Radiolabeling as a versatile tool in nanosafety research – Accurate quantification in complex media

Stefan Schymura[1], Heike Hildebrand[1], Iarsolav Rybkin[1,2], Thomas Fricke[3], Alexander Mansel[1], Marcel Neugebauer[4], Anette Freyer[5], Tomaz Rijavec[2], Ales Lapanje[2], Marko Strok[2], Thomas Lange[5], Uwe Holzwarth[6], Neil Gibson[6], Karsten Franke[1]

[1] HZDR, Institute of Resource Ecology, Leipzig, Germany [2] Jozef Stefan Institute, Environmental Sciences, Ljubljana, Slovenia
[3] Vita34 AG, BioPlanta, Leipzig, Germany [4] AUD, Chemnitz, Germany [5] IOM, Leipzig, Germany [6] European Commission, Joint Research Centre, Ispra, Italy

European Commission

HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

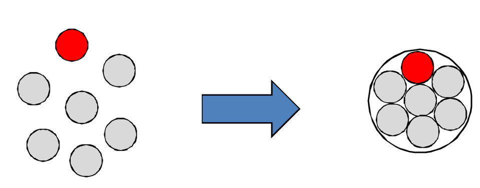
Motivation

Many studies in the field of nanosafety research „do not offer any kind of clear statement on the safety of nanomaterials“[1], as methodological problems considerably hinder the reliable detection of nanoparticles (NPs)[2] at the predicted low environmentally relevant concentrations[3].

The radiolabeling of nanoparticles has the potential for detecting nanoparticles at minimal concentrations in complex matrices, even against a same-element background, with unprecedented experimental ease, making it a versatile tool for NP release, transport, and uptake studies.

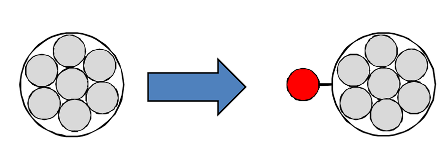
Radiolabeling methods

Radiosynthesis [4]



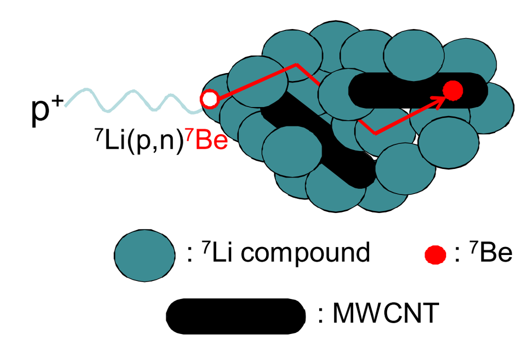
e.g.: [^{110m}Ag]Ag NPs

Radiochemistry [5]



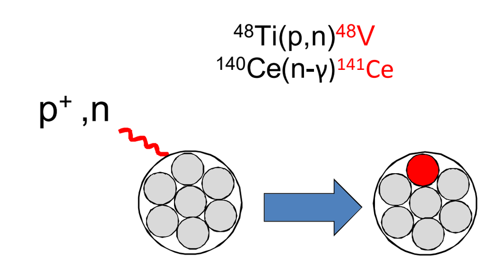
e.g.: [^{125}I]CNTs

Recoil-labeling [6]



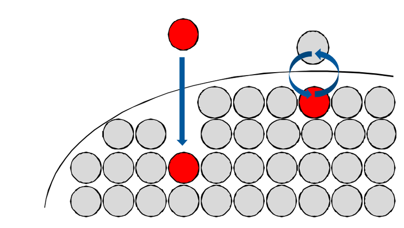
e.g.: [^{7}Be]MWCNTs

Activation [7]



e.g.: [^{48}V]TiO_2 NPs

In-diffusion [8]



e.g.: [^{139}Ce]CeO_2 NPs

stable nuclide ● radioactive nuclide

Cyclotron techniques

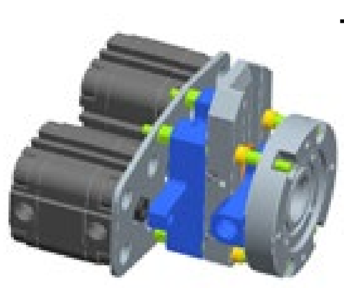
Cyclotron
IBA Cyclone 18/9

Radionuclide production

Established nuclide production routines:

^{11}C, ^{18}F, ^{45}Ti, ^{64}Cu, ^{135}La, ^{89}Zr, ^{48}V, ^{51}Cr, ^{85}Sr, $^{56/58}$Co, $^{86/88}$Y, ^{139}Ce

