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# Mobility of different nanomaterials in unsaturated soil columns

Umwelt  
Bundesamt

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UNIVERSITÄT  
DUISBURG  
ESSEN

# Release of NM from products



[www.hausjournal.net](http://www.hausjournal.net)



[www.wohzimmerz.club](http://www.wohzimmerz.club)



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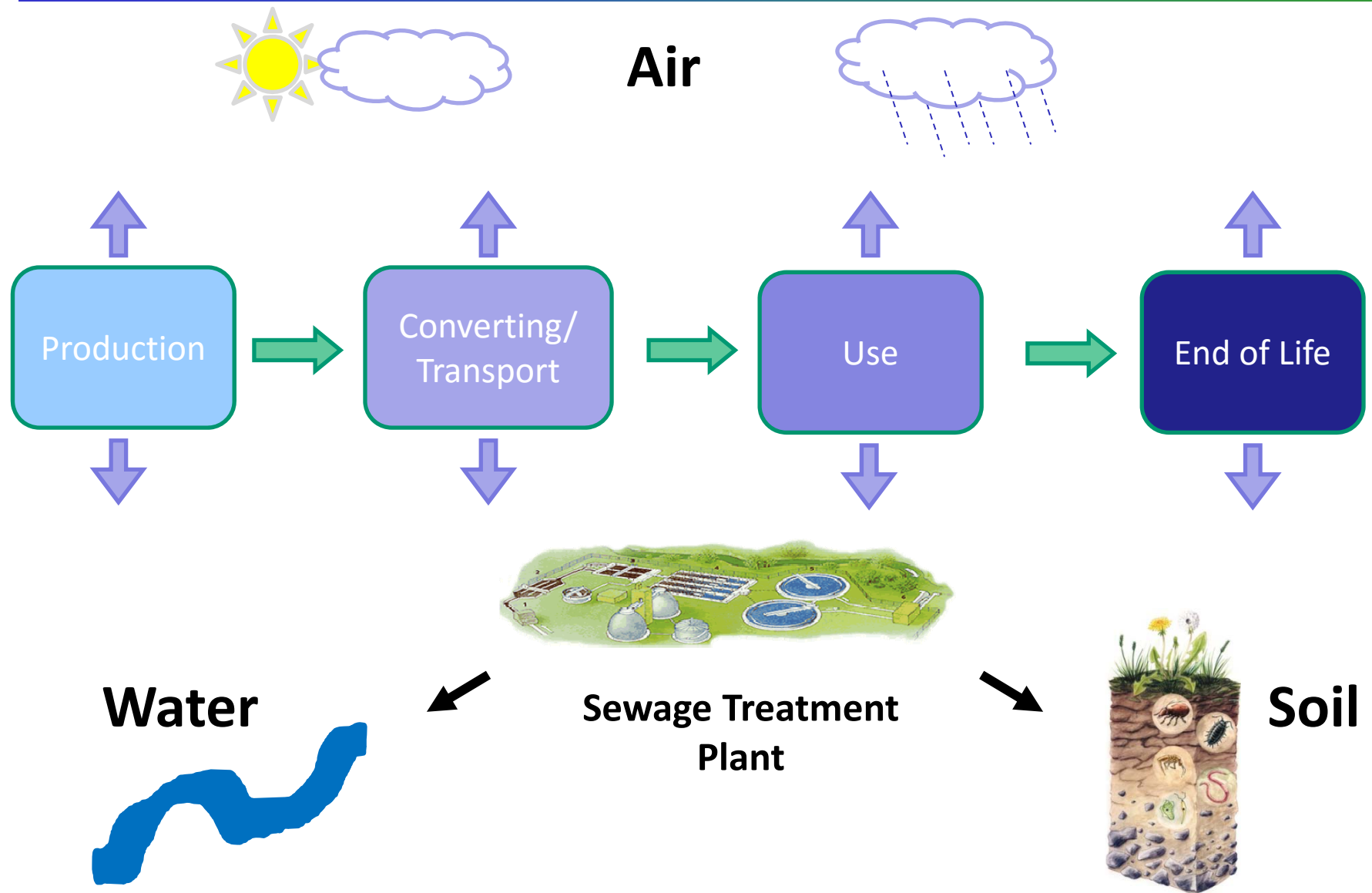


[www.vitavie.de](http://www.vitavie.de)



[www.ruhrnachrichten.de](http://www.ruhrnachrichten.de)

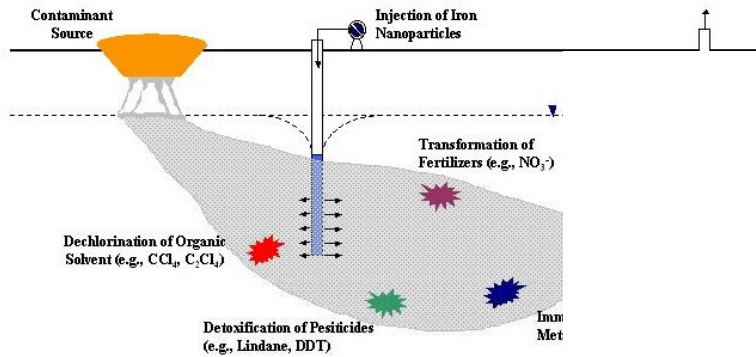
# Release of ENM in the environment





# Soils

## Remediation



Nano-Iron; Zangh et al., JNR 5: 323–3

direct

## Pesticides

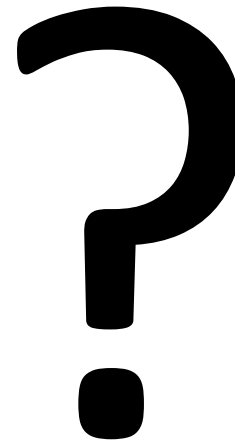


[www.umweltbundesamt.de](http://www.umweltbundesamt.de)

## Application of sewage sludge



<http://www.lauda-koenigshofen.de>



# Mobility of ENM?



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# Mobility of three different TiO<sub>2</sub> nanomaterials in soil columns

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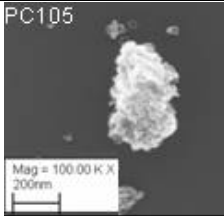
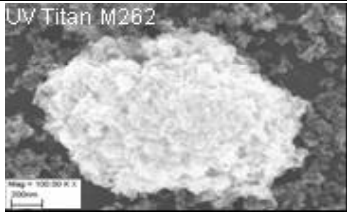
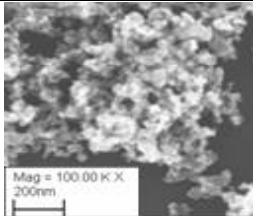
<sup>3</sup> Universitätsklinikum Heidelberg, Department of Infectiology, Hygiene and Medical Microbiology, Heidelberg

