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# Should we use wetlands to monitor emerging environmental pollutants of concern, since the regulations of them are so diverse between countries?

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**ABSTRACT**

Wetlands are areas with permanent or frequent high-water levels. They can be natural or constructed and used for both active and passive water treatment. They are often ideal both for removal and retention processes for many pollutants due to the variety of physical and chemical conditions, and their biodiversity. There was a trend towards the closing of creeks and water courses, this changed by the year 2000 and now we have an increasing number of wetlands at the benefit of flora and fauna alike.

In Norway the monitoring of the priority pollutants is determined by a number of limiting concentrations, for example for water bodies, the best class is the upper limit for the background concentrations, then there is a class defined as without risk of toxic effects (the chronic long-term toxicity quality standard), then a class of moderate toxic effects, the bad standard is defined by the risk of acute toxicity, and the lowest or very bad class is defined by the risk of comprehensive toxic effects.

What happens in wetlands? There are both removal and processes of storage of pollutants; physical such as flocculation, sedimentation, photo degradation and sorption. Biological; microbial transformation e.g. ammonia to nitrogen gas, dehalogenation, predation and uptake, Chemical such as coagulation, transformation and chemical sorption, and hydrological; retardation, diffusion and clogging.

There are two motivations; to investigate to prevent pollution and harmful effects, or to profit in one way or another, or a combination of the two. To profit is not harmful, unless it is based on consciously overlooking facts.

## POLLUTANTS OF CONCERN?

Emerging pollutants of concern (EPC), also called Constituents of emerging concern (CEC) and other names are regulated through several directives and guidelines, for example the Water framework directive (2000/60/EC), the Groundwater daughter directive (2006/118/EC), the Priority substances directive (2008/105/EC). The latter defines 33 priority substances + 8 other pollutants and requires the setting of threshold values for all pollutants which put the groundwater body at risk.

In Norway the EPA (Miljødirektoratet) issues quality standards for the environment, with classes I to V, see Fig. 1. Class I is the background or natural concentrations. The criteria for classes II and III upper limits used are the toxicological limits for chronical effect after long term exposure and for acute effects after short time exposure, respectively AA-EQS og MAC-EQS (EPA, 2016). The upper limit for class IV is for acute toxicity without any security factors so that for soils, class V is defined as hazardous waste.

## 2.1 Tilstandsklasser for ferskvann (µg/l)

| Nr | Navn på Navn substans | Klasse I | Klasse II | Klasse III | Klasse IV | Klasse V |
|---|---|---|---|---|---|---|
| | | Bakgrunn | AA-EQS | MAC-EQS | | Omfattende akutt tox eff. |
| 1 | Kadmium | *0.003* | *Fotnote 1* | *Fotnote 2* | *Fotnote 3* | *Fotnote 3* |
| 2 | Bly | *0.02* | 1.2 | 14 | 57 | > 57 |
| 3 | Nikkel | 0.5 | *4* | 34 | 67 | > 67 |
| 4 | Kvikksølv | 0.001 | 0.047 | 0.07 | *0.14* | > *0.14* |
| 5 | TBT | | 0.0002 | 0.0015 | 0.003 | > 0.003 |

Figure 1. Norwegian quality standard classes for freshwater (explained in the text, EPA, 2016).

**Table ES.1. Revised monitoring requirements for health-based and performance-based indicator CECs and performance surrogates for potable and non-potable reuse practices.**

