Approaches to assess and manage the risks of excessive contamination of food crops by toxic trace elements in agroecosystem soils exposed to diffuse contaminations

Christophe Nguyen, Zhongbing Lin, Thibault Sterckeman, Bofang Yan, M.-P. Isaure, Sandra Mounicou, Olaia Liñero, Yoann Viala, Benoît Méléard, Agathe Roucou, et al.

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Nguyen C.[1], Lin Z.[1], Schneider A.[1], Sterckeman T.[2], Yan B.[1], Isaure MP.[3], Mounicou S.[3], Linero O.[1], Viala Y.[1], Méléard B.[4], Roucou A.[4], Cornu JY.[1]

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119 Animine
Not only trace minerals

ICOBTE& ICHMET 2023
1st Joint International Conference in Wuppertal, Germany
Clean Environment.
Human Health. Our Future.
Bergische Universität Wuppertal

Hardening of regulations

11.8.2021 EN Official Journal of the European Union L 288/13

COMMISSION REGULATION (EU) 2021/1323

of 10 August 2021

amending Regulation (EC) No 1881/2006 as regards maximum levels of cadmium in certain foodstuffs

(Text with EEA relevance)

Cadmium (Cd)

- **38** new regulated products
- Lowering of some limits :

ex: Bread Wheat: 0.2 to 0.1 mg/kg

Durum Wheat 0.2 to 0.18 mg/kg

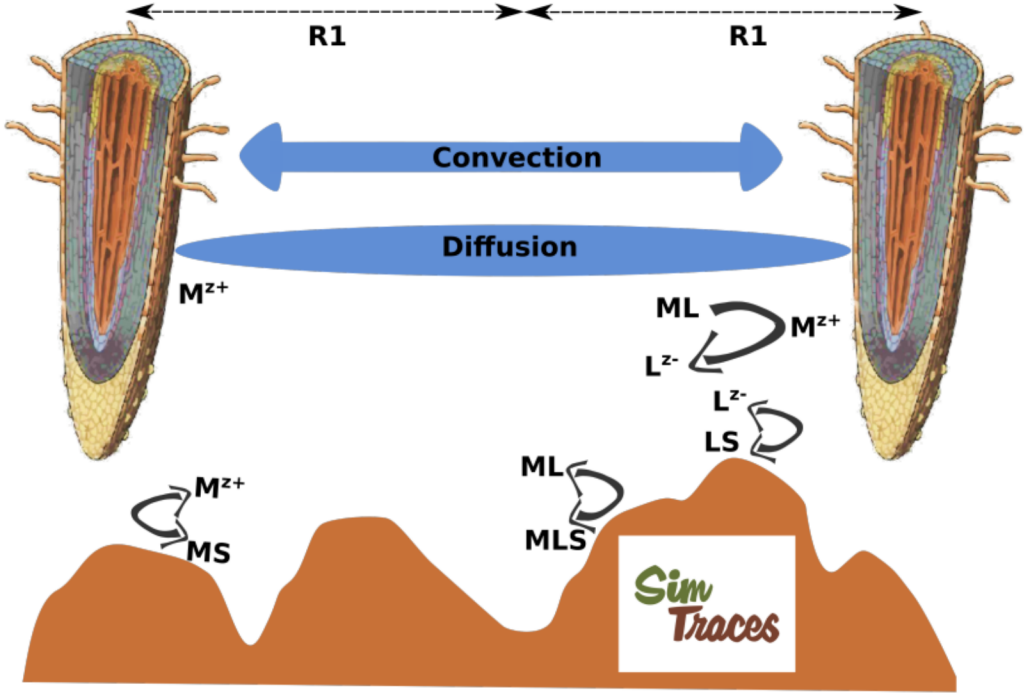
Nickel in preparation.....


Non compliance occurrences for Cd becomes a concern
France
Durum wheat: up to 12%
(Nguyen et al., 2017)
CaDON
INRA
ARVALIS
Linseed: 30-75%
(Traders, Pers. com.)

How to reduce crop contamination by toxic metals ?
Can modelling be helpful ?

Modelling of bioavailability: Simtraces

Lin et al., 2016 https://www6.inrae.fr/simtraces



3 species :
- M (free ion),
- L (free mean unique ligand),
- ML (the complex)

Transport by :
- diffusion
- convection

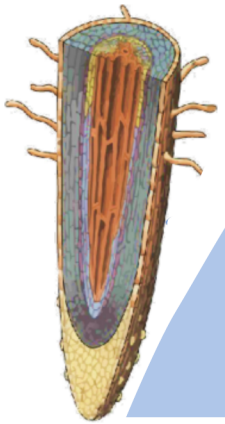
Kinetics for:
- Sorption
- Complexation for M, L, ML

Root uptake:
Only M (Michaelis kinetics)

