

Supporting information

Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

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Investigation of 15 sewage sludges

Table S1: Origin of the 15 investigated sewage sludges and sludge treatment at respective wastewater treatment plant (WWTP)

Sludge no.	Origin	Sewage sludge stabilization ^A	Sewage sludge dewatering	Sample matrix special feature
1	WWTP 1	none	centrifuge	rich in carbon
2	WWTP 1	none	centrifuge	rich in carbon
3	WWTP 2	humification	humification	rich in phosphorus
4	WWTP 3	anaerobic	chamber filter press	rich in calcium
5	WWTP 4	anaerobic	chamber filter press	rich in calcium
6	WWTP 4	anaerobic	chamber filter press	rich in calcium
7	WWTP 5	anaerobic	chamber filter press	rich in calcium
8	WWTP 6	simultaneously-aerobic	centrifuge	
9	WWTP 7	simultaneously-aerobic	centrifuge	
10	WWTP 8	simultaneously-aerobic	centrifuge	rich in carbon
11	WWTP 8	simultaneously-aerobic	centrifuge	rich in carbon
12	WWTP 9	anaerobic	chamber filter press	rich in calcium
13	WWTP 10	anaerobic	chamber filter press	
14	WWTP 11	anaerobic	centrifuge	rich in phosphorus
15	Interlaboratory comparison	mixture ^B	mixture ^B	

^A Sewage sludge stabilization is a process to reduce the sludge volume by aerobic or anaerobic degradation for disposal

^B The ILC sludge is a mixture of different, also stabilized and freeze-dried sludges from WWTPs 9, 10, and 11

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Table S2: Characterization of the 15 investigated sewage sludges and HNO₃ addition (for samples with more than 500 mg C on 3,000 mg according to EN 16174), contents related to dry matter

Sludge No.	P	Ca	C	N	Fe	Loss of ignition	C load in 3.0 g	extra HNO ₃	Moisture content
	[g/kg]	[g/kg]	[g/kg]	[g/kg]	[g/kg]		[g]	[ml]	[%]
1	19	24	432	39	35	81%	1.22	7.2	5.8
2	22	26	417	40	43	80%	1.18	6.8	5.4
3	36	33	266	33	44	58%	0.75	2.5	6.6
4	21	150	203	23	42	44%	0.56		7.6
5	21	187	193	16	50	37%	0.54		6.3
6	17	196	218	19	38	28%	0.62	1.2	5.3
7	17	239	168	18	35	28%	0.48		4.7
8	22	12	332	37	26	66%	0.92	4.2	7.4
9	23	20	310	46	14	62%	0.88	3.8	5.0
10	17	08	423	71	15	79%	1.20	7.1	5.0
11	24	11	401	69	18	78%	1.17	6.7	2.8
12	17	207	160	17	43	24%	0.46		4.4
13	20	34	324		30	61%	0.92	4.2	5.1
14	38	34	371	51	10		1.03	5.3	7.5
15	25	92	282	38	35		0.81	3.1	4.8

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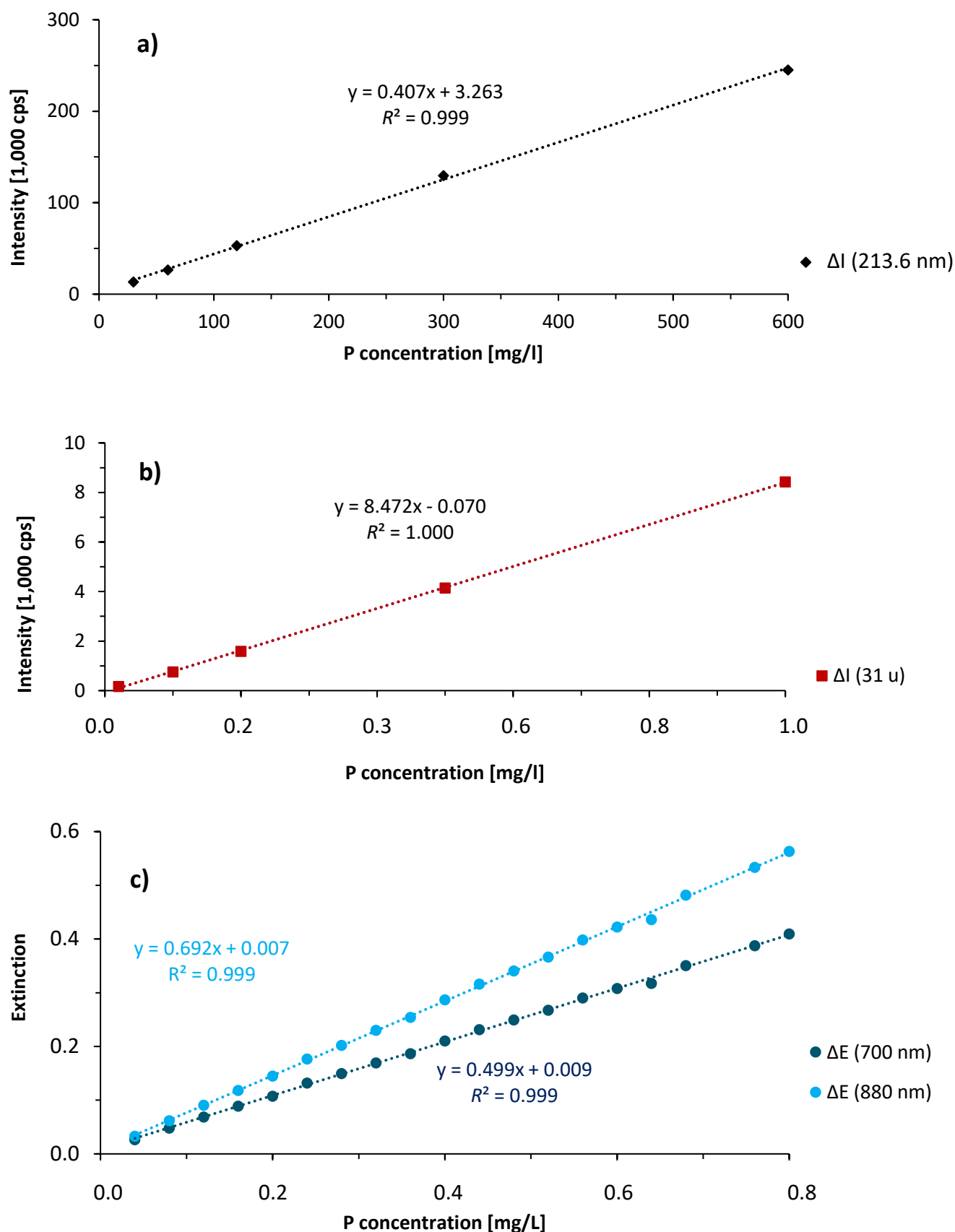


Figure S1: Exemplary calibration curves for ICP-OES (a), ICP-MS (b) and photometric phosphorus determination with ammonium molybdate (c)

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Table S3: Phosphorus recovery of certified reference materials (sewage sludges, Sigma-Aldrich, Laramie, USA); Averages (n=2) of respective measurement day related to fresh matter (FM) and dry matter (DM)

Analysis	Digestion	Measurement day	CRM029-50G: 21.1 ± 2.6 g/kg			CRM031-50G: 21.5 ± 1.5 g/kg		
			g/kg FM	g/kg DM	Recovery	g/kg FM	g/kg DM	Recovery
ICP-OES	Reflux	9	18.6	21.6	102%	16.2	18.3	85%
ICP-OES	Reflux	8	19.1	22.3	106%	18.3	20.7	96%
ICP-OES	Reflux	7	18.7	21.7	103%	18.4	20.8	97%
ICP-OES	Reflux	6	18.7	21.8	103%	17.3	19.6	91%
ICP-OES	Reflux	5	19.4	22.6	107%	17.0	19.2	90%
ICP-OES	Microwave	4	20.5	20.5	97%	19.2	21.7	101%
ICP-OES	Microwave	3	21.7	21.7	103%	20.5	23.2	108%
ICP-OES	Microwave	2	21.6	21.6	103%	19.3	21.8	102%
ICP-OES	Microwave	1	20.0	20.0	95%	19.1	21.5	100%
ICP-MS	Reflux	9	19.0	22.1	105%	17.2	19.4	90%
ICP-MS	Reflux	8	18.6	21.6	102%	18.8	21.3	99%
ICP-MS	Reflux	7	19.8	23.1	109%	17.5	19.7	92%
ICP-MS	Reflux	6	16.7	19.4	92%	15.6	17.6	82%
ICP-MS	Reflux	5	18.1	21.1	100%	16.9	19.0	89%
ICP-MS	Microwave	4	22.7	22.7	108%	19.7	22.2	103%
ICP-MS	Reflux	3	17.3	20.2	96%	15.2	17.2	80%
ICP-MS	Microwave	2	20.2	20.2	96%	18.3	20.7	96%
ICP-MS	Microwave	1	19.0	19.0	90%	20.3	23.0	107%

