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1 Location of Study site



Figure S-1: Location of the different sampling sites in Punjab, India. The pinkish wheat (Figure S-2) was taken on a rim just next to Field 2. For more details on the sampling, please refer to the Methods chapter.



Figure S-2: Wheat showing pink chlorosis (left); wheat with white chlorosis along the irrigation channel in Field-1 (middle); detailed picture of the wheat showing white chlorosis (right)

## 2 Data acquisition and quality assurance / quality control

#### 2.1 Analysis of Se and further element concentrations in soils

The Se concentration in soils was measured using two different methods namely the energy dispersive XRF and ICP-MS analysis based on microwave full acid digestions (HF, HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>). The idea was to firstly do some method development for the XRF and secondly to get a double check of the data quality with two different methods. A matrix specific calibration for low Se concentrations was done for the XRF analysis using a standard addition approach. Five predefined Se concentrations were added as liquid (Merck Se calibration standard) to an aliquot of the subsurface sample of Field-1 (> 15 cm) to prepare the individual standards. This ensures a similar matrix for standards and samples which is necessary with regard to reliable matrix dependent corrections of the XRF results. Using this approach it was possible to measure Se concentrations > 0.5 mg/kg. The advantage of XRF analysis is the large amount of sample (~2 g) that is used. The recovery of the certified reference (GXR5), which was included into the measurement procedure was 110%, indicating an overestimation of 10% (Table S-2). For the Se determination with ICP-MS analysis we decided to use a microwave acid digestion procedure to minimize losses of volatile Se that could be present. It is well known that Se volatilize in open digestions when the acids are evaporated at relatively high temperatures (>120 °C). In total, six acid blanks were included into the microwave digestion procedure. The mean of the blank values was subtracted from the measured concentration before calculating the final element content. For the quality assurance we did all samples of Field-1 in duplicate. The standard deviation of these duplicate measurements was 0.00-3.5% (Table S-1). The maximum standard deviation of 3.5% was used as error in all graphs and tables. The recovery of the GXR4 and GXR5 standard, that were digested once, was 88.3 and 89.2% indicating a loss of ~10% probably due to volatilization of Se (Table S- 2).

The xy-plot of Se<sub>XRF</sub> and Se<sub>ICP-MS</sub> illustrates the high correlation ( $r_P = 0.98$ , n = 17) between both methods (Figure S-3) with about 10% overestimation for XRF and about 10% underestimation for ICP-MS. Based on these results we corrected the mean of the ICP-MS analysis by 10%. This corrected value is given throughout the whole manuscript.



The concentration of Mn, Fe and As was also determined with ICP-MS using the same digestion. All other element concentrations are based on XRF analysis. The concentration of each element and the accuracy is given in Table S- 2).

	Selei	nium				Irc	on			
Depth	ICP	-MS	mean	Std.	dev.	ICP-	MS	mean	Std.	dev.
cm	mg	/kg	mg/kg	mg/kg	%	wt%	wt%	wt%	wt%	%
0-2	9.75	9.70	9.73	0.04	0.3	3.78	3.80	3.79	0.01	0.4
2-5	12.1	11.4	11.8	0.45	3.5	3.64	3.60	3.62	0.03	0.8
5-10	10.0	9.89	9.96	0.09	0.8	3.71	3.73	3.72	0.02	0.4
10-15	1.34	1.40	1.37	0.04	2.8	4.06	3.88	3.97	0.12	3.0
15-30	0.68	0.69	0.69	0.01	0.9	4.90	4.71	4.81	0.13	2.8
30-45	0.51	0.53	0.52	0.01	2.5	4.88	4.75	4.81	0.09	1.8
>45	0.39	0.39	0.39	0.00	0.00	5.05	4.82	4.93	0.17	3.4
	Arso	enic				Manga	anese			
Depth	ICP	-MS	mean	Std.	dev.	ICP-MS	mean	Std. dev.	ICP-MS	
[cm]	mg/kg	mg/kg	mg/kg	%	wt%	wt%	mg/kg	mg/kg	mg/kg	%
0-2	10.5	10.5	10.5	0.02	0.2	0.07	0.07	0.07	0.00	2.7
2-5	9.2	9.4	9.3	0.14	1.6	0.06	0.07	0.06	0.00	1.9
5-10	10.2	10.3	10.2	0.09	0.8	0.07	0.07	0.07	0.00	2.2
10-15	12.1	12.1	12.1	0.00	0.02	0.08	0.08	0.08	0.00	0.3
15-30	15.0	15.2	15.1	0.17	1.2	0.09	0.09	0.09	0.00	1.0
30-45	15.3	15.1	15.2	0.13	0.9	0.12	0.12	0.12	0.00	0.7
>45	14.7	14.5	14.6	0.12	0.8	0.11	0.11	0.11	0.00	0.3