Sensitivity analysis
100 000 simulations of 30 days root-uptake of Cd for agricultural conditions

Strong depletion of soluble Cd^{2+} at the root surface

Soil solution
Cd^{2+}concentration at the root surface
(% initial)



Mean: 9.7%

Median: 1.4%

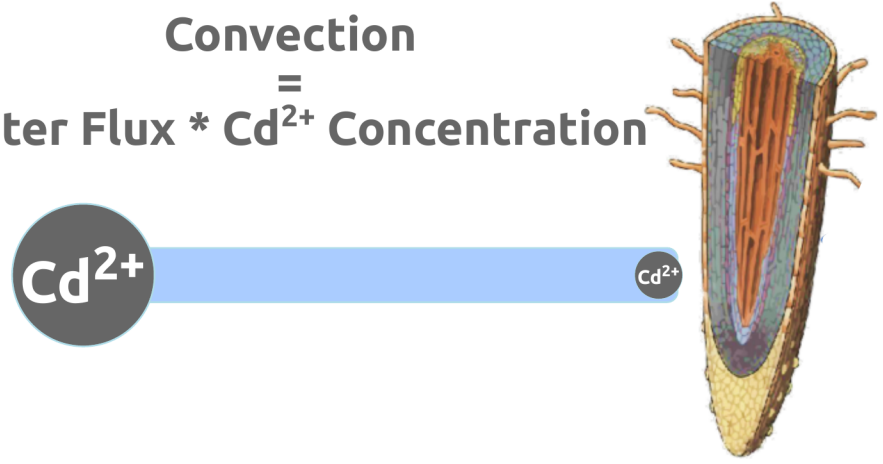
Q_{75}: 8.7%

In agricultural soils soluble Cd is few tens of nanomolar

The bioavailability of Cd is low compared to the capacity of uptake by roots

Strong depletion of Cd^{2+} = low contribution of convection

Convection
=
Water Flux * Cd^{2+} Concentration

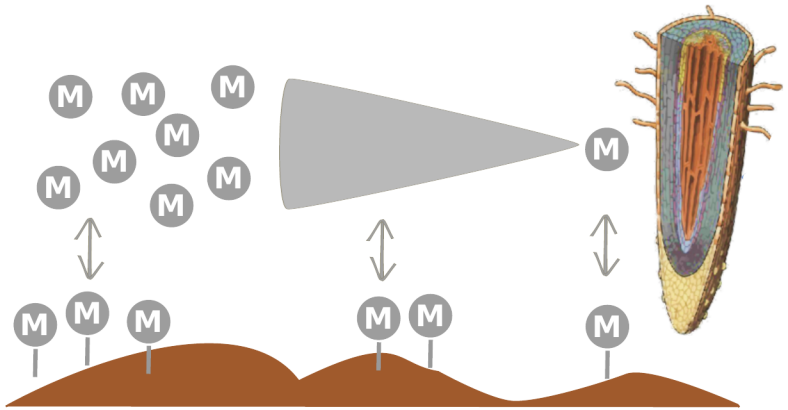


The low [Cd^{2+}] at the root surface leads to a low contribution of mass flow to Cd uptake

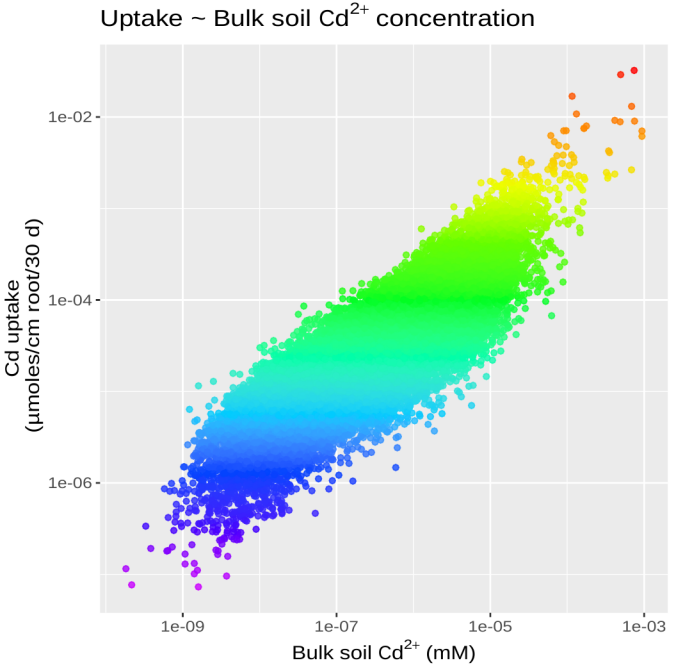
Reducing plant transpiration is not expected to be a strong lever to reduce crop contamination by Cd

