# PHOSPHORUS REMOVAL ON DAIRIES IN THE PACIFIC NORTHWEST:
## APPLYING A CONE SHAPED FLUIDIZED BED PHOSPHORUS CRYSTALLIZER.

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## Introduction

Some dairies use flush systems for removing waste from animal enclosure areas and irrigate some of the wastewater onto surrounding cropland. Concern has arisen that the crops' ability to take up phosphorus (P) in the wastewater falls short of the amount of P applied in the wastewater, thus leading to P accumulation and possible escape to surface water. Measures for reducing P in dairy wastewater are thus being sought. One possibility is the application of a phosphorus crystallizer technology that has been demonstrated in a North Carolina State University (NCSU) to be effective in removing P in swine wastewater (Bowers and Westerman, 2002). In the technology, ammonia and possibly magnesium are added to the wastewater, which then flows upward through a cone containing a fluidized bed of struvite, where P precipitates as struvite onto the bed. To explore the possibility of using this system at dairies, two tests of the technology were undertaken. One test investigated the technology at a 4,000-head dairy near Jerome, Idaho, and the other investigated it at a 600- head dairy near Monroe, Washington.

## Method

### *Idaho Test Set-up*

A system similar to the NCSU system was set up near a wastewater storage lagoon at the Si-Ellen dairy, about 5 miles east of Jerome, Idaho (Figure 1). On this dairy, approximately 4,000 cows are managed in an open lot set-up. Waste is flushed from lanes running under the feeding area and from the milking parlor. The wastewater passes through solids removal equipment and basins and then into three lagoons, each equipped with a surface aerator, for storage. The lagoons are filled sequentially during the cold months, and then emptied one by one for irrigation during the warm months. The test system was set up and operated in June and July, 2004, on the shore of one of the lagoons that remained nearly full during the test period.

The set-up in Idaho differed from the NCSU system in three ways. First, the entry point of the ammonia and magnesium was within the bottom of the cone itself rather than in the inlet pipe leading into the cone bottom. Second, while the NCSU system included means for adding magnesium, either in the form of carbonated magnesium oxide slurry or in the form of magnesium solution (chloride), only solution could be used in the Idaho system. The solution was prepared by dissolving magnesium oxide (MgO) in water containing hydrochloric acid, dissolving Epsom's salt (magnesium sulfate, $MgSO_4$) in water , or by dissolving magnesium chloride ($MgCl_2$) in water. Third, the Idaho system could use either anhydrous ammonia or ammonia water as the ammonia source, while the NCSU system used only anhydrous ammonia.

After an initial start-up period to achieve steady operation and build a bed in the cone, the system was run for 2-6 hours on each of six days, at a total liquid flow rate of 95 ± 5 gallons per hour. A summary of the operation conditions is included in Table 1 in the "results" section. On day 1, ammonia was added in the form of ammonia water at a rate sufficient to raise the pH by at least one point from that of the raw wastewater (7.5). Magnesium solution from acidified magnesium oxide was used to augment the magnesium concentration by 30 parts per million (ppm). Day 2 used the same conditions except magnesium was in the form of magnesium sulfate solution, and more Mg augmentation (60 ppm) was used. On the remaining days, magnesium chloride brine was used for Mg supplementation, and anhydrous ammonia was used in place of ammonia water, providing finer control on pH. On each of days

3 through 6, a different one of the four different sets of conditions resulting from two levels of pH (8.4 and 8.8) and two levels of magnesium addition (60 and 120ppm) were tested.

*Washington Test Set-up*

The system was set up at the Werkhoven dairy about 2 miles south of Monroe, Washington. On this dairy, about 600 cows are managed in a free-stall arrangement. Waste is flushed from the milking parlor and from lanes between the free stalls. The wastewater flows to a settling pond, through solids separation equipment, and then to a storage lagoon. This lagoon fills during the winter, when no irrigation is done. It is lowered during spring and summer by irrigation, and is nearly emptied by the end of October. The test system was set up and operated in September, October, and November, 2004 on the shore of the lagoon. The lagoon was more than half full at the beginning of the tests, nearly empty at the beginning of November, and less than one-half full at the end of November.

