

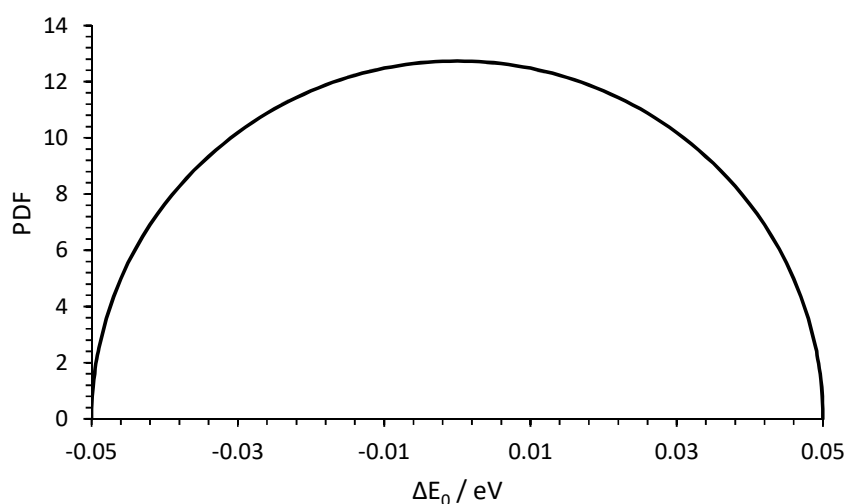
Supplementary materials to:

## A Probabilistic approach to Phosphorus Speciation of Soils using P K-edge XANES spectroscopy with Linear Combination Fitting

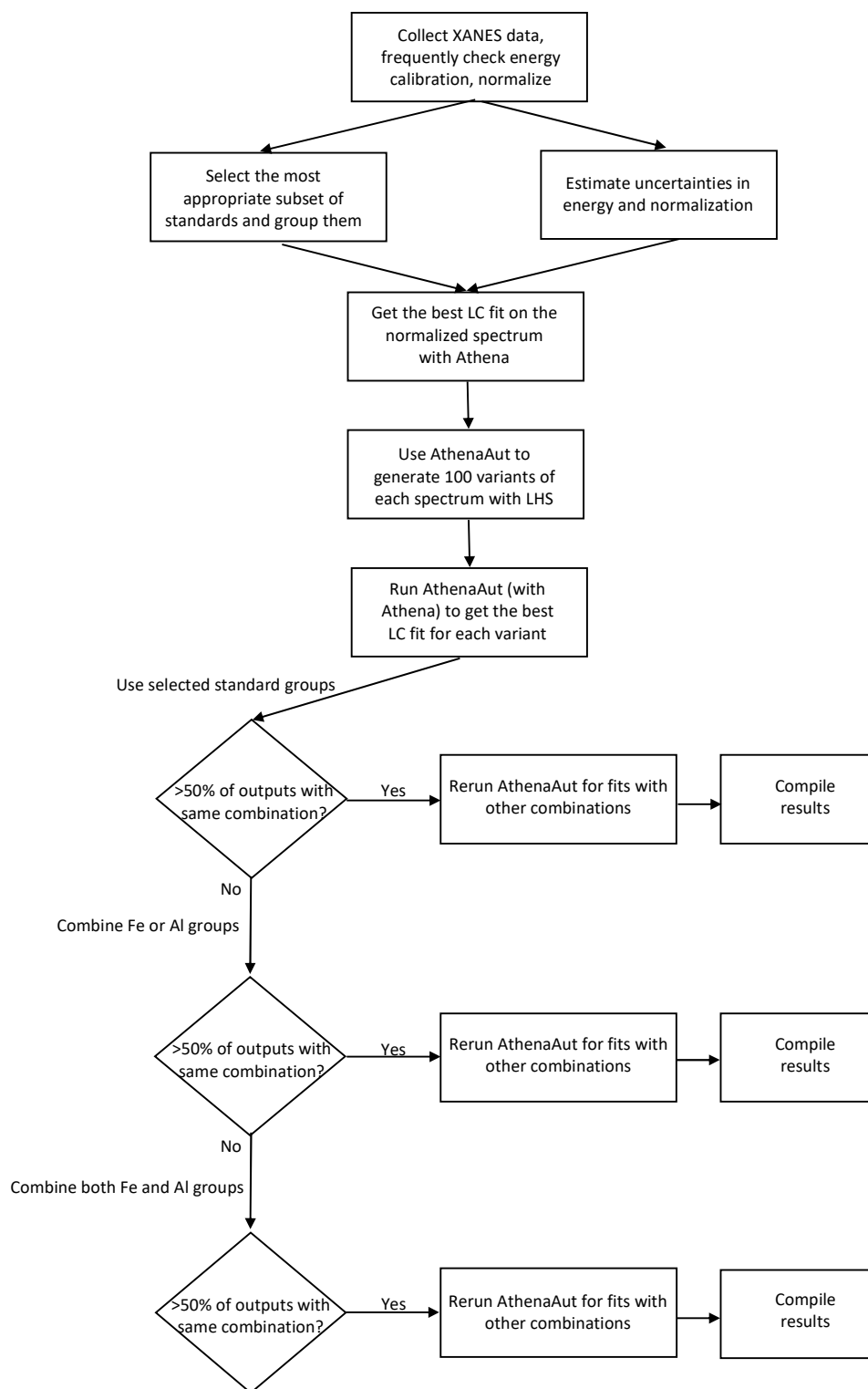
Jon Petter Gustafsson, Sabina Braun, J.R. Marius Tuyishime, Gbotemi A. Adediran, Ruben Warrinnier, Dean Hesterberg

