Sustainable use of phosphorus

Capturing the philosopher’s stone

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Chapter 2

Struvite: Towards a Circular Phosphorus Economy

Correspondence on Chen et al. Application of Struvite Alters the Antibiotic Resistome in Soil, Rhizosphere, and Phyllosphere.

Abstract: Recent work published by Chen et al. has been considered by the European Commission for guidance concerning the revised fertilizer regulation regarding the inclusion of the recovered phosphorus product, struvite. Chen et al. found that various antibiotics were detected in struvite, however, they did not describe their struvite recovery method and used a highly contaminated source. While other comparable studies have shown that organic contaminants are typically not present in struvite after precipitation. This chapter shows that since most struvite is recovered from municipal sources, with significantly lower levels of antibiotics than what is found in swine wastewater that Chen et al. investigated, significantly lower levels of antibiotics are detected in currently recovered struvite. Therefore, the use of the research of Chen et al. to guide policy for recovered phosphate products is inappropriate and might unnecessarily hamper the use of this renewable resource.

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2.1 Introduction

Phosphate fertilizers are essential to grow crops that are needed to feed all human beings on our planet. However, the primary fossil resource phosphate rock is finite and its current linear use is creating one of the biggest global environmental concerns (eutrophication), which demands immediate action.[1] To stay within the planetary boundaries and target the United Nations' Sustainable Development Goals, the development and implementation of phosphorus recovery and recycling techniques is essential in order to realize a circular phosphorus economy.[1,2] A promising way to recover phosphates is carried out by the precipitation of struvite ($MgNH_4PO_4{\cdot}6H_2O$) from phosphorus and nitrogen rich waste streams, such as manure, municipal wastewater and wastewater from food production, simply by the addition of magnesium salts (typically $MgCl_2$). A variety of struvite production processes are available that, also depending on the feedstocks used and the process conditions applied (e.g., washing and filtration steps, granule size and the amount of $MgCl_2$ added), afford struvite with differing quality.[3,4] For example, the P_2O_5-content of struvite precipitated with several technologies from municipal wastewater can range from 14.7 to 30.5% (Table 1). This means that just like phosphate rock deposits that contain impurities (e.g., fluorine, cadmium, uranium, radium, mercury, lead, chromium, zinc, iron, copper, and rare-earth elements), also secondary phosphates recovered from urban mines have variable quality. The presence of undesired substances (e.g., pharmaceuticals, pathogens and other micro-pollutants) needs to be considered before reuse becomes viable.[5]

Table 1. Struvite currently produced by various techniques, incl. elemental composition.

Struvite	**% P_2O_5**	**% N**	**% MgO**	**Source**
$MgNH_4PO_4\cdot 6H_2O$ (theoretical)	28.9	5.7	16.4	
Struvite obtained by crystallization				
PHOSNIX[6]	30.5	5.3	19.1	Liquor
AirPrex[6],[a]	19.8–22.9	3.0–5.0	10.2	Liquor
Pearl[6],[b]	28	5	16.7–17	Liquor
Struvia[6]	28–29	4.5–5.5	15.8–16.8	Liquor
NuReSys[6]	26.5–27.8	5.1–5.5	15.3–23.4[c]	Liquor
ANPHOS[6]	14.7	2.0	7.6	Liquor
REPHOS[7]	24.9	4.7	13.6	Liquor
Struvite obtained by leaching				
Gifhorn[6]	25.2–36.7	0.18	3.1–14.3	Sludge
Stuttgart[6]	25.9–59.6	1.2–5.0	10.9–13.3	Sludge
PHOXAN[8]	26.8	5.1	-	Sludge
Leachphos[6]	20–40	-	-	Ash

a. Related to WWTP influent; b. Moisture content of 14.9%; c. Formation of magnesium phosphate phases other than struvite

News Alert: European Commission

Last year, Chen et al. published a research article in Environmental Science & Technology entitled "Application of Struvite Alters the Antibiotic Resistome in Soil, Rhizosphere, and Phyllosphere",[9] which contained, in our view, some striking generalizations. The authors conclude that the application of struvite can facilitate the spread of antibiotic resistance via the human food chain. Since the EU included phosphates on its critical raw materials list and desires the local recovery and recycling of phosphates, these conclusions created considerable attention. On the 19th of April 2018, the European Commission published a News Alert entitled "Antibiotic resistance in struvite fertilizer from wastewater could enter the food chain",[10] where the European Commission states that the findings by Chen et al. may be relevant for the ongoing revision of the EU Fertilizers Regulation. This revision will have a significant impact, since it will also define under what circumstances struvite can be used as a component material for CE (circular economy) marked fertilizers. We feel that the conclusions of this specific case study by Chen et al. warrant a critical analysis before being used as a guideline.