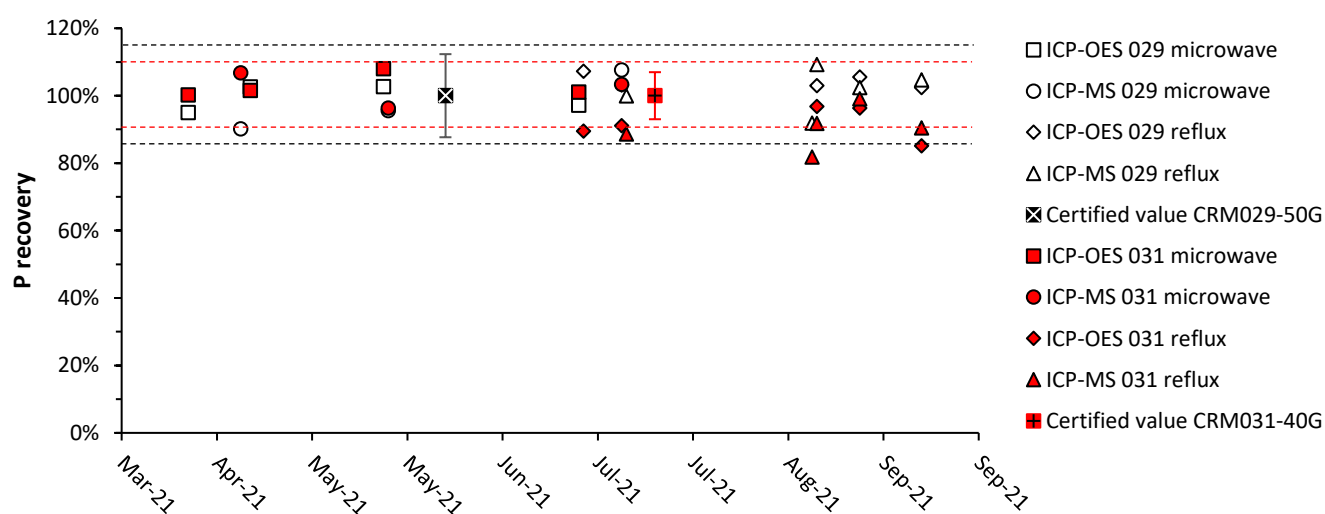


Figure S2: Phosphorus recovery rate from reference materials CRM029-50G (029) and CRM031-40G (031) by digestion and analysis

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Table S4: Recovery rates of spiked and diluted (1:5) samples by digestion (DG). Elemental P standards (10,000 mg/l for ICP-OES; 1,000 mg/l for ICP-MS diluted 1:10) of MERCK were used for spiking

Sludge No.	DG	ICP-OES					ICP-MS				
		Dilution for spiking	Spiking volume	Spiking Factor	Spiking Recovery	Dilution Recovery	Dilution for spiking	Spiking volume	Spiking Factor	Spiking Recovery	Dilution Recovery
			[µl]		[%]						
1	MW	2	100	1.1	96	94	1,000	10	0.6	101	122
	RF	5	100	1.0	109	104					93
	RF*	5	100	1.0	86	106	2,000	50	1.0	103	99
2	MW	2	100	1.0	96	94	1,000	10	0.5	105	90
	RF	5	100	0.9	121	103	2,000	50	0.9	103	102
	RF*	5	100	0.8	96	102	2,000	50	1.0	103	103
3	MW	2	100	0.5	97	102	1,000	20	0.5	99	99
	RF	5	100	0.5	117	111					92
	RF*	5	100	0.5	99	112	2,000	50	0.4	92	82
4	MW	2	100	1.0	102	100	1,000	10	0.5	104	103
	RF	5	100	1.0	120	116					97
5	MW	2	100	0.9	101	105	1,000	10	0.6	112	110
	RF	5	100	0.9	104	107	2,000	50	0.8	113	101
6	MW	2	100	1.2	94	101	1,000	10	0.6	96	94
	RF	5	100	1.1	98	109	2,000	50	1.0	108	100
	RF*	5	100	1.1	84	106	2,000	50	0.8	99	103
7	MW	2	100	1.2	101	106	1,000	10	0.7	99	118
	RF	5	100	1.2	125	98	2,000	50	1.0	111	95
8	MW	2	100	0.8	101	102	1,000	10	0.4	99	107
	RF	5	100	0.8	116	106	2,000	50	0.8	107	108
	RF*	5	100	0.8	101	93	2,000	50	0.7	96	107
9	MW	2	100	1.0	98	97	1,000	10	0.5	106	92
	RF	5	100	0.9	97	101	2,000	50	0.8	102	98
	RF*	5	100	0.9	96	107	2,000	50	0.9	92	105

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		ICP-OES					ICP-MS				
Table S4 continued											
10	MW	2	100	1.3	96	91	1,000	10	0.7	99	97
	RF	5	100	1.1	113	102	2,000	50	1.1	97	106
	RF*	5	100	1.1	80	104	2,000	50	1.1	103	102
11	MW	2	100	0.9	98	102	1,000	10	0.5	99	108
	RF	5	100	0.9	109	108	2,000	50	0.8	106	102
	RF*	5	100	0.8	99	104	2,000	50	0.8	103	95
12	MW	2	100	1.2	103	95	1,000	10	0.6	97	109
	RF	5	100	1.1	103	105	2,000	50	1.0	106	108
13	MW	2	100	1.1	106	96	1,000	10	0.5	94	101
	RF	5	100	0.9	102	106	2,000	50	0.9	89	107
	RF*	5	100	0.8	99	103	2,000	50	0.9	99	105
14	MW	2	100	0.6	95	109	1,000	20	0.6	95	105
	RF	5	100	0.4	92	100	2,000	50	0.5	86	95
	RF*	5	100	0.5	97	109	2,000	50	0.5	96	102
15	MW	2	100	0.8	89	97	1,000	10	0.4	95	105
	RF	5	100	0.7	95	107	2,000	50	0.6	99	96
	RF*	5	100	0.7	98	104	2,000	50	0.7	102	102

A recovery rate of 90-110% is permitted for diluted samples and a recovery rate of 75-125% is permitted for spiked samples (EN 16170, 16171)

MW: Microwave aqua regia digestion (EN 16174:2012)

RF: Reflux aqua regia digestion (EN 13346:2001)

RF*: Reflux aqua regia digestion with additional HNO₃ (EN 16174:2012, more details: Table S2)

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Table S5: Phosphorus contents by method combination in 15 sewage sludges in g/kg

	A1	A2	B1	B2	B*1	B*2	C1	C2	D1	D2	D*1	D*2	E1	E2	F1	F2	F*1	F*2
1	19.4	19.0	15.8	17.9	16.1	17.5	17.0	17.0	16.1	15.2	15.4	15.6	18.3	19.6	14.1	15.1	14.6	15.5
2	22.7	22.0	18.5	19.1	19.8	19.2	19.1	18.5	19.0	18.1	18.7	17.9	20.4	21.6	18.2	19.6	15.9	16.0
3	37.3	37.1	35.5	37.7	36.1	38.3	37.6	37.9	36.6	35.2	37.3	38.3	38.7	40.0	34.4	35.1	34.0	34.5
4	20.5	20.2	19.0	18.9			19.1	18.7	19.1	17.4			19.8	21.6	16.5	18.6		
5	18.8	19.6	17.6	18.1			21.3	21.7	19.7	20.0			23.7	25.9	18.7	20.2		
6	16.8	17.2	14.4	15.5	15.4	15.6	17.3	16.5	15.3	15.9	15.6	15.8	17.9	19.4	14.8	16.8	12.5	12.6
7	15.3	16.5	13.9	14.2			15.4	14.5	14.3	14.3			15.8		14.4			
8	23.4	23.2	21.1	21.8	22.5	22.2	22.7	22.6	19.5	21.1	20.0	21.1	23.2		20.2		19.0	
9	22.2	22.8	18.4	18.6	18.0	18.4	20.7	20.4	17.1	18.5	17.6	18.8	21.2	22.6	17.6	19.7	16.0	16.3
10	16.8	17.1	15.0	14.7	14.9	13.7	14.8	14.5	13.9	13.5	13.4	14.0	14.2	14.6	12.3	12.3	10.9	11.4
11	23.9	23.8	20.5	21.4	22.2	22.5	21.0	20.5	19.4	18.5	19.9	18.7	22.0	22.5	16.9	17.5	15.9	16.3
12	17.7	17.0	14.3	15.1			17.2	17.1	14.8	15.0			18.1	19.3	13.3	13.9		
13	21.9	21.0	19.1	18.0	17.3	17.8	19.1	17.9	17.2	15.8	17.8	18.0	21.0	23.3	18.2	19.0	15.0	15.4
14	38.8	37.2	32.5	36.4	34.7	35.8	34.9	34.4	32.3	33.9	32.7	32.0	35.6	37.7	30.0	30.8	30.6	31.0
15	23.9	22.9	24.3	24.0	24.9	25.0	24.8	24.1	23.4	23.1	23.8	25.0	25.6	27.2	21.0	21.8	21.5	21.9

