the **redox state**

RAW OW

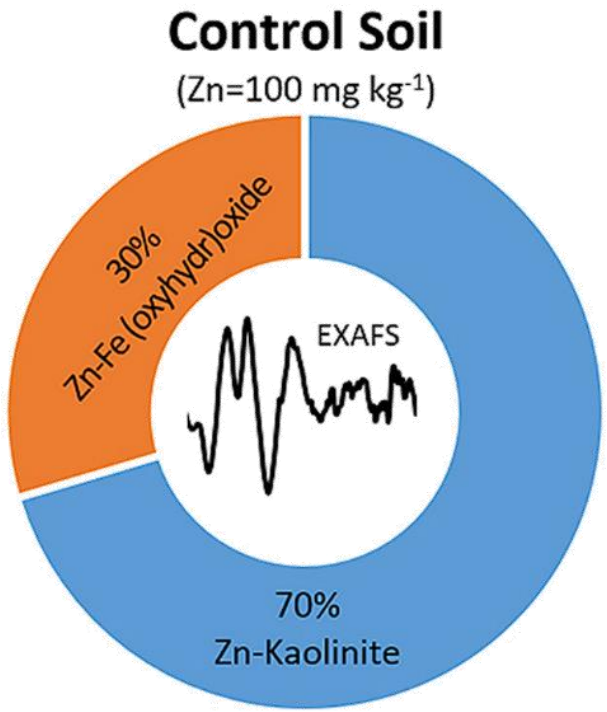


Legros et al. (2017) Environ. Sci. Technol. 51

Le Bars et al. (2018) Environ. Sci. Technol. 52

Mechanisms: 1. Organic residues

- Cu and Zn **sulfides evolved very quickly** in amended soils

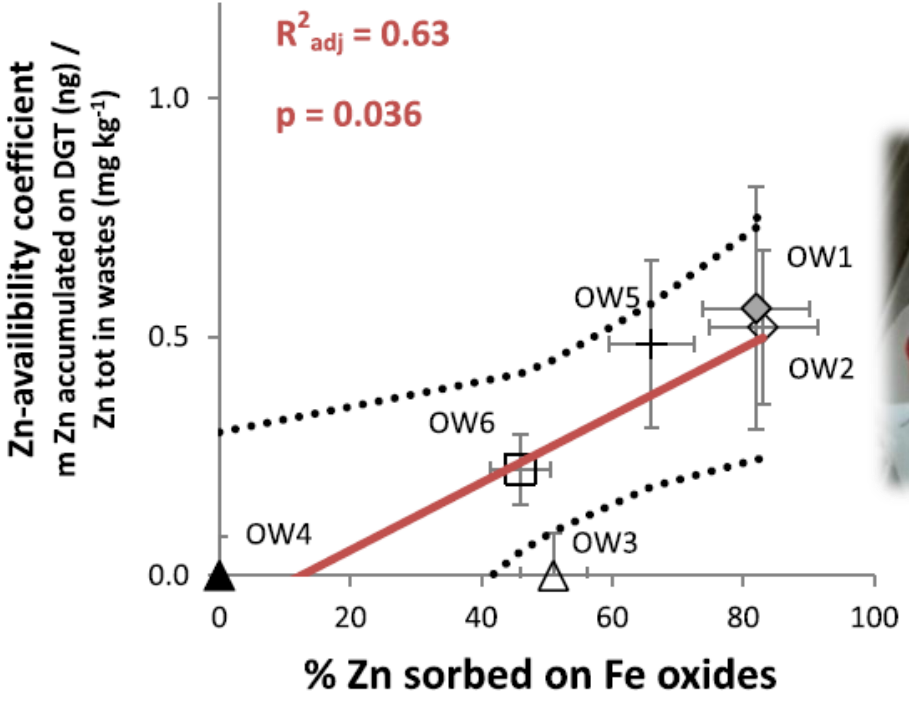


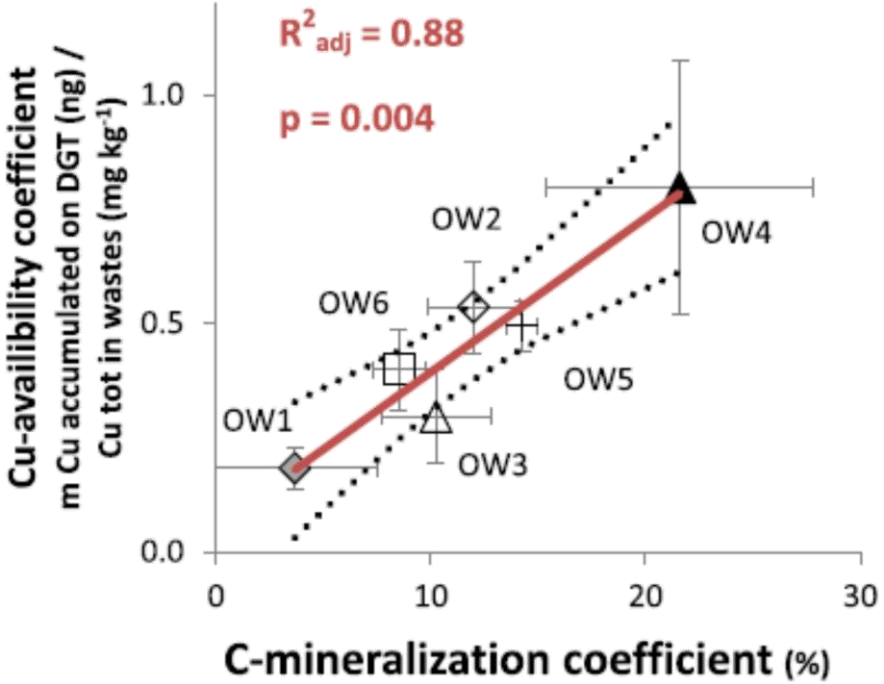
Formentini et al. (2017)
Environ. pollut. 222

Formentini et al. (2022)
Sci. Tot. Environ. 848

Mechanisms: 1. Organic residues

- Zn speciation in OR partly drives **soil Zn availability**
- Organic matter mineralization partly drives **soil Cu availability**

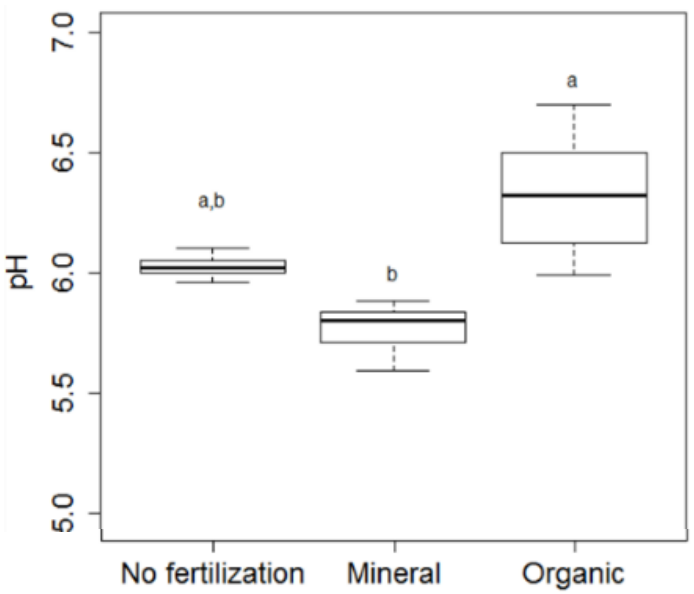


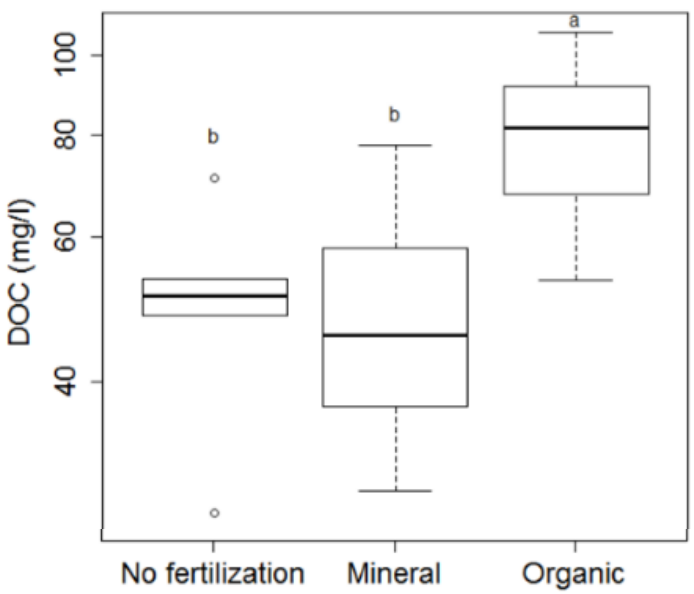


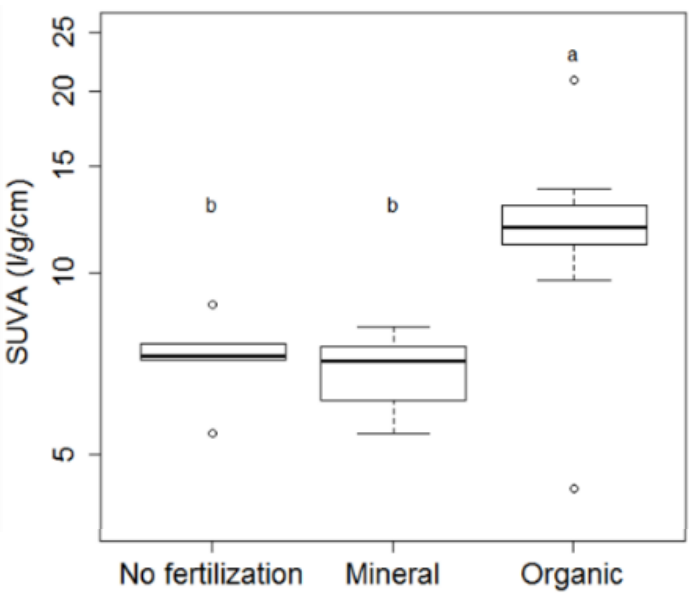
Tella et al. (2016) Environ. Pollut. 212

Mechanisms: 2. Amended soils

- Repetitive **organic residues** applications induce **soil pH and DOM increases**





