Sicherheit in Technik und Chemie

FOCUS AREA ENVIRONMENT

BAM Bundesanstalt für Materialforschung und -prüfung

# AN ALTERNATIVE SPECTROSCOPIC APPROACH FOR THE MONITORING OF MICROPLASTICS IN ENVIRONMENTAL SAMPLES

ANDREA PAUL[1]; ROLAND BECKER[1], LUKAS WANDER[1,2], STEFFEN BREITFELD[1,2], MARTIN KOEGLER[3], ANDREAS SAUER[1], ULRIKE BRAUN[1]

[1]Bundesanstalt für Materialforschung und –prüfung, Richard-Willstätter-Str.11, Berlin, Germany, andrea.paul@bam.de
[2]Humboldt University Berlin, Department of Chemistry, Brook-Taylor-Str. 2, 12489 Berlin, Germany
[3]Division of Pharmaceutical Biosciences, Centre for Drug Research, University of Helsinki, P.O. Box 56, 00014 Helsinki, Finland

www.bam.de

# Agenda

Microplastics – an analytical challenge

The alternative approach for microplastics in soil by process spectroscopic techniques

- cw process Raman spectroscopy
- timeGated Raman spectroscopy
- process – NIR spectroscopy

# Microplastics – an analytical challenge

**How much sampling & time do we need to gain representative information on possible contamination of soils with microplastics?**

- do we want to quantify small amounts precisely?

➡ TED-GC-MS (new!)

- or even want to learn about size distribution and age?

➡ microscopic techniques (standard)

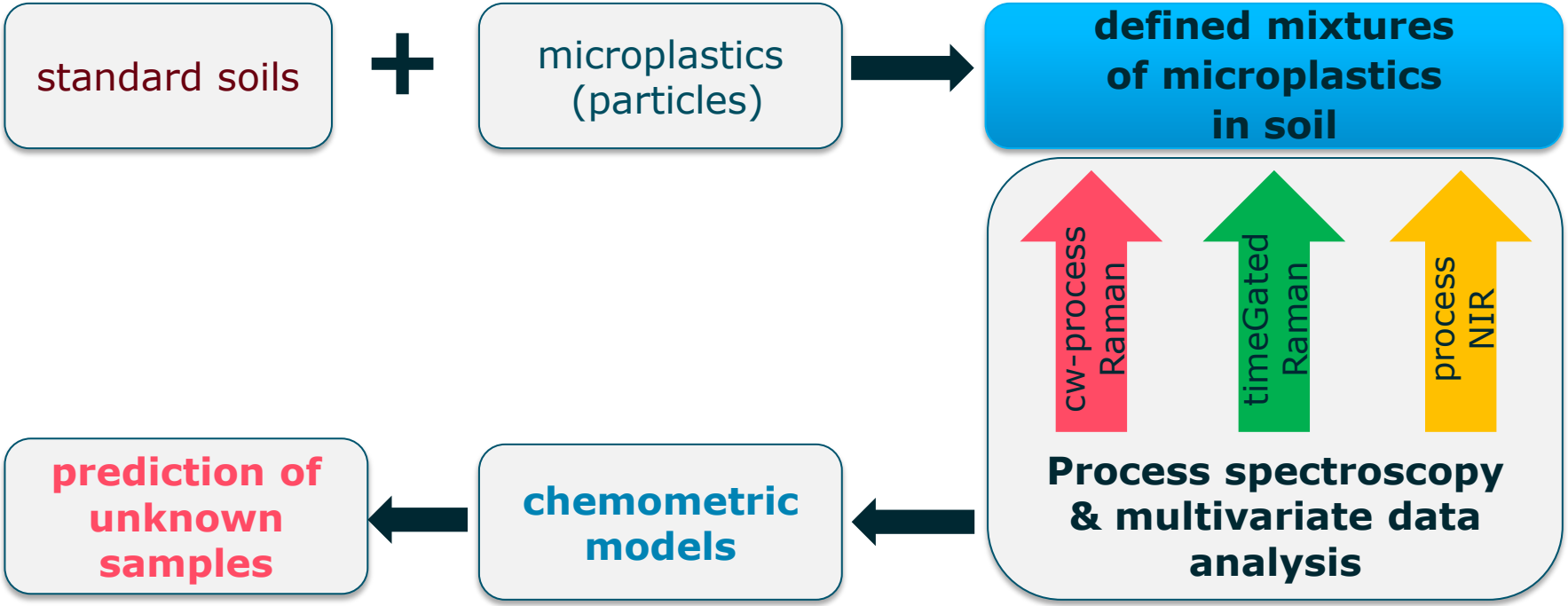
- **small volumes, long times**

- do we just want to know about if there is *some* contamination above a certain *level* but have to investigate huge amounts of material?

➡ process analytical approach
potential for online analysis

**„quick & dirty“**

# Process analytical approach for the quantification of microplastics in soils



# Preparation of „microplastics“ mixtures

standard soils

**Soils**

- coastal sand
- medium sand
- LUFA 2.2
- LUFA 2.3

LUFA Speyer

BEZIRKS VERBAND PFALZ

Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer
Obere Langgasse 40
67346 Speyer
Tel. 06232 136 0
Fax 06232 136 110
email: postalei@lufa-speyer.de
Internet: www.lufa-speyer.de

**Analyses Data Sheet for Standard Soils according to GLP**

(Mean values of different batch analyses +- standard deviation. All values refer to dry matter.)

| Standard soil type no. | 2.1 | 2.2 | 2.3 | 2.4 | 5M | 6S |
|---|---|---|---|---|---|---|
| Batch-No. (Sp=stored; F= field fresh | | | | | | |
| sampling-date | | | | | | |
| organic carbon in % C | 0,71+- 0,08 | 1,61 +- 0,15 | 0,67 +- 0,03 | 1,99 +- 0,21 | 1,02 +- 0,08 | 1,78 +- 0,08 |
| Nitrogen in % N | 0,06 +- 0,01 | 0,17 +- 0,01 | 0,08 +- 0,01 | 0,22 +- 0,02 | 0,13 +- 0,01 | 0,18 +- 0,01 |
| pH-value (0.01 M $CaCl_2$) | 4,9+- 0,3 | 5,4 +- 0,2 | 5,9 +- 0,6 | 7,4 +- 0,1 | 7,3 +- 0,1 | 7,2 +- 0,1 |
| cation exchange capacity ( meq / 100g) | 4,3 +- 0,6 | 9,7 +- 0,4 | 7,6 +- 0,8 | 32,9 +- 4,5 | 17,7 +- 3,7 | 27,3 +- 3,4 |
| Particle size (mm) distribution according to German DIN (%): | | | | | | |
| <0.002 | 3,1 +- 0,9 | 8,6 +- 1,2 | 6,9 +- 1,6 | 26,2 +- 1,4 | 10,8 +- 0,6 | 41,3 +- 0,7 |
| 0.002 - 0.006 | 1,5 +- 0,6 | 3,5 +- 1,0 | 5,3 +- 0,7 | 7,6 +- 0,5 | 3,7 +- 0,8 | 8,4 +- 0,9 |
| 0.006 - 0.02 | 3,5 +- 0,3 | 5,3 +- 0,9 | 11,5 +- 0,5 | 14,8 +- 1,0 | 9,3 +- 0,6 | 13,2 +- 0,6 |
| 0.02 - 0.063 | 7,2 +- 0,9 | 7,8 +- 1,6 | 18,8 +- 1,6 | 23,3 +- 0,7 | 21,7 +- 1,2 | 14,7 +- 0,8 |
| 0.063 - 0.2 | 28,2 +- 1,3 | 34,0 +- 3,5 | 24,7 +- 1,4 | 19,5 +- 1,0 | 39,0 +- 2,4 | 9,5 +- 0,3 |
| 0.2 - 0.63 | 54,0 +- 1,6 | 40,2 +- 1,7 | 30,1 +- 0,6 | 7,0 +- 2,2 | 14,4 +- 1,4 | 10,3 +- 0,7 |
| 0.63 - 2.0 | 2,5 +- 0,4 | 0,6 +- 0,1 | 2,7 +- 0,7 | 1,6 +- 0,2 | 1,1 +- 0,2 | 2,6 +- 0,6 |
| soil type | silty sand (uS) | loamy sand (lS) | silty sand (uS) | clayey loam (tL) | loamy sand (lS) | clayey loam (tL) |
| Particle size (mm) distribution according to USDA (%) | | | | | | |
| <0.002 | 3,0 +- 0,9 | 8,0 +- 1,7 | 6,8 +- 1,6 | 25,8 +- 1,8 | 10,6 +- 0,8 | 40,5 +- 1,6 |
| 0.002 - 0.05 | 11,0 +- 1,3 | 15,8 +- 3,1 | 33,6 +- 0,5 | 41,1 +- 1,2 | 30,1 +- 1,4 | 34,1 +-2,1 |
| 0.05 - 2.0 | 86,0 +- 0,9 | 76,2 +- 4,1 | 59,6 +- 1,4 | 33,1 +- 2,2 | 59,3 +- 1,5 | 25,4 +- 3,5 |
| soil type | loamy sand | sandy loam | sandy loam | loam | sandy loam | clay |
| maximum water holding capacity (g/100g) | 32,1 +- 1,7 | 44,8 +- 2,9 | 35,6+- 1,4 | 44,8 +- 2,1 | 40,1 +- 2,4 | 41,1 +- 1,4 |
| weight per volume (g/1000ml) | 1437 +- 41 | 1198 +- 38 | 1310 +- 43 | 1250 +- 39 | 1250 +- 88 | 1334 +- 63 |

Speyer,
By Order

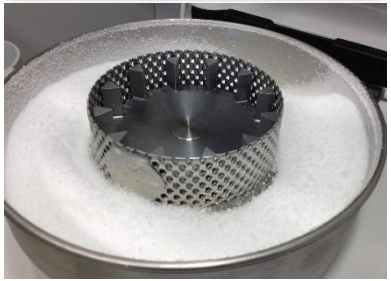
Speyer,
By Order

(Dr. Seibert - Phone: +49 (0) 6232 136 125; email: seibert@lufa-speyer.de) ab 15.03.16

# Preparation of „microplastics“ mixtures

cryo-milled polymers
& sieved

standard soils + microplastics (particles)



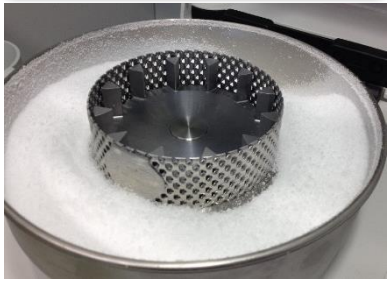
**Soils**
- coastal sand
- medium sand (1)
- Lufa 2.2 (2)
- Lufa 2.3 (3)

**Polymers**
- PE
- PS
- PP

**size**
- ≤ 2 mm
- ≤ 125 µm

# Preparation of „microplastics“ mixtures

standard soils + microplastics (particles) → **defined mixtures of microplastics (MP) and soils**



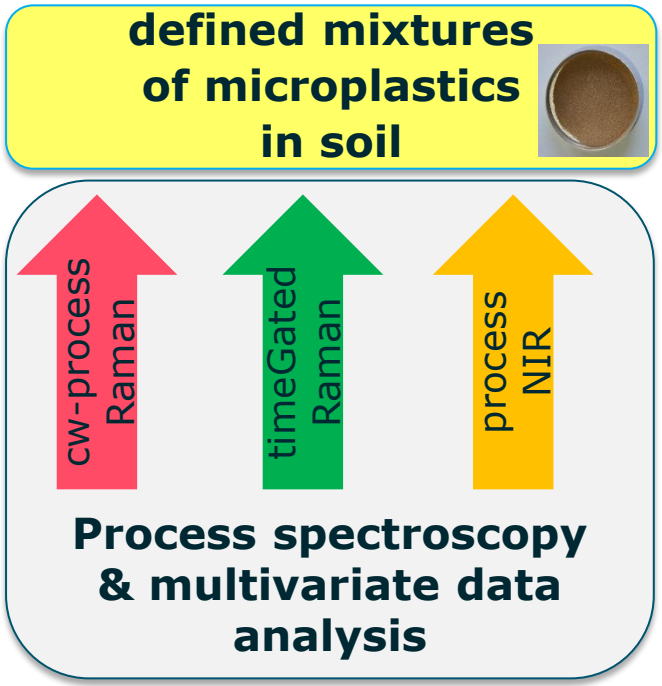
**Soils**
- coastal sand
- medium sand (1)
- Lufa 2.2 (2)
- Lufa 2.3 (3)

