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Applicability of IRMS to detect synthetic fertilizer addition to manure

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Introduction

Over-fertilizing is a serious environmental hazard in the Netherlands, and has resulted in a governmentally enforced system to regulate the application of nitrogen (N) and phosphorus (P) to farmland. All manure transports are routinely analyzed for N and P content, so that annual production and application of manure can be balanced. However, there are financial incentives to modify the N and P content in manure samples, for example by adding synthetic fertilizer. One of the possible approaches to verify the authenticity of manure is to use the low $\delta^{15}N$ values of synthetic fertilizers to discriminate between N of animal and synthetic origin.

Materials and Methods

A large database of manure N- and P-levels was obtained from the Dutch Ministry of Agriculture, Nature and Food Quality. Per class of manure, the combined result of two *t*-tests was used to estimate a sample being "normal" or "unusual". "Unusual" samples are unlikely ($p<0.001$) to belong to the population of that class of manure, based on N and P concentrations only.
This selection resulted in 10 normal and 6 unusual poultry manure samples, and 10 normal and 3 unusual pig manure samples. These and 10 typical synthetic fertilizer samples were analyzed for $\delta^{15}N_{total}$, $\delta^{15}N_{NH4}$, $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ at the ISOFYS-Laboratory of Applied Physical Chemistry at Ghent University, Belgium.

Results

The total $\delta^{15}N$ shows some differences between the classes of manure (*Fig. 1*), but the sample variation is too large compared to the absolute differences to be able to discriminate between authentic and unusual classes. Therefore, data were subjected to a multivariate approach. Using PCA the four measured variables per sample are reduced to two, allowing graphical representation (*Fig. 2*). The three different classes of manure are well separated from each other, indicating that isotope ratios have a discriminating potential. As seen from the loadings plot, the synthetic fertilizers are mainly discerned from the manures by their lower total $\delta^{15}N$ values. NO_3-$\delta^{18}O$ was an extra discriminating factor for pig manure, and $NH_4\delta^{15}N$ an extra factor to separate synthetic fertilizer from poultry manure.

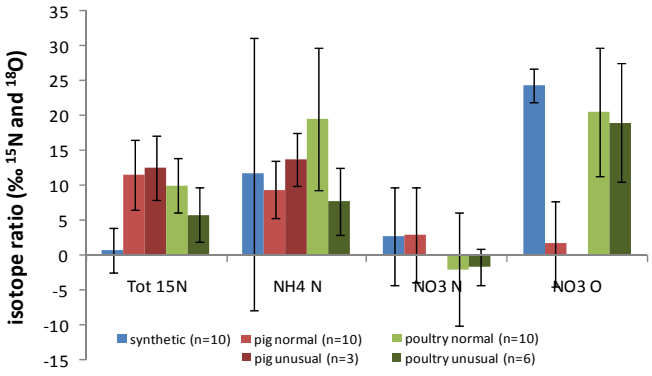

Fig. 1. Average isotope ratios per class of manure. Error bars represent class standard deviation, individual samples are analyzed in duplicate.

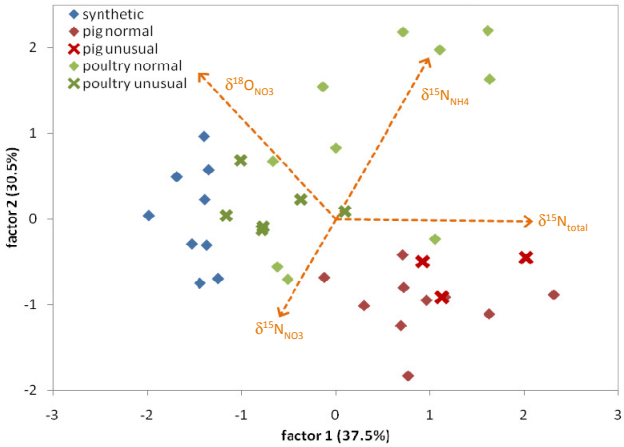

Fig. 2. PCA plot of auto-scaled isotope ratios ($\delta^{15}N$ in total N, NH_4 and NO_3, and $\delta^{18}O$ in NO_3) in three different manure classes. Samples that might contain synthetic fertilizer are indicated with ×-symbols. Loading vectors are given in orange arrows.

All poultry manure samples considered "unusual" based on their N- and P-levels appear close to the synthetic fertilizer samples in the PCA plot, indicating that their isotope ratios resemble those of synthetic fertilizer. However, some "normal" samples are equally close, which makes it impossible to draw definitive conclusions. The pig's manure samples that are considered "unusual" appear to have similar isotope ratios as the normal manures. For these samples, additional analyses such as $\delta^{11}B$ or trace element analyses could be valuable in the future. Based on the current set, it was not possible to detect addition of synthetic fertilizer to pig's manure samples.

Conclusions

The results confirmed that synthetic fertilizers generally have $\delta^{15}N$ values close to 0‰, while manures have higher values. This sample set was not sufficiently large, and the variation in $\delta^{15}N$ values was too large to achieve a clear detection on manure samples containing synthetic fertilizer. However, the four isotope ratio values combined, as visualized by principal component analysis (PCA), showed that notably the unusual poultry manure samples were very close to the synthetic fertilizers. Based on this small sample set, the approach seems promising to discriminate between manure and synthetic fertilizer samples. However, a larger set including guaranteed genuine manure samples and genuine manure with added synthetic fertilizer should be analyzed before this approach can be evaluated for its discriminative power.

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