

Appendix E

Ammonia Volatilization Study

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Introduction:

This report summarizes the results of studies concerning nitrogen (N) volatilization following the application of various organic amendments to soils. Three studies were begun in December 1995 and completed in September 1996. The studies were performed at Washington State University's Research and Extension Center in Puyallup, WA (Puyallup).

Ammonia-nitrogen (NH_3) and ammonium-nitrogen (NH_4^+) ions are added to the soil with biosolids applications or are produced during biological mineralization of organic N in biosolids. The concentration of NH_4^+ in solution and on exchange sites tends toward an equilibrium. Similarly, the concentration of NH_3 and NH_4^+ in solution tends toward an equilibrium. And, according to Henry's Law, the concentration of NH_3 tends toward an equilibrium relationship between its liquid (in solution) and its gaseous (in the atmosphere) phases. Because NH_3 is a gas at normal atmospheric temperatures and pressures, evolution of NH_3 into the atmosphere is a potential major loss of N under certain conditions. The primary factors known to contribute to NH_3 volatilization are:

- **Temperature:** As temperature increases, the constant in Henry's Law changes to favor greater volatilization. Secondly, as temperature increases the percentage of $\text{NH}_3/\text{NH}_4^+$ increases. Both of these increase the partial pressure differences and encourage volatilization.
- **Air turbulence:** Movement of air (such as wind speed) is very important in affecting NH_3 volatilization. Turbulence reduces the concentration of NH_3 in the atmosphere above the water (or soil water), thus increasing the driving force from liquid to gaseous. The extent of incorporation of biosolids affects the level of turbulence and gaseous dissipation from the biosolids.
- **Soil Moisture Levels:** Typically, all other things being equal, the lower the moisture level, the higher the volatilization rate. This is the case because as soil solution evaporates, the concentration of NH_3 in solution is increased relative to gaseous NH_3 , and the equilibrium must be reestablished by losses of solution NH_3 .
- **pH:** As pH increases the equilibrium ratio of $\text{NH}_3:\text{NH}_4^+$ in solution increases, and volatilization is more likely to occur because an increase in NH_3 in solution results in an inequilibrium between liquid NH_3 and gaseous NH_3 .

The two primary objectives of the studies were: 1) to examine the N volatilization rate of a specific biosolids receiving various treatments, and 2) to determine the N volatilization rate of various biosolids receiving typical application techniques and rates.

Materials and Methods:

The research was conducted in three studies:

1. An investigation of the progressive NH₃ volatilization loss at Puyallup for biosolids from the Renton Wastewater Treatment Plant in King County, WA, (Renton) over a 71 day period. Applications were made both in summer and winter, and used several treatments.
2. An investigation of the 71 day NH₃ volatilization rate of different biosolids at Puyallup utilizing typical application techniques and rates.

Plots established at Puyallup were chosen to represent typical application sites for the west side of the Cascades mountain range in Washington State. The results reported in this study may not be representative of those on eastern side of the Cascades, as the east side experiences harsher extremes in both summer and winter temperatures than experienced on the western side of the mountain range, and typically has much higher pH.

Biosolids and Characteristics

Biosolids characteristics and application rates (in terms of NH₄⁺-N) are summarized in Table 1.

Table 1. Initial characteristics of the biosolids examined.

<i>Location</i>	<i>Biosolids Type</i>	<i>Percent Solids</i>	<i>NH₄⁺-N (μg g⁻¹)</i>	<i>NH₄⁺-N applied (kg ha⁻¹)</i>
Kennewick	Lagooned	6.9	5500	14
Centralia liquid	Anaerobic liquid	6.5	2600	34
Birch bay	Aerobic	2.9	4000	57
Brewster	Lime stabilized	1.6	6600	74
Centralia	Drying Bed	40.5	3050	87
Vashon	Oxidation Ditch	14	15000	106
Renton	Anaerobic dewatered	21	11900	125

Treatments

For all studies, applications of biosolids were made to small plots laid out in a randomized block design.

