Sustainable sewage sludge management fostering phosphorus recovery and energy efficiency

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Quantification of nutritional value and toxic effects of each P recovery product

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List of abbreviations

AOX	adsorbable organic halogens
DM	Dry matter
FM	Fresh matter
PAH	polyaromatic hydrocarbons
PCB	polychlorinated biphenyls
PCDD	polychlorinated dibenzo-p-dioxins
PCDF	polychlorinated dibenzo-p-furans
WWTP	Wastewater Treatment Plant

1 Introduction

1.1 Objectives

The document will provide a compilation of all assessed P recycling products reflecting beneficial (nutritious) value and harmful (toxic) effects for health and environment. The aim is to identify the Best Available Techniques for P recovery by evaluation of all received results by the pot-test, the chemical analyses and the toxicity-tests conducted in the P-REX-project.

2 The P recycling products

All tests were done with three kinds of sewage sludge (sludge), with three products that were received by crystallization of the water-phase of sewage sludge (cryst) and five products that are based on ash that is received by incineration of sewage sludge (therm).

2.1 The sludge products

Sludge 1

Digested Bio-P sewage sludge (sludge 1or S1) directly sampled from the digester outlet (meaning un-dewatered). P removal is done with Enhanced Biological P Removal (EBPR).

Sludge 2

Sludge 2 or S2 is the same sludge as sludge 1, but sampled after centrifuge dewatering.

Sludge 3

Sludge 3 or S3 is digested Chem-P sewage sludge sampled after dewatering with centrifuge. P removal is done by precipitation as iron phosphate.

2.2 The crystallization products

Cryst 1

The first crystallization product (cryst 1 or C1) is the struvite (magnesium ammonium phosphate) of the company Ostara (Canada) which is produced by the Pearl-process. In the Pearl process sludge liquor after sludge dewatering is fed into an up-flow reactor. $MgCl_2$ and NaOH are dosed into the reactor which induced precipitation of the phosphorus in the mineral form of struvite. The struvite pellets are separated at the bottom of the reactor. The Pearl process is operated in full scale in North-America and Europe.

Cryst 2

The second crystallization product (cryst 2 or C2) is the struvite of the company Berliner Wasserbetriebe (Germany) operating the prototype of the AirPrex process. In the AirPrex process sludge from the anaerobic digester is fed to an airlift reactor. The reactor is aerated to strip CO_2 resulting in an increase of the pH. $MgCl_2$ is dosed into the reactor leading to struvite crystallization. Sedimented struvite crystals are harvested from the conic bottom of the reactor. The AirPrex process is operated at full scale at various WWTP in Europe and China.

Cryst 4

The third crystallization product (cryst 4 or C4) is a mixture of calcium phosphate (CaP) and struvite which is produced by the Stuttgarter process by the Stuttgart University (Germany). In the Stuttgart process phosphorus in the sewage sludge is solubilized by sulfuric acid. After solid/liquid separation and complexation of metals by citric acid, the dissolved phosphorus is precipitated in the mineral form of struvite and calcium phosphate by addition of NaOH and MgO. The Stuttgart process is operated in large pilot scale in Southern Germany.

2.3 The ash products

Therm 1

The first ash product (therm 1 or T1) is a raw (untreated) ash. So it is not a real P recovery product but used as a kind of control for the treatment processes of ashes. Ash from a mono-incineration facility located in Winterthur, Switzerland was used for the production of therm 2, therm 3 and therm 5. The input materials for therm 4 originate from another facility.

Therm 2

The second ash product (therm 2 or T2) is an ash treated with magnesium chloride ($MgCl_2$) by the Federal Institute for Materials Research and Testing (Germany) and the company Outotec (Finland). The production process is called Ash Dec. The Ash Dec process is a thermo-chemical process. In this process layout $MgCl_2$ is added to sewage sludge ash and the blend is treated at around 1000 °C. The sample was produced in technical scale in a rotary kiln with a corundum (Al_2O_3) tube at a throughput of about 2 kg/h.

Therm 3

The third ash product (therm 3 or T3) was produced by the same companies and with a similar process like Therm 2, but the treatment of the ash was done with sodium carbonate (Na_2CO_3). The Ash Dec process is a thermo-chemical process. In this process layout dry sewage sludge and Na_2CO_3 is added to sewage sludge ash and the blend is treated at around 1000 °C under reducing conditions. The sample was produced in technical scale in a rotary kiln with a Ni-base alloy-tube (65 % Ni, 25 % Cr) at a throughput of about 3 kg/h. Therm 3 is contaminated by chromium and nickel due to abrasion of the tube material. This is a specific problem of the experimental setup used for the trials but would not be problematic in industrial scale.

Therm 4

The fourth ash product (therm 4 or T4) was produced by the Mephrec process of the company Ingitec (Germany). Briquettes made of sewage sludge ash, sewage sludge and cement are thermally treated (gasification) in a shaft furnace at temperatures above 1450 °C. Therm 4 is produced during a pre-trial 2008 in Freiberg (Germany). A Mephrec product from current stage of development was not available for the plant availability and toxicity tests.

Therm 5

The fifth ash product (therm 5 or T5) is a product of the company BSH (Switzerland). The calcium phosphate product was produced by the LeachPhos process. The LeachPhos process consists of a leaching step in which phosphorus is solubilized and a precipitation step in which the phosphorus product is precipitated. The process was operated in full-scale mode in several intervals over a period of three months.

