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LAND POLLUTION (G HETTIARACHCHI, SECTION EDITOR)

Methods for Treatment of Animal Manures to Reduce Nutrient Pollution Prior to Soil Application

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Abstract For centuries, animal manures have been a traditional source of nutrients in agriculture. However, disposal of animal manure has become an environmental problem in recent times as a result of increased concentration of animal production within small geographic areas. Manure nitrogen (N) and phosphorus (P) applied in excess of the assimilative soil capacity have the potential to reach and pollute water resources through soil leaching or runoff. Yet, conservation and recovery of N and P is a concern in modern agriculture because of the high cost and future limited supply of commercial fertilizers, particularly P which is extracted from mineral deposits. Therefore, N and P recovery methods are necessary to reduce their excess prior to manure soil application and recover them as valuable products. This article is a review of existing technologies for animal waste treatment and additional new methods for recycling manure N and P and possible recovery as valuable byproducts.

Keywords Nutrient management · Animal waste · Phosphorus recovery methods · Nitrogen recovery methods · Nutrient pollution · Sustainable intensification

Introduction

Historically, animal manure has been used in agriculture as a soil amendment and a valuable source of nutrients for crop production. During the past 60 years, there has been a significant change on the structure of food animal production across the USA. Since the 1950s, the animal production has more than doubled while the number of operations has decreased by 80 % [1]. Animal production has increasingly moved to very large-scale operations. Most dairy cows, poultry, pigs, and beef cattle in the USA are now housed in high-density, confined spaces. As a result, thousands of animals concentrated in a small geographic area generate large amounts of manure beyond the crop nutrient needs and absorption capacity of the nearby land. Despite its value as a source of plant nutrients, manure is less frequently used as a fertilizer. For instance, in the USA between 2003 and 2006, only 10 % of the agricultural land growing the eight major crops received manure [2•]. Therefore, distribution and disposal of animal manure has become a problem. The application of excessive amounts of manure to soil can lead to accumulation of nutrients in soils with potential for surface and groundwater pollution. Therefore, methods are necessary for treatment of animal manure prior to soil application to reduce nutrient pollution.

Of all the nutrients found in manure, nitrogen (N) and phosphorus (P) cause the greatest concern regarding environmental pollution. In the USA, federal and state regulations require confined animal feeding operations (CAFOs) to implement a comprehensive nutrient management plan (CNMP) to land apply these nutrients in an environmentally safe manner [3]. Although animal manure also contains other pollutants that can contribute to pollution of water resources such as pathogens, heavy metals, antimicrobials, and hormones [4], this article is focused on methods to reduce manure nutrient pollution prior to soil application. In this context, a number of methods have been evaluated in the USA as potentially useful manure treatment methods for reducing the environmental impact of nutrient pollution. Therefore, an overview is provided on existing alternative technologies for animal waste

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treatment and additional new methods for the recycling of manure N and P and their recovery as valuable byproducts.

Nutrient Pollution Resulting From Land Application of Animal Manure

Typically, manure N is used on an agronomic basis to control the amount of this nutrient applied to the soil while minimizing N losses into the environment [5]. As a result of microbial mineralization of organic manure N, reactive N compounds are present in the soil such as ammonia (NH_3) and nitrate (NO_3) by subsequent oxidation of NH_3. These forms of reactive N are required for plant growth, but their losses into the environment can have detrimental effects on air and water quality [6]. The overall quality of water can be impaired by land applying excess manure N, leading to NO_3 leaching into groundwater or NO_3 enrichment of surface waters due to surface runoff [7]. Additional losses of manure N into the environment can occur as gaseous losses from animal houses where manure is excreted and during manure collection, storage, and land disposal [8]. These gaseous N losses in the form of NH_3 and nitrogen oxides (NO_x) result in emissions that can adversely affect both air and water quality through the following routes: (1) NH_3 emissions contribute to forming of N-containing fine particulate ($PM_{2.5}$) matter in air, which poses a substantial threat to animal and human health [9, 10]; (2) NO_x contribution to the formation of ground-level ozone, which can cause crop losses [10]; and (3) NO_x and NH_3 atmospheric deposition leading to acidification, water pollution by nitrates, and indirect contribution to global warming since N deposition enhances nitrous oxide (N_2O) emissions [10, 11].

