Isotopic techniques and their role in designing new P-availability tests for weathered, P-fixing soils

R. Merckx, L.Six, P. Pypers and E. Smolders

International Symposium on Managing Soils for Food Security and Climate Change Adaptation and Mitigation
23-26 July 2012, Vienna, Austria

DEPARTMENT OF EARTH AND ENVIRONMENTAL SCIENCES
K.U.LEUVEN - BELGIUM

Contents

- Introduction
  - P-availability
  - Isotopic techniques
  - Weathered soils, something specific?
- Anion Exchange Membrane-P
- E- and L-values
- Intensity or Quantity?
- DGT-P
- Conclusion

The available fraction of and element X equals that ***fraction*** *of the total amount of element X* ***present in the rootzone*** *which* ***can*** *be taken up by a given plant in* ***one single growing season*** *when* ***transport in the soil is not limiting*** *(infinite root density) and* ***uptake capacity infinitely high****. (de Willigen and van Noordwijk, somewhere in the 80's)*

- ✓ Only a part… out of a continuum
- ✓ Time dimension: kinetics…
- ✓ A potential…
- ✓ Plant dependent…

The role of isotopic techniques?

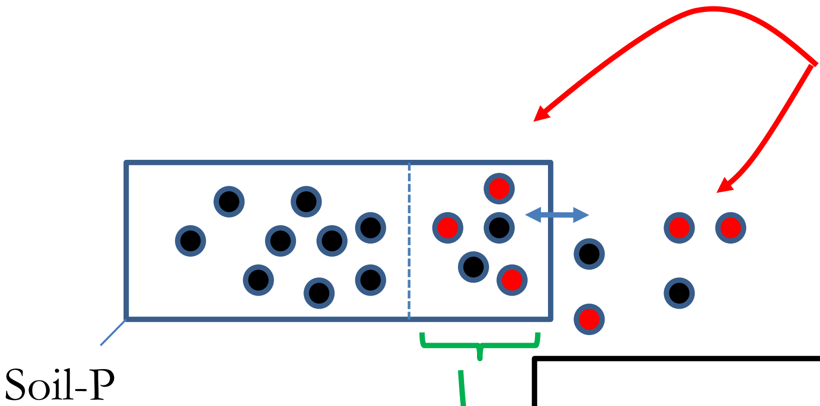
Hypothesis: A soil test that samples nutrients only from fractions that are accessible to plants will predict availability and uptake more robustly than empirical tests.

Hence: correspondence of specific activity (SA) values ($^{32}P/^{31}P$) between soil tests and plant P is a conceptual but not sufficient requirement for a good availability test

Or: If $SA_{shoot} = SA_{P\text{-}test}$ → The same pool of P is accessed during plant growth and soil P test.

Isotope dilution, something from the sixties…

E-value: a measure of the labile (= available?) P-pool



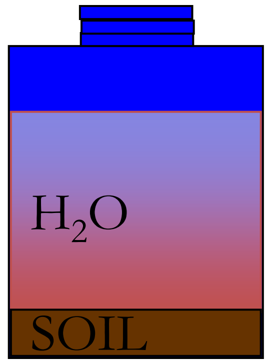
R= Bq added $^{32}P\text{-}H_2PO_4$
to M [kg] soil and V (L) soil solution

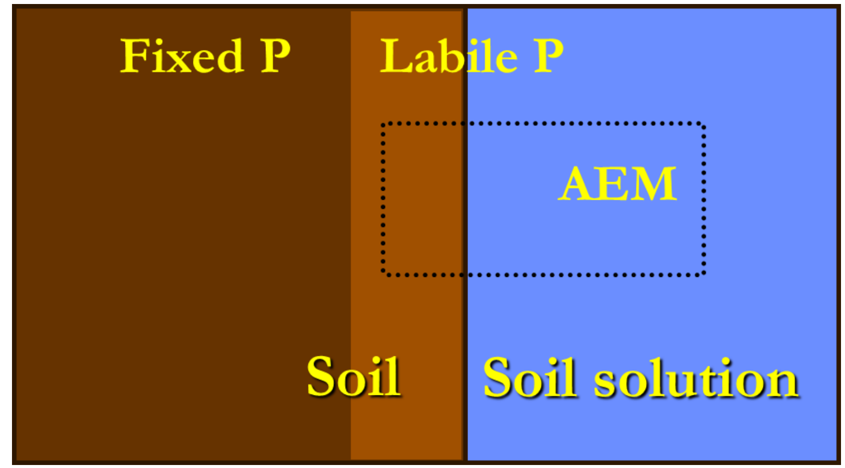
- ^{31}P
- ^{32}P

$$E = C_{H_2PO_4^-\,\text{soil solution}} \left[\frac{V}{M} + K_d\right] \text{ (mg P/kg soil)}$$

