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Influence of organics removal on pharmaceutical adsorption

MELiSSA conference 2022 – Aurea Heusser

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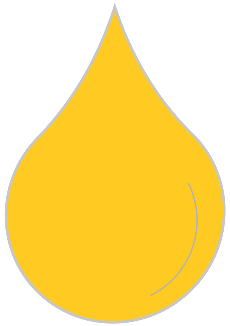
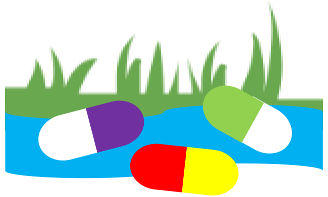
Introduction

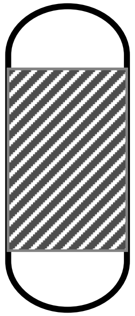
64% of active ingredients of the pharmaceuticals are excreted via urine - (Lienert et al. 2007)



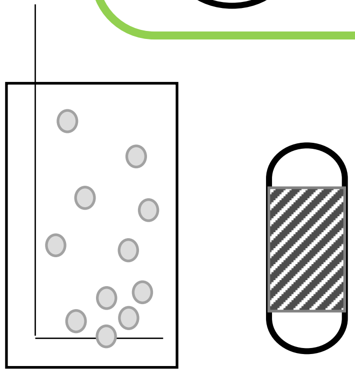
Removal by ozonation is not appropriate for urine - (Dodd et al. 2008)

Pharmaceuticals in the environment is an emerging issue - (Heberer 2002)





→ Removal by adsorption for untreated urine?



Removal by adsorption on GAC* works for nitrified urine - (Köpping et al. 2020)

* GAC = Granular Activated Carbon

Organics removal – but to what extent?

Hypothesis

Organics removal is required to adsorb pharmaceuticals from stored urine

- The removal of organics from stored urine prevents

    i. Extremely high carbon requirement due to competition with the bulk organics

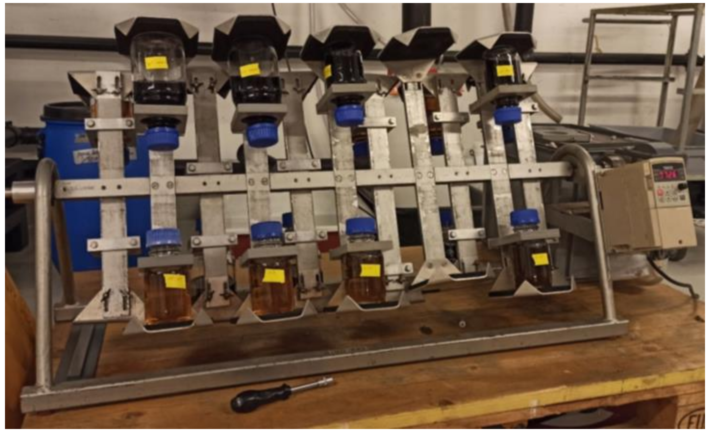
    ii. Extensive biomass growth and clogging in the GAC filter

Methods

Powdered Activated Carbon (PAC) experiments with filtered urine

1. Stored urine – urea hydrolized and organics fermented
2. 75% organics removal – aerobic treatment with short HRT (1-2 d)
3. 85% organics removal – aerobic treatment with long HRT (3-5 d)

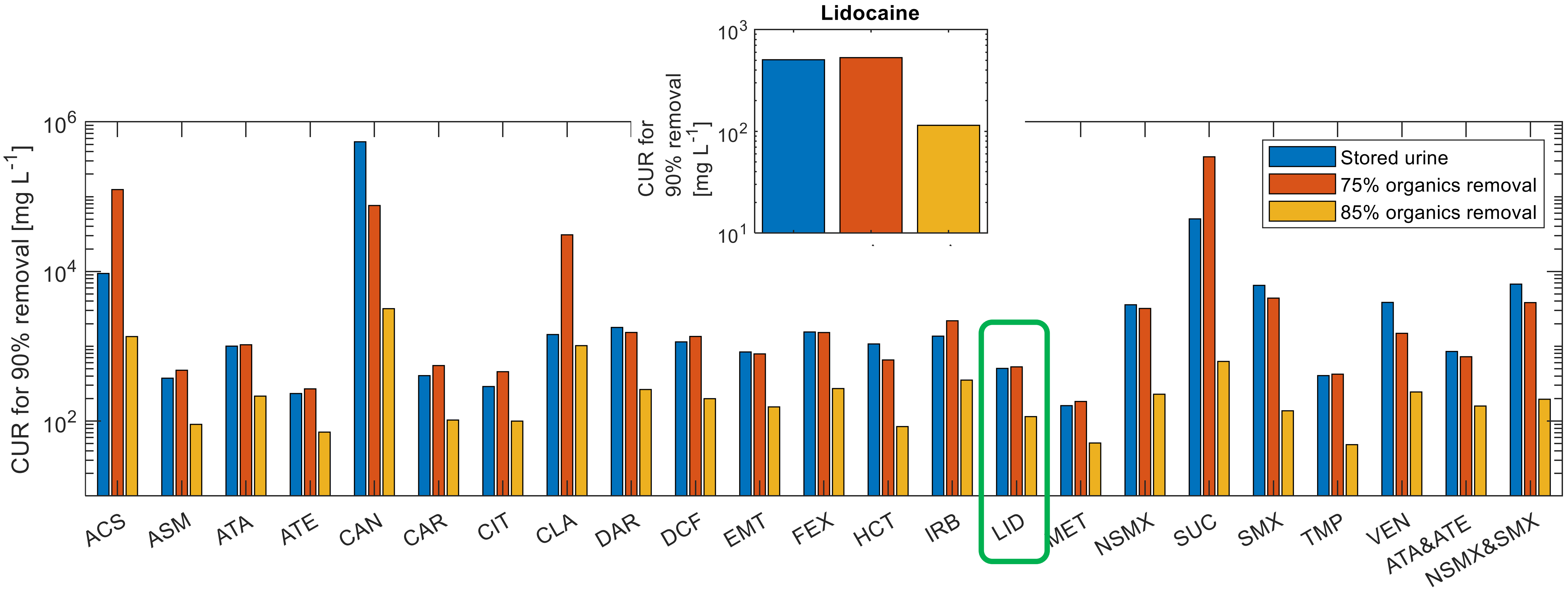
- 21 substances spiked @ 200 µg/L
- 16 different PAC concentrations



