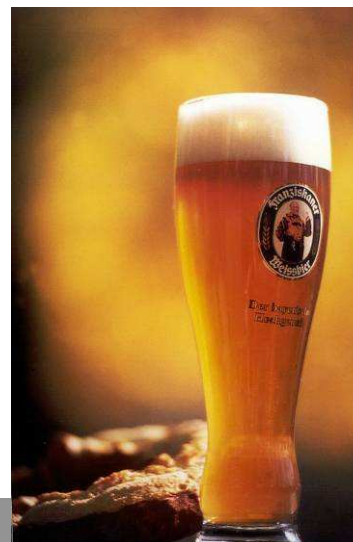
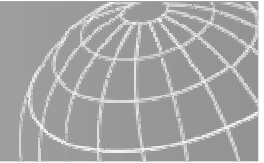


# Are pharmaceutical residues a problem for urine reuse in agriculture?

Dr.-Ing. Martina Winker, M.Sc.  
Sustainable Sanitation – ecosan program  
German Technical Cooperation (GTZ) GmbH

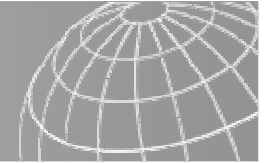




## What is a fertilizer?

- Fertilizers are substances which are determined to be applied directly or indirectly towards agricultural crops to support their growth, to enhance their yields or to improve their quality;
- Excluded are substances which are determined to protect plants from pests and diseases without supporting plant nutrition, determining plant nutrition, influencing life cycles in plants as well as soil conditioners, culture media, plant additives, carbon dioxide, peat and water.

(Düngemittelgesetz, 1977; BGBl. I S. 2134)

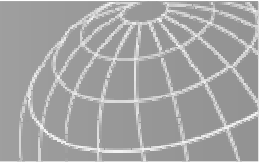


## Classification of Fertilizers

- Liquid ↔ Solid
- Mineral ↔ Organic

	Fertilizer type	
	mineral	organic
Nutrient concentration	high > 8%	low < 1-5%
Nutrient availability (Timing & Efficiency)	high	partially available N - hardly available P - medium term like MF K like MF
Soil structure	-	Improvement
CEC	-	Improvement
Hygiene	-	Treatment required
Price	high	Treatment required

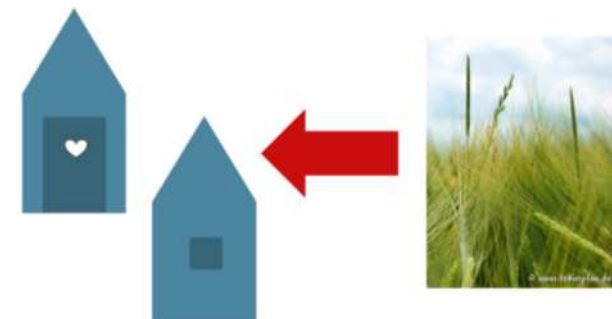
(Clemens, 2005)



## Change of perspective

Matching of capabilities of existing fertiliser application technologies:

- 10 - 50 m<sup>3</sup> ha<sup>-1</sup> – liquid fertilisers
- ≤ 40 t DM ha<sup>-1</sup> – solid fertilisers
- 100 - 600 kg ha<sup>-1</sup> – granulates





## Properties of products

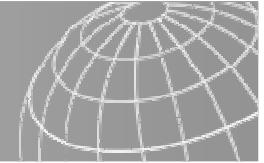
Fertilising type (FT)	Product	Level of knowledge	TS [%]	COD [g l <sup>-1</sup> ]	N [g l <sup>-1</sup> ]	P [g l <sup>-1</sup> ]	K [g l <sup>-1</sup> ]	Reference
Liquid mineral	Urine	+	1.5-3	4-11	1.8-17.5	0.2-3.7	0.7-3.3	Meininger and Oldenburg, 2008
	Concentrated urine e.g. Urevit	(+)		10	11	0.65	5.7	Boller, 2007
	Ammonia solution	(+)			120	n.r.	n.r.	Tettenborn et al., 2007
Liquid organic mineral	Digestate	-	≤ 1	2.8	1.5	-	0.14	Wendland, 2008
	Untreated sludge blackwater	-						
Solid mineral	Struvite	(+)			60	130	n.r.	Calculated stoichiometrically
Solid organic	Compost	-		100	5-20	2-4	3-10	Simons et al. (2005)
Solid organic mineral	Sludge with DM >20 %	-						



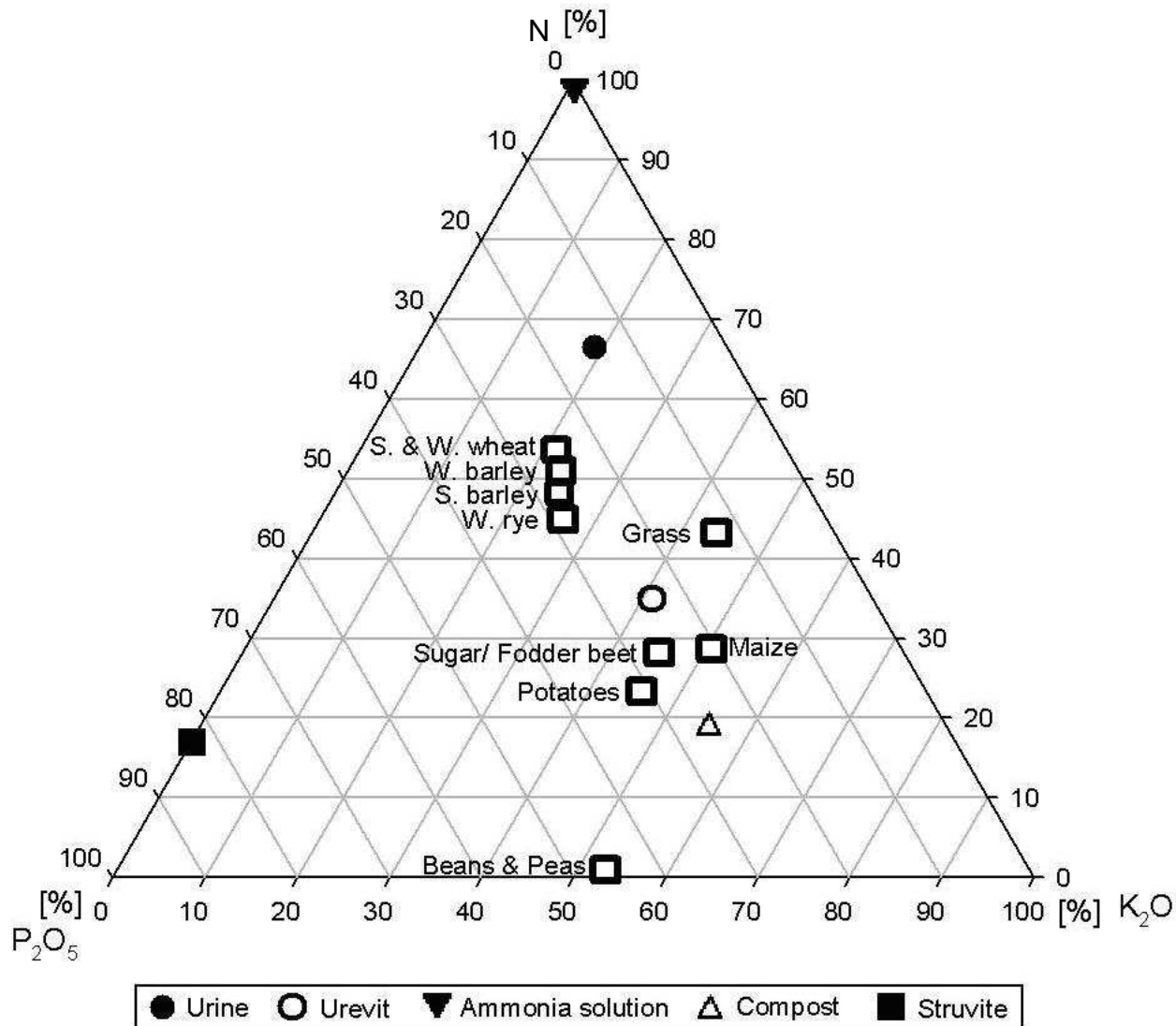
## Urine

- High concentrations of N and P as well as other nutrients
- Low ammonia emission
- Comparable to liquid manure after field application
- Multi-component fertiliser

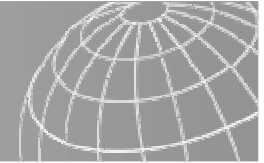




# Nutrient compositions and crop requirements







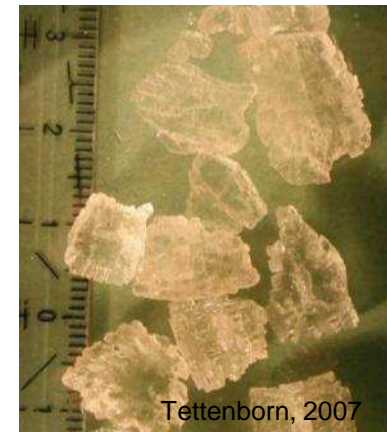
## Urine's fertiliser products

- Mostly derived in high-tech solutions
- Achieved through a combination of various treatment steps
- Limiting factor in production: energy costs
- Different plant availability of different MAP products according to specific crop (Simons, 2008)

