Impacts of Holding Time on the Analysis of Nonylphenol in Soil and Biosolids Samples

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Introduction

Annually, over 3 million dry tons of treated sewage sludge (or biosolids) are applied on agricultural lands in the U.S. Nonylphenol is a degradation product of nonylphenol ethoxylate, a surfactant used in industrial detergents and other products, and often found in biosolids. While nonylphenol is aerobically degradable, it is persistent in aquatic environments, moderately bioaccumulative, and extremely toxic. To evaluate land application of anaerobically digested biosolids at agronomic levels, a pilot-scale field research project was conducted. Nonylphenol-containing biosolids were applied to a rye grass and fescue field in outdoor conditions for a year, and samples were collected periodically over the year and placed into storage for 11 to 18 months prior to analysis. As shown in Figure 1, nonylphenol was observed in samples from both the liquid and solid biosolids applications, as well as biosolids-only controls, throughout the outdoor study period.

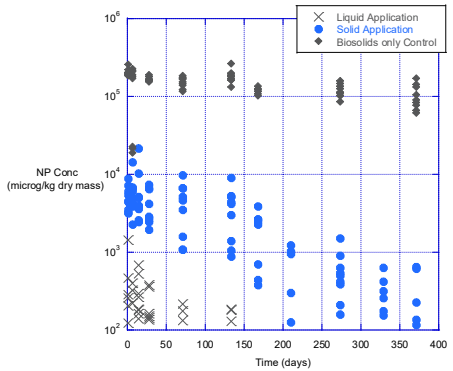

Figure 1. Nonylphenol (NP) concentration as a function of time after land application of biosolids (field study). Concentrations above the reporting limit of 120 microg/kg dry mass are shown.

Holding time is an important issue in analytical evaluation of chemical constituents. The integrity of samples and the stability of chemicals in those samples may depend on storage conditions, storage time, chemical volatility, matrix interactions, biodegradation, and other factors. To assess the usability of the nonylphenol data acquired from the land application of biosolids field study, a long-term holding time study was conducted to examine the influence of holding time on stability of nonylphenol concentrations when refrigerated (< 8 deg. C). Samples were randomly selected from the outdoor sample set, including samples from all application types, and re-analyzed 8 to 14 months after the initial analysis. Table 1 shows a timeline of the land application of biosolids field study and the holding time study.

Activity	Time Interval
Biosolids field application	
Field sampling (C_0)	13 months
Samples stored	11 – 18 months
Analysis of samples (C_1)	
Samples stored	8 – 14 months
Re-analysis of a subset of samples (C_2)	

Table 1. Timeline of land application of biosolids field study and holding time study.

If the concentrations of nonylphenol from the initial analysis (C_1) are equivalent to the concentrations of nonylphenol from the re-analysis of a sub-set of the samples (C_2), then it may be reasonably inferred that had the samples been analyzed immediately after being sampled, the concentrations of nonylphenol (C_0) would have been equivalent to C_1:

$$\text{If } C_1 = C_2, \text{ then } C_0 = C_1$$

Holding Time Data Analysis

An initial data analysis is shown in Figure 2. The concentrations in biosolids-only samples appeared to be stable throughout the holding period, indicating a strong correlation between C_1 and C_2, while both solid and liquid applications displayed higher variability between C_1 and C_2. Figure 2 also shows the laboratory duplicates analyzed at the same time as the C_1 samples. The variability in holding time study concentrations (C_2) was fairly consistent with the variability in C_1 laboratory duplicate concentrations for all application types. This observation may indicate that additional, application-based factors, such as non-representative sampling and/or sub-sampling, contributed to variability in nonylphenol concentrations between C_1 and C_2 for solid and liquid applications.