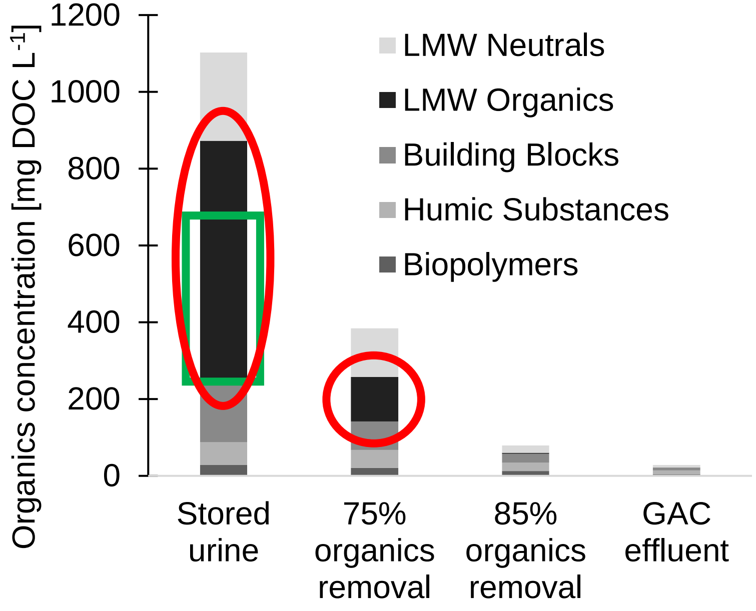
➢ Evaluation of Carbon Usage Rate (CUR) for a 90% removal

HRT: Hydraulic retention time

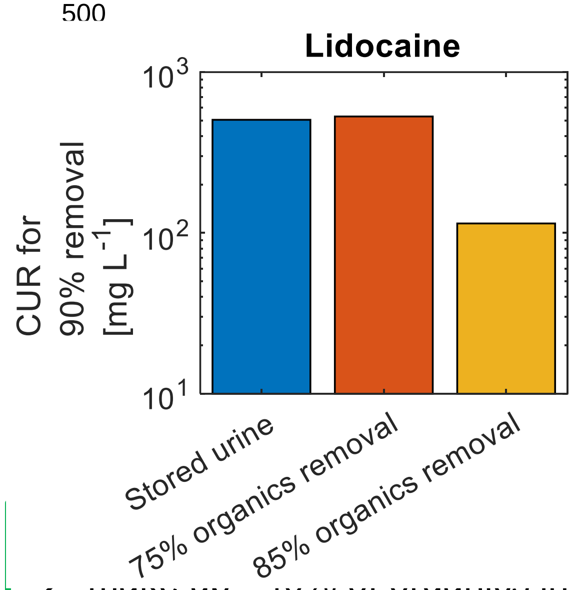
Carbon usage rate (CUR) for 90% removal



Bulk organics – LC-OCD[1] and IC for VFA[2]



		Stored urine	75% organics removal	85% organics removal
Acetate	mgC L^{-1}	217	0	0
Propionate	mgC L^{-1}	31	0	0
Share of total DOC	%	37%	0%	0%



Literature
claims that LMW[3] organics compete with pharmaceuticals for adsorption sites:
(Newcombe et al. 2002)
(Zietzschmann et al. 2014)
(Kennedy and Summers 2015)
(Velten et al. 2011)

