Atmospheric pressure gas chromatography triple quadrupole mass spectrometry as a powerful tool for trace analysis of legacy POPs in epidemiological studies

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INTRODUCTION

Legacy persistent organic pollutants (POPs) are still of interest in the research and regulatory community due to their continued presence in the environment. Such compounds biomagnify through food chains years after regulations on production and use. Although most of these compounds are banned from the market worldwide, dichlorodiphenyltrichloroethane (DDT) use is still permitted in parts of the southern hemisphere and Asia for malaria control, creating current emissions sources.
Analysis of DDTs and their metabolites, PCBs, PAHs and PBDEs is typically done by GC-EI-MS. Enhanced sensitivity for other halogenated legacy pesticides and PBDEs is achieved by applying NCI. Introduction of GC-MS/MS enhanced the analysis for environmental applications by minimizing background and matrix response on the analytical signal using MRM. Novel innovation has applied atmospheric pressure ionisation (API) with GC-MS/MS. API creates a softer ionisation process than EI. Ions are generated through charge transfer or protonation processes. Mass spectra are dominated by M[+•], [M+H]+ or [M-H]+, offering extensive capabilities for selection of precursor ions for targeted quantification in MRM. APGC-MS/MS methods applying wet and dry conditions in the ion source are under development for analysis of legacy POPs in human matrices. First results from the method development are presented.

INSTRUMENTS

APGC-MS/MS: Waters APGC-Xevo TQ-S
**GC:** Agilent 7890A with CTC PAL -AS
Positive ionisation mode: AP (dry condition, charge transfer mode) and APCI with H$_2$O as modifier in an open vial (wet condition, proton-transfer mode)