Although overabundance of N as a result of animal agriculture activities is a major environmental concern [6], P is the nutrient that most often may limit land application of manure in areas with concentrated animal production. Because of a disproportionate ratio of N and P in animal manure relative to crop needs, applications of manure at optimal N rates for crop growth result in accumulation of P in soils. For instance, the average N:P ratio in plant biomass of most grain and hay crops is 8:1, whereas animal manure has a smaller N:P ratio (<4:1) [12]. Due to this nutrient imbalance, eutrophication of river and lakes can be accelerated as excess soil P is lost through leaching and runoff into aquatic environments [13, 14]. As a result of P pollution, algal blooms in drinking water sources can drastically increase treatment costs and generate shortages in water supplies [15].

To reduce adverse effects of manure N and P losses into the environment, a substantial amount of N and P can be moved off the farm by transporting manure to nutrient-deficit croplands [16]. However, with increasing distance from manure production sites, the transportation of manure in bulk becomes more costly and less energy effective [17]. On the other hand, manure management in regions with dense, intensive livestock production could spur new technologies for nutrient recovery from manure. Eventually, economic incentives such as government subsidies, environmental credits, and tipping fees may be needed to promote wide adoption and integration of new methods to reduce nutrient pollution from animal production activities [1, 2•]. Thus, N and P recovery in a concentrated, usable form would allow a more economical long-distance transfer of manure nutrients while reducing agronomic N and P imbalances and adverse effects of soil nutrient losses on the environment.

Alternative Technologies for Animal Waste Treatment

Animal manures are usually a mixture of feces, urine, discarded bedding, and waste feed but with variable water content. Therefore, some manure treatment technologies can be more suitable than others to handle manure depending on if they are in solid, semi-solid, slurry, or liquid forms [18]. The technologies reviewed in this section are alternative in the sense that they do more to reduce environmental pollution than the traditional land application of untreated manure. These alternative technologies as part of waste management treatment may require additional treatment methods to improve the performance of the system to meet on-farm nutrient reduction goals. These additional treatment methods to reduce nutrients prior to soil application are further covered in this article under the section on methods for nutrient reduction and recovery.

Compaction

Compaction methods such as pelletizing and baling are physical processes that can enhance the storage and handling of bulk manure solids. These methods aim at a more economical and dust-free transport of manure nutrients as well as conditioning of manure prior to bio-energy conversion. Pelletizing a loose material such as poultry litter significantly increases its density. For instance, the bulk density of broiler litter was increased fourfold, from 200 to 790 kg m^{-3} by pelletizing poultry litter mixed with 3 % vegetable oil [19]. Optimum compaction of poultry litter using pelletizing equipment depends on moisture content and energy required to compact the poultry litter [20]. However, the high-energy input and equipment costs make the technology impractical for broiler farmers to purchase and operate a pellet mill on farm. As a lower energy alternative compaction method to pelletizing, baling is being developed for poultry litter waste. It combines compression and wrapping [21].

Composting

Composting is the aerobic microbial breakdown and stabilization of organic matter. Composting is a well-suited technology for on-farm management of agricultural residues, but it is not an environmentally sustainable technology for treating manure alone. Certain chemical and physical characteristics of animal manures are not adequate for composting and could limit the efficiency of the process: excess of moisture; low porosity; high N concentration versus organic C, which gives a low C/N ratio; and in some cases, high pH values [22]. As a result of composting animal manure, significant N loss can occur through NH_3 volatilization which is the main pathway of N loss during this process [23, 24]. Therefore, different aeration strategies, substrate conditioning-feedstock formulation, bulking agents, and amendments have been used in manure composting in order to control the process to reduce composting time and costs, enhance the quality of compost, and ultimately avoid NH_3 volatilization losses [24]. For instance, a full-scale study in a centralized solids processing facility evaluated the combined effect of feedstock formulation and bulking agent to optimize the composting process of pig manure [25]. The feedstock formulation included separated pig manure solids combined with cotton gin waste and wood chips. The composts produced met strict EPA Class A bio-solids quality standards due to low pathogen levels and conserved 95–100 % of the N. In another study, using zeolite or alum as amendments, NH_3 emissions were reduced 85–92 % with the finished pig manure compost retaining threefold more N than the unamended control; the addition of these amendments did not appear to significantly affect the composting process [26]. The advantages of composting animal manures compared with direct application to soil of untreated manure are sanitation, reduction of volume and moisture, odor removal, safe storage, and a more uniform, easier to transport byproduct than untreated manure [27]. On the other hand, possible disadvantages of composting are derived from the cost of installation and management, large areas for storage and operation, and additional cost of bulking agents and amendments. In this regard, composting of animal manure should be seen as a technology that adds value, producing a high quality product focused on specific agricultural markets such as soilless media for nursery crops, orchard mulching, and organic farming.

