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Research Article

Monitoring N : P Ratio and Cd, Cu, Pb, and Zn Contents in Different Types of Anaerobic Digestates: A Six-Year Study Case

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Depending on the quality of the input substrates, process parameters, and postfermentation treatments, digestates may contain a broad spectrum of potentially toxic elements. We suspected that these contents may vary on a broad scale even under seemingly stable process conditions at the biogas plant. Digestates from four biogas plants were therefore continuously analyzed for their contents of phosphorus, nitrogen, cadmium, copper, lead, and zinc over a period of six years. The input substrates varied between the plants (e.g., cattle and pig slurry and rye and maize silage), but were the same for each plant over the whole period. The N : P ratio of the digestates ranged from 2 to 24, with the digestate coming from cofermentation of pig slurry and energy crops ("DG Pig") having the widest range of N : P ratio over the years. Heavy metal loads of all digestates and during all evaluations did not exceed the limits set by European or German legislation, but as previously expected, showed a large variability especially if cattle or pig manure were used as substrates. Copper content of Cattle slurry before digestion was 897.7 mg kg^{-1} DM in one case, and zinc content of DG Pig reached 590.2 mg kg^{-1} DM also once during the investigation. As a result, we strongly recommend to monitor especially phosphorus, copper, and zinc contents in digestates very closely and in short intervals.

1. Introduction

In regions with intensive livestock production, there is often a surplus of plant nutrients when organic fertilizers exceed the nutrient requirements of the crops, leading to a discharge or to emission to the environment [1]. The focus often lies on the amount of nitrogen applied with liquid or solid manure [2], but the problem includes other nutrients as well. Phosphorus is of special importance because of the environmental problems it can cause, e.g., eutrophication of water bodies and algae bloom [2, 3]. The relative content of phosphorus in organic fertilizers is often much higher than the crops need [4]. In swine manure, for example, the N : P ratio ranges from 1 : 1 to 2 : 1, while the required N : P ratio of most crops is between 3 : 1 and 15 : 1. If these fertilizers are applied in an amount that satisfies the nitrogen demand of the crop, P is usually applied in excess [5, 6]. The majority of this phosphorus is rapidly adsorbed and then absorbed by soil particles [7]. Plant availability of P is, for example, reduced by complexation with iron and aluminum hydroxides in acidic soils or calcium in alkaline soils or by adsorption on external and internal surfaces of soil particles, especially clay [7, 8]. However, it is known that some organic fertilizers such as dairy manure improve plant availability of phosphorus through enhanced enzyme and soil microbial activities [9]. Since digestates usually also lead to an increase in soil microbial activity [10], they may likewise lead to an increase in phosphorus plant availability. And even if most of the phosphorus is not dissolved in the aqueous phase in the soil, erosion and run off of phosphorus bound to soil particles can still cause severe losses of phosphorus and thus negatively impact the surrounding environment [2]. This problem is not solved by anaerobic digestion in biogas plants: P may be lost during digestion due to leaching or retention via crystal deposition lignin, the reactor [11, 12], but on the other hand, P concentrations rise as carbon is lost from the substrate via methane production. Overall losses are reported to be somewhere between 10 and 36%, but are usually on the lower end of this range [5, 11, 13]. Digestates therefore contain, in most cases, almost as much P as the original substrate. While the ratio of organic to inorganic P does not change significantly during digestion, the fraction of dissolved P is mineralized and often becomes associated with suspended solids [14]. Water-extractable P is usually decreased as P crystallizes as struvite or as poorly soluble hydroxylapatite, but several studies have shown that the plant availability of the P in total is either not affected by the digestion process [15] or even increases after digestion [13, 16, 17]. Bachmann et al. [18], for example, reported that the proportion of readily soluble P fractions (H_2O-P, $NaHCO_3$-P) to total P was higher than 70% in digestates from two different biogas plants before and after solid-liquid separation. Other studies showed that plant availability of phosphorus in digested swine manure [19] and slurry [15, 20] is similar to that of their respective raw counterparts. This, however, reduces the risk of phosphorus losses only slightly if adequate fertilization practices are not performed (e.g., match application date and plant requirements, weather during application, and combination with inorganic fertilizers). Most digestates from agricultural biogas plants are applied in close proximity to the plant because of the high costs of transport of the hydrated material. This leads to a concentration of potentially problematic amounts of nutrients in the area around such plants because input substrates are often gathered from considerable distances [21].

