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Interactive adsorption of phenolic acids and amino acids on soil minerals

Implications for the formation and properties of soil mineral–organic associations

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Appendices

Appendix (A) to Chapter 3

Table A1 Composition of mobile phase with different buffer concentration.

Buffer concentration (mM)	Solvent A	Solvent B
2 (3.05) ^a	100% H ₂ O, 2 mM NH ₄ HCO ₂ , 0.03% FA	90% ACN, 10% H ₂ O, 2 mM NH ₄ HCO ₂ , 0.03% FA
4 (3.02)	100% H ₂ O, 4 mM NH ₄ HCO ₂ , 0.06% FA	90% ACN, 10% H ₂ O, 4 mM NH ₄ HCO ₂ , 0.06% FA
6 (3.04)	100% H ₂ O, 6 mM NH ₄ HCO ₂ , 0.09% FA	90% ACN, 10% H ₂ O, 6 mM NH ₄ HCO ₂ , 0.09% FA
8 (3.03)	100% H ₂ O, 8 mM NH ₄ HCO ₂ , 0.12% FA	90% ACN, 10% H ₂ O, 8 mM NH ₄ HCO ₂ , 0.12% FA
10 (3.00)	100% H ₂ O, 10 mM NH ₄ HCO ₂ , 0.15% FA	90% ACN, 10% H ₂ O, 10 mM NH ₄ HCO ₂ , 0.15% FA

^a Measured pH value of the solvent A was in the parenthesis.

Table A2 Composition of mobile phase with different pH.

pH value	Solvent A	Solvent B
3 (3.00) ^a	100% H ₂ O, 10 mM NH ₄ HCO ₂ , 0.15% FA	90% ACN, 10% H ₂ O, 10 mM NH ₄ HCO ₂ , 0.15% FA
5 (4.92)	100% H ₂ O, 10 mM NH ₄ OAc, 0.02% AcOH	90% ACN, 10% H ₂ O, 10 mM NH ₄ OAc, 0.02% AcOH
7 (6.60)	100% H ₂ O, 10 mM NH ₄ OAc	90% ACN, 10% H ₂ O, 10 mM NH ₄ OAc
9 (8.92)	100% H ₂ O, 10 mM NH ₄ OAc, 0.04% NH ₄ OH	90% ACN, 10% H ₂ O, 10 mM NH ₄ OAc, 0.04% NH ₄ OH

^a Measured pH value of the solvent A was in the parenthesis.

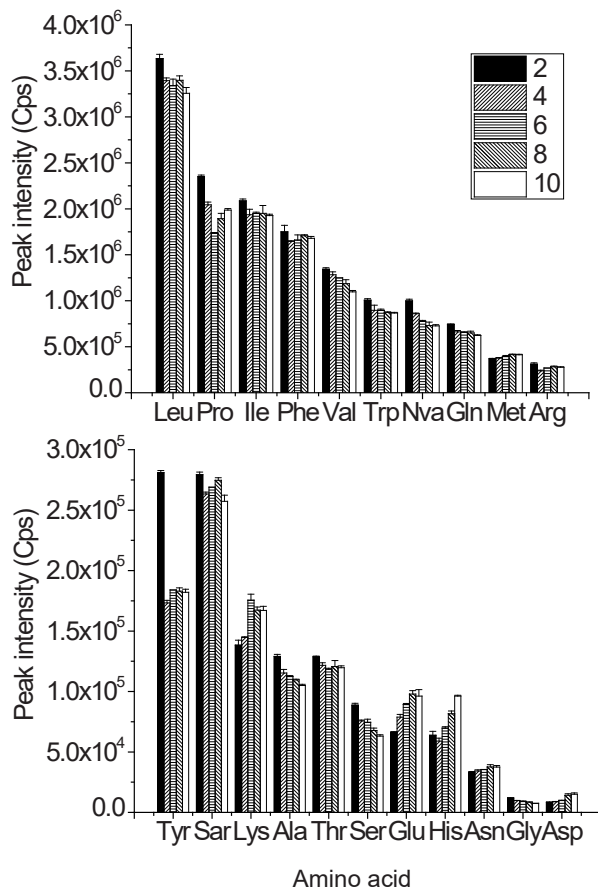


Figure A1 Influence of buffer concentration (mM) on peak intensity of the targeted amino acids. A standard mixture ($2.5 \mu\text{g ml}^{-1}$ for Asp and Gly, $0.5 \mu\text{g ml}^{-1}$ for the rest) was repeatedly injected under different mobile phase within around 10 hours to obtain the chromatograms. The composition of the mobile phase was presented in Table A1. The gradient method was 94–89% B from 0 to 6 minutes, 89–78% B from 6 to 10 minutes, 78–67% B from 10 to 12 minutes, constant 67% B from 12 to 13 minutes. The results are showed as average with standard deviation ($n = 3$).

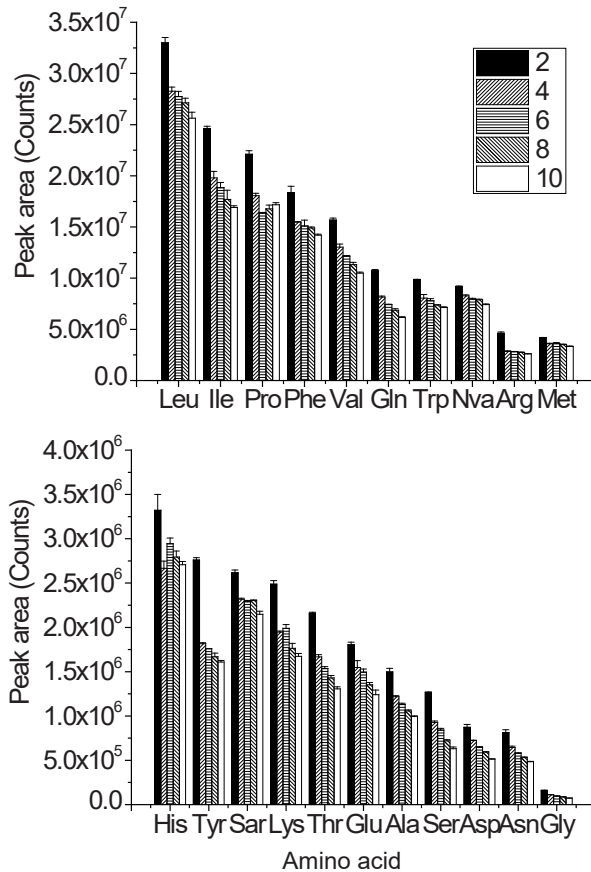


Figure A2 Influence of buffer concentration (mM) on peak area of the targeted amino acids. A standard mixture ($2.5 \mu\text{g ml}^{-1}$ for Asp and Gly, $0.5 \mu\text{g ml}^{-1}$ for the rest) was repeatedly injected under different mobile phase within around 10 hours to obtain the chromatograms. The composition of the mobile phase was presented in Table A1. The gradient method was 94–89% B from 0 to 6 minutes, 89–78% B from 6 to 10 minutes, 78–67% B from 10 to 12 minutes, constant 67% B from 12 to 13 minutes. The results are showed as average with standard deviation ($n = 3$).

