

Environmental impact of past and current military activities in Switzerland: an exploratory study

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DESCRIPTION

In Switzerland and worldwide, live military exercises, in particular firing activities and the resulting ammunition waste, are a potential source of soil contamination at exercise sites.

Today, it has become necessary to assess the risks associated with these ammunition residues and this assessment involves evaluating the amount of metals and energetic organic compounds present as residues in contaminated soils. Information on the amount of these munitions present in Swiss soils is still limited. However, it is necessary to know the extent of this contamination to be able to establish a monitoring system and to assess more precisely the risks and consequences caused by past and present military activities.

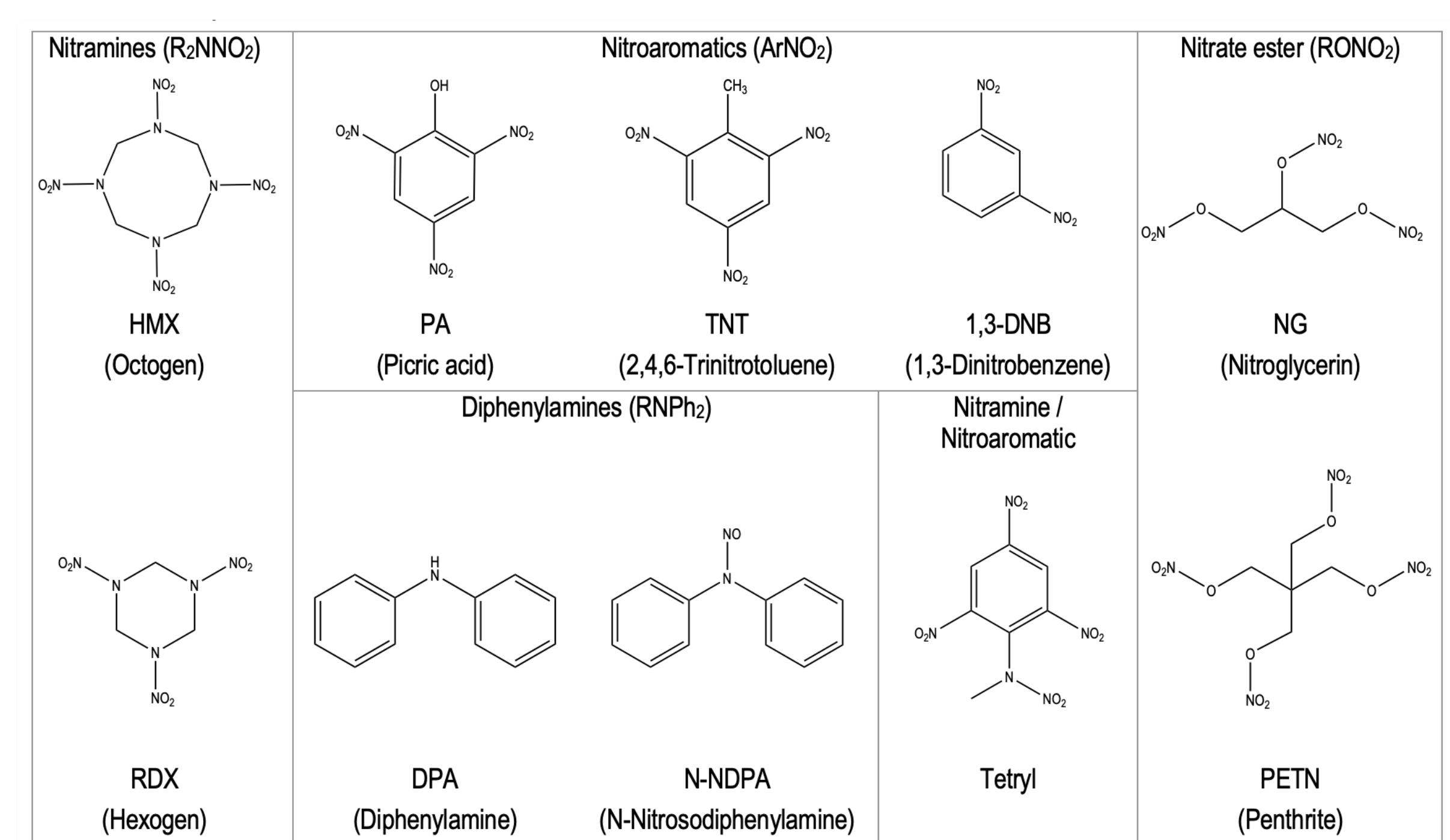
Once the extent of the distribution and the potential risks of contamination by residues of energetic compounds in the soils of the shooting ranges have been assessed, it will be possible to determine whether soil remediation measures should be taken.

