# EXPOSURE MONITORING AND BIOACCUMULATION POTENTIAL OF QUINOXYFEN RESIDUES IN SOIL AND AQUATIC SEDIMENT FOLLOWING REPEATED USE IN CEREAL GROWING REGIONS OF GERMANY

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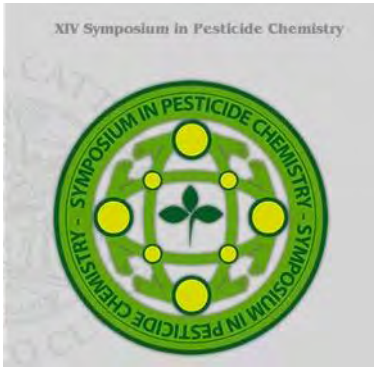


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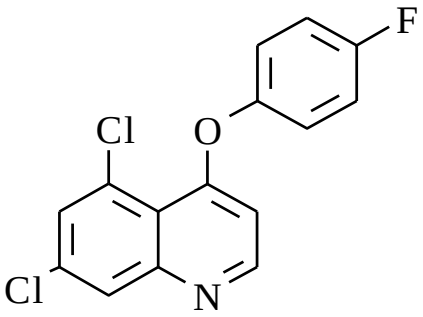
# Outline

- Quinoxyfen as Target Analyte
- Monitoring Sites
- Sampling and Processing
- Results
- Take Home Message




# Target Analyte Quinoxyfen

- **Fortress™**
- **Fungicide for protection against Powdery Mildew on winter cereals (other crops)**
- **Application time window (BBCH 25 – 51)**
- **Max. number of treatments per year = 2**
- **Max. dose per year = 250 g/ha**

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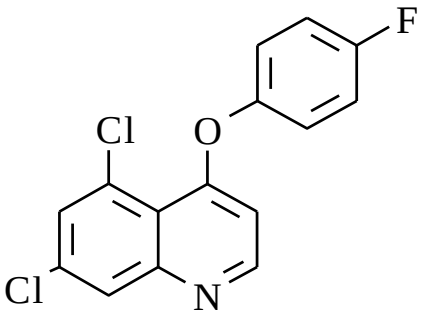


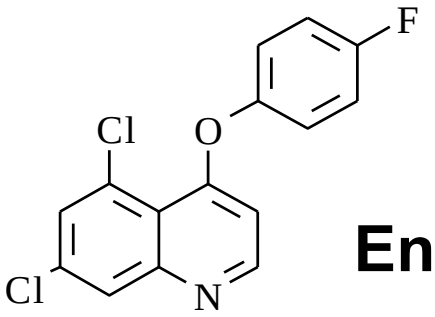

# Environmental Fate Profile[1)]

- **Soil**
  **Slowly degraded: $DT_{50lab}$ mean = 374 d; $DT_{50field}$ = 150 - 190 d (UK)**
  **Immobile: $K_{foc}$: mean = 22929 ml/g**

- **Water/Sediment**
  **Water phase: $DT_{50}$ = 3 - 7 days**
  **Sediment phase: $DT_{50}$ = 42 - 211 days**

- **Ecotoxicology Aquatic Organisms**
  **log $K_{ow}$ = 4.66**
  **Bioaccumulation: BCF rainbow trout = 5040**

[1)]EU Review Report (2003): Review Report for the Active Substance Quinoxyfen, Finalised in the Standing Committee on the Food Chain and Animal Health at its Meeting on 28 November 2003 in View of the Inclusion of Quinoxyfen in Annex I of Directive 91/414/EEC. 6781/VI/97-rev.19, 27 November, 2003.




# Environmental Fate Profile and its Consequences

- Based on the reported laboratory soil half-lives, and the field dissipation studies, Quinoxyfen has chemical properties which imply that it may be persistent in soil and aquatic sediment under certain conditions. Furthermore, with a log Kow of 4.66 and a BCF-fish of 5040 it may have bioaccumulation potential under certain conditions.

- In view of the Inclusion of Quinoxyfen in Annex I of Directive 91/414/EEC the purpose of addressing the environmental impact of residues of Quinoxyfen in soil (+biota) and aquatic sediment (+biota), monitoring was considered necessary.

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# Monitoring Sites: Cereal Growing Areas in Germany with Quinoxyfen Use


**Lehrte (Lower Saxony, flat)**

Field site: Lehrte

Water body: Billlerbach

**Northeim (Lower Saxony, low mountain)**

Field site: Krumberg

Water body: Krummel

Field site: Söhlen

Water body (Streamlet)

**Kraichgau (Baden Württemberg, hilly)**

Field site: Weiherbach

Water body: Weiherbach

## Monitoring Sites: Further Selection Criteria

• Field sites with historical long-term use of Quinoxyfen, and subsequent use in 2005/ 2006 at the maximum annual application rate (250 g a.i./ha)

## Water Bodies (Sediment) Vulnerable to Quinoxyfen Exposure Via:

- Aerial drift deposition (located in major downwind drift direction, small buffer strips)
- Run-off and erosion (slope of the adjacent treated field plot, small buffer strips)
- Drainage input via drainage pipes

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## Usage History:

- Application to cereals
- Applications since 1995-2002
- In total 3-6 application years
- Total amounts 533 – 950 g/ha

| | Lehrte | | Söhlen | | Krumberg | | Weiherbach | |
|---|---|---|---|---|---|---|---|---|
| Year | Crop | Amount applied a.i. (g/ha) | Crop | Amount applied a.i. (g/ha) | Crop | Amount applied a.i. (g/ha) | Crop | Amount applied a.i. (g/ha) |
| 1995 | - | - | - | - | - | - | Winter wheat | 150 |
| 1996 | - | - | - | - | - | - | - | - |
| 1997 | - | - | - | - | - | - | - | - |
| 1998 | - | - | - | - | - | - | Winter wheat | 150 |
| 1999 | - | - | - | - | - | - | - | - |
| 2000 | - | - | Winter barley | 100 | Sugar beet | - | - | - |
| 2001 | - | - | Winter wheat | 98 | Winter wheat | 98 | Winter wheat | 150 |
| 2002 | Sugar beet | - | Sugar beet | - | Winter wheat | 75 | - | - |
| 2003 | Winter wheat | 33 | Winter wheat | 100 | Sugar beet | - | - | - |
| 2004 | Sugar beet | - | Winter wheat | 75 | Winter wheat | 100 | Maize | - |
| 2005 | Winter wheat | 250 | Winter wheat | 250 | Winter wheat | 250 | Winter wheat | 250 |
| 2006 | Winter wheat | 250 | Winter wheat | 250 | Winter wheat | 250 | Winter wheat | 250 |
| **Sum** | | **533** | | **873** | | **773** | | **950** |