Assumption is that after time t:
SA of P in soil solution = SA of P in **available pool**

$E_{\text{Water extract}}$ versus E_{AEM}





$E_{\text{Water extract}}$

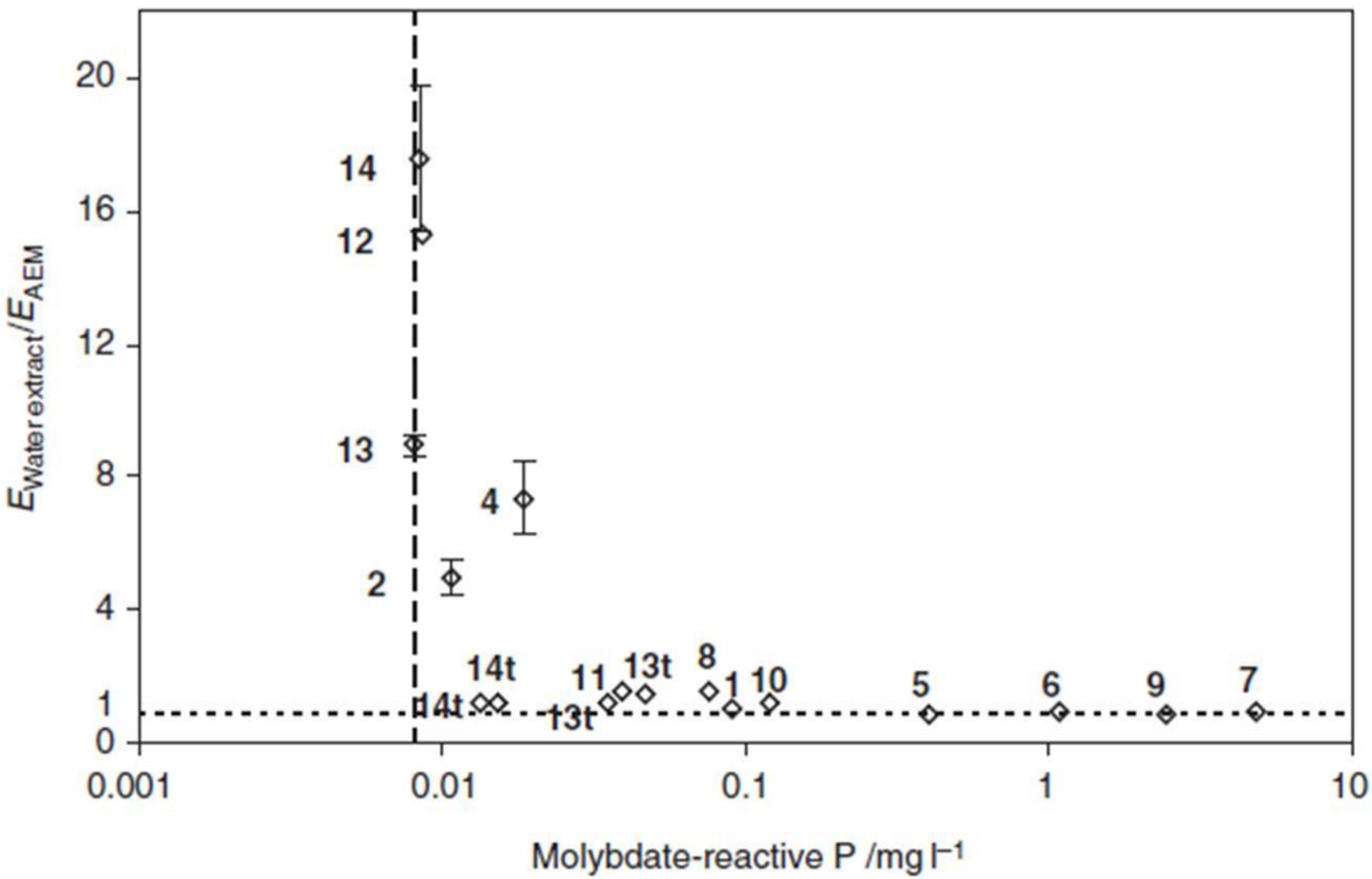
$$E_{WaterExtract}(t) = \frac{C_{^{31}\text{PO}_4,\text{solution}}}{C_{^{32}\text{PO}_4,\text{solution}}(t)} \frac{R}{M}$$

E_{AEM}

$$E_{AEM}(t) = \frac{C_{^{31}\text{PO}_4,\text{AEM}}}{C_{^{32}\text{PO}_4,\text{AEM}}(t)} \frac{R}{M}$$

