Non-target analysis to identify slowly degrading constituents in petroleum UVCBs

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Yves Verhaegen

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THIS PROJECT WAS EXECUTED BY:

SINTEF Ocean, Trondheim, Norway

Mari Creese
Lisbet Sørensen
Andy M. Booth

Oleolytics LLC, State College, PA, USA

J. Samuel Arey

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Agenda

01 A typical UVCB compositional ‘heat map’

02 Approach

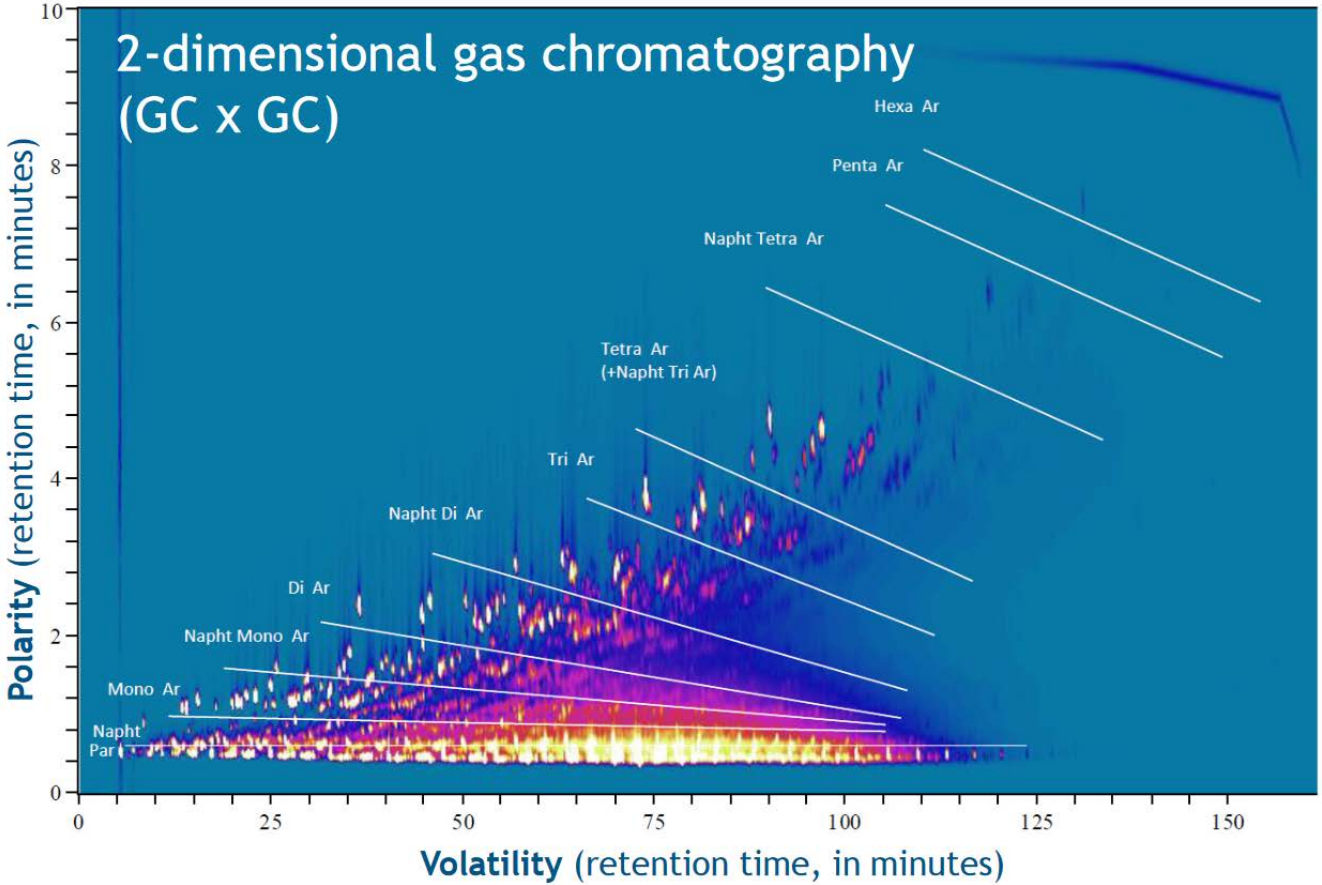
03 Peak quantification via GCxGC-FID

04 Deconvolution of FID peaks

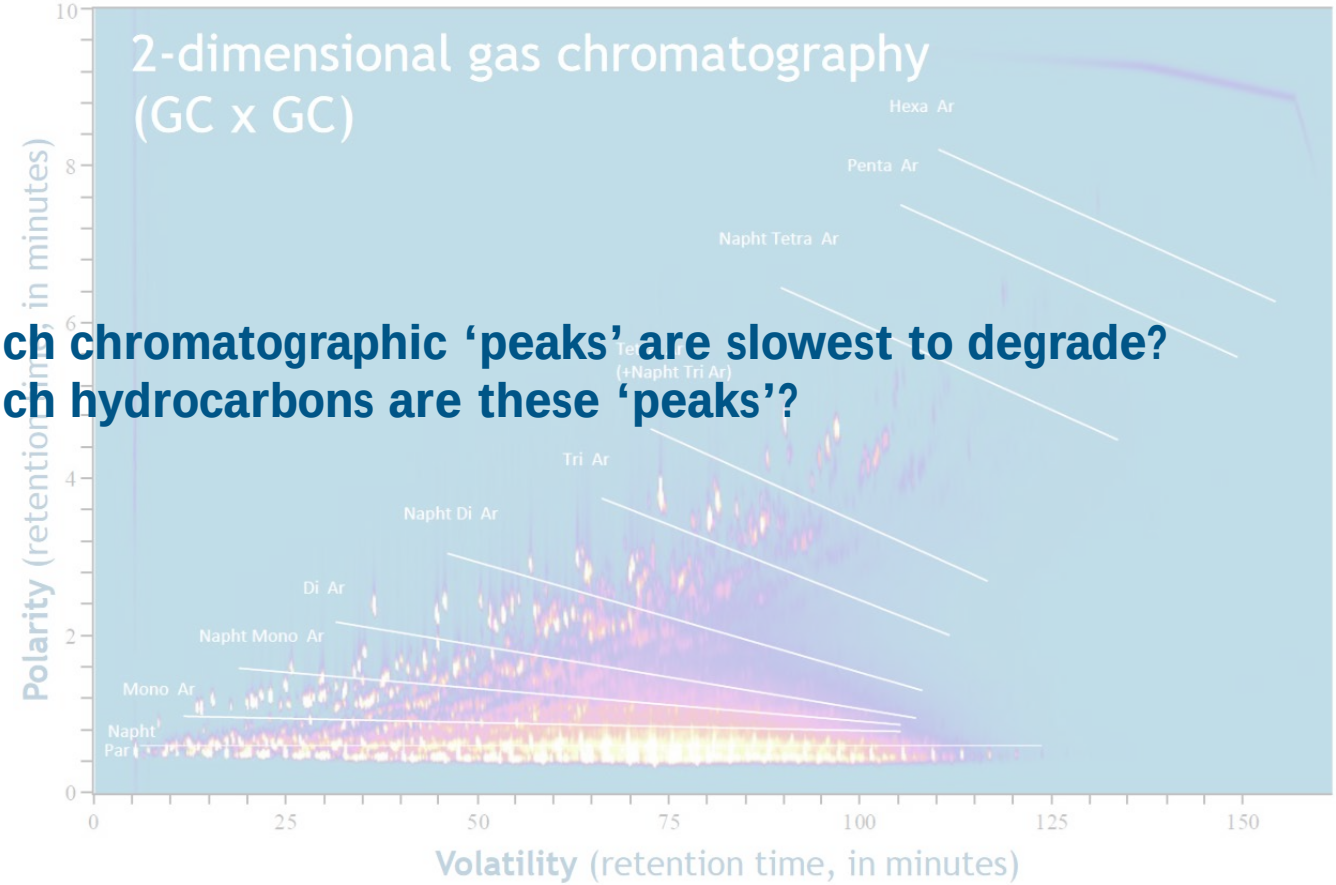
05 Quadrupole Time-of-Flight – Mass Spectrometry (qTOF –MS)

06 Conclusions

A typical UVCB compositional ‘heat map’



A typical UVCB compositional ‘heat map’



Which chromatographic ‘peaks’ are slowest to degrade?
Which hydrocarbons are these ‘peaks’?

