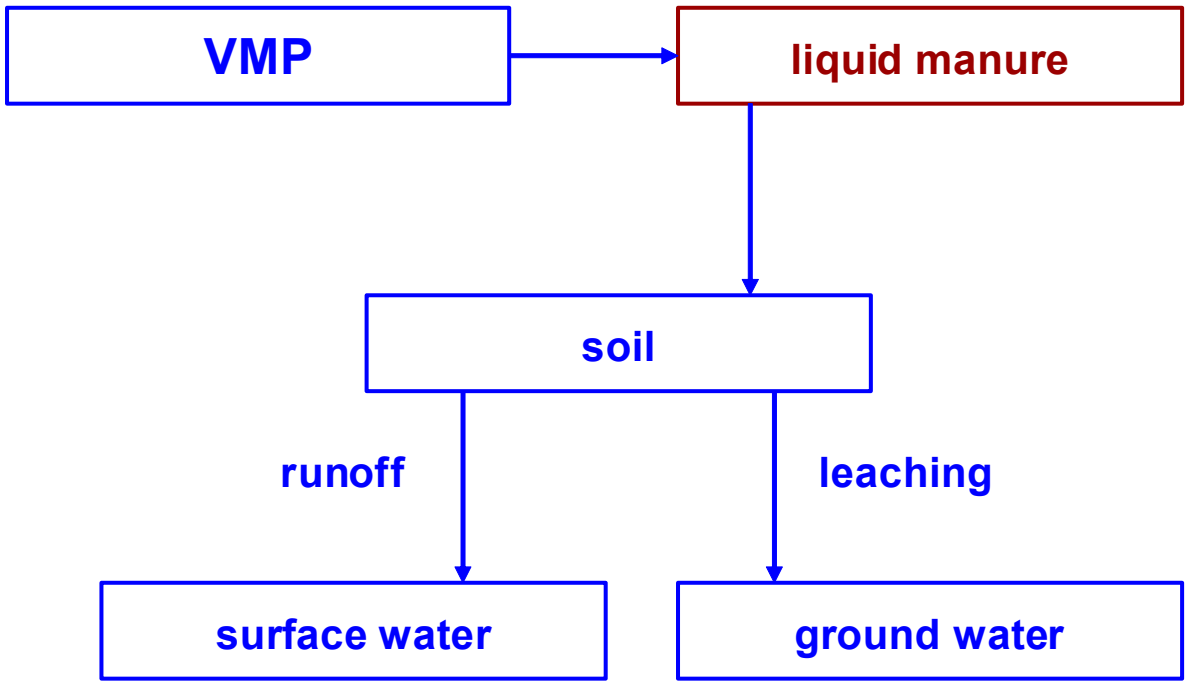
Technische Universität Braunschweig
Institut für Ökologische Chemie und Abfallanalytik

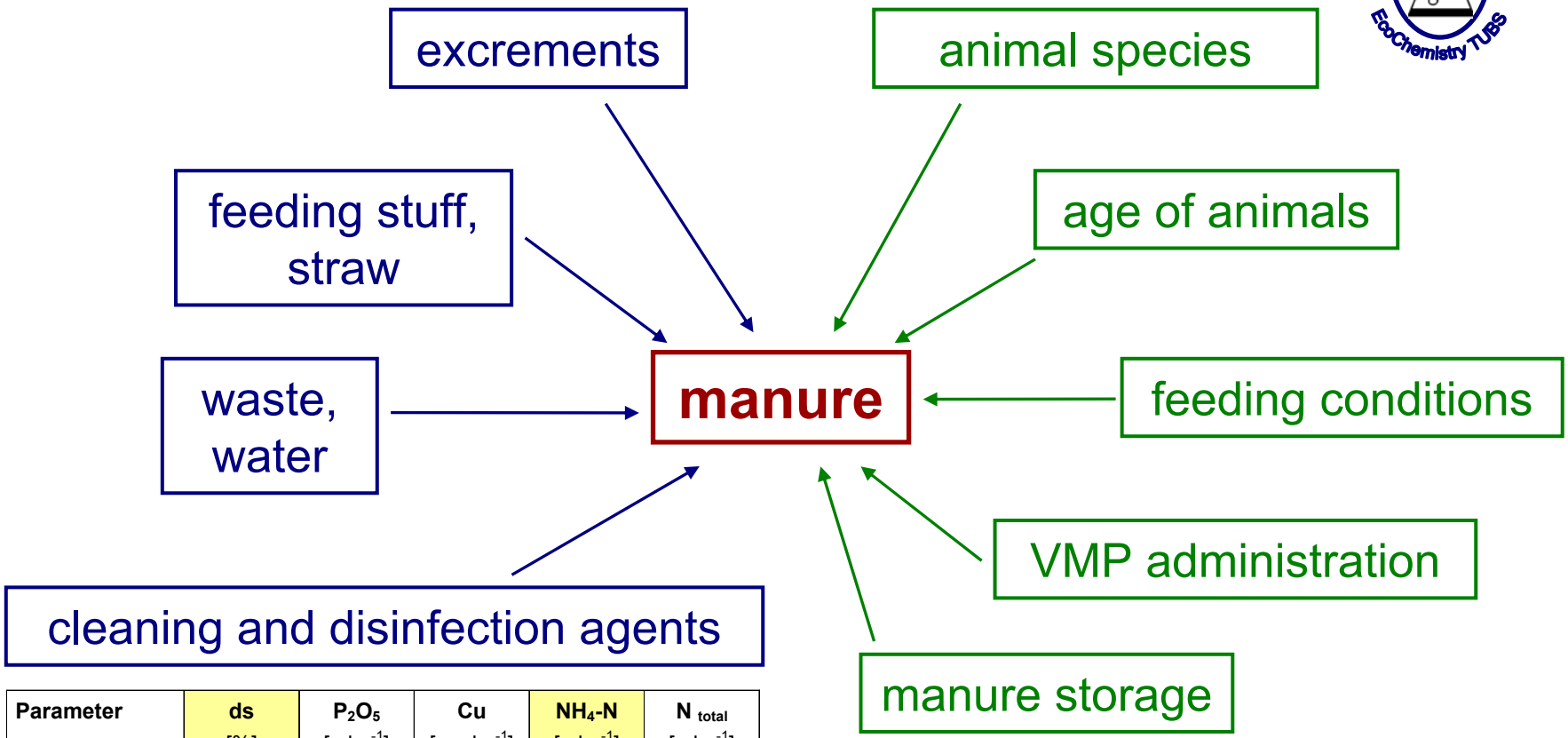
The Reference Manure Concept

R. Kreuzig



Manure Project: UBA-FKZ 207 67 455; 2004-2007
Biocide Project: UBA-FKZ 3 707 67 403; 2007-2009

Manure: Complexity, heterogeneity, variability



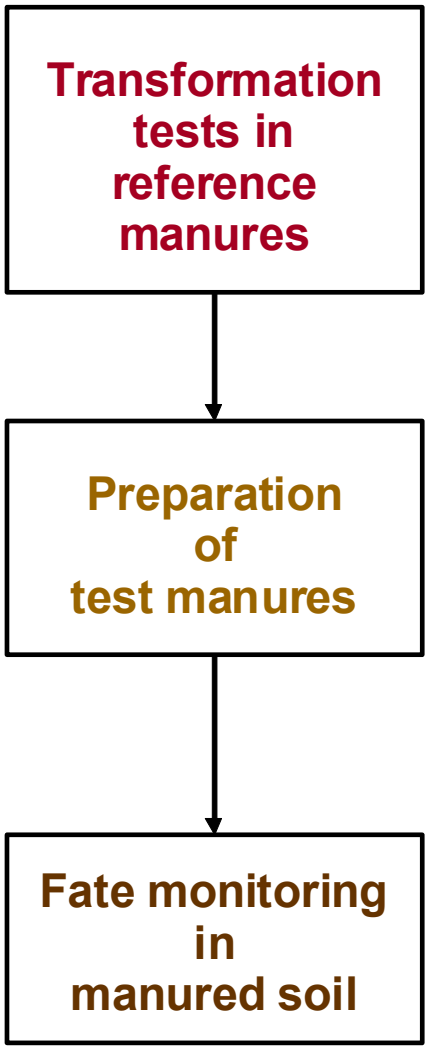
Parameter	ds [%]	P_2O_5 [g kg^{-1}]	Cu [mg kg^{-1}]	NH_4-N [g kg^{-1}]	N_{total} [g kg^{-1}]
Bovine manure					
minimum	0.4	0.05	0.08	0.01	0.43
median	8.7	1.7	3.9	1.7	4.0
maximum	12.3	2.7	12.1	2.9	5.7
Pig manure					
minimum	0.4	0.03	0.22	0.27	0.60
median	4.9	2.3	16.1	2.7	4.6
maximum	11.6	6.3	53.1	4.9	8.3