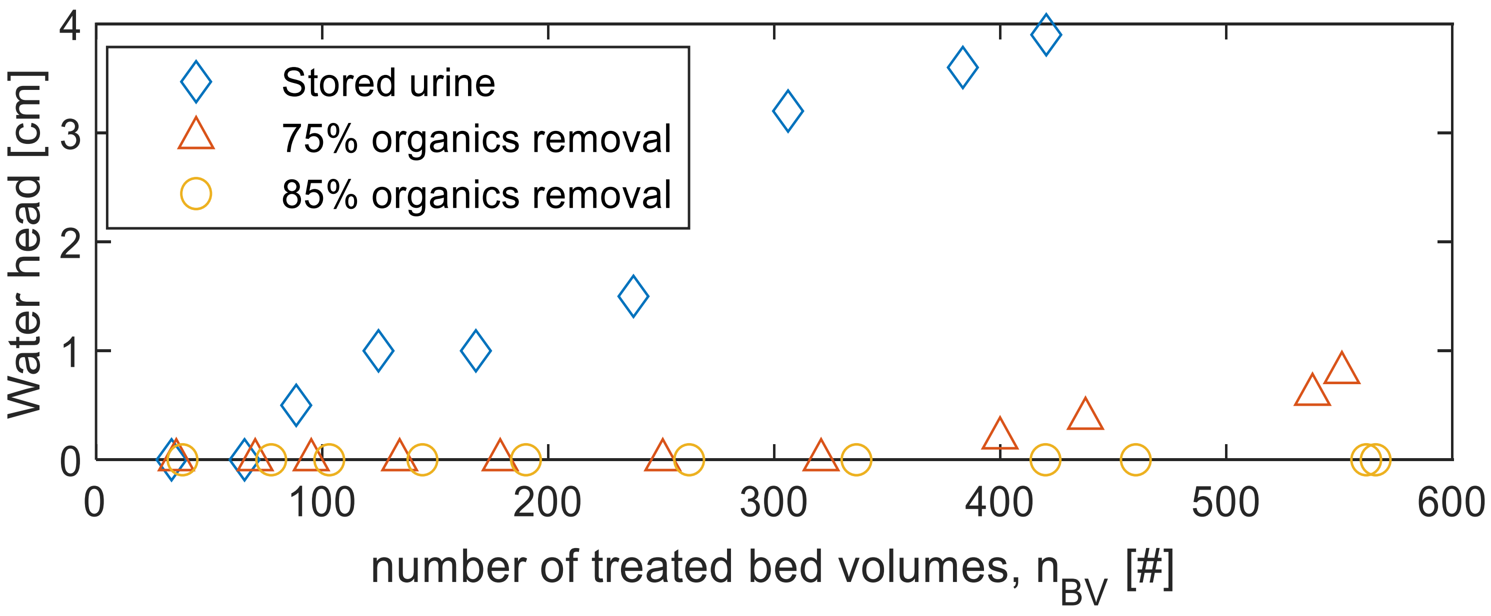
→ make up ~40% of organics in stored urine
→ are easily biodegradable
→ show as LMW[3] organics
→ do not adsorb on carbon

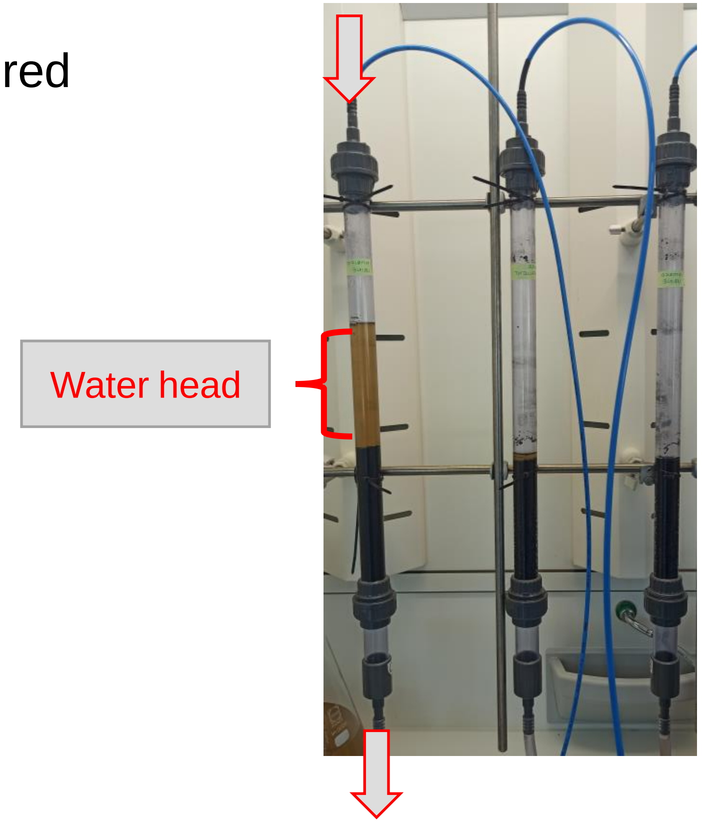
1: Liquid Chromatography – organic carbon detection
2: Ion Chromatography for Volatile Fatty Acids
3: LMW: Low Molecular Weight

Treatment of stored urine leads to clogging of the GAC

Granular activated carbon (GAC) experiment

- Stored urine, 75% organics removal, 85% organics removal – unfiltered





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Conclusions

Organics removal is required to adsorb pharmaceuticals from stored urine

Problem	Stored urine	75% organics removal	85% organics removal
Competition with bulk organics	✖	✖	✔
Clogging of the filter	✖	✔	✔

- ➢ Treatment of the organics in stored urine is required to optimally use the carbon
  - ➢ Less carbon required
  - ➢ No clogging

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Thank you ☺

Included literature

Heberer, T. (2002). "Occurrence, fate, and removal of pharmaceutical residues in the aquatic environment: a review of recent research data." Toxicology letters **131**(1-2): 5-17.