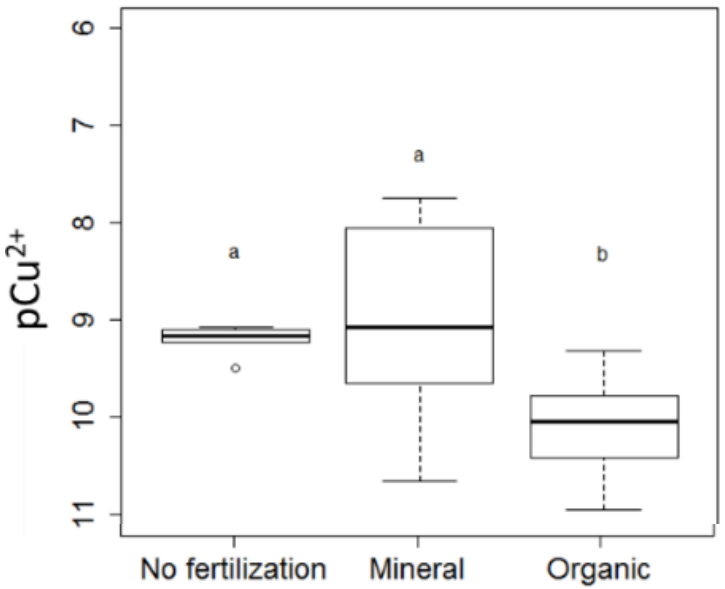


Laurent et al. (2020) Sci. Tot. Environ. 709

Mechanisms: 2. Amended soils

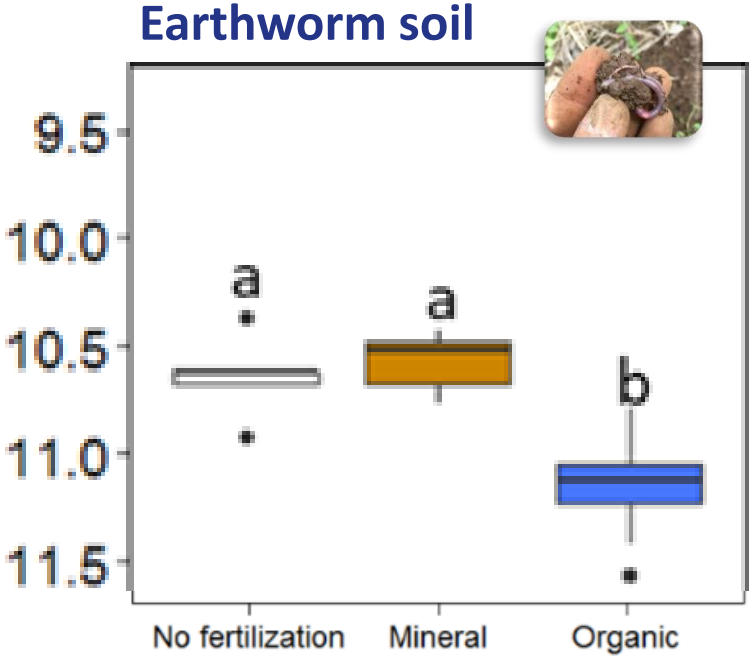
- **Organic residues** and **plants** mitigate **soil Cu and Zn availability**

Bulk soil



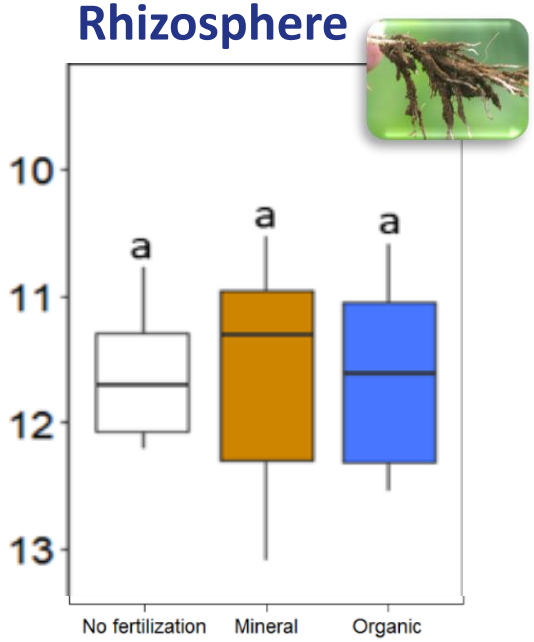
Laurent et al. (2020)
Sci. Tot. Environ. 709

Earthworm soil



Laurent et al. (2023a)
Environ. Sci. Pollut. Res. 30

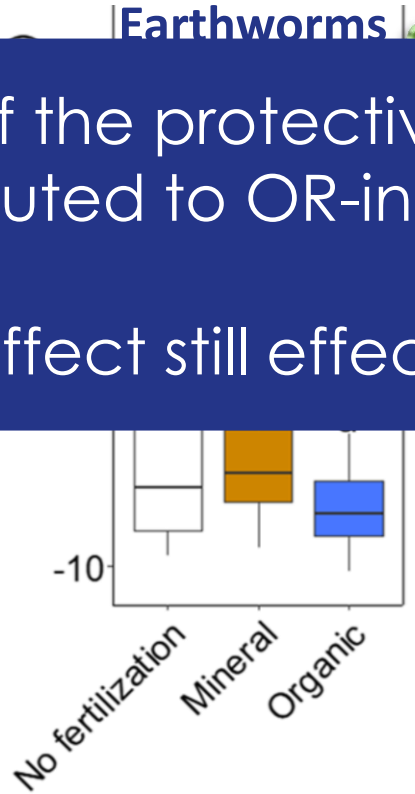
Rhizosphere



Laurent et al. (2023b)
under revision

Mechanisms: 2. Amended soils

- A decade of **organic residues applications** does not increase **Cu and Zn bioavailability**



- Validation of the protective effect over a decade
- Mainly attributed to OR-induced changes in soil pH and DOM

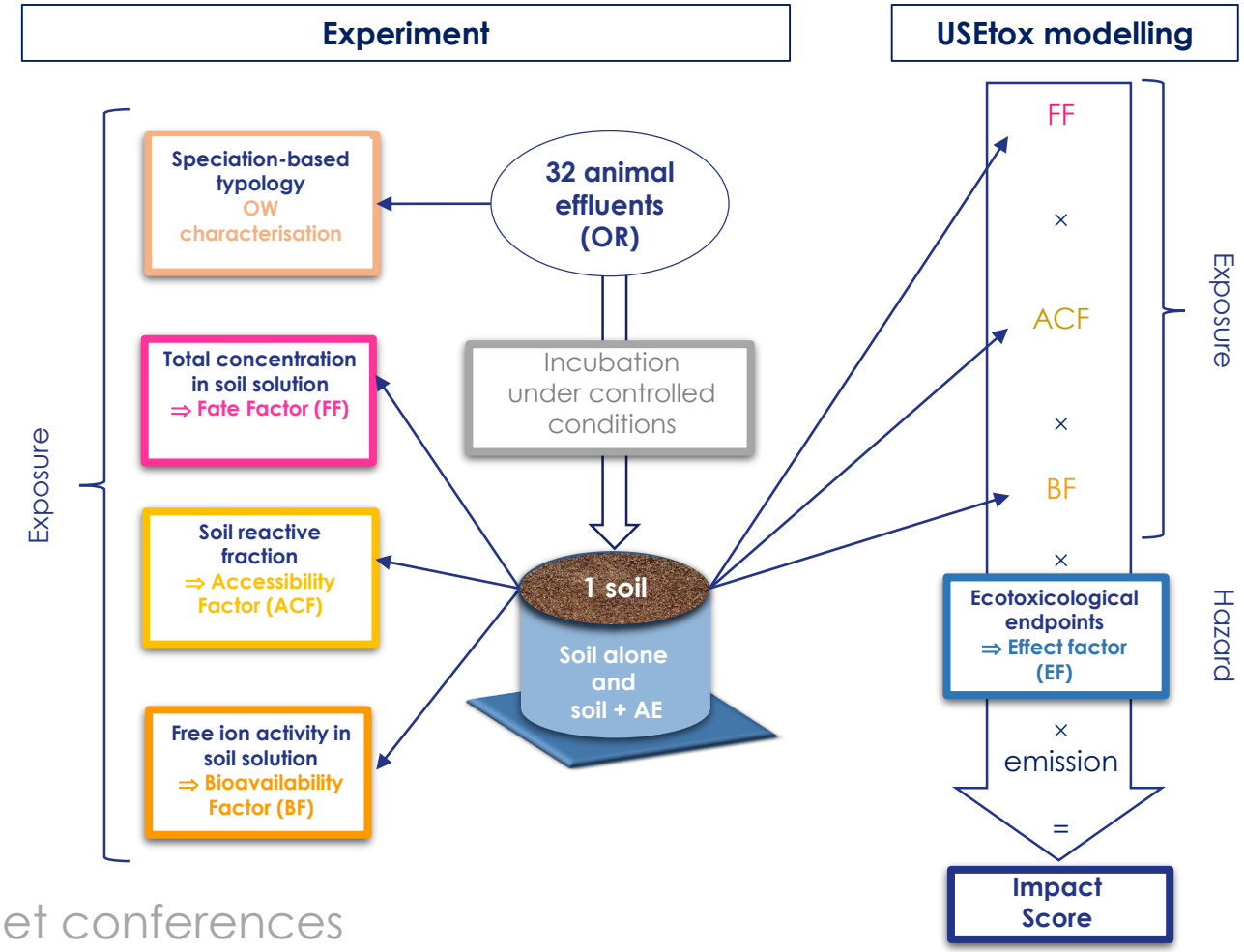
⇒ Protective effect still effective over several decades?

Laurent et al. (2023a)
Environ. Sci. Pollut. Res. 30

Laurent et al. (2023b)
under revision

USEtox vs soil biogeochemistry!

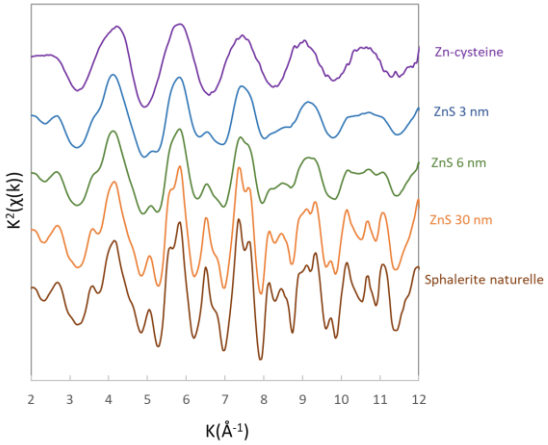
- A **unique** and **dedicated experiment**



Clément et al. (2023)
EAAP and Icobte-Ichmet conferences

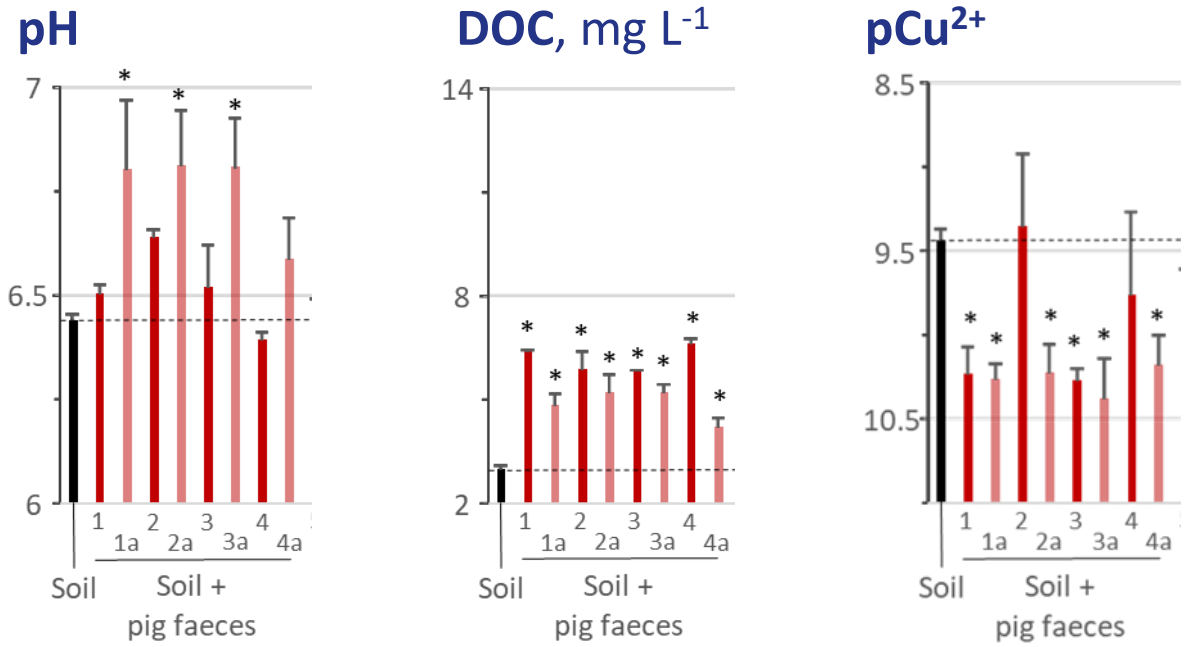
USEtox vs soil biogeochemistry!