Anaerobic Digestion

Driven by anaerobic microorganisms in an oxygen-free environment, anaerobic digestion converts organic matter into methane (CH_4), carbon dioxide (CO_2), hydrogen sulfide (H_2S), NH_3, other organic volatile organic compounds, and a nutrient-rich sludge. Anaerobic digestion is used around the world to stabilize manure, reduce pathogens and odor emissions, and produce energy through biogas generation. Anaerobic digestion is the basic process for biological treatment of animal manures in open anaerobic lagoons and anaerobic digesters (covered lagoons, plug flow, and complete mix reactors) [28]. Open anaerobic lagoons are widely used across the USA to store and treat wastewater generated from confined swine and dairy operations. Open anaerobic lagoons do reduce the N content of the material through NH_3 volatilization. For instance, estimates of NH_3 emissions from open anaerobic lagoons on an annual daily emission per finishing pig were reported in the range of 10 to 18 g NH_3 animal^{-1}d^{-1} [29, 30]. Moreover, the USDA-ERS estimates that large operations using open lagoons have NH_3 emissions of twice as much per animal than operations with pit storage systems under the animal housing [31]. Because of the adverse effects of NH_3 emissions on the environment, the use of supplemental strategies such as lagoon covers are needed to control these emissions. In itself, a lagoon cover is not a manure treatment technology but serves as a barrier between the lagoon waste and the environment. The use of an impermeable lagoon cover was reported as an effective measure to reduce NH_3 emissions and greenhouse gases [32], but accumulation of both biogas and NH_3 requires that the covered lagoons be retrofitted with a system for biogas utilization or flaring along with a nutrient management system to reduce the higher N concentrations of the covered lagoon effluent.

Since anaerobic digestion per se is not a nutrient pollution control practice, digester effluent from plug flow or complete mixed digesters must be managed similarly to digested manure from covered lagoons including treatment methods for sequestering nutrients prior to soil application. Due to economies of scale, most dairy and pig farmers in the USA are currently unable to take advantage of anaerobic digestion to treat their waste while simultaneously producing energy for farm use [33, 34•]. In addition, a widespread adoption and use of anaerobic digesters in US dairy farms without nutrient recovery technology would require twice as many acres of cropland to dispose nutrients in an environmentally safe manner [34•].

Methods for Nutrient Reduction and Recovery

Solid-Liquid Separation

Solid-liquid separation methods are used to divide the liquid and solid fractions of manure by gravity, mechanical, and chemical processes [35, 36]. Mechanical and gravity solid-liquid separation has been traditionally used to reduce lagoon solids buildup by separating solids from liquid raw manure prior to flowing into the anaerobic lagoon or other holding pond, or to recover solids from lagoon sludge [37]. Usually, solid-liquid separation efficiencies of mechanical manure separators are less than 60 % solids removal. However, new advances over the last 15 years in equipment and flocculant applications for chemically enhancing solid-liquid separation treatment have improved removal efficiency of solids and specific plant nutrients such as N and P [38, 39]. For example, swine manure treated using a high-rate solid-liquid separation system combined with flocculant (polyacrylamide) injection separated 89 % of total suspended solids, 72 % of organic N, and 66 % total P [40]. This separation process also efficiently removed heavy metals such as Cu (88 %) and Zn (87 %). Solids separation makes the storage of liquid and solids easier and safer by reducing the potential of contaminating surface and groundwater. In addition, solids separation facilitates the use of further methods to recover nutrients that would otherwise be unsuited for use with raw manure [41].

