Meta-Analysis of Strategies to Reduce NH₃ Emissions from Slurries in European Agriculture and Consequences for Greenhouse Gas Emissions

Christoph Emmerling 1, Andreas Krein 2 and Jürgen Junk 3,*

1 Department of Soil Science, University of Trier, Behringstraße 21, 54296 Trier, Germany; emmerling@uni-trier.de
2 Luxembourg Institute of Science and Technology (LIST), Environmental Health, 41 rue du Brill, 4422 Belvaux, Luxembourg; andreas.krein@list.lu
3 Luxembourg Institute of Science and Technology (LIST), Agro-environmental Systems, 41 rue du Brill, 4422 Belvaux, Luxembourg

* Correspondence: juergen.junk@list.lu; Tel.: +352-275-888-5011

Received: 21 June 2020; Accepted: 17 October 2020; Published: 23 October 2020

Abstract: The intensification of livestock production, to accommodate rising human population, has led to a higher emission of ammonia into the environment. For the reduction of ammonia emissions, different management steps have been reported in most EU countries. Some authors, however, have criticized such individual measures, because attempts to abate the emission of ammonia may lead to significant increases in either methane, nitrous oxide, or carbon dioxide. In this study, we carried out a meta-analysis of experimental European data published in peer-reviewed journals to evaluate the impact of major agricultural management practices on ammonia emissions, including the pollution swapping effect. The result of our meta-analysis showed that for the treatment, storage, and application stages, only slurry acidification was effective for the reduction of ammonia emissions (−69%), and had no pollution swapping effect with other greenhouse gases, like nitrous oxide (−21%), methane (−86%), and carbon dioxide (−15%). All other management strategies, like biological treatment, separation strategies, different storage types, the concealing of the liquid slurry with different materials, and variable field applications were effective to varying degrees for the abatement of ammonia emission, but also resulted in the increased emission of at least one other greenhouse gas. The strategies focusing on the decrease of ammonia emissions neglected the consequences of the emissions of other greenhouse gases. We recommend a combination of treatment technologies, like acidification and soil incorporation, and/or embracing emerging technologies, such as microbial inhibitors and slow release fertilizers.

Keywords: ammonia reduction; climate change mitigation; greenhouse gases; liquid manure management; meta-analysis; pollution swapping

1. Introduction

One-third of the earth’s arable land resources have already been severely degraded due to pollution through eutrophication, carbon and nutrient losses through soil management, and contamination with agrochemicals [1]. Ammonia (NH₃) and its salts are major contributors to eutrophication, and corresponding abatement strategies might lead to increased greenhouse gas (GHG) emissions [2]. Agriculture, mainly livestock production, is the greatest contributor to the emission of ammonia (NH₃) [2–4]. The GHGs from animal husbandry are nitrous oxide and methane. The latter is mainly produced by enteric fermentation and manure storage, and has an effect on global warming 28 times higher than carbon dioxide [5]. The general demand for measures to abate emissions of NH₃ due to the
rise in livestock production has led to the development of various manure management strategies, at different stages of the manure management chain (animal diets and housing, manure treatment, storage, and application) [3,6]. Livestock production is projected to double in the next century to accommodate the growing world population [7], which is expected to reach 9 billion by 2050 [8]. The consequence of these projected assumptions is a continued depletion of the environment due to NH$_3$ and GHG emissions. NH$_3$ is one of the major atmospheric pollutants leading to the deterioration of human health and ecosystems [9]. For example, apart from the eutrophication and acidification tendencies of NH$_3$, the nitrification of ammonium (NH$_4^+$), which can be formed from NH$_3$, may also contribute to ground water contamination [9], through nitrate leaching [10], nitric oxide (NO), and nitrous oxide (N$_2$O) emissions [11]. Large parts of the NH$_3$ emitted into the atmosphere form particulate matter (PM) [12] which have the potential to reduce human life expectancy via respiratory and cardiovascular diseases [13]. The estimated reduction of life expectancy due to exposure to particulate matter, in the Benelux region in 2005, accrued to an average of 9.0 months and 8.5 months in the EU-28 [14].

Due to the transboundary nature of NH$_3$ and GHGs, international cooperation is required to meet the air quality guideline values of the World Health Organization (WHO) [15], e.g., 20% of the nitrogen deposition on nature areas in the Netherlands emanates from Germany [14]. The sensitivity of agricultural practices to NH$_3$ and GHG emissions has paved the way for new policies, leading to changing trends and technologies compared to the old practices. New policies are still emerging [3,16]. For example, the new Danish regulation on pig production mandates pig farm owners to implement NH$_3$ abatement strategies, such as acidification and air-scrubbing techniques [17]. In France, various manure treatments and land application techniques are part of the national implemented nitrate and water framework directive [18]. For Spain, a study by Sanz-Cobena et al. (2014) showed that the implementation of the most effective region-specific mitigation strategy led to 63% NH$_3$ mitigation at the country level, compared to the reference situation of standard practices for the year 2008 [19]. Results for the UK were presented by Misselbrook et al. (2010), showing 231.8kt of NH$_3$ from livestock production and fertilizer used for 2009 [20].

In the EU-27 more than 1400 million tons of slurry is produced yearly, with a high percentage applied as fertilizers to agricultural lands [17,21]. A study by Ma et al. [22] on N use efficiency in China, reported that only 12% the of applied N was utilized by plants; 47% was lost to atmospheric emissions, and 41% to ground water, through leaching [23].

Research efforts are in place for the abatement of NH$_3$ emissions at the various stages of the manure management chain, namely; the feeding, housing, treatment, storage, and application stages to ensure a whole-farm management model [2,7]. However, the impact of these mitigation strategies on the emission of other GHGs has not received equal attention. Most studies have just focused on a single gas mitigation effort [2,11]. A few studies, where such impacts have been highlighted, pose contradictory results, and hence need to be accurately assessed [24]. A comprehensive analysis of the effects of NH$_3$ abatement strategies on emissions of different GHGs is so far missing. Therefore, our meta-analysis can contribute to the question of how the environmental impact of accepted mitigation strategies for NH$_3$ influences the emissions of N$_2$O, CH$_4$, and CO$_2$.