OBJECTIFS

The aim of this project is to develop a procedure for the quantification of energetic compounds potentially present as residues in the soils of exercise firing ranges used by the Swiss army. The entire procedure from sampling to quantification is to be developed.

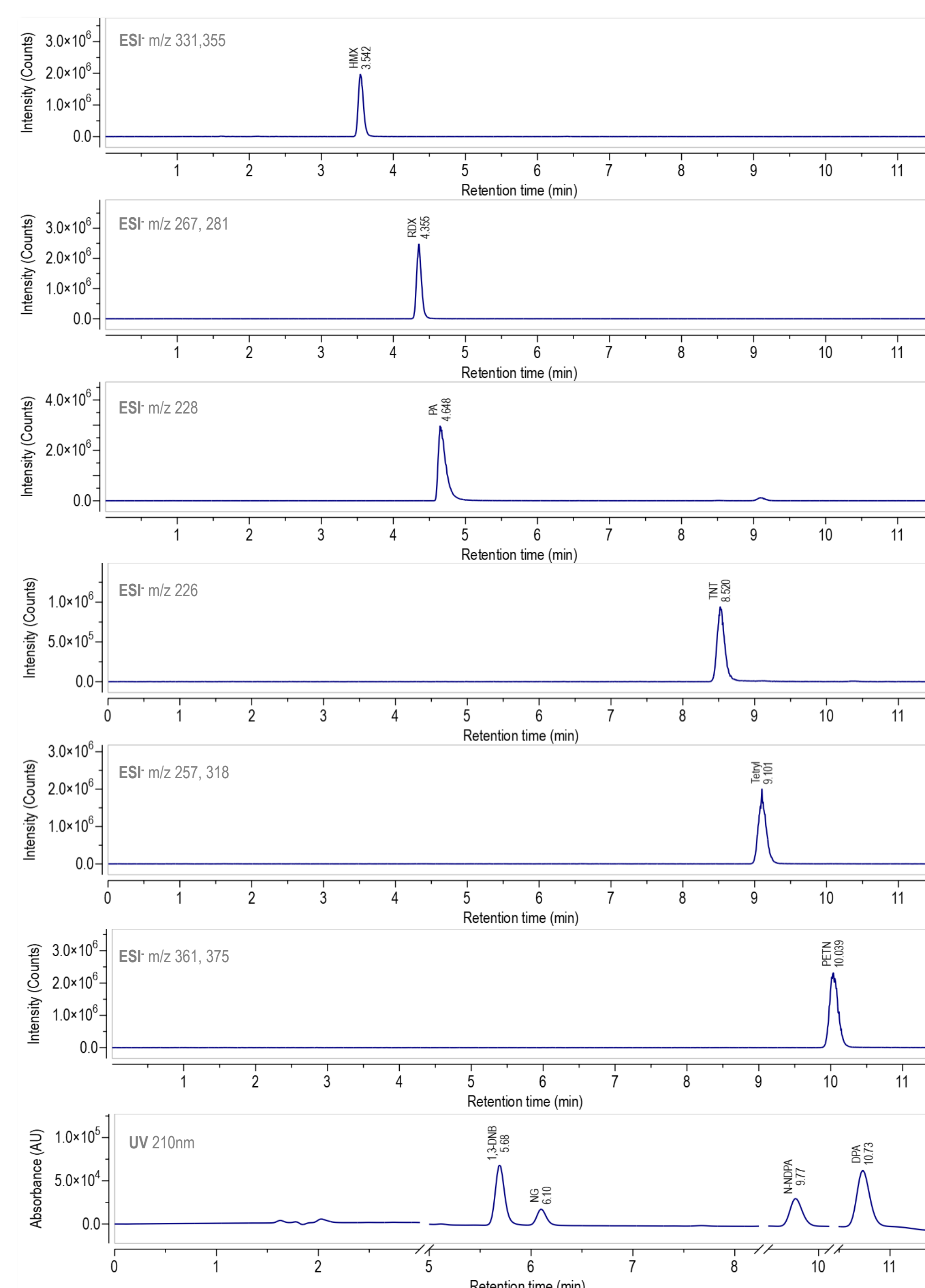


The following 10 energetic compounds (ECs) were determined as target compounds:



RESULTS

Development of a method for the detection and quantification of ECs by LC-MS/UV



For the separation and quantification of the target 10 ECs, different mobile phase compositions were investigated. Two stationary phases were tested: a Waters ACQUITY UPLC BEH C18 column and a Waters ACQUITY CSH Phenyl-hexyl column. The flow rate of the mobile phase and the elution gradient were optimised. All compounds could be separated with good baseline resolution.