Problems with detection limits, colour interference, non ionic species…

E_{water} and E_{AEM} deviate at low concentrations of P_i



(*Maertens et al. 2004, Eur. J. Soil Sci.* ***55****, 63-69.)*

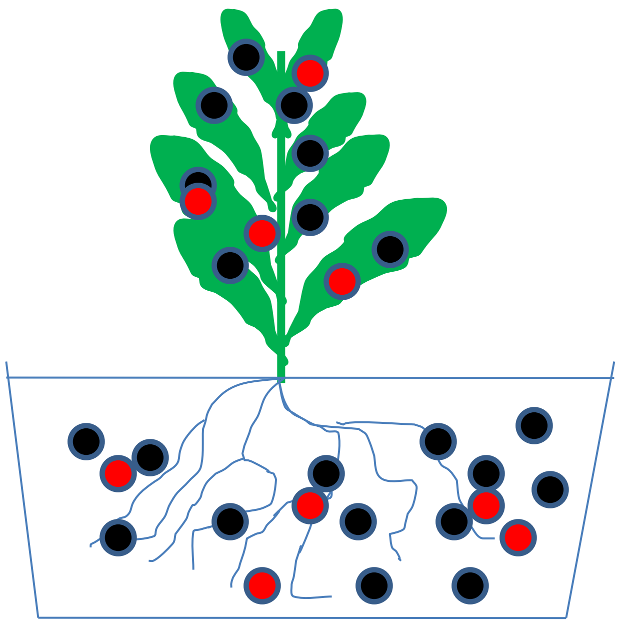
E_{AEM} works at low concentrations of P_i

E_{AEM} responds to treatments whereas E_{water} does not!

Soil	Treatment	MRP	$E_{water\ extract}$	E_{AEM}
		mg P L^{-1}	mg P kg^{-1}	mg P kg^{-1}
13	Control	0.008 (0.000)	172.51 (1.20)	19.26 (0.67)
	KH_2PO_4 + *Tithonia*	0.047 (0.006)	138.92 (7.37)	94.21 (2.77)
	KH_2PO_4 + *Mucuna*	0.036 (0.005)	122.11 (10.79)	98.82 (-)
14	Control	0.008 (0.000)	295.92 (28.49)	16.83 (1.31)
	KH_2PO_4 + *Tithonia*	0.013 (0.000)	120.30 (1.10)	100.75 (3.49)
	KH_2PO_4 + *Mucuna*	0.015 (0.001)	126.26 (8.44)	100.35 (0.23)