**Polymers**
- PE
- PS
- PP

**size**
- ≤ 2mm
- ≤ 125 µm

**powders & moldings**
- samples: 0.5 g – 4 g
- gravimetric
- 0.5 – 10 mass% MP

# Principle of process spectroscopy




**process spectrometers & fiber optical probes**

- easy to use

  - rapid measurement of many spectra
  - repeated measurements (online)
  - nead little time for adjustment
  - robust & reliable

- Raman – & NIR spectroscopic methods

# Principle of process spectroscopy

**defined mixtures of microplastics in soil**

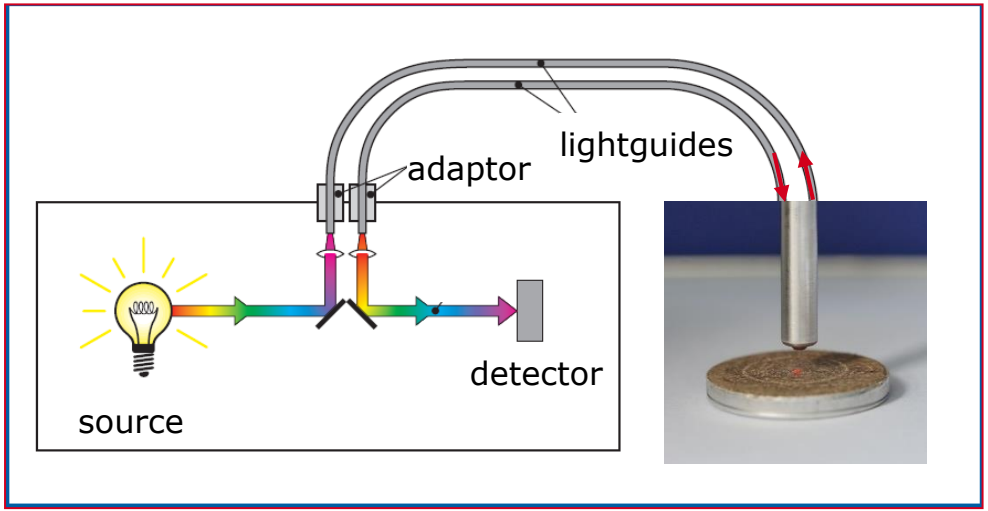
cw-process Raman

timeGated Raman

process NIR

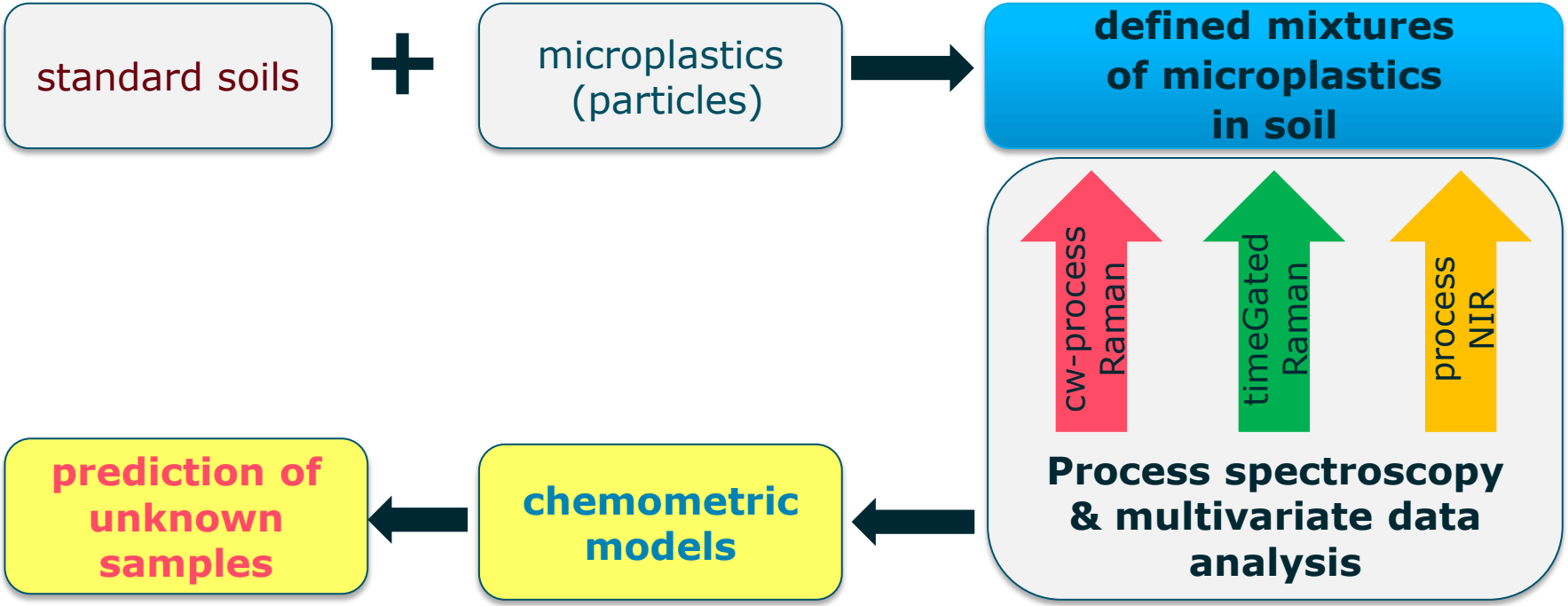
**Process spectroscopy & multivariate data analysis**

**process spectrometers & fiber optical probes**




*adopted from hellmaanalytics.com*

# Data evaluation & prediction



# Data evaluation & prediction

**multivariate data analysis = chemometrics**

- many spectra
- each spectrum contains many variables
- finding the *relevant* patterns and structures

*reduction* to principal components (PCA)

**chemometric models**

# Data evaluation & prediction

**multivariate data analysis = chemometrics**

- many spectra
- each spectrum contains many variables
- finding the *relevant* patterns and structures

*reduction* to principal components (PCA)

**chemometric models**

**prediction of new (unknown) samples**

**„real world" samples**

- compost & biowaste (1-2 mass% MP)
- washing-machine filter
- aged PP
- BAM-Reference

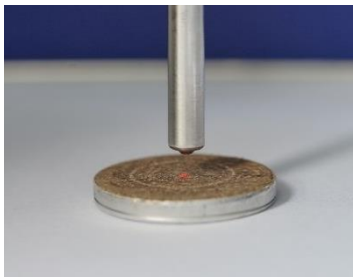
**1 mass% PE,PP,PS,PET**

# cw process Raman spectroscopy

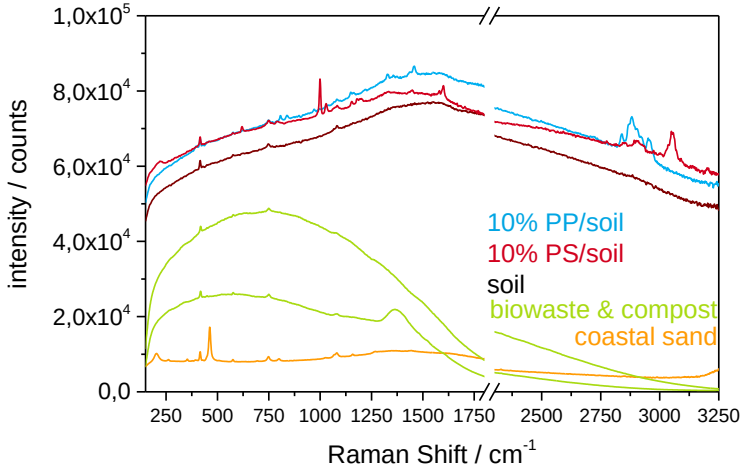
cw-process Raman spectroscopy

**defined mixtures of microplastics in soil**


**RXN1**



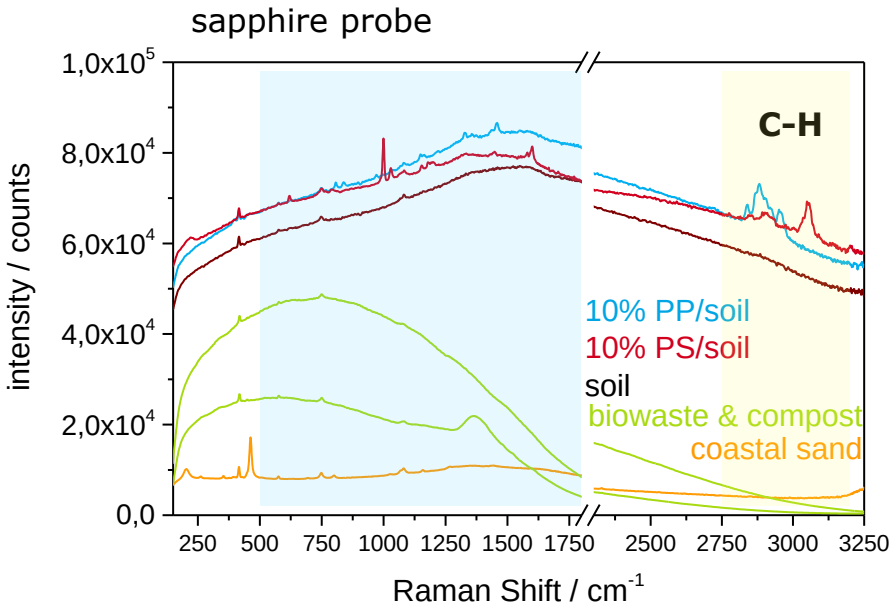
**optical probe & sample**




**spectra:** 5 x 3 s accumulation

# Raman spectroscopy

cw-process Raman spectroscopy



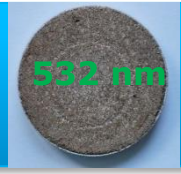

**not applicable for smaller particles ≤ 125 µm, < 5 mass% & real world samples**

- background fluorescence dominates weak Raman signal from microplastics
- future prospect: successful with additional treatment and / or enrichment?

# Time-resolved Raman spectroscopy

TimeGated Raman spectroscopy

**defined mixtures of microplastics in soil**





**principle of timeGate spectroscopy**

➡ **temporal separation**

of Raman scattering (≈ $10^{-12}$ s)
& fluorescence emission (≈ $10^{-9}$ s)

**Fluorescence suppression in Raman spectroscopy using a time-gated CMOS SPAD**

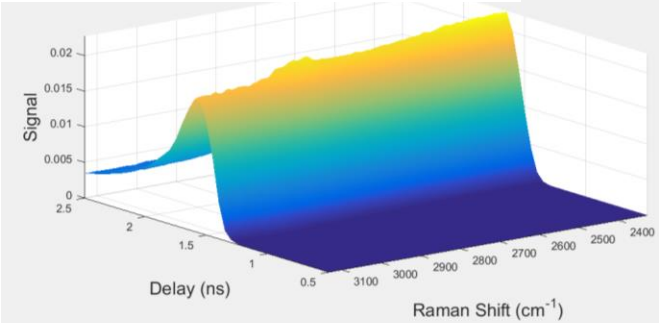
2013 | Vol. 21, No. 25 | DOI:10.1364/OE.21.031632 | OPTICS EXPRESS 31632

Martin Kögler,[*] Ilkka Nissinen,[1] Jan Nissinen,[1] and Pekka Keränen[1]