Renton Biosolids

Applications of Renton biosolids were made on 07/16/96 (excluding the winter application). The site received no irrigation in winter. However, during summer, all plots received irrigation when the adjoining corn crops were watered. The following treatments were explored:

- “Normal”: tilled the biosolids into the top 5 cm of the soil; applied at the agronomic rate
- “Acid Added”: 150 ml of hydrochloric acid (HCl) was added (intended to decrease the pH by one unit) to 5 kg of biosolids; a “normal” incorporation technique and application rate was utilized

- “Buried”: all biosolids buried beneath the upper 5 cm of soil—no biosolids left upon the surface; a “normal” application rate was utilized
- “Double Application”: 2x the agronomic rate was applied; a “normal” incorporation technique was utilized
- “Lime-stabilized”: the biosolids was applied with a similar weight of lime; a “normal” incorporation technique and application rate was utilized
- “No Incorporation”: all biosolids left upon the surface; a “normal” application rate was utilized
- “Winter Application”: applications were made on 12/14/96; a “normal” incorporation technique and application rate was utilized

Various Biosolids

Applications of the various biosolids products were made on 07/16/96. The biosolids were applied at agronomic rates and tilled into the top 5 cm of the soil. The site received no irrigation in winter. However, during summer, all plots received irrigation when the adjoining corn crops were watered.

Volatilization Method

Semi static sorption technique volatilization chambers were installed to capture NH_3 volatilized in the control and treatment plots. The 10 cm diameter PVC volatilization chambers had two foam pads soaked with a 2.2 *N* solution of phosphoric acid, glycerol and distilled water. The bottom pad collected NH_3 volatilized from the biosolids-treated soil, while the upper pad removed ambient NH_3 on the site. Only the lower pads were analyzed for treatment effects. Pads were changed after 24 hours in the field. Measurements were made at approximately 1, 3, 4, 7, 14, 28 and 71 days following application. Pads were individually bagged after removal from the chamber and returned to the laboratory in ice. Pads were rinsed repeatedly with distilled water then brought to 500 ml, and tested for NH_3 concentration using the idophenol blue method.

Volatilization losses were calculated by subtracting measured volatilized NH_3 mass from the initial mass of NH_3 present in the biosolids contained under the chamber. Three chambers measured volatilization loss per day for each treatment.

Results & Discussion

Renton Biosolids

Application technique for the biosolids from the Renton WWTP was investigated in this portion of the study. Application rate, interaction with the soil, irrigation scenario, and season of application was investigated. Average daily loss rates of ammonia from Renton biosolids treated in these different ways at Puyallup over 71 days are shown in Figure 1. Average initial NH_3 loss totals from these treatments are listed in Table 2.

