

# Investigations on Trace Elements in Biogas Slurry on Agricultural Areas

Leila Miganei, and Eberhard Gock

**Abstract**—Over several years, field tests were conducted on the experimental farm Hülsenberg (Germany), part of Union Agricole Holding AG, on corn monocultures fertilised with biogas slurry. The trace elements copper and nickel were investigated in consideration of phytoextraction. In order to verify the results, baseline investigations were conducted on the clear filtrate of biogas slurry in the presence of CO<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>S, and the resistance ranges of copper and nickel ions as well as copper and nickel glycine complexes were determined. Percolation tests were used to investigate the influence of the application quantity, degree of fermentation, metal concentration and types of bonding of the metals. The results were then correlated with the results of the field tests. In order to obtain a meaningful statement on the effect of biogas slurry over a period of 10 years, pressure oxidation tests were utilised to determine the natural contamination with metal in the soil and the additional metal content caused by biogas slurry, taking into consideration the phytoextraction. The mechanism: The application amount of biogas slurry, the metal content of the soil and phytoextraction in loamy sand soil over 10 years yielded an increase of 0.4 to 0.6% copper and 0.8 to 1.4% nickel on top of the natural contamination. The use of biogas slurry is, therefore, to be considered to be non-hazardous. This is of particular importance, since the generation of biogas will play an important role in the future supply of alternative forms of energy.

**Index Terms**—Biogas Slurry, Trace Elements Copper And Nickel, Field Test, Percolation Test, Pressure Oxidation Test.

## I. INTRODUCTION

With regard to the fermentation process for biogas generation, the German law distinguishes between three substance categories for the application of fertilisers:

- 1 Solid dung, slurry, agriculturally produced plant biomass,
- 2 Materials according to 1 and other produced plant biomass, biowaste generated from plants,
- 3 Materials according to 2 and biowaste of animal decent (category 2 and 3 as per the EG ordinance on hygiene 1069/2009).

In Germany, the residues from the fermentation of materials from category 1 are called biogas slurry. Waste from categories 2 and 3 are fermentation residues.

This study is limited to biogas slurry, i.e. the residues from category 1.

A study on the pure fermentation of renewable resources showed that it is impossible to completely do without animal manure due to acidification reactions [1]. This can be attributed

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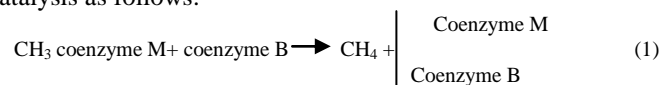
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to the lack of trace elements, which periodically stops the fermentation process. Fermentation plants for renewable raw materials are generally optimised by adding trace elements to stabilise the biocenosis. This article describes the impact of the trace elements copper and nickel associated with the application of biogas slurry on agricultural areas.

So far, the current literature does not provide a clear statement on the relevance of copper on biogas production. The question of whether copper is an essential trace element for methane bacteria has not been answered yet. Unlike zinc, of which significantly high concentrations have been found in all investigated types of bacteria, copper only occurs in a few types of bacteria [2,3].

In the mid-1970s, Zerner [4] pointed out the biological importance of nickel as part of the fermentation process. Nickel was found as a central atom in the urease, which catalyses the hydrolysis of urea to CO<sub>2</sub> and ammonia. Consequently, Thauer [5], a biochemist and microbiologist from Marburg, Germany, discovered the nickel dependence of methane bacteria. During this research and in cooperation with the ETH Zurich, the structure of a low-molecular yellow coenzyme - nickel tetra pyrrole - with the denomination F430 was discovered.

This coenzyme is characterised by a central nickel atom. During the last step of the methanogenesis, methane is released due to the reaction of the methyl coenzyme M reductase, to which the coenzyme F430 belongs, with the coenzyme B, which is necessary for redox reactions. Since the coenzymes M and B are available again after reductive cleavage, we are dealing with catalysis as follows:



Investigation on the use of trace element mixtures in agricultural biogas plants performed by a team of researchers from the University of Hohenheim and the ISF Schaumann Forschung GmbH [6] have shown that the trace elements already existent in commonly used substrates are generally insufficient for the metabolism of the microorganisms as well as for the optimisation and stabilisation of the fermentation process. Therefore, an adequate additive has to compensate the trace element deficit in the fermentation substrate of agricultural biogas plants. Such additives are mixtures of different trace elements, which are offered on the market as trace element mixtures with organic or inorganic liquid or solid compounds.