<sup>4</sup> BAuA, Dortmund, Germany

<sup>5</sup> Center for Nanointegration, University Duisburg-Essen, Germany



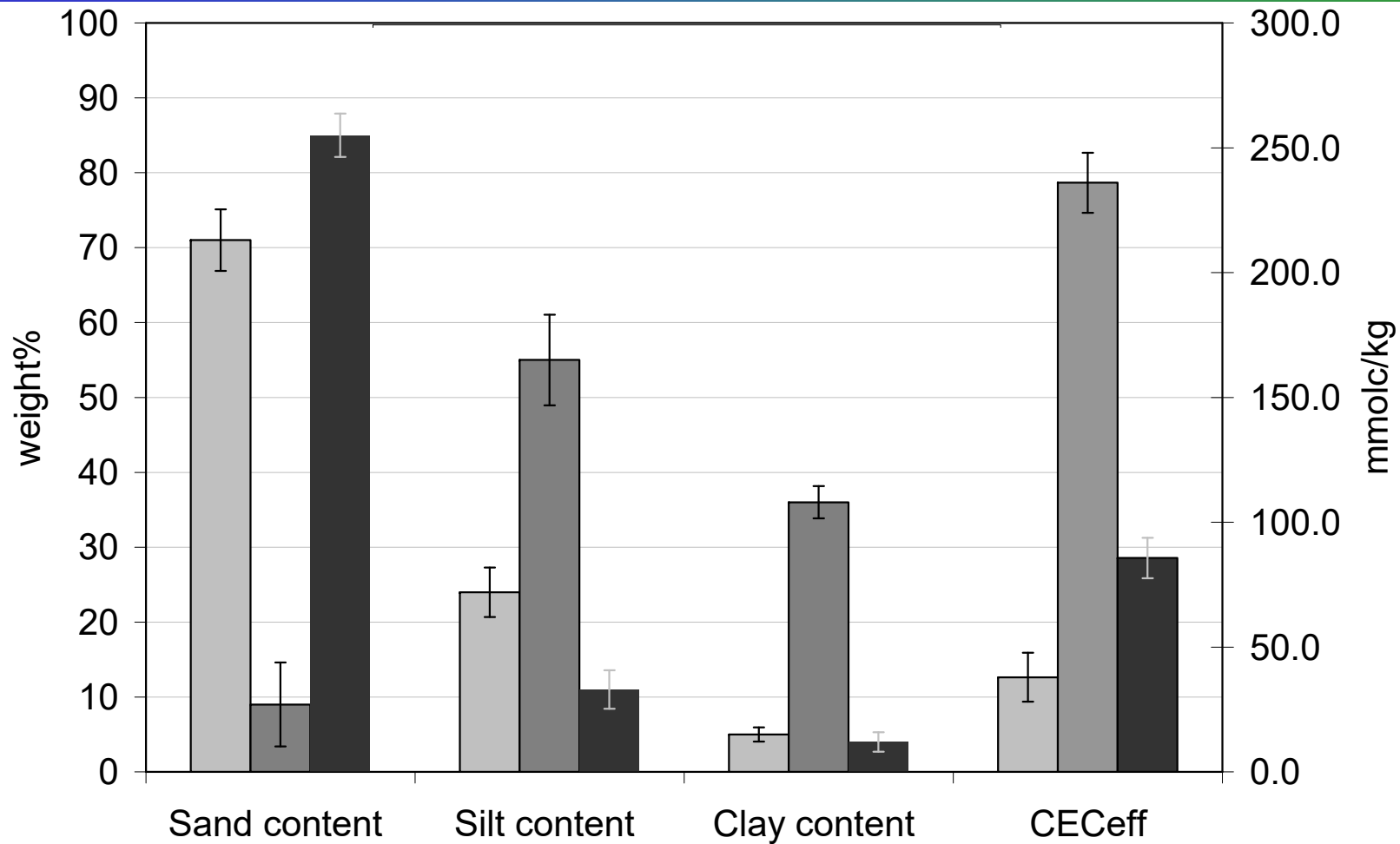
# TiO<sub>2</sub> test nanomaterials

|  | NM102<br>(PC105)   | NM103<br>(UV Titan M262)  | NM105<br>(P25)  |
|--|--|---|---|
| <b>Crystalline form</b>                      | anatase  | rutile  | anatase 86 %<br>rutile 14 %   |
| <b>Primary particle shape</b>                | essentially spherical  | essentially spherical   | spherical   |
| <b>Coating</b>                               | none   | Al <sub>2</sub> O <sub>3</sub> + dimethicone<br>(hydrophobic)                         | none  |
| <b>Primary particle size</b>                 | 15 – 25 nm   | 20 nm   | 21 nm   |
| <b>Particle size in suspension (pH 5) #</b>  | 560 nm (SD 4.62)*  | 180 nm (SD 3.1)*  | 220 nm (SD 1.01)*   |
| <b>Zeta potential in suspension (pH 5) #</b> | +29 mV*  | +26 mV (SD 1.06)*   | +23 mV (0.4)*   |
| <b>Use</b>                                   | photo catalyst   | cosmetics   | photo catalyst,<br>cosmetics  |
|  |  |  |  |

\* Average of DLS and Zetasizer measurements, 10 min sonication; n = 5

# Ultrasonic homogenizer 200 W pulse 0.2/0.8 – 10 min 100 mL

# Soil types



■ Dystric Cambisol

■ Cambic Rendzina

■ Gleyic Podsol

pH: 5.67

pH: 6.78

pH: 5.14

## Methods based on OECD Guideline 312

### Leaching in unsaturated soil columns

- Glas columns filled with the matrix (soils)
- Pre-wetted with 0.01 M  $\text{CaCl}_2$
- Application of the nanomaterials as suspension
- Application of 0.01 M  $\text{CaCl}_2$  solution on the top of the column for 48 h
- Chemical analysis of the eluate and different column segments