Aquatic exposure via:

- Aerial drift
- Drainage pipes
- Interflow
- Upper reaches

Aquatic exposure via:

- (Aerial drift)
- Run-off/erosion
- Interflow

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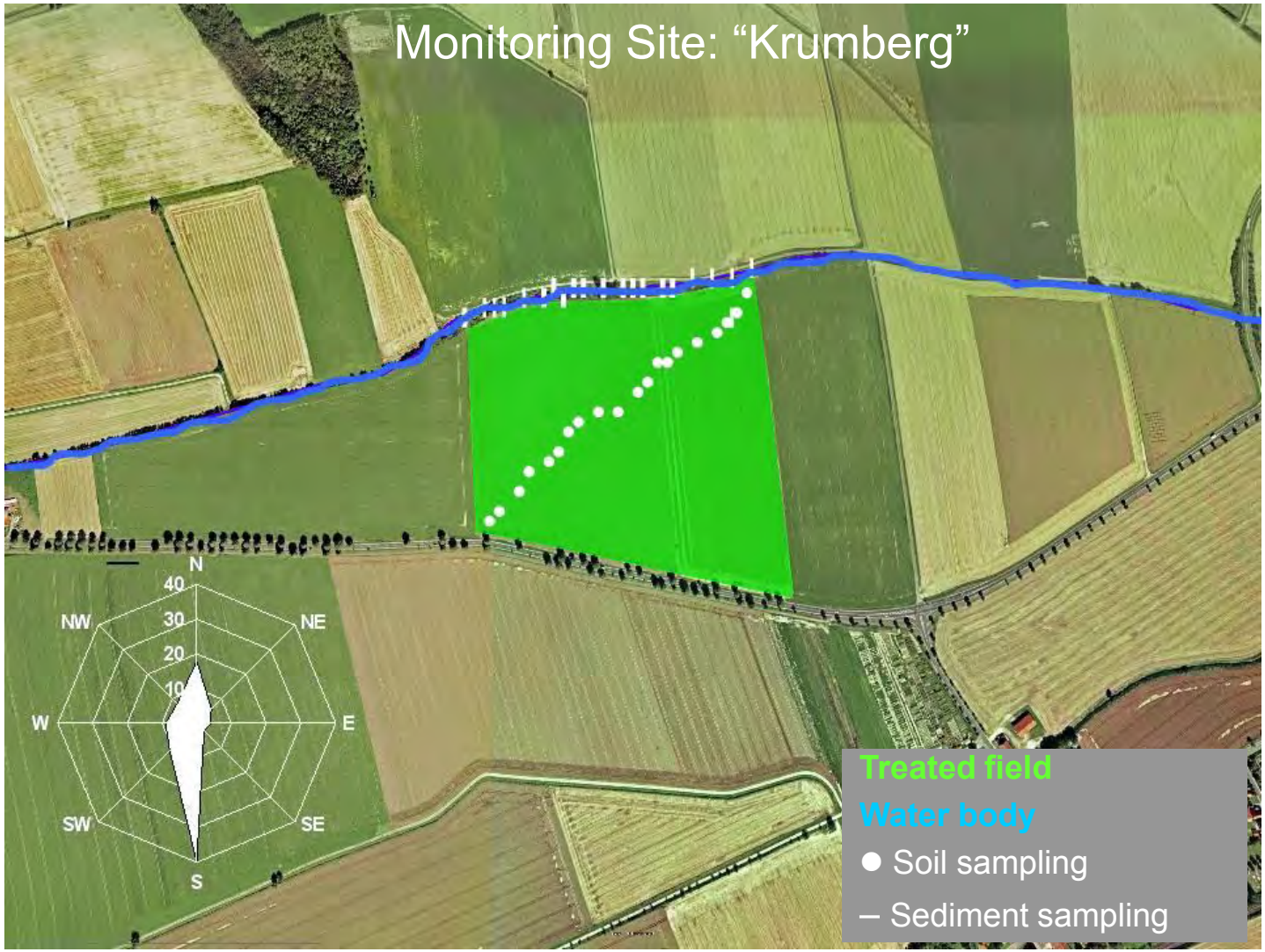
Aquatic exposure via:

- Aerial drift
- Upper reaches
- Interflow



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## Sampling Soil and Aquatic Sediment:

- Soil: For each field site one homogenized sample from 20 soil cores; 0-10 cm soil layer chosen due to strong sorption

- Sediment: For each water body one homogenized sample from 20 sediment cores taken from the boundary layer (5 cm depth)

**Sampling occasions in 2005 & 2006**:

- Prior to crop application in spring (Results from historical use)
- One week after application (Additional load)
- After crop harvest (August)
- In autumn (October)

**Earthworms were sampled because:**

- Their size and abundance
- Their feeding mode (saprophagous)
- Part of the food chain (e.g. hedgehog and birds)

Sampled with hot mustard extraction and hand sorting

**Sediment dwelling organisms were sampled because:**

- Potential exposure via contaminated sediment
- Part of the food chain

Sampled with surber-samplers and hand nets

**Fish were chosen:**

- To assess the biomagnification potential at a higher trophic level

Sampled by using a portable electro fishing device

**Sampling ocassions:**

- Simultaneously to soil sampling occasions “October 2005”, “Before treatment in spring 2006” and “October 2006”

## Sampling Biota:


■ Earthworm sampling areas (5 x 0.6 m²)

* Sediment dwelling organisms + fishes

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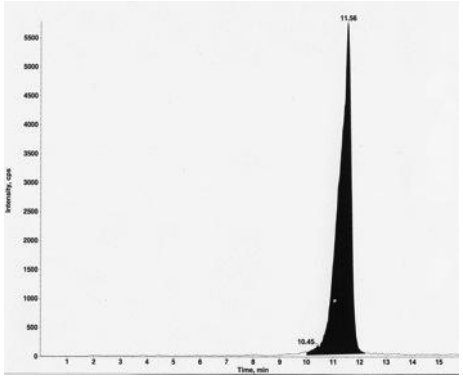
## Analytical Items:




- Soil, sediment and biota samples were extracted with organic solvents and cleaned up with SPE-cartridges
- Identification and quantification of Quinoxyfen by means of LC MS/MS
- Recovery depends on sample matrix = 80 – 109 %
- Coefficient of variation (n = 6) = < 11.8%
- LOD depends on sample matrix = 0.05 – 0.19 µg/kg
- LOQ depends on sample matrix = 0.16 – 0.59 µg/kg

