1. Phosphorus Concentrations in Environmental Samples

1.10 Organic and mineral fertilizers

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1.10.1 Organic fertilizers

By harvesting crops, nutrients are removed from soil. An average harvest of 8 t ha^{-1} of wheat removed 37 kg P, 124 kg K and 180 kg N from soil (LFL 2006 cited in Killiches 2013). Usage of fertilizers is necessary to compensate nutrient losses and maintain or increase soil fertility (soil fertility, German term: *Bodenfruchtbarkeit*).

Organic farm manure includes slurry (1-3 % dry matter, Schubert 2011), liquid manure (> 3 % solid substance), manure, compost, digestates from biogas plants and sewage sludge. Nutrients and therefore TP concentrations vary significantly and are especially affected by animal species especially in slurry, liquid manure and manure (different digestive system: ruminant, nonruminant with different feed efficiency), their nutrition and also the farm (Sharpley & Moyer 2000) or the feed processing as well as the water content (Tab. 1.10-1). TP concentrations in manure are additionally affected by litter (different plants/wood chips). Parent material and period of rotting process affect TP concentrations significantly. The degree of rotting explains the biological stability (maturation) of the compost (degree I = raw material of compost, II-III fresh compost, IV-V = finished compost). An increase in TP concentration in more mature compost can be explained by mass loss of non-P compounds (e.g. loss of volatile substances, CO_2-breathing) and following accumulation of P during rotting. In sewage sludge, besides parent material (waste water to be purified) the sludge type (depending on the period in waste water treatment) also affects TP concentration. An overview on P yield in different sludges (period of water treatment) with various processes can be found in Kabbe et al. (2015).

Table 1.10-1 Dry matter (DM) concentration, TP concentration per volume and per DM (g kg^{-1}) in organic farm manures

Matrix	Origin	DM (%)	TP (g l^{-1})	TP (g kg DM^{-1})	Reference
Slurry (Jauche)	Cattle		0		Chamber of Agriculture Schleswig-Holstein
	Pig		0.4		
Liquid manure (Gülle)	Dairy	8		7.6	Vadas (2006)
		30		1.5-7.8	Verma & Penfold (2017)
	Cattle	< 9.5		7.4-8.9	Sharpley & Moyer (2000)
	Pig	6.3		47.4	Vadas (2006)
		11		22.9-39.3	Verma & Penfold
	Poultry	38		19.5-36.1	(2017)
Manure (Mist)	Dairy	39		8.4-19.9	Sharpley & Moyer
	Poultry	70		6.4-12.2	(2000)
Compost (Kompost)	Wood chips			0.2	Verma & Penfold
	Garden refuse			2.4	(2017)
	Degree of rotting III (40-50 °C)[1]			1.2-1.6	Scherer (2004)
	Degree of rotting V (20-30 °C)			2.7-2.9	
Digestate (Gärreste)	Means from Europe	5.7		16.6	Wilken et al. (2013)
	liquid phase	5.7	0.9		Wendland &
	solid phase	24.3	2.2		Lichti (2012)
Sewage slude (Klär-schlamm)	2001-2006			22.0-27.3	UBA (2013)

[1] garden and kitchen waste (20/80 %) of North Rhine-Westphalia (NRW)

1.10.2 Mineral fertilizers

Mineral fertilizers are made from rock phosphate (chapter 1.2). The ground material can be used directly or TP concentration can be increased by industrial chemical processing. This processing mostly increases the percentage of soluble water and thereby potentially plant available percentage of P in the product (Killiches 2013). Mineral fertilizers are more homogeneous than organic fertilizers, because no biological processes such as digestion in animals are involved.

