

Uptake and translocation of arsenic species and cadmium in rice grain



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COMMISSION REGULATION (EU) 2015/1006

of 25 June 2015

amending Regulation (EC) No 1881/2006 as regards maximum levels of inorganic arsenic in

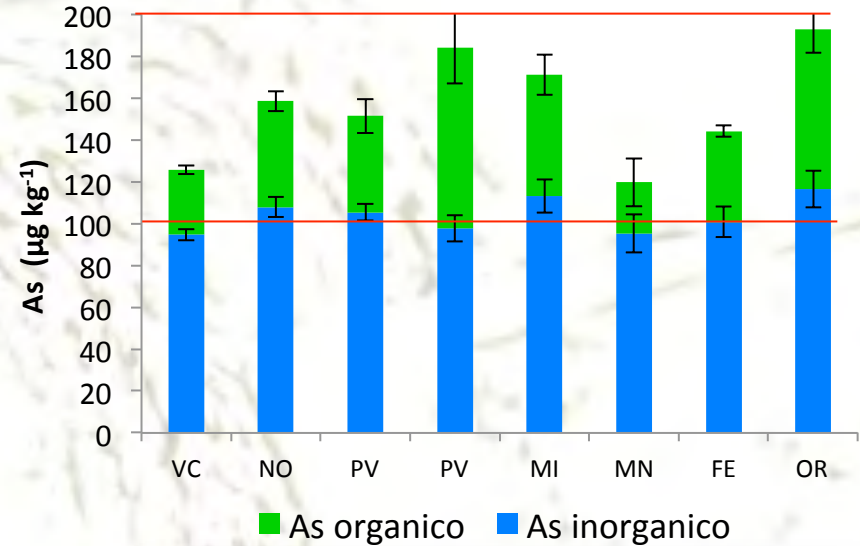
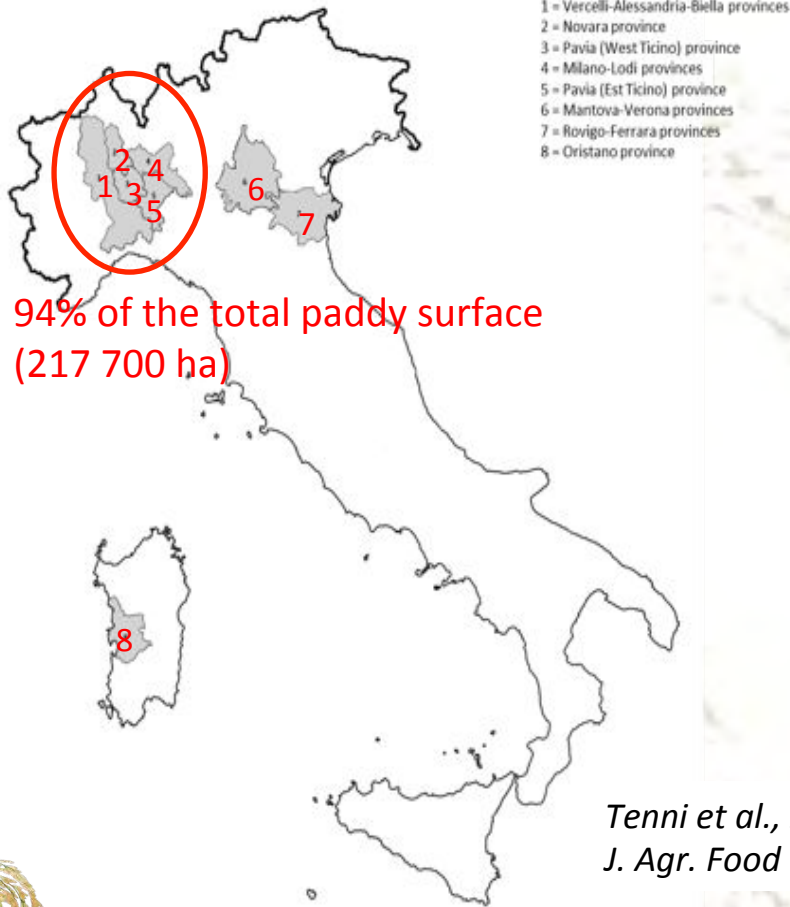
(1) the following subsection is introduced after Subsection 3.4 Tin (inorganic):

3.5	Arsenic (inorganic) ⁽⁵⁰⁾ ⁽⁵¹⁾	
3.5.1	Non-parboiled milled rice (polished or white rice)	0,20
3.5.2	Parboiled rice and husked rice	0,25
3.5.3	Rice waffles, rice wafers, rice crackers and rice cakes	0,30
3.5.4	Rice destined for the production of food for infants and young children ⁽⁷⁾	0,10

Regulation (EU) 488/2014

Total cadmium in rice and other cereals: 0.20 mg/kg; rice for baby-food: 0.040 mg/kg

