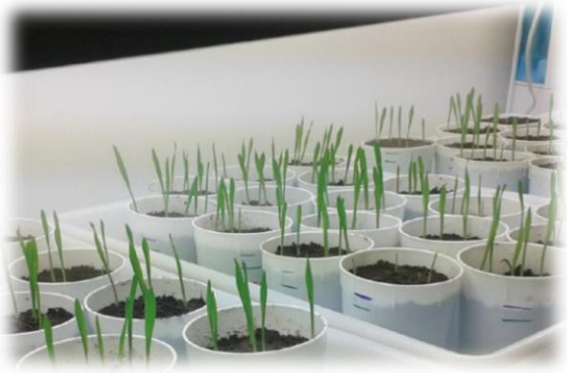
Invited lecture
Free University of Bozen-Bolzano
May 13th 2019

DOM biogeochemistry in agricultural soils as a major driver of **trace metal bioavailability** to **soil organisms**

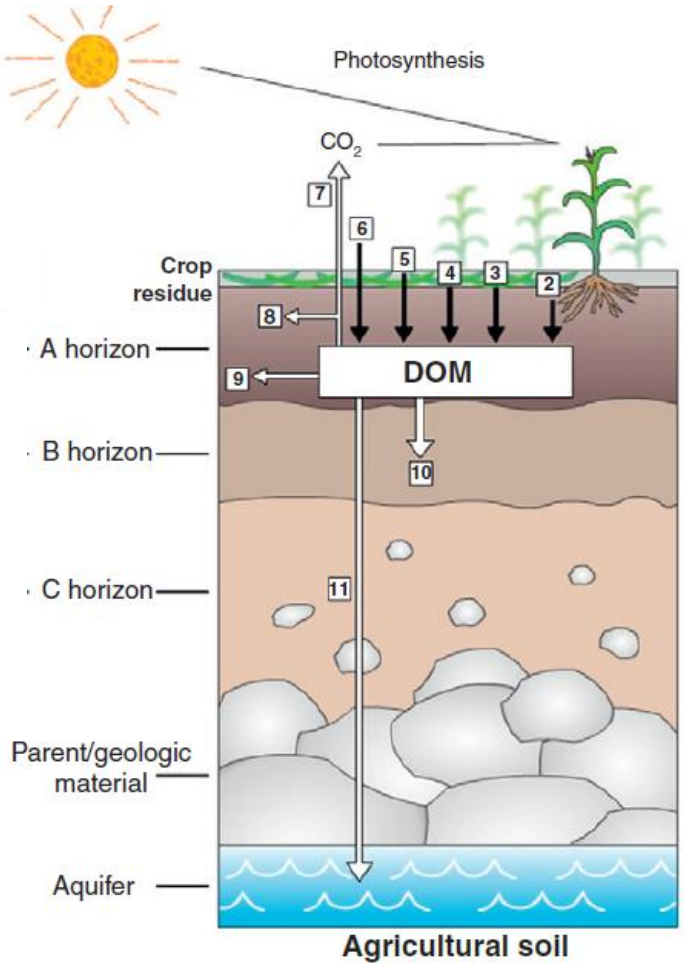

Matthieu Bravin
T. Djae, C. Garnier and E. Doelsch

cirad
LA RECHERCHE AGRONOMIQUE POUR LE DÉVELOPPEMENT

Environmental significance of DOM biogeochemistry

"*Dissolved organic matter comprises only a small part of soil organic matter; nevertheless, it affects many processes in soil and water including the most serious environmental problems like soil and water pollution and global warming*"

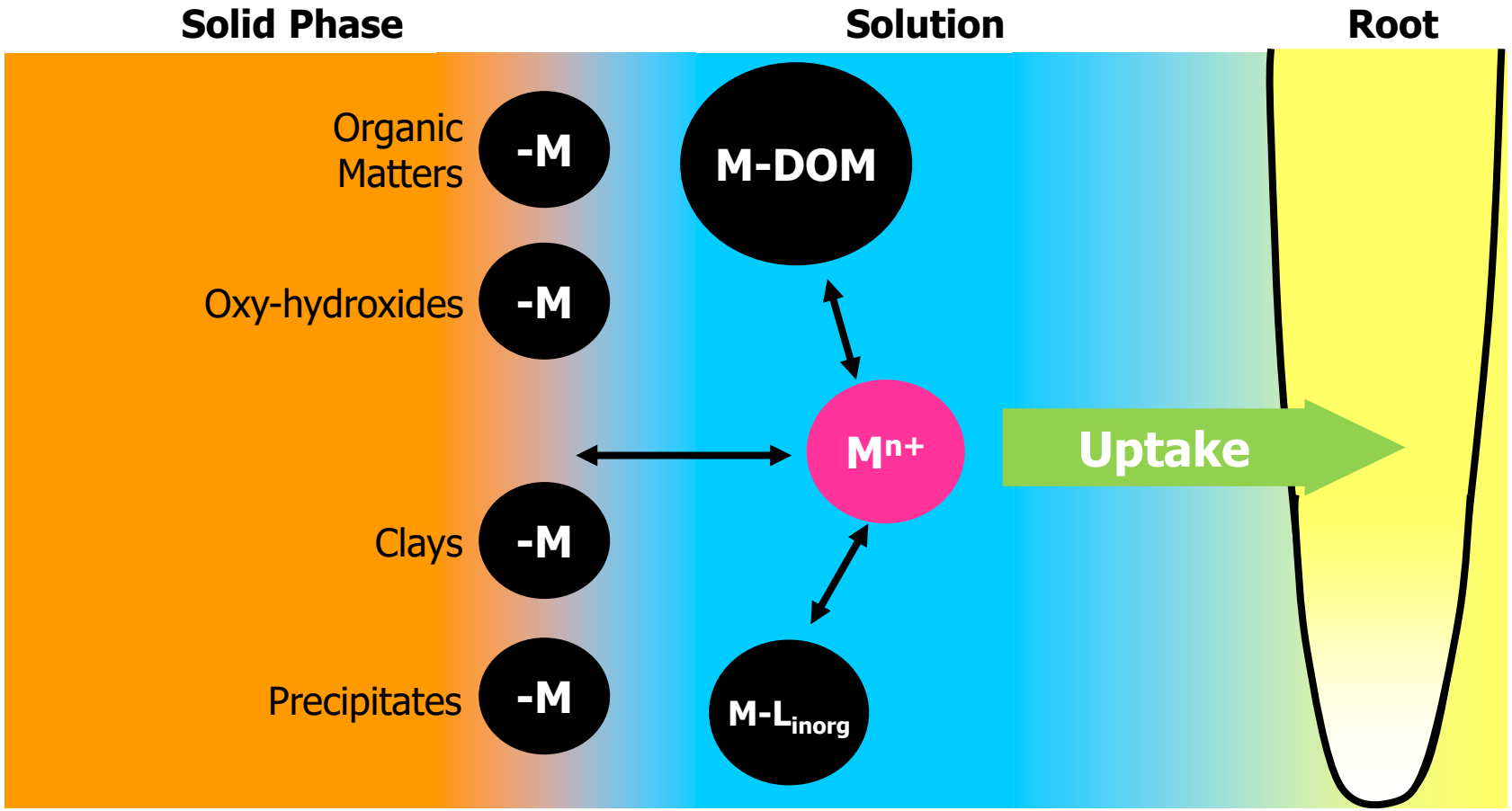
Kalbitz and Kaiser *2003*
Geoderma 113, 177-178



Bolan et al. *2011 Adv. Agron., 110, 1-75*

Importance of DOM for metal bioavailability

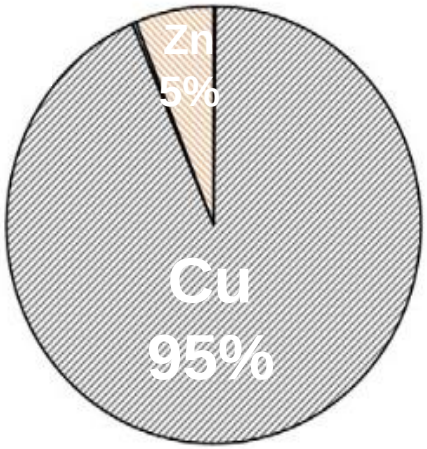
Soil organisms take up trace metal as the free ion in solution



Importance of DOM for metal bioavailability

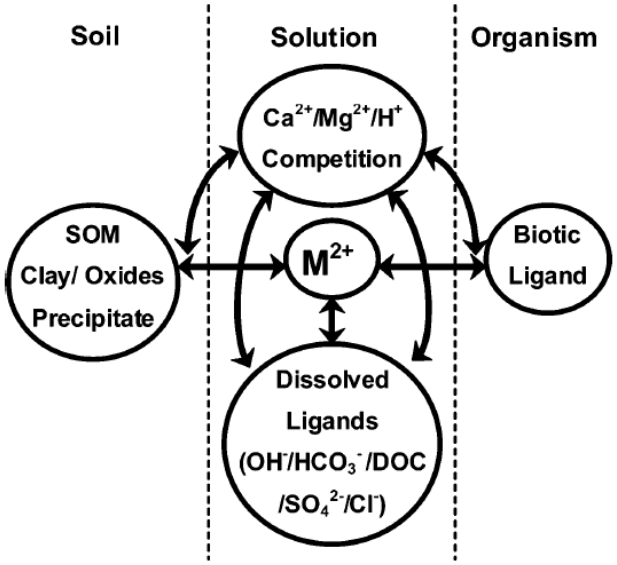
DOM is a key parameter in environmental risk assessment

Ecotoxicological impacts in LCIA



Leclerc and Laurent *(2017)*
Sci. Tot. Env. 590-591, 452-460
Sydow et al. *(2018) Sust. 10, 4094v*

Terrestrial ecotoxicity with the BLM



Thakali et al. *2006*
Environ. Sci. Technol., 40, 7085-7093

Determination of metal speciation

Several analytical techniques available to measure trace metal speciation…

e.g.

- Donnan membrane technique
- Voltammetry
- Potentiometry

But all have analytical drawbacks

e.g.

- Tedious and time-consuming
- Do not directly measure the free metal species
- Not sensitive enough
  to dealt with environmentally-relevant concentrations

⇒ **Necessity to develop modelling tool**

DOM consideration in speciation models

DOM binding properties are the corner stone of speciation models

Inputs

Analytical determination
pH
Major cations, anions
Total metals
DOM = 2 x DOC
x % DOM reacts as FA

Inorganic Database
Stoechiometry
log K_M

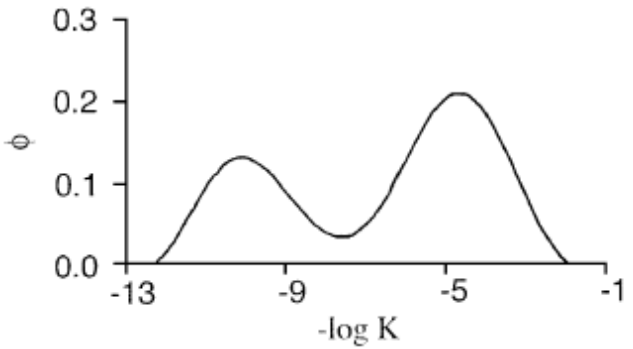
Speciation model

Nica-Donnan
WHAM

DOM database
Fulvic acid
Molecular weight
Site density
pK_a
log K_M

Outputs

Model estimation
Metal species
M^{n+}, $M\text{-}L_{inorg}$,
M-DOM

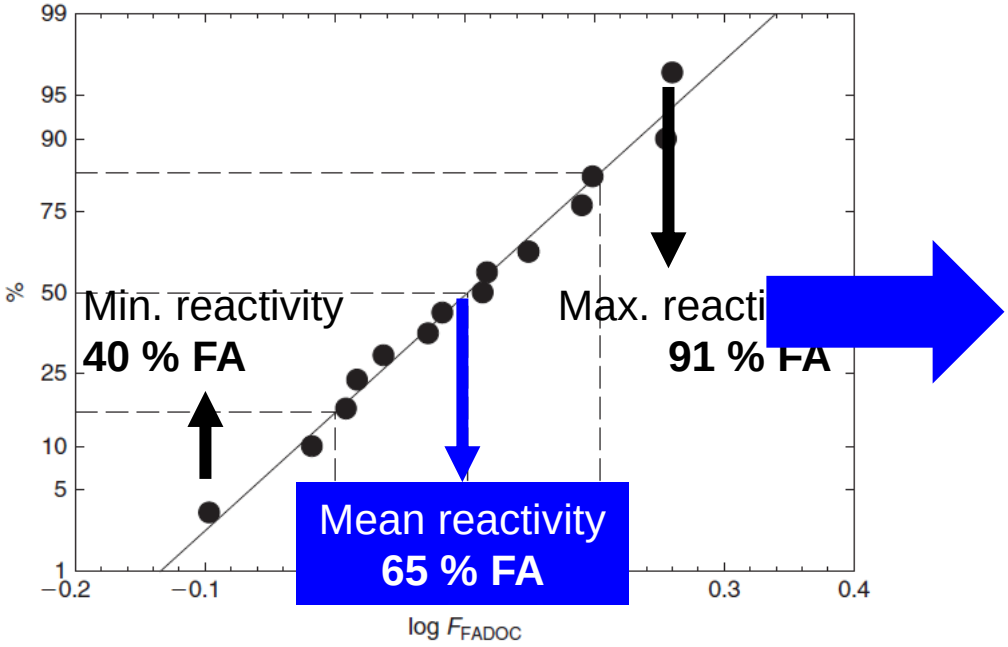


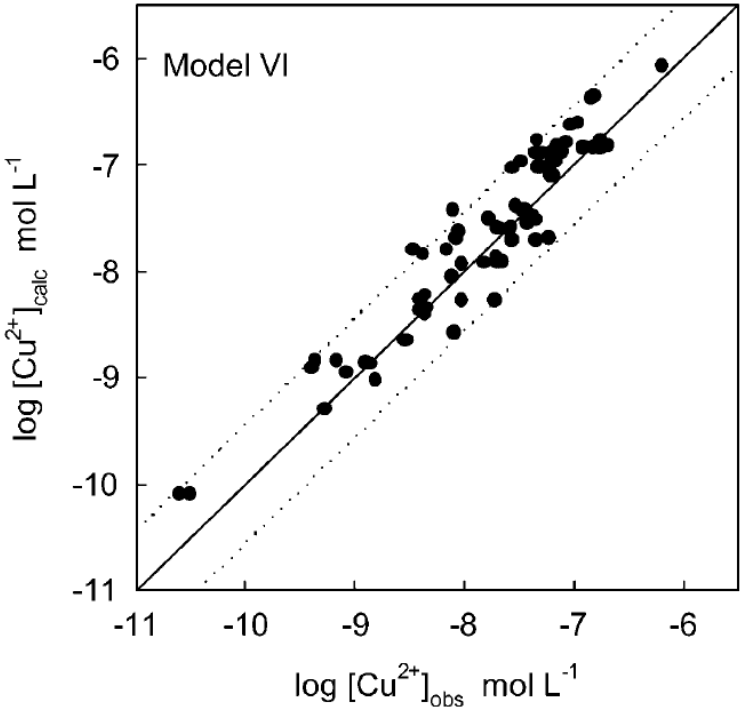
Dudal and Gérard *(2004)*
Earth-Sci. Rev., 66, 199-216