Furthermore, Webb et al. [23] highlighted that abatement efforts to suppress the emission of gases at initial stages of manure management do not guarantee complete abatement, but will only transfer the conserved gases to a later stage, thereby making the management of manure increasingly important as one moves down the chain. Seidel et al. [25] and Sajeev et al. [6] reported that manure storage, manure treatment, and field application are the major contributors to the total NH$_3$ emitted in European agriculture. Furthermore, at these last three stages the pollutant swapping effect plays a major role. Therefore, we investigated the consequences of the most effective measures to decrease NH$_3$ emissions, for the emission of other GHG (swapping effect).
2. Materials and Methods

2.1. Selection of Studies

A systematic literature search was conducted on the databases of Scopus, Google scholar, and gray literature, and from the websites of governmental/non-governmental agencies by combining the following keywords: ammonia emission, ammonia abatement, Europe, abatement strategies, integrated assessment, systematic review, meta-analysis, air quality, long-range transboundary air pollution (LRTAP), livestock, livestock management, animal housing, manure treatment, animal diet, Europe, France, Belgium, Germany, Netherlands, Spain, UK, Sweden, Finland. The keyword search and screening of the abstracts led to the identification of 289 documents with information on NH$_3$ abatement strategies, and a subset of 142 articles with information on abatement strategies across 11 EU countries in the period from 2008 to 2018. Due to the incomplete description in some papers, and lack of response from contacted authors (only 4 out of 19 contacted authors responded), only the papers listed in Annex I were included in the meta-analysis. A list of all studies used for the different treatment strategies can be found in the Table S1.

2.2. Slurry Treatment Methods

Based on the results of the literature research the following treatment methods were most common, and they are briefly described in this section. Slurry acidification is mainly achieved using sulfuric acid, with a pH-value between 5.1 and 6.5 [18]. Biological treatment means the conversion of slurry to biogas for energy purposes (anaerobic digestion) [2]. By separation slurry components are separated into the liquid and solid fractions, mainly by mechanical measures [6]. The use of covers as a further mitigation strategy is carried out to reduce the overall emitting surface, by the concealment of the liquid slurry with different materials like plastic, straw, or saw-dust [18]. Field application techniques of slurry can be divided into different categories, injection, incorporation, and band application [23]. Injection is mainly realized at a depth of 15 cm below the surface, while in incorporation the slurry is only covered by a few centimeters of soil [23]. With band spreading application technique, liquid manure, or fertilizers in general, are applied below crops in a concentrated layer in the soil, commonly 8–15 cm below the surface. This technique is considered as more efficient because of the uniform application of manure compared to surface application [23]. Furthermore, band application means application of fertilizers in a “band”, often 5 cm over and 5 cm below from the seed during planting [26].

2.3. Data Analysis

The treatment methods for NH$_3$ abatement included in this study were acidification, biological treatments (anaerobic digestion), and separation. They were compared to the worst practices, to identify the reduction potential (in percentage) attributed to each treatment strategy. In addition, the meta-analysis covered the aspects of storage (use of covers) and field application techniques. The number of selected papers and corresponding repetitions in relation to the different management strategy are shown in Table 1. The effectiveness of the treatments, reported as mean percentage reduction, was considered the primary outcome of interest for both NH$_3$ and GHGs. CO$_2$ released through biodegradation was considered carbon neutral. Biogenic carbon, which is not degraded in soil, increases the soil carbon pool and can be considered a carbon sink [6,23]. The considered time frame is of high importance, because, e.g., in 20 years less carbon will be degraded compared to 100 years. To assess the results of the different studies, the considered time frame must be the same. As these time frames are not indicated in most of the articles used in this study, a deeper assessment of total relevant greenhouse gas emission fluxes is not possible. Due to the higher global warming potential of CH$_4$ and N$_2$O, the release of those substances has a higher impact on global warming (Table S2).

All treatments were compared to a reference (no slurry treatment, no storage cover, and band spread application) to quantify the effect (Table 2). The percentage reduction in emissions (outcome variable) for each of the reported gases was calculated by comparing the differences between the abatement
strategy/treatment relative to the reference strategy/control. Negative values indicate a reduction, while positive values indicate an increased emission. To analyze the combined effect of different measures, taking sample sizes into account, testing for moderators, and obtaining corresponding forest plots, the meta-analytical software OpenMEE was used (http://www.cebm.brown.edu/openmee). A random effect model was used to aggregate the collected data into a meta-analysis, to satisfy the assumption of variance heterogeneity. We refrained from calculating the combined effects of the different abatement strategies, because in some of the studies only relative values were published and it was not possible to obtain the absolute values. The efficiency of greenhouse gases must be combined with their lifetimes to form a global warming potential (GWP) e.g., 20 or 100 years. A table with the different GWPs and atmospheric lifetimes is provided in the Table S2.

Table 1. Number of selected publications and number of observations per management strategy included in the meta-analysis. The numbers in brackets represent the total number of observations from all studies.

| Strategy | Reference Method | Number of Studies (Number of Observations) |
|----------|-----------------|--------------------------------------------|
|          | (worst practice) | NH\textsubscript{3} | N\textsubscript{2}O | CH\textsubscript{4} | CO\textsubscript{2} |
| Treatment | No Treatment | 14 | 5 | 9 | 9 | (103) | (15) | (33) | (41) |
| Acidification | No treatment | 4 | 7 | 7 | 3 | (16) | (26) | (30) | (14) |
| Biological | No treatment | 8 | 6 | 6 | 8 | (42) | (25) | (29) | (36) |
| Storage | No cover | 3 | 3 | 5 | 3 | (25) | (10) | (30) | (28) |
| Application | Surface incorporation | 3 | 2 | 2 | 2 | (12) | (7) | (5) | (16) |
| Injection | Surface application | 3 | 2 | 2 | 2 | (8) | (19) |
| Injection | Band spread | 2 | 1 | 1 | 1 | (30) | (3) |
| Band Application | Surface application | 3 | 1 | 1 | 1 | (5) | (6) | (2) | (2) |
| Incorporation | Surface application | 4 | 3 | 3 | 2 | (28) | (40) | (12) | (12) |

