**Identification of Marker Substances for Agricultural Liquids by SPDE-GC-MS**

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Frequently, agricultural liquids are suspected as cause of local spills of surface water. However, the determination of classical inorganic parameters such as nitrate or ammonia does not allow to distinguish e.g. between liquid manure and liquid from silage. Thus, in rather many real cases where the cause of the observed water pollution, often followed by death of fish, is not visible unambiguously, the source of contamination remains undetected.

Therefore, a method using the combination of solid phase dynamic extraction with gaschromatography coupled to mass spectrometry (SPDE-GC-MS) was established. A SPDE needle covered with a mixture of polydimethylsiloxane and activated carbon was used to extract (semi)volatile organic compounds from the gaseous phase of liquid samples heated to 85 °C in a headspace vial. Operating the quadrupole mass spectrometer in the scan mode the optimized SPDE-GC-MS method was applied to search for organic marker compounds possibly typical for a certain type of agricultural liquid.

SPDE-GC-MS analyses of samples of liquids from silage from different agricultural biogas production plants from various districts in the state of Bavaria, Germany, revealed the occurrence of ethyl and propyl ester of hexanoic acid in virtually all samples. Since these two compounds were neither detected in liquid samples from fermenters nor in liquid manure, hexanoic acid ethyl and propyl ester were identified as marker substances for liquids from silage. These liquids may enter the neighbouring surface water in various ways e.g. output of manure or leaks in a biogas production plant (silo, fermenter).

In most liquid samples from fermenters analyzed by SPDE-GC-MS, several 2-methyl ketones such as hexadecane-2-one and 6,8-dimethyl-2-undecanone were identified and elucidated as marker compounds for this type of agricultural liquids since they were neither found in liquids from silage nor in samples of liquid manure. Indole, p-cresole, p-ethylphenol and skatole, already known as typical substances in liquid manure, can also be identified by the same SPDE-GC-MS method.

SPDE-GC-MS is a sensitive analytical screening tool for the detection of the marker substances down to a 100,000-fold dilution of agricultural liquids. The method is meanwhile routinuously being applied for elucidation of the cause of local spills of surface water with the suspicion of agricultural liquids as source of contamination within the technical supervision of water bodiesin Bavaria.