Default DOM parameterisation

Very few studies suggest a relative homogeneity of DOM binding properties

Speciation in freshwaters



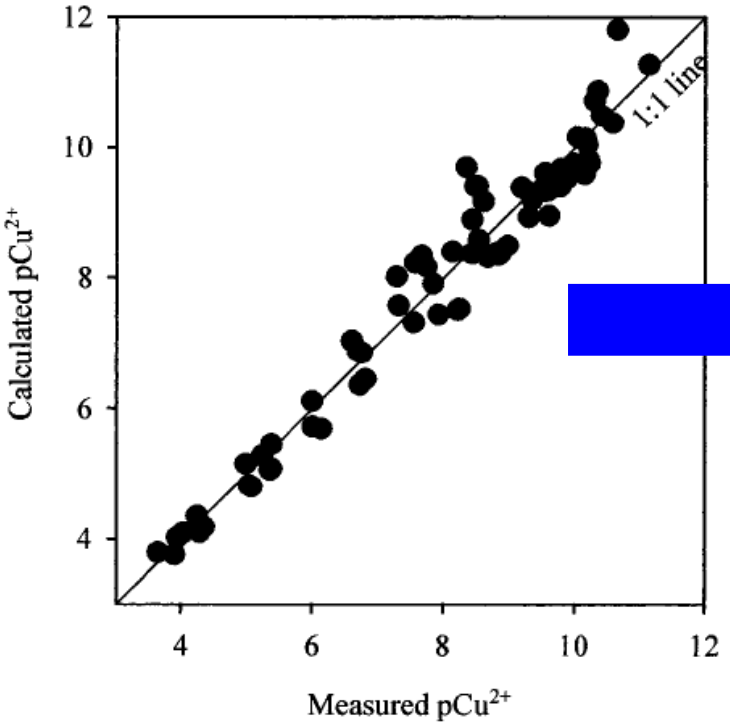


Bryan et al. *2002 Comp. Biochem. Physiol. Part C 133, 37-49*

Default DOM parameterisation

Very few studies suggest a relative homogeneity of DOM binding properties

Speciation in soils



Mean reactivity
69 % FA

Vulkan et al. 2000 Env. Sci. Technol. 34, 5115-5121

Default DOM parameterisation

65 % DOM reacts as FA
while 35 % was considered as inert

Inputs

Analytical determination
pH
Major cations, anions
Total metals
DOM = 2 x DOC
65 % DOM reacts as FA

Inorganic Database
Stoechiometry
log K_M

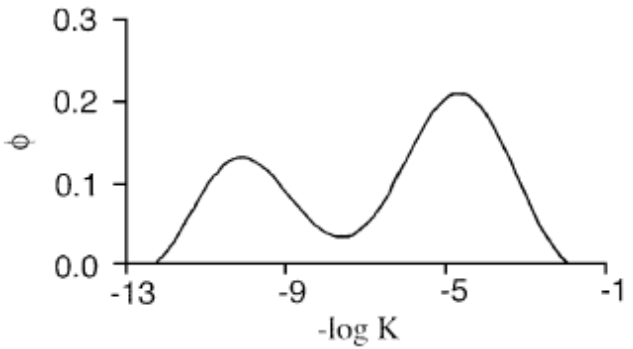
Speciation model

Nica-Donnan
WHAM

DOM database
Fulvic acid
Molecular weight
Site density
pK_a
log K_M

Outputs

Model estimation
Metal species
M^{n+}, $M\text{-}L_{inorg}$,
M-DOM



Dudal and Gérard (2004)
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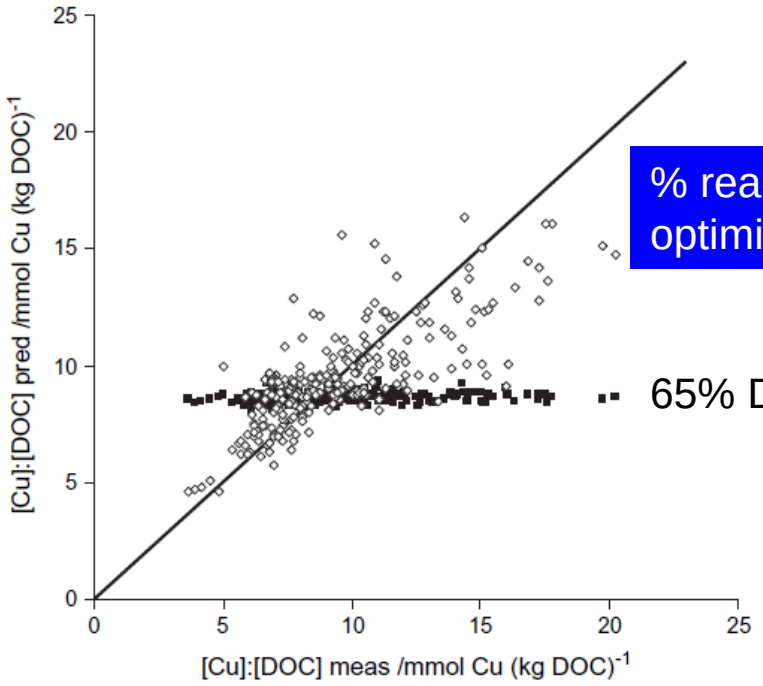
Current limits of DOM parameterisation

DOM binding properties appeared more variable than expected <u>in soil</u>

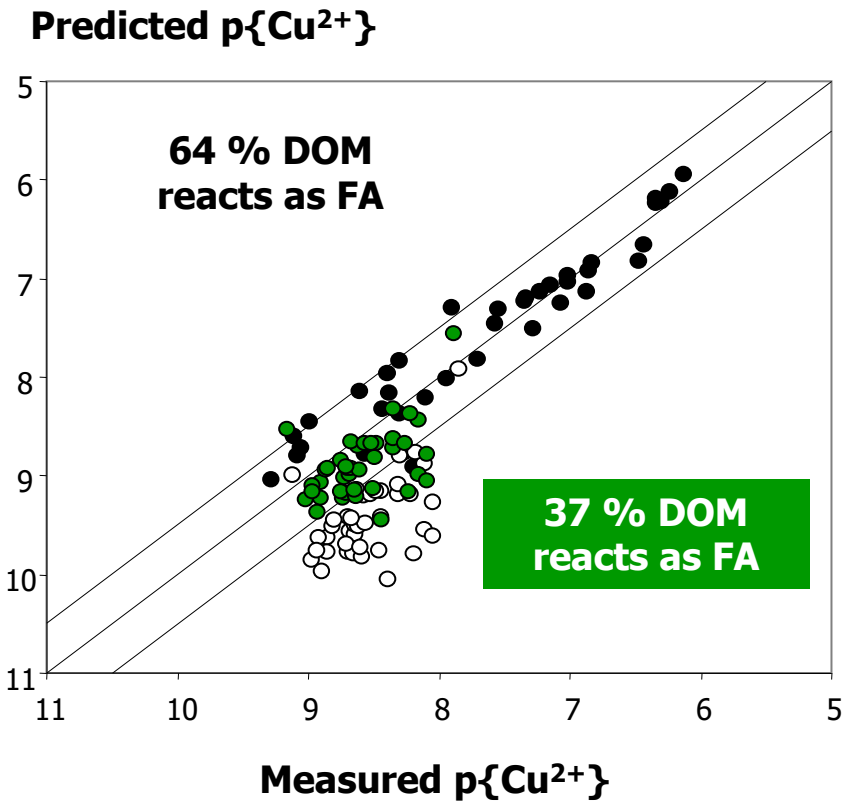


➢ But measured overtime in only one soil profile

Amery et al. 2008 Eur. J. Soil Sci. 59, 1087-1095

Current limits of DOM parameterisation

DOM binding properties appeared more variable than expected in the rhizosphere



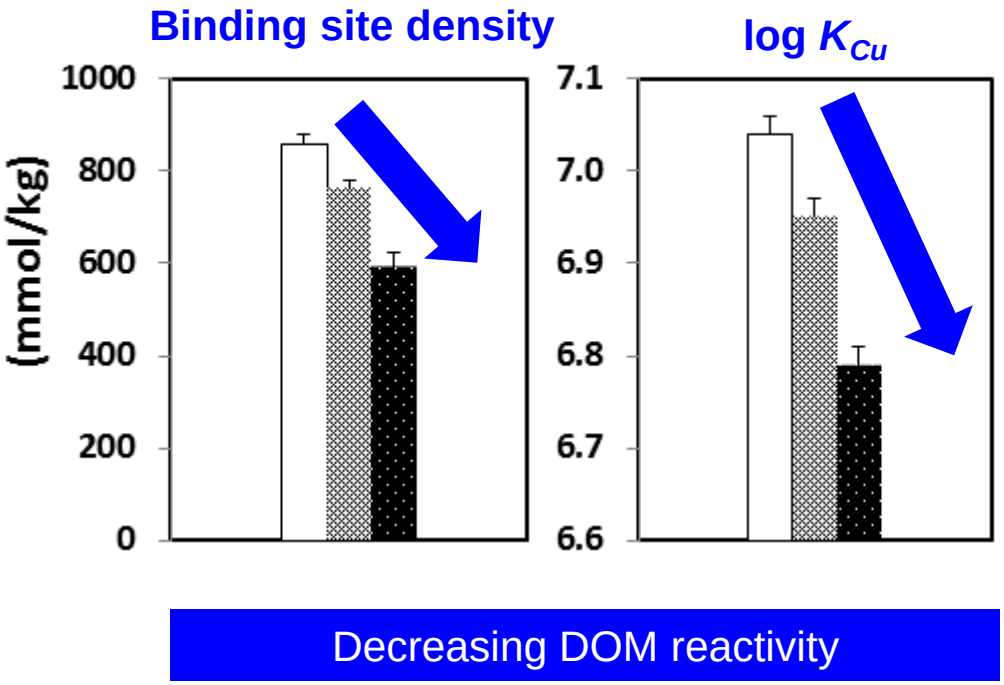
- Bulk Soil Solution
- Rhizosphere Solution
- Optimised rhizosphere

➢ But measured in only one soil limed ex situ at different pH

Bravin et al. *2012 Geochem. Cosmochem. Acta 84, 256-268*

Current limits of DOM parameterisation

DOM binding properties appeared more variable than expected <u>in amended soils</u>



➢ But measured on much more than only DOM as FA were extracted according to the IHSS procedure

Plaza et al. *2005 Chemo. 61, 711-716*

Objectives of my research

Evaluate how substantial is the variability of DOM binding properties in:

- Bulk soils
- Rhizospheres
- Soils amended with organic residues
- From the lab to the field

Evaluate the significance of this variability on trace metal:

- Speciation in soil solution
- Bioavailability and toxicity to soil organisms

Results – part I
Soil diversity

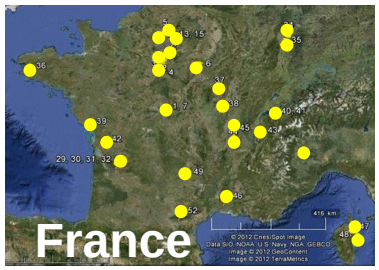
Methodology: Soil incubation procedure

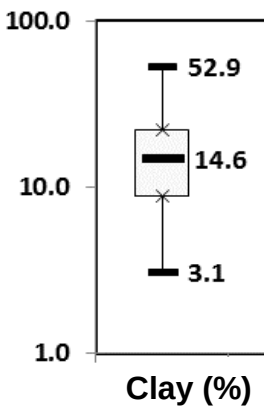
Bulk-soil

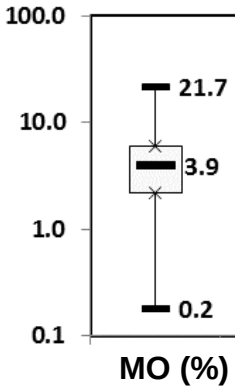
55 soils

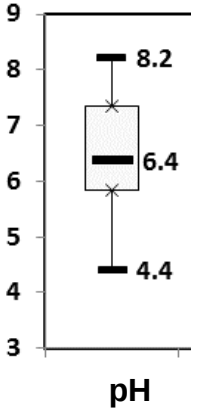
46 soils

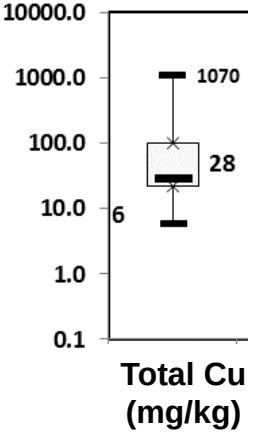
9 soils











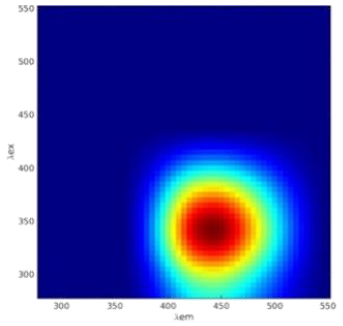
Djae et al. 2017 Environ. Toxicol. Chem. 36, 898-905

Results – part I
Soil diversity

Methodology: Analytics

- **55 soils** : determinations in 1/10 soil solution extracts
  - pH
  - Dom
  - Total major cations & anions
  - Total metals
  - Cu^{2+} activity