The equipment used for the Idaho test was moved to Washington for this test. However, two changes were made. First, after five days of operation, the ammonia and magnesium entry points were changed back to those used in the NCSU experiments: the pipe leading into the bottom of the cone. This change was made because bed build-up was observed to be slow and poor mixing of ammonia and magnesium into the wastewater was considered a possible cause. Second, after an additional three days of operation, an additional pump was used for feeding wastewater. The centrifugal pump used for feeding the cone in the NCSU and Idaho tests was piped into a surge tank with overflow back to the lagoon, and a second centrifugal pump drew from the surge tank and fed the cone. This change was made to avoid the flow unsteadiness and gas bubbles observed in the stream when only the original pump was used. The greater vertical distance of suction (15 feet or more when the lagoon level was at its lowest, as compared with 5-10 feet at the other two locations) probably caused these problems.

Magnesium chloride brine was used for the magnesium source, but was not always added due to the high magnesium content of the wastewater. Ammonia addition was in the form of anhydrous ammonia.

The system was operated for 2-7 hours on each of sixteen days during the period. On each of eleven days, only one set of conditions was tested, while multiple conditions were tested on each of five days. A summary of the operating conditions is included in Table 2 in the "results" section. Flow rates were 60-120 gallons per hour, Mg addition was 30 ppm when used, and pH was adjusted from that of the raw wastewater (7.8) to various levels between 7.8 and 8.8.

*Sampling and Analytical Procedures*

For each set of conditions tested each day, a raw wastewater sample and a treated wastewater sample were taken during a period of steady operation at the conditions being tested. The treated wastewater sample was taken from the overflow of the cone. Before the surge tank was added to the system, the raw wastewater sample was taken from the recycle line at the discharge of the feed pump. After the tank was installed, the raw wastewater sample was taken from the surge tank. Samples were analyzed for total phosphorus (TP), orthophosphate phosphorus (OP), Mg, and total ammoniacal nitrogen (TAN) as nitrogen. Samples were analyzed at commercial laboratories in the states where the samples originated. In addition, samples from days 15 and 16 in the Washington tests were also analyzed by the Environmental Analysis Laboratory at the Biological and Agricultural Engineering department at North Carolina State University (NCSU).

## Results

Tables 1 and 2 summarize the results in the Idaho and Washington tests, respectively. Calculated removal percentages of TP and OP showed no apparent trends in connection with the variation in conditions tested. In Idaho, the calculated TP removal averaged 19% and varied from zero to 55%. Calculated OP removal averaged 56% and varied from -59% to 89%. In Washington, average calculated P removals were lower. Calculated removal of TP averaged 8%, varying from -41% to 63%, while calculated OP removal averaged 4%, varying from -55% to 38%.

## Discussion

Sample-to-sample variation, which was most marked in the results from the commercial laboratory in Washington, may have obscured trends related to differing operating conditions. The variation could arise from any one, or a combination of, several factors, including actual variations in wastewater content, non-representative sampling, and laboratory analysis variability. Non-representative sampling appears unlikely to be a factor, as the same sampling procedures were used in Bowers and Westerman (2003), where far less sample-to-sample variability was observed. Actual variation in wastewater content is possible, though raw wastewater pumped from beneath a float off the shore of a lagoon with several days or weeks of residence time would be expected to exhibit variations of only a few ppm within one day. The laboratory results, however, show intraday variations in raw wastewater TP up to 30 ppm for Idaho and 140 ppm for Washington. In addition, commercial lab results for some of the Washington samples indicated OP content higher than TP, a condition that can only be explained by laboratory variability, since only one sample was provided for both parameters. Though only two days' samples were analyzed by the NCSU laboratory, the results showed little variability and were within a few ppm of the commercial laboratory.

Despite the variability, the results strongly suggest the system achieved TP removal, which is the aim of the tested system. Consistent with this interpretation was the observation of a build-up of bed, averaging around 2-3 inches of height (as settled bed) per day in Idaho and around 2 inches per day in Washington. However, the average calculated TP removal on average fell short of that observed in the earlier-reported tests in swine wastewater (Bowers and Westerman, 2003). In those tests, TP removals exceeding 60% were reliably achieved, peaking at near 80% at optimum conditions.

To aid in considering whether differences in wastewater content may have contributed to differences in TP removal, Table 3 summarizes raw wastewater content and TP removal in the NC swine tests of Bowers and Westerman (2003) and in the present tests. As the table shows, TP content of the raw wastewater was similar across the three series of experiments. The OP content was somewhat, though not markedly, higher, in the NC tests. However, the TAN and Mg content show larger differences, with the raw wastewater in the Idaho and Washington tests containing far more TAN and Mg than that in the NC tests.

