Eawag:
Swiss Federal Institute of Aquatic
Science and Technology

ETH zürich

eawag aquatic research

Broad-scope Groundwater Screening focusing on Persistent and Mobile Compounds from Urban Sources

Karin Kiefer, Heinz Singer,

Juliane Hollender

Kiefer et al. Water Research 2021
https://doi.org/10.1016/j.watres.2021.116994

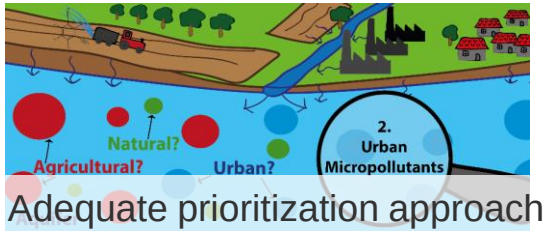
Goals of Groundwater Screening

…inform the authorities about emerging compounds to be monitored

Adequate analytical approach

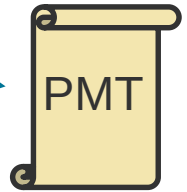
…focus on persistent & mobile compounds

…focus on urban compounds



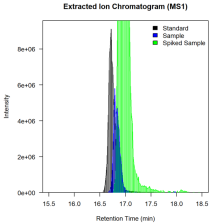
Adequate prioritization approach

…identify as many compounds as possible



Compound lists

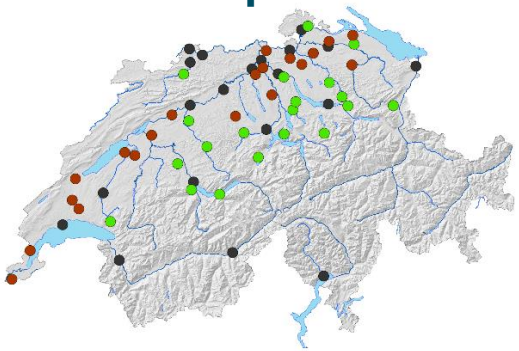
in silico tools, MS2 libraries



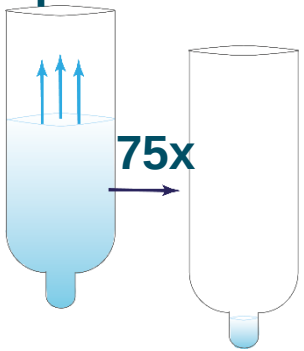
Confirmation

Samples & Analytical Approach

60 Groundwater Samples



Vacuum assisted evaporative enrichment



140 µL

RPLC-ESI-HRMS/MS

Atlantis® WatersT3
3 mm, 3.0 x 150 mm

Target screening (Trace Finder 4.1):
→ Quantification of 498 compounds with standards

