



Better Food. Better Health. Better World.

Semi-quantitative screening of PFAS in waters: feedback

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Where do we start from?



Publication :

www.elsevier.com/locate/chemosphere

Targeted and non targeted screening to assess the efficiency of the depuration systems



Controlling micropollutants in tertiary municipal wastewater by O_3/H_2O_2 , granular biofiltration and UV_{254}/H_2O_2 for potable reuse applications

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2nd phase of the project

Exploitation of the latest results of a list of more than 500 compounds including about 200 per-fluorinated compounds

The context: reclamation plant



*Tertiary treatment
plant and water
reservoir*

*Experimental
potable pilot
plant*

Storage basin

*Primary municipal
WWTP of Fasano*

FASANO, Italy

Project by

- AquaSoil S.r.l.
- Environmental Protection Agency- Arpa Puglia
- University of Salento
- **Mérieux NutriSciences**
- University of Western Ontario

GOALS

- Defining advanced treatment technologies suitable for potable purposes
- Adopting a **multilevel monitoring approach to guarantee safe water**
- Focus on **organic micropollutants of emerging concern at ultra-low concentrations**

Why looking for a combined approach?

The production and use of chemicals worldwide, and thus **the number of those that can potentially leach into the environment**, is constantly increasing



Also a depuration plant faces the challenge to deal with a multiplicity of **new emerging contaminants**

They could not be monitored by applying only targeted analysis: a **combined approach could be the key**



A **combined approach is a methodology:**

it is a way to select the significant parameters and to use that for the evaluation of the efficiency of the depuration system, including PFAS

The most known PFAS are monitored using conventional targeted analysis



Suspect and Non Targeted

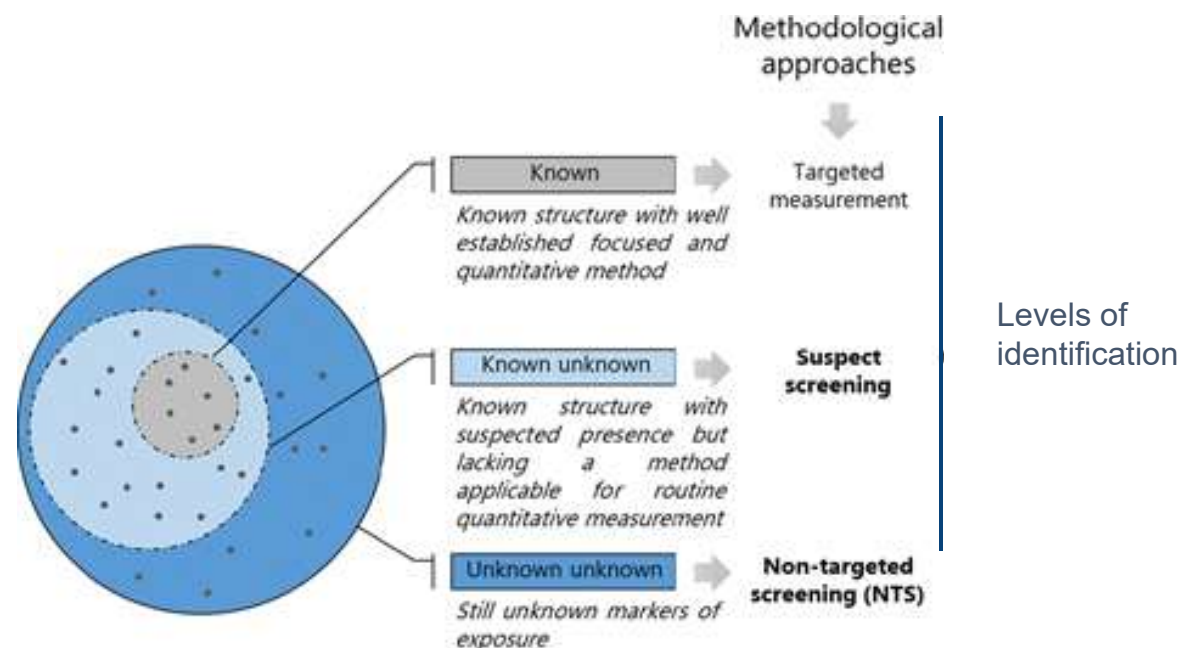
NON TARGETED ANALYSIS

It aims to analyse “unknown unknowns” without a priori criteria (the name and structure of potential analytes are not known).