Mean values in g/kg by method combination A1-F*2 (main text Figure 1) from replicates (n=5; except from sludge 15 reflux and expanded reflux: n=3)

No expanded reflux digestions (VK B*, D* und F*) of the sludges 4, 5, 7 and 12 due to low carbon contents

No photometric determination at 700 nm for the sludges 7 and 8 (method combinations E2, F2 und F*2)

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Table S6: Standard deviations of the phosphorus contents by method combination in 15 sewage sludges in g/kg

	A1	A2	B1	B2	B*1	B*2	C1	C2	D1	D2	D*1	D*2	E1	E2	F1	F2	F*1	F*2
1	0.1	0.1	0.4	0.3	0.4	0.1	0.8	0.6	0.4	0.6	0.6	0.5	0.7	0.8	0.8	0.3	0.3	0.4
2	0.3	0.2	0.4	0.1	1.5	0.1	0.5	1.3	0.7	0.2	0.7	0.5	1.8	1.8	0.4	0.5	0.3	0.3
3	0.7	0.5	2.0	2.2	2.5	0.4	1.3	1.1	1.9	0.8	2.2	0.8	0.9	0.9	0.6	0.6	0.7	0.7
4	0.2	0.1	1.4	0.5			0.4	1.1	0.7	0.7			0.8	0.4	0.6	0.5		
5	0.7	0.3	0.2	0.2			0.9	1.8	0.3	0.9			1.4	1.4	0.4	0.4		
6	0.3	0.3	0.4	0.4	0.6	0.6	0.5	0.1	0.4	0.6	0.9	0.2	0.7	1.0	0.6	0.7	0.7	0.7
7	0.3	0.3	0.2	0.2			0.4	0.8	0.8	0.3			0.5		0.5			
8	0.4	0.1	0.7	0.4	0.8	0.7	0.7	0.9	0.8	0.7	0.5	0.4	0.9		0.6		2.5	
9	0.2	0.1	0.3	0.4	0.2	0.8	0.5	0.4	1.0	0.7	0.8	0.7	1.0	1.1	0.3	0.4	0.9	1.0
10	0.3	0.1	0.5	0.4	1.1	1.2	0.4	0.8	0.5	0.6	1.3	0.9	0.4	0.4	1.9	2.0	0.2	0.3
11	0.4	0.3	0.4	0.3	1.1	1.4	0.2	0.6	0.7	0.4	1.1	1.4	1.8	1.8	0.4	0.4	0.6	0.7
12	0.5	0.4	0.4	0.3			1.1	0.6	0.8	0.6			0.7	0.8	0.3	0.3		
13	0.3	0.2	0.5	1.2	0.3	1.4	0.5	1.2	0.8	0.5	1.6	0.8	1.8	1.5	0.1	0.1	0.7	0.8
14	0.8	0.6	0.5	0.4	1.8	2.2	0.5	1.3	1.1	1.4	0.9	0.6	1.1	1.2	0.5	0.5	1.2	1.2
15	0.9	0.4	0.8	0.1	0.5	0.4	0.6	0.5	0.5	1.3	0.8	0.9	1.9	1.9	0.7	0.7	0.2	0.2

Standard deviation values in g/kg by method combination A1-F*2 (main text Figure 1) from replicates (n=5; except from sludge 15 reflux and expanded reflux: n=3)

No expanded reflux digestions (VK B*, D* und F*) of the sludges 4, 5, 7 and 12 due to low carbon contents

No photometric determination at 700 nm for the sludges 7 and 8 (method combinations E2, F2 und F*2)

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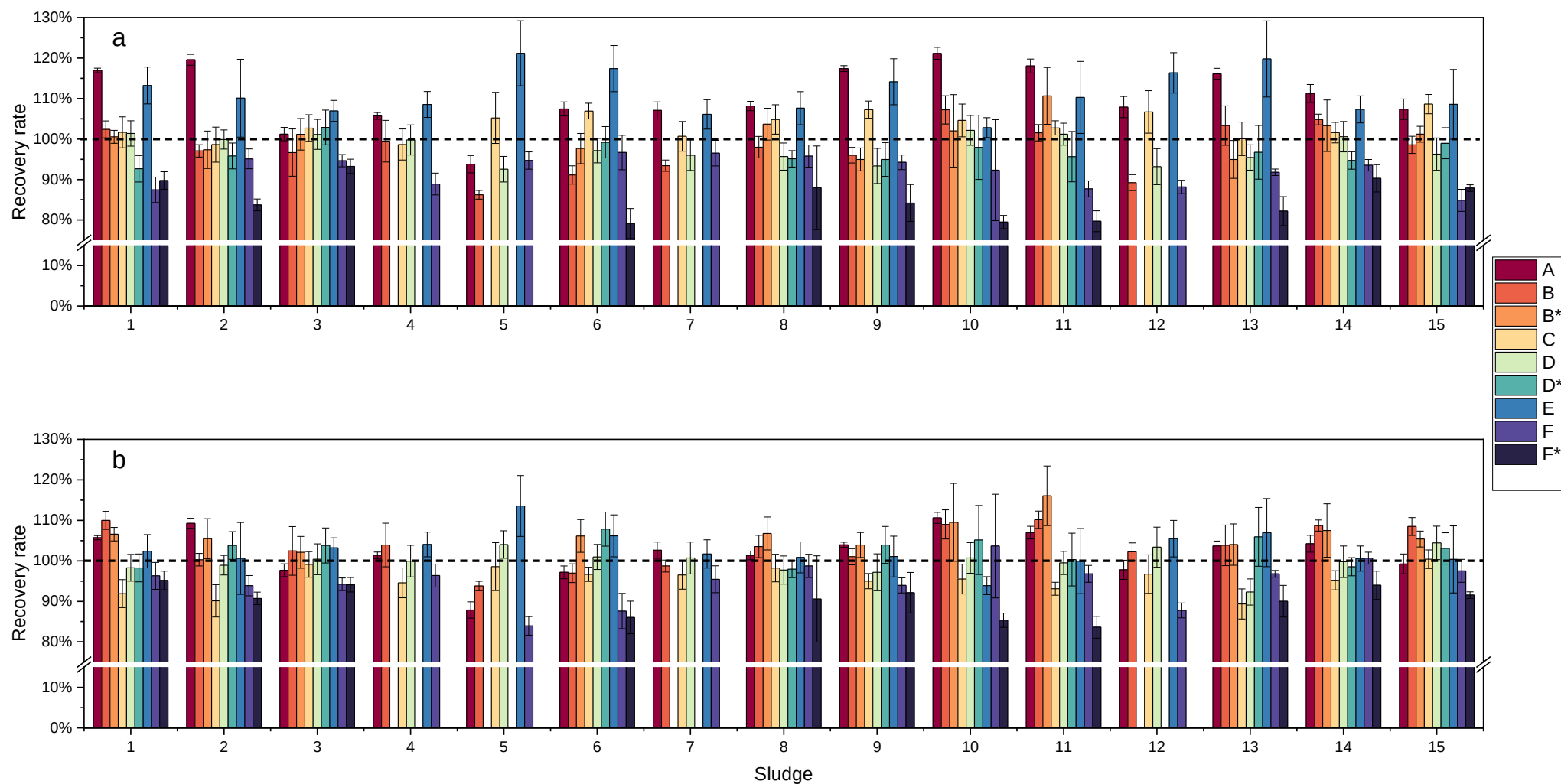


Figure S3: Phosphorus recovery from 15 sewage sludges as determined by method classes A-F* normalized to the grand mean (a) and normalized to the mean value by digestion (b). The error bars (a) represent the standard deviation of the five replicates (sludge 15 no. reflux digestions: three replicates) per sludge. For an explanation of the method class abbreviations see main text Figure 1

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Table S7: Phosphorus recovery rate of 15 investigated sewage sludges after normalization to the grand mean

Sludge	A	C	E	B	D	F	B*	D*	F*
1	117%	102%	113%	102%	101%	87%	101%	93%	90%
2	120%	99%	110%	97%	100%	95%	97%	96%	84%
3	101%	103%	107%	97%	101%	95%	101%	103%	93%
4	106%	99%	109%	99%	100%	89%			
5	94%	105%	121%	86%	93%	95%			
6	107%	107%	117%	91%	97%	97%	98%	99%	79%
7	107%	101%	106%	93%	96%	97%			
8	108%	105%	108%	98%	96%	96%	104%	95%	88%
9	117%	107%	114%	96%	93%	94%	95%	95%	84%
10	121%	105%	103%	107%	102%	92%	102%	98%	80%
11	118%	103%	110%	102%	101%	88%	111%	96%	80%
12	108%	107%	116%	89%	93%	88%			
13	116%	100%	120%	103%	95%	92%	95%	97%	82%
14	111%	102%	107%	105%	101%	94%	103%	95%	90%
15	107%	109%	109%	99%	96%	85%	101%	99%	88%
Mean	111%	103%	111%	98%	98%	92%	101%	97%	85%
SD	8%	3%	5%	6%	3%	4%	5%	3%	5%