| Reuse Practice | Health-based indicator | MRL (ng/L) | Bioanalytical methods | MRL (ng/L) | Performance-based Indicator | Expected Removal[6] | MRL (ng/L) | Surrogate | Method | Expected Removal[6] |
|---|---|---|---|---|---|---|---|---|---|---|
| Surface Spreading Application (SA) | NDMA[2] | 2 | ER-α | 0.5 | ΔGemfibrozil[3] | >90% | 10 | ΔAmmonia | SM | >90% |
| | NMOR[1] | 2 | AhR | 0.5 | ΔSulfamethoxazole[4] | >30% | 10 | ΔNitrate | SM | >30% |
| | 1,4-Dioxane[1] | 100 | | | ΔIohexol[3] | >90% | 50 | ΔDOC | SM | >30% |
| | | | | | ΔSucralose[5] | <25% | 100 | ΔUVA | SM | >30% |
| | | | | | | | | ΔTotal fluorescence | | >30% |
| Subsurface Application (Direct Injection) and Surface Water | NDMA[2] | 2 | ER-α | 0.5 | ΔSulfamethoxazole | >90% | 10 | ΔConductivity | SM | >90% |
| Augmentation (SWA) | NMOR[1] | 2 | AhR | 0.5 | ΔSucralose | >90% | 100 | ΔDOC | SM | >90% |
| | 1,4-Dioxane[1] | 100 | | | ΔNDMA | 25-50% | 2 | ΔUVA | SM | >50% |
| Non-potable reuse practices | | | | | None | | | Turbidity | SM | |
| | | | | | | | | $Cl_2$ residual or operational | SM | |
| | | | | | | | | UV dose<br>Total coliform | SM | |

[1]Industrial chemical; [2]Disinfection byproduct; [3]Pharmaceutical residue; [4]Antibiotic; [5]Food additive; [6]travel time in subsurface two weeks and no dilution, see details in Drewes *et al.*, 2008; SM – Standard Methods; MRL – Method Reporting Limit.

Figure 2. Recommended constituents of emerging concerns (CECs) in California, US.

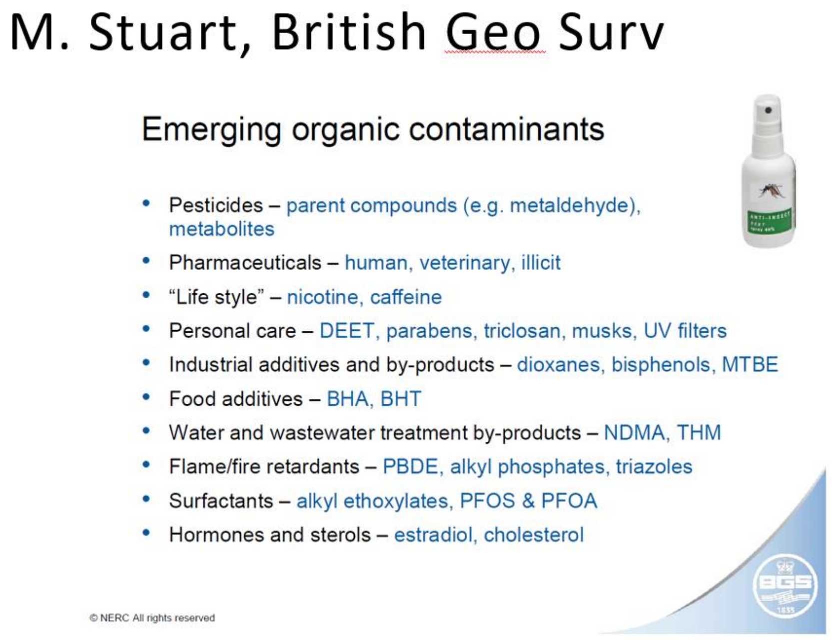


Figure 3. CECs from Britain (BHA are anisole antioxidants, DEET is insect repellent toluamide).