3 Fertilizer value

3.1 Pot test design and conduction

The pot test for evaluation of the nutrient availability of the P products was conducted with two soils differing in pH value (acidic and almost neutral soil) and with maize as test plant. The test has been conducted for a period of two years (2013 and 2014) after a single P-fertilization at the beginning of the test. For the conduction of the pot test all products were analyzed for their contents of plant nutrients. Additionally to the main nutrients nitrogen, potassium and phosphorus also the solubility of phosphorus in different solvents (acids) and the contents of magnesium, calcium and sulfur were analyzed (Table 1).

Table 1: Nutrient contents of P products and recyclates used in the pot experiment

Product	DM	P_2O_5 mineral acid soluble	P_2O_5 neutral ammonium citric acid + water soluble	P_2O_5 citric acid soluble	P_2O_5 water soluble	N	K_2O	MgO	CaO	S
	[% i. FM]	[% i. DM]								
S1	2.4	9.0	8.1	7.7	2.3	6.6	2.0	1.1	5.6	1.2
S2	23.3	10.3	9.3	8.8	0.6	6.5	0.4	3.6	5.6	1.2
S3	28.7	9.4	8.9	8.4	0.0	5.2	0.1	0.4	5.2	2.3
C1	100.0	30.5	28.6	29.7	0.6	5.7	0.1	18.2	0.1	0.0
C2	100.0	26.6	25.1	26.4	1.1	4.7	0.1	15.6	1.0	0.1
C4	100.0	23.0	22.0	23.0	0.6	5.0	0.3	12.5	1.6	1.3
T1	99.7	15.7	2.5	7.5	0.0	<0.1	0.6	2.5	19.1	1.3
T2	99.8	13.9	3.9	12.2	0.1	<0.1	0.3	10.3	17.4	1.0
T3	100.0	12.9	12.8	14.1	1.3	0.0	0.7	2.3	14.0	1.1
T4	99.9	9.5	0.6	4.1	0.0	<0.1	0.7	3.2	36.2	0.1
T5	97.5	28.3	26.9	27.2	1.2	<0.1	0.2	2.0	34.7	8.0
TSP	95.1	51.0	46.9	47.5	44.4	<0.1	1.0	1.3	26.2	1.1

The dry matter content of the cryst products (C1-C3) could not be detected correctly by drying, so they were determined as 100 %. Only the dry matter contents of the sludges (S1-S3) were of course significantly lower than 100 %, since sludge consists of a solid and an aqueous phase. The dry matter content of sludge 1 was only 2.4 % which in combination with the low P-content enables a very high application dose of the fertilizer.

The mineral acid soluble P_2O_5 content defined as total P content and was used for the calculation of the fertilizer amount in the pot test. The sludges had the lowest P_2O_5-contents between 9 and 10 % and the cryst products the highest values between 23 and 31 %. The therm products had inhomogeneous amounts between 10 and 28 %. The solubility in neutral ammonium citric acid and citric acid was relatively high in the most cases, but the water solubility was only high for the commercially available TSP. The quantities of N, K, Mg and S were used for the calculation of the nutrient solutions. The pot test was done with Mitscherlich-pots which are made for 6 kg soil. As the nutrient addition should be the same in all pots, nitrogen, potassium, magnesium and sulphur were added by considering the nutrient contents in the fertilizers. The nutrient values that have been aimed to be reached in 6 kg soil per pot were:

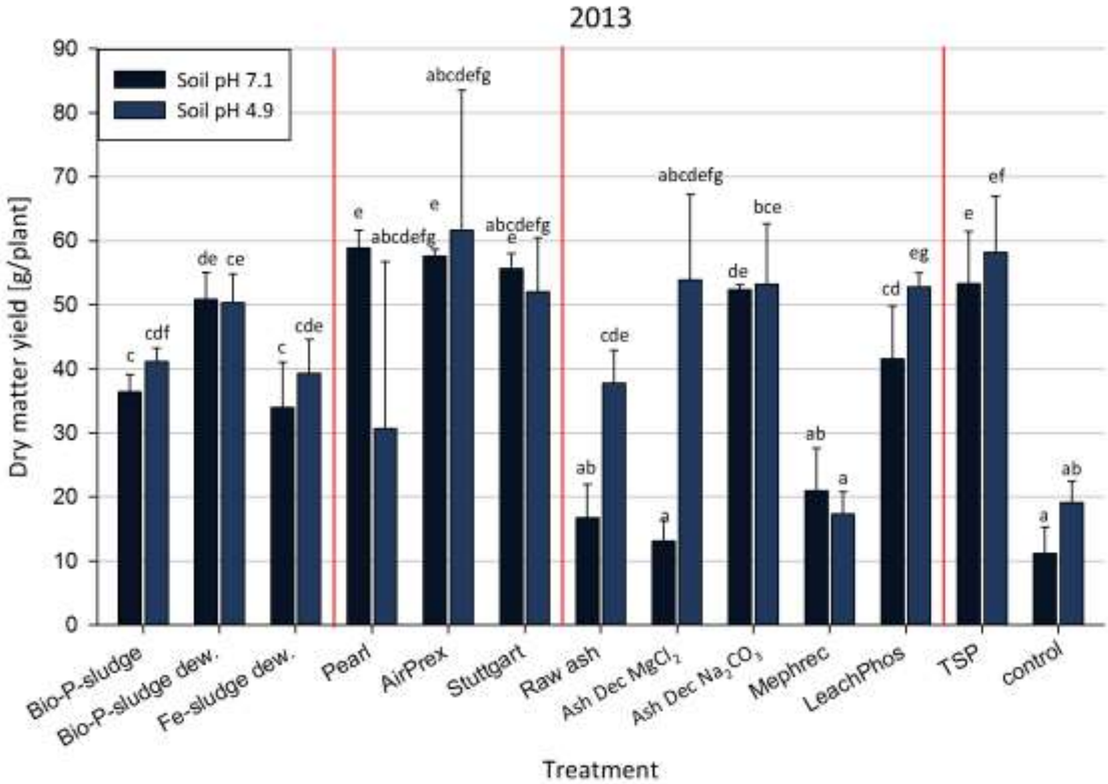
P: 750 mg (except control)
N: 2000 mg
K: 2000 mg
Mg: 200 mg
S: 200 mg