SD: Standard deviation

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Table S8: Phosphorus recovery rate of 15 investigated sewage sludges after normalization to digestion mean

Sludge	A	C	E	B	D	F	B*	D*	F*
1	106%	92%	102%	110%	98%	96%	107%	98%	95%
2	109%	90%	101%	100%	99%	94%	105%	104%	91%
3	98%	99%	103%	102%	100%	94%	102%	104%	94%
4	101%	95%	104%	104%	100%	96%			
5	88%	99%	114%	94%	104%	84%			
6	97%	97%	106%	97%	101%	88%	106%	108%	86%
7	103%	97%	102%	99%	101%	95%			
8	101%	98%	101%	104%	98%	99%	107%	98%	91%
9	104%	95%	101%	101%	97%	94%	104%	104%	92%
10	111%	96%	94%	109%	101%	104%	109%	105%	85%
11	107%	93%	100%	110%	100%	97%	116%	100%	84%
12	98%	97%	105%	102%	103%	88%			
13	104%	89%	107%	104%	92%	97%	104%	106%	90%
14	104%	95%	101%	109%	100%	101%	107%	99%	94%
15	99%	100%	100%	108%	104%	98%	105%	103%	92%
Mean	102%	95%	103%	104%	100%	95%	107%	103%	90%
SD	6%	3%	4%	5%	3%	5%	4%	3%	4%

SD: Standard deviation

Table S9: Two-way analysis of variance for the normalized (grand mean) 15 sewage sludges

Scattering cause	Square sum	Degrees of freedom	Mean square sum	Fobs	p value	F _{crit}
Sample (digestion)	0.47	1	0.47	145.91	< 0.01	3.91
Columns (instrumental analytics)	0.09	4	0.02	6.92	< 0.01	2.44
Interaction	0.06	4	0.02	4.67	< 0.01	2.44
Error	0.46	140	0.00			
Total	1.08	149				

Interlaboratory comparison of one sewage sludge

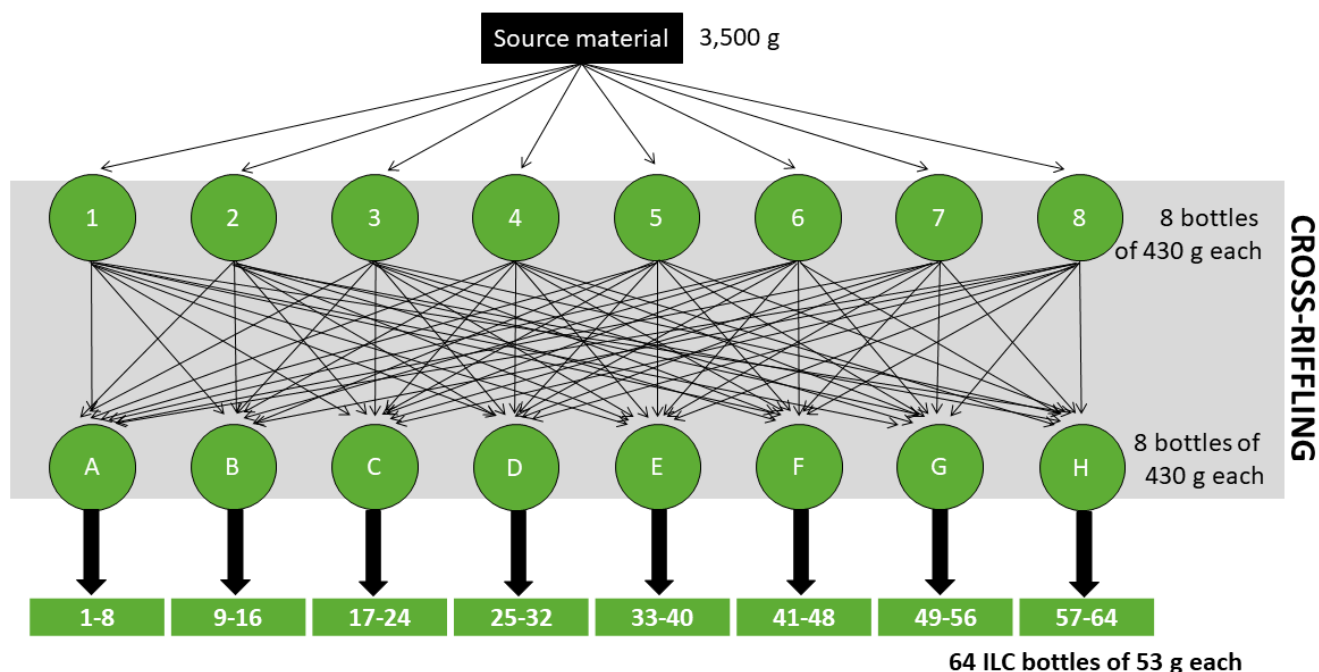


Figure S4: Schematic representation of the cross-riffling to generate bottles for interlaboratory comparison (ILC)

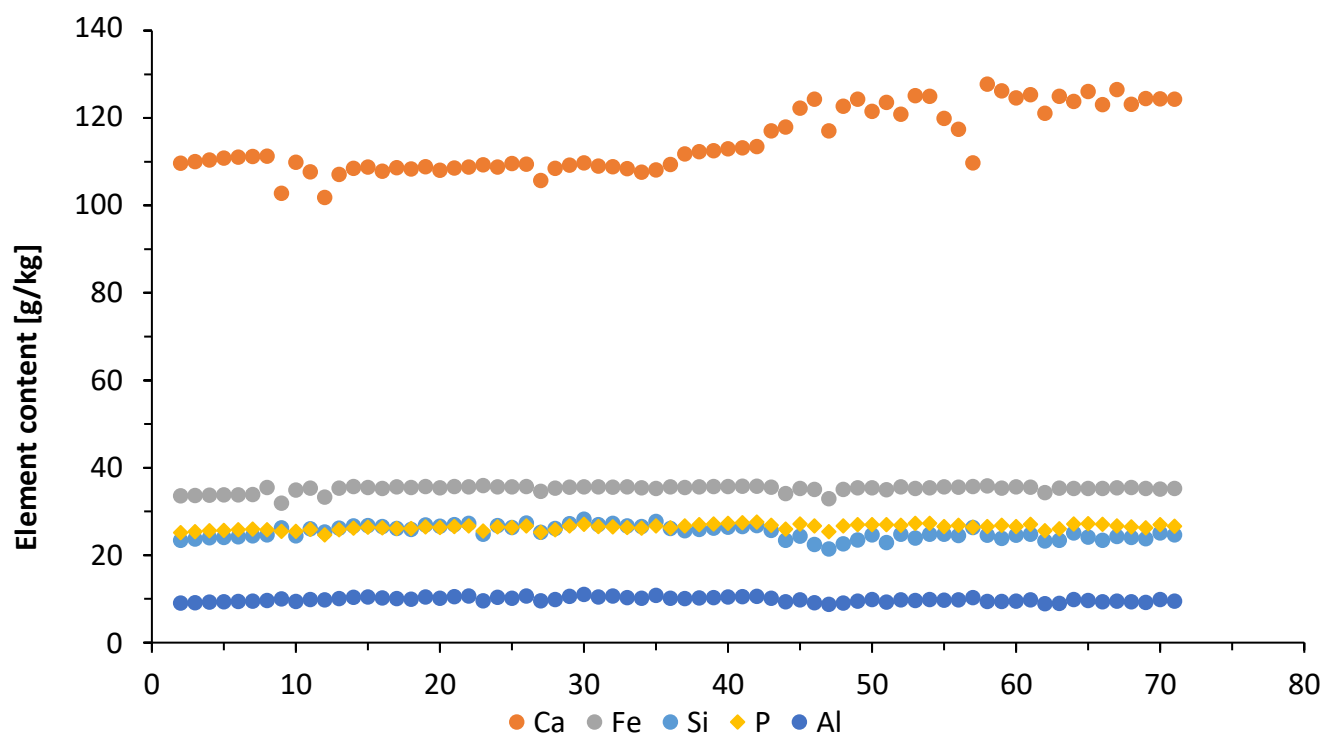


Figure S5: XRF homogeneity results of 10 bottles (six replicates). Measurement of three samples per bottle, shaking and new measurements from measurement number 42

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Table S10: XRF results in g/kg for homogeneity study of the sludge 15 for interlaboratory comparison. Powder analysis of 10 out of 64 bottles (regular intervals) from the line of bottling, three samples (x-1 to x-3) per bottle. After analysis sample shaking and remeasurement (x-4 to x-6).