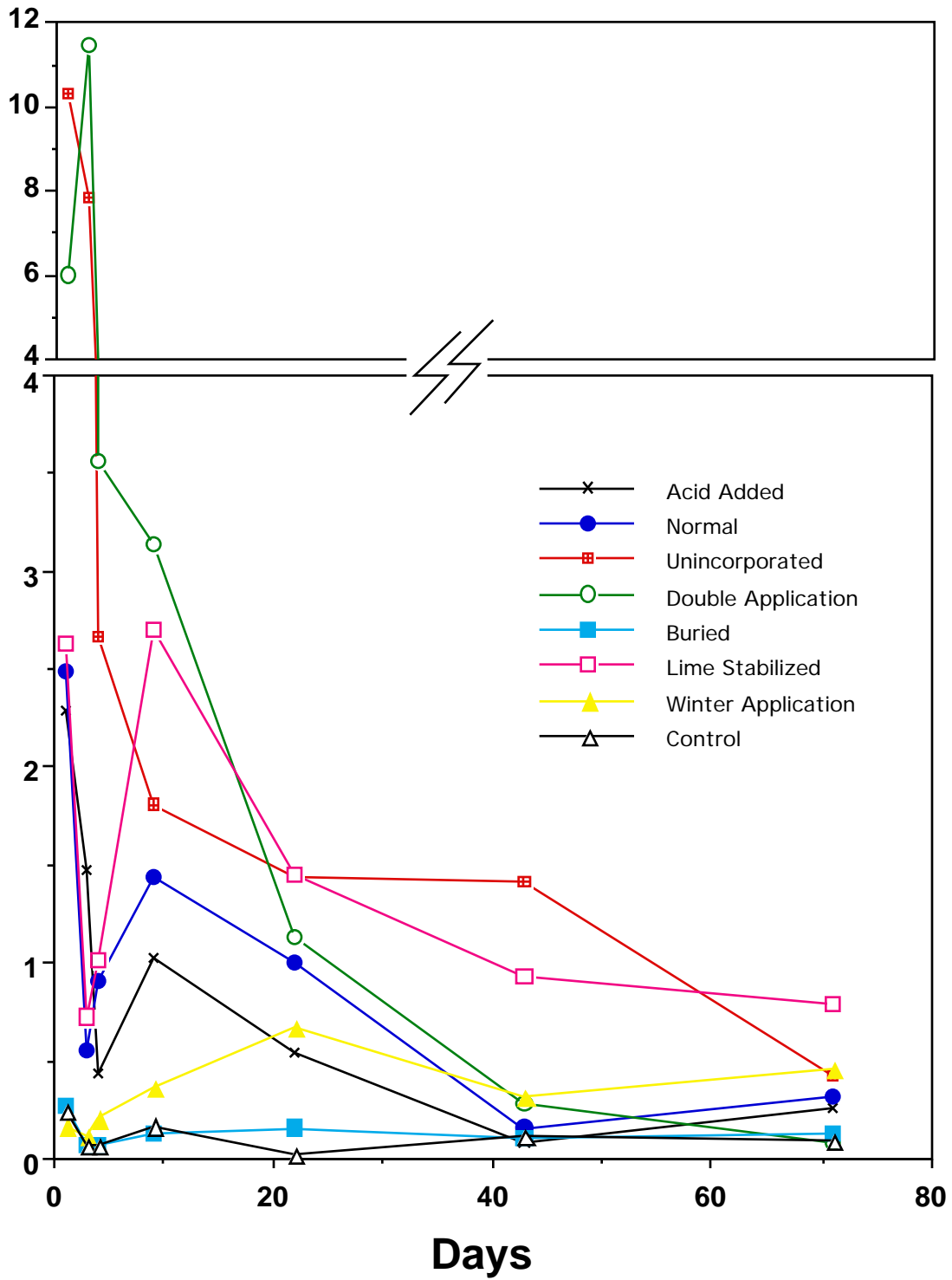


Figure 1: Average daily loss rate of ammonia (in kg/ha/d) from Renton biosolids treated in different ways at Puyallup over 71 days.

Table 2. Renton biosolids with various application treatments applied at Puyallup (percent of initial NH_3 loss totals after 71 days).

<i>Treatment</i>	<i>% of the initial NH_3 lost after 71 days</i>
Lime Stabilized	86%
Unincorporated biosolids	94%
Double application	43%
Normal incorporated	37%
Acid added	25%
Winter application	22%
Buried	7%

Effect of season: The volatilization rate was higher in summer than in winter. After 71 days, Renton biosolids incorporated into the soil had an average 37 percent of initial NH_3 loss following the summer application compared with 22 percent of NH_3 for biosolids applied in winter. Given the known effect of temperature on volatilization rates, this was an expected result. However, as summer and winter temperatures at Puyallup are not vastly different, it might be expected that sites with larger seasonal temperature differences would result in larger differences in volatilization rates.

Interaction with the soil: The most readily apparent result is that the unincorporated treatment produced vastly greater volatilization rates relative to the other treatments. Given the known effect of air movement on the volatilization rate, it was expected that loss patterns would follow: unincorporated treatment > normal incorporated > buried. This was true; loss rates were 94%, 37% and 7% respectively. Secondly, when biosolids are mixed into the soil, there is far more potential for pH of the matrix to change; lowered by the soil. Contact with the soil also allows NH_4^+ to be retained on soil exchange sites.