Table 2. Results of the meta-analysis of greenhouse gas (GHG) emission changes, following reduction strategies across different manure treatment strategies (numbers in brackets represent the 95% confidence intervals). Negative values represent emission reduction, and positive values show increase in emission.

| Strategy | Reference Method | Mean Emission Changes in Percentage (%) |
|----------|-----------------|-----------------------------------------|
|          | NH\textsubscript{3} | N\textsubscript{2}O | CH\textsubscript{4} | CO\textsubscript{2} |
| Treatment | no treatment | −77 | −21 | −86 | −15 | (−81, −73) | (−27, −15) | (−92, −80) | (−19, −11) |
| Acidification | raw slurry | (−81, −73) | (−27, −15) | (−92, −80) | (−19, −11) |
| Biological | no treatment | −14 | +10 | −46 | −26 | (−27, −1) | (−10, +30) | (−65, −27) | (−42, −10) |
| Separation | raw slurry | (−81, −73) | (−27, −1) | (−92, −80) | (−19, −11) |
| (raw slurry) | (−13, +11) | (−4, +52) | (−46, −8) | (−23, +95) |
3. Results and Discussion

3.1. Impact of Acidification in Reference to Raw Slurry

The acidification of slurry material during storage and soil application has been reported by various authors to decrease NH₃ emissions by shifting equilibrium between NH₃ and NH₄⁺, with low pH favoring NH₄⁺ dominance [16,21,26]. Furthermore, acidification is used to reduce the emissions of CH₄ [16,27,28], N₂O [29,30], and CO₂ [24,26,31,32]. In most of the studies acidification was achieved using sulfuric acid, with a pH-value between 5.1 and 6.5. Slurries amended with acids affected N-dynamics by delaying nitrification, and consequently N₂O emission [21,33]. Acidified slurries applied to agricultural lands inhibited the emission of NH₃, but also, released concurrently large amounts of NH₄⁺ [21]. Due to the delay in the nitrification activities of microbes as a result of acidification, which would have otherwise led to an increased formation of NO₃⁻ (with high leaching tendency), a successful NH₃ and N₂O inhibition was observed [7,21]. The activities of methanogens were also hampered when slurries were amended with acid, which reduced the possibility for their formation and consequently CH₄ and CO₂ emission [21,34].

In this meta-analysis results for the acidification of animal manure from 37 studies, with 192 measurement events, showed that acidification treatment was effective for the reduction of NH₃, and had no pollution swapping effect with other GHGs (Table 2). For NH₃, an average reduction in emission of −77% (CI −81, −73) was observed. Methane showed reductions of up to −86% (CI −80, −92), N₂O was reduced by −21% (CI −15, −27), and CO₂ had a reduction of up to −15% (CI −11, −19) (Figure 1).
3.2. Impact of Biological Treatment Relative to Raw Slurry

The conversion of slurry to biogas for energy purposes leads to the production of CH$_4$ and CO$_2$ prior to the storage of manure, leading to a reduction in GHG emission potentials in the subsequent management chain [35]. The available studies, however, show contrasting results. Some reports have related the emission of CH$_4$ to the quantity of total solid (TS) and volatile solid (VS) present in manure [18,36]. Digestate, the material remaining after the anaerobic digestion of a biodegradable feedstock, contains less TS and VS compared to raw slurries, and hence has less easily degradable carbon (C), compared to raw undigested slurry materials [37]. Rodhe et al. [38] attributed high production of CH$_4$ in digestate, relative to non-digestate, to the presence of more anaerobes, present as a result of TS conversion during and after anaerobic digestion, converting lignocellulose materials present in the soil to CH$_4$. Perazzolo et al. [37] also associated the reduced CO$_2$ emission to low carbon content (TS and VS), by comparing solid separated manure (with a higher TS and VS) to the liquid manure (with low TS and VS), and concluded that low CO$_2$ emission can be expected from digestate with low TS and VS, compared to non-digestate. Results from this present study showed an average reduction of $-46\%$ (CI $-65$, $-27$) in CH$_4$, and $-26\%$ (CI $-42$, $-10$) in CO$_2$ (Figure 2). It is also important to note that subsequent production of CH$_4$ and CO$_2$ can be provoked during storage when full methanogenesis is not achieved in anaerobic digestion, and that this can also lead to even more CH$_4$ and CO$_2$ in digestate compared to non-digestate during the land application of manure [39,40].

Figure 2. Forest plot of the impact of biological treatment of animal slurry with reference to raw slurry. The black square boxes show the individual mean points of each gas. Horizontal bars indicate the 95% confidence intervals.

Changes in manure characteristics are also expected following digestion of manure, which may provoke simultaneous emissions of other gases. Digestion is known to increase slurry pH [37,38], temperature [41], and N mineralization [37], leading to possible increase in NH$_3$ and N$_2$O emissions. Crust formation (which can mitigate NH$_3$ emission) is decreased by the gasification and removal of CH$_4$ and CO$_2$, which may lead to an increased NH$_3$ emission [2,7].

For biological treatment the results showed an aggregate NH$_3$ emission reduction of $-14\%$ (CI $-27$, $-1$) (4 studies and 16 observations). In contrast, Nyord et al. [41] attributed an increased NH$_3$ emission following anaerobic digestion to the increase of pH and total ammoniacal nitrogen (TAN), and backed up their findings with similar earlier reports [42,43]. For N$_2$O, biological treatment leads to an average increase of $10\%$ (CI $-10$, $30$) (7 studies and 26 observations). The result of the experiment by Regueiro et al. [32], showed a significant decrease in NH$_3$ and N$_2$O emissions when the digestate was acidified prior to storage. The activities of microbes are also reduced at low pH-values, and thus acidification may prove to be useful for the hindrance of methanogens (pH-value below 6); moreover, one of the requirements for nitrification is a neutral to slight alkaline condition. For both CH$_4$ ($-46\%$) and CO$_2$ ($-26\%$) biological treatment leads to a pronounced reduction of gas emissions (Figure 2).
3.3. Effect of Separation of Slurry into Solid and Liquid Fractions

The calculated emission changes reflect an aggregate of both, solid and liquid fractions to obtain an overall impact of separation on gaseous emissions. Slurry separation, as a treatment strategy, aims at trapping nutrients (nitrogen, phosphorous) in the various separated fractions [44,45] for an enhanced management and storage capacity (easy infiltration of liquid fraction, and a concentration of organic matter in the solid fraction) [23].

