How to investigate the fate of synthetic polymeric flocculants in a complex agricultural matrix - results of an experimental simulation study -

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Background

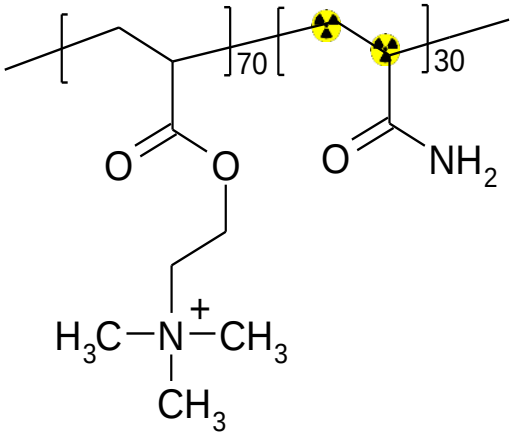
- Linear Polyacrylamides (“PAM”s) are a group of water-soluble polymers
- One of the major applications for PAM is sludge dewatering in municipal waste water treatment plants. With spreading sludge to agricultural land, the associated PAM used for dewatering enters the soil
- The German Fertilizer Ordinance (DüMV) requires to prove the degradability of synthetic polymers under environmental conditions!

But how to do that, since by now no analytical method is available to quantify / characterise a synthetic polymer in a complex environmental matrix?

Approach: ^{14}C-radiolabelled PAM

Why ^{14}C radiolabelling:

- No change of chemistry!
- Enables detection in complex matrix
- Mineralisation by $^{14}CO_2$ measurable also in low rates and high background
- Mass balance!



Challenges for the radiolabelling:

- not commercially available
- no experience with the downscaled process (finally 3.6 g ^{14}C-PAM were produced)
- radioactivity of monomer can induce polymerisation – high risk of failure
- specifications of the commercial product should be met but difficult to prove, as very specific instrumentation for characterisation is not available for ^{14}C-work

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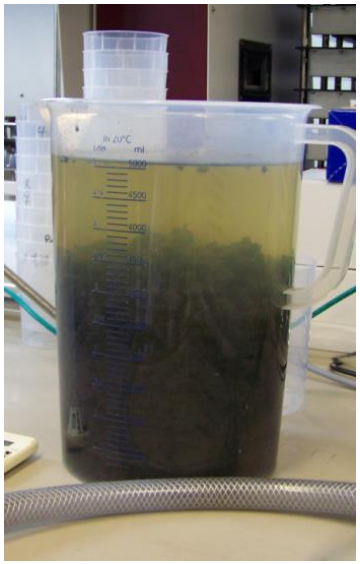
Flocculation of sludge with ^{14}C-PAM

Final prove of product specifications: viscosimetry and polymer function!

Flocculation of 105 L digested sludge (origin: MWWTP Maumke, ca. 0.8% dm)

Dosing ^{14}C-PAM: 4.33 g per kg sludge dm





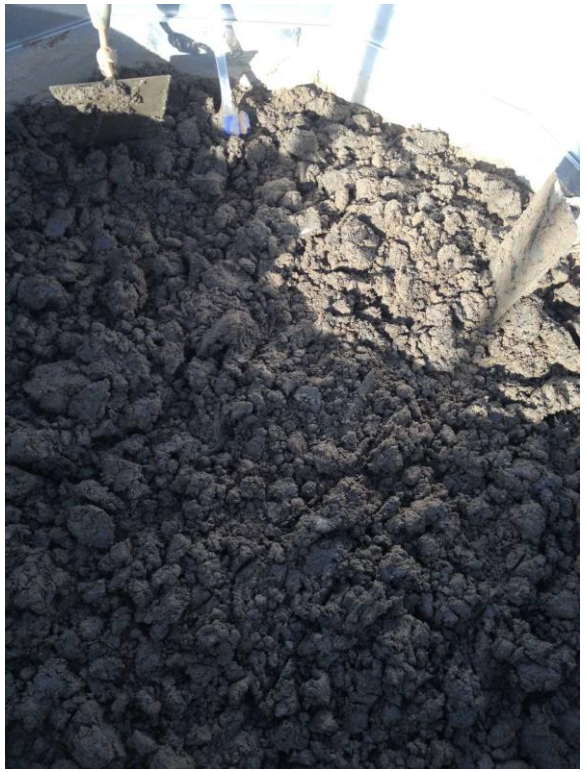

Flocculated sludge:

9247 g sludge with 872 g dm (9,4% dm) and 272 kBq per g dm

Sludge application in outdoor simulation experiment

7 kg sludge dm containing 179.7 MBq (=1,97 g ^{14}C-PAM) available

Surface area of the Lysimeter: 1.08 m^2 => **application rate: 18.2 kg PAM/ha**



mix into upper 5 cm

Maintainance of outdoor simulation experiment

Plot cultivation:	April 2013	summer wheat "Kadrilj"
	Mai 2014	Spinach "Emilia"
	April 2015	mustard seed (green manure)
	Juni 2015	summer wheat „Kadrilj“

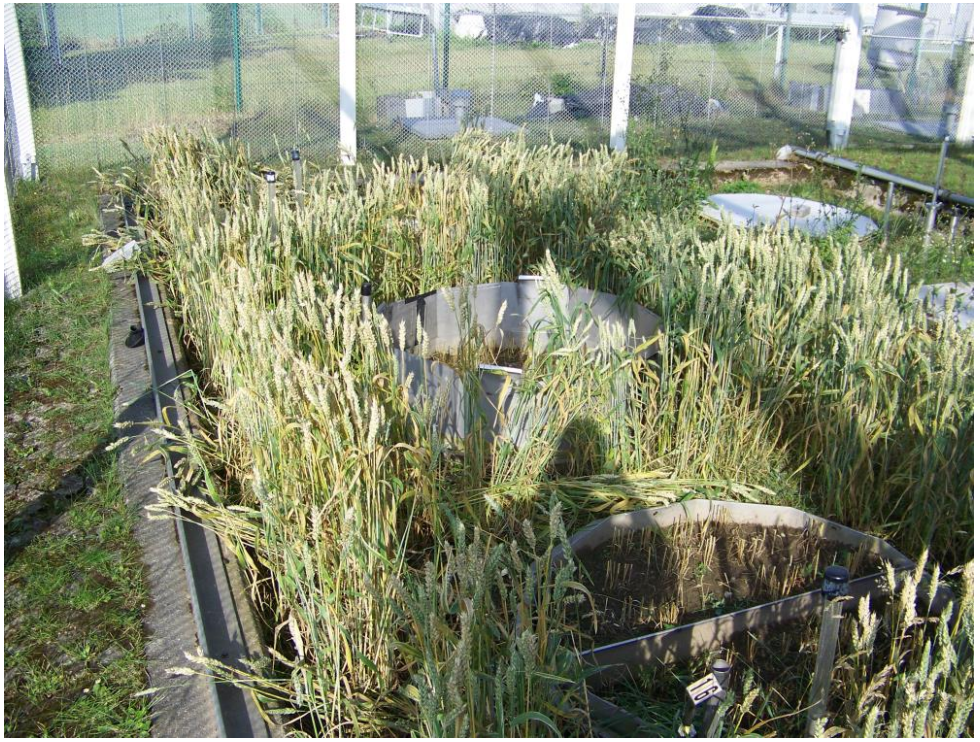
<u>Analysis of crops and leachate</u>

No radioactivity was detected in any crop sample at any time.

⇒ No plant uptake !

No radioactivity was detected in any leachate sample.

⇒ No leaching of PAM or metabolites



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Development of an extraction procedure

Extraction of dewatered sludge with:

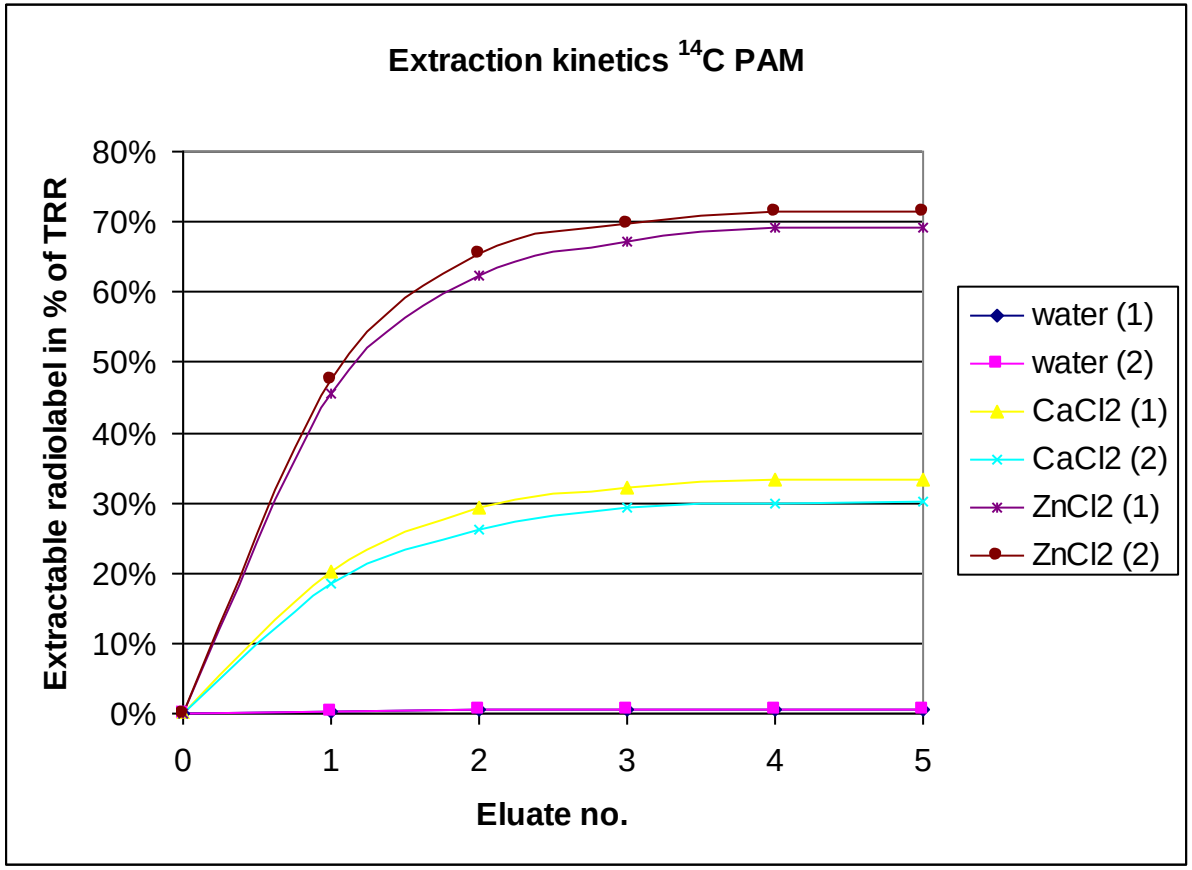
- water
- 5 m $CaCl_2$-Solution
- 5 m $ZnCl_2$-Solution

5 g sludge = 0,5 g dm with 20 mL solution

30 min shaken

centrifugation 5 min, 13.000 x g

Liquid scintillation Counting (LSC)



best extraction efficacy: 5 m $ZnCl_2$-solution

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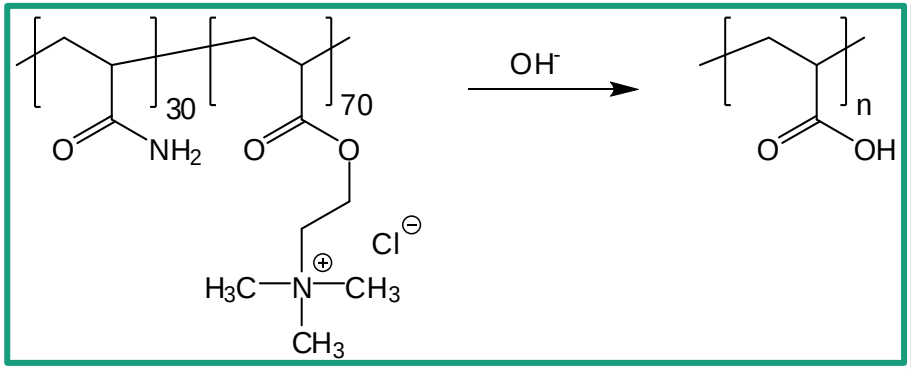
Development of an extraction procedure

Further extract treatment: dialysis to get rid of high salt load, but:

with decreasing salt concentration a precipitate occurred in the extract, which contains the entire extracted radioactivity and could not be re-solved in any solvent.

