Acidification of livestock slurry and digestate to reduce NH_3 emissions: predicting needed H_2SO_4 dosage and pH trends over time based on their chemical-physical composition

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Abstract

Acidification is a well-known treatment to reduce NH_3 emissions from livestock slurries by lowering their pH, but its application at the farm scale is still limited. The acid dosage depends on the acid strength and slurries composition. Acidification does not have a lasting effect and after the acid addition the slurry pH tends to rise due to its buffer system. By studying 54 samples of pig slurry, dairy cattle slurry and digestate, this study aimed to: (i) identify the chemical-physical parameters related to the sulphuric acid (98% w/w) dosage necessary to reduce pH at 5.5, and pH variation over time; (ii) develop predictive models for the acid dosage and the pH after one (pH1w) and two weeks (pH2w) of storage based on slurry composition by using regression trees (RT) and random forests (RF). Acid dosage ranged between 0.8-11.7 ml kg^{-1} increasing with slurry alkalinity, with digestate requiring significantly higher dosage than slurries. Pig slurry showed significantly higher pH increase than the other two slurries. Finally, the pH trend over time was negatively correlated with the solids content. The RF identified the alkalinity and the initial slurry pH as the most important variables in explaining the required acid dosage, while for pH1w and pH2w it identified the total organic carbon and volatile solids. Based on RF results, RT models accurately predicted required acid dosage

(r^2=0.881), the pH1w (r^2=0.728) and pH2w (r^2=0.667). Therefore, these simple models can have practical applications for reducing NH_3 emissions.

Keywords

Cattle slurry; pig slurry; digestate; sulphuric acid; random forests; regression trees

Nomenclature

ALK (mg $CaCO_3$ L^{-1})	Total alkalinity
CH_4	Methane
Cu (mg kg^{-1})	Copper
CO_2	Carbon dioxide
EC (mS cm^{-1})	Electrical conductivity
GHG	Greenhouse gases
H_2SO_4	Sulphuric acid
HCl	Hydrochloric acid
K (g kg^{-1})	Potassium
N_2O	Nitrous oxide
NH_3	Ammonia
P (g kg^{-1})	Phosphorus
pH1w	pH after 1 week acid addition to the sample
pH2w	pH after 2 weeks acid addition to the sample
RF	Random forest
RMSE	Root mean square error
RT	Regression tree
TAN (g kg^{-1})	Total ammoniacal nitrogen
TKN (g kg^{-1})	Total Kjeldahl nitrogen
TOC (%TS)	Total organic carbon
TS (g kg^{-1})	Total solids
VFA (mg kg^{-1})	Volatile fatty acid
VS (g kg^{-1})	Volatile solids
Zn (mg kg^{-1})	Zinc

1. Introduction

The livestock sector is one of the main producers of ammonia (NH_3) and greenhouse gases (GHG), as methane (CH_4) and nitrous oxide (N_2O), that are released into the environment (Kupper et al., 2020; Sommer et al., 2017). This sector is responsible for 78% of Europe's NH_3 emissions and 14%

of GHG emissions (particularly CH_4 and N_2O). Methane and nitrous oxide are 26 and 265 times more powerful than carbon dioxide (CO_2) in terms of global warming potential (De Pue et al., 2019; Feng et al., 2020; Gerber et al., 2013). The NH_3 emissions occur from different stages of manure management, accounting for 10-20% from storage and outdoor livestock, while the greatest proportion of NH_3 emissions arise from barns and after the manures land application, each of which account for 30-40% of NH_3 emissions (EEA, 2019). It is important to consider that in field application of manures more than 50% of the applied nitrogen can be lost, especially during the first 12-24 hours (Sommer and Hutchings, 2001).

Consequently, mitigation techniques can be introduced in several stages of the manure management to reduce the environmental impact of livestock emissions (European Commission, 2017). Among them, can be mentioned: improvements to animal housing (e.g., installation of air scrubbers and manure removal technique/frequency), manure treatments (e.g., anaerobic digestion, ammonia stripping), manure storage (e.g., tank covers), and manure application techniques (e.g., shallow injection) (Finzi et al., 2019; Sayeev et al., 2018). Although these mitigation strategies can have significant effects in reducing emissions, they act only on one specific step of the whole manure management chain. Conversely, the mitigation technique of the acidification treatment has the potential to display its effect from the production of slurry in the barn up to its field application.

Acidification consists of lowering the slurry pH to a sufficient level to minimise NH_3 emissions, both chemically through the addition of strong acids (e.g., sulphuric, hydrochloric or nitric acid), weak acids (e.g., lactic, acetic, citric acid) or other chemicals (e.g., aluminium chloride or sulphate, ferric chloride, superphosphate, elemental sulphur) and biologically by adding easily fermentable materials (e.g., saccharose, glucose, whey, sugar beet molasses) that stimulate endogenous anaerobic microorganisms to produce organic acids (Fangueiro et al., 2015; Regueiro et al., 2016a;

Gioelli et al., 2016; Gioelli et al., 2022; Kavanagh et al., 2021). However, the most applied chemical for the acidification of animal manure is sulphuric acid (H_2SO_4) due to its economic advantage and efficiency (Im et al., 2020).

With this treatment, NH_3 emissions can be reduced by 37-80% in the barn, 27-98% during storage, and 15-80% after field distribution (Fangueiro et al., 2015). The acidification enable an overall reduction in GHG emissions (Sommer et al., 2013), but with contrasting effects between CH_4 and N_2O. A significant reduction in CH_4 emissions (61-96%) can be expected both in storage (Kupper et al., 2020) and in field application (about 70%) (Fangueiro et al., 2017). Regarding N_2O emissions, acidification effect is contrasting both in storage (varying between no increase to 39% more) (Dalby et al., 2022; Kupper et al., 2020) and in field application (varying between no increase to two-three times more) (Fangueiro et al., 2017; Gomez-Munoz et al., 2016). This treatment is an already widespread solution in Northern European countries such as Denmark, and its effectiveness has been confirmed by many studies (Im et al., 2020; Petersen et al., 2016; Regueiro et al., 2016b; Sommer et al., 2017). In general, there are three main technologies for the acidification of slurries: in-house acidification, storage tank acidification, and acidification at field application (Fangueiro et al., 2015).

A reduction of emissions occurs when the pH is lowered to values below 7, and it is commonly recognised that reducing the pH to 5.5 is an optimal compromise between the acid dosage and the emission reduction (Regueiro et al., 2016a; Kai et al., 2008; Fangueiro et al., 2015).

The type of acid used and the slurry composition, especially its strong chemical buffer system (Sommer and Husted, 1995), affect the acid dosage needed to reach the target pH value, as well as its effect over time. The most important chemical components of slurry that control the buffer system and pH are the acid-base pairs: $H_2CO_3/HCO_3^-/CO_3^{2-}$, NH_4^+/NH_3, and CH_3COOH/CH_3COO^- (Christensen and Sommer, 2013; Sommer and Husted 1995).

However, after acidification, the pH increase over time can impact both NH_3 and GHG emissions. When acid addition is equivalent to the total alkalinity of the slurry the pH drops to approximately 4.2-4.5 and its rise is zero or very slow. In this case NH_3 emissions can be reduced up to 95% or even totally (Husted et al., 1991; Petersen et al., 2012). When acid addition lowers the pH to 5.5 it tends to rise faster, returning to the initial level between 12 and 60 days (Overmeyer et al., 2021; Regueiro et al., 2016a) and this also affects NH_3 and GHG emissions. Regueiro et al. (2016a) reports a reduction in NH_3 emissions of 70% for pig slurry and 85% for cattle slurry after 60 days from the addition of H_2SO_4, as result of a pH rise from 5.5 to approximately 7. Comparable results are shown by Husted et al. (1991) after 21 days from the addition of hydrochloric acid (HCl) at different dosages, highlighting reductions in NH_3 emissions of 35% with a pH lowered to 7.2; 60% with a pH of 6.8; 90% with a pH of 6.5; 100% with a pH of 5.8. Regarding methane emissions Petersen et al. (2012) report that acidification of slurry reduced the evolution of CH_4 from 67% with a starting pH of 5 to 87% with a pH of 4.5.

An economic evaluation of the acid requirements to keep the pH low enough to be effective while avoiding an increase in emissions is necessary.