In the presence of 500 ppm H<sub>2</sub>S in the biogas, the concentration of nickel ions can drop down to 5 μmol/l; in the case of copper ions, the sulphide precipitation is nearly quantitative. The type of anion is of no relevance for the corresponding trace elements in the presence of sulphide ions [6].

Over the last few years, research has been conducted at IFS Schaumann Forschungs GmbH on developing a process for the mechano-chemical production of organometallic compounds of copper, nickel, zinc, iron, manganese and magnesium.

The product "ACTILINC" was derived for the fermenter technology [7]. The twofold complexation of trace element metal ions without the absorption of anions makes the ACTILINC complex an optimum trace element supplement. ACTILINC complexes are electrically neutral. It is expected that precipitations in the form of metal sulphides or polymeric protein structures can be prevented.

The German fertiliser ordinance (DüMV) dated 5 December 2012, § 6 "Requirements for labelling", paragraph (1), point 3 "Nutrients..." lists the following elements, which are categorised as heavy metals: iron, cobalt, copper, manganese, molybdenum and zinc.

As per 1.4 "...harmful substances", **nickel** has to be identified and labelled starting at quantities of 40 mg/kg DM. The tolerance in % of the labelled value is 50%.

The maximum permissible value for nickel is 80 mg/kg DM.

## II. INVESTIGATIONS

The investigations described in this article on the behaviour of the trace elements copper and nickel in biogas slurry on agricultural areas was initiated by ISF Schaumann Forschung GmbH. Starting in 2009, and over a period of 5 years, field trials and percolation tests on farmland at the experimental farm Hülsenberg (53.9633°N, 10.1594° O) near Wahlstedt, Germany were conducted [8].

The focus was on questions regarding the reaction behaviour of the trace elements added during fermentation, as they penetrate the soil in the form of sulphides after the application of the biogas slurry. In view of a future substitution of inorganic metal compounds by complex organic metal compounds, the reaction behaviour of the glycines of copper and nickel were also investigated.

Three test fields were used for the field trials; two of them were fertilised with biogas slurry and one with pig and/or cattle slurry for reference purposes. The fertilisation took place in the spring, just before the sowing of the new seeds.

In order to check the influence of biogas slurry and animal slurry on the subsoil and percolation water, percolation tests were carried out at the same time as the field trials.

## III. FIELD TRIALS

The field trials were geared to the sampling campaigns. During the test period from 2009 to 2013, samples were taken prior to and after the application of biogas slurry and animal slurry, and plant samples were taken at the time of harvesting. Samples were taken from the topsoil, subsoil, plants and their roots. The meteorological data were taken into account for the evaluation of the field trial.

In the following, the three 1hectare trial fields are described:

### Field Hü1 (Hülsenberg 1)

This field features loamy sand soil. The field is surrounded by hedges to prevent excessive evaporation rates during the summer months. For the field tests, this field was defined as the reference field and fertilised with pig and cattle slurry.

### Field Hü2 (Hülsenberg 2)

This field also features loamy sand soil. This field was intended for the pure application of biogas slurry. This field is located right next to a residential area but is also bordered by a hedge.

### Field Hü3 (Hülsenberg 3)

Unlike the other fields, this field features half-bog loamy sand soil due to spring floods. This field was also fertilised with biogas slurry. The special characteristic of this field is its high groundwater level which was detected at a depth of 1 m by a shovel trench.

Grain sizes analyses were performed as per DIN 18123: 2011-04 [9]. Accordingly, the cut was defined at 0.063 mm. On average, the grain sizes of the topsoils and subsoils are < 1 mm; the number of grains > 1 mm is insignificantly small. The fine fraction of the samples taken from Hü1 and Hü2 show almost no difference at all. However, the topsoil of Hü3 shows a relatively high fine fraction of 18% < 0.063 mm.