Suspect Screening (enviMass, R workflow)
→ "Expected compounds

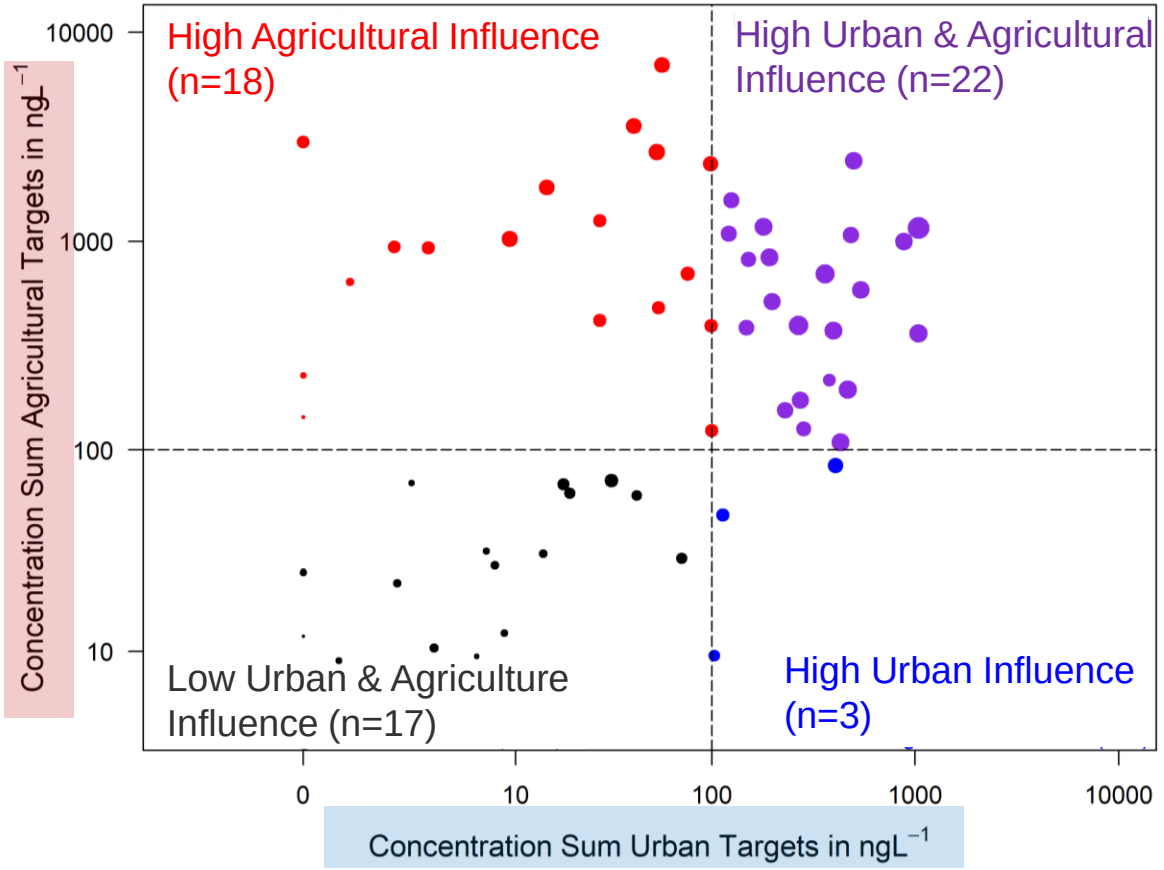
Prioritization

Nontarget Screening (enviMass, R workflow):
→ remaining signals without prior information

Kiefer et al. Water Research 2021
https://doi.org/10.1016/j.watres.2021.116994

Source Related Prioritization

Step 1:
classify ***samples*** based on their contamination with **269 urban** and **229 agricultural** target compounds.

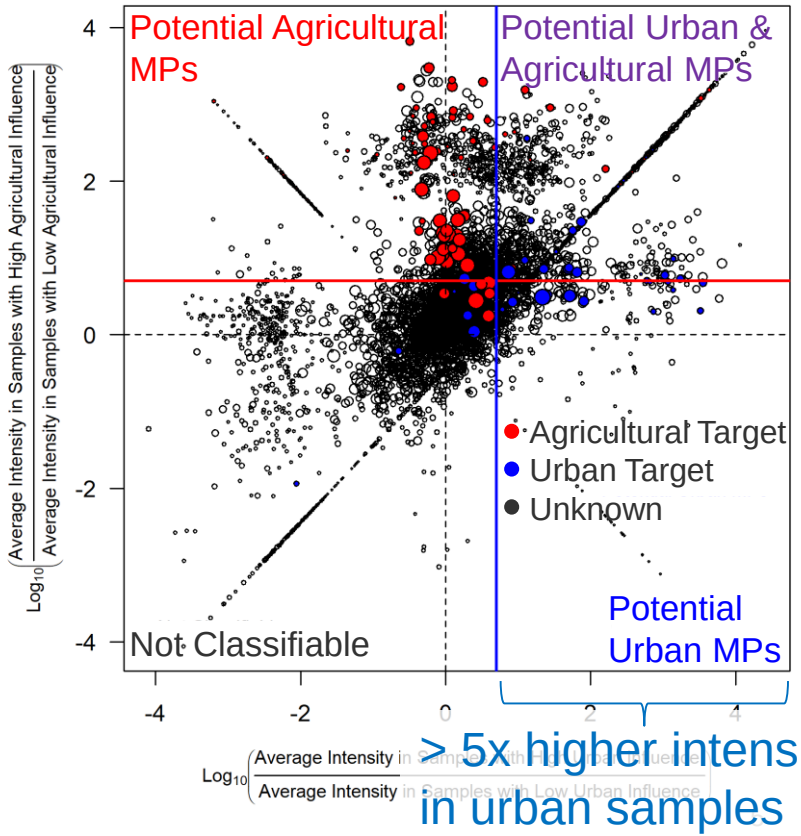


Kiefer et al. Water Research 2021

Source Related Prioritization

Step 2:
classify *detected* ***6500 compounds*** based on intensity and occurrence in samples