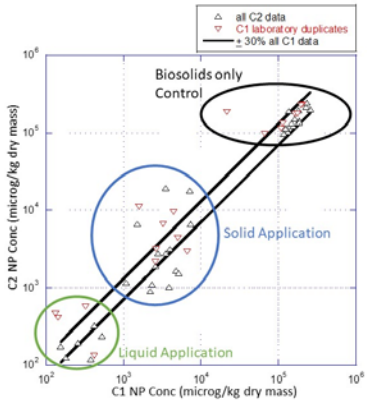

Figure 2. Nonylphenol (NP) concentrations from the holding time study (C_2) compared to data from initial analysis (C_1) and laboratory duplicates analyzed with C_1. Concentrations above the reporting limit of 120 microg/kg dry mass are shown.

A maximum likelihood estimation (MLE) regression approach was used for a two-group test that compared the holding time data (C_2) to the initial data set (C_1). MLE regressions were constructed[1] for the biosolids-only data and solid application data[2]. The liquid application data did not have enough detects (n = 3) to perform MLE regression analysis. The concentration data were plotted against an explanatory variable of indicators for group membership which were 0 for data from the initial analysis (C_1) and 1 for data from the final analysis (C_2). For each sample type, several distributions were run. The Anderson-Darling (AD) statistic was used to compare the fit of each distribution along with probability plots of the standardized residuals, which were calculated from the data subtracted from their group mean. Distributions were selected based on the lowest AD statistic and the best visual fit of the residuals. The resulting regressions were then used to examine the null hypothesis of no difference between the means of C_1 and C_2.

For the biosolids-only MLE regression, the lognormal distribution was selected (Figure 3). The slope of the explanatory variable provides a measure of the mean difference between C_1 and C_2. A Z-statistic was then calculated to test whether the two means are different, analogous to a t-test in least-squares regression. A Z-value of -0.98 was calculated for this regression analysis along with a probability value (or P-value) of 0.328, suggesting that the null hypothesis, that the means (of logarithmic data) from the initial and final biosolids samples are the same, cannot be rejected.

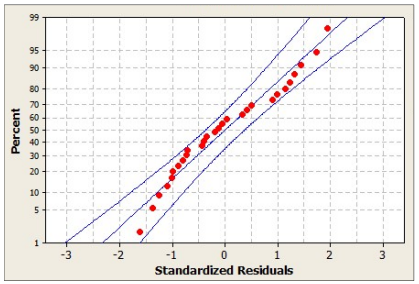

Figure 3. Probability plot for residuals from a regression of the biosolids-only nonylphenol concentration data versus group membership, compared to a lognormal distribution (center straight line). Data within 95% confidence interval.

For the solid application MLE regression, the Weibull distribution was selected (Figure 4) and a Z-value of 0.70 was calculated along with a P-value of 0.487, indicating that the null hypothesis, that the mean of logarithms are the same for the initial and final solids application samples, cannot be rejected.

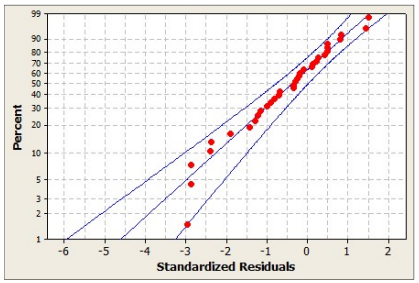

Figure 4. Probability plot for residuals from a regression of the solid application nonylphenol concentration data versus group membership, compared to a Weibull distribution (center straight line). Data within 95% confidence interval.

Conclusions

- For the biosolids-only control data, it may be reasonably inferred that $C_0 = C_1$, in most cases.
- For the solid application data, it may also be reasonably inferred that $C_0 = C_1$, but additional data analysis may be necessary.
- For the liquid application data, further data analysis is necessary to determine if $C_0 = C_1$.

[1]Minitab 16 [computer software]. State College, PA: Minitab, LLC.
[2]Helsel, D.R., 2011. Statistics for censored environmental data using Minitab and R (Vol. 77). John Wiley & Sons.