Table S- 1: Concentration of Se, Fe, As and Mn measured in duplicate at Field-1 using ICP-MS after microwave acid digestion. The table also includes the mean value and the standard deviation (total and percentage).

Table S- 2: Geochemistry at Field-1 to Field-3, the root zone soils of sugarcane, Indian Mustard, Clover, Wheat (pink chlorosis), and garlic. For Se, Fe, Mn and As, the mean of the duplicate measurements listed in Table S- 1 are given. Se concentrations were corrected as described in Chapter 2.1. Additionally the accuracy is given as recovery of the certified reference materials GXR4 and GXR5 (n.d. = not determined).

		ICP-MS				XRF					
D	epth	Se	Fe	Mn	As	CaO	Al <sub>2</sub> O <sub>3</sub>	K₂O	Y	Rb	Sr
	cm	mg/kg	wt%	wt%	mg/kg	wt%	wt%	wt%	mg/kg	mg/kg	mg/kg
	0-2	10.7	3.79	0.07	10.5	3.4	14.5	3.23	147	147	119
	2-5	13.0	3.62	0.06	9.3	3.3	12.9	3.21	142	142	121
Ę	5-10	11.0	3.72	0.07	10.2	3.3	13.7	3.24	144	144	119
ELD	10-15	1.5	3.97	0.08	12.1	3.3	14.0	3.29	150	150	110
Ē	15-30	0.8	4.81	0.09	15.1	3.1	15.0	3.39	168	168	104
	30-45	0.6	4.81	0.12	15.2	1.3	15.7	3.24	160	160	101
	>45	0.4	4.93	0.11	14.6	1.4	16.3	3.19	155	155	101
	0-2	5.1	2.97	0.05	6.2	4.4	11.0	3.0	134	134	136
	2-5	6.0	3.06	0.05	5.1	4.5	11.3	3.1	135	135	139
2	5-10	6.6	3.06	0.05	5.4	4.6	14.0	3.1	134	134	141
ELD	10-15	3.1	3.15	0.06	6.0	4.4	12.3	3.1	136	136	131
Ē	30-45	0.6	4.60	0.09	13.2	3.9	16.4	3.4	158	158	116
	30-45	0.5	4.68	0.09	11.9	3.0	15.4	3.4	165	165	112
	>45	0.5	4.99	0.10	12.9	2.1	15.3	3.5	174	174	112
	0-2	2.3	4.14	0.08	9.62	4.6	12.6	3.2	144	144	146
	2-5	3.7	4.11	0.08	8.43	4.6	13.6	3.1	139	139	153
m	5-10	2.4	4.18	0.08	9.22	4.6	14.7	3.2	141	141	158
ELD	10-15	2.1	4.35	0.09	10.7	4.5	13.0	3.2	143	143	142
Ē	15-30	0.6	5.66	0.12	15.9	2.5	16.7	3.3	174	174	100
	30-45	0.6	5.47	0.12	14.7	1.6	16.2	3.3	167	167	97
	>45	0.5	4.95	0.13	14.4	1.2	14.4	3.1	148	148	96
Sug	arcane	4.7	3.46	0.08	7.7	3.8	12.1	3.2	139	145	105

