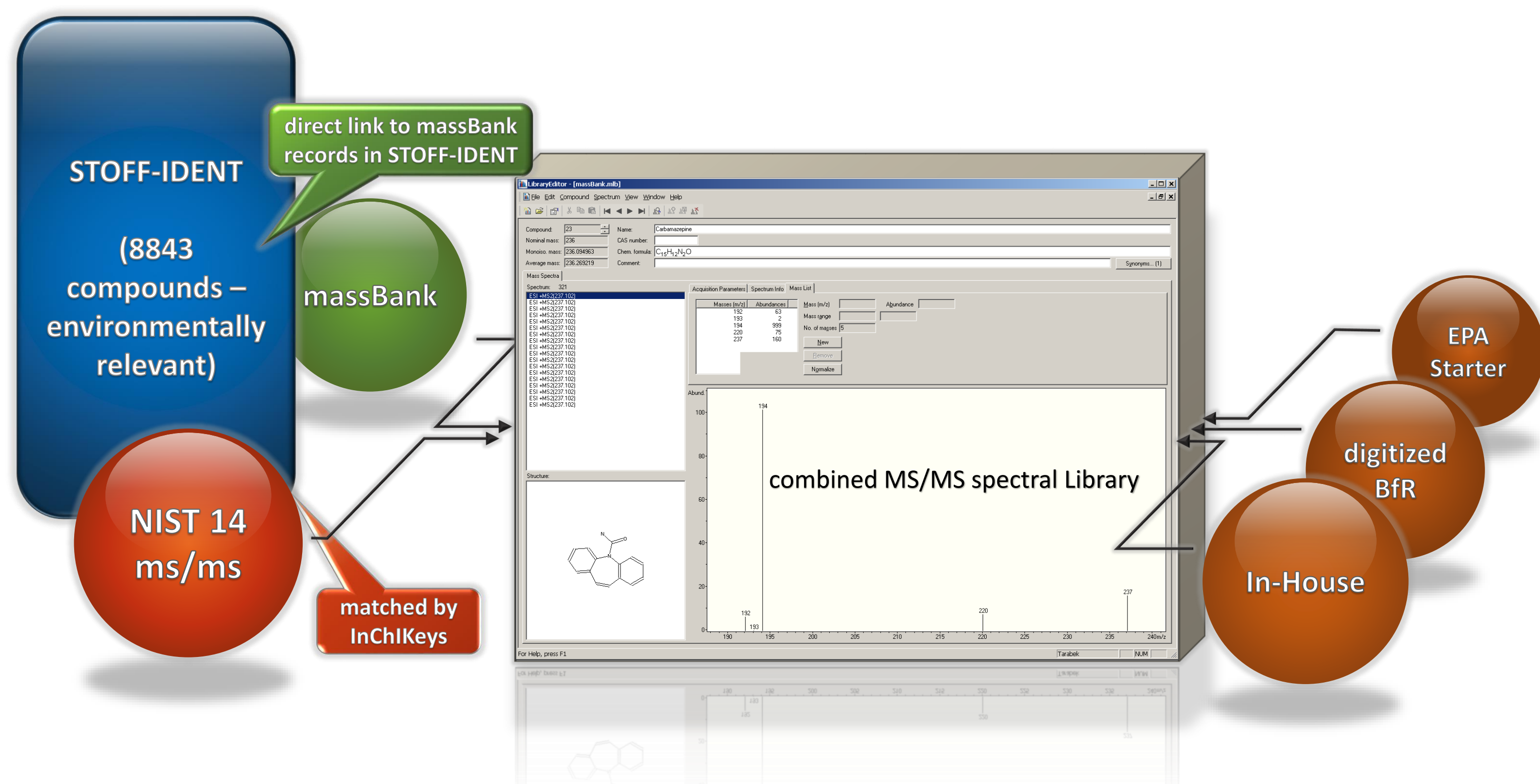# Combined MS/MS Library Search Based Screening for Water Pollutants – A LRMS Alternative

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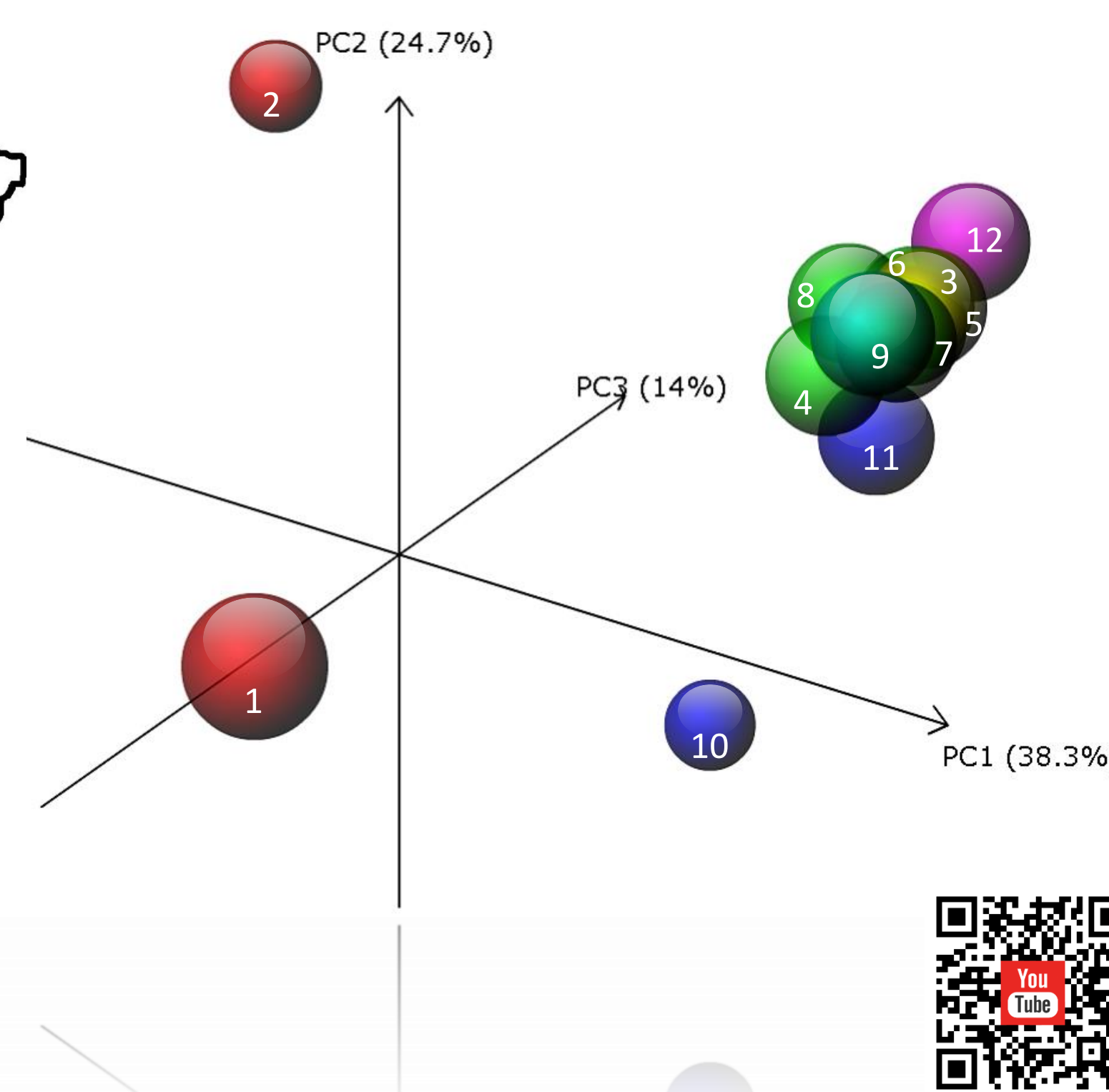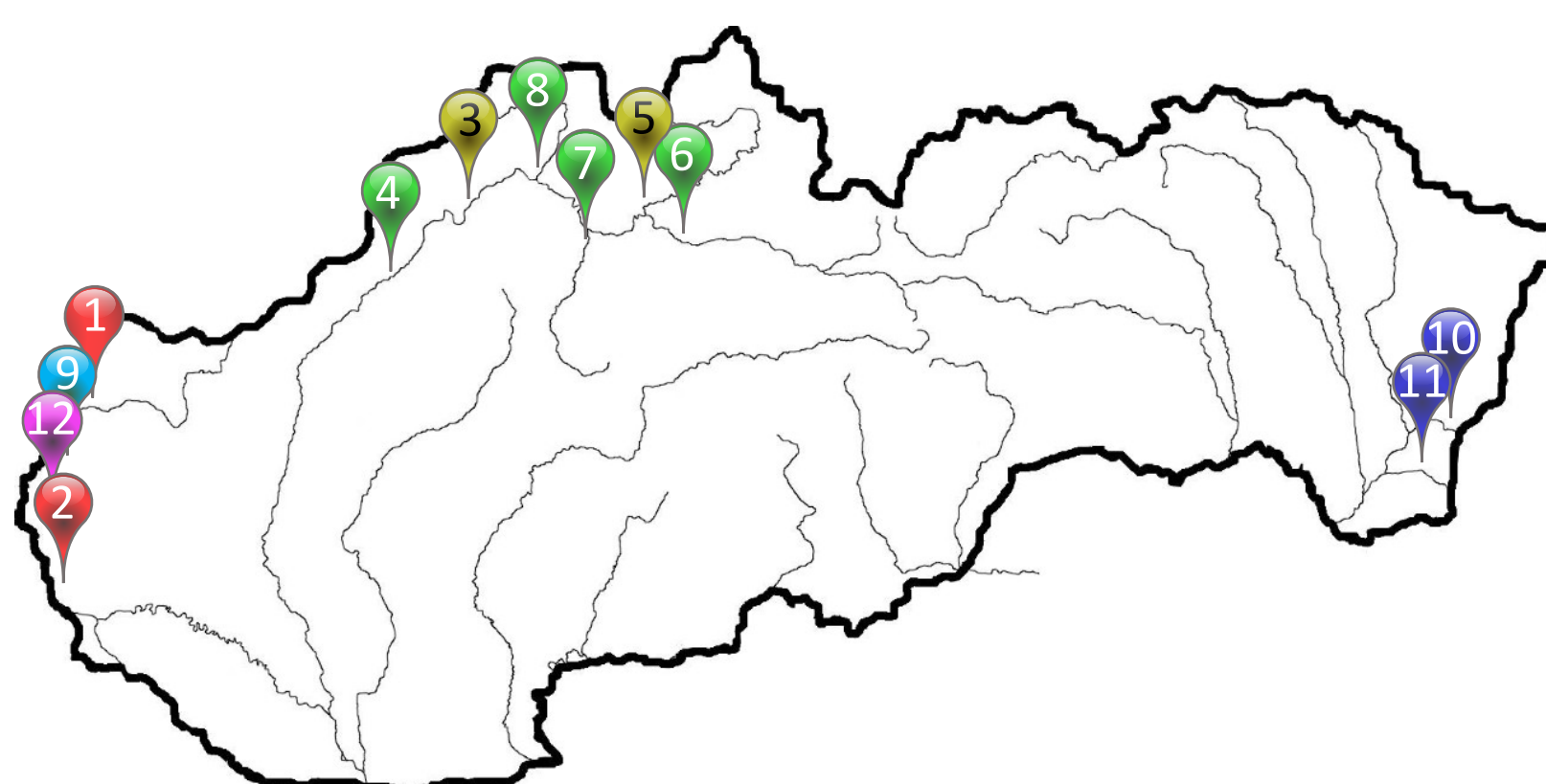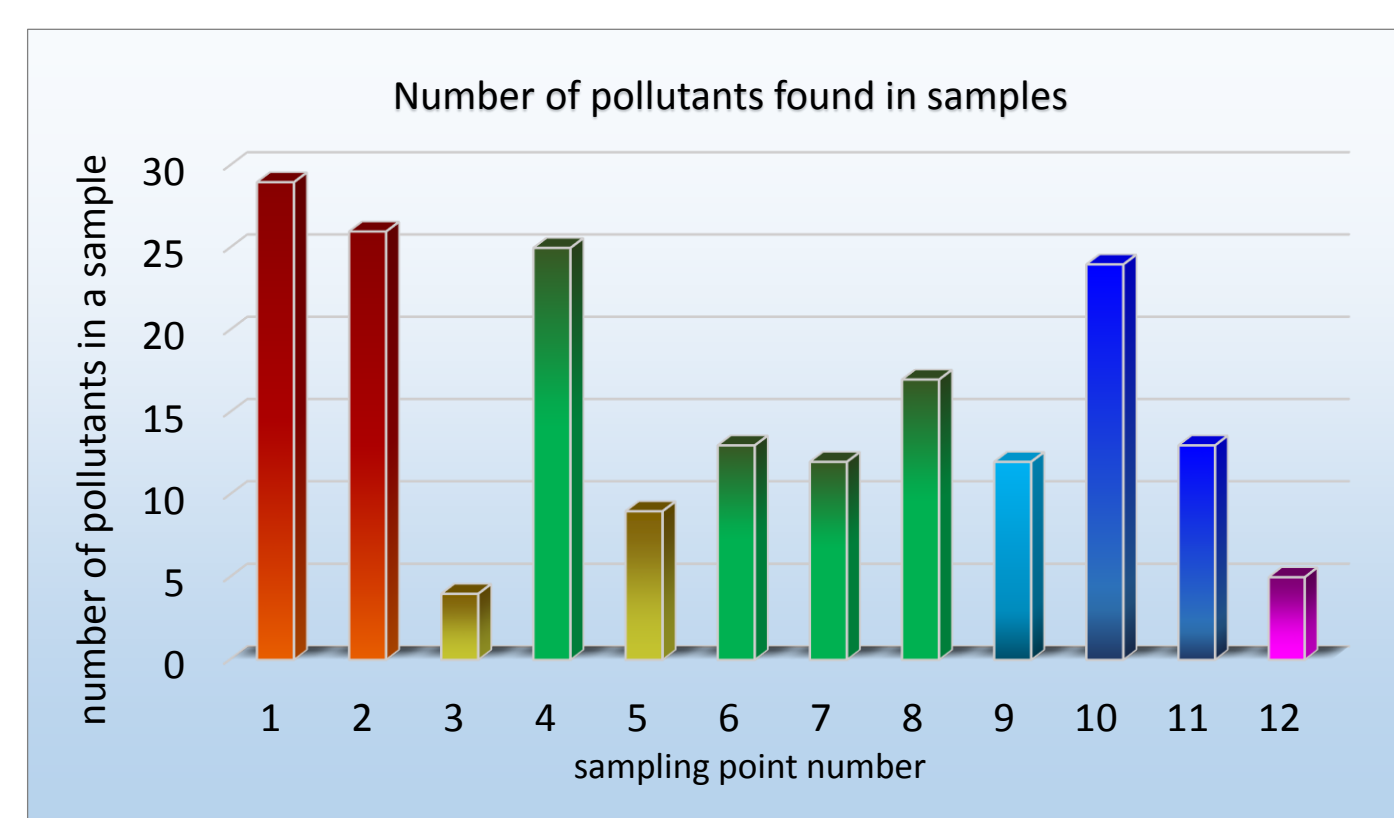
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Library	availability	#compounds original	#spectra original	selection	#compounds selected	#spectra selected
NIST 14 MS/MS	commercial	9,344	234,284	Matching InChIKeys in STOFF-IDENT	1217	27604
MassBank	http://www.massbank.jp/SVN/OpenData/record/	Unique compounds?	41,092	Direct link in STOFF-IDENT	1354	16436
EPA Starter	http://chemdata.nist.gov/mass-spc/ms-search/EPA_Starter.html	755	4064	Entire library	755	4064
BfR	http://www.bfr.bund.de/de/bfr_daten_fuer_die_mit_lc_ms_ms_analyse-5831.html	579	~4600	Pesticides not found either in NIST14 or MassBank (by matching CAS#)	218	231
in-house	-	30	260	Entire library	30	260

In order to perform a LC-MS/MS (with unit resolution) screening for water pollutants a sufficiently large but efficient mass spectral library should be available. Ion trap instruments are capable of generating tandem mass spectra – these are then searched within the library. In the presented study a combination of 5 libraries has been used for this purpose. To improve search performance and increase the relevance of hits only the compounds that are included in the STOFF-IDENT (database of environmentally-relevant substances) have been selected and fed into the combined library.