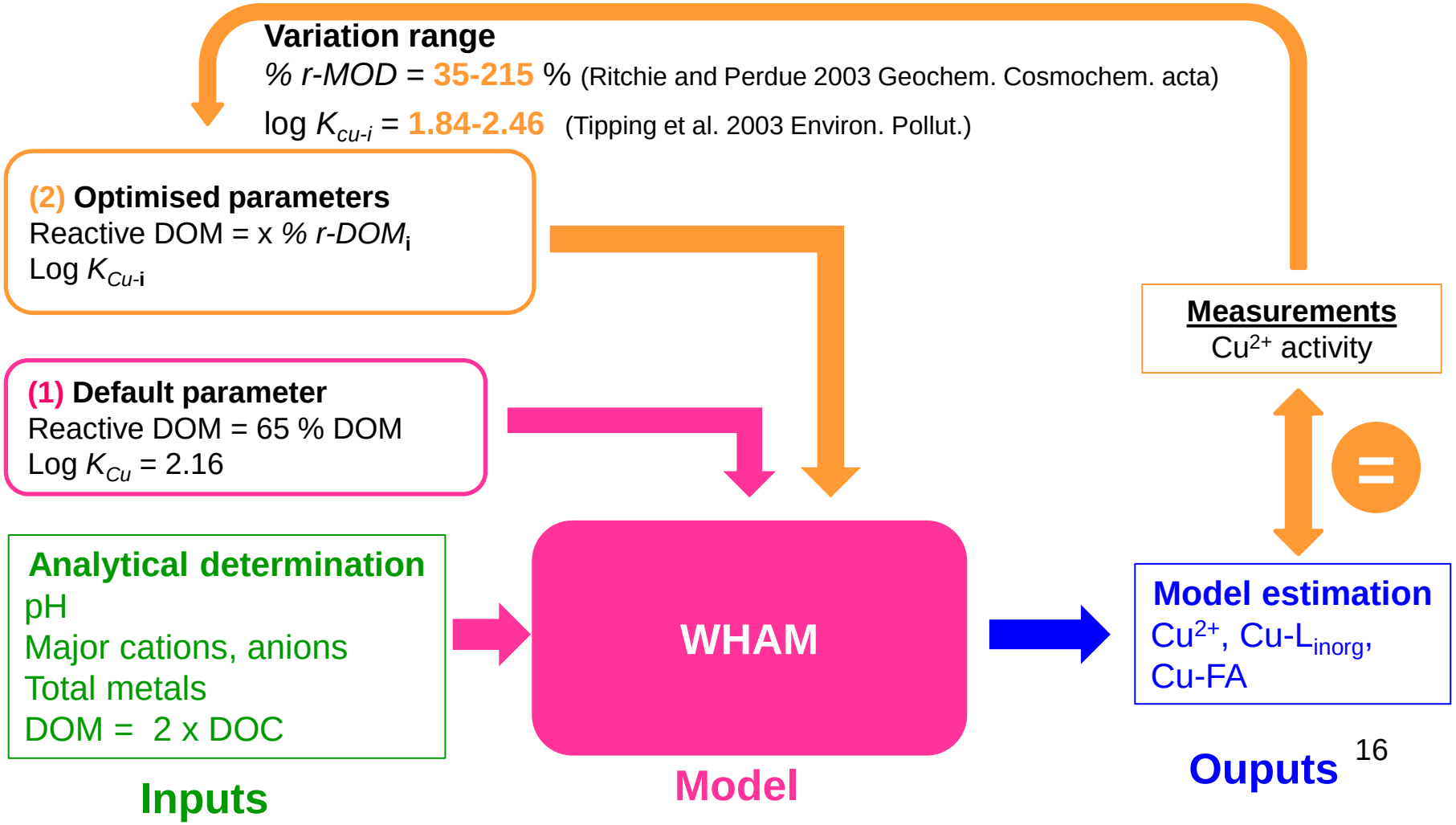
- **5 soils** : DOM analytical characterisation
  - SUVA 254 nm
  - E_{254}/E_{355} ratio
  - Organic anions
  - Parafac 3D fluorescence



Djae et al. 2017 Environ. Toxicol. Chem. 36, 898-905

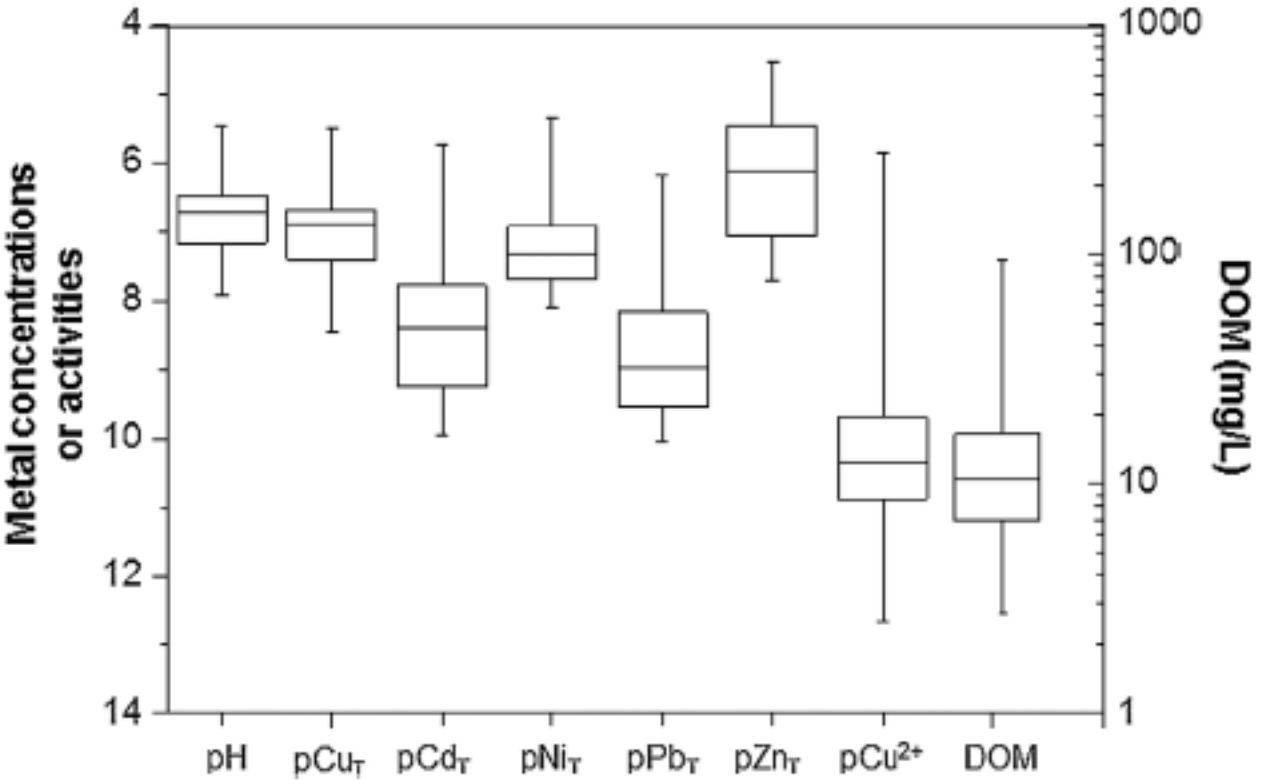
Results – part I
Soil diversity

Methodology: Modelling procedure



Results – part I
Soil diversity

Substantial variability of soil solution parameters

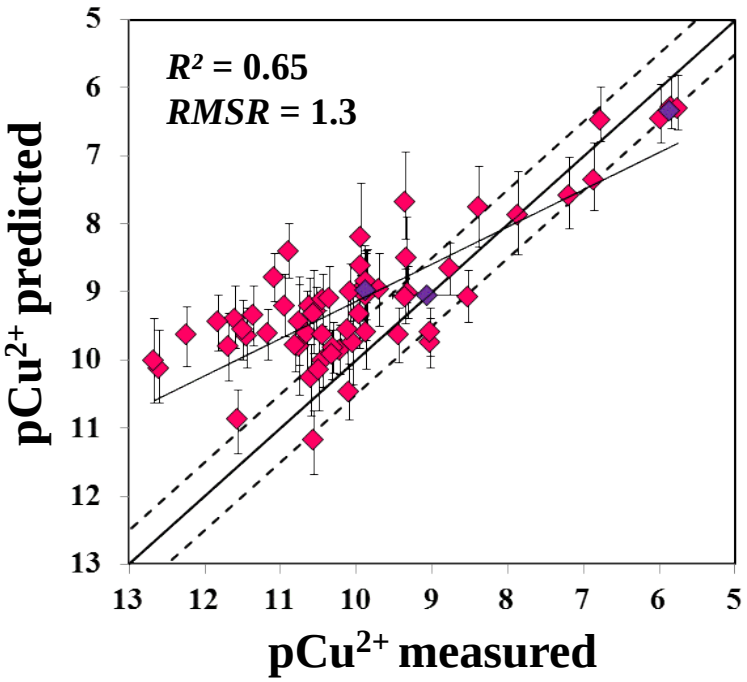


Djae et al. *2017 Environ. Toxicol. Chem. 36, 898-905*

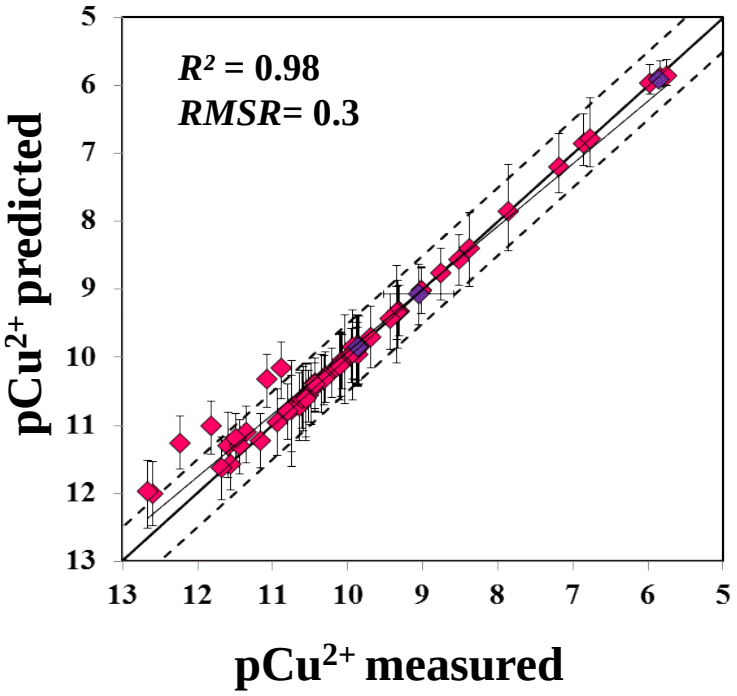
Results – part I
Soil diversity

Default vs. optimised Cu^{2+} modelling

Default parameterisation



Optimised parameterisation



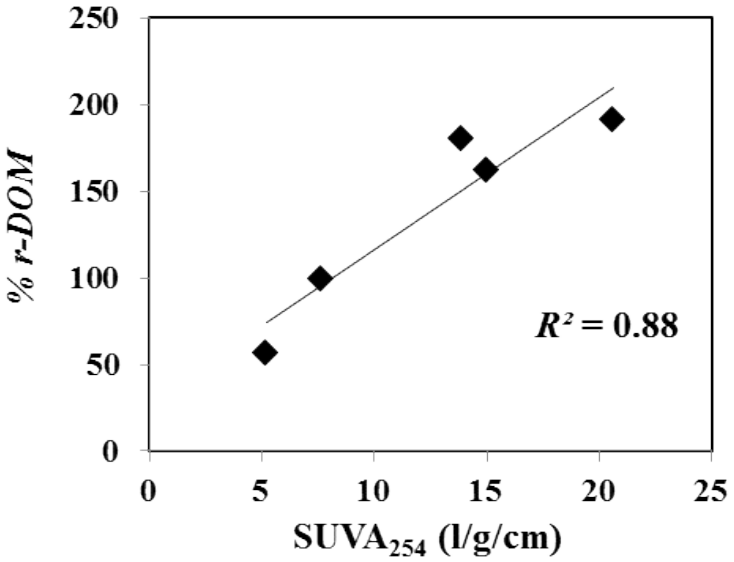
Djae et al. 2017 Environ. Toxicol. Chem. 36, 898-905

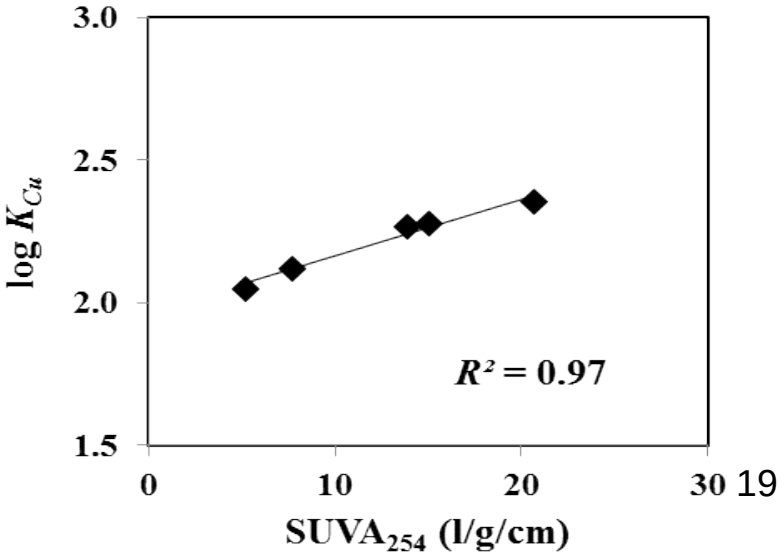
Results – part I
Soil diversity

DOM binding properties
Model optimisation vs. analytics

Djae et al. unpublished

	R^2	
	% r-MOD	Log K_{Cu}
SUVA (l/g/cm)	0,88	0,97
E2/E3	0,39	0,35
∑ acides organiques (mg_{MOD}/L)	0,34	0,19
∑ Contributions fluorescence (u.a)	0,02	0,01