	ICP-MS				XRF					
Depth	Se	Fe	Mn	As	CaO	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Y	Rb	Sr
CIII	rng/kg	Wl%	Wl%	ттg/кg	Wl%	Wl%	Wl%	під/кд	під/кд	під/кд
Indian Mustard	6.1	3.86	0.09	9.4	1.6	15.2	3.1	145	139	143
Clover	3.3	2.53	0.05	4.7	3.9	11.7	3.0	126	125	123
Pink Wheat	3.5	2.46	0.05	4.5	3.7	12.8	3.0	125	126	125
Garlic	2.0	3.03	0.06	6.7	3.9	11.8	3.1	139	139	120
Recovery GXR4 [%]	89.3	100.7	nd	94.3						
Recovery GXR5 [%]	89.3	97.7	100.0	90.20	103.7	98.3	101.9	92	94	94

# 2.2 pH-value in soils

In Germany two ways of pH determination in soil are regularly used and described in a German DIN standard procedure (DIN ISO 10390:2005-12). Apart from the solvent (pure water, 0.01 M CaCl<sub>2</sub>) used both procedures are similar. 5 g of soil is shaken for 1h. After settling for 1h the pH-value is measured in the supernatant solution. It is typical that the pH-value using CaCl<sub>2</sub> is up to 1 pH unit lower compared to the pH value determined using pure water. This can be explained by the exchange of Ca<sup>2+</sup> with H<sup>+</sup> which is present at mineral surfaces. As ions like Ca<sup>2+</sup> are often present in soil solutions, this pH-value is more realistic, but rarely used in international literature therefore both values are given. The pH-value was measured for each sample only once. For the three depth profiles, the mean of all 6 depth (Table S- 3) is given throughout the manuscript because of their similarity.

throughout the m											
Depth	Fie	ld-1	Fie	ld-2	Fie	ld-3					
[cm]	H <sub>2</sub> 0	CaCl <sub>2</sub>	H <sub>2</sub> 0	CaCl <sub>2</sub>	H <sub>2</sub> 0	CaCl <sub>2</sub>					
0-2	8.4	7.7	-	-	-	-					
2-5	8.4	7.7	8.6	7.7	8.4	7.8					
5-10	8.6	7.8	8.5	7.7	8.6	7.8					
10-15	8.7	7.9	8.7	7.8	8.8	7.9					
15-30	8.7	7.9	8.7	7.9	8.7	7.9					
30-45	8.6	7.8	8.8	7.9	8.6	7.8					
Mean	8.6	7.8	8.7	7.8	8.6	7.8					

0.1

0.1

0.1

0.1

Table S- 3: Individual pH-values of the depth profile of Field-1 to Field-3. The mean value of each depth profile is given throughout the manuscript. For Field- and Field-3, the top sample could not be measured due to a lack of sample material.

# 2.3 Organic carbon content

0.1

0.1

Std.dev.

The organic carbon content was measured using a carbon-sulfur analyser (Eltra, CS2000). Before the measurement the inorganic carbon was evaporated using diluted HCl (1:1) on a heating plate at low temperatures. All samples were treated in this manner and measured in duplicate. The standard deviation is <4.3 %. To check for the quality of the CSA measurement itself, a cement reference standard (90811-13) was used to check both accuracy (100±1%) and reproducibility (±0.8%, n=5).

