The Presence of Pharmaceuticals in Our Surface Waters and the Development of Effective Monitoring Strategies

Dylan O'Flynn [1], Blánaid White[1], Imogen Hands [1], Anne Parle-McDermott [1], Denise Harold [1], Thomas Mc Cloughlin [1], Linda Holland [2], Jenny Lawler [2], Fiona Regan [1]

1DCU Water Institute, School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland.
2DCU Water Institute, School of Biotechnology, Dublin City University, Glasnevin, Dublin 9, Ireland.

@EMPIRE_DCU

1 Introduction:

Pharmaceuticals play a pivotal role in human and animal health. The ever-increasing use and availability of pharmaceuticals in the last decade have led to the contamination of surface water ecosystems from ng/L to µg/L concentrations. The environmental fate and toxicological implications of many pharmaceuticals and their residues remain generally unknown. Additionally, the stability and biological activity of these "micro-pollutants" can lead to a "pseudo persistence" in the environment, with ensuing behavioural and health-related effects. This project highlights the occurrence, movement, and impact pharmaceuticals may have on surface water catchments. Findings from this review will highlight the importance of monitoring pharmaceuticals in surface waters, potential sources and factors that influence their concentrations. Furthermore, detailing strategic monitoring strategies will show the practicality of passive (long-term continuous) and grab (snapshot) sampling techniques in conjunction with effect based biomonitoring tools to give a detailed account of the passage of pharmaceuticals through an aquatic ecosystem. Outcomes from this research will aim to provide information on the relevant concentrations of pharmaceuticals in surface water systems while improving education surrounding appropriate use, disposal and waste management of pharmaceutical products.
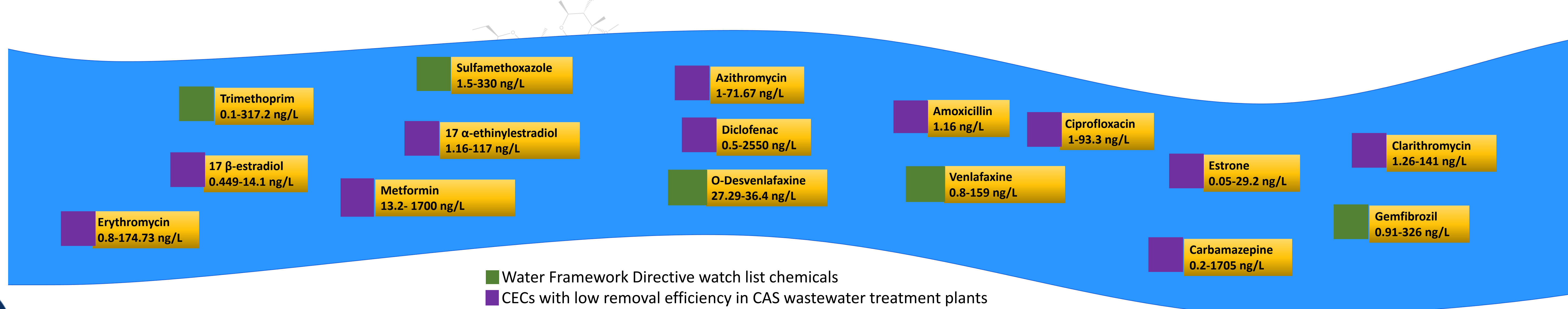
2 Life cycle of pharmaceuticals
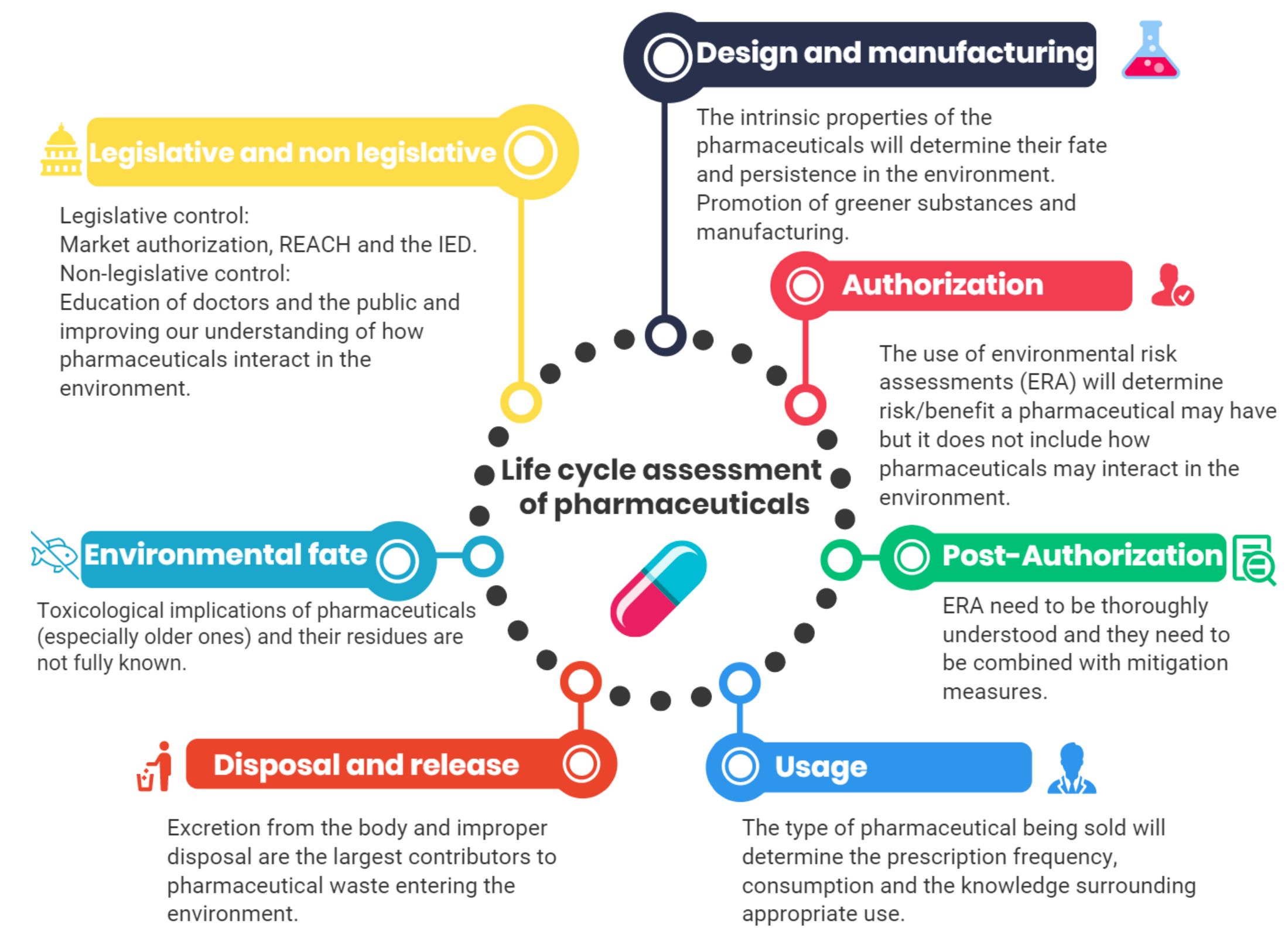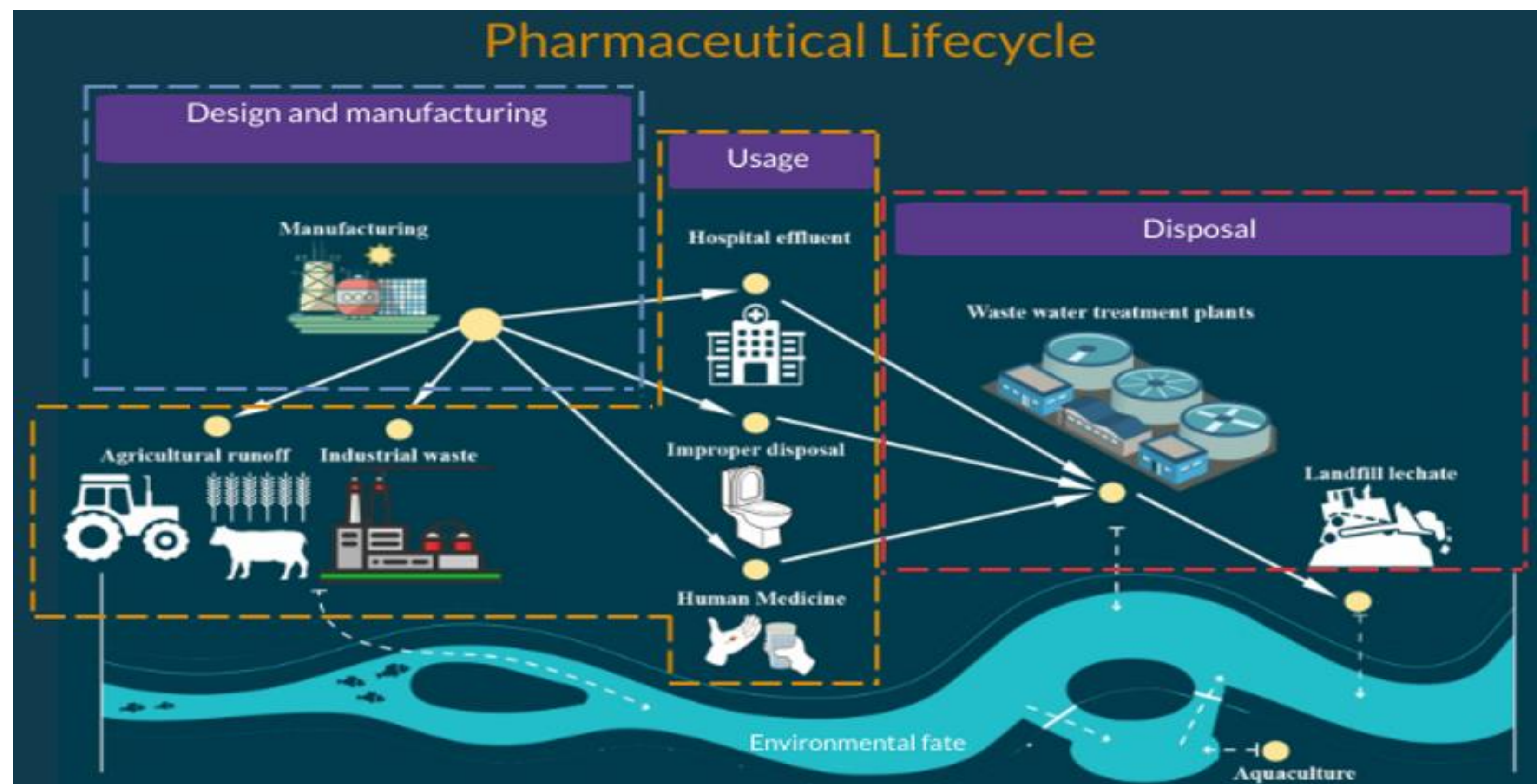
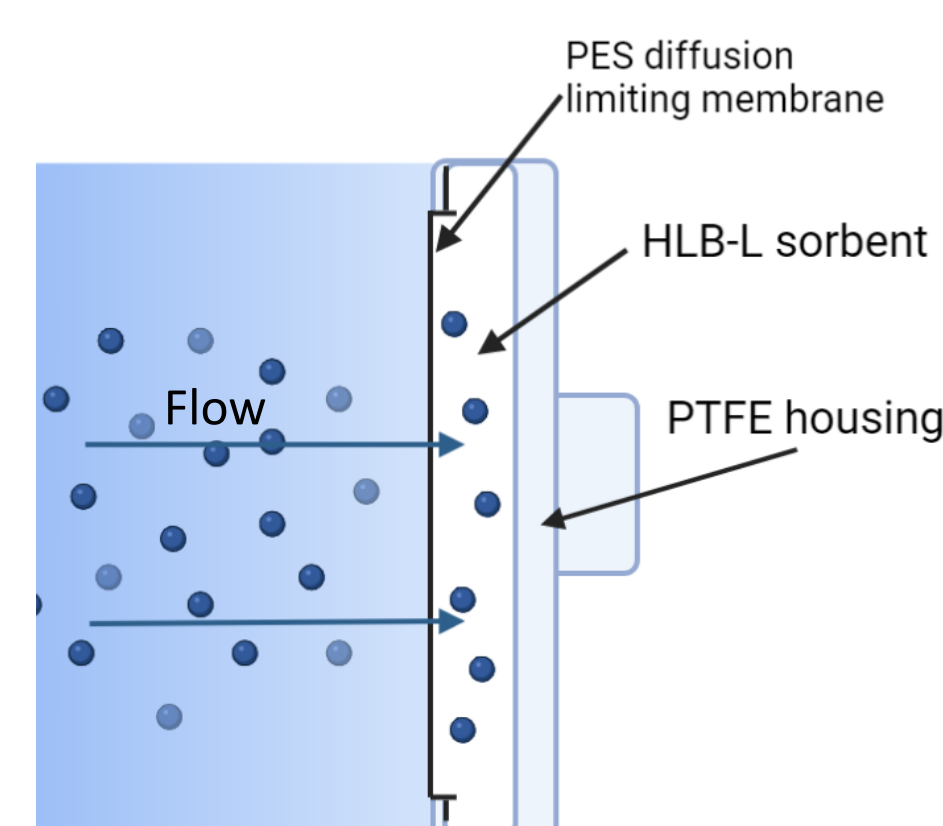## 3 Pharmaceuticals commonly found in surface water [1]