Each fertilizer was tested in four replications per soil except TSP and control which were tested in six replications. The pots were arranged randomized on tables in a wired house, so the temperature was like outside but the pots were sheltered from rain by a transparent roof. Watering was done almost every day by adding water until the normal weight (which was determined in the beginning of the experiment for each pot).

3.2 Results of the pot test

In both years the fresh and dry matter yields per pot were measured. The dry matter yields per plant are shown in Figure 1a and b.
All three sludge products lead to significant yield increases compared to the control in both years and on both soils. Although the water-soluble P fraction was lower in sludge 2 (Bio-P-sludge dewatered) compared to sludge 1 (Bio-P-sludge) the yields were higher for sludge 2 in the first year. One reason might be that after P-application in the first year the soil treated with the liquid sludge 1 was to wet (because of the high sludge amount) that seedling emergence was inhibited and the maize plants appeared later than all others did. The differences between sludge 1 and 2 disappeared in the second year. But in 2014 all three sludge products lead to lower yields on acidic soil which was not the case in 2013. The reason for this might be that the low pH value was not constant in 2013 (due to watering with tap water).

a)



b)

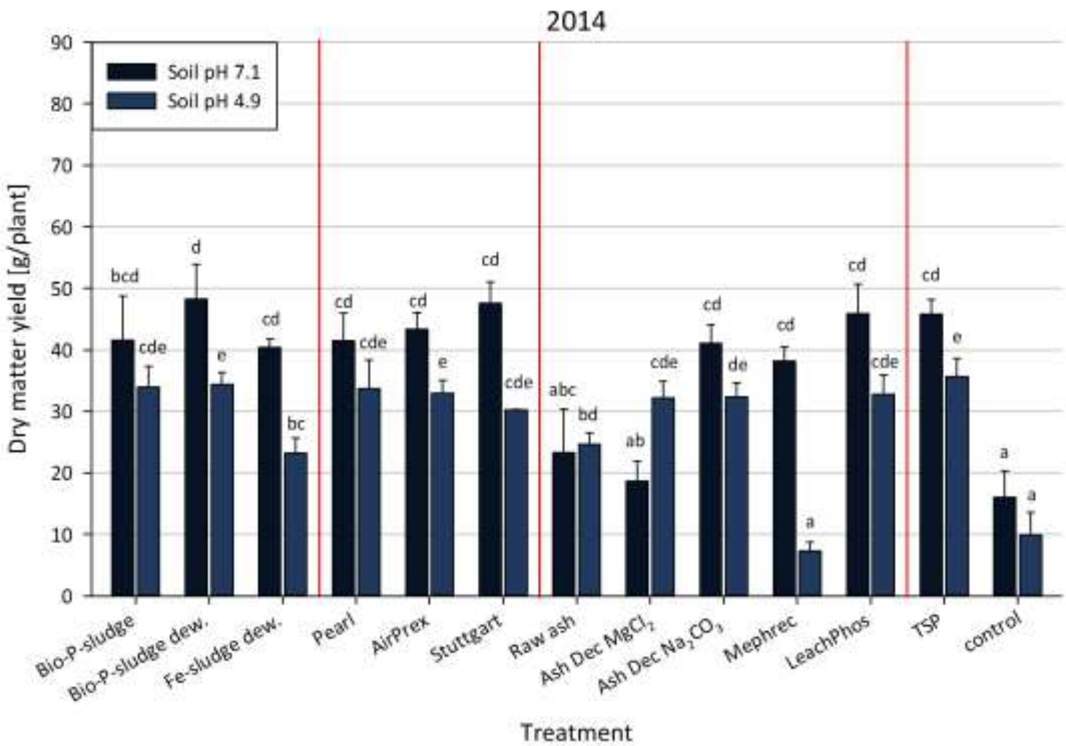


Figure 1: Dry matter yield (g/plant) of maize in a) 2013 and b) 2014 in dependence of different treatments of P-fertilization and of different pH-values of soil; Mean values of n=4 (except TSP and control are n=6); error bars are standard deviations; bars with the same letter within one year and soil do not differ significantly, Tukey-test or Dunnet T3-Test with $\alpha = 0.05$

The three struvite products led to yields as high as plants fertilized with TSP on both soils and in both years (exception: cryst 1 in the first year on acidic soil). In the first year standard deviations on acidic soil were so high that the yield increase was not significant compared to control plants. The reason for this is probably the rather low starting pH value of 4.9 and a following pH decrease due to ammonia nutrition (as ammonia is part of MAPs). Maybe due to this pH effect some of the plants emerged but stayed very small and stopped growing but most plants had a normal development. These differences in plant size (and therefore plant weight) may have led to high standard deviations.

