



Emerging Pollutants: Protecting Water Quality for the Health of People and the Environment

Identification and occurrence of the chlorination products of fipronil and its degradates in municipal wastewater treatment plants

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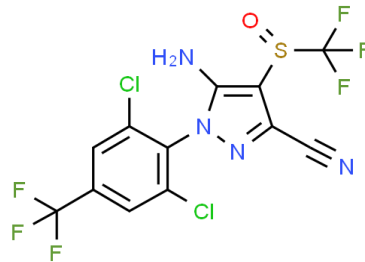
Fipronil was widely used in agricultural and non-agricultural application

Agricultural application

Insect pests control
 (herbivorous insects and mites, etc.)



Fipronil



Country	Regulation	Year
France	Be prohibited	2004
Italy	Be prohibited	2008
China	Not be used in crops	2009

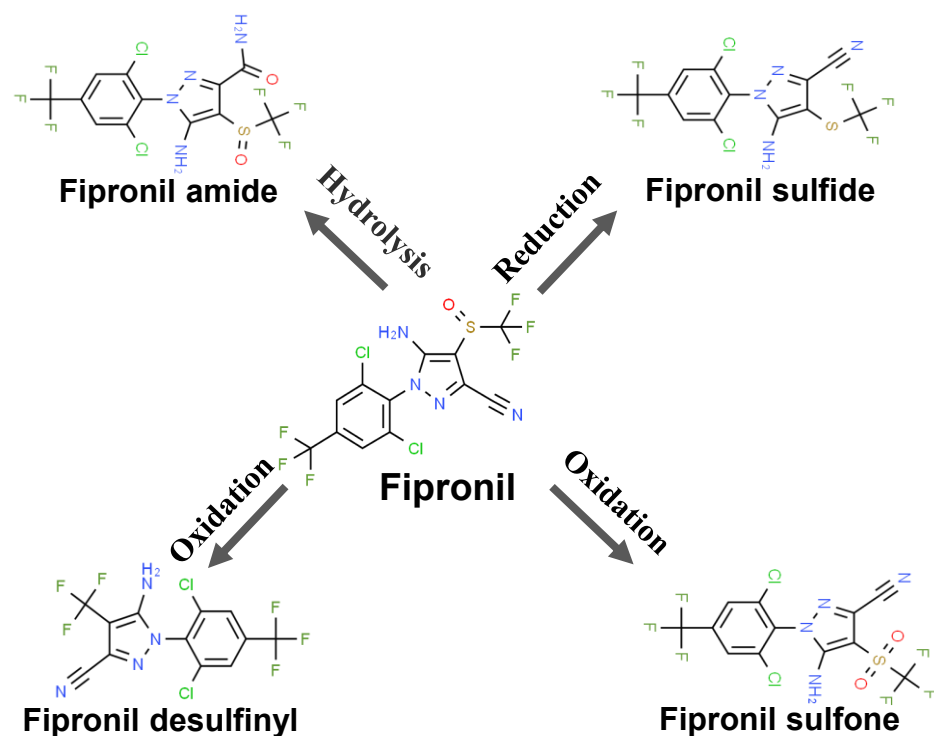
Non-agricultural application

- ✓ **Urban pests management**
 (cockroaches, ants, termites, etc.)
- ✓ **Veterinary applications**
 (fleas, ticks, etc. on pets)