Chemical Amendments

Chemical amendments such as alum [$Al_2(SO4)_3$•14 H_2O], sodium bisulfite ($NaHSO_3$), and acidified clays are used to control or reduce NH_3 release from poultry litter and manure [42–44]). Application of these chemical amendments reduces poultry litter or manure pH and suppresses NH_3 emissions. These amendments have been widely used in the USA to reduce NH_3 concentrations in the air of poultry houses to levels low enough to maintain bird health and productivity. Since the capacity of these amendments to neutralize NH_3 is depleted in time, repeated applications are needed at the beginning of a new flock of birds. By using these amendments, N is conserved un-volatilized in the poultry litter but not recovered as a separate product.

Thermochemical Conversion

Thermochemical methods such as incineration, pyrolysis, and gasification, employ high temperatures to convert biomass into gases, hydrocarbon fuels, and charcoal or ash residues. Incineration is the direct combustion of organic feedstock in the presence of air. For instance, incineration of poultry litter produced ashes with P average content of 110 g P kg^{-1} but with no N content because of its gaseous loss during the incineration process [45]. Other thermochemical conversion methods utilize heat under limited oxygen conditions to thermally decompose and convert biomass into gaseous (hydrogen, methane, carbon monoxide, hydrocarbons, etc.), liquid (bio-oil), and solid (char) products. Heating rates, reaction temperatures, and reaction fluid media (inert gas or liquid water) determine the composition and characteristics of the products [46, 47]. Gasification at reaction temperature of 800 °C produces mainly gaseous product called synthesis gas, while pyrolysis at lower reaction temperatures of 400 to 500 °C produces about equal distribution of gas, bio-oil, and solid charcoal called "biochar." Among these different thermochemical conversion technologies, the pyrolysis method looks promising for animal manure management because it produces value-added biochar for use as a soil amendment for carbon sequestration and soil fertility improvement [48]. Unlike incinerated manure ash, biochar generated from manure retains most of the P and up to one third of the N of original swine manure [49]. However, pyrolysis of wet animal manure alone is not energetically viable because of its low energy output versus the large energy required to evaporate moisture from the manure feedstock. Co-pyrolysis of animal manures with high-energy density feedstocks, such as plastics, can make the total pyrolysis process energetically sustainable. Pyrolysis of wet swine manure blended with spent plastic mulch wastes produced a solid biochar and combustible gas with a heating value higher than natural gas [50]. According to this report, pyrolysis of the swine solids could be energetically sustainable by co-pyrolyzing a feedstock consisting of dewatered swine solids (75 % moisture) with just 10 % plastic mulch waste.

On the other hand, hydrothermal carbonization methods can pyrolyze wet feedstock directly. Hydrothermal carbonization is a relatively low temperature (180–350 °C) process that treats wet waste streams under pressurized liquid water reaction medium and produces a valuable solid char called hydrochar [46]. The manure-based hydrochar surface properties make the char amenable to be used as an environmental sorbent for pollutants such as endocrine-disrupting chemicals, herbicides, and polyaromatic hydrocarbons [51–53]. Because evaporation of water is avoided, hydrothermal carbonization requires much less energy input than pyrolysis [46]. Despite its favorable energetics, hydrothermal carbonization of animal manure is still an emerging technology as the fate of nutrients and other beneficial uses of its byproducts need further investigation.

