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Identification and Characterization of Organic Compounds Present in Different Sources of Organic Matter Using Untargeted Metabolomics

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COLLEGE OF ENGINEERING

School of Chemical, Biological, and Environmental Engineering

Heavy Metal Pollution

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- Wastewater effluents and stormwater run-off are primary sources of heavy metal pollution
- This puts receiving waters at risk
- Copper levels below 3 µg/L can affect salmonid species
- High levels of Cu, Cr, Cd and Pb have been found in the liver, gills and kidney of the common carp and yellowhead catfish

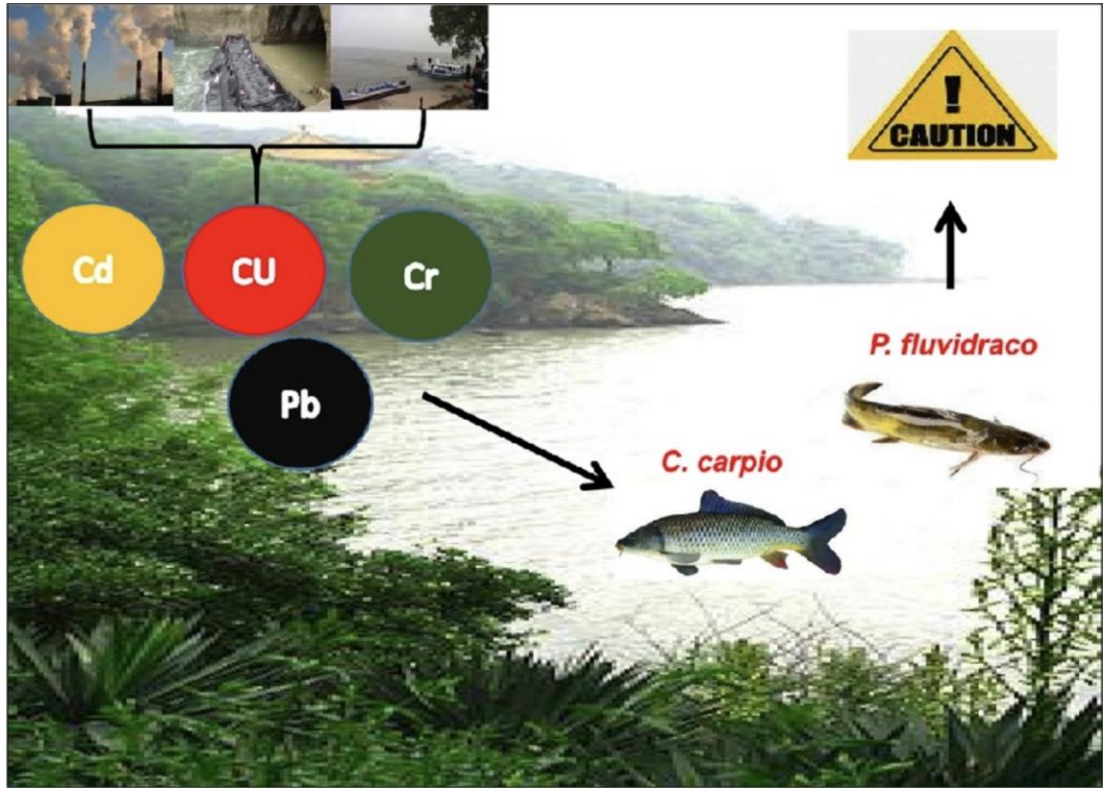

Image source: Rajeshkumar et al. 2018

Metals and Organic Matter

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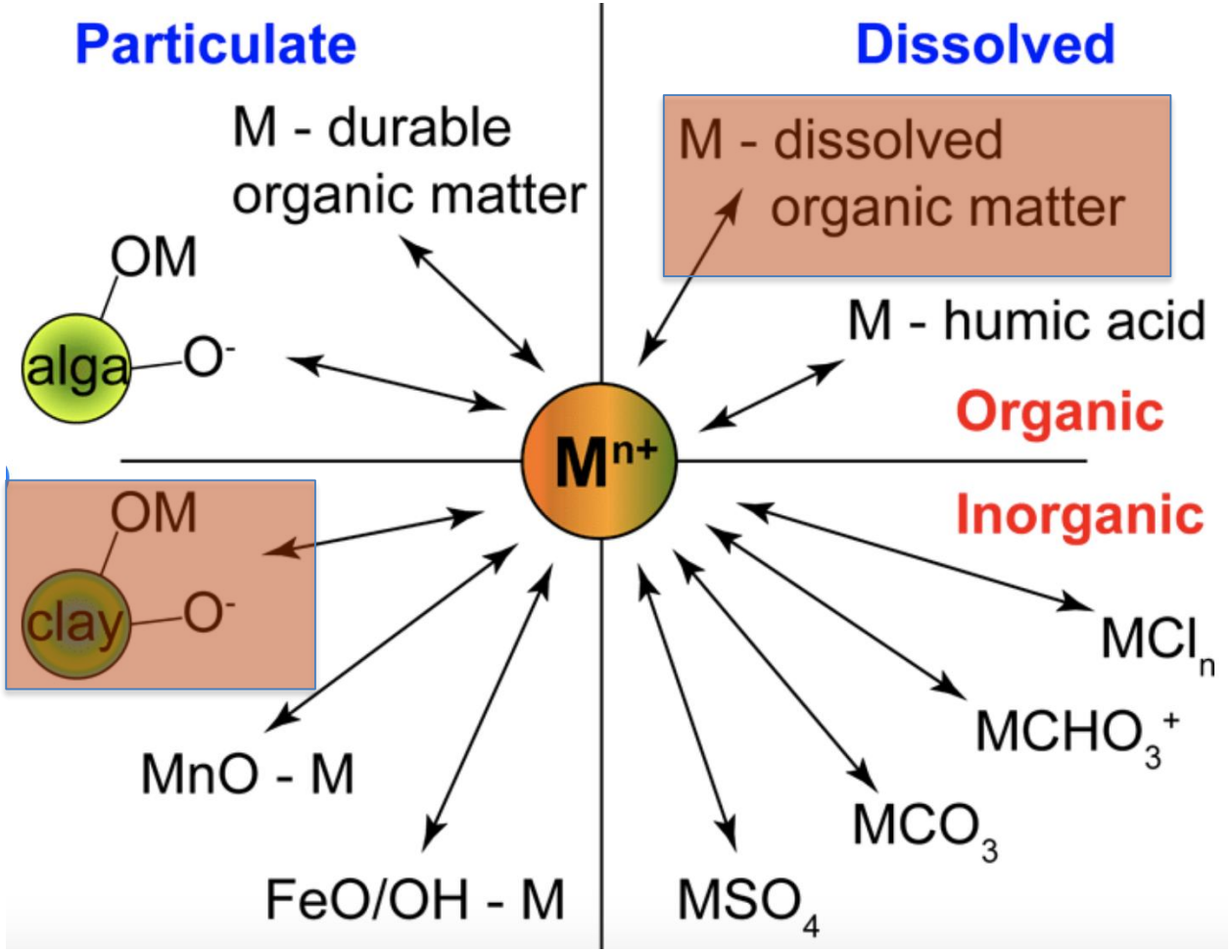