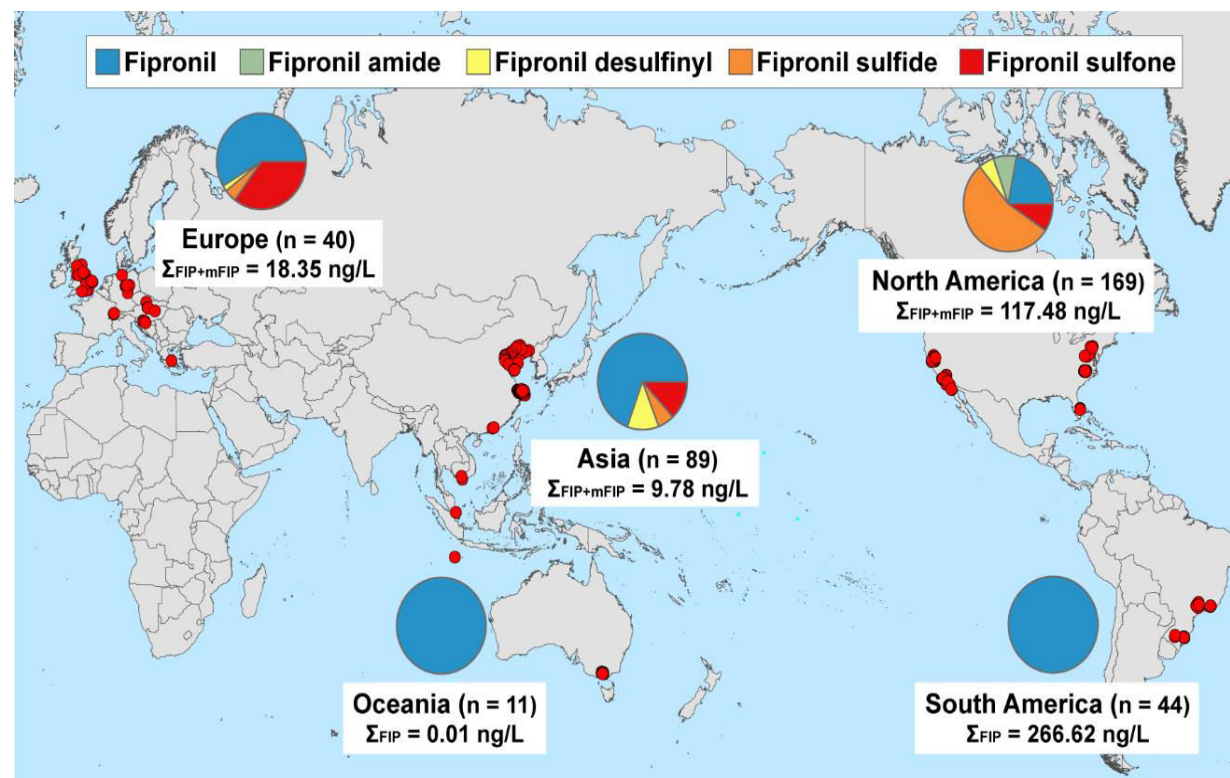


Degradation of fipronil in the environment

Degradation of fipronil in the environment



Worldwide distribution of fipronil and its four principal degradates in aquatic environment (including 353 sampling sites)



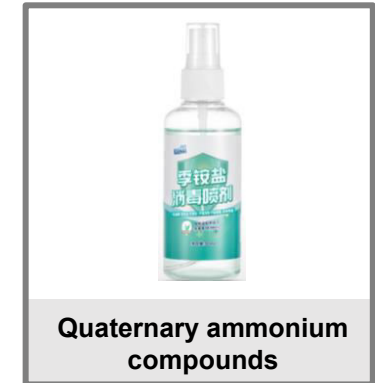
Increased use of disinfectants during the SARS-Cov-2 pandemic