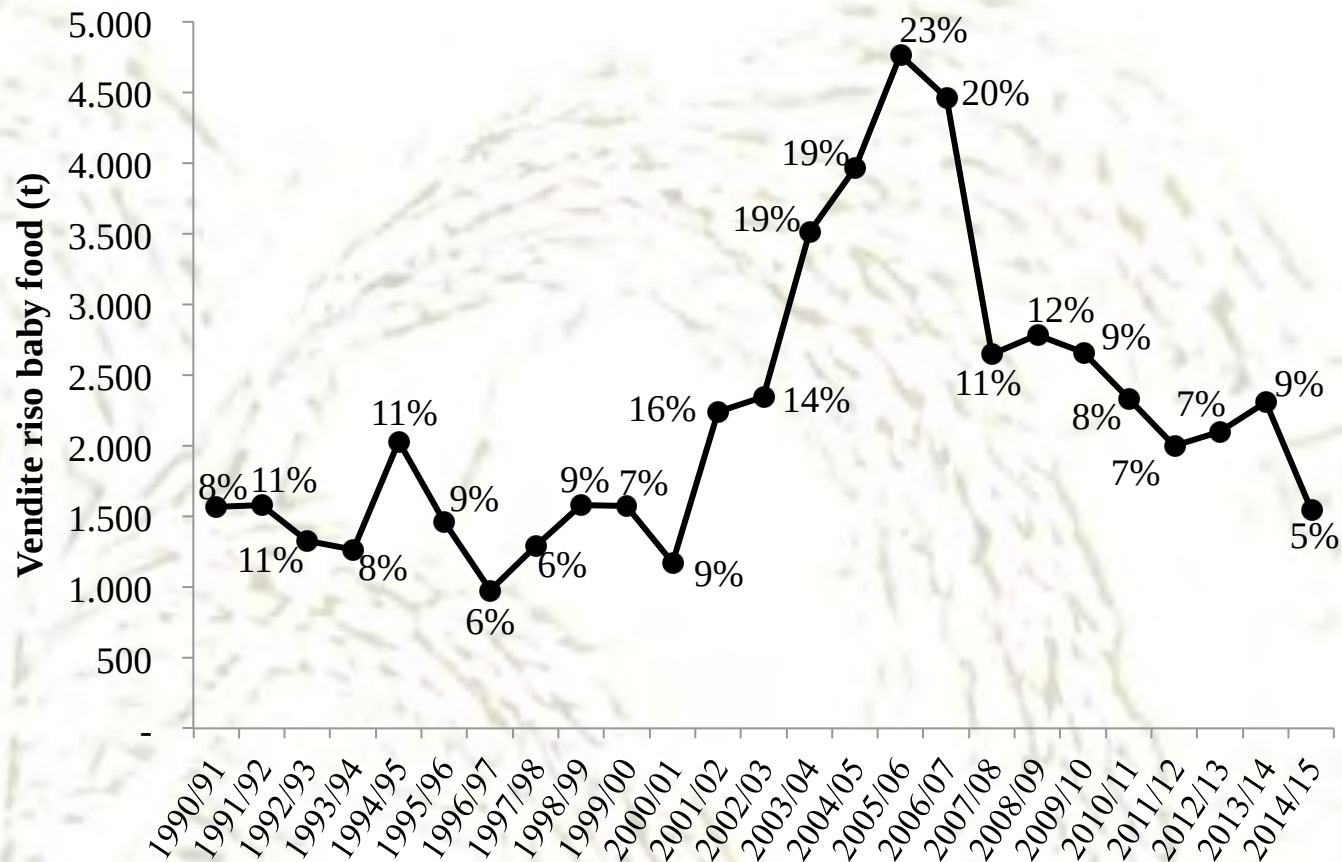
As in Italian rice



Italian mean:

Total As: **$155 \pm 65 \mu\text{g kg}^{-1}$**

Inorganic As: **$102 \pm 26 \mu\text{g kg}^{-1}$**



As in rice grain and in the paddy soils of the Po Plain

Grain total As ($\mu\text{g/kg}$)

Mean 161.7

Median 143.5

Standard deviation 83.3

Min. 55.8

Max. 585.9

Grain inorganic As ($\mu\text{g/kg}$)

Mean 98.5

Median 100.9

Standard deviation 28.6

Min. 44.3

Max. 158.0

Soil total As (mg/kg)

Mean 9.3

Median 7.6

St. dev. 6.5

Min. 2.9

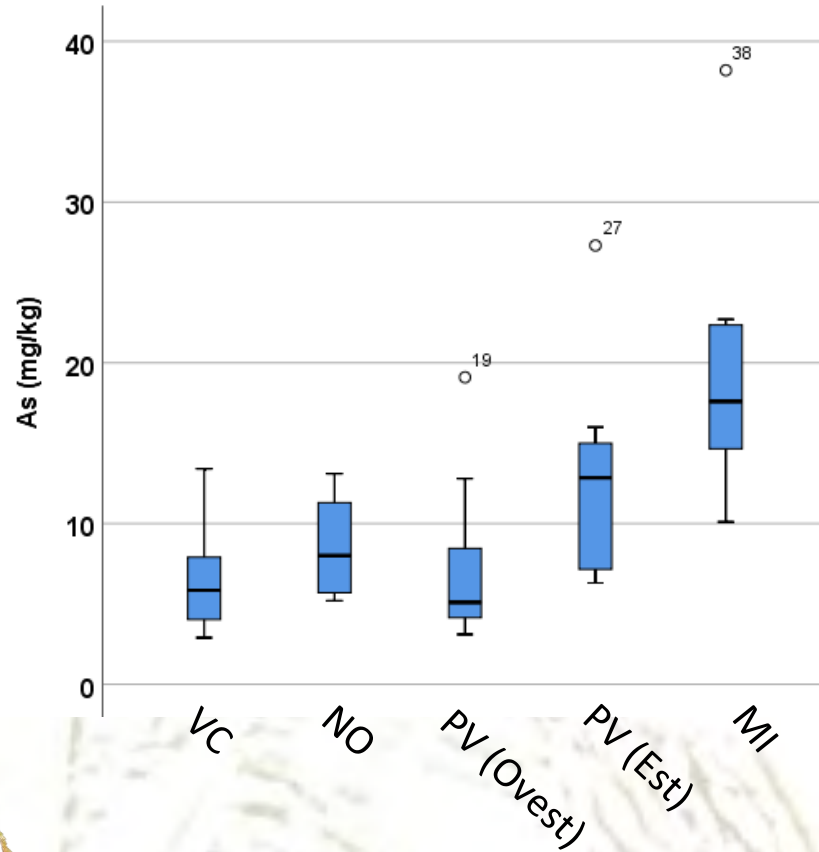
Max 38.2

Mean [As] in world : $\sim 7.5 \text{ mg/kg}$;

Mean [As] in european soils: $\sim 9 \text{ mg/kg}$

Italian [As] limit in green areas: 20 mg/kg

As in rice grain and in the paddy soils of the Po Plain



Soil total (mg/kg)

As

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Median 7.6

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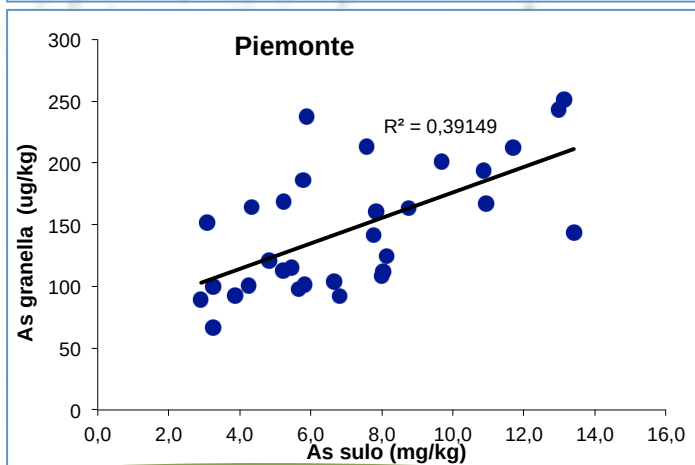
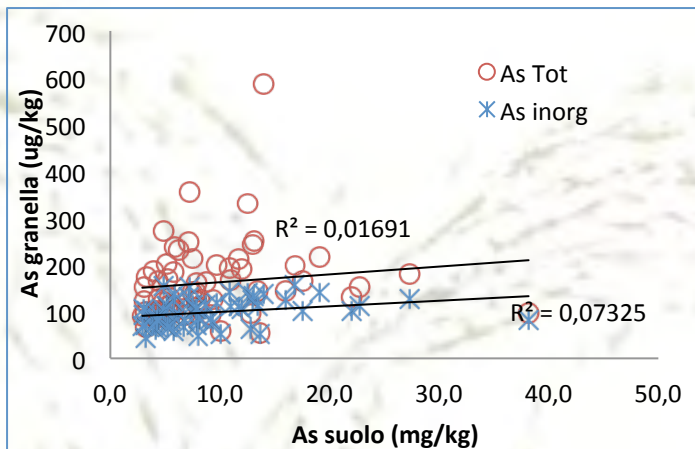
Max 38.2