Way out:

- Extraction with 1 m NaOH-solution: quantitativ extraction of radioactivity
- After dialysis the entire radioactivity stays in solution (partial hydrolysis of PAM)



Stability testing of PAM in up to 5 m NaOH:

- no quantitative hydrolysis of side chains (proven by H-NMR)
- no break of main chain („C-backbone“) by NaOH-treatment

Matrix-destructing extraction

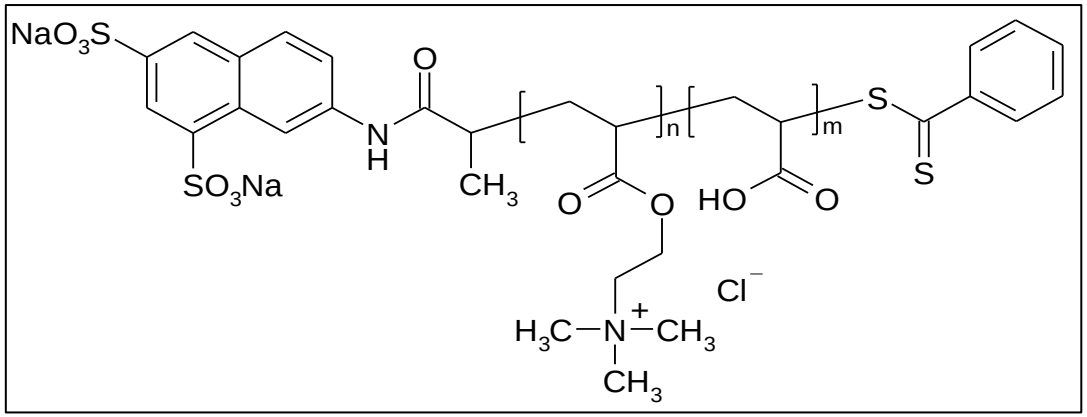
GPC-Analysis of extracts

GPC-column: combination of PSS MCX, 10^3 Å - 10^5Å, 10µ; 8,0 x 300 mm

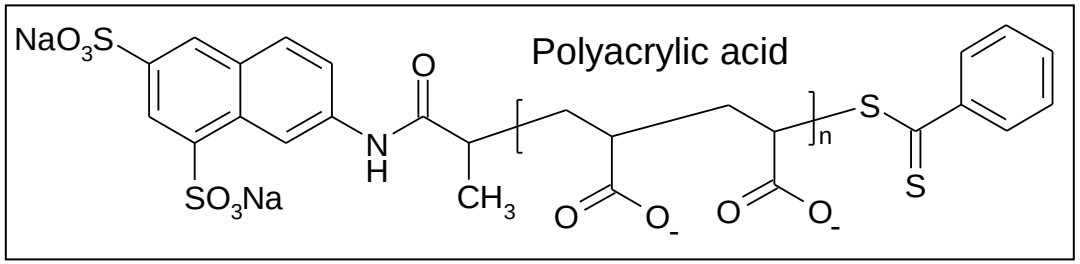
Detektion: UV (DAD) and ^{14}C, series connected

Evaluation of GPC-measurements

GPC molecular size standards (polystyrolsulfonate)
and taylor-made reference standards (Fh-IAP)



Standard	Retention time
SaSt140317-AS (300 000 Dalton)	13.8 min
SaSt140317-BS (92 000 Dalton)	15.2 min
SaSt140317-CS (24 000 Dalton)	16.4 min



LM-10 A (267 400 Dalton)	13.8 min
LM-10 B (94 000 Dalton)	15.2 min
LM-10 C (26 600 Dalton)	16.4 min