Some studies reported a small to medium (about −10%) reduction of NH\textsubscript{3} emissions due to manure separation during storage [24,37,42]. Regarding manure separation during application, Dinuccio et al. [2,46,47] and Regueiro et al. [32] highlighted an increased emission. The mean reduction in NH\textsubscript{3} emission for the present meta-analysis was very limited, i.e., −1% (CI −13, +11). N\textsubscript{2}O and CO\textsubscript{2} emissions were increased by +24% (CI −4, +52) and +59% (CI −23, +95), respectively, while a reduction of −27% (CI −46, −8) was achieved for CH\textsubscript{4} (Figure 3). Although soils amended with liquid manure tend to induce a higher crop yield, due to increased N-infiltration compared to untreated soils [23,48], some authors did not recommend separation as an effective treatment strategy without combining it with other treatment strategies, for the simple reason of increased net GHG emissions [47].

![Figure 3. Forest plot of the impact of separation of animal slurry with reference to unseparated slurry. The black square boxes show the individual mean points of each gas. Horizontal bars indicate the 95% confidence intervals.](image)

To highlight the importance of additional measures to this strategy, Hjorth et al. [43] showed a combination of separation and anaerobic digestion as an optimized version for manure management; NH\textsubscript{3} emission was largely reduced as well as the amount of VS due to separation. Acidification of slurry following separation has also proven to be more effective than simple separation in reducing the amount of N losses [32,37,49].

Increase in the emission of N\textsubscript{2}O [50] and CO\textsubscript{2} [37] due to separation of manure, especially from the liquid fraction relative to the untreated slurry and solid fraction, has been reported. These reports are in line with the outcomes of this present study. Separating manure is perhaps the abatement measure with the lowest impact on GHG mitigation potential [51].

3.4. Use of Covers for Manure Storage

The use of covers as a mitigation strategy is carried out to reduce the overall emitting surface [52]. The concealing of animal slurry with different material (plastic, straw, saw-dust, etc.) has been identified as an efficient mitigation strategy for the abatement of NH\textsubscript{3} emission [53,54]. Emission reductions for NH\textsubscript{3}, CH\textsubscript{4}, and CO\textsubscript{2} were achieved by −68% (CI −81, −55), −16% (CI −33, 1), and −31% (CI −45, −17) (Figure 4), respectively, while an increase in emission was noticed for N\textsubscript{2}O, by several orders of magnitude (+13502% (CI −25, +39600)).

It is also important to note that other environmental factors, such as temperature, can impact the emission potentials of these gases [2,31]. In addition, soil structure [6], crop type [42,43], and the composition of the slurry [35,39] strongly influence the emissions.
O, leading to an anaerobic environment which favors denitrifiers [60]. The results of the meta-analysis showed a reduction in NH$_3$ emission by −61% (CI −89, −31) and an increased N$_2$O emission by +196% (CI −39, +1365) when injection was compared to surface application.

3.5. Effects of Different Field Application Methods

Field application techniques were divided into different categories, injection (normally 15 cm depth), band application, and incorporation, to allow for the inclusion of some important findings in the literature, and to pitch various application techniques against one another (Table 2). A range of 30–50% of NH$_3$ emissions in the EU emanates from the application of livestock slurry [58–60]. Land application of organic fertilizers increases the amount of metabolizable-C in the soil. This leads to increased microbial activity, as evidenced by increased CO$_2$ emissions. This eventually leads to anaerobic denitrification whereby N$_2$O is produced [24].

While the emission of NH$_3$ is reduced after land application of liquid manure by injection, relative to surface application, N$_2$O is increased due to soil microbial N-mineralization and nitrification/denitrification processes. This is evidenced by the high concentration of NH$_4^+$ and subsequent oxic NO$_3^+$ increase as NH$_4^+$ depletes, ultimately leading to an increasing amount of N$_2$O production under anaerobic conditions [48]. Some of the pre-requisite processes enabling these nitrification/denitrification activities include; (i) the presence of metabolizable fatty acids and degradable C in slurry material, which increases the activities of soil micro-organisms [60,61]; and (ii) O$_2$ depletion with increasing application depth, or as a result of an increased microbial activity, leading to an anaerobic environment which favors denitrifiers [60]. The results of the meta-analysis showed a reduction in NH$_3$ emission by −61% (CI −89, −31) and an increased N$_2$O emission by +196% (CI −39, +1365) when injection was compared to surface application.
A similar emission trend was also noticed for NH$_3$ and N$_2$O, with changes in the emissions of $-19\%$ (CI $-100$, $+155$) and $+133\%$ (CI $-54$, $+300$), respectively, when injection of manure was compared to surface incorporation. There is no information in the individual studies explaining the wide range of results, presumably caused by different soil types or meteorological conditions. The same technique leads to an average decrease of CH$_4$ ($-23\%$ (CI $-34$, $-13$)) and CO$_2$ ($-20\%$ (CI $-50$, $+7$)).

