

MANURE STANDARDS PUBLICATION



Instructions for manure analysis

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1. Introduction

These instructions for manure analysis were formulated within the project Manure Standards (Advanced manure Standards for sustainable nutrient management and reduced emissions, Interreg Project No #R057). We aimed to compare and increase understanding of the manure analysing methods used within the Baltic Sea Region. The purpose of these instructions is to provide laboratory personnel, authorities, advisors, and farmers a tool to understand, use and modify, if necessary, the methods used in analysing manure samples.

In the Manure Standards project, three different methods for estimating characteristics of the manure have been used and also compared. In all Baltic Sea countries, there are existing national table values, that are based on previous knowledge from manure analysis and mass balance calculations for different farm animals and manure types. In WP3 of the Manure Standards project, a calculation tool, including data on animal categories, feeding, bedding materials, storage etc. was developed for providing a farm-specific estimate of manure characteristics. Analyses of manure samples will also give a farm-specific result but it also includes a seasonal effect, where i.e. recent weather and management methods will affect the results.

1.1. Manure definitions (KTBL, 2011)

The manure definitions used in this report are taken from the "Glossary of terms on livestock and manure management, 2011" issued by the Association for Technology and Structures in Agriculture (KTBL):

Slurry	Manure (faeces and	l urine) produced by	housed livestoc	k, usually mixed
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with some bedding material and some water during management to give liquid manure with dry matter content in the range 1-10%.

Solid manure Manure from housed livestock that does not flow under gravity and

cannot be pumped, but can be stacked in a heap. May include manure

from cattle, pigs, poultry, horses, sheep, goats and rabbits.

Semi-solid manure Manure that cannot be pumped or stacked in a heap.

Deep litter Faeces or droppings and urine mixed with large amounts of bedding

and accumulated over a certain time on the floor of animal houses.

Liquid fraction Varying degrees of separation of solids and liquid may occur during the

management of manures, giving rise to liquid and solid fractions. The properties of these liquid fractions vary with the proportion of urine,

faeces, bedding and water that they contain.

Solid fraction See "Liquid fraction" above. The solid fraction may include e.g. solids

remaining following drainage or seepage of the liquid fraction from cattle bedded on straw on a sloping floor and solid fibrous material

derived from mechanical separation of slurry.

Other terms, please see the Glossary: http://ramiran.uvlf.sk/doc11/RAMIRAN%20Glossary 2011.pdf

2. Background

Reliable information on the nutrient content of manure is necessary in order to develop an effective and comprehensive nutrient management plan that maximises the effectiveness of crop nutrient use and growth, while minimizing both nutrient runoff and pollution of adjacent waterways. Standard default values for manure properties are often used for nutrient balance planning when actual measurements are not available. Models can help to calculate standard mass balance values for manure properties based on feeding practices, production intensity, standard housing systems and storage practices. However, the chemical and physical properties of manure also vary greatly depending on other manure management factors. Therefore, sampling and analysis of manure provides farm-specific information, which may improve utilisation of manure resources.

Manure is a heterogeneous product and in addition of the appropriate sampling methodology solid and precise methods of analyses are a prerequisite to obtaining representative data from manure to be used e.g. as a basis for crop fertilisation.

Results from manure analyses contain several sources of error, including errors from sampling, sample preparation and sample analysis. The largest source of error is sampling, as shown in Figure 1. The more subsamples taken from different spots in stored manure, the more accurate the final sample sent to the laboratory. However, as sampling is time-consuming, a balance must be struck between sampling accuracy and the time required. In general, the larger the storage, the more subsamples should be taken.

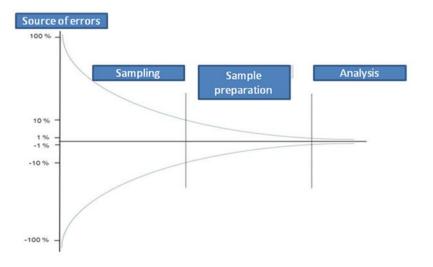


Figure 1. Contribution of different sources of error in sampling and analysing manure to the total error above and below the average. The greatest proportion of the error derives from the sampling procedure (Henkelmann, 2017).

Altogether 20 laboratories in 9 countries participated in the project. They analysed manure samples from the pilot farms and provided information on procedures for storage and preparation of the samples and methods of analyses.

There was a sampling scheme conducted in the Manure Standards-project, where variation coming from different sampling spots, times, samplers and laboratories could be estimated. Among the Finnish samples, we compared source of error from sampling spots (ex-housing and ex-storage), sampling times (spring, summer and autumn), three different laboratories and duplicate samples in laboratories

(Figure 2). We obtained similar result as shown by Henkelmann (2017) in Figure 1 with by far the greatest part of the errors being related to sampling rather than analysing.

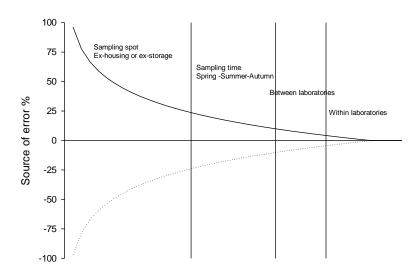


Figure 2. Contribution of different sources of error to the total error above and below average in total nitrogen analysis. The included sources of error are sampling spot, sampling time and errors between and within laboratories. Data are from the manure samples taken in Finland and analysed within the Manure standards project (samples n=169).

2.1. Available guidelines and standards

Manure analyses have been conducted since the basic understanding of plant nutrients was evolved from the developments in chemistry in the 19th century. The combustion analysis, i.e. burning organic material with oxygen, was used to determine carbon from the resulting gas. Minerals including those used by plants were extracted and analysed from the ash after combustion (Holmes 1963). Methods for analysing nitrogen were developed by Dumas already in 1826 and Kjeldahl in 1883. The principles for many of the analysis are still the same, although today we can use fine-tuned technical solutions by highly developed laboratory equipment.

There are various national and international standards used for manure analyses. In addition, there exist less formal recommendations. One widely known report is "Recommendations of manure analysis" by Peters et al. (2003). The current interest in recycled nutrients has brought an increase in organic fertilisers and soil improvers. The characteristics of these substances can be analysed with similar methods as manure. A recent review of methods to evaluate organic fertilizers was published by Wageningen University (Schoumans et al. 2019). The new European fertilizer legislation will most likely emphasise methods among European Committee of Standardization (CEN) standards that can be used for analysing the quality of organic fertilizers and manure.