Each of these chosen pharmaceuticals have been identified as Contaminants of Emerging Concern (CECs).[2] However, it is not just a single pharmaceutical in the environment, it is a chemical cocktail of many different types and their associated metabolites. This cocktail can lead to an unknown toxicity within the environment and to humans. The highest number of APIs are found in countries where monitoring is most frequently conducted, e.g. United States of America (USA), Germany, England, Spain. [3] This may suggest that countries with lower number detections may have similar levels, but they are not sufficiently investigated.

Trimethoprim 0.1–317.2 ng/L
Sulfamethoxazole 1.5–330 ng/L
Azithromycin 1–71.67 ng/L
Amoxicillin 1.16 ng/L
Ciprofloxacin 1–93.3 ng/L
Clarithromycin 1.26–141 ng/L
17 β-estradiol 0.449–14.1 ng/L
17 α-ethinylestradiol 1.16–117 ng/L
Diclofenac 0.5–2550 ng/L
Venlafaxine 0.8–159 ng/L
Estrone 0.05–29.2 ng/L
Erythromycin 0.8–174.73 ng/L
Metformin 13.2– 1700 ng/L
O-Desvenlafaxine 27.29–36.4 ng/L
Gemfibrozil 0.91–326 ng/L
Carbamazepine 0.2–1705 ng/L

Water Framework Directive watch list chemicals
CECs with low removal efficiency in CAS wastewater treatment plants