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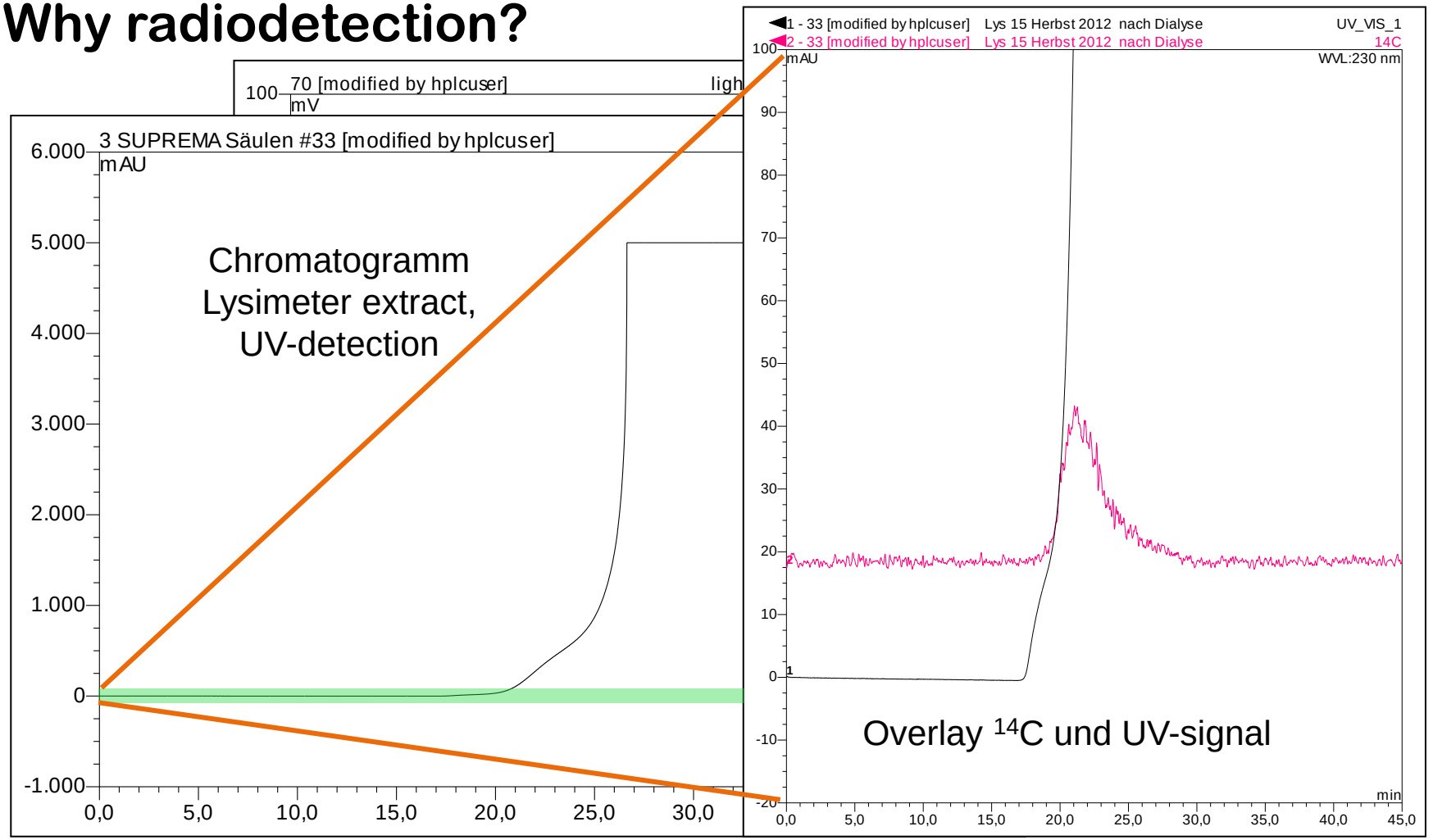
GPC-Analysis of extracts

Why radiodetection?



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GPC-Analysis

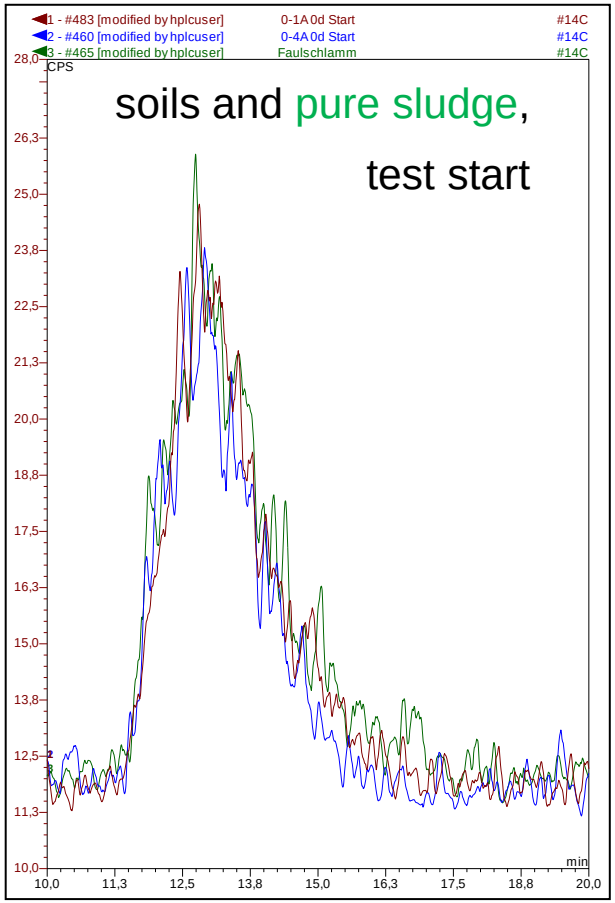
Peakshift depending on molecular mass of standards