Mean [As] in world : ~7.5 mg/kg;

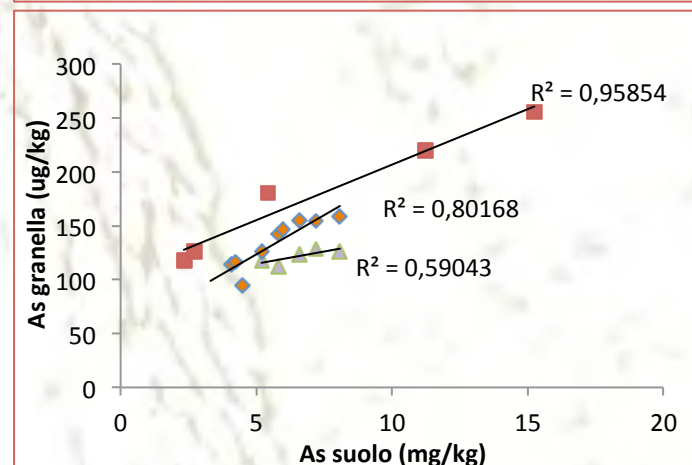
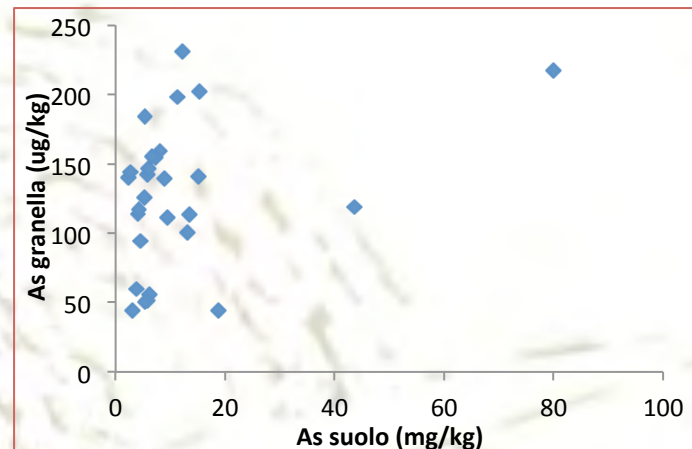
Mean [As] in european soils: ~ 9 mg/kg

Italian [As] limit in green areas: 20 mg/kg

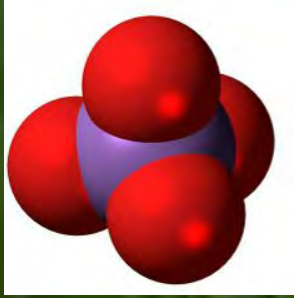
Survey 2008-2012



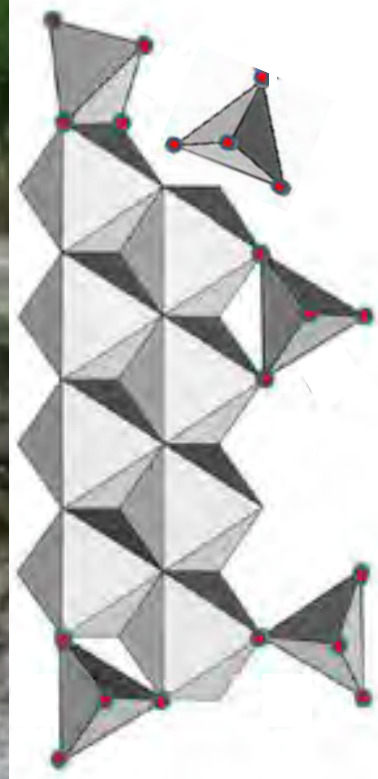
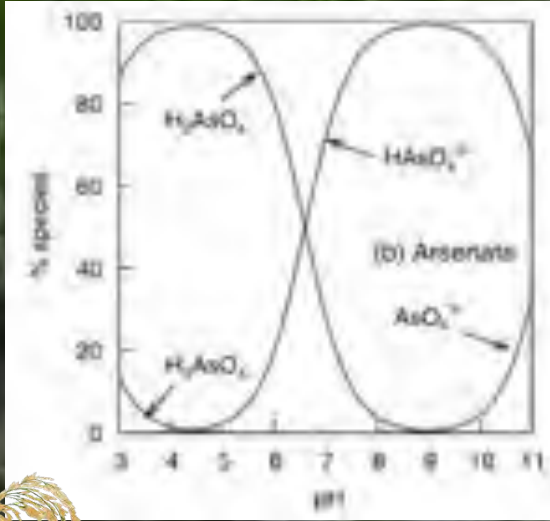
Progetto Babyrice (2016-18)



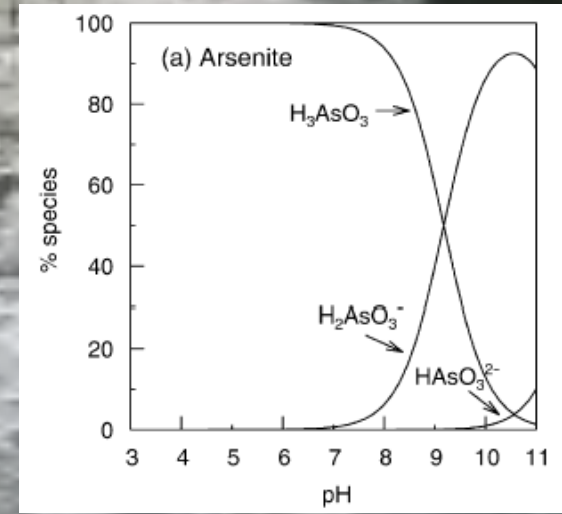
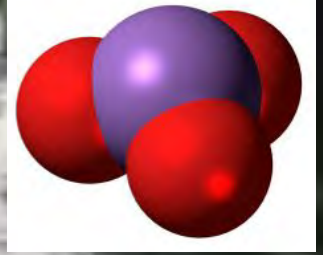
As dynamics in paddy soils...