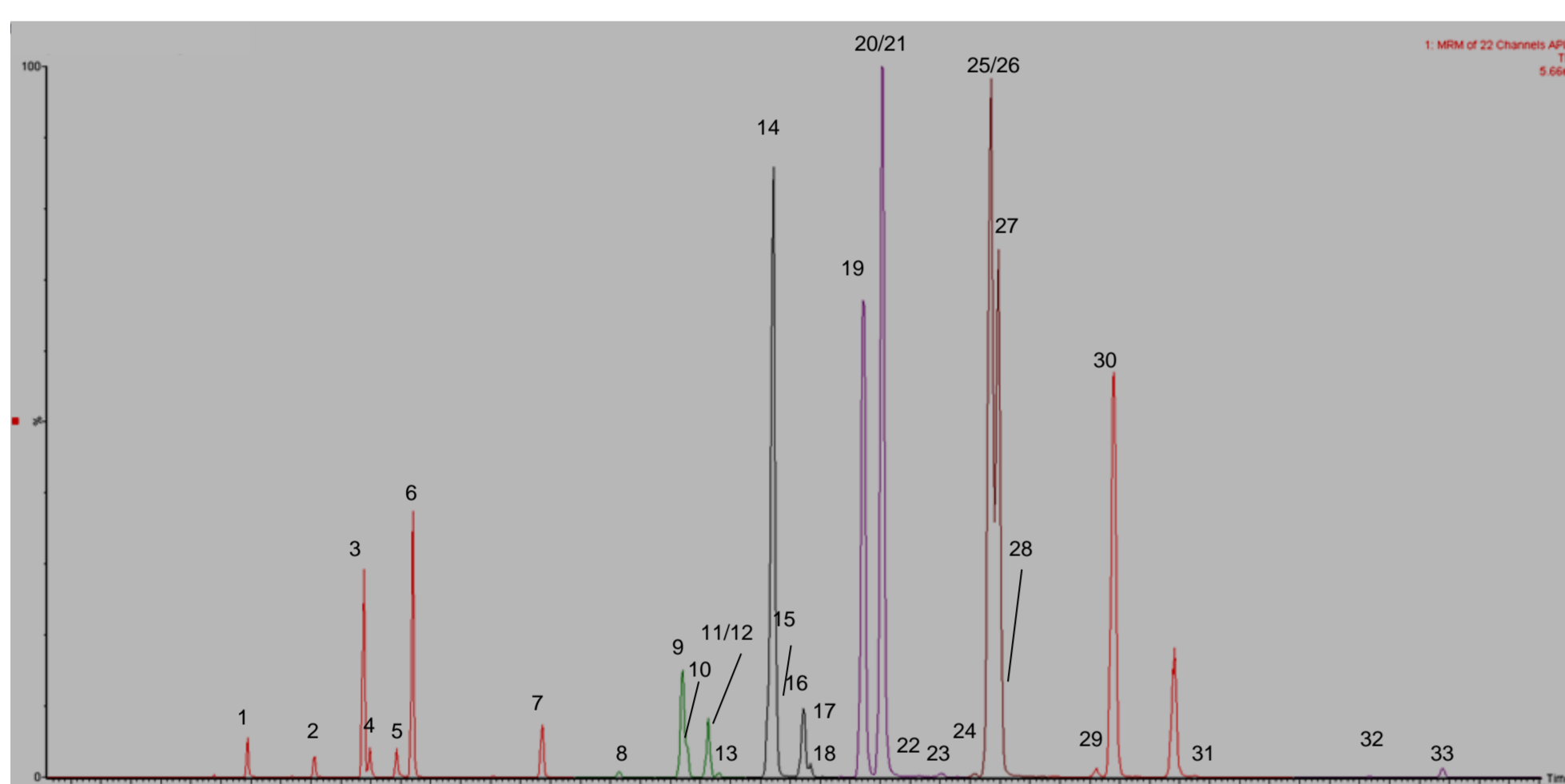**GC-EI/NCI-MS/MS:** Waters quattro micro GC-MS
GC: Agilent 7890A with 7683B AS or Agilent 6890N with CTC PAL -AS
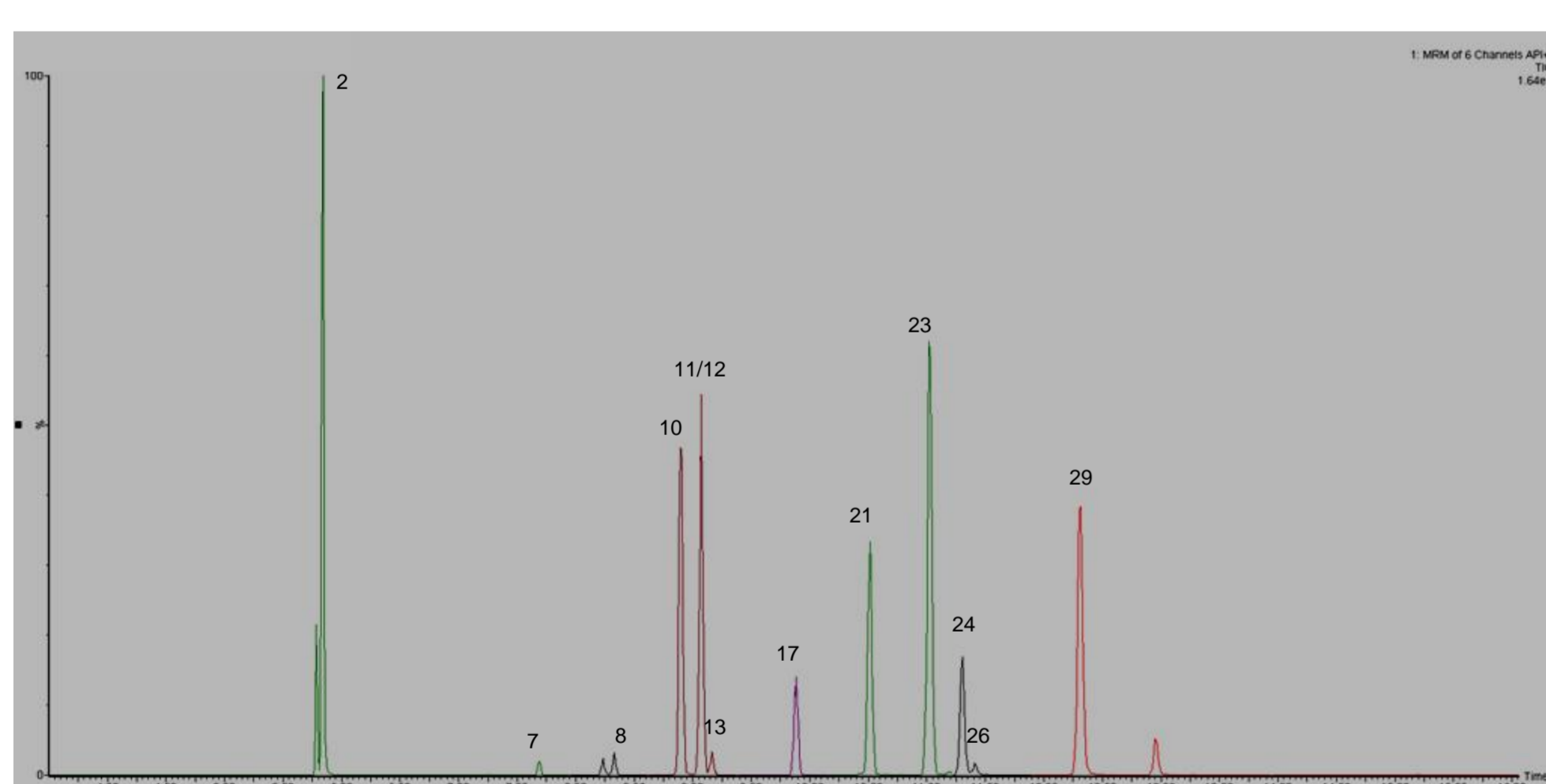**Ionisation mode:** EI and NCI with methane