Approach

Perform a biodegradation test on representative hydrocarbon UVCB(s)

Diesel Fuel

Adapted OECD 309 protocol, using seawater @ 13°C

Analytical separation & quantification

*via GCxGC - Flame Ionization Detection (**FID**)*

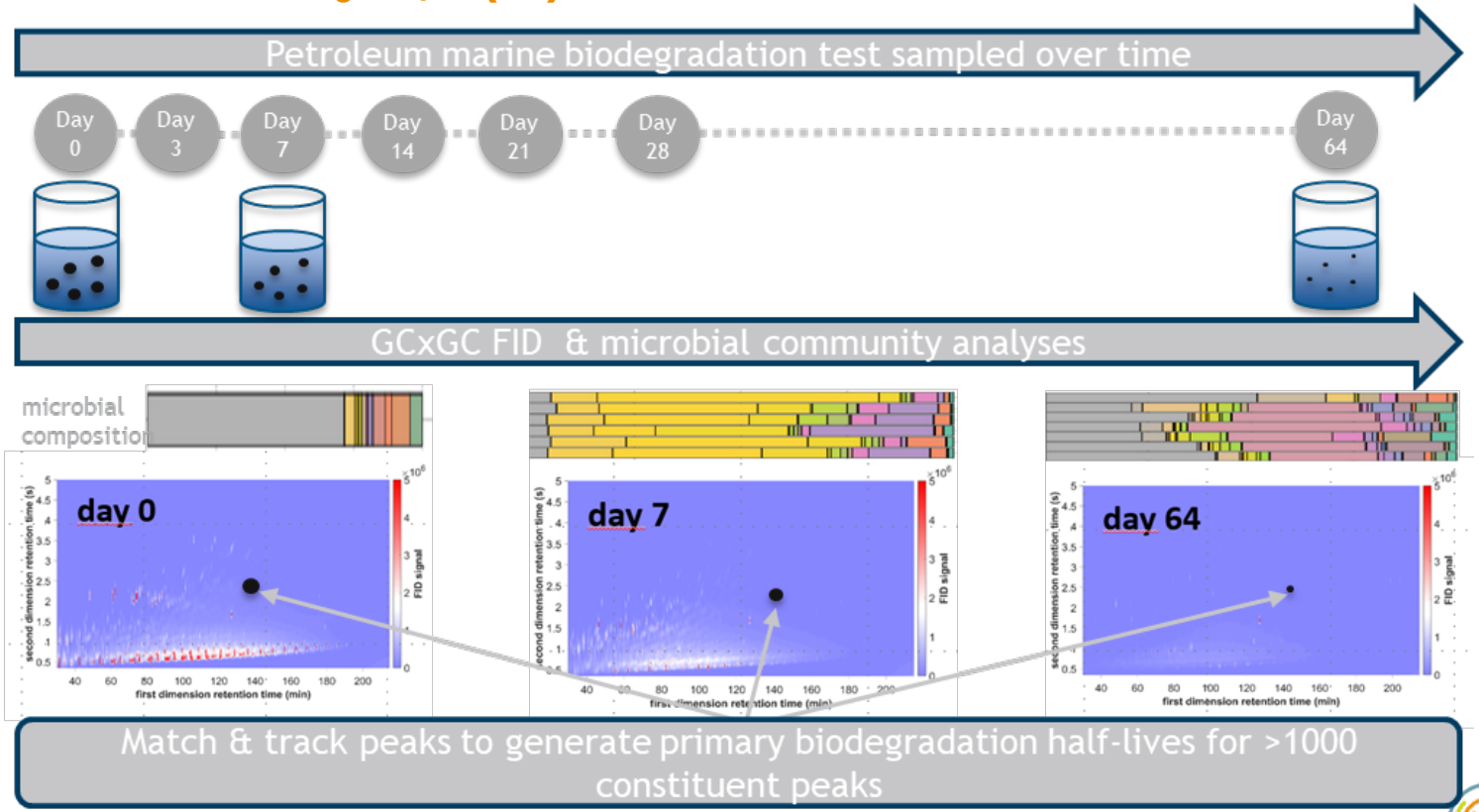
Mathematical 'deconvolution' of FID peaks