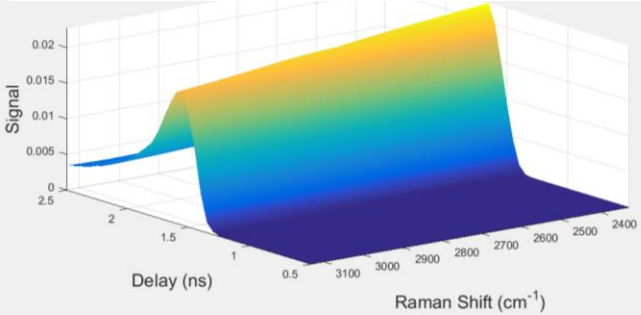
# Time-resolved Raman spectroscopy

TimeGated Raman spectroscopy

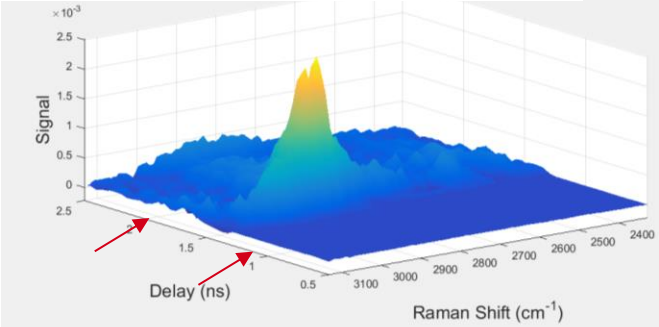
raw time-resolved spectra

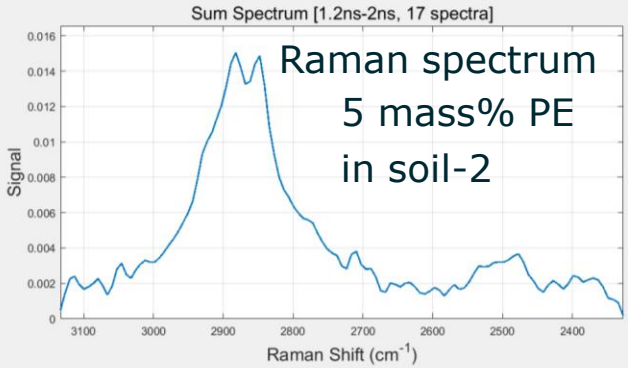



calculated background „fluorescence“



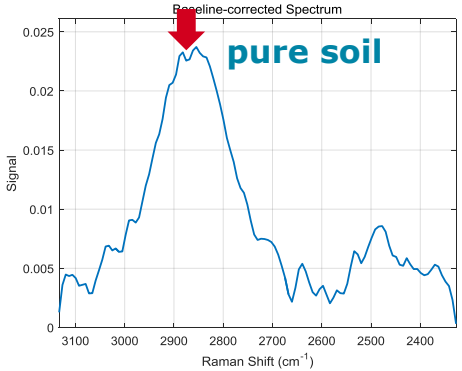

time-resolved Raman spectra

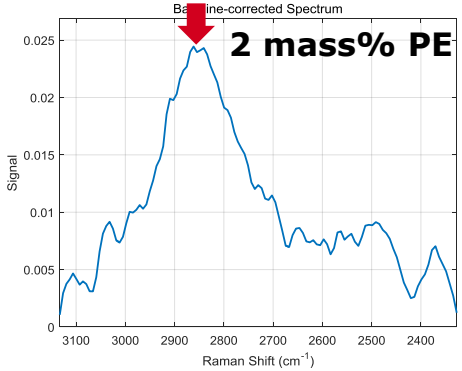


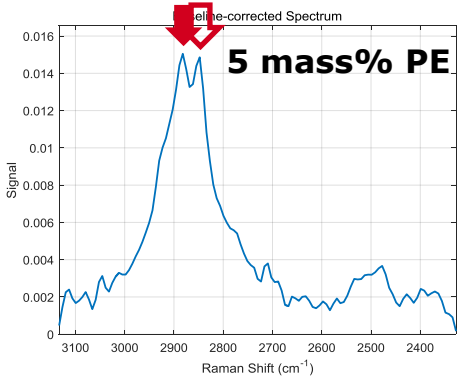



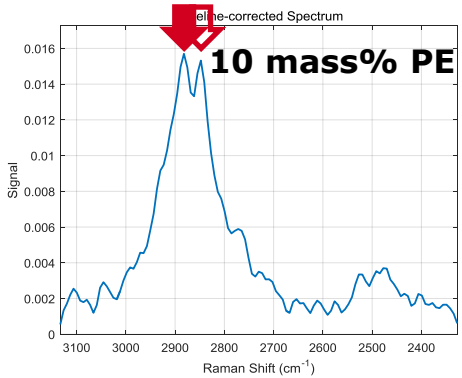
# Time-resolved Raman

TimeGated Raman spectroscopy




**not applicable for „real world" & reference samples**

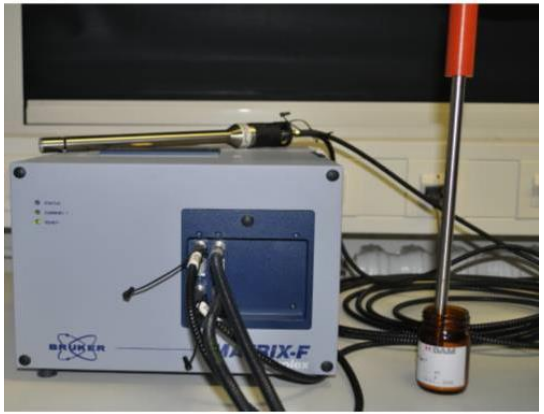
despite reduced fluorescence there is a strong signal from natural organic material

- not sensitive (≥ 5 mass%)

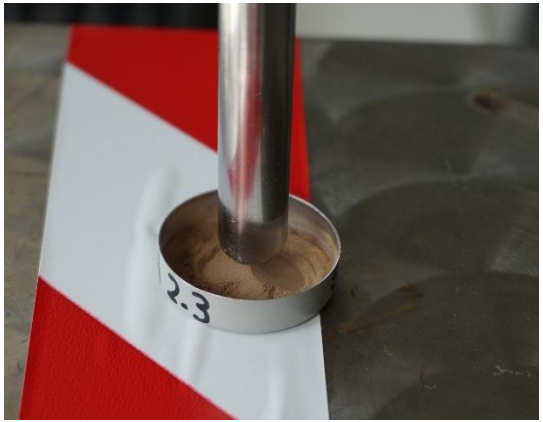
future prospect:
increase of sensitivity

# FT-NIR process spectroscopy

NIR spectroscopy

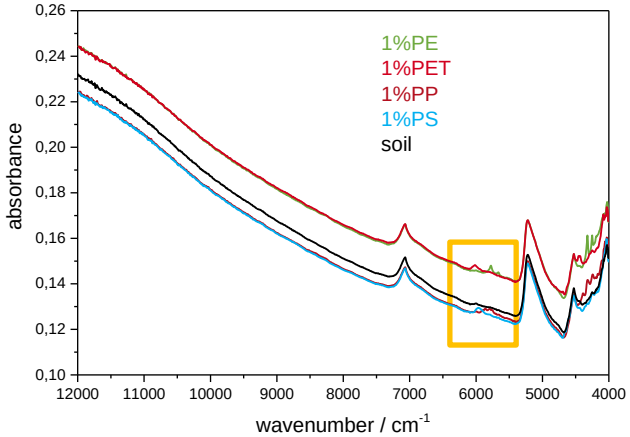


**NIR FT process spectrometer**



**reflection probe**

1 g of powder, 5 spectra per sample



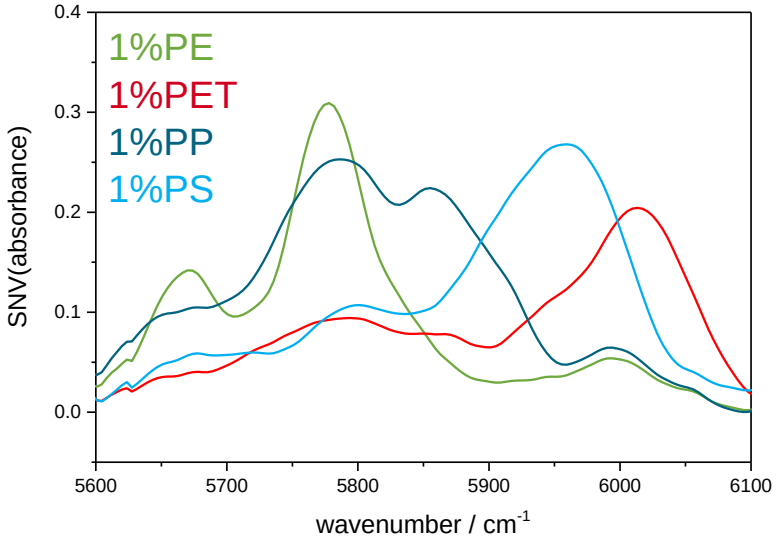

**typical spectra**

result of 64 scans (30 sec)