		Organic wt%	carbon <sub>wt%</sub>	Mean wt%	Std.dev. wt%	Std.dev. %
FIELD-1	0-2 2-5 5-10 10-15 15-30 30-45 >45	0.89 0.98 0.82 0.36 0.36 0.37 0.40	0.89 1.03 0.85 0.35 0.36 0.39 0.41	0.89 1.01 0.84 0.35 0.36 0.38 0.40	0.00 0.04 0.02 0.00 0.00 0.02 0.01	0.40 3.73 2.44 0.86 0.42 4.27 2.15
FIELD-2	0-2 2-5 5-10 10-15 15-30 30-45 >45	0.76 0.86 0.84 0.61 0.26 0.28 0.34	0.77 0.85 0.86 0.58 0.25 0.28 0.36	0.76 0.85 0.85 0.60 0.26 0.28 0.35	0.01 0.01 0.02 0.01 0.00 0.01	1.30 1.46 1.33 3.23 3.03 0.36 2.83
FIELD-3	0-2 2-5 5-10 10-15 15-30 30-45 >45	0.72 0.79 0.76 0.65 0.39 0.42 0.39	0.67 0.78 0.78 0.60 0.38 0.43 0.41	0.69 0.79 0.77 0.62 0.39 0.43 0.40	0.03 0.01 0.03 0.00 0.01 0.01	4.29 1.49 1.80 5.20 0.67 2.09 3.72
ROOT ZONE SOIL	Sugarcane Mustard Clover Pink Wheat Garlic	0.88 1.21 0.58 0.62 0.81	0.87 1.21 0.56 0.63 0.80	0.88 1.21 0.57 0.62 0.80	0.01 0.00 0.01 0.01 0.01	0.83 0.04 2.29 0.82 0.94

Table S- 4: Organic carbon content in wt% in all samples. The samples were pre-treated with HCl (1:1) to remove inorganic carbon. All samples were measured in duplicate. The mean and standard deviation is also given in the table.

#### 2.4 Sequential extraction

Sequential extractions were used to get an impression about the speciation and way of fixation of Se within the soils. This information is useful for mobility and bioavailability assessments or the identification of species transformation and thus to draw conclusions about the environmental behaviour of elements<sup>1-4</sup>. Sequential extractions are regularly used throughout the scientific world for these purposes<sup>3-4</sup> despite the general knowledge of severe shortcomings, especially its operational nature, possible re-distribution between phases, re-adsorption or precipitation of new phases during extraction<sup>3,5</sup>. The specific shortcoming of the extraction method used, a possible overestimation of elemental Se at the expense of organically associated Se, was mentioned within the discussion<sup>2</sup>.

The frequent application can partly be explained by the fact that other methods for species determination like XAS or PIXE are limited in the availability and also offer poor detection limits (especially with regard to trace elements). This explains why the application of XAS analysis on soil samples was only successful for one bulk sample and one single particle. In all other samples, the Se concentration was too low to get evaluable XANES signals. Furthermore, the actual interpretation of

the measured spectra is often not straightforward. The proportion of each species is determined using linear combination fits. The precision of these fits was previously estimated to be between 10 and 20%<sup>6-8</sup>.

The sequential extraction within this study was used to determine operationally defined species and get information about ways of fixation for all root zone soil samples and the top 10 cm at Field-1 to Field-3. The results allow valuable conclusions due to several reasons: 1) because of the similarity of the soil matrix and the protocol that was used, results are comparable among each other; 2) each sample could be measured thus enhancing the statistics and 3) quality assurance measures show a good reproducibility and accuracy (Table S-6).

Table S- 5: Results of the quality assurance measures for the sequential extraction procedure used. Listed are all individual values of two duplicate (Field-1, Indian Mustard root zone soil) and one triplicate sample (Field-2). Additionally the mean and standard deviation are given to determine the reproducibility of the extracted samples. The sum of all fractions is compared to the total Se concentration listed in Table S- 2. GXR4 as certified reference material was included twice into the procedure to test the accuracy (\*certified value).