Composition of bovine and pig manures (Merkel, 2005)

Parameter sets of different studies on degradation of VMP in manures submitted to UBA (Klein-Goedicke, 2009)

Study	Matrix	Test substance	Test conditions
01	pig manure, 9.25 % ds matrix: ds, ash, Eh, TOC, pH, NH_4-N, N_{total}, P, K, Mg, Na, bacteria, fungi, yeast	^{14}C	100 g, 0-30 d, anaerobic, 20 ± 1 °C
02	pig slurry matrix: ---	^{14}C	40 g, 0-64 d, 22 ± 2 °C
03	pig lagoon slurry matrix: pH, Eh, TOC, N, P, $solids_{total}$	unlabelled	20 mL, 22 °C
04	cow excreta matrix: pH	^{14}C	200 g
05	cattle manure matrix: Eh, microbial activity	^{14}C	133 g faeces + 66 mL urine, 100 d
06	poultry manure matrix: ds, TOC, microbial cell count	unlabelled	20 g, 0-40 d, aerobic, 25 ± 2 °C
07	chicken faeces matrix: ---	unlabelled	1 g, 0-15 d, aerobic, 21 ± 0.4 °C

Development of a technical protocol for fate monitoring of VMP in liquid manures and manured soils

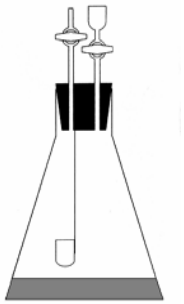


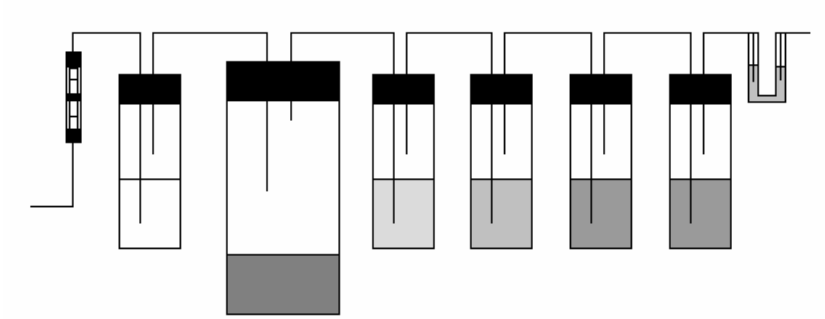
Reality:
- → composition of manures
- → storage conditions
- → entry route via manuring

Practicability:
- → feasibility
- → time and costs

Quality assurance:
- → "repeatability"
- → "reproducibility"

Manure Project (UBA-FKZ 204 67 455; 2004-2007)





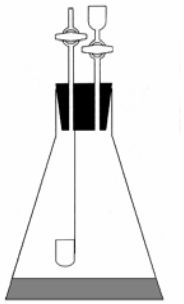
Reference manure versus tank manure for regulatory testing on transformation of novel VMP or biocides

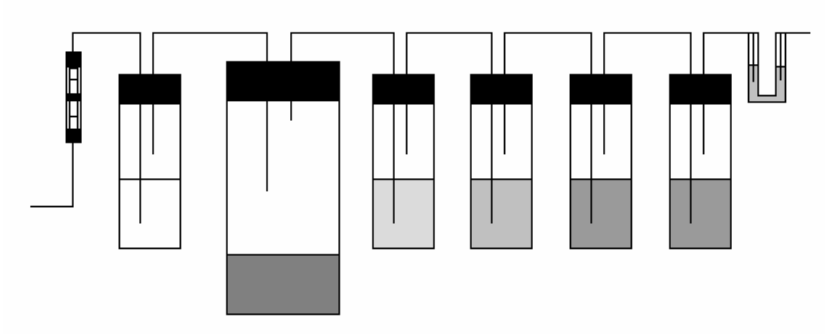
Numbers of tests for the tank-manure concept:

- ➡ Novel VMP or biocide applicable for cattle, pig and chicken
- ➡ 4 different tank manures each (according to OECD 307)
- ➡ Incubation intervals: 0, 1, 3, 7, 30, 72, 100 days, reserve (n =2)
- ➡ Matrix characterization of 12 tank manures (n =2)
- ➡ Matrix characterization of 12 tank manures: 0, 100 days (n =2)

$\sum_{\text{batch tests}}$: 3 x 4 x 8 x 2 = 192 !!! $\sum_{\text{matrix characterization}}$: 12 x 2 + 12 x 1 = 36 !!!

+ 12 LC/MS/MS screening analyses on interfering VMP and biocides !!!





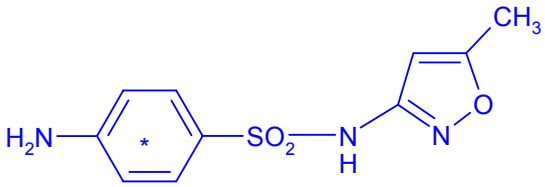
Reference manure versus tank manure for regulatory testing on transformation of novel VMP or biocides

Numbers of tests for the reference-manure concept:

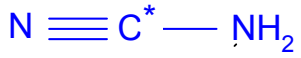
- ➡ Novel VMP or biocide applicable for cattle, pig and chicken
- ➡ 1 reference manure each
- ➡ Incubation intervals: 0, 1, 3, 7, 30, 72, 100 days, reserve (n =2)
- ➡ Matrix characterization of 3 excrements (n =2)
- ➡ Matrix characterization of 3 reference manures: 0, 100 days (n =2)

$\sum_{\text{batch tests}}$: 3 x 8 x 2 = 48 ! **$\sum_{\text{matrix characterization}}$: 3 x 2 + 3 x 2 x 2 = 18 !**

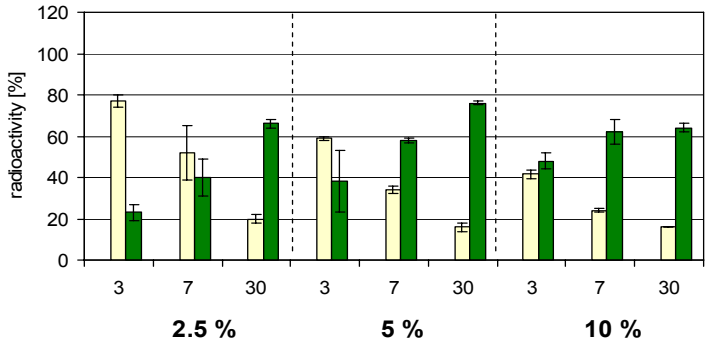
Excrements are operationally free of any VMP and biocide contamination !