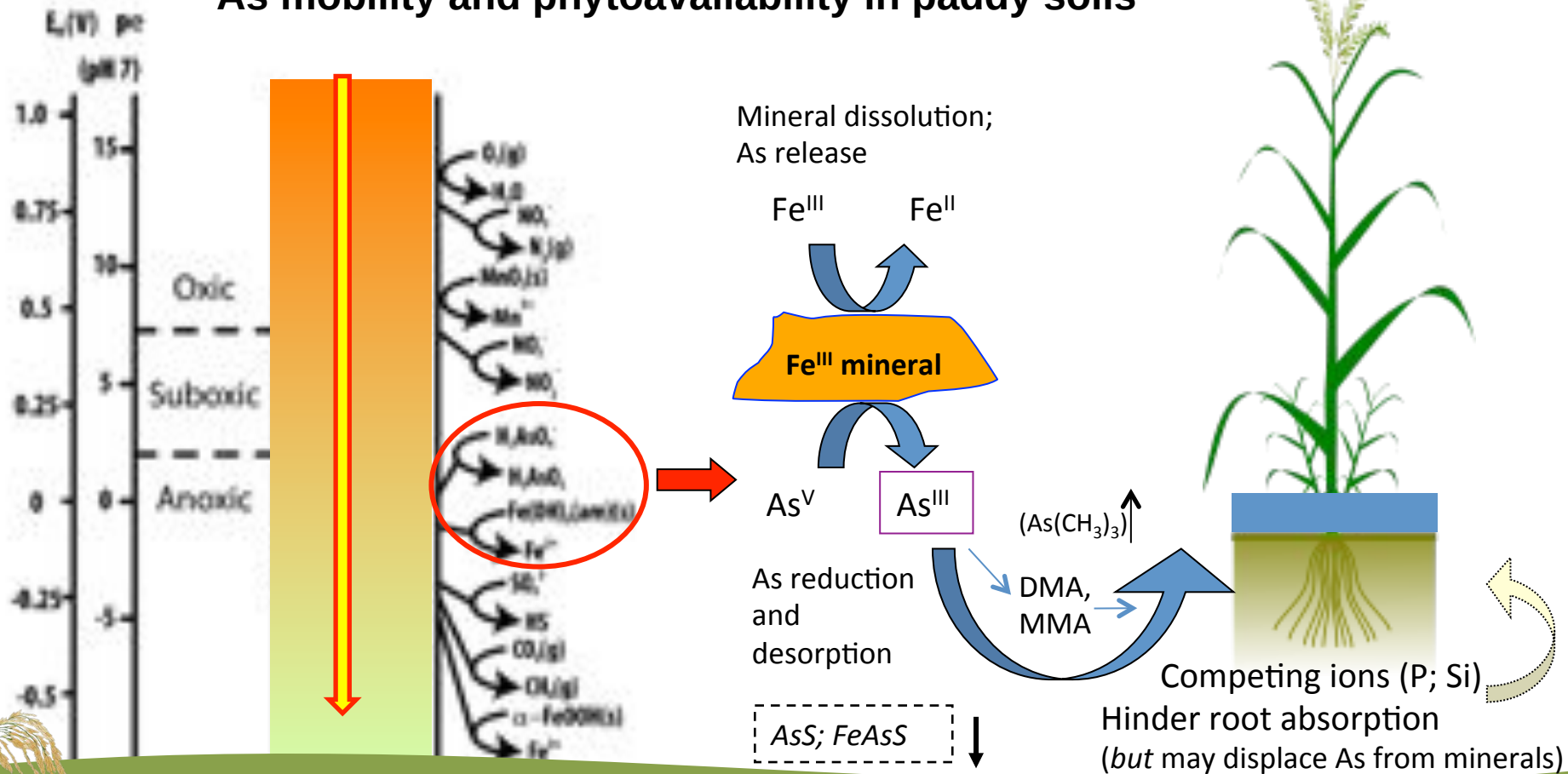
As(V)



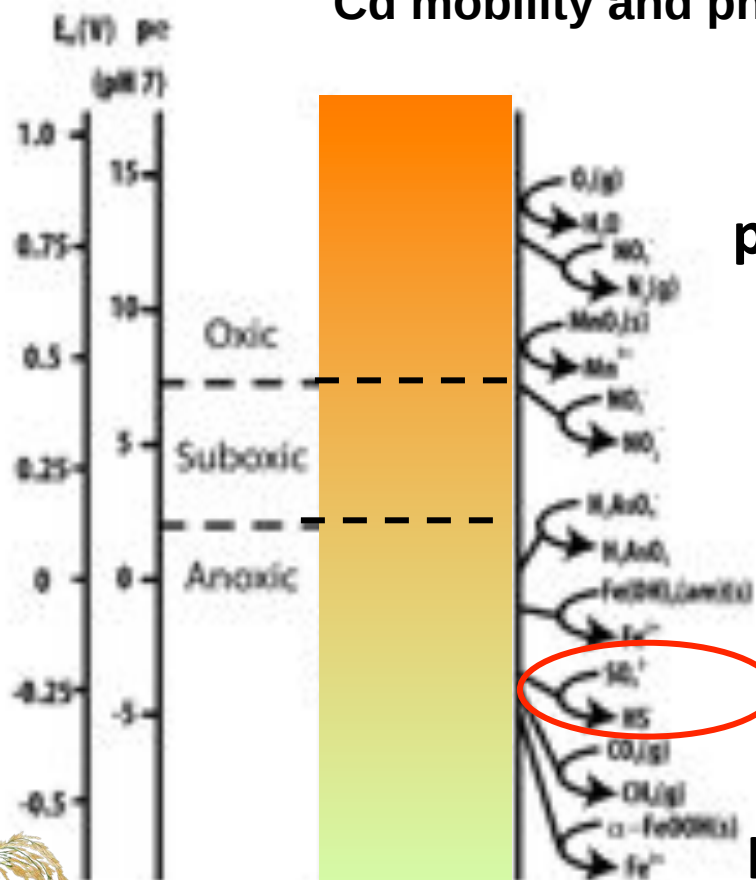
As(III)



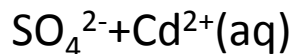
As mobility and phytoavailability in paddy soils



Cd mobility and phytoavailability in paddy soils



pH ↓
Increased solubility
solid phases
 CdCO_3 ; $\text{Cd}(\text{OH})_2$



CdS

*but: release Cd adsorbed
on Fe oxides*

pH ↑

Stable solid phases:
 CdCO_3 ; $\text{Cd}(\text{OH})_2$



How to estimate available As ...in paddy soils

Soil extractants

H₂O
0.01 M CaCl₂
0.05M (NH₄)₂SO₄
0.05M NH₄H₂PO₄
0.5M NaHCO₃
Ion exchange resins

Soluble, exchangeable

EDTA
DTPA

?