The ash products showed inhomogeneous results. The raw ash (therm 1) was used as a kind of reference as the P-availability is very low in untreated sewage sludge ash. The total P-amount of therm 1 is comparable with therm 2 and 3 (the two Ash Dec products) between 12.9 and 15.7 % i. DM, but the citric acid soluble P-amount is only half (7.5 compared to 12.2-14.1 %). Nevertheless the raw ash lead to significant yield increases on acidic soil in both years but not on neutral soil. The two Ash Dec products differed strongly in their effect on plants as the $MgCl_2$-treated product lead to good results only on acidic soil and the Na_2CO_3-treated product lead to comparable yield increases like TSP and the struvite products did. The Mephrec slag (therm 4) produced in 2008 lead to a significant higher yield than control plants only on neutral soil in the second year. This product had the lowest total P-content and also very low P-solubilities in the different acids. Due to this, it is remarkable that the yield was higher on neutral soil than on acidic soil in both years as acidic soil can increase the P-availability. The LeachPhos product (therm 5), together with the Na_2CO_3-treated Ash Dec product (therm 3), showed the best result among the therm products. The yields were significantly higher compared to the control plants on both soils and in both years and only slightly lower than TSP-treated plants in the first year.

The relative fertilizer efficiency (RFE) was calculated by determining the yield increase according to the control for each fertilizer. The yield increase of the TSP-fertilizer was set to 100 % and the proportion for the other P products was calculated. The results of both years of the RFE are shown in Table 2.

Table 2: Relative fertilizer efficiency (RFE) in dry matter yield per plant in percent compared to TSP (after subtraction of control yield) of maize plants in 2013 and 2014 in dependence of different treatments of P-fertilization and of different pH-values of soil; Mean values are marked in red if < 50, in orange if > 50 and < 80 and in green if > 80; Mean values of n=4 (except TSP and control are n=6)

P product	**Soil pH 7.1**			**Soil pH 4.9**			**Mean value pH 7.1 + 4.9**
	2013	**2014**	**Mean value**	**2013**	**2014**	**Mean value**	
	%						
Bio-P-sludge	60	**86**	**73**	56	**94**	**75**	**74**
Bio-P-sludge dew.	**94**	**108**	**101**	**80**	**95**	**88**	**94**
Fe-sludge dew.	54	**82**	**68**	52	52	**52**	**60**
Pearl	**113**	**86**	**100**	30	**93**	**62**	**80**
AirPrex	**110**	**92**	**101**	**109**	**90**	**100**	**100**
Stuttgart	**106**	**106**	**106**	**84**	79	**82**	**94**
Raw ash	13	24	**19**	48	57	**53**	**36**
Ash Dec $MgCl_2$	5	9	**7**	**89**	**87**	**88**	**47**
Ash Dec Na_2CO_3	**98**	**84**	**91**	**87**	**88**	**88**	**89**
Mephrec	23	75	**49**	-5	-10	**-8**	**21**
LeachPhos	72	**100**	**86**	**86**	**89**	**88**	**87**
TSP	100	100	100	100	100	100	100

Satisfying results of RFE values of 80 or more were reached by the dewatered Bio-P-sludge (sludge 2), all struvite products (cryst 1-4), Ash Dec (Na_2CO_3) (therm 3) and LeachPhos (therm 5). The yields of the three struvite products were comparable to the ones obtained by TSP.

4 Toxicity

For evaluation of the toxicity of the P products chemical analyses were made and furthermore six different eco-toxicity-tests were conducted.

4.1 Chemical analyses

The concentration of heavy metals was analyzed for all P products. Selected organic pollutants were analyzed only for the sludge- and cryst products as the ashes usually don´t contain organic substances anymore if incinerated properly. The results of the heavy metal analysis are presented in Table 3.

Table 3: Heavy metal contents in the P products, the recyclates and TSP and limit values in EU- and German legislation

Product	As	Cd	Cr	Cu	Fe	Hg	Ni	Pb	Zn
	[mg kg^{-1} DM]								
Sludge 1	4.0	1.2	27.9	214.9	18,934.4	0.7	25.5	28.7	885.9
Sludge 2	3.5	1.2	27.7	220.3	18,976.3	1.1	22.6	29.3	902.3
Sludge 3	4.7	1.0	17.6	831.7	120,629.1	1.1	17.6	35.7	945.6
MPV EU[1]	-	20.0-40.0	-	1000.0-1750.0	-	16.0-25.0	300.0-400.0	750.0-1,200.0	2,500.0-4,000.0
Cryst 1	4.9	<0.2	3.0	1.5	313.9	<0.7	6.1	<2.2	2.4
Cryst 2	1.5	<0.3	33.2	62.9	4,060.8	0.5	19.7	19.7	73.4
Cryst 4	1.6	0.1	5.5	58.9	19,648.7	0.6	6.7	10.9	87.5
Therm 1	11.2	6.9	96.1	893.0	147,296.6	<1.1	64.9	228.4	2434.4
Therm 2	9.4	1.9	50.4	494.1	119,545.3	<1.0	72.1	50.3	1133.2
Therm 3[3]	7.6	1.4	(311.4)	835.2	108,538.6	<1.2	(342.8)	87.4	1930.1
Therm 4	<4.5	0.1	103.0	97.0	21,744.8	<1.1	28.1	<3.3	69.3
Therm 5	16.0	4.3	28.0	659.9	15,697.7	0.4	11.8	8.5	1177.2
TSP	7.5	4.2 ≙ 8.2 mg kg^{-1}P_2O_5	121. 2	13.0	3,444.3	0.2	41.2	3.1	182.9
MPV Ger[2]	40.0	1.5 or*: 50 mg kg^{-1} P_2O_5	300.0** (2.0 for Cr_{VI})	-	-	1.0	80.0	150.0	-