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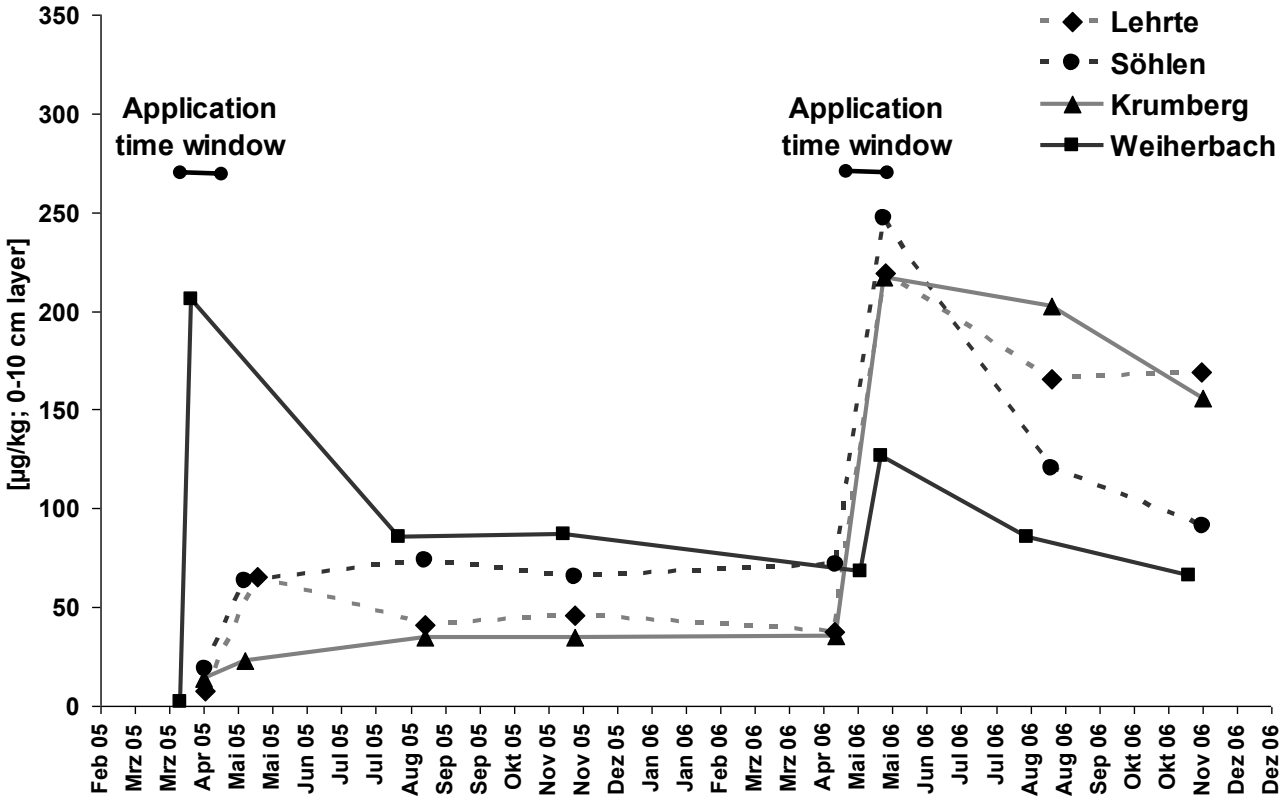
# Results: Quinoxyfen concentrations in soil [µg/kg]

- Historical use results in concentrations from 2.1 to 19.1 µg/kg
- Additional load in 2005 was between 10-204 µg/kg and between 59-182 µg/kg in 2006, but below that expected ($PEC_{initial}$ from single appn. = 208 µg/kg)*
- Concentration one year after 1st application was 25 -72 µg/kg in 2006 and 66 - 169 µg/kg after the 2nd application in 2006




* Based upon soil incorporation into 10 cm, b.d. 1.2 ml/g and single appn. rate of 250 g/ha

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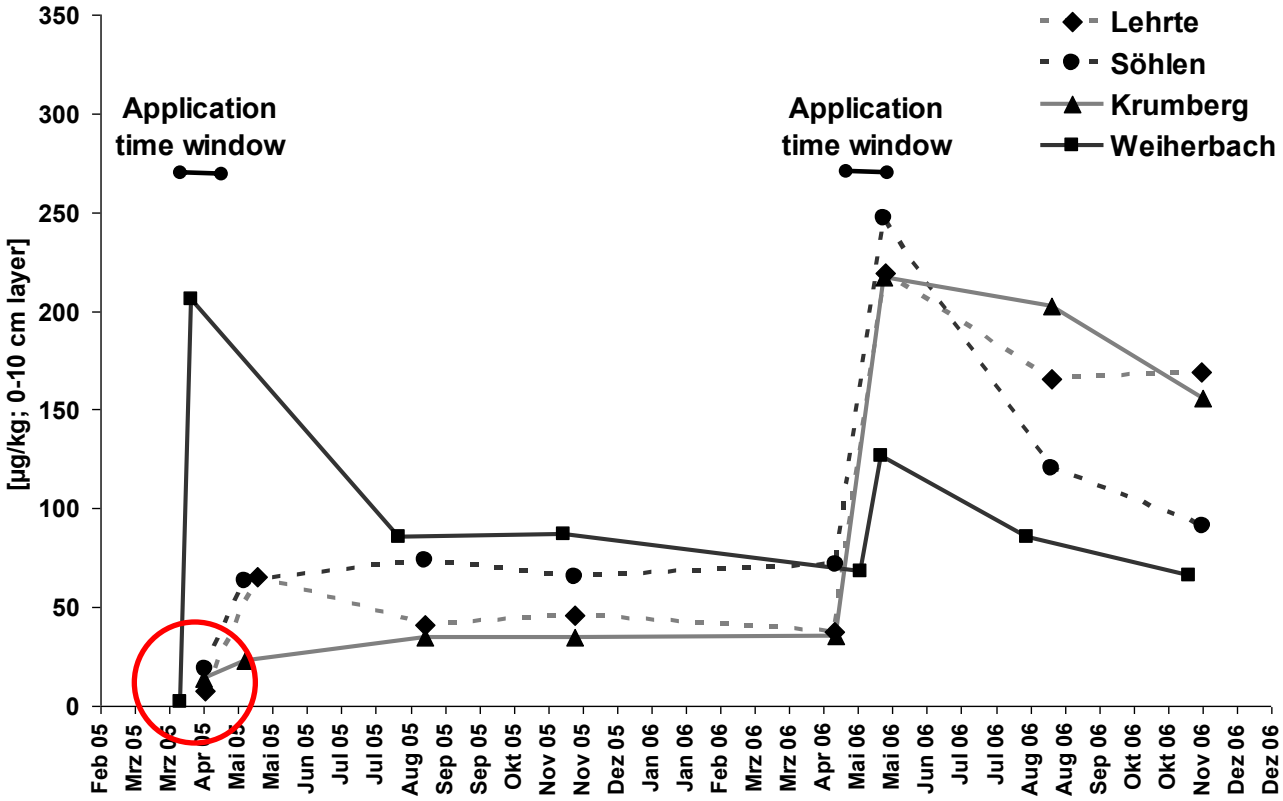