Diffusion is dominating → Strong effect of bulk soil Cd^{2+}

High Cd^{2+} gradient

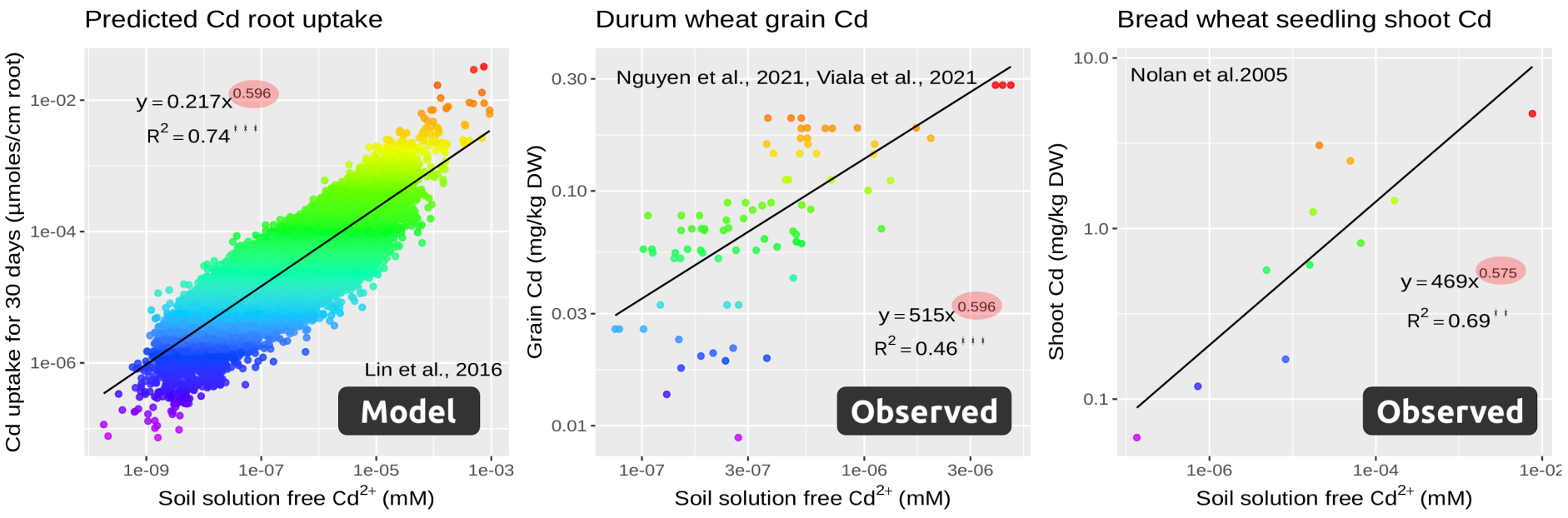


High Cd^{2+} gradient =
Diffusion controls Cd uptake



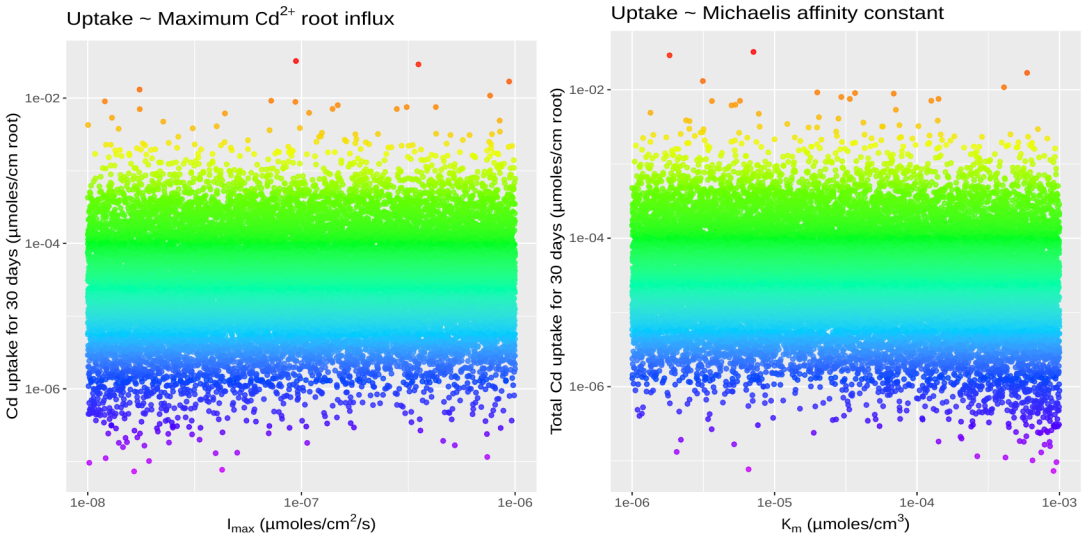
Bulk soil Cd^{2+} = Cd^{2+} gradient
= Cd uptake
Importance of pH, sorption (OM, clay, oxydes)

Is the model consistent with experimental data ?