# FT-NIR process spectroscopy

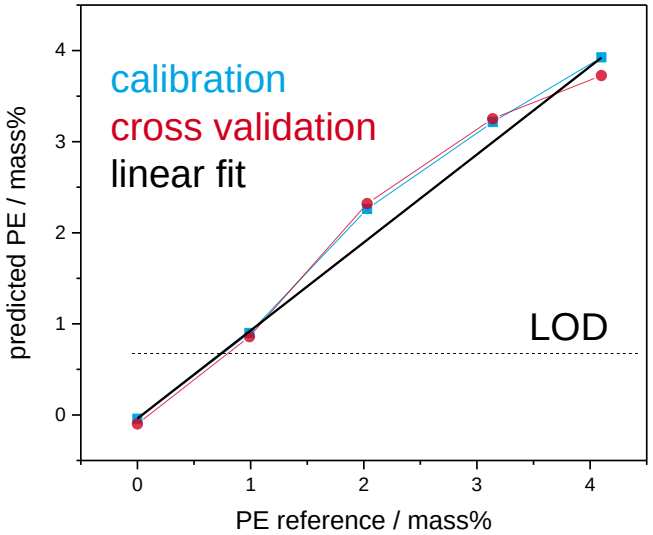
NIR spectroscopy
chemometrics

BAM




**spectra of microplastics in soil**

transformation: roi, bsl & SNV



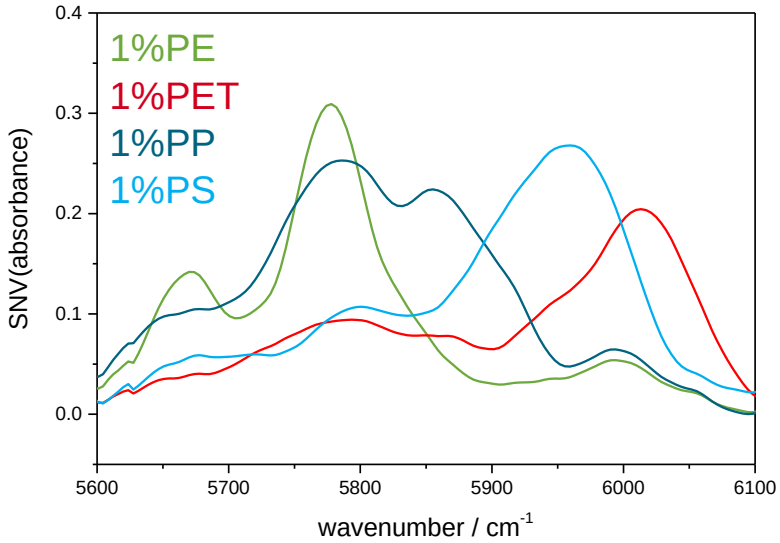

**calibration example PE (PLS-DA)**

**$R^2$ = 0.98 , RMSE-CV = 0.23 mass%**

# FT-NIR process spectroscopy

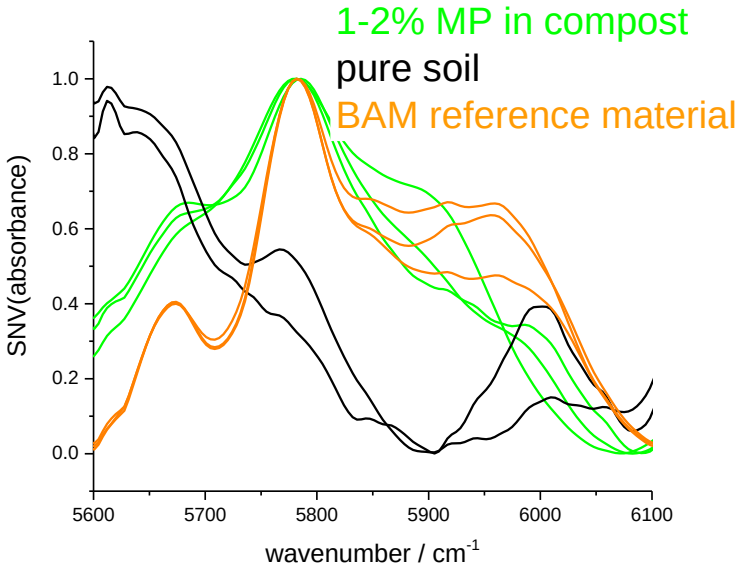
NIR spectroscopy
chemometrics

BAM




**spectra of microplastics in soil**

transformation: roi, bsl & SNV



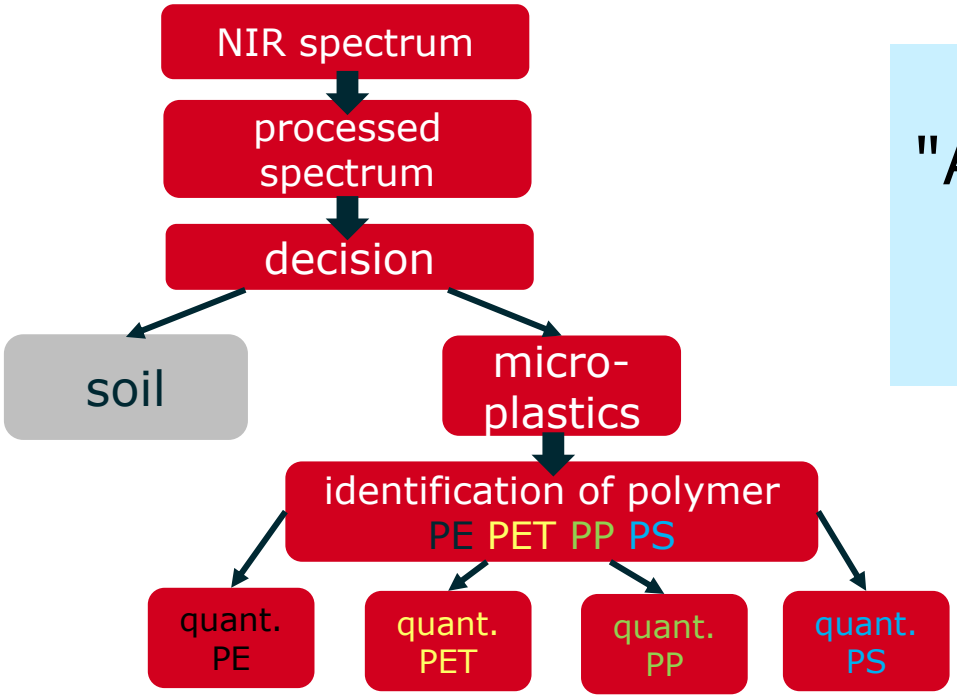

**spectra of „real world samples**

# NIR process spectroscopy

**method used: PLS-DA**

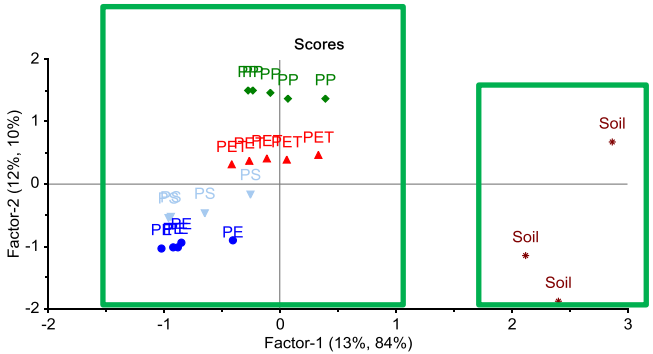
NIR spectroscopy chemometrics

BAM

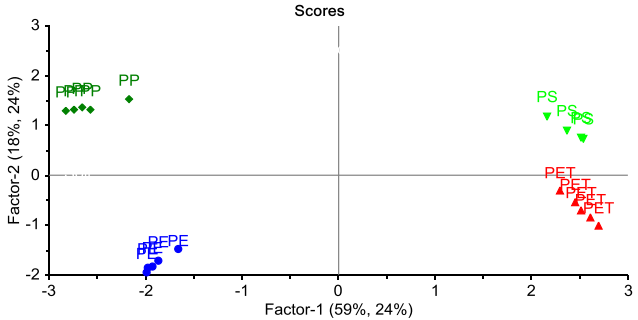


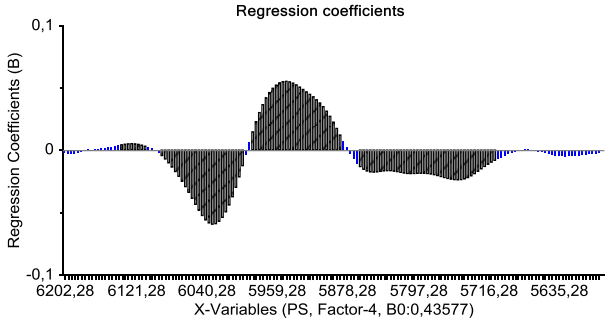

"All models are wrong but some are useful"
George Box, 1978

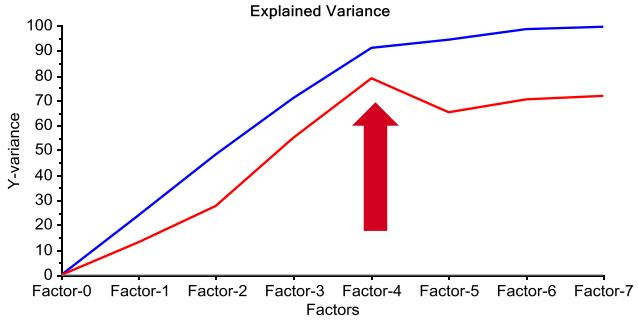
# PLS-DA models for NIR spectra
## 1- decision

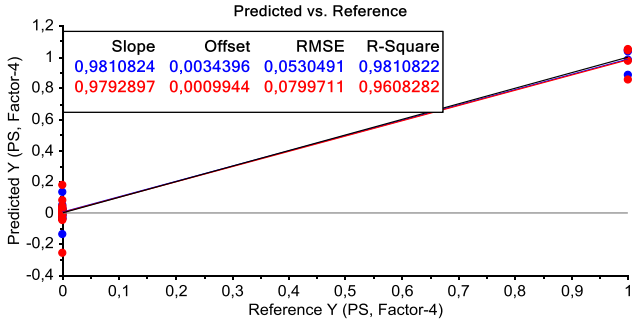


# PLS-DA models for NIR spectra
## 2- polymer

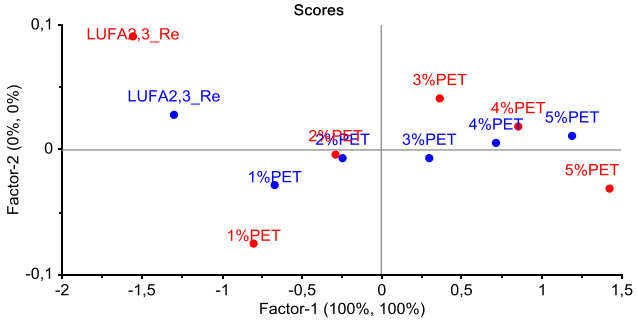


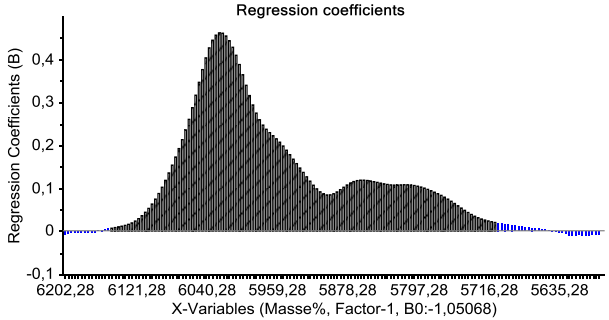



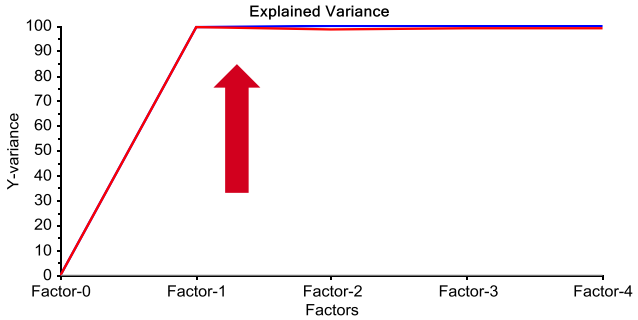



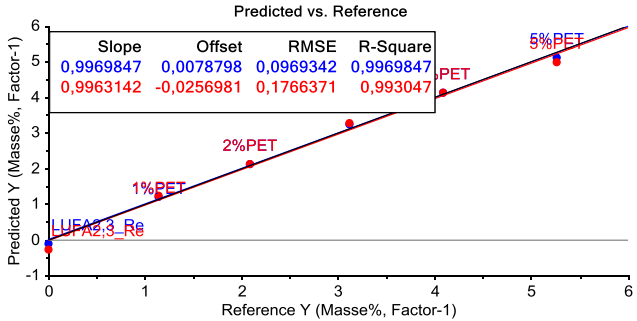



# PLS-DA models for NIR spectra
## 3- calibration for PET



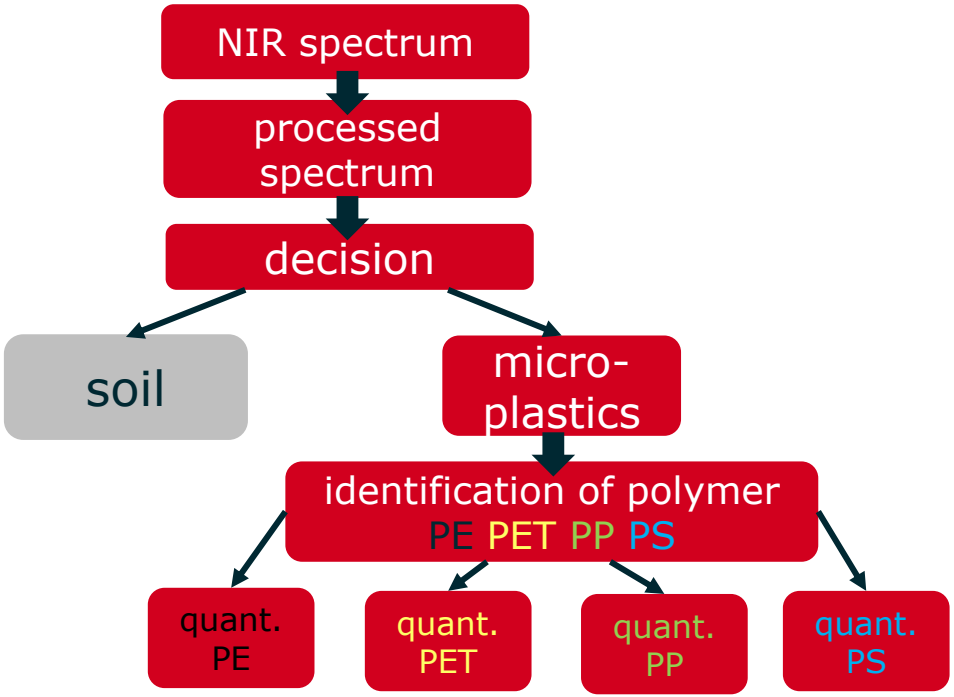



# NIR process spectroscopy
## method used: PLS-DA

NIR spectroscopy chemometrics

BAM




**works for „real world"**
**& reference samples**

- sensitive (≈ 1 mass%)
- specific for polymers (but not sensitive to soil matrix)
- fine materials ≤ 125 µm
- no chemical treatment
- short measurement time

prospect:
- optimized identification of polymers in mixtures
- online measurement

# Acknowledgement


- Dr. Michael Maiwald, BAM, head of division 1.4
- Dr. Ute Kalbe, BAM, soils and moldings
- Dr. Markus Ostermann, BAM, aluminium pots & reference soils from BONARES
- Dr. Andrea Karrasch, LLA Berlin, reference polymers