FULL SCAN SPECTRUM CHARACTERISTICS OF SELECTED PESTICIDES

⟹ **high abundance of M[+•] ions and/or higher m/z fragment ions with GC-APCI-MS**
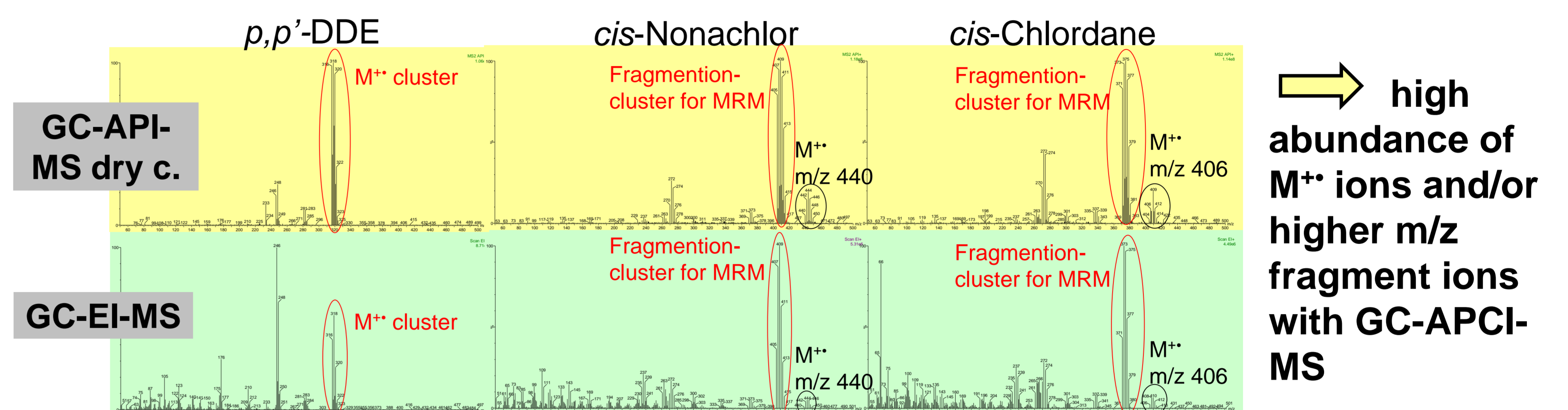
MRM-CHROMATOGRAMS OF PESTICIDES

GC-APCI-MS/MS chromatogram, measurement under charge- transfer condition (dry condition)

GC-APCI-MS/MS chromatogram, measurement under proton-transfer condition (wet condition)