Doubling the Cd^{2+} concentration in the bulk soil solution is expected to increase the uptake by x 1.5

Uptake of Cd ~ root system characteristics



Low Cd^{2+} at the root surface =
root uptake capacity not limiting

Thick few short roots favourable to a lower Cd uptake

Short/few roots
=
Low soil prospection

Large root radius
=
Least diffusion

Yu et al., 2016 — 18 herbaceous species grown in sand at 2 mg Cd/kg

		Total Cd in plants (µg plant^{-1})
Root length	RL (m)	0.899**
Root diameter classes	(0, 0.2]	0.335*
	(0.2, 0.4]	−0.416**
	(0.4, 0.6]	−0.250
	(0.6, 0.8]	−0.122
	>0.8	0.109

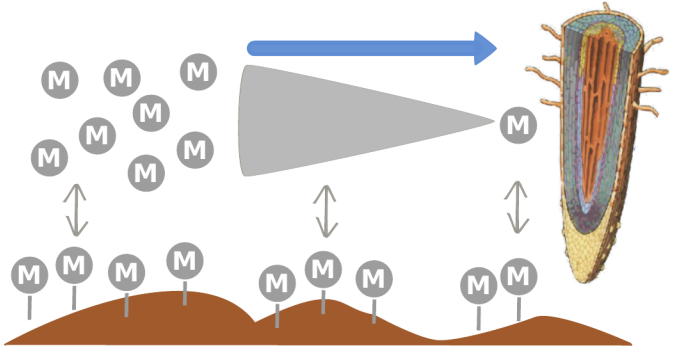
Environ Sci Pollut Res (2017) 24:4731–4740
DOI 10.1007/s11356-016-8210-z

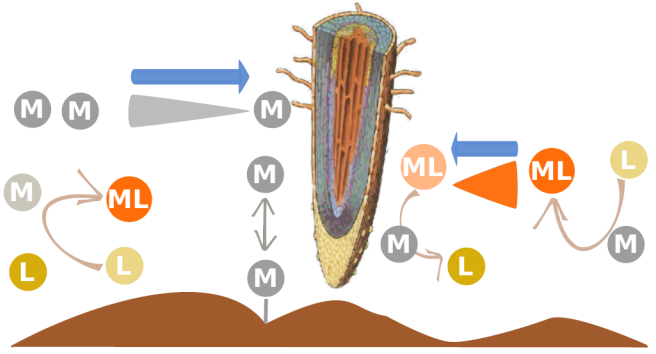
The contribution of complexes to root uptake

$$M^{2+} + L \leftrightarrow ML$$

No Complexation

With Complexation





+++

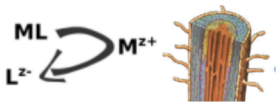
Diffusion of free metal towards the root

+

0

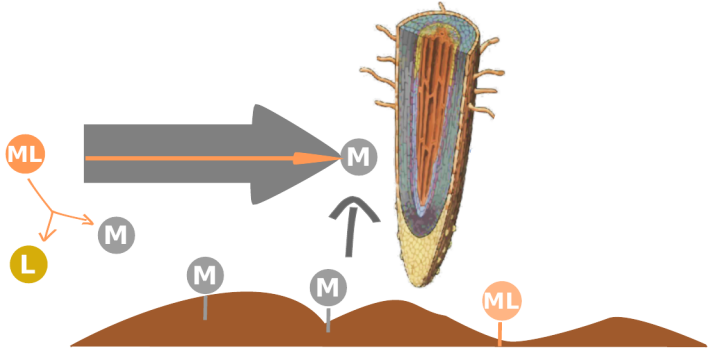
Buffering of free metal in the rhizosphere by complexe dissociation

+++



Contribution of CdL to Cd^{2+} uptake

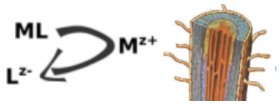
$$\text{Contribution of CdL} = \frac{\text{With CdL - Inert CdL}}{\text{With CdL}}$$

