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November 23, 2012

Mr. Hugh O'Riordan
Givens Pursley, LLC
601 West Bannock Street
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Subject: Preliminary Review of EPA-910-R-12-003

Dear Hugh:

At your request, I have conducted a preliminary review of the document, *Relation Between Nitrate in Water Wells and Potential Sources in the Lower Yakima Valley, Washington* (EPA-910-R-12-003). My preliminary comments are focused on nitrogen fate and transport beneath dairy lagoons as the document implies that nitrogen simply leaches from the lagoon to groundwater. This is an over-simplification, ignores nitrogen cycle dynamics, and, based on scientific research on the vadose zone beneath lagoon liners, is simply not accurate. It is my opinion that based on the information provided in the document it is not possible to distinguish between elevated nitrate in groundwater from lagoon seepage and background levels from nitrogen source applications to irrigated agricultural fields. My discussion focuses on research that has been conducted on soils (vadose zone) beneath lagoons that have demonstrated significant atmospheric loses of lagoon nitrogen through coupled nitrification-denitrification mechanisms.

**Nitrate Fate and Transport beneath Dairy Lagoons**

It is well documented that with the introduction of wastewater to a diary lagoon, the hydraulic conductivity of the earth lining will be reduce by at least an order of magnitude due to a process referred to as "seal formation", which is an organic seal at the bottom of the lagoon that results from a combination of biological, chemical, and physical processes (Tyner and Lee 2004; Tyner et al., 2006). Research shows that after a stable seal forms, which can be as soon as 10-days after wastewater additional to a lagoon, the seal properties, not the sediment or liner properties, are responsible for limiting infiltration (Cihan et al, 2006). Furthermore, studies have demonstrated that the soils beneath the seal (could be clay liner material or native material), becomes partially unsaturated. This soil zone beneath the seal has been shown to have favorable conditions for both nitrification and denitrification (Baram et al., 2012). This condition is termed *coupled nitrification-denitrification* (CND).

For an illustration of the nitrogen cycle please referred to Figure 2 in the document *Relation Between Nitrate in Water Wells and Potential Sources in the Lower Yakima Valley, Washington.* This figure provides a general overview of the nitrogen cycle, except that it leaves out ammonia volatilization, which can be an important nitrogen removal process from lagoon, manure piles, soil systems.

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For a wastewater lagoon system, the main forms of nitrogen (N) are organic-N, ammonium, and ammonia. Organic nitrogen can be microbially converted to ammonium and ammonia through *mineralization*. Microbial oxidation of ammonium and ammonia to nitrate (*nitrification*) requires the presence of molecular oxygen, which is almost always limiting in manure wastewater.

The overall process is as follows:

$$RNH_2 + H_2 \longrightarrow NH_4^+ + \text{energy}$$

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 2H_2O + 4H^+ + \text{energy}$$

$$2NO_2^- + O_2 \longrightarrow 2NO_3^- + \text{energy}$$

where R represents an organic compound.

Nitrification only occurs in oxidizing environments. Factors that influence this microbial reaction include temperature, moisture content, bacterial population, and pH. Nitrate, as an anion, is repelled by clays and is susceptible to leaching. Ammonium is a cation and is adsorbed by clay mineral and negatively charged organic matter. Ammonia is a gas and can exist in solution and as soil vapor, is in equilibrium with ammonium, and its concentration (ratio between ammonia and ammonium) is dependent upon solution pH.

Under low oxygen conditions (anoxic), nitrate can serve as an electron donor for microbial decomposition of organic matter. This reaction is expressed:

$$5C + 4NO_3^- + 2H_2O \longrightarrow 2N_2 + 4HCO_3 + CO_2$$

$N_2$ is a gas and is lost to the atmosphere. Nitrification does not occur (or minimally occurs) in dairy wastewater because there is not sufficient oxygen.

Baram et al. (2012) found that seal formation at the bottom of a dairy lagoon lead to the development of unsaturated conditions (70 percent saturation) in the underlying vadose zone. The authors describe a desiccation-crack network developing in the unsaturated material allowing air penetration and formation of aerobic conditions with anaerobic niches where CND occurred. Several findings were reported by these researchers:

- The formation of desiccant cracks beneath the seal zone enhanced vadose zone aeration and organic nitrogen and ammonium were completely oxidized to nitrate in the upper 2 feet of the soil beneath the lagoon.
- Ammonium oxidation was coupled with nitrate reduction, removing 90 percent of the leached N, with up to 100 percent N removal under regions of higher water contents.
- While nitrogen loss was near 100 percent complete for soils beneath the lagoon, seepage of wastewater near the lagoon margins (the outer banks of a lagoon that

> might get infrequent wastewater overflow) was favorable for nitrate formation and leaching. However, the "margin" areas have infrequent flooding (therefore I would expect the quantity of nitrate leached could be potentially low and could be controlled through best management practices).

In summary, scientific data supports the occurrence of CND zones beneath lagoons that can result in significant removal (loss) of nitrogen. Therefore, caution is warranted when making correlations between the presence of a dairy lagoon and downgradient water quality, especially when the lagoons occur in areas of manure and fertilizer applications to irrigated agricultural lands.

If you have questions, please contact me at (208) 387-7033.

Very truly yours,

HDR ENGINEERING

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Soil Scientist

References:

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