	F1	F2	F3	F4	F5	F6	Sum	Se <sub>tot</sub>	Recovery
Indicated	easily			Organically	oxidically		Sum of all		
form of Se	available	Adsorbed	Elemental	bound	bound	Residual	Fractions	mg/kg	%
				mg/l	kg				
Field-1									
2-5 cm – A	1.21	0.71	7.64	1.13	2.13	0.33	13.2	13.0	101
2-5 cm – B	1.26	0.72	8.08	1.09	1.46	0.39	13.0	15.0	100
Mean [mg/kg]	1.24	0.72	7.86	1.11	1.80	0.36	13.1		
Std.dev [%]	2.86	0.99	3.96	2.55	26.4	11.8	0.81		
Field-2									
0-2 cm – A	0.60	0.38	1.94	0.88	1.18	0.62	5.6		110
0-2 cm – B	0.59	0.35	2.34	0.91	1.28	1.38	6.9	5.1	134
0-2 cm – C	0.59	0.34	2.37	0.93	1.17	0.72	6.1		120
Mean [mg/kg]	0.59	0.36	2.22	0.91	1.21	0.91	6.2		
Std.dev [%]	0.97	5.84	10.83	2.78	5.03	45.6	10.1		
Indian Mus	tard								
root zone s	oil (IM)						0		
IM – A	0.46	0.64	2.17	1.13	1.96	0.47	6.8		112
IM – B	0.45	0.63	2.36	1.09	1.89	0.40	6.8	6.1	112
Mean [mg/kg]	0.46	0.64	2.27	1.11	1.93	0.44	6.8		
Std.dev [%]	1.55	1.11	5.93	2.55	2.57	11.4	0.1		
Certified St	andard								
GXR4 – A	0.77	0.43	0.44	0.77	1.84	1.71	5.96	5.6*	106
GXR4 – B	0.64	0.34	0.51	0.45	1.68	1.8	5.42	5.0	97

Sequential extractions were carried out with all root soil samples and the top three samples (0-2, 2-5, 5-10 cm) of the depth profile. Samples deeper than 10 cm were not used due to the low  $Se_{tot}$  concentration. Due to the relatively small differences between the three depths, the mean was used throughout the manuscript (Table S-6).

Table S-6: Results of sequential extraction at Field-1 to -3 in the depth of 0-2, 2-5, 5-10 cm. In addition, the mean and standard deviation of the topsoil of each field is given.

	F	1	F	2	F3		F4	L .	F:	5	F	6
	eas	sily					Organi	ically	Oxidi	cally		
	avai	lable	Adso	rbed	Eleme	ntal	bou	nd	bou	ınd	Resi	dual
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Field -1												
0-2 cm	1.18	10	0.69	6	6.77	57	1.10	9	1.46	12	0.62	5
2-5 cm	1.24	9	0.71	5	7.86	60	1.11	9	1.79	14	0.36	3
5-10 cm	1.31	11	0.73	7	6.72	56	1.08	9	1.8	15	0.47	3
Mean	1.24	10	0.71	6.0	7.12	58	1.10	9	1.68	13.7	0.48	3.6
Std.dev	0.07	1.0	0.02	1.0	0.64	2.1	0.02	0.0	0.19	1.5	0.13	1.2
Field -2												
0-2 cm	0.59	10	0.36	6	2.22	36	0.91	15	1.21	20	0.90	15
2-5 cm	0.83	12	0.46	7	2.52	37	1.03	15	1.29	19	0.68	10
5-10 cm	0.64	9	0.46	6	3.07	43	1.09	15	1.35	19	0.52	7
Mean	0.69	10	0.43	6	2.60	39	1.01	15	1.28	19	0.70	10.7
Std.dev	0.13	1.5	0.06	0.6	0.43	3.8	0.09	0.0	0.07	0.6	0.19	4.0
Field -3												
0-2 cm	0.24	9	0.23	8	0.66	23	0.24	9	1.39	49	0.08	3
2-5 cm	0.22	7	0.24	8	0.69	22	0.38	12	1.3	41	0.34	11
5-10 cm	0.27	8	0.27	8	0.77	23	0.48	14	1.28	39	0.28	8
Mean	0.24	8	0.25	8	0.71	22.7	0.37	11.7	1.32	43	0.23	7.3
Std.dev	0.03	1.0	0.02	0.0	0.06	0.6	0.12	2.5	0.06	5.3	0.14	4.0