- Metal speciation in aquatic environments is heavily impacted by organic matter (OM)
- Differences in OM composition affects the metal-OM binding interactions
- Different metals select for specific fractions or classes of OM
- Metal-OM interactions can influence metal treatment via adsorption

Image source: Egorova et al. 2017

Differences in Stormwater, Wastewater and Natural OM

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- Stormwater OM (SWOM) and Natural OM (NOM) have terrestrial origins (allochthonous) while wastewater OM (WWOM) tend to be of microbial origins (autochthonous)
- NOM have higher hydrophobic dissolved organic carbon compared to WWOM
- WWOM is more proteinaceous and less aromatic compared to SWOM and NOM
- Functional groups such as sulfides are more predominant in WWOM compared to SWOM and NOM

Common OM Characterization

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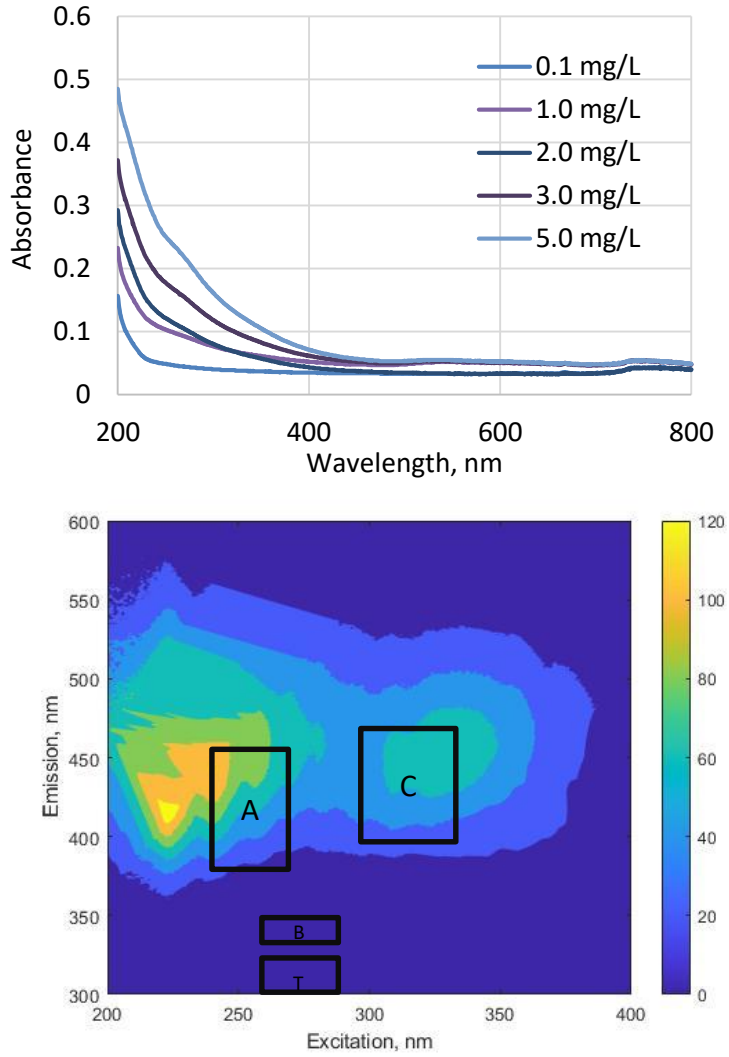
- **Specific Ultraviolet Visible Absorption Spectroscopy (SUVA):** SUVA values at 254 nm have been used to determine the aromaticity and origins of OM.

- **Fluorescence Emission Excitation Spectroscopy (EEM):** 3D-EEMs reveal Ex/Em fluorescent regions that are classified as humic-like or protein-like. Fluorescent Index (FI) also describes aromaticity and OM origin.