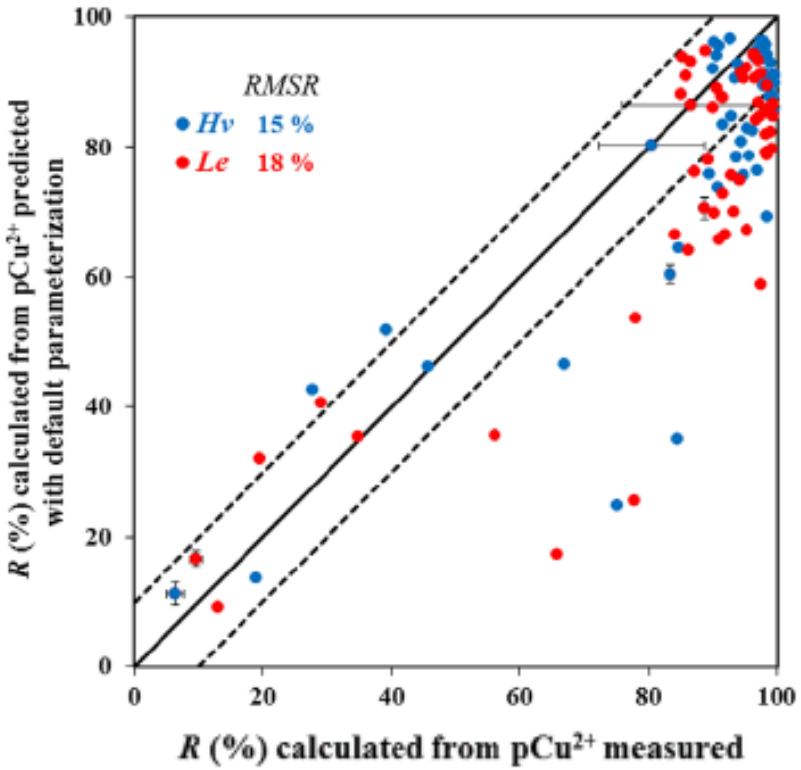




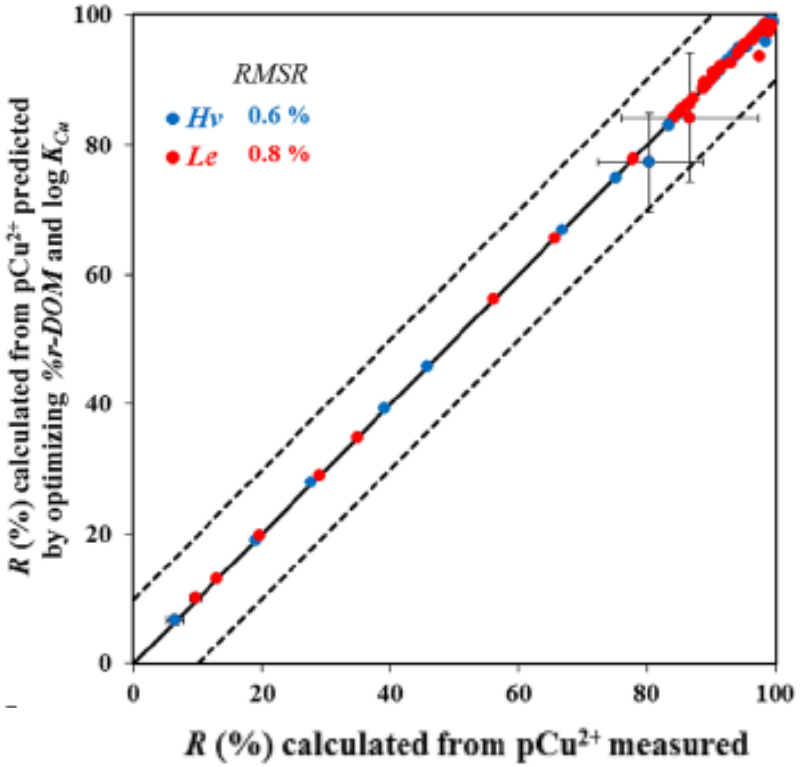
Results – part I
Soil diversity

Significance for soil Cu ecotoxicity

Default parameterisation



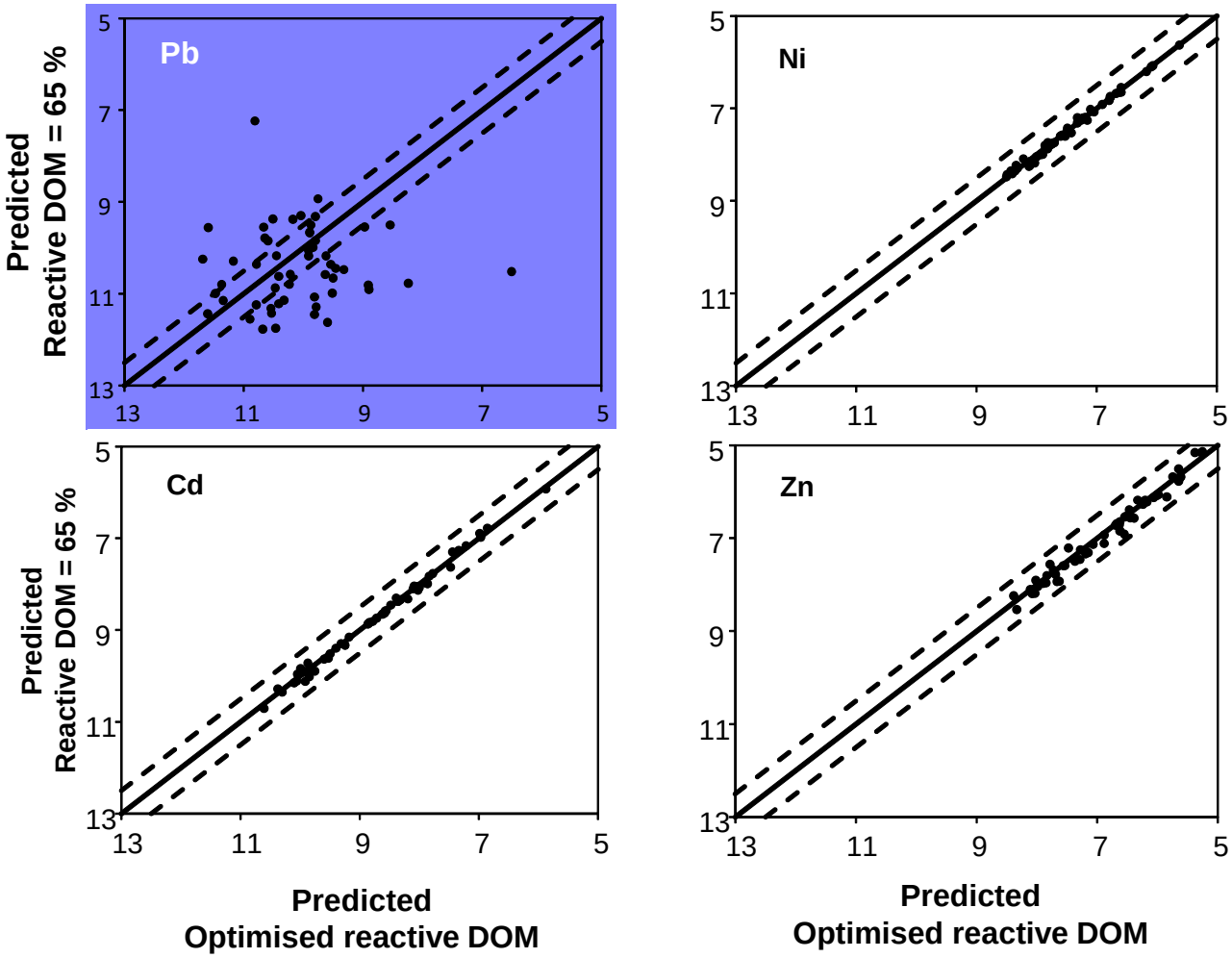
Optimised parameterisation



Djae et al. 2017 Environ. Toxicol. Chem. 36, 898-905

Results – part I
Soil diversity

What about other trace metals?



Djae et al.
unpublished

Results – part I
Soil diversity

Intermediate conclusions

- DOM binding properties vary in such a large extent that an optimised parameterisation of WHAM is necessary to predict adequately Cu speciation in soil solution and Cu toxicity to soil organisms

- Similar conclusion should be reached for trace metals exhibiting a high affinity for DOM such as Pb, but not for other trace metals such as Cd, Ni, and Zn

- DOM aromaticity may drive the variability of its binding properties and may be used as a proxy to optimise DOM binding properties in speciation models

Results – part II
Rhizosphere

Methodology: RHIZOtest & analytical procedure

Bulk-soil **Rhizosphere**

55 soils

3 plant species :
Cabbage et Tomato (dicots)
Fescue (monocot)

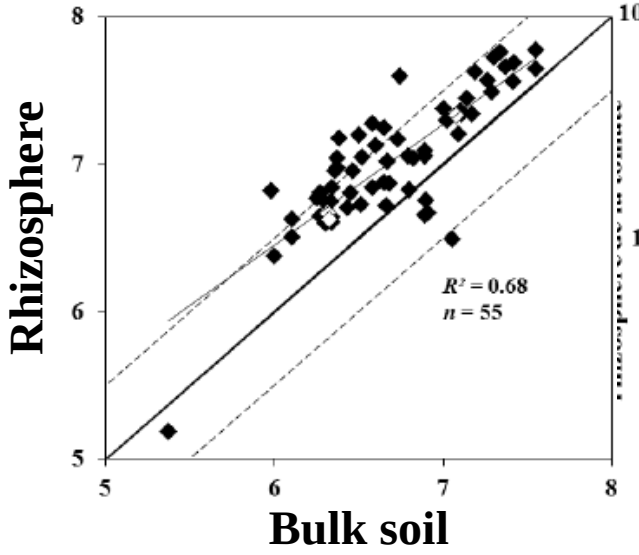
Analytics similar to bulk-soil :
DOM characterisation on 12 soils

Djae et al. in prep.

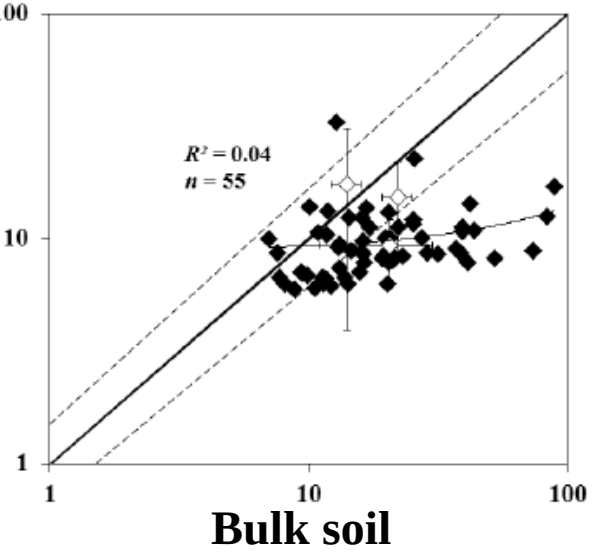
Results – part II
Rhizosphere

Substantal chemical changes in the rhizosphere

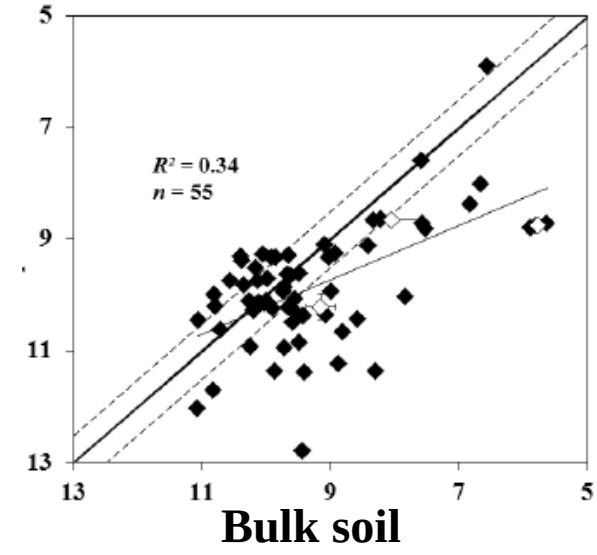
pH, fescue



DOM (mg/l), Tomato



pCu^{2+}, Cabbage



Djae et al. *in prep.*

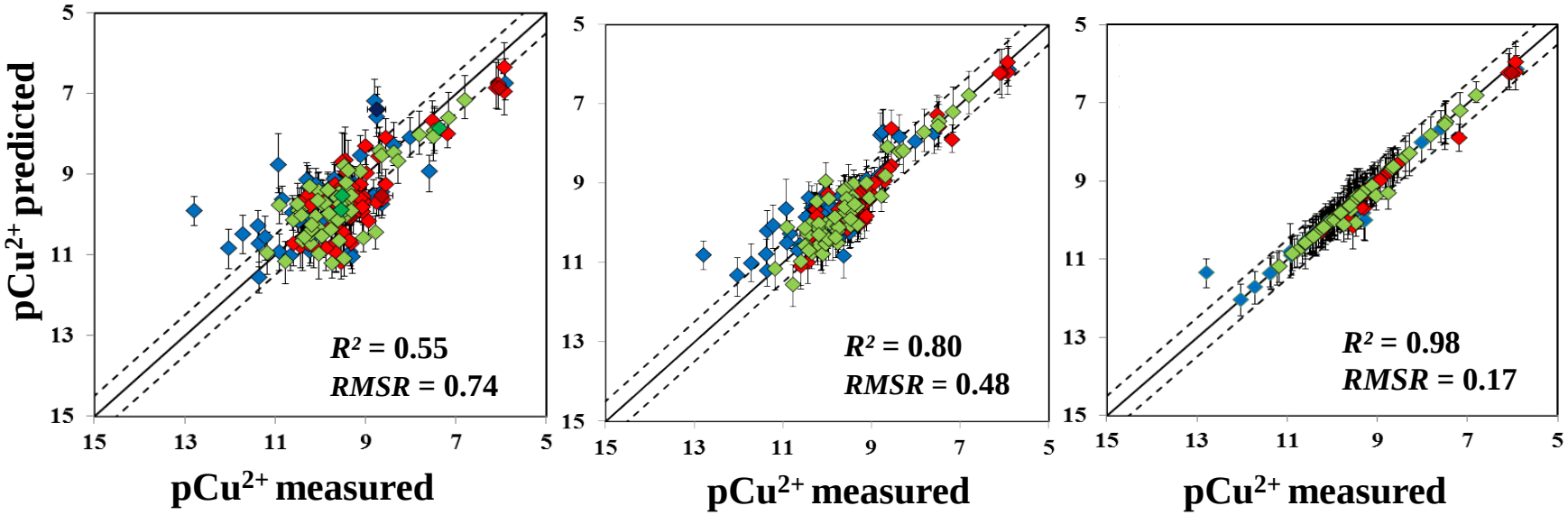
Results – part II Rhizosphere

Default vs. optimised Cu^{2+} modelling

Default parameterisation

Bulk-soil optimised parameterisation

Rhizoshere optimised parameterisation



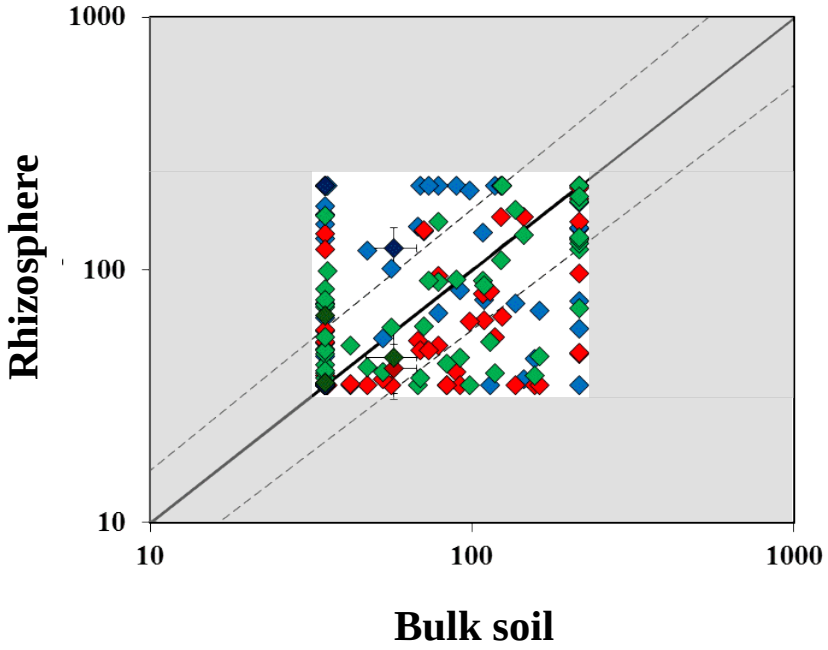
- Cabbage
- Tomato
- Fescue

Djae et al. in prep.