### Contents

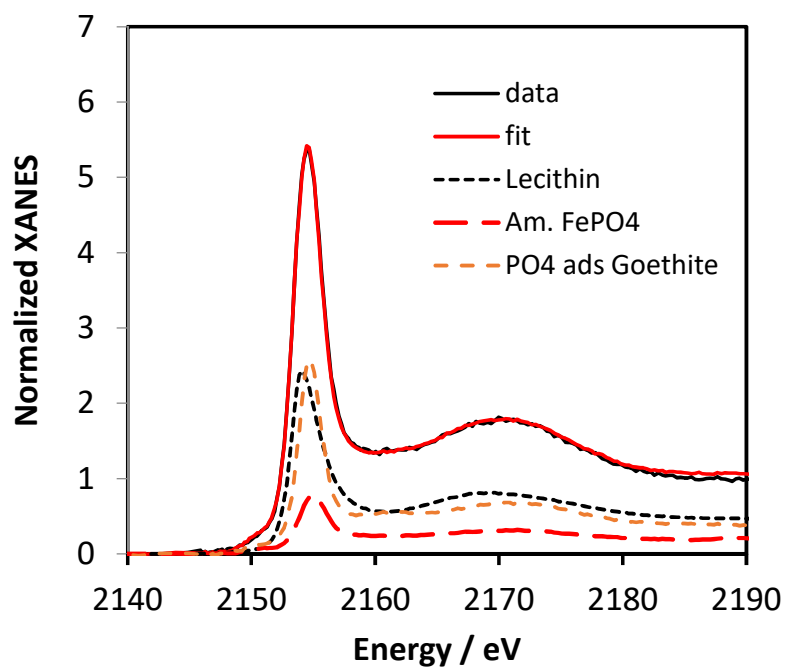
Fig. S1. Probability density function of the Beta distribution	1
Fig. S2. Flow chart illustrating the data treatment process	2
Fig. S3. Linear combination fitting of phytate adsorbed to ferrihydrite	3
Fig. S4. Stacked P K-edge XANES spectra of the 15 standards used for soils	4
Fig. S5. Stacked P K-edge XANES spectra of the 11 soils analysed	5
Table S1. Origin/synthesis method of the 34 standards used	6
Table S2. Prominent features of P K-edge XANES spectra of standards	9
Table S3. No. of occurrences of different standards in the best fits of 100 variants	11
Examples: Grouping of results in the output from AthenaAut	12