- **Fourier Transform Infrared Spectroscopy (FTIR):** FTIR has been used to identify functional groups and classes of OM due to differences in vibrational characteristics of chemical bonds.



UV-Vis Absorbance (top) and 3D EEM with common regions (bottom) of SRNOM

Project Objectives

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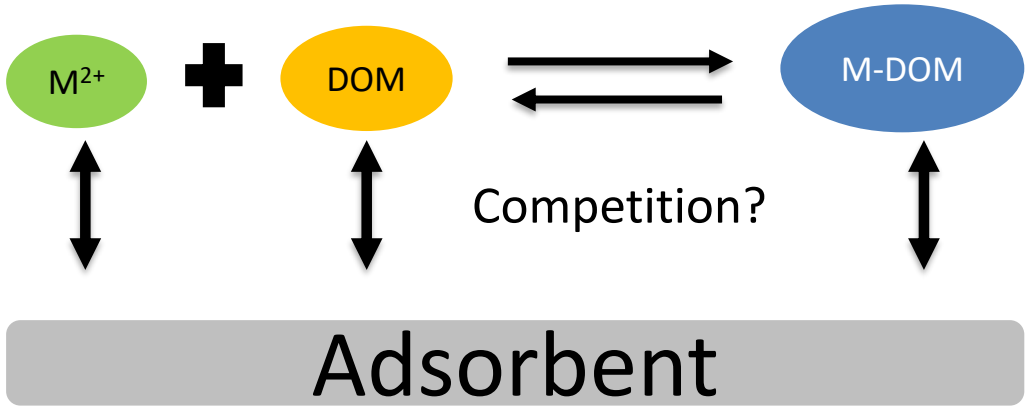
- Identify, characterize and quantify organic ligands that complex metals in storm water and wastewater using High Performance Liquid Chromatography coupled to Inductively Coupled Mass Spectrometry (HPLC-ICPMS) and to Electrospray Ionization Mass Spectrometry (HPLC-ESIMS)



- Describe the mechanisms by which commercial adsorbents take up metals and the effect of organic matter interactions

- Develop a framework that accounts for how both aqueous phase metal speciation and surface complexation explain these processes

Untargeted Metabolomics

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- Metabolomics involves the study of small molecules
- Can be discovery or validation driven
- Analytical techniques involve a separation step with gas or liquid chromatography (LC/GC) and detection with mass spectrometry
- Environmental samples contain common substances and as such a pure standard can be obtained and used to verify new compounds