Surface application followed by immediate or delayed incorporation follows the same nitrification/denitrification process as mentioned above. The importance of application depth for the reduction of N$_2$O has also been pointed out for the concurrent reduction of both NH$_3$ and N$_2$O. Velthof and Mosquera [61] highlighted that with increasing depth, complete denitrification of N$_2$O to N$_2$ will be achieved before the gas reaches the surface. Nevertheless, full denitrification is complicated, and might lead to additional N losses in form of N$_2$ instead of N$_2$. A comprehensive review by Almaraz et al. (2020) showed that for a better understanding of how denitrification rates vary across the soil profile, there is a need to more precisely investigate ecosystem N budgets. Therefore, surface and subsoil measurements should be included in future studies to determine controls on denitrification in surface soils vs. subsoils [62]. Fangueiro et al. [24] detected no N$_2$O emission when slurry material was injected to 30 cm depth. Furthermore, the authors also pointed out that a further N$_2$O reduction can be achieved for manure incorporation when soils are amended with acidified slurry in order to trigger nitrification inhibition as a result of slurry acidification. Manure incorporation, with reference to surface application with no incorporation, showed an emission reduction potential for NH$_3$ of $-68\%$ (CI $-96$, $+3$), and an increase in N$_2$O emissions of $+61\%$ (CI $-77$, $+412$), highlighting how no-incorporation affected N-dynamics. Infiltration of manure into soil was reduced in no-tillage management compared to a conventional tillage system, where surface exposure to air is minimized, resulting in a better N use efficiency (NUE), due to minimized environmental loss of N [62]. Moreover, urease activity is higher in the topsoil, and manure-soil contact and interaction is optimal, when the manure component is incorporated into the soil [63,64].

While promoting injection of fertilizers as the best manure application method for reduced NH$_3$ emissions [6,25,41], surface application using splash plates has been banned in most European countries because of its strong impact on NH$_3$ emission [23]. However, injection is accompanied by other flaws, such as the cutting of roots (especially of perennial crops) by injection materials, its impracticability on stony and sloped lands without the use of stronger tractors [23], and the great draught force hindering working perimeter [25,41].

In the band spreading application technique, fertilizers are applied below crops in a concentrated layer in the soil, commonly 8–15 cm below the surface, and are more efficient because of the uniform application of manure compared to surface application. Comparing the emission of gases from band application (applications of fertilizers in a “band” often 5 cm over and 5 cm down from the seed during planting) with reference to injection, the results of the meta-analysis showed an NH$_3$ reduction of $-51\%$ (CI $-84$, $-14$), and an increase in N$_2$O by $+3\%$ (CI $-50$, $+36$). Webb et al. [23] similarly concluded that the band application of fertilizers can be an efficient compromise when injection cannot be used. Bourdin et al. [65] showed that the band application of fertilizer, while conserving and elevating the concentration of NH$_4^+$ in the soil, may at the same time inhibit CH$_4$ oxidation due to competition for methanogenic enzymes by both NH$_4^+$ and CH$_4$. They concluded that when N is not volatilized, it remains in the soil where it carries out its inhibitory actions on CH$_4$ oxidation. Moreover, anaerobic sites are created and, consequently, CH$_4$ gas is emitted when fertilizers are applied in bands. These findings are in line with the outcomes of this study. A reduction of $-33\%$ (CI $-53$, $-4$) was achieved for NH$_3$ while increased N$_2$O, CH$_4$, and CO$_2$ were noticed, $+25\%$ (CI $-2$, $+57$), $+153\%$ (CI $+108$, $+197$), and $+18\%$ (CI $+10$, $+25$), respectively. Hansen et al. [55] stated that the use of additional draught to enable injection led to an increased CO$_2$ emission. Bourdin et al. [65] and Fangueiro et al. [24] attributed the high production of CO$_2$ to an initial increase in microbial respiration, following the application of metabolizable-C present in manure material (Table 2).
4. Conclusions

The results of the meta-analysis showed a reduction in NH\textsubscript{3} emission in all management strategies, but revealed mixed results for other GHGs; highlighting further that the management strategies were aimed at reducing the emission of NH\textsubscript{3}, while not considering the effect on GHGs. Thus, apart from acidification of manure, all management strategies affect N\textsubscript{2}O negatively. In addition, strategies to conceal manure (e.g., covering during storage, injecting, and incorporating manure during application), led to increased N\textsubscript{2}O emissions. This is possibly a result of the denitrification of already nitrified manure N-components, when oxygen is in limited supply as manure is concealed. Additional procedures, such as acidification, or the use of nitrification and urease inhibitors, are effective ways of ensuring reduced N\textsubscript{2}O emission, so that nitrification is delayed, or by acidification which obstructs the activities of microbial communities. A positive effect (reduced emission) was noticed in all strategies for CH\textsubscript{4}, except during band application, with reference to the surface application of fertilizers. Band application, compared to surface application, may also affect CO\textsubscript{2} negatively.

The effect of all application processes on CO\textsubscript{2} emission have remained unclear so far, as authors have attributed its emission to the initial increase in the activities and population of soil microbial communities in response to the introduction of substrates present in manure. Although the review by Webb et al. [23] claimed that readily degradable C will be in short supply after the storage of solid manure, and hence will have less impact on microbial metabolism. We attempted to relate CO\textsubscript{2} emission to soil profile (microbial presence with application depth), but a comparison between incorporation and surface application foiled the attempt, as an increased emission is noticed. Although it can still be argued that the incorporation depth, when not as deep as the injection depth, may have an increased presence of microorganisms, compared to the presence at the soil surface.

The separation of manure, although effective for CH\textsubscript{4} reduction, had a negligible impact on NH\textsubscript{3}, while N\textsubscript{2}O and CO\textsubscript{2} emissions were increased. We therefore conclude that although this treatment strategy is effective for crop-manure response and yield, this treatment is the least effective for NH\textsubscript{3} emission reduction, and at the same time has a negative impact on other GHGs (N\textsubscript{2}O and CO\textsubscript{2}) [47], and should only be used with an additional strategy, like slurry acidification, that is effective for the reduction of NH\textsubscript{3} emissions and has no pollution swapping effect with other greenhouse gases.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/ Table S1: List of the studies used in the meta-analysis, Table S2: Greenhouse Gas Global Warming Potentials and Atmospheric Lifetimes

Author Contributions: C.E. and J.J. are responsible for the concept of the paper. A.K. and J.J. performed the formal analysis and prepared the draft of the paper. All authors have read and agreed to the published version of the manuscript.

Funding: Parts of this research was funded by BLE (Federal Office for Agriculture and Food, Germany), grant No. 281B302816.