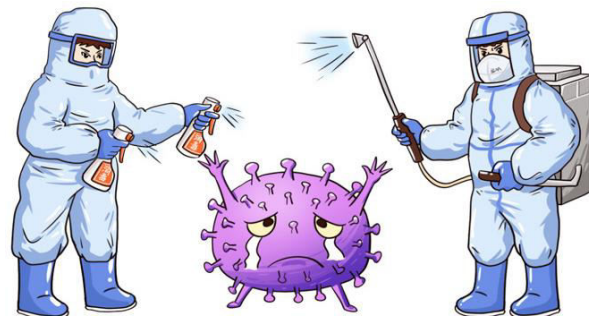
Chlorine-based
disinfectants



Alcohol



Quaternary ammonium
compounds



Formaldehyde



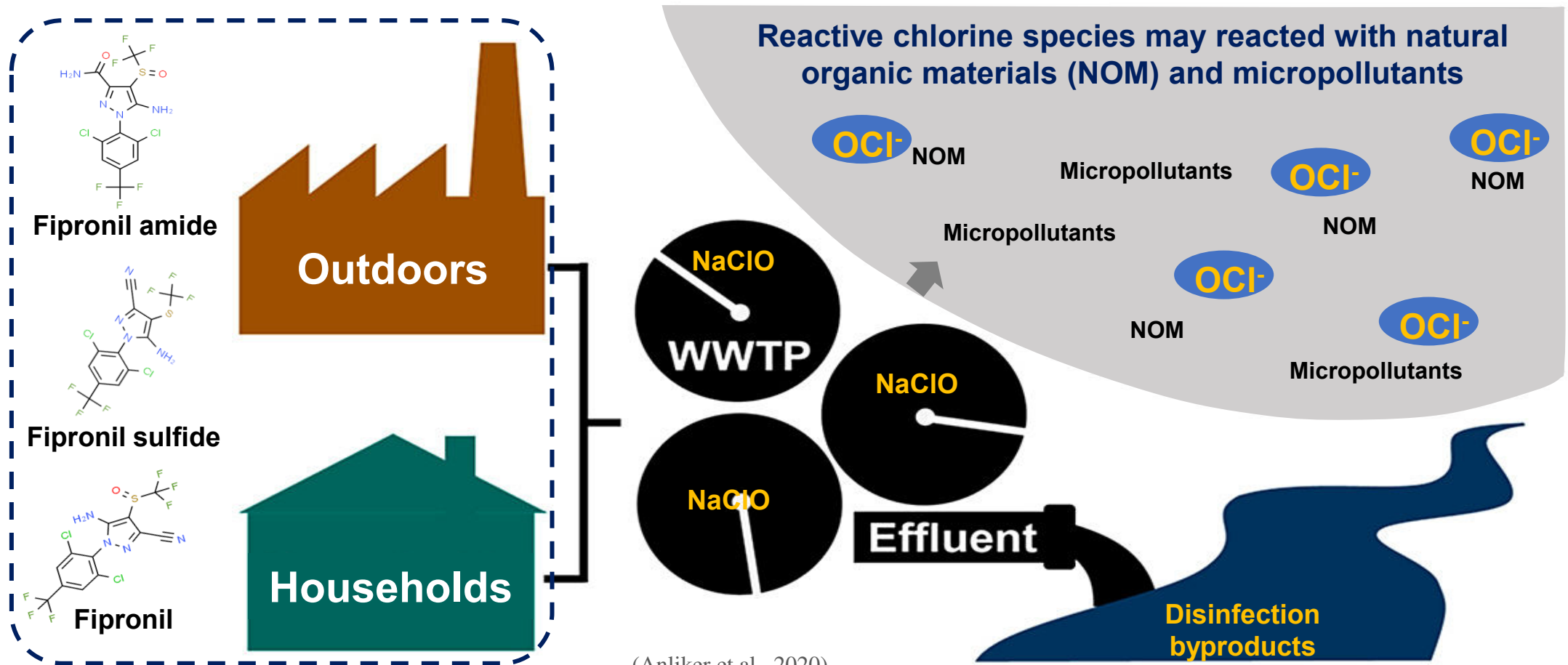
Povidone-iodine



Hydrogen peroxide

Chlorine-based disinfectants: chlorine (Cl_2), chloramine (NH_2Cl , NHCl_2), chlorine dioxide (ClO_2) and sodium hypochlorite (NaClO), etc.