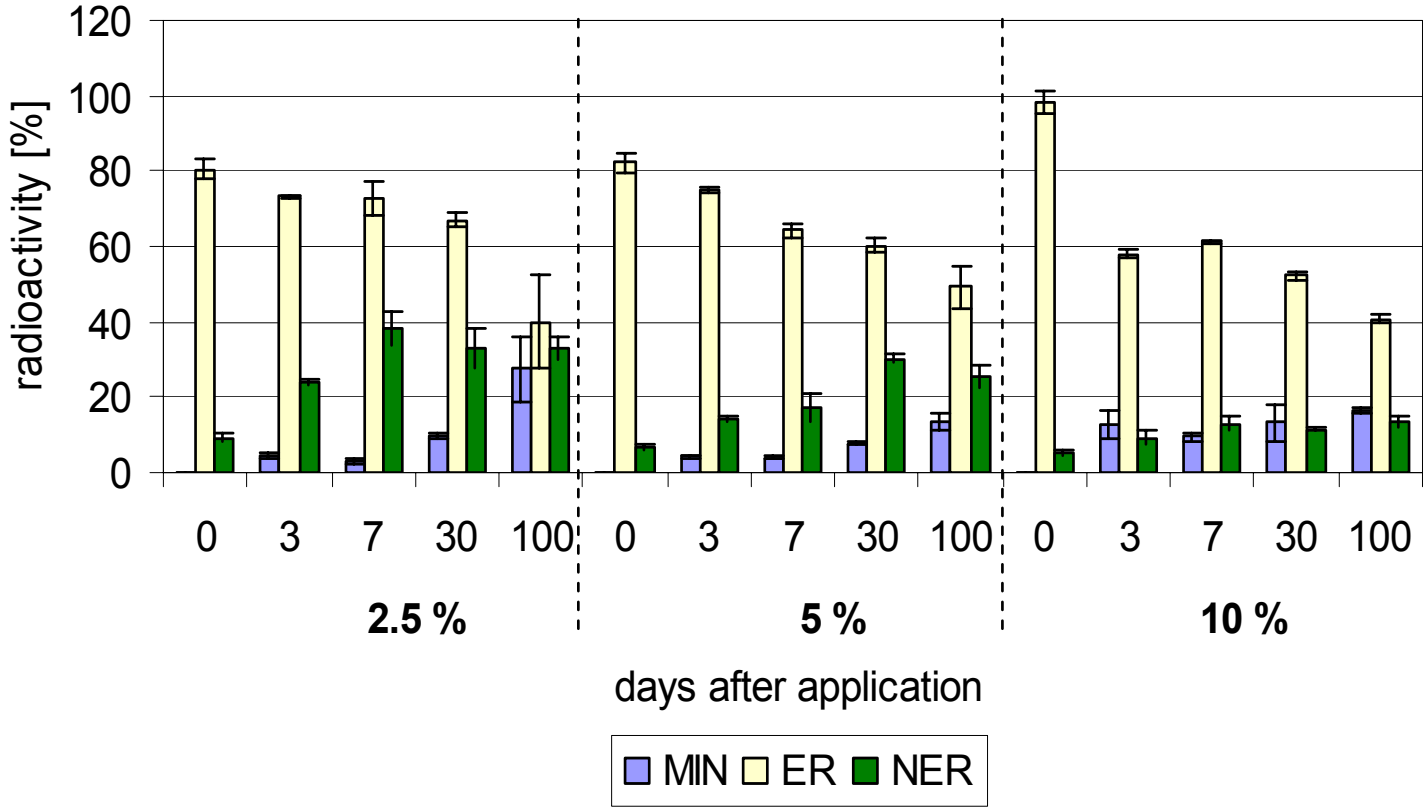
sulfamethoxazole



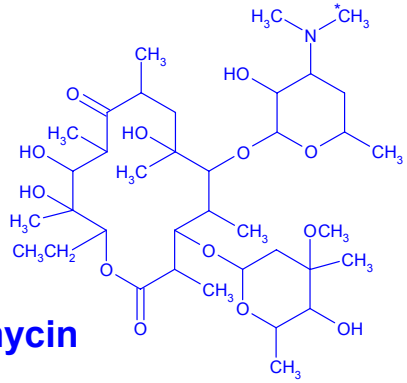
cyanamide



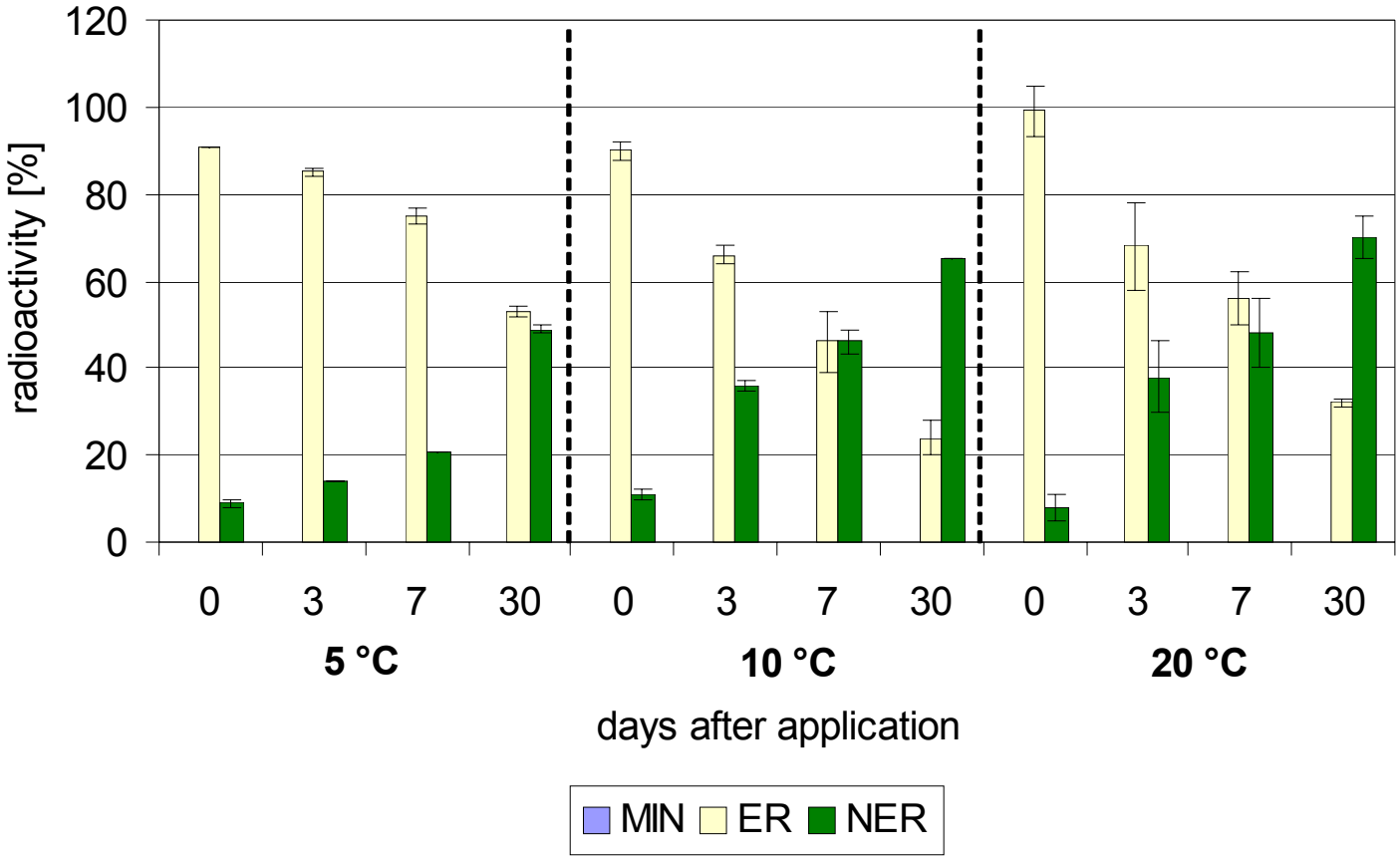
^{14}C-sulfamethoxazole in bovine reference manure



Transformation of ^{14}C-cyanamide in pig reference manure at different dry substance contents and at 20 ± 1 °C (balances: 92 ± 12%)



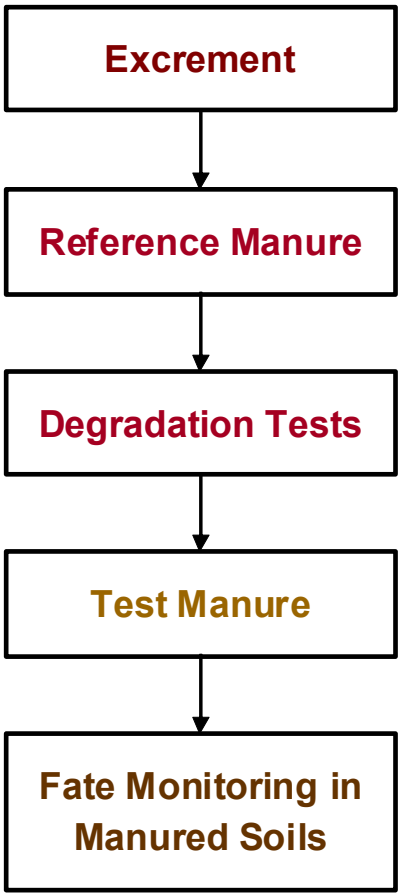
erythromycin



Degradation of ^{14}C-erythromycin in pig manure (PM-1) at different incubation temperatures (balances: 100 ± 5 %)

The Technical Guidance (Draft Version)

Transformation of VMP and Biocides in Bovine and Pig Manures and Degradation and Sorption in Manured Soils



A tiered experimental design in 5 parts:

I. **Sampling of excrements and preparation of reference manures.**

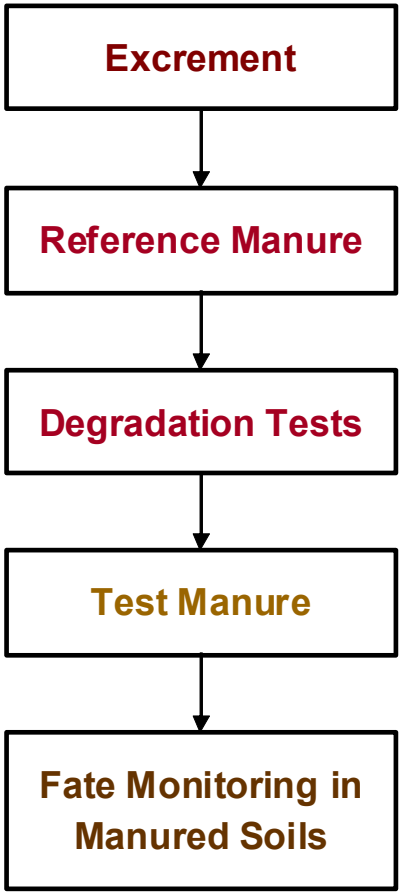
II. **Anaerobic degradation tests in reference manures.**