Sample number	Al	Ca	Fe	P	Si
test1	10.1	110.3	36.1	26.2	26.3
1-1	9.1	109.7	33.6	25.2	23.4
1-1	9.2	110.1	33.7	25.4	23.7
1-1	9.3	110.5	33.8	25.6	24.0
1-1	9.4	110.8	33.8	25.7	24.1
1-1	9.4	111.1	33.8	25.9	24.3
1-1	9.5	111.2	33.9	26.0	24.4
8-1	9.7	111.3	35.5	25.8	24.6
15-1	10.0	102.8	31.9	25.5	26.3
22-1	9.5	109.9	34.9	25.5	24.5
29-1	9.9	107.7	35.4	25.9	26.1
36-1	9.8	101.9	33.4	24.7	25.4
43-1	10.1	107.2	35.4	25.9	26.2
50-1	10.4	108.5	35.7	26.2	26.7
57-1	10.5	108.8	35.5	26.4	26.8
64-1	10.3	107.9	35.3	26.3	26.6
1-2	10.1	108.7	35.6	26.2	26.2
8-2	10.0	108.4	35.5	26.1	25.9
15-2	10.5	108.9	35.8	26.5	27.0
22-2	10.2	108.1	35.4	26.3	26.7
29-2	10.6	108.6	35.7	26.6	27.0
36-2	10.7	108.8	35.6	26.7	27.3
42-2	9.6	109.4	36.0	25.6	24.8
50-2	10.4	108.8	35.6	26.5	26.8
57-2	10.2	109.6	35.7	26.4	26.4
64-2	10.7	109.5	35.7	26.8	27.4
1-3	9.6	105.7	34.7	25.2	25.3

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Sample number	Al	Ca	Fe	P	Si
<i>Table S10, continued</i>					
8-3	9.9	108.6	35.3	25.9	26.1
15-3	10.6	109.2	35.6	26.7	27.2
22-3	11.0	109.8	35.7	27.1	28.3
29-3	10.5	109.0	35.6	26.6	27.0
36-3	10.7	108.9	35.6	26.5	27.3
42-3	10.3	108.5	35.6	26.3	26.7
50-3	10.2	107.7	35.4	26.2	26.6
57-3	10.9	108.2	35.3	26.7	27.8
64-3	10.2	109.4	35.6	26.3	26.1
1-4	10.1	111.8	35.5	26.7	25.7
1-4	10.2	112.3	35.6	27.0	26.0
1-4	10.3	112.6	35.7	27.2	26.2
1-4	10.4	113.0	35.8	27.3	26.4
1-4	10.5	113.2	35.8	27.5	26.6
1-4	10.6	113.5	35.8	27.6	26.8
8-4	10.2	117.1	35.6	26.8	25.7
15-4	9.4	117.9	34.2	26.0	23.4
22-4	9.8	122.3	35.3	27.1	24.4
29-4	9.2	124.4	35.1	26.7	22.5
36-4	8.8	117.1	33.0	25.4	21.5
42-4	9.1	122.7	35.1	26.7	22.6
50-4	9.5	124.4	35.4	27.0	23.5
57-4	9.9	121.5	35.4	27.0	24.7
64-4	9.3	123.6	35.0	27.0	22.9
1-5	9.8	120.9	35.7	26.9	24.8
8-5	9.7	125.2	35.3	27.3	24.0
15-5	9.9	125.0	35.5	27.3	24.8
22-5	9.7	119.9	35.7	26.6	24.8

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Sample number	Al	Ca	Fe	P	Si
<i>Table S10, continued</i>					
29-5	9.8	117.5	35.6	26.8	24.5
36-5	10.3	109.7	35.7	26.4	26.4
42-5	9.5	127.8	35.9	26.6	24.6
50-5	9.5	126.3	35.4	26.9	23.9
57-5	9.5	124.6	35.7	26.6	24.6
64-5	9.8	125.4	35.6	27.1	24.8
1-6	8.9	121.1	34.3	25.7	23.3
8-6	9.0	125.0	35.4	26.1	23.4
15-6	9.9	123.8	35.3	27.2	25.2
22-6	9.7	126.1	35.3	27.2	24.1
29-6	9.4	123.1	35.3	27.1	23.4
36-6	9.5	126.5	35.5	26.8	24.3
42-6	9.4	123.2	35.5	26.5	24.1
50-6	9.3	124.5	35.3	26.3	23.8
57-6	9.9	124.4	35.1	27.0	25.1
64-6	9.5	124.4	35.3	26.7	24.7

Table S11: One-way analysis of variance of homogeneity study (XRF results for phosphorus content)

Scattering cause	Square sum	Degrees of freedom	Mean square sum (MS)	F_{obs}	p value	$F_{crit.}$
Among the groups	0.0133	9	0.001478	0.53	0.84	2.39
Within the groups	0.0558	20	0.002793			
Total	0.0692	29				

According to ISO Guide 35 the uncertainty between bottles u_{bb} is in case of $F_{obs} < F_{crit.}$:

$$u_{bb} = \sqrt{\frac{MS_{within}}{n}} \sqrt{\frac{2}{N(n-1)}}$$

with N number of tested units and number of replicate determinations per unit $u_{bb}=0.172$ g/kg or 0.64%.

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Measurand: Phosphorus
 Mean $\pm U$ (Mean): 25.3 ± 0.4 g/kg
 Statistical method: ISO 5725-2
 No. of data sets: 67
 No. of measurement values: 248

Relative repeatability CV_r : 1.9%
 Relative reproducibility CV_R : 7.2%
 No. of Grubbs outliers: 1
 No. of Cochran outliers: 4
 No. of outlier values: 18

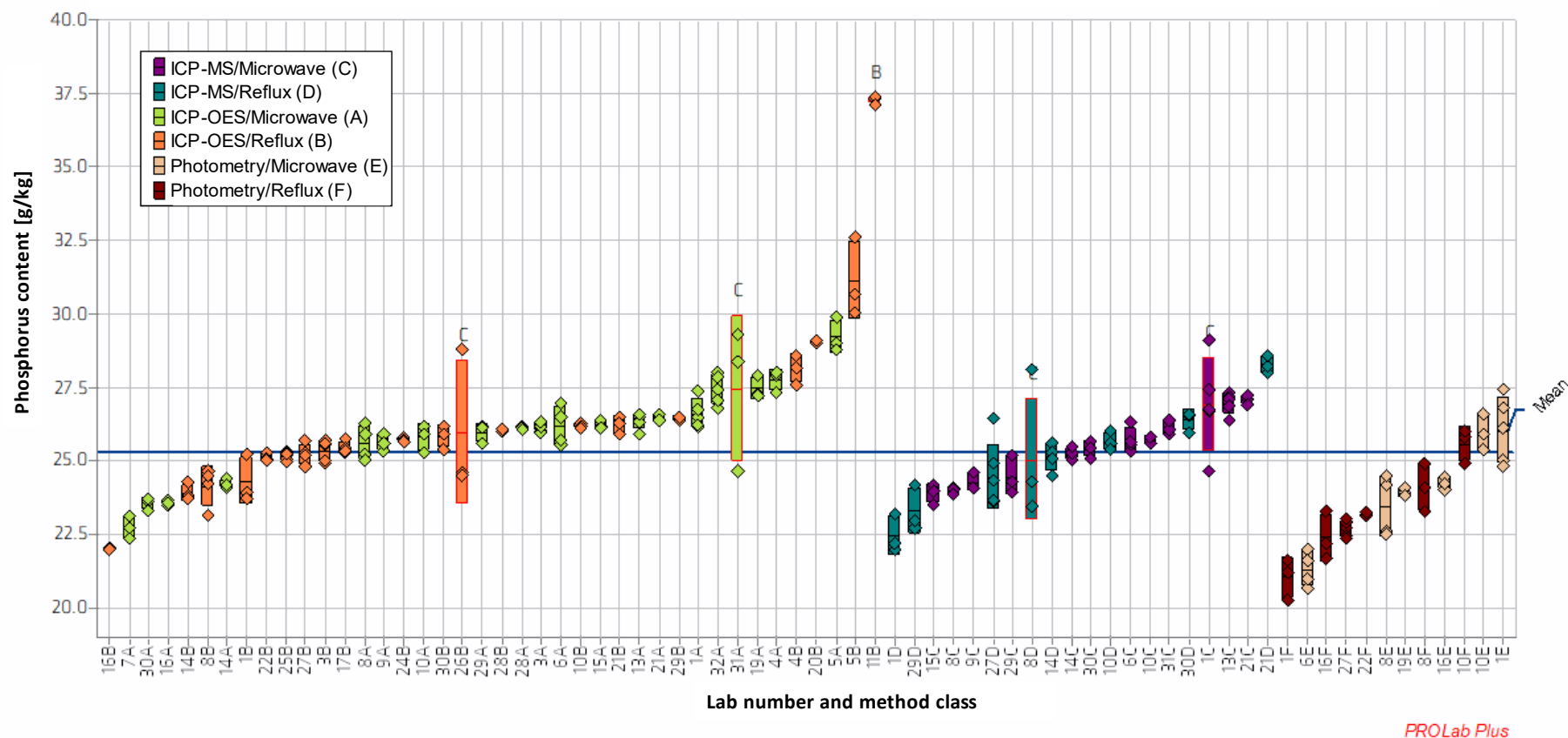


Figure S6: Interlaboratory comparison results sorted by analytical method (the bars represent laboratory means and standard deviations.). The method class lab code is shown on the x-axis and represents the lab number and the letter of the method class. Outliers have been eliminated for the calculations.