SUSPECT SCREENING

It is focused on analysing so-called “**known unknowns**” whose names and structures are clearly defined and suspected to be present in the sample.

They are less biased than traditional targeted analysis, since **the selection of the chemical domain is drastically minimized to assure the widest scope** of the analytical procedure.



Targeted and Non-targeted

TARGETED ANALYSIS



Standard for each targeted molecule



Instrumental analysis



Results

SUSPECT SCREENING of expected contaminants



List of compounds



Instrumental analysis



Results to be confirmed with standards

NON-TARGETED ANALYSIS



No preconception



Instrumental analysis



Results and consequential hypothesis on molecules



Suspect screening

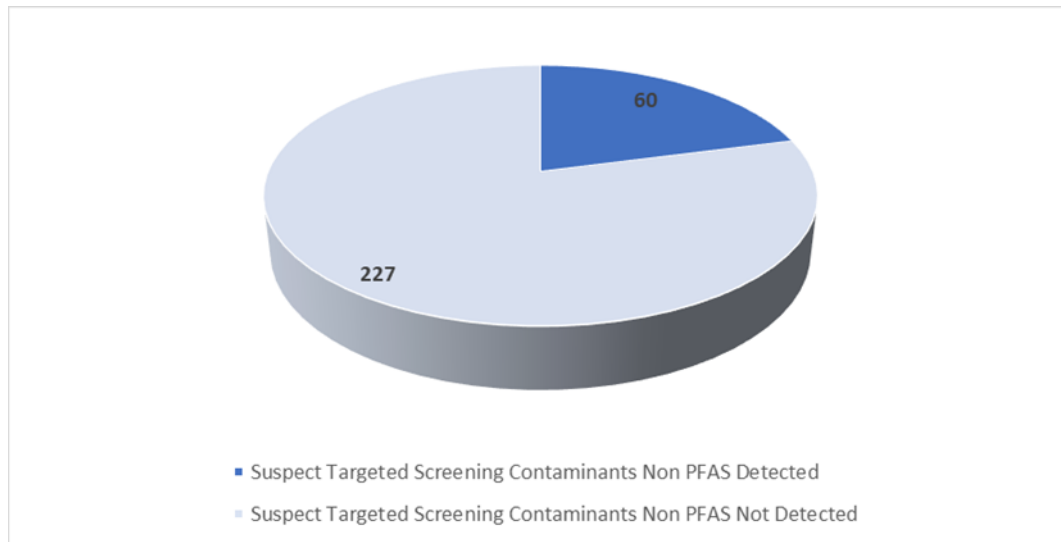
To compensate for the overwhelming amount of compounds, a **list of candidates** to be screened can be introduced to restrict the massive analysis or to **set some priorities**.

Suspect screening is not restrictive in terms of the preselection of the analytes to consider, but among the thousands of features pinpointed in the analysis, **only those corresponding to the interest or suspect list will be given priority to be evaluated and identified** at a higher or lower confirmation level.

Despite all the challenges, this approach could change environmental monitoring and assessment, making it **much more efficient and avoiding the misdetection of analytes**.



