Landesamt für Natur,
Umwelt und Verbraucherschutz
Nordrhein-Westfalen

Veterinary Pharmaceuticals in slurry, soils manured with slurry, ground water and vegetables

Dr. Annegret Hembrock-Heger
Mathilde Nießner
Christiane Ratsak
Rolf Reupert
Dr. Barbara Guhl

Structure of presentation

- Introduction
- Veterinary Pharmaceuticals in slurry (2009)
- Veterinary Pharmaceuticals in soils and groundwater (2008)
- Veterinary pharmaceuticals in vegetables (2011)
- Conclusion

Introduction

- **Veterinary pharmaceuticals are widely used in livestock husbandry.**
- **For decades slurry has been applied to agricultural fields as a sustainable principle of recycling of nutrients.**
- **To assess the concentrations of veterinary pharmaceuticals in North Rhine-Westphalia a literature study has been carried out in 2007 to identify environmentally relevant substances.**

  http://www.lanuv.nrw.de/veroeffentlichungen/fachberichte/fabe2/fabe2.pdf

- **Tetracyclines, sulphonamides and fluoroquinolones have been identified as environmentally relevant veterinary pharmaceuticals.**

Veterinary Pharmaceuticals in slurry

To assess the concentrations of tetracyclines, sulphonamides and fluoroquinolones in slurry and digestates in North Rhine-Westphalia a screening has been carried out in 2009:

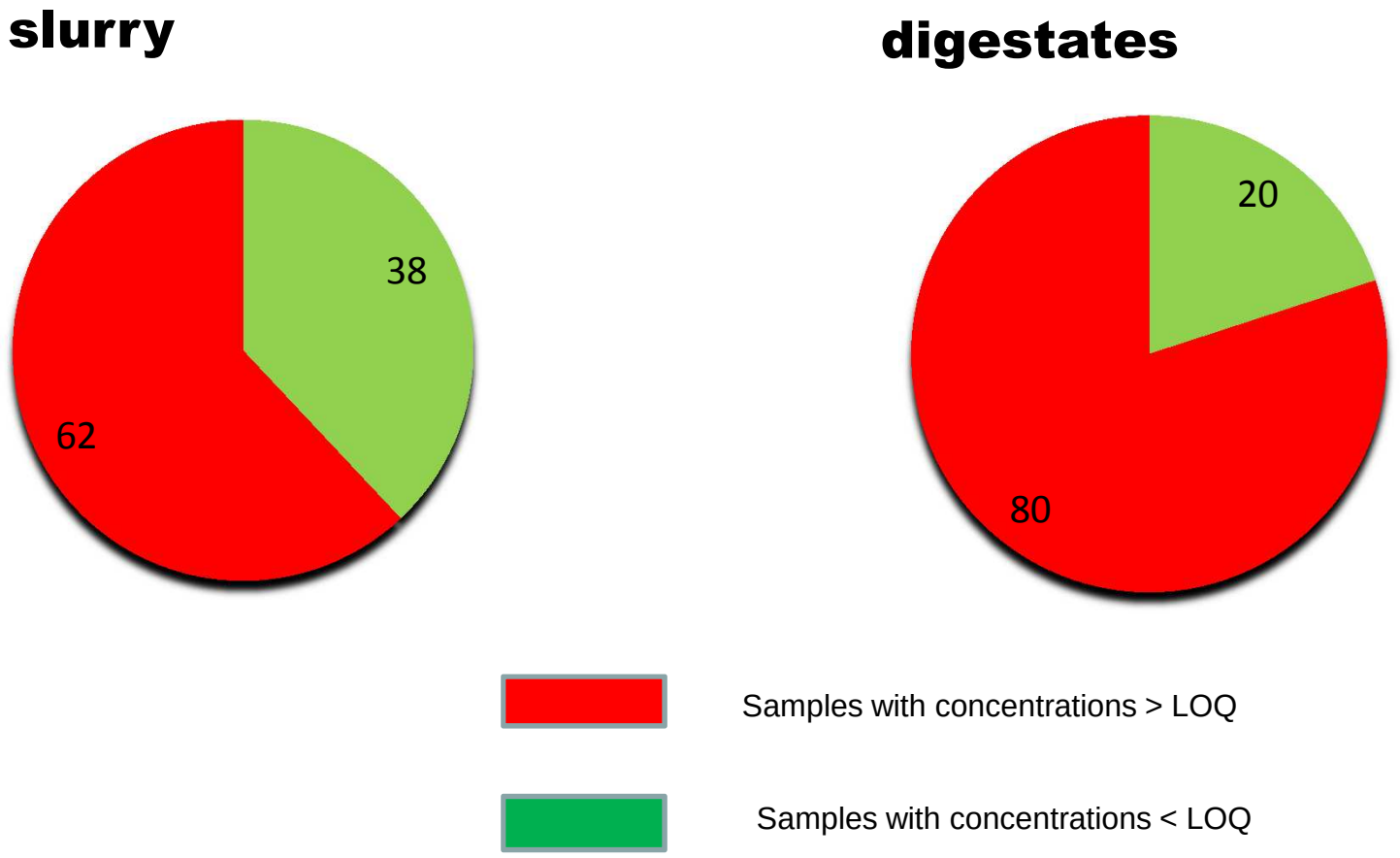
From october to december 2009 34 samples of slurry:

- Pig slurry (17)
- cattle slurry (10)
- poultry slurry (7)

and 35 digestate-samples have been investigated.