(Maertens et al. 2004, Eur. J. Soil Sci. ***55****, 63-69.)*

L-value uses the plant as the extractant…



$$\frac{l}{L} = \frac{r}{R}$$

● ^{31}P

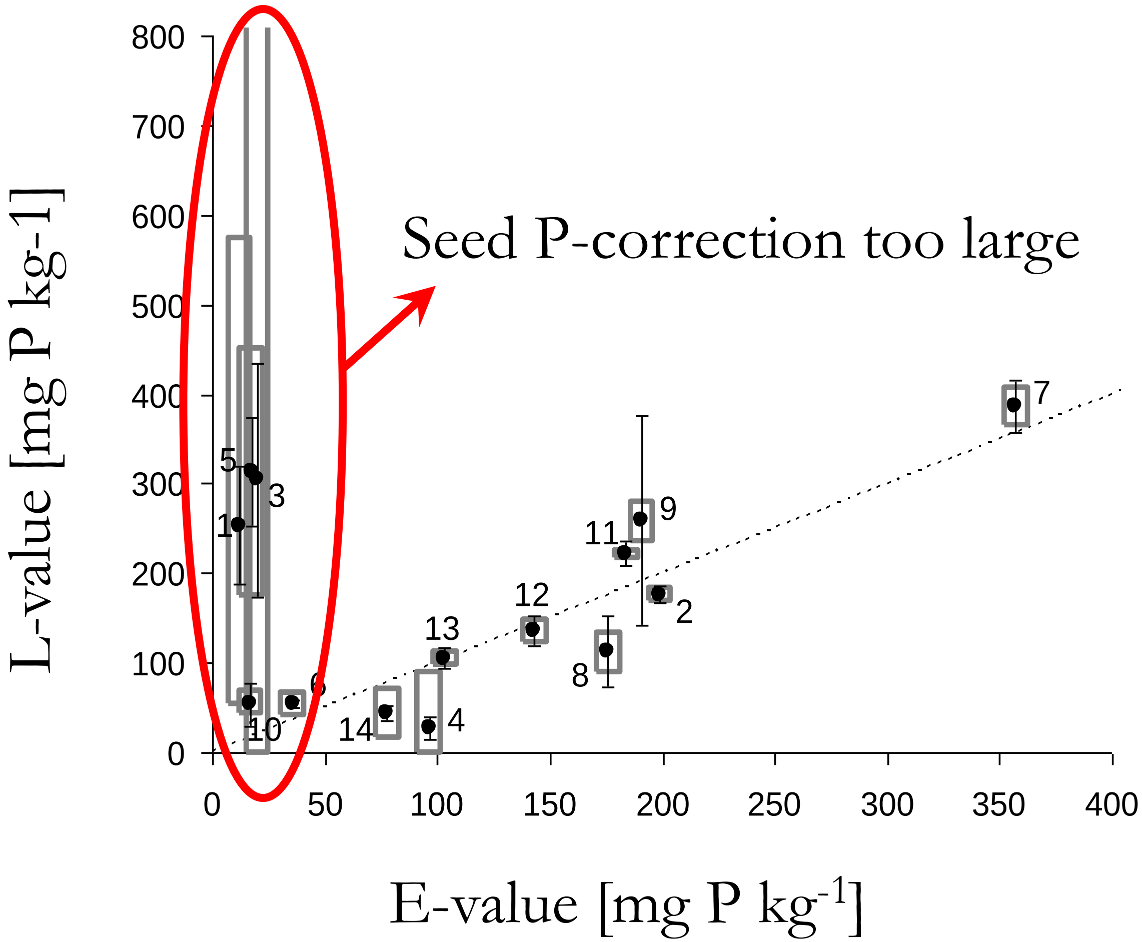
● ^{32}P

R = amount of ^{32}P in soil
r = amount of ^{32}P in plant
l = quantity assimilated P in plant
L = quantity of available P

$$L = \frac{l}{r} . R \quad \text{mg P/kg soil}$$

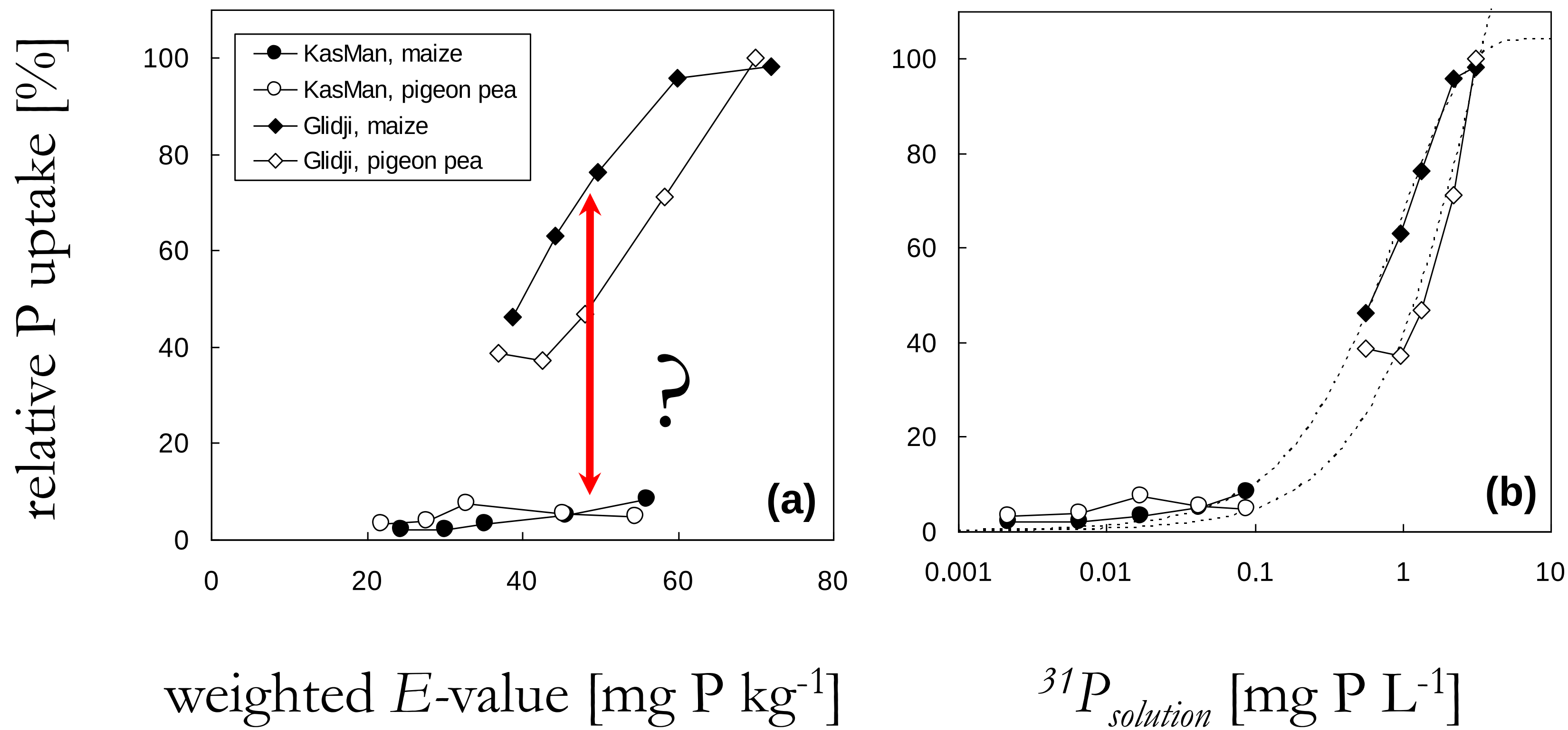
About the correspondence between L and E values…
L/E ratio > 1 indicates…?