Analytes
1 Pentachlorbenzene
2 Trifluralin
3 α-HCH
4 Hexachlorbenzene
5 β-HCH
6 γ-HCH
7 Heptachlor
8 Aldrin
9 Octachlorostyrene
10 Isodrin
11 cis-Heptachlorepoxide
12 Oxychlordane
13 trans-Heptachlorepoxide
14 trans-Chlordane
15 o,p'-DDE
16 cis-Chlordane
17 Endosulfan I
18 cis-Nonachlor
19 p,p'-DDE
20 o,p'-DDD
21 Dieldrin
22 Toxafen Parlar 26
23 Endrin
24 Endosulfan II
25 p,p'-DDD
26 trans-Nonachlor
27 Toxafen Parlar 32
28 o,p'-DDT
29 Endosulfan sulfate
30 p,p'-DDT
31 Toxafen Parlar 50
32 Toxafen Parlar 62
33 Mirex
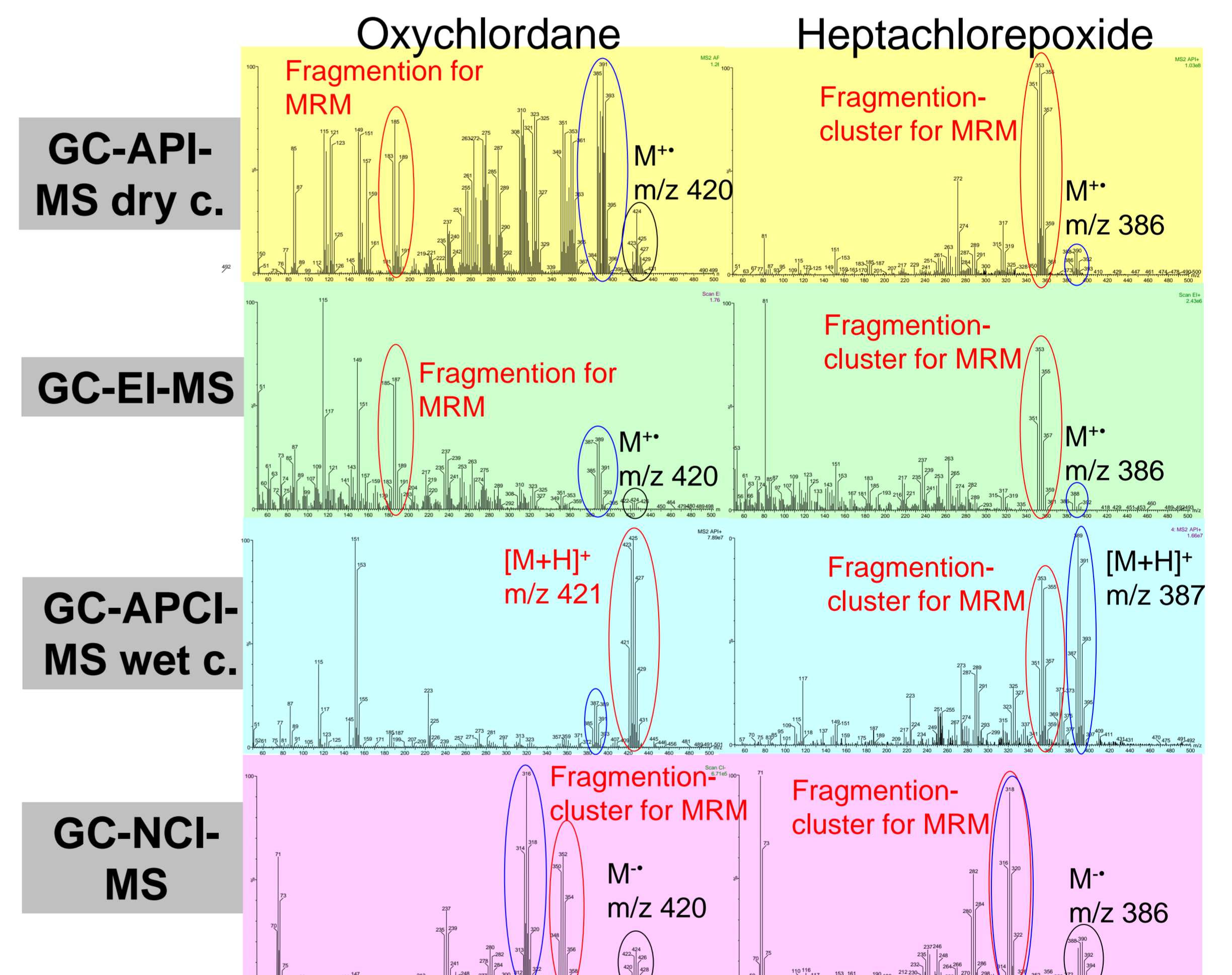
Heptachlorepoxide is coeluting with oxychlordane. An additional challenge is the presence of similar ions and fragment ion clusters in their spectra. The APCI application shows, compared to AP, EI and NCI, a better sensitivity and selectivity with regard to the [M+H]+ and fragment ion clusters.