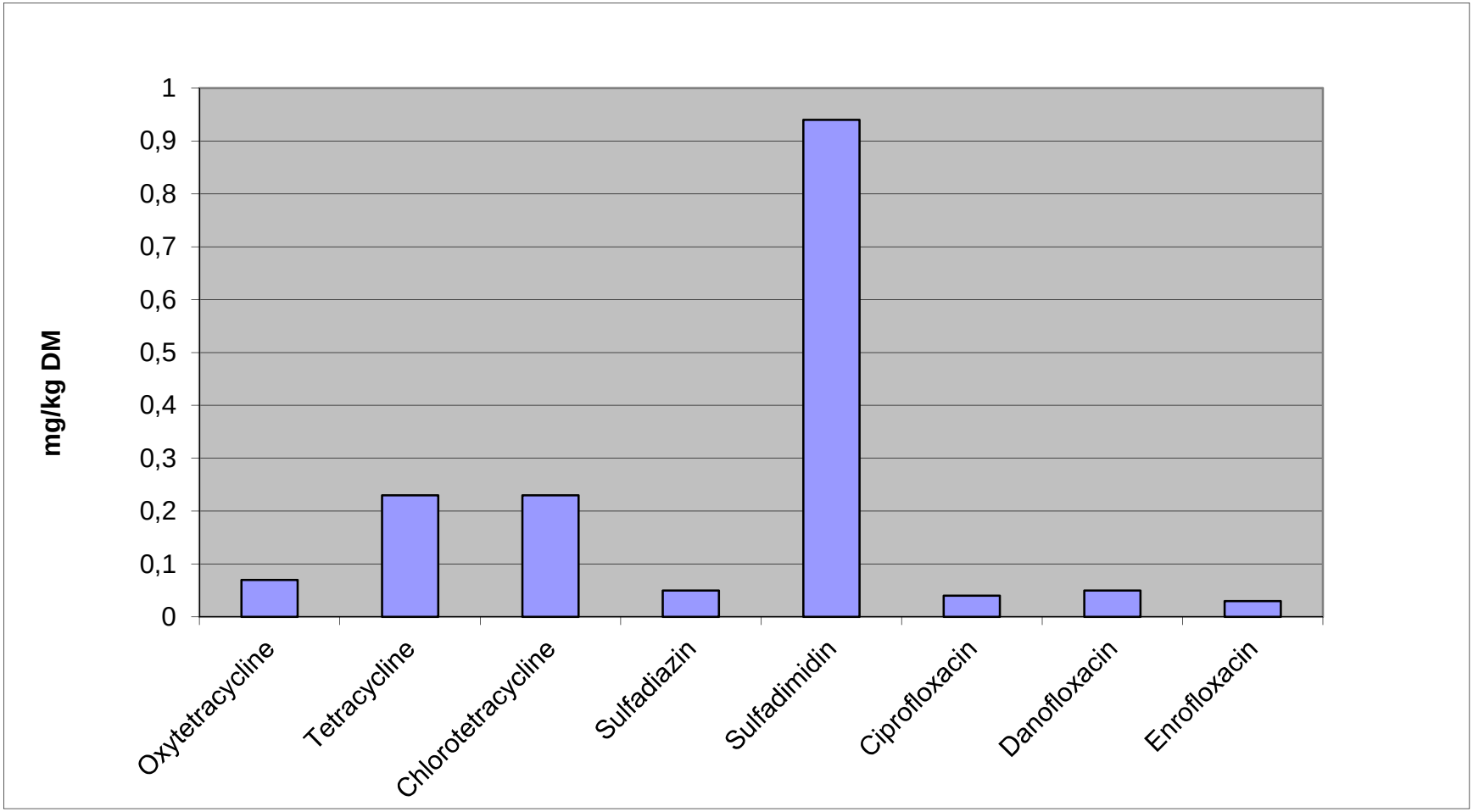
Veterinary Pharmaceuticals in slurry

Percentage of veterinary pharmaceuticals in slurry and digestates



Veterinary Pharmaceuticals in slurry

Veterinary pharmaceuticals in slurry from North Rhine-Westphalia, 2009 (n=34)
Median values of the samples with concentrations > LOQ



Veterinary Pharmaceuticals in soils and groundwater

To assess the concentrations of veterinary pharmaceuticals in soils and groundwater soils manured with slurry and groundwater in the catchment area of these plots have been investigated at 21 sites in North Rhine-Westphalia from october to december **2008**.

I. Sampling of **groundwater** from 21 selected measuring points of groundwater

Criteria for selection:

1. High amounts of animals per hectare
2. High concentrations of nitrate and ammonium in groundwater
3. Low distance between soil surface and groundwater surface