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Table S12: ILC results by laboratory and method class (MC) and outliers (Grubbs or Cochran) according to ISO 5725-2 (total summarized values main text, Table 3)

Lab no.	MC	P content mean [g/kg]	P content <i>RSD</i> [%]	Moisture means [%]	Moisture <i>CV_r</i> [%]	Method for moisture analysis
1	A	26.61	1.8	6.2	2	Moisture balance
	B	24.30	3.3			
	C	26.93	Cochran: 5.9			
	D	23.43	5.7			
	E	26.03	4.3			
	F	21.02	3.3			
3	A	26.17	0.6	6.9	< 1	Drying chamber (DIN EN 15934)
	B	25.36	1.4			
4	A	27.75	1.3	3.0	18	Drying chamber
	B	28.12	1.8			
5	A	29.21	2.0	6.3	1	Drying chamber
	B	31.11	Cochran*: 4.3			
6	A	26.18	2.5	6.3	3	Moisture balance and drying chamber (DIN EN 15934)
	C	25.70	1.7			
	E	21.33	2.9			
7	A	22.74	1.8	4.9	41	Drying chamber (DIN EN 15934)
8	A	25.62	2.2	5.6	< 1	Drying chamber (DIN EN 12280)
	B	24.14	2.8			

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	MC	P content mean [g/kg]	P content <i>RSD</i> [%]	Moisture means [%]	Moisture <i>CV_r</i> [%]	Method for moisture analysis
<i>Table S12, continued</i>						
8	C	23.97	0.5	5.6	< 1	Drying chamber (DIN EN 12280)
	D	25.05	Cochran: 8.3			
	E	23.45	4.5			
	F	24.10	3.3			
9	A	25.62	1.1	5.8	2	Drying chamber
	C	24.26	1.2			
10	A	25.80	1.8	3.3	1	Drying chamber
	B	26.20	0.4			
	C	25.73	0.4			
	D	25.67	1.2			
	E	25.97	2.3			
	F	25.57	2.3			
11	B	Grubbs: 37.28	0.3	5.9	< 1	Drying chamber (DIN EN 13040)
13	A	26.33	1.0	6.0		Drying chamber (DIN EN 15934)
	C	26.97	1.3			
14	A	24.20	0.6	0.9	1	Moisture balance
	B	23.88	1.2			
	C	25.25	0.8			

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	MC	P content mean [g/kg]	P content RSD [%]	Moisture means [%]	Moisture CV _r [%]	Method for moisture analysis
<i>Table S12, continued</i>						
14	D	25.13	1.8	0.9	1	Moisture balance
15	A	26.23	0.6	6.5	13	Drying chamber
	C	23.90	1.5			
16	A	23.57	0.3	7.0	< 1	
	B	22.01	0.2			
	E	24.24	0.8			
	F	22.39	3.6			
17	B	25.46	0.8	6.0	1	
19	A	27.47	1.4	7.7	2	Moisture balance
	E	23.93	0.6			
20	B	29.07	0.2	5.7	< 1	Drying chamber
21	A	26.47	0.4	7.0	1	Drying chamber (DIN EN 15934)
	B	26.23	1.2			
	C	27.07	0.6			
	D	28.27	1.1			
22	B	25.10	0.5	5.4	1	Drying chamber
	F	23.16	0.2			
24	B	25.71	0.3	5.4	6	Drying chamber (DIN EN 12880)

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	MC	P content mean [g/kg]	P content RSD [%]	Moisture means [%]	Moisture CV _r [%]	Method for moisture analysis
<i>Table S12, continued</i>						
25	B	25.16	0.5			
26	B	25.97	Cochran: 9.5	0.1	< 1	Drying chamber (DIN EN ISO 12048)
27	B	25.18	1.4	1.9	2	Drying chamber
27	D	24.44	4.6	1.9	2	Drying chamber
	F	22.70	1.1			
28	A	26.13	0.2	9.3	1	Moisture balance
	B	26.03	0.1			
29	A	25.97	1.2	6.2	5	Drying chamber (DIN EN 12880)
	B	26.47	0.2			
	C	24.47	2.7			
	D	23.30	3.4			
30	A	23.53	0.9	0.9	< 1	Drying chamber (DIN ISO 11465)
	B	25.83	1.6			
	C	25.40	1.1			
	D	26.37	1.3			
31	A	27.45	Cochran: 9.1	4.1	4	Drying chamber 40 °C (DIN 19747)
	C	26.13	0.9			
32	A	27.44	1.8	6.8	< 1	Drying chamber (DIN EN 15934)

* Not in all cases: outlier according to evaluation by analysis method (ICP-OES) and by method class (B)

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Table S13: Interlaboratory comparison, instrumental parameters by laboratory sorted by analytical method

Lab no.	Analysis	Standard	Acc.	Digestion	Standard	Acc.	Replicates	Calibration points	Calibration min. [mg/l]	Calibration max. [mg/l]	Wavelength [nm]
1	ICP-OES	ISO 11885		Microwave	EN 16174		5	5	30	600	213.6
1	ICP-OES	ISO 11885		Reflux	EN 16174		3	5	30	600	213.6
3	ICP-OES	ISO 11885		Microwave	EN 16174		6	5	1	10	178.2
3	ICP-OES	ISO 11885		Reflux	EN 16174		5	5	3	15	178.2
4	ICP-OES	ISO 11885		Microwave	EN 16174		3	5	0	2.5	213.6 214.9
4	ICP-OES	ISO 11885		Reflux	EN 16174		3	5	0	10	213.6 214.9
5	ICP-OES	EN 16170		Microwave	EN 16174		3	6	1	100	213.6
5	ICP-OES	EN 16170		Reflux	EN 16174		3	6	0	100	213.6
6	ICP-OES	ISO 11885	x	Microwave	EN 16174	x	4	8	0	1000	213.6
7	ICP-OES	ISO 11885	x	Microwave	EN 16174		3	5	5	50	213.6
8	ICP-OES	ISO 11885	x	Microwave	EN 16174	x	4	10	0.5	50	213.6 177.4
8	ICP-OES	ISO 11885	x	Reflux	EN 16174	x	4	10	0.5	50	213.6 177.4
9	ICP-OES	ISO 11885		Microwave	EN 16174		3	4	50	500	214.9
10	ICP-OES	ISO 11885	x	Microwave	EN 16174	x	3	5	10	50	213.6 177.4

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	Analysis	Standard	Acc.	Digestion	Standard	Acc.	Replicates	Calibration points	Calibration min. [mg/l]	Calibration max. [mg/l]	Wavelength [nm]
<i>Table S13, continued</i>											
10	ICP-OES	ISO 11885	x	Reflux	EN 16174	x	3	5	10	50	213.6 177.4
11	ICP-OES	ISO 11885	x	Reflux	EN 16174	x	3	8	2.5	300	214.9
13	ICP-OES	ISO 11885		Microwave	EN 16174		5	4	0.5	20	213.6
14	ICP-OES	EN 16170		Microwave	EN 16174		4	7	0.05	10	213.6 214.9 177.4
14	ICP-OES	EN 16170		Reflux	EN 16174		4	7	0.05	10	213.6 214.9 177.4
15	ICP-OES	ISO 11885	x	Microwave	EN 16174	x	3	5	20	200	185.9
16	ICP-OES	ISO 11885		Microwave	EN 16174		3	5	0.5	50	178.3
16	ICP-OES	ISO 11885		Reflux	EN 13346		3	5	0.5	50	178.3
17	ICP-OES	ISO 11885	x	Reflux	EN 16174	x	4	4	75	300	185.9
19	ICP-OES	ISO 11885	x	Microwave	EN 16174	x	3	6	0.25	5	213.6
20	ICP-OES	EN 16170		Reflux	EN 16174		3	5	20	300	177.4
21	ICP-OES	EN 16170	x	Microwave	EN 16174	x	3	2	0	326.1	213.6
21	ICP-OES	EN 16170	x	Reflux	EN 16174	x	3	2	0	326.1	213.6