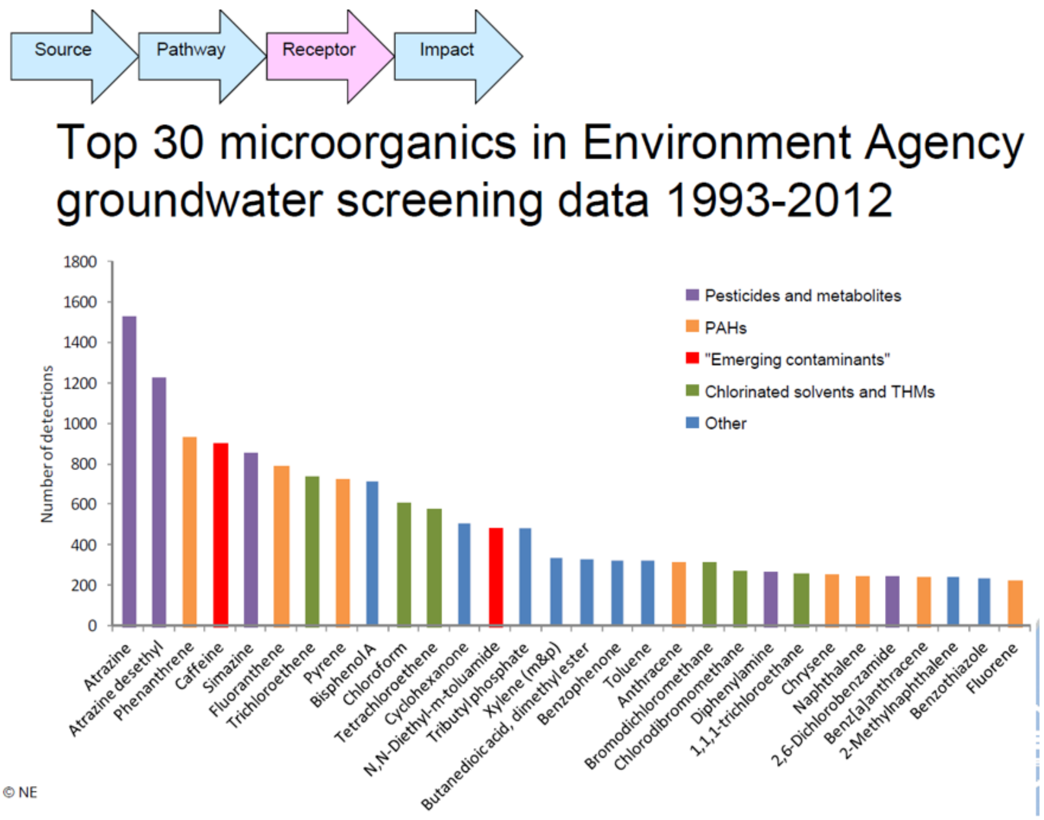


Figure 4. Occurrence of selected CECs (Drewes et al, 2018).

In the US a framework was then used to develop a list of monitoring parameters, including four health-relevant and four performance-based ("indicator") CECs to demonstrate a consistent capacity for reduction of CECs by recycled water treatment processes (Figure 2). This initial list of eight CECs, representing multiple source classes (e.g., pharmaceuticals, personal care products, food additives, and hormones), were identified for groundwater recharge (GWR) potable reuse applications.  This comparison revealed that potential exposures and potential human health risks associated with CECs in non-potable use scenarios are expected to be 10% or lower than exposure to CECs in water intentionally consumed in the potable reuse scenario.