- **Speciation** in animal effluents
  - Cu sulfides dominate whatever the animals
  - Zn sulfides for pig and piglets
  - Zn phosphate for broilers



Tella et al. (2023) Chemosphere 340

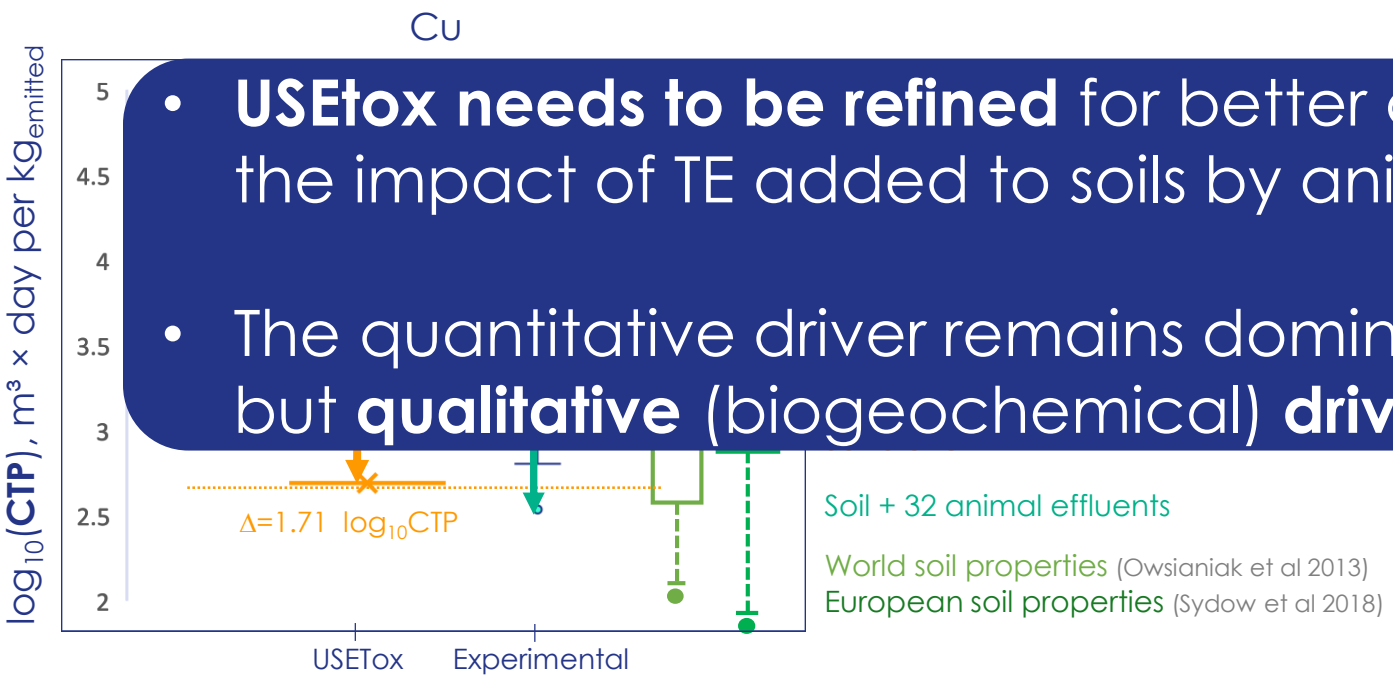
- Induced changes in **soil Cu and Zn availability**

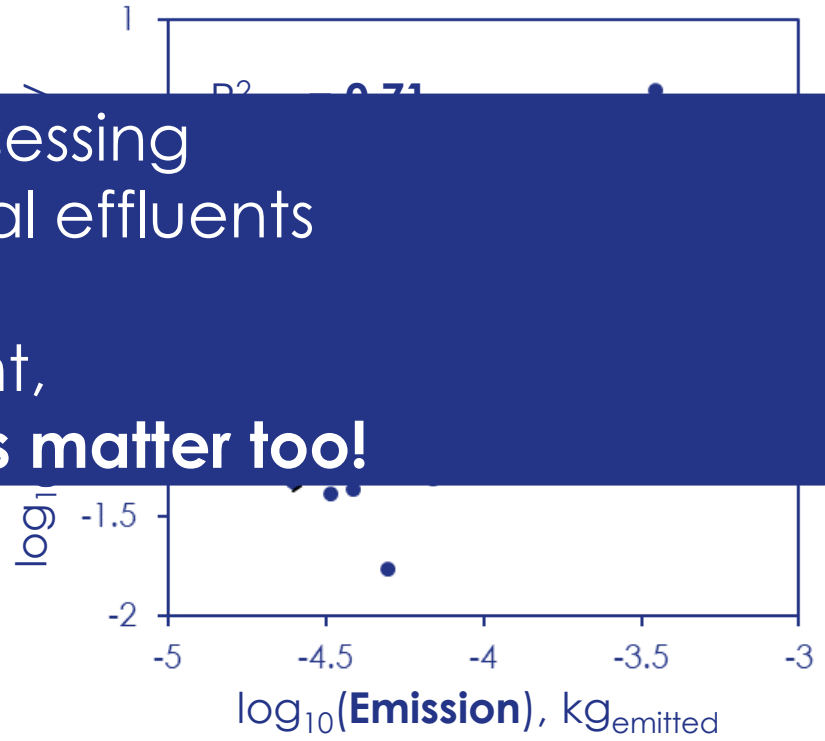


Clément et al. (2023) EAAP and Icobte-Ichmet conferences

USEtox vs soil biogeochemistry!

- USEtox cannot reproduce the **huge AE effect on CTP**
- **Impact** less driven by **emissions** than at the country scale





- **USEtox needs to be refined** for better assessing the impact of TE added to soils by animal effluents
- The quantitative driver remains dominant, but **qualitative** (biogeochemical) **drivers matter too!**

Clément et al. (2023) EAAP and Icobte-Ichmet conferences

Risk assessment: field case study

- **Field trial**
  - 14 cropping cycles, 7 years
  - Market-garden crops
  - 3 fertilizations
    - Synthetic fertilizers
    - Pig slurry and poultry litter composts: 30-60 t (ha y)$^{-1}$

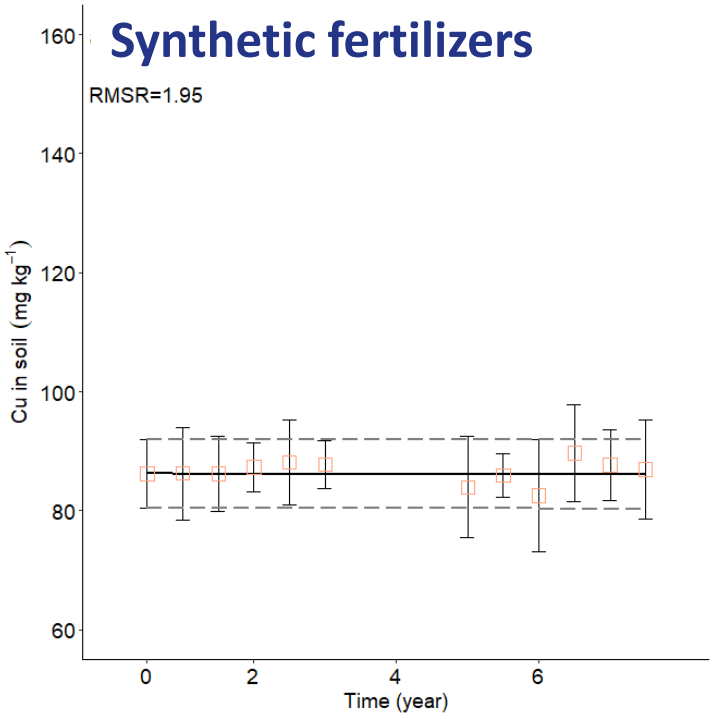
- **Analytical determinations**
  - TE total concentrations in fertilizers, soils and plants
  - Soil pH and OM

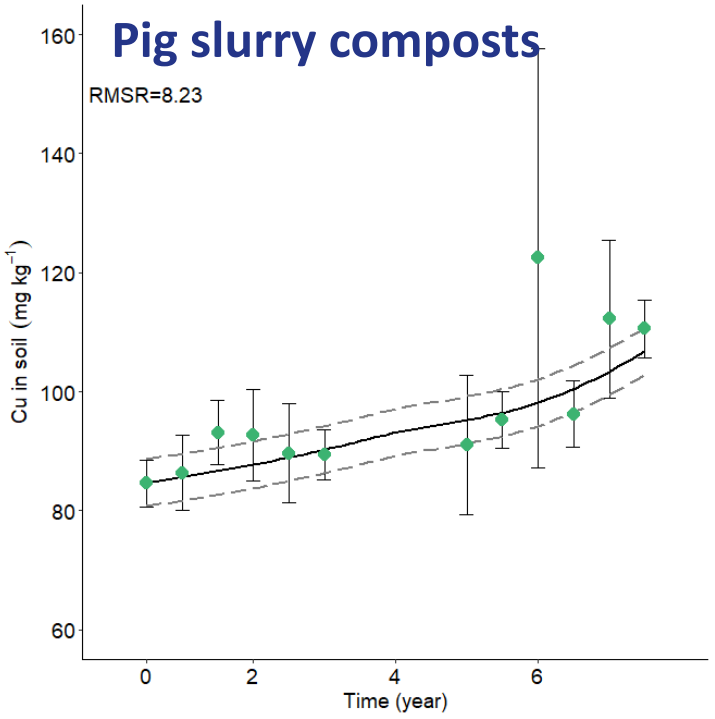
- **Modelling**
  - TE mass-balance in soil
  - Extrapolation over 1 century
  - Calculator for soil ecotoxicity assessment