The chemical analyses of the sampled areas focused on 18 elements [10]. The complete analysis of the elements was performed by means of aqua regia pressure dissolution. Unlike DIN 38 414 part 7 (S7) [11], distilled water was added to the aqua regia dissolution in order to reduce the pressure, and hydrogen peroxide was added in order to destroy the organic matter. In order to be able to determine the siliceous parts, hydrofluoric acid and cold saturated boric acid were added for the analysis of silicon, aluminium, sodium, barium, calcium and sulphur. Following the dissolution, the sample solutions were diluted to 50 ml and their elements were measured by means of ICP (Inductively Coupled Plasma). Table I shows the chemical analyses of the original states of the samples from Hü1, Hü2 and Hü3, dated 11 March 2009 taken at depths of 0-30 cm and 30-60 cm as examples. The elements were measured in mg/kg DM.

TABLE I  
CHEMICAL ANALYSES OF THE SOILS SAMPLES FROM FIELDS HÜ1, HÜ2 AND HÜ3 AFTER SAMPLING ON 11 MARCH 2009 [10].

Elements [mg/kg DM]	Hü1		Hü2		Hü3	
	0-30 cm	30-60 cm	0-30 cm	30-60 cm	0-30 cm	30-60 cm
As	2.68	3.2	1.78	<29	1.41	<1.27
Cd	<1.50	<1.19	<1.30	<0.52	<0.60	<0.51
Co	<1.50	1.34	1.67	1.34	<1.35	0.53
Cr	5.24	2.745	6.46	3.61	6.61	2.66
Cu	8.54	1.41	10.78	0.98	8.82	<0.81
Fe	4,093	3,766	4,504	3,117	1,614	1,214
Hg	<1.50	<1.19	<1.34	<1.29	<1.43	<1.27
K	530.9	445.3	722.4	688.3	590.1	364.9
Mg	361.4	379.3	503.1	551.0	378.6	266.6
Mn	214.9	72.06	346.7	90.4	75.6	28.1
Mo	<0.30	<0.23	<1.34	<0.52	<0.60	<0.51
Ni	<1.40	<1.84	1.5	<1.39	1.5	<1.27
P	915.8	238.1	1,033	216	742.8	217.9
Pb	11.63	2.22	11.73	<2.58	10.19	1.53
Se	<3.01	<2.30	<2.68	<1.29	<2.87	<2.55
Tl	<1.50	<1.15	<1.34	<1.29	<1.43	<1.27
W	1.51	<1.15	1.49	<1.29	<1.43	<1.27
Zn	36.97	11.5	29.56	13.39	32.72	3.82
Al	9,80	12,75	13,41	13,58	8,53	11,07
Ba	130	140	159	141	103	139
Ca	1,719	1,244	2,073	1,361	1,940	1,095
Na	2,15	2,87	2,51	3,08	1,42	3,29
S	112	47	111	39	423	46
Si	26,11	35,46	23,47	28,44	6,29	22,12

Significant differences in the contents of elements in topsoil and subsoil are obvious. For copper, the value varies between factor 7 and 14. In the case of nickel, no significant differences are evident. The relatively high calcium content shows sufficient carbonate and, therefore, there is sufficient buffer capacity to form hardly soluble alkaline carbonates of copper and nickel [10].

The mineralogical diagnosis was done using diffractometry. The analysis was conducted on the grain size ranges of < 0.063 mm and > 0.063 mm. For the grain sizes > 0.063 mm, quartz (SiO<sub>2</sub>), albite (NaAlSi<sub>3</sub>O<sub>8</sub>) and microcline (KAlSi<sub>3</sub>O<sub>8</sub>) were identified. In the material < 0.063 mm, the primary decomposition component was identified as the clay mineral montmorillonite.

Diffractometry cannot provide any information on the mineralogical form of appearance of copper and nickel. However, it can be assumed that in the weathered soil at hand, copper and nickel can only be present in the form of hardly soluble oxides, independent or bound in the crystal lattice of other minerals. During the pressure oxidation test of the soils, the oxidic compounds of copper and nickel are not mobilised [10].