III. Preparation of test manures.

IV. Aerobic degradation in manured soils.

V. Sorption tests in manured soils.

Preparation of Reference Manures



- **Sampling of excrements from individual production animals**
  - animals´ age: cattle : 8 – 60 months
    pigs : 4 – 12 months
  - nutrition: cattle : silage (maize, grass), pellets
    pig : barley, wheat, potatoes, soya
- **Matrix characterisation of excrement samples**
- **Adjustment of excrement samples to definied water contents**
  - bovine manure : 2.5 %, 5 %, **10** % ds
  - pig manure : 2.5 %, **5** %, 10 % ds
- **Matrix characterisation of reference manure samples**

Matrix characterisation
of excrement and reference-manure samples

- **dry substance (ds)**
- mineral content (R_{min})
- copper and phosphor content (Cu, P)
- **total organic carbon (TOC)**
- **pH value**
- **redox potential (Eh)** — **Eh < 0 mV: anaerobic conditions**
- **dissolved oxygen (O_2)** — **O_2 < 0.1 mg kg^{-1}: anaerobic conditions**
- **ammonium (NH_4-N)**
- **total nitrogen (N_{total})** — NH_4/N_{total}: ageing of excrements/manures
- **biological oxygen demand (BOD_5)**
- chemical oxygen demand (COD); — BOD/COD > 0.5 mg kg^{-1}: readily degradable

Microbial activity in liquid bovine and pig manures

By means of the BOD_5 measurement, the activity of aerobic microorganisms is merely comprised. Thus, the validity of the biological oxygen demand in anaerobic manure samples may be limited. Certainly, there is not any alternative method without any other interferences. The determination of the dehydrogenase activity, feasible to determine the activities of aerobic and anaerobic microorganisms, may be limited by its final photometric measurement of triphenyl formazan at λ = 485 nm or λ = 546 nm because of the deeply colored excrement and manure extracts [29]. The application of a readily degradable reference substance, e.g., sodium benzoate, in parallel batch experiments causes other inadequacies. In order to check the microbial activity of manure samples at the start of the transformation test series, this test is too time consuming due to its 4-week test period specified by the OECD guideline 311 [30]. Due to the different experimental designs, the degradability of this test substance is only measured by the gas production, this test is not appropriate to check the microbial activity at longer incubation intervals. So far the application of an external standard substance should be followed in the future, there is the need to identify an appropriate ^{14}C-labeled reference substance that shows a characteristic behavior in bovine and pig manure within incubation intervals up to 100 days.

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Sterile batch experiments

Regarding the question if tests with sterile manures should be added, the risk of **artifical surface changes** during the sterilization process (autoclav method, UV, γ-irradition, NaN_3) was depicted.

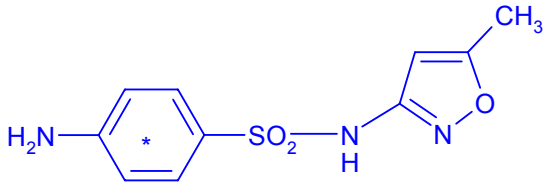
So far ^{14}C-labeled test substances are used, there is not any further information on the transformation of VMP or biocides in liquid manures.
In case, there is the need of applying an unlabeled test substance, the **process understanding** may be increased.

However, it should be considered relevant that **long-term trans-formation** tests cannot be performed **under permanent sterile conditions** because spores of bacteria and fungi may be very persistent and may be reactivated under the incubation conditions. This fact has been already shown for soil samples.

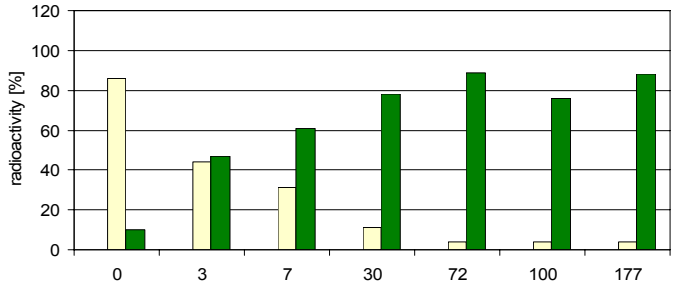
Effects of the storage at –20 °C on matrix properties

	Bovine excrement (BE-1)		Pig excrement (PE-1)	
Parameter	**fresh sample**	**reserve sample**	**fresh sample**	**reserve sample**
ds [%]	13	13	22	22
TOC [g kg^{-1}]	53	46	77	96
pH	6.8	7.4	7.3	7.3
Eh [mV]	60	-140	-140	-30
O_2 [mg kg^{-1}]	< 0.1	< 0.1	< 0.1	< 0.1
NH_4-N [g kg^{-1}]	1.7	1.7	8.3	9.0
N_{total} [g kg^{-1}]	4.3	4.0	14.0	13.8
NH_4-N/N_{total}	0.4	0.4	0.6	0.7
BOD_5 [g kg^{-1}]	7.6	9.1	29	23
COD [g kg^{-1}]	80	63	182	179
BOD_5/COD	0.1	0.1	0.2	0.2

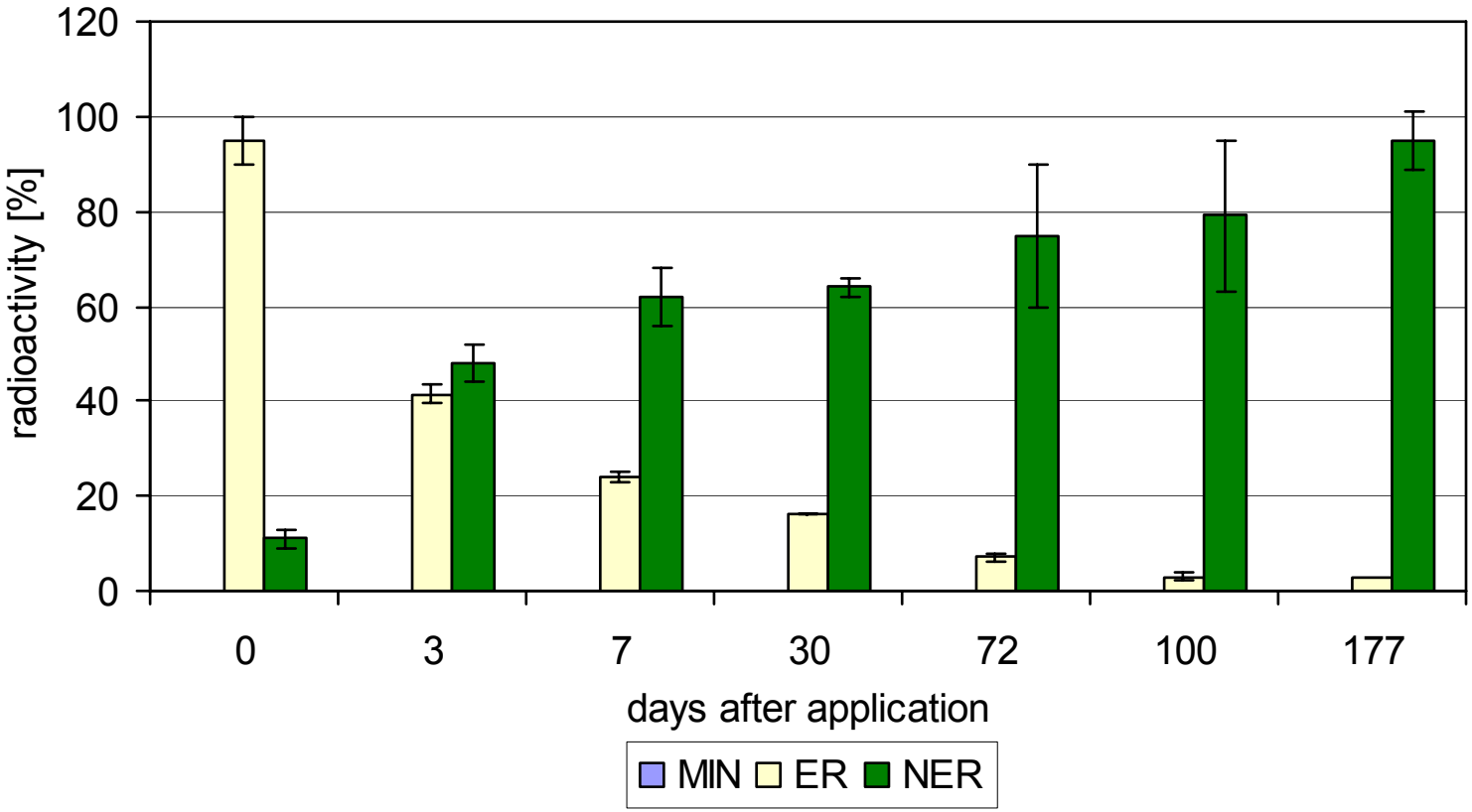
storage periods: 378 d for BE-1, 322 d for PE-1 reserve samples



sulfamethoxazole



Degradation test in 2006 (1250 µg kg^{-1})