Higher TAN and Mg content could explain the lower TP removals observed. In concept, the system removes phosphorus by stimulating (through pH rise and, if used, Mg augmentation) its precipitation as struvite. If, however, the wastewater contains so much Mg, TAN, and OP (the components of struvite) that it is already beyond the equilibrium solubility point for struvite at the pH of the raw wastewater, then much of the precipitable phosphorus already may have converted to solid struvite, which could exist as fine suspended solid that would pass through the fluidized bed rather than be captured by it.

Figure 3 shows the condition of three raw wastewaters (North Carolina, Idaho, and Washington series) as related with the conditional equilibrium solubility curve for struvite from Ohlinger et al. (2000). The position indicated for each of the three wastewaters was determined by converting the Mg, TAN, and OP concentrations indicated in Table 3 for that wastewater to molarities, multiplying them together to calculate the conditional solution product, and converting the product to precipitable phosphorus form by taking its negative base-10 logarithm. The figure shows the North Carolina wastewater is not quite saturated in struvite, the Idaho wastewater is slightly beyond equilibrium, and the Washington wastewater is farther beyond equilibrium. This order, which corresponds with the ranking of the three test series in average TP removal, is consistent with the explanation that TP removal could be suppressed if Mg and/or TAN are high enough that struvite already exists as fine suspended solid in the raw wastewater.

## Conclusions

The cone-shaped fluidized-bed crystallizer removed phosphorus from wastewater at the two northwest dairies where it was tested. However, removal fell short of that previously reported for the system in swine wastewater in North Carolina. The lower degree of removal may be explained by the fact that the dairy wastewater contained higher amounts of Mg and TAN, indicating that much of the struvite may already be precipitated in fine suspended form, unavailable for capture by the fluidized bed.

Experiments exploring this possibility could be conducted. For example, dairy wastewater could be acidified prior to being fed to the system. Acidification would aim to reduce the pH sufficiently to shift to the left in Figure 3 and cross the equilibrium line. Increased phosphorus removal would support the explanation, while failure to increase removal would indicate that other factors are primarily responsible for the poorer removal observed in dairy wastewater.

## Acknowledgements

The authors are grateful for support from the Si-Ellen Dairy, which contributed site support and funding for the Idaho tests, and the Werkhoven Dairy, which provided site support for the Washington tests. The Washington Technical Center, an agency of the State of Washington, contributed funding for the Washington tests. The Environmental Analysis Laboratory in the Biological and Agricultural Engineering Department at NCSU provided chemical analysis of samples taken during two days of the Washington tests.

## References

Bowers. K.E. and P.W. Westerman. 2003. Phosphorus removal in a novel fluidized bed. Proceedings of the 2003 Annual Meeting of the American Society of Agricultural Engineers. Paper number 03-4123 of the ASAE. St. Joseph, MI.

Ohlinger, K.N., T.M. Young, and E.D. Shroeder. 2000. Post-digestion struvite using a fluidized bed reactor. Journal of Environmental Engineering April(2000):361-367.

**Table 1. Summary of operating conditions and results in Idaho**

| Day | gpm flow | Mg added (ppm) | pH | Mg source | $NH_3$ form | P removal (%) | | Raw wastewater (ppm) | | | | Treated (ppm) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | TP | OP | TP | OP | Mg | TAN | TP | OP |
| 1 | 1.6 | 30 | 8.8 | MgO | water | 10 | 71 | 98 | 31 | 145 | 337 | 88 | 9 |
| | 1.6 | 30 | 8.7 | MgO | water | 22 | 75 | 128 | 36 | 134 | 349 | 100 | 9 |
| | 1.6 | 30 | 9.1 | MgO | water | 0 | -59 | 113 | 29 | 135 | 319 | 113 | 46 |
| 2 | 1.6 | 60 | 8.7 | $MgSO_4$ | water | 6 | 63 | 111 | 35 | 147 | 329 | 104 | 13 |
| | 1.6 | 60 | 8.6 | $MgSO_4$ | water | 22 | 42 | 91 | 12 | 194 | 485 | 70 | 7 |
| | 1.6 | 60 | 8.9 | $MgSO_4$ | water | 55 | 69 | 83 | 26 | 129 | 358 | 37 | 8 |
| 3 | 1.6 | 60 | 8.4 | $MgCl_2$ | anhyd. | 22 | 50 | 72 | 6 | 134 | 279 | 56 | 3 |
| | 1.6 | 60 | 8.4 | $MgCl_2$ | anhyd. | 14 | 83 | 97 | 18 | 139 | 293 | 83 | 3 |
| 4 | 1.6 | 60 | 8.8 | $MgCl_2$ | anhyd. | 14 | 89 | 74 | 18 | 138 | 245 | 64 | 2 |
| | 1.6 | 60 | 8.8 | $MgCl_2$ | anhyd. | 16 | 75 | 90 | 44 | 146 | 326 | 76 | 11 |
| 5 | 1.6 | 120 | 8.4 | $MgCl_2$ | anhyd. | 23 | 67 | 106 | 24 | 139 | 330 | 82 | 8 |
| | 1.6 | 120 | 8.4 | $MgCl_2$ | anhyd. | 31 | 64 | 84 | 22 | 312 | 355 | 58 | 8 |
| 6 | 1.6 | 120 | 8.8 | $MgCl_2$ | anhyd. | 19 | 62 | 84 | 26 | 139 | 332 | 68 | 10 |
| | 1.6 | 120 | 8.8 | $MgCl_2$ | anhyd. | 16 | 30 | 74 | 44 | 139 | 304 | 62 | 31 |