Bundesministerium für Bildung und Forschung
Behörde

Bundesministerium für Bildung und Forschung

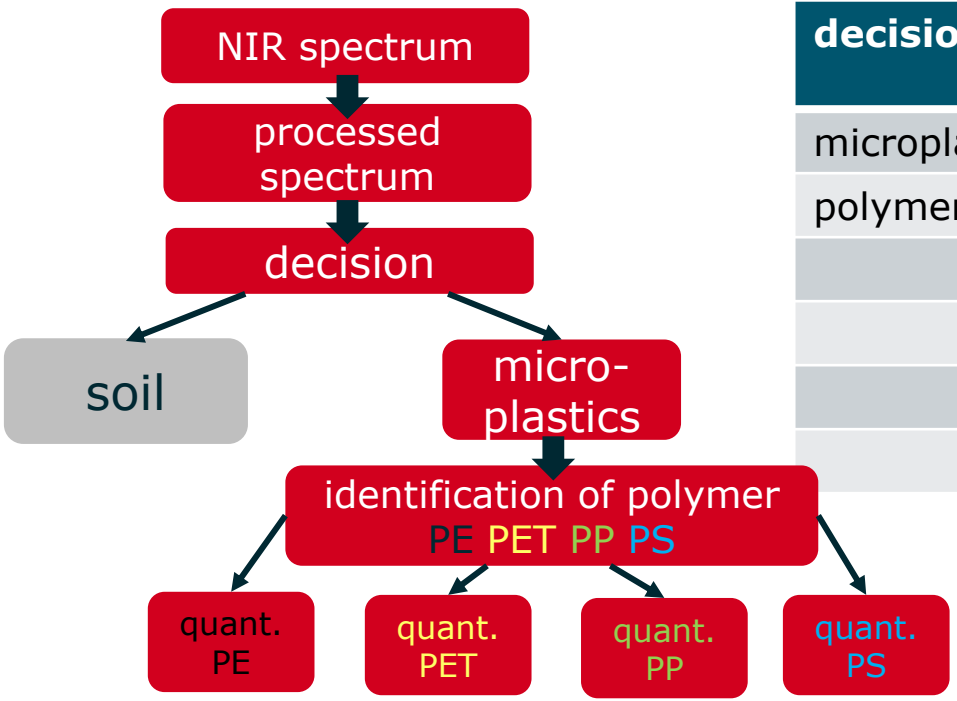
MiWA

FOCUS AREA
ENVIRONMENT

# NIR process spectroscopy
## method used: PLS-DA

NIR spectroscopy chemometrics

BAM




| decision | quantification 1 – 5 mass% | RMSE / mass% | f |
|---|---|---|---|
| microplastics*) | | 0.13 | 3 |
| polymer | | 0.28 | 4 |
| | PE | 0.23 | 1 |
| | PET | 0.18 | 1 |
| | PP | 0.20 | 1 |
| | PS | 0.17 | 1 |

*) one out of 6 samples failed

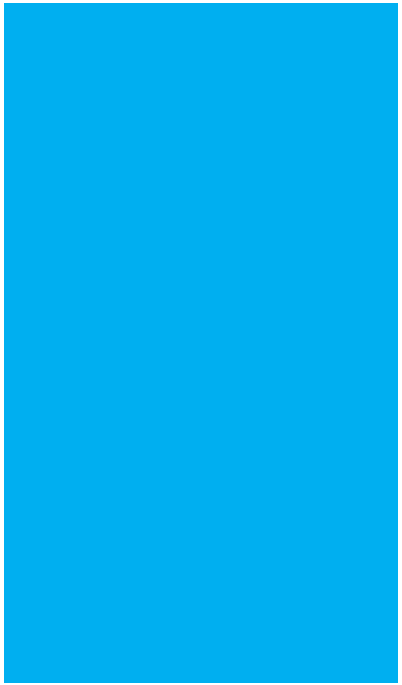
# Assesment of the methods (Anna, nur für mich zum Vgl.)

| Parameters | Raman scanning | FTIR imaging | TED-GC-MS | Chemical extraction |
|---|---|---|---|---|
| Sample amount | 1 µg | 1 mg | 20 mg | 500 mg |
| Sample preparation | Single particle | Single particle layer on IR transparent substrates | As received | As received |
| Measurement time for representative results | ~ 40 min | 3-6 h | 3 h | 2 h |

| | | | | | |
|---|---|---|---|---|---|
| Result information | Identification | PE, PP, PS, PET | PE, PP, PS, PET | PE, PP, PS, PET | PS, PET |
| | Quantification | No | No | Yes | Yes |
| | Particle size distribution | Yes | Yes | No | No |
| | Aging Status | Yes | Yes/No | No | Yes |

# Vibrational spectroscopy

ab hier kommen ergänzende Folien für die Diskussion



# Microplastics: Samples for calibration





**Soils**

- coastal sand
- medium sand (1)
- Lufa 2.2 (2)
- Lufa 2.3 (3)

**Polymers**

- PE
- PS
- PP
- PET
- PVC

Foto kleine Partikel!

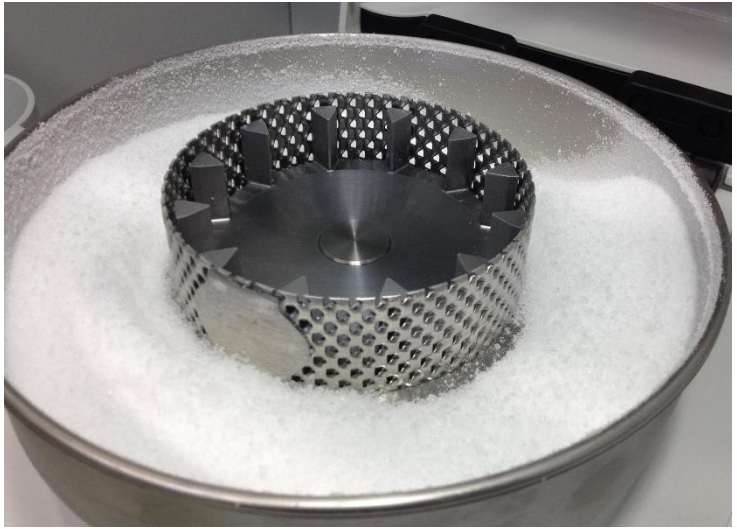
**polmer size**

- ≤ 2mm
- ≤ 125 µm

# preparation of polymers for artificial microplastics

## 2016

- PE, PP and PS
- cry-milling (Ultra Zentrifugalmühle (ZM200), 16000 rpm with liquid nitrogen
- ring sieve, 2 mm



# medium sand

| Probennummer IV.31-12-09-228 | | Festoff mg/kg |
|---|---|---|
| **Bodenart** | | MS |
| **G** | % | 7,68 |
| **S** | | 92,32 |
| **U** | | 0,79 |
| **T** | | - |
| **Korngrößenverteilung [Gew.-%]** **DIN ISO 18123 (Trockensiebung)** | 10-6,3 mm | 0,13 |
| | 6,3-2 mm | 7,55 |
| | 2 - 0,63 mm | 7,94 |
| | 0,63 - 0,2 mm | 56,58 |
| | 0,2 -0,063 mm | 27,01 |
| | 0,063-0,0020 mm | 0,79 |
| | < 0,0020 mm | - |
| **Restfeuchte DIN ISO 12880** | [Gew.-%] | 0,509 |
| **pH-Wert (H2O) DIN ISO 10390** | - | 8,48 |
| **Leitfähigkeit** | [µS/cm] | 110,0 |
| **Korndichte DIN 66137-2** | [g/cm3] | 2,582 |
| **Glühverlust DIN ISO 18128** | [Gew.-%] | 0,65 |

# Lufa 2.2 & 2.3

LUFA Speyer

BEZIRKS VERBAND PFALZ

Landwirtschaftliche Untersuchungs- und Forschungsanstalt Speyer

Obere Langgasse 40
67346 Speyer
Tel. 06232 136 0
Fax 06232 136 110
email: poststelle@lufa-speyer.de
Internet: www.lufa-speyer.de

**Analyses Data Sheet for Standard Soils according to GLP**

(Mean values of different batch analyses +- standard deviation. All values refer to dry matter.)

| Standard soil type no. | 2.1 | 2.2 | 2.3 | 2.4 | 5M | 6S |
|---|---|---|---|---|---|---|
| Batch-No. (S=stored; F= field fresh | | | | | | |
| sampling-date | | | | | | |
| organic carbon in % C | 0,71+- 0,08 | 1,61 +- 0,15 | 0,67 +- 0,03 | 1,99 +- 0,21 | 1,02 +- 0,08 | 1,78 +- 0,08 |
| Nitrogen in % N | 0,06 +- 0,01 | 0,17 +- 0,01 | 0,08 +- 0,01 | 0,22 +- 0,02 | 0,13 +- 0,01 | 0,18 +- 0,01 |
| pH-value (0.01 M $CaCl_2$) | 4,9+- 0,3 | 5,4 +- 0,2 | 5,9 +- 0,6 | 7,4 +- 0,1 | 7,3 +- 0,1 | 7,2 +- 0,1 |
| cation exchange capacity ( meq / 100g) | 4,3 +- 0,6 | 9,7 +- 0,4 | 7,6 +- 0,8 | 32,9 +- 4,5 | 17,7 +- 3,7 | 27,3 +- 3,4 |
| Particle size (mm) distribution according to German DIN (%): | | | | | | |
| <0.002 | 3,1 +- 0,9 | 8,6 +- 1,2 | 6,9 +- 1,6 | 26,2 +- 1,4 | 10,8 +- 0,6 | 41,3 +- 0,7 |
| 0.002 - 0.006 | 1,5 +- 0,6 | 3,5 +- 1,0 | 5,3 +- 0,7 | 7,6 +- 0,5 | 3,7 +- 0,8 | 8,4 +- 0,9 |
| 0.006 - 0.02 | 3,5 +- 0,3 | 5,3 +- 0,9 | 11,5 +- 0,5 | 14,8 +- 1,0 | 9,3 +- 0,6 | 13,2 +- 0,6 |
| 0.02 - 0.063 | 7,2 +- 0,9 | 7,8 +- 1,6 | 18,8 +- 1,6 | 23,3 +- 0,7 | 21,7 +- 1,2 | 14,7 +- 0,8 |
| 0.063 - 0.2 | 28,2 +- 1,3 | 34,0 +- 3,5 | 24,7 +- 1,4 | 19,5 +- 1,0 | 39,0 +- 2,4 | 9,5 +- 0,3 |
| 0.2 - 0.63 | 54,0 +- 1,6 | 40,2 +- 1,7 | 30,1 +- 0,6 | 7,0 +- 2,2 | 14,4 +- 1,4 | 10,3 +- 0,7 |
| 0.63 - 2.0 | 2,5 +- 0,4 | 0,6 +- 0,1 | 2,7 +- 0,7 | 1,6 +- 0,2 | 1,1 +- 0,2 | 2,6 +- 0,6 |
| soil type | silty sand (uS) | loamy sand (lS) | silty sand (uS) | clayey loam (tL) | loamy sand (lS) | clayey loam (tL) |
| Particle size (mm) distribution according to USDA (%) | | | | | | |
| <0.002 | 3,0 +- 0,9 | 8,0 +- 1,7 | 6,8 +- 1,6 | 25,8 +- 1,8 | 10,6 +- 0,8 | 40,5 +- 1,6 |
| 0.002 - 0.05 | 11,0 +- 1,3 | 15,8 +- 3,1 | 33,6 +- 0,5 | 41,1 +- 1,2 | 30,1 +- 1,4 | 34,1 +-2,1 |
| 0.05 - 2.0 | 86,0 +- 0,9 | 76,2 +- 4,1 | 59,6 +- 1,4 | 33,1 +- 2,2 | 59,3 +- 1,5 | 25,4 +- 3,5 |
| soil type | loamy sand | sandy loam | sandy loam | loam | sandy loam | clay |
| maximum water holding capacity (g/100g) | 32,1 +- 1,7 | 44,8 +- 2,9 | 35,6+- 1,4 | 44,8 +- 2,1 | 40,1 +- 2,4 | 41,1 +- 1,4 |
| weight per volume (g/1000ml) | 1437 +- 41 | 1198 +- 38 | 1310 +- 43 | 1250 +- 39 | 1250 +- 88 | 1334 +- 63 |

Speyer,
By Order

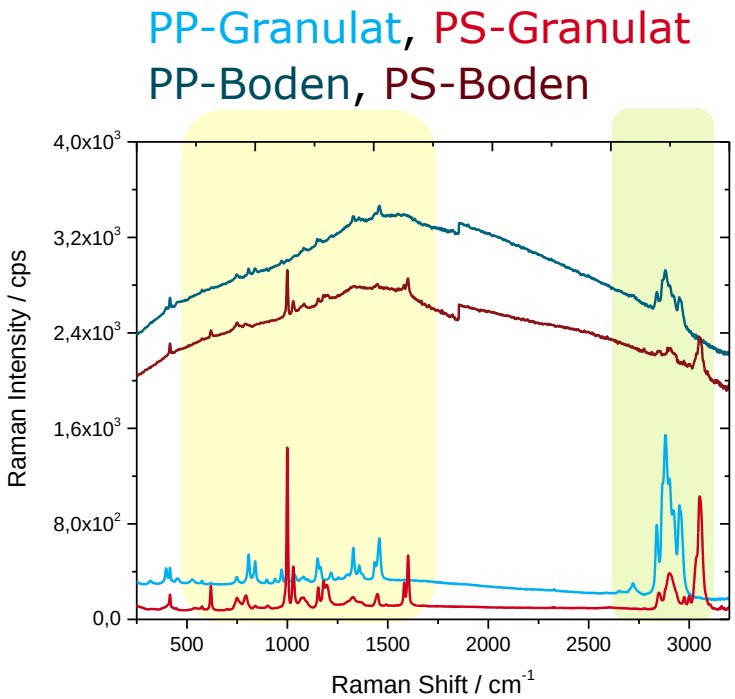
Speyer,
By Order

(Dr. Seibert - Phone: +49 (0) 6232 136 125; email: seibert@lufa-speyer.de) ab 15.03.16