Degradation of ^{14}C-sulfamethoxazole in bovine manure BM-1 in 2005 (560 µg kg^{-1})

Origin of bovine excrements (dairy cow and calf)

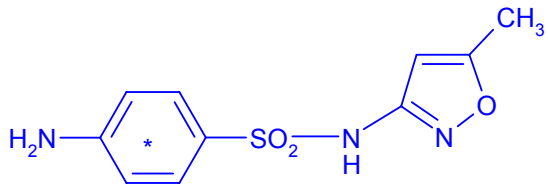
Excrement	Origin	Age	Feeding conditions
BE-1	FLI	5 years	maize, grass, wheat silage, pellets, mineral food
BE-2	FLI	8 months	maize, grass, wheat silage
BE-3	farm	5 years	maize, grass silage, hay, pellets, mineral food
BE-4	FLI	5 years	maize silage, pellets, mineral food
BE-5	FLI	4 years	grass, maize silage, pellets, mineral food
BE-6	FLI	5 years	grass, maize silage, pellets, mineral food

FLI: Friedrich-Löffler-Institut, Braunschweig, Germany; experimental stable

Farm: Beyer Farm, Erpsen, Germany; conventional animal husbandry

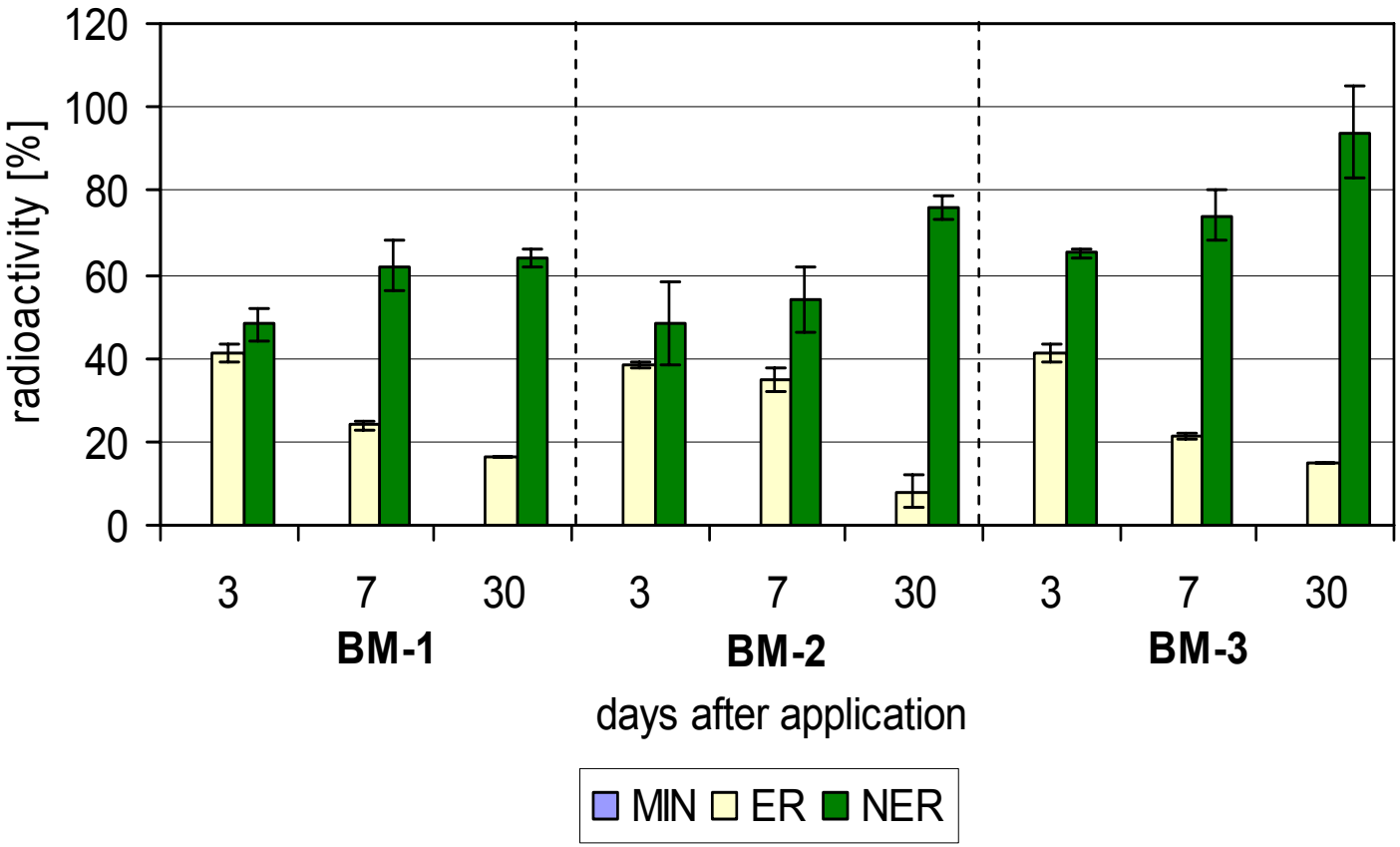
Matrix characteristics of bovine excrements and reference manures

	Excrements						Reference manures					
Matrix / Parameter	**BE-1**	**BE-2**	**BE-3**	**BE-4**	**BE-5**	**BE-6**	**BM-1**	**BM-2**	**BM-3**	**BM-4**	**BM-5**	**BM-6**
ds [%]	13	13	10	13	12	13	adjusted to 10 %					
R_{min} [% TS]	19	15	24	15	12	13	---	---	---	---	---	---
Cu [mg kg^{-1}]	13	7	6	12	6	7	10	5	6	9	5	5
P [g kg^{-1}]	0.9	0.7	1.1	1.0	0.7	0.9	0.7	0.6	1.1	0.8	0.6	0.8
TOC [g kg^{-1}]	47	54	40	50	42	57	39	42	39	39	37	44
pH	6.9	8.4	8.0	6.2	6.5	6.3	7.0	8.1	8.0	6.6	6.6	6.7
Eh [mV]	40	10	-20	-40	-40	-100	-40	-80	-20	10	-100	-160
O_2 [mg kg^{-1}]	< 0.1						< 0.1					
NH_4-**N** [g kg^{-1}]	1.6	4.5	4.0	1.6	1.2	2.3	1.3	3.2	4.0	1.3	0.9	1.6
N_{total} [g kg^{-1}]	4.1	6.4	6.5	3.5	3.1	4.4	3.2	5.0	6.5	2.6	2.5	3.8
BOD_5 [g kg^{-1}]	9.4	11	6.0	23	8.5	18	8.3	7.3	6.0	14	9.3	9.9
COD [g kg^{-1}]	76	70	65	83	62	120	71	60	65	50	59	112



sulfamethoxazole

LabTestSysTeam
EcoChemistry TUBS



Degradation tests of ^{14}C-sulfamethoxazole in different bovine manures

Compositions of bovine excrements

Parameter	ds [%]	pH	Eh [mV]	O_2 [mg L^{-1}]	NH_4-N [g kg^{-1}]	N_{total} [g kg^{-1}]	TOC [g kg^{-1}]	BOD [g kg^{-1}]
Minimum[1]	10	6.2	-100	---	1.2	3.1	40	6
Median[1]	13	6.7	-30	< 0.1	2.0	4.3	49	10
Maximum [1]	13	8.4	40	---	4.5	6.5	57	23
Excrements[2]	13	6.2	-80	< 0.1	1.8	4.7	54	11
Excrements[3]	13	6.6	-120	< 0.1	4.5	8.2	57	18

[1] Sampling within the Manure Project from 2004-2007,21-d conditioning, matrix characterisation

[2] Sampling within the Biocide Project in November 2007, 21-d conditioning, matrix characterisation

[3] Sampling within in the Biocide Project in August 2008, 21-d conditioning, matrix characterisation