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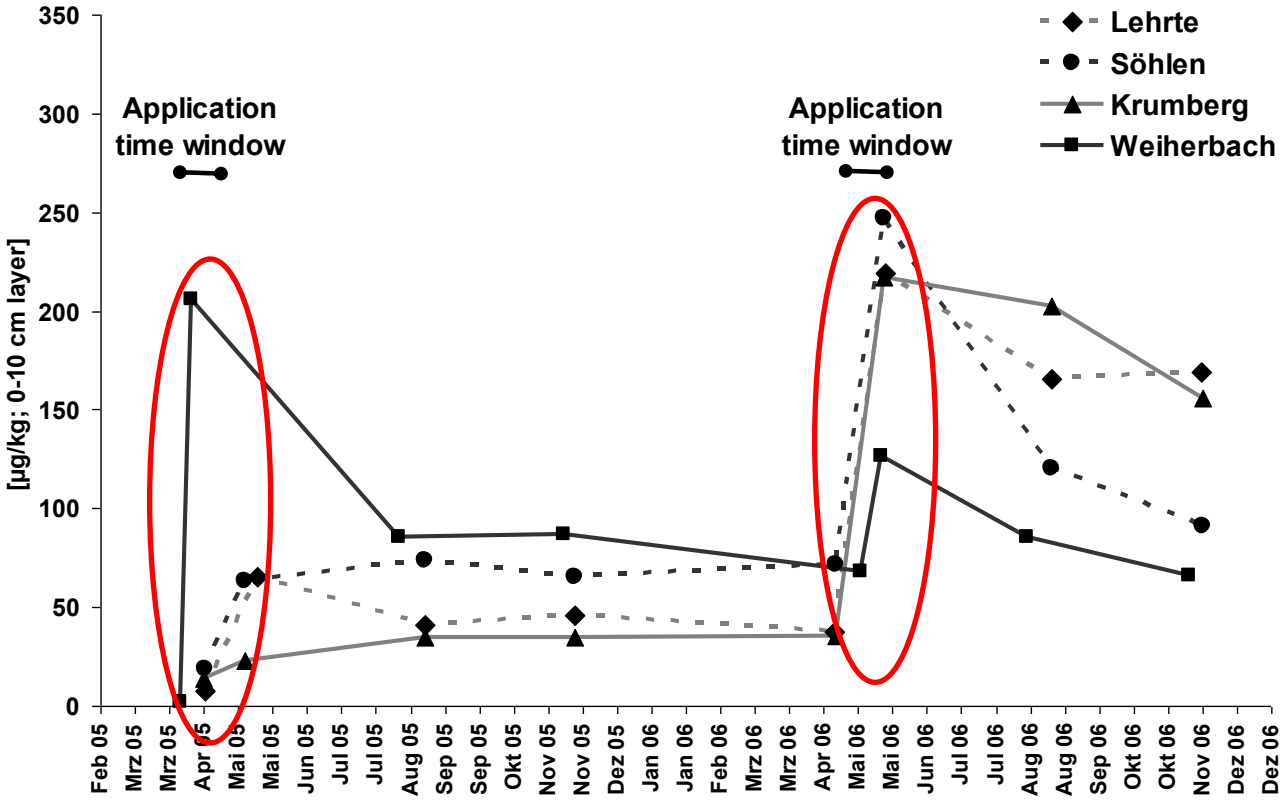


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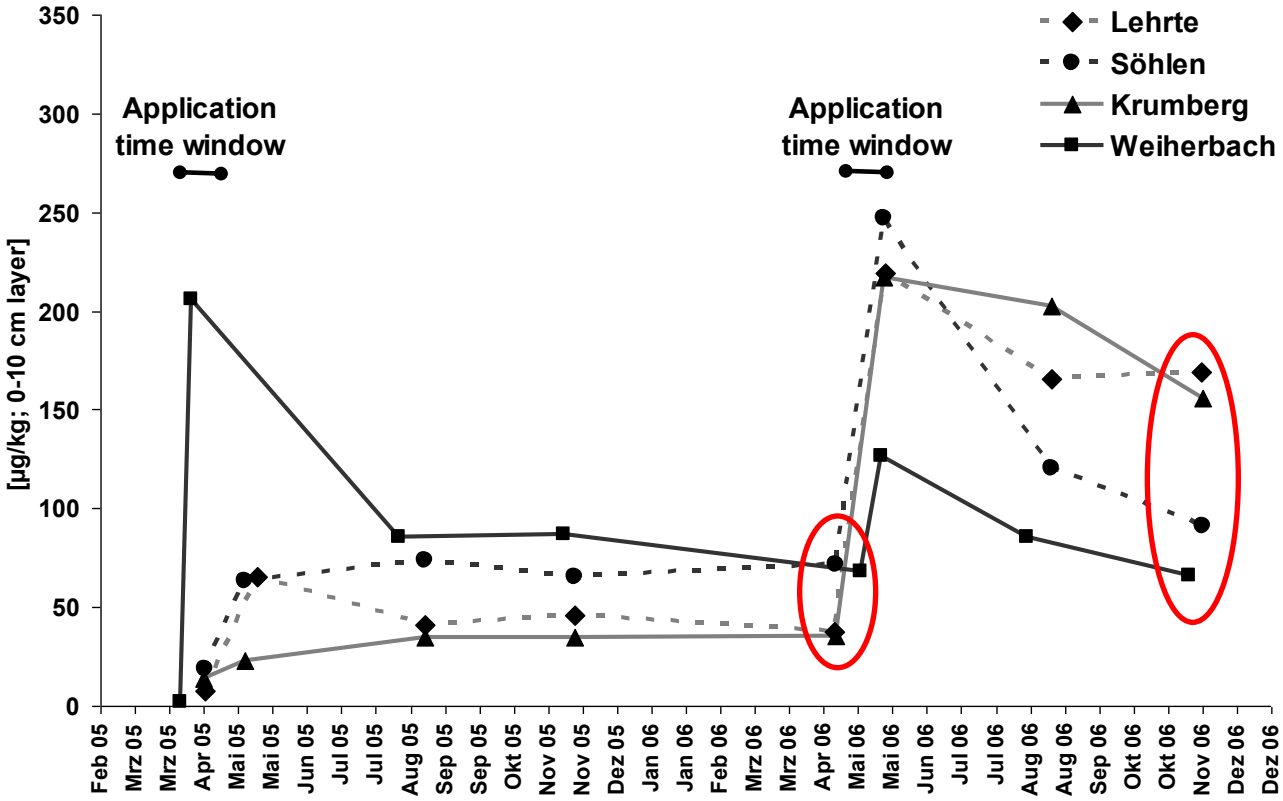