## soils from M. Ostermann (BONARES)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Böden | Lufa2.3 ungemahlen | | | | | | B3-raw |
| | Lufa2.3 Referenzmaterial Charge-1 | | | | | | B3-ref |
| | Lufa2.3 Referenzmaterial Charge-2(grob) | | | | | | B3-grob |
| | Lufa2.3 gemahlen (Lukas) | | | | | | B3milled |
| | Aschebergsand 0-30cm | | | | | | B5-G1 |
| | Ascheberg tonig 0-30cm | | | | | | B6-G2 |
| | CKA_AP_Löss 0-30cm | | | | | | B7_G3 |
| | CKA_Löss B0-150cm | | | | | | B8_G4 |
| | Marquardt 0-25cm | | | | | | B9_A1 |

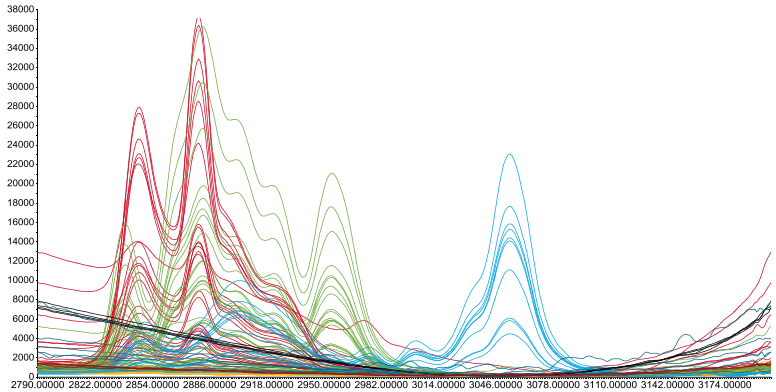
# Microplastics - cw Raman



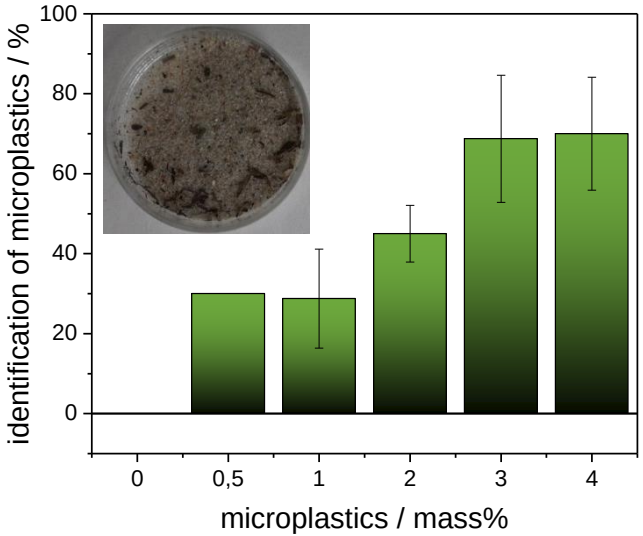
# cw process Raman spectroscopy
# Microplastics in coastal sands

**spectra of: PE, PP, PS, Sand, kelp**

polymers: ≤ 2mm



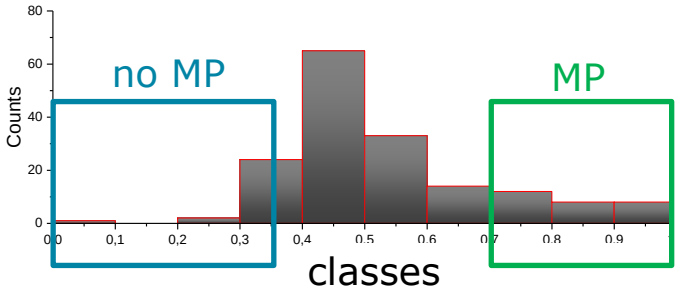

**recovery (pooled data)**



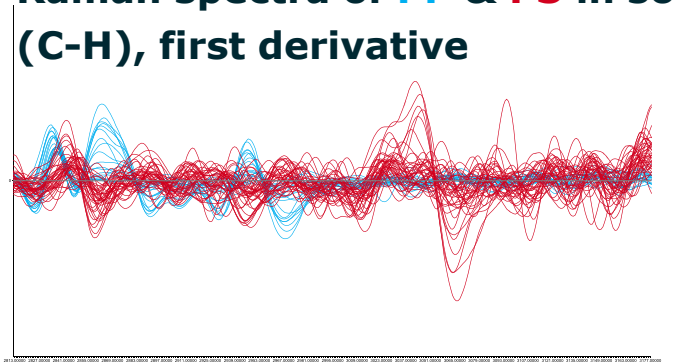
# Raman spectroscopy

cw-process Raman spectroscopy

- **detection of particles with diameters ≤ 2 mm in 10 mass% MP samples**




**Raman spectra of PP & PS in soil (C-H), first derivative**

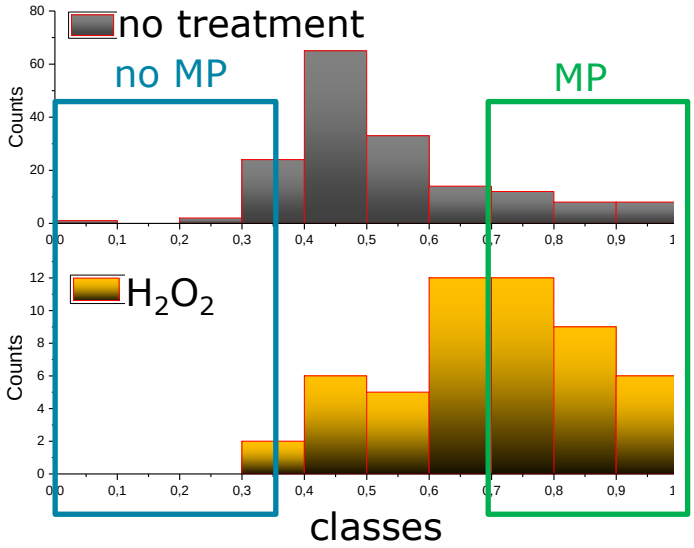


- prediction by PLS-DA

# Raman spectroscopy

cw-process Raman spectroscopy

- **detection of particles with diameters ≤ 2 mm in 10 mass% MP samples**



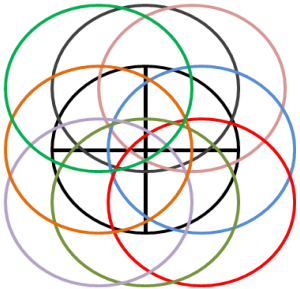

**not applicable for smaller particles ≤ 125 µm, < 5 mass% & real world samples**

- background fluorescence dominates weak Raman signal from microplastics
- future prospect: successful with additional treatment and / or enrichment?

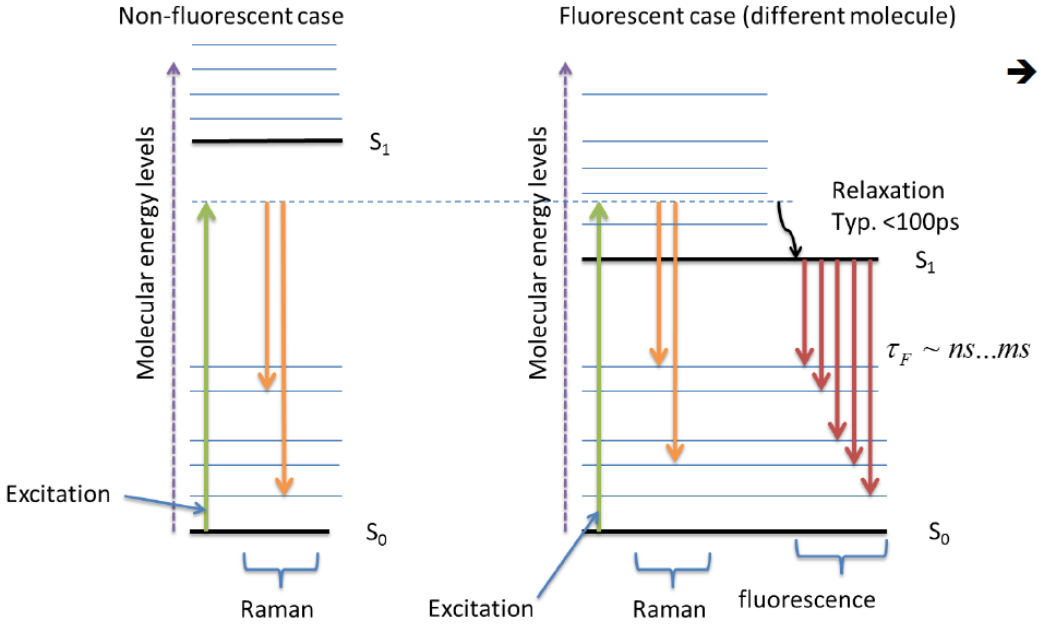
# cw process Raman spectroscopy positioning of probe

**for cw process spectrometer**

- X, Y according to mask
- Z: manual adjustment
- measurement: 3 x 5 seconds
- repeated measurements for each sample at 9 different positions



# Raman spectroscopy




➔ Quantenmechanisches Energie-Diagramm nach *Perrin-Jablonski* mit:

**$S_0$** = Energiegrundzustand;
**$S_1$** = Angeregter Zustand eines Valenzelektrons.

➔ hellblaue Linien = Vibrationsstadien der Atome des angeregten Moleküls

➔ etwas verschwommenen hellblauen Linien = Vibrationsstadien der Atome angeregter Moleküle miteinander; diese entspechen den Vibrationsenergiezuständen, die mit Raman-Spektroskopie oder IR-Absorbtion detektiert werden können