L-values correspond with E-values measured with the AEM method (for maize)



DEPARTMENT OF EARTH AND ENVIRONMENTAL SCIENCES
K.U.LEUVEN - BELGIUM

L and E values correspond, but fail to predict P-uptake



(Relative P-uptake is wrt maximal P uptake in Glidji soil)

Rotation effects?

P-uptake by maize following a legume or maize

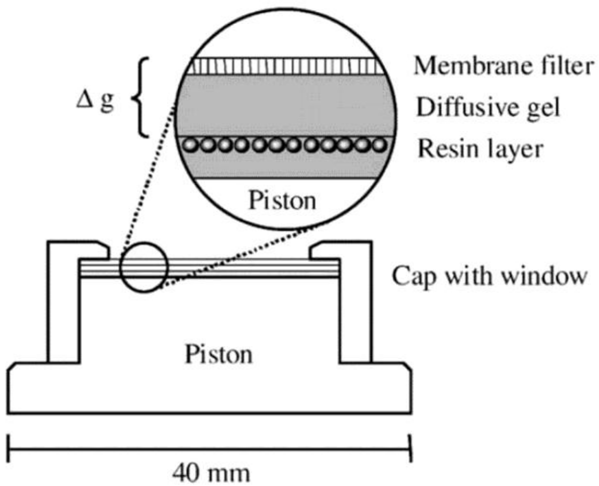
variable(s)	R	multiple regression equation
$^{31}P_{solution}$	0.75	$P\ uptake = 794^{***} + 92.5^{***} \ln(^{31}P_{solution})$
E-value	0.54	$P\ uptake = 108^{***} + 7.59^{***}\ E\text{-value}$

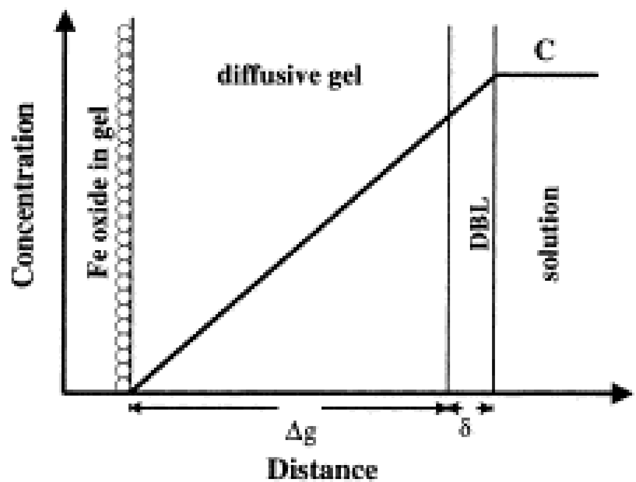
Only 56 and 29% of variation explained by I or Q

Still in search for a better method?

(Pypers et al., 2007, Soil Biol. Biochem. ***39****, 2555-2566.)*

DGT (Diffusive Gradient in Thin films) technique

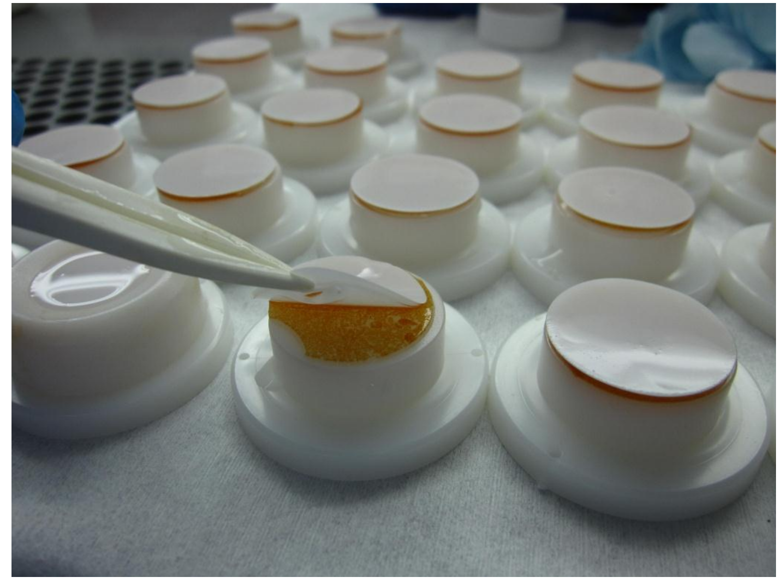




- Principle
  - Binding layer: Ferrihydrite gel = zero sink
  - Diffusive gel -> Fick's 1st law
- Assumptions:
  - P conc in ferrihydrite gel is negligible
  - DBL is negligible

$$C_{DGT} = \frac{M\Delta g}{DtA}$$

M = adsorbed P mass
D = Diffusion coefficient
t = deployment time
A = Exposure Area