Lienert, J., et al. (2007). "Reducing micropollutants with source control: substance flow analysis of 212 pharmaceuticals in faeces and urine." Water Science and Technology **56**(5): 87-96.

Dodd, M. C., et al. (2008). "Ozonation of source-separated urine for resource recovery and waste minimization: process modeling, reaction chemistry, and operational considerations." Environmental science & technology **42**(24): 9329-9337.

Köpping, I., et al. (2020). "Removal of pharmaceuticals from nitrified urine by adsorption on granular activated carbon." Water research X **9**: 100057.

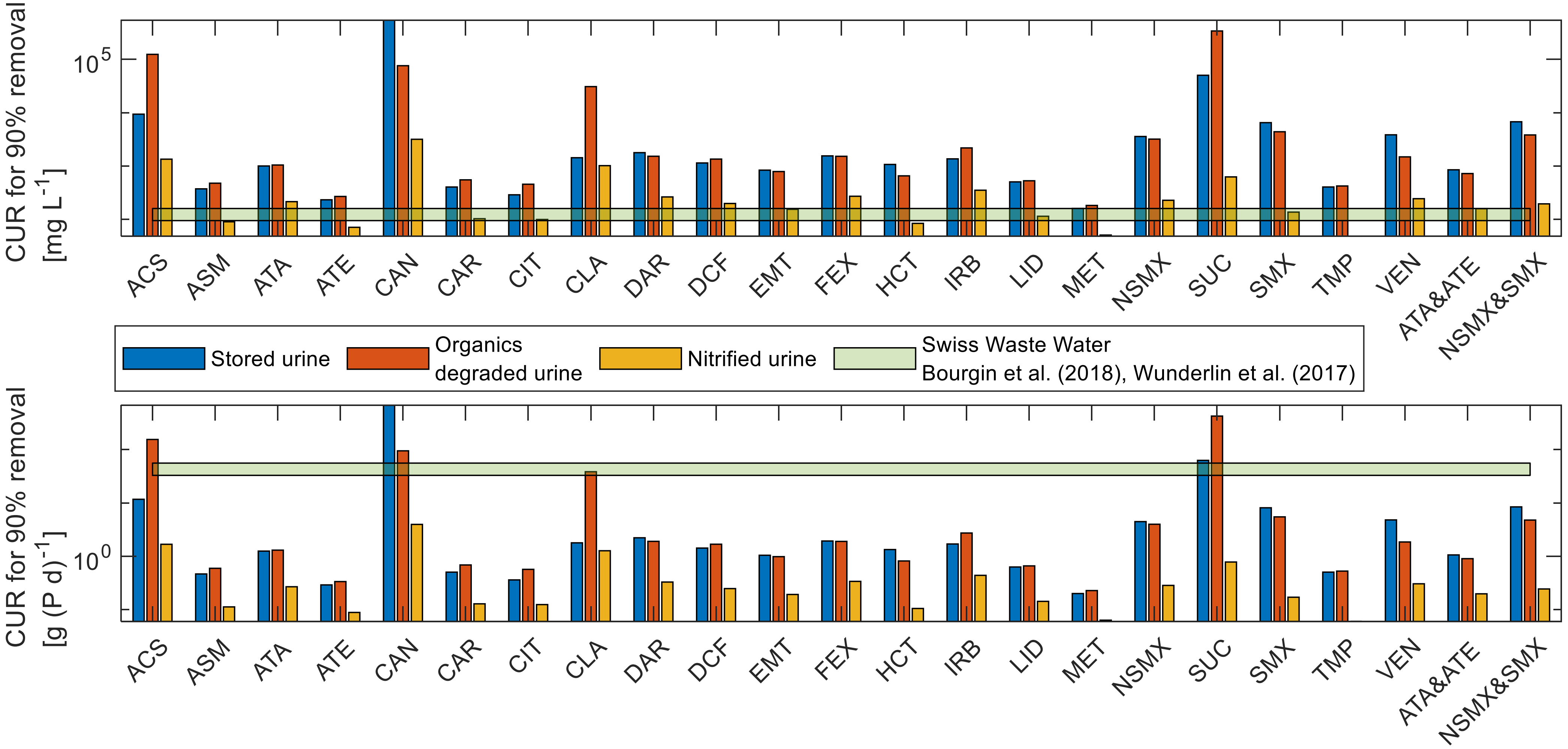
Newcombe, G., et al. (2002). "Simultaneous adsorption of MIB and NOM onto activated carbon. I. Characterisation of the system and NOM adsorption." Carbon **40**(12): 2135-2146.

Zietzschmann, F., et al. (2014). "Impact of EfOM size on competition in activated carbon adsorption of organic micro-pollutants from treated wastewater." Water research **65**: 297-306.

