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Publication date:
2013

Document Version
Publisher's PDF, also known as Version of record

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Citation (APA):

Polesel, F., Lehnberg, K., Dott, W., Trapp, S., Thomas, K. V., & Plósz, B. (2013). Modelling sorption of ciprofloxacin using the ASM-X framework – Evaluation of factors influencing activated sludge treatment and implications on environmental risk assessment. Poster session presented at 13th Nordic Wastewater Conference (NORDIWA), Malmö, Sweden.

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Modelling sorption of ciprofloxacin using the ASM-X framework – Evaluation of factors influencing activated sludge treatment and implications on environmental risk assessment

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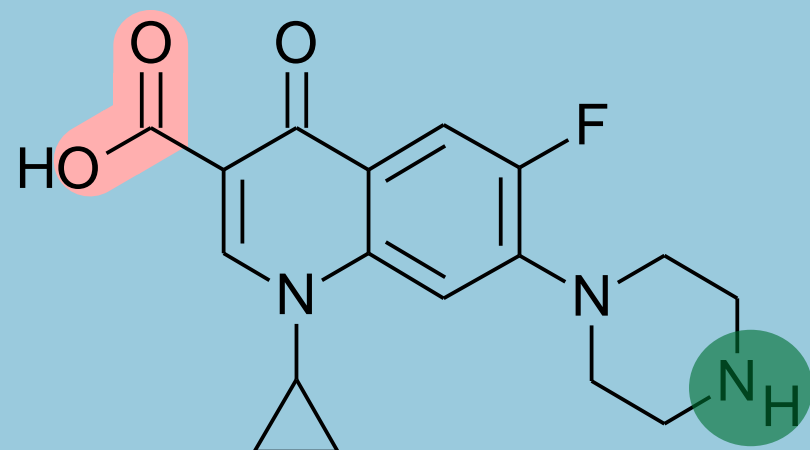


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1. Introduction

Ciprofloxacin:

- ~ 1 t/a in Nordic countries [1][2]
- Highly toxic to cyanobacteria [3]
- Zwitterionic ($pK_a=6.16, 8.63$) [4]



Fate in wastewater

Ciprofloxacin is mostly removed from sewage via sorption to activated sludge [5]. Its relatively high sorption capacity was found to be the result of electrostatic interactions with solid matrices – e.g., cation bridging [6].

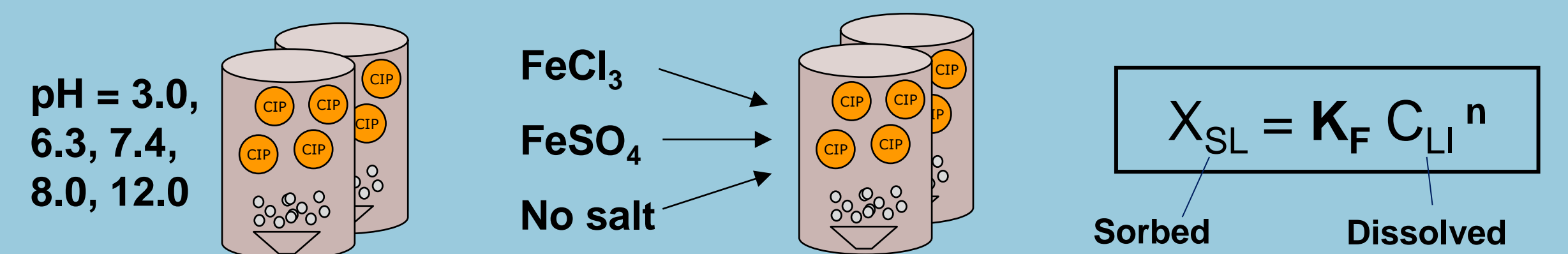
Case study
Systematic reduction of removal of ciprofloxacin in Bekkelaget WWTP (Oslo, Norway) [7]