# Time-resolved Raman spectroscopy

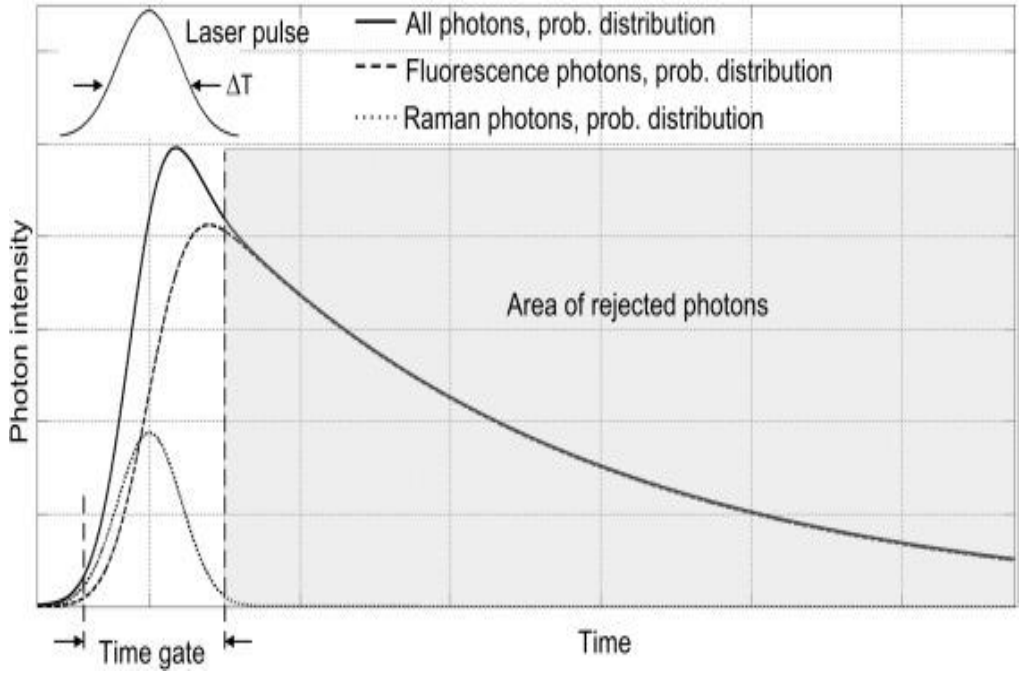
TimeGated Raman spectroscopy


**Fluorescence suppression in Raman spectroscopy using a time-gated CMOS SPAD**

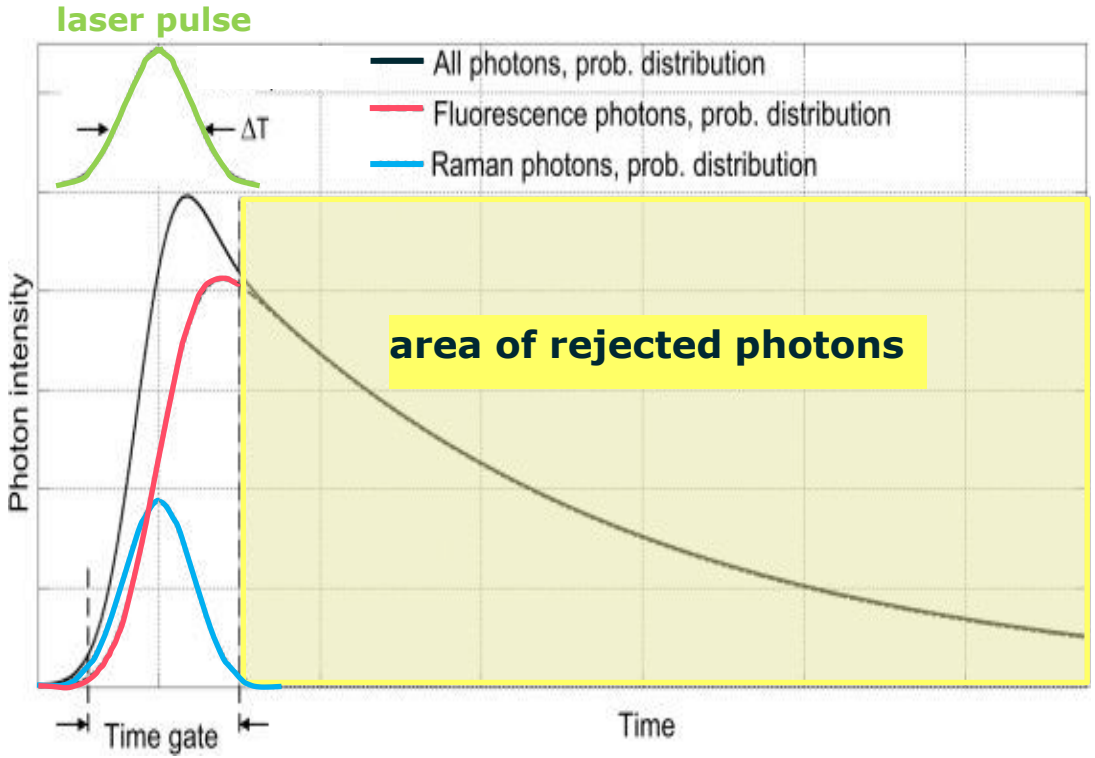
Juha Kostamovaara,[1,*] Jussi Tenhunen,[2]
Martin Kögler,[2] Ilkka Nissinen,[1] Jan Nissinen,[1] and Pekka Keränen[1]

2013 | Vol. 21, No. 25 | DOI:10.1364/OE.21.031632 | OPTICS EXPRESS 31632

**defined mixtures of microplastics in soil**

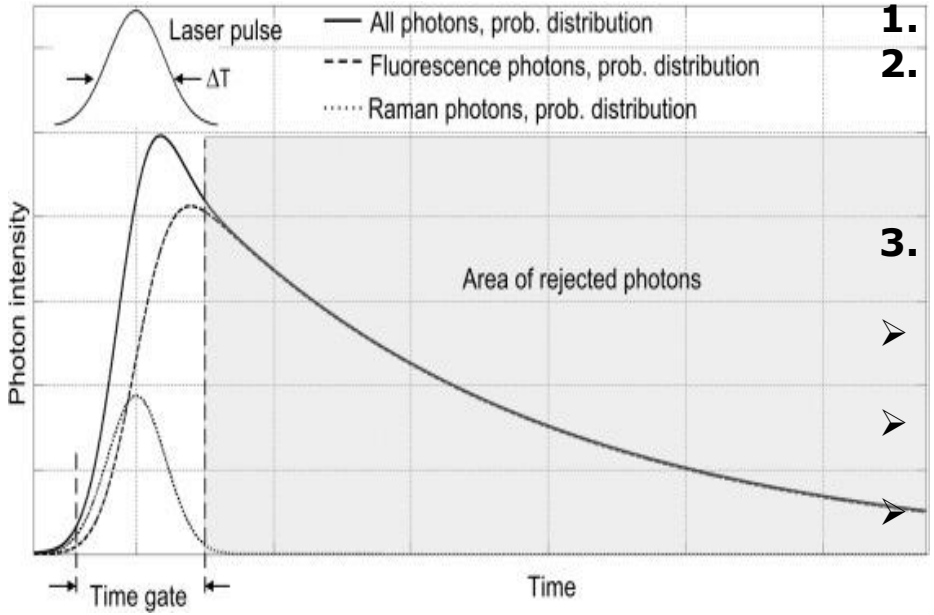



# Time-resolved Raman
# Principle of Time-Gated (TG) Raman spectroscopy




1. **Short Laser pulse (50-150 ps)**
2. **Detector is synchronised with an adjustable start and end-time-point of LASER pulse (adjustment depending on sample-related fluorescence decay time)**
3. **System runs in pulsed operation according to the set gating-time**

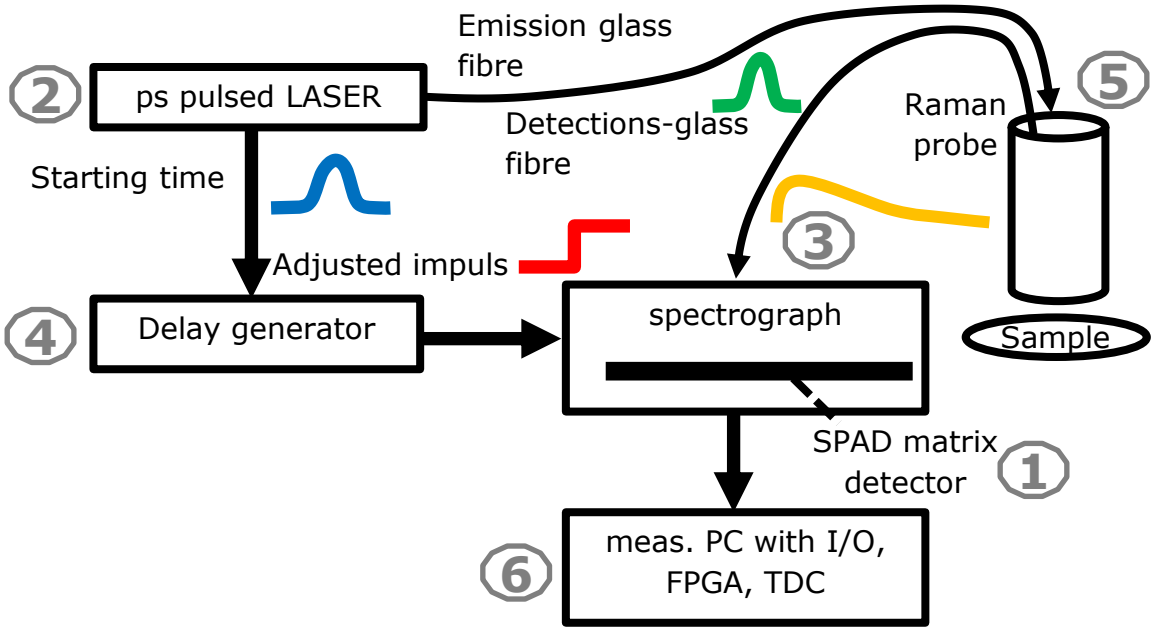
# Time-resolved Raman
# Principle of Time-Gated (TG) Raman spectroscopy




1. **Short LASER pulse Δ 50-150 ps**
2. **Detector is synchronised with an adjustable start and end- time-point of LASER pulse (adjustment depending on sample-related fluorescence decay time)**
3. **System runs in pulsed operation according to the set gating-time**

- High pulse frequency to needed to excite Raman scattering photons
- CW-Raman reaches high amplitudes after a short measurement time
- TG-Raman operating in pulsed-mode compensates it with an automated integration of each individual erratic value

# Principle set-up of the commercial Time-Gated (TG) Raman spectrometer

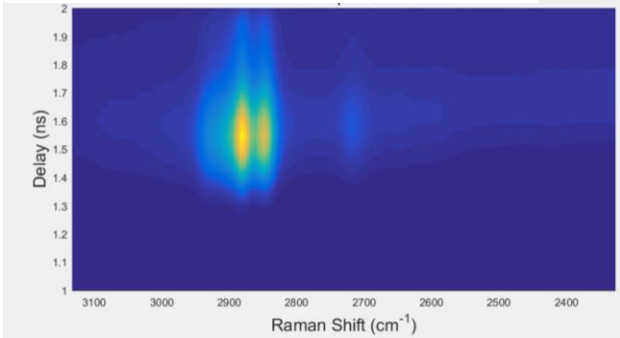



**Time-gated Raman spectrometer:**

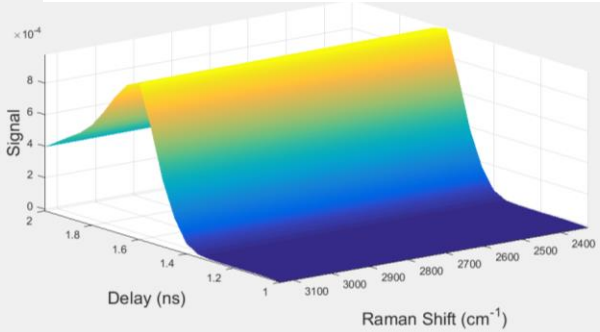
1. CMOS-SPAD (Single-Photon Avalanche Photodiode) array detector which consists of 128 x 8 actively quenched SPAD elements and associated gating electronics that overall have timing resolution on the order of 100 ps
2. Pulsed Nd:YVO microchip laser at 532 nm
3. Spectrograph
4. Delay generator synchronized with the laser,
5. Optical Raman probe
6. Control electronics (FPGA and connected PC).