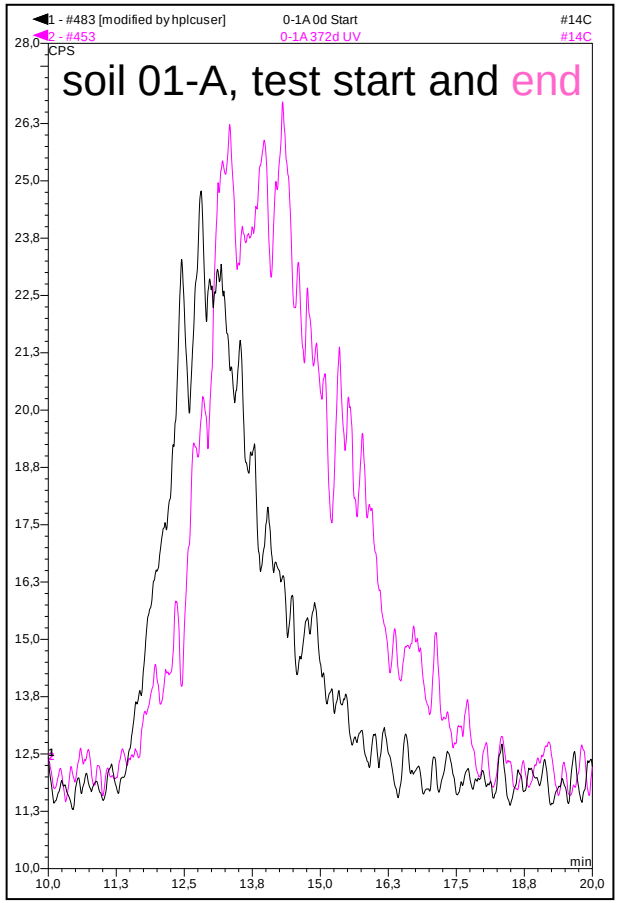
Standard	Molecular weight [Da]	Retention time [min]	Shift [min]	Reduction factor molecular mass
GPC-Standard „light blue“	708000	13.4		
	107000	15.3	1.9	7
	9600	18.3	4.9	74
	504	22.0	8.6	1405
PAM (SaSt140317)	300000	13.8		
	92000	15.2	1.4	3.3
	24000	16.4	2.6	12.5
Polyacrylic acid (LM-10)	267400	13.2		
	94000	14.0	0.8	3
	26600	15.1	1.9	10

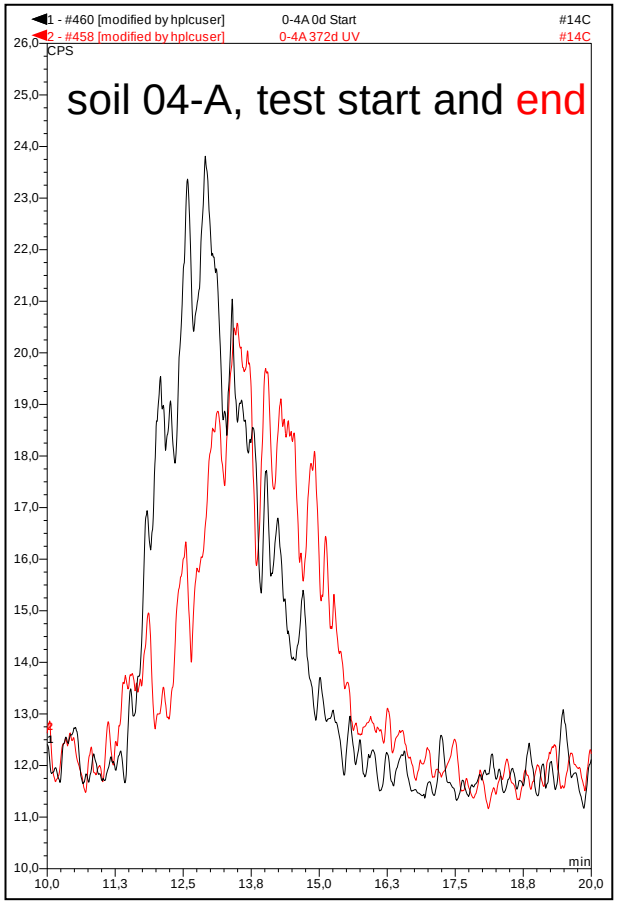
A shift of 2 min corresponds to a factor of about 10 in molecular size reduction

Lab soil degradation experiment, GPC results

Extractable radioactivity, GPC:







Significant reduction of molecular weight distribution at test end!