The updated measured environmental concentration (MECs) and monitoring trigger levels (MTLs) were employed to screen a total of 489 CECs (increased from 418 in 2010) using the same screening framework used by the 2010 Panel to identify candidate compounds for monitoring. This exercise indicated that regular monitoring of three of four 2010 health-based indicator CECs (17β-estradiol, triclosan and caffeine) is no longer necessary, as the monitoring data set collected over the past several years (2008-2017) indicate that concentrations are consistently below MTLs (i.e., the MEC/MTL ratio is less than 1). In contrast, the collected monitoring data indicated that concentrations of N-nitrosodimethylamine (NDMA) were eight times higher than the MTL and, therefore, NDMA should be retained as a human health-based indicator. Of the remaining CECs screened, the 90th percentile MECs for two compounds, NNitrosomorpholine (NMOR) and 1,4-dioxane, exceed their respective MTLs by factors of 9 and 7, respectively, thus warranting their addition as human health indicators. Figure 2 summarizes the updated 2018 health-based and performance-based indicators for CECs and performance surrogates. The Panel reiterates that the MEC/MTL ratio employed in the risk-based, screening framework is operationally defined and should not be compared to (or confused with) regulatory criteria (i.e. enforceable maximum contaminant levels or MCLs). Furthermore, a large margin of safety is incorporated into this framework. Therefore, a MEC/MTL ratio of greater than 1 does not represent an immediate threat to public health. With this in mind, the very small percentage of CECs that are recommended for health-based monitoring (3 of 489 or < 1%) reinforces the inherent low potential risk of CECs in recycled water to human health currently attributable to water reuse applications that include most Title 22 nonpotable uses and potable reuse via groundwater and surface water augmentation under current regulatory practices. The Panel recommends that the Estrogen Receptor alpha (ER-α) and the Aryl Hydrocarbon Receptor (AhR) bioassays be used to respectively assess estrogenic and dioxin-like biological activities in recycled water.

Figure 5. Strategies for electing constituents of emerging concern (CECs).

In an earlier study from Europe MTBE and oxygenates (fuel additives), 1,4-dioxane (solvent), perchlorate and NMDA (industrial chemicals), pharmaceuticals, PFOS (polyfluonated alkyls, flame retardants), APEOs (surfactants, emulgents and flame retardants in textile and other industries), and emerging pathogens was suggested as CECs (Alvarez-Cohen, L, Sedlak, D L, 2003). The same authors also discussed the motivation for applying CECs, see Figure 3.

From Alvarez-Cohen et al, 2018,Univ. of California, Berkely

## Why Emerging Contaminants?

### Analytical Advances Produce new Generations of Emerging Water Contaminants

| | Priority Pollutants | Emerging Contam. |
|---|---|---|
| Analysis | GC, GC/MS, LC, IC | GC/MS/MS, LC/MS Orbitrap LC/MS GC/GC, FTICR/MS LC/ICP/MS, NMR |
| Log $K_{ow}$ | 2 to 7 | -2 to 10 |
| Biodegradable? | Mostly | good question!! |
| Detection limits | ppm, ppb | ppb, ppt, ppq! |

Figure 6. CEC motivation.

**EXAMPLES FROM WETLANDS**

Figure 7 shows the timeline for a small Norwegian MSW landfill, being closed in 1997. Even though being an extremely low strength leachate with ammonia at 10 to 50 mg/l, high concentrations of pesticides started to show up in the early 2000, and dioxins in the leachate sediment from 2015.

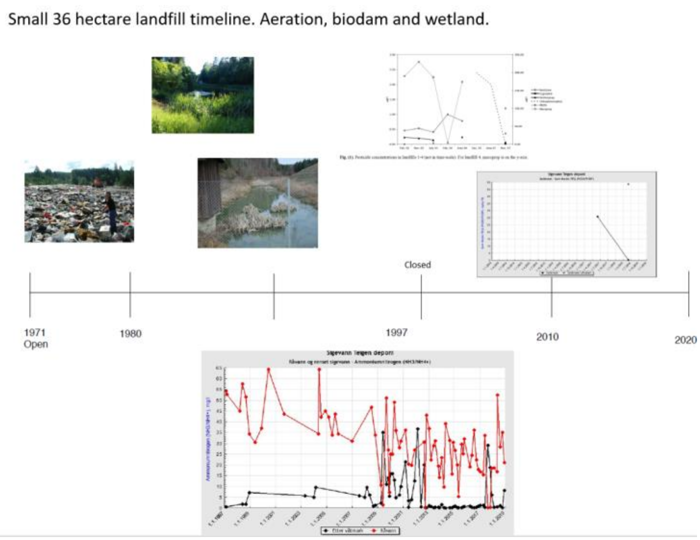


Figure 7. Timeline for small municipal solid waste landfill.