Biological Conversion to Non-Reactive N

Nitrification-Denitrification

The aim of the nitrification-denitrification process is to transform NH_3 into innocuous N gas (N_2). Nitrification is a very limiting process in animal waste treatment but a necessary process to be able to remove large amounts of reactive N using biological nitrification-denitrification systems. Nitrification depends on the ability of nitrifying bacteria to oxidize NH_3. Ammonia is in solution as the ammonium ion (NH_4^+) and unionized or free NH_3. These two forms of NH_3 are in equilibrium, controlled by the pH and temperature of the manure. Nitrifying bacteria needs oxygen, low organic carbon, favorable temperature, and a growth phase before sufficient numbers are present for effective nitrification. Low nitrification rates during cold weather are often a problem for adoption of biological treatment of NH_3 in livestock effluents. This problem has been circumvented by the discovery of a high performance nitrifying sludge (HPNS) with excellent NH_3 removal performance during cold weather conditions [54]. The unique microbial community composition that contained NH_3 oxidizers, cold tolerant, and floc-forming microorganisms provided a nitrifying sludge capable of very high rates of nitrification at cold temperatures as low as 5 °C [55]. The HPNS was used for rapid start-up of full-scale plants for swine wastewater treatment; the biological process removes more than 95 % of the NH_3 from wastewater containing 1000–2700 mg NH_3 L^{-1}. [40, 56]. This technology is well suited for economical nitrification of high-NH_3 livestock wastewater under cold weather conditions. Once in NO_3^- form, the transformation of N into N_2 (or denitrification process) needs two conditions: a source of carbon and an anaerobic environment. These conditions are typically found in liquid manure storage units. Thus, a denitrification tank can be incorporated into the treatment system in fluid connection with a nitrifying tank to provide total N removal [40].

Deammonification

The use of the anaerobic ammonium oxidation (anammox) as a new pathway to biologically remove NH_3 has created great expectations in the field of wastewater treatment because it could significantly reduce aeration needs and cost of treatment. The anammox process uses carbon dioxide as its C source to produce biomass ($CH_2O_{0.5}N_{0.15}$) and nitrite (NO_2) as an electron acceptor for ammonium (NH_4^+) oxidation but also as an electron donor for the reduction of carbon dioxide (see Eq. 1) [57].

$$NH_4^+ + 1.32NO_2 + 0.066HCO_3^- + 0.13H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2.03H_2O + 0.066CH_2O_{0.5}N_{0.15} \quad (1)$$

In the USA, a novel anammox bacterium strain was discovered (Candidatus *Brocadia caroliniensis*) that oxidizes NH_3 and releases N_2 gas under anaerobic conditions [58, 59]. This novel anammox bacterium was isolated from livestock manure sludge. The bacterium isolate can be used for the treatment of wastewater contaminated with animal waste and/or having undesirable high levels of NH_3, including agricultural, industrial, or municipal wastewaters [60]. Partial nitritation of NH_4^+ to NO_2^- is needed to produce a suitable influent for the anammox process [61]. This partial nitritation conversion can be done by ammonia-oxidizing bacteria in a separated reactor or combining both processes in a single reactor [62]. Compared to conventional biological N removal methods, the anammox process can save more than 50 % of the oxygen supply and 100 % of the external organic C source for denitrification [62]. This leads to the development of new anammox-based treatment for livestock wastewater with a significant decrease in operational costs.

Nitrogen Recovery Methods

N Recovery From Air

There is major interest from producers and the public on implementing best control technologies that can abate NH_3 emissions from confined animal operations by capturing and recovering N. There are three approaches to recover NH_3 from air in livestock operations: (1) treating the NH_3 in the exhaust air from the houses using scrubbing or filtration techniques, thus preventing its release into the environment [63, 64]; (2) to selectively pull and treat the air near the source, where NH_3 levels are more concentrated, using dedicated ventilation systems or systems that are independent of the house ventilation system [65]; and (3) the passive use of gas-permeable membrane modules inside the houses [66]. The scrubbing methods consist of removal of NH_3 from livestock houses by forcing the house air through an NH_3 trap, such as an acidic solution (scrubbers), or through a porous filter with nitrifying biofilms that oxidize NH_3 to nitrate (bio-trickling or organic filters) [63]. The use of acid scrubber is promising, as it simultaneously mitigates and recovers NH_3 emission to form a salt with value as fertilizer. A new scrubber, described by Moore [64], consisted of a two-stage exhaust scrubber system where the carbon dioxide, particulate matter, and alkalinity of the barn exhaust air is reduced by a first scrubber, and a second scrubber subsequently reduces the amount of NH_3 and volatile organic compounds. The second scrubber used potassium bisulfate ($KHS0_4$) which functions as a proton donor scrubber solution to remove NH_3 from exhausted barn air. Combining the $KHS0_4$ scrubber solution with exhausted NH_3, N is recovered in a solution also rich in K that could be used as a liquid fertilizer. On a full-scale study, an acid spray scrubber was evaluated to recover NH_3 emissions from poultry waste composting facilities and produce N fertilizer [67]. The scrubber, installed with a 1.3-m exhaust fan, consisted of 15 spray scrubber modules each equipped with three full-cone nozzles that used dilute sulfuric acid as the medium. The scrubber effluents containing 22–36 % (*m*/*v*) NH_3SO_4 were comparable in grade to commercial N fertilizer.