> 5x higher intensity in agricultural samples

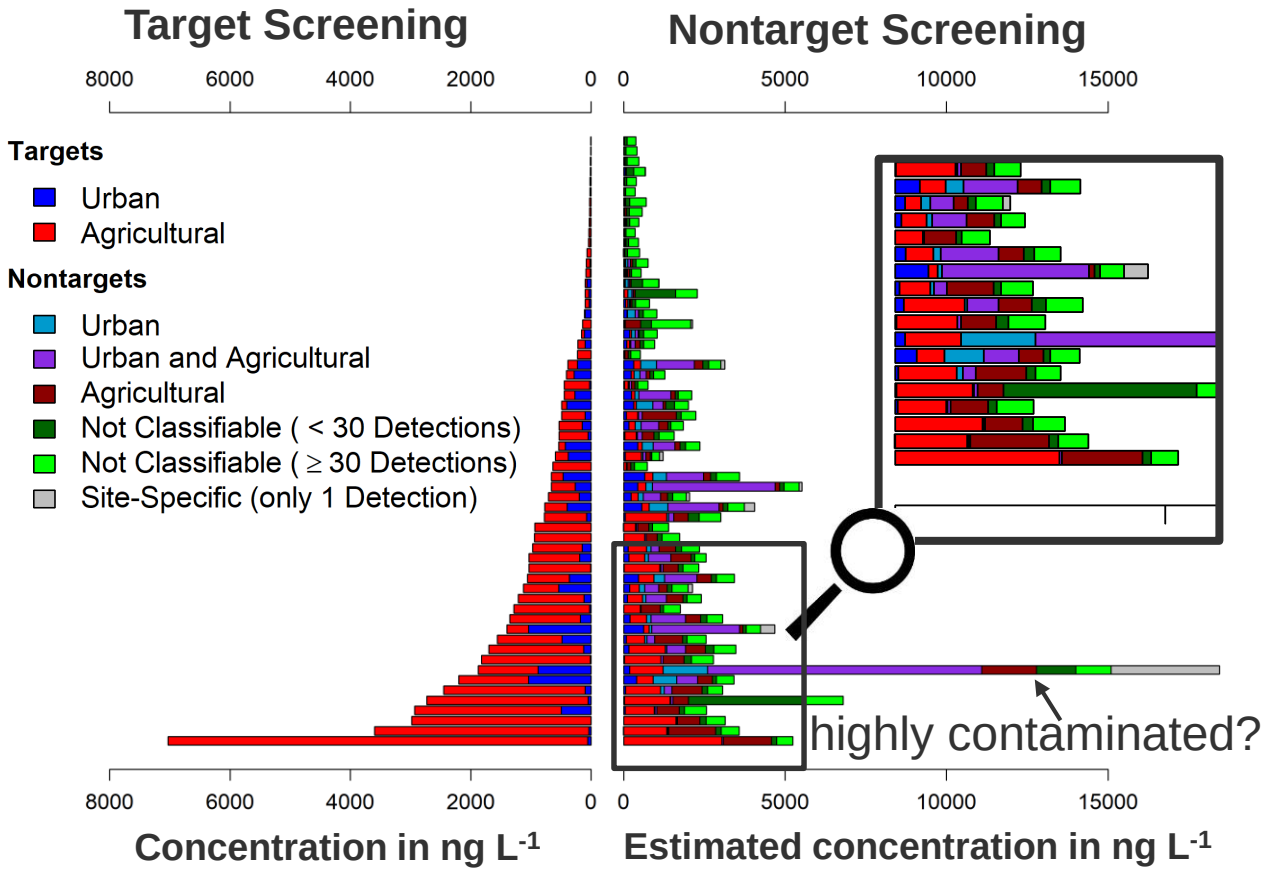


> 5x higher intensity in urban samples

Kiefer et al. Water Research 2021

Source Related Prioritization

Step 3:
estimate still **unknown contamination** from different sources

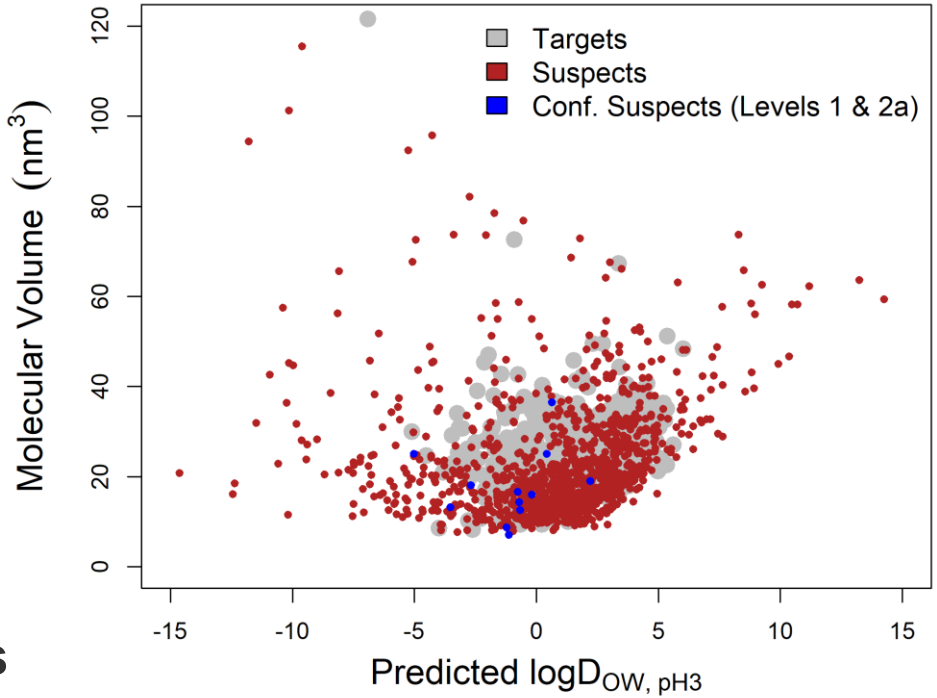


Kiefer et al. Water Research 2021

Annotation of Compounds

1162 Suspects

- UBA PMT (607, Arp & Hale 2020)
- Extended PMT (215, mobile, high production, Arp & Hale)
- Selected PMT compounds (64, Schulze et al. 2019)