### 2.5 Selenium concentration in plant material

The Se concentration in plant material was measured using ICP-MS after microwave acid digestion. 200 mg sample was digested using 1 mL MilliQ water, 5 mL HNO<sub>3</sub> (subboilded) and 1 mL H<sub>2</sub>O<sub>2</sub>. The vessels were cooled down over night to avoid any volatilization. One sample batch consisted of 8 samples, 1 acid blank and one certified standard (tomato leaves). The acid blank was subtracted from the measured Se concentration in the digestion solution before calculating the actual Se content of each sample. Unfortunately, a quantitative Se measurement of the certified standard was not possible with any of the Se isotopes due to heavy Br interferences and very low Se concentration (0.054 wt%). The recovery of other elements that were measured (n = 6) was of good to excellent quality (P: 94.6%; Cr: 99.4 %; Mn: 101.8%; Fe: 101.5%; Cu: 97.9%; Zn: 90.9%); therefore, we assume a full digestion without considerable losses. The reproducibility of the digestion procedure was very high for the just mentioned elements with a standard deviation of 0.8 (Fe) to 5.4% (Zn) (n =6). Three samples were digested in duplicate (Table S-7). With a standard deviation of  $\leq 4.5\%$ , the reproducibility of the Se data can be considered as high.

		Repl	icate			
		Α	В	Mean	Std.dev.	Std.dev.
		mg	/kg	mg/kg	mg/kg	%
Garlic	bulb	14.2	13.8	14.0	0.28	2.0
	leaves	35.9	34.1	35.0	1.27	3.6
Wheat Field-3	leaves	5.16	5.5	5.33	0.24	4.5

Table S-7: Selenium concentrations in duplicates of three different plant samples including mean and standard deviation.

If available, material of two different plants from the same site was used. Furthermore, different plant parts and in some cases also different pieces of the same plant parts were digested. All results are listed in Table S-8. The mean of all subsamples of one plant part were used within the manuscript.

Table S-8: Selenium concentrations in different plant parts. Several subsample were digested and measured using ICP-MS from the same plant parts and if possible also from different plants of the same site to account for the natural variability within and between individual plants.

	Plant 1	Plant 2	Mean	Std.Dev.
	n	ng/kg	mg	;/kg
Wheat Field 2				
root	47.3			
stom	47.5			
stem	28.8			
lower leaves (piece 1)	22.1			a
lower leaves (piece 2)	24.6		35.8	21.5
upper leaves	60.6			
head	35.5			
Wheat Field-3				
root	6.14	5.88	6.01	0.18
stem	1.36	1.23	1.30	0.09
lower leaves	9.73	3.75	6.83	2 76
upper leaves	8.49	5.33	0.05	2.70
head	3.37	3.07	3.22	0.21
Sugarcane				
root (piece 1)	43.1	32.9		
root (piece 2)	77.8	49.1	55.8	17.5
root (piece 3)	73.3	58.7		
stem (piece 1)	62.0	63.8	57.1	16.3
stem (piece 2)	69.6	33.1	07.12	10.0
lower leaves	64.5	61.6		
middle leaves	89.1		85.6	30.3
upper leaves	127			
Indian Mustard				
root	186			
stem (piece 1)	133			
stem (niece 2)	127		130	4.2
leaves	931			
flower	541			
Garlic				
Surfic	41 3			
root	12.0			
leaves (piece 1)	35.0		24.5	14.9
hulb	14 0			
lower leaves (piece 1) lower leaves head Wheat Field-3 root stem lower leaves upper leaves upper leaves head Sugarc→ Foot (piece 1) root (piece 2) root (piece 2) root (piece 3) stem (piece 1) stem (piece 1) stem (piece 2) lower leaves middle leaves upper leaves stem (piece 2) lower leaves middle leaves indidle leaves middle leaves flower Foot stem (piece 1) stem (piece 2) leaves flower	22.1 24.6 60.6 35.5 6.14 1.36 9.73 8.49 3.37 43.1 77.8 73.3 62.0 69.6 64.5 89.1 127 186 133 127 931 541 541 541	5.88 1.23 3.75 5.33 3.07 32.9 49.1 58.7 63.8 33.1 61.6	35.8 6.01 1.30 6.83 3.22 55.8 57.1 85.6 130 24.5	21.5 0.18 0.09 2.76 0.21 17.5 16.3 30.3 4.2