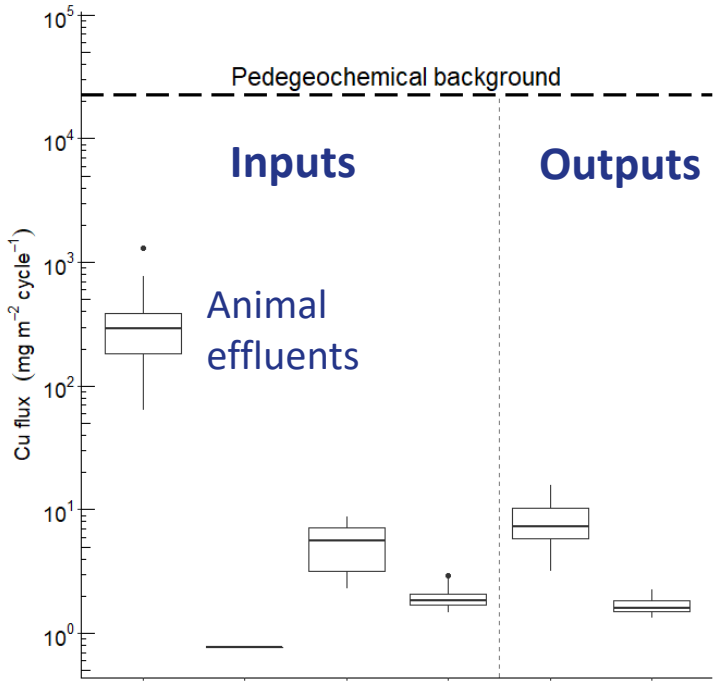
Laurent et al. (2023) in preparation

Risk assessment: field case study

- **Animal effluents** induced **soil Cu and Zn contamination**



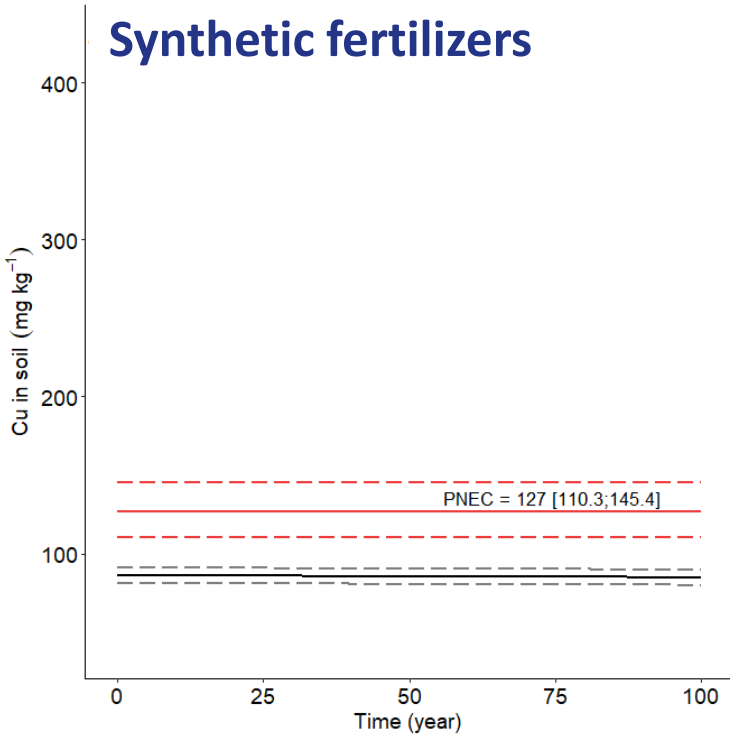


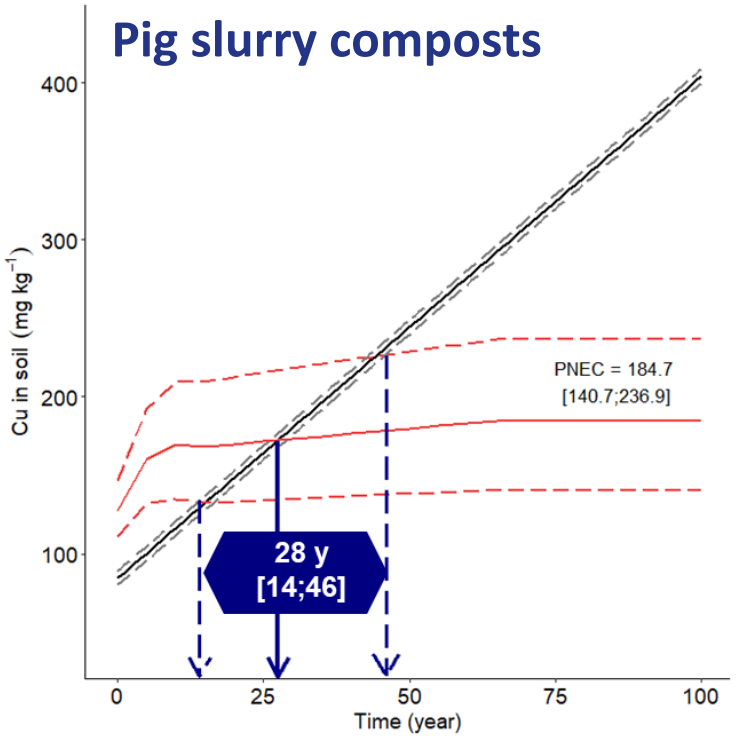


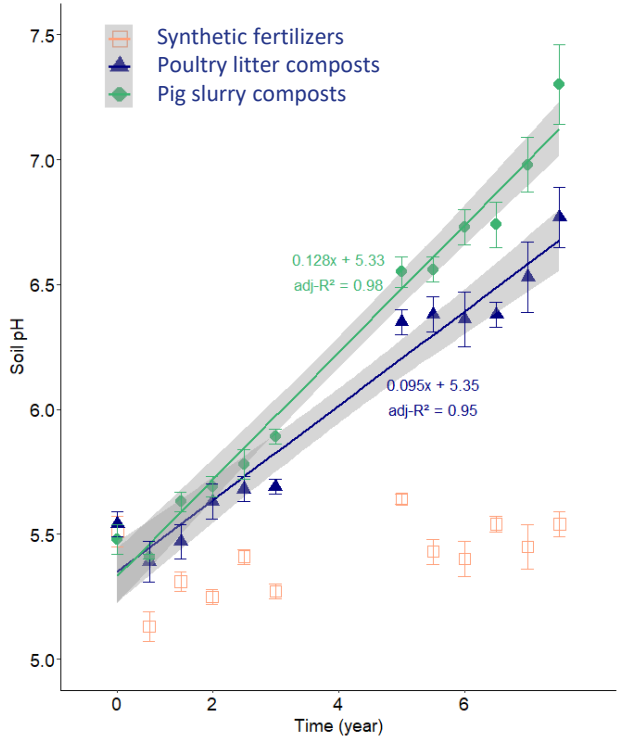
Laurent et al. (2023) in preparation

Risk assessment: field case study

- **Soil Cu and Zn contamination** could induce **ecotoxicological impacts** within a few decades







Laurent et al. (2023) in preparation

Conclusion

and perspectives

Take-home messages

- AE-induced soil TE (Cu and Zn) contamination may have an **ecotoxicological impact over several decades**
- The **quantitative driver** seems **dominant**
- **Qualitative drivers matter** too!
- **Further information** in our recent **review**

CHAPTER TWO

Trace contaminants in the environmental assessment of organic waste recycling in agriculture: Gaps between methods and knowledge

Angel Avadí[a,b], Pierre Benoit[c], Matthieu N. Bravin[b,d], Benoit Cournoyer[e], Frédéric Feder[a,b], Wessam Galia[e], Patricia Garnier[c], Claire-Sophie Haudin[c], Samuel Legros[b,f], Laure Mamy[c], Sylvie Nazaret[e], Dominique Patureau[g], Valérie Pot[c], Laure Vieublé Gonod[c], Tom Wassenaar[a,b], and Emmanuel Doelsch[a,b,*]

[a]CIRAD, UPR Recyclage et risque, F-34398 Montpellier, France
[b]Recyclage et risque, Univ Montpellier, CIRAD, Montpellier, France
[c]Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, F-78850 Thiverval-Grignon, France
[d]CIRAD, UPR Recyclage et risque, F-97743 Saint-Denis, La Réunion, France
[e]Univ Lyon, Université Claude Bernard Lyon 1, VetAgro Sup, CNRS, UMR5557, INRA UMR1418, Laboratoire d'Ecologie Microbienne (LEM), Research Team "Bacterial Opportunistic Pathogens and Environment", Marcy L'Etoile, France
[f]CIRAD, UPR Recyclage et Risque, 18524 Dakar, Senegal
[g]LBE, Université de Montpellier, Narbonne, France
*Corresponding author: e-mail address: emmanuel.doelsch@cirad.fr

Contents

Advances in Agronomy, Volume 174
ISSN 0065-2113
https://doi.org/10.1016/bs.agron.2022.03.002

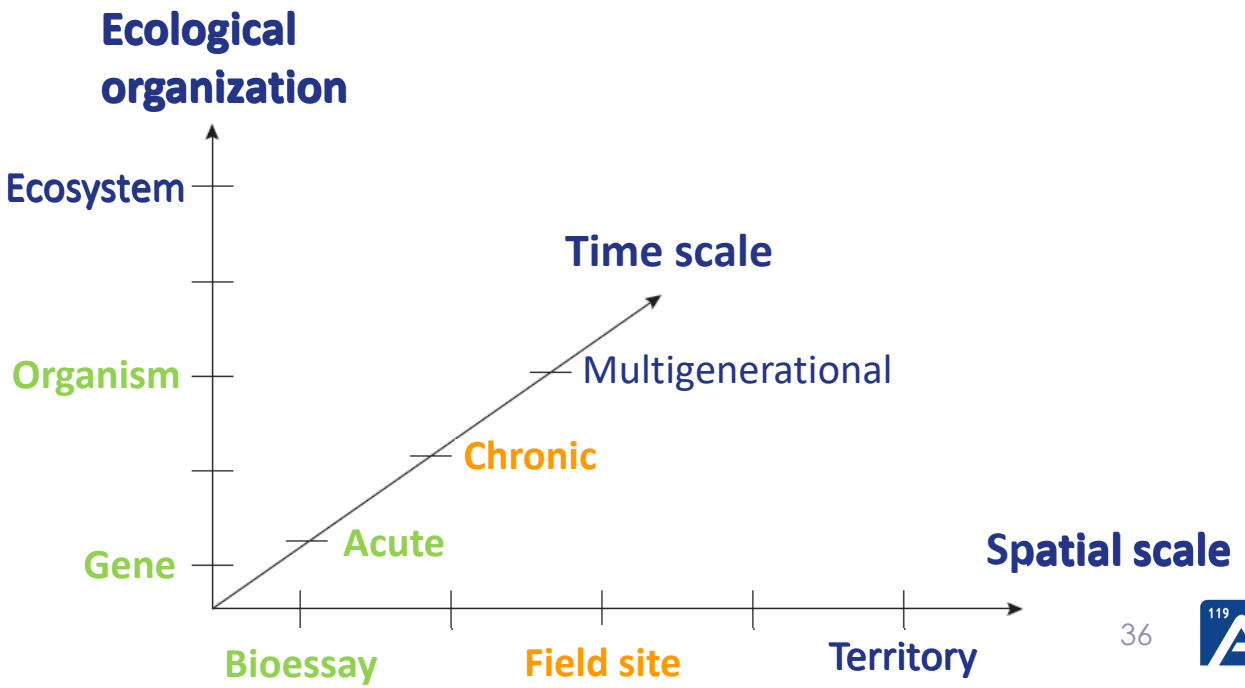
53

Avadi et al. (2022)
Adv. Agron. 174

Perspectives

- Accounting for the potential **mixture effect**
  - Antagonisms and synergisms **between TE**
  - Between **TE, antibiotics, and human pathogens**
    ⇒ Antimicrobial resistance

- More **environmental** and **ecological realism**
  ⇒ Towards Eco-Health



Lamy et al. (2022)
L'écotoxicologie en questions, Quae ed.