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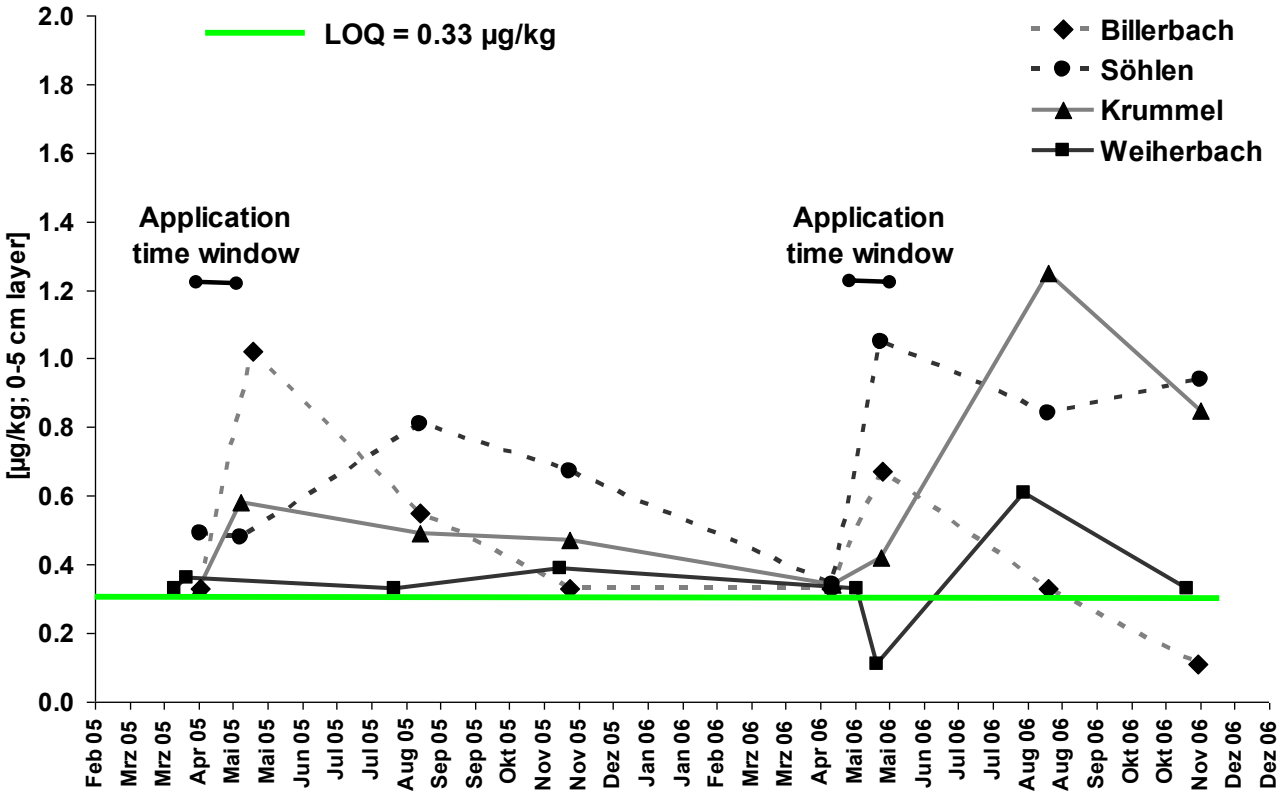
# Results: Quinoxyfen concentrations in aquatic sediment [µg/kg]

- Historical use results in concentrations from < LOQ to 0.5 µg/kg
- Sediment concentration after application always ≤1 µg/kg ($PEC_{sedinitial}$ = 3.5 µg/kg)*
- Additional load after application was not meaningful and always < 1 µg/kg
- In certain cases very minor increase in sediment concentration (< 1 µg/kg) was observed outside the application window (run-off, erosion, interflow?)