#### 2.6 XANES measurements

Bulk sample means that a pressed pellet was made from powdered bulk material of the respective sample. Several mg of sample material was mixed with cellulose powder which acts as binder. The amount of powdered sample that is used depends on the Se concentration of the soil. Single particle means that the original soil material was embedded into a resin to prepare thin sections. At the SUL-X beamline, spatially resolved XANES measures are possible so we could measure the XANES spectra within individual grains. We did this at Se hotspots to assure sufficient Se concentrations for a good XANES spectra (Figure S- 4).



Figure S-4: Microscopic picture of the soil particle agglomerate that was measured at the SUL-X beamline. The red cross indicates the spot where XANES spectra was taken.

Each spectra is the merge of two to six individual scans (Figure S- 5). Each individual scan was taken at a slightly different spot (shift of few  $\mu$ m) because it is known that Se speciation can change over time due to a beam induced damage. The differences between the individual spectra was mainly far less than 5%. The merge was done using the Athena software of the IFEFFIT software package. The precision of these fits was previously estimated by other studies to be between 10 and 20%<sup>6-8</sup>.





Figure S-5: Merge and standard deviation of the individual XANES spectra of each plant part.

The XANES spectra were fitted using elemental Se (Se<sup>0</sup>), selenate (Se<sup>VI</sup>, Na<sub>2</sub>SeO<sub>4</sub>x10H<sub>2</sub>O) and selenite (Se<sup>IV</sup>, Na<sub>2</sub>SeO<sub>3</sub>) in a diluted form as inorganic references. The spectra of organic Se species included Secysteine (SeCys), Semethionine (SeMet), Dimethyl-selenide (DMeSe), Se-methyl-selenoL-cysteine (SeMeCys). Apart from SeMet, all organic spectra were kindly provided by G. Sarret. The individual fits of the plant material is given in Figure S- 6



Figure S-6: XANES spectra and linear combination fit of (a) sugarcane (roots, leaves), (b) Pink wheat (roots, leaves) and (c) Clover (stem, leaves).

# 3 Hydrochemistry

Groundwater, which is used for irrigation, could only be sampled from two wells (W1, W2; depth >90 m, sampled at same day) near site 1 because electricity for the pumps is generally switched off during non-irrigation times. All samples were filtered (cellulose acetate, 0.45  $\mu$ m) and stored in plastic bottles at 4°C till further analysis in Karlsruhe. In order to avoid sampling of stagnant water in the wells, water was pumped before sampling until the values of pH and electrical conductivity were stable. A portable system WTW Multi 340i (John Morris Scientific Pty Ltd.) was used to measure Eh-/pH-values and oxygen on-site. Selenium was determined by ICP-MS (X-Series2, Thermo Scientific). The accuracy (Se  $\leq$  1%) was tested by including the certified standard HPS CRM-TMDW (High Purity Standards, USA) into the measurements.

		Well 1	Well 2	HPS certified standard	Recovery [%]
рН		7.1	7.1		
Electrical conductivity	μS cm <sup>-1</sup>	714	728		
Eh	mV	177	151		
т	°C	25.8	24.9		
Se	μg L <sup>-1</sup>	130	259	2.2	99
Fe	μg L <sup>-1</sup>	10	47	19	105
Mn	μg L <sup>-1</sup>	34	64	8.2	102
Sr	mg L <sup>-1</sup>	1.2	1.4	60.5	101
Alkalinity	mg L <sup>-1</sup>	537	512		
Chloride	mg L <sup>-1</sup>	3.7	4.2		
Nitrate	mg L <sup>-1</sup>	7	6.1		
Sulfate	mg L <sup>-1</sup>	2.3	3.3		

Table S-9: Hydrochemistry of Well 1 and Well 2. Additionally the measured values of the HPS certified water standard and the recovery are listed as quality assurance measure.

# 4 References

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