



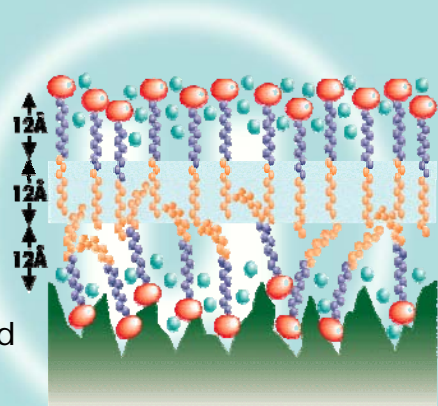
Determination of selected veterinary antibiotics and quaternary ammonium compounds in digestates of biogas plants in Austria

CODIS
27.02.2008 – 29.02.2008
Oliver Gans





Quaternary Ammonium Compounds (QAC)

- Cationic surfactants
- Disinfectants
- Production volume: approx. 2 Mio t/a
- > 300 substances
- Hospitals, laundries, agriculture, household products, etc.



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Selected compounds


**Benzalkoniumchloride
BAC**

N-alkyl chain length between 10 and 18 C

**Dialkyldimethylammoniumchloride
DDAC**

N-alkyl chain length between 8 and 18 C


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Veterinary antibiotics

- Tetracycline
 - TC, OTC, CTC
 - Still the most important group > 50 %
 - Persistent in manure
- Sulfonamides
 - Sulfadimidin, Sulfamethoxazole and Sulfadiazin
 - Trimethoprim
- Fluoroquinolones
 - Enrofloxacin, Ciprofloxacin
 - Persistent in manure


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Antibiotics and QACs in biogas plants

- potential inhibitory effects ?
- Possible soil contamination
- QACs
 - High concentration levels of QACs in sewage sludge (> 100 mg/kg)
 - High concentrations of surfactants (LAS, NPEOs, etc.) present in digestates
- Antibiotics
 - Contaminated manure up to 100 mg/kg per compound


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Analysis of selected compounds in digestate

- QACs
 - Martínez-Carballo E., Sitka A., González-Barreiro C., Kreuzinger N., Scharf S., Gans O. (2007): Determination of selected quaternary ammonium compounds by liquid chromatography with mass spectrometry. Part II. Application to sediment and sludge samples in Austria. Environ. Pollut. 146, 543-547.
- Veterinary antibiotics
 - Martínez-Carballo E., González-Barreiro C., Scharf S., Gans O. (2007): Environmental monitoring study of selected veterinary antibiotics in animal manure and soils in Austria. Environ. Pollut. 148, 570-579

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Analysis of QACs

- Freeze drying of the digestate
- Soxhlet extraction with acidic MeOH
- Evaporation of the solvent
- Residue is redissolved in CHCl_3
- Clean-up with water
- Solvent exchange to MeOH
- Determination with LC-MS/MS
- In each series:
 - Blank
 - Standard addition of a sample

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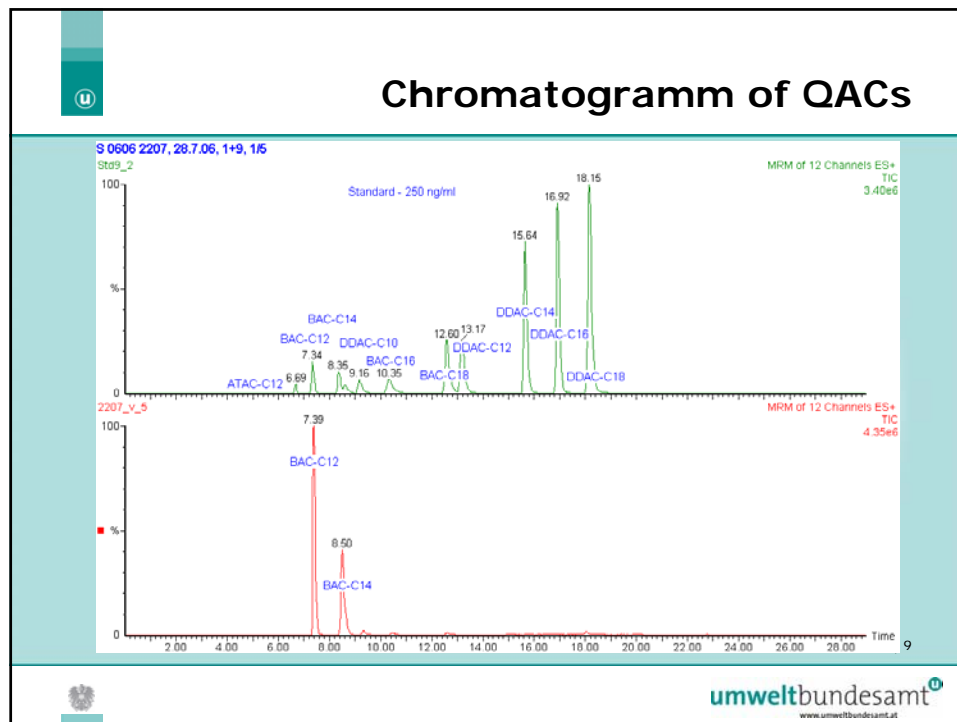
Analysis of Veterinary Antibiotics