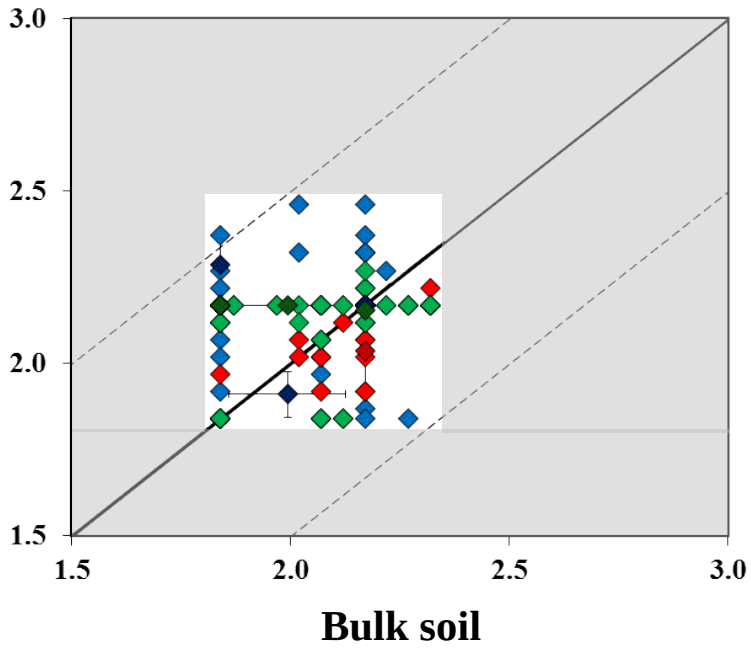
Results – part II Rhizosphere

Optimised DOM binding properties Rhizosphere vs. bulk soil

Optimised *% r-DOM*



Optimised log K_{Cu}



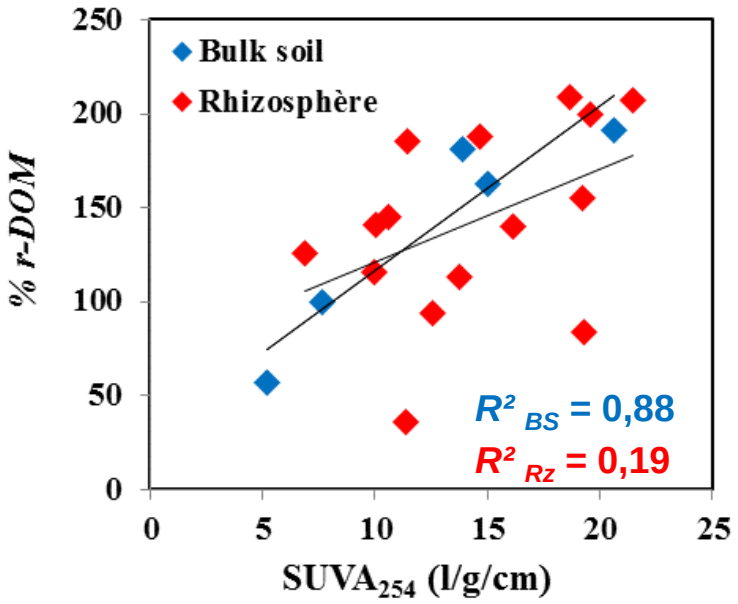
- Cabbage
- Tomato
- Fescue

Djae et al. *in prep.*

Results – part II
Rhizosphere

DOM binding properties
Model optimisation vs. analytics

Optimised *% r-DOM*



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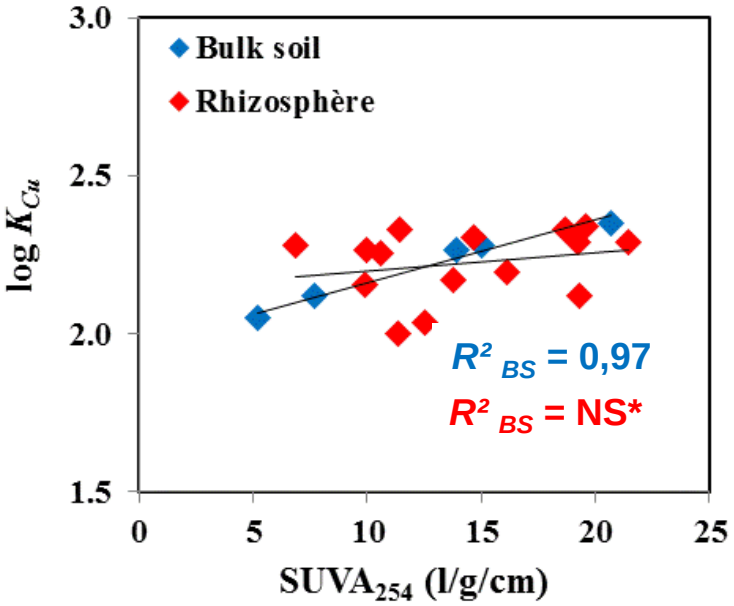


Djae et al. *in prep.*

Results – part II Rhizosphere

Intermediate conclusions

- Usual chemical properties in the rhizosphere substantially differ from that in bulk soil

- Model optimisation based on bulk soil is not sufficient to predict adequately Cu speciation in the rhizosphere solution

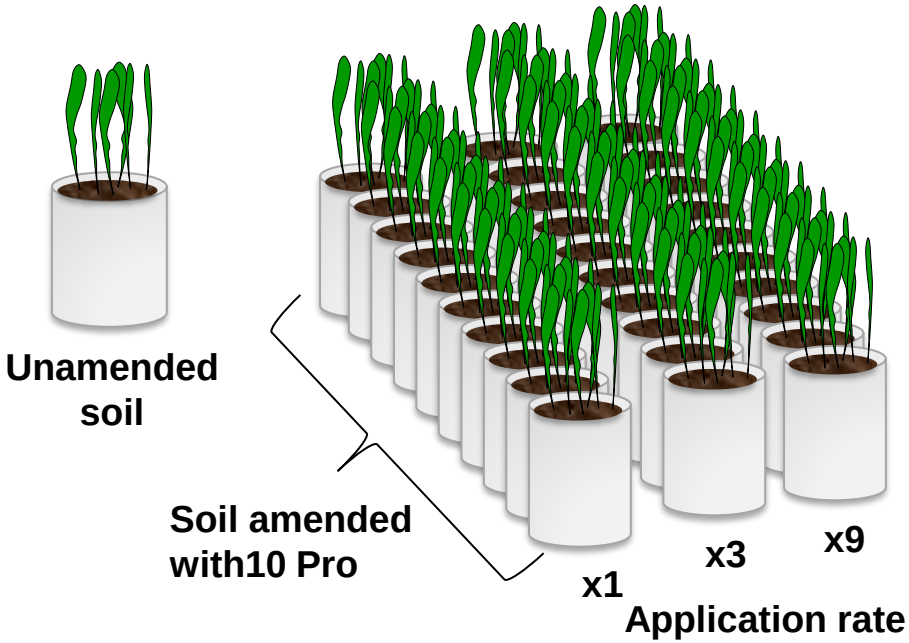
- DOM binding properties in the rhizosphere differ substantially from that in bulk soil

- We did not find yet an adequate proxy to optimise DOM binding properties in the rhizosphere

Results – part III
Organic residues

Methodology: Exp. & analytical procedure

4 days soil incubation exp.



Analytics similar to RHIZOtest exp.

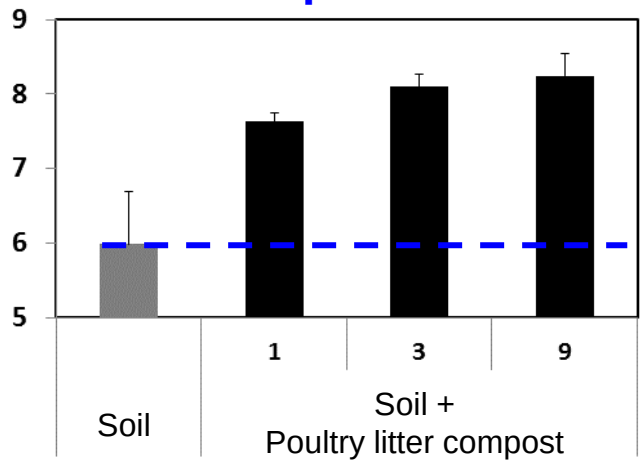
Soil solution collected by centrifugation

Djae et al. *in prep.*

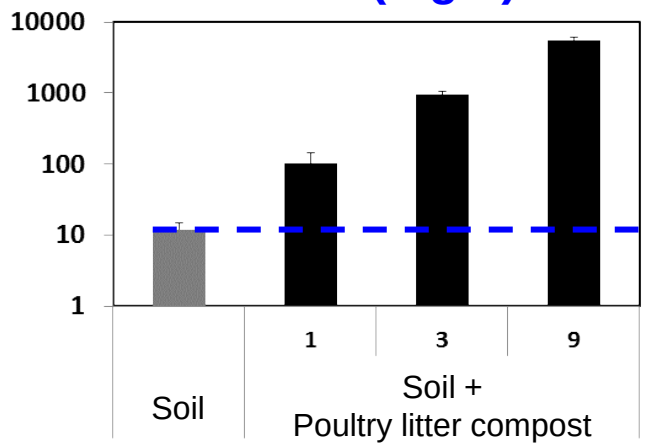
Results – part III
Organic residues

Substantial chemical changes in amended soils

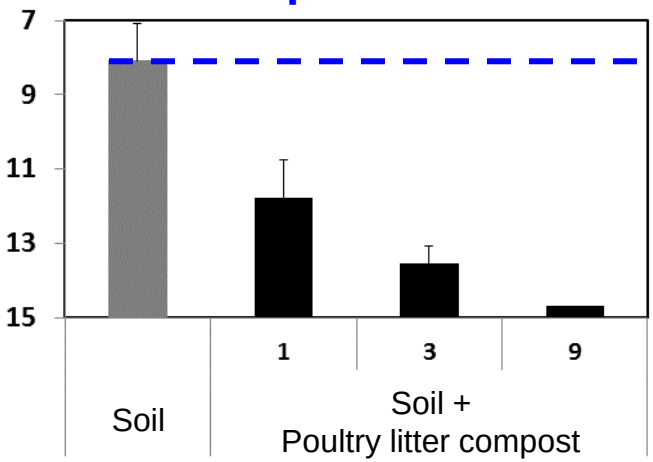
pH



DOM (mg/L)