The analysis of manure is not separately included in any working groups or technical committees of standardization organisations. Relevant methods for manure are often included in methods used for analysing soils, sludges, composts, growing media or water (Table 1). So far the most targeted attempt to harmonise these methods was Project Horizontal (2002-2006) that collected and recommended standards in the field of sludge, soil and treated biowaste (https://horizontal.ecn.nl/).

The relevant standards of CEN for manure analyses are mostly developed and administered in six technical committees (TC) listed in Table 1. The recommended standards from Project Horizontal have been realised under TC 444. International standardisation organisation (ISO) covers relevant standards

for manure analyses mostly in four technical committees (Table 1). In Russia, standard methods exist for determination of moisture in fresh manure by sample drying at 105° C (State Standard GOST 26713-85). Determination of total nitrogen and phosphorus is performed after the mineralization of the organic substance in concentrated sulfuric acid with hydrogen peroxide according to State Standard GOST 26715-85 (Briukhanov et al. 2016). Ammonium-N determination after 0.05 M HCl extraction (GOST 26716-85) and organic matter determination by loss on ignition (GOST 26714-85) are also standard methods. The laboratories analysing samples from Manure standards-project often used above mentioned standard methods. There were both commercial laboratories and laboratories combined with research institutes (Table 2).

Table 1. Technical committees of CEN (European Committee of Standardization and ISO (International standardisation organisation), that manage standards applicable for manure analysis.

CEN	ISO
TC 223, Soil improvers and growing media	TC 134/WG2, Fertilizers, soil conditioners
	and beneficial substances
TC 230, Water analysis	TC 147/SC2, Water quality
TC 345, Characterization of soils	TC 190/SC3, Soil quality
TC 335, Solid biofuels	TC 238, Solid biofuels
TC 308, Characterisation and management of	
sludges	
TC 444, Test methods for environmental	
characterization of solid matrices	

Table 2. Laboratories of participated countries divided as commercial and research laboratories.

Country	Commercial laboratories	Research laboratories
Denmark	3	
Estonia		2
Finland	3	1
Germany	3	
Latvia		2
Lithuania	2	
Poland		1
Russia		1
Sweden	2	_
Total	13	7

3. Handling and transport to laboratory

Manure samples should be tightly sealed to prevent leakage and double-bagged as an extra precaution. To ensure that samples sent for analysis are representative of the nutrient content in the original manure, proper precautions must be taken to avoid leakages, nutrient losses by volatilisation, moisture losses and nutrient transformations. The following approaches are recommended:

Make sure containers and plastic bags are tightly sealed, to avoid ammonia losses.

Keep samples cool in a refrigerator or by placing on ice. Warm temperatures promote nutrient conversion, which will change the nutrient content of the sample. The temperature should not be above 5°C. Do not allow the samples to be in a warm environment, such as a car or the cabin of a truck, for longer than a few hours.

Freezing the samples before transport to the laboratory is recommended. If a freezer is not available, transport samples to laboratory within a few days. Samples kept at room temperature should be analysed within 24 hours.

Send samples Monday-Wednesday, to ensure they can be processed by the laboratory before the weekend.

Clearly label all samples with permanent marker. At the very least, the label should state: farm name, type of manure, contact information, and date and time when the sample was collected.

Send samples together with a completed laboratory-specific order form. If not available, the Manure Standards survey form should be used (https://www.luke.fi/manurestandards/en/results/). The following analyses are recommended:

- ✓ Total solids (TS)/dry matter (DM) content
- ✓ Total-N
- ✓ Ammonium-N
- ✓ Total P
- ✓ Total K
- √ (Total C)*
- ✓ pH

Laboratories can have their own recommendations of sample volumes needed. Liquid and slurry samples are usually easier to homogenise, so the requested volume of them is usually small and approximately one litre. Solid and deep litter manure are more difficult to homogenise in the laboratory and thus they often have higher request of volume (usually 1–2 litres).

^{*}At several laboratories within the Baltic Sea Region, total C is not included in the standard analysis package for manure and may be excluded. Dry ashing to determine organic matter content is sometimes available as an alternative for total C determination.

4. Pre-treatment in laboratory

Manure samples contain active microbial population and volatile compounds, which will make manure samples unstable and hence may affect the analytical results. The homogenisation for subsampling is often difficult. Manure sample may contain pathogens and parasites, which would cause risks for humans while analysing the samples or after sample disposal. When laboratory personnel are handling manure samples, they should wear normal protective equipment used in laboratories (i.e. gloves, eye protection). In case of handling dried manures, the risks of dust inhalation should be minimised by using safety cabinets and inhalation masks. When cleaning dust from equipment and surfaces, vacuum cleaner or equipment venting air directly outside should be used.

4.1. Storage in laboratory

Samples should be stored in a way so that manure characteristics do not change. Laboratories taking part in the project stored manure samples in about 4°C usually for 1-4 weeks before analysis. If storage period was known to be longer before analysis, the samples were frozen. After freezing, samples were thawed usually in room temperature before the analysis. However, there exist recommendations that samples should not be stored unfrozen for more than one week before analysis (Peters et al. 2003).

Recommendation:

Samples are transferred to 4°C directly after arrival to laboratory. The holding times in 4°C before specific analysis as suggested by Peters et al (2003.)

рН	7 days
Dry matter	7 days
Total nitrogen	7 days
Ammonia nitrogen	7 days
Electrical conductivity	6 months
Mineral nutrients –total P, K, Ca, Mg, Cu, Zn	6 months

If holding times would be exceeded, samples should be frozen to suspend microbial and chemical activity.

Among international standards there are ISO 18512, "Soil quality—Guidance on long and short-term storage of soil samples" and 5667 "Water quality. Sampling. Part 15: Guidance on the preservation and handling of sludge and sediment samples. ISO 18512 suggests maximum storage time of one week regarding analyses of pH and available nutrients and storage time of one month for analysis of total nutrients when storing moist soil samples in 4°C. Considering sludge samples stored in 1-5°C, ISO 5667 suggests maximum storage time of 24 hours for analysis of all nitrogen fractions, total phosphorus and pH, seven days for dry matter and one month for metals.

4.2. Homogenisation of sample

In the participated laboratories, liquid manure samples were mostly mixed manually and only one laboratory reported automatic shaking of 30 minutes. Fresh solid samples were mixed manually or using household blenders.