1) Maximum permissible value in EU Directive 86/278/EEC
2) Maximum permissible value in the German fertilizer ordinance (DüMV)
3) The increased mass fractions of chromium and nickel resulted from abrasion of the Ni-base alloy tube material of the trail rotary kiln and are not representative for an industrial process

* For products with more than 5 % P_2O_5 in FM the limit of 50 mg Cd kg^{-1} P_2O_5 has to be observed (which is the case for TSP)
**DüMV does not define a limit value but an obligation of labeling for concentrations ≥ 300 mg kg^{-1} DM for Chromium

All three sludges met the limit values of the EU Sludge Directive and are allowed for agricultural application. But, regarding the stricter limits of the German fertilizer ordinance sludge 2 and 3 were not allowed to be used on arable land due to a mercury content of 1.1 mg kg^{-1} DM exceeding the limit of 1.0 mg kg^{-1} DM. While sludge 1 and sludge 2 have similar concentrations of heavy metals in some cases sludge 3 has much higher values especially regarding copper and lead. Since iron is not considered harmful and therefore not limited, higher contents pose no matter of concern.

The three crystallization products show very low levels of heavy metals and do not exceed any limit values. Another picture is given by the products from the thermal processes.

The raw ash (T1) exceeds the limit for lead and contains also very high concentrations of cadmium, copper and zinc. Therm 3 (T3) exceeds the threshold for chromium and nickel with 311 and 343 mg kg^{-1} DM originating from the kiln used for the ash processing. Therm 2, 4 and 5 complied with all legal thresholds.

The concentrations of adsorbable organic halogens (AOX), perfluorated tensides (PFOA and PFOS), polycyclic aromatic hydrocarbons (PAHs) and of some pharmaceuticals and other organic chemicals in the sludges and cryst products are shown in Table 4.

Table 4: Contents of AOX, PFTs, PAHs and of some pharmaceuticals and other organic chemicals of concern in sludge and cryst products analyzed in the P-REX project

Product	AOX	Perfluorated Tensides (PFT)		Polycyclic aromatic hydrocarbons (PAH)						Others					
	Adsorbable organic halogens	Perfluor-octanoic acid	Perfluor-octanesulfonic acid	Fluoranthene	Benzo(b) Fluoranthene	Benzo(k) fluoranthene	Benzo(a)pyrene	Benzo(ghi) perylene	Indeno(1,2,3) Pyrene	Carbamazepin	Benzotriazol	Sulfamethoxazol	Mecoprop	Diclofenac	Estron
	[mg kg^{-1} DM]									[ng kg^{-1} DM]					
Sludge 1	125.8	<0.01	<0.01	0.38	0.16	0.07	0.11	0.09	0.11	2105.8	6122.5	<LOD	<LOD	1935.4	<LOD
Sludge 2	153.1	<0.01	0.02	0.42	0.19	0.08	0.13	0.11	0.14	546.3	697.1	<LOD	<LOD	254.4	<LOD
Sludge 3	80.9	<0.01	0.01	0.32	0.11	< 0.05	0.09	0.07	0.07	872.7	12766.7	<LOD	<LOD	347.8	<LOD
Cryst 1	< 85.1	< 0.02	< 0.02	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	< 0.09	0.72	11.7	<LOD	<LOD	1.8	<LOD
Cryst 2	< 71.3	< 0.01	< 0.01	1.10	0.44	0.20	0.34	0.24	0.24	55.6	15.7	<LOD	<LOD	2.7	<LOD
Cryst 4	< 78.1	< 0.02	< 0.02	0.13	< 0.11	< 0.11	< 0.11	< 0.11	< 0.11	176.3	168.5	<LOD	<LOD	13.2	<LOD

The concentrations of AOX are higher for sludge 1 and 2 than for sludge 3. For the cryst products the concentrations were below the detection limit. The concentrations of PFTs were very low for all six products. The concentrations of the PAHs were in all cases the highest for cryst 2. The antibiotic Sulfamethoxazol, the herbicide Mecoprop and estrogen Estron were below the limit of detection (LOD). The concentrations of the pharmaceuticals Carbamazepine and Diclofenac and of the sequestrant Benzotriazole were higher in the sludges than in the cryst products, which is not surprising since pharmaceuticals are by purpose mostly polar and therefore hydrophilic compounds posing concerns for the WWTP effluents and not for the sludge solids. In all cases sludge 2 had the lowest amounts compared to sludge 1 and 3.