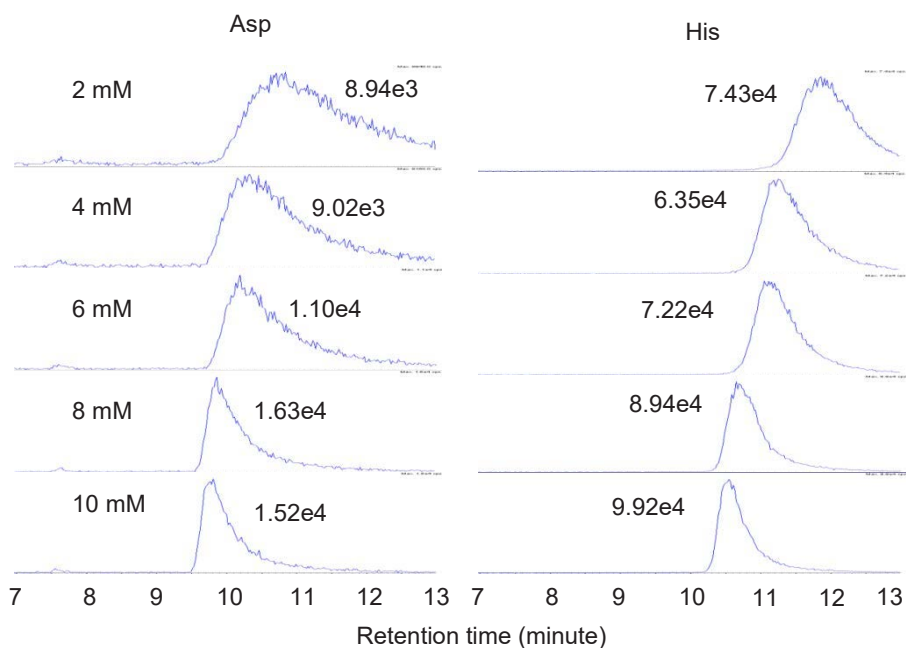


Figure A3 Extracted chromatograms of Asp and His (labelled with peak intensity in cps) under different buffer concentration in mobile phase obtained from standard mixture ($0.5 \mu\text{g ml}^{-1}$ for His and $2.5 \mu\text{g ml}^{-1}$ for Asp). The composition of the mobile phase were presented in Table A1. The gradient method was 94–89% B from 0 to 6 minutes, 89–78% B from 6 to 10 minutes, 78–67% B from 10 to 12 minutes, constant 67% B from 12 to 13 minutes.

Table A3 Eluted percentage of 20 amino acids in pure water and soil extracts for three consecutive elution steps with varied eluent pH through SPE procedure ($n = 3$).

Analyte	Eluent pH (%NH ₄ OH) ^a	H ₂ O	Soil 1	Soil 2	Soil 3
Trp	1.25	99	94	87	92
	3.75	1	5	11	6
	7.5	0	1	2	2
Phe	1.25	99	97	94	96
	3.75	1	2	4	3
	7.5	0	1	1	1
Leu	1.25	99	98	96	98
	3.75	1	1	3	2
	7.5	0	1	1	1
Ile	1.25	99	98	96	97
	3.75	1	2	3	2
	7.5	0	1	1	1
Met	1.25	100	100	100	100
	3.75	0	0	0	0
	7.5	0	0	0	0
Val	1.25	99	98	98	98
	3.75	0	1	2	1
	7.5	0	0	0	1
Pro	1.25	100	98	98	99
	3.75	0	1	2	1
	7.5	0	0	1	1
Tyr	1.25	100	97	97	98
	3.75	0	2	3	2
	7.5	0	1	0	0
Sar	1.25	98	97	98	98
	3.75	1	1	1	1
	7.5	1	1	1	1
Ala	1.25	100	99	98	99
	3.75	0	1	1	0
	7.5	0	0	1	0

(continued)

Table A3 Eluted percentage of 20 amino acids in pure water and soil extracts for three consecutive elution steps with varied eluent pH through SPE procedure ($n = 3$) (continued).

Analyte	Eluent pH (%NH ₄ OH) ^a	H ₂ O	Soil 1	Soil 2	Soil 3
Thr	1.25	100	98	97	99
	3.75	0	1	2	1
	7.5	0	0	1	0
Gly	1.25	100	100	100	100
	3.75	0	0	0	0
	7.5	0	0	0	0
Gln	1.25	100	99	98	99
	3.75	0	1	2	1
	7.5	0	0	0	0
Ser	1.25	100	96	94	97
	3.75	0	2	3	1
	7.5	0	2	2	1
Asn	1.25	100	100	100	100
	3.75	0	0	0	0
	7.5	0	0	0	0
Glu	1.25	100	100	95	95
	3.75	0	0	5	4
	7.5	0	0	0	1
Asp	1.25	100	100	100	100
	3.75	0	0	0	0
	7.5	0	0	0	0
Arg	1.25	1	10	2	2
	3.75	29	14	3	4
	7.5	70	76	95	94
His	1.25	92	83	68	84
	3.75	8	17	32	16
	7.5	0	0	0	0
Lys	1.25	94	91	76	56
	3.75	6	8	24	37
	7.5	0	2	0	7

^a The percentage of NH₄OH in MeOH.

Table A4 Intra-day and inter-day precision of amino acids overall recoveries for soil 3.

Analyte	Intra-day (% , <i>n</i> = 5)			Inter-day (% , <i>n</i> = 3)		
	Mean	STD	RSD	Mean	STD	RSD
Trp	82	2	3	85	3	3
Phe	83	3	3	86	5	6
Leu	80	4	5	85	6	7
Ile	76	3	5	83	9	10
Met	5	0	2	6	1	14
Val	69	3	5	74	7	10
Pro	57	1	1	57	2	4
Tyr	113	2	2	97	14	14
Sar	79	1	2	81	2	2
Ala	98	3	3	96	3	3
Thr	127	2	2	121	6	5
Gly	100	4	4	100	2	2
Gln	85	1	1	86	2	2
Ser	83	2	2	83	1	1
Asn	77	4	5	81	5	6
Glu	108	5	4	112	4	4
Asp	77	4	5	80	3	4
Arg	29	1	3	30	1	3
His	93	1	1	92	4	5
Lys	108	1	1	104	4	4

Table A5 Free amino acids content extracted from soil ($\mu\text{g g}^{-1}$).

Analyte	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10
Trp	19 ± 1	4.6 ± 0.3	34 ± 1	60 ± 4	33 ± 1	244 ± 10	2 ± 0.1	ND	12 ± 1	15 ± 1
Phe	520 ± 15	64 ± 2	453 ± 15	357 ± 16	250 ± 5	1955 ± 64	12.4 ± 0.3	6 ± 0.3	51 ± 2	127 ± 9
Leu	679 ± 22	116 ± 3	934 ± 40	625 ± 17	349 ± 3	2946 ± 97	17.7 ± 0.4	7.9 ± 0.3	84 ± 4	186 ± 13
Ile	360 ± 8	73 ± 4	429 ± 19	290 ± 11	267 ± 6	1208 ± 32	8.8 ± 0.4	4.2 ± 0.2	35 ± 2	107 ± 7
Met	2.1 ± 0.2	1.1 ± 0.1	ND	80 ± 17	22 ± 7	820 ± 23	ND	ND	1.2 ± 0.4	1.2 ± 0.1
Val	374 ± 16	112 ± 2	683 ± 48	433 ± 23	463 ± 8	1528 ± 74	11.9 ± 0.6	3 ± 0.2	60 ± 1	189 ± 13
Pro	526 ± 16	64 ± 6	89 ± 4	197 ± 16	113 ± 8	349 ± 13	ND	ND	24 ± 1	73 ± 7
Tyr	588 ± 26	38 ± 2	155 ± 3	228 ± 16	200 ± 4	944 ± 11	5.3 ± 0.8	ND	54 ± 1	84 ± 1
Sar	93 ± 1	6.8 ± 0.4	13 ± 0	13 ± 0	7.8 ± 0.2	10 ± 0	1.9 ± 0.1	1.6 ± 0.1	3.5 ± 0.2	2.7 ± 0.1
Ala	924 ± 2	288 ± 1	885 ± 38	1005 ± 21	747 ± 6	3106 ± 53	17.4 ± 0.4	10.2 ± 0.3	150 ± 2	304 ± 0

(continued)

Table A5 Free amino acids content extracted from soil^a ($\mu\text{g g}^{-1}$, continued).