# Results



Cubic  
Rendzina

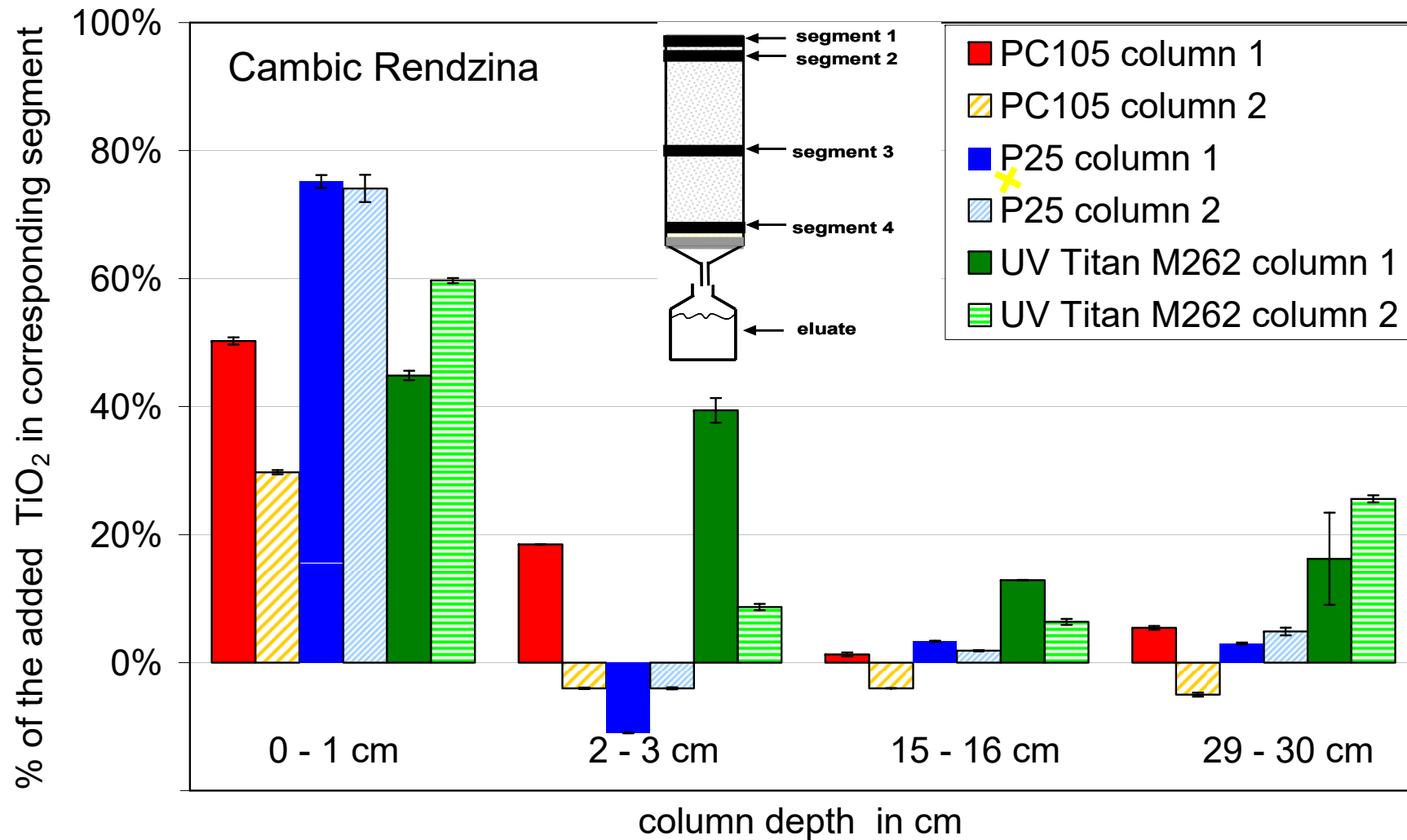


Dystric  
Cambisol



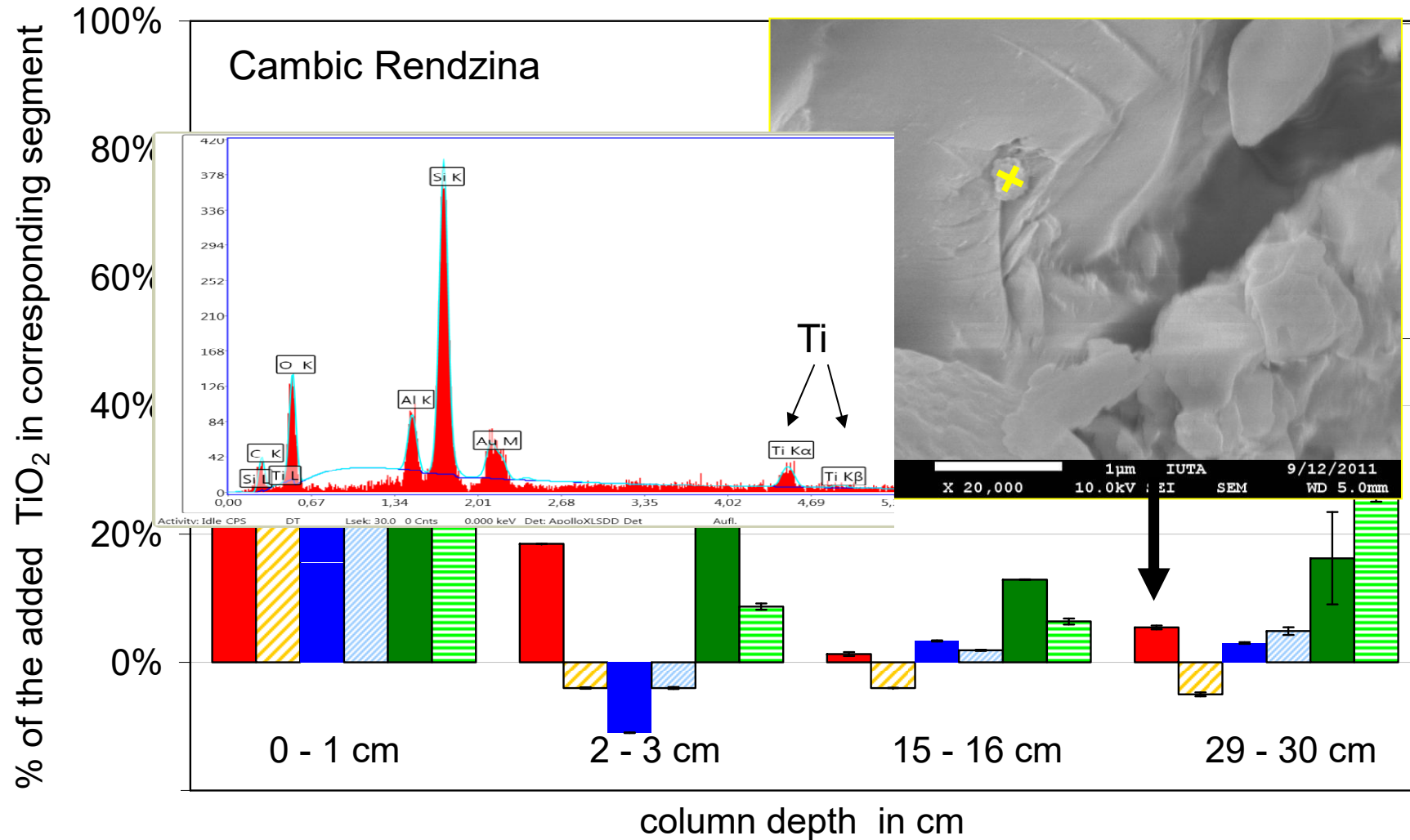
Gleyic  