pCu^{2+}

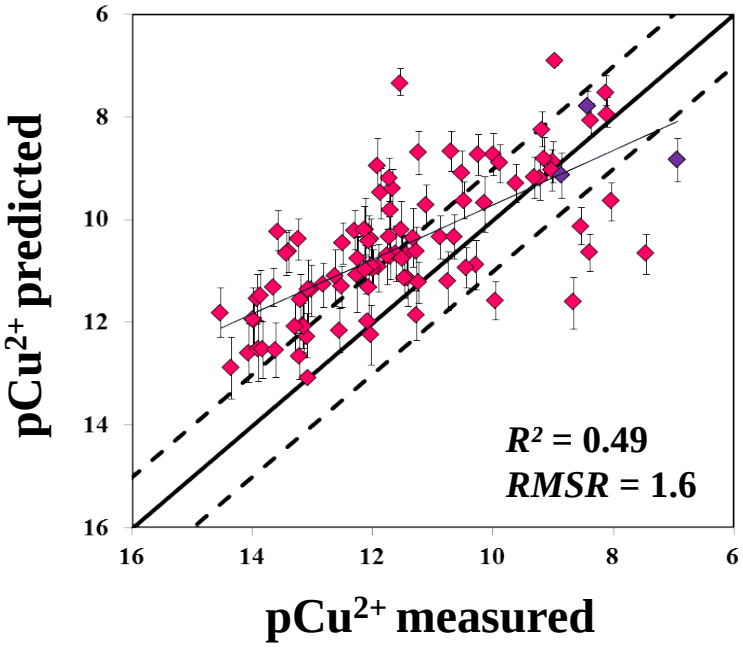


Djae et al. *in prep.*

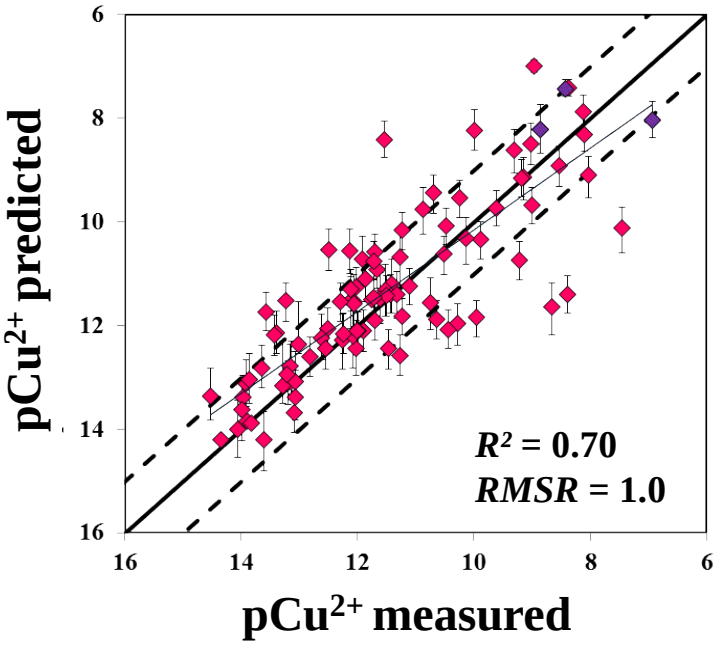
Results – part III
Organic residues

Default vs. optimised Cu^{2+} modelling

Default parameterisation



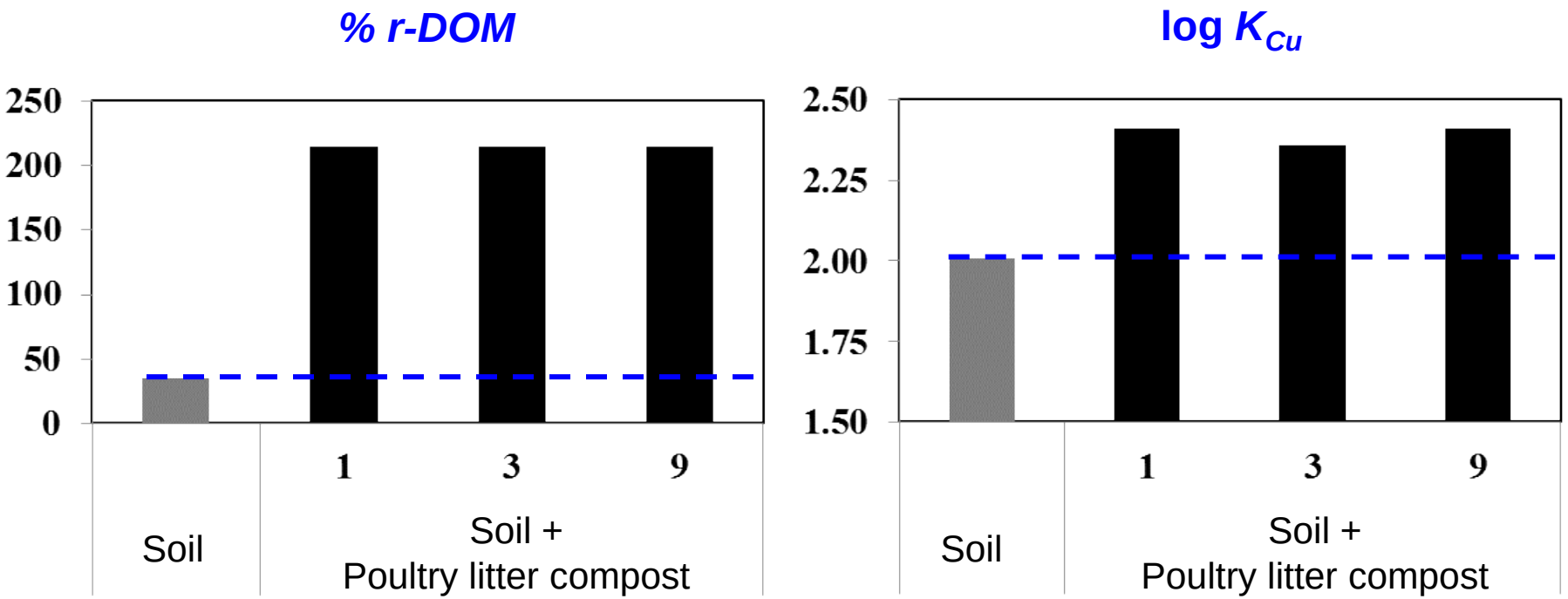
Optimised parameterisation



Djae et al. in prep.

Results – part III
Organic residues

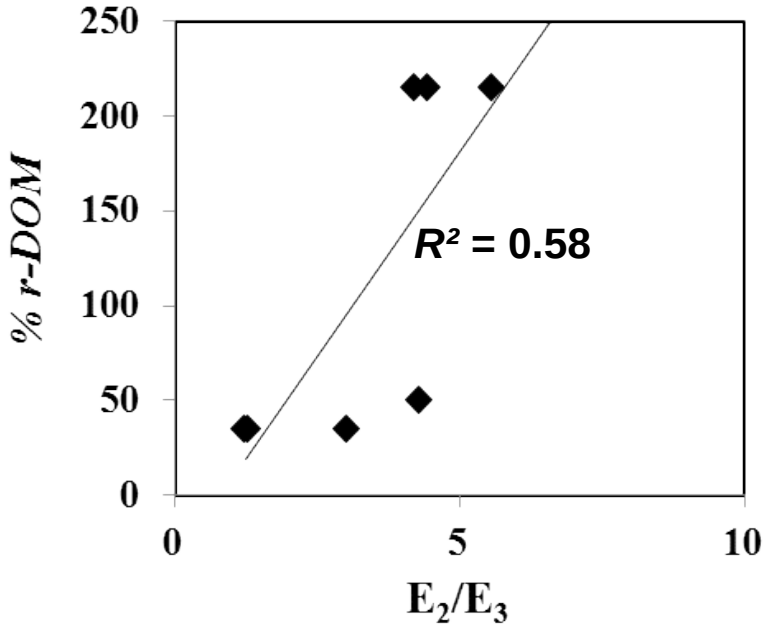
Optimised DOM binding properties
Amended vs. unamended soil

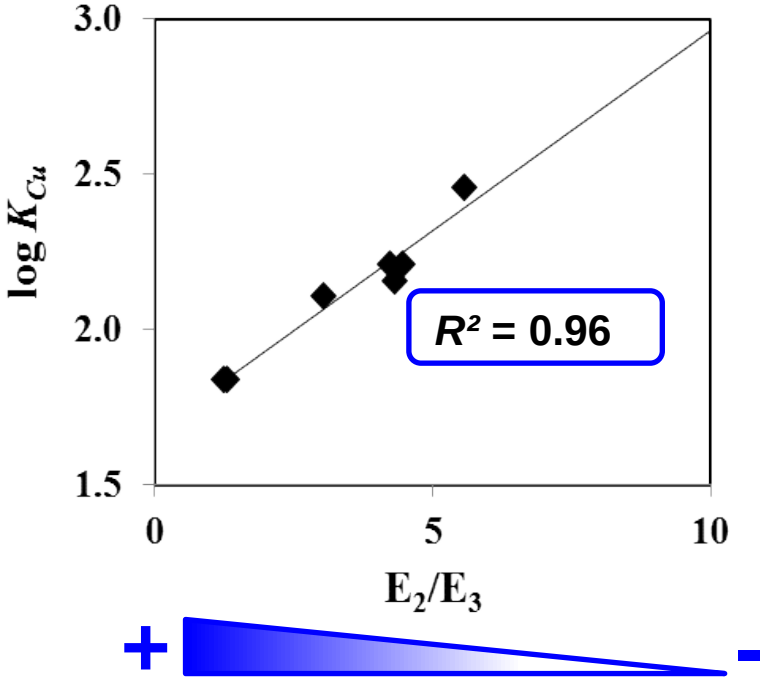


Djae et al. *in prep.*

Results – part III
Organic residues

DOM binding properties
Model optimisation vs. analytics





Djae et al. in prep.

Results – part III
Organic residues

Intermediate conclusions

- Organic residue application changes substantially soil chemical properties and Cu speciation in soil solution

- Optimisation of DOM binding properties is necessary to improve Cu speciation prediction in an amended soil

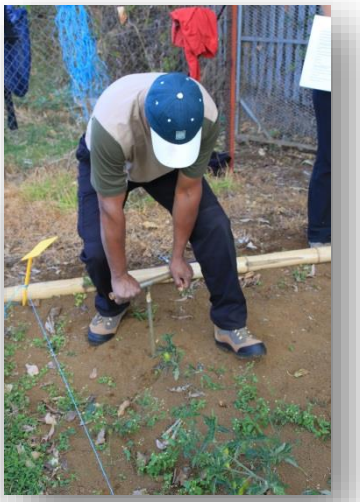
- DOM binding properties increase in an amended soil

- DOM molecular weight may drive the variability of its binding affinity and may be used as a proxy to optimise this parameter in speciation models

Results – part IV
Field-scale validation

Methodology: 10-year filed trial

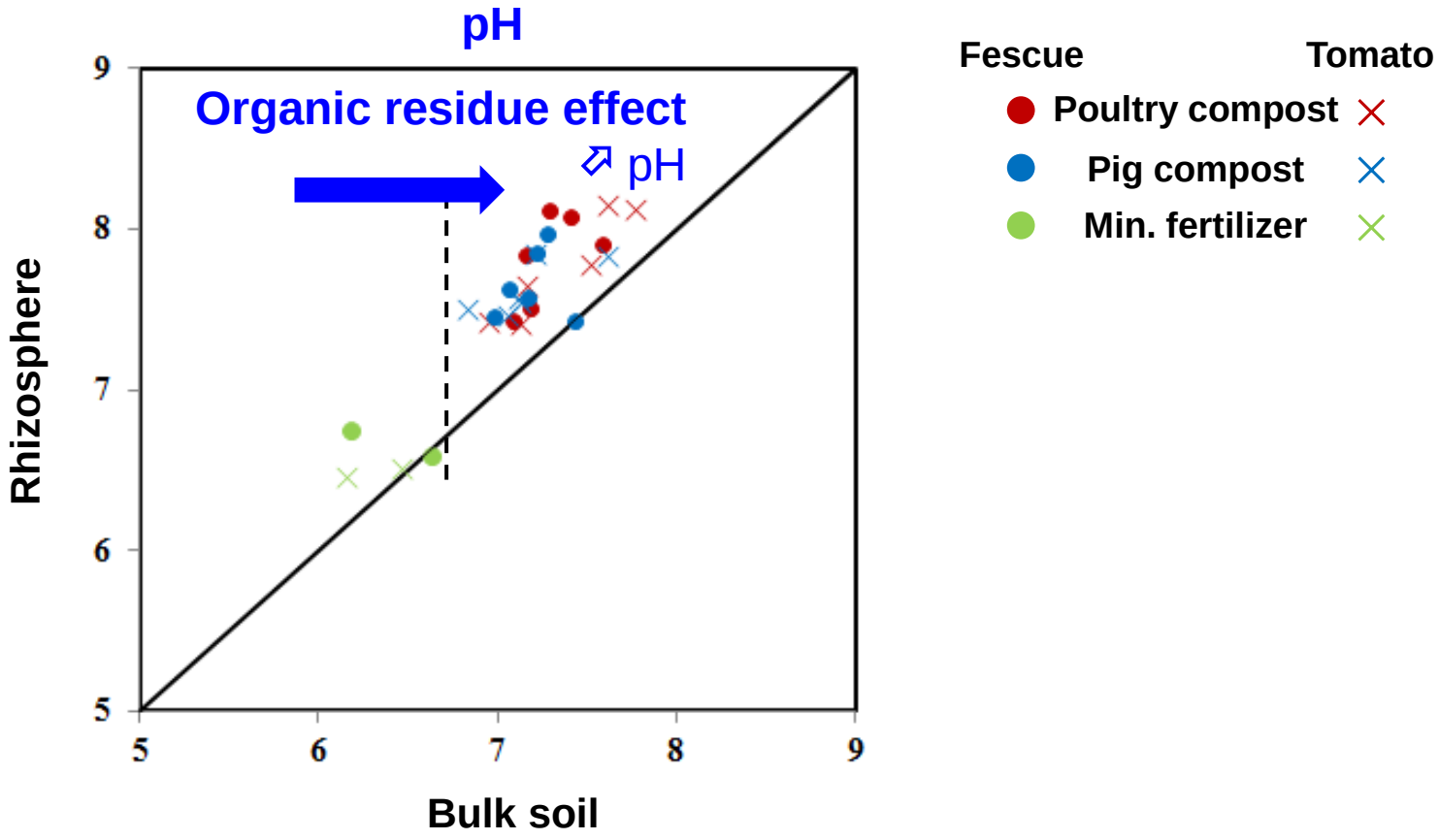
- **2 species**
  - Tomato = dicot
  - Fescue = monocot
- **3 fertilizations**
  - Mineral
  - Pig slurry compost
  - Poultry litter compost
- **Soil sampling**
  - Bulk soil
  - Rhizosphere
- **Analyses**
  - As for lab exp.



Djae et al. unpublished

Results – part IV
Field-scale validation

Organic residue vs. plant effects : pH



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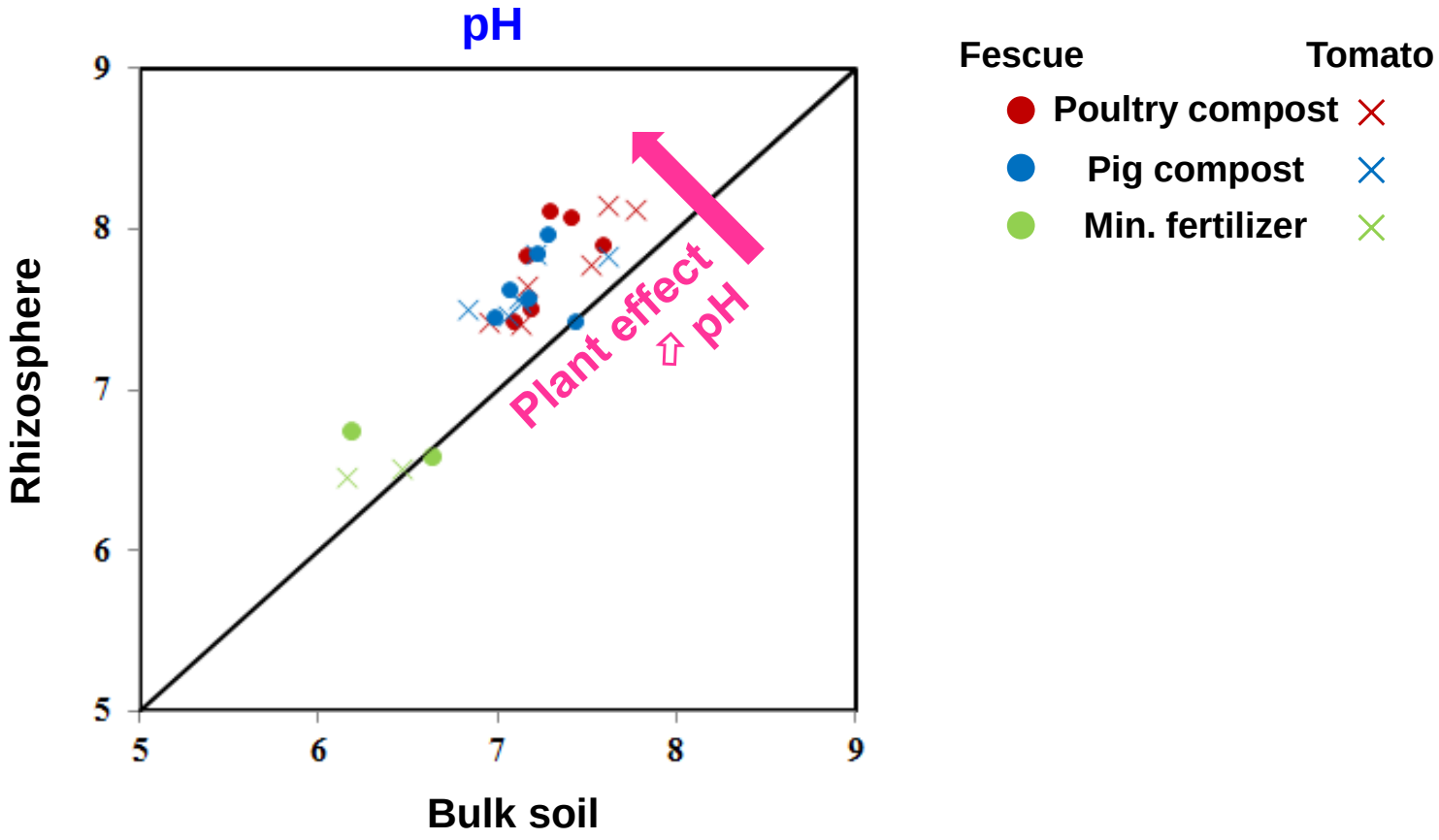
Results – part IV
Field-scale validation