# Removal....

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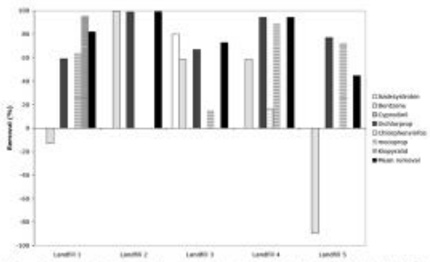


Fig. (2). Mean removal of pesticides in on-site treatment systems and number of samples from the treated leachate (Landfill 1= aeration, n=3; 2=reverse osmosis, n=1, 3=natural attenuation+aeration+CW, n=1; 4=aeration+biodam+CW n=7; 5=SBR, n=1), see also Table 2.

**Table 5. Pesticide Emissions**

| | Reverse Osmosis | Aeration /Wetlands | SBR |
|---|---|---|---|
| Pesticides detected after treatment | Phenoxy acids | Phenoxy acids<br>Chlorphenvinphos<br>Isoproturon<br>Azoxystrobin<br>Chlopyralid<br>Mecoprop | Phenoxy acids |
| Concentration range (µg/l) | 0.01-0.08 | 0.16-50 | 0.03-1.1 |

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Figure 8. Removal of pesticide in leachate treatment systems (Haarstad & Mæhlum, 2008)

# Per- and poly fluorized alkanes (PFAS)

*Table 1 Average PFAS concentrations (ng/l) in landfill leachates from landfill I-X (sampled in 2018). Values < LOQ are excluded from the calculations. PFDS, PF-3.7-DMOA, PFTrA, PFTA, PFHxDA, and PFAS precursors (EtFOSA, MeFOSA, EtFOSE, MeFOSE) were not detected > LOQ in any of the samples, and are thus excluded from the calculations. n.a. = not analysed. I-S to III-S and VI-S = supplementary PFAS results obtained from the landfill operators (site-owner measurments) at the same sampling points as in this study (I-III and IV).*

| ID | Year, month (n) | ∑Short-chain PFSAs (< C6)[1] | ∑Long-chain PFSAs (≥ C6)[2] | ∑Short-chain PFCAs (< C7)[3] | ∑Long-chain PFCAs (≥ C7)[4] | ∑Short-chain PFAS (PFSAs and PFCAs) | ∑Long-chain PFAS (PFSAs and PFCAs) | Short:long-chain ratio | PFOS | PFOA | ∑PFAS |
|---|---|---|---|---|---|---|---|---|---|---|---|
| I | 2018, Jan. (1) | 30 | 51 | 142 | 85 | 172 | 136 | 1.3 | 29 | 66 | 320 |
| I-S | 2017, Apr., June, Aug., Nov. – 2018, May (5) | 24 ± 10 | 151 ± 205 | 158 ± 24 | 109 ± 17 | 181 ± 26 | 261 ± 211 | 0.70 | 100 ± 140 | 69 ± 10 | 466 ± 235 |
| II | 2018, April (1) | 260 | 90 | 240 | 144 | 500 | 234 | 2.1 | 70 | 94 | 780 |
| II-S | 2016, April (1) | 320 | 113 | 263 | 165 | 583 | 277 | 2.1 | 74 | 100 | 900 |
| III | 2018, April (1) | 100 | 109 | 253 | 183 | 353 | 292 | 1.2 | 70 | 120 | 670 |
| III-S | 2018, April (1) | 110 | 113 | 261 | 195 | 371 | 308 | 1.2 | 65 | 130 | 740 |
| IV | 2018, April (1) | 47 | 26 | 380 | 112 | 427 | 138 | 3.1 | 15 | 72 | 590 |
| V | 2018, May (1) | n.a. | 87 | 68* | 98 | 68* | 185 | 0.4 | 51 | 98 | 432 |
| VI | 2018, April (1) | 4200 | 196 | 2570 | 2688 | 6770 | 2884 | 2.3 | 120 | 1800 | 11000 |
| VI-S | 2017, Sept. (1) | 660 | 73 | 490 | 419 | 1150 | 492 | 2.3 | 36 | 270 | 2500 |
| VII | 2018, May (1) | 850 | 215 | 1930 | 998 | 2780 | 1213 | 2.3 | 65 | 660 | 4200 |
| VIII | 2018, May (1) | n.a. | 98 | 95* | 241 | 95* | 339 | 0.3 | 59 | 203 | 592 |
| IX | 2018, May (1) | 7.3 | 71 | 125 | 210 | 132 | 281 | 0.5 | 36 | 170 | 420 |
| X | 2018, June (1) | 7.2 | 204 | 126 | 195 | 133 | 399 | 0.3 | 160 | 120 | 540 |
| Median | 2016-2018 (18) | 105 | 103 | 247 | 189 | 362 | 286 | 1.3 | 65 | 120 | 631 |
| Mean ± SD | | 551 ± 1181 | 114 ± 58 | 507 ± 758 | 417 ± 694 | 980 ± 1810 | 531 ± 728 | 1.8 | 68 ± 38 | 284 ± 462 | 1725 ± 2873 |
| Min-max | | 7.1 - 4200 | 26 - 215 | 68 - 2570 | 85 - 2688 | 68 - 6770 | 136 - 2884 | 0.5 – 2.3 | 15 - 160 | 66 - 1800 | 320 - 11000 |
| Most abundant | | (PFBS) | PFOS | PFHxA | PFOA | PFBS | PFOA | - | - | - | PFBS |