Hypothesis
Reduced elimination caused by decrease of sorption capacity

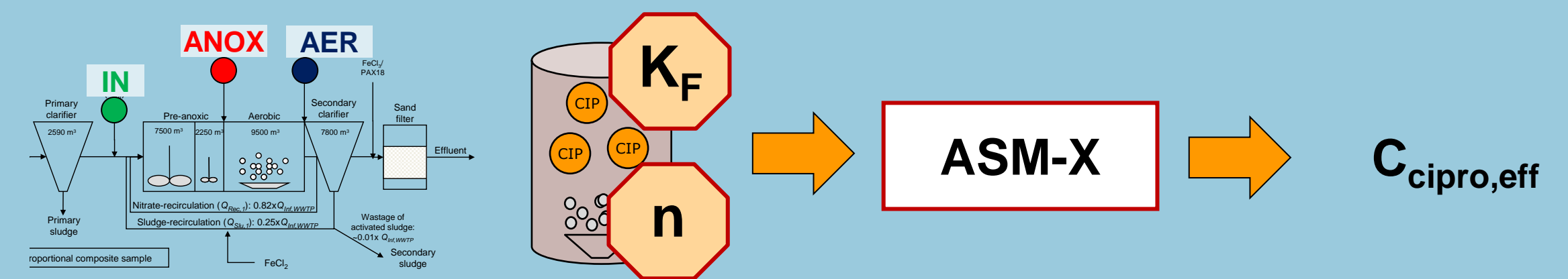
Objective of the study
To investigate how
• pH conditions
• salt dosing for P removal affect sorption of ciprofloxacin on activated sludge by using
1. Batch experiments
2. Full-scale fate (ASM-X)

2. Methods

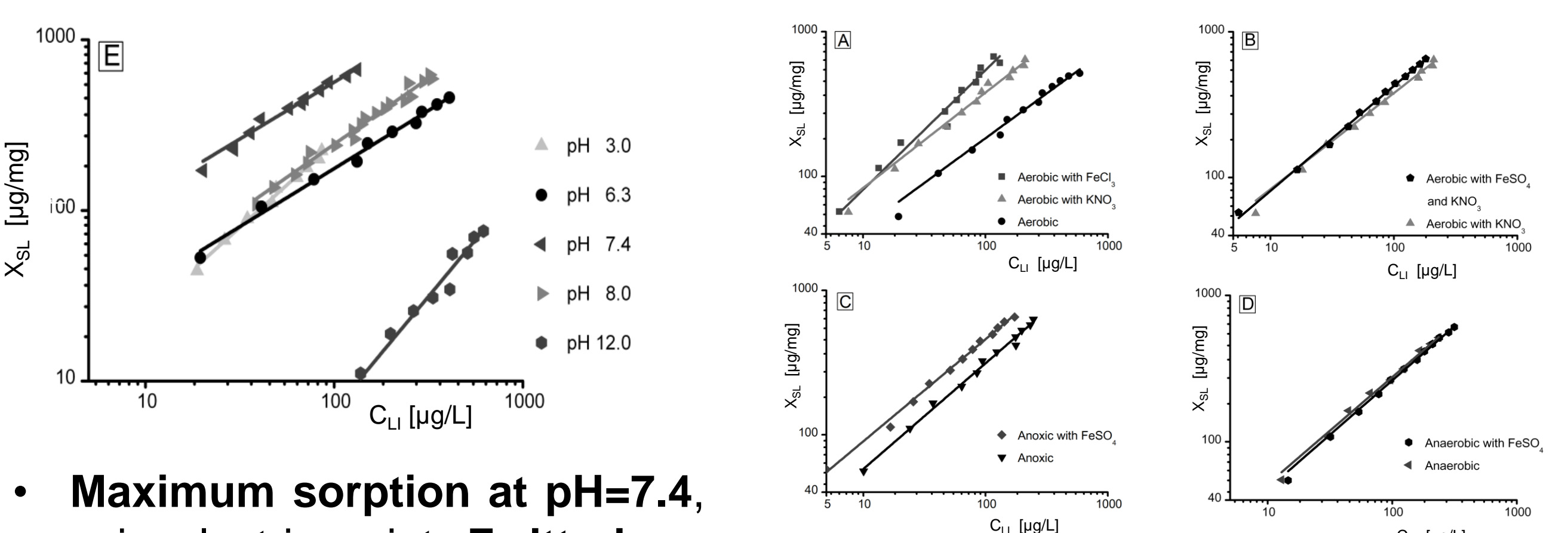
1) Targeted batch experiments were performed to evaluate sorption onto activated sludge under different pH and iron salt dosing conditions using Freundlich isotherms.



2) The Activated Sludge Model for Xenobiotics – ASM-X ([7]) was used to predict measured ciprofloxacin's concentrations at Bekkelaget WWTP (Oslo). Freundlich parameters estimated in batch were used for ASM-X calibration. Effluent concentrations of ciprofloxacin ($C_{cipro,eff}$) could also be estimated.