Analyte	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6	Soil 7	Soil 8	Soil 9	Soil 10
Thr	512 ± 12	138 ± 2	582 ± 12	541 ± 20	537 ± 8	1832 ± 68	9.7 ± 0.4	5.5 ± 0.4	74 ± 8	139 ± 1
Gly	566 ± 22	293 ± 3	556 ± 25	652 ± 14	1000 ± 11	1193 ± 29	21 ± 2.2	19.2 ± 2.3	147 ± 10	136 ± 10
Gln	103 ± 1	108 ± 6	137 ± 5	296 ± 11	89 ± 4	1735 ± 52	7 ± 0.1	4.9 ± 0.2	436 ± 21	259 ± 7
Ser	597 ± 11	139 ± 5	388 ± 12	483 ± 2	356 ± 5	1470 ± 61	ND	ND	88 ± 17	125 ± 3
Asn	136 ± 9	59 ± 1	171 ± 8	138 ± 4	256 ± 4	1434 ± 94	ND	ND	197 ± 27	150 ± 5
Glu	569 ± 17	205 ± 8	2024 ± 95	3240 ± 63	1405 ± 20	12987 ± 198	53.4 ± 2.6	45.5 ± 2.2	321 ± 3	136 ± 1
Asp	1581 ± 130	193 ± 20	464 ± 43	1068 ± 36	1239 ± 10	1556 ± 97	ND	ND	160 ± 15	109 ± 1
Arg	187 ± 2	77 ± 5	124 ± 2	180 ± 6	264 ± 15	10832 ± 125	6.8 ± 0.2	6.9 ± 0.4	62 ± 3	72 ± 3
His	46 ± 2	ND	16 ± 0	38 ± 2	96 ± 2	227 ± 8	ND	ND	4.6 ± 0.5	4.8 ± 0.5
Lys	252 ± 1	16 ± 1	53 ± 1	55 ± 1	345 ± 4	673 ± 15	5.6 ± 0.8	1.6 ± 0.1	13 ± 1	27 ± 3
sum	8636	1996	8189	9979	8039	47049	181	116	1977	2245

^a The data are presented as means with standard deviation ($n = 3$). ND: not detectable.

Appendix (B) to Chapter 4

Table B1 Summary results of two way analysis of variance (ANOVA) for the adsorption of PAs on different minerals (goethite and montmorillonite) in the control experiment.

Source of variation	Degrees of freedom	Mean square	F ratio	P
Mineral	1	4.568	31503.7	<0.001
Concentration	2	0.926	6386.2	<0.001
Interaction	2	0.084	582.1	<0.001
Residual	12	0.000145		
Total	17	0.388		

Note: the data were transformed using function $Y = \ln(X + 1)$ prior to analysis, X and Y represent the initial and transformed value, respectively.

Table B2 Summary results of two way ANOVA for the adsorption of AAs on different minerals (goethite and montmorillonite) in the control experiment.

Source of Variation	Degrees of freedom	Mean square	F ratio	P
Mineral	1	0.382	176.0	<0.001
Concentration	2	0.363	167.0	<0.001
Interaction	2	0.170	78.5	<0.001
Residual	12	0.00217		
Total	17	0.0867		

Note: the data were transformed using the function $Y = X / (10 - X)$ prior to analysis, X and Y represent the initial and transformed value, respectively.

Table B3 Increase in solution pH after adsorption of PAs and AAs on goethite (G) and montmorillonite (M).

Mineral	Initial concentration /mM	Increase in pH			
		Control	PAs	AAs	PAs & AAs
G	0	0.80 (0.08)	NA	NA	NA
	0.01	NA	0.68 (0.05)	0.64 (0.02)	0.72 (0.04)
	0.05	NA	0.72 (0.02)	0.66 (0.02)	0.75 (0.03)
	0.10	NA	0.73 (0.01)	0.67 (0.01)	0.76 (0.01)
M	0	0.52 (0.02)	NA	NA	NA
	0.01	NA	0.42 (0.02)	0.40 (0.01)	0.42 (0.03)
	0.05	NA	0.44 (0.01)	0.41 (0.02)	0.42 (0.02)
	0.10	NA	0.43 (0.01)	0.40 (0.01)	0.44 (0.01)

Note: the results are presented as mean values with standard deviation ($n = 3$). Control: 10 mM NaN_3 solution. NA: not applicable.

Table B4 Mean values of total adsorption of PAs and AAs on goethite and montmorillonite, respectively, with competition and surface conditioning.

Compounds	Effects	Mineral	IC ^a /mM	Mean ^b / $\mu\text{mol g}^{-1}$	SEM ^c	LSD ^d	
PAs	Comp. ^e	G ^g	0.01	1.86		0.08	0.24
			0.05	4.76			
			0.10	4.77			
		M ^h	0.01	0.28	(0.39)	0.01	0.03
			0.05	0.48	(0.93)		
			0.10	0.54	(1.16)		
	Surf. ^f	G	0.01	2.08		0.09	0.27
			0.05	7.29			
			0.10	10.0			
		M	0.01	2.62	(0.38)	0.03	0.08
			0.05	0.80	(1.26)		
			0.10	0.57	(1.77)		
AAs	Comp.	G	0.01	0.36		0.25	0.77
			0.05	0.65			
			0.10	2.83			
		M	0.01	0.61		0.04	0.12
			0.05	2.86			
			0.10	5.81			
	Surf.	G	0.01	0.66		0.35	1.09
			0.05	2.69			
			0.10	4.05			
		M	0.01	0.40	(0.67)	0.00	0.01
			0.05	0.75	(3.03)		
			0.10	0.87	(6.76)		

^a Initial concentration; ^b Original mean values are presented in the bracket if transformed data are used for ANOVA; ^c Standard error of the transformed mean determined using the residual MS (12 d.f.); ^d Least significant difference, $P < 0.05$; ^e Competition; ^f Surface conditioning; ^g Goethite; ^h Montmorillonite.

Table B5 Summary results of two way ANOVA for effects of competition on the adsorption of PAs on goethite in the competition experiment.

Source of Variation	Degrees of freedom	Mean square	F ratio	P
Competition	1	3.056	164.7	<0.001
Concentration	2	25.11	1353.0	<0.001
Interaction	2	1.561	84.1	<0.001
Residual	12	0.0186		
Total	17	3.330		

Table B6 Summary results of two way ANOVA for effects of competition on the adsorption of AAs on goethite in the competition experiment.

Source of Variation	Degrees of freedom	Mean square	F ratio	P
Competition	1	0.379	2.02	0.181
Concentration	2	5.641	30.09	<0.001
Interaction	2	1.051	5.61	0.019
Residual	12	0.187		
Total	17	0.942		

Table B7 Summary results of two way ANOVA for effects of competition on the adsorption of PAs on montmorillonite in the competition experiment.

Source of Variation	Degrees of freedom	Mean square	F ratio	P
Competition	1	0.0030	11.9	0.005
Concentration	2	0.1280	498.4	<0.001
Interaction	2	0.000542	2.1	0.163
Residual	12	0.000256		
Total	17	0.0154		

Note: the data were transformed using the function $Y = X / (1 + X)$ prior to analysis, X and Y represent the initial and transformed value, respectively.

Table B8 Summary results of two way ANOVA for effects of competition on the adsorption of AAs on montmorillonite in the competition experiment.

Source of Variation	Degrees of freedom	Mean square	<i>F</i> ratio	<i>P</i>
Competition	1	1.611	378.3	<0.001
Concentration	2	32.80	7703.8	<0.001
Interaction	2	0.430	101.1	<0.001
Residual	12	0.00426		
Total	17	4.007		

Table B9 Summary results of two way ANOVA for effects of conditioning by AAs on the adsorption of PAs on goethite in the conditioning experiment.

Source of Variation	Degrees of freedom	Mean square	<i>F</i> ratio	<i>P</i>
Conditioning	1	15.31	644.8	<0.001
Concentration	2	63.31	2666.3	<0.001
Interaction	2	3.685	155.2	<0.001
Residual	12	0.0237		
Total	17	8.799		

Table B10 Summary results of two way ANOVA for effects of conditioning by PAs on the adsorption of AAs on goethite in the conditioning experiment.

Source of Variation	Degrees of freedom	Mean square	<i>F</i> ratio	<i>P</i>
Conditioning	1	9.814	26.16	<0.001
Concentration	2	8.225	21.93	<0.001
Interaction	2	1.727	4.60	0.033
Residual	12	0.375		
Total	17	2.013		

Table B11 Summary results of two way ANOVA for effects of conditioning by AAs on the adsorption of PAs on montmorillonite in the conditioning experiment.