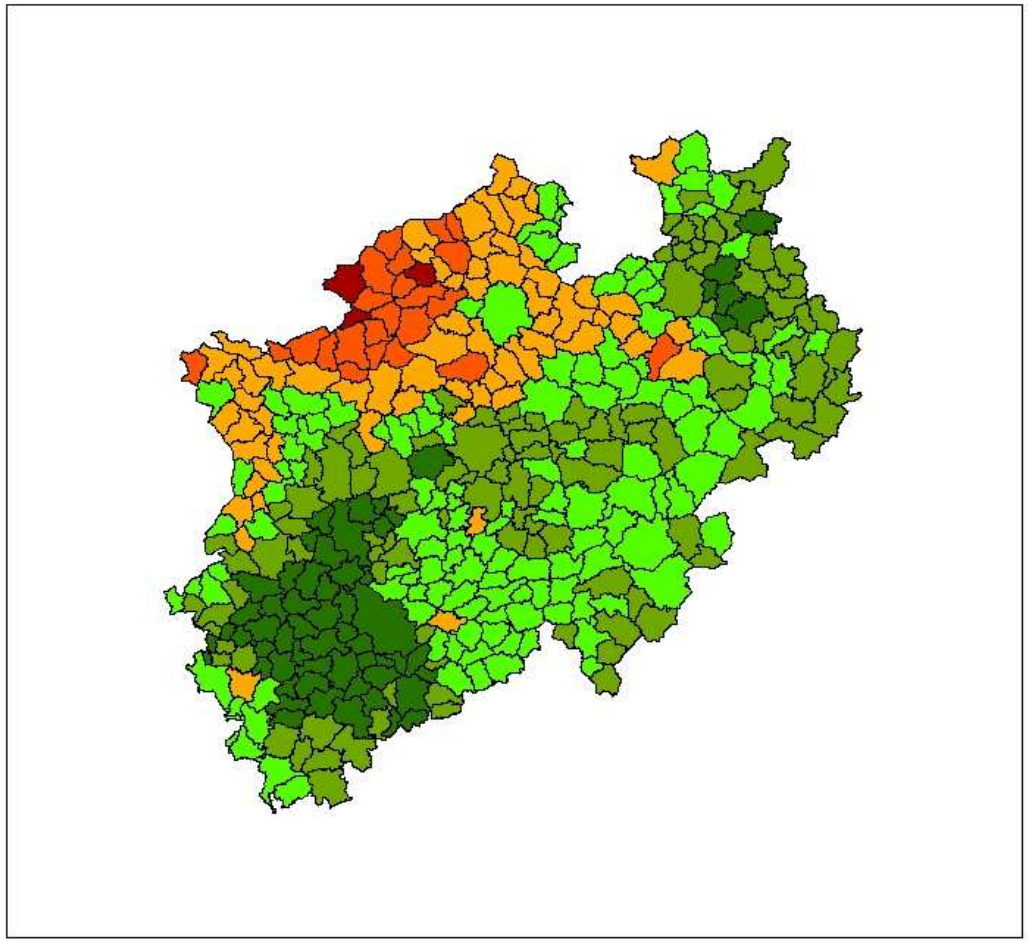
II. Sampling of 3 **soil** samples respectively at 21 sites from the depth: 0 - 30 cm, 30 – 60 cm and 60 – 90 cm

Veterinary Pharmaceuticals in soils and groundwater

Amounts of animals per hectare

Viehbesatz in NRW 2003

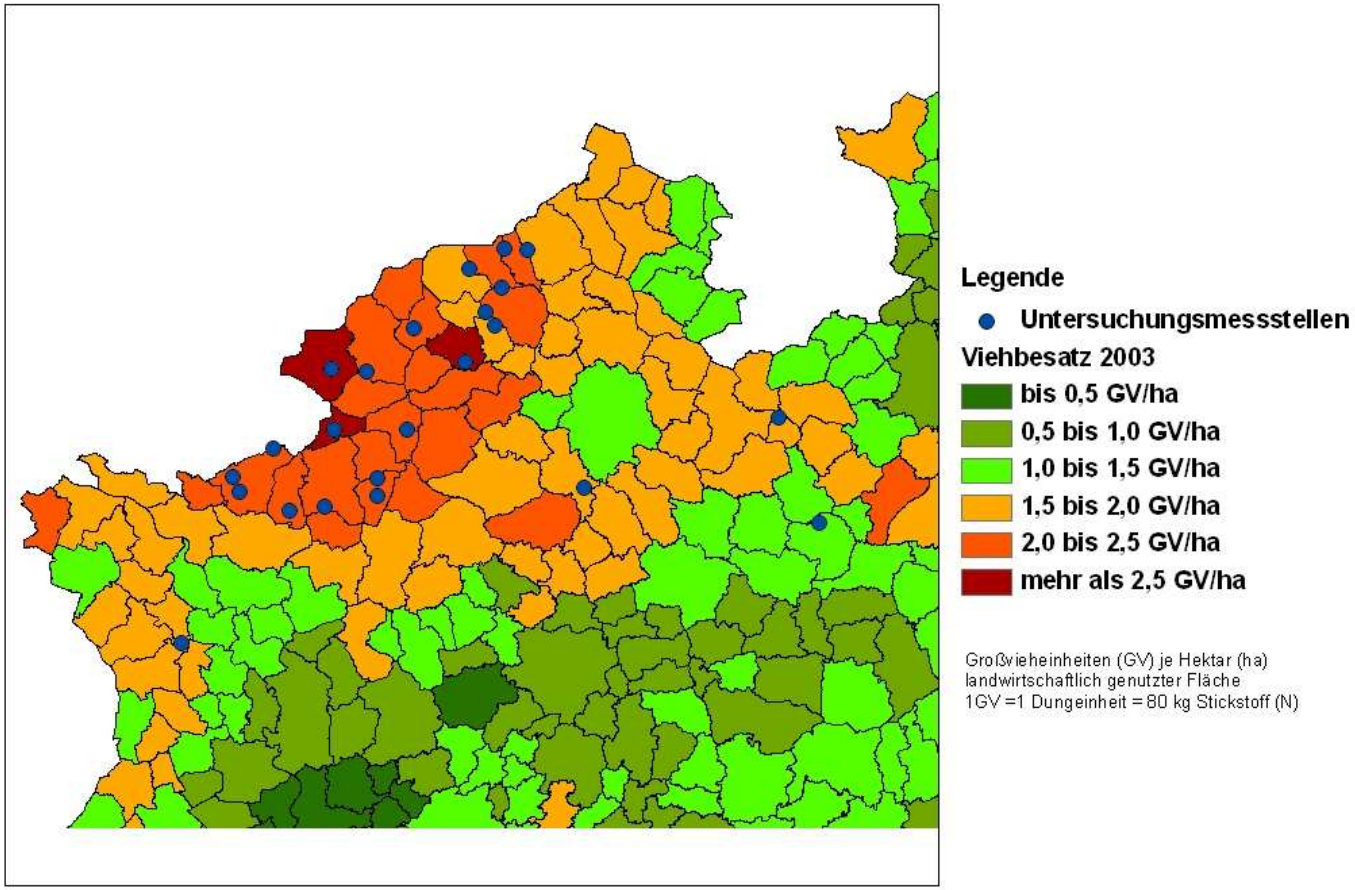
Großvieheinheiten (GV) je Hektar (ha) landwirtschaftlich genutzter Fläche
1GV =1 Dungeinheit = 80 kg Stickstoff (N)