0.2M NH₄-oxalate pH 3
0.2M NH₄-oxalate + ascorbic ac. /DCB
Aqua regia (+ H₂O₂)
Acid mixture+HF

Bound to solid phases



Determination of As forms in soils ...

Sequential extractions (a few examples):

Chang and Jackson (1957)

1M NH_4Cl ; 0.5M NH_4F ; 0.1M NaOH ; 2M H_2SO_4 ; DCB

Tessier et al. (1979)

1M MgCl_2 ; 1M NaOAc ; 8.8 M $\text{H}_2\text{O}_2/\text{HNO}_3 + 0.8 \text{ M } \text{NH}_4\text{OAc}$; 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$; HF/HClO_4

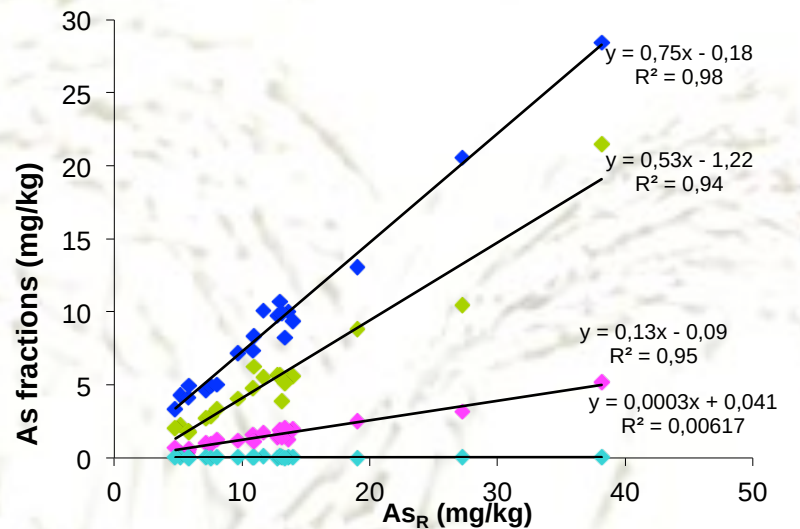
Hedley and Stewart (1982)

Resins in H_2O ; 0.5M NaHCO_3 ; 0.1M NaOH ; 1M HCl ; $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$

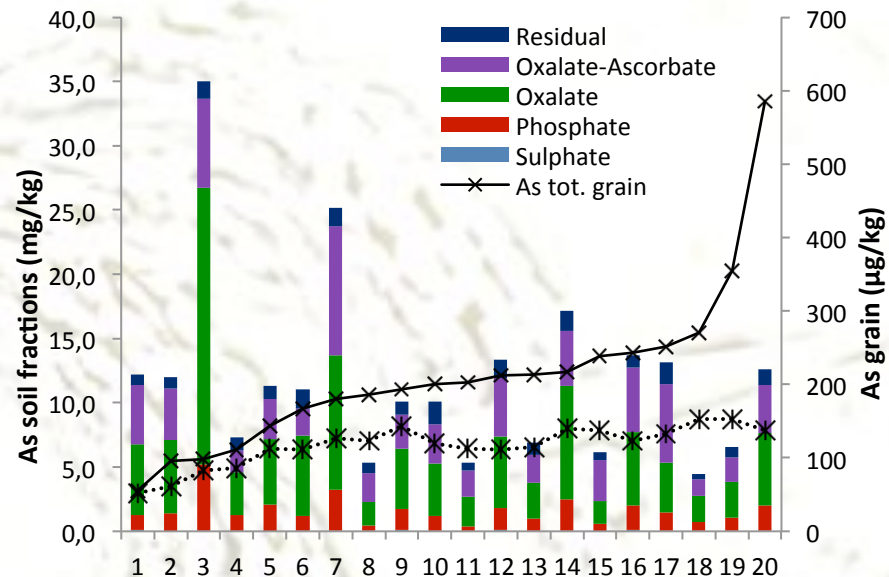
Wenzel et al. (2001)

- 0.05M $(\text{NH}_4)_2\text{SO}_4$ ----- weakly bound (soluble)
- 0.05M $\text{NH}_4\text{H}_2\text{PO}_4$ ----- adsorbed (exchangeable)
- 0.2M NH_4 -oxalate pH 3 ----- poorly ordered oxides
- 0.2M NH_4 -oxalate+ ascorbic acid ----- crystalline Fe oxides
- $\text{HNO}_3/\text{H}_2\text{O}_2$ ----- residual





◆ Free Fe oxides ◆ Poorly ordered oxides ◆ Exchangeable ◆ Soluble



Babyrice 2018	As-T grain	As-I grain	As-Org. grain
As Olsen	0.600*	0.527*	0.595*
As citrate	0.504	0.452	0.546*
As oxalate	0.254	0.289	0.288
As DCB	0.305	0.299	0.352
As regia	0.545*	0.516*	0.595*

...to estimate available As in paddies ...