Source of Variation	Degrees of freedom	Mean square	F ratio	P
Conditioning	1	0.024	11.7	0.005
Concentration	2	6.687	3278.7	<0.001
Interaction	2	0.028	13.5	<0.001
Residual	12	0.00204		
Total	17	0.793		

Note: the data were transformed using the reciprocal function prior to analysis.

Table B12 Summary results of two way ANOVA for effects of conditioning by PAs on the adsorption of AAs on montmorillonite in the conditioning experiment.

Source of Variation	Degrees of freedom	Mean square	F ratio	P
Conditioning	1	0.0143	397.0	<0.001
Concentration	2	0.377	10463.2	<0.001
Interaction	2	0.000265	7.3	0.008
Residual	12	0.0000360		
Total	17	0.0453		

Note: the data were transformed using the function $Y = X / (1 + X)$ prior to analysis, X and Y represent the initial and transformed value, respectively.

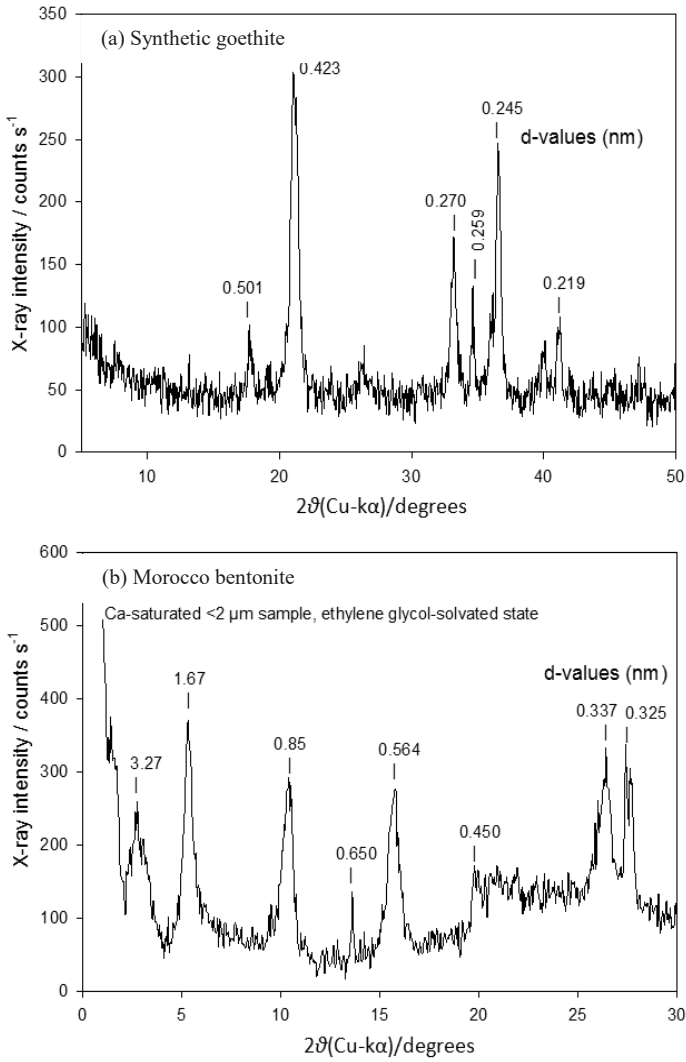


Figure B1 X-ray diffraction patterns of (a) the synthetic goethite and (b) the < 2 μm fraction of Morocco bentonite.

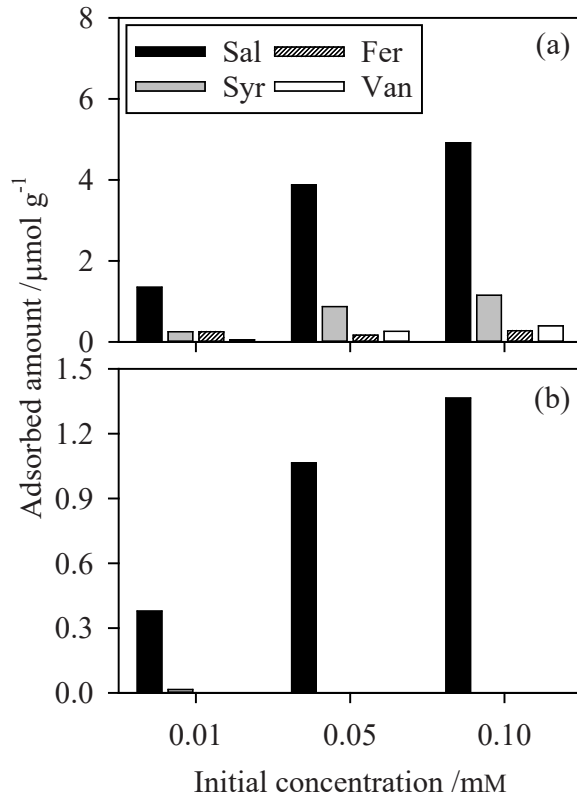


Figure B2 Adsorption of individual PAs (Sal, Syr, Fer and Van) on (a) goethite and (b) montmorillonite in the control experiments. The results are presented as mean values without transformation ($n = 3$). Sal, salicylic acid; Syr, syringic acid; Fer, ferulic acid; Van, vanillic acid.

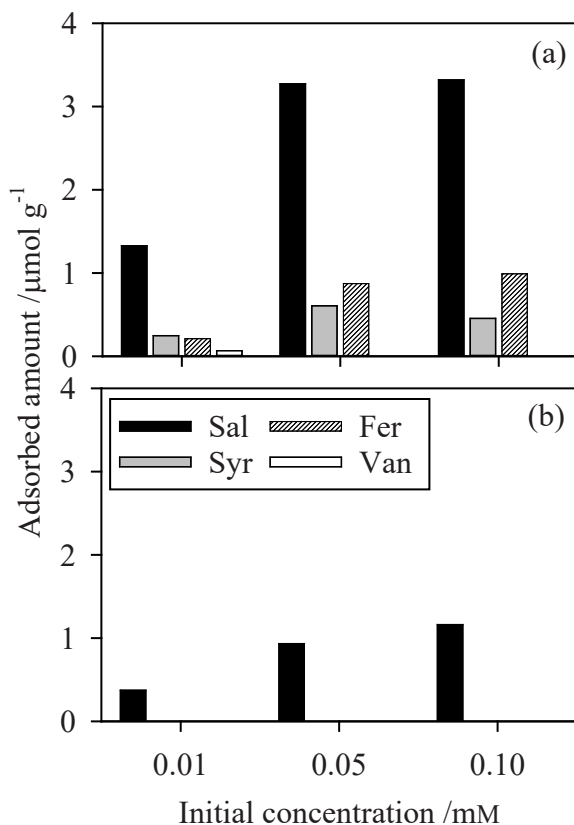


Figure B3 Adsorption of individual PAs (Sal, Syr, Fer and Van) on (a) goethite and (b) montmorillonite in the competition experiment. The results are presented as mean values without transformation ($n = 3$). Sal, salicylic acid; Syr, syringic acid; Fer, ferulic acid; Van, vanillic acid.

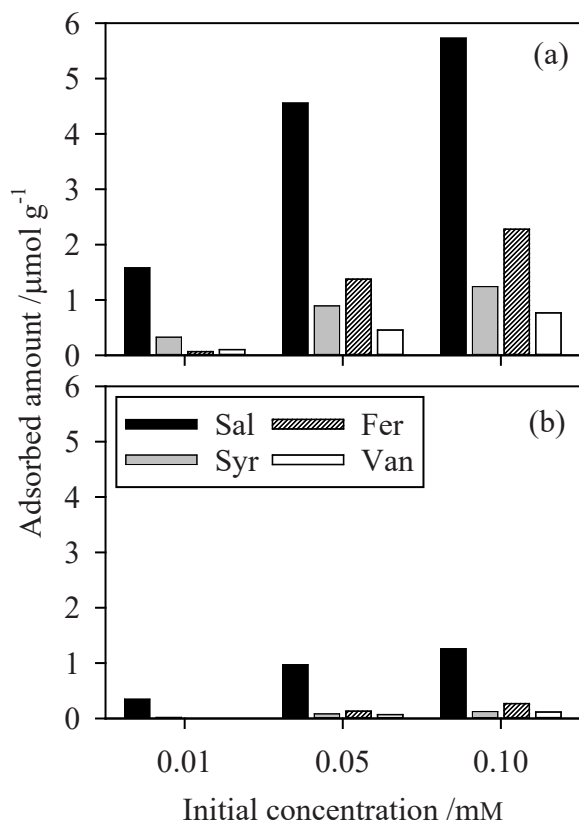


Figure B4 Adsorption of individual PAs (Sal, Syr, Fer and Van) on (a) goethite and (b) montmorillonite after adsorption of AAs. The results are presented as mean values without transformation ($n = 3$). Sal, salicylic acid; Syr, syringic acid; Fer, ferulic acid; Van, vanillic acid.