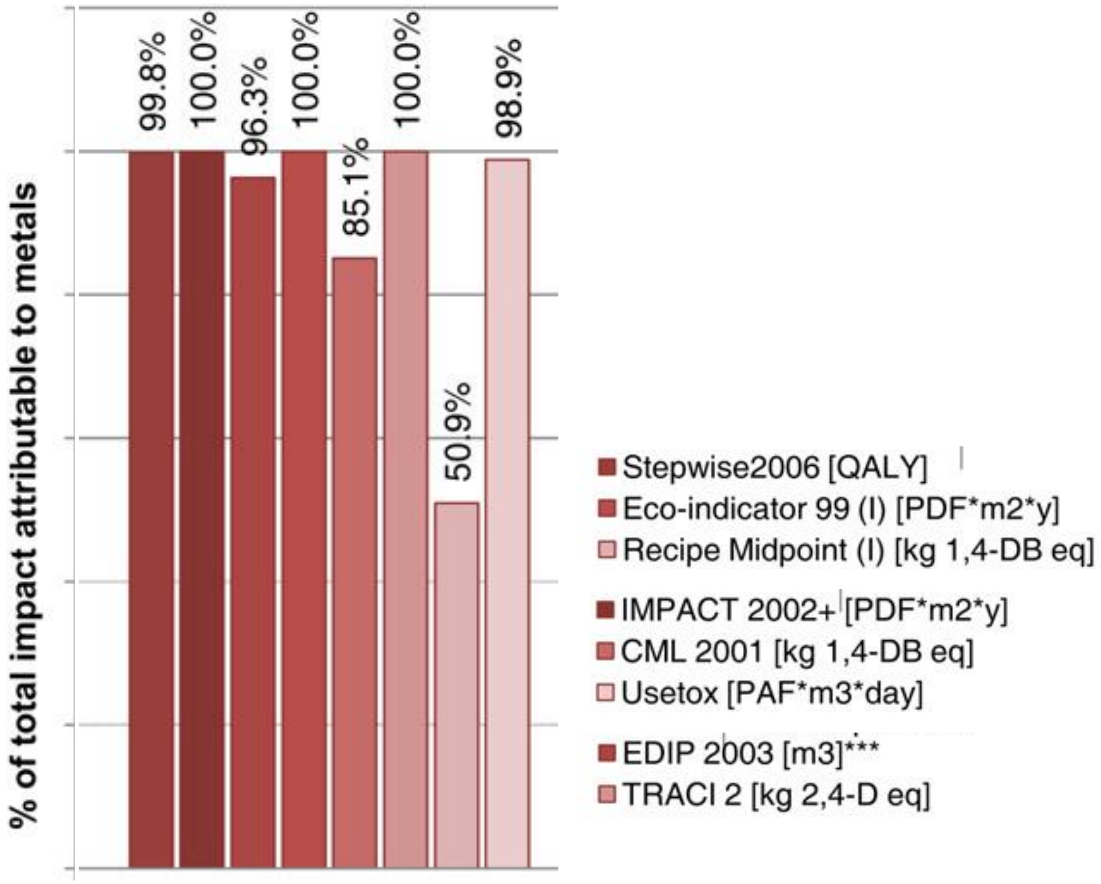
Thank you for your attention!

Matthieu N. Bravin, matthieu.bravin@cirad.fr

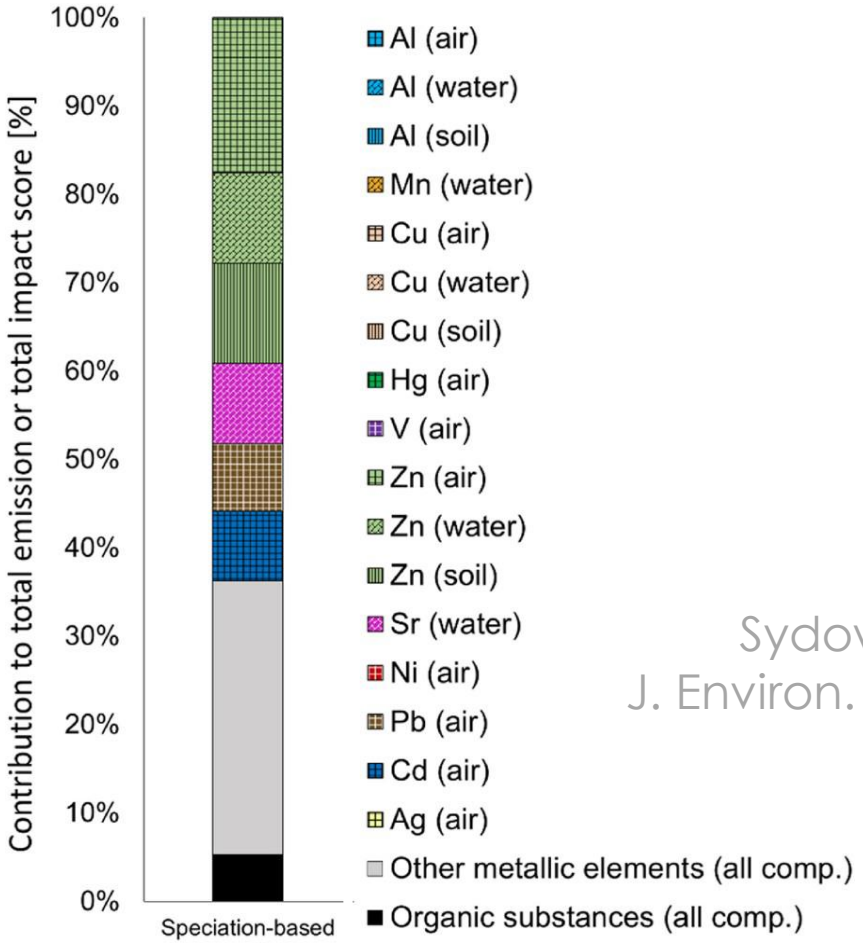
S. Legros, E. Clément, M. Tella, A. Avadi, and E. Doelsch

TE vs organic contaminants

- TE most contribute to **ecotoxicological impacts in LCA**



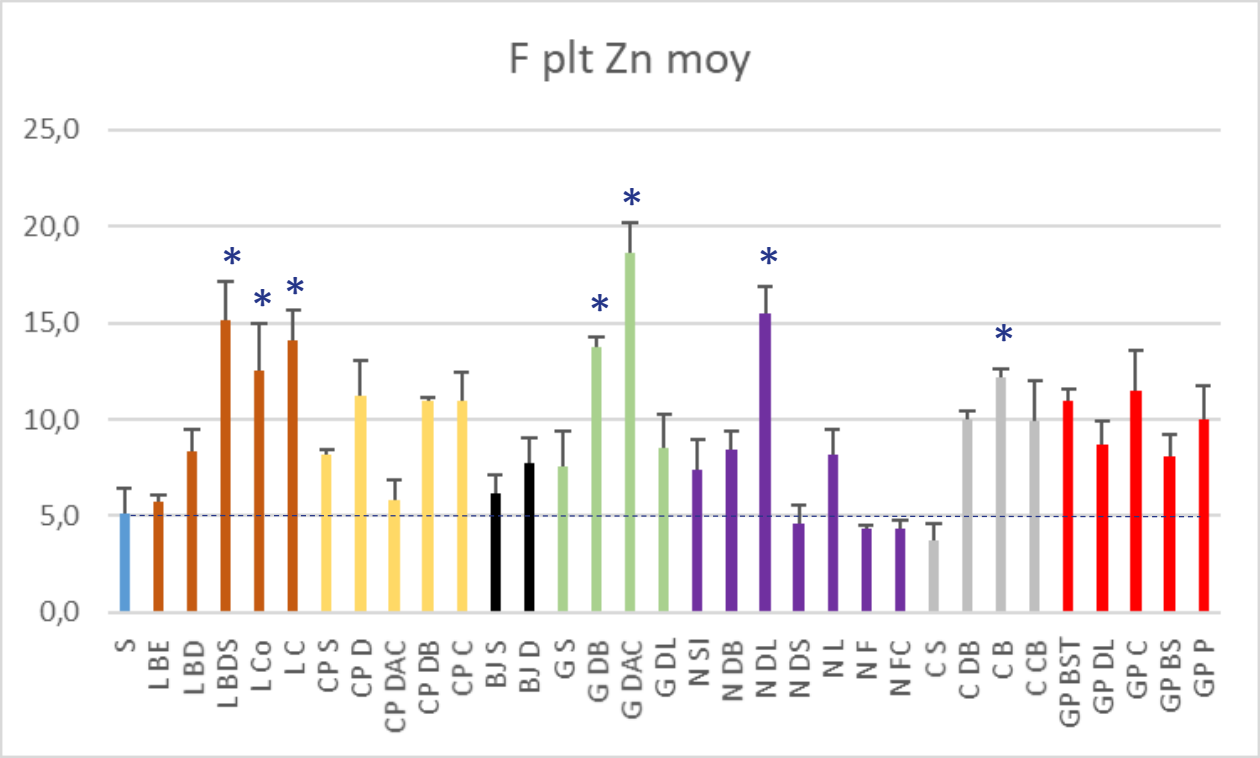
Pizzol et al. (2011) J. Clean. Prod. 19

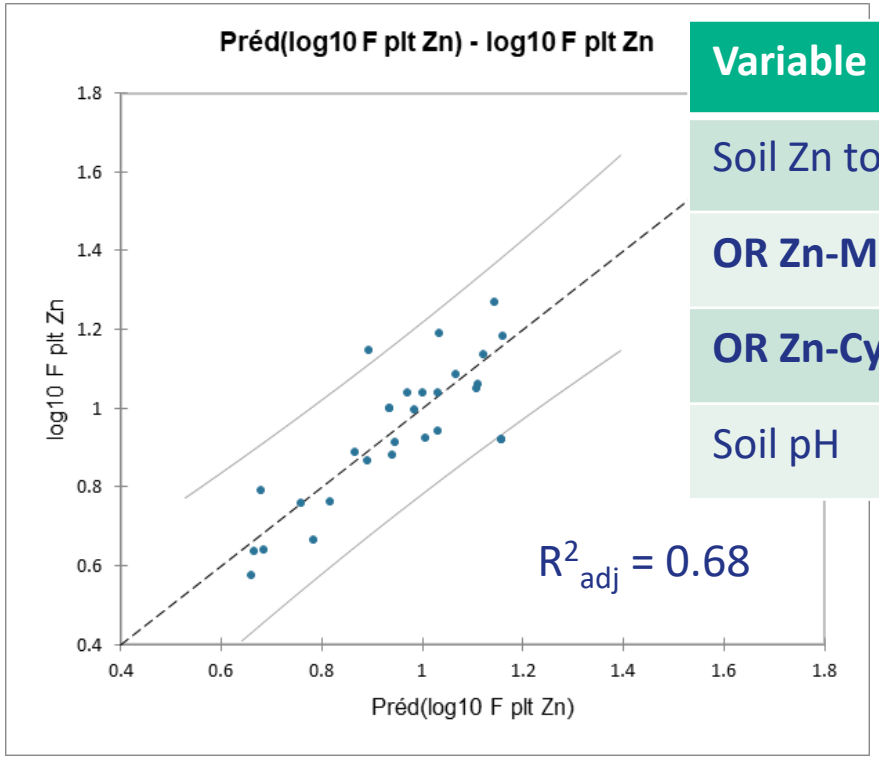


Sydow et al. (2020)
J. Environ. Manage. 266

TE speciation in organic residues

- **Zn speciation in organic residues** contributes to determine **Zn phytoavailability**



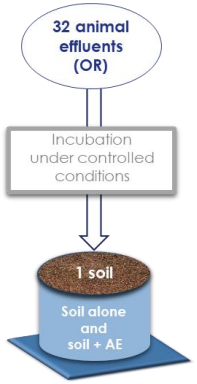


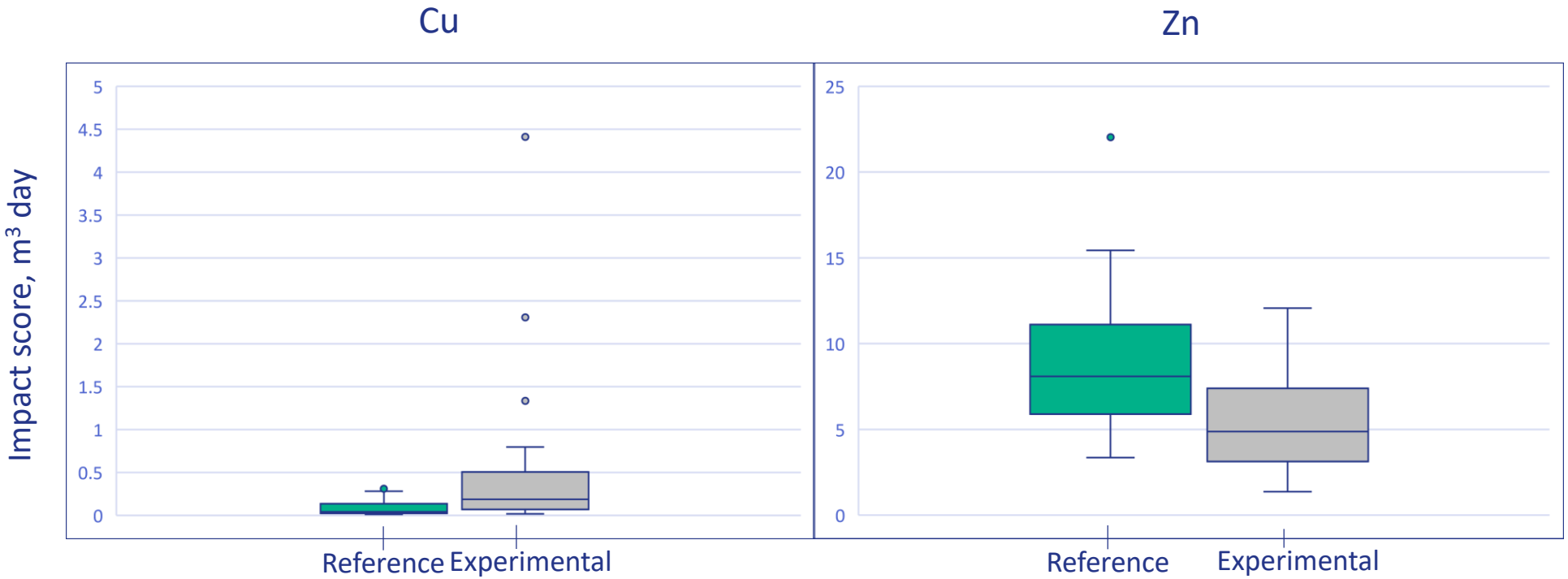
Variable	Effect
Soil Zn tot	+
OR Zn-MO	-
OR Zn-Cys	-
Soil pH	-

Bravin et al. unpublished

USEtox vs soil biogeochemistry !