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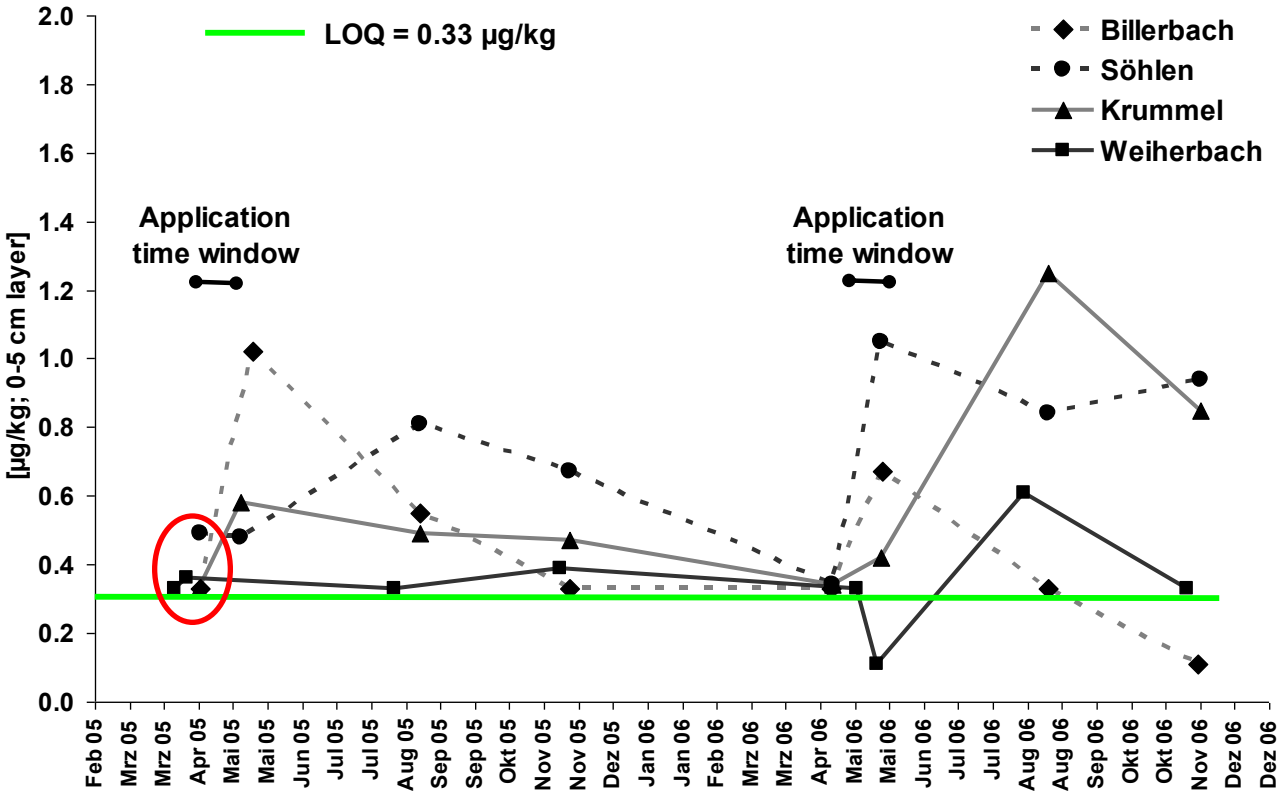


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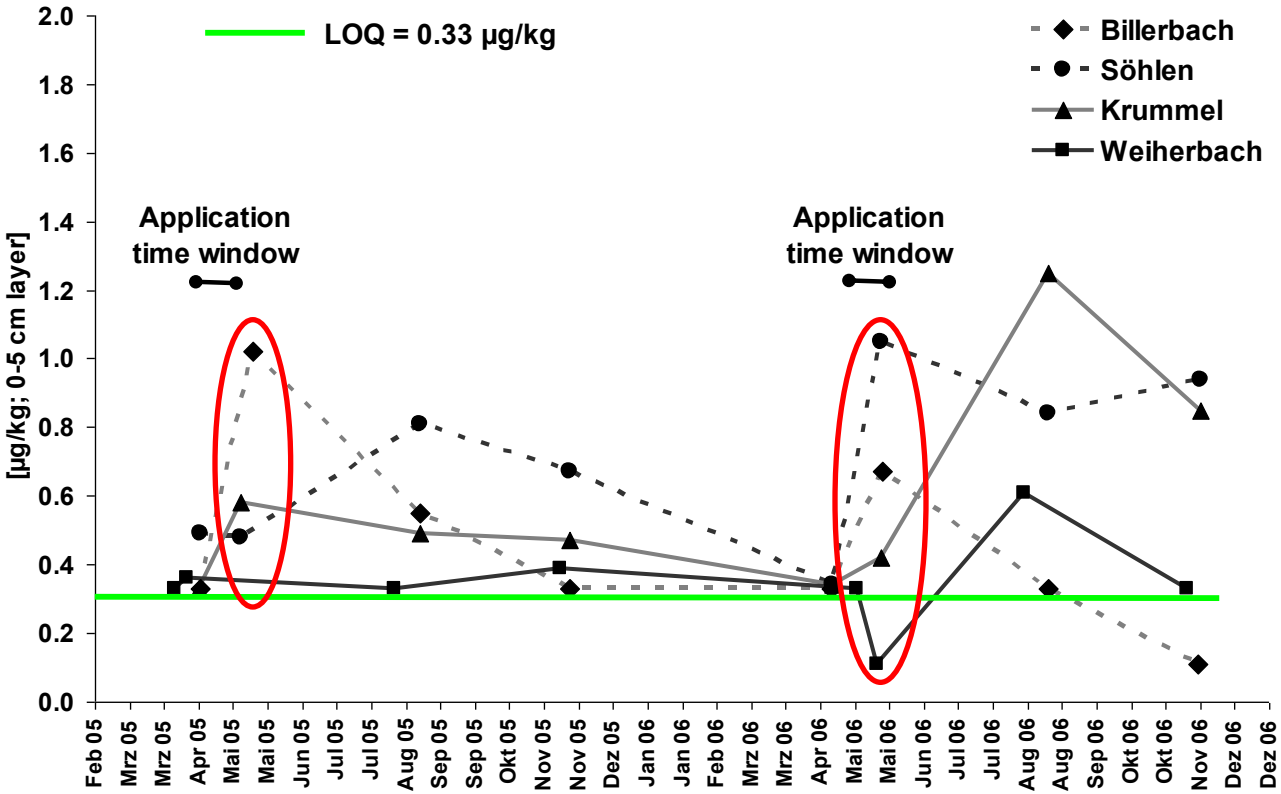