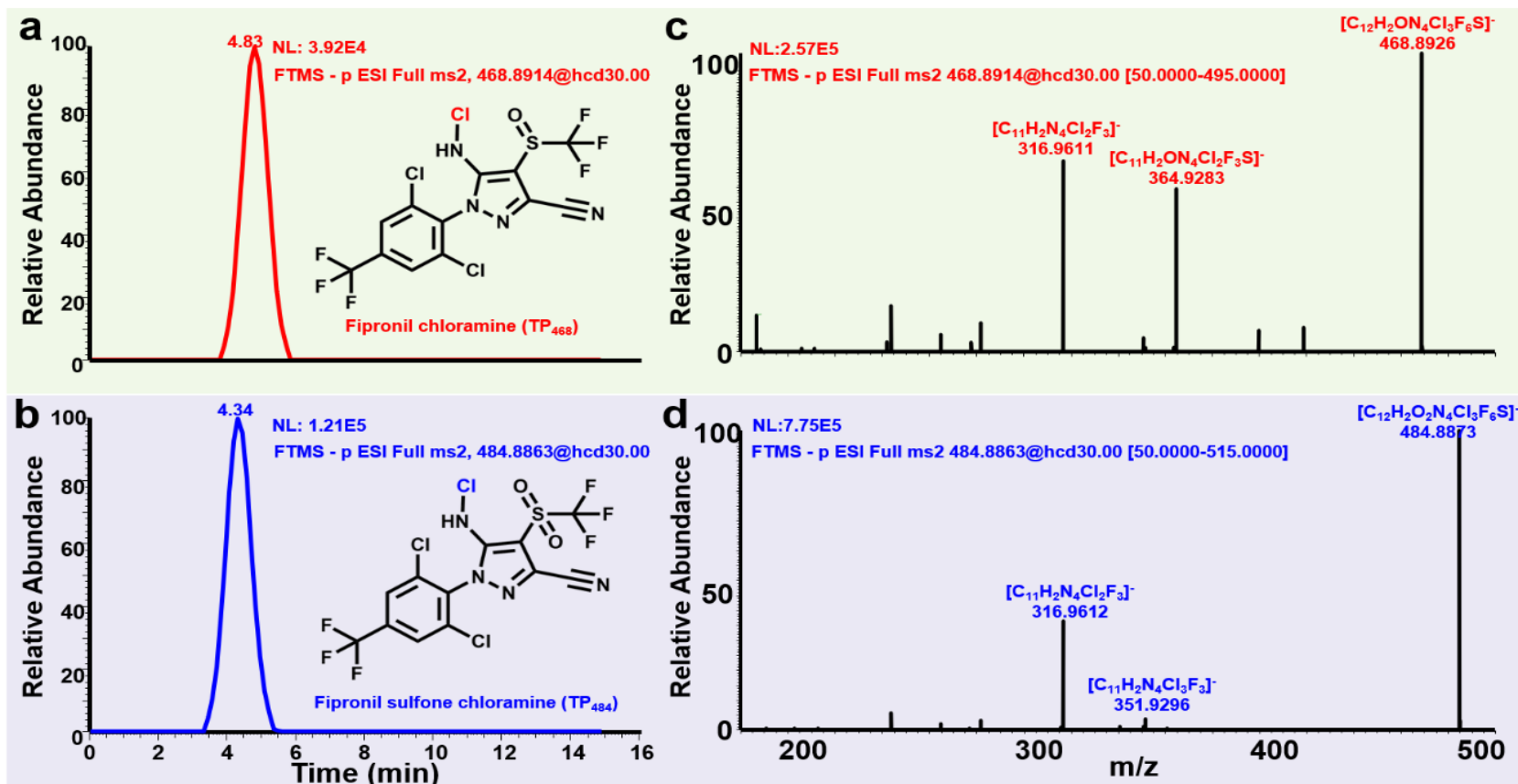
Formation of disinfection byproducts



Objectives

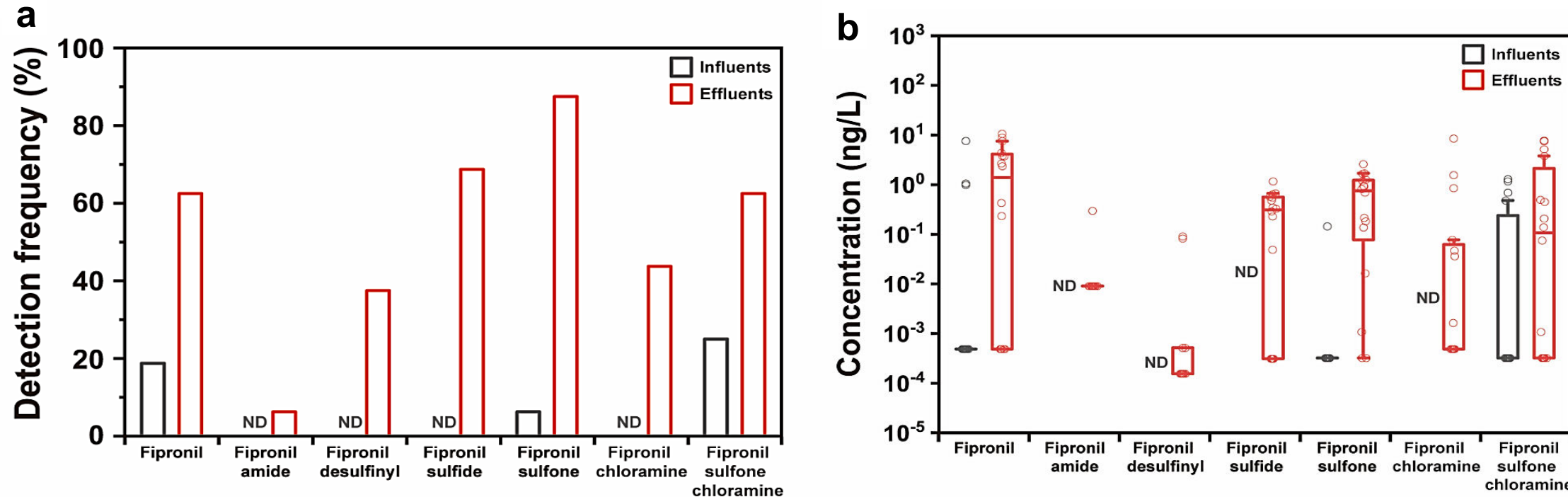
- **To identify the chlorinated disinfection byproducts of fipronil and its degradates in municipal wastewater treatment plants (MWWTPs);**
- **To investigate the difference of fipronils (fipronil and its transformation products) between municipal wastewater influents and effluents;**