Effect of pH: Renton biosolids were pH 8.2, whereas the pH of the upper 7.5 cm of soil was 6.2. At this soil pH, NH_4^+ is greatly favored over NH_3 . Addition of acid to the biosolids would change the also lower the ratio of $\text{NH}_3/\text{NH}_4^+$. In contrast, adding lime and increasing the pH would increase the ratio of $\text{NH}_3/\text{NH}_4^+$. Thus the expected result was lime stabilized > normal > acid added. The acid treatment showed a somewhat lower rate of volatilization relative to the normal treatment and a significantly lower rate relative to the lime-stabilized treatment. Since this treatment was applied to a slightly acidic soil, there would be a combined effect on lowering the pH of the biosolids/soil matrix. The lime-stabilized treatment resulted in a significantly greater volatilization rate relative to all other treatments. Such an increase in pH moves the $\text{NH}_3/\text{NH}_4^+$ equilibrium relationship such that as the pH increases, the percent NH_3 of the total $\text{NH}_3 + \text{NH}_4^+$ increases; with this increase in NH_3 in solution, liquid NH_3 becomes out of equilibrium with gaseous NH_3 and is eventually lost from solution as the equilibrium of solution and gaseous NH_3 is reestablished. Such transformations clearly were occurring during this study.

Application rate: The double application treatment had slightly higher volatilization rates than normal application rate. However, the difference was not great. It was expected that the total volatilization loss would be less, as there was a reduced surface area to mass ratio.

Various Products

Average daily loss rates of ammonia from various products examined at Puyallup over 71 days are shown in Figure 2. Average initial NH₃ loss totals from these products are listed in Table 3.