- At water saturation instead of soil suspensions
- Both AEM and DGT promote resupply from soil
- DGT has less interferences from other anions
- Diffusive layer limits maximum flux
- No shaking of soil

DGT is a good predictor of nutrient uptake if diffusion controls bio-availability *(Degryse et al. Environ. Chem, 2009).*

Hypothesis: diffusion of P controls P supply to plants in highly weathered soil

Experimental testing for P:

Eight different P availability tests, including DGT, compared for predicting growth response to P in different weathered soils

- comparison of SA's
- comparison of growth response (pot trial: 9 soils, P response curve; 2 plants)

Ratio of the specific activity in shoot to that in soil extract of conventional and new P availability tests. An asterisk (*) represents a significant difference between SA_{shoot} and $SA_{P\text{-}test}$.

	Teso		Sega	
	Low P	High P	Low P	High P
Oxalate	1.35 (0.08)*	1.19 (0.05)	2.36 (0.08)*	1.35 (0.04)*
Olsen	1.05 (0.06)	1.21(0.05)	3.01 (0.19)*	1.35 (0.05)*
Colwell	1.10 (0.07)	1.24 (0.05)*	2.56 (0.20)*	1.26 (0.05)*
Bray-1	0.90 (0.05)	1.16 (0.02)*	1.77 (0.05)*	1.27 (0.04)*
Mehlich-3	0.95 (0.05)	1.18 (0.03)*	1.71 (0.03)*	1.26 (0.04)*
AEM	0.80 (0.06)	1.10 (0.02)	1.42 (0.04)*	1.18 (0.04)*
$CaCl_2$	0.79 (0.05)*	1.01 (0.02)	nd.	1.13 (0.04)*
DGT	1.00 (0.06)	1.04 (0.02)	1.01 (0.02)	1.06 (0.12)

Ratios > 1 indicate sampling from pools not accessible by plants…

(Six et al. 2012 Plant Soil; DOI: 10.1007/s11104-012-1192-9)