When some of the analyses were made from the dried matrix, samples were dried usually in 105°C, but a few laboratories used 60 or 70°C. There were no specific details if samples prepared for analyses from dried material would be treated otherwise than samples for dry matter determination. Some laboratories might use lower drying temperatures for samples prepared for further elemental analysis. Dried samples were milled.



Figure 3. Homogenisation of dried manure samples with a laboratory mill (Photos: Lauris Leitans).

EN 16179, Guidance for sample pretreatment, gives instructions for drying and homogenisation of sludge, treated biowaste and soil samples.

Recommendation:

The sample must thoroughly be mixed and homogenized before taking subsamples for individual analysis. Liquid samples must be subsampled immediately after manual or mechanical shaking to avoid sedimentation. Solid samples without long-fiber materials can be mixed in a blender (e.g. kitchen mixer). If sample contains long-fiber materials like straw or hay, chopping, dividing and recombining before mixing might be necessary (Peters et al. 2003). Mechanical shaking or mixing would minimise the effect of personnel on homogenisation.

It is strongly recommended that ammonium and total nitrogen will be analysed from the subsample kept in fresh matter, if the sample is dried and milled for other analyses. The guidelines of EN 16179 should be followed in sample pretreatment.

5. Methods of analyses

5.1. Total solids (TS)/dry matter (DM)/moisture content

Procedures in laboratories

In participated laboratories, drying temperature was mostly 105°C. A few laboratories reported that they are using 60° or 70°C. No details were reported from the used drying times or if change of dry weight was followed. Standards for dry matter determination used included the ones from groups: "Characterization of Sludges" and "Soil Improvers and Growing Media".

Available standards

Standards determine the drying temperature to be 103 +/- 2°C. The loss of weight is determined after successive measurements, and drying can be stopped when loss of weight is less than 0.2 % or 2 mg (dry mass of sample at least 500 mg) of the previous weighting (CEN 12880).

ISO 11465, ISO 18134-1, EN 13040, EN 12880. EN 15934, (EN 14346, withdrawn), GOST 26713-85

Discussion

Dry matter (DM) content is important for estimating the handling characteristics and the relative nutrient contents between different manures. Often part of the analysis is done from dried manure and converted from dry weight to fresh weight basis, thus causing possible errors in DM determination to affect also in those results.

Hoskins et al. (2003) tested three temperatures (50°C, 70°C and 110°C) with 6, 16, 25 and 48 hours each. Several different manures were dried in three different laboratories. Forced draft ovens were used, and different containers were used. Sample size was below 2 g in DM. The minimum drying time in each temperature was determined, when no significant weight loss was observed between successive time intervals. Residual moisture content of samples dried to constant weight was determined in drying samples afterwards in 110°C.

Hoskins et al. (2003) observed that residual water content of manures after drying in 50°C or 70°C was insignificant excluding poultry manures. Open cubicles decreased the time needed in drying. They concluded a following table for drying times and sample sizes:

Table 3. Maximum fresh samples size for dry matter determination in open vessels (Hoskins et al. 2003).

	Drying temperatures		
Drying time	50°C	70°C	110°C
6 hours	Not recommended	5 g	10 g
16 hours	5 g	10 g	20 g
24 hours	10 g	20 g	20 g

Hoskins et al. 2003 suggest that all solid and semi-solid manure samples should be replicated, and the difference higher than 2% units would result to run larger sample size and longer drying time. For liquid manure, replicate in every 10 samples is recommended.

Recommendation:

For determining dry matter content, different combinations of drying time, mass and temperature are possible. Drying temperatures recommended in standards (103°-105°C) seem to be appropriate. In this drying temperature, 30-50 g of moist sample is recommended and the sample dry weight should be at least 0.5 g. Replicated samples should be included in the batches and special attention should be paid for solid manures due to their heterogeneousness.

5.2. Total-N

Procedures in laboratories

The prevailing method was Kjeldahl digestion, followed by distillation and titration of NH_3 -N. Laboratories used several standard methods that are aimed for different matrices. The differences in methods between laboratories originated from the sample size, catalysts to improve digestion and reduction of nitrate-N in digestion. Sample size varied from 1 to 20 g of fresh manure, for slurry sample size of 15-20 g was mostly used. In case of dried samples, approximately 1 g was used.

Mostly nitrate-N concentration in raw manures should be minimal, and thus reduction of nitrate-N to include for total-N is seldom important. Deep litter and especially composted manures can accumulate nitrate and thus in their analyses nitrate determination should be kept in mind. In a few laboratories, Dumas method using dry combustion and dried samples were used. At least one of the laboratories aimed to volatilise all ammonia in drying and then added the result of ammonia-N determination to result of total-N from Dumas method.

Available standards

Kjeldahl method has standards for growing media, sludge, soil, soil improvers, treated biowaste and water. Although Dumas method is also approved as a valid standard for e.g. sludge, treated biowaste and soil (EN 16168), there is a considerable risk of ammonia loss during the drying of samples. Standard methods of Dumas consider ammonia loss, for example in recommendations of Project horizontal: "During the drying procedure there is taken care not to lose amounts of ammonium-N and/or nitrate-N. Therefore, excessive drying (105°C) should be avoided. Rapid microwave drying may be a good choice. In special situations moist samples can be used." The standard, EN 16168, states "During the drying procedure or a milling process take care not to lose ammonium-N and/or nitrate-N. Prolonged drying at 40°C or at room temperature may cause losses of nitrogen due to microbial activity within the sample. Therefore rapid drying methods should be used."

Kjeldahl: EN 16169, ISO 11261, EN 13342, EN 13654-1, EN ISO 16948

Dumas: EN 16168, ISO 13878, EN 13654-2

Discussion

Kjeldahl and Dumas methods have been used for the analysis of plant tissue and soils, and both of them have also been adapted for the determination of N in manure. Dumas and Kjeldahl methods have usually good correlation in agricultural samples, at least when wet samples can be used for sludges and manures in Dumas method (Watson & Galliher 2001). Laboratories can base the selection of the used method on cost, safety and ease of operation, especially when manure samples might be only a small proportion of analysed samples.

Watson et al. (2003) present Kjeldahl method with 5 g (Macro-Kjeldahl) and 0.5-2 g (Micro-Kjeldahl) sample sizes. In their presentation of Dumas method, sample size is 0.5-1.0 g of harmonized sample. Watson et al. (2003) mention that it is recommended that total-N analysis would be analysed an as-is-basis (without drying), and emphasise that laboratories should determine and verify which sample preparation methods meet their procedures.