Acknowledgments: We thank Melody Njoku for contributing to parts of an earlier version of this manuscript.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

References
1. Gomiero, T.; Pimentel, D.; Paoletti, M. Is there a need for a more sustainable agriculture? Crit. Rev. Plant. Sci. 2011, 30, 6–23. [CrossRef]
2. Hou, Y.; Velthof, L.G.; Oenema, O. Mitigation of ammonia, nitrous oxide and methane emissions from manure management chains: A meta-analysis and integrated assessment. Glob. Chang. Biol. 2015, 21, 1293–1312. [CrossRef] [PubMed]
3. Aneja, V.P.; Schlesinger, W.H.; Li, Q.; Nahas, A.; Battye, W.H. Characterization of the global sources of atmospheric ammonia from agricultural soils. J. Geophys. Res. Atmos. 2020, 2020, 125, e2019JD031684. [CrossRef]
4. Ndegwa, P.M.; Hristov, A.N.; Argo, J.; Sheffield, R.E. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. Biosyst. Eng. 2008, 100, 453–469. [CrossRef]
5. Grossi, G.; Pietro, G.; Andrea, V.; Adrian, G.W. Livestock and climate change: Impact of livestock on climate and mitigation strategies. *Anim. Front.* 2018, 9, 69–76. [CrossRef] [PubMed]

6. Sajeev, M.E.P.; Winiwarter, W.; Amon, B. Greenhouse gas and ammonia emissions from different stages of liquid manure management chains: Abatement options and emission interactions. *J. Environ. Qual.* 2018, 47, 30–41. [CrossRef]

7. Petersen, S.O.; Sommer, S.G. Ammonia and nitrous oxide interactions: Roles of manure organic matter management. *Anim. Feed Sci. Tech.* 2011, 166–167, 503–513. [CrossRef]

8. UN. United Nations-Department of Economic and Social Affairs DESA: World Population Projected to Reach 9.7 Billion by 2050. 2015. Available online: http://www.un.org/en/development/desa/news/population/2015-report.html (accessed on 8 January 2019).

9. Ti, C.; Xia, L.; Chang, S.X.; Yan, X. Potential for mitigating global agricultural ammonia emission: A meta-analysis. *Environ. Poll.* 2019, 245, 141–148. [CrossRef]

10. Rose, T.J.; Wood, R.H.; Rose, M.T.; Van Zwieten, L. A re-evaluation of the agronomic effectiveness of the nitrification inhibitors DCD and DMPP and the urease inhibitor NBPT. *Agric. Ecosyst. Environ.* 2018, 252, 69–73. [CrossRef]

11. De Vries, J.W.; Hoogmoed, W.B.; Groenestein, C.M.; Schröder, J.J.; Sukkel, W.; De Boer, I.J.M.; Groot Koerkamp, P.W.G. Integrated manure management to reduce environmental impact: I Structured design of strategies. *Agric. Syst.* 2015, 139, 29–37. [CrossRef]

12. Backes, A.M.; Aulinger, A.; Blieser, J.; Matthias, V.; Quante, M. Ammonia emissions in Europe, part II: How ammonia emission abatement strategies affect secondary aerosols. *Atmos. Environ.* 2016, 126, 153–161. [CrossRef]

13. Wagner, S.; Angenendt, E.; Beletskaya, O.; Zeddies, J. Costs and benefits of ammonia and particulate matter abatement in German agriculture including interactions with greenhouse gas emissions. *Agric. Syst.* 2015, 141, 58–68. [CrossRef]

14. Maas, R. Ammonia Abatement Strategies to Reduce Health Risks and Biodiversity Loss in the Benelux-Plus Region. 2018. Available online: http://www.benelux.int/files/4815/2835/5618/Ammonia_report_Benelux_Air_Working_group_03042018.pdf (accessed on 8 October 2019).

15. EEA. European Union Emission Inventory Report 1990–2016 under the UNECE Convention on Long-Range. 2018. Available online: https://www.eea.europa.eu/publications/european-union-emission-inventory-report-1990–2016 (accessed on 8 October 2019).

16. Petersen, S.O.; Hutchings, N.J.; Hafner, S.D.; Sommer, S.G.; Hjorth, M.; Jonassen, K.E.N. Ammonia abatement by slurry acidification: A pilot-scale study of three finishing pig production periods. *Agric. Ecosyst. Environ.* 2016, 216, 258–268. [CrossRef]

17. Danish Ministry of Energy; Utilities and Climate. Denmark’s Seventh National Communication and Third Biennial Report: Under the United Nations Framework Convention on Climate Change. 2017. Available online: https://unfccc.int/sites/default/files/resource/8057126_Denmark-NC7-BR3-2-Denmark-NC7-and-BR3_1January2018-12MB.pdf (accessed on 8 October 2019).

18. Loyon, L. Overview of manure treatment in France. *Waste Manag.* 2017, 61, 516–520. [CrossRef] [PubMed]

19. Sanz-Cobena, A.; Lassaletta, L.; Estellés, F.; Del Prado, A.; Guardia, G.; Abalos, D.; Aguilera, E.; Pardo, G.; Vallejo, A.; Sutton, M.A.; et al. Yield-scaled mitigation of ammonia emission from N fertilization: The Spanish case. *Environ. Res. Lett.* 2014, 9, 125005. [CrossRef]

20. Misselbrook, T.H.; Chadwick, D.R.; Gilhespy, S.L.; Chambers, B.J.; Smith, K.A.; Williams, J.; Dragosits, U. Inventory of Ammonia Emissions from UK Agriculture 2009. North Wyke Research, 34pp. (DEFRA Contract: AC0112, CEH Project Number: C03642). 2010. Available online: http://www.nora.nerc.ac.uk/13234/ (accessed on 10 October 2019).