The unacidified liquid manure undergoes minor fluctuations in pH during storage. These fluctuations could be insignificant (Sommer et al., 2017; Regueiro et al., 2016a) or have a slight upward trend (Petersen et al., 2012).

Acidification has been shown to reduce NH_3 emissions in pig and cattle slurry, but there is limited research on its effects on digestate (Fangueiro et al., 2015). Existing literature highlights considerable variability in both acid dosage and its impact over time, but each study focuses on a very limited number of samples, no more than 5 (Habtewold et al., 2018; Petersen et al., 2014; Regueiro et al., 2016a; Sokolov et al., 2020). Therefore, to evaluate the applicability of acidification techniques in a wide context of livestock farms, we investigated the application of acidification on a dataset of 54 different samples of livestock slurries (pig and cattle slurry and digestate) to (i) identify the chemical-physical parameters that have a significant influence on the acid dosage and its effect on pH over time and (ii) develop predictive models on acid dosage based on the composition of the effluents but also on the duration of the acidification effect. This would enable more effective planning and management of the acidification treatment (dosage and time of use) in livestock farms by optimising the acid consumption and supply, minimising the risk of pH rises which would consequently reduce the risk of an increase in emissions.

2. Materials and methods

2.1. Sample collection and analysis

A total of 54 samples, including 19 pig slurries, 18 dairy cattle slurries and 17 digestates, were collected from 35 farms in Lombardy, Italy. Fresh slurry samples of 10 L each were taken from the slurry reception pits on dairy farms with concrete floor and scrapers or during the emptying process in dairy and pig farms with slatted floor, while digestate was collected directly from the digesters.

The characteristics of farms, such as livestock housing system, slurry removal technique and feedstock used in the biogas plant, are reported in Table S1.

Immediately after delivery to the laboratory, three subsamples were taken from each sample: (i) 0.5 L for carrying out the chemical-physical analyses; (ii) 2.25 L for the acidification test; (iii) 1.5 L as a control for the acidification test. The samples were stored at +4 °C and analysed within 24 hours. Analyses of the content of total solids (TS), volatile solids (VS), ash, total Kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN), total alkalinity (ALK), pH, and electrical conductivity (EC) were performed on all samples. All parameters were analysed using standard methods (APHA, 2012). In detail, for the TS determination approximately 25ml of raw manure was dried in the oven at 105 °C for 24h. The resulting dried sample was dried in the muffle furnace at 550 °C until the complete combustion of the organic fraction to determine Ash and the VS as difference of Ash with TS. TKN was determined through a sulphuric acid digestion plus acid distillation and a titration, while TAN was determined directly by an acid distillation and a titration. EC and pH were determined potentiometrically. Total alkalinity (ALK) was determined by a two points titration at pH levels 5.75 and 4.3. Regarding Phosphorus (P), potassium (K), copper (Cu) and zinc (Zn) their contents were determined according to an international standardised method (EPA, 2007). In brief, 500 mg of dried samples were digested with concentrated HNO_3 (1:10, w/v) solutions, using a vapor recovery digestion system. These solutions were analysed by inductively coupled plasma mass spectrometry (ICP-MS, Varian, Fort Collins, USA). Slurry samples were also analysed for total organic carbon (TOC) after dry combustion (ISO, 10694:1995) and volatile fatty acids (VFAs) by ion chromatography on filtered and diluted slurry samples. Specifically, a Metrohm ECO IC 1.925.0020 was used with metrosep organic acids 250/7.8 column. Afterward, the ratios of VS/TS, TAN/TKN, and VFA/ALK ratio, were determined.

2.2. Acidification test

For each sample, acidification was conducted in triplicate, and the control test (no acidification) was performed in duplicate. Each replicate consisted of a 1 L beaker filled with 0.75 L of sample. Acidification was conducted by adding H_2SO_4 (98% w/w) to the slurry sample to adjust the pH to 5.5. The acid was added 0.2 mL at time using a micropipette while mixing the slurry manually and measuring pH (pH meter HI 902, Hanna instruments, Inc.). Finally, the acid dosage to lower the pH to 5.5 and the pH level reached were recorded.

Beakers were stored at 15 °C for two weeks, and daily manual measurement of pH was carried out on all beakers after gentle mixing.

Acidification can be carried out in a storage tank shortly before the slurry field application and two weeks can be considered an adequate timing (Fangueiro et al., 2015; Petersen et al., 2012).

2.3. Statistical analyses

To determine significant differences among types of slurry for each chemical-physical parameter, an analysis of variance (one-way ANOVA) followed by Tukey post hoc tests at $p<0.05$ was conducted. Correlation analyses were performed using Pearson correlation tests to verify the relations among all variables. This evaluation was useful to (i) understand the role of each parameter representing the chemical-physical characteristics of the slurries on the acid dosage to lower the pH to 5.5 and on its capacity to keep it low over time and (ii) verify the collinearity among variables. Indeed, strong correlations between two or more predictors can inflate the variance of the parameters estimated by the models (Sokal and Rohlf, 2012).

In addition, a more in-depth evaluation of the pH evolution over time was set up by comparing the slopes of linear regressions related to the pH increase rate of the three types of slurries during the two weeks of monitoring, both for acidified and nonacidified samples. This comparison was performed using the slope of linear regression models. These statistical analyses were performed with IBM ®SPSS® 27 software (IBM Corp., Armonk, NY, USA).

Furthermore, predictive models were developed to estimate the acid dosage (ml kg^{-1}), pH1w (pH after 1 week acid addition to the sample), or pH2w (pH after 2 weeks) by using regression trees (RT) and random forests (RF).

RT and RF are classification methods with high classification accuracy and can uncover complex relations between the response and the predictor variables (Cutler et al. 2007). RT build the classification rule by recursive binary partitioning of the dataset into regions (nodes) that are increasingly homogeneous to the response variable. At each step of the procedure, an optimisation procedure (pruning) is used to select a predictor variable and a cutoff value, continuing until any further subdivision does not create more homogeneous groups (terminal nodes).

RF are machine-learning methods that have proven superiority to other statistical tools to produce accurate predictions with complex datasets. They are a development of RT that fit many trees to a dataset and then combine the predictions from all of them (Cutler et al. 2007).

RF were fitted using the randomForestSRC package in R (Ishwaran and Kogalur 2022, R Core Team 2020) to determine the chemical-physical characteristics of the slurries that were the most important in explaining added acid and slurry pH1w and pH2w. The number of RT per forest was set to 5000, and other parameters were set to default values (Ishwaran and Kogalur 2022). Based on variable importance, we selected the important variables from each RF and used these variables as inputs in an RT analysis using the rpart package in R (Therneau and Atkinson 2019). This step allowed us to identify threshold variables for each selected variable, which can be used for predictions. We stress that, albeit RF are a development of RT, we preferred to base our final model on the latter because of the easier interpretation of their results, which should boost their application in real-world cases.

Model performances were assessed by calculating the squared Pearson correlation coefficient (R-squared) and root mean square error (RMSE) between the observed values and those predicted by different models.

3. Results and discussion

3.1. Descriptive statistics on chemical-physical characteristics

Table 1 provides an overview of the chemical-physical characteristics of the samples divided for the type of slurry (pig slurries, dairy cattle slurries and digestates). The values reported are similar to those observed by other researchers (Moral et al., 2005; Cabassi et al., 2015; Finzi et al., 2015).

Table 1 also includes the results of the ANOVA test performed to assess significant differences among the three types of slurries, considering the chemical-physical parameters analysed.

The latter showed significant differences ($p<0.001$) in initial pH among the slurries, where dairy cattle slurry had a lower initial pH, while digestate had a higher average value ($p<0.001$). It is well known that pH is influenced by the TAN and VFA contents, which are two important components of the slurry buffering system on which the pH strictly depends (Christensen and Sommer, 2013); in fact, the dairy cattle slurry had lower values of TAN and higher values of VFA than the digestate. This is due to the prior anaerobic digestion treatment that mineralises the organic nitrogen into ammonia and VFAs into CH_4 and CO_2.