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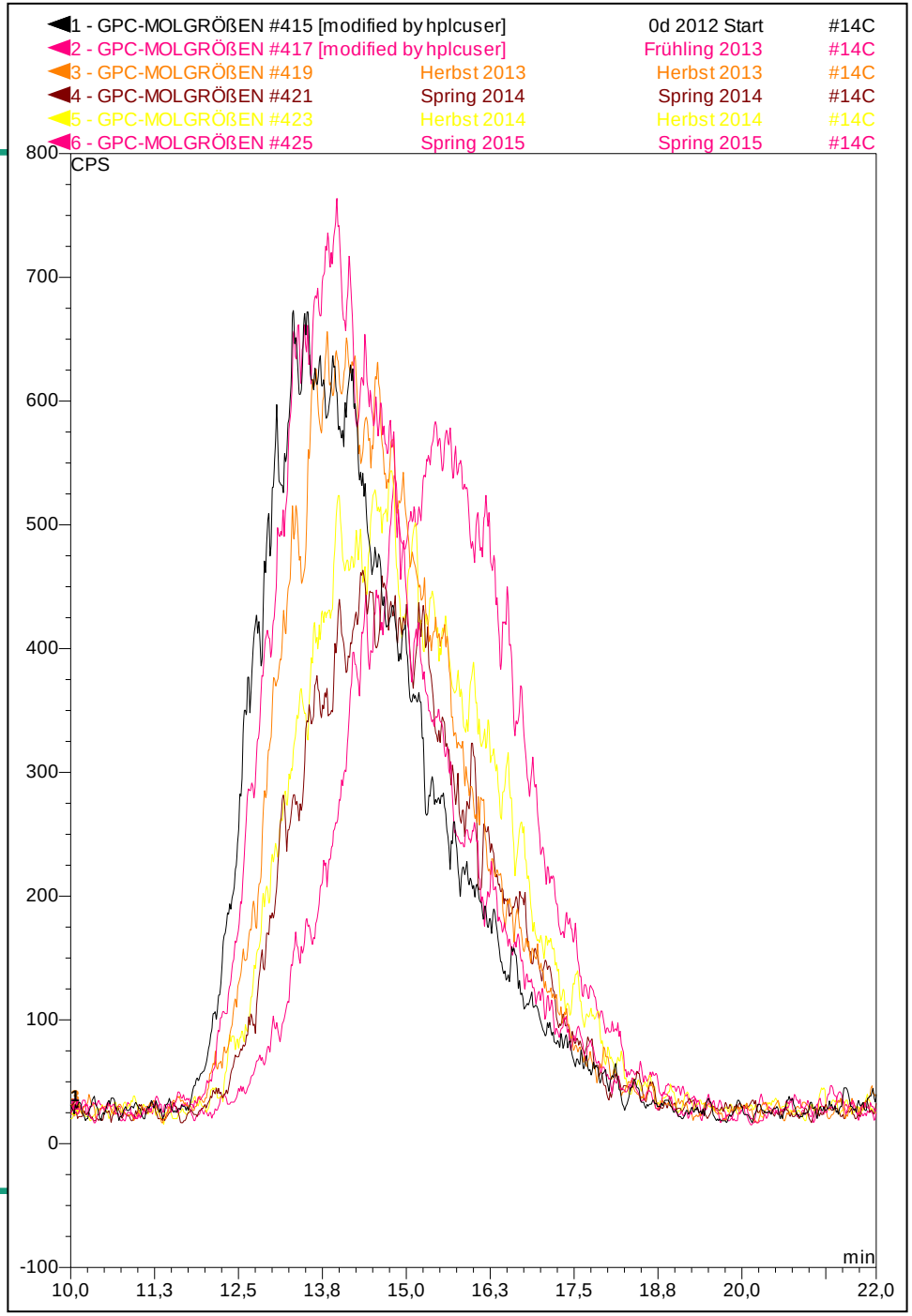
Outdoor simulation experiment, GPC results

Sample	Retention time [min]	Shift [min]
Start Fall 2012	13.318	
Spring 2013	13.967	0.649
Fall 2013	13.819	0.501
Spring 2014	14.353	1.035
Fall 2014	14.789	1.471
Spring 2015	15.434	2.116