However we should have some suspicion against Dumas with samples of high ammonia content and low dry matter. The analysed sample size can be higher in Macro-Kjeldahl compared to Dumas, while the homogenization of sample is easier with dried samples used in Dumas. The ammonia loss during drying is a well-known process and can be high, when dry matter content is low and ammonium-N content is high. We tested with 28 manure samples taken in Finland, what was the difference in ammonium-N contents when samples were analysed fresh, freeze-dried or dried in 60°C ventilated oven. Considering slurry samples with low dry matter content, 87–97% of ammonia was lost in oven drying (Figure 5). This shows, that the method aiming to volatilise as much ammonia as possible in drying and adding the determined NH4-N concentration to total-N result from Dumas can result satisfactory results in case of slurries. In deep litters, 34–95% of ammonia was lost in drying, and in solid manures 76–87%, respectively.

For quality control, Watson et al. (2003) recommended that 10% of samples would be replicated and a known reference sample would be measured daily or in every batch.





Figure 4. Kjeldahl system. Left there are macro-Kjeldahl tubes used in digestion and right there is a distillation and titration unit. (Photo: Tapio Salo)

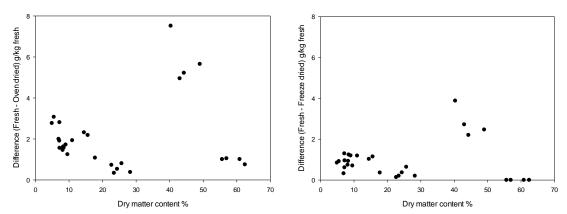


Figure 5. The difference in ammonium-N content (fresh g/kg – dried g/kg) between fresh samples and oven dried (60°C) samples (a) or freeze-dried samples (b) classified by their dry matter content in x-axis (n=28). Tested samples are a selection from the Finnish manure samples.

Recommendation:

Kjeldahl-method with abundant sample size and fresh samples can be considered as a most reliable method for total N. Micro-Kjeldahl method has advantages of using fresh samples, but the small sample size creates demands for sample preparation. If Dumas with dry and grind samples is the only option to be used, the loss of ammonia during drying should be carefully considered.

5.3. Ammonium-N (including nitrate-N and soluble organic N)

Procedures in laboratories

The available N in manures was mostly analysed as ammonium-N. Common methods were distillation/titration and colorimetric determination. Water or salt extraction (Table 4) was also used for liquid manures while extraction had to be used for solid manures. Solutes and time of extractions varied. Most common method was distillation with base (e.g. MgO) which releases ammonia that can be titrated. In colorimetric methods, filtering or centrifugation was used to get a solution suitable for colorimetric determinations in flow injection analyser (FIA) or autoanalyser.

A few laboratories performed Kjeldahl digestion of the extracted and filtered/centrifuged sample. Thus their results include also organic N in small soluble particles. The main difference towards determination of sole NH4-N comes from the inclusion of small-size particles passing the filtration paper or remaining in the solution after centrifugation. Because these small particles contain organic N, the digestion of filtrate will lead to higher N concentration than the direct NH4-N determination. Digestion of filtrate with autoclavation and FIA measurement after that, is another route to include N from small organic particles.

Table 4. Extraction solutions and methods of NH4-N determination in the participated laboratories.

Extraction solution	Water			KCI	K ₂ SO ₄	HCl or HCl + CaCl₂
Number of laboratories	8			2	1	2
Determination method	Distillation	Kjeldahl + distillation	FIA	FIA	Kjeldahl + distillation	Distillation
Number of laboratories	5	2	1	2	1	2



Figure 6. Flow injection analyser (FIA) used for determining ammonium-N in solution (Photo: Åsa Myrbeck).

Available standards

The existing standards for extraction methods in a scope of "Soil improvers and growing media (CEN/TC 223)" are 1:5 water extraction (EN 13652) and 1:5 $CaCl_2$ -DTPA extraction (EN 13651). In the scope of "Sludge, soil and treated biowaste CEN/TC 444" the standard for determination of ammonium, nitrate and nitrite has 1:20–80 extraction ratio with 1 M KCl (EN 16177). ISO-standards for soil have the extraction with 1 M KCl in 1:5 ratio (ISO 14256-1 and 2). The Russian standard, GOST 26716-85, advices the extraction of a sample with 0.05 M HCl. For determination of NH₄-N after the extraction, there are several standards available and auto-analysers also have their own protocols that can be followed.

Extraction: EN 13652 (1:5 water extraction), EN 13651 (CAT-DTPA extraction), EN 16177 (1 M KCl extraction), ISO 14256-1 and 2 (1 M KCl extraction), GOST 26716-85 (0.05 M HCl)

Determination: EN ISO 11732:2005 (Flow spectrophotometric), ISO 5664:1984 (Distillation), ISO 7150-1:1984 (Manual spectrophotometric), ISO 7150-2:1986 (Automated spectrophotometric method), ISO 14256-2: 2005 (Segmented flow analysis), GOST 26716-85 (distillation or photometric)

Discussion

Peters et al. (2003) describe three recommended methods for determining ammonium nitrogen and they were distillation/titration, colorimetric method and electrode. The recommended distillation

method has the sample size of 3-10 g and sample is diluted in 425 ml water and distilled immediately with magnesium oxide. In the recommended electrode method, 1-2 g of sample is mixed with 100 ml of water and shaken for one hour before the electrode measurement. In colorimetric determination of NH_4^+ Peters et al. (2003) suggested that liquid manures would be filtered to remove solids clogging the tubes of autoanalyser. For semi-solid and solid manures they suggest extraction of 0.5 g sample with 30 ml 2 M KCl, shaking of 20 min, followed by centrifugation or filtration.

The extraction of ammonium-N is probably most variable part of the measurement. We can only state that water or salt solutions are possible extractants and then centrifugation or filtration should take out the distracting particles for colorimetric analysis.

When comparing NH₄-N or soluble N after Kjeldahl digestion of the extractant, we think that it is clearer to determine only NH₄-N. Then there is no need to discuss the method to produce to filtrate, what is the pore size of paper or the time and speed of centrifugation. N retained in small organic particles can be quite well available for plants, but that is not fully clear or consistent with all manure types.

One additional aspect in NH₄-N determinations is to remember to minimize the NH₃-evaporation during extraction and filtration. In some manure types, nitrate-N can be formed in aerobic conditions and thus nitrate-N should be considered in analyses of them. For quality control, the same procedure as for total N is suggested by Peters et al. (2003), 10% of samples should be replicated and a reference sample included with each batch of samples.