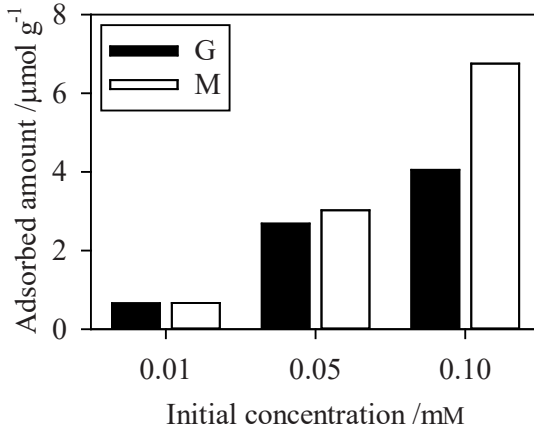


Figure B5 Adsorption of AAs on goethite (G) and montmorillonite (M) after adsorption of PAs. The results are presented as mean values without transformation (SE = 0.321, 12 d.f.). SE: standard error of mean.

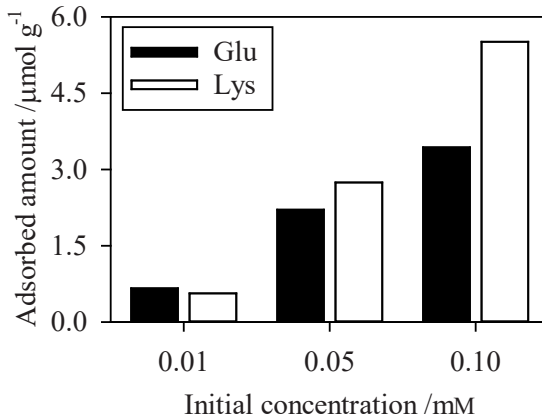


Figure B6 Adsorption of glutamic acid (Glu) on goethite after conditioning with PAs, and lysine (Lys) on montmorillonite after conditioning with PAs. The results are presented as mean values without transformation ($n = 3$). Transformed mean values were used for ANOVA analysis (SE = 0.025, 12 d.f., $P < 0.05$ for the initial concentration of 0.05 and 0.1 mM). SE: standard error of mean.

Appendix (C) to Chapter 5

Measurement of PAs

The standard mixture solution of four PAs and internal standard (IS) were prepared in ultrapure H₂O. Separation was done with a LiChrospher/Superspher RP-18 100-Å column (125 mm × 2 mm, 4 μm; Phenomenex, Torrance, CA, USA) and an RP-18 4-μm guard column. The mobile phase was solvent A (MeOH, 0.1% FA, v/v%) and solvent B (ultrapure H₂O, 0.1% FA, v/v%) with an isocratic elution of 27% solvent A for 15 minutes. Solvent A (90%) was used to wash the column between injections for 5 minutes, followed by a 15-minute equilibration period. The rate of flow of the mobile phase was 0.3 ml minute⁻¹. The injection volume was 10 μl and the oven temperature was 35 °C. Sal, Van, Syr, Fer and Eva were detected at 240, 260, 270, 320 and 280 nm, respectively.

Calibration lines were made by plotting the ratio of analyte to IS concentration versus analyte to IS peak area. Quantification of all measurements was performed with a eight point calibration line. For each different level of analyte concentration, the IS concentration was the same (4 mg l⁻¹). The high coefficients of determination (r^2) in Table C1 indicated the reliability of the calibration line over a wide range of concentration.

Table C1 Regression linear range and coefficients of determination of the PAs.

Analyte	IS	Linear range /mg l ⁻¹	r^2
Van	Eva	0.1–20	0.9999
Syr	Eva	0.1–20	0.9999
Fer	Eva	0.1–20	0.9998
Sal	Eva	0.1–20	0.9998

Table C2 Accuracies of the analytical methods for mixture of PAs and AAs.

Analyte	Concentration /mM		
	0.01	0.05	0.10
PAs			
Van	90 (4)	92 (5)	91 (5)
Syr	92 (4)	91 (5)	92 (5)
Fer	86 (2)	93 (15)	94 (13)
Sal	87 (3)	93 (4)	94 (5)
AAs			
Leu	105 (9)	100 (8)	108 (10)
Glu	99 (6)	115 (8)	110 (5)
Lys	93 (12)	107 (12)	99 (11)
Phe	101 (8)	110 (7)	107 (7)

Notes: The accuracies (%) are calculated as the ratio of measured value to calculated value. The results are presented as mean values with standard deviation ($n = 6$).

Table C3 Desorption of adsorbed OC from OM-coated minerals^a.

Mineral	Adsorbed OC /mg g ⁻¹	First cycle		Second cycle	
		Desorbed OC /mg g ⁻¹	Desorbed fraction /%	Desorbed OC /mg g ⁻¹	Desorbed fraction /%
L-G ^b	8.85 (0.01)	0.30 (0.02)	3.4 (0.2)	ND	ND
O-G ^c	18.2 (0.02)	1.51 (0.04)	8.3 (0.2)	0.33 (0.00)	1.8 (0.0)
L-K ^d	1.07 (0.00)	0.07 (0.00)	6.4 (0.4)	ND	ND
O-K ^e	1.13 (0.00)	0.12 (0.02)	10.2 (2.0)	ND	ND
L-M ^f	0.73 (0.00)	0.19 (0.01)	26.7 (0.7)	0.02 (0.00)	2.1 (0.6)
O-M ^g	0.80 (0.00)	0.18 (0.02)	22.2 (2.0)	0.01 (0.00)	1.7 (0.3)

^a The results are presented as mean values with standard deviation ($n = 3$). ^b Goethite coated with L-DOM; ^c Goethite coated with O-DOM; ^d Kaolinite coated with L-DOM; ^e Kaolinite coated with O-DOM; ^f Montmorillonite coated with L-DOM; ^g Montmorillonite coated with O-DOM; ND: not detectable.

Table C4 Desorption of previously adsorbed PAs and AAs after addition of AAs and PAs, respectively, in the conditioning experiment^a.

Mineral	DOM coating	Compounds	IC ^g /mM	Desorption / $\mu\text{mol g}^{-1}$	Desorbed proportion /%	
G ^b	L ^e	PAs	CK ^h	ND		
			0.01	0.17 (0.01)	73 (7)	
			0.05	0.56 (0.00)	70 (1)	
				0.10	0.85 (0.03)	96 (6)
		AAs	CK	0.12 (0.01)		
			0.01	0.17 (0.04)	8 (6)	
			0.05	0.46 (0.04)	18 (12)	
				0.10	0.72 (0.30)	21 (13)
		O ^f	PAs	CK	ND	
	0.01			NA		
	0.05			NA		
	0.10			NA		
	AAs		CK	0.01 (0.00)		
			0.01	ND		
			0.05	ND		
0.10			ND			
K ^c	L	PAs	CK	ND		
			0.01	0.07 (0.00)	43 (1)	
			0.05	0.23 (0.00)	49 (2)	
				0.1	0.35 (0.00)	60 (1)
		AAs	CK	0.02 (0.00)		
			0.01	0.10 (0.01)	15 (1)	
			0.05	0.26 (0.05)	10 (2)	
			0.10	0.41 (0.10)	11 (4)	

(Continued)

Table C4 Desorption of previously adsorbed PAs and AAs after addition of AAs and PAs, respectively, in the conditioning experiment (continued)^a.