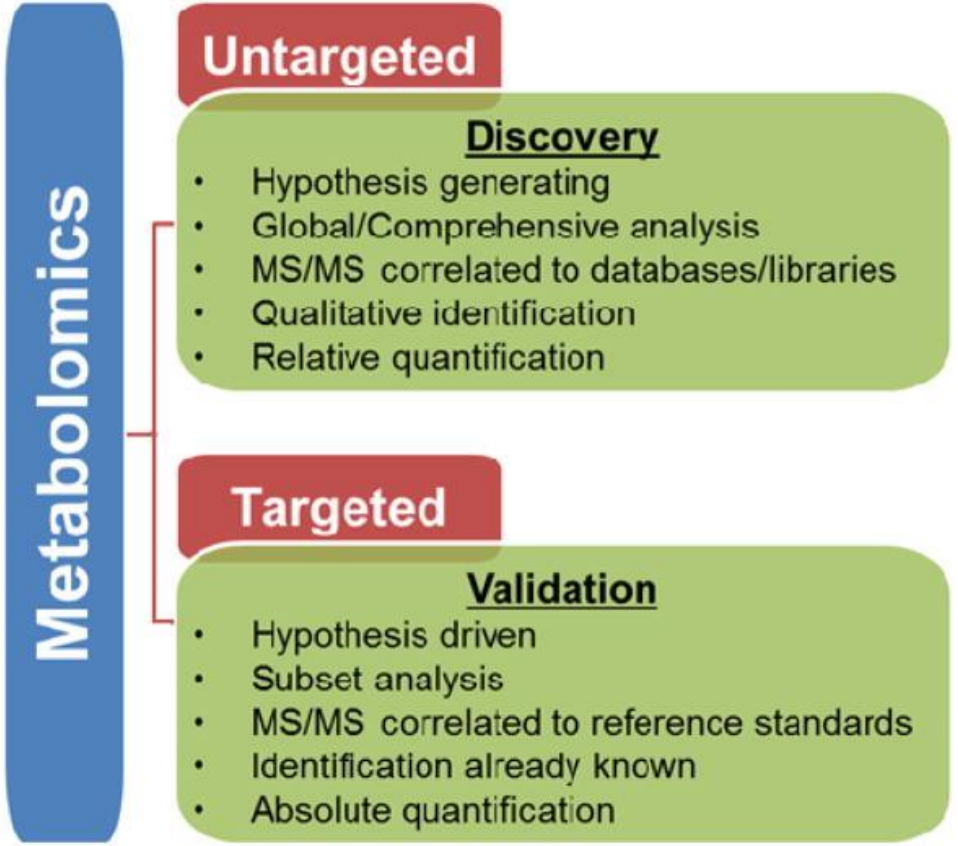

Image source: Schrimpe-Rutledge et al. 2016

Experimental Procedure

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Sampling

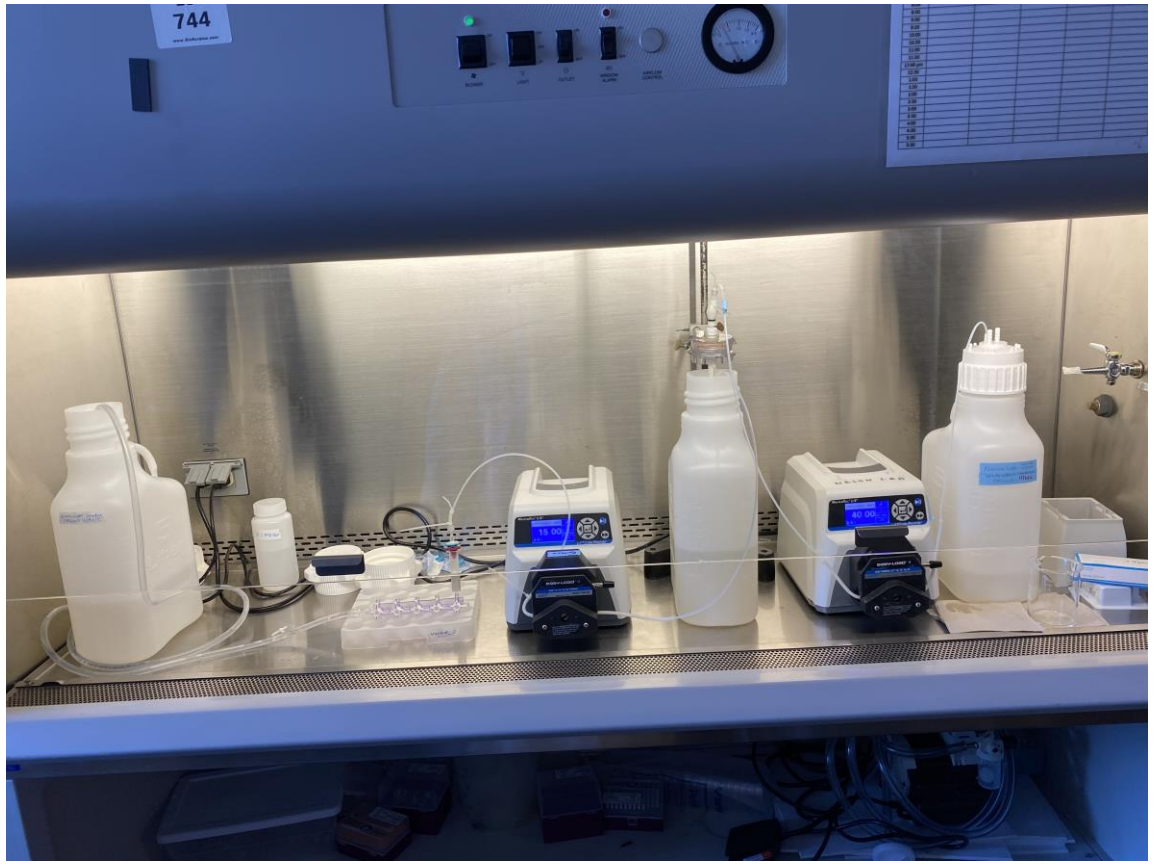
River, Stormwater, Wastewater

OM Extraction

Solid Phase (SPE) with ENV

Analysis

LC-ICPMS and LC-ESIMS



Data Processing with MSDIAL

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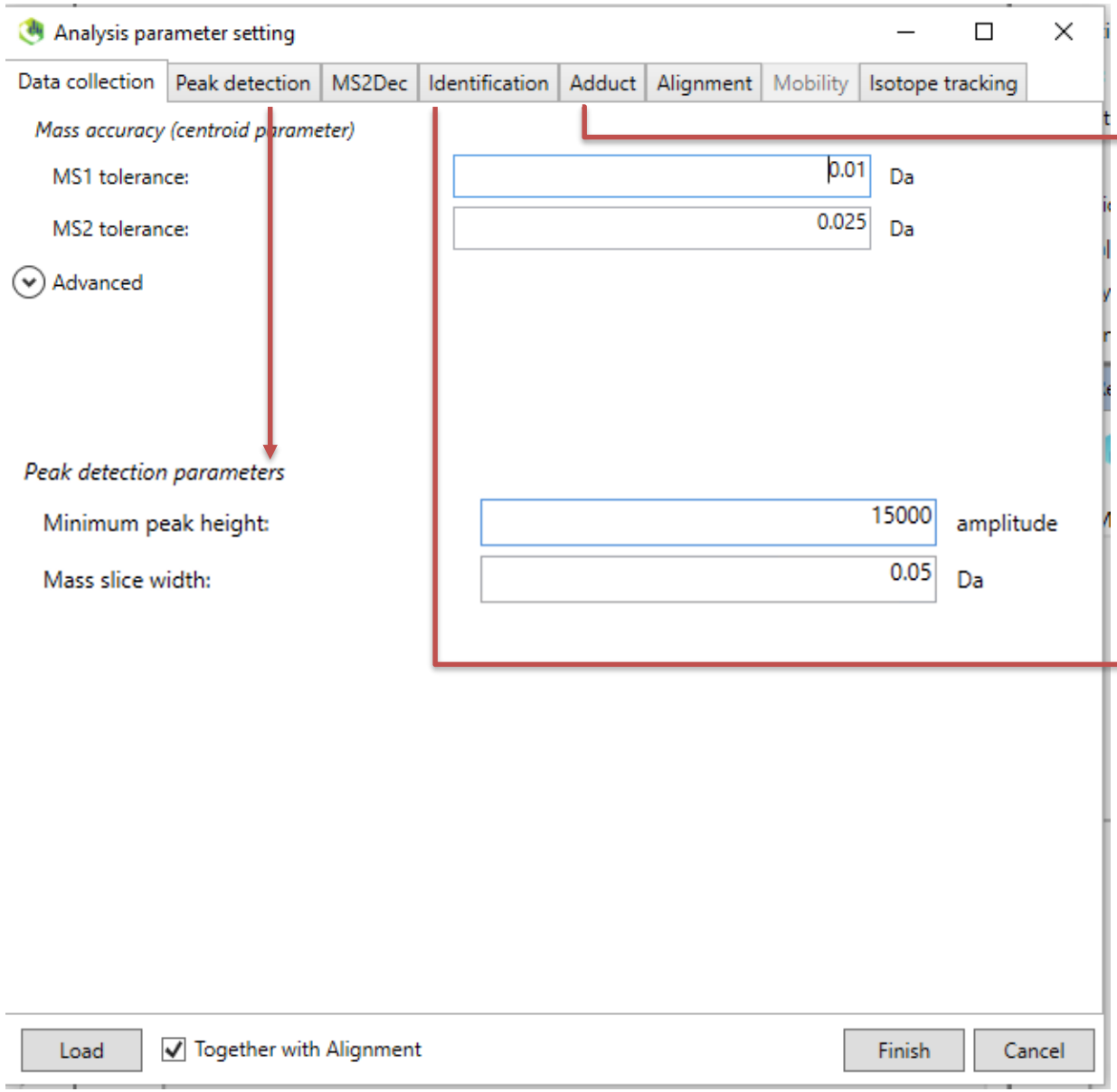