Veterinary Pharmaceuticals in soils and groundwater

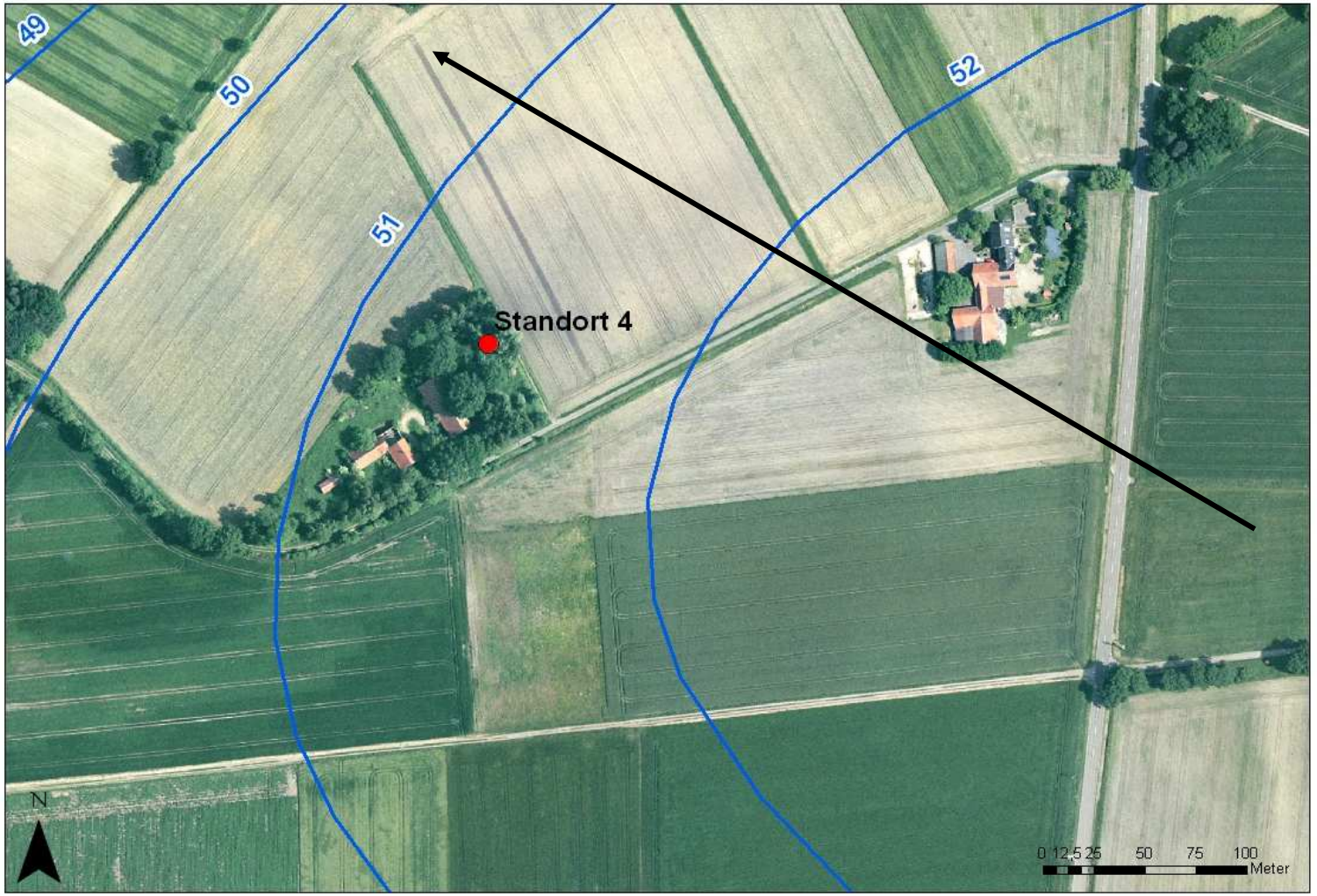
Selected measuring points of groundwater