21. Fanguero, D.; Surgy, S.; Fraga, I.; Monteiro, F.G.; Cabral, F.; Coutinho, J. Acidification of animal slurry affects the nitrogen dynamics after soil application. *Geoderma* 2016, 281, 30–38. [CrossRef]

22. Ma, L.; Ma, W.Q.; Velthof, G.L.; Wang, F.H.; Qin, W.; Zhang, F.S.; Oenema, O. Modeling nutrient flows in the food chain of China. *J. Environ. Qual.* 2010, 39, 1279–1289. [CrossRef]

23. Webb, J.; Pain, B.; Bittman, S.; Morgan, J. The impacts of manure application methods on emissions of ammonia, nitrous oxide and on crop response-A review. *Agric. Ecosyst. Environ.* 2010, 137, 39–46. [CrossRef]
Agronomy 2020, 10, 1633

24. Petersen, S.O.; Højberg, O.; Poulsen, M.; Schwab, C.; Eriksen, J. Methanogenic community changes, and emissions of methane and other gases, during storage of acidified and untreated pig slurry. J. Appl. Microbiol. 2014, 117, 160–172. [CrossRef]

25. Seidel, A.; Pacholski, A.; Nyord, T.; Vestergaard, A.; Pahlmann, I.; Herrmann, A.; Kage, H. Effects of acidification and injection of pasture applied cattle slurry on ammonia losses, N₂O emissions and crop N uptake. Agric. Ecosyst. Environ. 2017, 247, 23–32. [CrossRef]

26. Fangueiro, D.; Pereira, J.L.S.; Macedo, S.; Trindade, H.; Vasconcelos, E.; Coutinho, J. Surface application of acidified cattle slurry compared to slurry injection: Impact on NH₃, N₂O, CO₂ and CH₄ emissions and crop uptake. Geoderma 2017, 306, 160–166. [CrossRef]

27. Hjorth, M.; Cocolo, G.; Jonassen, K.; Abildgaard, L.; Sommer, S.G. Continuous in-house acidification affecting animal slurry composition. Biosyst. Eng. 2015, 132, 56–60. [CrossRef]

28. Wang, K.; Huang, D.; Ying, H.; Luo, H. Effect of acidification during storage on emissions of methane, ammonia and hydrogen sulfide from digested pig slurry. Biosyst. Eng. 2014, 122, 23–30. [CrossRef]

29. Fangueiro, D.; Hjorth, M.; Gioelli, F. Acidification of animal slurry—A review. J. Environ. Manag. 2015, 149, 46–56. [CrossRef]

30. Regueiro, I.; Coutinho, J.; Fangueiro, D. Alternatives to sulfuric acid for slurry acidification: Impact on slurry composition and ammonia emissions during storage. J. Clean. Prod. 2016, 131, 296–307. [CrossRef]

31. Misselbrook, T.; Hunt, J.; Perazzolo, F.; Provolo, G. Greenhouse gas and ammonia emissions from slurry storage: Impacts of temperature and potential mitigation through covering (Pig Slurry) or acidification (Cattle Slurry). J. Environ. Qual. 2016, 45, 1520–1530. [CrossRef]

32. Regueiro, I.; Coutinho, J.; Gioelli, F.; Balsari, P.; Dinuccio, E.; Fangueiro, D. Acidification of raw and co-digested pig slurries with alum before mechanical separation reduces gaseous emission during storage of solid and liquid fractions. Agric. Ecosyst. Environ. 2016, 227, 42–51. [CrossRef]

33. Chadwick, D.; Sommer, S.; Thorman, R.; Fangueiro, D.; Cardenas, L.; Amon, B.; Misselbrook, T. Manure management: Implications for greenhouse gas emissions. Anim. Feed Sci. Technol. 2011, 166–167, 514–531. [CrossRef]

34. Ottosen, L.D.M.; Poulsen, H.V.; Nielsen, D.A.; Finster, K.; Nielsen, L.P.; Revsbech, N.P. Observations on microbial activity in acidified pig slurry. Biosyst. Eng. 2009, 102, 291–297. [CrossRef]

35. Petersen, S.O.; Blanchard, M.; Chadwick, D.; Del Prado, A.; Edouward, N.; Mosquera, J.; Sommer, S.G. Manure management for greenhouse gas mitigation. Anim. Consort. 2013, 7, 266–282. [CrossRef] [PubMed]

36. Amon, B.; Kryvoruchko, V.; Amon, T.; Zechmeister-Boltenstern, S. Methane, nitrous oxide and ammonia emissions during storage and after application of dairy cattle slurry and influence of slurry treatment. Agric. Ecosyst. Environ. 2006, 112, 153–162. [CrossRef]

37. Perazzolo, F.; Mattachini, G.; Tambone, F.; Misselbrook, T.; Provolo, G. Effect of mechanical separation on emissions during storage of two anaerobically codigested animal slurries. Agric. Ecosyst. Environ. 2015, 207, 1–9. [CrossRef]

38. Rodhe, L.K.K.; Ascue, J.; Willén, A.; Persson, B.V.; Nordberg, Å. Greenhouse gas emissions from storage and field application of anaerobically digested and non-digested cattle slurry. Agric. Ecosyst. Environ. 2015, 199, 358–368. [CrossRef]

39. Clemens, J.; Trimborn, M.; Weiland, P.; Amon, B. Mitigation of greenhouse gas emissions by anaerobic digestion of cattle slurry. Agric. Ecosyst. Environ. 2006, 112, 171–177. [CrossRef]

40. Nicholson, F.; Bhogal, A.; Cardenas, L.; Chadwick, D.; Misselbrook, T.; Rollett, A.; Taylor, M.; Thorman, R.; Williams, J. Nitrogen losses to the environment following food-based digestate and compost applications to agricultural land. Environ. Pollut. 2017, 228, 504–516. [CrossRef]

41. Nyord, T.; Hansen, M.N.; Birkmose, T.S. Ammonia volatilisation and crop yield following land application of solid-liquid separated, anaerobically digested, and soil injected animal slurry to winter wheat. Agric. Ecosyst. Environ. 2012, 160, 75–81. [CrossRef]

42. Hjorth, M.; Nielsen, A.M.; Nyord, T.; Hansen, M.N.; Nissen, P.; Sommer, S.G. Nutrient value, odour emission and energy production of manure as influenced by anaerobic digestion and separation. Agron. Sustain. Dev. 2009, 29, 329–338. [CrossRef]
43. Moeller, K.; Stinner, W. Effects of different manuring systems with and without biogas digestion on soil mineral nitrogen content and on gaseous nitrogen losses (ammonia, nitrous oxides). *Eur. J. Agron.* 2009, 30, 1–16. [CrossRef]