RESULTS FROM MRM EXPERIMENTS

➢ **APGC-MS/MS vs GC-MS/MS for analysis of pesticides:** Signal enhancement resulting in better sensitivity as e.g. factor 160 – 600 for DDTs and metabolites, ~20 for Chlordanes and 120 for Nonachlors (same GC-programme and transitions on both instruments).

➢ **Charge-transfer vs proton-transfer condition:** Compound specific results are observed. Charge transfer condition favours PCBs, PAHs and majority of investigated pesticides, while proton-transfer condition gives enhanced sensitivity for trifluralin, dieldrin, aldrin, endrin, isodrin and endosulfanes and better selectivity for oxychlordane and heptachlorepoxides (adapted GC-programmes and transitions).

➢ **PAHs:** Application of pseudo MRM (parent-parent MRM) due to almost no fragmentation and instable product ions when using parent-daughter transitions.
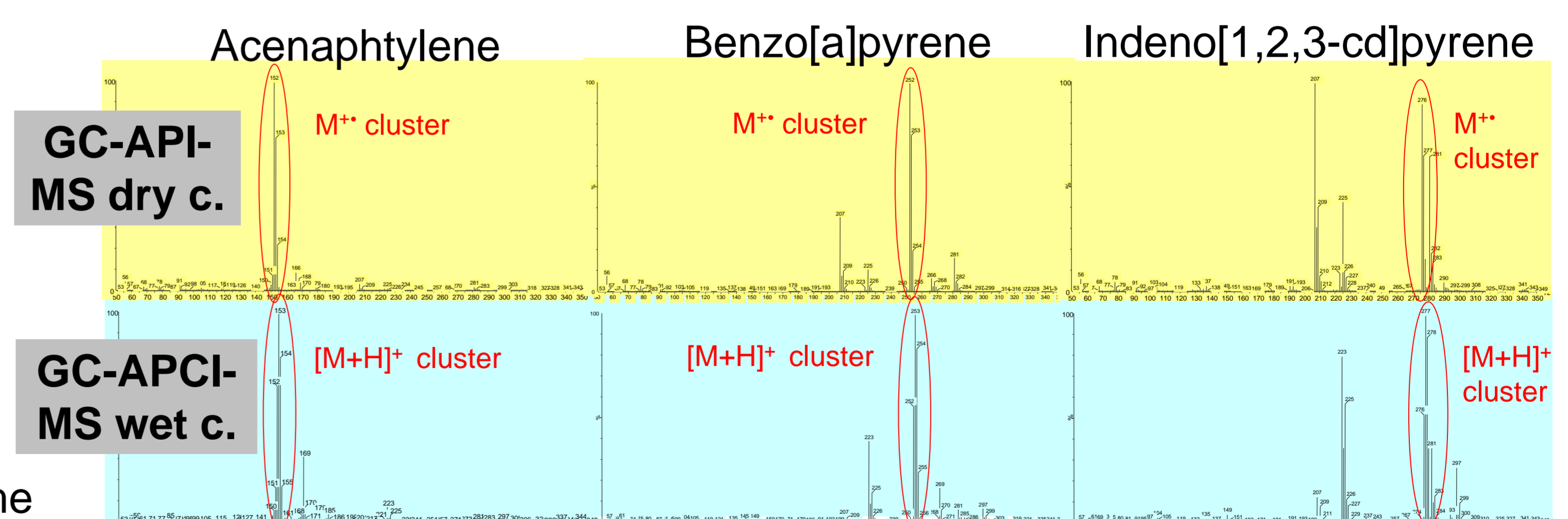
CONCLUSIONS

The soft ionisation processes in the API source generate reduced fragmentation patterns with higher abundance of M[+•] or [M+H]+ ions and high m/z fragmentation clusters, resulting in better sensitivity on the APGC system compared to the GC-MS/MS system. Faster scan rates associated with new generation instrumentation and latest design of the MS origin further enhance the sensitivity on the APGC-MS/MS.
The APGC-MS/MS system is a powerful tool for trace analytical work on legacy POPs and promising for applications related to human matrices where sample material is limited and therefore highly valuable.

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