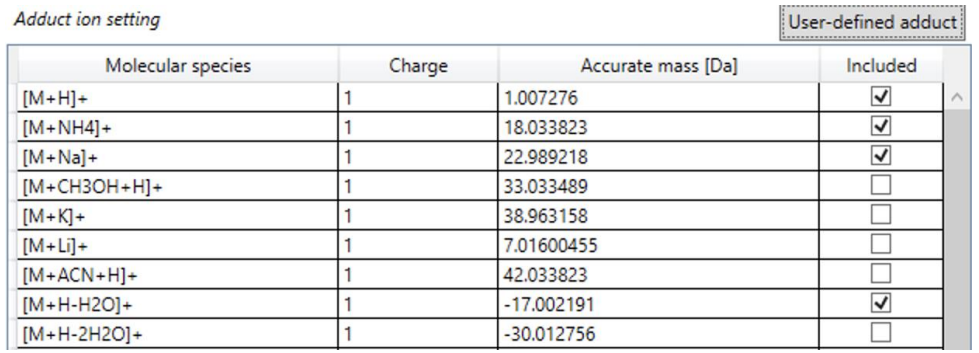
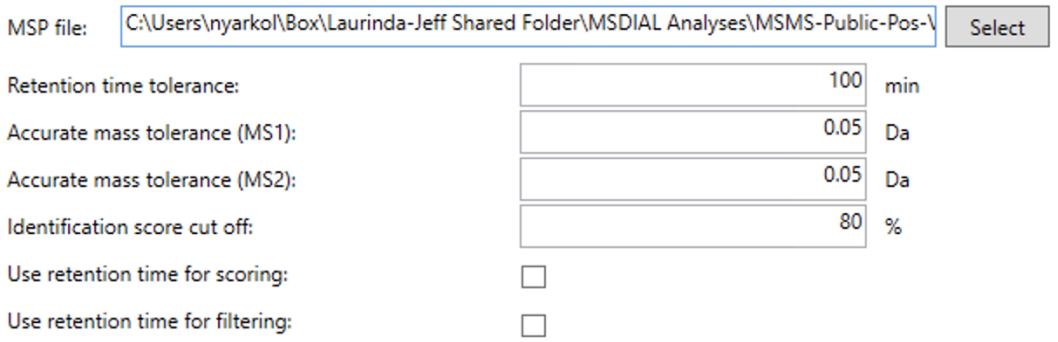




Molecular species	Charge	Accurate mass [Da]	Included
[M+H]+	1	1.007276	☑
[M+NH4]+	1	18.033823	☑
[M+Na]+	1	22.989218	☑
[M+CH3OH+H]+	1	33.033489	☐
[M+K]+	1	38.963158	☐
[M+Li]+	1	7.01600455	☐
[M+ACN+H]+	1	42.033823	☐
[M+H-H2O]+	1	-17.002191	☑
[M+H-2H2O]+	1	-30.012756	☐