- **To estimate and discuss the potential persistence and bioaccumulation of novel transformation products.**

RESULT-Screen and identification of the chlorination products of fipronil and its degradates in MWWTPs



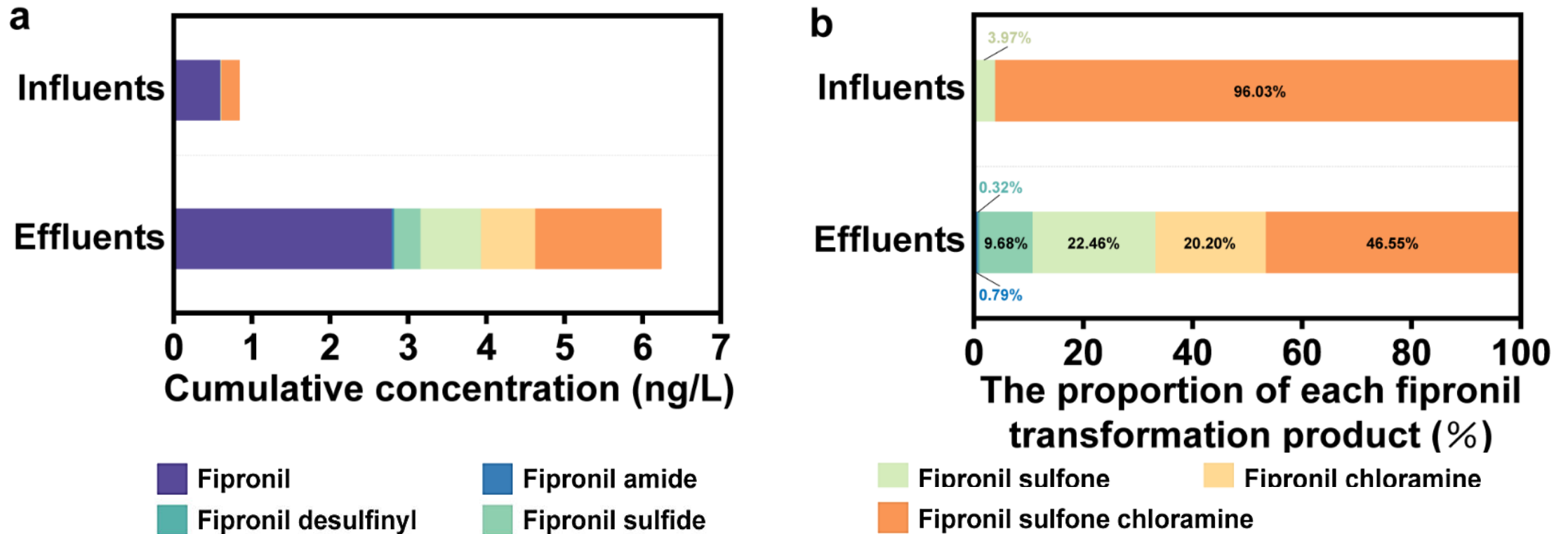
Novel transformation products: **TP₄₆₈ (fipronil chloramine)** and **TP₄₈₄ (fipronil sulfone chloramine)**.