- KEMI Market List (796, mobile, high water exposure)



Annotation of prioritized nontargets
Using list of >988,000 compounds

EPA CompTox, NORMAN SusDat, PubChemLite, Extended PMT, list with pesticide TPs…

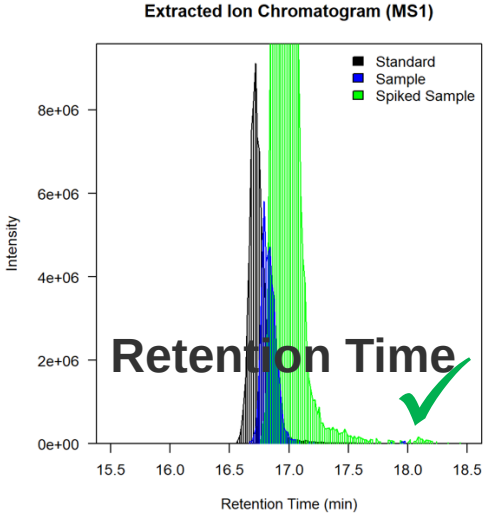
Evaluation & Confirmation of Identity

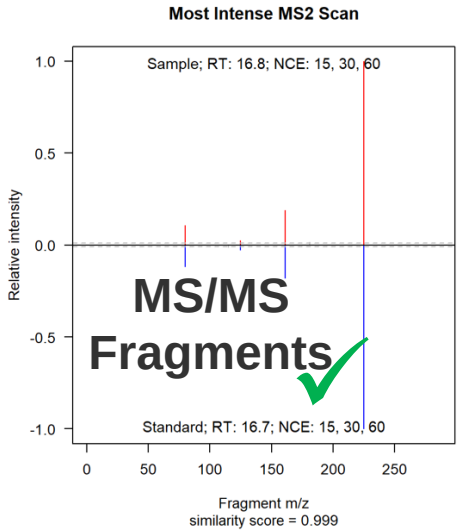
Evaluation of annotated compounds

- 2 *in silico* fragmenters (MetFrag, SIRIUS4/CSI:FingerID)
- MS/MS library search (MassBank, MoNA, NIST17, mzCloud)
- Peak shape, intensity, retention time