Results and Discussions

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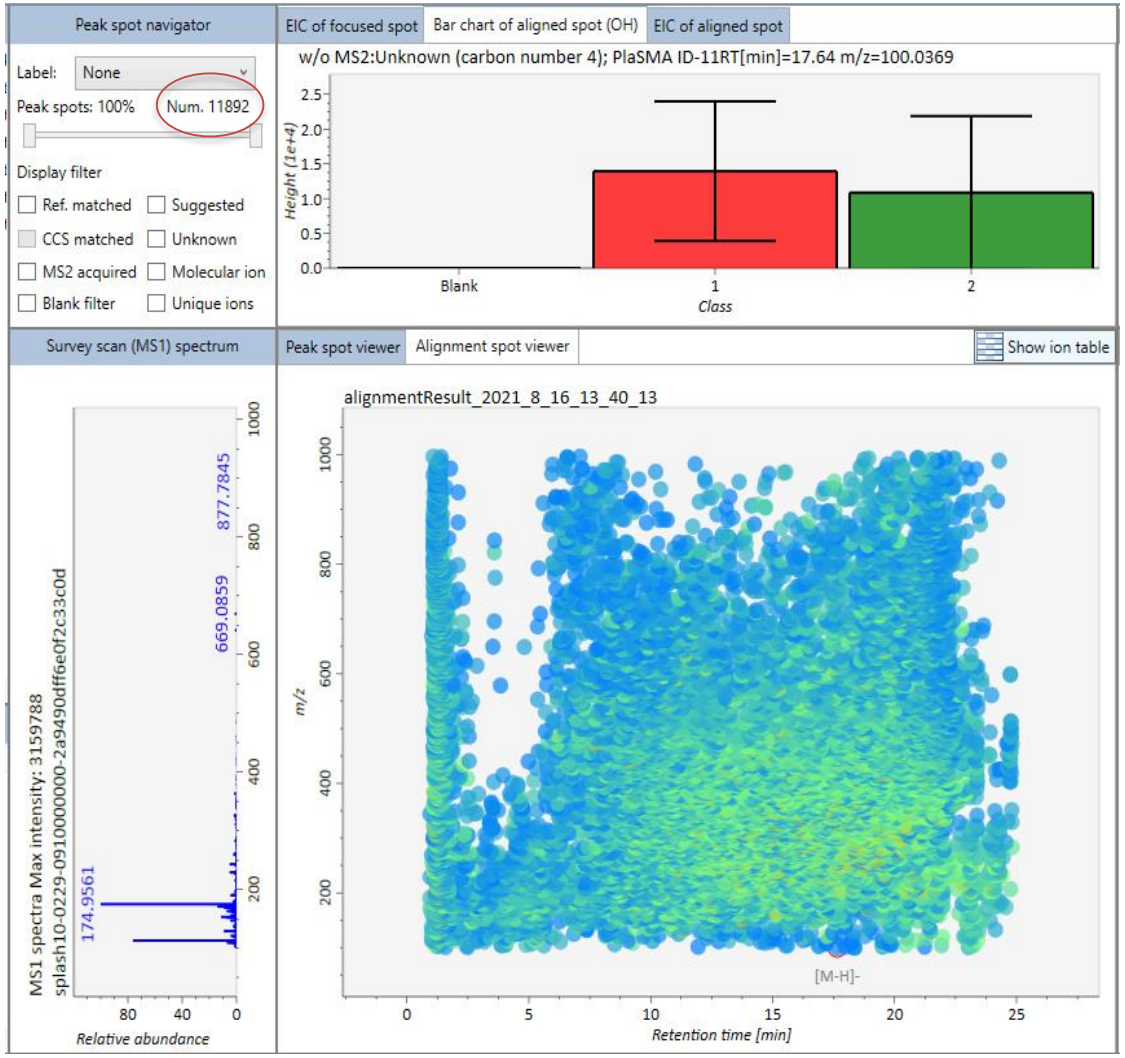