To evaluate the differences among slurries based on solids content, an overall evaluation was performed considering the parameters of TS ($p<0.001$), VS ($p<0.001$), ash ($p=0.002$) and TOC ($p<0.001$). The pig slurry had significantly lower TS ($p<0.001$) and VS ($p<0.001$) values than the other two slurries and significantly lower ash content ($p=0.001$) than the digestate. This occurs because in dairy farms bedding materials and rests of fibrous feed are typically removed with the manure, while in the anaerobic digesters solid biomasses are added to increase biogas production. Dairy cattle slurry had significantly higher VS ($p=0.007$) and TOC contents ($p<0.002$) than other slurries. Since digestate samples were taken from biogas plants fed mainly with livestock slurries and secondly with energy crops and agrifood byproducts (see Table S1), the TS content was similar to that of dairy cattle slurry but slightly lower.

The VS/TS ratio of digestate was intermediate between cattle and slurry and all of them were significantly different ($p<0.001$). Although in the digesters there is a drop in the VS/TS ratio as the VS are converted into biogas, the value reported in table 1 could depend on the addition of energy crops and by-products in the digesters (Table S1). These substrates have a higher VS/TS ratio than slurries and a residual amount could be found in digestate.

The nitrogen content, described by the parameters of TKN ($p=0.007$), TAN ($p<0.001$) and TAN/TKN ($p<0.001$), significantly differed among the three slurries. The TAN of dairy cattle slurry was significantly lower than that of pig slurry and digestates ($p<0.001$). This result is in line with the findings of other authors (Martinez-Suller et al., 2008; Finzi et al., 2015; Tambone et al., 2017).

The other macronutrients, P and K, have comparable values with the characteristics of livestock manure and digestates of the study area (Martinez-Suller et al., 2008; Finzi et al., 2015; Tambone et al., 2017). Observing the P content, no significant differences ($p=0.260$) emerged among the types of slurries; in contrast, K ($p=0.002$) had a significantly higher value ($p<0.007$) in the digestate. Contrary to what was reported by Finzi et al. (2015) and Martinez-Suller et al. (2008), in which the P and K contents of dairy cattle slurry were higher than those of the other slurries.

Total alkalinity (ALK) is the parameter that best describes the buffer capacity (Husted et al., 1991), and it is significantly different among slurries ($p<0.001$) and higher in the digestates than in the other slurries ($p<0.001$). In the digestates, the acidifying component constituted by VFA has been partly removed with the anaerobic digestion process, and the CO_2 derived from the degradation of VFA is not immediately emitted; therefore, CO_2 can act as a buffer in the form of carbonates (HCO_3^- and CO_3^{2-}) (Overmeyer et al., 2020). Although the ALK of dairy cattle and pig slurries does not differ significantly, it is slightly lower in dairy cattle slurry, probably because the lower TAN content, which also differed significantly between dairy cattle and pig slurries.

The VFA content that is linked with the ALK also showed significant differences among slurries ($p<0.001$). In dairy cattle and pig slurries, the VFA concentration was higher than that in digestates ($p<0.001$).

Electrical conductivity (EC) measures the major cation and anion contents in livestock slurry and can be used to indirectly estimate the nutrient content (Moral et al., 2005). The three slurries showed significant differences in this parameter ($p<0.001$), with dairy cattle slurry having significantly lower EC values than other slurries ($p<0.001$). Lower EC values of dairy cattle slurry compared to pigs were also found by other authors (Finzi et al., 2015; Martínez-Suller et al., 2008; Scotford et al., 1998), while EC values of dairy cattle slurry were higher than those of digestate (Finzi et al., 2015).

The heavy metals typical of livestock manure, such as copper (Cu) and zinc (Zn), do not reached high concentrations due to limitations in their use in animal feeding. In this study were found slightly lower values than those reported by other authors (Nicholson et al., 1999; Provolo et al., 2018; Rodrigues et al., 2021). Overall, there were no significant differences among slurries for Cu (p=0.096) and Zn (p=0.092), while pig slurries were usually more endowed with respect to dairy cattle slurries. Digestates reported slightly higher values than slurries, probably because other biomasses are used together with the slurry for the feeding of the biogas plants and increase the heavy metal content.

Table 1 Means and range (min-max) values of the chemical-physical parameters analysed for each slurry and digestate sample. Univariate ANOVA was conducted to determine significant differences among the effluents (differences are within rows). Letters next to mean values indicate significant differences (, **, *** significantly different at P<0.05, 0.01, 0.001, respectively).*

	Cattle (n° 18)		**Pig (n° 19)**		**Digestate (n° 17)**		**Anova**	
	range	**mean**	**range**	**mean**	**range**	**mean**	**$F_{2,51}$**	**p**
Initial pH	6.5-7.3	6.8a	6.7-8	7.3b	7.6-8.6	7.9c	54.3	***
TS (g kg^{-1})	9.3-110.2	70.3b	8.7-83.9	28.3a	27.7-85.2	55.8b	21.1	***
VS (g kg^{-1})	5.8-86.9	57.2c	4.7-55.3	18.4a	16.6-65.1	40.1b	27.5	***
Ash (g kg^{-1})	3.5-23.3	13.1ab	3.6-28.6	9.9a	11-22.2	15.6b	7.0	**
VS/TS (%)	62.2-84.1	80.2c	43.2-79.3	61.5a	60.2-77.1	71.1b	35.0	***
TOC (%TS)	35.5-42.5	40.7b	25.4-42	34.6a	31.7-40.6	36.7a	16.38	***
TKN (g kg^{-1})	0.6-4.3	2.9a	1.3-5.1	3.2ab	3-5.3	3.9b	5.5	**
TAN (g kg^{-1})	0.3-1.8	1.2a	1-3.5	2.3b	1.3-3.5	2.1b	18.9	***
TAN/TKN (%)	28.8-51.2	42a	52.5-83.8	71.7c	39.9-66.7	53.5b	87.2	***
P (g kg^{-1})	0.1-0.8	0.5ns	0.1-3.2	0.7ns	0.5-1.3	0.7ns	1.4	ns
K (g kg^{-1})	0.7-2.9	1.8a	0.9-3.1	1.9a	1.2-3.5	2.6b	7.2	**
Cu (mg kg^{-1})	0.4-7.1	3.4ns	0.6-17.7	5.9ns	2.9-24.7	6.7ns	2.5	ns
Zn (mg kg^{-1})	1.4-28.1	12.6ns	1.2-40.4	16.8ns	6.8-53.3	21.3ns	2.5	ns
EC (mS cm^{-1})	6.1-20.3	14.5a	10.8-29.5	21b	16.5-26.8	20.5b	12.1	***
ALK (mg $CaCO_3$ L^{-1})	2136-12500	8167a	3667-15976	10122a	10585-20016	13881b	17.0	***
VFA (mg kg^{-1})	919-9228	5703b	759-8931	4647b	397-1472	810a	36.4	***
VFA/ALK	0.4-1.1	0.7a	0.1-1.1	0.5b	0-0.1	0.1c	54.8	***

3.2. Parameters involved in the acidification process

Table 2 shows the parameters useful for understanding the applicability of the acidification treatment to livestock slurry. These parameters are the added acid expressed both in ml kg^{-1} slurry and in meq kg^{-1} slurry, pH1w and pH2w , the last two representing the evolution of pH over time after acidification.

Concerning the added acid, digestate had a significantly higher value than the dairy cattle and pig slurries. The overall range of acid dosage to lower pH to 5.5 was consistent with other studies (Habtewold et al., 2018; Petersen et al., 2014; Regueiro et al., 2016a; Sokolov et al., 2020).

Regarding the pH trend over time following acidification (Table 2), it is known that the pH value of the slurry tends to return close to its initial pH value after acidification, which is due to the buffer capacity of the slurry (Regueiro et al., 2016a; Petersen et al., 2012). Possible reasons for such an increase in pH value can be the degradation of VFAs, the mineralisation of organic nitrogen, or the dissolution of carbonates with the consequent CO_2 release (Husted et al., 1991; Sommer and Husted, 1995). The pH1w and pH2w of the pig slurry reached significantly higher values than those of the other two slurries, meaning that the acidification effect was reduced faster. This probably happens because cattle slurry and digestates have more organic matter than pig slurry and therefore have a greater catabolic activity, that leading to accumulation of CO_2 in the slurry would keep a lower pH (Petersen et al., 2012).