4 Monitoring strategies

Passive and grab sampling

PES diffusion limiting membrane
HLB-L sorbent
Flow
PTFE housing

Chemcatcher deployment kit

Passive sampling:
- Provides a time weighted average of pharmaceutical concentrations.
- More likely to capture periods of increased concentrations (2 week deployment).
- More environmentally relevant due to larger sampling period [4].
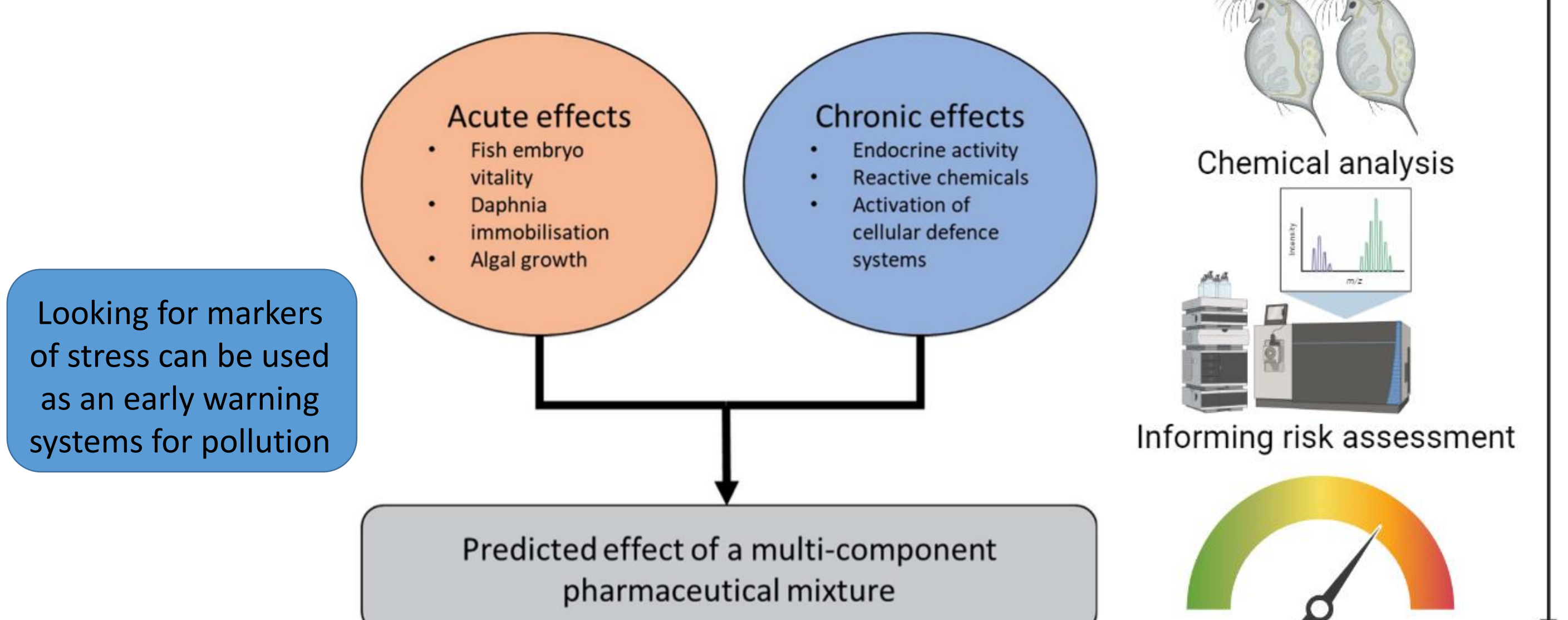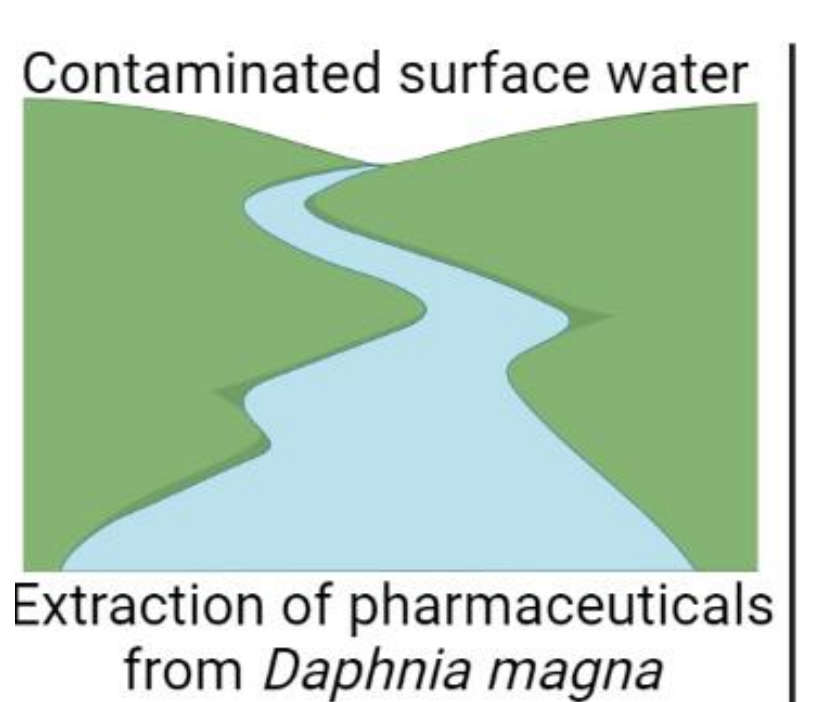- Requires tandem grab sampling increasing labour and costs.

