Localised Flux-Maxima of Arsenic, Lead and Iron around Root Apices in Flooded Lowland Rice.

Paul N. Williams, Jakob Santner, Morten Larsen, Niklas J. Lehto, Eva Oburger, Walter Wenzel, Ronnie N. Glud, William Davison, Hao Zhang

SUPPORTING INFORMATION

7 Pages, 2 Figures and 2 Tables

TABLE OF CONTENTS

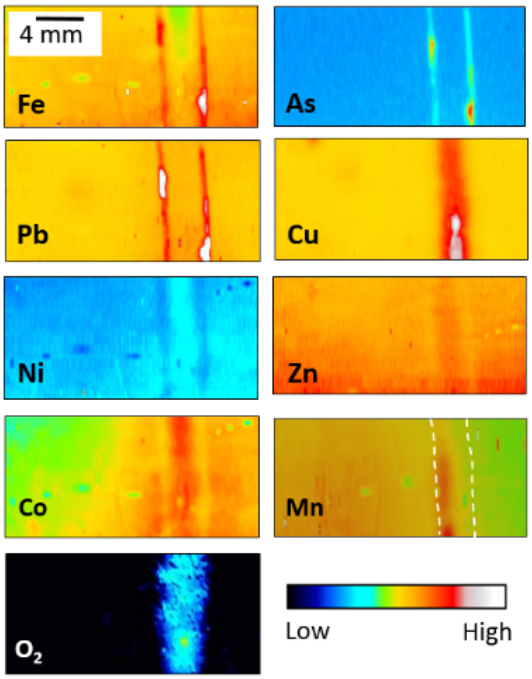
		Page
Table S1	Soil characterisation……..	*S3*
Table S2	Limits of detection…….....	*S4*
Figure S1	Artificial root experiment……..	*S5*
Figure S2	Comparison of geochemical trends in the root tip and microniche zones….	*S6*
	References……..	*S7*

	Total		Sodium Citrate-Bicarbonate-Dithionite (CBD) extractable Fe	Acid ammonium oxalate extraction in darkness (amorphous Fe oxides)	10 mmol L^{-1} $Ca(NO_3)_2$
	(mg kg^{-1})		(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})
Fe	**17399** ± 1%	*	**6616** ± 6%	**3005** ± 5%	**42** ± 19%
Mg	**6100**	**	~	~	~
Ca	**1836**	**	~	~	~
Mn	**674** ± 3%	*	**493** ± 9%	~	~
P_{total}	**478**		~	~	~
Zn	**56** ± 2%	*	**8.6** ± 39%	~	~
Pb	**20** ± 3%	*	**3** ± 1%	**11** ± 18%	~
Ni	**19** ± 6%	*	**3.9** ± 6%	~	~
Cu	**12** ± 1%	*	**5.4** ± 27%	~	~
Co	**8.6** ± 2%	*	**4.4** ± 24%	~	~
As	**< 2**	**	~	~	~
pH_{H20}	**6.3**		~	~	~
pH_{CaCl2}	**5.4**		~	~	~
Corg	**49,000**		~	~	~