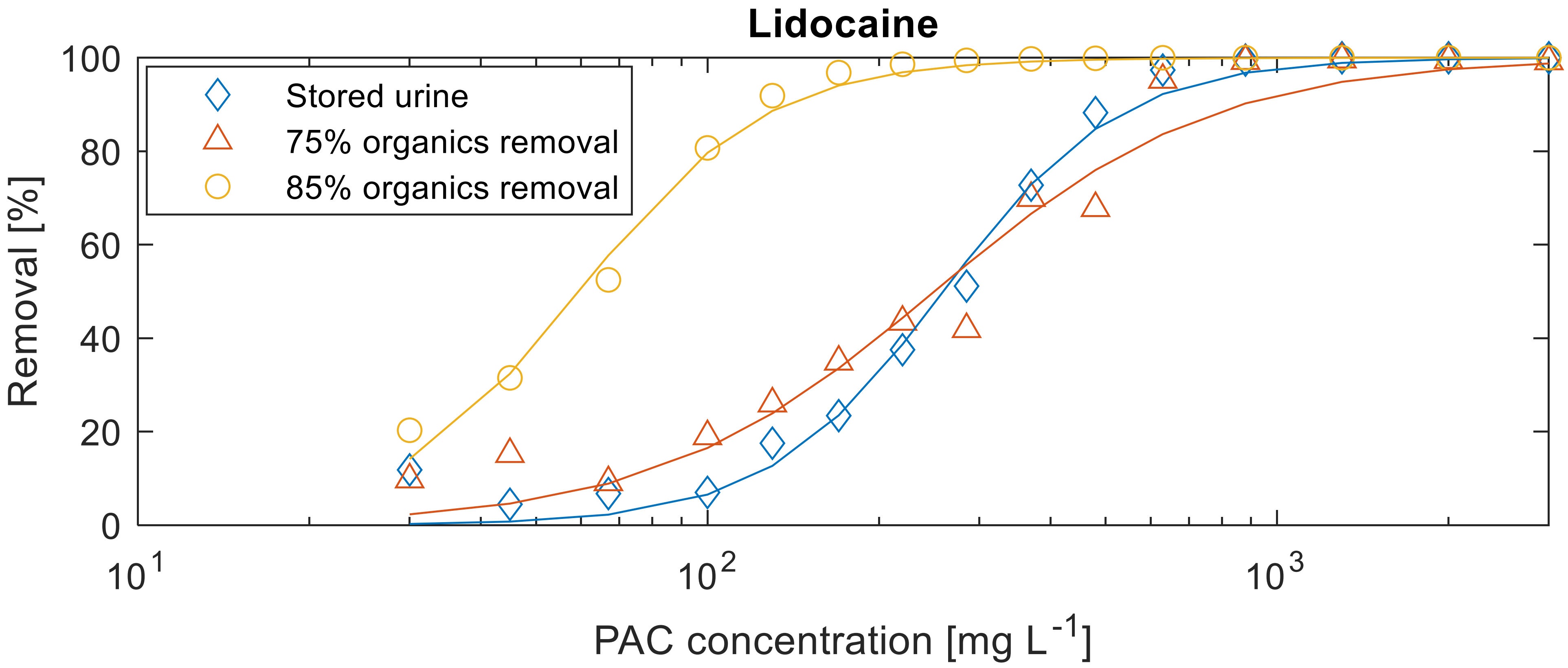
Kennedy, A. M. and R. S. Summers (2015). "Effect of DOM size on organic micropollutant adsorption by GAC." Environmental science & technology **49**(11): 6617-6624.

Velten, S., et al. (2011). "Characterization of natural organic matter adsorption in granular activated carbon adsorbers." Water research **45**(13): 3951-3959.