Potassium Ammonium Phosphate



Stercorit



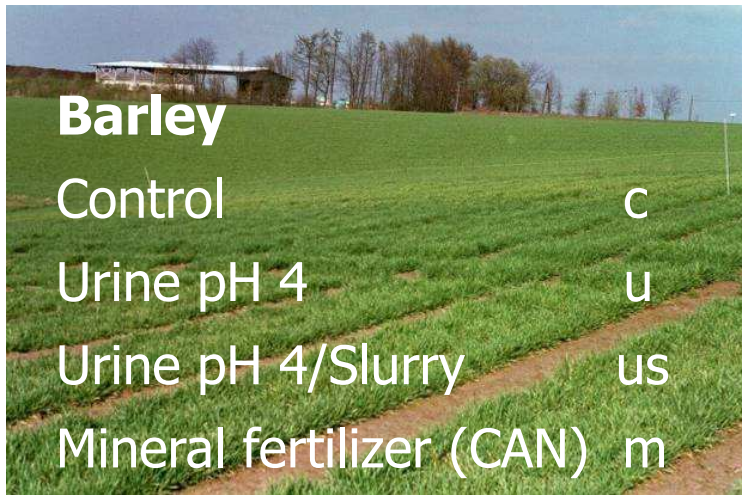
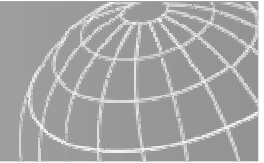


# History – E. Wolff

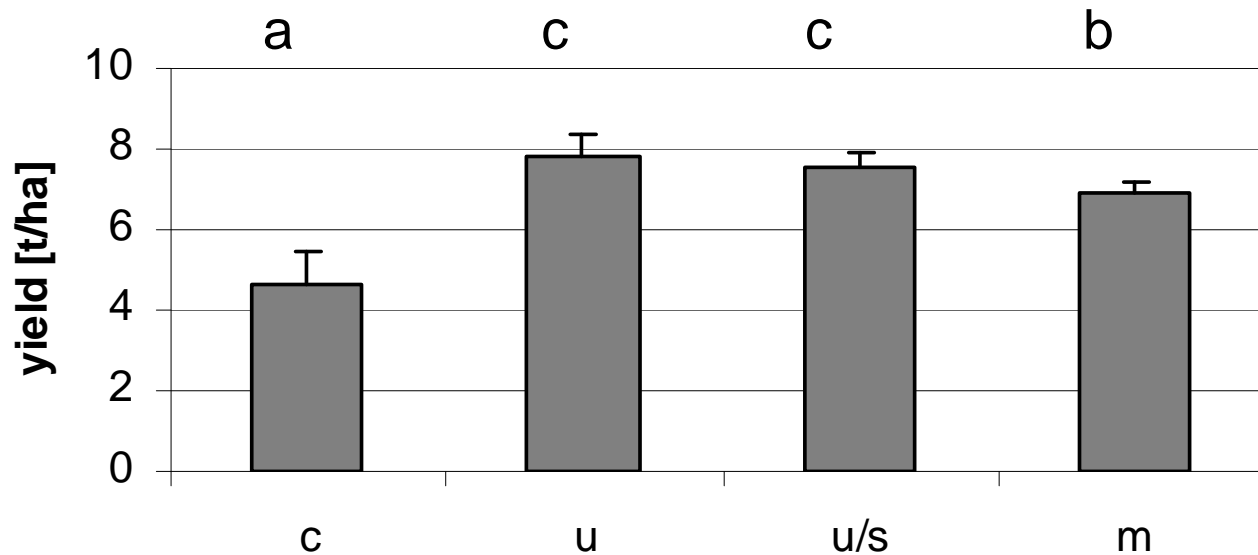
Es handelt sich in den Städten zunächst um Beseitigung der Fäkalien, also des Grubeninhalts oder Latrinendüngers. Aus zahlreichen Untersuchungen ergibt sich, daß ein Mensch (Erwachsene und Kinder zusammengerechnet) durchschnittlich im Jahr an Excrementen liefert:

	Frische Substanz.	Trocken- substanz.	Mineral- Stoffe.	Stick- Stoffe.	Phosphor- stoffe.	Kali.	Chlor- natrium.
Fäces . kg	48,5	11,0	1,65	0,75	0,5	0,25	0,15
Harn . . "	422,0	19,8	4,85	4,0	0,85	0,75	3,0
In Sa. kg	470,5	30,8	6,5	4,75	1,35	1,0	3,15
In Proz. der frisch. Subst. %	100	6,54	1,38	1,01	0,29	0,21	0,67
In Proz. der trockn. Subst. "	—	100	21,1	15,4	4,4	3,3	10,2

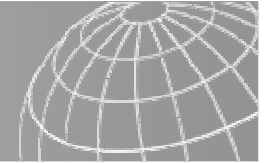
(Emil Wolff, 1868)



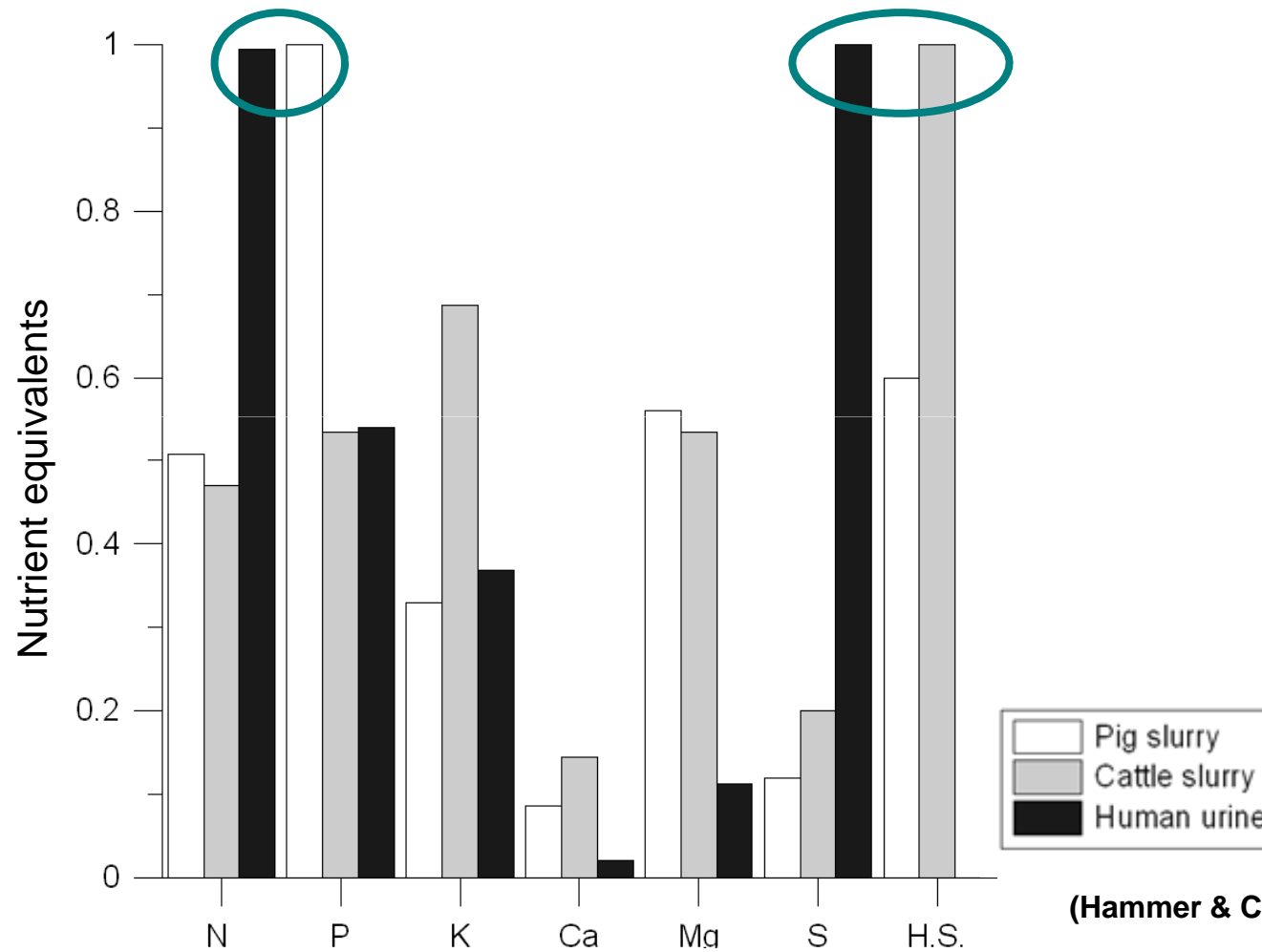
## Fertilizing Effect of Urine



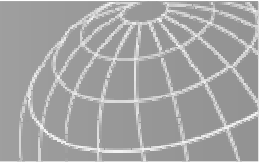
(Clemens, 2005)



## Comparison with Manure

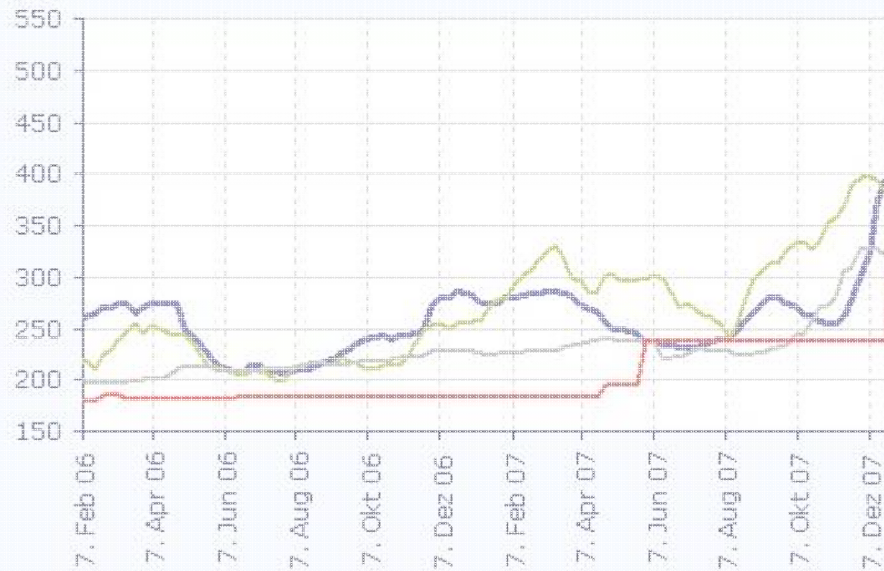


(Hammer & Clemens, 2007)