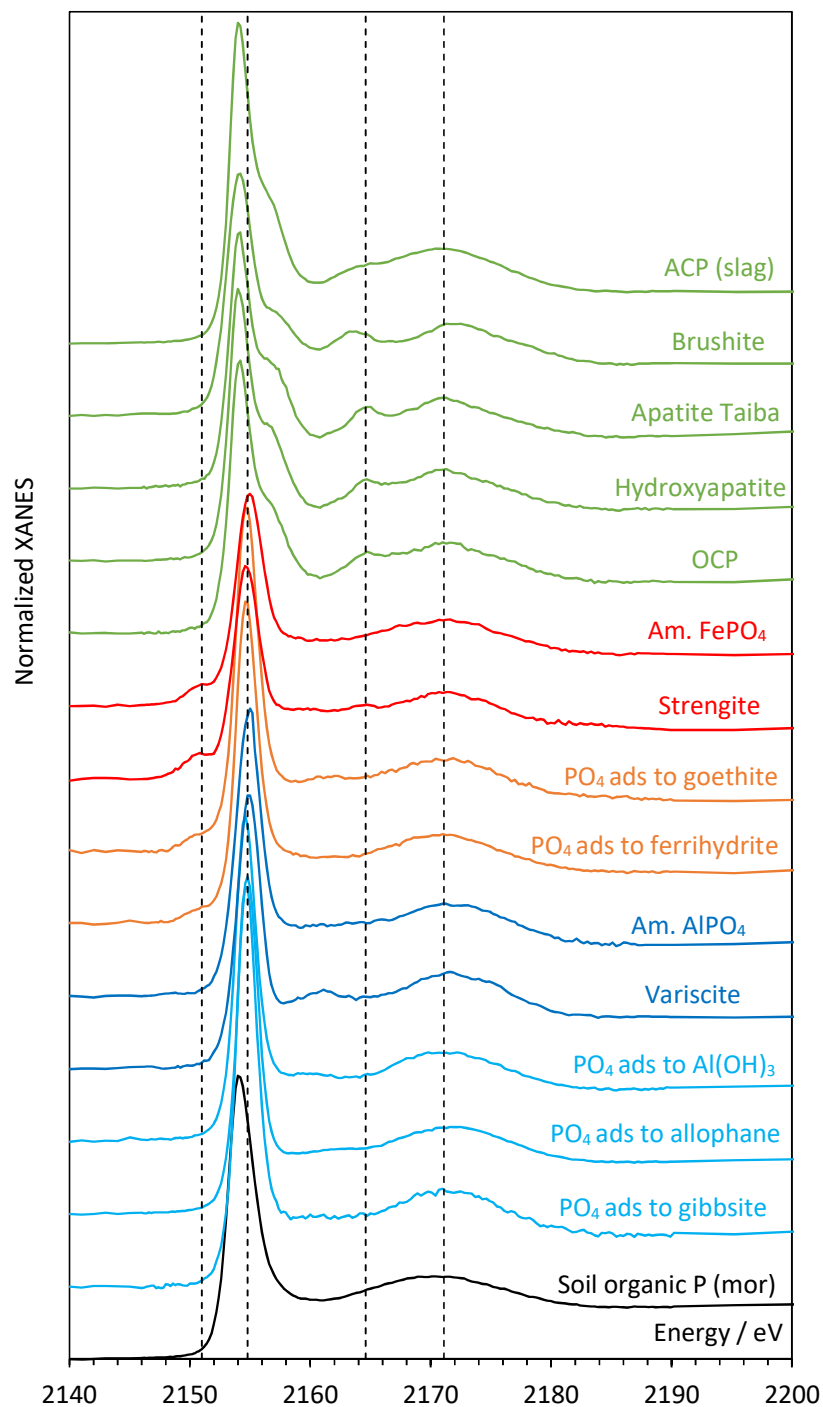
**Figure S1.** Probability density function of the Beta distribution used for linear hypercube sampling of the misalignment of the energy calibration, with the shape parameters fixed at  $\alpha = \beta = 1.5$ .  $\Delta E_0$  is defined as the difference between the assigned energy and the real energy.



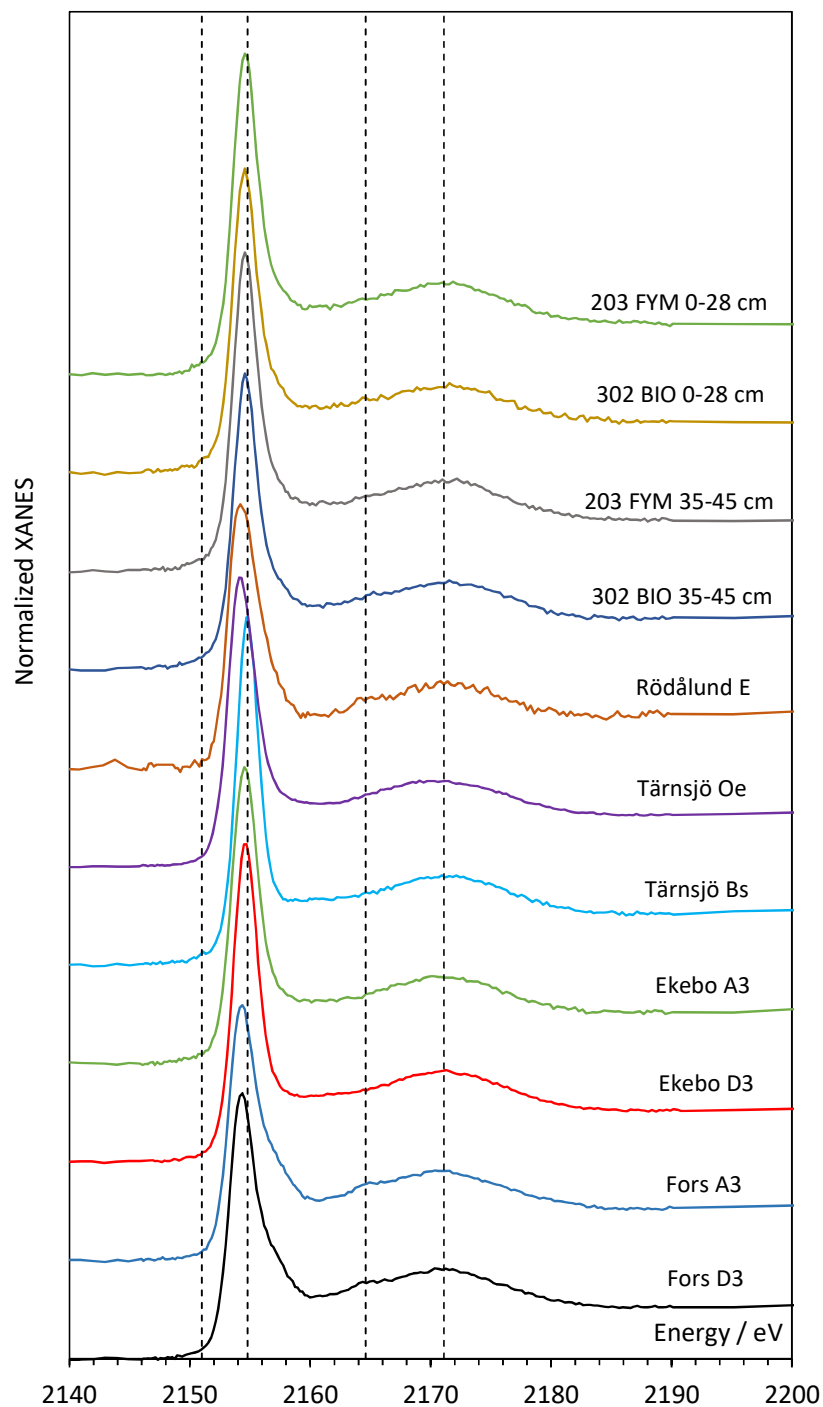
**Figure S2.** Flow chart illustrating the data treatment process as described in the paper. LC = linear combination, LHS = latin hypercube sampling.