Within the EU, there are increasing concerns about inevitably high phosphorus loads being applied to arable land with nitrogen-based organic fertilization and the environmental risks related to this [3, 22, 23]. Some countries such as Germany have recently adopted national laws setting limits for both nitrogen and phosphorus. According to these laws, fertilizer application is capped by whichever of these two nutrients reaches first the respective limit [24]. Regarding this idea of defining limits for several critical elements in organic fertilizers, the authors want to present phosphorus contents and N : P ratios of digestates from a range of biogas plants with different manure and/or plant-based substrates and with subsequent separation of digestates.

Apart from the nutrient contents, there are often also concerns about potentially toxic elements in digestates [25]. The contents of those differ significantly depending on the substrates. Especially biowastes can be contaminated with Cd, Co, Cr, Cu, Ni, Pb, and Zn [26], but digestates from purely agricultural substrates may also be the source of heavy metals [27, 28], especially if they contain great amounts of livestock manure [29, 30]. While some of these elements such as Ni, Cu, and Zn are needed for biological processes in plants and animals including humans, they still hold the toxic potential to disrupt critical physiological processes when they occur in excess [31]. Many plants are able to exclude bioavailable elements either from uptake into the roots or from further transport in other plant tissues. However, some plants accumulate potentially toxic elements in organs that are later harvested and used as a human food source or as fodder. Heavy metals and other toxic elements can thus enter the food web [31, 32]. Reaching humans, they can cause a wide variety of health problems, including gastrointestinal distress and diarrhea (Zn), kidney damage (Cd), headaches and neurological disorders (Pb, Cu), and carcinogenic effects (Cu) [33, 34]. The risk is highest if pig manure is used as substrate [35], whereas cattle manure is usually not thus contaminated [36].

The digestates in this study were analyzed twice a year over a period of six (in one case five) years and are also compared to the liquid cattle manure that serves as a substrate in one of the plants. Substrate composition was stable over the years for each plant, leading to a unique data set, since most comparable investigations analyze a high number of digestates, but this should be done only once (e.g., [14, 18, 37]). Based on previous experiences and reports from farmers, we assumed that the contents of phosphorus and certain potentially toxic elements would vary significantly not only between the different products but also for the same product between different sampling dates.

2. Material and Methods

Digestates from four biogas plants were analyzed twice a year (in late spring and early autumn) for N, P, Cd, Cu, Pb, and Zn contents over a period of five to six years. Average inputs and operating parameters of the biogas plants are given in Table 1.

Plant D uses liquid/solid separation of the digestate as subsequent treatment. Therefore, five products were obtained from these four plants. The cattle slurry that serves as substrate in plant A was analyzed over the same period of time and used as reference.

For each sampling, 1 m^3 of the respective digestate was drained from the plant. From this cubic meter, several random samples were taken with a dipper after thorough stirring and poured together to a mixed sample of approximately 1 l volume. For the solid digestate from plant D, 1-2 m^3 were put together by taking material from different points of the stack. From this material, a mixed sample was taken for the laboratory. Inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific, USA) was used to analyze phosphorus and heavy metals in the digestates. Nitrogen was measured with the Kjeldahl method. All analyzes were performed from fresh material with two repetitions. All values presented are a mean of these two analysis. Contents in dry matter are calculated from the fresh matter results and the determined content of dry matter.

The results were analyzed for significant differences using SPSS Statistics Desktop 20.0 for Windows (one-way

Table 1: Input material and operating parameters of the four biogas plants included in the study and given designations of the resulting digestates ("DG").

Plant	A	B	C	D
Input	53% cattle slurry 37% maize silage 5% grass silage 5% other remains	38% pig slurry 38% maize silage 14% millet silage 10% grass silage	50% maize silage 50% grass silage	25% Cattle slurry 25% Grass silage 19% Maize silage 16% Cattle manure 15% Rye and rye silage
Operating temperature	Mesophile	Mesophile	Thermophile	Mesophile
Retention time	70 days	60 days	50 days	80 days
Related products	"DG cattle" and "Cattle slurry"	"DG pig"	"DG renew"	"DG Mix liquid" and "DG Mix solid"

ANOVA after Levene's test for variance homogeneity followed by Scheffé's test (due to unequal sample sizes)), $p \leq 0.05$.