Results: non-PFAS Suspect Targeted Screening

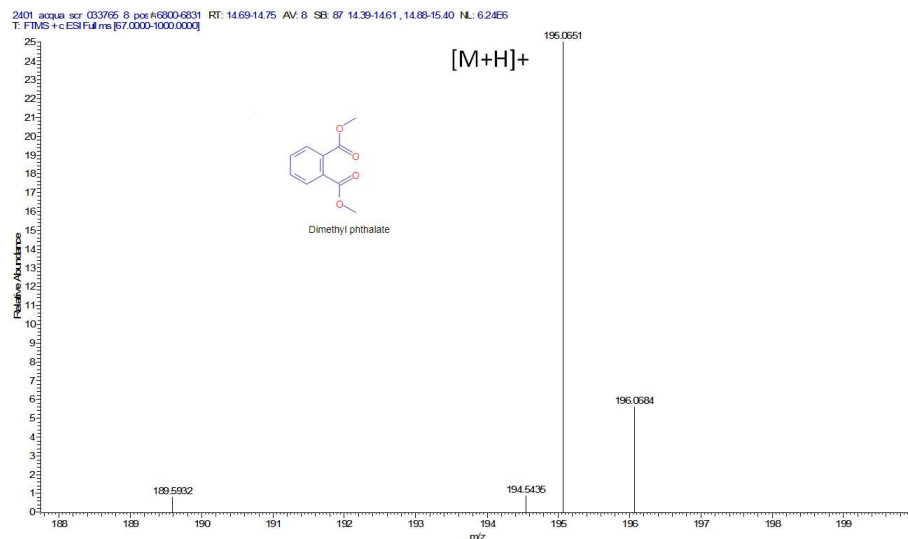


- Contaminants (non PFAS) that are recognised or not recognised thanks to the Suspect Screening

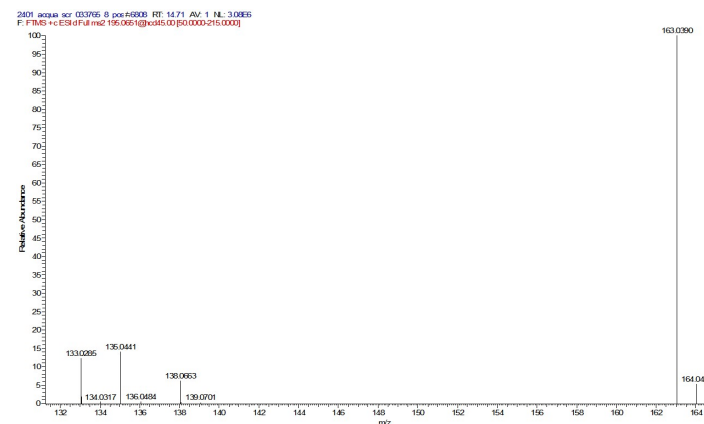
This allows to go on in the study **excluding contaminants that are not present.**

It is also the way to chose the **contaminants that can be use to test depuration efficiency.**

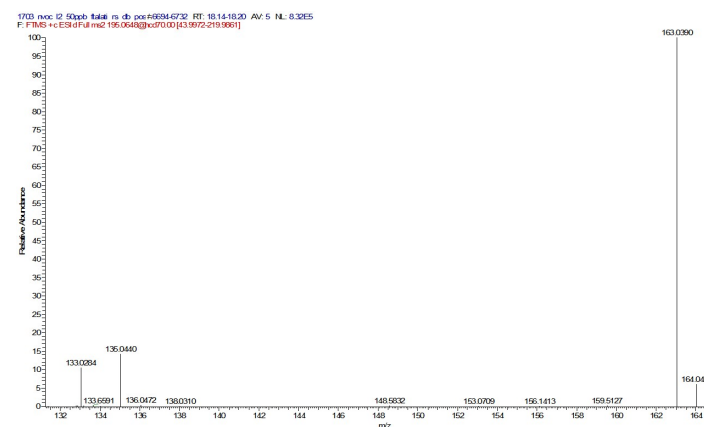
Dimethyl phthalate



Full ms of the peak identified as Dimethyl phthalate (DMP) CAS 131-11-3

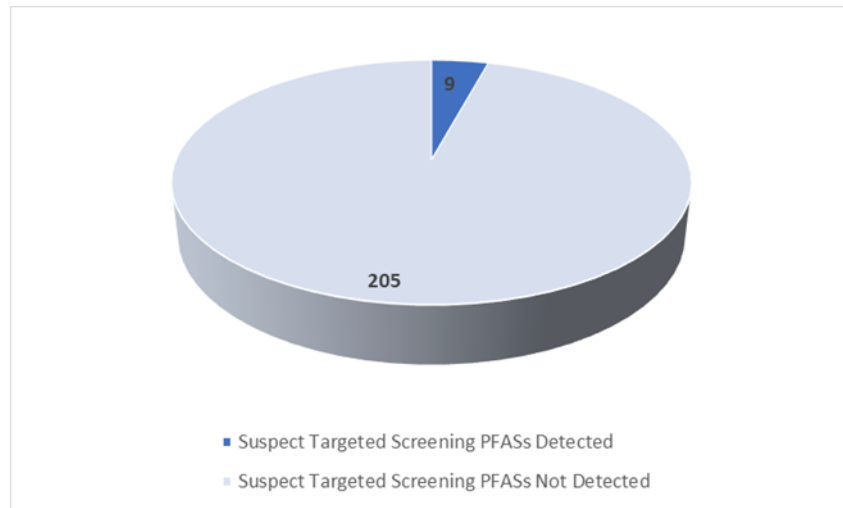


Full ms2 of m/z ratio identified as adduct [M+H]⁺ from Dimethyl phthalate



Full ms2 of adduct [M+H]⁺ from Dimethyl phthalate (standard)