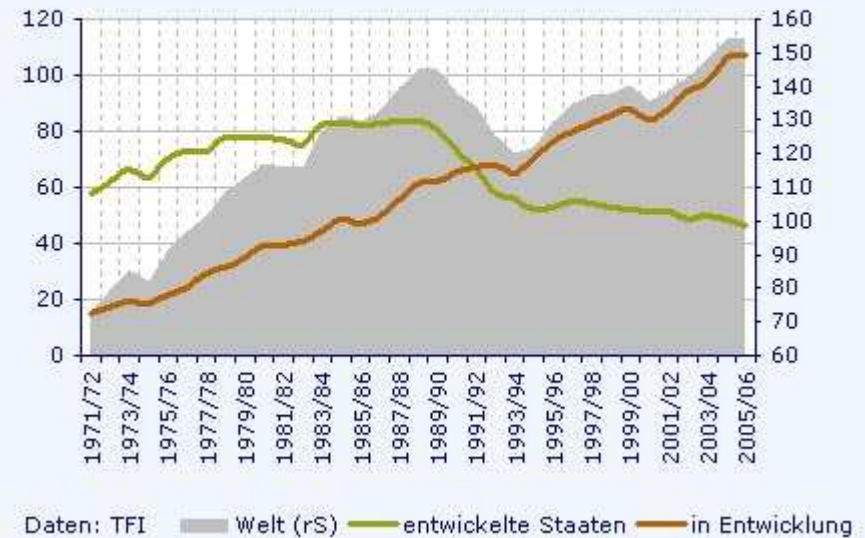
# Fertiliser demands worldwide

**Düngemittelpreise** = Fertilizer prices  
in Dollar je Tonne = \$/t



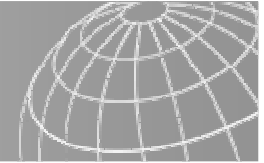
Daten: Yara — Ammonia — Urea — CAN — Phos acid (rS)

**Düngemittelverbrauch**  
in den vergangenen Jahren, in Millionen Tonnen = Mio. t

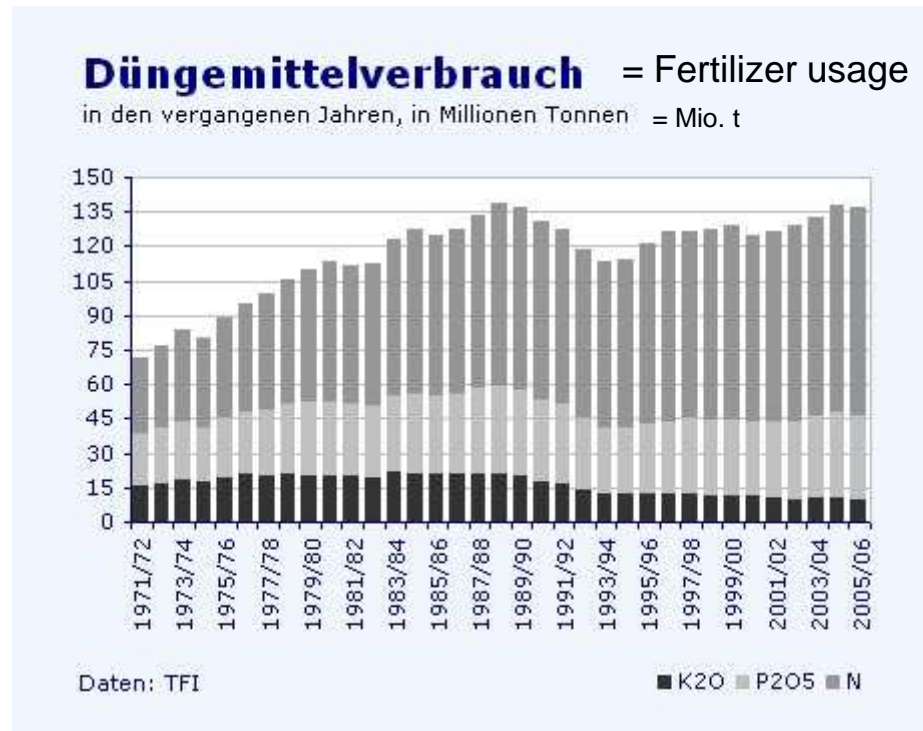
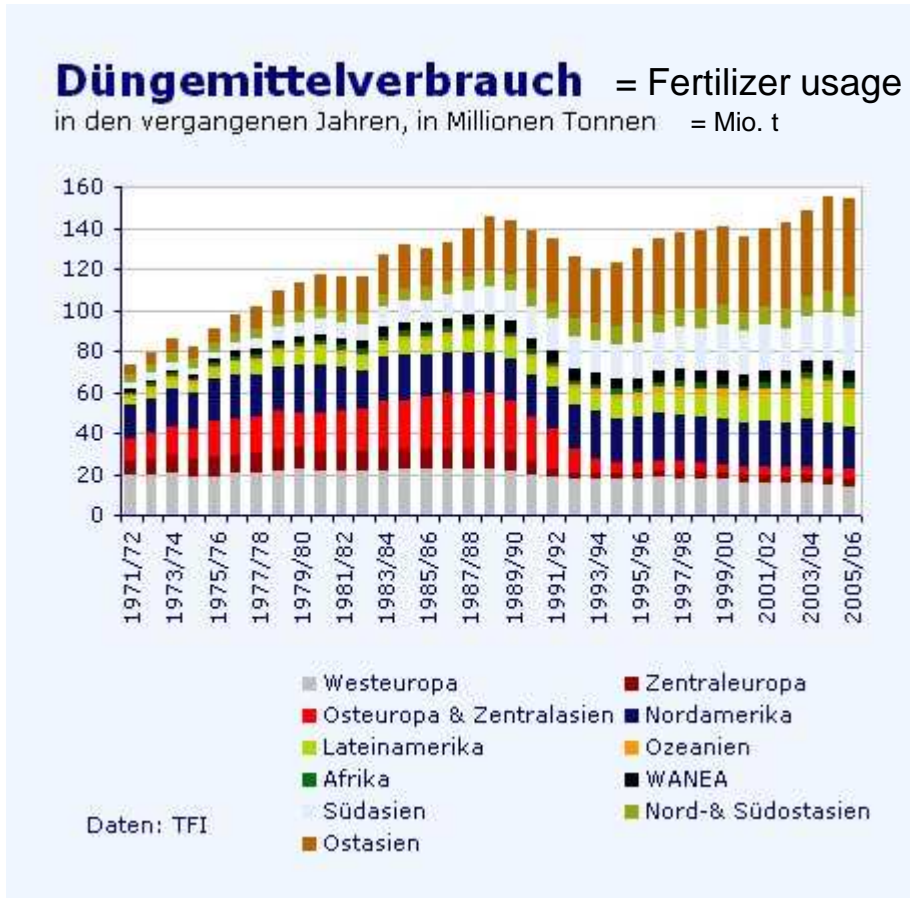


Daten: TFI — Welt (rS) — entwickelte Staaten — in Entwicklung

(FAZ.NET, 2008)



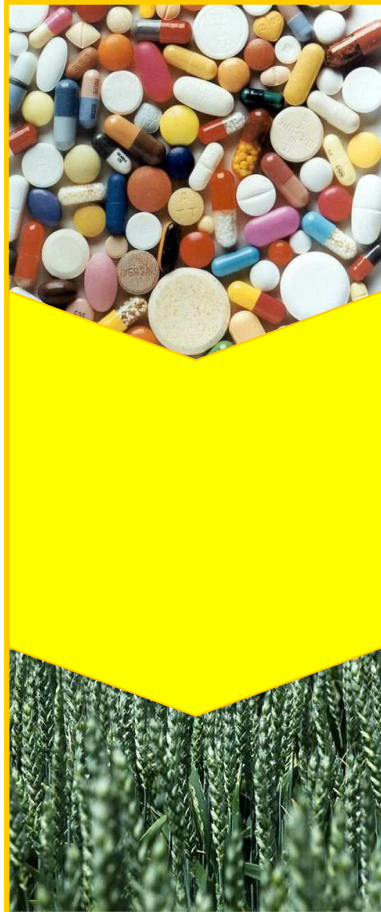
# Fertiliser demands worldwide



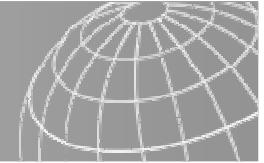
(FAZ.NET, 2008)