## Table 2. Summary of operating conditions and results in Washington

| Day | Flow (gpm) | Mg added (ppm) | pH | Mg, $NH_3$ entry point | Surge tank? | P removal (%) | | Raw wastewater (ppm) | | | | Treated (ppm) | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | TP | OP | TP | OP | Mg | TAN | TP | OP |
| 1 | 1.5 | 30 | 8.5 | cone | no | 10 | -6 | 82 | 49 | 320 | 1040 | 74 | 52 |
| | 2 | 30 | 8.5 | cone | no | -8 | -30 | 83 | 54 | 316 | 1060 | 90 | 70 |
| 2 | 2 | 30 | 8.5 | cone | no | 3 | 7 | 75 | 54 | 310 | 960 | 73 | 50 |
| 3 | 2 | 30 | 8.5 | cone | no | -10 | -4 | 73 | 52 | 340 | 1150 | 80 | 54 |
| 4 | 2 | 30 | 8.5 | cone | no | -33 | 35 | 90 | 34 | 306 | 800 | 120 | 22 |
| 5 | 2 | 30 | 8.5 | cone | no | 8 | 17 | 76 | 12 | 245 | 600 | 70 | 10 |
| 6 | 1.5 | 30 | 8.5 | inlet | no | 9 | 11 | 76 | 18 | 254 | 650 | 69 | 16 |
| | 1.5 | 0 | 8.5 | inlet | no | 27 | 9 | 105 | 22 | 289 | 550 | 77 | 20 |
| 7 | 1.5 | 30 | 8.3 | inlet | no | -3 | 13 | 74 | 32 | 230 | 550 | 76 | 28 |
| | 1.5 | 0 | 7.8 | inlet | no | 16 | -7 | 87 | 30 | 252 | 650 | 73 | 32 |
| | 1.5 | 30 | 7.8 | inlet | no | 63 | -55 | 211 | 22 | 384 | 650 | 78 | 34 |
| | 1.5 | 30 | 8.8 | inlet | no | 15 | 7 | 71 | 28 | 224 | 600 | 60 | 26 |
| | 1.5 | 0 | 8.3 | inlet | no | 23 | 0 | 91 | 24 | 239 | 550 | 70 | 24 |
| | 1.5 | 0 | 8.8 | inlet | no | 19 | 38 | 109 | 32 | 217 | 550 | 88 | 20 |
| 8 | 1.5 | 0 | 7.8 | inlet | no | 46 | -14 | 153 | 28 | 268 | 640 | 82 | 32 |
| | 1.5 | 30 | 8.8 | inlet | no | 26 | 24 | 62 | 34 | 185 | 620 | 46 | 26 |
| | 1.5 | 30 | 8.3 | inlet | no | 29 | 35 | 102 | 34 | 222 | 600 | 72 | 22 |
| | 1.5 | 0 | 8.8 | inlet | no | 10 | 13 | 99 | 30 | 219 | 565 | 89 | 26 |
| | 1.5 | 30 | 7.8 | inlet | no | -41 | 14 | 66 | 42 | 182 | 610 | 93 | 36 |
| | 1.5 | 0 | 8.3 | inlet | no | 22 | 15 | 74 | 40 | 167 | 490 | 58 | 34 |
| 9 | 1 | 0 | 7.8 | inlet | yes | 47 | 12 | 55 | 50 | 203 | 700 | 29 | 44 |
| | 1 | 0 | 8.8 | inlet | yes | 16 | 13 | 58 | 48 | 209 | 700 | 49 | 42 |
| | 1 | 0 | 8.3 | inlet | yes | 19 | 13 | 32 | 48 | 177 | 640 | 26 | 42 |
| | 1 | 30 | 8.3 | inlet | yes | -4 | 21 | 28 | 48 | 178 | 700 | 29 | 38 |
| | 1 | 30 | 7.8 | inlet | yes | -33 | 9 | 30 | 44 | 180 | 645 | 40 | 40 |
| | 1 | 30 | 8.8 | inlet | yes | -29 | 23 | 51 | 44 | 195 | 720 | 66 | 34 |
| 10 | 1 | 30 | 8.5 | inlet | yes | 5 | 0 | 77 | 58 | 229 | 875 | 73 | 58 |
| 11 | 1.5 | 0 | 8.5 | inlet | yes | no samples | | | | | | | |
| 12 | 1.5 | 0 | 8.5 | inlet | yes | -4 | 0 | 78 | 60 | 213 | 880 | 81 | 60 |
| 13 | 1.5 | 0 | 8.5 | inlet | yes | -4 | 3 | 79 | 60 | 222 | 780 | 82 | 58 |
| 14 | 1.5 | 0 | 8.5 | inlet | yes | no samples | | | | | | | |
| 15[1] | 1.5 | 0 | 8.5 | inlet | yes | 2 | 9 | 102 | 46 | - | - | 100 | 42 |
| 16[1] | 1.5 | 0 | 8.5 | inlet | yes | 5 | -9 | 102 | 42 | - | - | 97 | 46 |