Grab Sampling:
- Provides a snapshot of pharmaceuticals a specific point in time.
- Can miss periods of increased concentrations.
- Significantly less labour intensive

Effect Based Biomonitoring and chemical analysis

Effect based biomonitoring involves the use of in vitro effect based methods using non-target organisms. Effect based methods are a valuable screening tool to reduce the burden of chemical and analytical monitoring [5]. However, examining wild aquatic organisms can identify priority pharmaceuticals and indicate long-term exposure [6].

Contaminated surface water

Extraction of pharmaceuticals from *Daphnia magna*

Acute effects
- Fish embryo vitality
- Daphnia immobilisation
- Algal growth

Chronic effects
- Endocrine activity
- Reactive chemicals
- Activation of cellular defence systems

Looking for markers of stress can be used as an early warning systems for pollution

Chemical analysis

Predicted effect of a multi-component pharmaceutical mixture

Informing risk assessment

References:
1. https://docs.google.com/spreadsheets/d/1Ach93CdFk5PKBnqvUFreV2HU6t-O1JX9tuSLQD6GHDM/edit?usp=sharing
2. NORMAN, LIST OF EMERGING SUBSTANCES, https://www.norman-network.com/sites/default/files/files/Emerging_substances_list_Feb_16/NORMAN%20list_2016_FINAL.XLSX
3. OECD, Pharmaceutical Residues in Freshwater, 2019
4. A. C. Taylor, G. R. Fones, A. Gravell and G. A. Mills, Use of Chemcatcher® passive sampler with high-resolution mass spectrometry and multi-variate analysis for targeted screening of emerging pesticides in water, Anal. Methods, 2020, 12, 4015–4027.
5. D. O'Flynn, J. Lawler, A. Yusuf, A. Parle-McDermott, D. Harold, T. M. Cloughlin, L. Holland, F. Regan and B. White, A review of pharmaceutical occurrence and pathways in the aquatic environment in the context of a changing climate and the COVID-19 pandemic, Anal. Methods, 2021, 13, 575–594.
6. T. H. Miller, K. T. Ng, S. T. Bury, S. E. Bury, N. R. Bury and L. P. Barron, Biomonitoring of pesticides, pharmaceuticals and illicit drugs in a freshwater invertebrate to estimate toxic or effect pressure, Environment International, 2019, 129, 595–606.
7. Images were created using biorender.com