Podsol

# Results



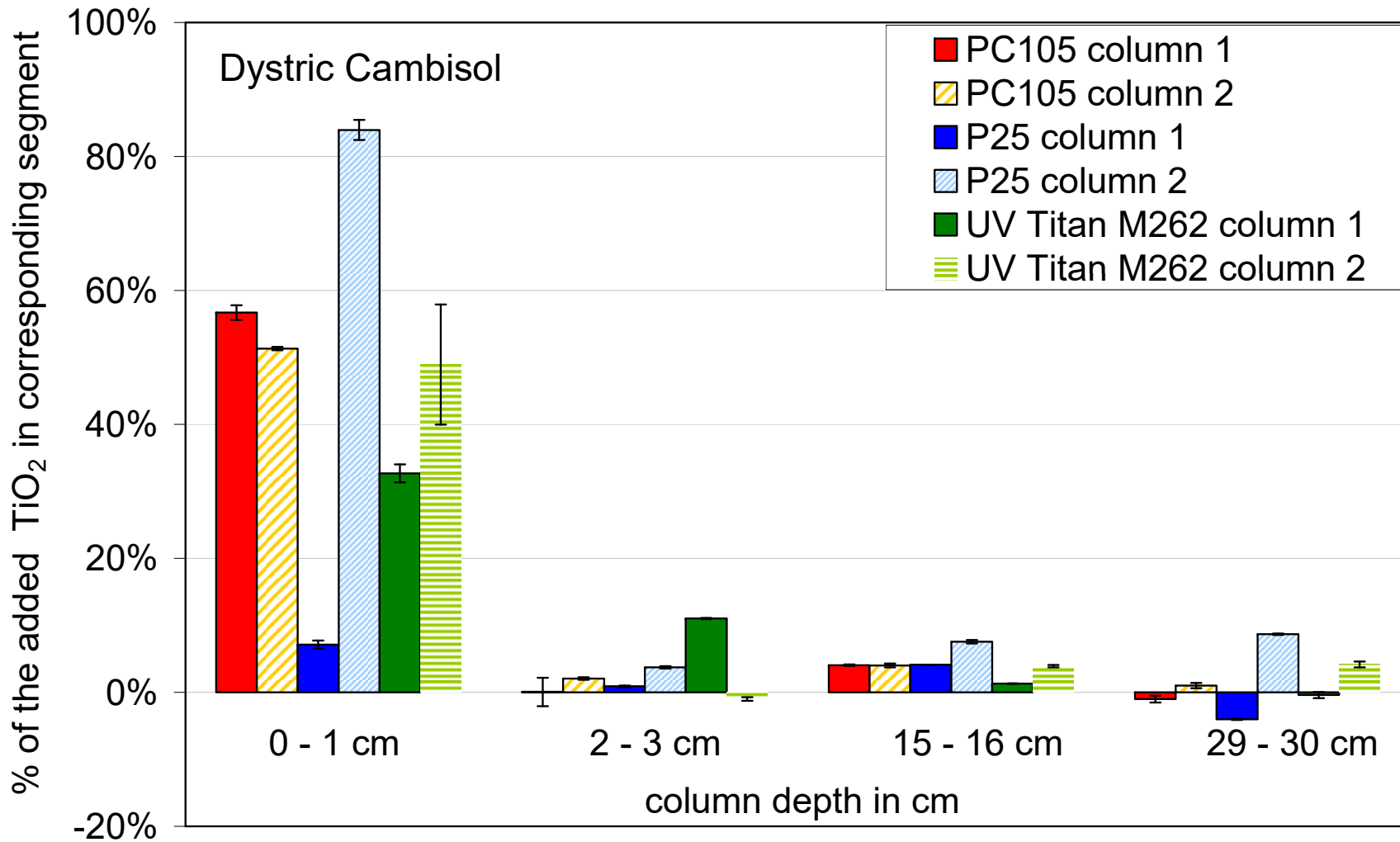
Background Ti: 0.42 % (4.2 g/kg)

# Results



Background Ti: 0.42 % (4.2 g/kg)