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	Analysis	Standard	Acc.	Digestion	Standard	Acc.	Replicates	Calibration points	Calibration min. [mg/l]	Calibration max. [mg/l]	Wavelength [nm]
<i>Table S13, continued</i>											
22	ICP-OES	ISO 11885	x	Reflux	EN 13346	x	4	6	3	98	213.6
24	ICP-OES	ISO 11885	x	Reflux	EN 16174		3	5	10	100	178.3
25	ICP-OES	EN 16170		Reflux	EN 13346		10	4	5	100	213.6 177.5 178.3
26	ICP-OES	ISO 11885	x	Reflux	EN 13346	x	3	2	5	50	213.6
27	ICP-OES	ISO 11885	x	Reflux	EN 16174	x	6	10	5	50	213.6
28	ICP-OES	ISO 11885		Microwave	EN 16174		4	7	0.013	200	178.3
28	ICP-OES	ISO 11885		Reflux	EN 16174		4	7	0.013	200	178.3
29	ICP-OES	EN 16170	x	Microwave	EN 16174	x	3	3	0	100	213.6
29	ICP-OES	EN 16170	x	Reflux	EN 16174	x	3	3	0	100	213.6
30	ICP-OES	ISO 11885	x	Microwave	EN 16174		3	3	1	10	213.6 617
30	ICP-OES	ISO 11885	x	Reflux	EN 13346	x	3	3	1	10	213.6 617
31	ICP-OES	ISO 11885	x	Microwave	EN 16174	x	3	6	0.25	200	213.6
32	ICP-OES	ISO 11885	x	Microwave	EN 16174		5	3	5	50	213.6 177.4
1	ICP-MS	EN 16171		Microwave	EN 16174		5	5	0.02	1.00	

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	Analysis	Standard	Acc.	Digestion	Standard	Acc.	Replicates	Calibration points	Calibration min. [mg/l]	Calibration max. [mg/l]	Wavelength [nm]
<i>Table S13, continued</i>											
1	ICP-MS	EN 16171		Reflux	EN 16174		3	5	0.02	1.00	
6	ICP-MS	ISO 17294-2	x	Microwave	EN 16174	x	4	5	0	5	
8	ICP-MS	ISO 17294-2	x	Microwave	EN 16174	x	4	5	2.5	25	
8	ICP-MS	ISO 17294-2	x	Reflux	EN 16174	x	4	5	2.5	25	
9	ICP-MS	EN 16171		Microwave	ISO 54321		3	6	1	50	
10	ICP-MS	EN 16171	x	Microwave	EN 16174	x	3	5	10	50	
10	ICP-MS	EN 16171	x	Reflux	EN 16174	x	3	5	10	50	
13	ICP-MS	ISO 17294-2		Microwave	EN 16174		5	4	0.5	10	
14	ICP-MS	EN 16171		Microwave	EN 16174		4	7	0.005	1	
14	ICP-MS	EN 16171		Reflux	EN 16174		4	7	0.005	1	
15	ICP-MS	ISO 17294-2	x	Microwave	EN 16174	x	3	6	0.2	3	
21	ICP-MS	EN 16171		Microwave	EN 16174	x	3	4	0	100	
21	ICP-MS	EN 16171		Reflux	EN 16174	x	3	4	0	100	
27	ICP-MS	EN 16171		Reflux	EN 16174	x	6	4	0.0125	0.10	
29	ICP-MS	EN 16171	x	Microwave	EN 16174	x	3	3	0	2	
29	ICP-MS	EN 16171	x	Reflux	EN 16174	x	3	3	0	2	

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	Analysis	Standard	Acc.	Digestion	Standard	Acc.	Replicates	Calibration points	Calibration min. [mg/l]	Calibration max. [mg/l]	Wavelength [nm]
<i>Table S13, continued</i>											
30	ICP-MS	ISO 17294-2		Microwave	EN 16174		3	6	0.1	10	
30	ICP-MS	ISO 17294-2		Reflux	EN 13346	x	3	6	0.1	10	
31	ICP-MS	ISO 17294-2	x	Microwave	EN 16174	x	3	3	1	10	
1	Photometry	ISO 6878		Microwave	EN 16174		5	10	0.08	0.80	880
1	Photometry	ISO 6878		Reflux	EN 16174		3	10	0.08	0.80	880
6	Photometry	ISO 6878	x	Microwave	EN 16174	x	4	6	0.02	1.00	880
8	Photometry	ISO 6878	x	Microwave	EN 16174	x	4	15	0.01	0.50	880
8	Photometry	ISO 6878	x	Reflux	EN 16174	x	4	15	0.01	0.50	880
10	Photometry	ISO 6878	x	Microwave	EN 16174	x	3	10	0.08	0.80	880
10	Photometry	ISO 6878	x	Reflux	EN 16174	x	3	10	0.08	0.80	880
16	Photometry	ISO 6878		Microwave	EN 16174		3	6	0.05	0.50	880
16	Photometry	ISO 6878		Reflux	EN 13346		3	6	0.05	0.50	880
19	Photometry	ISO 6878	x	Microwave	EN 16174	x	3	10	0.01	2.00	880
22	Photometry	ISO 6878	x	Reflux	EN 13346	x	4	10	0.05	1.50	880
27	Photometry	ISO 6878		Reflux	EN 16174	x	6	10	0.12	12.00	880

No results received from laboratory 12 and 23, invalid results (wrong standards) received from laboratory 2 and 18

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Table S14: Interlaboratory comparison, deviations of lab from the sample digestion prescribed in the sample instruction letter

Lab no.	Digestion type	Sample intake	Aqua regia volume	Acid ratio	Digestion process
5	Reflux	2.5 instead of 3.0 g			
8	Microwave			HCl:HNO ₃ 1:5 instead of 3:1	120 instead of 10 min.
9	Microwave			HCl:HNO ₃ 1:4 instead of 3:1	
10	Microwave	1.0 instead of 0.5 g	12 instead of 8 ml		
10	Reflux		30 instead of 28 ml		
11	Reflux		8 instead of 28 ml		50 instead of 120 min.
13	Microwave		12 instead of 8 ml		90 instead of 10 min.
15	Microwave	0.35 instead of 0.5 g			60 instead of 10 min.
17	Reflux		32 instead of 28 ml		
18	Reflux		24 instead of 28 ml		140 instead of 175 °C; digestion according to VDLUFA MB I A 2.4.3. instead of prescribed DIN standards
20	Reflux		30 instead of 28 ml		
21	Reflux	1.25 instead of 3.0 g	14 instead of 28 ml		
25	Reflux		30 instead of 28 ml		
26	Reflux				180 instead of 120 min.
28	Microwave		10 instead of 8 ml		

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Lab no.	Digestion type	Sample intake	Aqua regia volume	Acid ratio	Digestion process
Table S14, continued					
29	Microwave				120 instead of 10 min.; 220 °C instead of 175 °C
29	Reflux				300 instead of 120 min.
30	Microwave	1.0 instead of 0.5 g	10 instead of 8 ml		
30	Reflux	2.0 instead of 3.0 g			
31	Microwave		12 instead of 8 ml		
32	Microwave	Different: 0.5 g; 1.0 g and 3.0 g			

Results from laboratory 18 were not evaluated due to the unauthorized special digestion process

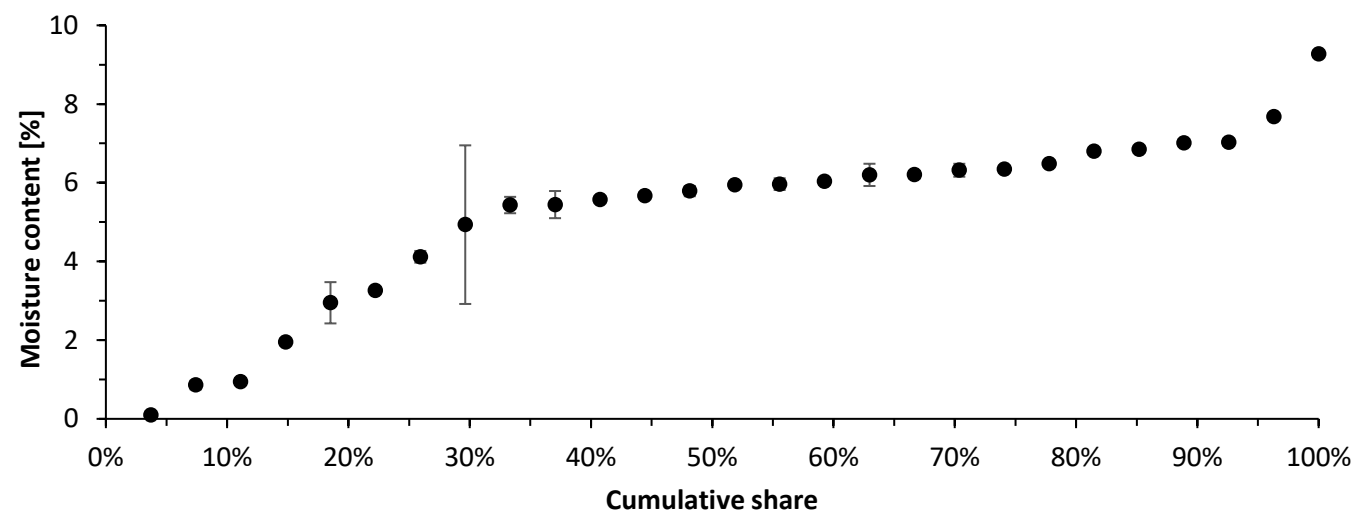


Figure S7: Cumulative curve of the moisture content analyzed by the labs during the interlaboratory comparison. The error bars mark the standard deviation (n=2 to 6)

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

Table S15: Interlaboratory comparison, deviations by of lab of from the analytical method prescribed in the sample cover instruction letter