Recommendation:

Ammonium-N is measured from fresh samples. As an extractant for solid samples, salt solutions are usually more efficient then water, but both methods must be considered usable. The NH_4 -N determination either by distillation and titration or by colorimetric methods are both viable and standardized methods. Distillation and titration have less requirements for pretreatment, as only dilution during the actual determination is necessary. Colorimetric methods need centrifuged or filtrated samples. In manure samples, that can contain nitrate-N, its measurement should be included in the analysis.

5.4. Total P and K (and other nutrients)

Procedures in laboratories

In participating laboratories several methods were used with strong acids as extractant. Methods included either dry ashing before acid treatment or wet digestion with the acid (Table 4). Determinations of elemental concentrations were done either with ICP or AAS (Table 5). One laboratory used X-ray method. All methods should lead to similar results from manures that are mostly organic and do not contain chemicals or minerals that bind phosphorus or potassium strongly.

Table 5. The number of participated laboratories using different digestion methods. A few laboratories used different methods depending on matrices or work load.

Nitric	Sulfuric	Hydrochloric	Aqua Regia (HNO ₃
acid	acid	acid	+ HCl)

Dry ashing		1	4	
Wet digestion (digestion vessels, microwave oven or autoclave)	4	2	1	2





Figure 7. Microwave oven to digest samples with acid (Photo: Lauris Leitans), and samples that have been extracted with nitric acid (Photo: Åsa Myrbeck).

For determination of elements, most laboratories had inductively coupled plasma-atomic/optical emission spectroscopy (ICP-AES/ICP-OES) in their use. A few laboratories used the methods where phosphorus was determined with colorimetric methods and other elements with atomic absorption spectrometer (AAS).

Available standards

Aqua regia extraction is common standard method among different matrices, and it is available for growing media, sludge, soil, soil improvers, treated biowaste, sludge and water. Nitric acid is another strong acid, where standards are available for soil, sludge, treated biowaste and water. There are respective standards for determining P and other elements from the digestates. Regarding phosphorus, there are also FIA-methods grouped in Water quality – subcommittee of ISO.

Digestion: Aqua regia: EN 13650:2001, EN 13657:2002, EN 16173:2012, EN ISO 11885:2007, EN ISO 54321; Nitric acid: EN 16174:2012, ISO 16729:2013; Nitric acid + Hydrofluoric acid: EN ISO 16967:2015

Determination: EN 14672:2005, EN 16170:2016 (ICP-OES), EN 16171:2016 (ICP-MS), EN 16188:2012 (AAS), ISO/TS 16965:2013 (ICP-MS), ISO 11047: 1998 (AAS), EN ISO 11885: 1998 (ICP-AES), ISO 9964-3: 1993 (Flame emission), EN ISO 6878:2004 (Spectrometric), EN ISO 15681-1:2003 (FIA), EN ISO 15681-2:2003 (CFA)

Discussion

Strong acids destroy the organic matter of manure and make the elements of interest soluble. Wolf et al. (2003) mention three predominant methods: 1) heating the sample in muffle furnace and adding acid to the resulting ash; 2) adding concentrated acid to the sample and incorporating heat; and 3) adding concentrated acid to the sample in sealed vessel and heating the sample with microwave energy. Regarding comparison between dry ashing and wet digestion, Ali et al. (1988) did not found differences in total Ca, Mg, K and P concentrations of the tested peat soil. Twyman (2005) reviewed different use of different acids in wet digestion and methods to avoid contamination and losses of studied elements.

Kovar (2003) lists atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES/ICP-OES) and colorimetry as the most commonly used methods in laboratory to determine elemental concentrations.

Recommendation:

For organic matter breakdown in manure most combinations of ashing or wet digestion with strong acids should produce sufficient result. For determination of elements, the ICP-OES is the most reliable method. If the size or capacity of the laboratory do not support purchasing ICP-OES, the older method determining phosphorus with colorimetric methods and other elements with AAS is also fully viable. In case of trace elements determinations, ICP-OES is usually not detecting precisely very small concentrations, whereas ICP-MS is recommended when low concentrations of trace elements are of interest.

5.5. Total C and organic matter

Procedures in laboratories

There are usually two methods used in determination of manure organic matter or total carbon content. The difference in mass before and after ignition in the furnace is used to calculate loss on ignition that is suggested to describe organic matter. The second method (Dumas) is based on high temperature combustion to oxidise carbon and measure the released carbon. In the participated laboratories both dry ashing with temperatures 450–600°C and up to 800°C in Russia and Dumas method were used.

Available standards

When measuring organic matter with loss on ignition, in most recommendations the furnace is heated up to 550°C, although in EN 13039 for Soil improvers and growing media the maximum temperature is only 450°C. In the Russian standard GOST 26714-85 for organic fertilisers, temperature of furnace is risen to 800°C. It should be remembered while loss on ignition is often used as an estimate of organic matter, inorganic substances or decomposition products (e.g. H₂O, CO₂, SO₂, O₂) are released or absorbed and some inorganic substances are volatile under the reaction conditions.

This dry combustion method (Dumas) has mostly replaced chemical oxidation methods due to often toxic chemicals of them. It must be kept in mind that Dumas method measures all carbon and thus also inorganic carbon is included in the result. Available standards are EN 15936:2012 and ISO 10694:1995.

Discussion

The relation between organic matter and carbon contents is widely studied for soil samples. The Van Bemmelen factor, 1.724, is often used to estimate relationship between soil carbon and organic matter, and it is based on assumption that organic matter is 58% carbon. However, there exist considerable variation among relationship between carbon and organic matter in different soils, and based on the variation on the soil organic matter composition, range of conversion factor can be between 1.4 and 2.5 (Pribyl 2010). There are few comparisons between total carbon and organic matter of manures. In the dataset of this project, we had only 8 samples from both carbon and organic matter content were determined. In these samples organic matter/total C (OM/TC) was 2.0 ranging from 1.7 to 2.4. Moral et al. 2005 tested manures of eight different farm animal groups and got OM/TC averaged to 1.72 (n=32). Larney et al. (2005) analysed 3000 manure and compost samples resulting to average OM/TC of 1.9, while the range was from 1.5 to 2.6.



Figure 8. Unit used for measuring total carbon and nitrogen content of dry samples with Dumas method (Photo: Åsa Myrbeck).