Table 2 - Means and range (min-max) values of the parameters related to acidification effects for each slurry and digestate sample. Target pH of acidified samples was 5.5. Univariate ANOVA was conducted to determine significant differences among the effluents (differences are within rows). Letters next to mean values indicate significant differences (, **, *** significantly different at P<0.05, 0.01, 0.001, respectively).*

	Cattle (n° 18)		Pig (n° 19)		Digestate (n° 17)		Anova	
	range	Mean	range	Mean	range	Mean	$F_{2,51}$	p
Added acid (ml kg^{-1})	0.8-5.3	3.3a	1.6-9.4	4.5a	6.1-11.7	8.2b	42.0	***
Added acid (meq kg^{-1})	28.9-191.3	119.1	57.7-339.2	162.4	220.1-422.3	295.9	42.0	***
pH1w	5.7-6.9	6.0a	5.7-7.8	6.5b	5.9-6.5	6.2ab	6.9	**
pH2w	6.1-7.7	6.5a	6-8.2	7.0b	6-6.8	6.5a	6.1	**

Fig. 1 shows the pH trends and linear regression models in both acidified and non-acidified samples during the first (Fig. 1a and 1c) and the second week (Fig. 1b and 1d).

Evaluating the slope of the regression models (referring to pH units increased weekly), for acidified samples all types of slurries showed an increase in pH in the days following acidification. This increase showed higher rates in the first week than in the second week, varying from 1.3 times for dairy cattle slurry to 4.3 times for digestate. Among the tested slurries, pig slurry had the highest slope values in both the first (0.1422) and second weeks (0.0652). For this reason, the pig slurry pH reached neutrality (pH=7) in two weeks, while dairy cattle slurry and digestate maintained acidic values after two weeks (pH approximately 6.5) (Fig. 1b), which limits ammonia emissions more effectively than in pig slurry. Furthermore, the final pH of these acidified samples remained lower than the pH before acidification.

Regarding the nonacidified samples, the increase in the first and second weeks differed depending on the slurry; in particular, pig slurry showed 1.8 times higher rates of pH increase in the first week than in the second, while for digestate, a similar trend in both weeks was observed, while a slightly opposite trend occurred in cattle slurry (higher rate in the second week). The comparison among slurries highlighted that pig slurry had the fastest trend in the first week, while digestate increased more in the second. The increases in pH that occurred in all slurries resulted in a final pH ranging between 7.0 for dairy cattle slurry and 8.4 for digestate (Fig. 1c and 1d).

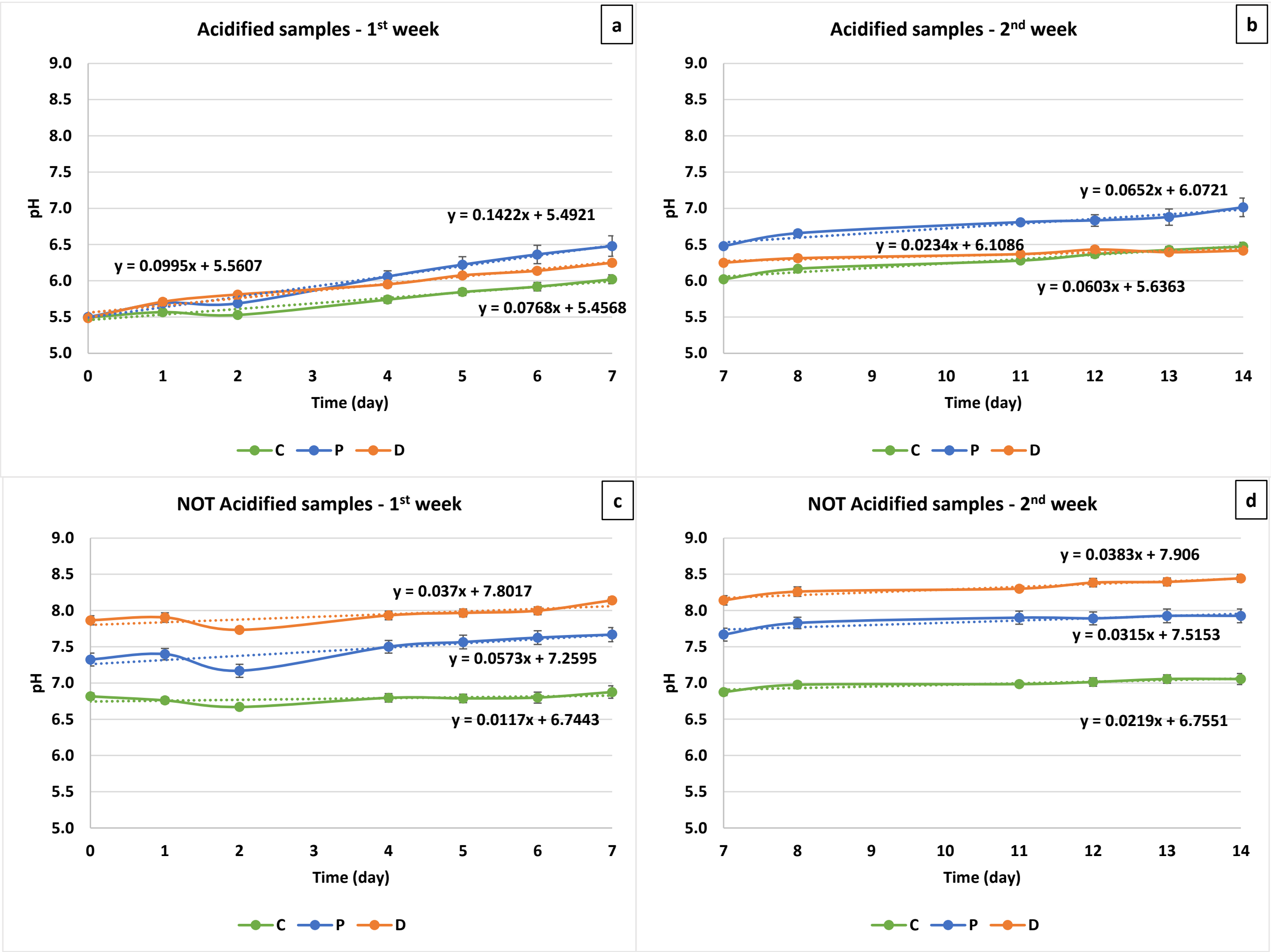

Fig. 1

The results shown in Fig. 1 are consistent with literature findings that report an increase in pH after slurry acidification carried out at pH 5.5. Sommer et al. (2017) reported a change in pH from 5.4 to 7 over 45 days of storage after acidification of liquid cattle manure with H_2SO_4. In the acidification of digested pig slurry, Wang et al. (2014) adjusted the pH to 5.5 and 6.5 using H_2SO_4. They found a rapid increase from 5.5 to 7.2 in the first 25 d and from 6.5 to 7.75 in the first 20 d, respectively. A considerable increase in pH occurred from days 54-55 in the slurry acidified to 5.5. Instead, no pH change was observed in the control groups with an initial pH of 7.5 until 10 days, although there was a gradual increase to 8.4 on day 38 (Wang et al., 2014). Rodrigues et al. (2021) showed faster pH increases in dairy slurry compared to pig slurry, which may be due to a higher initial pH of the dairy slurry (7.1) compared to that of pig (6.7), as well as a lower content of TS, TKN and TAN, which can indicate a lower buffering capacity.

Regueiro et al. (2016a) studied alternative substances to the use of H_2SO_4 for acidification of dairy and pig slurry, including lactic acid, citric acid, acetic acid and alum. A rapid increase in the pH of the acidified pig and dairy slurries from 5.5 to 6.8 - 7.3 was observed in both slurries at 20 days after the start of storage. In contrast to our findings, the increase of dairy slurry pH was faster than that of pig slurry. However, after the first 20 days, pig slurries had higher pH values than dairy slurries. Only for acidification with H_2SO_4 and alum, the pH values did not exceed the initial pH after 40 days of storage for both slurries acidified to pH 5.5.

In addition, Petersen et al. (2012) studied the acidification of fresh cattle slurry with alternative acids: HCl and potassium sulphate (K_2SO_4). They observed a pH evolution from approximately 4.5 to 6-6.5 during the 3 months of storage, while for the unacidified fresh cattle slurry, the pH increased from 7 to 7.5.