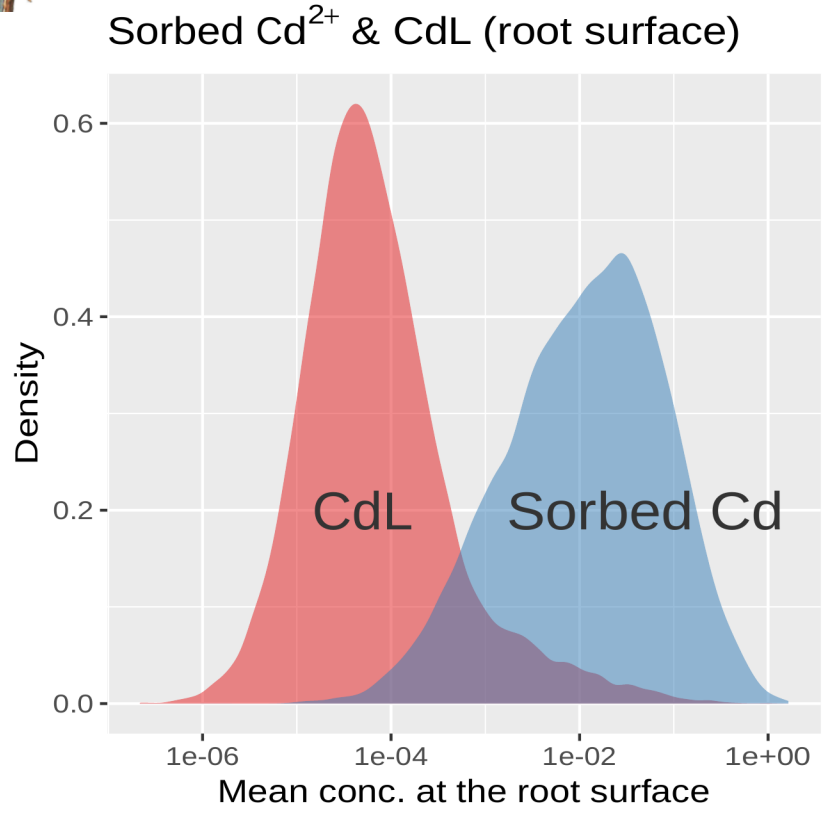


Very low contribution of CdL dissociation to Cd uptake

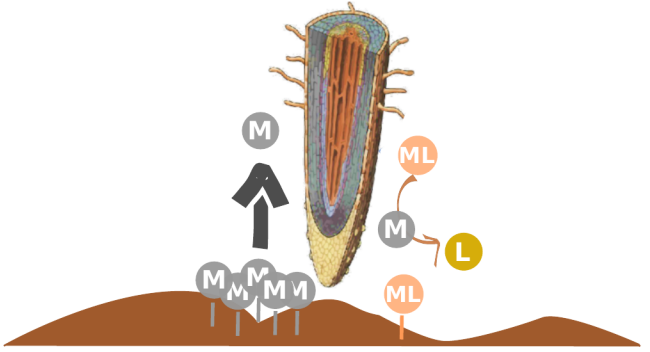
Median = 1.6% Mean=10% Q_{75}=7.5% Q_{90}=23.6%

At the root surface, there is more sorbed Cd^{2+} than CdL



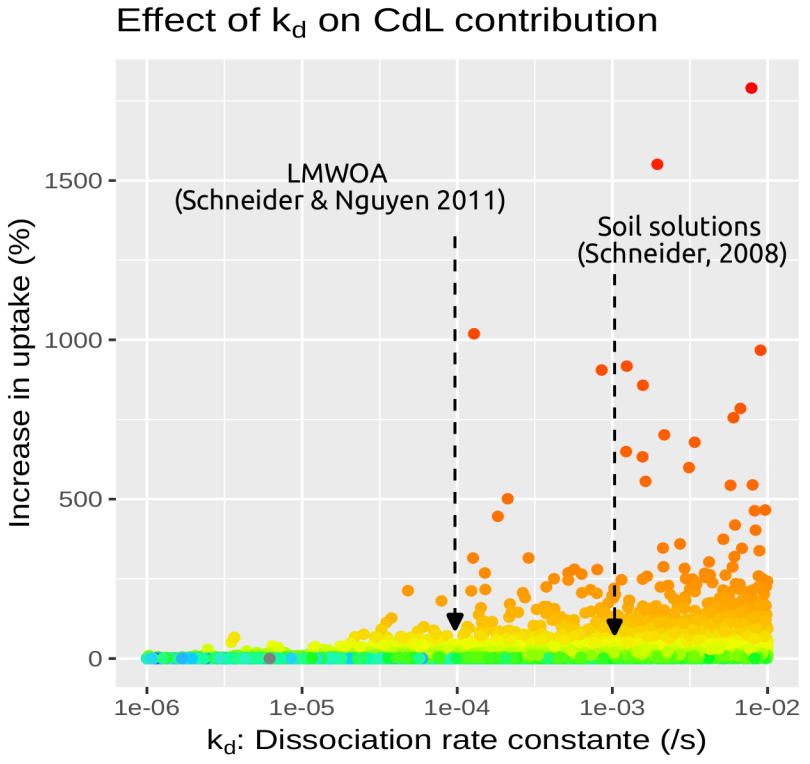


Amount of sorbed Cd > quantity of CdL in the rhizopshere



A significant contribution of CdL to Cd uptake requires dissociation constant >$10^{-5}s^{-1}$

$$Cd^{2+} + L \underset{k_d}{\overset{k_a}{\rightleftharpoons}} CdL$$

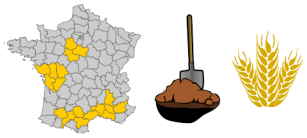


Will this soil give a crop that complies with the regulation limit for Cd ?