An optimisation of the detection by mass spectrometry using an ESI⁺ system was carried out by means of the realisation of an experimental design allowing the search for an optimal signal according to a set of ionisation parameters. ESI⁻ detection has been developed for the detection of nitroaromatics, nitramines and ester nitrates while ESI⁺ detection has been developed for diphenylamine compounds. Only 1,3-DNB could not be detected by ESI detection.

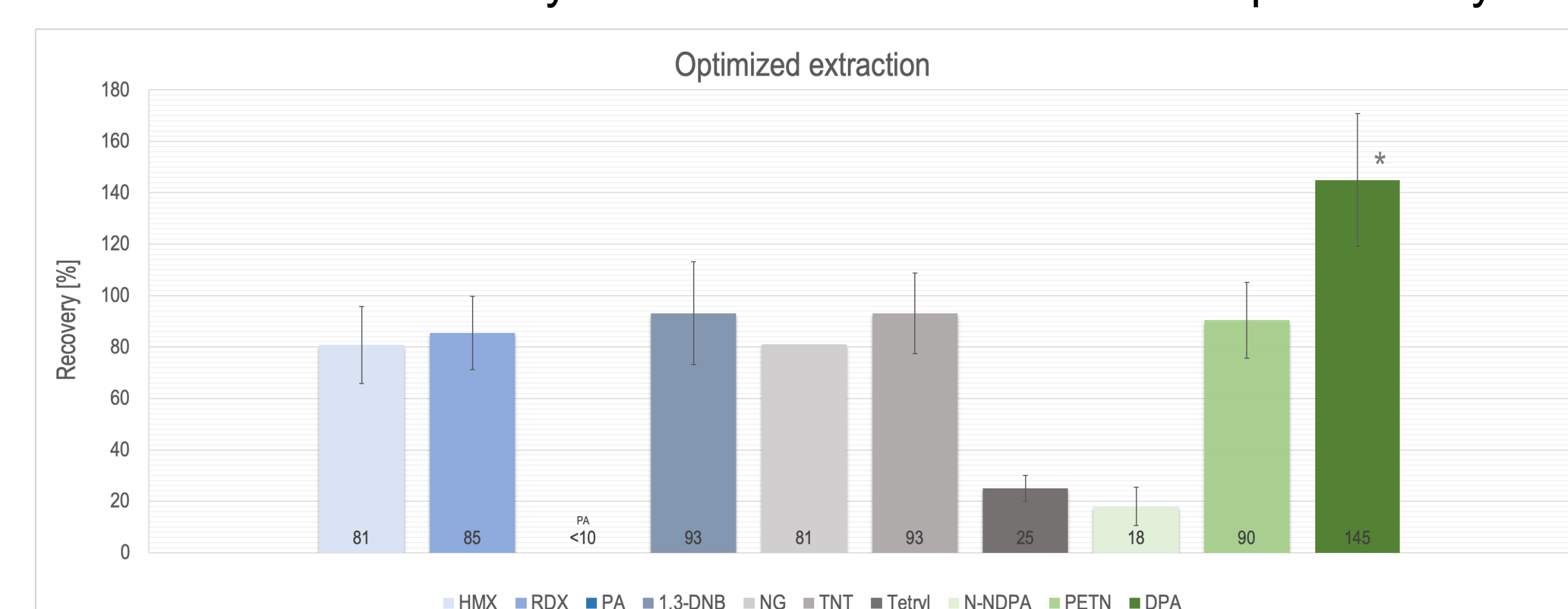
Different performance factors such as LOD, LOQ, linearity and precision were determined for each EC and UV and MS detection were compared. The optimal detection method to be applied to each EC for quantification in a single 15min analysis could be determined by compromising between detection sensitivity and analysis time.