Recommendation:

Loss on ignition in furnace would give organic matter content and Dumas method would measure total carbon and they are both well-known methods. Regarding temperature for loss on ignition, the recommended temperature of 550°C in EN 15935 is preferred. The proportion of carbon and organic matter can vary between manures, so interpretations between total carbon of Dumas method and organic matter from loss on ignition should be used with precaution.

Standards and references:

Loss on ignition: EN 12879:2000, EN 13039:2011, EN 15169:2007, EN 15935:2012, GOST 26714-85 Dumas: EN 15936:2012, ISO 10694:1995, ISO 16948:2015

5.6. pH

Procedures in laboratories

In participated laboratories, pH was measured with electrode. Usually solid samples were diluted with 1:5 water ratio but also 1:2.5 was used. One laboratory used 1 M KCl (1:5) and three German

laboratories used 0.01 M CaCl₂ with the ratio of 1:5. Measuring pH with salt solutions should usually lead in lower values than water-pH.

Available standards

Standard for determining pH of growing media (EN 13037:2011) uses 1:5 water extraction from moist samples. Standard for sludge, treated biowaste and soil (EN 15933:2012) starts with extraction either with water or $0.01~M~CaCl_2$ using the ratio of 1:5 for solid samples. pH of liquid sludge can be determined without water addition. Standard of pH determination from soil samples (ISO 10390:2005) mentions three possible extraction methods with the ratio of 1:5, which are water, 1~M~KCl and $0.01~M~CaCl_2$. This standard is applicable for all types of air-tried soil samples. All standards recommend measurement immediately after or whilst being stirred.

Discussion

For liquid manure, pH can be directly measured by electrode. In case of solid and semi-solid manures, slurry must be formed and different manure to water or salt solution can be used. Wolf (2003) describes a method based on 1:2 manure to water ratio. Solid samples with high amount of straw or sawdust may require more water to create enough slurry for proper pH electrode operation (Wolf 2003).

Wolf (2003) recommends perform replicated analysis on 10% of samples. Reference material should be included in each batch of samples or each group of 30 samples.



Figure 9. pH-meter. Photo: Lauris Leitans.

Recommendation:

Measurement with electrode is the prevailing method. Dilution and shaking with 1:5 ratio of water is a common method and approved in both CEN and ISO standards. If the practice has been based on other standards using salt solutions with 1:5 ratio, it is also fully approved method.

Standards and references:

EN 13037:2011, EN 15933:2012, ISO 10390:2005.

5.7. Volume weight (Bulk density)

Procedures in laboratories

Volume weight of manure samples were usually not analysed in this project. Most laboratories did either not use any method or did not report it. The reported methods had sample sizes of 100-1000 ml. Mostly the method was based on EN13040.

Available standards

The standard applied for soil improvers and growing media (EN13040) uses a pressure (9.17 g/cm²) to compact the sample in a test cylinder having diameter of 10 cm and height of 13 cm. Test cylinder should have a capacity of approximately one litre. The bulk density standard of solid biofuels (EN ISO 17828) has options for 5 or 50 litre cylinders, where test portions or densified by shock exposure.

Standards and references: EN13040, EN ISO 17828

Discussion

The laboratory determined volume weight can be used to convert results between volume and weight basis in the laboratory conditions. We must, however, keep in mind that in practice the volume weight of solid manure and deep litter will be very heterogeneous and it will depend on handling and transport of the manure.

Recommendation:

Weight of one litre sample (EN13040) is useful in laboratory purposes to convert values from mass to volume, but its use for farm conditions is not reliable, especially for solid manure and deep litter.



Figure 10. Test cylinder of one litre, removable collar and weight used in volume weight measurements. (Photo Tapio Salo).

5.8. Quality control

Procedures in laboratories

Only two labs from Sweden reported using standard samples and taking part in ring tests. Replication of samples varied from duplicating every sample, to every 5th or 10th replicated. Nitrogen analysis tended not to get different treatment regarding replicates. One laboratory reported that it replicated especially N-analysis. German laboratories reported that they are following the guidelines of German Accreditation Body.

Available standards

Even if laboratories did not mention in the questionnaire, most of them likely follow ISO 9001:2015 and ISO 17025:2017 standards. ISO 9001:2015, "Quality management system requirements", addresses the general requirements for integration of quality management system. ISO 17025:2017, "General requirements for the competence of testing and calibration laboratories" includes general requirements regarding impartiality and confidentiality, structural requirements, and requirements for resources needed such as personnel and facilities, as well as technical resources such as equipment and environmental conditions.

Standards:

ISO 9001:2015, ISO 17025:2017,

Discussion

Ring tests (also called as proficiency tests) specifically for manure samples are rare. Majority of available and relevant tests are aimed for compost or sludge samples. Survey conducted in UK identified 20 proficiency test schemes suitable for composts (WRAP 2015).

The French run BIPEA scheme (PTS 45 Organic fertilizing materials / PTS 38 - Activated sludge & sediments) covers the majority of parameters required by manure analysis https://www.bipea.org/soils/.

WEPAL scheme is run from the Netherlands and has two tests possible for manures. In the BIMEP test for solid biofuels (http://www.wepal.nl/website/products/BIMEP.htm), the products to be examined are solid organic materials like wood, straw, pulp, manure and compost. Four ring tests are planned annually. This test is developed for the purposes of using standards that are among the technical TC/335). committees of Solid biofuels (ISO/TC 238 and CEN MARSEP (http://www.wepal.nl/website/products/MARSEP.htm) has samples of dried compost, manure and refuse of which total elemental concentrations will be determined.

LÜRV-A Bioabfall scheme is organised amongst German laboratories to ensure compliance with general characterisation of compost in Germany (https://www.lfl.bayern.de/zentrale_analytik/031890/index.php).

There can exist national reference laboratories that organize proficiency tests. For example, the Finnish national environmental reference laboratory makes regularly interlaboratory comparison tests for composts, sludges, soil improvers and waste water, that can be used validating the methods used in manure analysis (https://www.syke.fi/en-US/Services/Quality and laboratory services).

There can be national organisations like German Quality Assurance Organisation for Compost - Bundesgütegemeinschaft Kompost e.V. (BGK) that can recognize laboratories based on qualification demands of BGK. For the quality assurance systems of BGK, the laboratories are obliged to take part successful in a ring test for biowaste every 2 years. With this certificate of the ring test they can be acknowledged for the quality assurance.