via Fourier transformation algoritm

Analytical identification of FID peaks

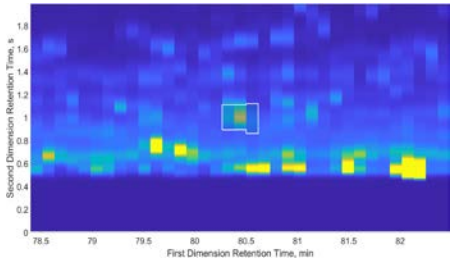
via Quadruple pole Time of Flight – Mass Spectroscopy (**qTOF-MS**)

Booth, et al. Comprehensive Two-Dimensional Gas Chromatography with Peak Tracking for Screening of Constituent Biodegradation in Petroleum UVCB Substances. Environ Sci Technol. 2023 Aug 29;57(34):12583-12593. doi: 10.1021/acs.est.3c01624.



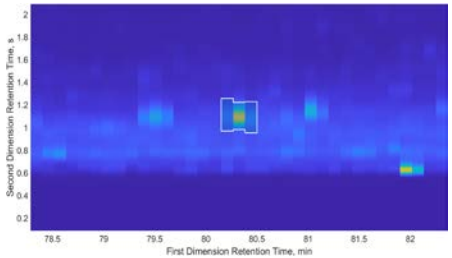
Deconvolution of FID peaks

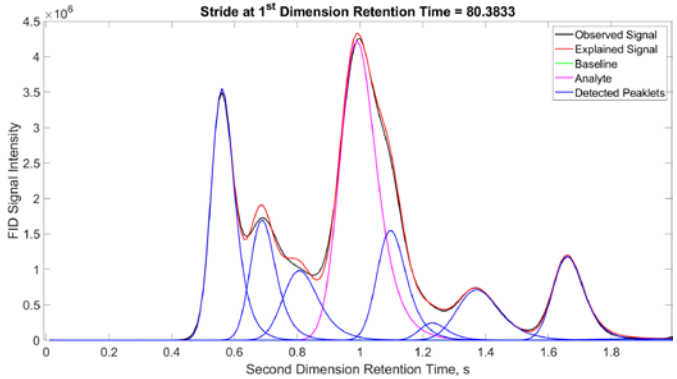
day 0

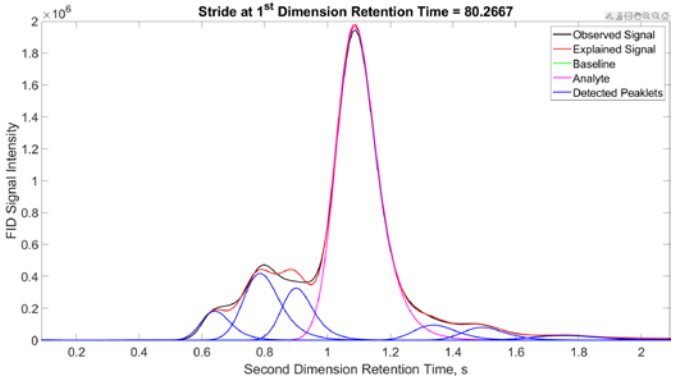


“Peak # 4”