- **Calculated impacts differ** between **reference** and **experimental** approaches

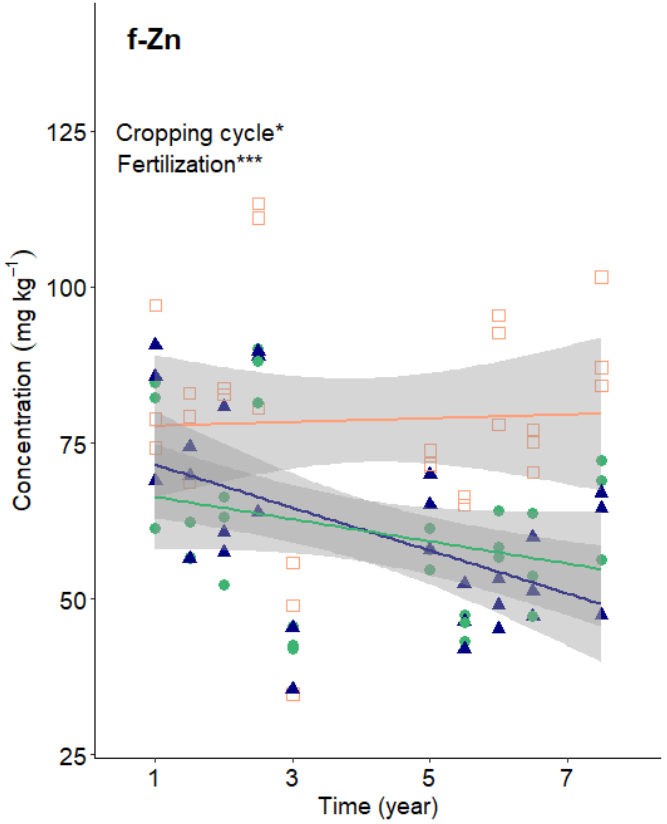




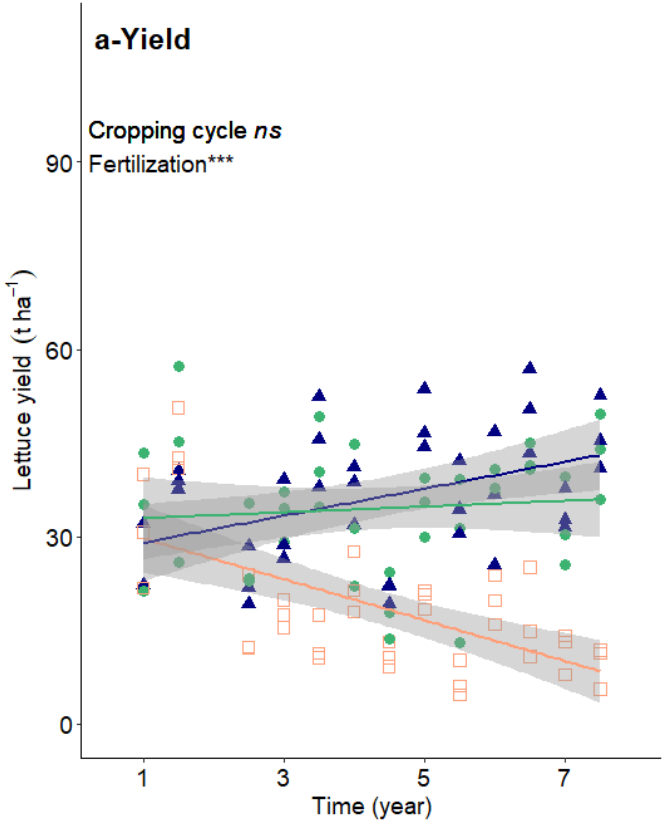
Clément et al. (2023) EAAP and Icobte-Ichmet conferences

Risk assessment: field case study

- **TE does not bioaccumulate more in plants** in soils amended with animal effluents



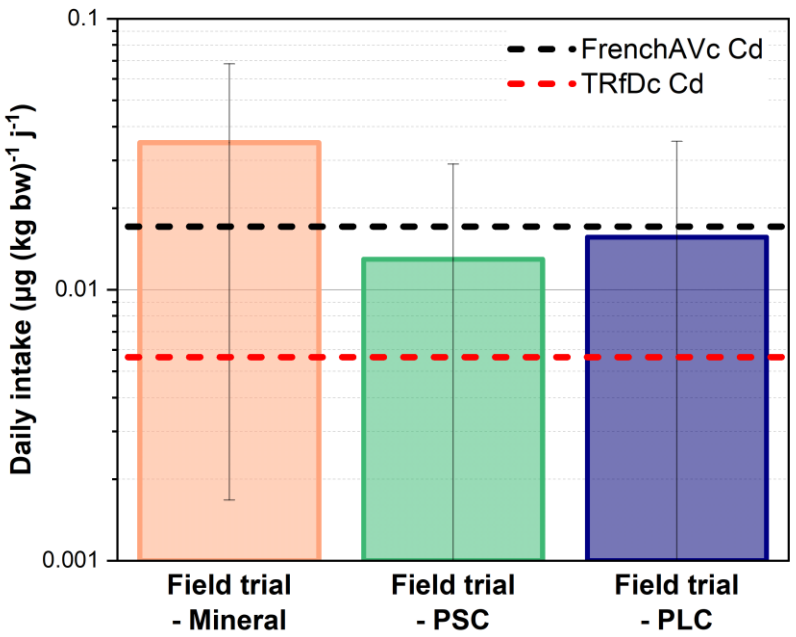
Synthetic fertilizers
Poultry litter composts
Pig slurry composts