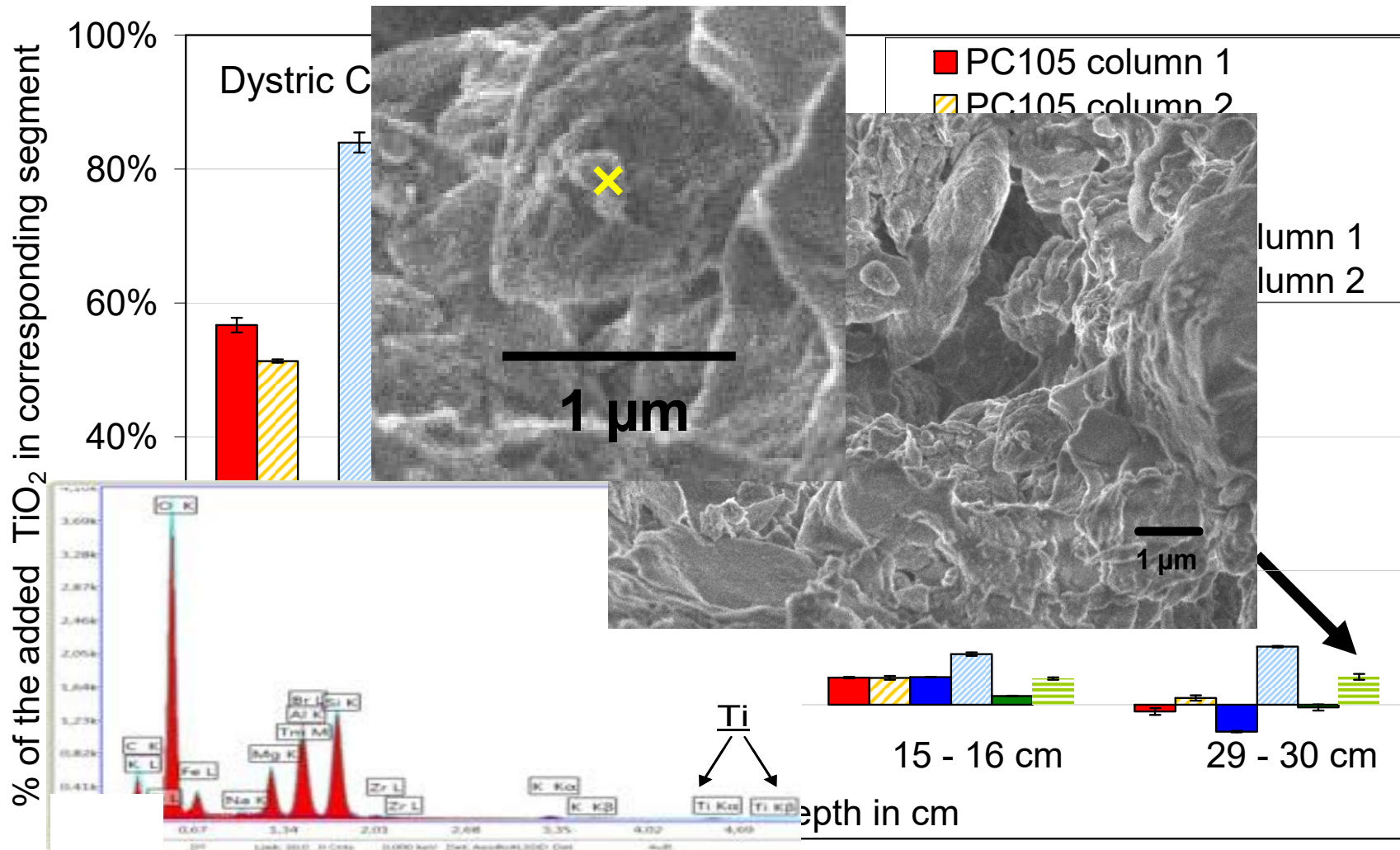
# Results



Background Ti: 0.19 % (1.9 g/kg)



# Results



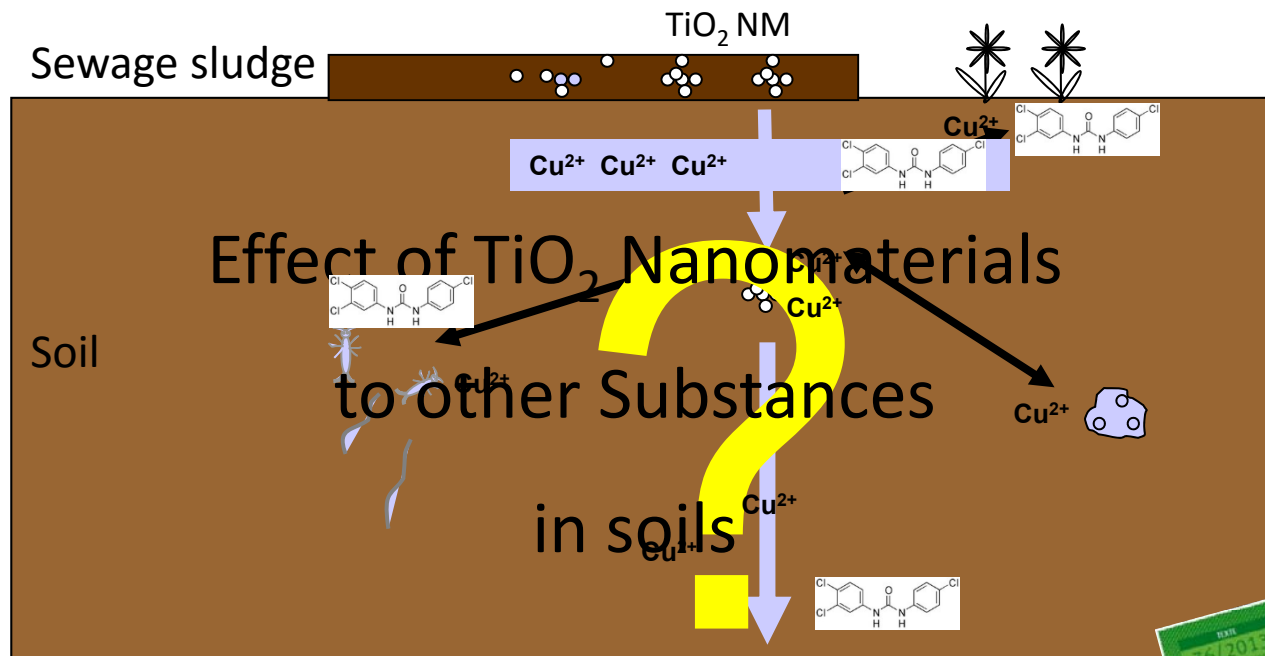
Background Ti: 0.19 % (1.9 g/kg)

# Summary

| Soil             | NM102<br>(PC105)  | NM103<br>(UV Titan M262)                                  | NM105<br>(P25)  |
|------------------|---|---|---|
| Dystric Cambisol | -   | +   | -   |
| Conclusion       | no significant transport detected   | transport indicated, between the first and second segment | no significant transport detected   |
| Cambic Rendzina  | (+)   | +   | (+)   |
| Conclusion       | chemically no transport detected. SEM / EDX indicate a transport of single agglomerates | transport indicated, down to segment four                 | chemically no transport detected. SEM / EDX indicate a transport of single agglomerates |

- Low mobility → no risk for the Groundwater
- ICP-OES analysis – Transport indicated for the coated NM in the soil with high CEC, pH, carbon content
  - Comparable particle size (NM103 and NM105) and zeta potential in suspension (all)
  - coating effect?

# Trojan Horse Effect



Carmen Nickel<sup>1</sup>, Bryan Walter<sup>1</sup>, André Nogowski<sup>2</sup>, Frank Babick<sup>2</sup>,  
 Michael Stintz<sup>2</sup>, Hanna Maes<sup>3</sup>, Andreas Schaeffer<sup>4</sup>, Thomas Kuhlbusch<sup>5,6</sup>

<sup>1</sup>Air Quality & Filtration, IUTA e.V., Duisburg, Germany

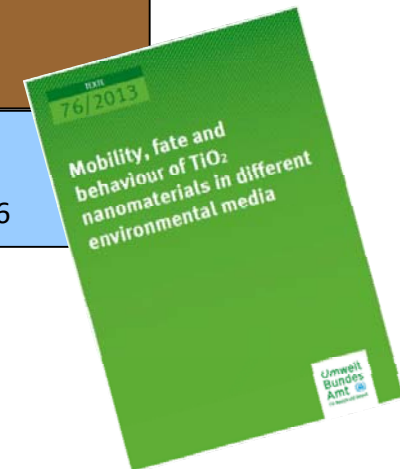
<sup>2</sup>Research group mechanical Process Engineering, TU Dresden, Germany