2.2 Results & Discussion

A closer look at the article by Chen et al. shows that they used struvite produced from swine wastewater, which, not surprisingly, contains considerable quantities of antibiotics such as four types of tetracycline antibiotics (360.1–742.07 mg/kg struvite; Table 2). This is striking since related studies show that the incorporation of impurities in the struvite formed is much lower. For example, Ye et al.[11] analyzed struvite precipitated from swine wastewater, but in their case this resulted in much lower concentration levels of several antibiotics (see Table 3). This raises questions on the methodology used by Chen et al. and, in particular, the process they applied to produce struvite, which unfortunately is not described in their research article.

Analysis of pharmaceuticals in different influents

Both municipal and swine wastewater contain significant amounts of antibiotics. The concentration of most of the selected antibiotics are on average significantly higher in swine wastewater than in communal wastewater, especially the concentrations of doxycycline and sulfamethazine (see Table 2). The concentration is dependent on the amount of antibiotics in the feed addition of the swines. Antibiotics are poorly taken up by swines, which results that 70-90% of the used antibiotics end up in the wastewater in unchanged form or as metabolites.[12] The amounts of antibiotics analysed in swine wastewater differ among the sampling locations and depends on the antibiotic intake of the pigs.

Table 2. Concentrations of selected antibiotics in communal wastewater influent in WWTP samples and in swine wastewater influent samples from multiple locations.

Compound	**Municipal wastewater influent μg/L** [13]	**Swine wastewater influent μg/L** [12]
Tetracycline (TC)	Wisconsin, U.S., 48[13] Sweden, 0.16[14] Singapore, 50[15] Hunan Province, China, ND[16] Mexico, <0.01–0.1[17]	Jiangsu, China, ND–84.30 Beijing, China, 126.0–388.70 South China, 1.45–10.59
Oxytetracycline (OTC)	Wisconsin, U.S., 47[13] Singapore, 75[15] Hunan Province, China, 50[16] Mexico, 0.04–0.13[17]	Beijing, China, 6.18–25.36 South China, 18.70 Shandong, China, 8.05 East China, 23.80 Taiwan, ND–5.33
Chlortetracycline (CTC)	Wisconsin, U.S., 0.31[13] Singapore, 7.5[15] Hunan Province, China, ND[16]	East China, 13.70 Shandong, China, 8.05 Beijing, China, 2.65–32.67 Germany, 4.10 Taiwan, ND–4.32
Doxycycline (DC)	Wisconsin, U.S., 10[13] Hunan Province, China, ND[16]	East China, 685.60
Sulfadiazine (SDZ)	Wisconsin, NA[13] Hunan Province, China, 39[16] Mexico, 0.22–1.2[17]	East China, 98.90
Sulfamethazine (SMZ)	Wisconsin, U.S., 0.30[13] Singapore, 0.3[15] Hunan Province, China, 22[16]	Beijing, China, 0.44–324.40 Jiangsu, China, ND–63.60 Shandong, China, 14.56 Bayer, Germany, 18.50–19.20 Germany, 49.50
Ciprofloxacin (CIP)	Wisconsin, U.S., 0.31[13] Sweden, 0.39[14] Singapore, 5.0[15] Hunan Province, China, ND[16] Mexico, 0.48–1.9[17]	0.01[18]
Enrofloxacin (ENR)	Wisconsin, U.S., 0.25[13] Hunan Province, China, ND[16]	0.01[18]

NA. Not analysed; ND. Not detected.

Struvite quality from different feedstocks

Interestingly, struvite produced from municipal wastewater, currently the main source for struvite production (75%, the remaining 25% comes from industrial wastewater, mainly food processing),[19] contains hardly any of these impurities and the concentration of all measured substances are below any health or environmental limits calculated with the acceptable daily intake limits (Table 3). The sheer amount of antibiotics in the recovered struvite in the Chen study could well have affected the antibiotic resistance in the soil to which it was applied, but this is not the case with the analysed struvite by Ye et al. and from municipal wastewater. Therefore, the conclusion "struvite as an organic fertilizer can facilitate the spread of antibiotic resistance into human food chain" should not be applied to all types of struvite.