day 64

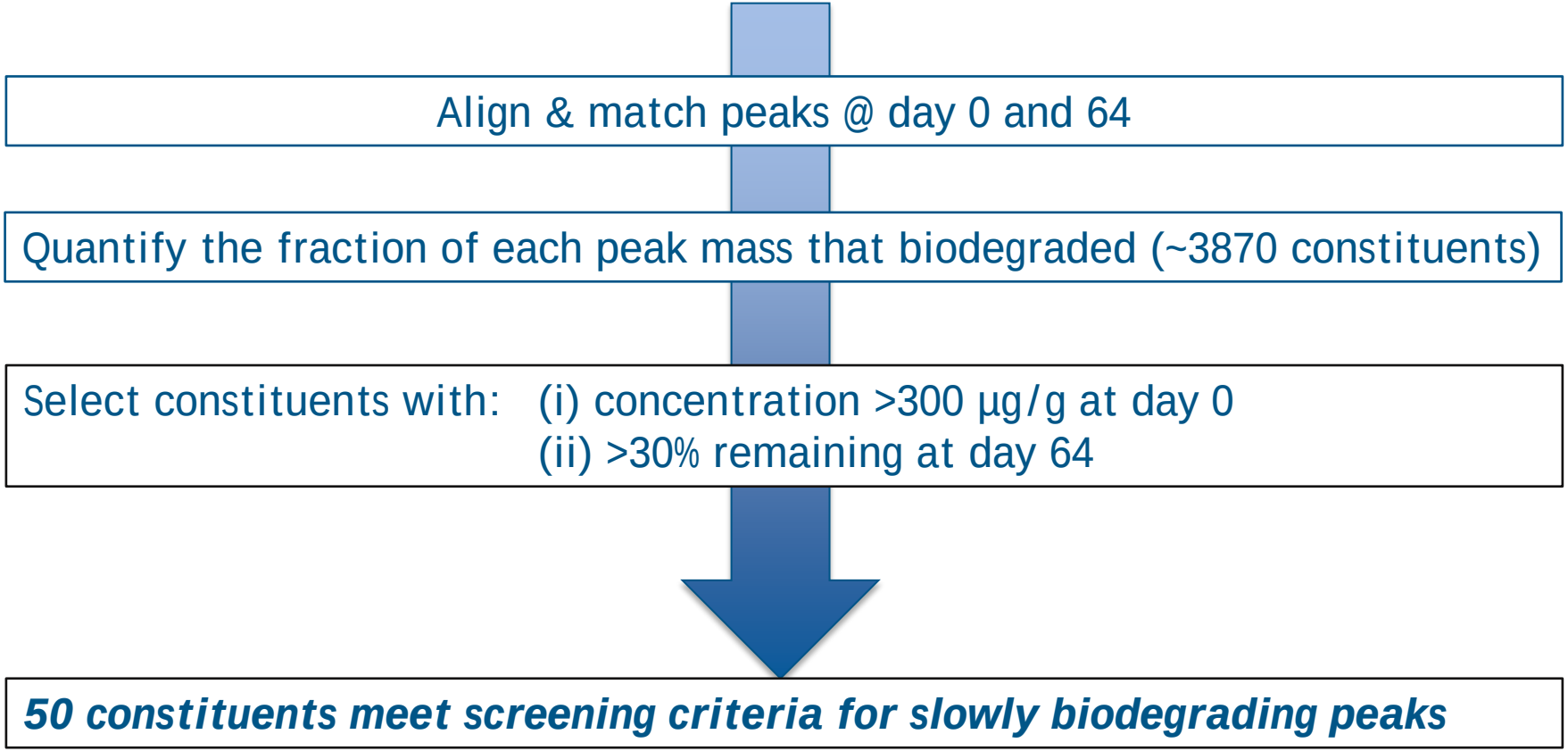






Black line: Observed FID signal Pink line: FID signal attributed to peak #4 Blue lines: FID signal attributed to other constituents