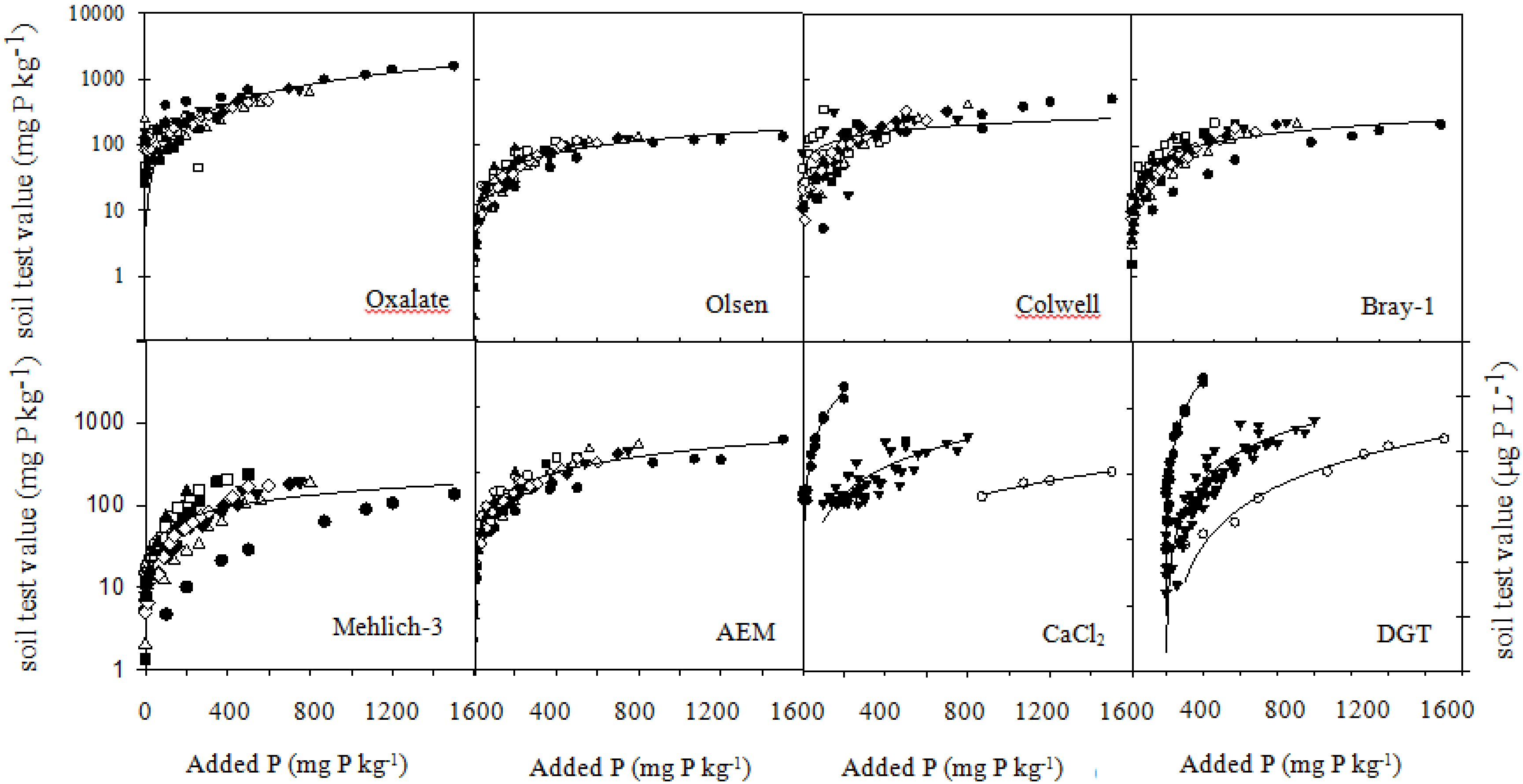
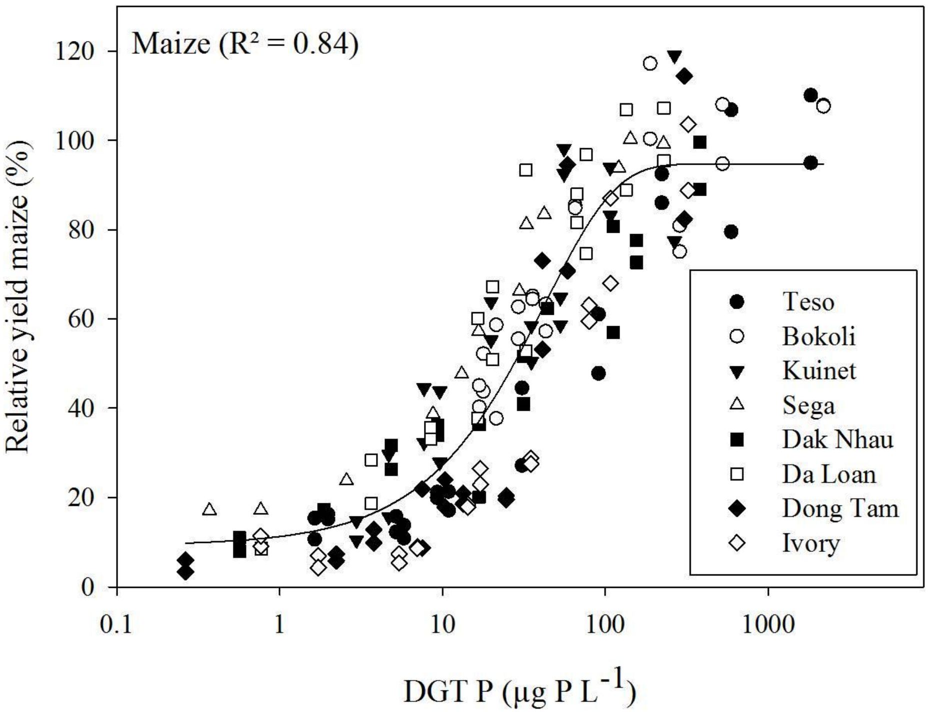
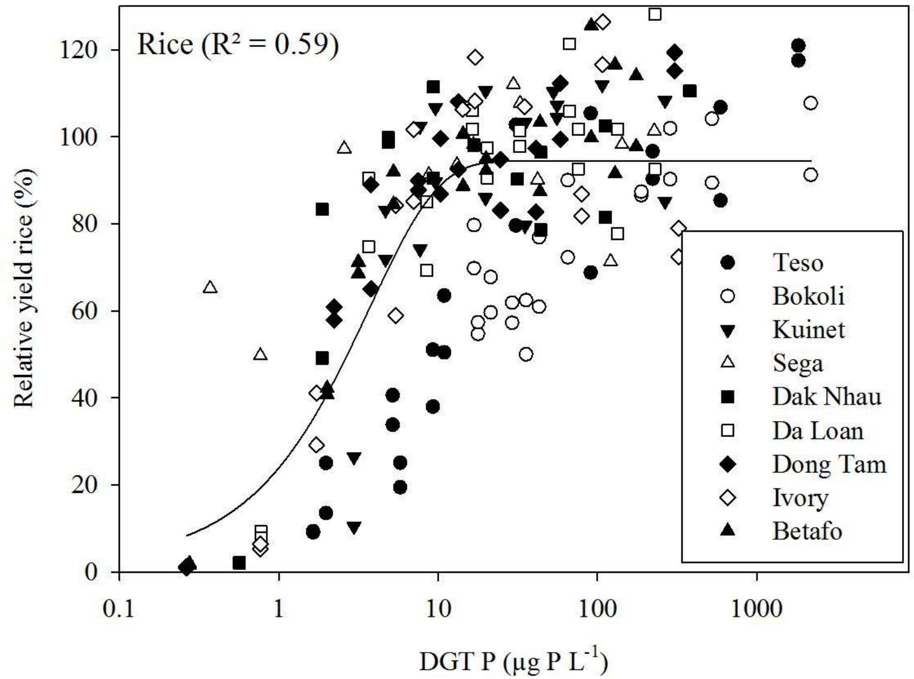