**Figure S3.** Results from linear combination fitting of phytate adsorbed to ferrihydrite. The black solid line represents the data, whereas the red solid line is the fit.



**Figure S4.** Stacked P K-edge XANES spectra of the 15 standards used for routine LCF analyses of soil samples. The dashed lines corresponds to the pre-edge of Fe-bound P (2151 eV), the white-line maximum energy of variscite (2154.8 eV), the first post-edge peak of hydroxyapatite (2164.6 eV), and the second post-edge peak of hydroxyapatite (2171.1 eV).



**Figure S5.** Stacked P K-edge XANES spectra of the 11 soils analysed in this study. The dashed lines corresponds to the pre-edge of Fe-bound P (2151 eV), the white-line maximum energy of variscite (2154.8 eV), the first post-edge peak of hydroxyapatite (2164.6 eV), and the second post-edge peak of hydroxyapatite (2171.1 eV).

**Table S1.** Origin/synthesis method of the 34 standards used for P K-edge XANES spectroscopy, with abbreviations as used in the main text

Standard	Origin and/or synthesis method
ACP, Slag	Amorphous calcium phosphate from slag. AOD-P sample of Zuo et al. [1,2]
Apatite Taiba	Natural carbonate apatite from Taiba, Sudan. Mineral collection of the James Hutton Institute.
Brushite	Mineral collection of the James Hutton Institute.
Hydroxyapatite	Mineral collection of the North Carolina State University.
OCP	Octacalcium phosphate. Mineral collection of the North Carolina State University.
Amorphous FePO <sub>4</sub>	Synthesized according to Roncal-Herrero et al. [3]
Strengite	Mineral collection of the James Hutton Institute.
PO <sub>4</sub> ads. to goethite	PO <sub>4</sub> adsorbed to goethite. Goethite was synthesized by hydrolysing FeCl <sub>2</sub> •4H <sub>2</sub> O with 1 M NaHCO <sub>3</sub> following Schwertmann and Cornell [4]. Phosphate was adsorbed at 150 mmol P kg <sup>-1</sup> at pH 6 following procedures described for ferrihydrite by Khare et al. [5], and the final moist-paste sample was freeze dried.
PO <sub>4</sub> ads. to ferrihydrite	PO <sub>4</sub> adsorbed to ferrihydrite. Ferrihydrite was synthesized according to Gustafsson [6] and confirmed to be 2-line by XRD. 100 μmol PO <sub>4</sub> L <sup>-1</sup> (as NaH <sub>2</sub> PO <sub>4</sub> ) was equilibrated for 24 h with 1 mmol Fe L <sup>-1</sup> (as ferrihydrite) at pH 6.5, centrifuged and dried at 25°C.
Amorphous AlPO <sub>4</sub>	Synthesized according to Roncal-Herrero et al. [3]
Amorphous AlPO <sub>4</sub> II	Synthesized according to Hsu and Sikora [7] using an OH/Al molar ratio = 2 and aging for 10 days (verified by XRD) as reported by Hesterberg et al. [8].
Variscite	Mineral collection of the James Hutton Institute.
PO <sub>4</sub> ads. to Al(OH) <sub>3</sub>	PO <sub>4</sub> adsorbed to Al hydroxide. Amorphous Al hydroxide was synthesized according to Larsson et al. [9] and confirmed to be amorphous by XRD. 100 μmol PO <sub>4</sub> L <sup>-1</sup> (as NaH <sub>2</sub> PO <sub>4</sub> ) was equilibrated for 24 h with 1 mmol Al L <sup>-1</sup> (as Al hydroxide) at pH 6.5, centrifuged and dried at 25°C.
PO <sub>4</sub> ads. to allophane	PO <sub>4</sub> adsorbed to allophane. Allophane was synthesized according to Ohashi et al. [10] and confirmed to be allophane by XRD. 100 μmol PO <sub>4</sub> L <sup>-1</sup> (as NaH <sub>2</sub> PO <sub>4</sub> ) was equilibrated for 24 h with 1 mmol Al L <sup>-1</sup> (as allophane) at pH 5.5, centrifuged and dried at 25°C.
PO <sub>4</sub> ads. to gibbsite	PO <sub>4</sub> adsorbed to gibbsite. Gibbsite (specific surface ~80 m <sup>2</sup> g <sup>-1</sup> ) was synthesized according to Wierenga et al. [11]. Phosphate was adsorbed on gibbsite at 120 mmol kg <sup>-1</sup> (maximum adsorption capacity) at pH 6, then freeze-dried.
Soil organic P	Spodosol Oe sample from Paskalampa, central Sweden, with 54% organic C, 15 mmol kg <sup>-1</sup> oxalate-Al and 5 mmol kg <sup>-1</sup> oxalate-Fe [12]