NP irradiation



COSTIS target station

Target capsules for NP irradiation

[^{48}V]TiO_2
[^{139}Ce]CeO_2
[^{194}Au]Pt
[^{7}Be]NP

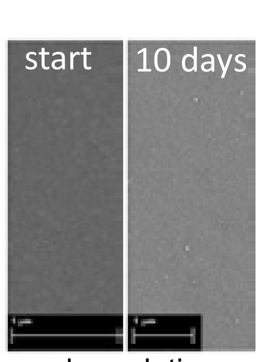
Method	Particle	Halflife	Activity	Detection limit
Radiosynthesis	[^{110m}Ag]Ag	250 d	1.5 MBq/mg	33 ng/L
	[^{105}Ag]Ag	41.3 d	0.65 MBq/mg	77 ng/L
	[^{64}Cu]CuS	12.7 h	0.45 MBq/mg	111 ng/L
	[^{64}Cu]SiO_2	12.7 h	1.0 MBq/mg	50 ng/L
	[^{65}Zn]CdSe/ZnS	244 d	0.69 MBq/mg	73 ng/L
	[^{75}Se]CdSe	119.8 d	0.10 MBq/mg	504 ng/L
Radiochemistry	[^{124}I]CNT	4.2 d	8.0 MBq/mg	6 ng/L
	[^{125}I]CNT	59.4 d	19.9 MBq/mg	2 ng/L
	[^{131}I]CNT	8.0 d	3.7 MBq/mg	14 ng/L
	[^{125}I]fulvic acid	59.4 d	1.4 MBq/mg	37 ng/L
Recoil-labeling	[^{7}Be]TiO_2	53.0 d	0.3 MBq/mg	170 ng/L
	[^{7}Be]MWCNT		0.18 MBq/mg	275 ng/L
Activation	[^{48}V]TiO_2	16.0 d	15.2 MBq/mg	3 ng/L
	[^{139}Ce]CeO_2	137.6 d	0.97 MBq/mg	52 ng/L
	[^{141}Ce]CeO_2	32.5 d	0.25 MBq/mg	202 ng/L
	[^{194}Au]Pt	1.6 d	0.76 MBq/mg	66 ng/L
In-diffusion	[^{110m}Ag]Ag	250 d	1.0 MBq/mg	50 ng/L
	[^{45}Ti]TiO_2	3 h	140 MBq/mg	0.4 ng/L
	[^{44}Ti]TiO_2	49 a	10 kBq/mg	5 µg/L
	[^{139}Ce]CeO_2	137.6 d	1.24 MBq/mg	41 ng/L

Application: (Nano-)Particle Tracing

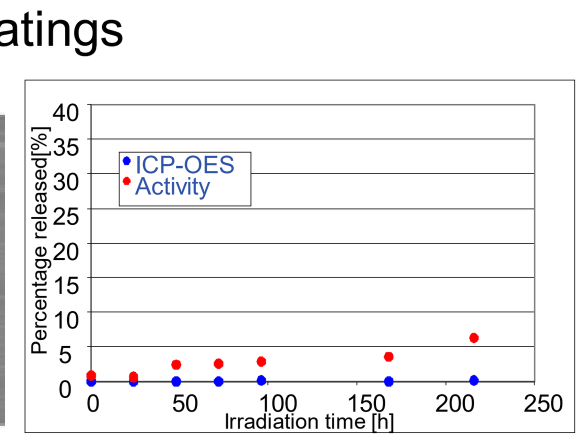
Release from solids:

IOM

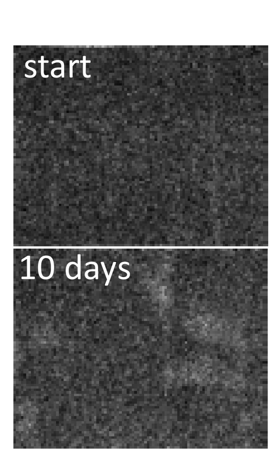
Release of [^{48}V]TiO_2 NPs from UV-degraded surface coatings



no degradation visible with SEM



NP release detectable by radiolabeling



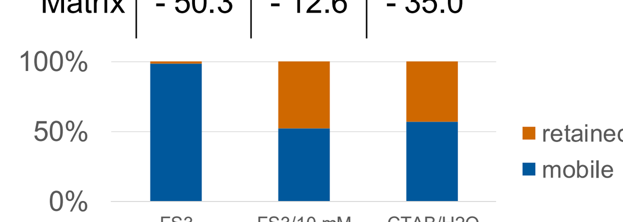
localization of NP release

Transport in liquids:

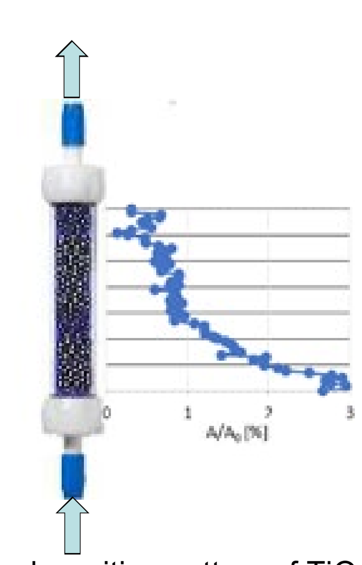
Transport of [^{48}V]TiO_2 NPs

ζ-Potential [mV]