Recommendation:

Laboratories follow standardised or well validated methods, and participate regularly in ring tests. Use of replicated and standard samples is based on Quality management system. Accreditation of suitable organisation is highly supported. Special attention in quality control should be paid for ammonia and total nitrogen analyses, where loss of ammonia can lead to smaller results than real.

6. Understanding the manure test report (same as in the Instructions for sampling)

6.1. Wet basis or dry matter basis

The results of manure analysis can be reported in different ways, for example based on wet or dry matter weight (assembled basis or dry matter basis). If expressed on a dry weight basis (kg/kg DM), the values can be converted to a wet-weight basis as:

Nutrient content (%) on a wet weight basis = Nutrient content (%) on a dry weight basis x (% total solids/100)

The value obtained is then kg nutrient/kg wet weight slurry. Multiplying by 1000 will convert to kg/tonne slurry.

6.2. Volume and weight

Slurry and urine are in most cases considered to have a volume weight of 1 kg per litre or one tonne per m³. The volume weight of solid, semi-solid and deep litter manure varies greatly depending e.g. on the type and amount of litter used.

6.3. Phosphorus versus P₂O₅

The manure test results may be expressed as total elemental P or P_2O_5 . Conversion between the two can be made using:

 $P_2O_5 = Total P x 2.29$

6.4. Potassium versus K₂O

The manure test results may be expressed as total elemental K or K₂O. Conversion between the two can be made using:

 $K_2O = Total K x 1.2$

7. Conclusions

The survey of used methods in 20 laboratories around Baltic Sea shows that there is need for communication and knowledge sharing related to manure analysis. Because laboratories usually analyse many different matrices, the specific properties of manure are not necessarily considered in details by laboratories. Use of international standards and participating in proficiency tests is part of the knowledge sharing between countries and laboratories. Although liquid and solid manure samples are challenging matrices for internal reference samples, laboratories should include proper manure samples in their references.

Analyses of total and ammonia nitrogen concentration are usually the most challenging methods as volatilisation of ammonia and microbial activity in the sample can change concentrations. Another challenge for methods is related to certain manure types (e.g. poultry and fur manure) that usually have high nutrient concentrations.

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Appendix 1: Standards

Following list includes standards considered relevant for manure analysis. Standards are classified according to Technical Committees (TC) of European Standardszation Organisation (CEN) and International Standardszation Organisation (ISO). Standards used in Russia are also listed.

Soil quality (ISO/TC 190):

- ISO 10390:2005. Soil quality Determination of pH. (1:5 in water or 1 M KCl or 0.01 M CaCl2). 7 p.
- ISO 10694:1995. Soil quality -- Determination of organic and total carbon after dry combustion (elementary analysis). 7 p.
- ISO 11261:1995 Soil quality -- Determination of total nitrogen -- Modified Kjeldahl method. 4 p.
- ISO 11465: 1993. Soil quality–Determination of dry matter and water content on a mass basis Gravimetric method. 3 p.
- ISO 13878:1998. Soil quality Determination of total nitrogen content by dry combustion ("elemental analysis"). 5 p.
- ISO 14255:1998. Soil quality Determination of Nitrate Nitrogen, Ammonium Nitrogen and Total Soluble Nitrogen In Air-Dry Soil Using Calcium Chloride Solution As Extractant.
- ISO 14256-1: 2003. Soil quality Determination of nitrate, nitrite and ammonium in field-moist soils by extraction with potassium chloride solution part 1: manual method
- ISO 14256-2: 2005. Soil quality Determination of nitrate, nitrite and ammonium in field-moist soils by extraction with potassium chloride solution part 2: automated method.
- ISO 14869-3:2017. Soil quality Dissolution for the determination of total element content Part 3: Dissolution with hydrofluoric, hydrochloric and nitric acids using pressurised microwave technique. 9 p.
- EN ISO 16720:2007. Soil quality Pretreatment of samples by freeze-drying for subsequent analysis (ISO 16720:2005). 8 p.
- ISO 16729:2013. Soil quality Digestion of nitric acid soluble fractions of elements. 8 p.
- ISO/TS 16965:2013. Soil quality –Determination of trace elements using inductively coupled plasma mass spectrometry (ICP-MS). 13 p.
- ISO 18512:2007. Soil quality-Guidance on long and short-term storage of soil samples. 15 p.

Water quality (ISO/TC 147 and CEN/TC 230):

- ISO 5663:1984. Water quality -- Determination of Kjeldahl nitrogen -- method after mineralization with selenium. 4 p.
- ISO 5664:1984. Water quality Determination of ammonium: distillation and titration method
- EN ISO 5667-15: 2009. Water quality. Sampling. Part 15: Guidance on the preservation and handling of sludge and sediment samples. 21 p
- EN ISO 6878:2004: Water quality Determination of phosphorus Ammonium molybdate spectrometric method. 21 p.
- ISO 7150-1. 1984. Water quality Determination of ammonium Part 1: Manual spectrometric method. 7 p.
- ISO 7150-2. 1986. Water quality Determination of ammonium Part 2: Automated spectrometric method. 7 p.
- ISO 7980: 1986. Water quality Determination of calcium and magnesium Atomic absorption spectrometric method. 3 p.
- ISO 10523:2008. Water quality Determination of pH. 13 p.
- EN ISO 11732:2005. Water quality Determination of ammonium nitrogen by flow analysis (CFA and FIA) and spectrometric detection. 18 p.

- EN ISO 11885:2007. Water quality Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES). 28 p.
- EN ISO 11905-1:1998. Water quality. Determination of nitrogen. Part 1: Method using oxidative digestion with peroxodisulfate (ISO 11905-1:1997). 16 p.
- EN ISO 13395:1996. Water quality- Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection. 18 p.
- ISO 15587-1: 2002: Water quality Digestion for the determination of selected elements in water Part 1: Aqua regia digestion. 18 p.
- ISO 15587-2:2002. Water quality Digestion for the determination of selected elements in water Part 2: Nitric acid digestion. 17 p.
- EN ISO 15681-1:2003. Water quality Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) Part 1: Method by flow injection analysis (FIA). 19 p.
- EN ISO 15681-2:2003. Water quality Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) Part 2: Method by continuous flow analysis (CFA). 18 p.