ACP, Synthetic	Synthetic amorphous calcium phosphate. Synthesized according to Eveborn et al. [13]
Apatite Gafsa	Natural carbonate apatite from Gafsa, Tunisia. Mineral collection of the James Hutton Institute.
Apatite Templeton	Natural hydroxyfluorapatite from Templeton, Canada. Mineral collection of the James Hutton Institute.
Monetite	Mineral collection of the James Hutton Institute.
Wavellite	Mineral collection of the North Carolina State University, originally provided by Dr. Willie Harris, Univ. of Florida.
PO <sub>4</sub> ads. to TiO <sub>2</sub>	PO <sub>4</sub> adsorbed to TiO <sub>2</sub> . Amorphous TiO <sub>2</sub> was produced from the hydrolysis of TiCl <sub>4</sub> , following the method of Poznyak et al. [14]. 100 μmol PO <sub>4</sub> L <sup>-1</sup> (as NaH <sub>2</sub> PO <sub>4</sub> ) was equilibrated for 24 h with 1 mmol Ti L <sup>-1</sup> (as TiO <sub>2</sub> ) at pH 6.5, centrifuged and dried at 25°C.
Phytate ads. to ferrihydrite	Phytate adsorbed to ferrihydrite. Ferrihydrite was synthesized according to Gustafsson [6] and confirmed to be 2-line by XRD. 100 μmol Na phytate was equilibrated for 24 h with 3 mmol Fe L <sup>-1</sup> (as ferrihydrite) at pH 6.5, centrifuged and dried at 25°C.
Phytate ads. to Al(OH) <sub>3</sub>	Phytate adsorbed to Al hydroxide. Al hydroxide was synthesized according to Larsson et al. [9] and confirmed to be amorphous by XRD. 100 μmol Na phytate was equilibrated for 24 h with 3 mmol Al L <sup>-1</sup> (as Al hydroxide) at pH 6.5, centrifuged and dried at 25°C.
Phytate ads. to allophane	Phytate adsorbed to allophane. Allophane was synthesized according to Ohashi et al. [10] and confirmed to be allophane by XRD. 100 μmol Na phytate was equilibrated for 24 h with 3 mmol Al L <sup>-1</sup> (as allophane) at pH 5.5, centrifuged and dried at 25°C.
K-Taranakite	Mineral collection of the James Hutton Institute.
Struvite	Mineral collection of the James Hutton Institute.
Vivianite	Mineral collection of the James Hutton Institute.
Mg-Al LDH	Mg-Al layered double hydroxide. Synthesized according to Everaert et al. [15]
Na phytate	Phytic acid, Na salt. Purchased from Sigma-Aldrich (St. Louis, MI, USA)
Ca phytate	Phytic acid, Ca salt. Purchased from Sigma-Aldrich (St. Louis, MI, USA)
Lecithin	Purchased from Sigma-Aldrich (St. Louis, MI, USA)
Phosphonate	Purchased from Sigma-Aldrich (St. Louis, MI, USA)
Sphagnum organic P	Sphagnum peat from Paskalampa, central Sweden, with 45% organic C, 4 mmol kg <sup>-1</sup> oxalate-Al and 7 mmol kg <sup>-1</sup> oxalate-Fe [12]

## References

- 1 Zuo, M.; Renman, G.; Gustafsson, J.P.; Renman, A. Phosphorus removal performance and speciation in virgin and modified argon oxygen decarburisation slag designed for wastewater treatment. *Water Res.* **2015**, *87*, 271-281.