Result-Detection frequency, concentrations and spatial distribution of in MWWTPs



- **Influents:** Detection frequency (6.25% - 25.0%); the median concentration of fipronil was 1.52 times higher than that of fipronil sulfone and fipronil sulfone chloramine.
- **Effluents:** detection frequency (6.25% - 87.5%); fipronil sulfone were the most prevalent fiproles in wastewater samples by their concentration.

Result-Difference of fiproles in the municipal wastewater influents and effluents



- The cumulative concentration of fiproles in the effluents was closed to the toxic dose for some sensitive species (7-10 ng/L).
- The formation of fipronil sulfone and fipronil sulfone chloramine were induced by sodium hypochlorite (NaClO) oxidation during wastewater treatment.

Result-Persistence and bioaccumulation (P&B) properties of fiproles

Name	Molecular formula	WATERNT (25°C, mg/L)	Log K _{ow}	Water half-life (t _{1/2} , w, day)	Sediment half-life (t _{1/2} , day) ^a	Bioconcentration factor (BCF) (L/kg wet-wt)
Fipronil	C ₁₂ H ₄ ON ₄ Cl ₂ F ₆ S	0.374	4.01 ^a	180	25.1-91.2	202.4
Fipronil amide	C ₁₂ H ₆ O ₂ N ₄ Cl ₂ F ₆ S	0.032	5.43	180	—	1769
Fipronil desulfinyl	C ₁₂ H ₄ N ₄ Cl ₂ F ₆	0.486	4.63 ^a	180	217-497	218.9
Fipronil sulfide	C ₁₂ H ₄ N ₄ Cl ₂ F ₆ S	0.0937	4.77 ^a	180	195-352	705.1
Fipronil sulfone	C ₁₂ H ₄ O ₂ N ₄ Cl ₂ F ₆ S	0.130	3.68 ^a	180	502-589	382.8
TP₄₆₈ (Fipronil chloramine)	C ₁₂ H ₃ ON ₄ Cl ₃ F ₆ S	0.00127	6.64	180	—	11200
TP₄₈₄ (Fipronil sulfone chloramine)	C ₁₂ H ₃ O ₂ N ₄ Cl ₃ F ₆ S	0.0785	4.42	180	—	382.9

a. The data of log K_{ow} and half-life were collected from references.

Conclusion

- **Two novel chlorinated byproducts (fipronil chloramine and fipronil sulfone chloramine) were identified and detected in MWWTPs in China;**
- **Fipronil chloramine and fipronil sulfone chloramine were primary transformation products in both influents (96.0%) and effluents (66.8%);**
- **Both fipronil chloramine and fipronil sulfone chloramine were more persistent and bioaccumulative than fipronil;**

Thanks for your attention