[1] Samples from these days analyzed by the laboratory in the Biological and Agricultural Engineering Department at North Carolina State University in Raleigh, NC. Samples from all other days analyzed by Soiltest Farm Consultants, Inc. at Moses Lake, WA.

## Table 3. Average raw wastewater content and TP removal for three series of tests.

| PARAMETER | Bowers and Westerman, 2003 | Idaho Dairy | Washington Dairy |
|---|---|---|---|
| TP (ppm) | 88 | 93 | 83 |
| OP (ppm) | 42 | 27 | 39 |
| Mg (ppm) | 60 | 155 | 241 |
| TAN (ppm as N) | 178 | 332 | 662 |
| pH | 7.7 | 7.5 | 7.8 |
| TP removal (%)[1] | 66 | 19 | 6 |

[1] Numbers shown include all results for periods in which ammonia was being added to the system for pH adjustment.

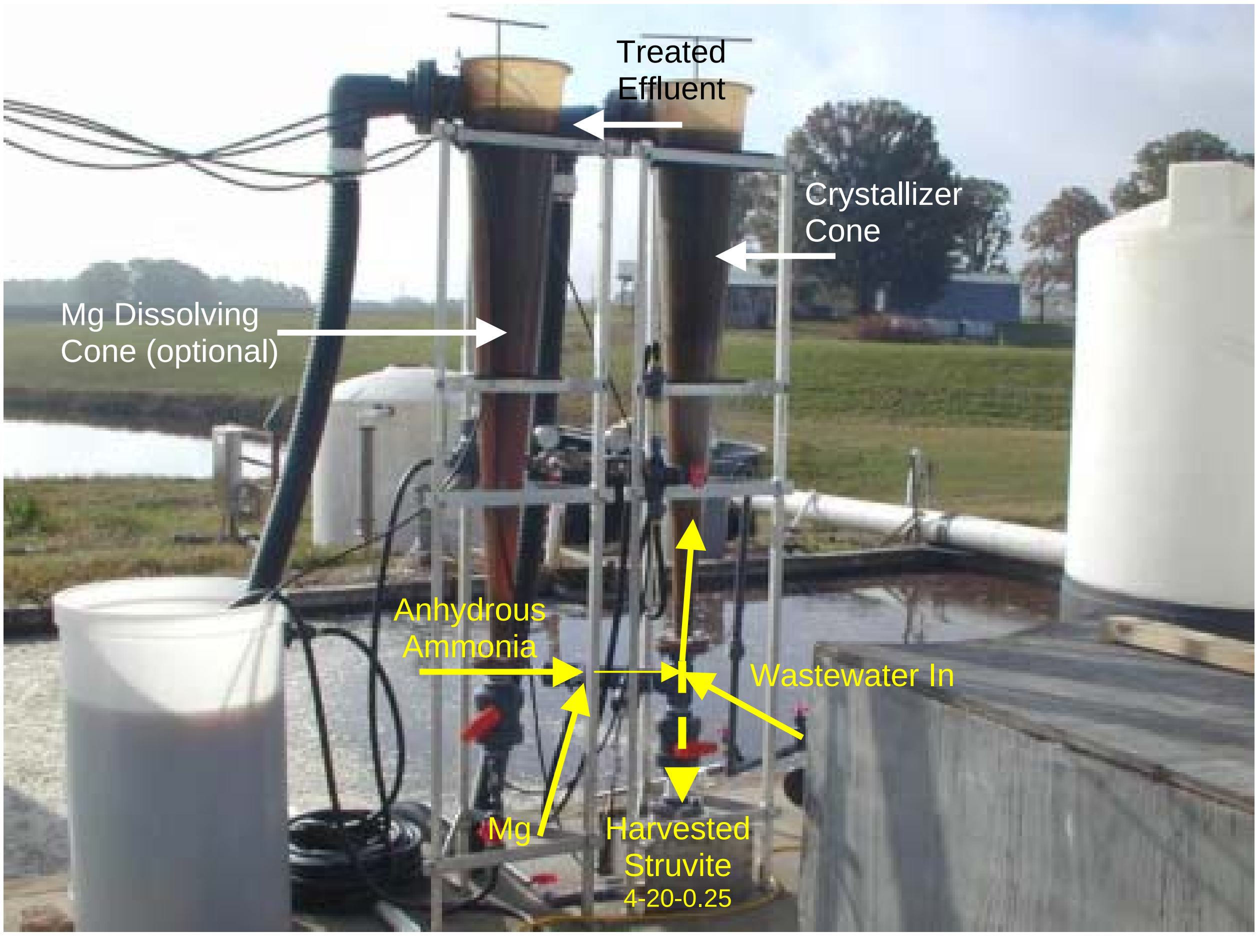

**Figure 1 Pilot-Scale Cone Shaped Fluidized bed Phosphorus Crystallizer.**

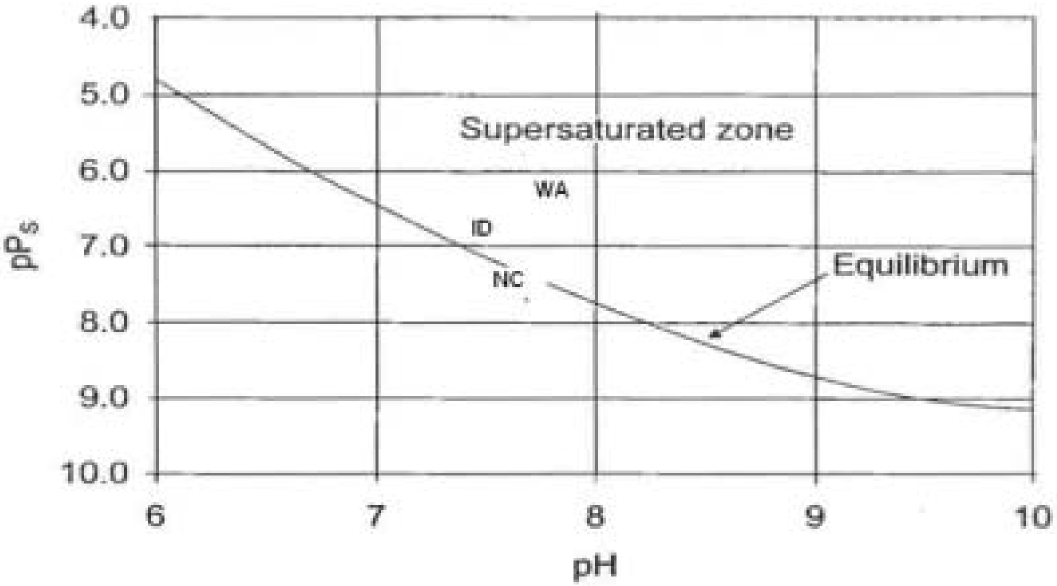

**Figure 2: Conditional solubility product of raw wastewaters compared with equilibrium. (From Ohlinger et. al [2000], with “NC,” “ID,” and “WA” inserted, representing the conditions of raw wastewater from the North Carolina, Idaho, and Washington tests respectively.)**