Analysis of pharmaceuticals present in struvite

We have compared the amounts of antibiotics in the struvite used in the research of Chen et al.[4] with struvite produced from swine wastewater described in the research of Ye et al.[5] and struvite produced at a WWTP from sludge water of municipal wastewater.[6] The comparison in Table 3 clearly illustrates the differences in magnitude concerning the amount of antibiotics present in the three types of struvite. The struvite analyzed by Chen et al. contains significantly higher levels of all the analysed antibiotics. Especially the difference between the analysis of the struvite of Chen et al. and Ye et coworkers, both from swine wastewater, is an interesting observation. The difference is almost for all antibiotics more than 100 fold higher in the struvite of Chen et al. do not mention in their paper how they produced the used struvite.

Only cyprofloxacin was detected just above the detection limit, in the analysis of antibiotics in struvite from the aqueous phase of municipal wastewater, more specifically 0.009 mg/kg, 567 times lower than the amount found in the struvite used by Chen et al., see Table 3. The difference in quality is even more apparent in the case of doxycycline: struvite used by Chen et al. contains 742 mg/kg, whereas the amount of doxycycline in the struvite produced from municipal wastewater was found to be below the detection limit (<0.005 mg/kg), therefore at least 148,000 times lower. The only micro-pollutants above the detection limit in the analysis of the struvite from the aqueous phase are triclosan (0.013 mg/kg), caffeine (0.014 mg/kg), carvedilol (0.007 mg/kg) and carbamazepine (0.006 mg/kg).

Table 3. Comparison of different types of struvite and the UBM Norm.

	Struvite Chen et al. from swine wastewater (mg/kg)[9]	Struvite Ye et al. from swine wastewater by using a fluidized bed (mg/kg)[11]	AirPrex struvite from municipal wastewater (mg/kg)[a]	Crystal Green struvite from municipal wastewater (mg/kg)[b]	Struvite from municipal WWTP Amsterdam (mg/kg)[21]	Struvite from municipal WWTP Echten (mg/kg)[21]	Struvite from municipal WWTP Leuven (mg/kg)[21]	Struvite from municipal WWTP Land van Cuijk (mg/kg)[21]	Theoretical struvite	Norm UBM
Total Carbon	35.39		1.63%						0	
Total Nitrogen	43.28		5.99%		21.2 g N/kg	30.0 g N/kg	20.0 g N/kg	55.4 g N/kg	57.1 g N/kg	
Cr	10.01		8		10.64	16.02	5.74	5.0	0	1875
Cu	71.55		48		20.62	7.01	4.02	<2.12	0	1875
Pb	1.47		11		17.96	2.32	1.43	<1	0	2500
Zn	521.50		90		71.85	21.05	23.52	3.0	0	7500
Tetracycline	415.21	0.3-2	<0.005	<0.01						
Oxytetracycline	360.1	0.5-2	<0.005	<0.01						
Chlorotetracycline	420.32	0.2-0.7	-	<0.01						
Doxycycline	742.07	0.3-1.9	<0.005	<0.01						
Sulfadiazine	13.63	NA	<0.005	<0.01						
Sulfamethazine	1.86	NA	<0.005	<0.01						
Ciprofloxacin	5.10	0.1-1.1	0.009	<0.01						
Enrofloxacin	59.10	0-0.2	<0.005	<0.01						

a: One sample. Detection level is <0.005 mg/kg; NA: Not analysed

b: Four samples. Detection limit of 0.01 mg/kg; <0.01mg/kg means not detected.

2.3 Conclusion

Mined phosphate rock, the primary source of phosphorus-based fertilizers, has its challenges due to toxic and radioactive elements, such as cadmium and uranium, that naturally occur in phosphate rock deposits and can be transferred into fertilizers and further accumulate into the soil. Similarly, recovered, secondary phosphates have their challenges too concerning pollutants from their (waste) sources. Notwithstanding, the use of secondary phosphates is essential for obtaining a circular phosphorus economy. Therefore, it is essential that the quality of the renewable fertilizers should be guaranteed and the risk minimized. Currently, organic fertilizers are used on large scale, including the spreading of sewage sludge and manure on arable land.[20] These phosphate sources are undoubtedly less clean and safe to use than the majority of recovered phosphates in struvite. This clearly unveils the need for standardized analytical methods and quality assurance (e.g., ISO standardization) as well as appropriate policy measures for struvite and all other recovered phosphates, which will bridge the gap between phosphate recovery and recycling enabling the safe and sustainable (re)use of phosphorus.

2.4 References

[1] H. Ohtake, S. Tsuneda, *Phosphorus Recovery and Recycling*, Springer, Singapore, **2018**.