Bléssur a tool for predicting compliance of durum wheat to Cd regulation

560 Paired Samples

CaDON
2016-2018



Soil: Total Cd, pH, organic C, clay, loam, calcareous
Grain: Cd

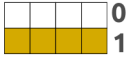
Statistical Modeling

Proba(Y=1) =f(Soil predictors+Variety)

Machine learning
Random Forest
Logistic regression

Cross validation for model selection

Calibration



Test

Model performances

	Detection	Reliability
Compliance	**88%**	**89%**
Non-compliance	**82%**	**75%**

Web application

Bléssûr

https://ispa.bordeaux.inra.fr/services/blesur/

INRAE Interactions Sol Plante Atmosphère
ARVALIS Institut du végétal
ANR-10-LBX-45

Nguyen *et al.*, 2021. *J. Hazard. Mat.*

Compliance models

Details and application to other crops

Efficient models for predicting the non-compliance of food crops with regulation limits for metallic contaminants

Nguyen[1] C., Denaix[1] L., Vivien[1] E., Cornu[1] JY., Roucou[2] A., Méléard[2] B.

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2: Arvalis Institut, Boigneville France

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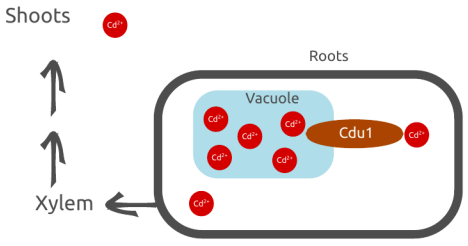
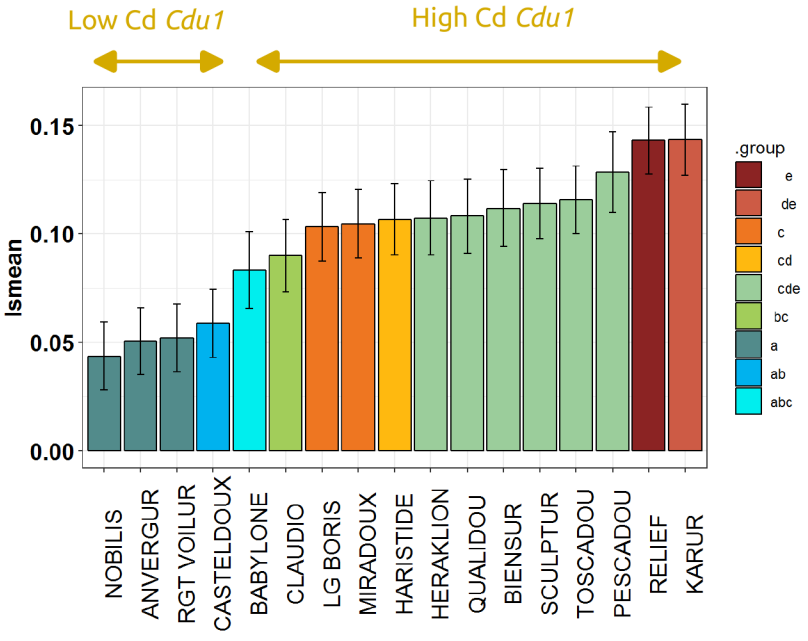
Will this future harvest comply with the regulation limits for toxic metals in food products?