# Time-resolved Raman spectroscopy
# Spectra

raw time-resolved spectra

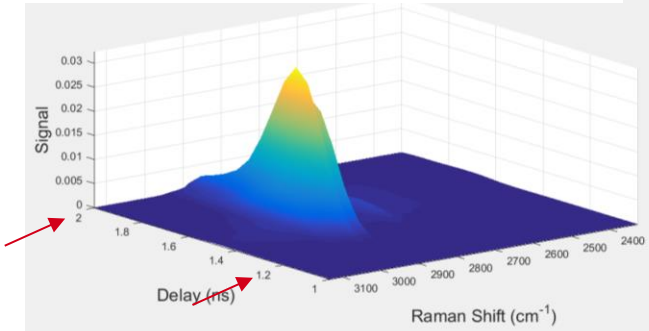



calculated background „fluorescence“

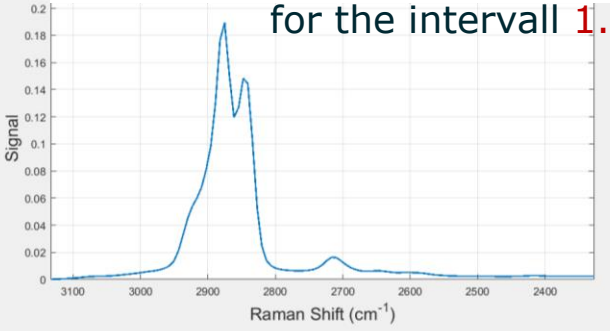



**Sample**
**PE**

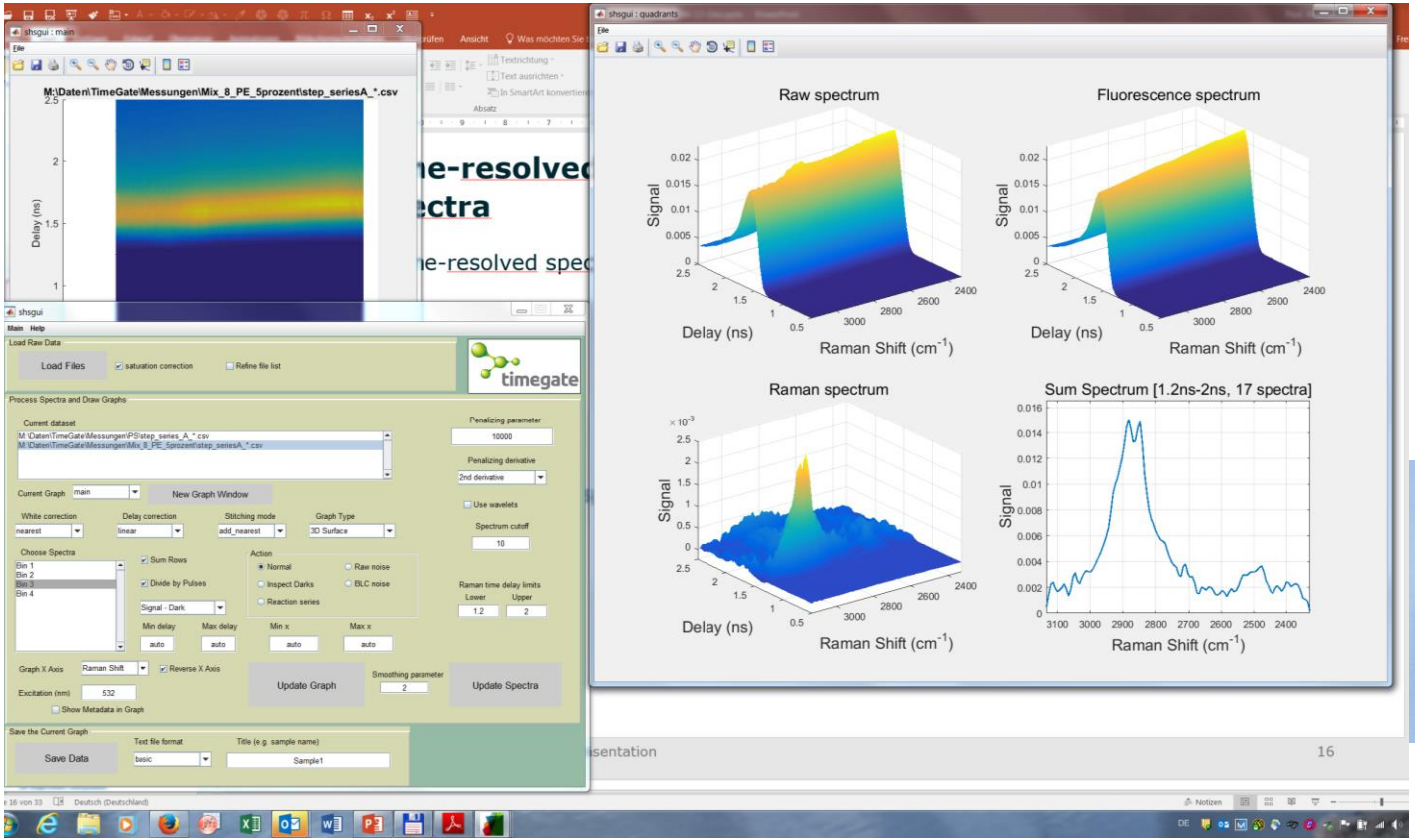
time-resolved Raman spectra

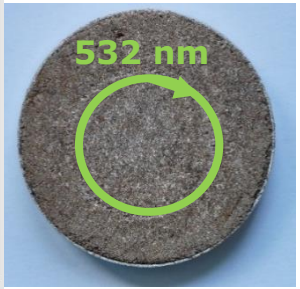



averaged Raman spectrum
for the intervall 1.2 – 2 ns



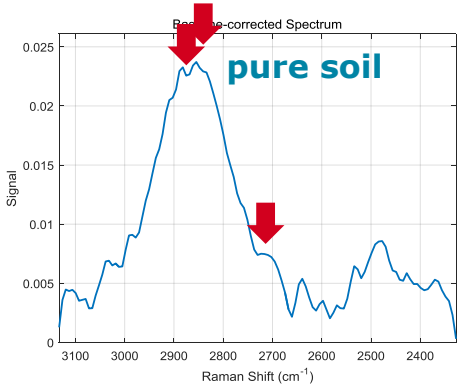
# screenshot on timegate

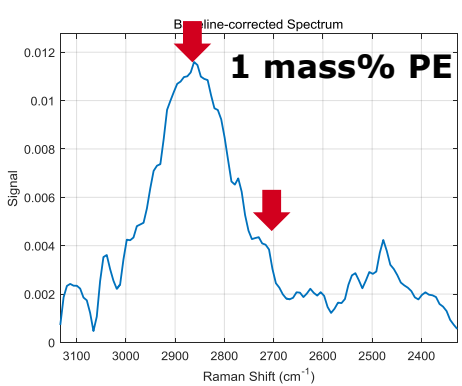


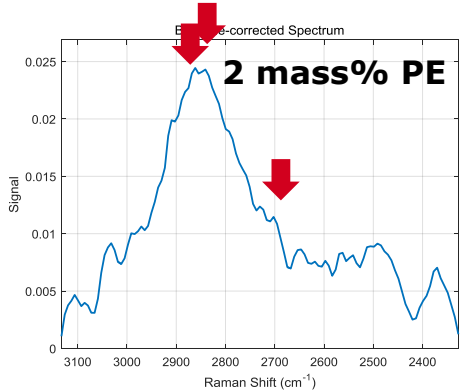



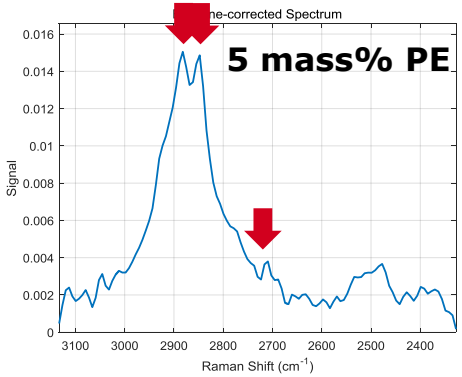
# Time-resolved Raman

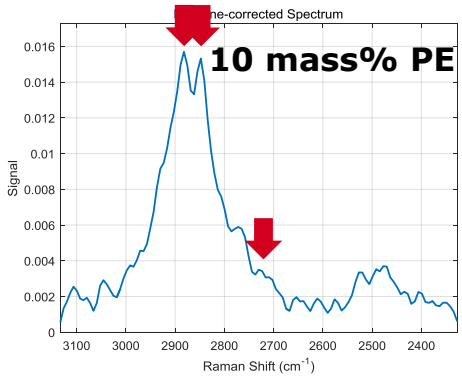
TimeGated Raman spectroscopy

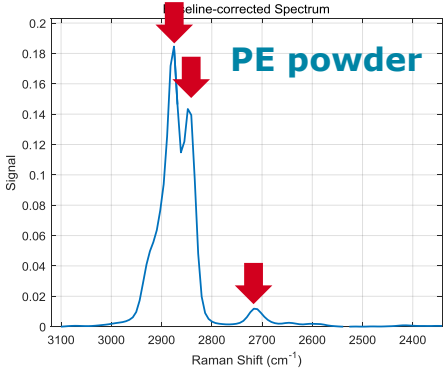


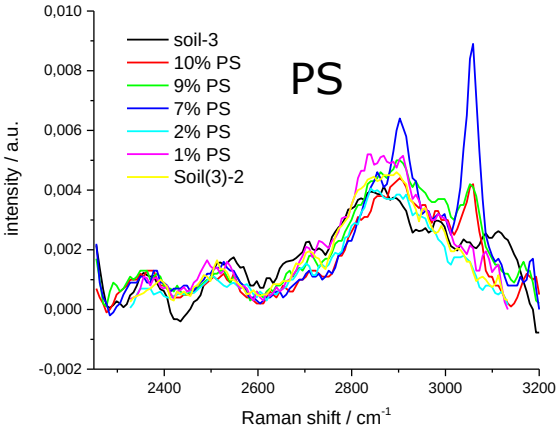



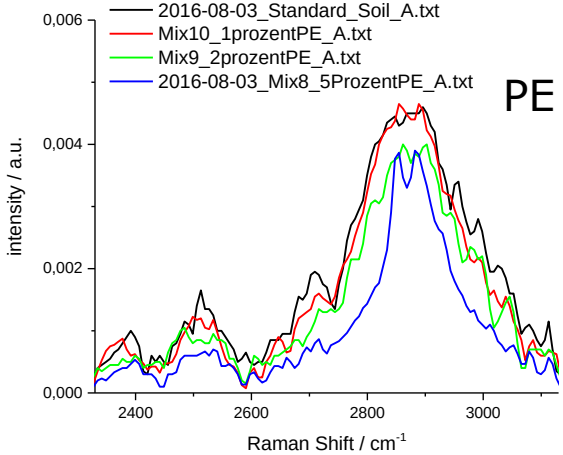



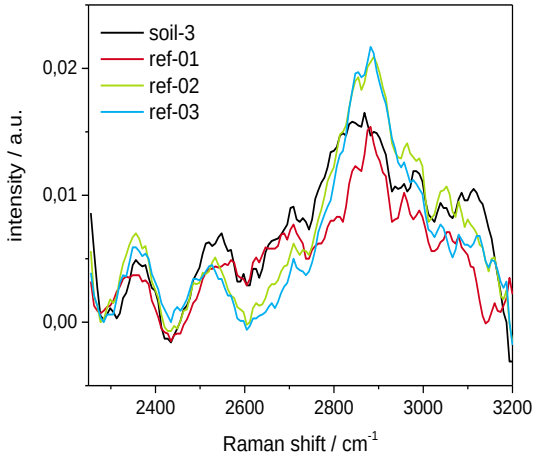



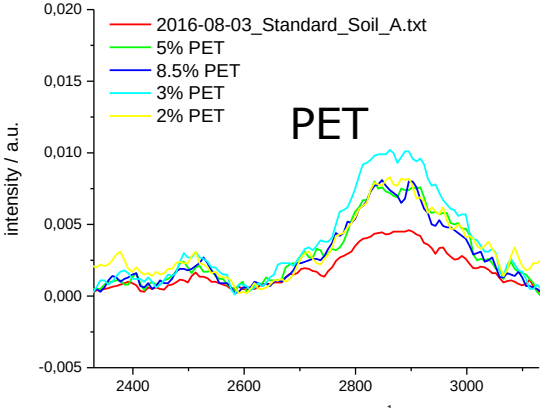



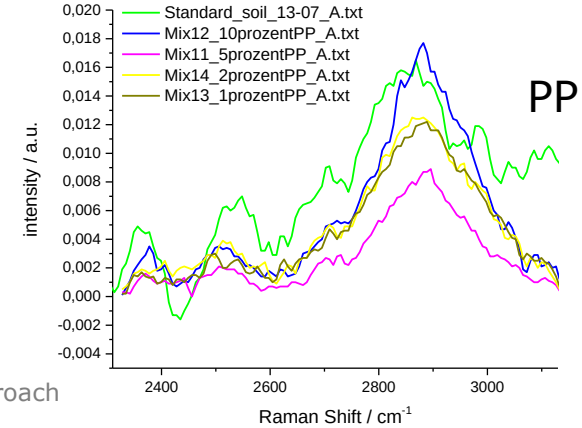
# Spectra TimeGated Raman

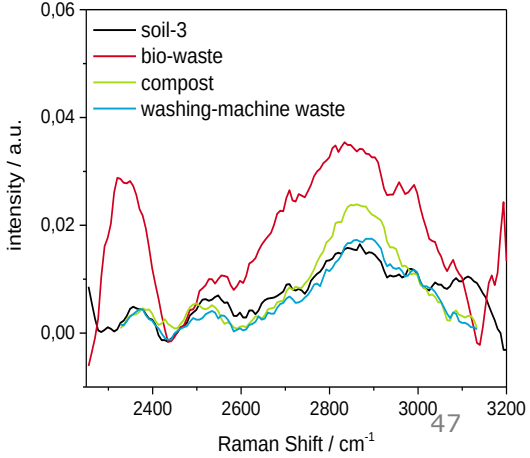



BAM
Sample No.: 01
BAM
FOCUS AREA
ENERGY