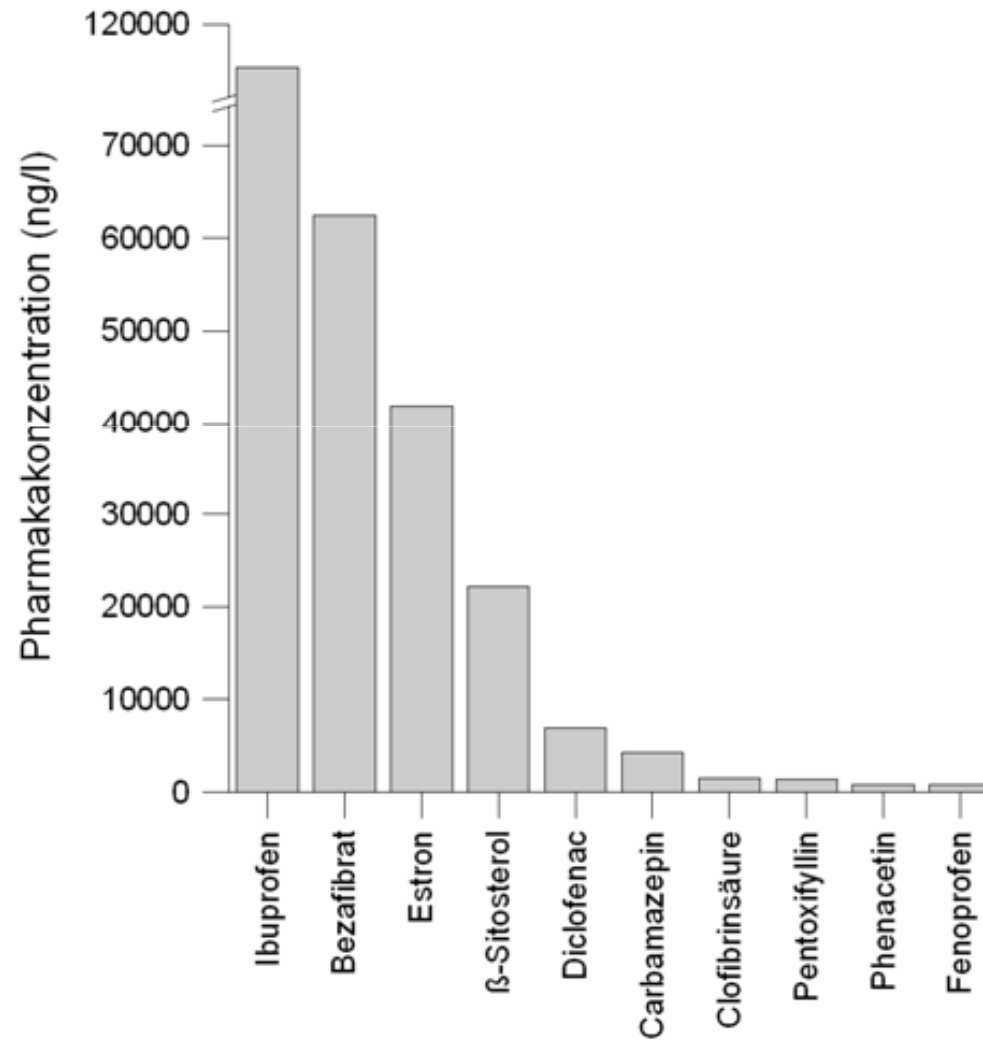
## Urine as fertiliser



- Consume of pharmaceuticals is common in everyday life.
  - Urine is a component in new sanitation systems.
- 
- Urine has a good potential as liquid fertilizer.
  - But: Urine might contain pharmaceutical substances...

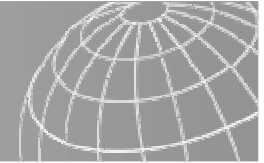


# Pharmaceuticals

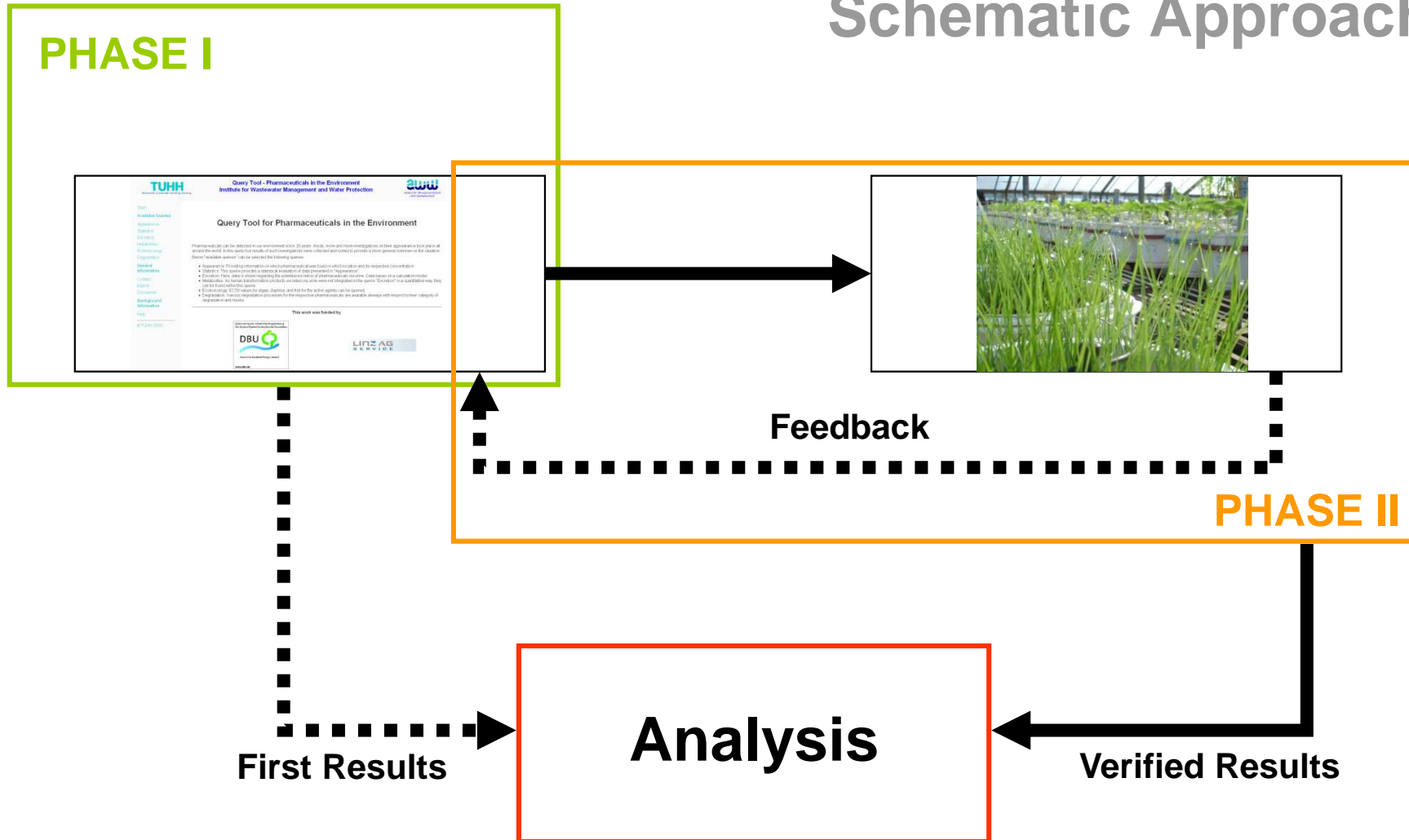


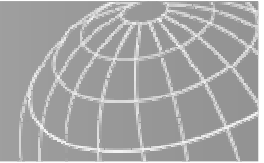
(Winker et al., 2008)