For production of P fertilizers, rock phosphate is mixed with sulfuric acid, which react to phosphoric acid and gypsum ($CaSO_4$ x $2H_2O$). Phosphoric acid can be used in food and beverage industry or can be further processed to P fertilizer. Depending on the reaction partner, mixing and reactions with other compounds different P fertilizers such as diammonium phosphate (DAP), monoammonium phosphate (MAP) or triple superphosphate can be produced (table 1.10-2)

For production of superphosphates, insoluble calcium phosphate reacts with sulfuric acid to about 40 % water-soluble Ca dihydrogen phosphate and about 60 % water-insoluble Ca phosphate. The latter reacted with phosphoric acid to Ca dihydrogen phosphate for production of double superphosphate. For production of triple superphosphate, very pure phosphoric acid is used to increase P concentration in fertilizer, but the reaction and the molecular formula is the same. Only the TP concentrations of double and triple superphosphate products vary: in triple superphosphate the TP concentration is around 200 g TP kg^{-1} dry matter compared to double superphosphate with around 150 g TP kg^{-1} dry matter.

Thomas slag (Thomas phosphate) is a by-product in steel industry from phosphate containing pig iron. Nowadays, steel industry mainly uses phosphate-poor ores and hence the Thomas slag virtually disappeared from the marked (Dittrich und Klose 2008). Another mineral fertilizer is magnesium ammonium phosphate (or struvite or MAP), which can be produced from waste water (see chapter 1.5). TP concentration of mineral fertilizers is mostly expressed in % P_2O_5. This can be converted to TP concentrations (g TP kg^{-1} dry $matter^{-1}$) in the following way:
Molar masses of P and O are 30.97 and 15.999 g mol^{-1}, respectively, which means that the molar mass of P_2O_5 = (2 x 30.97) + (5 x 15.999) = 141.94 g mol^{-1}.P_2O_5 comprises 2 P atoms (2 x 30.97 = 61.94 g mol^{-1}), therefore, divide 141.94 g mol^{-1} by 61.94 g mol^{-1} to get the factor for converting P to P_2O_5: 2.29.

The reciprocal factor for converting P_2O_5 to P is then: 0.44. Note that both data (P_2O_5 and P) need to have the same unit. In case one data is given in %, the factor for converting % into g kg^{-1} is 10: multiply with 10 (% into g kg^{-1}) and vice versa divide by 10 (g kg^{-1} into %).
Therefore, the conversion factor from:
P_2O_5 in % to TP in g kg^{-1} is: 4.4
TP in g kg^{-1} to P_2O_5 in % is: 0.23

Table 1.10-2 Commercial Phosphorus fertilizers, their chemical compound with phosphorus (molecular formula), percentage (%) of P_2O_5

Acronym	Molecular formula	% of P_2O_5	TP g kg^{-1}	Reference
Rock phosphate	$Ca_5(F,Cl,OH)(PO_4)_3$	27-28	119-123	HELM-AG (chemistry marketing company) Gwosdz et al. 2006
		5-37[2]	22-163	
Diammonium phosphate	$(NH_4)_2HPO_4$	42	185	
Mono-ammonium-phosphate	$NH_4H_2PO_4$	48	211	
Superphosphate	$Ca(H_2PO_4)_2$ + 2 $CaSO_4 \cdot H_2O$	18-22	79-88	
Double superphosphate	$Ca(H_2PO_4)_2 \cdot H_2O$	35	154	wikipedia about double superphosphate
Triple superphosphate	$Ca(H_2PO_4)_2 \cdot H_2O$	43-46	189-202	HELM-AG (chemistry marketing company)
Mono-ammonium phosphate		20-46	88-202	
		7-20[2]	31-88	raiffeisen.com
Thomas slag	$Ca_3(PO_4)_2 \cdot (Ca_2SiO_4)$	15	66	wikipedia about Thomas slag
Thomas phosphate - potassium		7-14	31-63	raiffeisen.com, gartendialog.de
Complete fertilizer (NPK)		6-26	26-114	HELM-AG (chemistry marketing company)
Struvite	$(NH_4)Mg(PO_4) \cdot 6H_2O$	23	101	BWB: Berliner Pflanze

[2] water-soluble

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