CUR comparison with wastewater

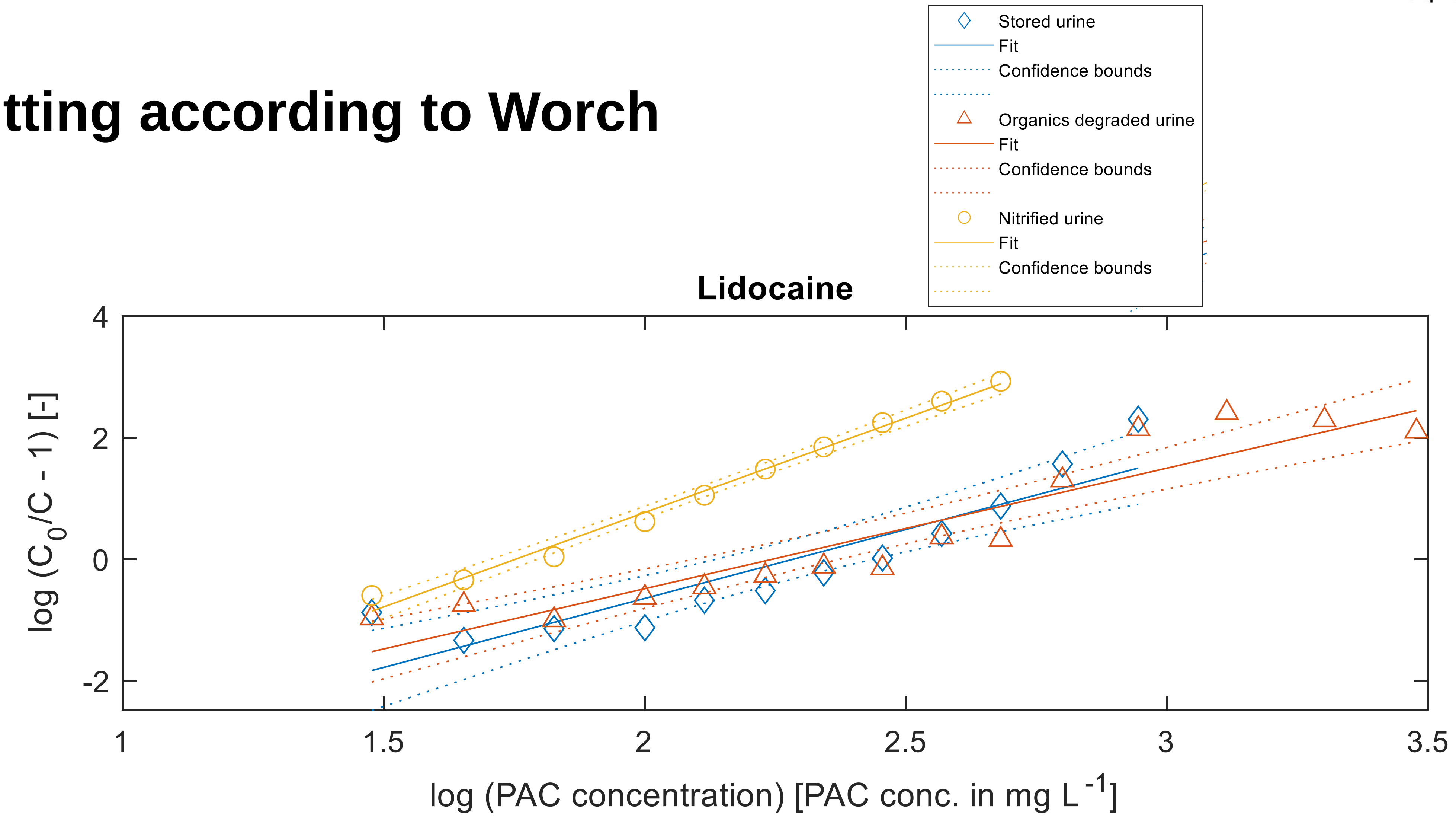


Removal



Lidocaine
Stored urine
75% organics removal
85% organics removal
Removal [%]
100
80
60
40
20
0
10^1
10^2
10^3
PAC concentration [mg L^{-1}]

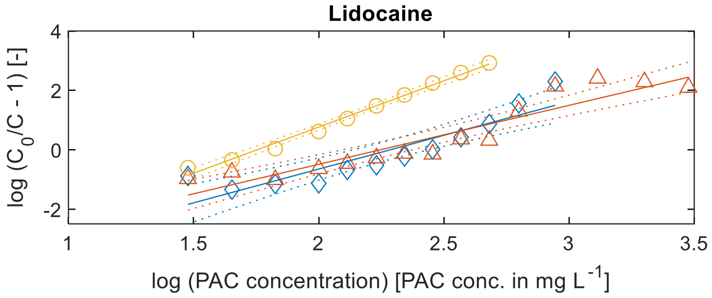
Fitting according to Worch



Fitting according to Worch (equations)

Find A and n by linear fitting:

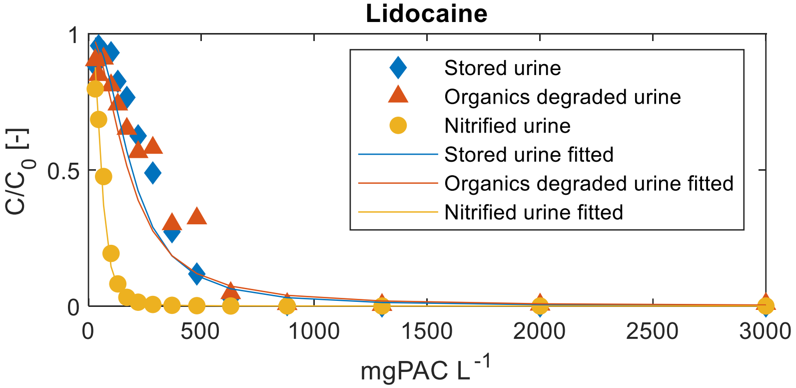
$$\ln\left(\frac{C_0}{C}-1\right)=\frac{1}{n}*\ln\left(\frac{m_A}{V_L}\right)-\ln(A)$$