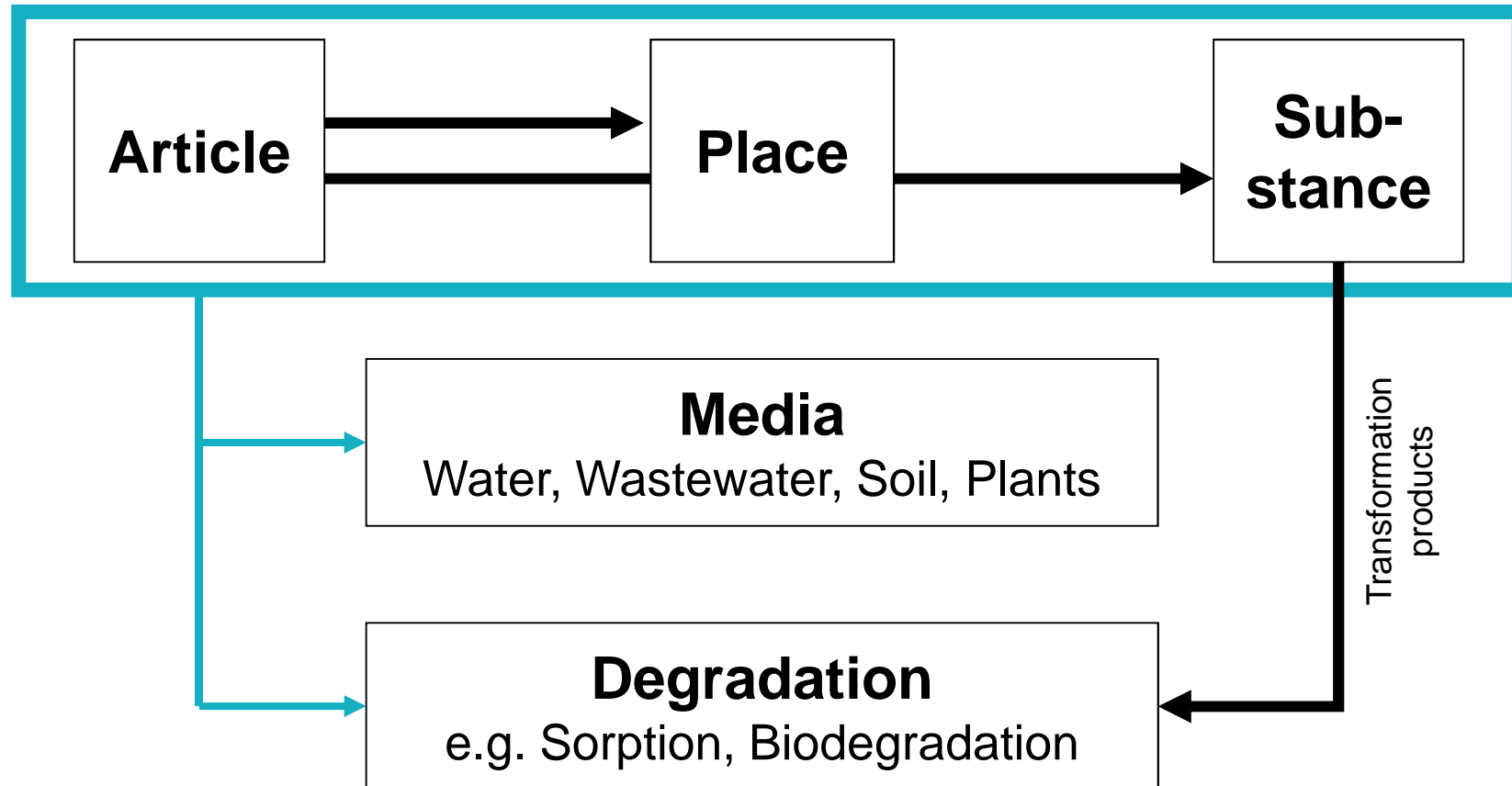


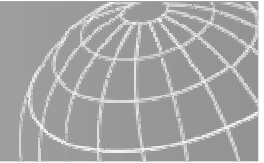
# Schematic Approach



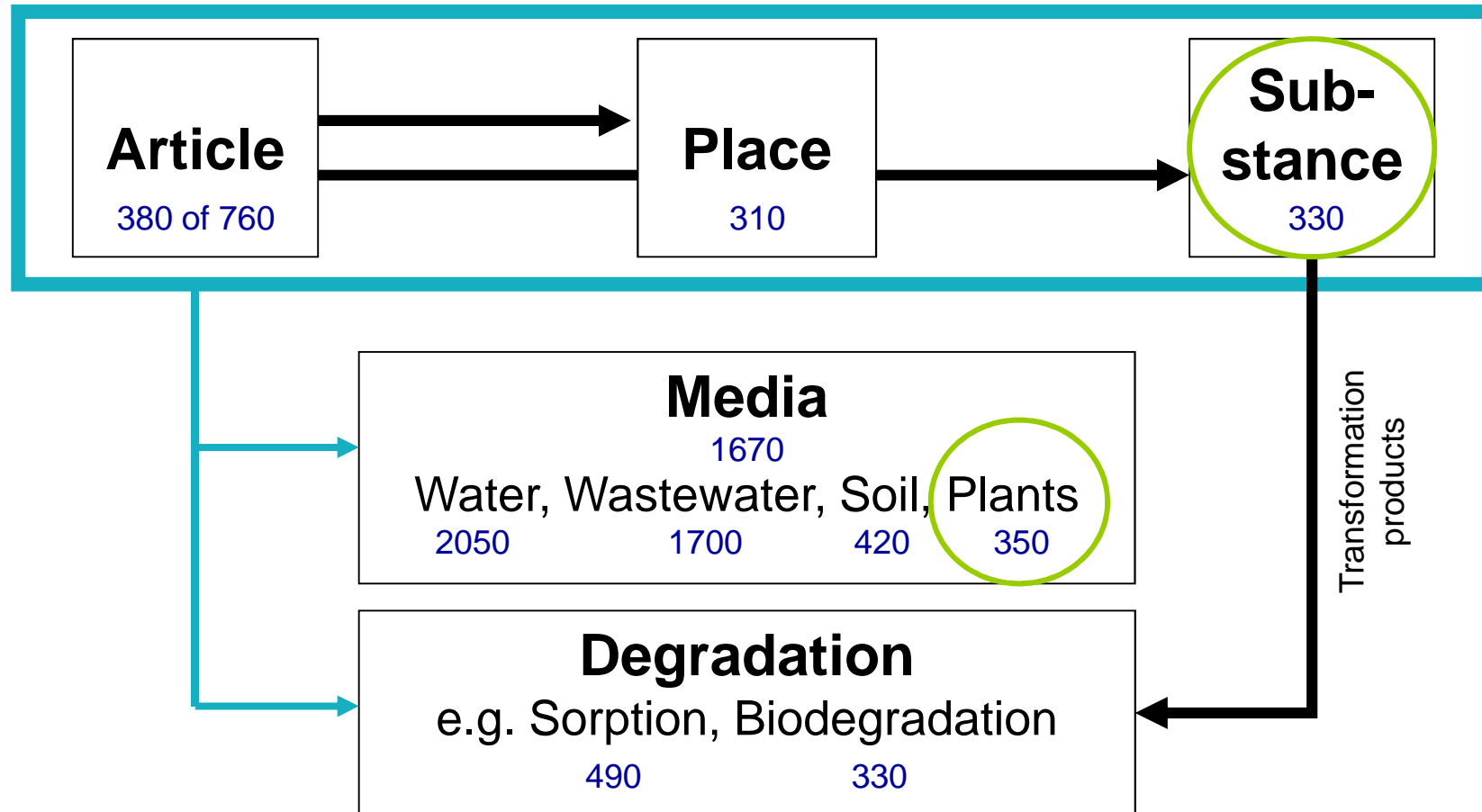


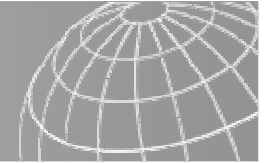
# Database





# Database

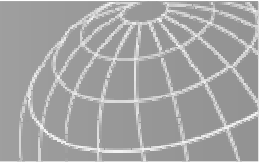




## Evaluation of Database

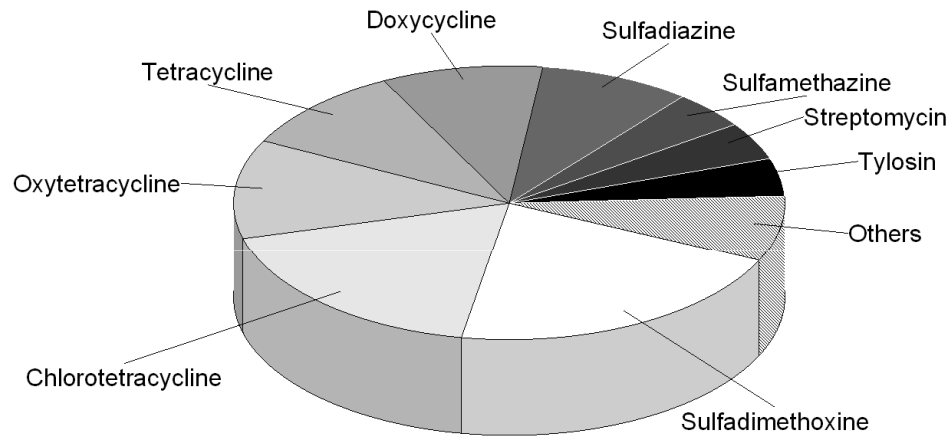
- Two aspects investigated regarding plants:  
Uptake and Phytotoxicity

	Uptake	Phytotoxicity
Datasets	162	348
Substances	14	30
Plant species	25	30
Plant families	16	11

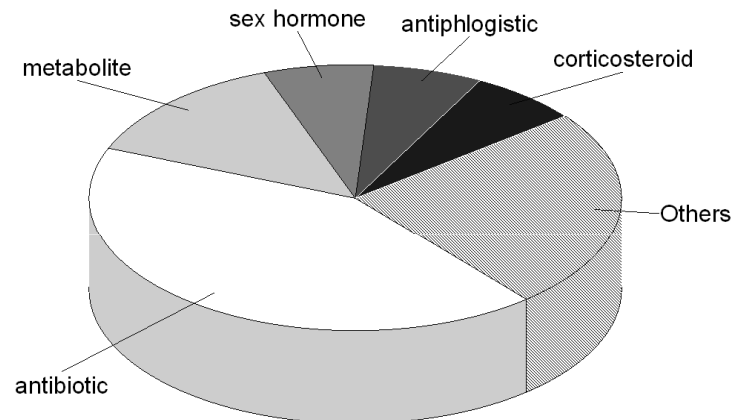


# Evaluation of Database - Substances

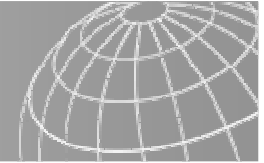
## Uptake



## Phytotoxicity

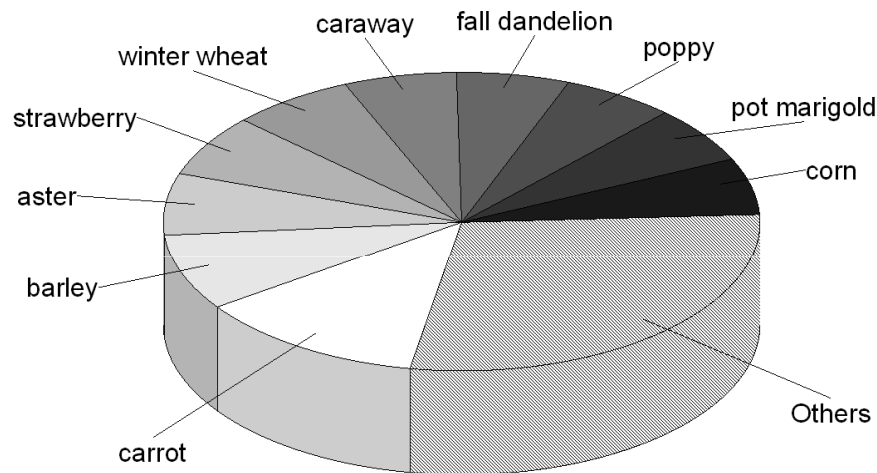


Mainly antibiotics investigated!