NP	- 41.8	- 12.3	+ 41.3
Matrix	- 50.3	- 12.6	- 35.0



retention rates of 100 ng TiO_2 on 7x1 cm glass bead (200 µm) column

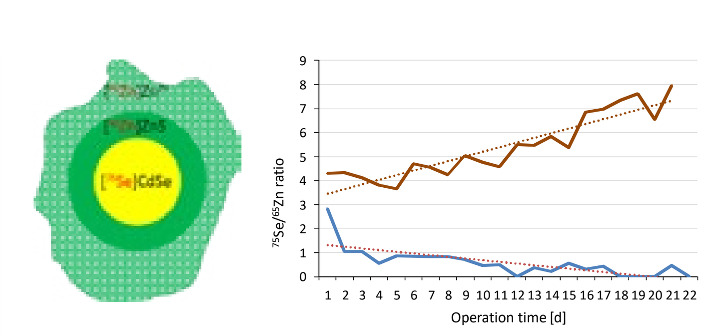


deposition pattern of TiO_2 along the column

Fate in waste water treatment:

AUD

Dissolution of [^{75}Se]CdSe/[^{65}Zn]ZnS NPs

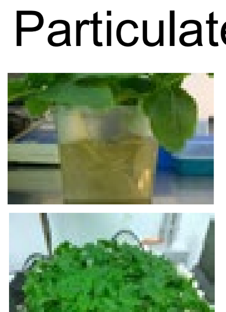


development of Zn/Se ratio in effluents

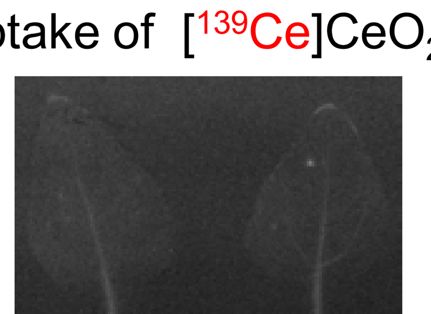
Uptake by plants:[9]

VITA34 BioPlanta

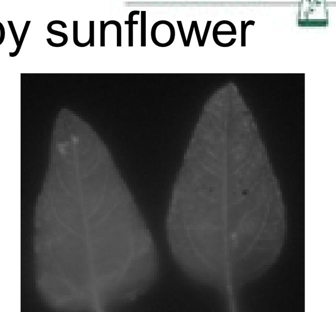
Particulate uptake of [^{139}Ce]CeO_2 by sunflower



experiment setup



[^{139}Ce]CeO_2 NPs accumulate in leaf veins and edges

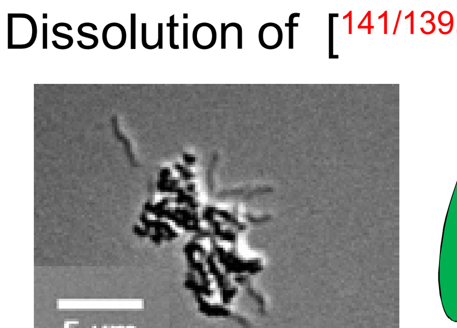


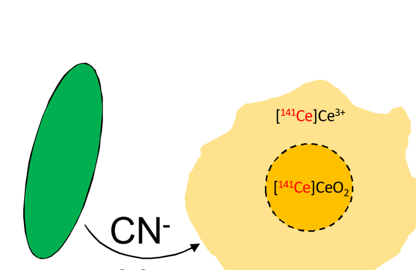
aq. [^{139}Ce]$CeCl_3$ shows equal distribution

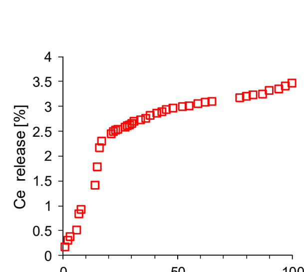
Interaction with soil bacteria:

Jožef Stefan Institute

Dissolution of [$^{141/139}$Ce]CeO_2







dissolution of CeO_2 at pH 3

Conclusion

Visualization and **quantification** of **complex processes** in **complex systems** with very low **detection limits**

References [1] Krug, *Angew. Chem. Int. Ed.* 53, 2014. [2] Von der Kammer *et al.*, *J. Environ. Toxicol. Chem.* 31(1), 2012. [3] Gottschalk *et al.*, *Environ. Pollut.* 181, 2013. [4] Ichedef *et al.*, *J. Nanopart. Res.* 15(11), 2013. [5] Franke *et al.*, *ES&T* 42(11), 2008. [6] Holzwarth *et al.*, *J. Nanopart. Res.* 16(9), 2014. [7] 2014 Hildebrand *et al.*, *J. Nanopart. Res.* 17(278), 2015. [8] Hildebrand & Franke, *J. Nanopart. Res.* 14(10), 2012. [9] Schymura et al., *Angew. Chem. Int. Ed.* 56, 2017.

Dr. Stefan Schymura | Institute of Resource Ecology | Reactive Transport | s.schymura@hzdr.de | www.hzdr.de

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES
PIE-0007
QualityNano
Federal Ministry of Education and Research
DFG
JRC-TAF-23,119,167,168,341,348
03X0144A
03X007881
FR1643/3-1