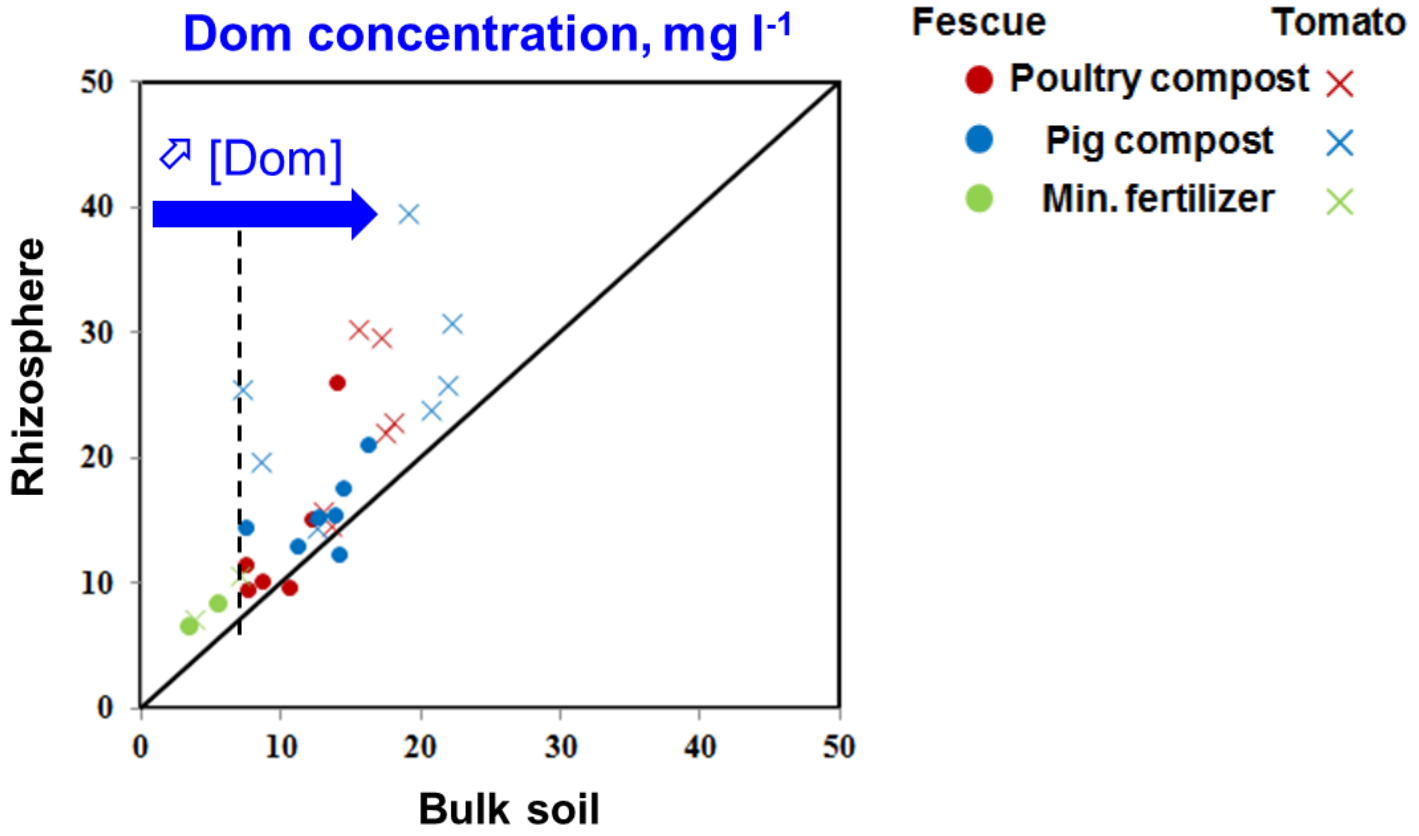
Organic residue vs. plant effects : pH



Djae et al. unpublished

Results – part IV
Field-scale validation

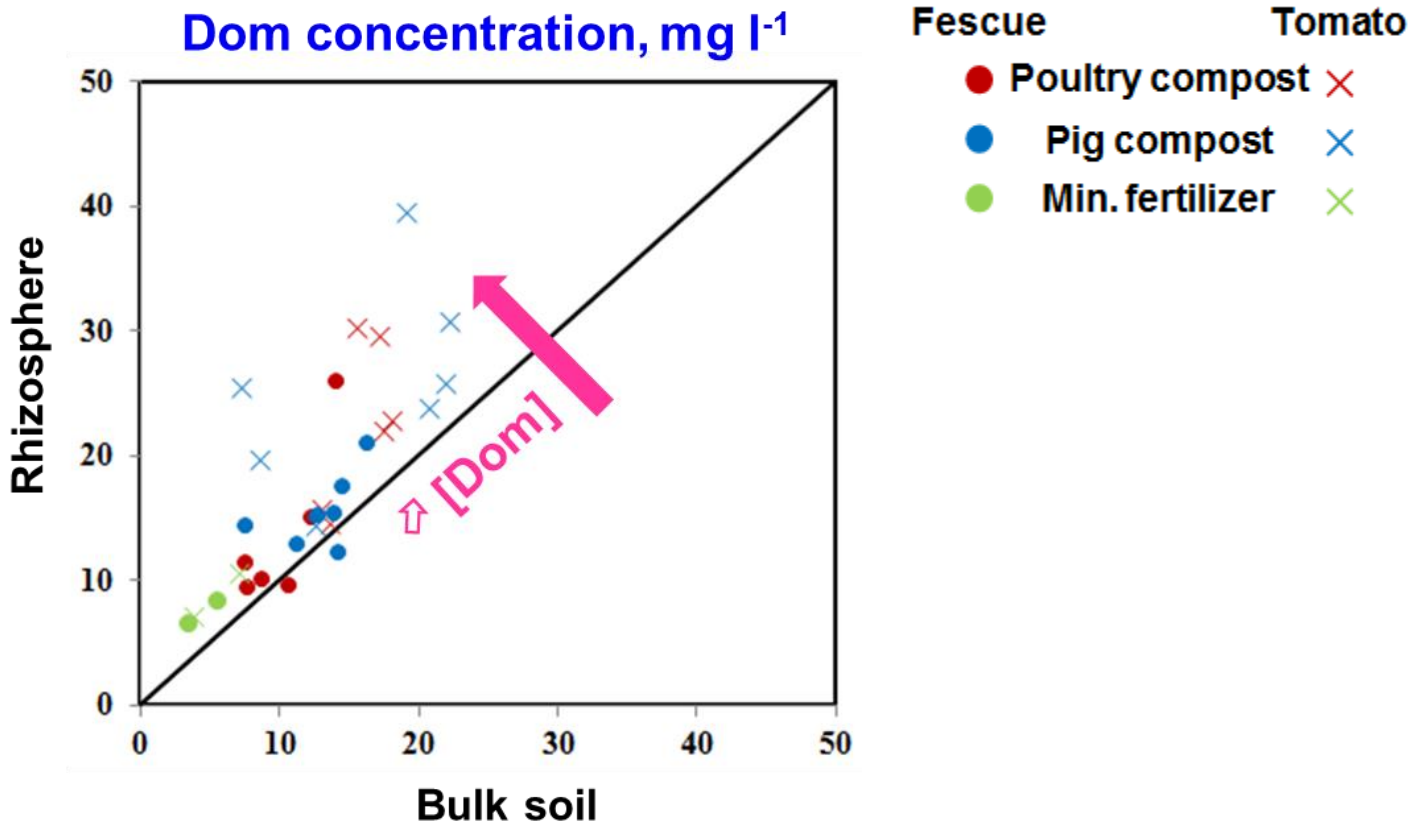
Organic residue vs. plant effects : DOM conc.



Djae et al. unpublished

Results – part IV
Field-scale validation

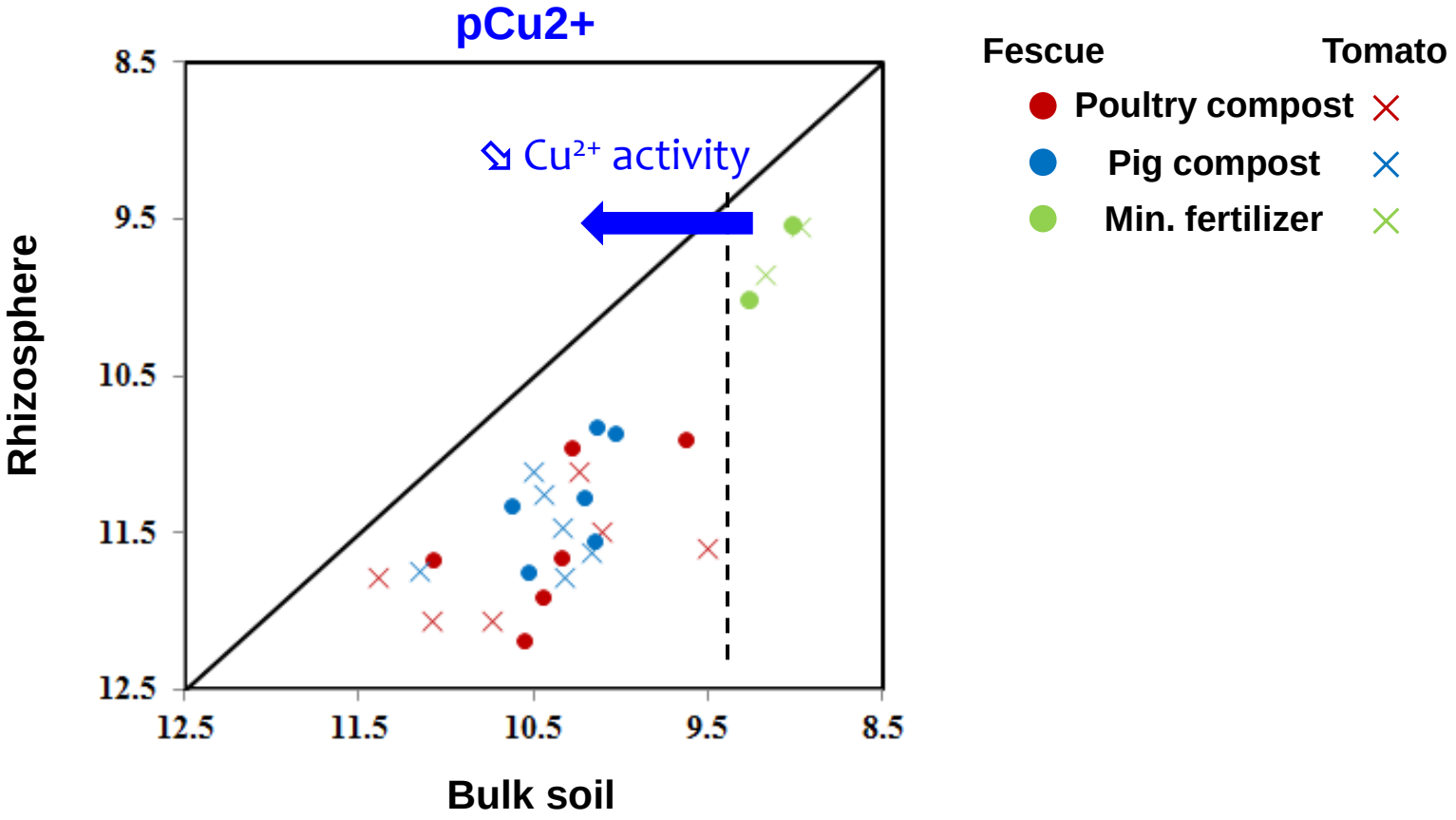
Organic residue vs. plant effects : DOM conc.