Various energy crops were grown on the selected fields (Hü1, Hü2 and Hü3) over the trial period from March 2009 to September 2013. **Table II** shows the crop sequence on the trial fields Hü1, Hü2 and Hü3 over the entire trial period. On field Hü1, the reference field, winter rye was grown in 2009 and 2011. In 2010, it was corn and in the last two years of 2012 and 2013 agricultural grass was grown.

TABLE II

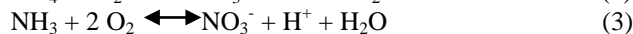
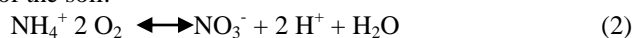
SCHEDULE FOR SAMPLING CAMPAIGNS AND CROP ROTATION ON THE TEST FIELDS HÜ1, HÜ2 AND HÜ3 DURING THE TRIAL PERIOD OF 2009 TO 2013.

Year	Date of sampling	Crop		
		Hü1	Hü2	Hü3
2009	11 March	Rye	Corn	Corn
	20 May	(Askari)	(Subito)	(Agrogas)
	28 Sept.			
2010	16 April	Corn	Corn	Corn
	28 Sept.	(Subito)	(Arolux)	(Aventura)
2011	24 March	Rye	Corn	Corn
	28 May	(Askari)	(Susann)	(Avro)
	28 Sept.			
2012	22 March	Agric. grass	Rye	Corn
	15 May	(Graenstar)	(Askari)	(Susann)
	06 Sept.			
2013	11 April	Agric. grass	Corn	Corn
	12 June	(Graenstar)	(Subito)	(Kairo)
	17 Sept.			

Fig. 1 shows the development of the pH levels on the topsoil of fields Hü2 and Hü3 compared to the reference field Hü1 in dependence of the precipitation events. After the application and over the entire period, the pH level significantly dropped after the application of biogas slurry on fields Hü2 and Hü3 as well as after the application of pig and cattle slurry on field Hü1.

In the literature [12], this is explained with the ongoing ammonification of NH<sub>4</sub>-N, which leads to the formation of NO<sub>3</sub> and to the release of H<sup>+</sup> ions, causing a temporary acidification

of the soil:



Apart from phytoextraction the precipitation events also have a regulating effect on the pH level. Figure 48 shows that the pH level increases with increasing precipitation. The influence of precipitation events on the topsoil of fields Hü2 and Hü3 is particularly evident in the years 2010 and 2011.

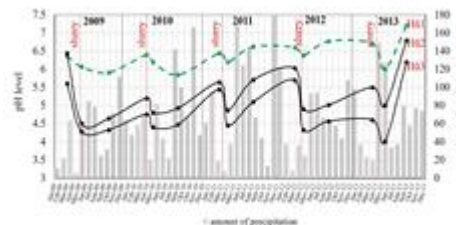


Fig. 1: Development of the pH level in the topsoil on fields Hü2 and Hü3 compared to the reference field Hü1 over a period of 5 years (March 2009 to September 2013).

The metal analysis of the topsoils of fields Hü1, Hü2 and Hü3 was performed down to a sampling depth of 30 cm. **Fig. 2** shows the measured copper contents of the topsoils over the trial period of 5 years. Considering the interval of 10 years, which is the legally prescribed interval in the German slurry ordinance for performing the metal analyses of soil, it is legitimate to generate yearly averages for the corresponding metal analysis. These levels are within the normal range for copper (2 to 40 mg/kg), as defined for copper in the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV) of 1991.

The high solubility of copper in the half-bog soil of Hü3 can be attributed to the drop in the pH level, especially after the application of biogas slurry and the contact with oxygen from the air. With the decrease of the pH level, the mobility of copper significantly increases starting at pH < 5. This observation is verified in tests on the resolution of CuS at pH 6 [8].