Results PFAS Suspect Targeted Screening

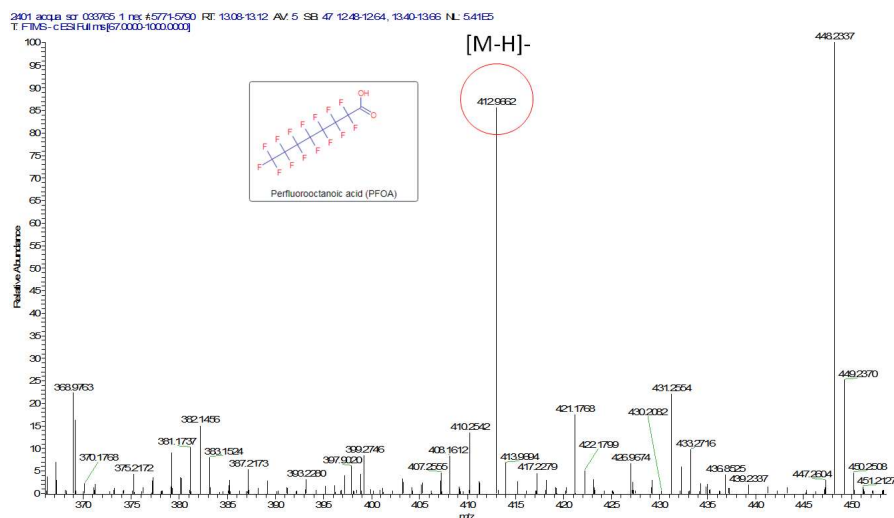


- PFAS that are recognised or not recognised thanks to the Suspect Screening

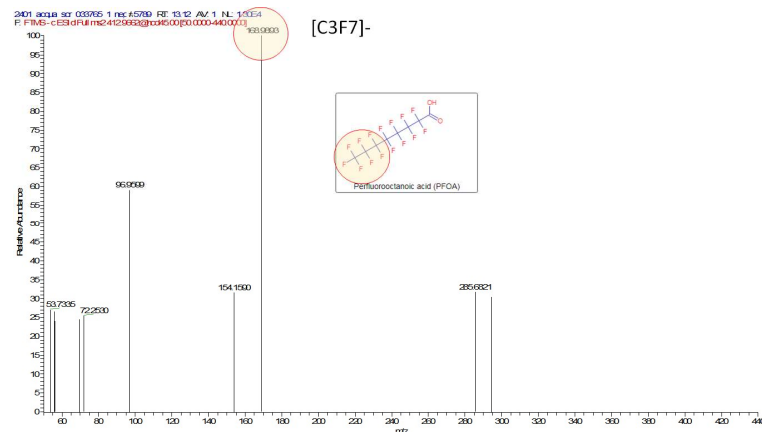
As with the other suspected contaminants, it is a way to **restrict the scope** and to **select the parameters that should be used** in the study.

From this screening I have a **qualitative result**, to be confirmed thanks to the standard.