3. Results and Discussion

Total nitrogen content in the fresh matter ranged over all years and all products between 0.2 and 0.6%. DG Pig and Cattle slurry had on average the lowest N contents in the fresh matter and DG Mix solid and DG Renew had the highest (Table 2). The nitrogen content in the dry matter ranged on a much wider scale from 1.9 to 11.3%. The digestate from pig slurry substrate and the liquid fraction of the separated digestate showed both the absolute highest nitrogen contents in the dry matter and the widest range of measured nitrogen contents.

The P content in the fresh matter was on average the highest in the solid fraction of the separated digestate, whereas the P content in the dry matter was the highest in DG Pig. In the separated digestates, phosphorus was mostly found in the fresh matter of the solid fraction, with contents up to 3.6 times higher than that in the liquid phase. Nitrogen on average was also higher in the solid phase, but with far lesser and, in some years, no difference between the separated fractions. This is in accordance with the experiences of other authors who also found that phosphorus mainly accumulates in the solid fraction where it is bound to ions and precipitates in salt form [38], while nitrogen is usually partitioned equally between solid and liquid [39, 40].

The pH values of the digestates were higher than 7 in all cases and in DG Mix solid even higher than 9 (Table 2). There was a significant difference between pH values of the separated fractions with the solid fraction having higher pH at all analyzing dates. This confirms the finding of other studies, in which separation also lead to solid fractions with higher pH than the liquid fraction [4, 9]. Digestion also leads to a significant raise of pH from the Cattle slurry to the related digestate DG Cattle on all dates. It is known that a raise in pH promotes the formation of dissociated phosphate ions, which then precipitate as insoluble Ca and Mg phosphates [5, 13]. The same mechanism is used to recover phosphorus and nitrogen from wastewater and liquid digestates via enforced struvite ($MgNH_4PO_4{}^*6H_2O$) formation [41–43]. The high pH of the digestates also increases the risk for NH_3 volatilisation after digestion either during storage or after field application [44]. A higher soil pH also reduces plant availability of the four potentially toxic elements included in this study (Cd, Pb, Cu, and Zn) [45–48]. It is, however, debatable whether the application of digestates could influence the soil pH significantly, since the applicable amounts are usually restricted by nitrogen content.

The N : P ratio of the digestates was on average between 4.9 : 1 and 7.5 : 1 (Figure 1).The means of the N : P ratio

Table 2: Range of total N and P contents and pH of five digestates and cattle slurry (analyzed twice a year over six years; therefore, $n = 12$ (DG Mix liquid five years, $n = 10$), and different letters within columns mark significant differences between means (Scheffé's test, $p \leq 0.05$)).

	N (% FM)	N (% DM)	P (% FM)	P (% DM)	pH
DG Pig	0.2–0.5[a]	4.7–11.3[c]	0.01–0.15[a]	0.5–2.1[b]	7.4–8.2[b]
DG Cattle	0.4–0.5[b]	5.5–8.2[c]	0.04–0.09[a]	0.6–1.3[ab]	7.6–8.3[bc]
DG Renew	0.4–0.6[c]	4.6–9.5[c]	0.05–0.18[a]	0.6–1.6[ab]	7.8–8.4[c]
DG Mix solid	0.5–0.6[c]	1.9–2.9[a]	0.11–0.26[b]	0.5–1.1[a]	8.5–9.3[d]
DG Mix liquid	0.3–0.6[b]	6.1–11.3[c]	0.03–0.08[a]	0.6–1.2[ab]	7.3–8.4[bc]
Cattle slurry	0.3–0.4[a]	3.7–4.8[b]	0.03–0.09[a]	0.4–1.1[ab]	6.4–7.4[a]

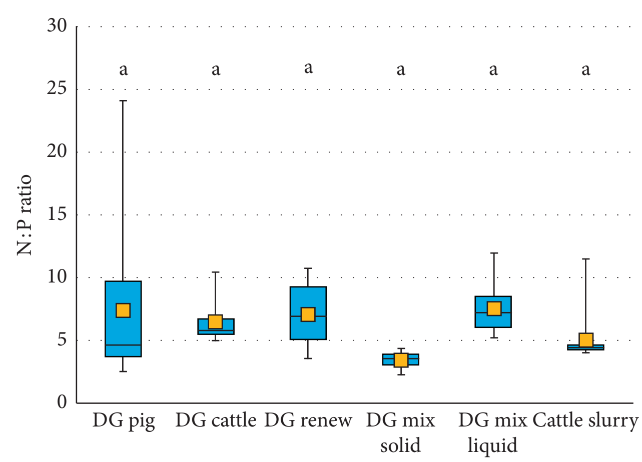

Figure 1: Range of N : P ratio of five digestates and cattle slurry (analyzed twice a year over six years; therefore, $n = 12$ (DG Mix liquid five years, $n = 10$), and different letters above bars mark significant differences between means (Scheffé's test, $p \leq 0.05$)).