<sup>4</sup>Eurofins, Niefern-Öschelbronn, Germany

<sup>4</sup>Bio V, RWTH Aachen, Germany

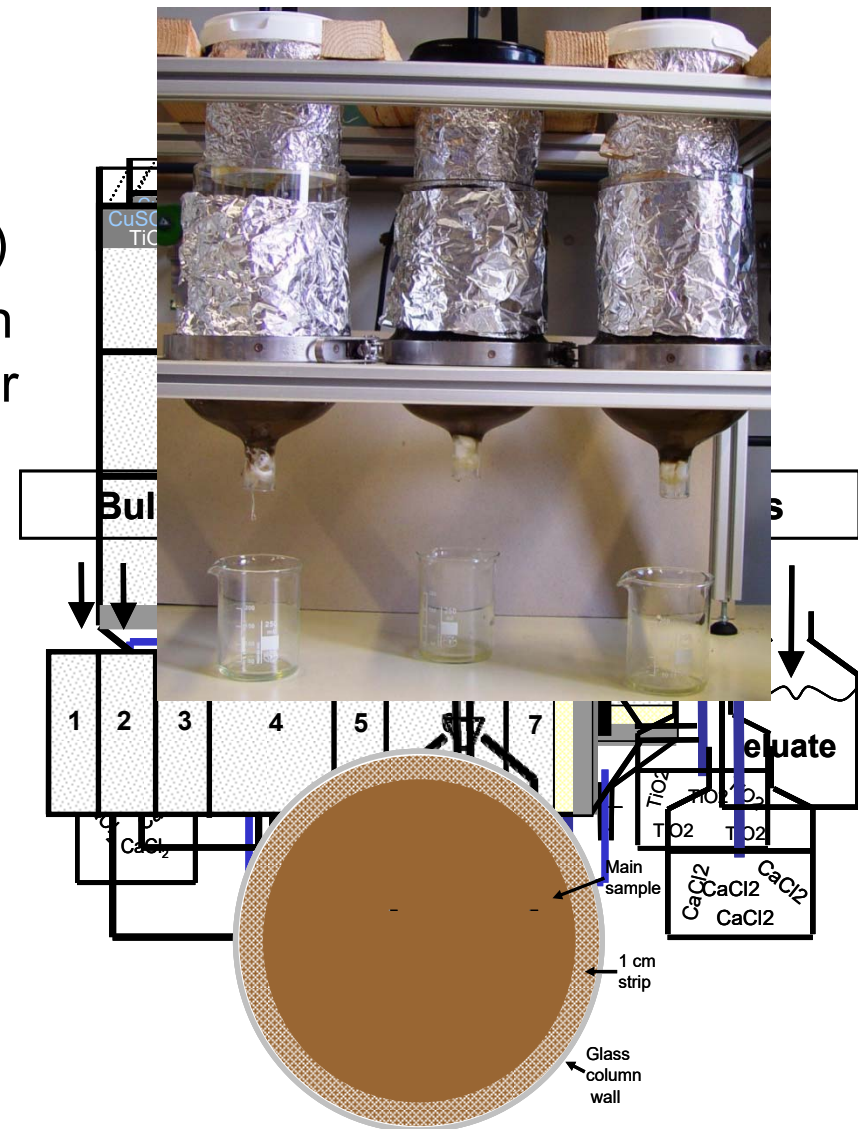
<sup>5</sup>BAUA, Dortmund, Germany

<sup>6</sup>Center for Nanointegration, University Duisburg-Essen, Germany



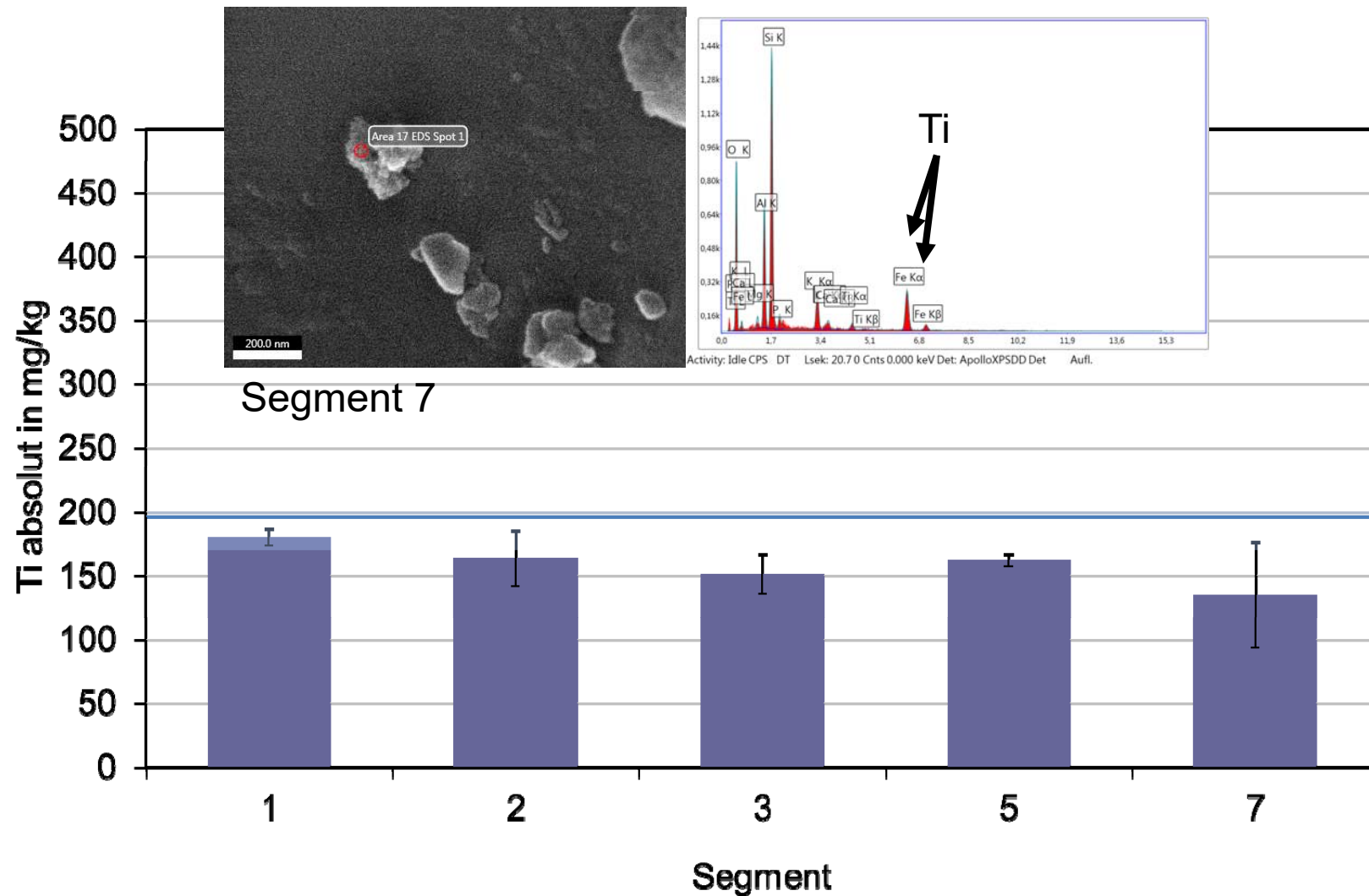
## Experimental design

- Saturation 0.01 M  $\text{CaCl}_2$
- Application of 1cm spiked soil layer (Cu (43 mg/kg) or  $^{14}\text{C}$  TCC (2 mg/kg))
- Application of 100 ml P25 Suspension pH 5 test system and 100 ml DI water pH 5 reference system
- 48 h application of „rain“ – 42 ml/min 0.01 M  $\text{CaCl}_2$
- Sampling of the eluate and soil
- Chemical analysis (Cu and Ti)
- Radioanalytic ( $^{14}\text{C}$  TCC)
- Different diameter (12 cm)
- Glas wall sample omitted