A new approach was developed for NH_3 capture from the air near the source without intense air movement using gas-permeable membranes. This method has the potential to reduce ventilation and energy needs along with lowering NH_3 in the air of poultry barns and composting systems [66]. This new method recovers NH_3 in a concentrated, purified form using the concept of integrated membrane separation and gas absorption also shared by hollow fiber membrane contactor techniques. This process includes the passage of gaseous NH_3 through a microporous hydrophobic membrane, capture with a circulating diluted acid on the other side of the membrane, and production of a concentrated ammonium salt. In a bench-scale prototype study using tubular expanded polytetrafluoroethylene (ePTFE) membranes and a 1 *N* acidic solution (sulfuric acid), about 96 % of the NH_3 lost from poultry litter was captured and recovered [68]. The results obtained in this study show that the use of gas-permeable membrane technology could be an effective approach to recover NH_3 from poultry litter. On a second study, bench- and pilot-scale prototype systems using flat expanded polytetrafluoroethylene (ePTFE) membranes and a 1 *N* sulfuric acid solution reduced headspace NH_3 concentrations from 70 to 97 % and recovered 88 to 100 % of the NH_3 volatilized from poultry litter [69]. The potential benefits of this technology include cleaner air inside poultry houses, reduced ventilation costs, and a concentrated liquid NH_3 salt for use as a liquid fertilizer.

N Recovery From Liquid Phase

A promising new method to recover NH_3 from the liquid phase is the use of gas-permeable membranes [70, 71]. The membranes can be assembled in modules or manifolds. Diluted sulfuric acid (H_2SO_4) is continuously circulated through the tubular gas-permeable membrane placed in the liquid waste and back into an acid tank to recover NH_3. For liquid manure applications, the membrane manifolds are submerged in the liquid and the NH_3 could be removed from the liquid matrix in barn pits or storage tanks before it goes into the air. The concept was successfully tested using concentrated swine and dairy manure effluents containing 140 to 1400 mg L^{-1} NH_3-N. The removal efficiency of the gas-permeable process was higher than 90 %. By using the same stripping solution in 10 consecutive batches treating raw swine manure, the recovered N was concentrated in a clear solution containing 53 g L^{-1} NH_4-N [70, 71]. On another trial, the process was optimized by controlling the pH using manures of various strengths (low, medium, and high) with NH_3 concentrations ranging from 1070 to 2290 mg L^{-1} and total solids concentrations from 8.6 to 24.9 g L^{-1}. As NH_3 content increased in manure, more N was captured by the process. With no pH adjustment, NH_3 recovery from manure was 55 %. When pH of manure was adjusted (8.5–9.0 units), the process recovered more than 80 % of the NH_3 contained in the raw manure [72]. These results suggested that this new method that makes use of submerged gas-permeable membrane manifolds is useful for recovering and concentrating the NH_3 contained in raw swine manure, reducing environmental pollution potential while converting NH_3 into a valuable plant fertilizer.

Phosphorus Recovery

Chemical Precipitation

Chemical precipitation of P from animal wastewater comprises well-studied methods for P recovery. Phosphorus can be removed as a precipitate by adding metal salts of aluminum, iron, magnesium (Mg), or calcium (Ca). Because of the limited value of aluminum or iron phosphates for industrial and agricultural applications [73], the most common precipitation technologies to recover P for use as fertilizer use Mg or Ca phosphate precipitation processes [74–76].