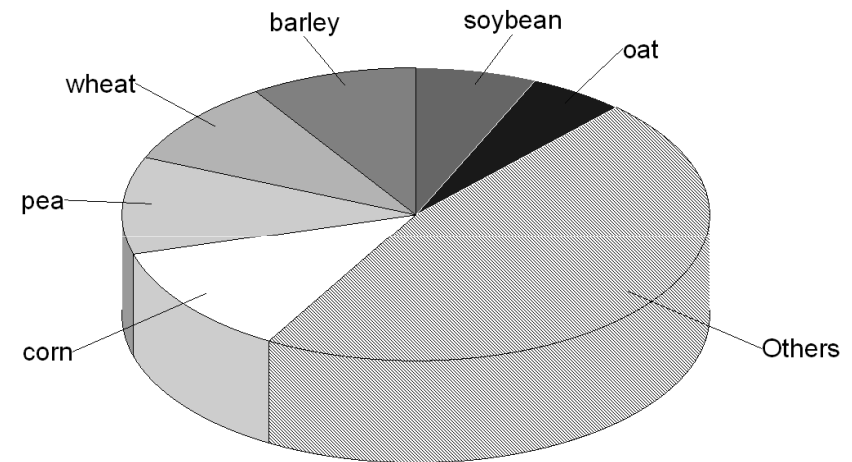


## Evaluation of Database – Plant types

Uptake



Phytotoxicity



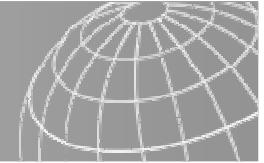
Mainly cereals and umbellifers reg. uptake.  
Mainly cereals and legumes reg. phytotoxicity.



## Evaluation of Database

- Comparison of collected data with urine
- Tests with liquid medium
  - Urine-water mix assumed
  - 112 DS - 12 pharmaceuticals
  - Only two articles comparable reporting on uptake by very old bioassays.
- Tests with solid medium
  - Application of urine:  $25 \text{ m}^3 \text{ ha}^{-1}$
  - Infiltration of 0.5 m assumed
  - 45 DS - 9 pharmaceuticals

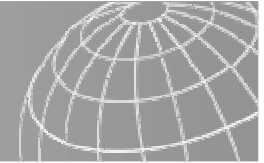
Hammer & Clemens. 2007. A tool to evaluate the fertilizer value and the environmental impact of substrates from wastewater treatment. *Water Science & Technology* 56 (5), pp 201 – 209



## Evaluation of Database

Substance	Plant species	Reported impacts	Factor (DB/U)
Chloroquine	soybean	Phytotoxic: neg. on w, h, r, s, l	182
Chlorotetracycline	spring wheat	Phytotoxic: pos. on h, r	82
Chlorotetracycline	pinto bean	Phytotoxic: neg. on w, h, r, s, l	82
Chlorotetracycline	green onion	Bioaccumulation: 0.013 ng kg <sup>-1</sup> FW in stalk & leaves	51
Chlorotetracycline	cabbage	Bioaccumulation: 0.01 ng kg <sup>-1</sup> FW in stalk & leaves	51
Metronidazole	soybean	Phytotoxic: neg. on w, h, r, s, l	67
Oxytetracycline	spring wheat	Phytotoxic: pos. on h, r	2
Oxytetracycline	pinto bean	Phytotoxic: neg. on w, h, r, s, l	2





## Evaluation of Database

- **Pharmaceuticals found in guttation drops.**  
(Stokes, 1954; Brian et al., 1951;)
- **Uptake via peel observed for carrots and potatoes.**  
(Dolliver et al., 2007; Boxall et al., 2006)
- **Different behavior regarding pharmaceutical substances by different plants.**  
(Batchelder, 1982)
- **Uptake of oxytetracycline detected in barley grain.**  
(Jacobsen et al., 2004)



Applied amount are much higher then in case of fertilization with urine.

# Design of Pot Experiments with Rye Grass



Winker et al. 2008. Fertilisation of rye grass using urine spiked with carbamazepine, ibuprofen, and 17 $\alpha$ -ethinylestradiol – a greenhouse experiment. *Handed in.*

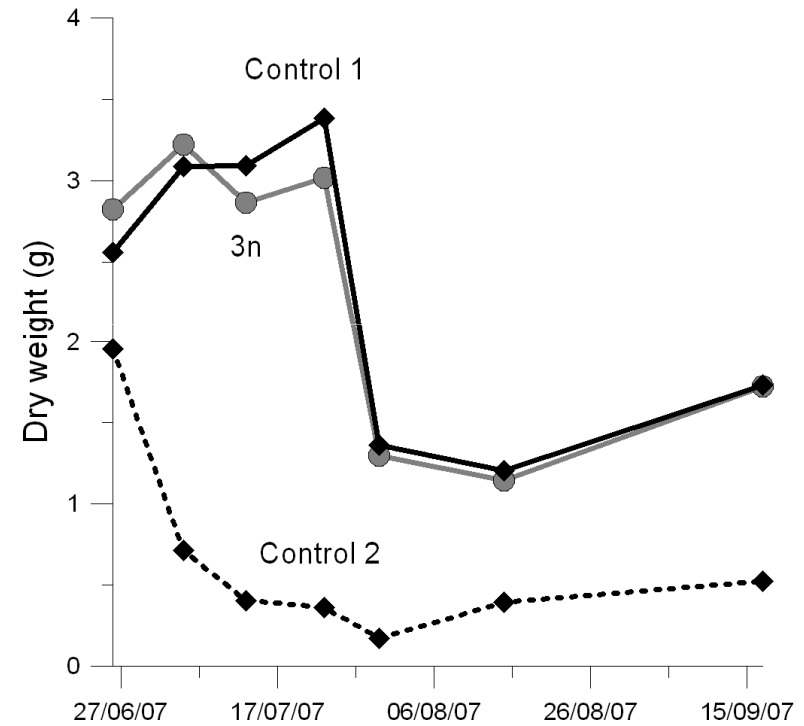
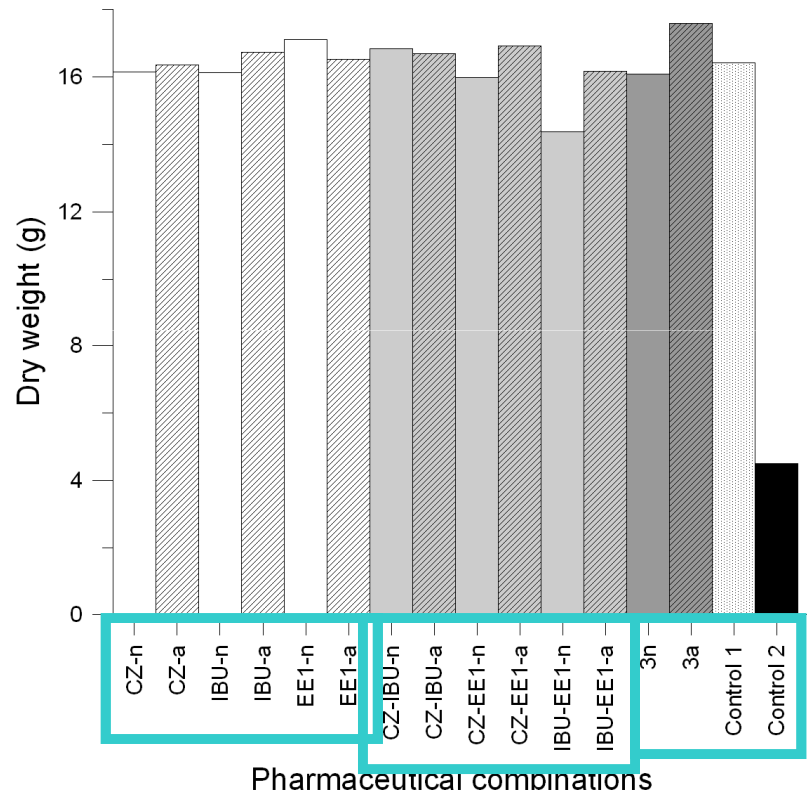
## Results of Pot Experiments

- Only Carbamazepine (CZ) found in soil.
- No effect on biomass production visible.
- Aside of well-known fertilizing effect of urine.
- No differences of biomass production course of the vegetation period
- Analytics: (Reich & Er)

  - EE2 not measurable (matrix effects)
  - IBU only in roots (LOQ:  $20 \mu\text{g kg}^{-1}$  TM)
  - CZ – LOQ in roots:  $30 \mu\text{g kg}^{-1}$  TM
    - LOQ in aerial plant parts:  $75 \mu\text{g kg}^{-1}$  TM