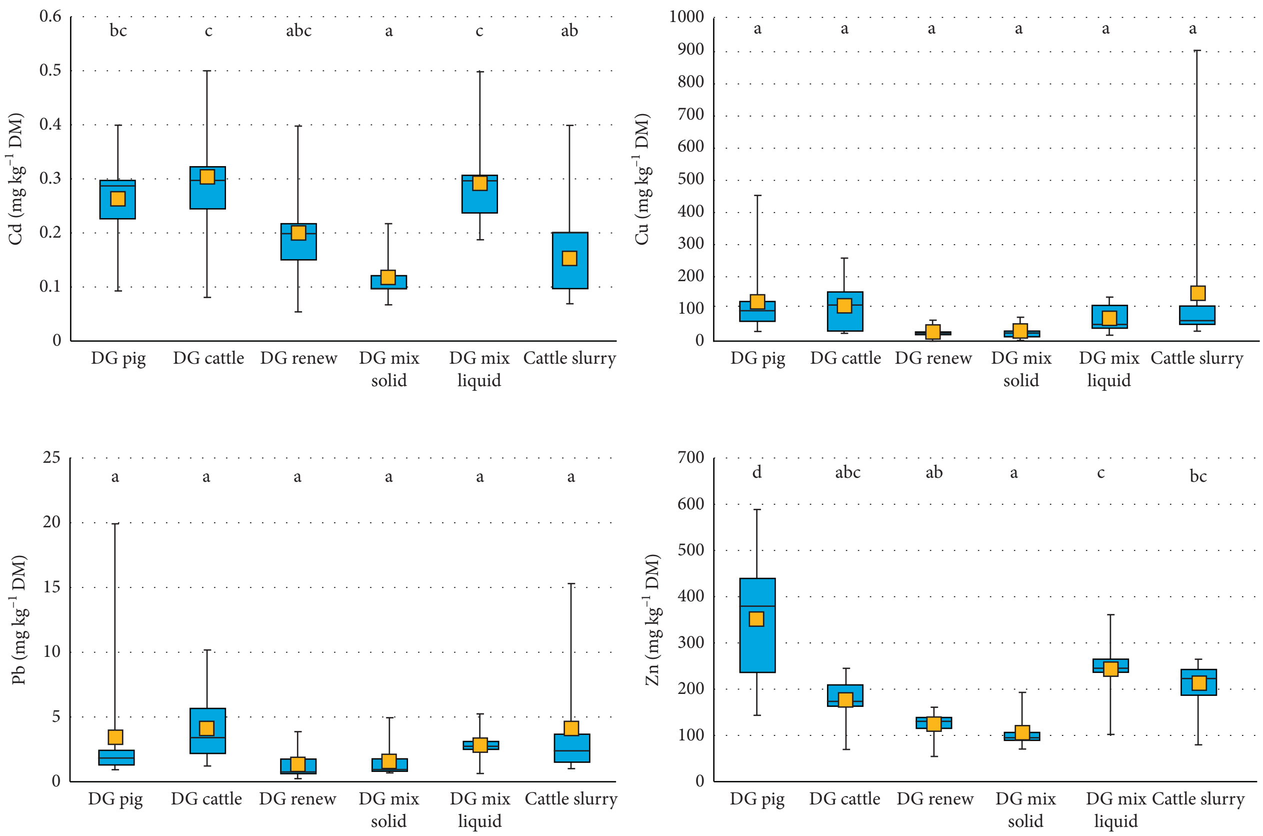

Figure 2: Range of contents of cadmium, copper, lead, and zinc in five digestates and cattle slurry (analyzed twice a year over six years; therefore, $n = 12$ (DG Mix liquid five years, $n = 10$). Different letters above bars mark significant differences between means (Scheffé's test, $p \leq 0.05$)). Yellow boxes mark the mean values.

showed no significant differences between the analyzed products (Scheffés test, $p \leq 0.05$), but the range of the ratio was especially large for DG Pig. The minimal N : P ratio of this digestate was 2.4 : 1 and the maximum ratio was 24, 1 : 1. The minimal N : P ratio of the DG Mix solid was even lower with 2.2 : 1.