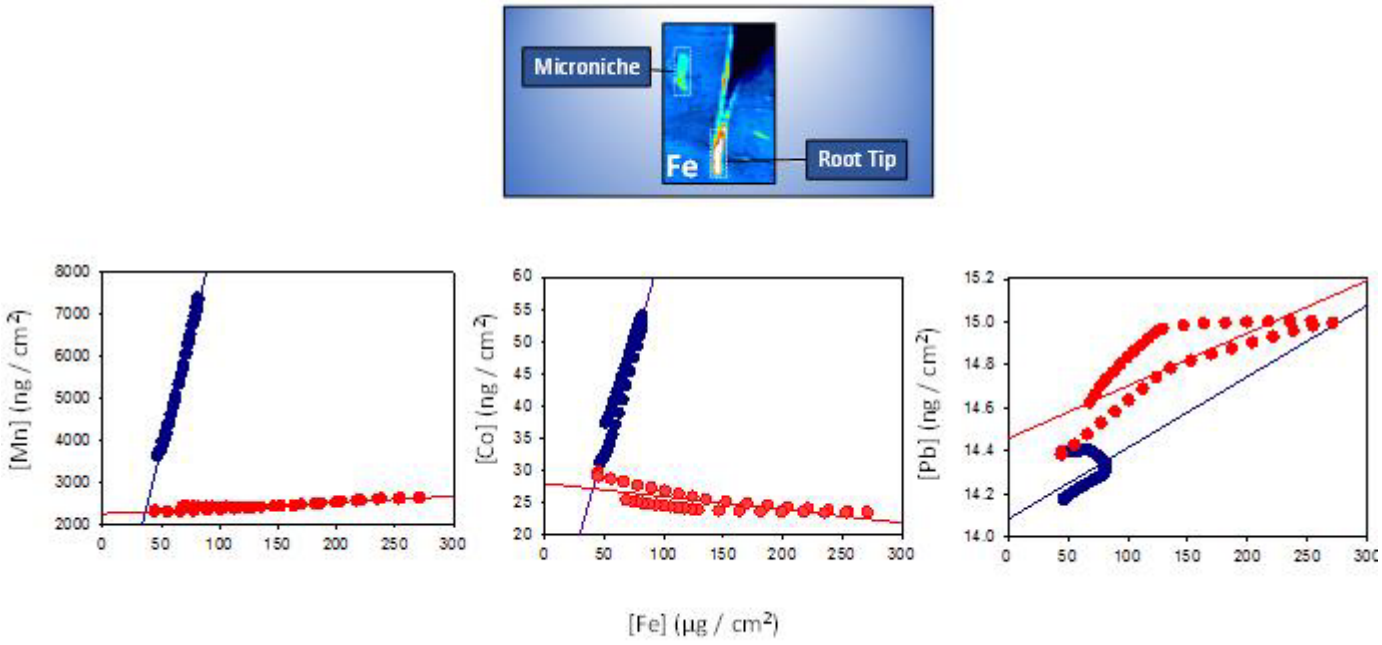
Supplementary Table S1. Soil characterisation. Average of four sub-samples ± relative standard deviation. **Aqua regia digestion*. 0.5 g of dried, ground soil digested in 4.5 mL HCl + 1.5 mL HNO_3 at 150 ^oC in open glass tubes. 1 drop of octanol was added to inhibit foaming. ** 3 g of dried, ground soil digested were pressed into a pellet and analysed by ED-XRF (Rigaku NEX CG series, Japan). *DCB extractable*. 0.5 g of soil extracted in 18.8 mL Sodium citrate (0.3 M) + 2.8 mL Sodium bicarbonate (1 M) at 80^oC (water bath), followed by the addition of 2 x 0.4 g of Sodium dithionite powder for 25 min. *Acid ammonium oxalate extraction.* 0.5 g of soil extracted in 30 mL of ammonium oxalate (0.175 M; acidified to pH 3) in darkness for 2 hours on a shaker. *$Ca(NO_3)_2$ extract.* 5 g soil extracted in 50 mL 0.01 M $Ca(NO_3)_2$ for 2 hours on a shaker.

LOD					
	ng cm^{-2}			pg cm^{-2} s^{-1}	
	min	*max*		*min*	*max*
iron	71	76		0.824	0.880
manganese	33	52		0.382	0.602
zinc	23	45		0.266	0.521
copper	3.1	24		0.036	0.278
arsenic	0.8	9.2		0.009	0.106
nickel	0.3	4.3		0.003	0.050
lead	0.2	18		0.002	0.204
cobalt	0.05	4.4		0.001	0.051
	µM				
oxygen	1.9		pH	6.48*	

Supplementary Table S2. Limits of detection (LOD). The LOD was calculated as three times the standard deviation of the blank. Each sample run had a unique element specific LOD, this table reports the minimum and maximum LOD's from the entire analytical campaign. Values in ng cm^{-2} are the LOD based on the analyte surface concentration on the DGT gel, while pg cm^{-2} s^{-1} values are the LOD given as flux onto the DGT gel.*Lowest pH that can quantified, with the blank being defined as the mean value from the pH range where there is no response from the optode.



Supplementary Figure S1. Metal mobilisation trends observed around the rice roots were replicated using an artificial root composed of silicone tubing. The tubing was inserted into the rhizotron so that it extended from a 5 cm length in the overlying water into the flooded soil to a depth of c. 5 cm. The end of the tubing residing in the soil was sealed while the opposite end remained open; this enabled oxygen to diffuse into the tubing. Silicone was selected because of its high gas permeability at room temperature. The tubing was orientated so that direct contact was made with the membrane overlying the optode-DGT assembly. Metal fluxes are presented in f_{DGT} pg cm^{-2} s^{-1}. The scales in the figure range from 0.88-71 for Fe, 0.11-0.61 for As, 0.005-0.01 for Pb, 0.28-0.37 for Cu, 0.003-0.27 for Ni, 0.27-0.93 for Zn, 0.001-0.002 for Co, and 0.6-6 for Mn. Oxygen concentrations ranged from 0 -100 (% air saturation). The white dashed line indicates the location of the silicone tubing.



Supplementary Figure S2. **Comparison of geochemical trends in the root tip (●) and microniche zones (●)**. Fifty 0.24 mm^2 averaged measurements were obtained from both the microniche and root tip zones. The key distinguishing features are i) greater Fe mobilisation in the root tip zone ii) Strong positive correlations between Fe and Mn with proportionally greater Mn mobilisation in relation to Fe in the microniche. iii) Opposite patterns of Co mobilisation with increasing Fe release between the root tip and microniche iv) localised differences in Pb mobilisation with increases in Fe supply. Metal mobilisation trends observed in the microniche were similar to those reported for microniches in Fones *et al.*[1]

REFERENCES

1) Fones, G. R.; Davison, W.; Hamilton-Taylor, J. The fine-scale remobilization of metals in the surface sediment of the North-East Atlantic. *Cont. Shelf Res.* **2004**, 24, 1485-1504.