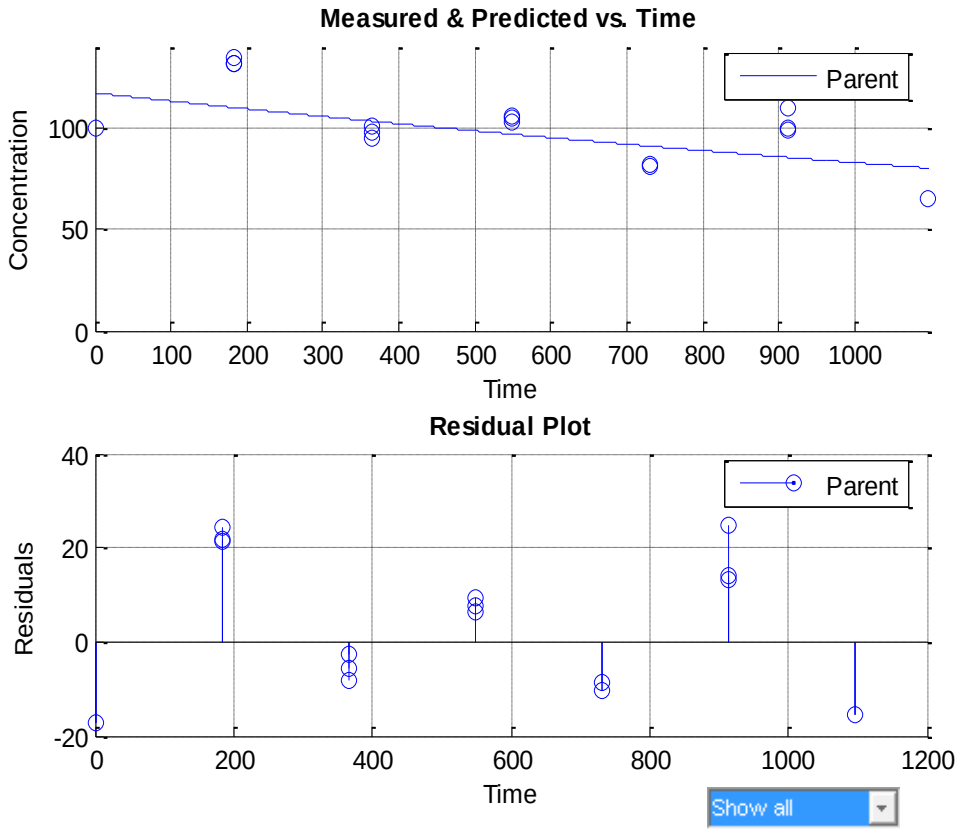
Significant reduction of molecular weight distribution at test end!

According to standard shift reduction by factor of about 10



Outdoor simulation experiment, results

Radioactive Mass balance, kinetics of 0-10 cm layer



KinGUI, first order kinetics

$Chi^2 = 12.00$

$k = 3.5*10^{-4}$

$DT_{50} = 1980\ d = 5.4\ a$

(for disappearance of ^{14}C)

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Outdoor simulation experiment, results

Formation of „NER“

sampling	24.10.2012	24.04.2013	02.10.2013	05.05.2014	28.10.2014	05.05.2015
extractable*	98.1	102.6	83.4	79.6	62.9	63.9
non-extractable*	8.0	10.0	9.7	10.8	8.4	8.7

* in % of the combustion result of 1d sampling

- A constant amount of about 10% is not extractable with 1 m NaOH. Similar findings in the lab degradation experiment
- Does NOT represent the „classical NER“ since a matrix destructive extraction procedure is used.
- Extraction of freshly flocculated sludge + soil with 5 m $ZnCl_2$ recovered only 50% (04-A) to 25% (01-A) of the applied radioactivity (1 m NaOH: 100%).

=> NaOH-extraction leads to significant underestimation of „NER“

Summary

- ^{14}C-labelled PAM was successfully synthesized in a downscaled procedure
- Simulation experiments were performed under realistic exposure and incubation conditions
- Extraction- and clean-up procedures were developed to characterise the fate of PAM in complex environmental matrix

- Under outdoor conditions a significant reduction of the molecular weight of PAM was determined, break of the C-C backbone!
- A formation of at least 10% *„NER“* was found. Due to the matrix destructive extraction procedure this is a massive underestimation of NER.
- The mass balance prove disappearance of the radioactivity over time. Based on the recovery data a degradation kinetic could be established.
- No leaching, no plant uptake, no effects in ecotox-testing were observed.

^{14}C-radiolabelling suitable technique to follow the fate of polymers in complex matrices!

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