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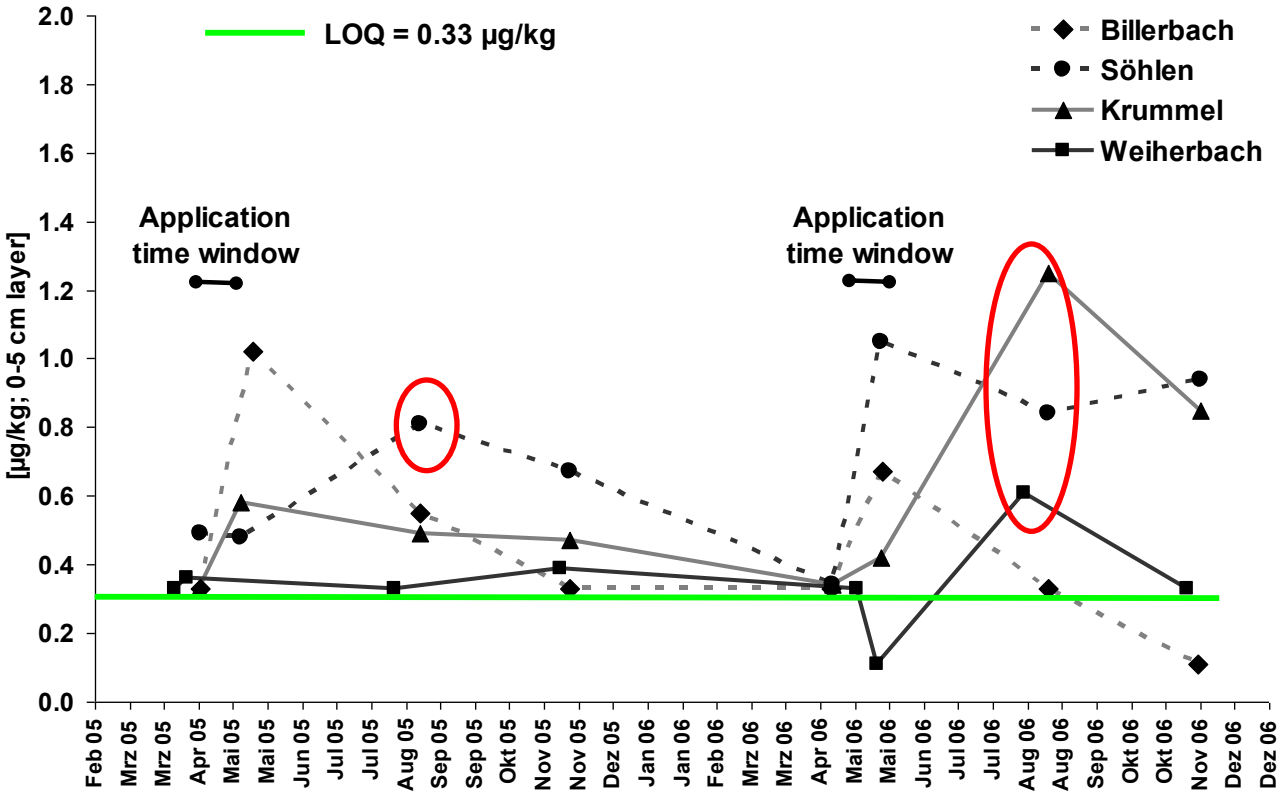


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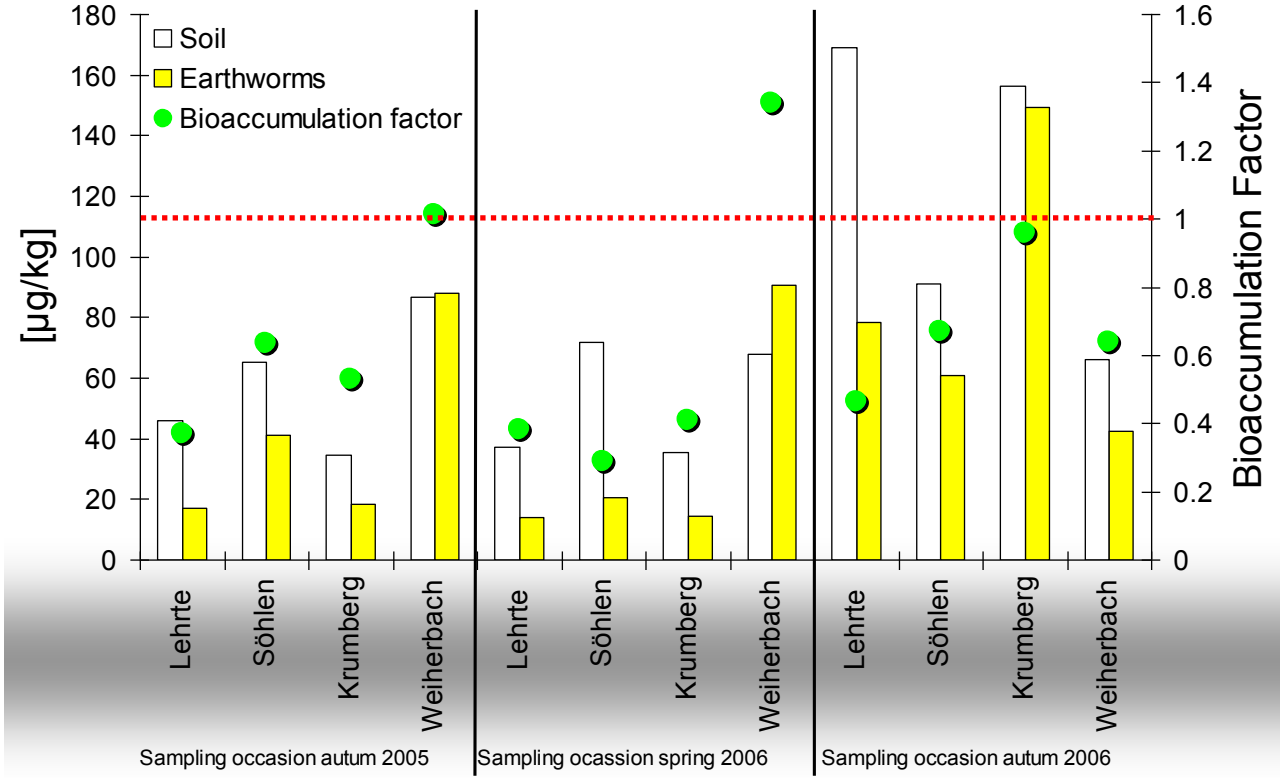
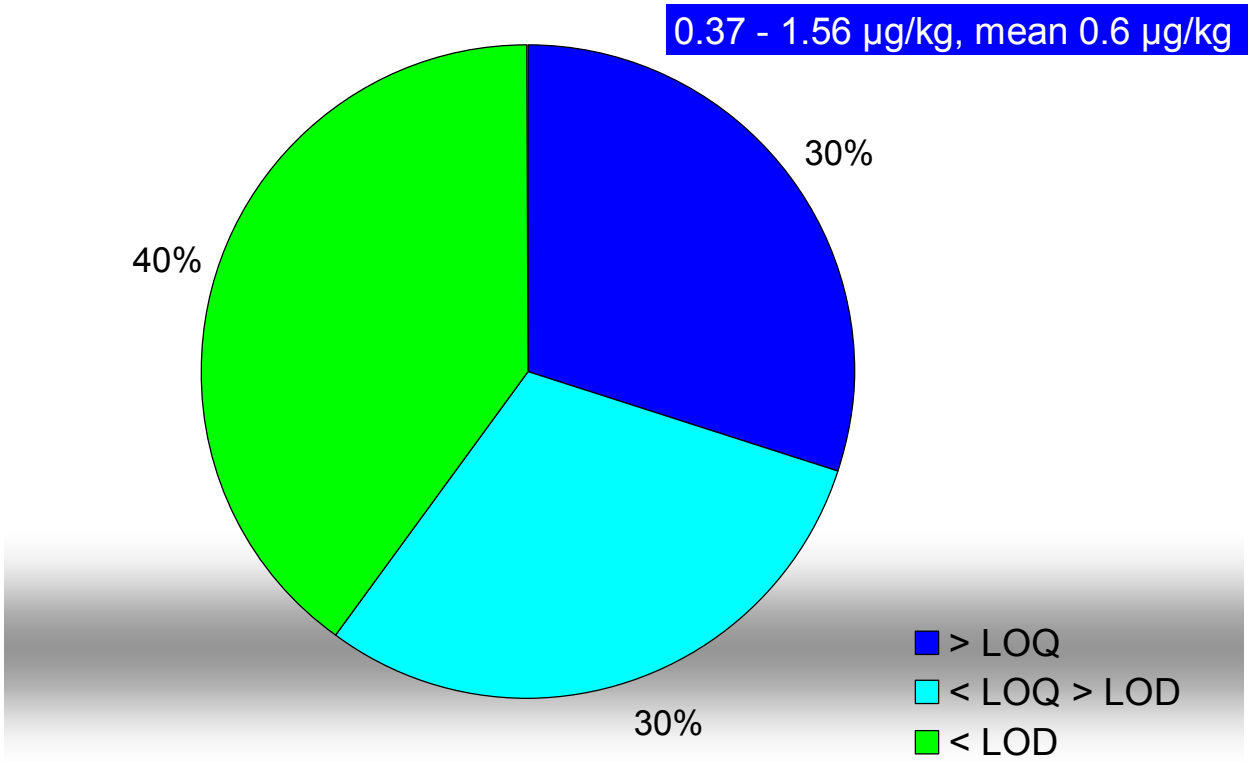
# Results: Field study Earthworm Bioaccumulation