Field studies: Soil solution

- Lisimeters (porous cups; Rhizon samplers)
- Anion exchange resins
- DGT



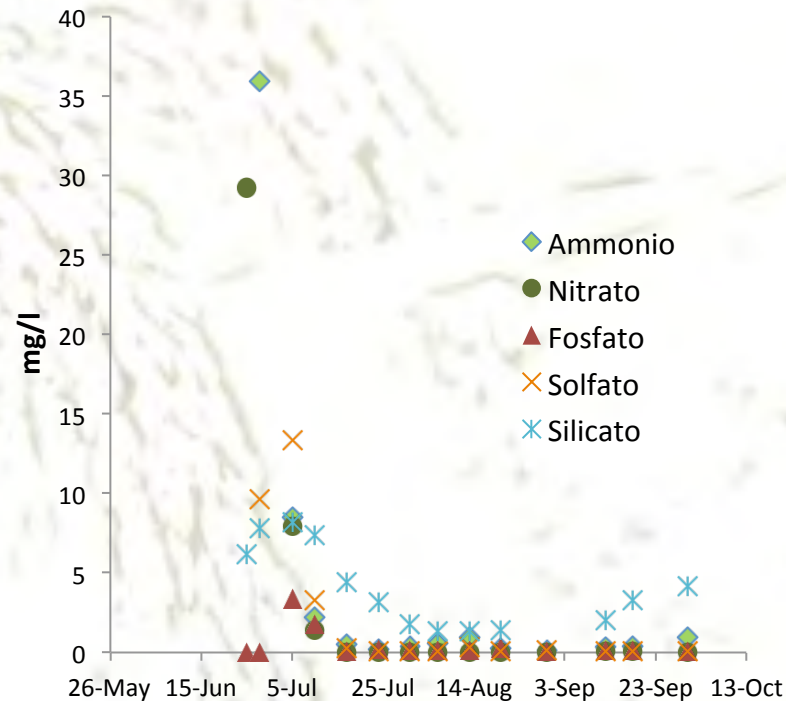
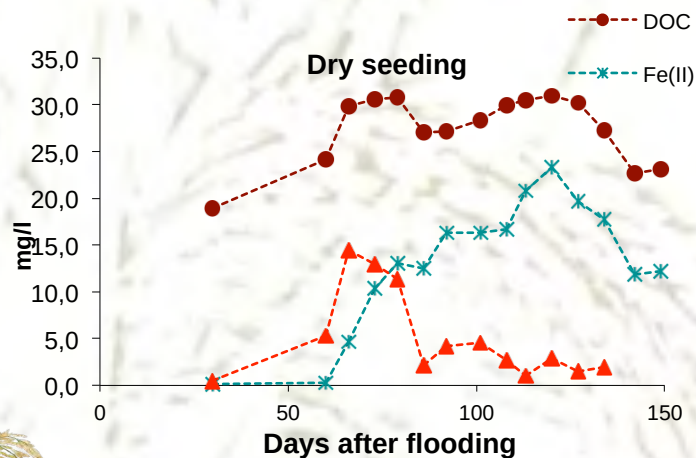
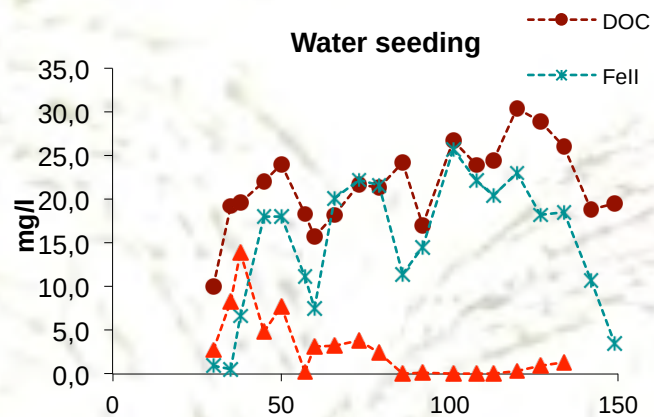
Preservation of As speciation:

- Sample uptake
- Extraction
- Storage
- analysis

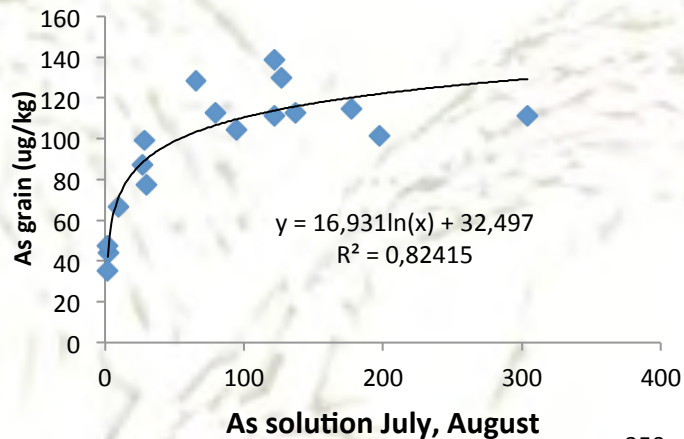
- Vacuum/inert gas
- Cooling/Freezing
- Acidification (HNO_3 ; HCl)
- Fe-complexing molecules (EDTA; DTPA; ...)

- Oxidation:
 - As (speciation changed)
 - Fe (coprecipitation Fe-As)
- Changes in extractability (from solids)
- Artifacts

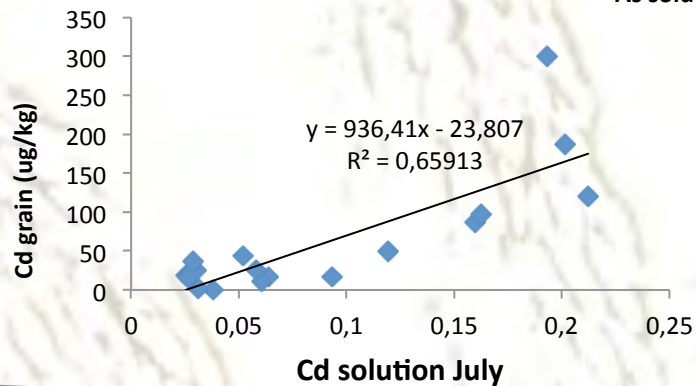
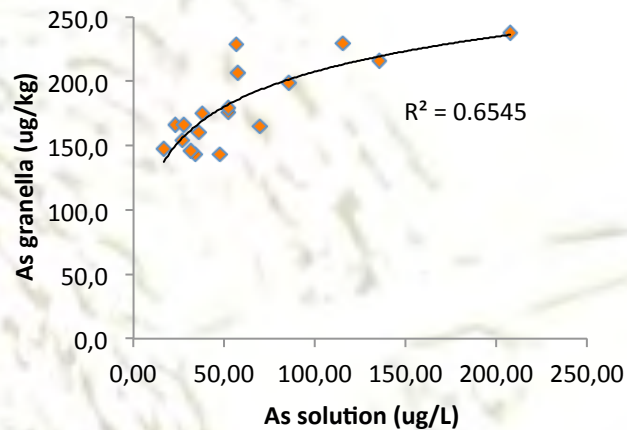




Babyrice project 2017



Babyrice project 2018



Analisi e speciazione dell'As nella granella di riso



AISETOV- PIACENZA

21 giugno 2019

As extraction from plant tissues and rice grain

Total As:

HNO₃

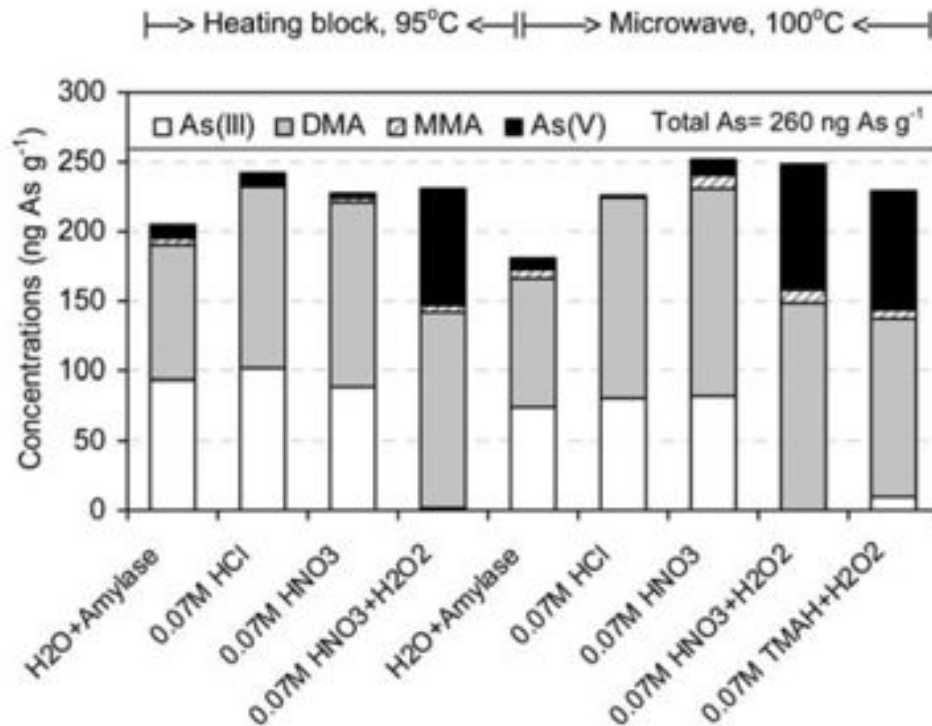
HNO₃ + H₂O₂

Incineration + HCl

.....