While the other digestates and also the Cattle slurry meet the abovementioned crop requirements (between 3 : 1 and 15 : 1) in most cases, the solid fraction after separation and the digestate obtained from pig slurry apparently need special attention with regard to the nitrogen-phosphorus relation. If products like these are applied on a nitrogen-based calculation, phosphorus will either be applied in far too high or too low amounts. Mean values do also not serve as a calculation basis, as can be seen from the wide range of N : P ratios over the years. Instead, continuous measurements are required, which precede each application. Contents of cadmium, lead, zinc, and copper in the digestates are given in Figure 2. The European Union has adopted new regulations for fertilizers produced from phosphate minerals and from organic materials in 2019. According to these, organic fertilizers may not contain more than 1.5 mg kg^{-1} DM cadmium and 120 mg kg^{-1} DM lead [49]. These limits were not exceeded by any of the digestates or the Cattle slurry on any date. For zinc and copper, there are currently no limits set by the European Union with regard to organic fertilizers from agricultural background. Limits on EU level exist only for sewage sludge and are set to 1000–1750 mg kg^{-1} DM for Cu and to 2500–4000 mg kg^{-1} DM for Zn [50]. These limits were not exceeded by either element. German legislation requires that contents of Zn and Cu must be declared if they exceed 0.1% and 0.05%, respectively [51]. Zn remained under this threshold on all dates, but Cu contents exceeded these limits in some cases. However, contrary to the expectations derived from literature, maximum Cu contents were observed in the Cattle slurry, with the maximum content of Cu in DG Pig being only half as high. While the lower content in the DG Pig can be explained by the cofermentation of the pig slurry with plant material, which leads to a dilution, the origin of the high contents of copper and lead in the Cattle slurry on some dates remain so far unexplained and need further investigation.

When applying digestates, a certain attention should also be given to possible interactions between the different components. An increasing content of soluble P may, for example, decrease the plant availability of Zn due to the formation of only slightly soluble zinc phosphates [52]. Zn in lower doses is a plant nutrient, but becomes toxic in higher doses. Borkert et al. [53], for example, determined critical toxicity levels of Zn in soils for 4 crop species: 36 mg dm^{-3} for peanut, 70 mg dm^{-3} for soybean, between 160 and 320 mg dm^{-3} for rice, and >300 mg dm^{-3} for corn. In case of high Zn loads, high amounts of soluble P may reduce the accumulation in plants and in doing so reduce the risk of damaging the plants or causing health issues along the food chain. On the other hand, since Zn is also a plant nutrient, a reduced uptake may negatively impact the plant nutrition. Similar interactions are known for other potentially toxic elements as well. Large amounts of plant-available lead can promote the absorption of cadmium [54], while according to some authors, zinc can reduce the uptake of cadmium if it equals or exceeds its concentration [55]. Other studies report of contrasting results and showed that Cd and Zn [56] and Cd and Pb [57] may have synergetic effects. Increasing Cd and Zn or Cd and Pb contents in soils could thus increase the accumulations of both of the combined elements in crops.

4. Conclusions

The N : P ratio of digestates meets on average the requirements for most of the crops. Nevertheless, up-to-date analyzes are mandatory since the range of the N : P ratio is wide, even though the substrate composition of the digestates did not differ to a great extent. In this study, the N : P ratio was in some cases between 2 : 1 and 3 : 1, and the P content of these digestate was therefore far higher than the need of most crops. Digestates from pig slurry and solid fractions after digestate separation are especially prone to excessive P application if fertilization is based on N contents. Separation of digestates can be used to drain the liquid fraction of high phosphorus loads, but nitrogen is more or less equally distributed between solid and liquid. More efficient treatment methods are required in order to separate the nutrients from each other and to further reduce water content and volume. In cases where further treatment is impossible or uneconomic, a combination with mineral fertilizers may be useful to balance inadequate nutrient ratios.

Heavy metal loads of digestates did not exceed the limits set by European legislation. Copper and zinc, however, should be monitored, especially if animal manure is used as substrate.

Further research into interactions between potentially toxic elements regarding plant uptake is necessary. A wide variety of factors (soil parameters, plant species, source of the elements, and content of organic matter in the fertilizer and soil) appears to influence the existence and extent of such effects. It is, however, of vital importance to understand these interactions because they may necessitate legal limits for combinations of potentially toxic elements in addition to existing limits for single elements.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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