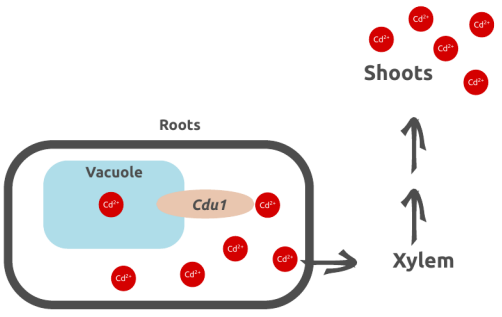
See poster # ***P236***

Varietal differences in Cd accumulation as a lever to manage crop contamination



Maccaferri et al., 2019



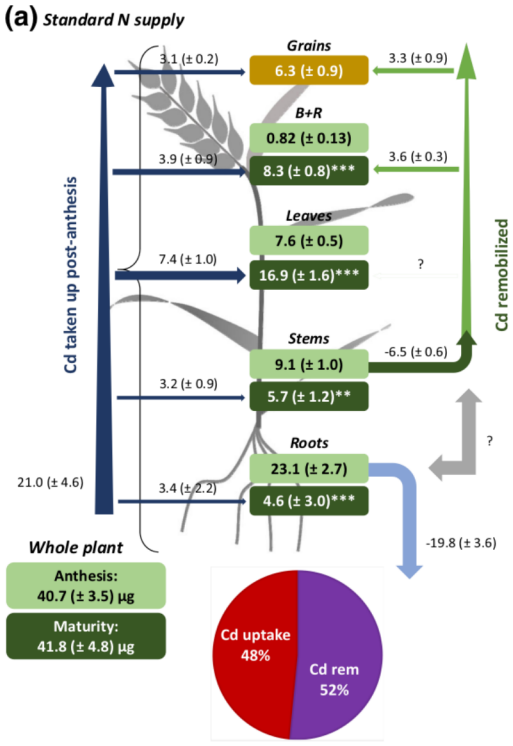


BSWheat: Breeding Safe Wheat

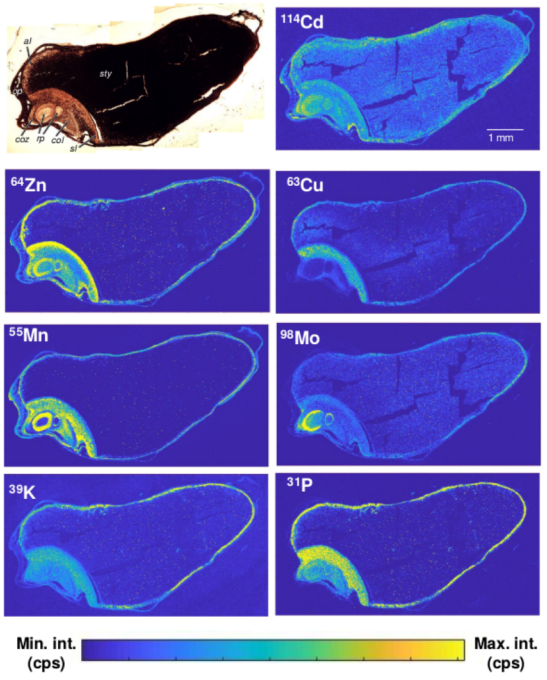
Identifying genetic markers and ecophysiological traits in wheat
for reducing the accumulation of toxic metal(oid)s (Cd, As, Ni, Pb)

https://bswheat.hub.inrae.fr/

Traits for the varietal differences in Cd accumulation



Yan *et al.*,2018. *Plant Soil.*



Yan *et al.*, 2020. *Envir. Pollut.*

Plant traits potentially related to Cd accumulation in grains

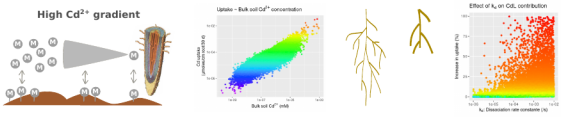
- Remobilization efficiency
- Spike /grain structure
- Biomass allocation
- etc....

Summary: *Yes modelling can help reducing crop contamination!*

On average for Cadmium

- Root uptake capacity and plant transpiration affect little Cd uptake
- Uptake of Cd favored by high lengths of thin and branched roots
- Cd^{2+} bulk soil x2 = uptake x1.5
- Possible important contribution of CdL complexes for $k_d > 10^{-5} s^{-1}$

SimTraces
anr ANR-2011-CESA-008-01
https://bswheat.hub.inrae.fr/
Lin *et al.* 2016, Plant & Soil, n°399



- *Cd^{2+} strongly depleted at the root surface*
- *Convection contributes little to root uptake of Cd*
- *Roots are supplied with Cd^{2+} by diffusion*
- *Cd complexes contribute little to Cd uptake compared to desorption*
- *The contribution of CdL is governed by the rate constant of CdL dissociation*

- Machine learning- based models can efficiently predict compliance

Web application

Blessûr
https://ispa.bordeaux.inra.fr/services/blesur/
INRAE ARVALIS ANR-10-LBX-45

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B-SWheat
BREEDING SAFE WHEAT
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anr ANR-22-CE34-0023

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SimTraces — https://bswheat.hub.inrae.fr/
anr — ANR-2011-CESA-008-01

Web application
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anr — ANR-10-LBX-45

B-SWheat BREEDING SAFE WHEAT — https://bswheat.hub.inrae.fr/
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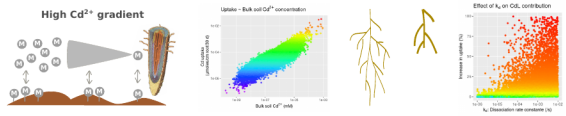