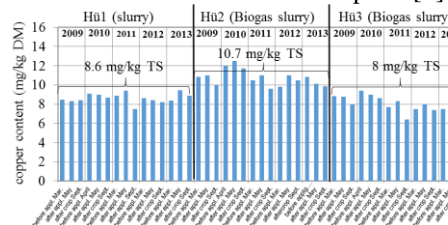


Fig. 2: Copper content measurements of the topsoils of fields Hü1, Hü2 and Hü3 over the trial period of 2009 to 2013.

The nickel content of the investigated topsoil over the period from 2009 to 2013 was determined in the same way (see **Fig. 3**). The average contents compared to the normal content of nickel in the soil, which is defined at < 50 mg/kg [12], do not constitute any impairment of the crop growth.

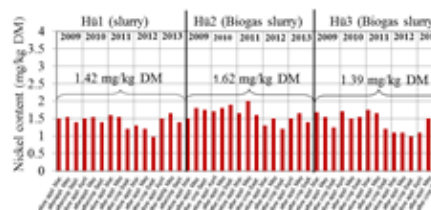


Fig. 3: Nickel content measurements of the topsoils of fields Hü1, Hü2 and Hü3 over the trial period of 2009 to 2013.

IV. PERCOLATION TESTS

These investigations used open Plexiglas cylinders with a diameter of 140 mm, a length of approx. 1,000 mm and an outlet. The peripheral equipment used was a metering pump with an apportioning vessel as well as a receptacle. The percolators were covered in order to prevent evaporation losses. In correspondence with the meteorological data, an annual average precipitation of 800 l/m<sup>2</sup> was assumed for the Wahlstadt region. This corresponds to an average precipitation of 15.4 l/m<sup>2</sup> per week.

Groundwater replenishment of 220 mm/a was also assumed. The weekly irrigation amount results from the following formula:

$$\text{precipitation} = \text{evaporation loss} + \text{drainage} \quad (4)$$

The corresponding percolation area was 153.93 cm<sup>2</sup>. At a weekly amount of rain of 15.4 l/m<sup>2</sup> this corresponds to 177 ml per week.

In order to get realistic conditions regarding the density, a core drilling was performed on the occasion of the sampling. The average density of the topsoil was determined to be 1.21 g/cm<sup>3</sup>. For the subsoil, the determined density was 1.38 g/cm<sup>3</sup> [10]. The flow chart in fig. 4 shows the concept of the percolation tests. The eluates of the topsoils are the load for the percolation tests with the subsoil. During weekly checks, the pH levels and conductivity were measured and element analyses were performed.

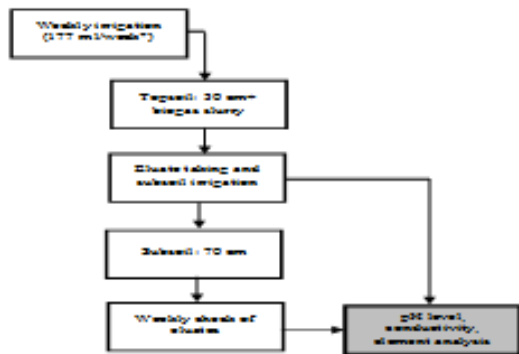


Fig. 4: Concept of percolation tests, percolator volume 15,393 cm<sup>3</sup>.

The general advantage of percolation tests is the reproducibility of the parameters. The percolation tests performed as part of these investigations focused on effects, e.g. triggered by changes in the operating conditions. The influence of the amount applied, degree of fermentation, metal concentrations and types of metal bonds were investigated.

It was possible to prove that a reduction of the biogas slurry from 35 to 17 m<sup>3</sup>/ha, i.e. by 50%, significantly decreases the reduction of the pH level. This is particularly evident in the case of the half-bog soil of Hü3 (see Fig. 5).

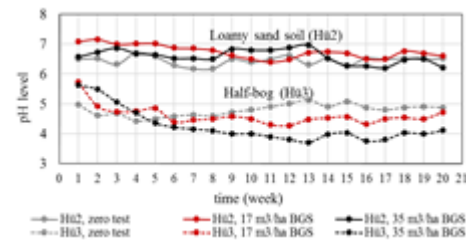


Fig. 5: pH level development during percolation tests with topsoil and subsoil from fields Hü2 and Hü3 as a function of the reduction of biogas slurry over 20 weeks.