Mineral	DOM coating	Compounds	IC /mM	Desorption / $\mu\text{mol g}^{-1}$	Desorbed proportion /%	
K	O	PAs	CK	ND		
			0.01	0.05 (0.00)	74 (9)	
			0.05	0.19 (0.00)	81 (10)	
		0.10	0.30 (0.00)	101 (3)		
		AAs	CK	ND		
			0.01	0.06 (0.01)	11 (1)	
	0.05		0.24 (0.03)	11 (1)		
	M ^d	L	PAs	CK	ND	
				0.01	0.11 (0.00)	52 (1)
				0.05	0.39 (0.01)	57 (1)
			0.10	0.64 (0.01)	68 (1)	
			AAs	CK	0.02 (0.00)	
0.01				0.07 (0.02)	7 (2)	
0.05		0.21 (0.01)		6 (0)		
O		PAs	CK	ND		
			0.01	0.11 (0.00)	44 (1)	
			0.05	0.39 (0.00)	49 (1)	
		0.10	0.64 (0.01)	58 (1)		
		AAs	CK	ND		
	0.01		0.06 (0.00)	9 (0)		
0.05	0.28 (0.02)		8 (1)			
	0.10	0.60 (0.07)	11 (1)			

^a The results are presented as mean values with standard deviation ($n = 3$); ^b Goethite; ^c Kaolinite; ^d Montmorillonite; ^e L-DOM; ^f O-DOM; ^g Initial concentration; ^h Desorption from adsorbed OM on mineral surface; NA: not applicable due to no adsorption of PAs; ND: not detectable.

Table C5 Recovery of PAs and AAs spiked to the solutions desorbed from OM-coated minerals^a.

Compound	OM-coated minerals						
	L-G ^b	O-G ^c	L-K ^d	O-K ^e	L-M ^f	O-M ^g	
PAs	Van	90.9 (1.6)	91.4 (0.6)	91.1 (1.2)	90.9 (0.9)	90.9 (0.6)	91.0 (0.1)
	Syr	91.4 (1.3)	91.9 (0.4)	91.6 (1.0)	91.4 (0.7)	91.3 (0.8)	91.4 (0.4)
	Fer	92.5 (1.2)	93.1 (0.4)	92.8 (1.1)	92.6 (0.7)	92.4 (0.8)	92.6 (0.5)
	Sal	91.9 (1.1)	92.4 (2.0)	91.9 (2.3)	92.2 (1.8)	91.7 (3.4)	92.0 (2.6)
AAs	Leu	91.0 (6.6)	85.7 (6.2)	88.7 (6.7)	93.5 (3.8)	87.5 (8.0)	90.6 (6.0)
	Glu	92.3 (7.3)	87.8 (10.7)	90.4 (9.3)	97.2 (4.7)	87.9 (8.4)	92.7 (6.8)
	Lys	98.5 (9.1)	88.8 (12.6)	95.3 (9.4)	101.3 (4.1)	92.2 (9.1)	96.4 (4.6)
	Phe	89.4 (7.1)	85.3(7.4)	87.8 (4.2)	92.7 (5.2)	87.7 (8.9)	91.1 (7.8)

^a The results (in %) are presented as mean values of four different spiking concentrations with standard deviation. ^b Goethite coated with L-DOM; ^c Goethite coated with O-DOM; ^d Kaolinite coated with L-DOM; ^e Kaolinite coated with O-DOM; ^f Montmorillonite coated with L-DOM; ^g Montmorillonite coated with O-DOM.

Table C6 Langmuir parameters obtained by fitting the adsorption isotherms of L-DOM (L) and O-DOM (O) on goethite (G), kaolinite (K) and montmorillonite (M).

Mineral	DOM	$Q_{max}/\text{mg C g}^{-1}$	$Q_{max}/\text{mg C m}^{-2}$	$k/\text{g mg}^{-1}$	r^2
G	L	14.29	0.205	0.1203	0.9985
	O	31.15	0.447	0.0834	0.9968
K	L	1.70	0.068	1.1351	0.9990
	O	1.96	0.078	1.4140	0.9993
M	L	1.45	0.015	0.1752	0.9805
	O	1.44	0.015	0.8933	0.9996

Note: The equilibrium concentration of adsorbates after adsorption referred to the ratio of the amount of remaining OC in the solution to the amount of minerals in fitting of adsorption data. Q_{max} = adsorption capacity, k = affinity coefficient.

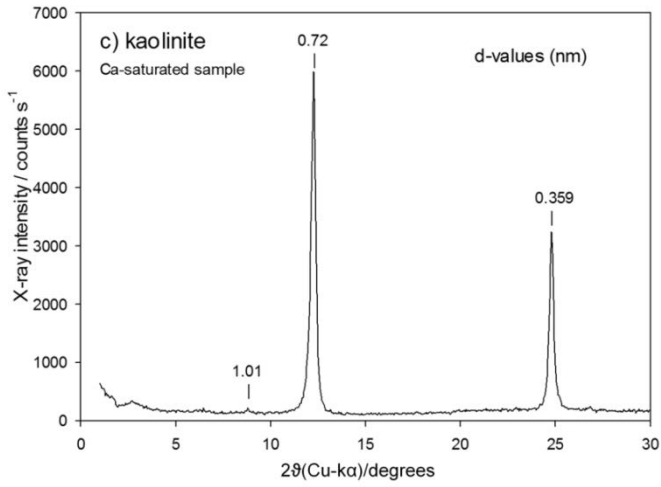


Figure C1 X-ray diffraction patterns of kaolinite.

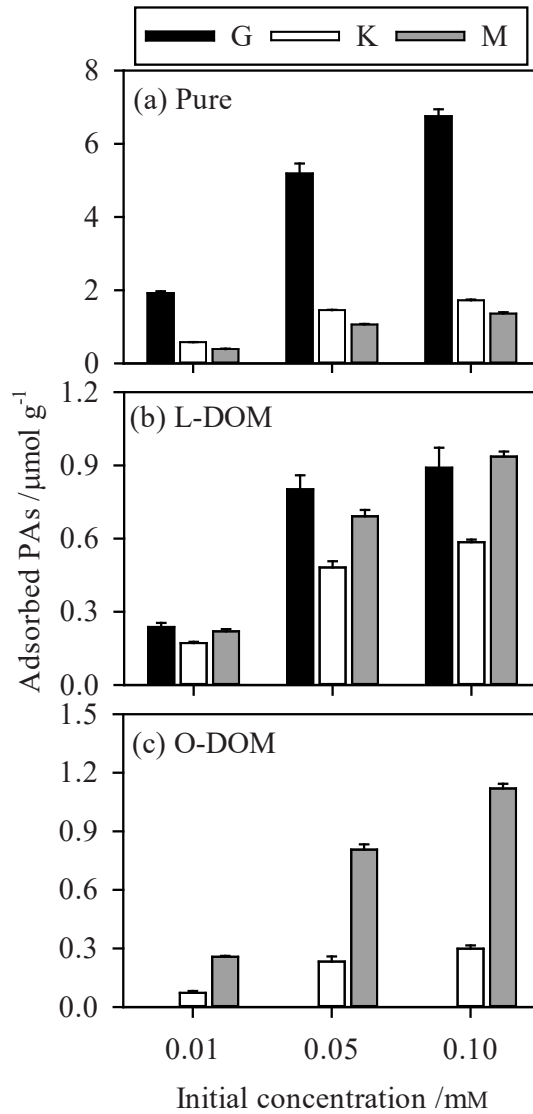


Figure C2 Adsorption of PAs on (a) pure minerals, (b) coated minerals with L-DOM and (c) coated minerals with O-DOM. Data are presented as mean values with 95% confidence intervals ($n = 3$). G, goethite; K, kaolinite; M, montmorillonite.