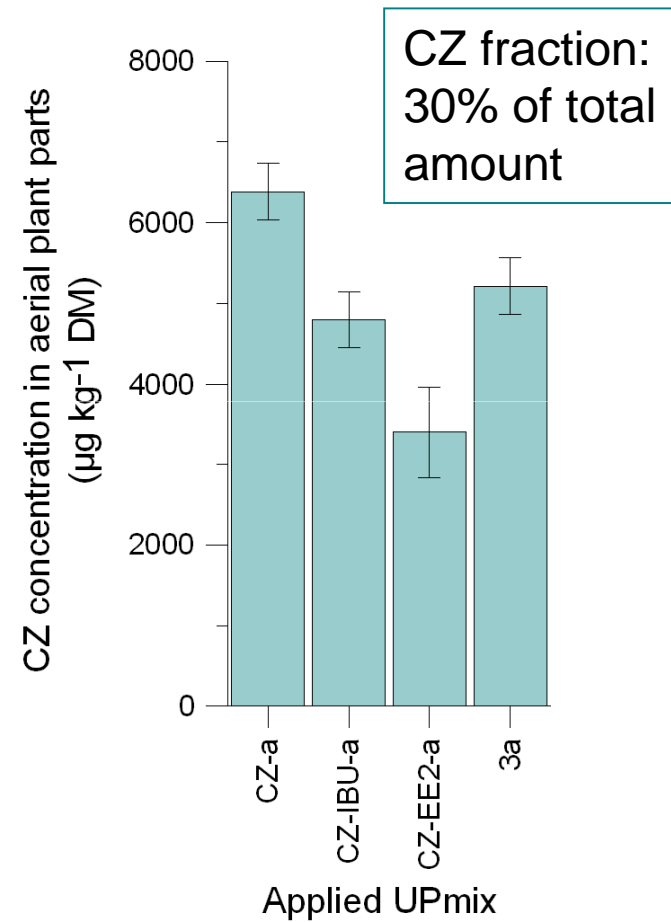
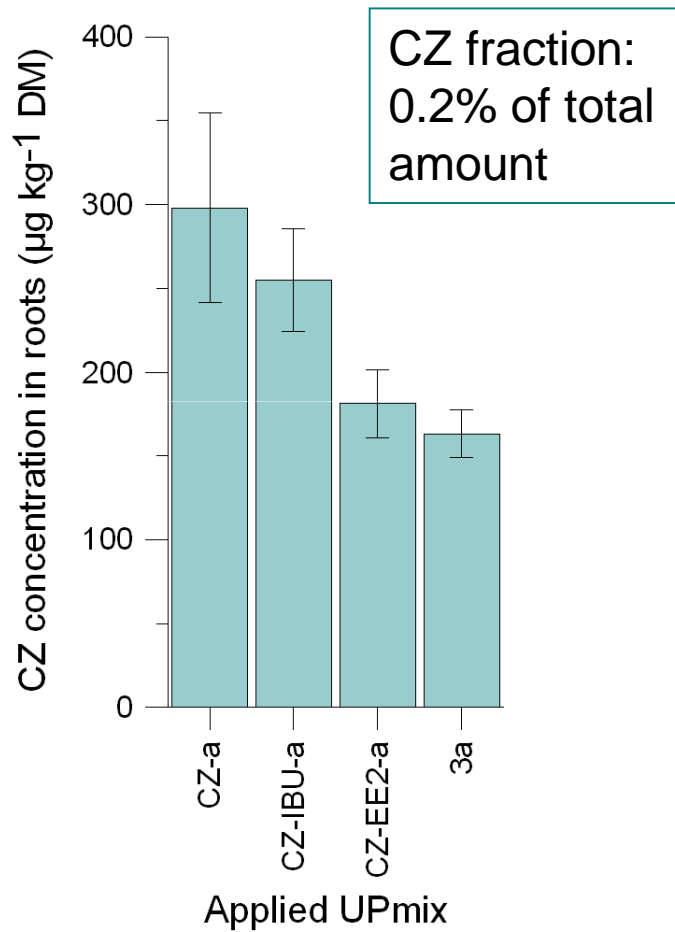


# Plant Tests with Rye Grass



(Winker et al., 2008)

# Results of Pot Experiments



## Results of Pot Experiments



**Dairy Cow**  
(Weight: 600 kg / Milk production: 50 kg d<sup>-1</sup>)

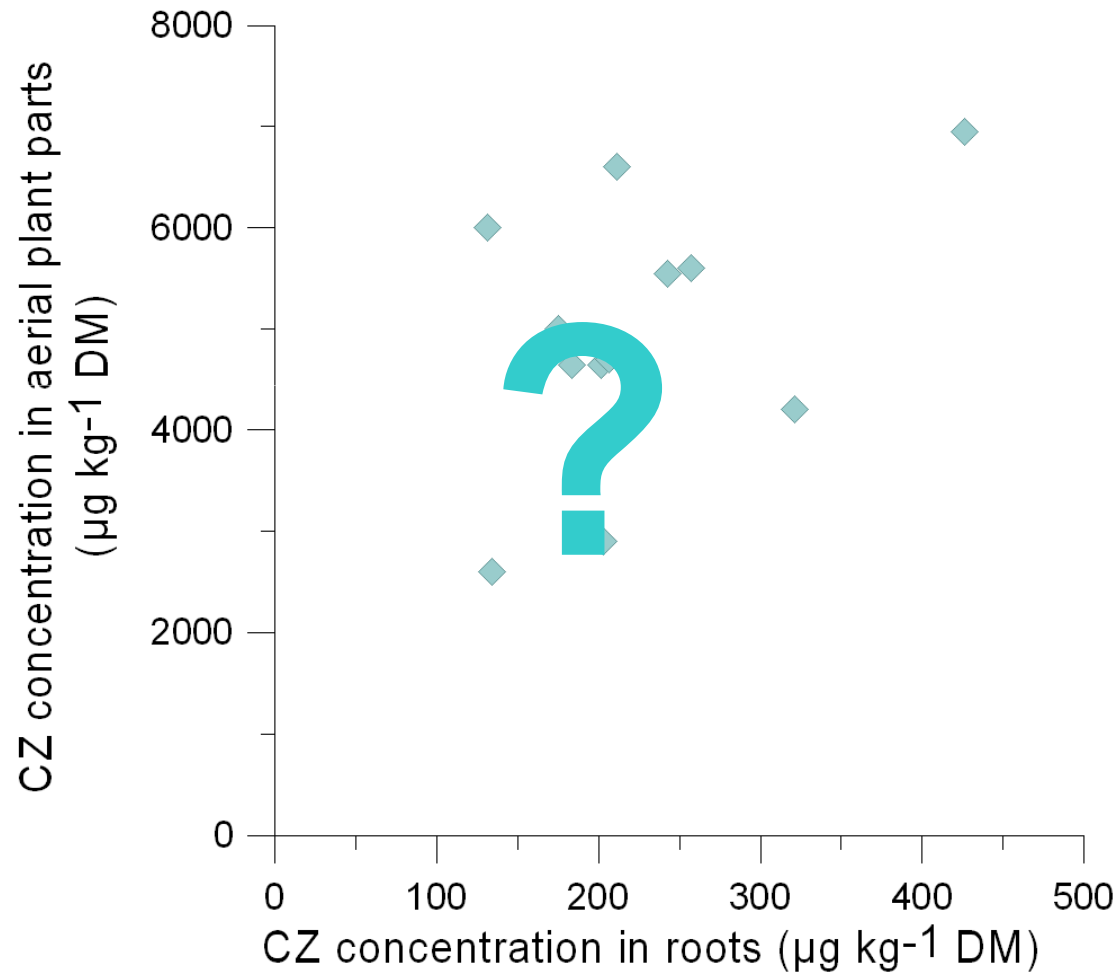
Dry matter: approx. 10 kg d<sup>-1</sup> (DLG, 2005)

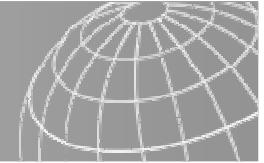
CZ uptake: 1.4 mg d<sup>-1</sup>

Human being: 0.8 - 2 g d<sup>-1</sup> (Mutschler et al., 2001)

Kanton Solothurn, 2007

# Results of Pot Experiments





## Pot experiments

- Biodegradation seems to be an important factor.
- Biomass production was not influenced in the pharmaceutical concentrations applied via urine.
- CZ was found in roots and aerial plant parts of rye grass.
- Assumption: Pharmaceutical substances persistent in soil can be taken up by plants in higher concentrations.



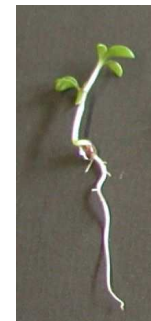
Only first results!!!



## Germination Tests

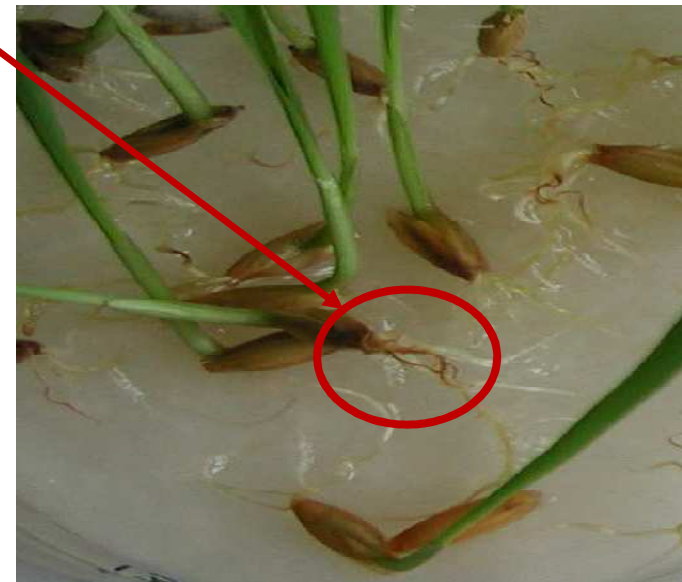
- 5 pharmaceuticals used
- At different concentration levels to identify phytotoxicologic effects.
- Duration of test: 10 days
- Applied in a water-urine-mix
- Evaluated: successful germination and dry weight

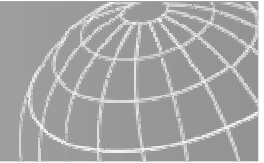
Winker et al. 2008. Comparison of analytical and theoretical pharmaceutical concentrations in human urine in Germany. *Water Research* 42 (14), pp. 3633 -3640.



