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Degradation of synthetic polymeric flocculants in land spreading of MWWTP sludge

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1. Introduction

Polyacrylamides (PAMs) are a group of watersoluble polymers with a wide range of applications in industry, food processing, agriculture and waste management. One of the major applications for PAM is sludge dewatering in municipal waste water treatment plants (MWWTPs). Spreading of the sludge on agricultural land is currently one of the most important recycling routes.

In Germany, the maximum application rate of sewage sludge on agricultural land is 5 MT per hectare every three years. Considering that the dewatered sludge contains between 3 and 10 kg/MT significant amounts of PAM are added to the soil..

Even though PAM has been reported to be non-toxic to the ecological system concern has been expressed concerning potential adverse effects [3]. PAM does not appear to be toxic to soil organisms but currently less is known about microbial degradation of PAM in soils [1],[2]. Since it is irreversibly bound to the sludge matrix it is not possible to determine degradation processes without the use of an isotope-labelled polymer.

Based on these concerns and the precautionary principle which is one of the basic tenets of the German soil protection act, the German Fertilizer Ordinance DüMV of December 5th, 2012 introduced a trigger value for degradation of synthetic polymers of 20% in a 2-year period.

The current study investigated the fate and effects of PAM applied to soils through land-spreading of treated sludge. Degradability, leaching, uptake of degradation products and effects on soil microorganisms were studied in both standard laboratory experiments and outdoor simulations at a realistic exposure scenario.

2. Materials and methods

Radiolabelled polymer was synthesized using ^{14}C-labelled acrylamide in a downscaled synthesis procedure with the labeling positioned at the carbon-carbon backbone of the amide units. The ^{14}C-labelled polymer met the product specifications of commercially available polymer used in sludge dewatering. The ^{14}C-polymer was used to dewater digested sewage sludge from a local MWWTP in a standard way and the dewatered sludge containing the ^{14}C-polymer was used for the subsequent degradation tests. By this procedure a 100 % realistic exposure scenario for the subsequent degradation experiments was achieved.

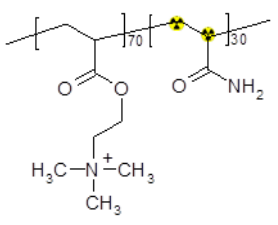

Figure 1: structure of synthetic polymer and labelling

Degradation of the polymer in a real-life matrix was initially assessed using a modified OECD 307 test. The modifications from the standard setup included an extended test duration of one year and exposure of a second set of samples to simulated sunlight in a 12-hour day / night sequence. Samples were incubated in a flow through system to measure mineralisation and enable a full mass balance at each point. After extraction the soil residues were subject to combustion analysis to quantify the amount of non-extractable residues (NER).

Additionally, an outdoor simulation study was conducted using a Lysimeter device. The fate of the polymer in agricultural soil was monitored along with frequent soil and eco-toxicological testing. Site treatment in the three years after the spreading the sludge followed good agricultural practice including cultivation of typical agricultural crops (wheat and spinach) used to analyse plant uptake of ^{14}C-PAM or radiolabelled degradation products. At regular intervals of six months, soil samples were taken from the Lysimeter surface for analysis. Leachate was sampled whenever generated by natural rainfall events. After three years samples were taken up to a depth of 50 cm to determine the shift of the applied substance into deeper soil layers.

OECD 222 (earthworm reproduction) and ISO 15685 (microbial nitrification) were used for soil ecotox-testing, ISO 6341 (Daphnia immobilisation) and ISO 11348 (Luminescent inhibition) for soil eluates.

3. Results and discussion

3.1. OECD 307 standard lab test

Radioactivity recovered using 1 N NaOH decreased from 100% at the outset to about 90% at day 100. After 100 days, no further significant changes were observed. All of the missing radioactivity was identified as NER. Mineralization was not a relevant process and no difference was observed between the dark incubation conditions and simulated sunlight.

Further characterisation of the extractable radioactivity indicated strong binding to the extracted sludge/soil matrix. Radio-GPC showed significant reduction of the MW proving degradation of the polymer backbone which is considered to be the most stable part of the macro-molecule. However, the degradation kinetic could not be derived from the GPC data.

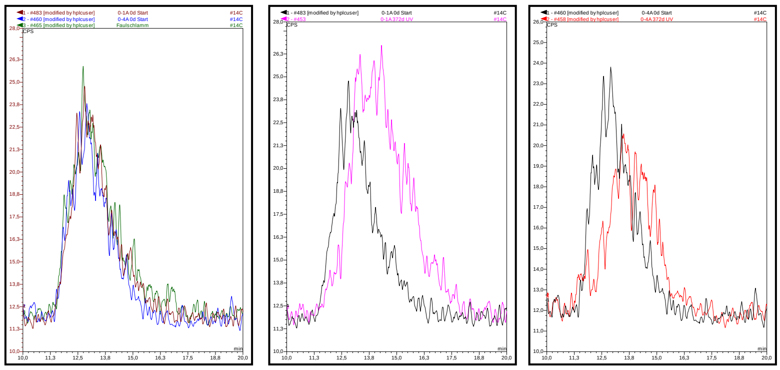

Figure 2: radio-GPC chromatograms of extracts from OECD 307 samples

left: extracts from study start (*d*0)

centre: soil 1 at start (black) and at d***372 (pink)***

right: soil 2 at start (black) and at d372 (red)

3.2. Lysimeter outdoor study

Plant uptake and leaching of radioactivity was not observed. There was practically no vertical shift found at study end. Radio-GPC confirmed the results obtained in the OECD 307 lab degradation study.

The radioactive mass balance showed a permanent decrease of the applied radioactivity. Based on this data, a half-life of 1980 days could be calculated using the KinGUI software. This half-life does not take in consideration the degradation of the polymer backbone which is also degradation although it is not mineralisation. The ecotox-tests did not show any effect over control in any of the samples.

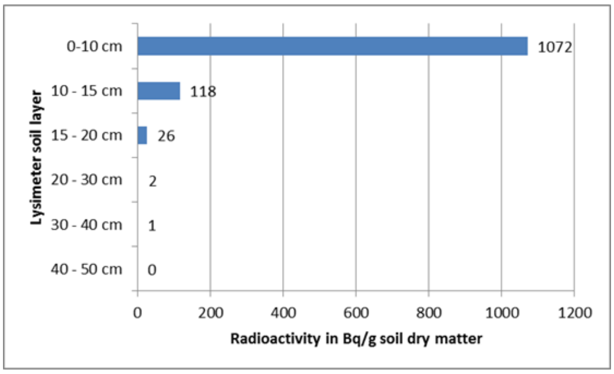

Figure 3: Vertical distribution of radioactivity after 3 years

4. Conclusions

This project demonstrated that the synthetic polymer degrades in soil after land-spreading as a component of MWWTP sludge and has no adverse effect on the soil environment. Even in a very conservative evaluation which considered only disappearance of radioactivity, the degradation rate was greater than 20% within two years which complies with the requirements of German Fertilizer Ordinance. However, degradation is not exclusively mineralisation and, therefore, the breakdown of the polymer backbone and subsequent integration into the soil matrix have to be taken into account when determining the fate of the polymer.

5. References

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