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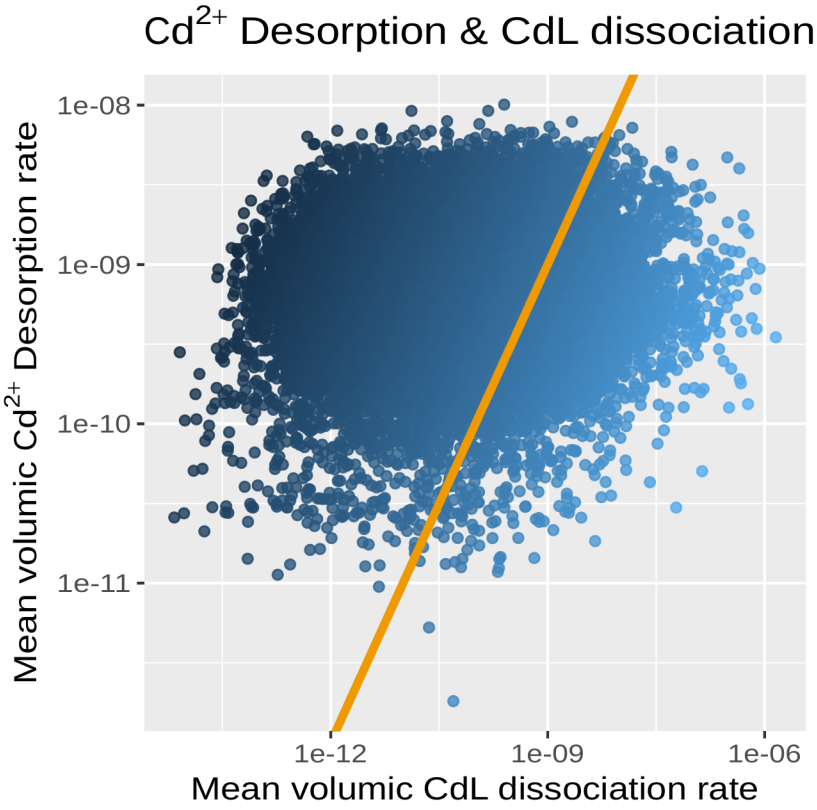
anr ANR-22-CE34-0023

That's all Folks!

Thank you !

At the root surface, Desorption of Cd^{2+} dominates compared to CdL dissociation

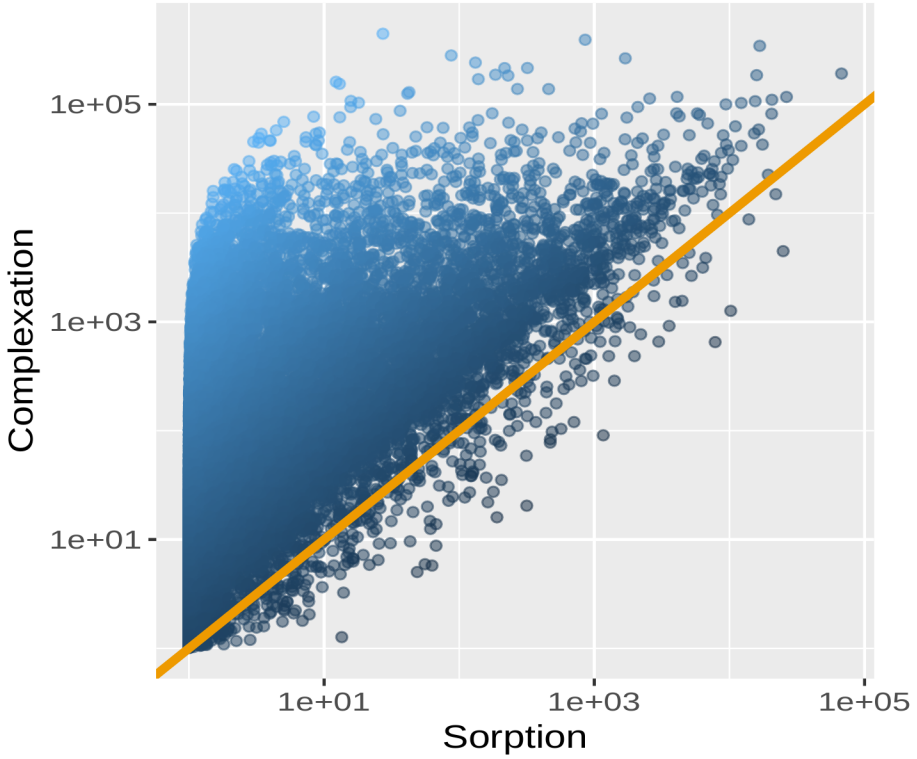


For 78% of cases
Desorption > CdL dissociation

At the root surface, replenishment of Cd^{2+} mainly results from desorption and less from CdL dissociation

Kinetics of CdL dissociation is low compared to that of desorption

Departure from equilibrium (Values >1)



CdL dissociates more slowly than the desorption of Cd^{2+}