Origin of pig excrements

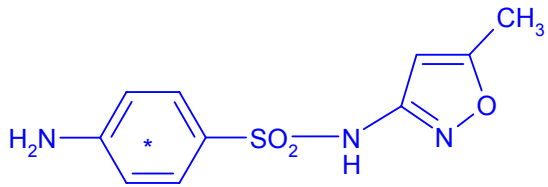
Excrement	Origin	Age	Feeding conditions
PE-1	FLI	6 months	46 % barley, 35 % wheat, 15 % soya pellet,1.5 % soya oil, 2 % vitamins/ minerals/trace elements, 0.5 % amino acids
PE-2	FLI	12 months	25 % barley, 50 % wheat, 20 % soya pellet, 2 % soya oil, 3 % vitamins/minerals/trace elements
PE-3	farm	7 months	60 % potato refuse, 30 % wheat/barley, 7 % soya pellet/soya oil, 3 % vitamins/minerals/trace elements
PE-4	FLI	4 months	46 % barley, 35 % wheat, 15 % soya pellet,1.5 % soya oil, 2 % vitamins/ minerals/trace elements, 0.5 % amino acids
PE-5	FLI	4 months	37 % barley, 27.5 % wheat, 18 % soya pellet,12.5 % triticale, 2 % soya oil, 3 % vitamins/minerals/trace elements
PE-6	FLI	7 months	46 % barley, 35 % wheat, 15 % soya pellet,1.5 % soya oil, 2.5 % vitamins/minerals/trace elements/amino acids

FLI: Friedrich-Löffler Institute, Braunschweig, Germany; experimental stable

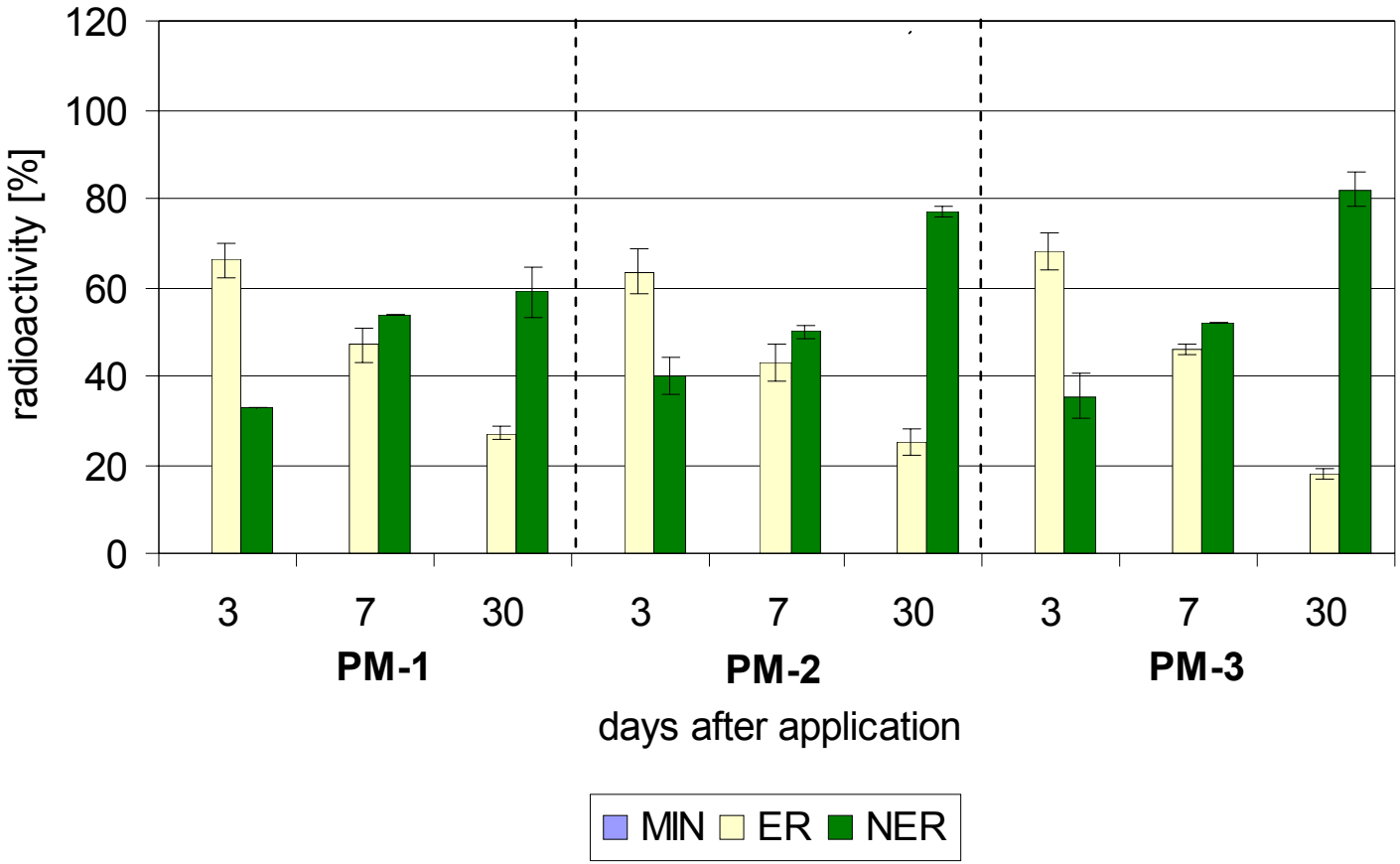
Farm: Beyer Farm, Erpsen, Germany; conventional animal husbandry

Matrix characteristics of bovine excrements and reference manures

	Excrements						Reference manures					
Matrix / Parameter	**PE-1**	**PE-2**	**PE-3**	**PE-4**	**PE-5**	**PE-6**	**PM-1**	**PM-2**	**PM-3**	**PM-4**	**PM-5**	**PM-6**
ds [%]	23	18	21	17	16	13	adjusted to 5 %					
R_{min} [% TS]	22	19	15	21	17	16	---	---	---	---	---	---
Cu [mg kg^{-1}]	25	29	29	16	16	8	6	8	7	5	5	3
P [g kg^{-1}]	4.4	3.8	2.2	2.3	3.0	2.4	1.0	1.1	0.5	0.7	0.9	1.0
TOC [g kg^{-1}]	74	93	103	66	70	56	19	20	21	22	20	18
pH	7.4	7.3	5.7	6.3	6.1	6.8	7.7	7.0	5.8	7.5	6.7	7.3
Eh [mV]	- 130	-90	40	-50	-100	-180	-180	-90	60	-170	-110	-180
O_2 [mg kg^{-1}]	< 0.1						< 0.1					
NH_4-N [g kg^{-1}]	9.2	6.2	3.4	5.8	5.7	4.5	1.9	2.0	0.9	2.0	1.7	1.8
N_{total} [g kg^{-1}]	13.8	9.9	9.4	9.0	8.9	6.8	3.0	3.0	2.3	2.6	2.7	2.8
BOD_5 [g kg^{-1}]	27	23	28	25	21	21	10	10	10	12	9.5	9.1
COD [g kg^{-1}]	173	98	153	124	147	103	40	41	41	32	49	48



sulfamethoxazole



Degradation of ^{14}C-sulfamethoxazole in different pig manures (balances: 99 ± 6 %)

Compositions of pig excrements

Parameter	ds [%]	pH	Eh [mV]	O_2 [mg L^{-1}]	NH_4-N [g kg^{-1}]	N_{total} [g kg^{-1}]	TOC [g kg^{-1}]	BOD [g kg^{-1}]
Minimum[1]	13	5.7	-180	---	3.4	6.8	56	21
Median[1]	18	6.6	-95	< 0.1	5.8	9.2	72	24
Maximum[1]	23	7.4	40	---	9.2	13.8	103	28
Excrements [2]	14	6.0	-30	< 0.1	4.4	8.8	67	18
Excrement [3]	15	6.1	49	< 0.1	4.8	8.6	57	21
Excrements [4]	14	6.3	-80	< 0.1	4.5	8.2	57	18

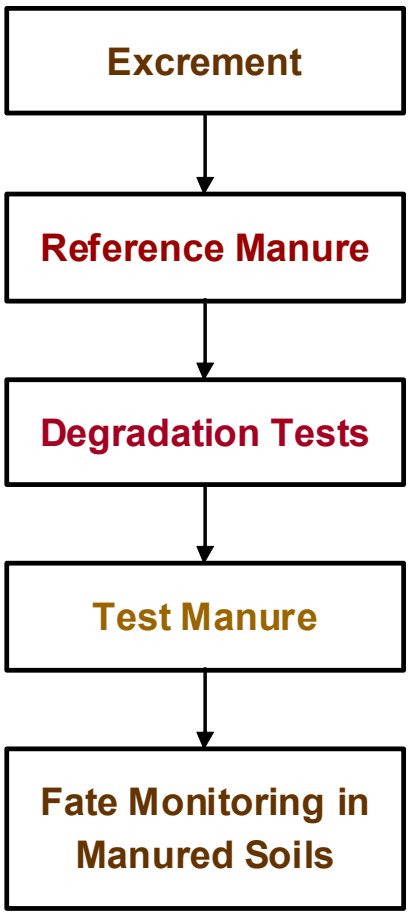
[1] Sampling from 2004-2007, 21-d conditioning, matrix characterisation

[2] Sampling in November 2007, 21-d conditioning, matrix characterisation

[3] Sampling in November 2007, frozen after conditioning and matrix characterisation at -20 °C until July 2008, reconditioned at ambient temperature, matrix characterisation

[4] Sampling in August 2008, 21-d conditioning, matrix characterisation

Standardization of transformation tests of VMP and biocides in bovine and pig manures



- The application of reference-manure samples reduces heterogeneity and variability of tank manure samples.
- The reference-manure concept facilitates reproducible laboratory testing at minimized experimental efforts !
- Matrix parameters: ds, TOC, pH, Eh, O_2, N_{total}, NH_4-N, BOD.
- ^{14}C-labelled test substances allow for setting up mass balances: MIN, ER, NER.
- The application of unlabelled test substances only describes the disappearance of parent compounds.
- Test conditions should be standardised:
  0-100 d, 20 °C, anaerobic: cattle, pig, aerobic: poultry.