This allowed the definition of a separation and detection method allowing the quantification of the 10 target ECs. As a result, ESI⁻ ionisable compounds except NG are quantified using MS detection while the others and NG are quantified using UV 210nm detection.

Quantification method for the separation and the quantification of the 10 target ECs with a Waters ACQUITY CSH Phenyl-hexyl 2.1x150mm, 1.7µm column, a mobile phase of MeOH:2.5mM acetate buffer pH 4.8, flow rate of 0.2ml/min, temperature of 25°C and performed using a 50%-60% MeOH gradient for 0.25 min, followed by an increase in MeOH concentration from 60%-64% for 8 min.

Development of a method for the extraction of the 10 target ECs

Two extraction methods were tested on spiked soil samples: an ultrasonic extraction and an extraction using a Thermo Scientific Dionex ASE 150 accelerated solvent extractor system. The ASE extraction was optimised by varying certain parameters, such as the solvent used, the extraction temperature, the extraction time and the number of successive extractions for one sample. The extraction performed with the ASE Dionex 150 extractor thus allowed to obtain good recovery yields higher than 80% for 6 target ECs out of 10. PA could not be extracted with this method and the extraction at 100°C induces the probable decomposition of some compounds such as Tetryl and N-NDPA



Optimized extraction of all ECs in soil with the ASE Dionex 150 extractor in one extraction with ACN at a temperature of 100°C. (95% confidence intervals: Student, k=2, α=0.05). *Probable decomposition of N-NDPA in DPA

CONCLUSION

During this project, a method for the separation of the 10 target ECs was developed with good resolution of all compounds. An operational UPLC-MS-ESI method has been developed for the screening of 9 compounds out of the 10 ECs targeted by the project. A separation and detection method allowing the quantification of the 10 target ECs was developed. This quantification method was then transferred to armasuisse where it is planned to use it in the future. An extraction method has been developed with the ASE Dionex 150 extractor which allows the extraction of 9 target ECs out of 10 and allowed to obtain good recovery yields higher than 80% for 6 target ECs.

The chromatographic peak representing PA shows a very broad distribution along the column and thus a widening, probably due to insufficient mobile phase buffer capacity. Extraction at 100°C with ASE causes decomposition of certain compounds such as Tetryl or N-NDPA. PA, due to its high affinity for the soil matrix could not be extracted with low-polarity solvents. Regarding the perspectives, the sampling and drying methods still need to be determined and characterised. The extraction method can be further optimised by reducing the time during which the ECs are subjected to high temperature to reduce the degradation of the compounds. A solvent gradient can also be considered to improve the extraction of more polar compounds such as PA.