- With one exception the BCF was ≤1 (mean 0.6) indicating no bioacummulation potential of Quinoxyfen residues under field conditions
- BCF was more affected by sampling site than sampling occasion



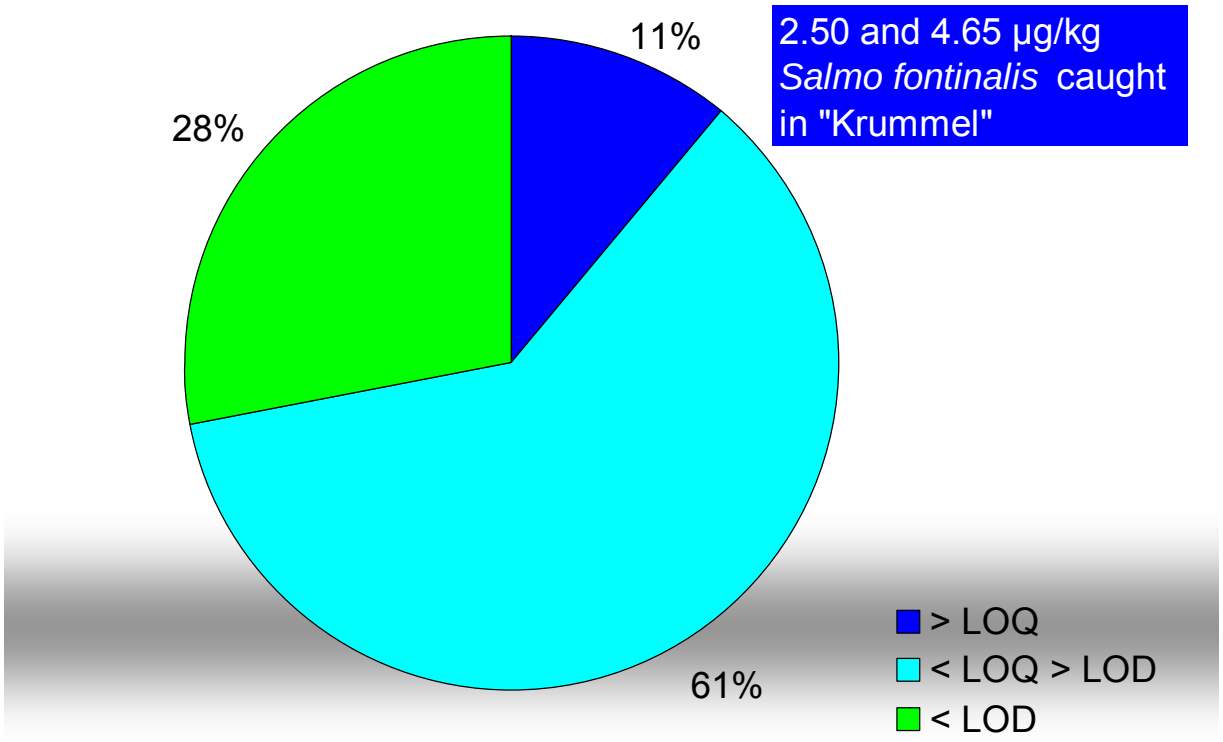
# Results: Bioaccumulation in sediment dwelling organism (SDO)

- In total 20 samples (9 different taxa) were sampled and analysed.
- With one exception (1.56 µg/kg Gastropoda from Billerbach) the concentration was ≤1 µg/kg
- 70% of samples contained no Quinoxyfen above the LOD or LOQ
- Concentrations in SDO were below, or comparable to the sediment concentration observed in the corresponding sediment layer



# Results: Biomagnification in Fishes

- In total 18 samples (8 different species) were sampled and analysed.
- With one exception all other species contained no target analyte in concentrations above the LOQ (0.59 µg/kg). Therefore there is no evidence that uptake via sediment or SDO leads to biomagnification of Quinoxyfen in fishes



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# Take Home-Messages

- The monitoring quantified Quinoxyfen residues in soil and adjacent aquatic sediment + biota resulting from the long-term and recent use of Quinoxyfen in cereal growing regions of Germany
- Low levels of Quinoxyfen in soil sampled before application in 2005 confirmed the historical use, with subsequent applications in 2005 and 2006 not increasing the burden beyond that of the PECinitial
- Except for one water body (Billerbach), the historical use led to aquatic sediment concentrations below the LOQ
- Increases in sediment concentrations were generally low following the Quinoxyfen applications in 2005 and 2006 (<1 µg/kg), and the results showed no trend towards accumulation
- In most cases the corresponding biota concentrations (earthworms, SDOs and fish) were considerably lower than the concentrations observed in the soil and sediment, indicating little or no biomagnification