The cited studies show variability in the response times of the slurry pH to the acidification treatment. The lower the pH is, the longer it takes to return to the initial value (Petersen et al., 2012; Wang et al., 2014). The effect is not associated with the animal species from which the slurry originated; instead, it stems from the composition of the slurry (Regueiro et al., 2016a; Rodrigues et al., 2021).

3.3. Correlation analysis

The correlations between parameters used to evaluate the applicability of acidification (added acid, pH1w and pH2w) and the chemical-physical parameters are shown in Tables 3, 4 and 5 divided by type of slurry. The correlations provide insights facilitating the identification of potential strategies to enhance the acidification process by minimising acid consumption and extending its effectiveness. For dairy cattle slurry (Table 3), significant correlations emerged between the added acid and most of the parameters that describe its composition, above all EC, Ash and ALK ($r>0.921$).

Other significant correlations were found with the parameters related to the solid content, TS and VS (r>0.868) and nutrient content (r>0.828) but also with VFAs (r=0.711).

Furthermore, for pig slurry (Table 4), significant correlations emerged between the added acid and most of the parameters describing its composition, above all Ash and ALK (r>0.853). Solids, nutrients and EC showed lower correlations in pig compared to dairy cattle slurry, although they remained significant. Specifically, the correlated parameters were TS and VS (r>0.658), nutrients (r>0.706) and EC (r=0.706). In contrast, compared to the dairy cattle slurry, the initial pH of pig slurry showed a significant correlation with the added acid (r=0.690).

Regarding digestate (Table 5), a general reduction in significant correlations was observed among the considered parameters and added acid with respect to dairy cattle and pig slurry. This was probably due to the limited variability of the sample set. In this case, a high correlation could be observed between the added acid and ALK (r=0.934), while for TKN, TAN and EC, there were significant but lower correlations than for ALK (r>0.741).

These results are consistent with those reported by Sommer and Husted (1995) and Husted et al. (1991) that highlighted the ALK had a leading role in the buffering power of the effluents, able to regulate the pH, followed by the TS, EC, VFA and initial pH. Based on findings of Husted et al. (1991) the role of ALK was expected since it is determined by adding acid to the slurry.

In all the slurries, ALK was significantly correlated with EC and nitrogen content TKN and TAN, and strong correlations emerged also with TS, VS and Ash in dairy cattle and pig slurry (while not in digestate). The result on TAN was consistent with the findings of Heidarzadeh et al. (2022), while the correlations with solids content confirmed what is reported by Husted et al. (1991). Concerning EC, as this parameter is well positive correlated with TAN (Martínez-Suller et al., 2008; Scotford et al., 1998), the reduction in TAN also determines the decrease of EC as a consequence of ALK. Since the reduction of EC itself involves a reduction of TAN, TAN stands as the key parameter to control.

Regarding the role of P, K, Cu and Zn in acid consumption the correlations identified were consistent with the findings of Sommer and Husted (1995) and Rodrigues et al. (2021).

P, K, Cu, and Zn, as well as inorganic minerals in general, play a role in the buffering system of slurry, albeit secondary to TAN, VFA, and ALK (Fangueiro et al., 2015; Sommer and Husted, 1995). The impact of these minerals on pH and, consequently, on the acidification treatment, while limited, does not seem to warrant their exclusion a priori from the assessments made with RF. Specifically, among these, phosphorus has the greatest potential effects in the forms of $H_3PO_4/H_2PO_4^-$, $H_2PO_4^-$ $/HPO_4^{2-}$, HPO_4^{2-}/PO_4^{3} (Fangueiro et al., 2015), while an increase in the concentration of the K+ ion in slurry promotes a rise in pH (Christensen and Sommer, 2013).

Focusing on the pH1w of the 3 slurries, Table 3 shows that it was significantly and negatively correlated with TOC, TS and VS (r>-0.694) in dairy cattle slurry, where the importance of the other parameters that were correlated with the added acid also decreased. A similar result emerged for the pH1w of pig slurry, that was significantly correlated with TOC, TKN, VS and Zn (r>-0.758), followed by TS, P, Cu and TAN (r>-0.697). In addition, the pH1w and pH2w of pig slurry showed significant correlations with solids and nutrients, while the importance of ALK and ash decreased.

The pH1w values of the digestate did not show significant correlations with the other parameters except for the initial pH (r=0.535); the same occurred for the pH2w.

In contrast, the pH2w of dairy cattle slurry showed significant negative correlations with TOC, TS and VS (r>-0.797), while it was more correlated with TKN, P, ALK and VFAs than pH1w (r>-0.683). The initial pH of the dairy cattle slurry, on the other hand, did not show significant correlations with the added acid, confirming what was reported by Husted et al. (1991) and Overmeyer et al. (2020) and with pH1w and pH2w.

Regarding the pH2w of pig slurry, significant correlations emerged with the same parameters correlated with pH1w, although slightly stronger than at 1 week. In addition, for pig slurry, the initial pH showed no significant correlation with pH1w and pH2w.

The negative correlations between solids and pH1w and pH2w show that high solids contents, especially in the form of organic matter and organic carbon (VS and TOC), slow the pH rise after acidification, which is a positive aspect for the acidification process.

*Table 3. Correlations among the chemical-physical parameters of dairy cattle slurry. ** Pearson's correlation coefficient at the 0.01 level; * Pearson's correlation coefficient at the 0.05 level*

	acid ml kg^{-1}	pH1w	pH2w	pH	TS g kg^{-1}	VS g kg^{-1}	Ash g kg^{-1}	VS/TS %	TAN g kg^{-1}	TKN g kg^{-1}	TAN/TKN %	P g kg^{-1}	K g kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	EC mS cm^{-1}	ALK mg CaCO$_3$ L^{-1}	VFA mg kg^{-1}	VFA/ALK
acid	--																		
pH1w	-.565*	--																	
pH2w	-.606**	.897**	--																
pH	.420	.021	.106	--															
TS g kg^{-1}	.888**	-.681**	-.755**	.239	--														
VS g kg^{-1}	.868**	-.694**	-.770**	.220	.998**	--													
Ash g kg^{-1}	.926**	-.576*	-.634**	.314	.946**	.922**	--												
VS/TS %	.491*	-.839**	-.882**	-.071	.681**	.711**	.495*	--											
TAN g kg^{-1}	.858**	-0.375	-.521*	.274	.806**	.790**	.824**	.524*	--										
TKN g kg^{-1}	.905**	-.577*	-.674**	.296	.950**	.944**	.918**	.645**	.921**	--									
TAN/TKN %	-.240	.615**	.520*	-.077	-.461	-.484*	-.321	-.421	.083	-.306	--								
P g kg^{-1}	.828**	-.497*	-.619**	.386	.916**	.915**	.863**	.626**	.851**	.937**	-.308	--							
K g kg^{-1}	.845**	-.479*	-.543*	.386	.883**	.875**	.861**	.542*	.874**	.908**	-.181	.903**	--						
Cu mg kg^{-1}	.594**	-.478*	-.501*	-.004	.731**	.728**	.698**	.483*	.640**	.722**	-.263	.658**	.788**	--					
Zn mg kg^{-1}	.583*	-0.441	-.568*	-.136	.714**	.700**	.736**	.415	.557*	.682**	-.365	.639**	.608**	.817**	--				
EC mS cm^{-1}	.921**	-.485*	-.565*	.306	.842**	.834**	.825**	.553*	.926**	.914**	-.097	.837**	.873**	.618**	.506*	--			
ALK mg CaCO$_3$ L^{-1}	.963**	-.585*	-.683**	.347	.889**	.878**	.883**	.598**	.909**	.926**	-.188	.853**	.847**	.552*	.521*	.956**	--		
VFA mg kg^{-1}	.711**	-.565*	-.637**	.111	.834**	.837**	.763**	.641**	.813**	.879**	-.241	.777**	.785**	.724**	.627**	.798**	.878**	--	
VFA/ALK	.037	-.341	-.328	-.199	.314	.336	.193	.494*	.279	.351	-.148	.286	.271	.473*	.360	.174	.346	.685**	--
TOC %TS	.273	-.680**	-.797**	-.107	.517*	.547*	.344	.895**	.407	.523*	-.375	.517*	.386	.390	.414	.319	.511*	.578*	.627**