Lab no.	Analysis	Calibration	Dilution	Other special aspects
2	ICP-MS	Standard addition calibration		No analysis by standard
5	ICP-OES		Not sufficient: above calibration (reflux +1,000%)	
6	Photometry	Up to 1.0 instead of 0.8 mg/l: above DIN safe working space		
8	ICP-OES		Not sufficient: above calibration (microwave +100%, reflux +200%)	
8	ICP-MS		Not sufficient: above calibration (microwave +300%, reflux +20%)	
16	ICP-OES		Not sufficient: above calibration (reflux +25%)	
16	Photometry		Not sufficient: above calibration (microwave +150%, reflux +400 %)	Treated according to ISO 6878 part 6: Further digestion of aqua regia digestions (H ₂ SO ₄)
18	ICP-OES			Analysis according to ISO 22036 instead of prescribed standards
19	Photometry	Up to 2.0 instead of 0.8 mg/l: above DIN safe working space		
25	ICP-OES		Not sufficient: above calibration (reflux +650%)	
27	Photometry	Up to 12.0 instead of 0.8 mg/l: above DIN safe working space		
30	ICP-OES		Not sufficient: above calibration (microwave and reflux +400%)	

Results from laboratories 2 and 18 were not evaluated due to unauthorized special sample analysis

Supporting information - Phosphorus determination in sewage sludge – comparison of different aqua regia digestion methods and ICP-OES, ICP-MS and photometric determination

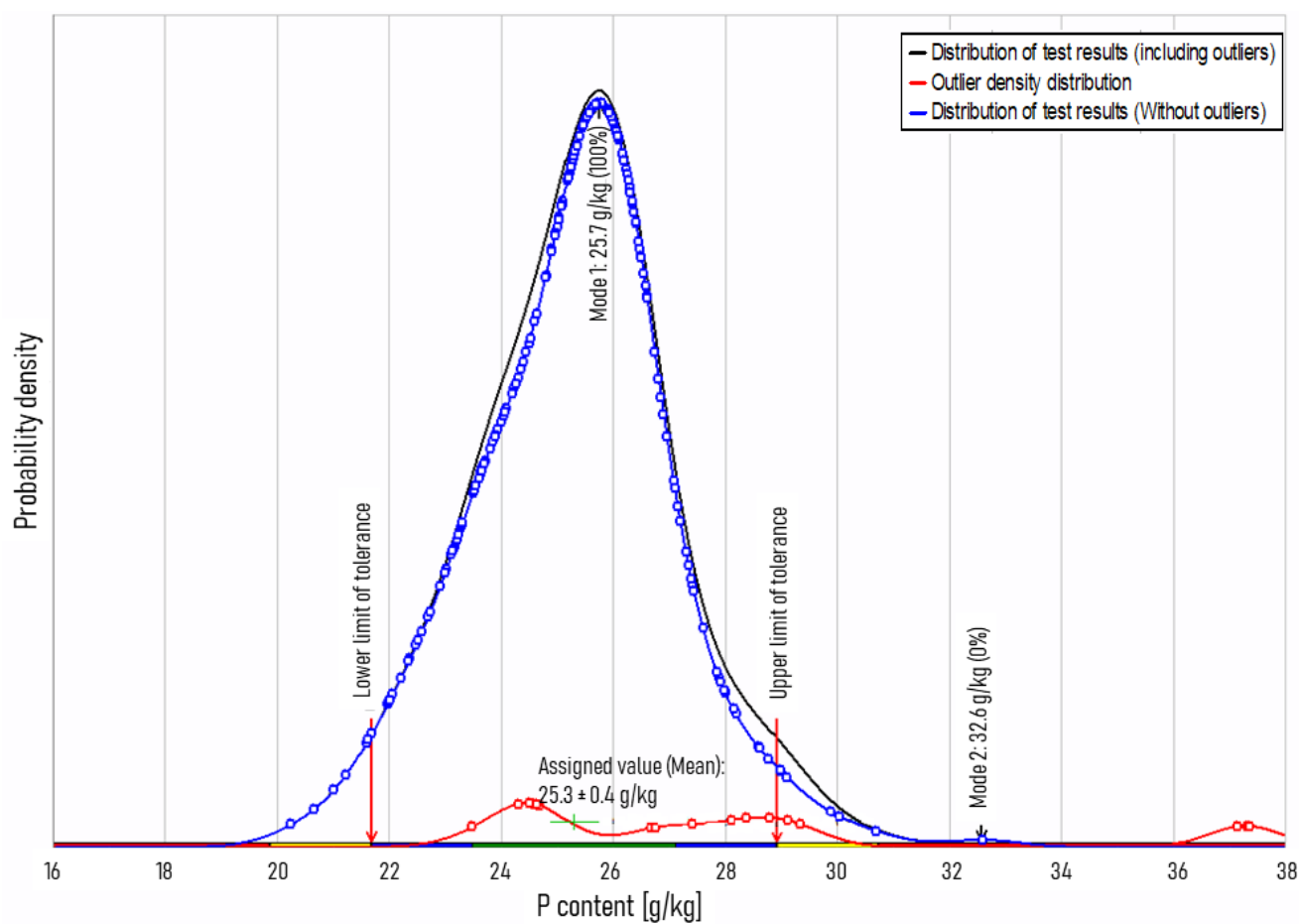


Figure S8: Interlaboratory comparison, distribution obtained with a kernel density estimator

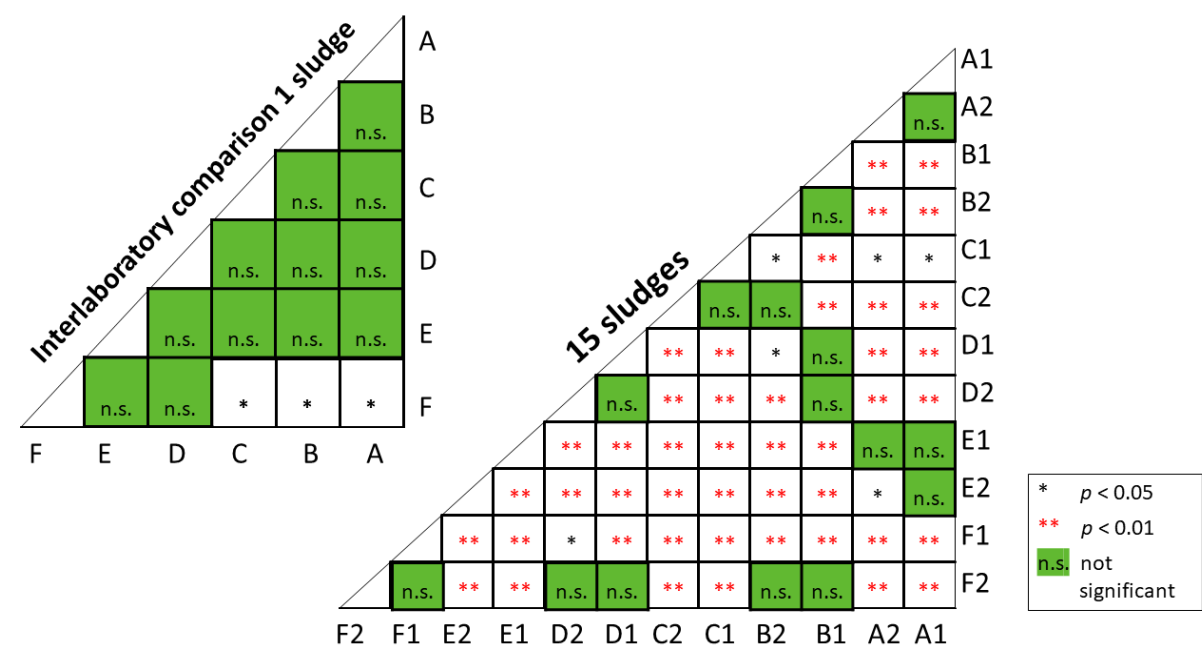


Figure S9: Significant differences by method combination and method class (main text, Figure 1) from the interlaboratory comparison and investigation of 15 sewage sludges t-test

Supporting References

ISO 5725-2:2019. Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

ISO-Guide 35:2017. Reference materials — Guidance for characterization and assessment of homogeneity and stability.

ISO 22036:2009. Soil quality - Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP-AES)

EN 12880:2001-02. Characterization of sludges - Determination of dry residue and water content; German version EN 12880:2000

EN 12048:1996-11. Solid fertilizers and liming material - Determination of moisture content - Gravimetric method by drying at $(105 \pm 2) ^\circ\text{C}$ (ISO 8190:1992, modified); German version EN 12048:1996

EN 15934:2012-11. Sludge, treated biowaste, soil and waste - Calculation of dry matter fraction after determination of dry residue or water content; German version EN 15934:2012

ISO 11465:1993-12. Soil quality; determination of dry matter and water content on a mass basis; gravimetric method

19747:2009-07. Investigation of solids - Pre-treatment, preparation and processing of samples for chemical, biological and physical investigations