- 2 Zuo, M.; Renman, G.; Gustafsson, J.P.; Klysubun, W. Dual slag filters for enhanced phosphorus removal from domestic waste water: performance and mechanisms. *Environ. Sci. Pollut. Res.* **2018**, *25*, 7391-7400.
- 3 Roncal-Herrero, T.; Rodríguez Blanco, J.D.; Benning, L.G.; Oelkers, E.H. Precipitation of iron and aluminum phosphates directly from aqueous solution as a function of temperature from 50 to 200°C. *Cryst. Growth Design* **2009**, *9*, 5197-5205.
- 4 Schwertmann, U.; Cornell, R.M. Iron oxides in the laboratory: preparation and characterisation. VCH Publ Co., Weinheim, Germany, 1991.
- 5 Khare, N.; Hesterberg, D.; Beauchemin, S.; Wang, S.L. XANES determination of adsorbed phosphate distribution between ferrihydrite and boehmite in mixtures. *Soil Sci. Soc. Am. J.* **2004**, *68*, 460-469.
- 6 Gustafsson, J.P. Modelling molybdate and tungstate adsorption to ferrihydrite. *Chem. Geol.* **2003**, *200*, 105-115.
- 7 Hsu, P.H.; Sikora, F. Effects of aluminum and phosphate concentrations and acidity on the crystallization of variscite at 90 degrees C. *Soil Sci.* **1993**, *156*, 71-78.
- 8 Hesterberg, D.; Zhou, W.Q.; Hutchison, K.J.; Beauchemin, S.; Sayers, D.E. XAFS study of adsorbed and mineral forms of phosphate. *J. Synchrotron Radiat.* **1999**, *6*, 636-638.
- 9 Larsson, M.A.; d'Amato, M.; Cubadda, F.; Raggi, A.; Öborn, I.; Kleja, D.B.; Gustafsson, J.P. Long-term fate and transformations of vanadium in a pine forest soil with added converter lime. *Geoderma* **2015**, *259-260*, 271-278.
- 10 Ohashi, F.; Wada, S.-I.; Suzuki, M.; Maeda, M.; Tomura, S. Synthetic allophane from high-concentration solutions: nanoengineering of the porous solid. *Clay Miner.* **2002**, *37*, 451-456.
- 11 Wierenga, A.M.; Lenstra, T.A.J.; Philipse, A.P. Aqueous dispersions of colloidal gibbsite platelets: synthesis, characterisation and intrinsic viscosity measurements. *Coll. Surf. A* **1998**, *134*, 359-371.
- 12 Makselon, J.; Campos Oliveira, H.; Kleja, D.B.; Gustafsson, J.P. Manuscript in preparation.
- 13 Eveborn, D.; Gustafsson, J.P.; Hesterberg, D.; Hillier, S. XANES speciation of P in environmental samples: an assessment of filter media for on-site wastewater treatment. *Environ. Sci. Technol.* **2009**, *43*, 6515-6521.
- 14 Poznyak, S.K.; Kokorin, A.I.; Kulak, A.I. Effect of electron and hole acceptors on the photoelectrochemical behaviour of nanocrystalline microporous TiO<sub>2</sub> electrodes. *J. Electroanal. Chem.* **1998**, *442*, 99-105.
- 15 Everaert, M.; Warrinnier, R.; Baken, S.; Gustafsson, J.P.; de Vos, D.; Smolders, E. Phosphate-exchanged Mg-Al layered double hydroxides: a new slow release phosphate fertilizer. *ACS Sust. Chem. Eng.* **2016**, *4*, 4280-4287.