*Table 4. Correlations among the chemical-physical parameters of pig slurry. ** Pearson's correlation coefficient at the 0.01 level; * Pearson's correlation coefficient at the 0.05 level*

	acid ml kg^{-1}	pH1w	pH2w	pH	TS g kg^{-1}	VS g kg^{-1}	Ash g kg^{-1}	VS/TS %	TAN g kg^{-1}	TKN g kg^{-1}	TAN/TKN %	P g kg^{-1}	K g kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	EC mS cm^{-1}	ALK mg $CaCO_3$ L^{-1}	VFA mg kg^{-1}	VFA/ALK
acid	--																		
pH1w	-.358	--																	
pH2w	-.282	$.916^{**}$	--																
pH	$.690^{**}$	.209	.365	--															
TS g kg^{-1}	$.733^{**}$	$-.697^{**}$	$-.724^{**}$	.180	--														
VS g kg^{-1}	$.658^{**}$	$-.725^{**}$	$-.768^{**}$	.097	$.990^{**}$	--													
Ash g kg^{-1}	$.853^{**}$	$-.572^{*}$	$-.562^{*}$	.363	$.943^{**}$	$.886^{**}$	--												
VS/TS %	.055	$-.804^{**}$	$-.835^{**}$	-.393	$.558^{*}$	$.649^{**}$	.297	--											
TAN g kg^{-1}	$.731^{**}$	$-.605^{**}$	$-.614^{**}$	.158	$.689^{**}$	$.635^{**}$	$.761^{**}$	.258	--										
TKN g kg^{-1}	$.711^{**}$	$-.733^{**}$	$-.765^{**}$	.072	$.826^{**}$	$.801^{**}$	$.819^{**}$	$.477^{*}$	$.959^{**}$	--									
TAN/TKN %	-.088	$.644^{**}$	$.710^{**}$	.253	$-.615^{**}$	$-.703^{**}$	-.354	$-.887^{**}$	-.114	-.386	--								
P g kg^{-1}	$.706^{**}$	$-.644^{**}$	$-.668^{**}$	.189	$.940^{**}$	$.915^{**}$	$.923^{**}$	$.477^{*}$	$.608^{**}$	$.719^{**}$	$-.516^{*}$	--							
K g kg^{-1}	$.723^{**}$	-.360	-.334	.340	$.571^{*}$	$.494^{*}$	$.709^{**}$	-.021	$.842^{**}$	$.779^{**}$	.006	$.494^{*}$	--						
Cu mg kg^{-1}	.258	$-.623^{**}$	$-.676^{**}$	-.112	$.505^{*}$	$.511^{*}$	.449	$.554^{*}$	.415	$.528^{*}$	$-.580^{**}$	$.565^{*}$	.330	--					
Zn mg kg^{-1}	$.526^{*}$	$-.725^{**}$	$-.782^{**}$	.079	$.787^{**}$	$.795^{**}$	$.703^{**}$	$.655^{**}$	$.610^{**}$	$.755^{**}$	$-.701^{**}$	$.751^{**}$	.430	$.805^{**}$	--				
EC mS cm^{-1}	$.706^{**}$	-0.351	-.331	.300	$.493^{*}$	.419	$.632^{**}$	-.025	$.920^{**}$	$.822^{**}$	.115	.361	$.893^{**}$	.204	.379	--			
ALK mg $CaCO_3$ L^{-1}	$.873^{**}$	$-.539^{*}$	$-.517^{*}$	.385	$.779^{**}$	$.723^{**}$	$.848^{**}$	.251	$.928^{**}$	$.927^{**}$	-.219	$.660^{**}$	$.831^{**}$	.366	$.671^{**}$	$.891^{**}$	--		
VFA mg kg^{-1}	-.082	-.441	$-.477^{*}$	-.423	.143	.165	.079	.339	$.519^{*}$	$.499^{*}$	-.100	.006	.368	.256	.215	.447	$.693^{**}$	--	
VFA/ALK	$-.617^{**}$	-.153	-.123	$-.577^{**}$	-.337	-.284	-.437	.178	-.196	-.204	.033	-.341	-.258	.012	-.231	-.280	-.016	$.644^{**}$	--
TOC %TS	-.089	$-.758^{**}$	$-.808^{**}$	$-.514^{*}$	$.457^{*}$	$.540^{*}$	.223	$.900^{**}$	.302	$.472^{*}$	$-.722^{**}$	.368	-.026	$.506^{*}$	$.563^{*}$	.035	.449	$.593^{**}$	.444

*Table 5. Correlations among the chemical-physical parameters of the digestate. ** Pearson's correlation coefficient at the 0.01 level; * Pearson's correlation coefficient at the 0.05 level*

	acid ml kg^{-1}	pH1w	pH2w	pH	TS g kg^{-1}	VS g kg^{-1}	Ash g kg^{-1}	VS/TS %	TAN g kg^{-1}	TKN g kg^{-1}	TAN/TKN %	P g kg^{-1}	K g kg^{-1}	Cu mg kg^{-1}	Zn mg kg^{-1}	EC mS cm^{-1}	ALK mg $CaCO_3$ L^{-1}	VFA mg kg^{-1}	VFA/ALK
acid	--																		
pH1w	.199	--																	
pH2w	-.041	.897**	--																
pH	.384	.535*	.439	--															
TS g kg^{-1}	.357	.281	.223	.185	--														
VS g kg^{-1}	.320	.290	.247	.135	.994**	--													
Ash g kg^{-1}	.466	.209	.091	.370	.895**	.842**	--												
VS/TS %	.028	.252	.328	-.080	.789**	.841**	.472	--											
TAN g kg^{-1}	.791**	.173	-.001	.654**	.083	.028	.302	-.309	--										
TKN g kg^{-1}	.782**	.332	.140	.561*	.573*	.530*	.678**	.134	.811**	--									
TAN/TKN %	.348	-.179	-.225	.304	-.593*	-.631**	-.356	-.714**	.651**	.094	--								
P g kg^{-1}	.553*	-.089	-.316	.115	-.210	-.227	-.109	-.337	.609**	.443	.461	--							
K g kg^{-1}	.300	.353	.363	.526*	.592*	.552*	.680**	.323	.150	.416	-.340	-.207	--						
Cu mg kg^{-1}	.413	-.157	-.313	.063	-.468	-.464	-.423	-.410	.518*	.159	.685**	.861**	-.485*	--					
Zn mg kg^{-1}	.370	-.222	-.355	.110	-.554*	-.554*	-.480	-.561*	.562*	.181	.731**	.800**	-.461	.938**	--				
EC mS cm^{-1}	.741**	.187	.081	.616**	.279	.223	.477	-.176	.862**	.783**	.451	.315	.455	.150	.236	--			
ALK mg $CaCO_3$ L^{-1}	.934**	.196	.046	.536*	.413	.364	.564*	.058	.804**	.776**	.360	.354	.469	.213	.201	.849**	--		
VFA mg kg^{-1}	.441	.151	.078	.624**	.426	.361	.638**	-.027	.644**	.704**	.192	-.019	.466	-.200	-.110	.747**	.497*	--	
VFA/ALK	-.005	.037	.039	.410	.257	.207	.433	-.094	.314	.398	.043	-.247	.271	-.374	-.248	.422	.186	.876**	--
TOC %TS	-.142	.227	.309	-.129	.720**	.763**	.445	.894**	-.477	-.011	-.825**	-.501*	.338	-.595*	-.686**	-.319	.033	-.132	-.150

3.4. Regression trees and random forest analysis

The RF analysis showed that the key variables in predicting the acid dosage were ALK and initial pH of the slurry, confirming that the type of slurry has a low importance (Fig. S1). Alkalinity confirms what emerged from the analysis of the correlations reported in Tables 3, 4 and 5, while the importance of the initial pH emerged only for pig slurry (Table 4). However, observing the correlation analysis performed on the entire sample dataset (Table S2), the initial pH shows a high correlation with the added acid. The acid dosage increased at increasing values of both ALK and initial pH, albeit nonmonotonically for initial pH values (Fig. 2). When we refitted the RF by including these variables only, the R-squared value was 0.894 (see also Fig. S2), indicating that the RF was able to accurately predict the observed values (Fig. 2). RT analysis fitted including these predictors only showed that the initial pH was the main driver of the acid dosage, discriminating slurries between an initial pH above or below 7.6. Depending on the values of this variable, the acid dosage varied according to the ALK of the slurry, with the only exception of samples with ALK between 8924 and 13385 mg $CaCO_3$ L^{-1}, where it varies again according to initial pH values (Fig. 3a). The R-squared value of this model was 0.881 (Fig. S2), slightly lower than that of the final RF model. Therefore, with an initial pH<7.6, the discriminating threshold of ALK was 8924 mg $CaCO_3$ L^{-1}, which led to the addition of either 2.7 or 4.4 ml kg^{-1} (97.4 or 158.8 meq kg^{-1}). In the RT-branch leading to 2.7 ml kg^{-1}, there were 12 samples of cattle slurry and 8 of pigs, while the branch ending with 4.4 ml kg^{-1} included 6 samples of cattle slurry and 6 of pig. When the initial pH>7.6, ALK discriminated between above and below 13385 mg $CaCO_3$ L^{-1}, finally requiring 7.0 or 8.9 ml kg^{-1} (252.6 or 321.2 meq kg^{-1}). The lowest value of this RT-branch included 8 samples of digestate and 2 of pig slurry, similarly for the higher value that listed 9 digestates and 3 pig slurry samples.