- LLE with acidified acetonitrile
- Filtration of the extracts
- Clean-up with n-hexane
- Evaporation under 5 ml
- Clean-up with n-hexane
- Solvent change to acetonitrile-water
- Determination with LC-MS/MS
- Standard addition of each sample
- Additional a blank determination in each series

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Results - Antibiotics

- 6 biogas plants (fed by pig or veal manure)
 - All digestates were contaminated with TCs
 - MAX: 1,4 mg/kg dw. (OTC), 1,3 mg/kg dw. (CTC), 1 mg/kg dw. (TC)
 - Concentration levels in digestates << in manure
 - Sulfadimidine occasionally measured
 - MAX: 0,27 mg/kg dw.
 - Factor 100 less than in pig manure
 - Other sulfonamides / trimethoprim not present
 - Fluoroquinolones not detected


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Antibiotics in biogas plants

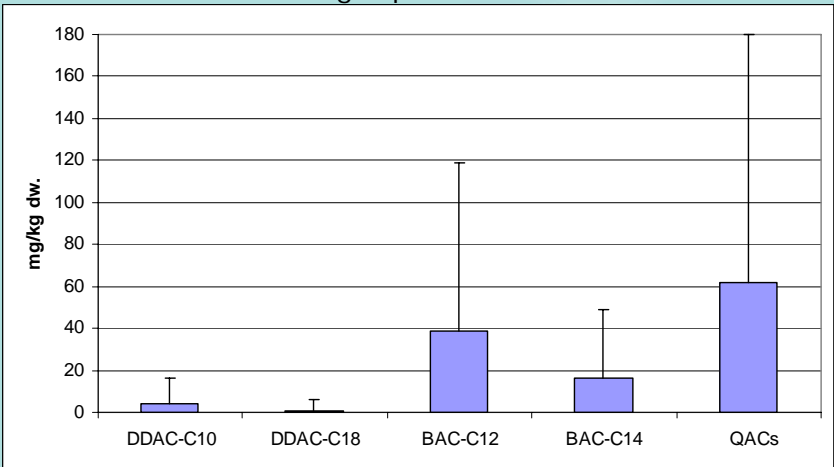
- Arikan et al. (2006)
 - Reduction of OTC from 10 mg/l to 4 mg/l
 - Inhibitory effects: biogas production was reduced by 27 %
- Lallei et al. (2002)
 - Inhibitory effects at OTC concentration > 125 mg/l
- Sanz et al. (1996)
 - IC₅₀ of CTC were at 40 mg/l
- 6 Austrian digestates: 0,07 µg/l OTC and 0,065 µg/l CTC
- STERCUS TERRA

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Results - QACs


- 12 biogas plants



Substance	mg/kg dw.
DDAC-C10	~5
DDAC-C18	~2
BAC-C12	~38
BAC-C14	~18
QACs	~62

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QACs in biogas plants

- Tezel et al. (2006) - anaerobic
 - DDAC: Inhibitory effects at 25 mg/l for short C-chain (>50%)
 - BAC: Inhibitory effects at 25 mg/l for mixture C10 – C16 (-15 % methane production)
 - C8 > C10 > C16 > C18
 - Limitation: Analysis done by disulfine blue method
 - BACs used in a commercial mixture
- Madsen et al. (1996)
 - EC₅₀ level for BACs: 6,7 mg/l


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QACs in biogas plants

- Umweltbundesamt (2005) - aerobic
 - BACs
 - Effect levels for acute and chronic inhibitions: 1 mg/l
 - DDACs
 - Effect levels for acute and chronic inhibitions: 5 mg/l
 - BACs > DDACs; C8 > C10 > C16 > C18
- EU Risk Assessment for DDAC-C18 – aerobic
 - EC₅₀ of 2.1 mg/l

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QACs concentration vs effects


- Maximum concentration of 9 mg/l (sum of 12 QACs)
- Maximum concentration of 6 mg/l BAC-C12
- Effect concentrations:
 - Anaerobic: 6,7 mg/l – 25 mg/l
 - Aerobic: 1 mg/l – 5 mg/l

⇒ Effects on the fermentation process cannot be ruled out


⇒ Methane gas production might be reduced

⇒ Possible soil contamination if digestates are used as fertilizer

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Conclusions

- Antibiotics
 - Tetracycline, occasionally sulfadimidine
 - Manure >> digestates
 - No effects on the fermentation process expected
- QACs
 - Highly contaminated up to 180 mg/kg dw. (9 mg/l)
 - Methane gas production probably affected
 - Soil contamination possible

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Outlook Antibiotics

- Number of samples was small
- Fluoroquinolones ???
- Effect concentration as well as determination of half life times of different groups – reduction of antibiotics through biogas plants possible
- Soil contamination possible by utilizing digestates as fertilizer ?
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Outlook QACs

- Source identification
- Behavior and fate of QACs in biogas plants
- Effects on methane gas production of different QACs using LC-MS/MS analysis
- Effects on microorganism in biogas plants
- Soil contamination ??
- Effects on soil microorganism

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 **Acknowledgement**

Federal state of Vorarlberg
Austrian Agency for Health and Food Safety

 for your attention



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