Precipitation of P with Mg as magnesium ammonium phosphate crystals [$MgNH_4$ $(PO_4).6H_2O$], also known as struvite, is the most common method of P recovery because it allows the simultaneous recovery of N and P from waste streams [77]. Struvite is formed when the activity of Mg, NH_4, and phosphate ions exceeds the solubility product of struvite as described in Eq. 2.

$$Mg^{2+} + NH_4{}^{+} + PO_4{}^{3+} + 6H_2O \rightarrow MgNH_4PO_4.6\,H_2O \tag{2}$$

Methods for P recovery from animal wastewater by struvite precipitation include crystallizers and fluidized bed reactors requiring seeding material to promote aggregation of fine phosphate particles for subsequent recovery by filtration devices [78–80]. Recovery of P as struvite is a suitable method for treatment of swine wastewater. However, precipitation of struvite from dairy manure effluents can be a challenge due to the interference with Ca. Zhang et al. found that the majority of P in anaerobically digested dairy effluent was tied up in finely suspended Ca phosphate solids [81]. They demonstrated that the P removal efficiency was improved up to 82 % by removing the Ca interference with an acid pre-treatment of dairy effluents using either hydrochloric acid or ethylene di-amine tetra-acetic acid. This acid pre-treatment dissolved the Ca phosphate solid phase allowing subsequent precipitation of struvite at alkaline pH by the addition of sodium hydroxide and magnesium chloride. Thus, recovery of phosphate from dairy wastes in struvite form may require additional acid pre-treatment to improve the initial phosphate solubility and significant addition of chemicals to adjust pH (sodium hydroxide) for its precipitation.

Removal of P using Ca compounds may initially precipitate a number of Ca phosphate minerals (brushite, monetite, octacalcium phosphate, hydroxyl apatite, or amorphous calcium phosphate). However, hydroxylapatite

[$Ca_5(PO_4)_3OH$] is the most common of these minerals and its formation is described in Eq. 3 [82].

$$10Ca^{2+} + 6\,PO_4{}^{3-} + 2OH^- \rightarrow 2Ca_5(PO_4)_3OH \qquad (3)$$

When calcium hydroxide is added to liquid manure, the hydroxide reacts with the existing bicarbonate to form carbonate, with $NH_4{}^+$ to form NH_3, and with phosphate to form phosphate precipitate compounds [82, 83]. Since a large part of the inorganic C in liquid manure is released during decomposition of organic compounds, carbonate and $NH_4{}^+$ alkalinity are the most important chemical components in liquid manure. Both contribute to the buffering capacity in the alkaline pH range. However, precipitation of P in animal wastewater using an alkaline compound such as calcium hydroxide is very difficult due to the inherent high buffering capacity of liquid manure. This buffering effect prevents rapid changes in pH. This problem is solved using a pre-nitrification step that reduces the concentration of $NH_4{}^+$ and bicarbonate alkalinity [84]. The pre-nitrification step provides a less buffered liquid in optimum pH conditions for effective P removal with the addition of small amounts of calcium hydroxide. With this process, the use of a crystallizer or fluidized bed reactor with seeding to induce P nucleation is not required. In practice, the soluble P was removed from pre-nitrified liquid swine manure in a settling tank by adding hydrated lime to form a fine precipitate at pH 10.5 [40]. Thereafter, the fine precipitate was aggregated by adding a polymer and dewatered using filter bags, recovering 99 % of total P with respect to unfiltered material [40, 85].

This calcium phosphate removal process [84] was conceived to both remove P in animal waste treatment systems with anaerobic lagoons [82, 83] and in newer systems that eliminate lagoons [40, 56]. In a pilot field study at ten swine farms in North Carolina, USA, this technology effectively recovered 95–98 % of the P from the anaerobic lagoon effluent as a phosphate precipitate [82]. In systems without a lagoon, raw liquid manure was first treated through an enhanced solid-liquid separation process with polymers to remove most of the carbonaceous material from the wastewater. The separated water was then treated with the nitrification and soluble P removal sequence. A denitrification tank was incorporated into the treatment system to provide total N removal in addition to the P removal. This configuration was tested full-scale in swine farms in North Carolina. In a first generation evaluation, removal efficiencies of 94 % for soluble P were obtained [84]. On average, the recovered P precipitate solid had a concentration of 10.7 % P. A second generation improved version of the technology was developed for municipal and agricultural wastewater and includes the simultaneous separation of solids and P from wastewater effluents [40, 86]. A third generation system allowed the P recovery from diluted flushed swine manure [87•]. In the latest improved versions, the incorporation of a combined solid-liquid separation and P recovery process became more efficient in terms of equipment needs and chemical use [88].