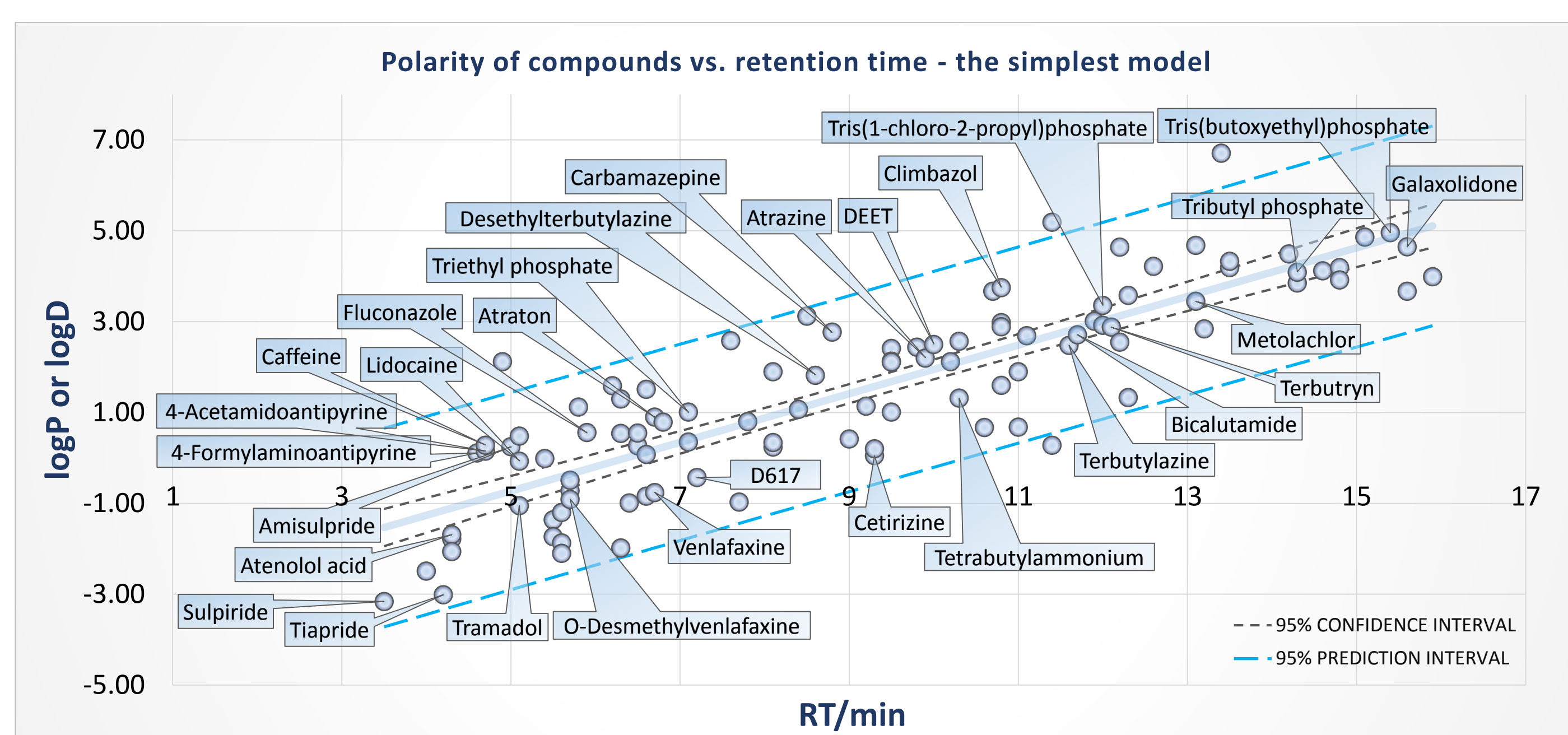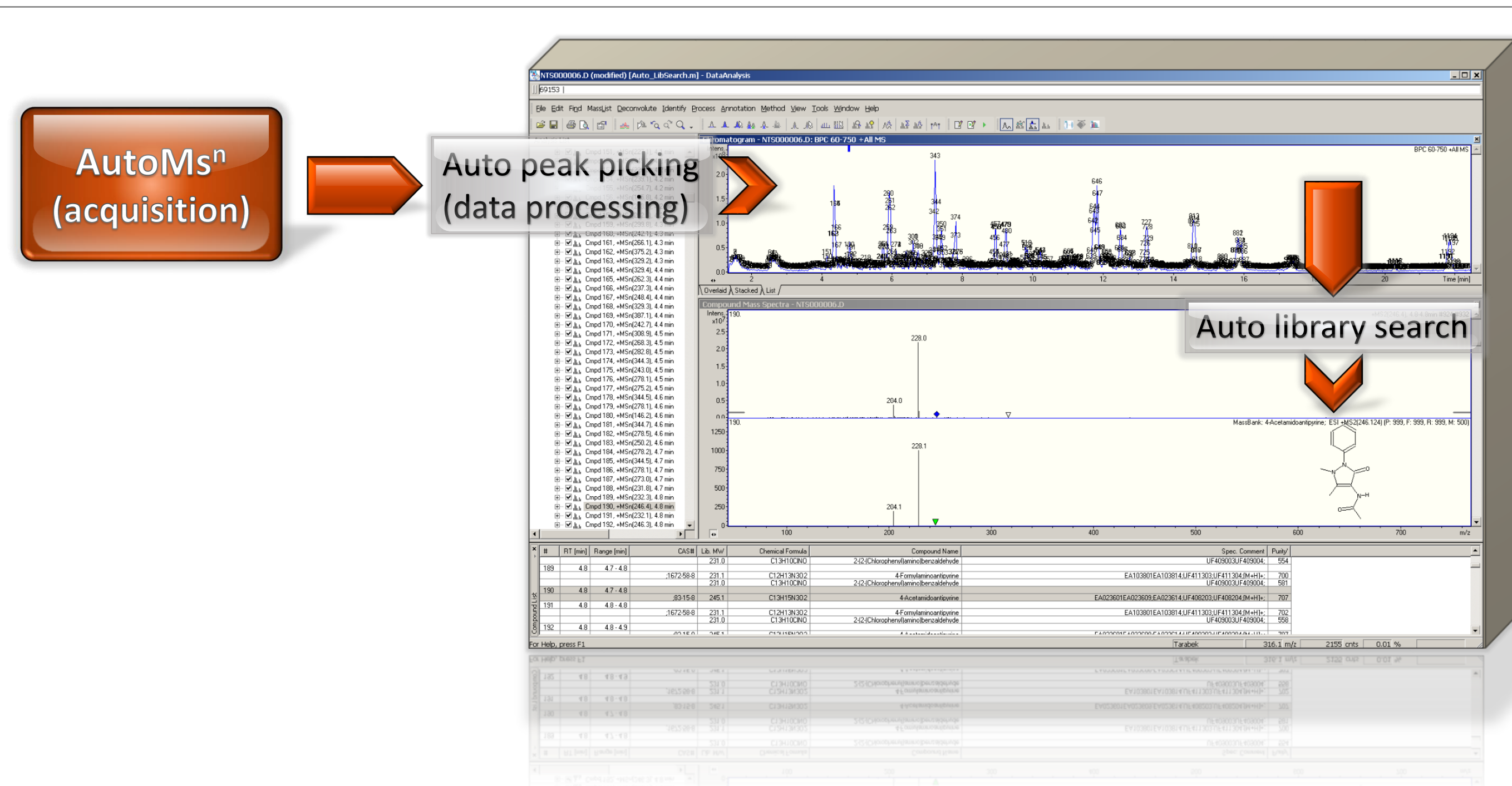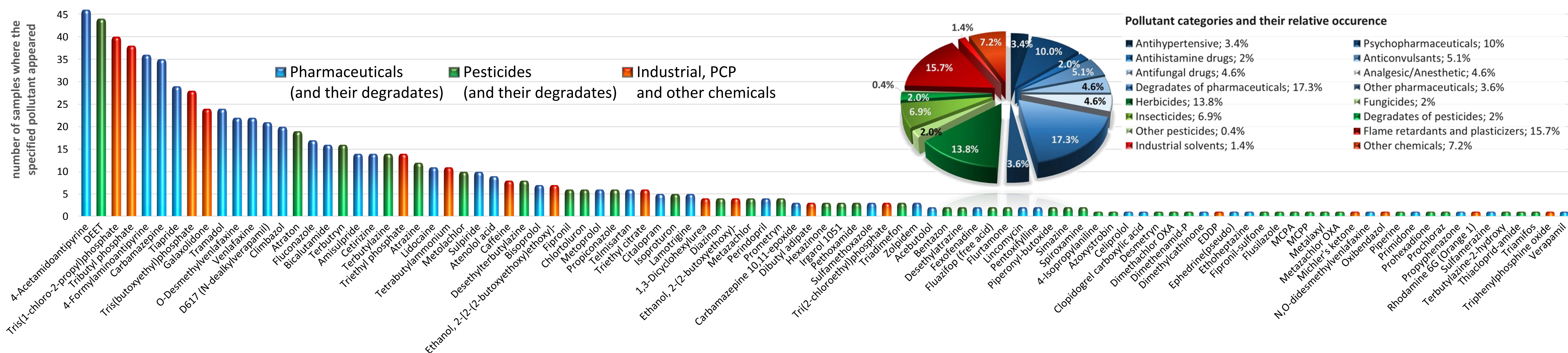

Analysis of water samples is carried out in "AutoMs(n)" mode. For a given retention time from a full MS scan, two highest MS peaks are selected for isolation and fragmentation. About 110 MS/MS spectra per min are generated this way. The amount of data produced during a 20 min LC/MS chromatographic run requires a high level of automation also in terms of data processing. A peak picking procedure (without deconvolution) specified within the processing method is followed by a library search of compounds resulting from the peak picking – all in one click. All search hits are thereafter inspected and evaluated based on spectral match, retention time – polarity relationships and isotopic patterns, where applicable. The described procedure represents a "quick-and-dirty" approach to untargeted screening of water pollutants.

The above described method has been applied within a chemical status of surface waters monitoring program in Slovakia. 61 samples in total have been analyzed and evaluated during the years 2013-2015. For illustration only the results from summer 2015 are presented in the following diagrams. From left to right: plot of numbers of pollutants found and tentatively attributed to certain substances in each sample; map of Slovakia with the largest rivers and categorized sampling points (each category colored separately). The categorization reflects spatial distribution as well as the results of principal component analysis of the relative amounts of pollutants (far right).

Principal component analysis of 48 pollutants found in 12 samples. Quantification is only relative - based on peak areas of extracted MS chromatograms. The three principal components explain together 77 % of the variance in the data set. The outliers clearly showing the highly polluted areas/sampling sites.

Frequency of occurrence of 99 pollutants found present in 61 samples collected in the years 2013-2015. The screening scope of pollutants is limited by the actual mass spectral library records.
Potential for future development: Increasing the number of compounds/spectra in the mass spectral library. Confirmation of structure assignments by reference standards plus quantitative analysis. Improvement of additional supporting methodologies – relating retention time to the structure of a solute, application of more isotope patterns etc.