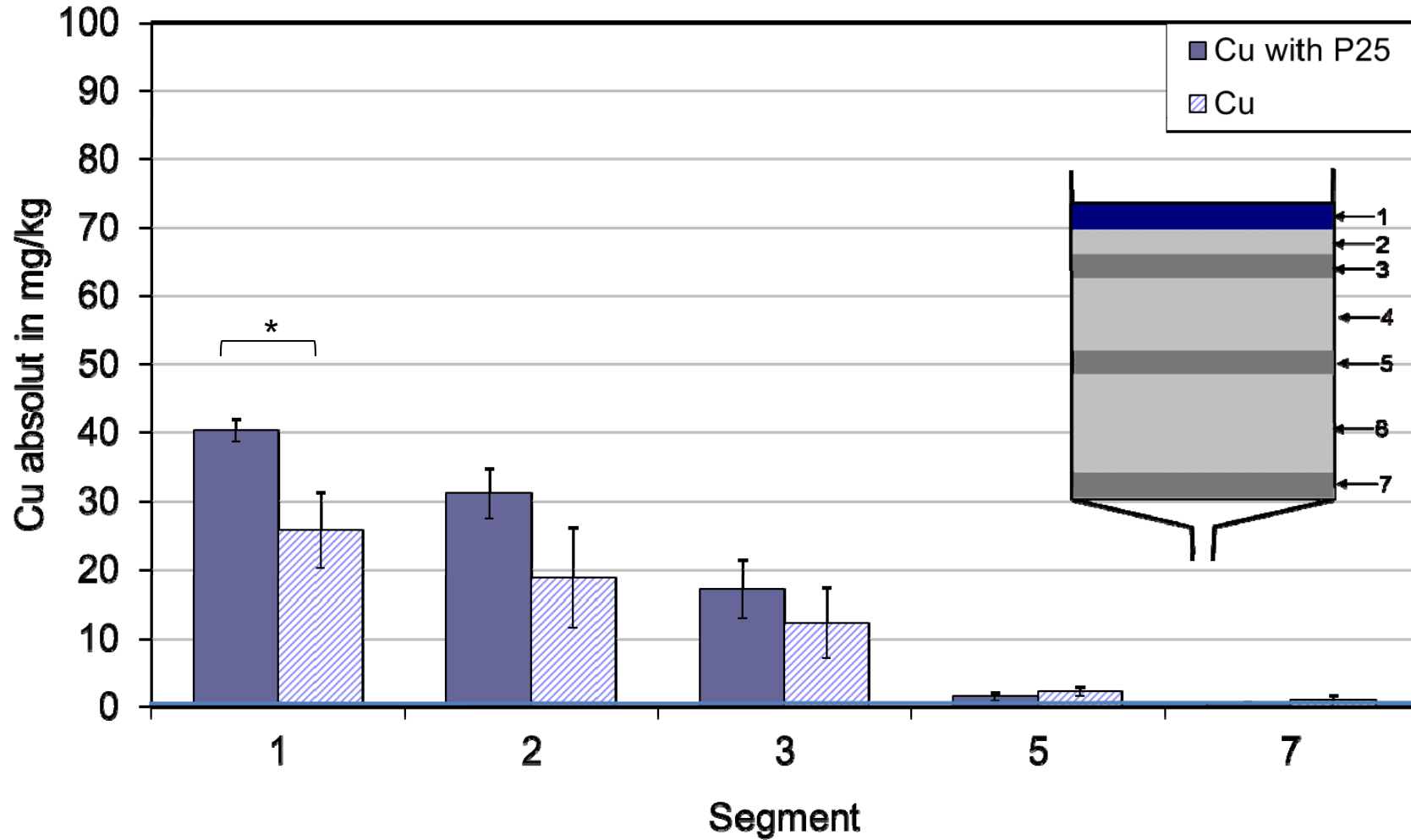


# Ti Transport – Example - Soil type Dystric cambisol (A01)

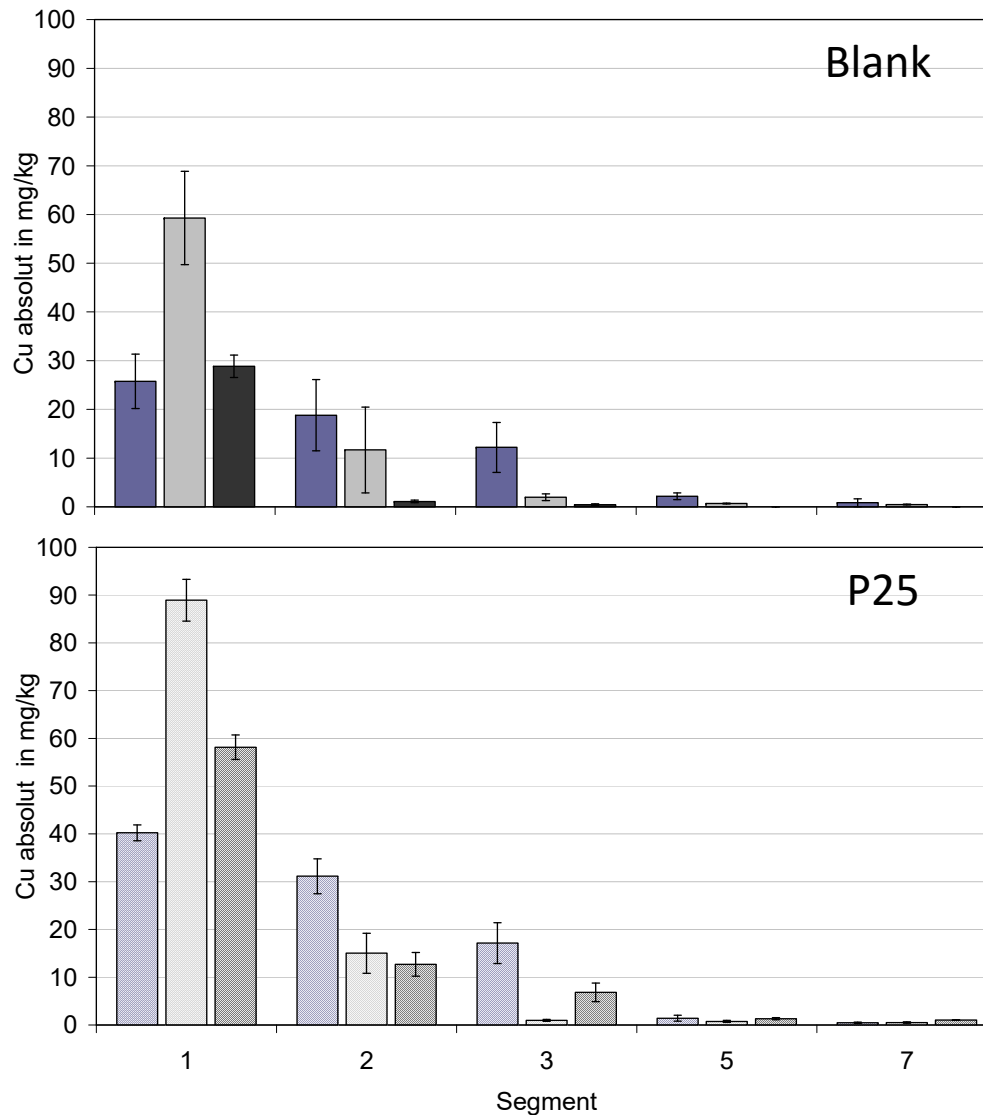


→ Transport of isolated P25 agglomerates

# Cu Transport – Example - Soil type Dystric cambisol (A01)



# Cu Transport



## Reference:

Soil type dependent low transport:  
 Dystric cambisol (A01) > Eutric cambisol (G03) > Stagnic luvisol (A02)

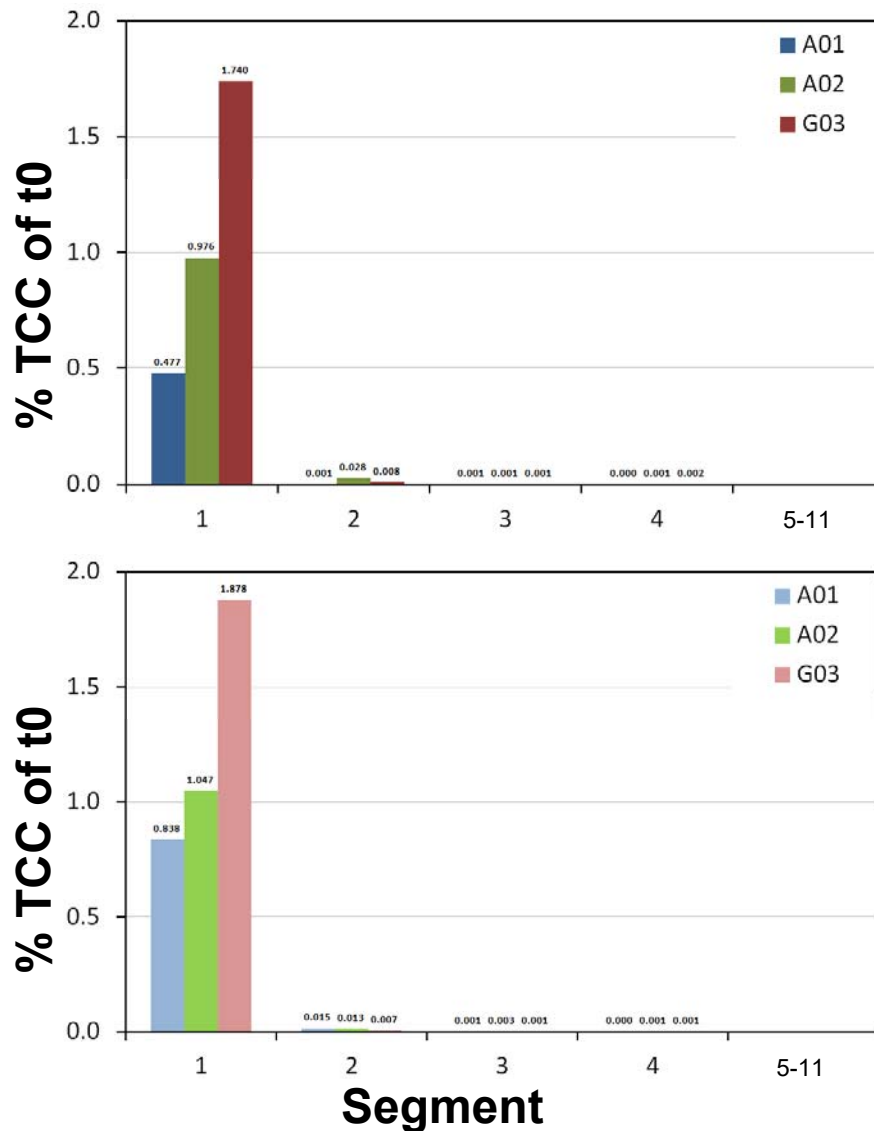
## Test system:

Soil type dependent low transport, Cu transport lower compared with the blank

Dystric cambisol (A01) > Eutric cambisol (G03) > Stagnic luvisol (A02)

➔ P25 reduced Cu-transport

# TCC Transport



## Reference:

Low mobility, no breakthrough of TCC, TCC concentration higher as LOD only in the first 4 cm

Dystric cambisol (A01) > Stagnic luvisol (A02) > Eutric cambisol (G03)

## Test system:

Low mobility, no breakthrough of TCC, TCC concentration higher as LOD only in the first 4 cm

→ No differences if P25 is available (slightly lower transport for soiltype A01)



## Conclusion

- Low mobility of Ti ENM (only single agglomerates)
  - Low Cu and very low TCC transport
  - Soiltype with the lowest pH (5.7) and CEC (38 mmolc/kg) shows the highest transport - Dystric Cambisol
  - Significant lower Cu transport if P25 is available for all soiltypes
  - No significant effect of P25 on TCC transport
- Accumulation of Ti or Cu in the upper soil layers → higher availability for plants → concentration hot spots possible
- Transferability of other substances → lower transport of nutrients possible?

## Outlook

- Literature → No / low mobility of ENM in soils
- Are these information enough for a comprehensive Risk Assessment?

### Open questions?

- Some ENM show a higher mobility
  - Identification of important ENM paramaters which determine the behaviour
  - Identification of important soil parameter like AWI affecting the ENM mobility
- Transformation processes → change of the mobility possible?
- Relevance of the low mobility → Concentration hot spots?
  - Bioavailability for soil organisms / plants?
- Lack of long term studies and mesocosm studies

# Thank you for your attention!!!



**Bryan Hellack, Christof Asbach,  
Stephan Gabsch, Michael Stintz,  
Lothar Erdinger,  
Hanna Maes,  
Andreas Schäffer,  
Thomas Kuhlbusch**

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