Based on this finding, the application amount was increased to 105 m<sup>3</sup>/ha in order to make the behaviour of copper and nickel in 30 cm topsoil and in 70 cm subsoil from the fields Hü2 and Hü3 clearly reproducible. Fig. 6 and 7 show the contamination from copper and nickel in g per hectare due to biogas slurry in the topsoil and subsoil of fields Hü2 and Hü3 at an application amount increased from 35 to 105 m<sup>3</sup>/ha.

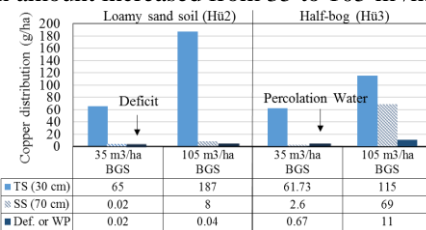


Fig. 6: Copper distribution in the fields Hü2 and Hü3 at increasing amounts of applied biogas slurry.

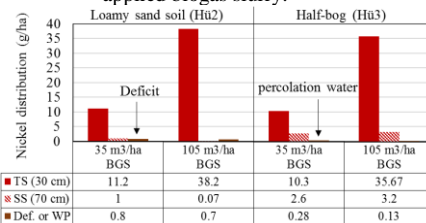


Fig. 7: Nickel distribution in the fields Hü2 and Hü3 at increasing amounts of applied biogas slurry.

It is certain that under half-bog conditions and at excessive amounts of applied biogas slurry, the migration of copper into the subsoil and/or groundwater takes place relatively fast. Since the natural pH level of biogas slurry is around 8, a drastic reduction of the pH level during the application of overdosed biogas slurry is prevented by the correspondingly increased organic content. Fig. 8 shows that this neutralisation effect does not apply to soil such as Hü3 with a low buffer capacity. In dry loamy sand soil the pH level will even increase in case of overdosing of biogas slurry. The mentioned increase of the organic content during the overdosing of biogas slurry leads to an intermediary precipitation of the copper in the topsoil.

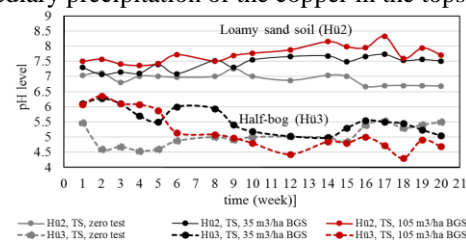


Fig. 8: pH level development during percolation tests with topsoils from Hü2 and Hü3 at increased application amounts of biogas slurry.

These observations on the behaviour of copper correspond with the findings by Somasundaran from 2006 [13].

In the case of nickel and the application of overdosed biogas slurry, no significant changes in the distribution compared to the control test were observed, neither for the subsoil of Hü2 nor for the half-bog subsoil of Hü3 (see figure 58). Nickel is bound absorptively in the topsoil. The topsoils of Hü2 and Hü3 were also contaminated in the same way with the threefold application amount and the threefold nickel content.

The percolation tests were also used to investigate the influence of types of metal bonds on the soils on fields Hü2 and Hü3. Solutions of copper and nickel sulphate or glycinate were added to the top soil, to which biogas slurry had previously been applied.

**Fig. 9** and **10** show the copper and nickel distribution in the topsoil and subsoil and in the percolate water of Hü2 and Hü3 regarding the types of copper and nickel bonds.

Figure 63 shows that during the percolation tests over 20 weeks there was no migration of copper into the subsoil or the percolation water, neither with the addition of copper sulphate nor with the addition of copper glycinate solution.

The background for this behaviour is the precipitation of copper humate from a copper sulphate solution at pH 6 and the adsorption of copper glycinate complexes in the topsoil [8].

In all tests, the addition of nickel sulphate or nickel glycinate solutions to the topsoil of Hü2 and Hü3 led to nickel output into the subsoil (see figure 10), since unlike copper solutions, nickel sulphate and nickel glycinate solutions are mostly stable at pH 6 [8].