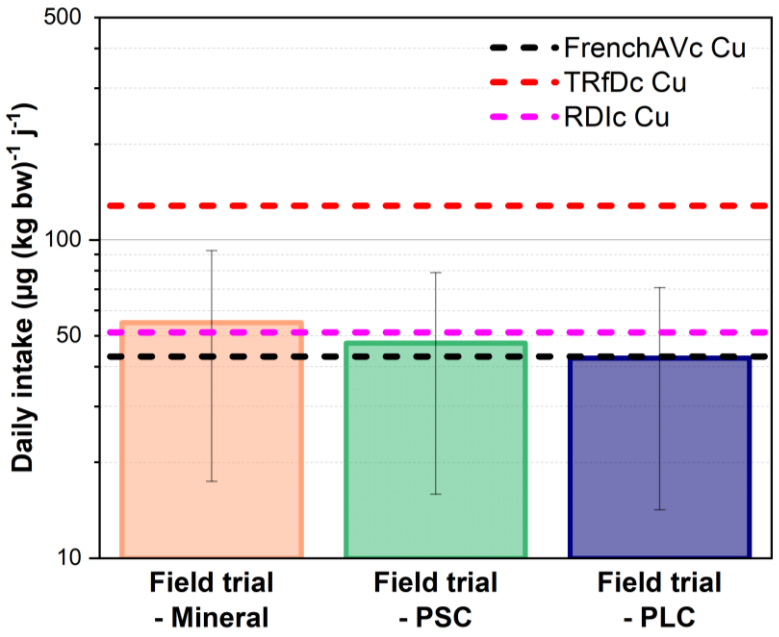
Laurent et al. (2023) in preparation

Risk assessment: field case study

- Vegetable contribution to **Cd daily intake** is **excessive**



- Vegetable contribution to **Cu and Zn daily intake** is **deficient**

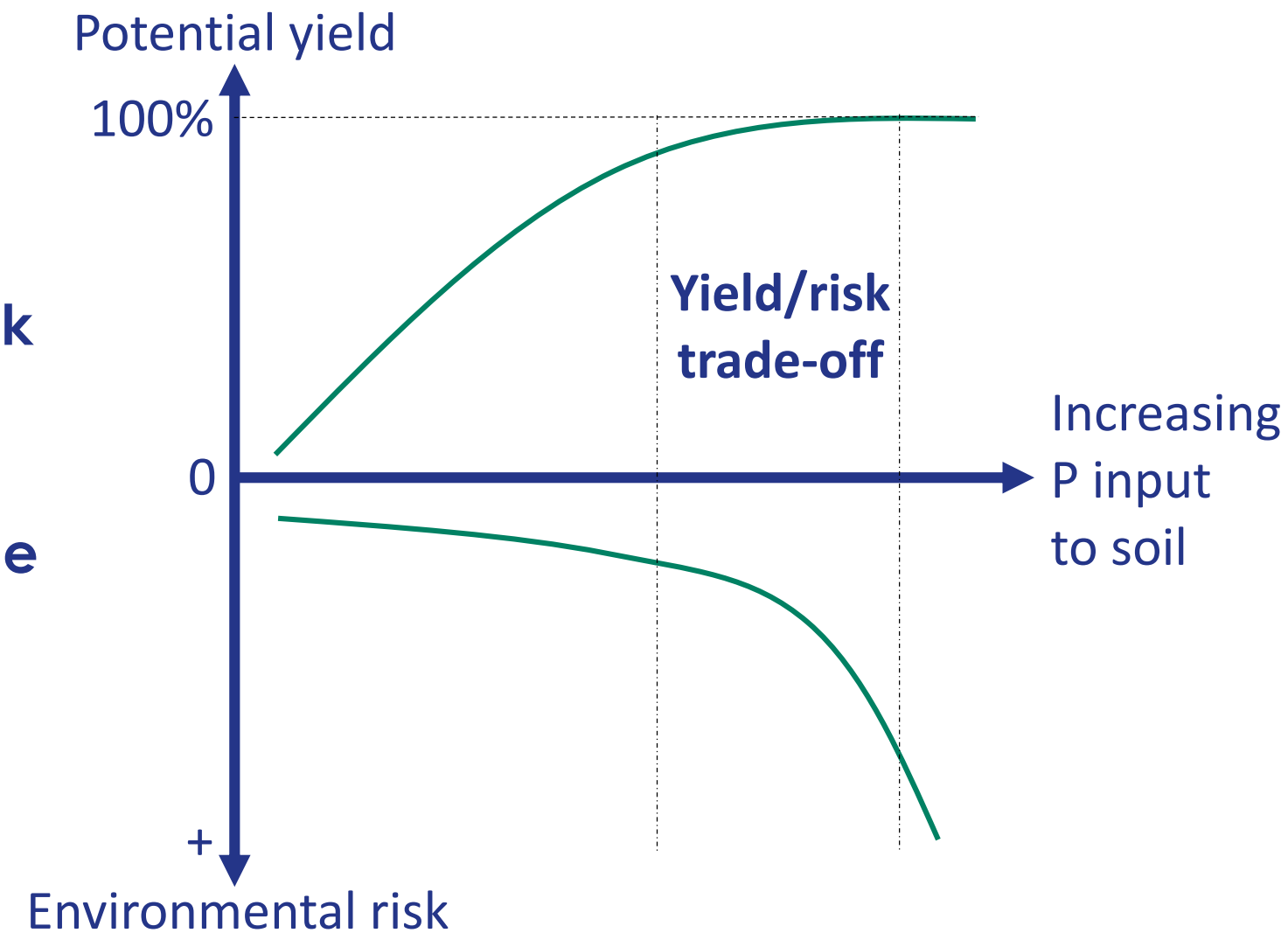


Laurent et al. (2023) in preparation

Phosphorus

The **quest**
for the **trade-off** between
yield and **environmental risk**

⇒ Closing
the **P biogeochemical cycle**
in agro-ecosystems

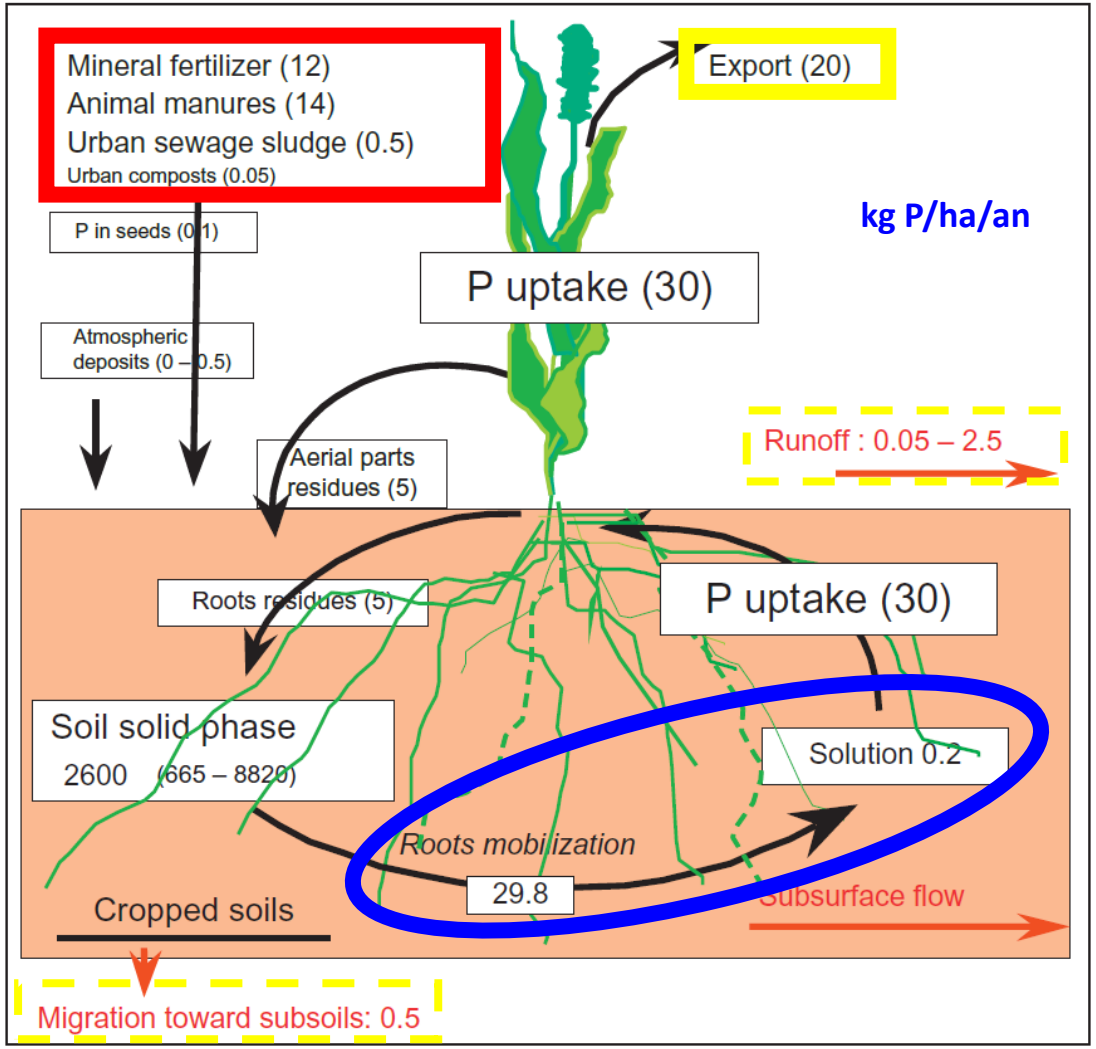


Lemaire (2022) *in* La fabrique de l'agronomie, de 1945 à nos jours. Quae ed.

Phosphorus

P biogeochemical cycle is driven by the **balance** between **harvest outputs** and **fertilization**

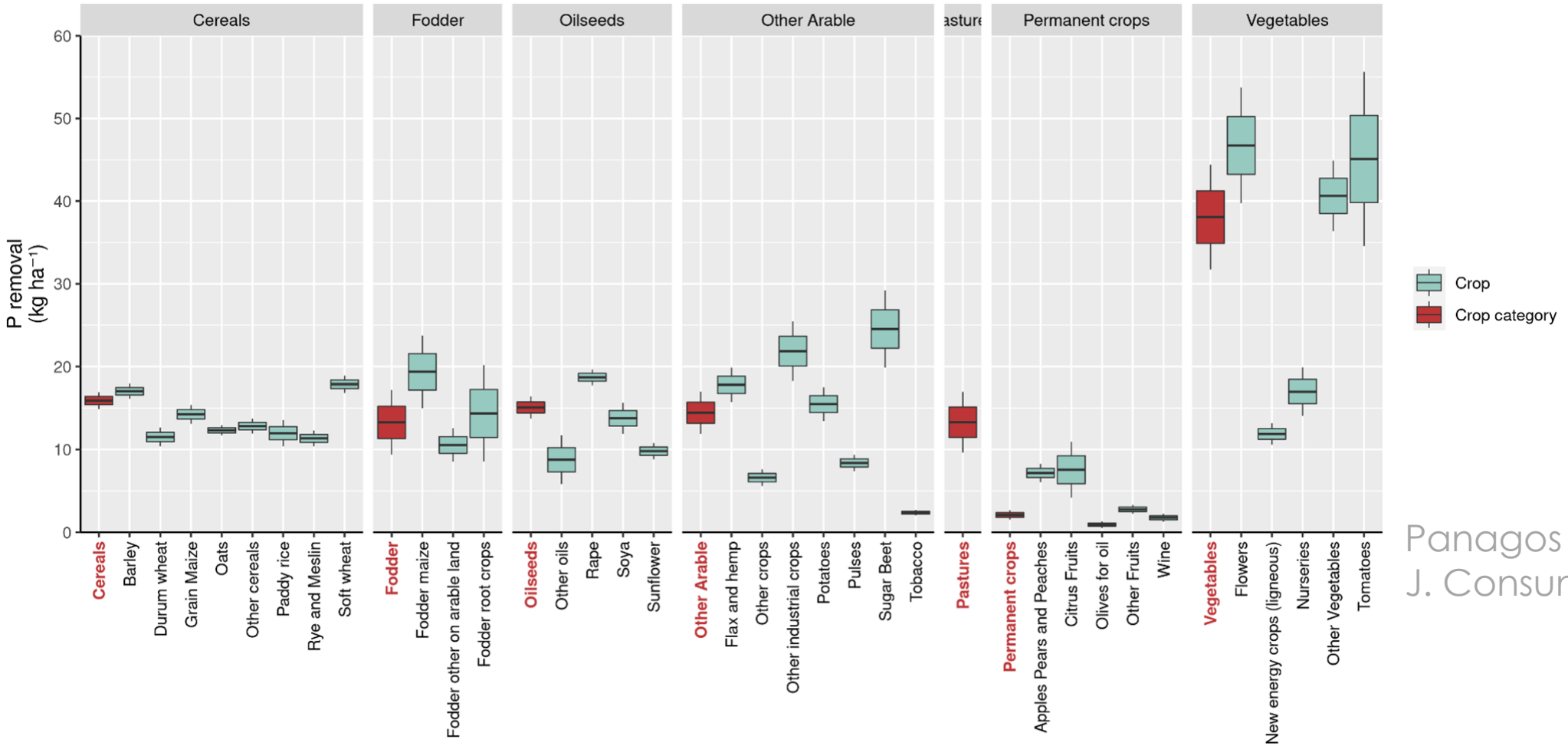
- Satisfy **plant requirements**
- Sustain **soil P availability**



Ziadi et al. (2013) Adv. Agron. 122

Phosphorus

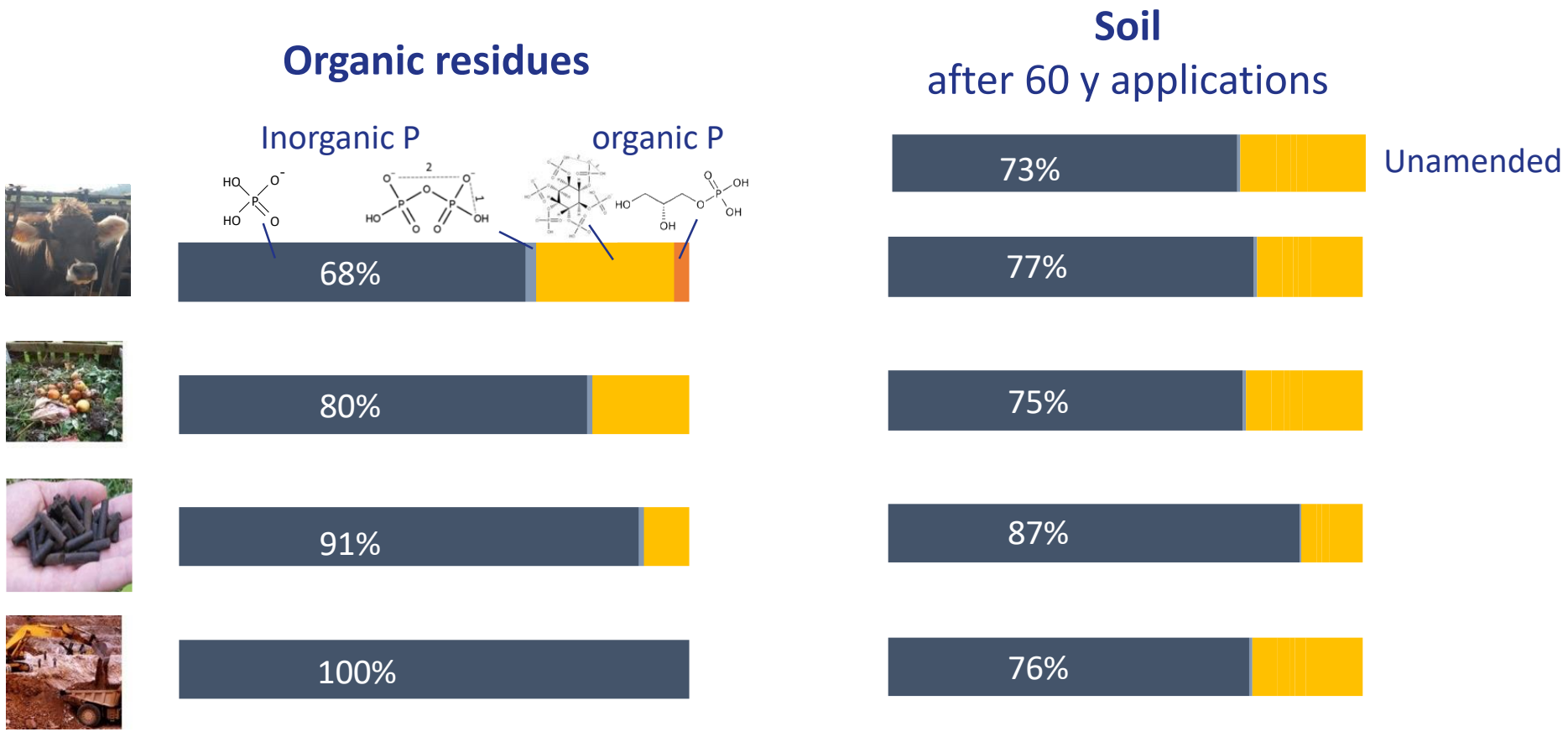
- **Plant P requirements** vary substantially between plant species