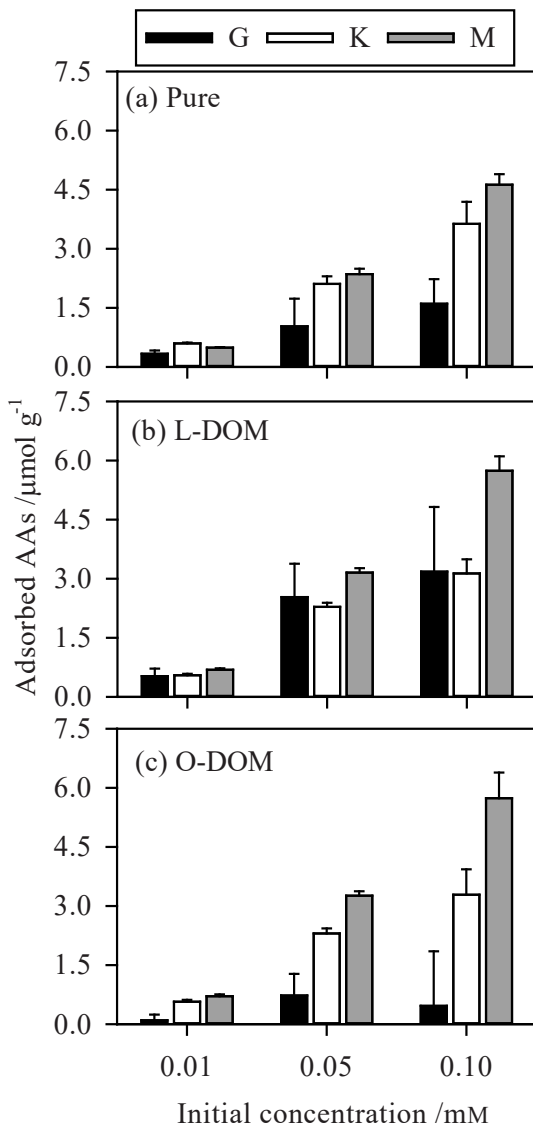


Figure C3 Adsorption of AAs on (a) pure minerals, (b) coated minerals with L-DOM and (c) coated minerals with O-DOM. Data are presented as mean values with 95% confidence intervals ($n = 3$). G, goethite; K, kaolinite; M, montmorillonite.

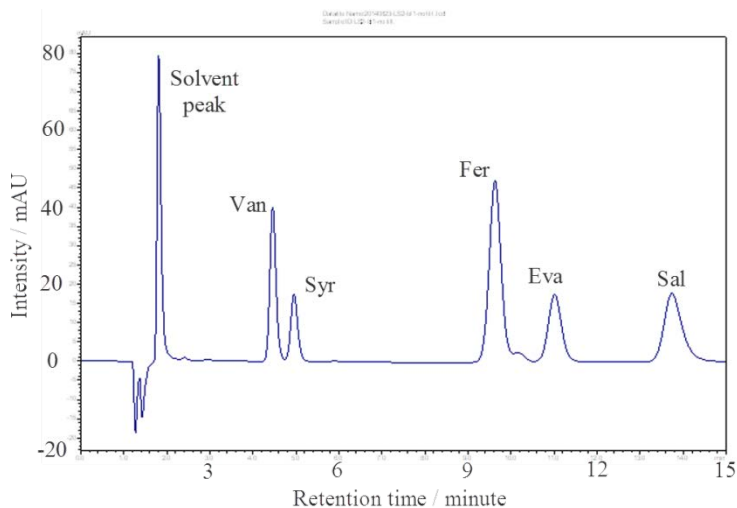


Figure C4 Typical chromatograms of the targeted PAs and IS (Eva) obtained from a mixture solution of PAs and AAs. The injection concentrations of targeted PAs and IS were 0.05 and 0.03 mM, respectively. The wavelength of the detection was 240 nm.

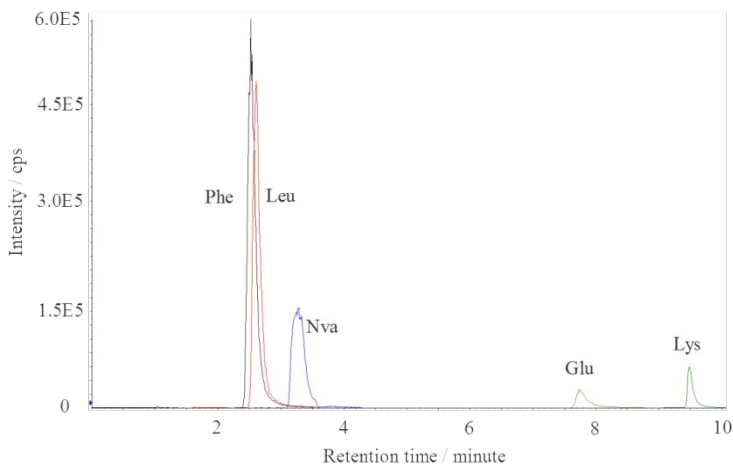


Figure C5 Typical chromatograms of the targeted AAs and IS (Nva) obtained from a mixture solution of PAs and AAs. The injection concentrations of targeted AAs and IS were 1.0 and 0.9 μM , respectively.

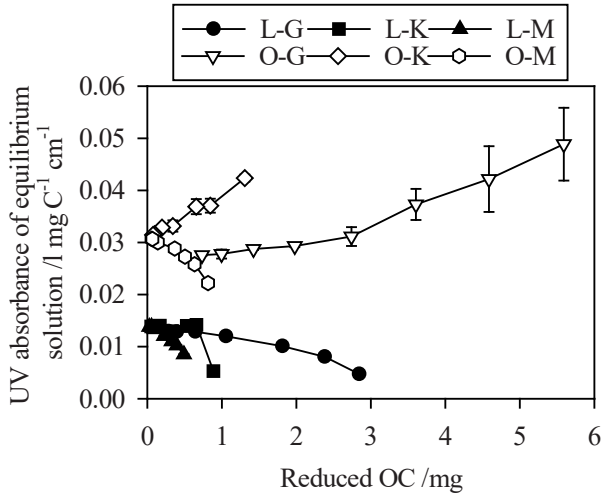


Figure C6 Changes of the UV absorbance (280 nm) of equilibrium solution with reduced OC in solution for all combinations of minerals and DOM. The results are presented as mean values with standard deviation ($n = 2$). G, goethite; K, kaolinite; M, montmorillonite; L, L-DOM; O, O-DOM.

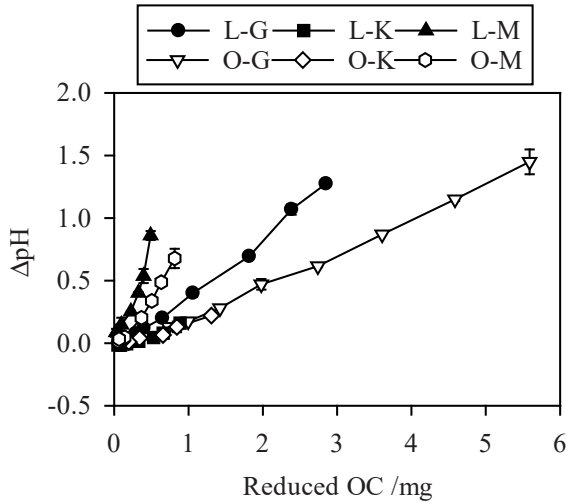


Figure C7 Changes of equilibrium solution pH with reduced OC in the solution for all combinations of minerals and DOM. The results are presented as mean values with standard deviation ($n = 2$). G, goethite; K, kaolinite; M, montmorillonite; L, L-DOM; O, O-DOM.

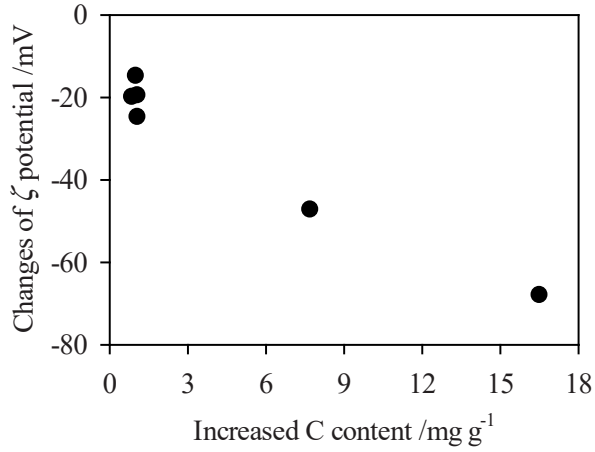


Figure C8 Relation between the increased C content of all OM-coated minerals and the changes of ζ potential.