**Table S2.** Prominent features of P K-edge XANES spectra of the 34 standards considered

Reference	Pre-edge	White line			Post-edge			Comments
		E <sub>0</sub>	Maximum	Normalized intensity	Shoulder	Peak 1	Peak 2	
<i>Selected for soils</i>								
ACP, Slag	-	2153.3	2154.1	6.2	2156.7	2165.0	2170.6	Used only at pH > 7.5
Apatite Taiba	-	2153.4	2154.2	4.9	2157.4	2164.8	2171.1	
Brushite	-	2153.1	2154.1	4.7	2157.6	2163.4	2171.7	
Hydroxyapatite	-	2153.4	2154.1	5.3	2156.8	2164.6	2171.2	
OCP (octacalcium phosphate)	-	2153.4	2154.2	5.3	2157.1	2164.6	2171.1	
Amorphous FePO <sub>4</sub>	2151.1	2154.0	2154.9	4.1	-	-	2170.8	
Strengite	2150.9	2153.8	2154.7	4.1	-	-	2170.7	
PO <sub>4</sub> adsorbed to goethite	2150.6	2153.9	2154.7	6.7	-	2160.9	2170.7	
PO <sub>4</sub> adsorbed to ferrihydrite	2151.0	2153.9	2154.7	6.3	-	-	2170.7	
Amorphous AlPO <sub>4</sub>	-	2154.0	2155.0	5.6	-	-	2171.3	
Variscite	-	2154.0	2154.8	5.4	-	2161.1	2171.6	
PO <sub>4</sub> adsorbed to Al(OH) <sub>3</sub>	-	2153.8	2154.7	6.3	-	2160.4	2170.3	
PO <sub>4</sub> adsorbed to allophane	-	2153.9	2154.8	6.6	-	2161.4	2171.1	
PO <sub>4</sub> adsorbed to gibbsite	-	2153.9	2154.7	7.8	-	-	2171.0	
Soil organic P	-	2153.2	2154.1	5.5	-	-	2169.8	
<i>Other references</i>								
ACP, Synthetic	-	2153.2	2154.1	3.9	2156.7	2164.3	2170.6	Probable self-absorption
Apatite Gafsa	-	2153.3	2154.1	3.2	2156.8	2164.6	2171.1	”
Apatite Templeton	-	2153.3	2154.0	4.3	2156.8	2164.6	2170.8	Similar to Apatite Taiba, possible self-absorption
Monetite	-	2153.4	2154.4	4.4	-	2164.9	2169.6	Similar to other Ca phosphates, less common
Wavellite	-	2154.0	2154.8	5.4	-	2160.6	2168.8	Similar to variscite, more noise
Amorphous AlPO <sub>4</sub> II	-	2154.0	2154.9	5.8	-	2162.8	2172.0	Similar to amorphous AlPO <sub>4</sub> , more noise
PO <sub>4</sub> adsorbed to TiO <sub>2</sub>	2151.1	2154.2	2155.2	5.1	-	-	2170.2	Less common in soils
Phytate adsorbed to ferrihydrite	2150.9	2153.4	2154.6	5.4	-	-	2170.1	Can be described by other standards
Phytate adsorbed to Al(OH) <sub>3</sub>	-	2153.4	2154.6	5.2	-	-	2169.8	”

Phytate adsorbed to allophane	-	2153.4	2154.5	5.0	-	-	2170.0	”
K-Taranakite	-	2153.4	2154.9	3.0	-	-	2169.9	Less common in soils
Struvite	-	2153.2	2154.2	4.5	-	2158.5	2168.9	Not present in soils
Vivianite	-	2153.4	2154.5	4.2	-	2159.5	2165.9	+ additional peak at 2170.3 eV; less common in soils
Mg-Al LDH	-	2153.5	2154.5	4.8	-	2158.9	2170.1	Less common in soils
Phytic acid, Na salt	-	2152.8	2154.3	3.3	-	-	2169.6	Probable self-absorption
Phytic acid, Ca salt	-	2153.2	2154.2	4.6	-	-	2170.0	Similar to soil organic P, more noise
Lecithin	-	2153.0	2153.8	5.0	-	-	2168.6	Similar to soil organic P
Phosphonate	-	2151.9	2153.0	2.3	-	2158.3	2169.8	Probable self-absorption
Sphagnum organic P	-	2153.3	2154.2	5.5	-	-	2170.3	Similar to soil organic P, more noise

---

**Table S3.** Number of occurrences of different standards in the best fits of 100 LHS-generated P K-edge XANES spectral variants

Reference	203 FYM 0-28 cm	302 BIO 0-28 cm	203 FYM 35-45 cm	302 BIO 35-45 cm	Tärnsjö Oe	Tärnsjö Bs	Rödälund E	Ekebo A3	Ekebo D3	Fors A3	Fors D3
Apatite Taiba	10	7	10	52		2		7	2	86	62
Hydroxyapatite	78	68	85	48		2	100	9	4	21	33
Brushite	1	4	4	28	72				1	22	52
ACP, Slag	nc	nc	nc	nc	nc	nc	nc	nc	nc	2	4
OCP	12	25	5	1		4		3	9	2	6
Strengite	1			1		2		2	7	4	4
Am. FePO <sub>4</sub>	26		3	7	4	5	1	25	31	57	24
PO <sub>4</sub> ads. to goethite	69	99	98	76	62	91		37	31	4	41
PO <sub>4</sub> ads. to ferrihydrite		1	4	50				8	9	3	6
Variscite			6		43	1	1	1	29	3	7
Am. AlPO <sub>4</sub>	12	6	16	63	27	61	94	90	44	64	51
PO <sub>4</sub> ads. to Al(OH) <sub>3</sub>		10	1	3					7	5	6
PO <sub>4</sub> ads. to gibbsite	92	56	67	27	20	70	41	93	84	2	9
PO <sub>4</sub> ads. to allophane	9	29	29	29	3	100	10	19	41	4	2
Soil organic P	85	85	66	15	100	46	100	100	100	100	89

nc = not considered during the LCF, see text

## Examples: Grouping of results in the output from AthenaAut

Here we provide three examples on the grouping of standards as detailed in section 2.3 of the main paper, also summarized in Fig. S2.