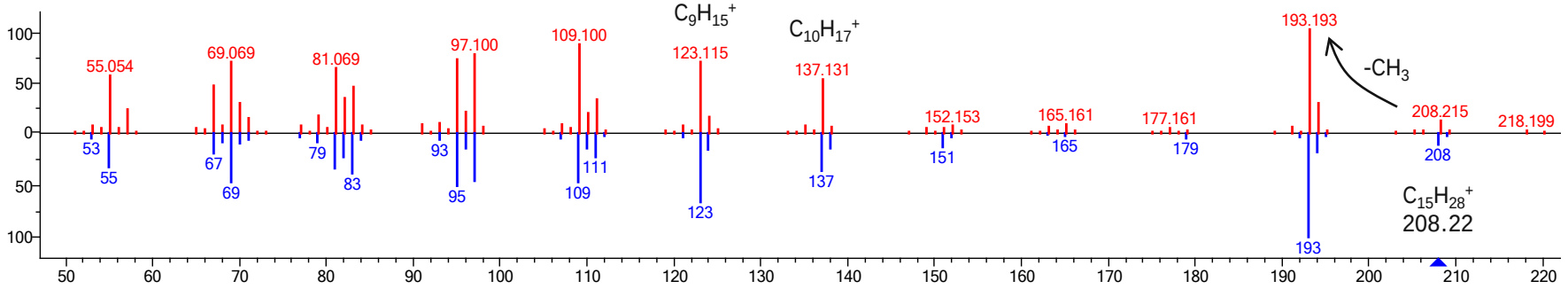
Deconvolution of FID peaks



Quadrupole Time-of-Flight – Mass Spectroscopy (qTOF-MS)

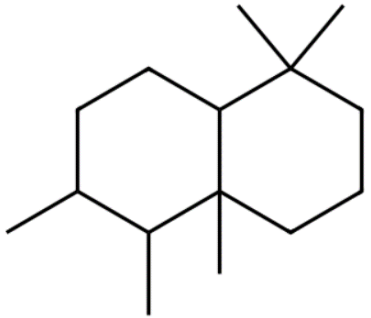
Series 55.054, 69.070, 81.070, 95.086, 109.101, 123.117, and 137.133 are characteristic of many naphthenes

Red sticks show the deconvoluted spectrum of peak #4



Substructure Analysis evaluates the chemical structure features that appear in the top 100 best-match spectra within the combined three libraries. The analysis accounts for both the frequency of substructure appearance and similarity of those spectra.

Peak #4 is a $C_{15}H_{28}$ naphthenic with two rings which likely contains quaternary carbon(s). This is likely a drimane

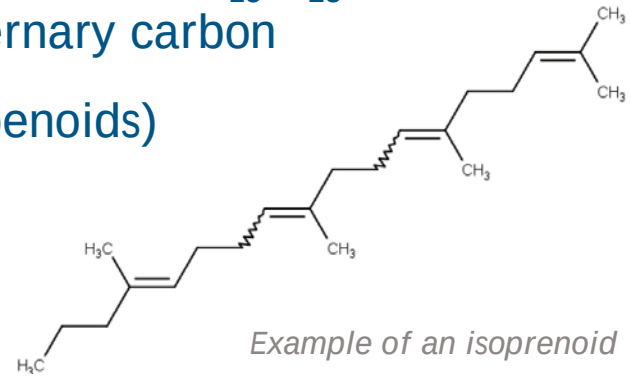


Conclusions

43 out of the 50 prioritized constituents are interpreted as C_{15}-C_{23} two-ring naphthenics, of which 30 likely containing a quaternary carbon

5 constituents are C_{21}-C_{23} acyclic isoprenoids (terpenoids)

2 constituents were not successfully interpreted



Example of an isoprenoid

The technique of whole substance testing with constituent tracking can generate biodegradation data (primary half-lives) for thousands of constituents. The redesigned workflow presented here, which includes deconvolution and non-target analysis, improves the detection, quantification, and identification of slowly-biodegrading constituents

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Thank you for your attention

Yves Verhaegen
yves.verhaegen@concawe.eu