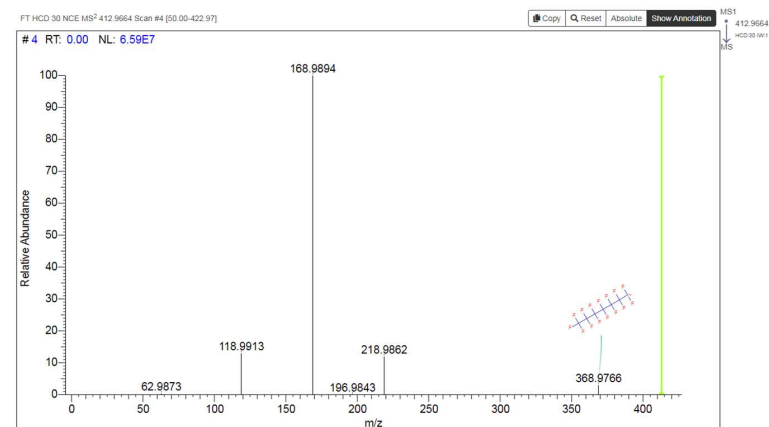
Perfluorooctanoic acid



Full ms peak identified as perfluorooctanoic acid
CAS 335-67-1

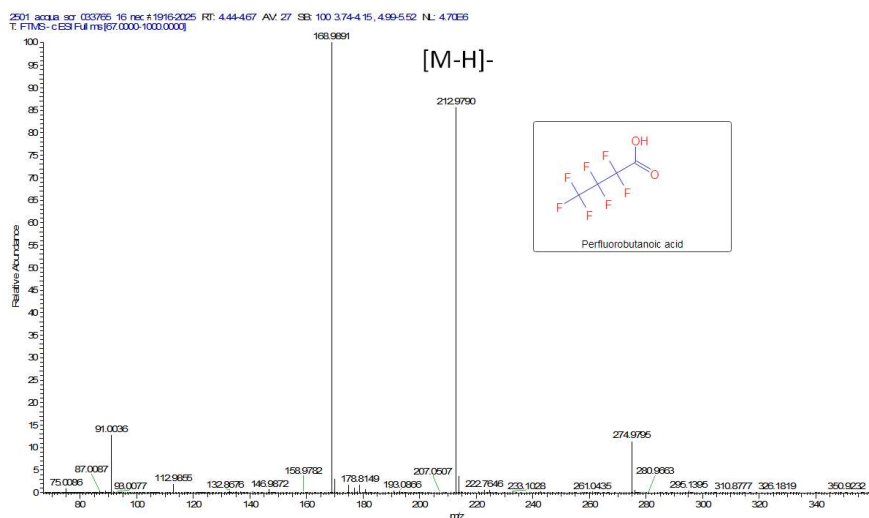


Full ms2 of
m/z ratio identified
as adduct [M-H]- of
perfluorooctanoic
acid

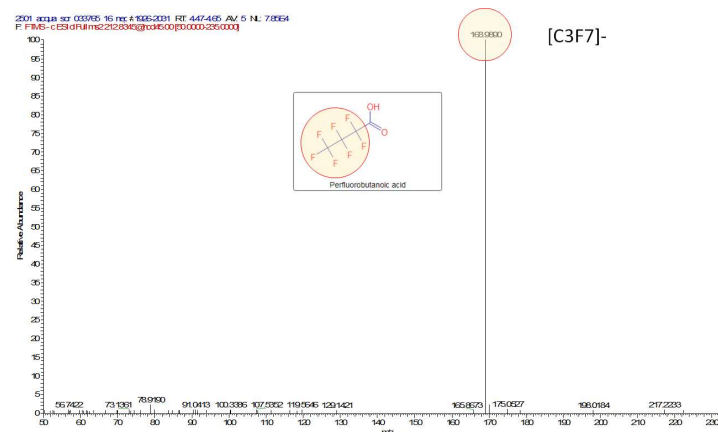


Full ms2 of the
adduct
[M-H]- of
perfluorooctanoic
acid present in **mz
cloud, online
library**

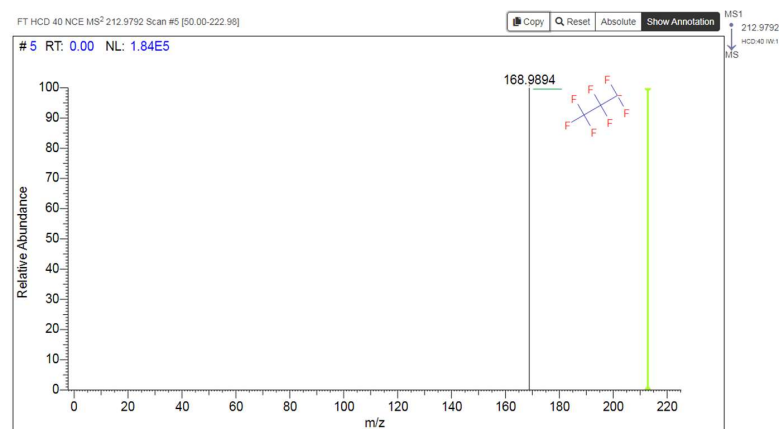
Perfluorobutanoic acid



Full ms of the peak identified as perfluorobutanoic acid CAS 375-22-4 acid, m/z 168 [M-COOH]- present as fragmentation product in the source