44. Nyord, T.; Kristensen, E.F.; Munkholm, L.J.; Jorgensen, M.H. Design of a slurry injector for use in growing cereal crop. *Soil Tillage Res.* 2010, 107, 26–35. [CrossRef]

45. Fangueiro, D.; Senbayran, M.; Trinidad, H.; Chadwick, D. Cattle slurry treatment by screw press separation and chemically enhanced settling: Effect on greenhouse gas emissions after land spreading and grass yield. *Bioresour. Technol.* 2008, 99, 7132–7142. [CrossRef]

46. Dinuccio, E.; Berg, W.; Balsari, P. Gaseous emissions from the storage of untreated slurries and the fractions obtained after mechanical separation. *Atmos. Environ.* 2008, 42, 2448–2459. [CrossRef]

47. Dinuccio, E.; Berg, W.; Balsari, P. Effects of mechanical separation on GHG and ammonia emissions from cattle slurry under winter conditions. *Anim. Feed Sci. Technol.* 2011, 166–167, 532–538. [CrossRef]

48. Fangueiro, D.; Surgy, S.; Fraga, I.; Cabral, F.; Coutinho, J. Band application of treated cattle slurry as an alternative to slurry injection: Implications for gaseous emissions, soil quality, and plant growth. *Agric. Ecosyst. Environ.* 2015, 211, 47, 94–99. [CrossRef]

49. Perazzolo, F.; Mattachini, G.; Tambone, F.; Calcante, A.; Provolo, G. Nutrient losses from cattle co-digestate slurry during storage. *J. Agric. Eng.* 2016, 45, 96–109. [CrossRef]

50. Fangueiro, D.; Pereira, J.; Bichana, A.; Surgy, S.; Cabral, F.; Coutinho, J. Effects of cattle-slurry treatment by acidification and separation on nitrogen dynamics and global warming potential after surface application to an acidic soil. *J. Environ. Manag.* 2015, 162, 1–8. [CrossRef]

51. Wang, Y.; Dong, H.; Zhu, Z.; Gerber, P.J.; Xin, H.; Pote, S.; Opio, C.; Steinfeld, H.; Chadwick, D. Mitigating greenhouse gas and ammonia emissions from swine manure management: A system analysis. *Environ. Sci. Technol.* 2017, 51, 4503–4511. [CrossRef]

52. Portejoie, S.; Martinez, J.; Guiziou, F.; Coste, C.M. Effect of covering pig slurry stores on ammonia emission processes. *Bioresour. Technol.* 2003, 87, 199–207. [CrossRef]

53. Wulf, S.; Vandré, R.; Clemens, J. Mitigation options for CH₄, N₂O and NH₃ emissions from slurry management. In *Non-CO2 Greenhouse Gases: Scientific Understanding, Control Options and Policy Aspects, Proceedings of the Third International Symposium, Maastricht, The Netherlands, 21–23 January 2002*; Van Ham, J., Baede, A.P.M., Guicherit, R., Williams-Jacobse, J.G.F.M., Eds.; IOS press: Amsterdam, The Netherlands, 2002; pp. 487–492.

54. Matulaitis, R.; Juskiene, V.; Juska, R. The effect of covering pig slurry stores on ammonia emission. *Chem. J. Agric. Res.* 2015, 75, 232–238. [CrossRef]

55. Hansen, M.N.; Sommer, S.G.; Niels, P.M. Reduction of ammonia emission by shallow slurry injection: Injection efficiency and additional energy demand. *J. Environ. Qual.* 2003, 32, 1099–1104. [CrossRef]

56. Chadwick, D.R. Emissions of ammonia, nitrous oxide and methane from cattle manure heaps: Effect of compaction and covering. *Atmos. Environ.* 2005, 39, 787–799. [CrossRef]

57. Sommer, S.G.; Dahl, P. Nutrient and carbon balance during the composting of deep litter. *J. Agric. Eng.* 1999, 74, 145–153. [CrossRef]

58. Hänö, C.; Sintermann, J.; Kupper, T.; Jocher, M.; Neftel, A. Ammonia emission after slurry application to grassland in Switzerland. *Atmos. Environ.* 2016, 125, 92–99. [CrossRef]

59. Viguria, M.; Sanz-Cobeña, A.; López, D.M.; Arriaga, H.; Merino, P. Ammonia and greenhouse gases emission from impermeable covered storage and land application of cattle slurry to bare soil. *Agric. Ecosyst. Environ.* 2015, 199, 261–271. [CrossRef]

60. Severin, M.; Fuß, R.; Well, R.; Garlipp, F.; Van den Weghe, H. Soil, slurry and application effects on greenhouse gas emissions. *Plant. Soil Appl. Environ.* 2015, 61, 344–351. [CrossRef]

61. Vethof, G.L.; Mosquera, J. The impact of slurry application technique on nitrous oxide emission from agricultural soils. *Agric. Ecosyst. Environ.* 2011, 140, 298–308. [CrossRef]

62. Almaraz, M.; Wong, M.Y.; Yang, W.H. Looking back to look ahead: A vision for soil denitrification research. *Ecology* 2020, 101, e02917. [CrossRef]

63. Afshar, R.K.; Lin, R.; Mohammed, Y.A.; Chen, C. Agronomic effects of urease and nitrification inhibitors on ammonia volatilization and nitrogen utilization in a dryland farming system: Field and laboratory investigation. *J. Clean. Prod.* 2018, 172, 4130–4139. [CrossRef]
64. Rochette, P.; Angers, D.A.; Chantigny, M.H.; MacDonald, J.D.; Bissonnette, N.; Bertrand, N. Ammonia volatilization following surface application of urea to tilled and no-till soils: A laboratory comparison. *Soil Tillage Res.* 2009, 103, 310–315. [CrossRef]

65. Bourdin, F.; Sakrabani, R.; Kibblewhite, M.G.; Lanigan, G.J. Effect of slurry dry matter content, application technique and timing on emissions of ammonia and greenhouse gas from cattle slurry applied to grassland soils in Ireland. *Agric. Ecosyst. Environ.* 2014, 188, 122–133. [CrossRef]

**Publisher’s Note:** MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).