Wet Extraction

There is much interest around the world on P recovery from animal manure by wet extraction of P from the byproducts of thermal treatment such as the ash after incineration and the biochar after pyrolysis. For instance, P was recovered in a two-step precipitation process from chicken manure incineration ash extracted with a 1.0*M* hydrochloric acid solution. Heavy metal impurities were first precipitated at pH 3.0 using sodium hydroxide and removed by filtration. Phosphorus was then recovered by raising the pH of the filtrate to 8.2 forming a precipitate containing 92 % of its P as Ca phosphate [89]. Following pyrolysis of pig manure, about 92 to 97 % of the P present in fresh manure was recovered in the biochar fraction, much of which (60 to75%) was extracted as inorganic P using a 0.2*M* sulfuric acid solution [90]. Hydrochar produced by hydrothermal carbonization of poultry, swine, and cattle retained more than 90 % of the initial total P of the wet manure feedstock. About 80 to 90 % of the P content of these hydrochars was recovered using acid extraction (4*M* HCl) and precipitation at pH 9 by addition of 5*M* NaOH to well-stirred acid extract solutions [91].

A new method called “quick wash”, conceived to improve the N and P balance in poultry litter waste prior to soil application, used wet extraction of P from raw poultry litter and recovered manure P in solid concentrated form [92]. This process consists of selectively extracting P (but not the N) from solid manure and municipal sludge prior to soil application using mineral or organic acid solutions and recovery of P from the extract by adding lime and an organic polymer forming a calcium-containing P precipitate [93]. The quick wash process has three products: (1) a washed solid with an N:P ratio optimal for use in crop production; (2) a concentrated solid P material that can be transported long distance and used as an effective P fertilizer; (3) a liquid effluent that could be applied to nearby cropland as liquid fertilizer or recycled into the treatment system. This method can recover 80 to 90 % of P in concentrated solid Ca phosphate form from poultry litter and raw swine manure. After treatment, it leaves a washed residue with an N:P ratio >4, which makes the residue more environmentally safe for soil application [93, 94]. The recovered phosphate is a good plant fertilizer with P contents of more than 10 % P_2O_5 with over 90 % as plant available P [95, 96]. Compared with thermal conversion methods, the quick wash process avoids loss of oxidizable organic C and N from treated manure because it is conducted at ambient temperature. Most C and N remain untouched in the washed residue. Therefore, the washed manure with most of the P removed can be land applied on an N basis because its N:P ratio is better balanced to match specific nutrient needs of crops. In addition, the recovered P product can be transported to P-deficient croplands for use as a plant fertilizer.

Conclusions

As a result of increasing global demand on protein consumption, animal production has progressively moved to larger scale operations in agglomerated geographic distribution. Usually, a large concentration of animals and manure in a limited land area can lead to accumulation of nutrients in nearby soils with potential for surface and groundwater pollution. As a consequence of this trend in animal production, the management and treatment of large amounts of manure are becoming increasingly difficult via conventional methods. The integration of N and P recovery methods in manure management systems can help to maintain sustainability of confined animal production while recycling these nutrients into agriculture. New regulations and current trends of animal production concentration will require environmentally safe technologies for handling excess manure nutrients. Therefore, affordable technologies for N and P recovery from manures will be needed in the near future. A strategy to reduce costs of new nutrient reduction technologies is to install these technologies on a sufficient number of farms to facilitate continued engineering improvement and development of the market for their byproducts. Eventually, economic incentives such as government subsidies, environmental credits, and tipping fees may be needed to initiate adoption and integration of new methods to reduce nutrient pollution from animal production activities.

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Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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