The concentrations of polychlorinated dibenzodioxins and -furans (PCDD/Fs) are presented in Table 5.

Table 5: PCDDs, PCDFs (with toxicity equivalents) in sludges and cryst products analyzed in the P-REX project

Product	Polychlorinated dibenzodioxins (PCDD)							Polychlorinated dibenzofurans (PCDF)										Tox.eq.
	2,3,7,8-TCDD	**1,2,3,7,8-PeCDD**	**1,2,3,4,7,8-HxCDD**	**1,2,3,6,7,8-HxCDD**	**1,2,3,7,8,9-HxCDD**	**1,2,3,4,6,7,8-HpCDD**	**OCDD**	**2,3,7,8-TCDF**	**1,2,3,7,8-PeCDF**	**2,3,4,7,8-PeCDF**	**1,2,3,4,7,8-HxCDF**	**1,2,3,6,7,8-HxCDF**	**1,2,3,7,8,9-HxCDF**	**2,3,4,6,7,8-HxCDF**	**1,2,3,4,6,7,8-HpCDF**	**1,2,3,4,7,8,9-HpCDF**	**OCDF**	**WHO-PCDD/F-TEQ incl. detection limit**
	[ng kg^{-1} DM]																	
Sludge 1	<0.56	<0.56	<1.11	2.75	<1.11	108.13	866.37	1.50	1.01	1.67	<1.11	1.17	1.21	3.17	30.51	2.43	76.84	4.66
Sludge 2	<0.55	<0.55	<1.10	2.64	1.76	92.18	726.87	2.20	1.95	2.34	2.63	2.84	<1.10	5.76	50.99	3.51	117.84	5.58
Sludge 3	<0.53	<0.53	<1.06	<1.06	<1.06	93.53	954.40	1.46	<0.53	1.01	<1.06	<1.06	<1.06	<1.06	9.52	<2.12	41.57	3.62
Cryst 1	<0.34	<0.43	<0.85	<0.85	<0.85	<3.41	<17.00	0.82	<0.43	<0.43	<0.85	<0.85	<0.85	<0.85	<3.41	<3.41	<17.0	1.7
Cryst 2	<0.29	<0.36	<0.71	<0.71	<0.71	10.60	71.4	0.93	<0.36	0.37	<0.71	<0.71	<0.71	<0.71	<2.85	<2.85	<14.3	1.54
Cryst 4	0.38	0.50	<0.78	<0.78	<0.78	19.30	191.0	1.19	<0.39	0.41	3.57	1.22	<0.78	1.58	3.4	<3.12	<15.6	2.39

The concentrations of PCDDs and PCDFs are in almost all cases much higher in the sludges than in the cryst products. In contrast to the results of the heavy metal analytics sludge 3 shows in most cases the lowest concentrations of PCDDs and PCDFs compared to sludge 1 and 2.
The concentrations of polychlorinated biphenyls (PCBs) are shown in Table 6.

Table 6: Contents of PCBs (with toxicity equivalents for dl-PCBs) in the sludges and cryst products analyzed in the P-REX project

Product	Dioxin-like polychlorinated biphenyls (dl-PCBs)												Tox.eq.		Polychlorinated biphenyls (PCBs)					
	PCB 77	PCB 81	PCB 105	PCB 114	PCB 118	PCB 123	PCB 126	PCB 156	PCB 157	PCB 167	PCB 169	PCB 189	WHO-dl-PCBB-TEQ incl. DL	Sum WHO-PCDD/F-TEQ + dl-PCB-TEQ	PCB 28	PCB 52	PCB 101	PCB 138	PCB 153	PCB 180
	[ng kg^{-1} DM]														[mg kg^{-1} DM]					
Sludge 1	129.2	<22.3	674	54.1	2523	64.5	16.5	787	107.1	368	<3.3	129.2	1.90	6.56	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sludge 2	189.4	<22.0	887	74.0	3046	72.6	3.9	990	116.7	417	<3.3	160.8	0.69	6.28	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Sludge 3	58.6	<21.2	286	32.1	1073	<15.9	4.7	317	56.5	117	<3.2	41.7	0.64	4.25	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cryst 1	<34.1	<34.1	119	<25.5	1379	<25.5	6.8	318	<25.5	166	<5.1	<51.1	0.90	2.61	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cryst 2	<28.5	<28.5	166	<21.4	880	<21.4	5.6	460	42.1	208	<4.3	92.3	0.76	2.30	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cryst 4	56.6	<31.2	252	<23.4	1329	<23.4	<4.7	715	46.5	267	<4.7	52.4	0.70	3.11	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02

The results of the PCB analysis were comparable to those of the PCDD/Fs: in most cases the concentrations were lower in the cryst products than in the sludges (except PCB 118 and 156). Sludge 3 contains lower concentrations than sludge 1 and 2.