Ausgesuchte Grundwassermessstellen für Tierarzneimitteluntersuchungen



Veterinary Pharmaceuticals in soils and groundwater

location of measuring point of groundwater, direction of flow of groundwater and the location of the agricultural land manured with slurry at one site



Veterinary Pharmaceuticals in soils and groundwater

Results
- groundwater -

- In 21 samples of groundwater tetracyclines and fluoroquinolones could not be detected (LOQ: 0,05 µg/l)
- Sulphonamides could not be detected in 20 of a total of 21 samples (LOQ: 0,05 µg/l)
- In one groundwater-sample sulfamethoxazol has been detected (2008: 0,30 µg /l; follow-up-sampling 2009: 0,37µg/l) but the other sulphonamides were below LOQ
- The concentrations of all sulphonamides in soil in the catchment area of this measuring point of groundwater were below LOQ (5 µg/kg DM). The source for sulfamethoxazol in groundwater could not be detected.

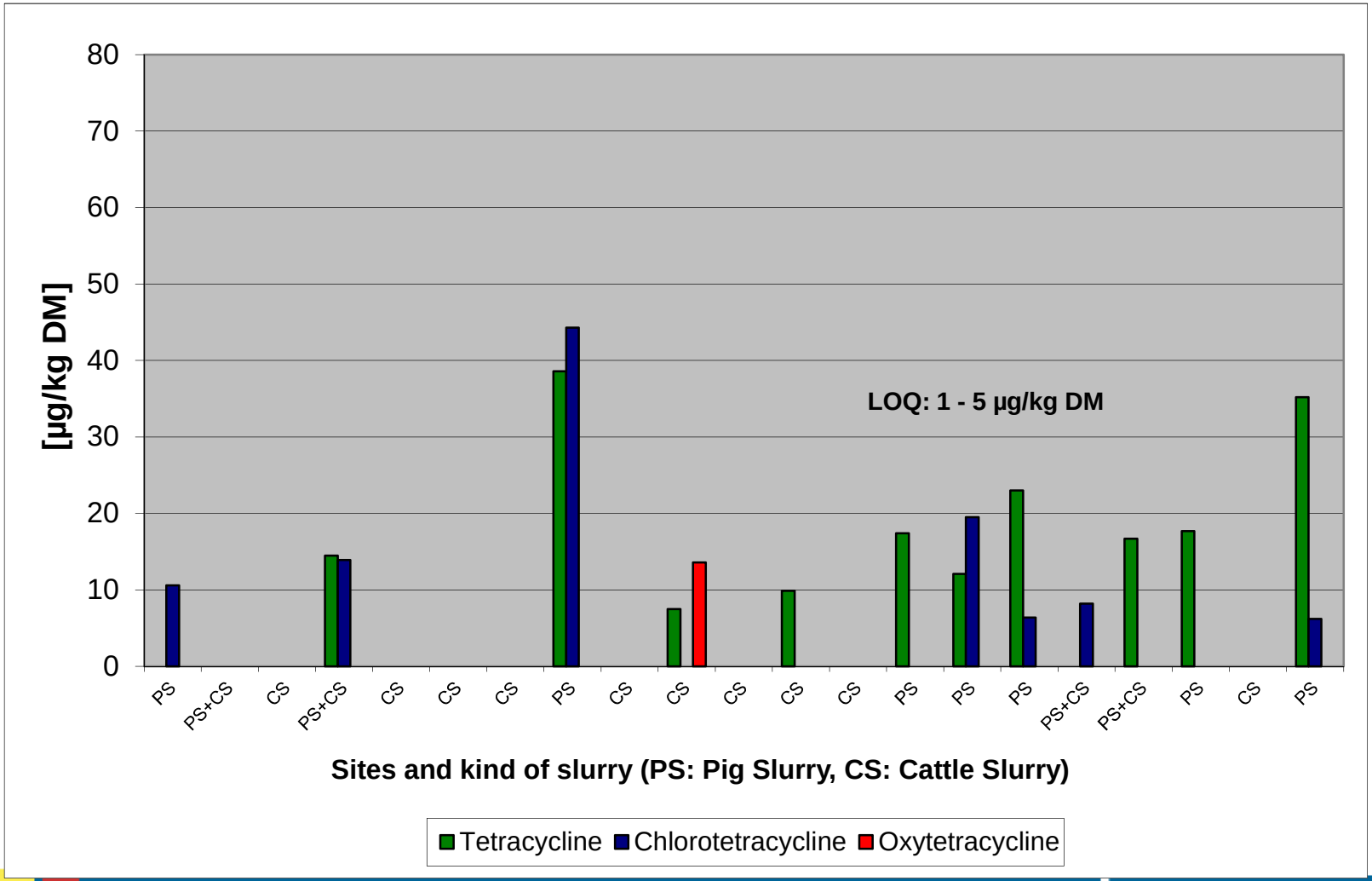
Veterinary Pharmaceuticals in soils and groundwater

Results
- soil -

- In soils sulphonamides and fluoroquinolones could not be detected (LOQ: 5 µg/kg DM)
- In 12 top-soils (0 – 30 cm) tetracyclines have been detected with maximum concentrations of
  13,6 µg oxytetracycline/kg DM
  44,3 µg chlorotetracycline/kg DM
  38,6 µg tetracycline/kg DM
- In three soil samples of the layer 30 – 60 cm tetracyclines have been detected, but in the layer 60 – 90 cm tetracyclines have not been found.