In the dry loamy sand soil of Hü2, the mobility of nickel increases with the use of nickel glycinate solution. Under half-bog conditions there are no significant differences between the addition of nickel sulphates and nickel glycinate.

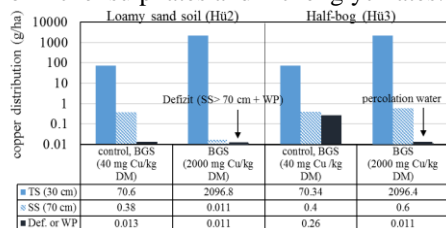


Fig. 9: Precipitation of copper in the topsoil in dependence on its types of bond (sulphate, glycinate).

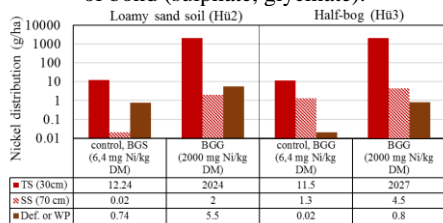


Fig. 10: Precipitation of nickel in topsoil in dependence on its types of bond (sulphate, glycinate).

## V. RESULTS AND DISCUSSION

The natural contamination is the general contamination with metals in the soil without the addition of biogas slurry.

Percolation tests with topsoil and subsoil from the fields Hü2 and Hü3 showed that without the addition of biogas slurry, the eluate output for copper and nickel is generally less than 1% of

the metal content of the soil. **Table III** shows the percolation results from the treatment of the topsoil prior to the use of biogas slurry. It shows that the soil without any vegetation is a relatively stable system regarding the immobility of heavy metals.

TABLE III.

EVALUATION OF THE NATURAL CONTAMINATION WITH COPPER DURING PERCOLATION TESTS WITH TOPSOIL AND SUBSOIL FROM HÜ2 AND HÜ3 PRIOR TO THE APPLICATION OF BIOGAS SLURRY

Specimen	Material	TS		SS	
		Cu content soil [%]	Cu aluate appl.	Cu content soil	Cu aluate appl.
Hü2 without BGS	BGS				
	TS				
Hü3 without BGS	BGS				
	TS				
	SS	99.90	0.10	99.45	0.55
	SS	99.91	0.09	99.05	0.95

Pressure oxidation tests with the untreated topsoils from Hü2 and Hü3 support the statement that the natural contamination of the topsoils with copper and nickel is stable, i.e. no mobilisation is evident (see also **fig. 11**). The results of the pressure oxidation tests with the subsoil of the objects Hü2 and Hü3 show the same tendency.

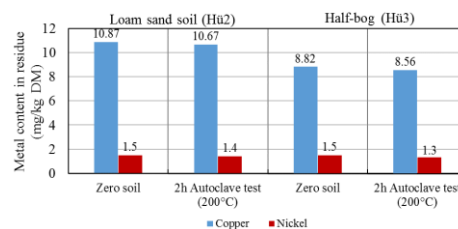


Fig. 11: Copper and nickel contents in the dry substance of the topsoils of fields Hü2 and Hü3 during pressure oxidation test (p:20 bar O<sub>2</sub>; T:200°C; t:2h).

In connection with the percolation water prognosis of the mine dumps containing heavy metals, we developed the pressure oxidation test at the Institute for Mineral and Waste Processing, Waste Disposal, and Geomechanics [14]. The test uses a so-called agitation autoclave, type 1220, by Ernst Haage GmbH; 100 g test substance per litre H<sub>2</sub>O are stirred at a temperature of 120°C and 200°C under an oxygen partial pressure of 20 bar. The reaction period is 2 hours. This process was initially developed for heavy metal sulphides and later extended for heavy metal oxides [15]. The test assumes natural pH levels for the prepared suspensions. The sulphatisation of the existing sulphides triggered under oxygen pressure simulates and shortens the long-term reactions taking place under natural conditions. It is possible to make reliable statements on the potential for forming acid water and the corresponding hazard potential.

**Fig. 12** shows the result of the pressure oxidation test with the use of 100 g of biogas slurry in 1 litre of distilled H<sub>2</sub>O. It is clear that the sulphides of copper and nickel and the organic matter in the biogas slurry completely dissolve.