## Results and discussion

Roots of winter barley in contact with ibuprofen.



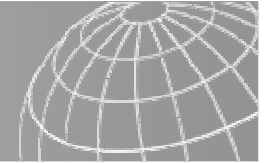


## Germination Tests

- The different types of cereals as well as cress react differently.
- Application of urine had a much larger effect on germination.
- It seemed that certain pharmaceutical substances might even have a positive effect.

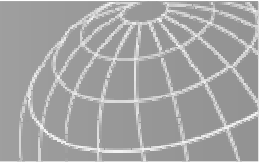


An effect on germination due to “naturally” expected pharmaceutical concentrations in urine is not expected.



## Conclusion I

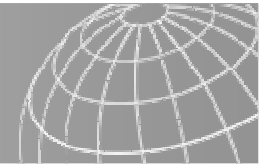
- An evaluation of potential toxic effects for human beings is not possible at the moment.
- If urine is reused in agriculture, some of the pharmaceutical residues will enter the human food chain.
- Moreover, research carried out so far shows that the expected concentrations of pharmaceutical residues in average urine do not reach concentration levels which affect plant growth and development.
- Load of hormones and antibiotics in human urine are much lower than in animal manure which is already used in agriculture.



## Conclusion II

Statement of Jörn Germer (cited in von Münch and Winker (2009))

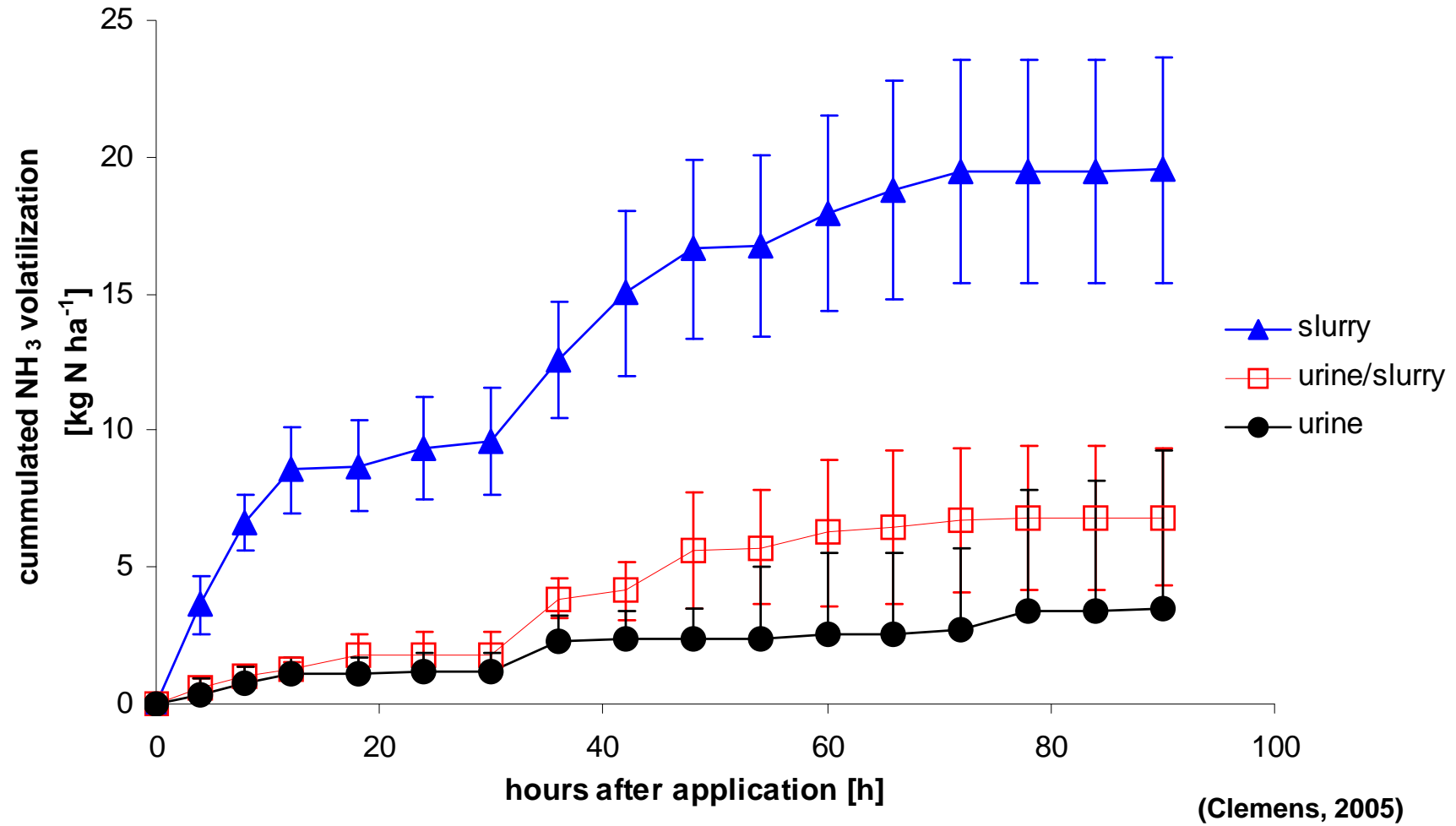
*“Drug residues in sustainable sanitation products used to supply plant nutrients can hardly be a serious issue in regions where malnutrition, groundwater and surface water pollution due to inappropriate sanitation and irrigation with untreated wastewater is a reality”.*

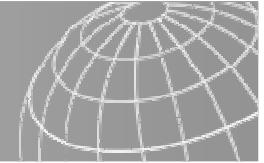


GRACIAS!

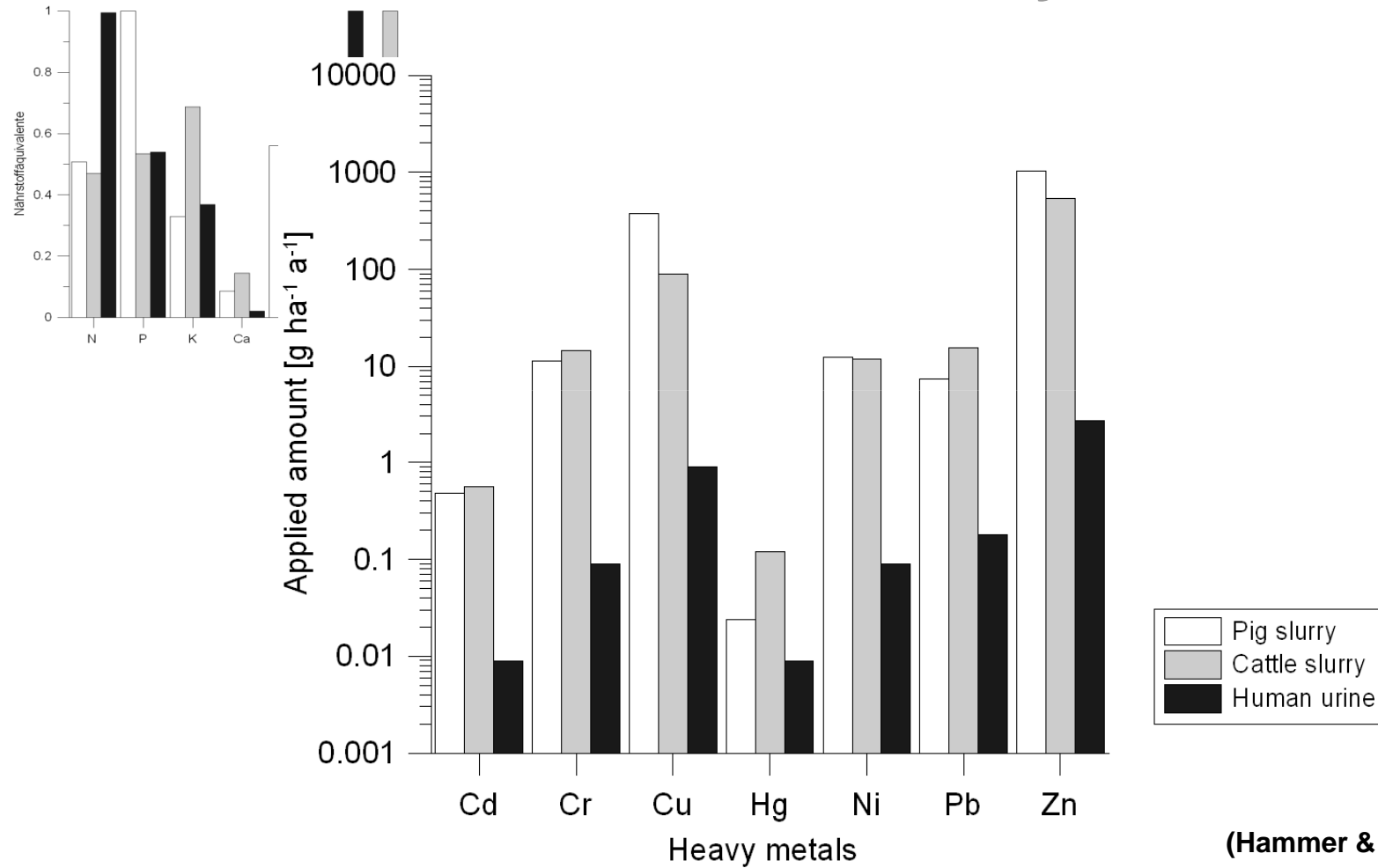


# NH<sub>3</sub>-Emissions





# Micro nutrients vs. Heavy Metals



(Hammer & Clemens, 2007)