*[1]PFBS; [2]PFHxS, PFHpS and PFOS; [3]PFBA, PFPeA and PFHxA; [4]PFHpA, HPFHpA, PFOA, PFNA, PFDeA, PFUdA and PFDoA*

**PFBS was not analysed in these samples, which could explain their relatively lower ∑short-chain concentrations*

Figure 9. PFAS in landfill leachate in Norway (in Press)

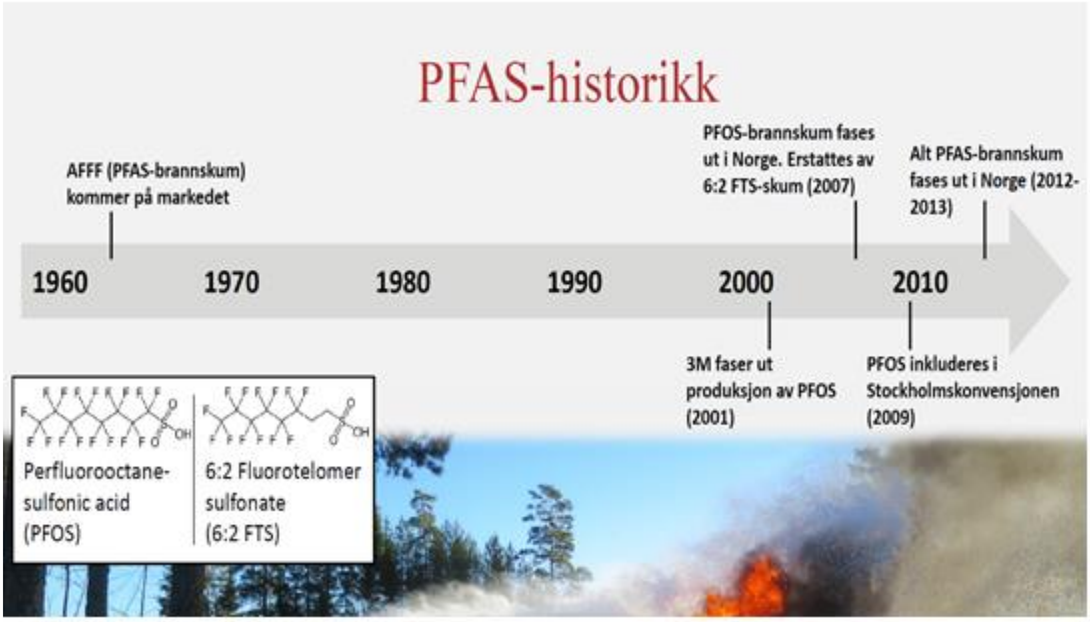


Figure 10. Timeline of PFAS use; on the market early 60-ies, long chained phased out from 2007.