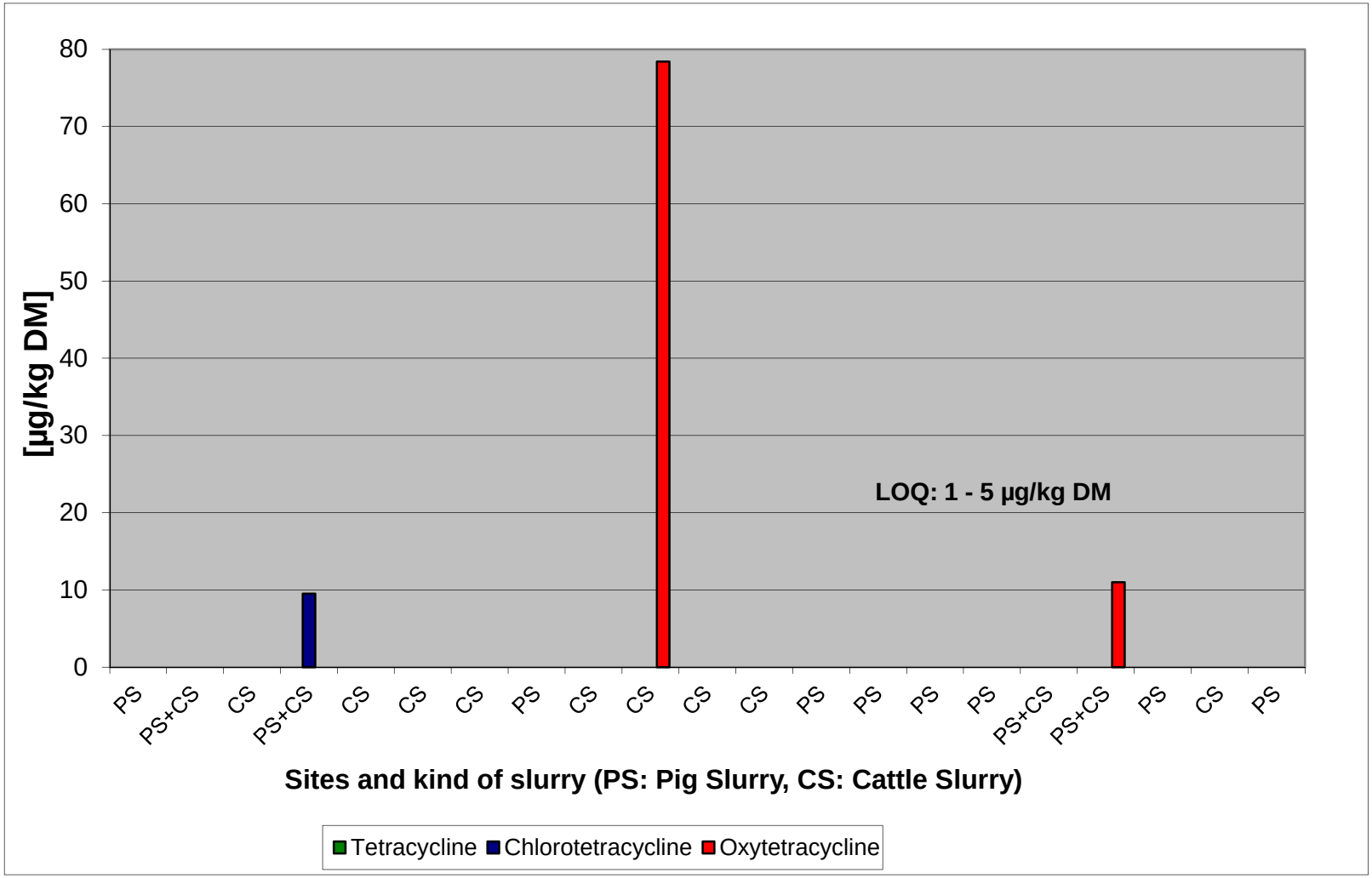
Veterinary Pharmaceuticals in soils and groundwater

Tetracycline-, Chlorotetracycline- and Oxytetracycline-concentrations in soils manured with slurry (0 – 30 cm, Soil- and groundwater-Screening, 2008:)



Veterinary Pharmaceuticals in soils and groundwater

Tetracycline-, Chlorotetracycline- and Oxytetracycline-concentrations in soils manured with slurry (30 – 60 cm, Soil- and groundwater-Screening, 2008)



Veterinary Pharmaceuticals in soils and groundwater

Number of slurry-, digestate, soil- and groundwater-samples with tetracycline- and fluoroquinolone- concentrations above limit of quantitation (LOQ)