Confirmation using reference material

- 23 compounds confirmed
- 6 rejected

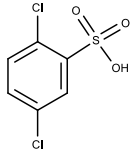




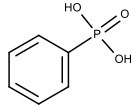
Identified Suspects & Nontargets

13 “Novel” Micropollutants

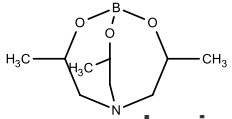
Industrial Chemicals



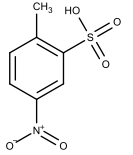
2,5-Dichlorobenzene-sulfonic Acid



Phenylphosphonic Acid

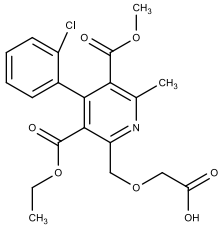


Triisopropanolamine borate

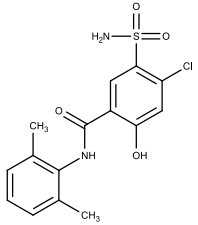


2-Methyl-5-Nitrobenzene-sulfonic Acid

Pharmaceuticals



TP of Amlodipine

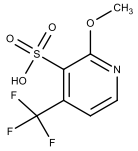


Xipamide

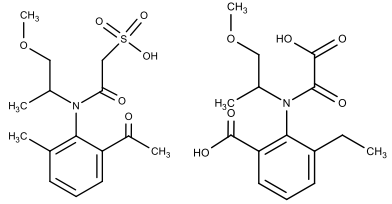
27 “Known” Micropollutants

17 x Level 1
10 x Level 2a/3

Pesticide TPs



Pyroxsulam TP PSA
Level 3



6 Metolachlor TPs
Level 3

Levels according to Schymanski et al. (2014), Environ Sci Technol, 48.

Classification of Identified Compounds

eawag aquatic research
ETH zürich

Pre-classification correct?

Urban

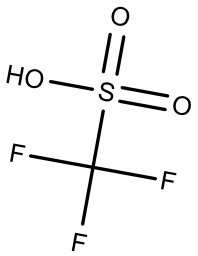
- Edetic acid (EDTA)
- Methenamine
- Oxypurinol
- Iomeprol TP 629
- Isomer of 5,6-Dimethyl-2H-benzotriazole

Agricultural

- Atrazine-desethyl-desisopropyl
- Trifluoromethanesulphonic acid
- Metolachlor TP SYN542490
- Metolachlor TP SYN547969 / SYN542488
- Metolachlor TP SYN547977

Not Classifiable

- p-Toluenesulfonic acid
- Trifluoroacetic acid
- Hexa(methoxymethyl)melamine



Urban and Agricultural

- 2,5-Dichlorobenzenesulfonic Acid
- 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS)
- Pyrimidinol (2-Isopropyl-6-methyl-4-pyrimidone)
- 2-Methyl-5-nitrobenzenesulfonic Acid
- 5-Methoxy-2H-benzotriazole
- Dimethylbenzenesulfonic acid (isomers)
- Fluometuron
- O-Des[2-aminoethyl]-O-carboxymethyl dehydroamlodipine
- Perfluorobutylsulphonamide
- Perfluoropropanesulfonic Acid
- Phenylphosphonic Acid
- Propyphenazone
- Triisopropanolamine borate
- Xipamide
- Iopromide TP 643
- Iopromide TP 701 A
- Triphenylphosphine oxide
- Isomer of 5-Methoxy-2H-benzotriazole
- Methyldiphenylphosphine oxide
- Naphthalenedisulfonic Acids (various isomers)
- Pyroxsulam TP PSA

Conclusions

- **Prioritization approach** needs to be appropriate for research question
- **Regulatory suspect lists** are highly valuable for monitoring
- **Confirmation** with reference material or library MSMS spectra is important!
  - **Research community** should add more MS/MS spectra to openly accessible libraries, e.g. MassBank
  - **Industry** should provide reference material or/and MSMS spectra of compounds and their transformation products
- Still **many compounds might be unknown**
  - analytical approach
  - incomplete compound lists
  - TPs of industrial chemicals largely unknown?
  - …

Acknowledgements

Support for sampling and lab work

Letian Du, Bernadette Vogler, Birgit Beck, Philipp Longrée, Jennifer Schollée, Eawag

Support for data processing

Martin Loos, envibee GmbH, Jennifer Schollée, Michael Stravs, Eawag

Support for suspect lists

Hans Peter Arp, Norwegian Geotechnical Institute

Emma Schymanski, University of Luxembourg

Financial support and selection of monitoring wells

Miriam Reinhardt, Ronald Kozel, Federal Office for the Environment