The most important variables identified from RF in predicting slurry pH1w were TOC and VS. In both cases, pH values decreased nonmonotonically with both variables (Fig. 2). The R-squared value of the RF model was 0.574 (Fig. S2).

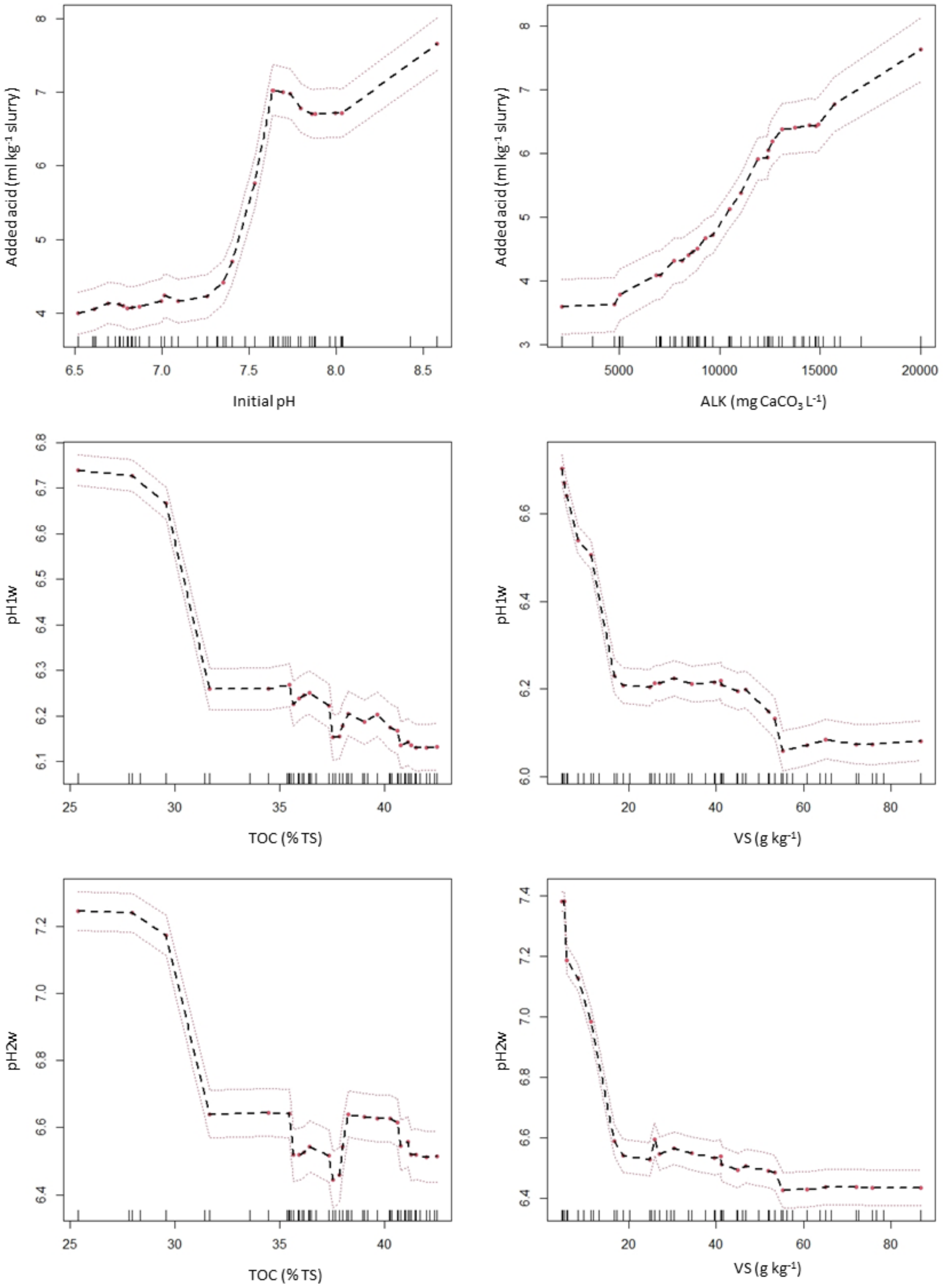

Fig. 2

RT analysis showed that pH1w was mainly determined by TOC being less or more than 31.5 %TS. In the first case, the predicted pH was 7.2, while in the second case, the pH varied according to VS (Fig. 3b). The R-squared for the RT model was 0.728, higher than that of the RF (Fig. S2). Pig slurries were included in the case with TOC below 31.5 %TS.