Acitive pharmaceutical ingredient	**slurry** (n=34)	**digestate** (n=35)	**soil** (n=63)	**groundwater** (n=21)
Chlorotetracycline	7	<5 µg/kg DM	8	<0,05 µg/l
Oxytetracycline	5	<2,5 µg/kg DM	3	<0,05 µg/l
Tetracycline	12	9	10	<0,05 µg/l
Enrofloxacin	5	20	< 5 µg/kg DM	<0,05 µg/l
Ciprofloxacin (main metabolite of Enrofloxacin)	3	15	< 5 µg/kg DM	<0,05 µg/l
Difloxacin	<3 µg/kg DM	6	< 5 µg/kg DM	<0,05 µg/l
Sarafloxacin (Metabolite of Difloxacin)	1	1	< 5 µg/kg DM	<0,05 µg/l
Marbofloxacin	3	<3 µg/kg DM	< 5 µg/kg DM	<0,05 µg/l
Danofloxacin	1	7	< 5 µg/kg DM	<0,05 µg/l

= below LOQ

Veterinary Pharmaceuticals in soils and groundwater

Number of slurry-, digestate, soil- and groundwater-samples with sulphonamides and trimethoprim- concentrations above limit of quantitation (LOQ)

Acitive pharmaceutical ingredient	**slurry** (n=34)	**digestate** (n=35)	**soil** (n=63)	**groundwater** (n=21)
Sulfachlorpyridazin	<1,5 µg/kg DM	1	< 5 µg/kg DM	< 0,05 µg/l
Sulfadiazin	5	14	< 5 µg/kg DM	< 0,05 µg/l
4-Hxdroxy-Sulfadiazin	8	10	n.a.	n.a.
N-Acetyl-Sulfadiazin	6	4	n.a.	n.a.
Sulfadimidin/ Sulfamethazin	6	11	< 5 µg/kg DM	< 0,05 µg/l
Sulfamerazin	<1,5 µg/kg DM	1	< 5 µg/kg DM	< 0,05 µg/l
Sulfameter	<1,5 µg/kg DM	2	n.a.	n.a.
Sulfamethoxazol	<1,5 µg/kg DM	3	< 5µg/kg DM	1
Sulfaquinoxalin	3	<1,5 µg/kg DM	< 5 µg/kg DM	< 0,05 µg/l
Trimethoprim	1	<1,5 µg/kg DM	< 5 µg/kg DM	< 0,05 µg/l

= below LOQ

n.a.: not analysed

Veterinary Pharmaceuticals in soils and groundwater

Comparison of tetracycline-concentrations in slurry and in soils manured with slurry

There is no information on the concentration of veterinary pharmaceuticals in slurry that has been used as manure at the soil- and groundwater-screening-sites

Therefore the maximum load of veterinary pharmaceuticals is alternatively estimated on the basis of the concentration in slurry of the slurry-and digestate-screening in 2009:

Assumptions:
Application of 30 tons slurry per hectare and year
Concentration in slurry (maximum): 2,45 mg tetracycline/kg DM resp.
3,60 mg chlorotetracycline/kg DM
Depth: 0 – 30 cm, 10 % DM in slurry
→ concentration in soils: 1,6 µg tetracycline/kg DM resp.
2,4 µg chlorotetracycline/kg DM.

The concentration measured in soils is higher than the estimated concentration.

→ Indication for the enrichment of veterinary pharmaceuticals in soils by repeated application of slurry

Veterinary Pharmaceuticals in vegetables

In different publications the transfer of veterinary pharmaceuticals from soil into plants with different test conditions is described.

To ascertain the possible transfer of veterinary pharmaceuticals from soils manured with slurry into vegetables, soils and vegetables have been investigated at 20 sites in North Rhine-Westphalia in 2011.

- Sampling of **soil-samples** at 20 sites (0 – 30 cm)
- Sampling of 10 samples of **white cabbage** and 10 samples of **onions**