Laboratory testing of poultry manures

Status quo:

- ➡ Many different animal husbandry systems.
- ➡ Differences in manures´compositions, e.g., moisture contents, litter content.
- ➡ Aerobic storage conditions: self-heating processes.
- ➡ Changes of matrix characteristics during long-term storage.

Solution:

- ➡ Administration of ^{14}C-labeled VMP to test animals.

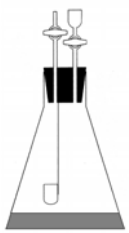
Problem:

- ➡ Simultaneous occurrence of parent compounds and metabolites.

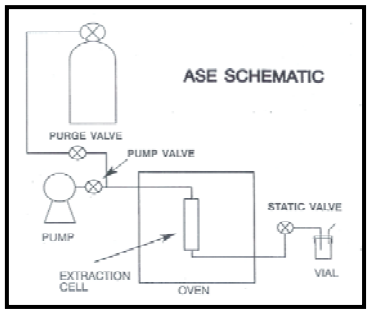
Recommendation:

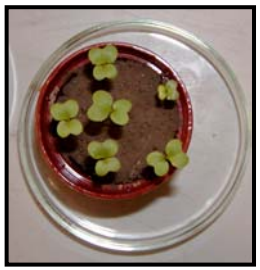
- ➡ Regulatory requirements should be defined first before research laboratories starts to develop the experimental design of laboratory tests !

not under study within Manure Project and Biocide Project



Chemical and biological characterization of non-extractable residues for environmental risk assessment





Open questions:

- ➡ parent compound or metabolites ?
- ➡ non-hazardous or hazardous substances ?
- ➡ physically entrapped or chemically bound ?
- ➡ reversible or irreversible processes ?
- ➡ benefit or environmental risk ?
- ➡ limits of soils´ buffer capacity ?

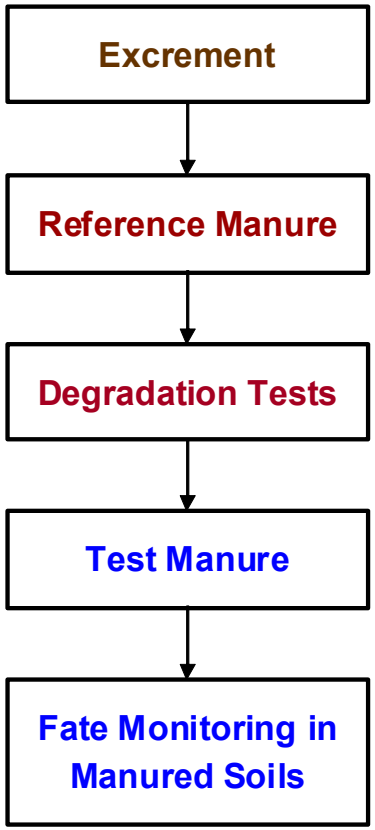
Possible measures:

- ➡ operational definition of non-extractability !
- ➡ definition of persistence criteria or NER triggers:

  MIN < 5 %; NER <10 %, 10-70 %, > 70 % in 100 days !

The Technical Protocol (Draft Version)

Transformation of VMP and Biocides in Bovine and Pig Manures and Degradation and Sorption in Manured Soils



A tiered experimental design in 5 parts:

I. Sampling of excrements and preparation of reference manures.

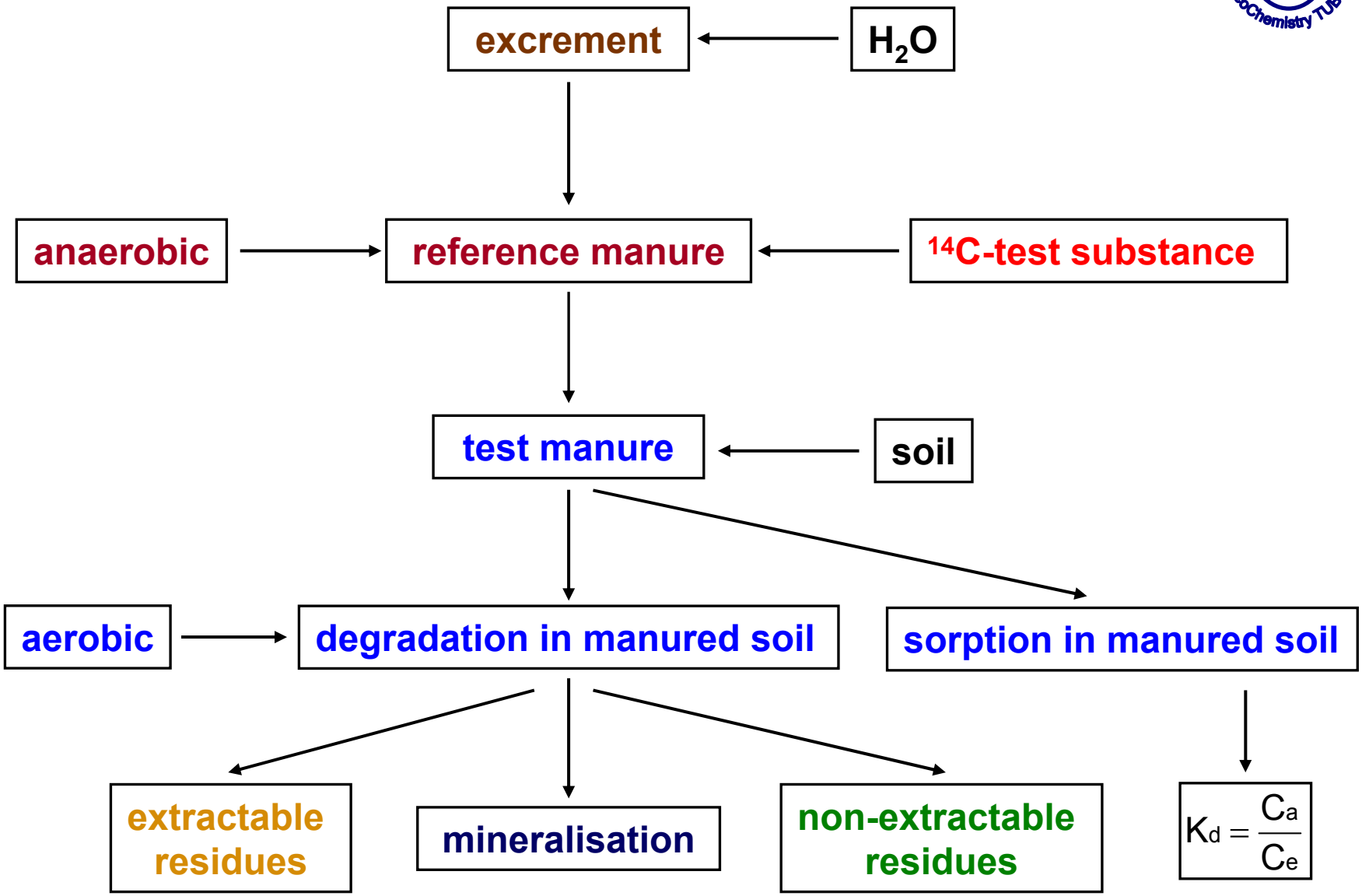
II. Anaerobic degradation tests in reference manures.

III. Preparation of test manures.

IV. Aerobic degradation in manured soils.

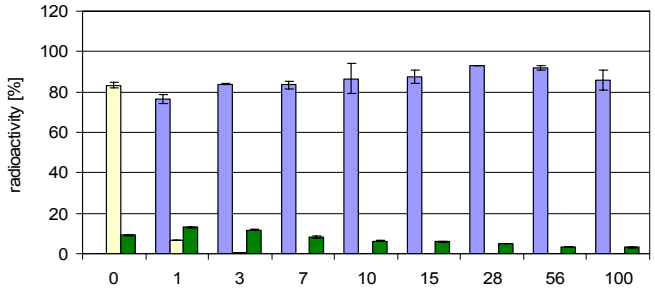
V. Sorption tests in manured soils.