### Example 1. 302 BIO 0-28 cm

In the best fits of the LCFs from the 100 outputs, 11 standards occurred (see Table S3 for details). As a first step in the data treatment, these 11 standards were grouped according to the groups as defined in section 2.3 in the manuscript.

As every single LCF output contains a maximum of four standards, there is a large number of combinations of groups that occur in the output. The purpose of the data treatment is to identify which combination that is most likely to describe the data. The output combinations may be termed *models*, and for the output from 302 BIO 0-28, we obtain the following models (in decreasing order of frequency):

Model 1: CaP, PO<sub>4</sub> ads Al, PO<sub>4</sub> ads Fe, SOP (79 occurrences)

Model 2: CaP, PO<sub>4</sub> ads Al, PO<sub>4</sub> ads Fe (12 occurrences)

Model 3: CaP, PO<sub>4</sub> ads Al, PO<sub>4</sub> ads Fe, AIP (3 occurrences)

Model 4: CaP, PO<sub>4</sub> ads Fe, SOP (3 occurrences)

Model 5: CaP, AIP, PO<sub>4</sub> ads Fe, SOP (3 occurrences)

As model 1 is able to describe > 50 % (79 %) of all outputs, we accept this model, in accordance with the criterion given in point 2 of the grouping procedure in the main paper (also shown in Fig. S2). Having done so, the second step of the data treatment is to rerun the remaining 21 spectral variants in AthenaAut while excluding those standards not present in model 1 from the standards database, i.e. those included in the FeP and AIP groups. This is needed to get all 100 outputs consistent with model 1. Calculation of average weights and standard deviations, as given in Table 3, is then made for the sum of the 79 original outputs that matched model 1 and the output from the 21 rerun variants.

### Example 2. 302 BIO 35-45 cm

In this case the following models were obtained based on the 100 generated outputs:

Model 1: CaP, PO<sub>4</sub> ads Fe, AIP (28 occurrences)

Model 2: CaP, PO<sub>4</sub> ads Fe, PO<sub>4</sub> ads Al, AIP (25 occurrences)

Model 3: CaP, PO<sub>4</sub> ads Fe, PO<sub>4</sub> ads Al (22 occurrences)

Model 4: CaP, PO<sub>4</sub> ads Fe, AIP, SOP (10 occurrences)

Model 5: CaP, PO<sub>4</sub> ads Fe, PO<sub>4</sub> ads Al, FeP (8 occurrences)

Model 6: CaP, PO<sub>4</sub> ads Fe, PO<sub>4</sub> ads Al, SOP (4 occurrences)

Model 7: CaP, PO<sub>4</sub> ads Fe (2 occurrences)

Model 8: CaP, PO<sub>4</sub> ads Fe, SOP (1 occurrence)

As no model could describe > 50 % of the outputs, we test if a better result is obtained by combining the PO<sub>4</sub> ads Fe and FeP groups to a new and larger group called Fe-bound P, or by combining the PO<sub>4</sub> ads Al and AIP groups to another large group called Al-bound P. To do this, all standards belonging e.g. to the PO<sub>4</sub> ads Fe and FeP groups are now instead put in a single group called Fe-bound P. When we use the Fe-bound P group we get the following frequencies:

Model 1: CaP, Fe-bound P, PO<sub>4</sub> ads Al (30 occurrences)

Model 2: CaP, Fe-bound P, AlP (28 occurrences)

...etc.

This did not help, because we still cannot describe > 50 % of the outputs. Instead let us try with using the Al-bound P group:

Model 1: CaP, PO<sub>4</sub> ads Fe, Al-bound P (79 occurrences)

Model 2: CaP, PO<sub>4</sub> ads Fe, Al-bound P, SOP (14 occurrences)

...etc

Here model 1 fulfils the criteria, and therefore we rerun the remaining 21 spectral variants while excluding the FeP and SOP standards to get the final output.

### Example 3. Fors A3

For this soil, it does not help to use either the Fe-bound P or Al-bound P groups. The next step is then to investigate if a better model can be obtained by using *both* the Fe-bound and Al-bound groups. We get:

Model 1: CaP, Fe-bound P, Al-bound P, SOP (40 occurrences)

Model 2: CaP, Al-bound P, SOP (37 occurrences)

Model 3: CaP, Fe-bound P, SOP (23 occurrences)

No, this did not help either. There is only one option remaining, which is to combine Fe-bound P and Al-bound P into a single group called "Fe- and Al-bound P". As can be realized from the models obtained above, we can now describe all 100 outputs, so there will be only one model and no rerun of variants is needed.