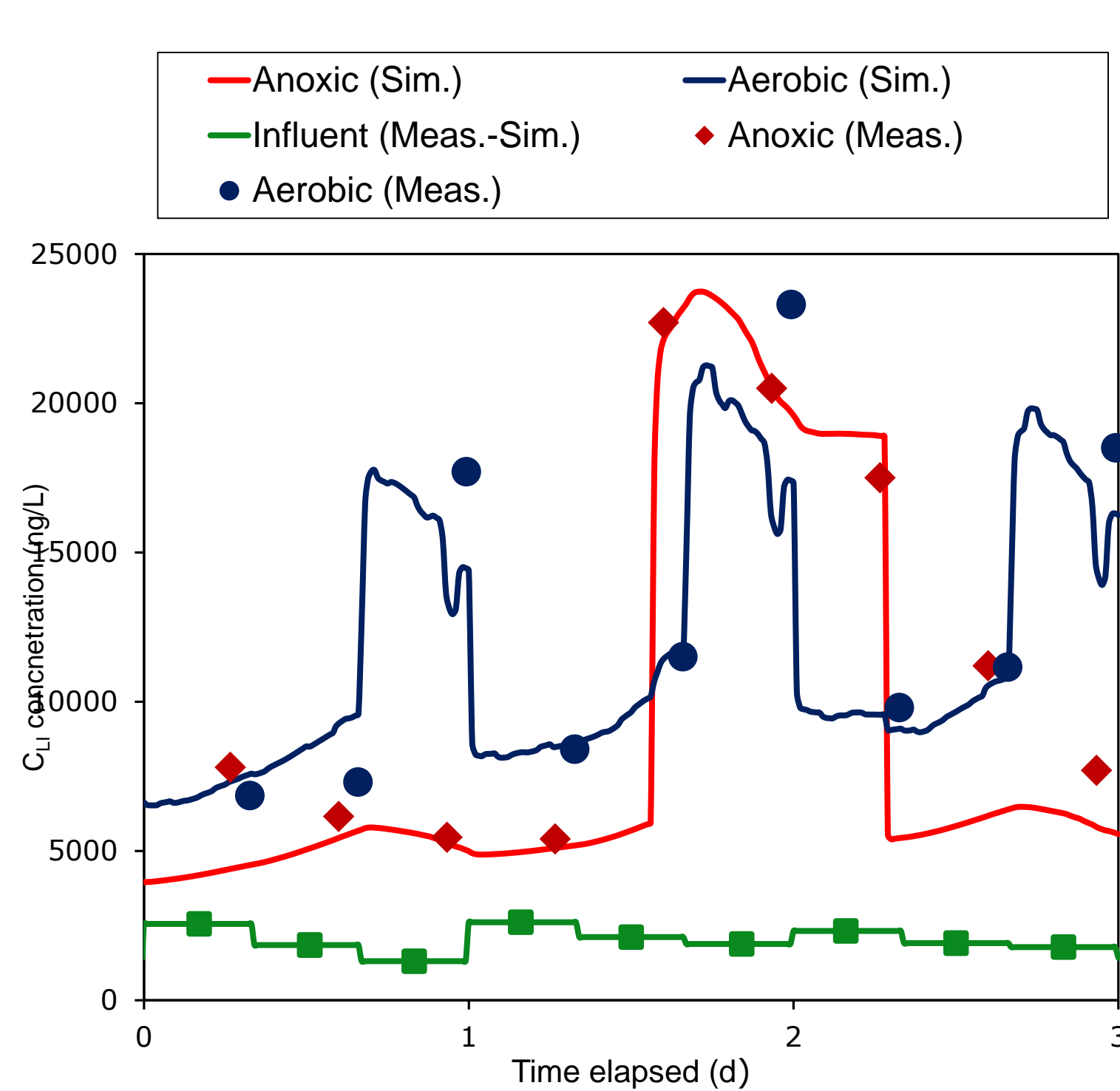


3. Results – pH and iron effect



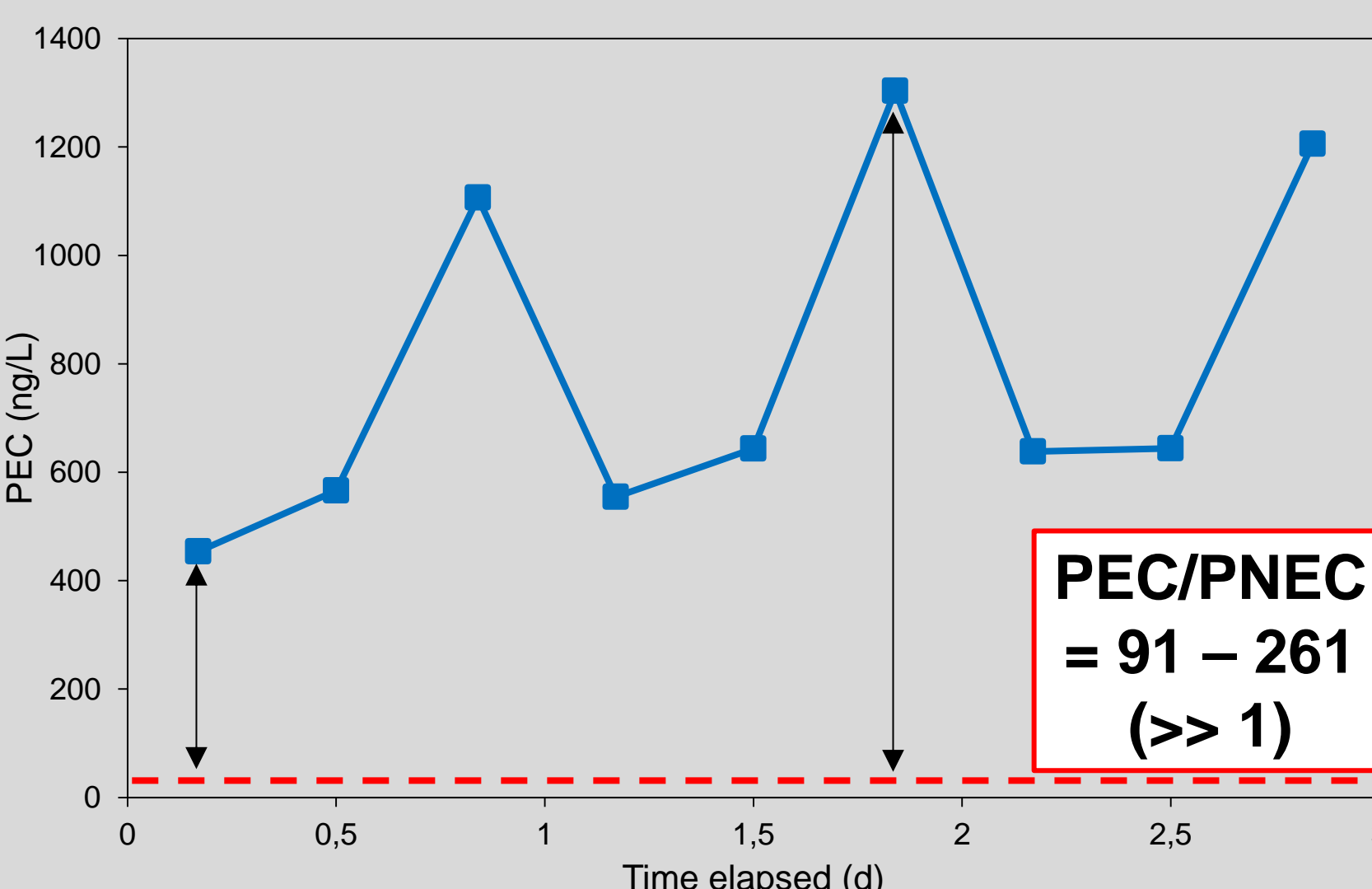
- Maximum sorption at pH=7.4, ~ isoelectric point. Zwitterions had highest sorption capacity (via bound cations on sludge)
- Anions (pH=12) had negligible sorption capacity, possibly due to repulsion to sludge [8]
- Increase of sorption by spiking iron salts (except for anaerobic exp.), with possible complexation
- Redox conditions affected sorption only in the presence of iron

4. Full-scale simulations



Intermittent ciprofloxacin's removal ($C_{LI} > 15 \mu\text{g/L}$) occurred in Bekkelaget full-scale WWTP and was associated to sorption deterioration [7]. Full-scale simulations using batch-estimated Freundlich parameters showed that pH increase (> 8) was more likely to have caused reduced removal. No specific effect could be associated to the reduction in salt dosing (usually occurring in night hours).

5. Implications for risk assessment



PECs (*) of ciprofloxacin, calculated by using a dilution factor $DF=10$, varied of a factor of ~ 3 over the sampling period, as a result of changes in sorption capacity. In general, PECs were 2 orders of magnitude higher than PNECs. A situation of potentially high risk was therefore identified for Bekkelaget, with regard to release of ciprofloxacin. Similar evidences were obtained by [1].

*** Additional notes**
 $PEC = C_{cipro,eff} / DF$
Predicted Environmental Concentration
 $PNEC = 5 \text{ ng/L}$
Predicted Non-Effect Concentration
 $PEC/PNEC = 91 - 261 (>> 1)$

6. Conclusions

- When present as zwitterion in solution, ciprofloxacin was found to sorb at a higher extent as compared to other ionic species. Presence of iron salts increased sorption extent under aerobic and anoxic conditions.
- Full-scale simulations with ASM-X associated the intermittent removal of ciprofloxacin in activated sludge to a pH increase in the biological reactors, rather than to the reduction in iron salt dosing regimes.
- Predicted environmental concentrations (PECs) of ciprofloxacin had evident time variations, as a result of dynamic loading and operational conditions typical to WWTPs. Potentially high risk, due to high PECs of ciprofloxacin, was associated to the water bodies, receiving Bekkelaget WWTP effluent.

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