Transformation and Sorption Tests in Manured Soils

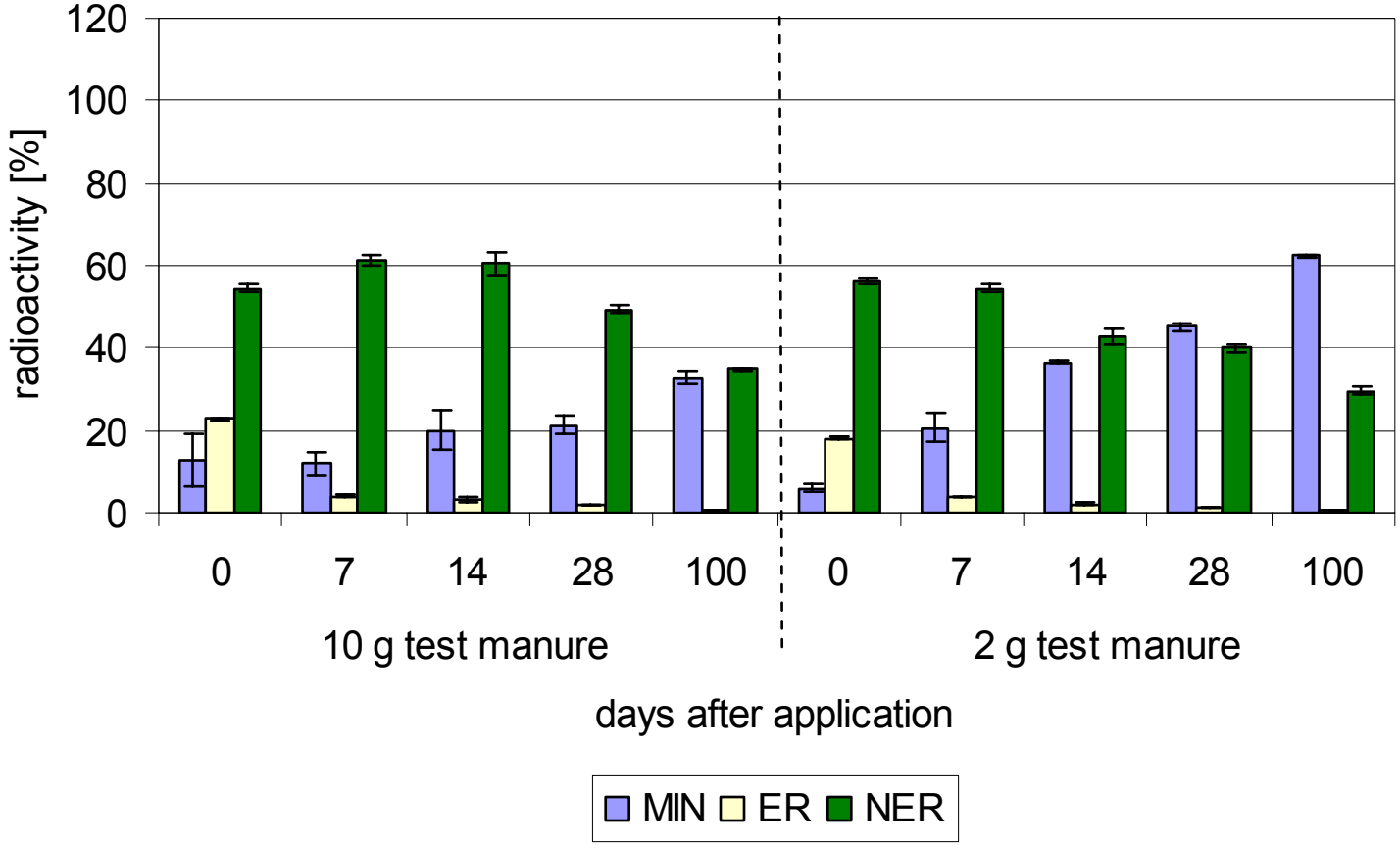


$N \equiv C^* - NH_2$

cyanamide



Standard application (balances: 94 ± 3 %)



Transformation of ^{14}C-cyanamide in silty clay soil after application of different amounts of bovine test manure (balances: 84 ± 13 %)

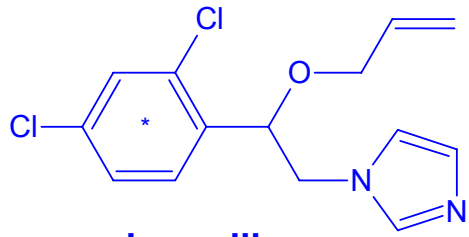
Sorption in silty clay soil
after standard and test-manure application

$$K_d = \frac{C_a}{C_e}$$

$$K_{OC} = \frac{K_d}{OC} \cdot 100$$

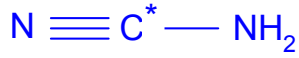
Application technique	OC [%]	K_d [L kg^{-1}]	K_{OC} [L kg^{-1}]
Standard	1.3	68	5291
Bovine test manure	4.5	49	1063
Pig test manure	3.4	36	1108

Application technique	OC [%]	K_d [L kg^{-1}]	K_{OC} [L kg^{-1}]
Standard	1.7	4.6	266
Bovine test manure	2.7	2.6	97
Pig test manure	2.6	2.1	79



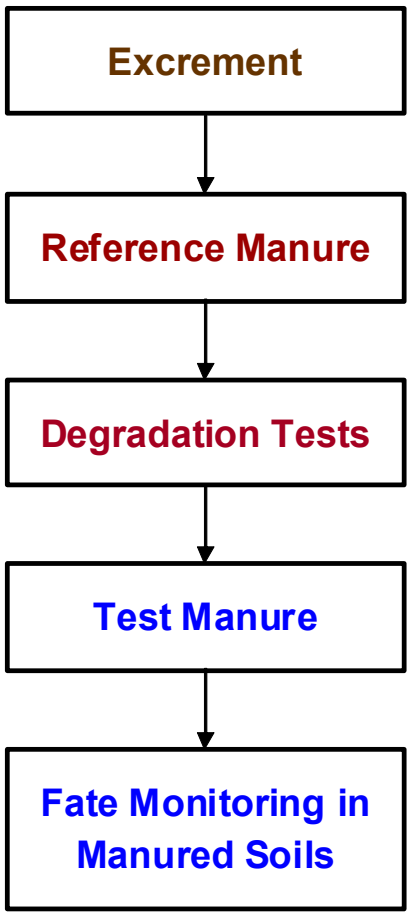
imazalil

Mobility classes (Hollis, 1991)	K_{OC} [L kg^{-1}]
immobile	> 4000
slightly mobil	500 - 4000
moderately mobil	75 - 499
mobile	15 - 74
very mobily	< 15



cyanamide

Transformation tests of VMP and biocides in liquid manures and transformation and sorption in manured soils



From excrements to reference manures:
The reference-manure concept facilitates reproducible laboratory testing at minimized experimental efforts !

Entry route and matrix effects define fate in soil:
The persistence of VMP and biocides in manures defines their entry into soil environments !

Transferability from laboratory to field:
Manure application to soil already under laboratory conditions improves understanding of VMP´s and biocides´ fate under field conditions !

Conclusion and outlook

1. The TGD of EMEA could be based on the current experiences of the Reference Manure Concept.

+ Harmonization of data sets submitted for novel VMP.
+ Minimization of experimental expenditures.
- Availability of matrix characterized excrements and reference manures.

2. The tank manure concept is preferred.

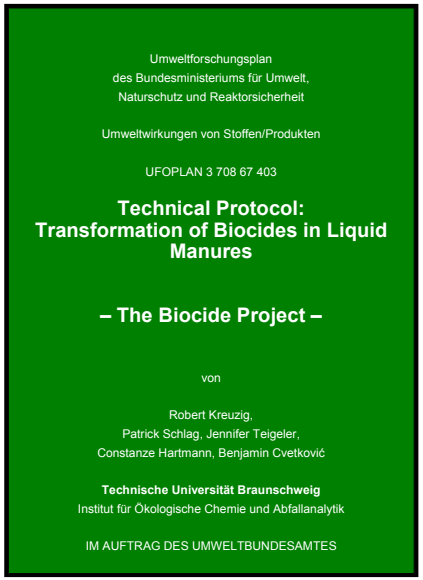
+ Higher availability of tank manures.
- Higher variabilities of matrix parameters.

3. The current experiences do not justify the TGD of EMEA.

+ A joint research project has to close the lacks.
- Time will be consumed for further 3 years.

4. The VICH concept will be continued without any change.

+ Regulatory authorities may reject submitted manure studies.
- The scientific state-of-the-art will be disregarded. Return to 2004.



available soon at
www.umweltbundesamt.de

Acknowledgments

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... and many thanks for your attention !

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