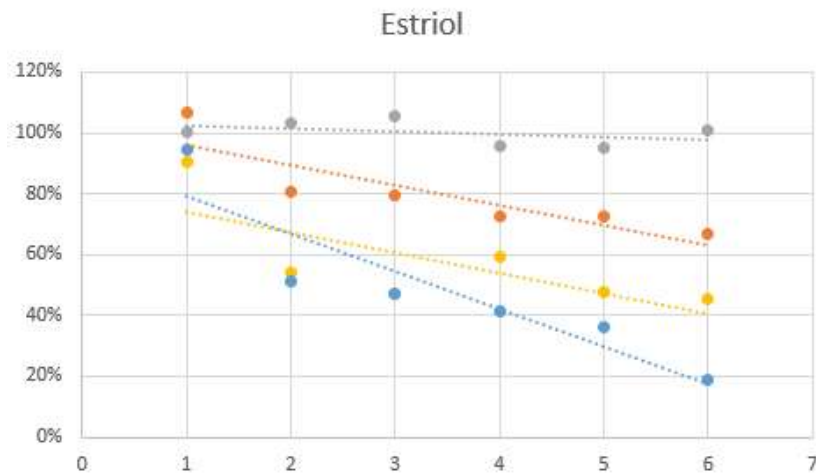


Full ms2 of m/z ratio identified as adduct [M-H]- perfluorobutanoic acid



Full ms2 of the adduct [M-H]- of perfluorobutanoic acid present in **mz cloud, online library**

Contaminants results and Depuration process



Trend of contaminants concentration after different phases of the depuration treatment

PROCESS 1 (under patent) - 5 step growing trend

PROCESS 2 (under patent) - 5 step growing trend

PROCESS 3 (under patent) - 5 step growing trend

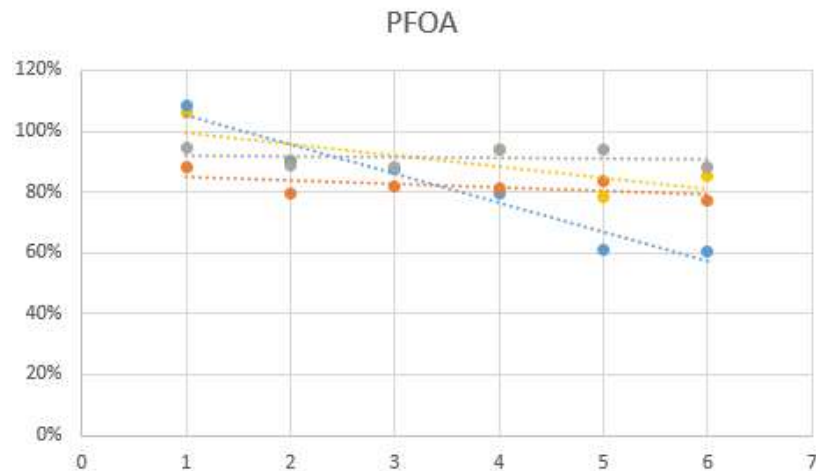
PROCESS 4 (under patent) - 5 step growing trend

In this way we can make an **analytical evaluation** of the depuration phases.

Although the Suspect analysis **is not quantitative**:

- it outlines a **trend of pollutant removal** over the processes of purification,
- it allows **hypotheses to be made by extrapolating semi-quantitative data**

PFAS results and Depuration process



Trend of PFAS concentration after different phases of the depuration treatment

PROCESS 1 (under patent) - 5 step growing trend

PROCESS 2 (under patent) - 5 step growing trend

PROCESS 3 (under patent) - 5 step growing trend

PROCESS 4 (under patent) - 5 step growing trend

Conclusions

Suspect analysis are highly challenging, requires state-of-the-art equipment, but represent a **promising strategy applied to the study of environmental contamination**, where it is necessary to deal with a multiplicity of pollutants.

- Use of LC-HRMS, IC-HRMS, GC-HRMS
- Strong methodology
- Collaboration with partners for the data interpretation

are the key to investigate and discover *unknowns*





Thank you

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