- Unique features that are in database

Results and Discussions

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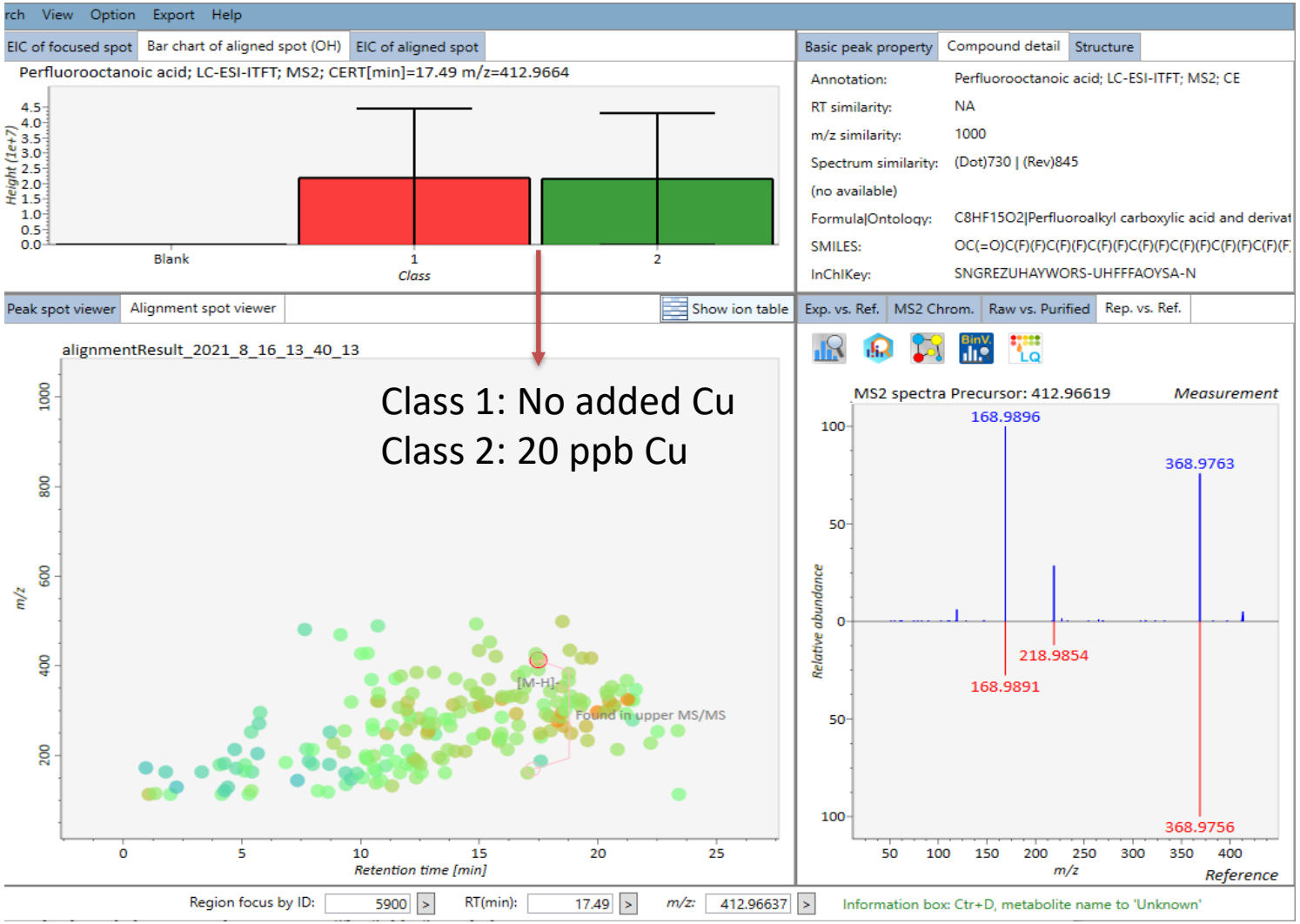
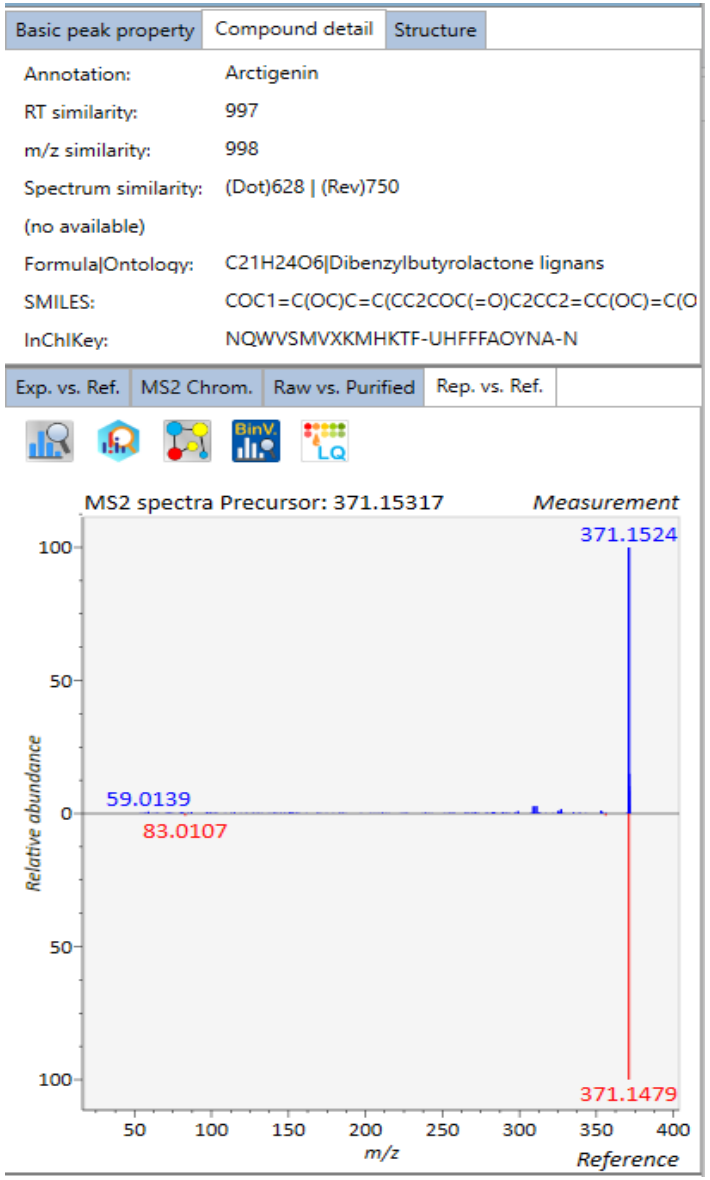
- Clear match and unclear match with database





