

Compound-specific stable isotope analysis on chemical and enzymatic hydrolysis of organophosphorus pesticides (OPs) in slurry of biogas reactor

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Waste products from agriculture, food production, industries or municipalities are used as carbon sources for biogas production. Sludge and liquid of biogas plants contain carbon, nitrogen, and phosphorous-rich substances which are potentially valuable fertilizer, however also residues of pesticides, pharmaceutical, and chemical compounds. To close carbon, nitrogen and phosphor cycle for sustainable agriculture, sludge and liquid from biogas production are needed in agriculture. For prevention of the deposition of chemical residues in soil, it is important to study the capacity of biogas plants for degradation of chemicals if materials from biogas plants are used as fertilizers.

For this study we developed a concept based on stable isotope fractionation (carbon and hydrogen fractionation) for identification of degradation mechanisms of organic phosphate (OP) pesticides. Studies on stable isotope concepts to trace the transformation of persistent organic pesticides have been published, but the research for elucidation of the degradation process during the biogas process is lacking. Multi-element isotope fingerprinting of OPs can be used to trace the degradation mechanisms and metabolic pathways involved. The chemical and enzymatic hydrolysis of the OPs exists simultaneously under biogas production. Hydrolysis and biodegradation are probably the most important mechanisms for degradation of OPs.

In this study, we take the slurry from a full-scale biogas reactor to measure the enzymatic activity in the biogas reactor system on OPs degradation. The slurry after filtration should be homogenized by French pressure cell press to get microbial enzymatic activity. Cell free digester is set as control experiment. The chemical hydrolysis of parathion and parathion-methyl under acid (pH 5), neutral (pH 7) and alkaline (pH 9) conditions was conducted as comparison experiment to evaluate the kinetics of enzymatic hydrolysis. The concentrations were measured by GC, isotope compositions of OPs were measured by GC-C-IRMS.

The objective of this study is to determine the enzymatic hydrolysis degradation in slurry of biogas reactors by 2D-CISA. The carbon and hydrogen fractionation was evaluated for enzymatic hydrolysis of OPs from slurry of the biogas reactor under neutral condition compared with chemical hydrolysis. The carbon enrichment factors (ϵ_c) of parathion under chemical hydrolysis are $-6.4 \pm 0.8\text{‰}$ (pH 5), $-5.8 \pm 0.5\text{‰}$ (pH 7) and $-3.5 \pm 0.6\text{‰}$ (pH 9), respectively. And ϵ_c of parathion-methyl are $-10.2 \pm 2.3\text{‰}$ (pH 5), $-9.9 \pm 0.9\text{‰}$ (pH 7) and $-6.4 \pm 0.6\text{‰}$ (pH 9), respectively. It demonstrates that hydrolysis of parathion has different degradation mechanisms under acid, neutral and alkaline conditions. The OPs degradation in full scale continuous biogas reactor under neutral condition can be compared with the fractionation factor of chemical hydrolysis under pH 7.

This study shows that multi isotope pattern of OPs can be developed to characterize and quantify degradation processes in full scale technical biogas plants. The isotope fractionation factors can directly demonstrate the degradation mechanisms during the biogas production.