Djae et al. unpublished

Results – part IV
Field-scale validation

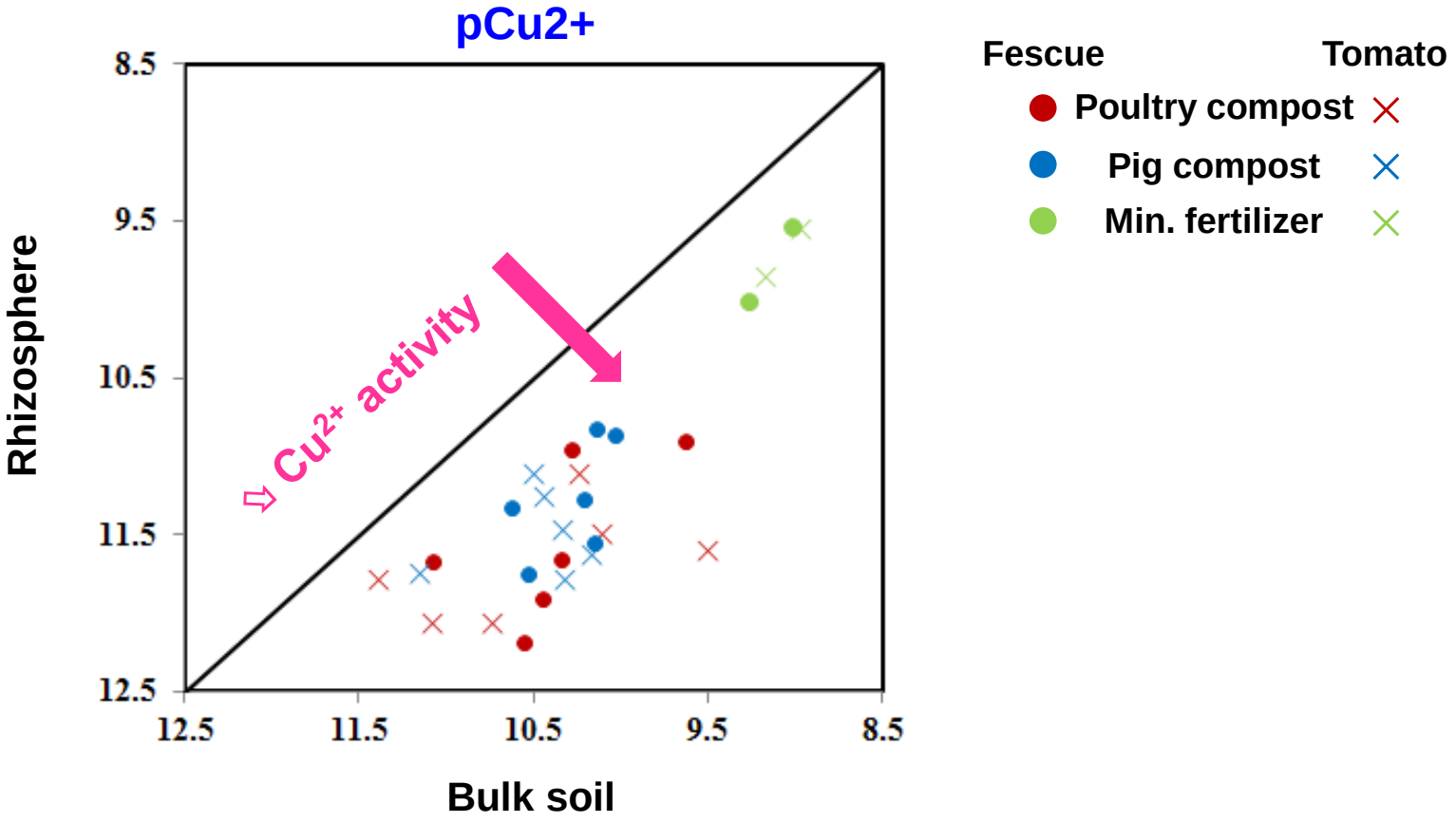
Organic residue vs. plant effects : Cu^{2+} activity



Djae et al. unpublished

Results – part IV
Field-scale validation

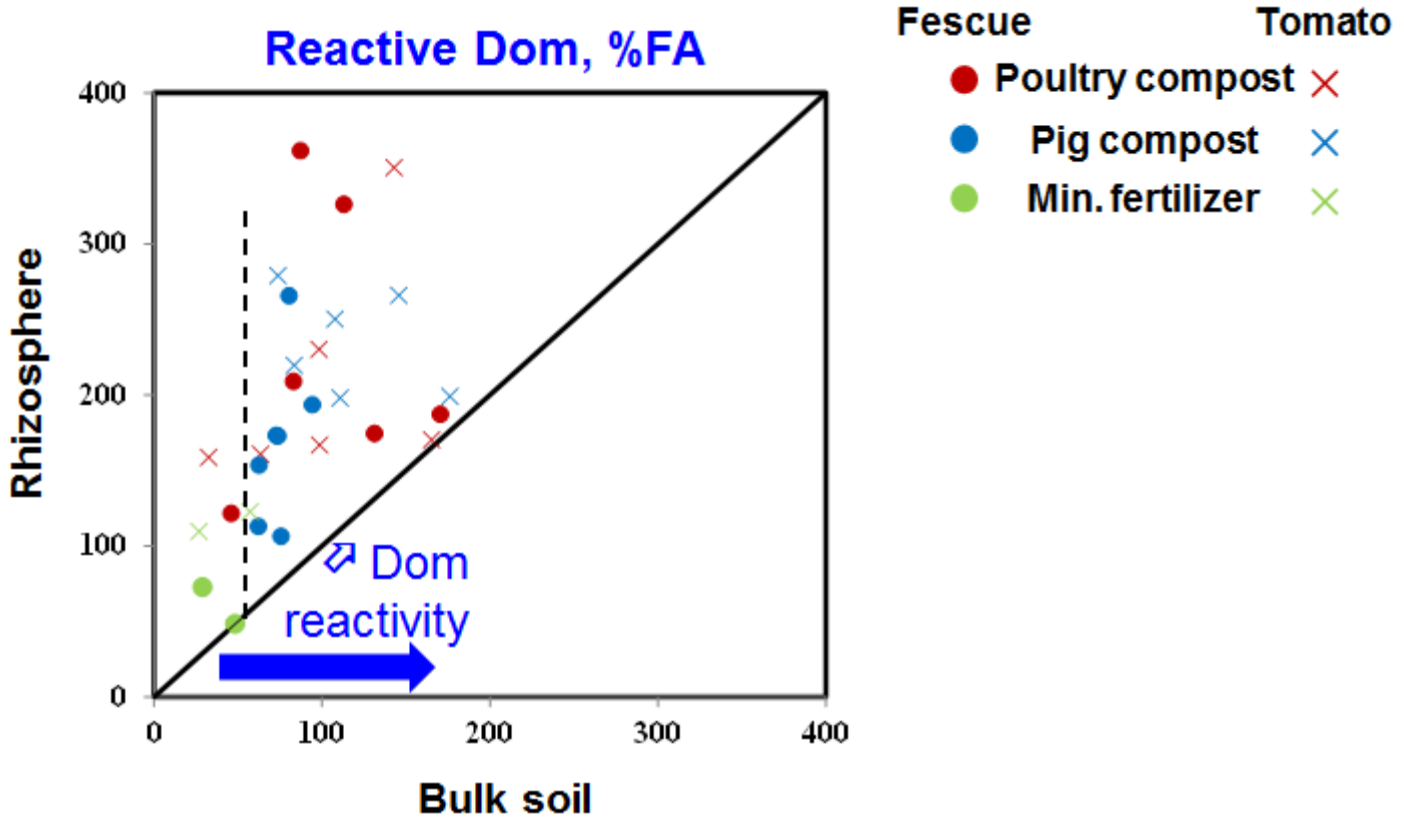
Organic residue vs. plant effects : Cu^{2+} activity



Djae et al. unpublished

Results – part IV
Field-scale validation

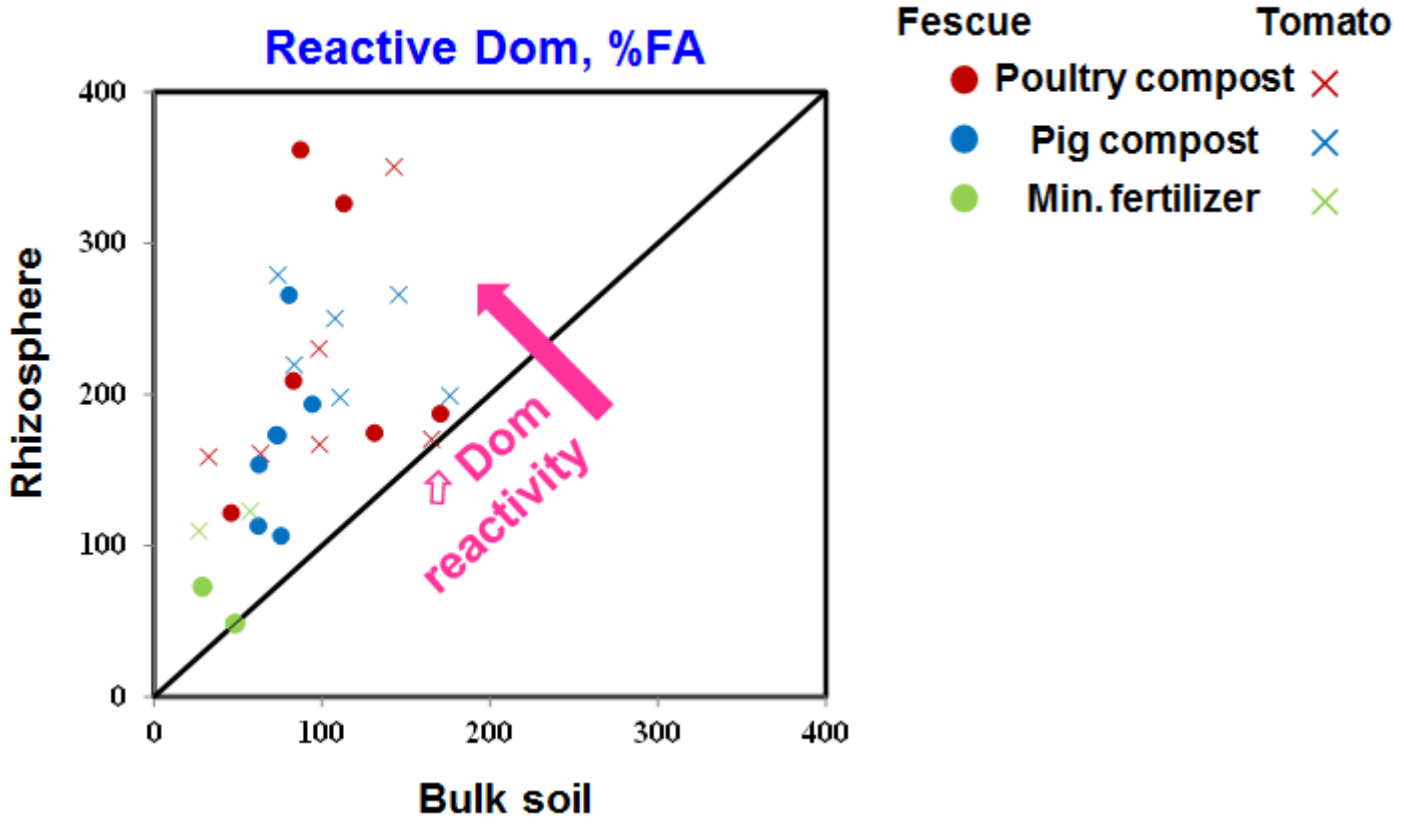
Organic residue vs. plant effects : DOM reactivity



Djae et al. unpublished

Results – part IV
Field-scale validation

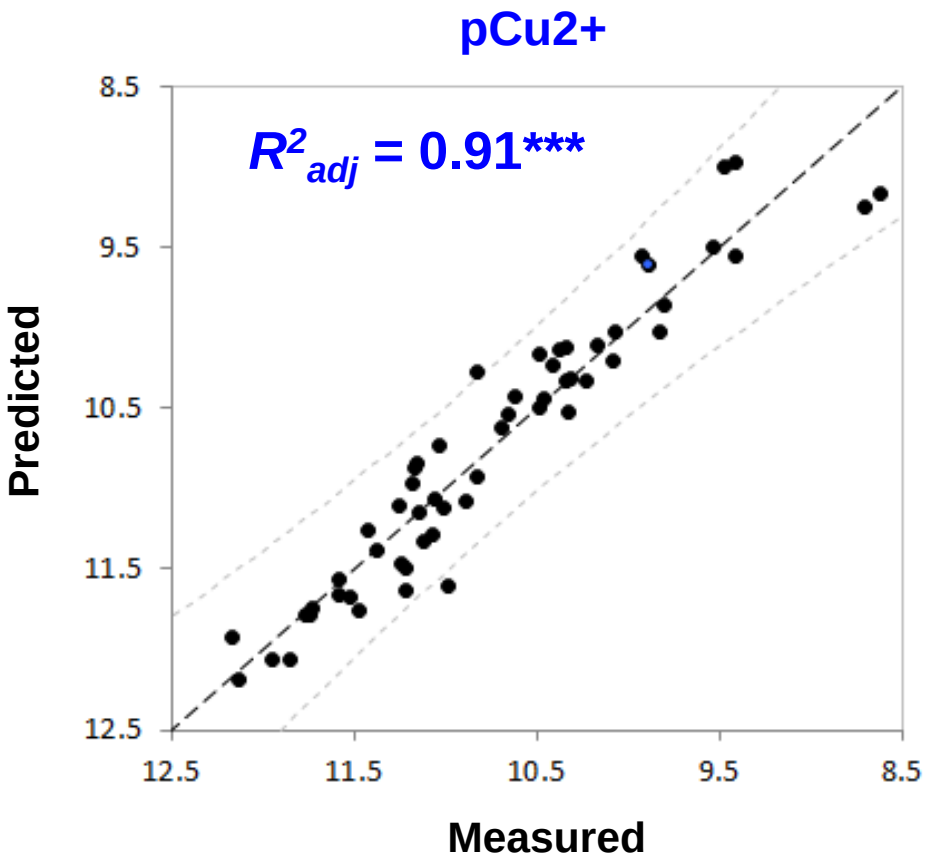
Organic residue vs. plant effects : DOM reactivity



Djae et al. unpublished

Results – part IV
Field-scale validation

Cu^{2+} prediction with pH and DOM reactivity



pCu^{2+} = 1.0 ± 0.2 **pH**

+ 1.5 ± 0.4 $\mathbf{log_{10}[\%FA]}$

+ 0.4 ± 1.1

Djae et al. *unpublished*

Final conclusions

DOM binding properties seem to vary much more than previously expected

Soil diversity, rhizosphere specific properties, and organic residue applications at least induce a large variability in DOM binding properties

The variability in DOM binding properties should be accounted for in speciation models and predictive ecotoxicology

Necessity to find some proxy(s) to parameterise DOM binding properties in speciation models

A few perspectives

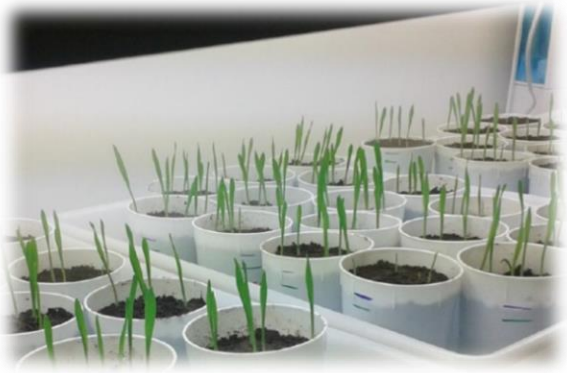
(Re-)examining DOM binding properties
with adequate and some new analytical techniques

A way could be to determine
the relative but comprehensive metabolomic profile
of DOM molecules in some relevant study cases
to better parameterise speciation models

Further evaluate the kinetic aspects
of DOM binding properties

Invited lecture
Free University of Bozen-Bolzano
May 13th 2019

DOM biogeochemistry in agricultural soils as a major driver of **trace metal bioavailability** to **soil organisms**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LA RECHERCHE AGRONOMIQUE POUR LE DÉVELOPPEMENT