[2] W. Steffen, K. Richardson, J. Rockström, S. E. Cornell, I. Fetzer, E. M. Bennett, R. Biggs, S. R. Carpenter, W. De Vries, C. A. De Wit, et al., *Science (80-.).* **2015**, *347*, DOI 10.1126/science.1259855.

[3] M. A. de Boer, M. Hammerton, J. C. Slootweg, *Water Res.* **2018**, *133*, 19–26.

[4] N. Ahmed, S. Shim, S. Won, C. Ra, *L. Degrad. Dev.* **2018**, DOI 10.1002/ldr.3010.

[5] P. Kemacheevakul, S. Chuangchote, S. Otani, T. Matsuda, Y. Shimizu, *Water Sci. Technol.* **2015**, *72*, 1102.

[6] P-REX, "Main P-REX deliverables," DOI 10.5281/ZENODO.242550can be found under https://zenodo.org/record/242550#.WzEFPKczZdj, **2017**.

[7] M. Lebek, S. Lohmar, *Remondis Aqua* **2013**.

[8] L. Egle, H. Rechberger, M. Zessner, *Resour. Conserv. Recycl.* **2015**, *105*, 325–346.

[9] Q. L. Chen, X. L. An, Y. G. Zhu, J. Q. Su, M. R. Gillings, Z. L. Ye, L. Cui, *Environ. Sci. Technol.* **2017**, *51*, 8149–8157.

[10] European Commission, *Sci. Environ. Policy* **2018**.

[11] Z.-L. Ye, Y. Deng, Y. Lou, X. Ye, S. Chen, Z.-L. Ye, Y. Deng, Y. Lou, X. Ye, S. Chen, *Front. Environ. Sci. Eng.* **2018**, *12*, 7.

[12] D. L. Cheng, H. H. Ngo, W. S. Guo, Y. W. Liu, J. L. Zhou, S. W. Chang, D. D. Nguyen, X. T. Bui, X. B. Zhang, *Sci. Total Environ.* **2018**, *621*, 1664–1682.

[13] K. G. Karthikeyan, M. T. Meyer, *Sci. Total Environ.* **2006**, *361*, 196–207.

[14] M. Östman, R. H. Lindberg, J. Fick, E. Björn, M. Tysklind, *Water Res.* **2017**, *115*, 318–328.

[15] N. H. Tran, H. Chen, M. Reinhard, F. Mao, K. Y.-H. Gin, *Water Res.* **2016**, *104*, 461–472.

[16] H. Lin, H. Li, L. Chen, L. Li, L. Yin, H. Lee, Z. Yang, *Ecotoxicol. Environ. Saf.* **2018**, *147*, 530–536.

[17] E. B. Estrada-Arriaga, J. E. Cortés-Muñoz, A. González-Herrera, C. G. Calderón-Mólgora, M. de Lourdes Rivera-Huerta, E. Ramírez-Camperos, L. Montellano-Palacios, S. L. Gelover-Santiago, S. Pérez-Castrejón, L. Cardoso-Vigueros, et al., *Sci. Total Environ.* **2016**, *571*, 1172–1182.

[18] L. Tong, P. Li, Y. Wang, K. Zhu, *Chemosphere* **2009**, *74*, 1090–1097.

[19] Based on our analysis there are currently 82 struvite precipitator installations operational worldwide, of which 61 are located at municipal wastewater treatment plants and 21 at industrial wastewater treatment plants, with a total production of 32.000 tonne struvite/year.

[20] For more information on the spread of antibiotic resistance genes to the soils with the use of manure, see: a) Xie, W. Y.; Shen, Q.; Zhao, F. J. Antibiotics and Antibiotic Resistance from Animal Manures to Soil: A Review. Eur. J. Soil Sci. 2018, 69 (1), 181–195; b) Heuer, H.; Schmitt, H.; Smalla, K. Antibiotic Resistance Gene Spread Due to Manure Application on Agricultural Fields. Curr. Opin. Microbiol. 2011, 14 (3), 236–243; For more information on the spread of antibiotic resistance genes to the soils with the use of manure and biosolids, see: c) Munir, M.; Xagoraraki, I. Levels of Antibiotic Resistance Genes in Manure, Biosolids, and Fertilized Soil. J. Environ. Qual. 2011, 40 (1), 248.

[21] STOWA, *Verkenning van de Kwaliteit van Struviet Uit de Communale Afvalwaterketen*, **2015**.