Manure Chemistry – Nitrogen, Phosphorus, & Carbon

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INTRODUCTION

It's hard to talk about manure management without referring to the complex chemistry involved. It's also hard to remember all that stuff we learned so long ago--- especially when somebody starts throwing around words like 'anoxic,' 'mineralization,' and 'redox.' This document is intended to provide a compact overview of what happens to three critical elements—nitrogen, phosphorus, and carbon—during manure storage and treatment.

NITROGEN

The element nitrogen (N) has many oxidation states and can form numerous compounds. Elemental N_2, or diatomic nitrogen, composes 78% of the air we breathe, and nitrogenous compounds are components of all living tissue. In manure, N occurs as nearly all of these forms at one time or another:

Nitrogen Species	Formula	Oxidation State
Organic nitrogen	Org-N	
Ammonia,	NH_3	-3
Ammonium ion	NH_4^+	-3
Hydrazine	N_2H_4	-2
Hydroxylamine	NH_2OH	-1
Nitrogen gas	N_2	0
Nitrous oxide	N_2O	+1
Nitric oxide	NO	+2
Nitrous acid	HNO_2	+3
Nitrite ion	NO_2^-	+3
Nitrogen dioxide	NO_2	+4
Nitric acid	HNO_3	+5
Nitrate ion	NO_3^-	+5

Nitrogen is of concern to agriculture both as an essential plant nutrient for building proteins and amino acids and as a potential water pollutant. Nitrogen, as nitrate or ammonium, is highly soluble and moves rapidly in runoff and in soil solutions. Buildup of nitrate in groundwater is a health concern; the concentration limit in drinking water is 10 mg per liter. While in surface waters the concentration is rarely that high, nitrogen still contributes to eutrophication (excess plant growth). Excessive use of nitrogen fertilizers is implicated in the expansion of a hypoxic area or "Dead Zone" in the Gulf of Mexico.

The ammonia form of nitrogen can be an air quality concern. Manure nitrogen is often converted into the ammonium (soluble) form by bacteria. If the pH is above neutral, the manure is warm, and there is nothing to work against ammonification, the ammonium changes into the ammonia (gaseous) form and volatilizes into the atmosphere. Ammonia in significant concentrations is harmful to livestock and agricultural workers; it is also a precursor to harmful particulates and facilitates the formation of undesirable gases.

There are five ***natural*** processes that transform N from one form to another: Fixation, ammonification, synthesis, nitrification, and denitrification.

- Fixation: the conversion of nitrogen gas [N_2] from the atmosphere into any form of nitrogen used by plants and animals. The most familiar example is the work done by *Rhizobia* bacteria attached to the roots of legumes, which can reduce N_2 from the atmosphere into NH_3. A certain amount of N_2 is also transformed into NO_3 by lightening and delivered to the soil in rain. Plants utilize N as either ammonium (from bacteria) or nitrate (from bacteria, lightening, or fertilizer). Animals get their N by eating plants or other animals.

- Ammonification: the degradation of organic-N to ammonium, usually by bacteria. This can happen under both aerobic and anaerobic conditions if the appropriate bacteria are present.

- Nitrification: converting ammonium to nitrite and then nitrate, in a type of biological oxidation. The two bacterial species *Nitrobacte*r and

Nitrosomonas are most commonly associated with this transformation.

- Synthesis: the biochemical mechanism that converts ammonium or nitrate into living cells, either plant cells or bacterial cells. (Animals cannot eat straight ammonium or nitrate and convert it.)
- Denitrification: The completion of the nitrogen cycle by returning N to the atmosphere as N_2 gas. Denitrifying bacteria convert NO_3 to N_2 under anoxic (low oxygen) conditions. This can occur in soils that undergo periods of saturation, either naturally or under cultivation as in rice production.

After manure is excreted, the organic nitrogen, ammonium, and urea in the feces and urine are subjected to treatment and storage. Urea is quickly converted to ammonium. Here are some of the transformations that might occur, depending on how the manure is handled:

- Storage: What happens to nitrogen in structures designed to store, rather than treat, manure depends on whether conditions are aerobic (plenty of oxygen) or anaerobic (no free oxygen.) In aerobic conditions, the N will largely remain in the manure as organic N or ammonium. Aerobic conditions may exist in dry stack storage, poultry litter storage, or systems specifically designed to aerate the manure. In anaerobic conditions, which usually apply, a portion of N will probably be lost to the atmosphere as NH_3.
- Anaerobic lagoons: Structures specifically designed as anaerobic lagoons are not just for storage. In a properly operating lagoon, conditions foster anaerobic decomposition. pH will be at or above neutral, in contrast to storage facilities which are more acidic. Manure has a long residence time in most anaerobic lagoons, allowing for complex chemical and biological interactions. Nitrogen will be converted into NH_4 and NH_3 by biological activity. When conditions favor ammonia volatilization, NH_3 will be lost to the atmosphere. Ammonification is accelerated by high pH and warmth.
- Aerobic lagoons: Under aerobic conditions, where oxygen is freely available, far less ammonia is generated than in anaerobic conditions. In these situations, N will be retained in solution as NO_3 and NH_4, and in the bodies of aerobic microorganisms as organic N. Nitrogen converted to ammonium will be mineralized as NO_3. If the conversion from NH_4 to NO_3 is interrupted or slowed by lack of oxygen, the intermediate NH_3 will be driven off.
- Anaerobic digestion: Passing through a digester has little effect on the total nitrogen content of manure. A negligible amount of N may be emitted as NH_3, but the majority will be found as organic N and NH_4 in solution in the digester sludge. The ammonium content of digester sludge will be higher than that of raw manure. Although the anaerobic conditions should favor production of ammonia, the ammonium is held in solution by the pressurization of the vessel, and the slightly acidic pH favorable to methanogenic bacteria.
- Gasification: a portion of the N in manure will be gasified into either N_2 or N_2O. This process is still poorly understood and may be highly variable depending on conditions. The ash and char remaining after gasification is usually low in nitrogen.
- Pyrolysis: Some N will be found in the oil products, where it is considered a contaminant. The remaining N is usually found in solution in the watery waste remaining after the oils have been distilled off.
- Composting: A portion of the N in the compost pile is volatilized as NH_3, and a small amount may be emitted as N_2O. The remainder is found either in the bodies of microorganisms as organic N, or as NO_3, which is available to plants.
- Land application: Raw (untreated) manure applied to land contains nitrogen in the form of organic compounds and ammonium. Dryer manure from feedlots and poultry litter will also contain some nitrate-N. The organic nitrogen in manure is broken down into forms plants can absorb over time. Nitrate is highly mobile in soil solution, as is ammonium to a lesser degree. Both are readily used by crop plants. Unfortunately, they are also mobile in surface runoff, and may cause water pollution if not properly managed. Manure management calculations generally assume that most available nitrogen in manure will be utilized by plants or denitrified by soil microorganisms in three years. When land applied, manure can also lose nitrogen as ammonia through volatilization. This occurs during application and as the manure sits on the soil surface. Incorporation or injection reduces these losses, because the ammonium will be nitrified by soil bacteria. In wet soils and under appropriate conditions, anaerobic bacteria may then denitrify the nitrate and give off nitrogen gas.

PHOSPHORUS

Phosphorus is a non-metal found in the same chemical family as nitrogen. The most common oxidation states found in nature are +3, +5, and -3. Phosphorus generally forms compounds with oxygen, hydrogen, and halides [e.g. fluoride]. In agriculture, we're most familiar with it in fertilizer compounds such as mono- and di-ammonium phosphate, triple super-phosphate, and as the plant-available ion in soils, orthophosphate ($H_2PO_4^-$). Regardless of the actual chemical form of the phosphorus, the analyses of phosphorus fertilizers are given as phosphate (P_2O_5).

Phosphorus (P) is an essential nutrient for both plants and animals. All DNA molecules contain phosphorus. Plants need it for flowering and reproduction, as well as energy exchange. Animals need phosphorus for a number of processes including energy processes, formation of bone, and building eggshells.

In manure, P is present in organic matter and as dissolved reactive phosphorus—DRP or orthophosphate. The dissolved form is easily transported from crop fields to surface water in runoff, where it can cause nutrient imbalances leading to eutrophication and other water quality problems.

Because P does not easily form gases, it stays in the manure through storage and treatment. Organic phosphorus is contained in the bodies of microorganisms in the manure. Dissolved reactive P in solution can be coagulated with metal compounds and then aggregated into clumps that will settle out by treating the manure with flocculating polymers. Solids separation technology may partition up to 90% of P into the solid portion of the manure if the separation process is augmented with coagulants and flocculants. Solids separation without chemical assistance may remove anywhere from a few percent of total P up to 60%, depending on how efficiently the method separates out fine manure particles, where most of the P is contained.

Under certain conditions, (pH between 7 and 11 and a sufficient amount of dissolved magnesium) P can combine with magnesium and ammonium to form the crystalline compound struvite [magnesium ammonium phosphate hexahydrate, $MgNH_4PO_4 \cdot 6H_2O$]. Forced precipitation of struvite has been investigated as a way of removing P from manure effluent.

Under acidic anaerobic conditions, P can form the gas phosphine (PH_3). However, rather than volatilizing like ammonia, phosphine usually recombines with other constituents of the manure and is not lost.

Note that in treatments that reduce the mass of the manure, like composting, gasification, pyrolysis, and digestion, the concentration of P increases because it does not go away.