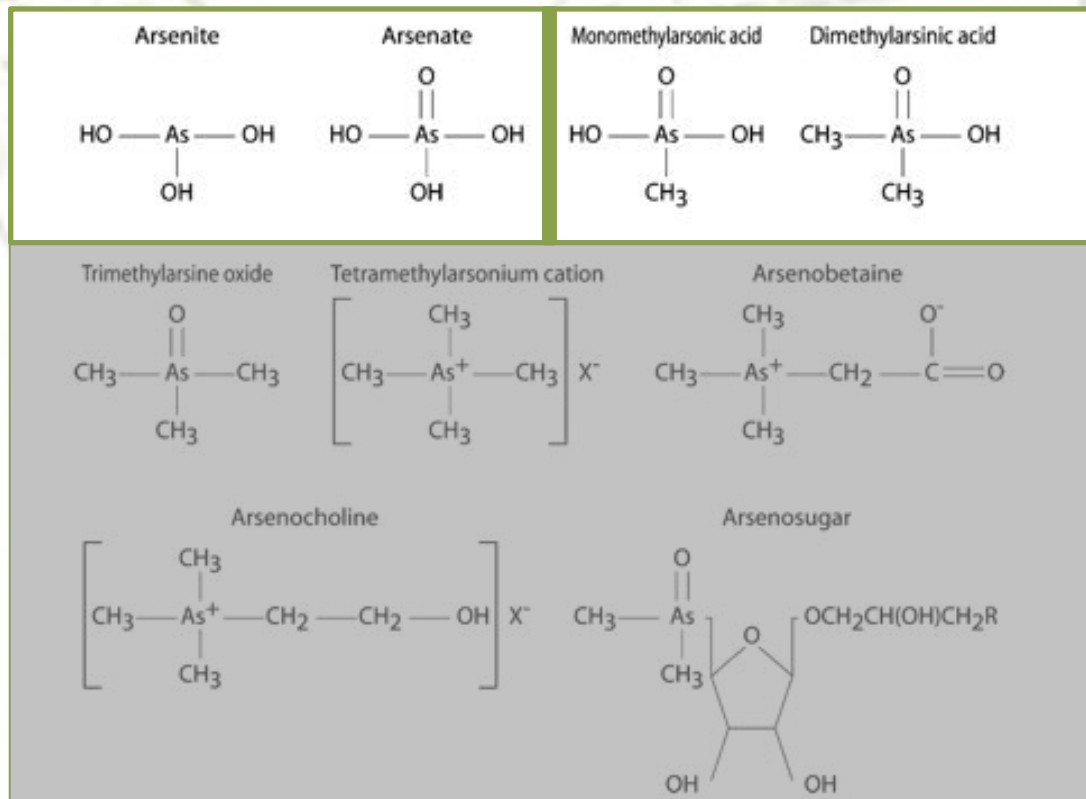
Speciation

- 2M Trifluoroacetic Ac
- Enzymatic extractions
- HCl (H₂O₂)
- HNO₃ (H₂O₂)
- 1-2% HNO₃ (95°C)
-



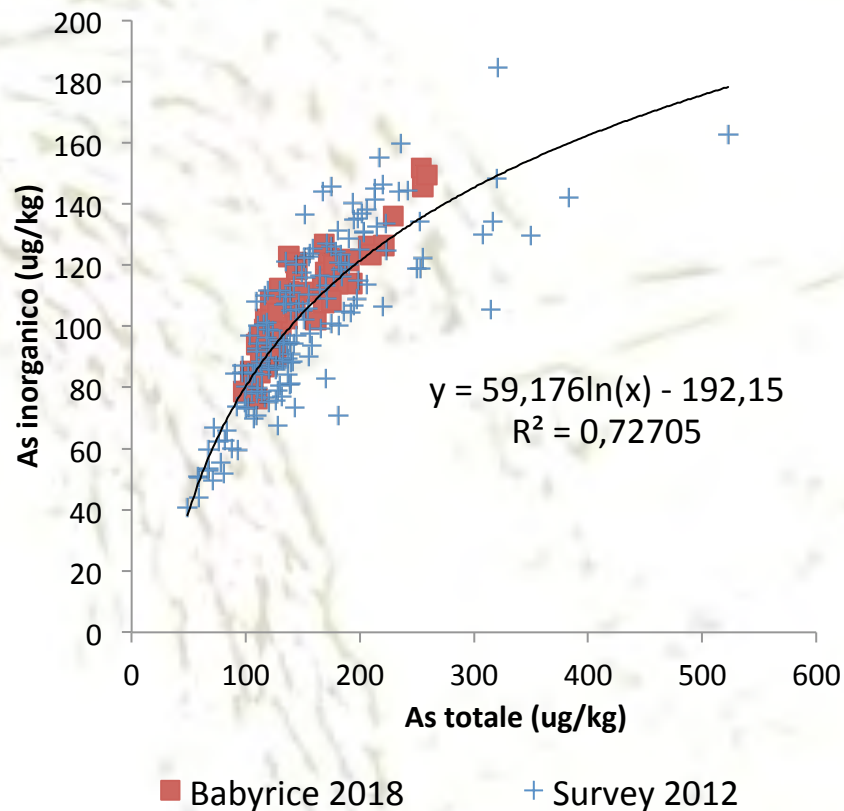
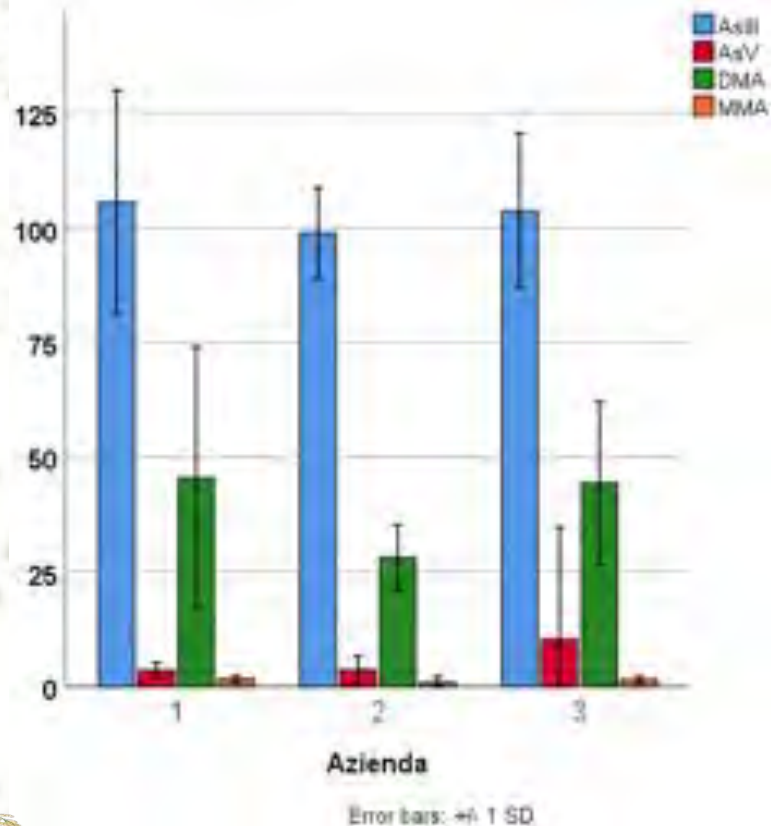
Huang et al. (2010)