Solid biofuels (ISO/TC 238 and CEN/TC 335):

- EN ISO 17828:2015. Solid biofuels Determination of bulk density. 11 p.
- EN ISO 18134-1:2015. Solid biofuels Determination of moisture content Oven dry method Part 1: Total moisture Reference method. 5 p.
- EN ISO 16948:2015. Solid biofuels Determination of total content of carbon, hydrogen and nitrogen. 9 p.
- EN ISO 16967:2015. Solid biofuels Determination of major elements Al, Ca, Fe, Mg, P, K, Si, Na and Ti. 13 p.

Soil improvers and growing media (CEN/TC 223):

- EN 13037:2011. Soil improvers and growing media Determination of pH. (1:5 water).
- EN 13039:2011. Soil improvers and growing media Determination of organic matter content and ash.
- EN 13040:2007. Soil improvers and growing media. Sample preparation for chemical and physical tests, determination of dry matter content, moisture content and laboratory compacted bulk density). 16 p.
- EN 13650:2001. Soil improvers and growing media Extraction of aqua regia soluble elements.
- EN 13651:2001. Soil improvers and growing media Extraction of calcium chloride/DTPA (CAT) soluble nutrients. 29 p.
- EN 13652:2002. Soil improvers and growing media Extraction of water soluble nutrients and elements. 30 p.
- EN 13654-1: 2001. Soil improvers and growing media. Determination of nitrogen. Part 1: Modified Kjeldahl method. 11 p.
- EN 13654-2: 2001. Soil improvers and growing media. Determination of nitrogen. Part 2: Dumas method. 9 p.

Test methods for environmental characterization of solid matrices (CEN/TC 444):

- EN 13656:2002. Characterization of waste Microwave assisted digestion with hydrofluoric (HF), nitric (HNO3) and hydrochloric (HCl) acid mixture for subsequent determination of elements.
- EN 13657:2002. Characterization of waste Digestion for subsequent determination of aqua regia soluble portion of elements.
- EN 15169:2007. Characterization of waste Determination of loss on ignition in waste, sludge and sediments. 16p.

- EN 15933:2012. Sludge, treated biowaste and soil Determination of pH. (1:5 water and 0.01 M CaCl₂).
- EN 15934:2012. Sludge, treated biowaste and soil Calculation of dry matter fraction after determination of dry residue or water content. 20 p.
- EN 15935:2012. Sludge, treated biowaste, soil and waste Determination of loss on ignition. 12 p.
- EN 15936:2012. Sludge, treated biowaste, soil and waste Determination of total organic carbon (TOC) by dry combustion. 25 p.
- EN 16168:2012. Sludge, treated biowaste and soil. Determination of total nitrogen using dry combustion method. 12 p.
- EN 16169: 2012. Sludge, treated biowaste and soil. Determination of Kjeldahl nitrogen. 13 p.
- EN 16170:2016. Sludge, treated biowaste and soil Determination of elements using inductively coupled plasma optical emission spectrometry (ICP-OES). 25 p.
- EN 16171:2016. Sludge, treated biowaste and soil Determination of elements using inductively coupled plasma mass spectrometry (ICP-MS). 23 p.
- EN 16173:2012. Sludge, treated biowaste and soil Digestion of nitric acid soluble fractions of elements. 12 p.
- EN 16174:2012. Sludge, treated biowaste and soil Digestion of aqua regia soluble fractions of elements. 13 p.
- EN 16177: 2012. Sludge, treated biowaste and soil. Extraction for the determination of extractable ammonia, nitrate and nitrite. 14 p.
- EN 16179:2012. Sludge, treated biowaste and soil Guidance for sample pretreatment. 48 p.
- EN 16188:2012. Sludge, treated biowaste and soil Determination of elements in aqua regia and nitric acid digests Flame atomic absorption spectrometry method (FAAS).
- EN ISO 54321:2019. Soil, treated biowaste, sludge and waste Digestion of aqua regia soluble fractions of elements. 37 p.

Characterization and management of sludge (CEN/TC 308):

- EN 12879:2000. Characterization of sludges Determination of the Loss on Ignition of Dry Mass. 14 p.
- EN 12880:2000. Characterisation of sludges Determination of dry residue and water content
- EN 13342:2000. Characterization of sludges Determination of Kjeldahl nitrogen
- EN 14671:2006. Characterisation of sludges Pretreatment for the determination of extractable ammonia using 2 mol/l potassíum chloride.
- EN 14672:2005. Characterization of sludges Determination of total phosphorus.

Standards in Russia:

- State Standard GOST 26713-85 Organic fertilizers. Method for determination of moisture and dry residue. http://docs.cntd.ru/document/gost-26713-85
- State Standard GOST 26714-85 Organic fertilizers. Method for determination of ash content. http://docs.cntd.ru/document/gost-26714-85
- State Standard GOST 26715-85 Organic fertilizers. Methods for determination of total nitrogen. http://docs.cntd.ru/document/1200019311
- State Standard GOST 26716-85 Organic fertilizers. Methods for determination of ammonium nitrogen http://docs.cntd.ru/document/gost-26716-85
- State Standard GOST 26717-85 Organic fertilizers. Method for determination of total phosphorus. http://docs.cntd.ru/document/gost-26717-85

Appendix 2. Project partners

Project Partner	Country	Organisation
PP 1	FI	Natural Resources Institute Finland (Luke)
PP 2	PL	Institute of Soil Science and Plant Cultivation
PP 3	SE	RISE - Research Institutes of Sweden
PP 4	FI	HELCOM
PP 5	LT	Lithuanian University of Health Sciences
PP 6	EE	Estonian University of Life Sciences
		Julius-Kühn-Institute (JKI), Federal Research Centre for
PP 7	DE	Cultivated Plants
PP 8	FI	Finnish Environment Institute SYKE
PP 9	DK	Aarhus University
PP 10	DK	Danish Agriculture & Food Council, SEGES
PP 11	SE	Swedish Board of Agriculture
PP 12	LV	State Plant Protection Service
PP 13	EE	Estonian Crop Research Institute
		Central Union of Agricultural Producers and Forest
PP 14	FI	Owners (MTK)
PP 15	PL	Agricultural Advisory Center in Brwinów
PP 16	LV	Farmers' Union Parliament
		State budgetary vocational educational institution of
PP 18	RU	the Pskov region "Pskov Agrotechnical College"
		Interregional Public Organization "Society for
PP 19	RU	Assistance of Sustainable Rural Development"
		Federal State Budgetary Scientic Instition, Federal
		Scientific Agroengineering Center VIM IEEP-branch of
PP 20	RU	FSBSI FSAC VIM



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