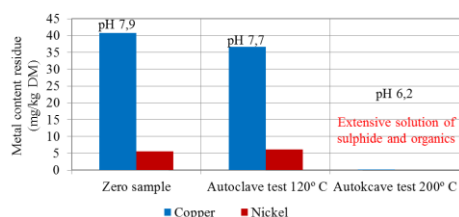


Fig. 12: Copper and nickel contents of biogas slurry after digestion under p-T-conditions (p: 20 bar O<sub>2</sub>; T: 120, 200°C; t:2h).

The pressure oxidation test also provides information about the acid formation potential of biogas slurry (see **fig. 13**). At 200°C, over a period of 2 h the potential for total organic acids was approx. 2,000 mg per litre. As opposed to untreated biogas slurry, this is an increase by a factor of 100. The initial pH level was 7.9; at the end of the test, a pH level of 6.2 was measured.

If the representation of a period of 100 years by means of the pressure oxidation test is assumed [14], the soil fertilised with 35 m<sup>3</sup> of biogas slurry per hectare would mean an average annual mobility of 4 g of copper or nickel per hectare.

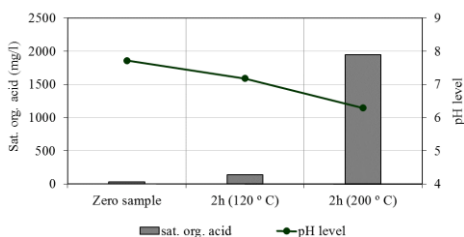


Fig. 13: Acid formation and pH level development after digestion of biogas slurry under p-T-conditions (p: 20 bar O<sub>2</sub>; T: 120, 200°C; t:2h).

In order to be able to make a prognostic statement on the efficiency of biogas slurry, we are looking at a time period of 10 years. This methodical approach is supported by the German slurry ordinance, which demands soil analyses to be done every 10 years and thereby expresses that soil is a stable system if there is no external impact [8].

For loamy sand soil (Hü2), the pressure oxidation test results yield a natural contamination in the topsoil of 40,000 g of copper and 6,000 g of nickel per hectare. The discovered additional contamination on top of the natural contamination caused by the use of copper and/or nickel sulphates in a biogas fermenter over a time period of 10 years taking into account phytoextraction is 0.7% for copper and 1.4% for nickel.

For half-bog loamy sand soil (Hü3), the result is more favourable due to a higher phytoextraction rate. The natural contamination in the topsoil is 30,000 g Cu or 5,000 g Ni per hectare. The use of copper and/or nickel sulphates in a biogas fermenter causes an additional contamination on top of the natural contamination caused by the biogas slurry, taking into account phytoextraction of 0.8% for copper as well as for nickel (see **fig. 14**) over a period of 10 years.

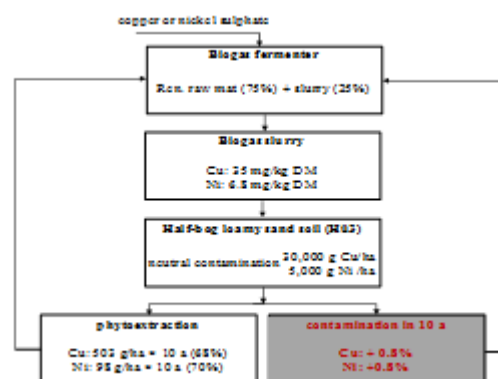


Fig. 14: Prognosis on the development of the copper or nickel content during fertilisation with biogas slurry on the test field of Hü3 over 10 years (35 m<sup>3</sup>/ha- 74 g Cu/ha; 14 g Ni/ha) × 10 a.

The use of biogas slurry as fertiliser, therefore, does not cause any environmental contamination regarding the metal load, if the amount applied is adapted to the fertiliser demand and if monocultures are avoided. Prior to setting up a biogas plant, the fields to be used and the capacity of the long-term fertiliser demand have to be calculated or determined by means of field trials as done in this study.

## VI. AKKNOWLEDGMANT

F. A. would like to thank the Union Agricole Holding AG for financial support during her PhD studies.

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