4.2 Eco-toxicity tests

Six biological eco-toxicity tests were selected to assess the toxicity of three sewage sludges and nine P products and recyclates. Two of the tests were aquatic and four were soil tests:

1) Earthworm Avoidance Test (ISO 17512-1:2008)
2) Phytotoxicity Test (ISO 11269-2:2012)
3) N-transformation Test (OECD Guideline for the testing of chemicals Nr. 217)
4) C-transformation Test (OECD Guideline for the testing of chemicals Nr. 216)
5) Lemna Growth Inhibition Test (ISO 20079:2005)
6) Gammarus Acute Toxicity Test (EPA, 1996)

For the two aquatic tests the maximum concentration was chosen too low for the cryst and therm products so that no negative effects occurred and no statement about the toxicity of the products and about the sensitivity of the tests can be given. The other four tests were soil tests. The results of the C- and N-transformation test could not be evaluated as the validity criteria were not met (N-transformation) or mainly also no inhibiting/positive effects occurred even at very high concentrations of the tested substances in soil (10 %). Only two tests lead to evaluable results: the earthworm avoidance test and the phytotoxicity test. For some tests more than one test criteria /test endpoint is available, so for the phytotoxicity test the emergence and the biomass were evaluated. All evaluable results are shown in Table 7.

Table 7: EC_{50} values of the conducted eco-toxicity tests for all sludges and P products assessed in the P-REX project

Product	**EC_{50} values for soil tests**			**EC_{50} values for aquatic tests**	
	***Eisenia fetida* – Avoidance behavior**	***Brassica rapa* – Emergence**	***Brassica rapa* – dry matter per plant**	***Lemna minor* – growth inhibition**	***Gammarus fossarum* – mortality**
	[% FM in soil]			**[Vol-% FM in water]**	
Sludge 1	1.7	5.9	5.7	5.0	2.1
Sludge 2	5.3	3.7	3.4	2.9	0.6
Sludge 3	5.3	1.8	5.7	3.4	0.6
Cryst 1	0.2	6.7	8.6	>1	>1
Cryst 2	0.7	1.1	>10	>1	>1
Cryst 4	0.1	0.4	3.8	>1	>1
Therm 1	0.9	>10	>10	>1	>1
Therm 2	6.7	>10	>10	>1	>1
Therm 3	1.7	0.1	>6	>1	>1
Therm 4	-	>10	>10	>1	>1
Therm 5	1.0	6.3	>10	>1	>1
TSP	0.3	0.5	3.1	0.20	0.03

Regarding the EC_{50} values only the sensitivities of the different tests against the products can be compared. But for an evaluation of the toxicity of the products the P-concentration or the expected application amount (predicted environmental concentration, PEC) must be considered. The PEC and the predicted no effect concentrations (PNEC) and furthermore their ratio (PEC/PNEC) are calculated in Table 8. If the PEC/PNEC ratio is >1 the evaluation or the tests must be refined or the substance is evaluated with "of concern".

Table 8: Calculation of PEC/PNEC ratio for all sludges and P products assessed in the P-REX project

Product	P_2O_5-content	Amount of fertilizer containing 60 kg P_2O_5	Resulting fertilizer-concentration in soil (PEC)*	Lowest EC/LC_{50} value from soil tox-tests	PNEC (calculated by assessment factor 1000)	PEC/ PNEC ratio
	[% i. FM]	[kg FM]	[%]	[%]	[%]	-
Sludge 1	0.22	27,272.73	0.802	1.7	0.0017	472
Sludge 2	2.39	2,510.46	0.074	3.4	0.0034	22
Sludge 3	2.69	2,230.48	0.066	1.8	0.0018	37
Cryst 1	30.51	196.66	0.006	0.2	0.0002	30
Cryst 2	26.60	225.56	0.007	0.7	0.0007	10
Cryst 4	23.00	260.87	0.008	0.1	0.0001	80
Therm 1	15.60	384.62	0.011	0.9	0.0009	12
Therm 2	13.90	431.66	0.012	6.7	0.0067	2
Therm 3	12.90	465.12	0.014	0.1	0.0001	140
Therm 4	9.46	634.25	0.019	>10	0.0100	2
Therm 5	27.60	217.39	0.006	1.0	0.0010	6
TSP	48.50	123.71	0.004	0.3	0.0003	13

General problems occurred when trying to evaluate the test results by risk assessment as for calculating the PNEC for short term tests an assessment factor of 1000 is recommended by the Technical Guidance Document on Risk Assessment (IHCP, 2003). This leads to high PEC/PNEC values of >1, so validity of toxicity tests results is low. Following this approach, risk cannot be excluded. This is the consequence of common approaches for dealing with uncertainties in risk assessment, not a consequence of toxicity test results

The evaluation of the test results indicates that sludge 1 is most toxic with a PEC/PNEC ratio of 472. The other two sludges showed much lower values of 22 and 37. The cryst products showed values between 10 and 80 with cryst 4 with the highest. The therm products had very low values between 2 and 12 except therm 3 which had a high PEC/PNEC ratio of 140. TSP had a low PEC/PNEC ratio of 13 because of the low PEC due to the high P_2O_5 content. The reason for the high toxicity of therm 3 might be the high chromium and nickel content of 311 and 343 mg/kg DM, respectively. These high heavy metal concentrations are caused by the Cr-Ni-based alloy in the kiln used in the experiments, which is not relevant for full-scale facilities. The higher toxicity could also be confirmed by the results of the C- and N-transformation tests (which were not evaluated). This shows also that the tests make sense but are not very sensitive. Of course solubility of the matrix has an important impact on these results, since dissolved materials (ions) are much more mobile than inert materials.