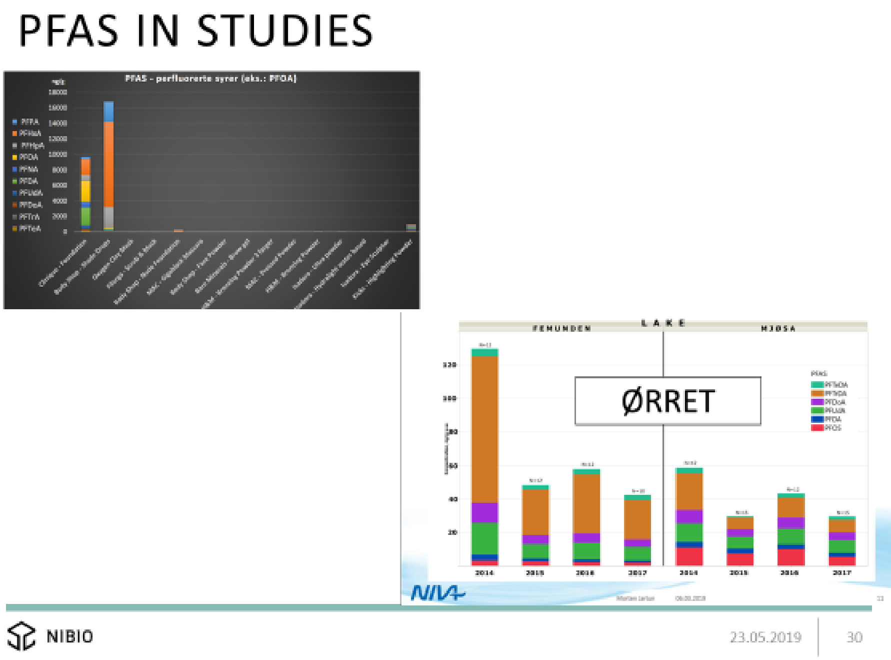


Figure 11. PFAS in the “environement”; personal care products and in trout.