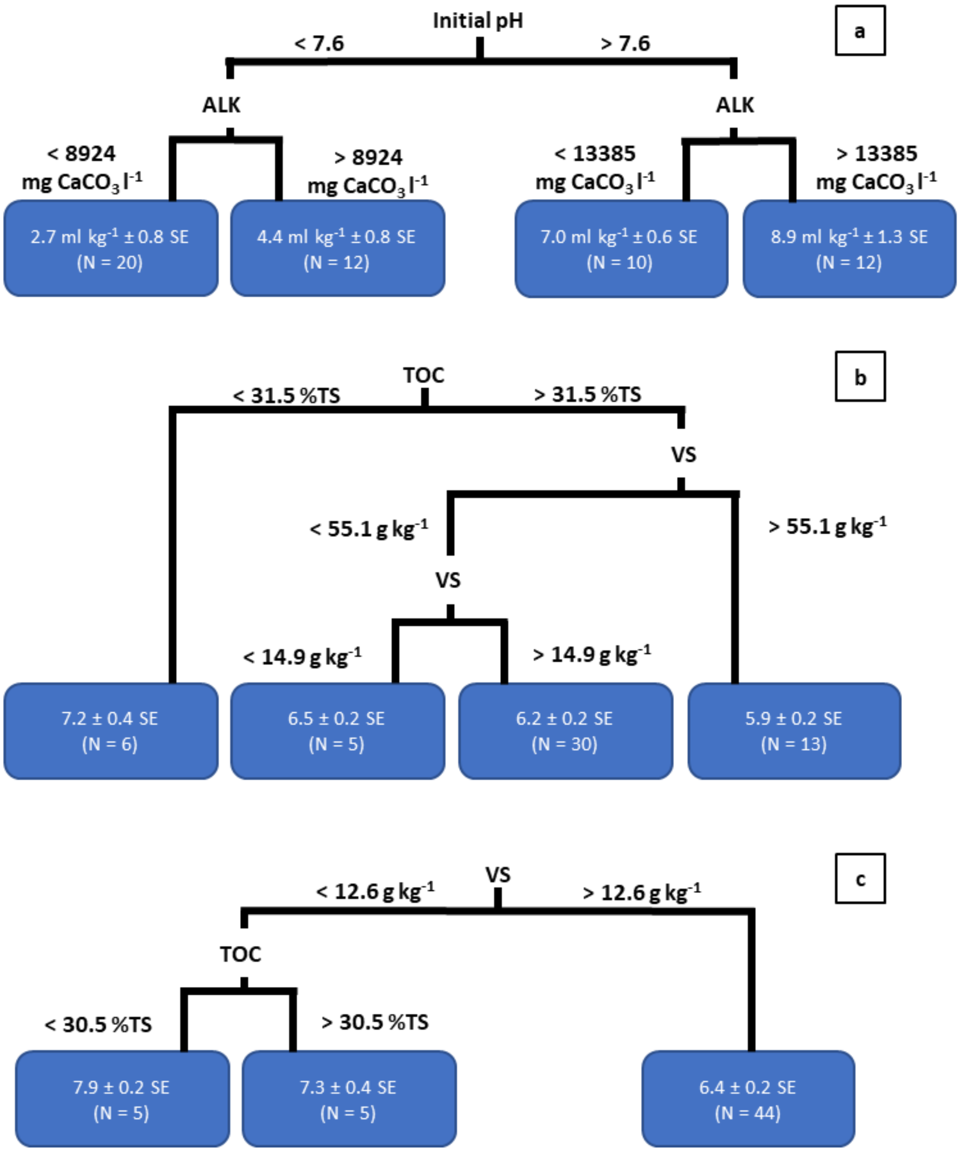

Fig. 3

Conversely, with higher TOC and VS>55.1 mg kg^{-1}, cattle slurries were predominant (11 out of 13 samples), and when VS<55.1 mg kg^{-1} but higher than 14.9 mg kg^{-1}, almost all digestates (16 samples) and both pig and cattle slurries (8 and 6 samples, respectively) were included. If VS<14.9 mg kg^{-1}, then almost only pig slurry was present. In these three cases, pH1w ranged between 5.9-6.5.

The same variables also predicted slurry pH2w, and in this case, pH values decreased nonmonotonically with both variables (Fig. 2). The R-squared value of the RF model was 0.692 (Fig. S2). However, RT analysis indicated that VS was the main driver of pH, while TOC was relevant only at low values of the first variable (Fig. 3c). The main driver parameter to predict pH2w was inverted compared to pH1w prediction, probably because, as also shown in Fig. 1, digestate has a higher pH rise rate than cattle slurry in the first week, while in the second week the opposite occurs, and both reach the same pH value. This is reflected in the pH1w and pH2w models. The R-squared for the RT model was 0.667, slightly lower than that of the RF (Fig. S2). When VS<12.6 mg kg^{-1}, pig slurries were predominant (9 out of 10 samples), whereas when VS>12.6 mg kg^{-1}, digestates, cattle slurries and the remaining pig slurries were included.

It is noteworthy that the parameters used by the predictive models differed in the prediction of the added acid (initial pH and ALK) compared with the prediction of pH1w and pH2w (TOC and VS). For this reason, no direct connection among the results of the 3 models could be made.

As first assessment of the predictive accuracy of the RT models with a view to full-scale application treatments, the predictive error was evaluated by calculating the RMSE. The predictive model for added acid had a higher RMSE in digestate (1.0 ml kg^{-1}) than in cattle and pig slurry (0.8 ml kg^{-1}), although the RMSE of digestate was 12.5% of the average acid dosage, while in cattle and pig slurry, the RMSE was 18.7% and 23.8%, respectively. Regarding the predictive models on pH1w and pH2w, the RMSE was very similar both between the two parameters and among the slurries. For pH1w, it was 0.17 for cattle slurry, 0.21 for digestate and 0.25 for pig slurry, while for pH2w, it was 0.23 for cattle slurry and digestate and 0.29 for pig slurry. This meant that RMSE was approximately 3-4% of the average value of pH1w and pH2w for all the slurries.

3.5. Practical implications and future perspectives

Livestock farms considering acidification can use these models for improved adoption planning and more aware management. This leads to optimised treatment through better planning of acid supply, enabling the prediction of treatment effects over time. These measures contribute positively to emission reduction. Consistently maintaining the proper acidification of the slurry has the potential to lead to a reduction in NH_3 emissions by up to 95% (Finzi et al., 2019).

Some slurries (e.g. digestates) require high dosage of acid while others have a rapid rise in pH after acidification (e.g. pig slurry) which may require frequent additions of acid to lower the pH to the target value. In these cases, acidification could become very expensive. In the attempt to reduce the consumption of acid, pretreatments of effluents able to reduce TAN or alkalinity, and therefore the need of acid, could be adopted. Among them, can be found a slow-release ammonia stripping treatment (Heidarzadeh et al. 2022) that reduces the TAN content and consequently the alkalinity, a CO_2 stripping to reduce only alkalinity (Flotats et al., 2011), or the solid–liquid separation to reduces the TS content, which is highly correlated with alkalinity in dairy cattle and pig slurry (Table 3 and 4). Regarding the cost-effectiveness of emission reduction of these treatments coupled with acidification, NH_3 stripping would have an additional cost of 3.5 €/m^3 (Provolo et al., 2017) but would have a greater impact on reducing emissions being able to remove up to 90% of TAN, also producing a valuable mineral fertiliser (Provolo et al., 2017; Heidarzadeh et al. 2022). CO_2 stripping should be much less expensive than NH_3 stripping and still effective in reducing alkalinity but needs to be studied further (Flotats et al., 2011). Solid-liquid separation is an already widespread technique, therefore often it would not have an additional cost. Acidifying only the liquid fraction would not avoid emissions of the solid fraction, but overall there would still be a reduction in emissions (Dinuccio et al., 2008). Reducing the solid content through solid-liquid separation leads to a saving of acid, but at the same time tends to reduce the effect on pH. Although, this aspect needs to be further explored, this pre-treatment may be suitable when it is necessary to acidify the slurry before field application. In this condition the rise in pH does not represent a critical aspect because the slurry is acidified a few days before distribution and its incorporation into the soil occurs in a short time. Instead, solid-liquid separation before acidification at the housing and storage level may be less advisable because the slurry is stored for long time and therefore the pH rise must be slow.

4. Conclusions

This study represents comprehensive research on the parameters that affect the acidification process of livestock slurries and digestates with the aim to reduce ammonia emissions. Prediction models were developed to give valuable and practical information on the parameters to be considered when applying acidification at farm scale, before field application. To assess acidification effects on housing and storage, investigation longer than two weeks is needed.

Several variables were investigated, highlighting the overwhelming importance of alkalinity and of the initial pH in predicting the acid dosage, as well as of VS and TOC in predicting the pH at 1 and 2 weeks after dosage. The main advantage of this model is that is based on data from different samples of pig slurry, dairy cattle slurry and digestate, thus allowing a wide applicability on different farm conditions. In particular, the acidification of digestate has not been studied much in literature.

Although acidification is not frequently adopted, its use should be promoted as it is a valuable mitigation technique for ammonia emissions. However, among the main disadvantages to the acidification process, the purchase cost of the acid can be mentioned.

The next to their wide applicability, the developed models, are also easily interpretable. Therefore, if appropriately translated into operational tools, they can provide practical indications to farmers and stakeholders on how to deal with and manage this treatment in practice.

Acknowledgements

This research was funded by the project AGROCLEAN (Development of a system for the indirect measurement of the characteristics of livestock slurry during field application), funded by Lombardy Region, call Innodriver – S3 F 2019 edition, under the POR FESR 2014 –2020; and partly by the project LIFE CLINMED-FARM (Towards a Mediterranean Climate Neutral Farm model), grant number LIFE20 CCM/ES/001751, funded by the European Union under the LIFE 2020 program.

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Figure captions

Fig. 1 pH trends of acidified (a and b) and nonacidified (c and d) samples during the two weeks of the experiment (first week: a and c; second week: b and d). The regression intercept is the initial pH value. The regression models are reported close to the lines of different slurries (C: dairy cattle slurry; P: pig slurry; D: digestate).

Fig. 2: RF outputs showing the predicted values of added acid according to initial pH and ALK; pH1w according to TOC and VS, pH2w according to TOC and VS. The dashed lines show the predicted values and the red dotted lines their confidence intervals.

Fig. 3: RT outputs showing the influence of initial pH and ALK on a) the acid dosage; b) pH1w; c) pH2w. Coloured boxes at the end of the RT branches report the predicted values and the sample sizes. For instance, with reference to Fig. 3a, the acid dosage to lower pH to 5.5 in a slurry with initial pH = 6 and alkalinity = 9000, can be estimated in 4.4 ml kg^{-1} slurry, according to the model.