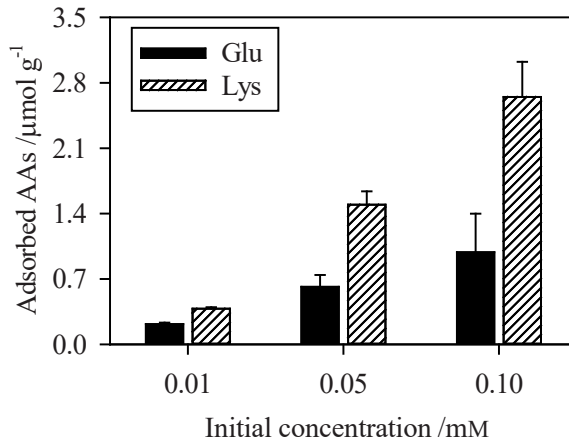


Figure C9 Adsorption of Glu and Lys on kaolinite. The results are presented as mean values with standard deviation ($n = 3$). Glu, glutamic acid; Lys, lysine.

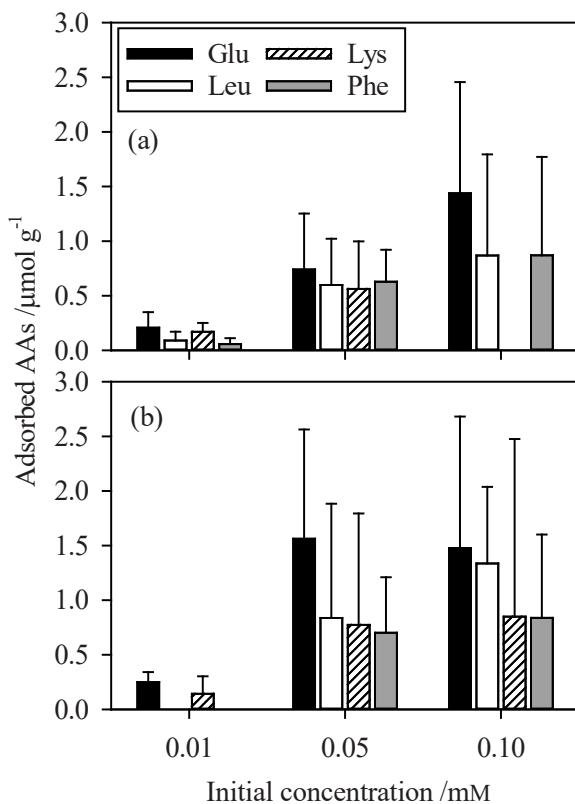


Figure C10 Adsorption of individual AA on (a) L-goethite and (b) L-goethite with pre-conditioning by PAs. The results are presented as mean values with standard deviation ($n = 3$). Glu, glutamic acid; Leu, leucine; Lys, lysine; Phe, phenylalanine.

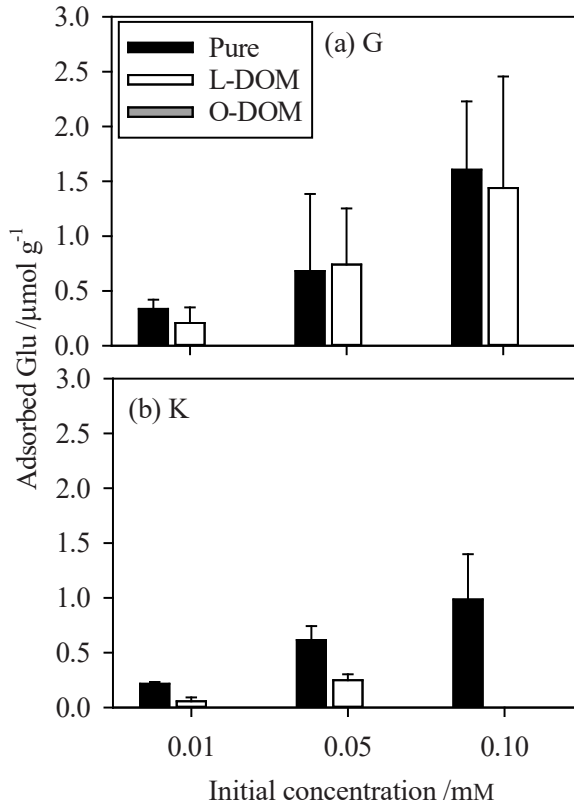


Figure C11 Adsorption of Glu on (a) pure and coated goethite with L-DOM and O-DOM and (b) pure and coated kaolinite with L-DOM and O-DOM. The results are presented as mean values with standard deviation ($n = 3$). No adsorption was observed on O-goethite and O-kaolinite for all initial concentrations and L-kaolinite at the high initial concentration. G, goethite; K, kaolinite.

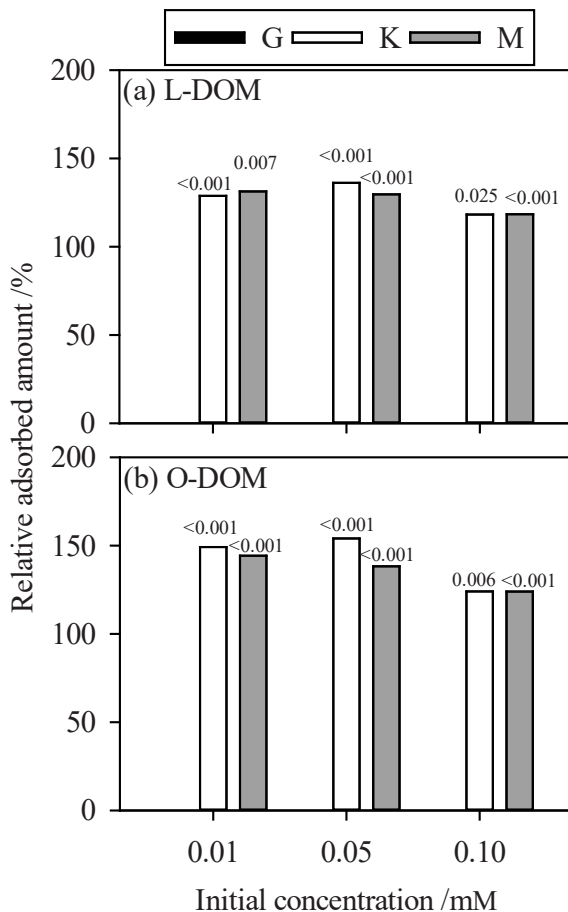


Figure C12 Relative adsorption of Lys on (a) coated minerals with L-DOM and (b) coated minerals with O-DOM. The results are expressed relative to the adsorption (mean value) on pure minerals (reference, expressed as horizontal line). Data are presented as mean values ($n = 3$). P values above each column indicate significant level of differences compared with the references. The adsorption results on coated goethite were not displayed because the values of the references were zero. G, goethite; K, kaolinite; M, montmorillonite.

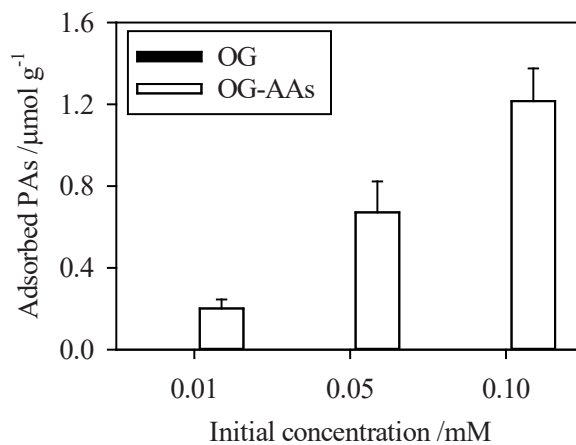


Figure C13 Adsorption of PAs on O-goethite (OG) and after pre-conditioning by AAs (OG-AAs). The results are presented as mean values with standard deviation ($n = 3$). No adsorption of PAs was observed on OG.