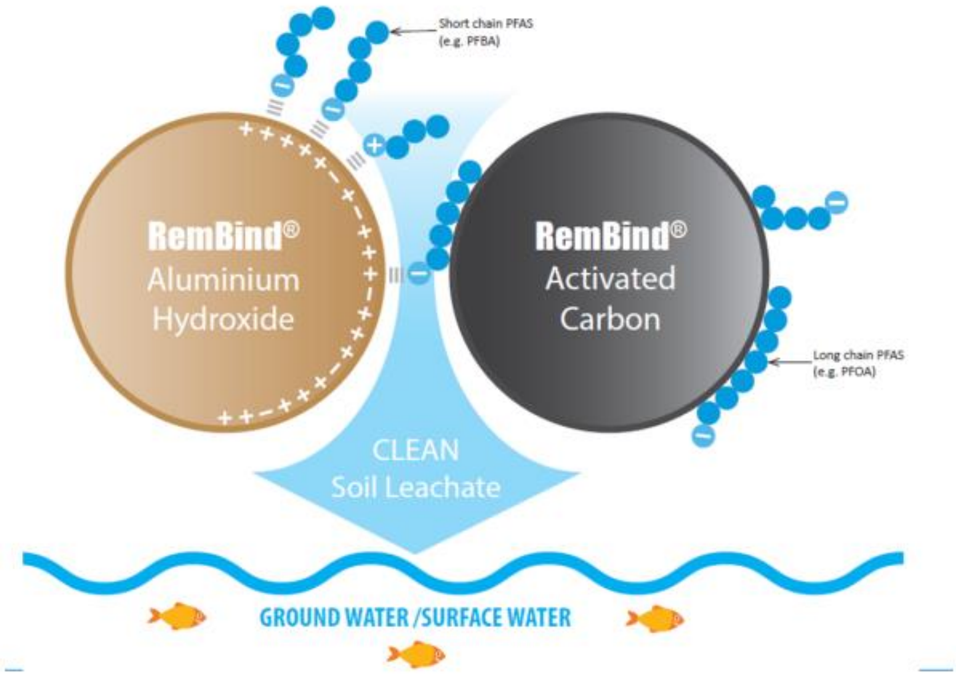


Figure 12. Adsorption of PFAS.

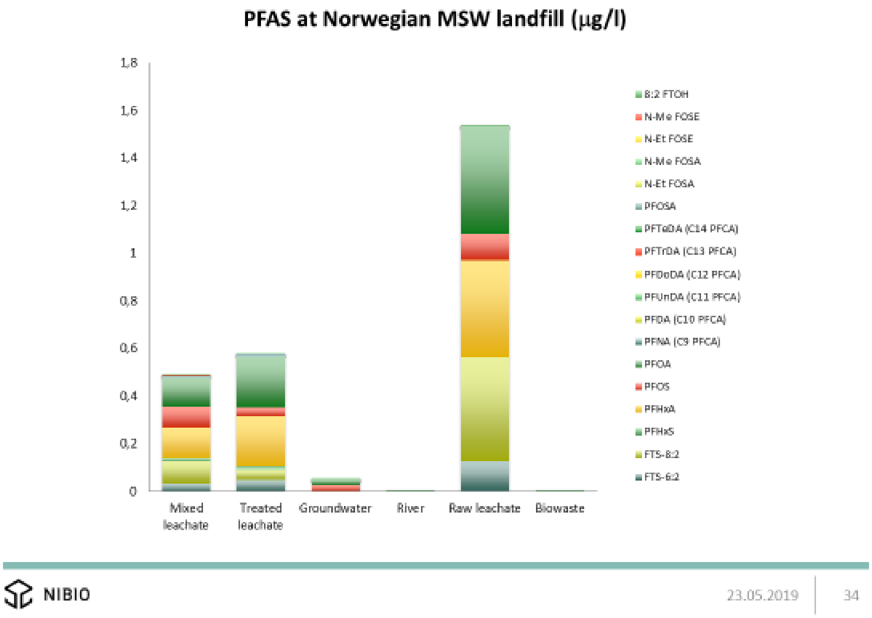


Figure 13. PFAS in leachate systems.

**CLOSING REMARKS**

Emerging pollutants or constituents of emerging concern (CECs) emerge over time at different locations and countries depending on a number of factors. This variation might be a problem when comparing across countries and continents. The waste industry is dealing with most of the CECs, thus wetlands that receive landfill leachate might be good locations for CEC monitoring since they provide a large number of physical, chemical and biological processes. Even small and seemingly insignificant landfills can pollute over very long timescale.

**REFERANSER**

Alvarez-Cohen, L, Sedlak, D L, 2003. Emerging contaminants in water. Env. Eng. Sci, 20, 287—388.

Drewes. R. et al., 2018. Monitoring strategies for constituents of emerging concern (CECs) in recycled water. Recommendations of a science advisory panel convened by the state water resources control board. California Water Boards, SCCWRP Technical Report 103, 155 pp.

EPA (Norway). 2016. Quality standards for the classification of water, sediments and biota. Report M608, Oslo , Norway, 24 pp.

Haarstad, K., Mæhlum, T. 2008. Pesticides in Norwegian Landfills. The Open Environmental & Biological Monitoring Journal, 1, 8-15