Results and Discussions

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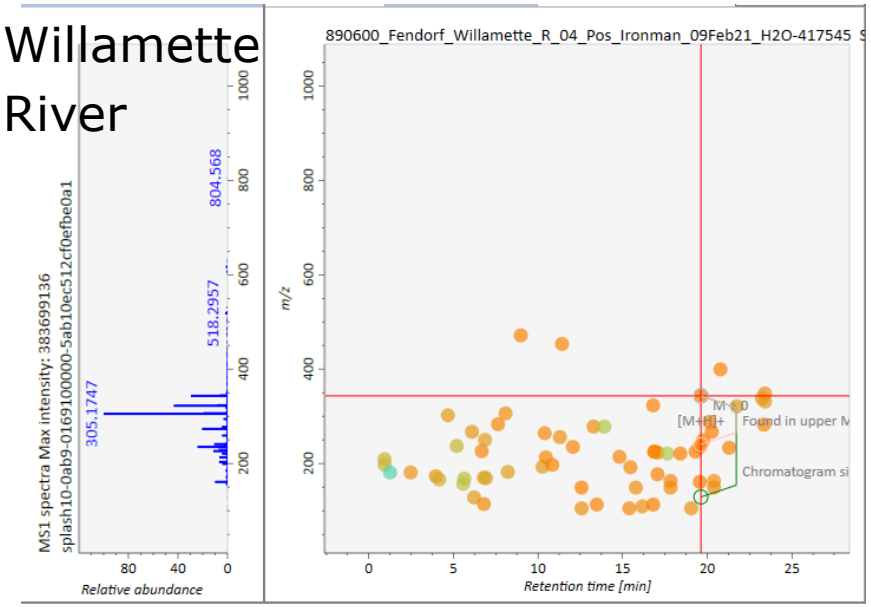
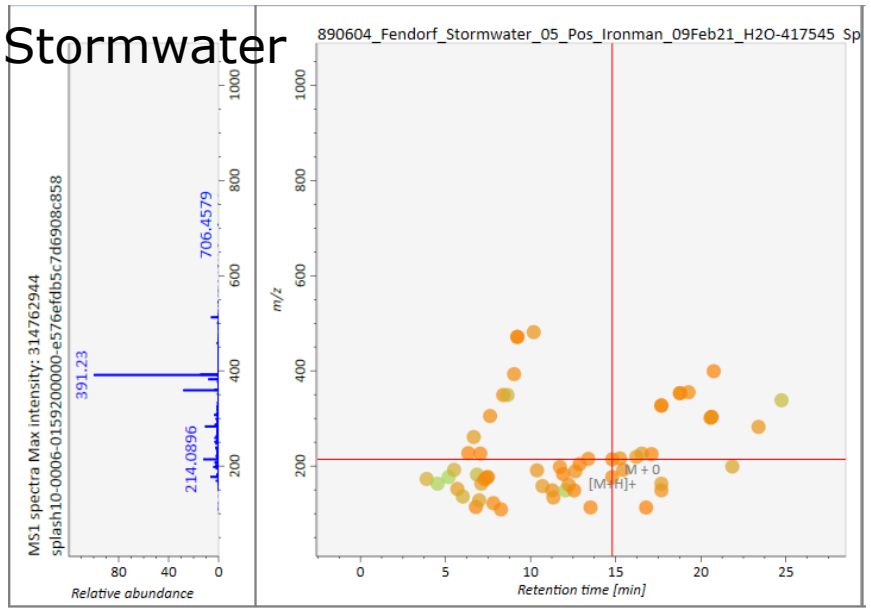
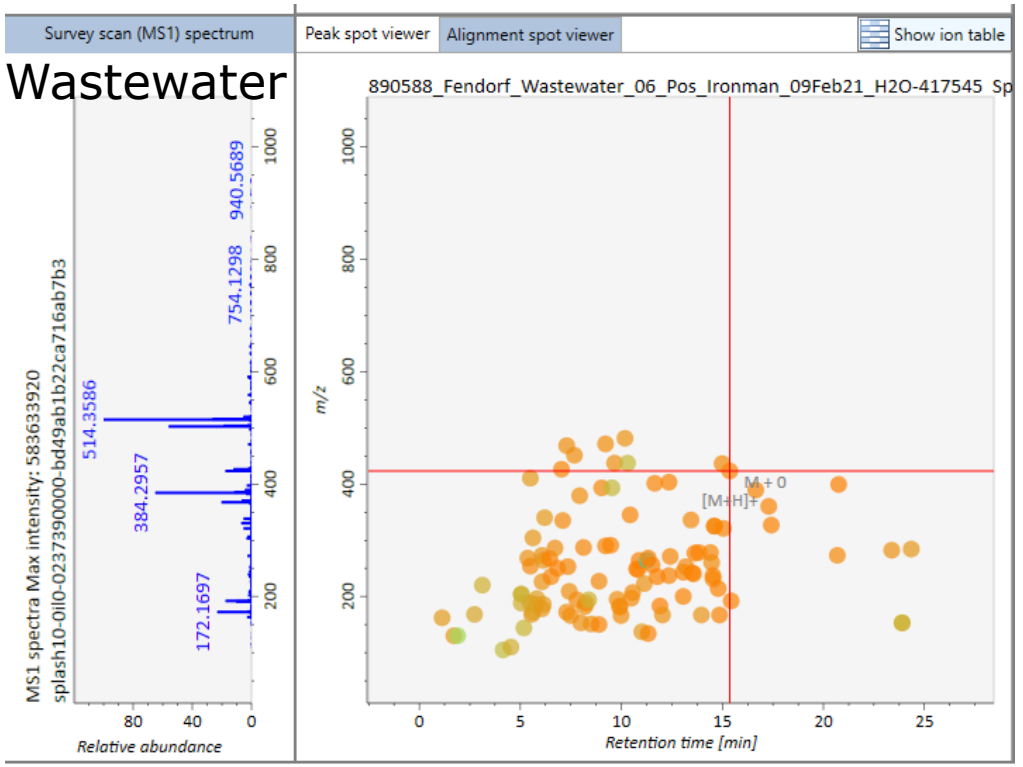
Willamette River



Stormwater





- 63 database matches out of 796 MS2 collected for SWOM, 70 out of 901 for WROM and 113 out of 959 for WWOM
- More polar compounds in WWOM
- Lots of medication in WWOM

Next Steps

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- Perform further data analysis to identify compounds that are common and unique to these OM pools
- Identify unique ligands that bind preferentially to certain metals
- Assign molecular formula to unmatched features
- Collect mass spectra of known compounds and validate matches
- Add new compounds to database

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