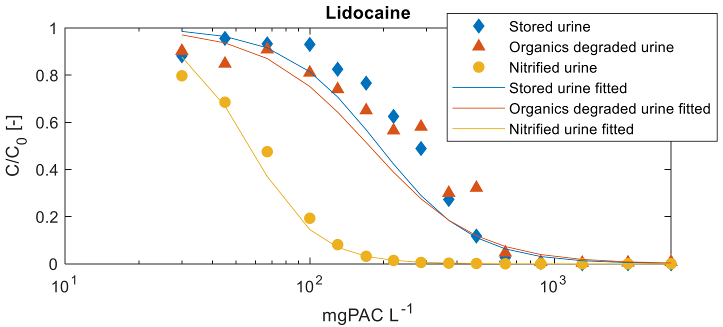


$$\left(\frac{m_A}{V_L}\right)=PAC\ concentration\ [mg\ L^{-1}]$$

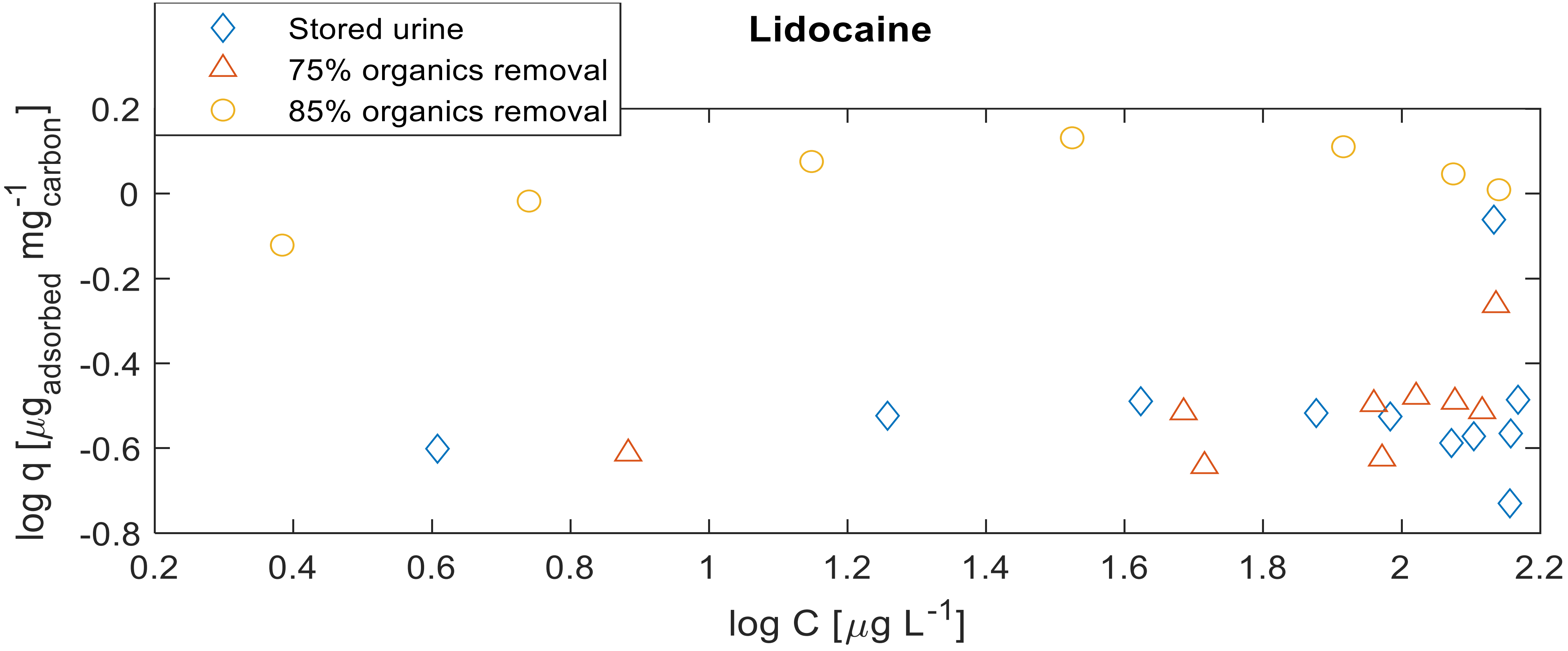
Find CUR for a given removal:

$$\left(\frac{m_A}{V_L}\right)=A^n*\left(\frac{C_0}{C}-1\right)^n$$

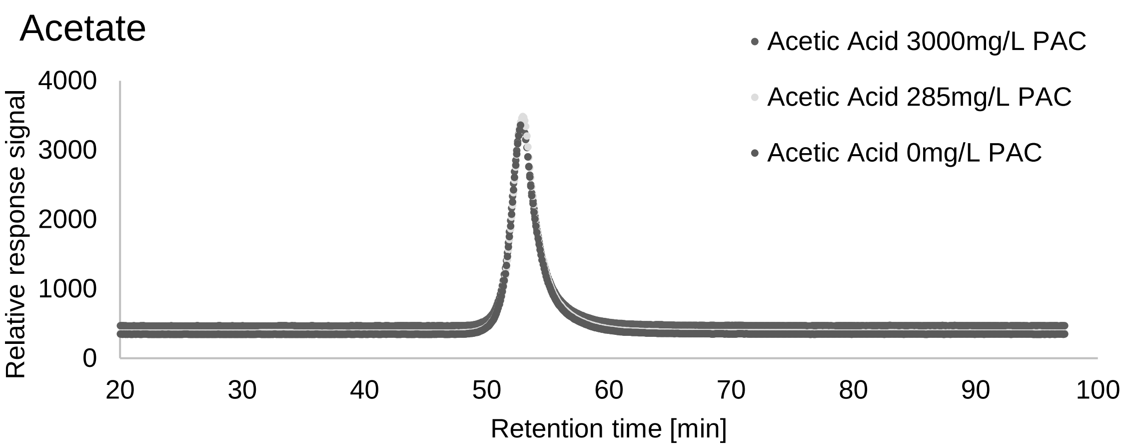


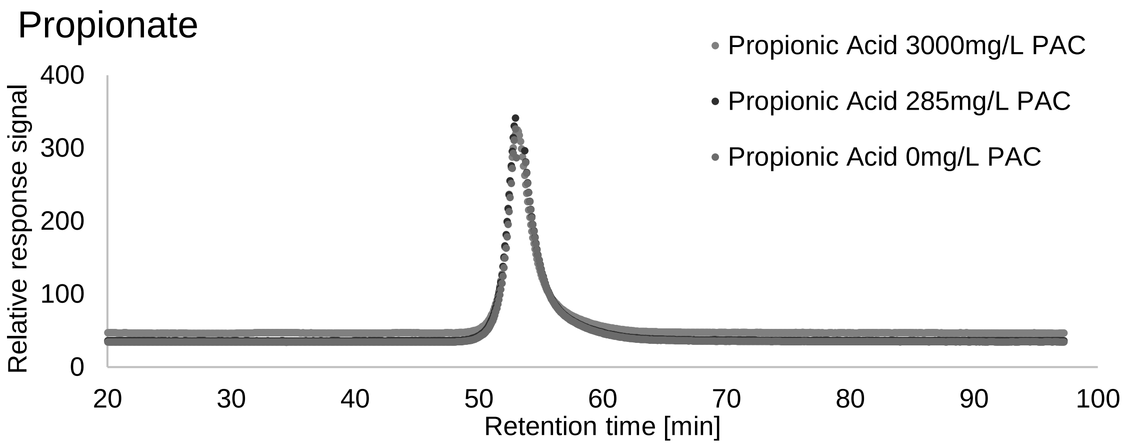


Isotherm

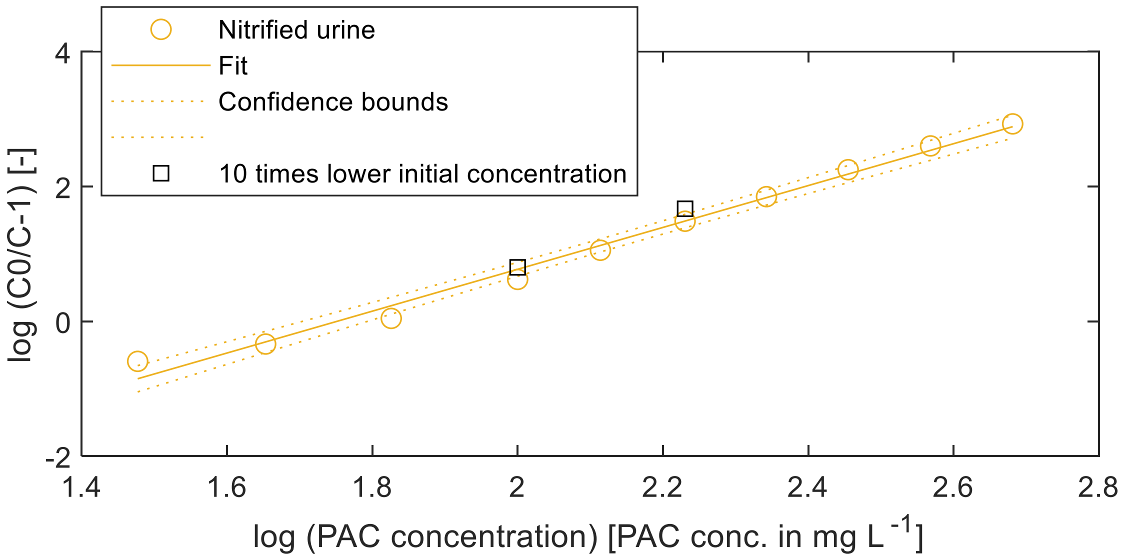

Lidocaine
Stored urine
75% organics removal
85% organics removal
log q [μg_adsorbed mg^-1_carbon]
log C [μg L^-1]
0.2
0
-0.2
-0.4
-0.6
-0.8
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2

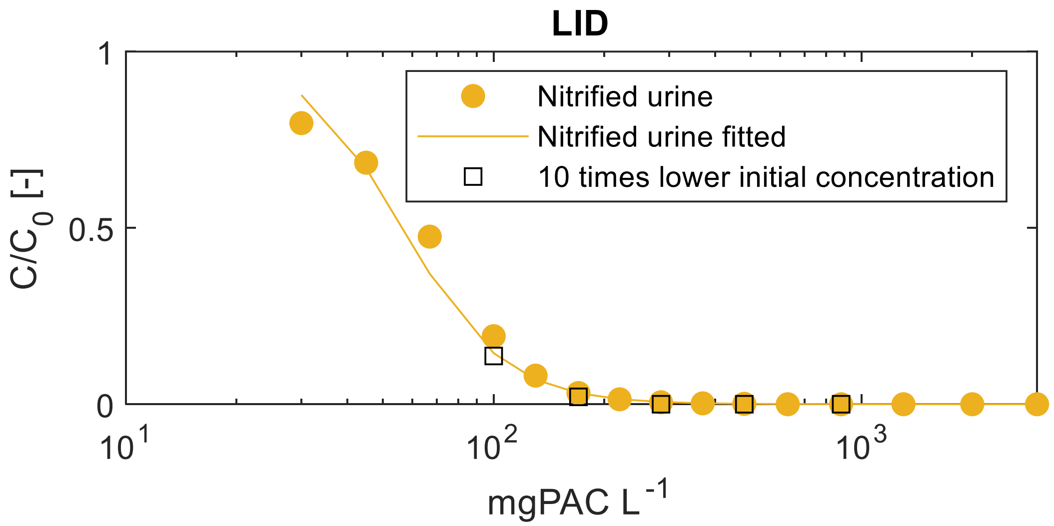
Chromatographs of acetate and propionate





Low concentration - Lidocaine





Removal and isotherm at low initial concentration