The very high ratio observed for sludge 1 must be discussed as there are no noticeable results within the chemical analytics compared with sludge 2. The low EC_{50} value results from a negative result in the Earthworm Avoidance Test. The sludge was very liquid (only 2.4 % dry matter) and had a high ammonia content. Earthworms react very sensitive on ammonia. This shows that the evaluation method can be influenced very easily by outliners as for the calculation of the PEC/PNEC ratio only the smallest EC_{50} value is used also if diverse test results are available.

5 Conclusions

A summary of all results is given in Table 9. It has to be considered that sludge 1-3 are not real technical recovery products but relevant for phosphorous recycling in agriculture. Furthermore therm 1 and TSP are no recovery products but were used as a kind of references.

Table 9: Summary of the results of the pot test, the chemical analyses (heavy metals and organic contaminants) and the eco-toxicity tests conducted in the P-REX project; + means good results, +/- means moderate result and – means negative result

Product	P-availability	Toxicity		
	pot test	**heavy metal contamination**	**organic contaminants**	**eco-toxicity-tests**
Sludge 1	+/-	+	-	-
Sludge 2	+	-	-	+/-
Sludge 3	+/-	+ (but high Fe-content)	+/-	+/-
Cryst 1	+	+	+	+/-
Cryst 2	+	+	+	+/-
Cryst 4	+	+	+	+/-
Therm 1	-	-	n.a. (+)	+/-
Therm 2	-	+ (but high Fe-content)	n.a. (+)	+
Therm 3	+	(-)*	n.a. (+)	-
Therm 4	-	+	n.a. (+)	+
Therm 5	+	+	n.a. (+)	+
TSP	+	+	n.a.	+/-

n.a. = not analyzed (because ash products are thermally treated and therefore should not contain organic contaminants)

* The increased mass fractions of chromium and nickel resulted from transfer of the Ni-base alloy tube material of the trail rotary kiln and are not representative for an industrial process

The sludge products show inhomogeneous results within the four categories. The P-bio-availability determined with the pot test was good to moderate. But sludge 1 and 2 had both two negative results in the toxicity evaluation. Only sludge 3 had no negative result.

The three struvite products had positive results in the pot tests and in the chemical analyses (heavy metals and organic contaminants). The results of the eco-toxicity tests were moderate with cryst 2 showing the best results and cryst 4 with the worst result.

The ash products also had very inhomogeneous results. Good results within the toxicity assessment showed therm 2, 4 and 5. But therm 2 and 4 had negative results for the P availability. Therm 3 was the other way round: good results for P availability but negative results in the heavy metal analysis and likely due to this also a negative result in the eco-toxicity tests. But as mentioned above the high chromium and nickel concentrations are due to the pilot scale production process and would not be a problem in full-scale production. Probably this product would have had good results within the toxicity tests with lower heavy metal concentrations, but this must be tested in future. So of the tested ash products therm 5 was the only product that reached positive results in all four categories.

As a conclusion therm 5 and cryst 2 and 1 showed the best results regarding P-availability and toxicity of the product.

For the determination of the Best Available Technique also costs of production and application (in agriculture) must be considered. Under this aspect it must be said, that only for the struvites representative data and quantities are available to date. Sewage sludge is a very heterogeneous matrix and ash processing products mainly depend on the sludge fed into the incinerator facilities. Also reliable data on decontamination rates for these processes are rare. The risk assessment done in the P-REX project clearly indicates and allows to conclude, that technical P recovery and recycling can provide advantages regarding P bio-availability and risk reduction compared to sludge application on land.

It can further be concluded, that dewatering (solid-liquid-separation) is an effective measure to reduce contamination of the solids by pharmaceuticals. Since pharmaceuticals are by purpose mostly polar organic compounds and therefore hydrophilic, elevated concentrations are measurable in aqueous phases (wastewater and sludge liquor) and not in the sludge solids. This is also the reason, why WWTPs have to consider the installation of advanced so-called tertiary treatment steps to reduce the pharmaceutical concentration in their effluents to meet the discharge limits. Here the Water Framework Directive and it national implementations by Member States provides the regulative framework to be met.

Further information can be found in this literature:

- Deliverable 7.1 – Guidance document for “safe sludge” monitoring (www.p-rex.eu)
- Deliverable 9.1 – Quantitative risk assessment of potential hazards for humans and the environment: quantification of potential hazards resulting from agricultural use of the manufactured fertilizers (www.p-rex.eu)

6 References

EPA U.S. (1996): Ecological Effects Test Guidelines. Gammarid Acute Toxicity Test OPPTS 850.1020.

IHCP (2003): Technical Guidance Document on Risk Assessment – Part II: Environmental Risk Assessment. European Union – Institute for Health and Consumer Protection.

ISO (2005): BS ISO 20079: Water quality. Determination of the toxic effect of water constituents and waste water on duckweed (*Lemna minor*). Duckweed growth inhibition test. Geneva.

ISO (2008): BS ISO 17512-1: Soil quality. Avoidance test for determining the quality of soils and effects of chemicals on behavior. Part 1: Test with earthworms (*Eisenia fetida* and *Eisenia andrei*). Geneva.

ISO (2012): ISO 11269-2: Soil quality – Determination of the effects of pollutants on soil flora – Part 2: Effects of chemicals on the emergence and growth of higher plants.

OECD Guidelines for the testing of chemicals Nr. 216: Nitrogen Transformation of Soil Microorganisms.

OECD Guidelines for the testing of chemicals Nr. 217: Carbon Transformation of Soil Microorganisms