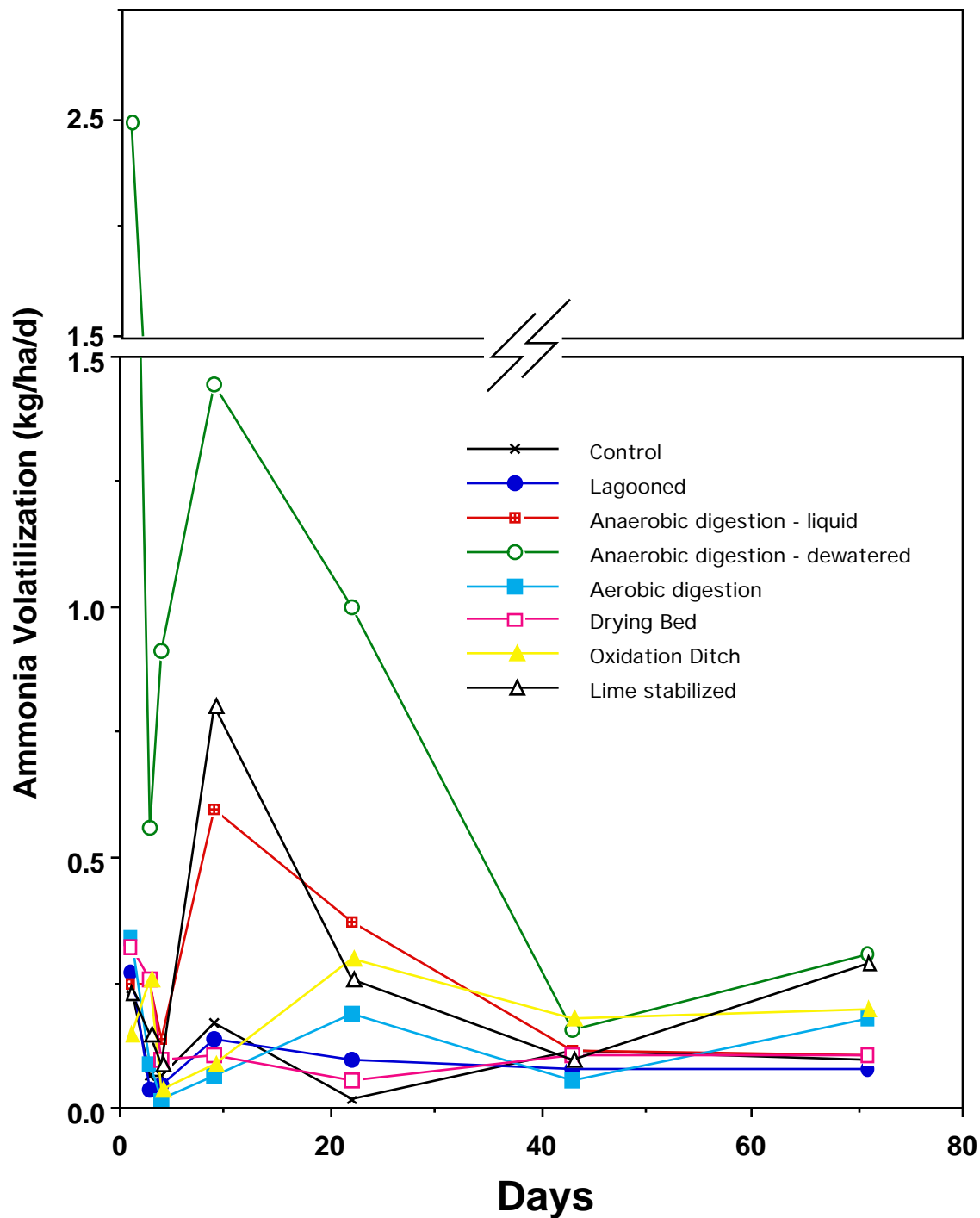


Figure 2. Average daily loss rate of ammonia from biosolids produced at different treatment plants using different biosolids management techniques.

Table 3. Various biosolids with normal application treatment applied at Puyallup (percent of initial NH_3 loss totals after 71 days).

<i>Biosolids Product</i>	<i>% of the initial NH_3 lost after 71 days</i>
Anaerobic digestion - dewatered (Renton)	37%
Anaerobic digestion - liquid (Centralia)	51%
Lime stabilized (Brewster)	26%
Oxidation Ditch (Vashon)	24%
Lagooned (Kennewick)	48%
Aerobic digestion (Birch Bay)	15%
Drying Bed (Centralia)	12%

Effect of pH: The lime-stabilized product from Brewster presumably had the highest pH of all the products tested. This biosolids product would likely show the greatest losses of NH_3 volatilization. Such was the case in the study where lime was added to Renton biosolids. However, Brewster's lime-stabilized product did not have a higher volatilization rate than either anaerobically-treated biosolids. This result and the effect of initial $\text{NH}_3/\text{NH}_4^+$ levels discussed below suggest that there likely was another factor significantly affecting the NH_3 volatilization rates in this study.

Effect of initial $\text{NH}_3/\text{NH}_4^+$ applications: Table 1 presents the total amount of NH_4^+ applied, in the order of: anaerobic dewatered, oxidation ditch, drying bed, lime stabilized, aerobic, anaerobic liquid, and lagooned. However, percent loss of NH_4^+ did not follow this pattern. Overall, the two anaerobically-digested and the lagooned biosolids had the highest rates of volatilization, and the drying bed biosolids showed the lowest rate. The results in this study in addition to the results from the other studies (discussed above) suggests that the initial NH_4^+ levels may be a less significant factor in determining the volatilization rate following the application of biosolids products than other potential factors.

Conclusion

The results of these studies suggest that NH_3 volatilization is affected by temperature, pH, air turbulence, more so than initial $\text{NH}_3/\text{NH}_4^+$ levels and the treatment and stabilization processes/techniques utilized. The widely and somewhat unexpected variability of the results suggest strongly that different biosolids with different characteristics be tested before a large-scale application program is embarked on.