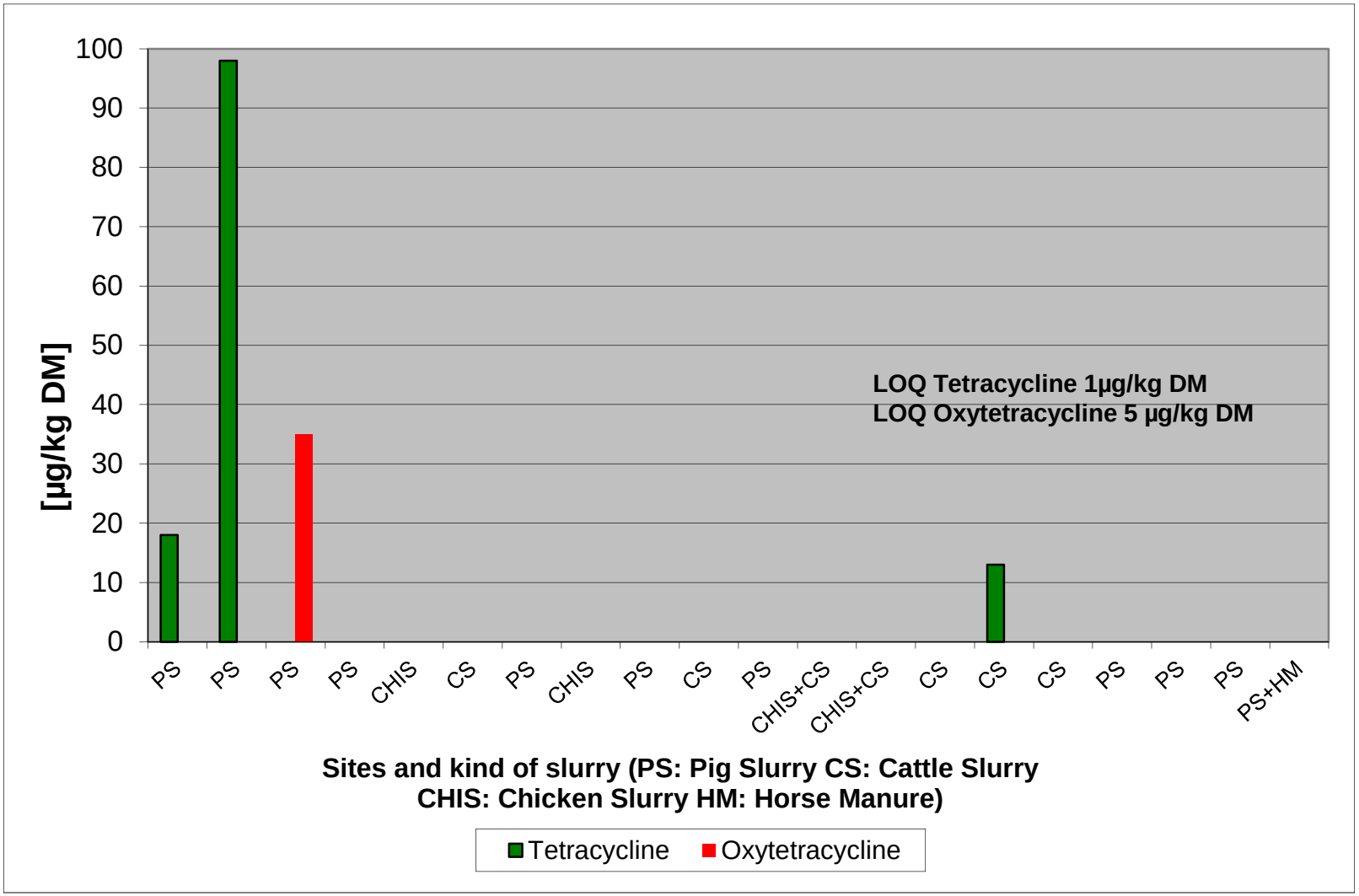
Veterinary pharmaceuticals in vegetables

Results

- In all analysed 20 samples of **vegetables** tetracyclines, sulphonamides and fluoroquinolones could not be detected
  LOQ:
  Tetracyclines: 0,3 – 1,1 µg/kg FW
  Sulphonamides: 0,2 – 36 µg/kg FW
  Fluoroquinolones: 0,05 – 0,65 µg/kg FW
- in **soils** sulphonamides and fluoroquinolones could not be detected (LOQ: 5 µg/kg DM)
- In 4 top-soils (0 – 30 cm) **tetracyclines** have been detected with maximum concentrations of
  35 µg oxytetracycline/kg DM
  98 µg tetracycline/kg DM

Veterinary pharmaceuticals in vegetables

Tetracycline-, Chlorotetracycline- and Oxytetracycline-concentrations in soils manured with slurry (0 – 30 cm, Vegetable-Screening, 2011)



Conclusion (1)

- By application of slurry to agricultural land in amounts usually used in agricultural practice veterinary pharmaceuticals can be found in soils.
- In slurry tetracyclines, sulphonamides and fluoroquinolones were detected.
- In soils only tetracyclines were found, sulphonamides and fluoroquinolones could not be detected.
- The concentrations of tetracyclines in soils are below the threshold limit value of 100 µg/kg (EMEA/VICH phase I).
- Repeated application of slurry leads to enrichment of veterinary pharmaceuticals in soils.

Conclusion (2)

- In groundwater tetracyclines and fluoroquinolones were not found. Only at one site the active ingredient sulfamethoxazol has been detected, but the other sulphonamides were below LOQ.
- The application of slurry to agricultural land in amounts usually used in agricultural practice does not yet lead to a relevant input into groundwater.
- In vegetables tetracyclines, sulphonamides and fluoroquinolones could not be detected. Under the conditions of agricultural practice there is no indication that transfer of veterinary pharmaceuticals from soils manured with slurry into vegetables is a relevant problem.
- Due to the antibiotic effects of these compounds the input into soils should be minimized to avoid spreading of antibiotic resistance.

Many Thanks to

Reinhard Lemke, Rainer Isermann
Chamber of Agriculture North Rhine-Westphalia

Prof. Dr. Gerd Hamscher
Institute of Food Chemistry and Food Biotechnology, University of Gießen

Prof. Dr. Michael Spiteller
Institute of Environmental Research (INFU) Faculty of Chemistry, TU Dortmund

Dr. Armin Mehlich, Dr. Wilfried Hackmann
Institute of Chemical and Veterinarian Analysis Eastwestphalia-Lippe, Detmold

Annette Poschner, Dr. Olaf Haeger
Institute of Veterinarian Analysis, Arnsberg

Rolf Reupert, Dorothea Selke, Dorothea Sopczak
North Rhine-Westphalian State Agency for Nature, Environment and Consumer Protection

...and thank you for your attention!

Landesamt für Natur,
Umwelt und Verbraucherschutz
Nordrhein-Westfalen

Veterinary Pharmaceuticals in slurry, soils manured with slurry, ground water and vegetables

Remarks? Questions?

Dr. Annegret Hembrock-Heger
Mathilde Nießner
Christiane Ratsak
Rolf Reupert
Dr. Barbara Guhl