- Storage: When manure is stored as a solid, not much happens to the phosphorus; it will still be present as it was when stored. When stored as a liquid, the P tends to accumulate in the sludge at the bottom of the storage unit, as organic P present in the bodies of microorganisms.
- Anaerobic digestion: Digestion has little effect on P, other than moving some of the dissolved portion into the bodies of bacteria that carry out the anaerobic digestion process. All of the P present in the manure will still be present in the digester sludge.
- Gasification: Since P is not a component of any of the gases produced in this process, all the P present in the manure at the beginning of the process will still be there at the end, contained in the ash and char residuals.
- Pyrolysis: As with gasification, all of the P will end up in char and other residuals.
- Composting: At the end of the composting process, most of the P will be in organic form, contained in live or dead microorganism bodies. All of the initial P will still be present.
- Land application: Ideally, all the P in land-applied manure would be taken up by crop plants. In reality, some is transported in runoff, some moves into the soil profile, and some is bound by metal ions (calcium, aluminum, and iron.) Soils have varied capacity for binding P, depending on pH, cation exchange capacity, rainfall, type of clay present, and presence of metals (primarily aluminum and iron oxides.) Over time, all the easily available P in the root zone will be used by crops as long as the amount of manure applied is in balance with crop needs. In many parts of the country, excess manure has been applied for years and soils are heavily loaded with phosphorus that is slowly traveling down the soil profile, and may never be fully utilized.

CARBON

The abundant carbon atom is present in all forms of terrestrial life. Carbon cycles through the soil, oceans, atmosphere, earth's geology, and living things, entering into more chemical compounds than any other element.

Plants fix carbon from carbon dioxide (CO_2) in the atmosphere, converting most of it into sugars and starches. Animals eat the plants and convert the carbon into animal tissue. The carbon in manure comes from plant (and some animal) materials in livestock feed. A portion of the carbon consumed is exhaled as methane (CH_4), and of course, animals breathe in oxygen and exhale CO_2.

A large amount of the organic matter in manure is actually the bodies of bacteria from the animal's gut, along with some partly digested feed. Carbon is present in proteins, fatty acids, lipids, carbohydrates, cellulose, and lignins.

During storage and treatment, much of the carbon in manure may be mineralized into CO_2 or converted to CH_4.

- Storage: Biological activity continues in the manure during storage. If the conditions are aerobic, CO_2 will be given off, and if anaerobic, CH_4 and smaller amounts of CO_2 will be emitted. When manure is stored in anaerobic lagoons, significant amounts of carbon are lost as methane.
- Anaerobic digestion: Simple sugars, volatile fatty acids, and alcohols degrade quickly – within hours–and are converted into CH_4 and CO_2 with traces of hydrogen sulfide [H_2S] and water vapor. If the residence time is long enough, hemicellulose, fat, and protein will degrade in a few days. Cellulose and lignin are usually left intact. The gasses given off by the digester will contain 40% to 70% methane.
- Gasification: Under low-oxygen conditions and high temperatures, carbon compounds are converted into combustible gasses, leaving behind mineral ash. The gasses contain CO, CO_2, CH_4, C_2H_4, N_2, and H_2.
- Pyrolysis: Manure is converted under high temperatures, pressure, and absence of oxygen into oil, char, and waste gasses. Carbon monoxide (CO) is actually pumped into the process to scavenge free oxygen, and the carbon in the manure is transformed into burnable hydrocarbons similar to light crude oil. This process is a variant of the methods used to make charcoal from wood.
- Composting: Carbon-containing compounds are attacked by bacteria, actinomycetes, and fungi under aerobic conditions, and the carbon is primarily mineralized into CO_2. Some CH_4 is produced in the interior of particles where there is little oxygen. So much carbon is consumed that the mass may shrink by 50% or more.
- Land application: The transformation of carbon-containing compounds is similar to the composting process but takes place more slowly and without the increase in temperature. Organisms in the soil mineralize carbon in manure into CO_2, which is given off into the atmosphere or retained in soil gasses. Some of the carbon is bound into the soil as humic acid (soil organic matter.) If the ratio of carbon to nitrogen is high—for example, if the manure contains a lot of sawdust or other bedding, or there is a large amount of residue on the soil surface— the available nitrogen in the soil may be immobilized by bacteria decomposing the carbonaceous material, leaving plants with less nitrogen than they need for successful crop production. High-carbon manures, including poultry litter and horse manure, benefit from composting before being land applied for this reason.

ADDITIONAL INFORMATION

The fate of crop nutrients during digestion of swine manure in psychrophilic anaerobic sequencing batch reactors. D.I. Massé, F. Croteaua and L. Massea, Bioresource Technology Vol 98, Issue 15, November 2006

The Fate of Nutrients and Pathogens During Anaerobic Digestion of Dairy Manure. Patrick Topper, Robert Graves, Thomas Richard, Penn State Agricultural and Biological Engineering Cooperative Extension Publication G-71 June 2006

Livestock and Poultry Environmental Stewardship (LPES) Curriculum, Lesson 25, Manure Treatment Options. [All of the LPES series are worth studying.] Can be downloaded at http://www.lpes.org/les_plans.html

Evaluation of On-Farm Composting of Turkey Brooder Litter. John Chastain, P. Andrew Rollins, Kathy Moore, ASAE Paper # 054064, July 2005