Panagos et al. (2022)
J. Consum. Prot. Food. Saf. 17

Phosphorus

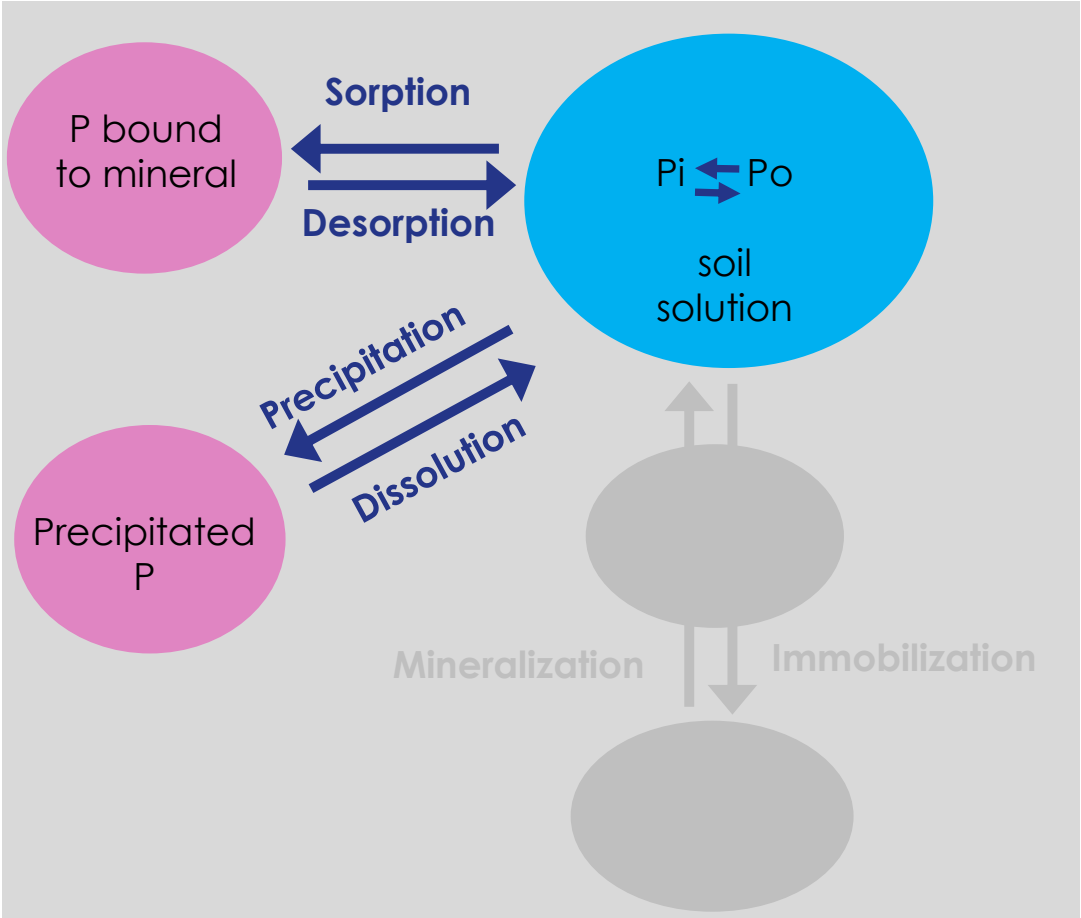
- **P speciation in organic residues** does not determine P speciation in soil



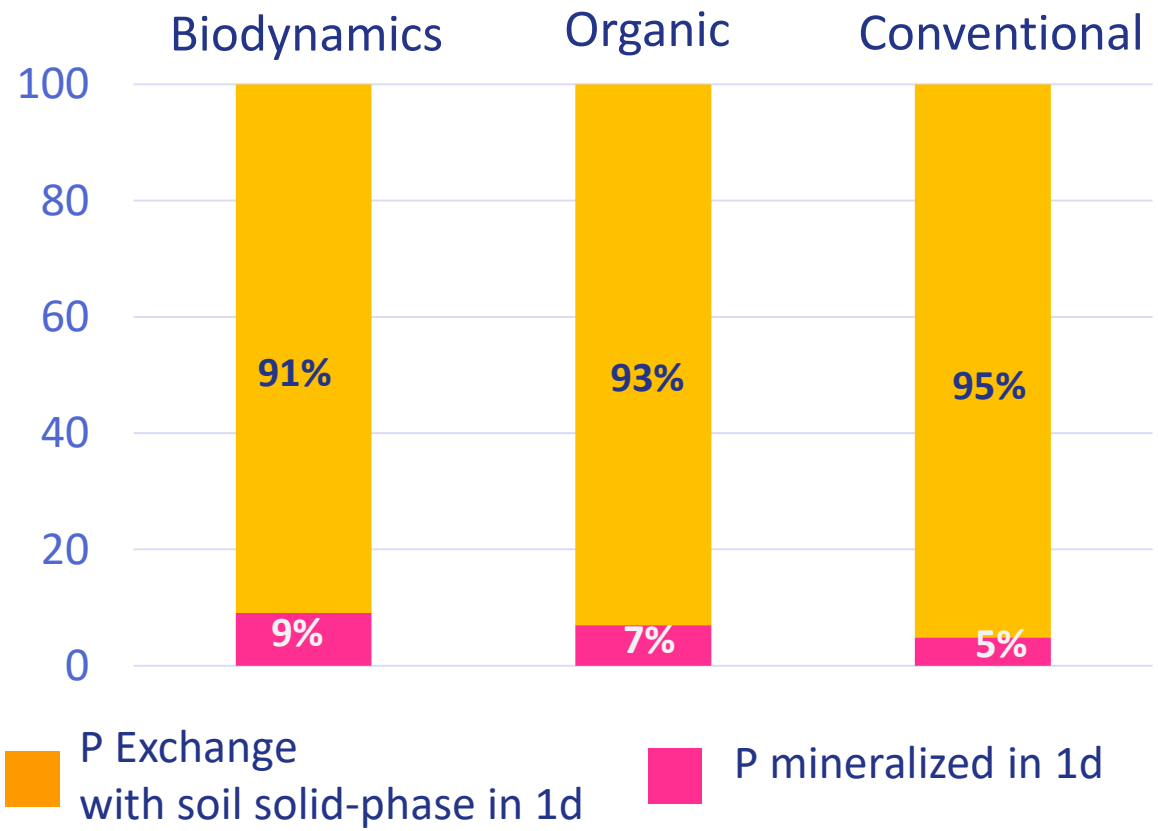
Annaheim et al. (2015) Geod. 257-258

Phosphorus

- **P availability in soil**



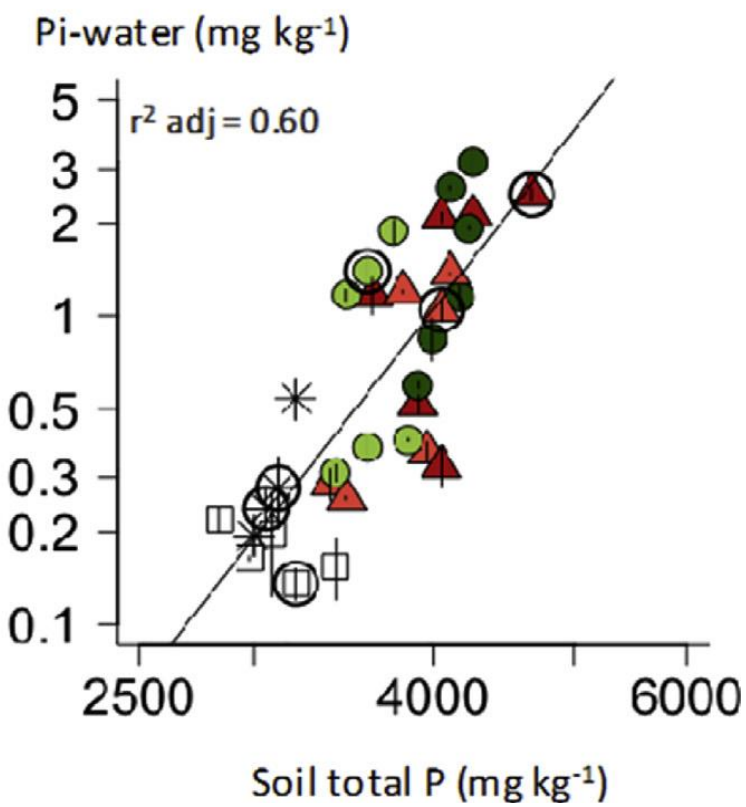
20-y old cropping systems

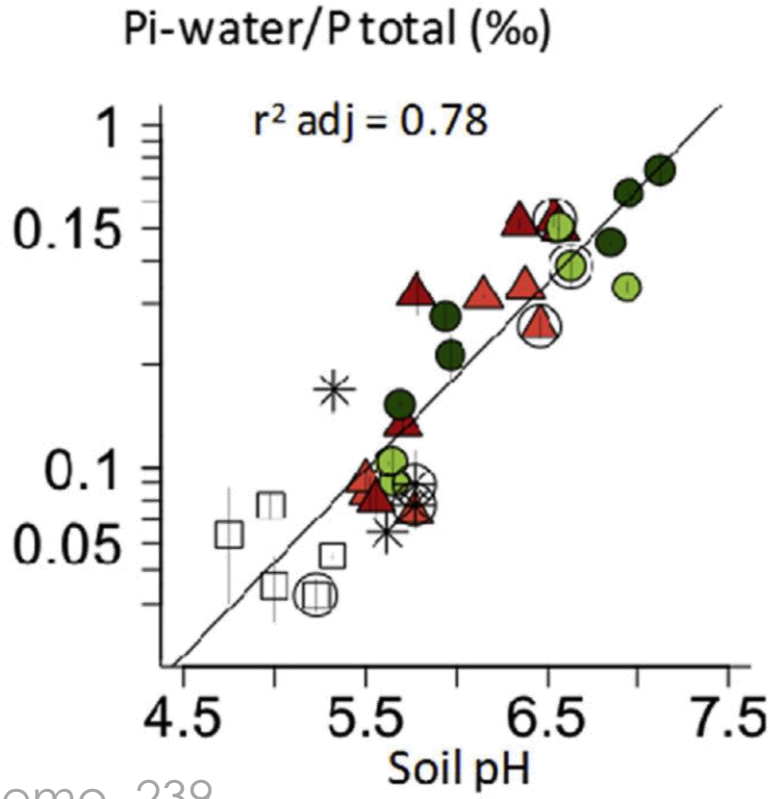


Oehl et al. (2004) Soil Biol. Biochem. 36

Phosphorus

- The **quantitative driver** of soil P availability
- **Qualitative drivers** of soil P availability





Nobile et al. (2020) Chemo. 239