Figure 1 Relationship of added P with soil P based on the ammonium oxalate, Olsen, Colwell, Bray-1, Mehlich-3, AEM, $CaCl_2$ and DGT method.

DGT responds to P additions, just like $CaCl_2$ and separates the soils into three groups according to K_d

(Six et al., 2012, PLSO DOI: 10.1007/s11104-012-1192-9)





DGT predicts relative yield of maize, irrespective soil type

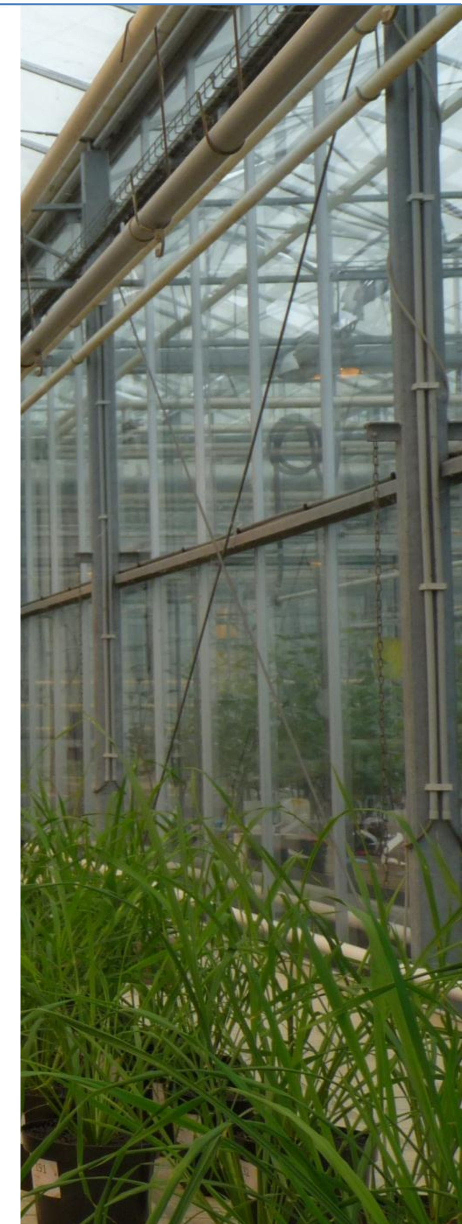
DGT fails to predict relative yield of rice…

(Six et al., 2012, PLSO, DOI 10.1007/s11104-012-1375-4)

Only when demand for P is high and hence diffusion of P limiting

r^2 of Mitscherlich curves relating relative yield of maize or rice (%) to the soil P test values

	Maize	Rice
Soil test	r^2	r^2
Oxalate	0.53	0.44
Olsen	0.52	**0.76**
Colwell	0.41	0.62
Bray-1	0.45	**0.73**
Mehlich-3	0.50	**0.76**
AEM	0.51	**0.77**
$CaCl_2$	0.69	0.12
DGT	**0.84**	0.59



DEPARTMENT OF EARTH AND ENVIRONMENTAL SCIENCES
K.U.LEUVEN - BELGIUM

Conclusions

- ✓ Zero-sink based methods reflect P-availability better than 'conventional' soil tests because of mimicking plant root action
- ✓ Most chemical exctractants and even AEM sample from P-pools inaccessible for plants
- ✓ In most cases measures of Intensity predict uptake better than those of Quantity
- ✓ DGT as a compromise between Intensity and Capacity measures is promising when P-demand is high.
- ✓ Under these conditions, DGT-P is independent from soil PBC

- ✓ In all the above, isotope tracing proved indispensable