As species commonly detected in plants



From: Quaghebeur and Rengel, *Microchim Acta* 151, 141–152 (2005)

As species commonly detected in rice



Monothioarsenate Uptake, Transformation, and Translocation in Rice Plants

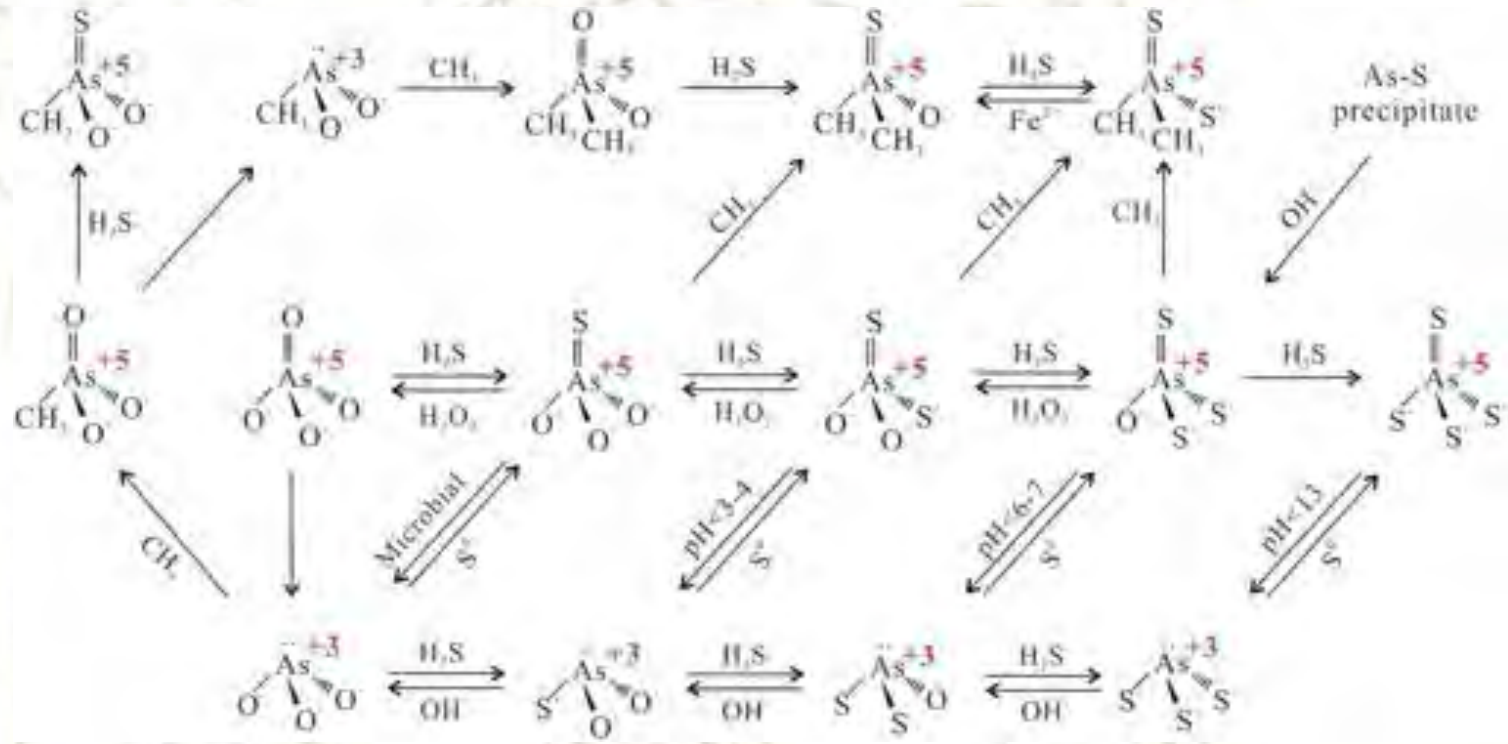
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[†]Environmental Geochemistry, Bayreuth Center for Ecology and Environmental Research (BayCEER), University of Bayreuth, D-95440 Bayreuth, Germany

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Thio-As species

have been detected in rice fields and in rice grain





***Thank you
for your attention***

AISETOV- PIACENZA

21 giugno 2019

Total As concentrations in rice and other cereals

TABLE 1. Arsenic Distribution in Rice, Wheat, and Barley Grain, Shoot, and Soil by Production Region

crop	country	region	As level, $\mu\text{g g}^{-1}$
rice (<i>Oryza</i>)	France	Carmarque	grain
			shoot
	Spain	Doñana	soil
			grain
		Cadiz	shoot
			soil
	U.S.A.	California	grain
			shoot
		Arkansas	soil
			grain
wheat (<i>Triticum</i>)	Scotland	East Coast	shoot
			soil
	England	Cornwall, Devon	grain
			shoot
barley (<i>Hordeum</i>)	Scotland	East Coast	soil
			grain
	England	Cornwall, Devon	shoot
			soil

Rice grain
mean: 0.19

Wheat and Barley grain
mean: 0.06

*Williams et al., Environ.
Sci. Technol.* **2007**, 41,
6854-6859

