NATIONAL CENTRE FOR SCIENTIFIC RESEARCH "DEMOKRITOS"

Degradation of 2-Methylisoborneol and Geosmin in Water via Radiolysis: Reactive Radical Species and Pathways of Transformation

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Industrial Fellowships Program 2017

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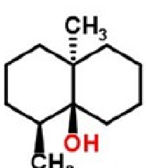
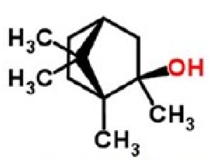
water taste & odour (T&O) compounds

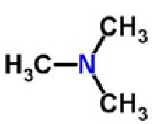
- Substances that cause strong taste and distinctive odour in water
- Common odors: earthy, mold, fishy, egg, etc.
- Perceived by the human sense of smell in extremely low concentrations
- Difficult to remove from water using conventional methods
- Responsible for most cases of complaints from water consumers, which significantly reduces the reliability of water companies
- They are not necessarily related to public health effects, but they degrade overall water quality



geosmin
(earthy)

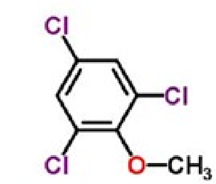


2-methylisoborneol
(musty)

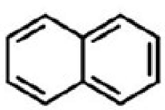


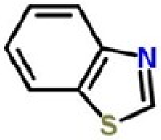
trimethylamine
(fishy)

Dimethyl trisulfide
(septic)

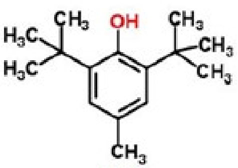


2,4,6-trichloroanisole
(musty)


naphthalene
(mothballs)



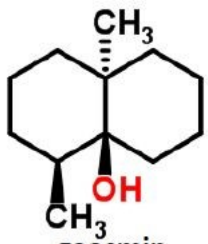
benzothiazole
(plastic)



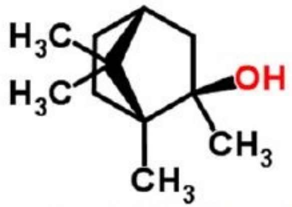
BHT
(plastic)

Sources and occurrence of T&O

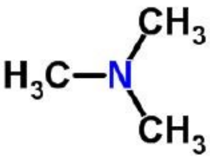
Surface Water Reservoirs
Algal metabolites



geosmin
(earthy)



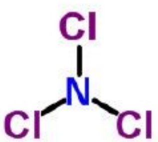
2-methylisoborneol
(musty)



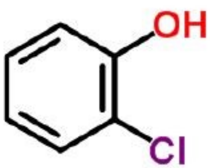
trimethylamine
(fishy)

Dimethyl trisulfide
(septic)

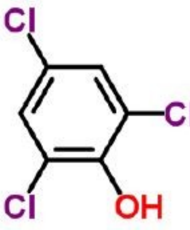
Water treatment
Chlorination products



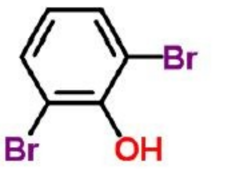
Trichloramine
(swimming pool)



2-chlorophenol
(chemical)



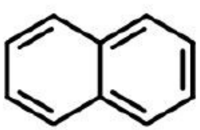
2,4,6-trichlorophenol
(medicinal)



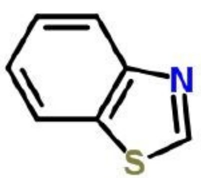
2,6-dibromophenol
(medicinal)

Distribution network
biofilm activity, materials in contact

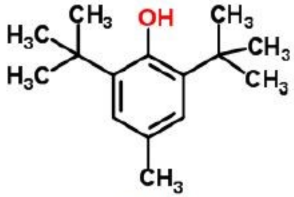
2,4,6-trichloroanisole
(musty)



naphthalene
(mothballs)



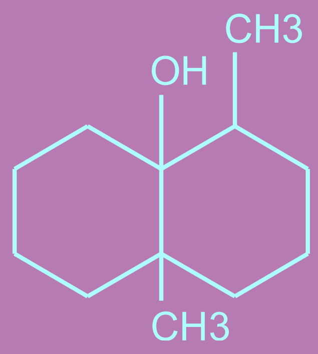
benzothiazole
(plastic)



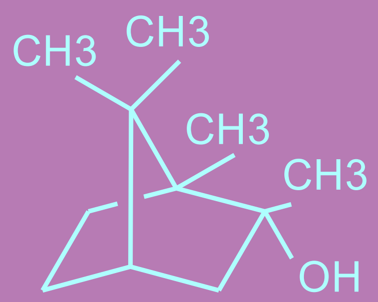
BHT
(plastic)

Geosmin (GSM) and 2-methylisoborneol (MIB)

- **Geosmin** (GSM)
- Semi-volatile
- Earthy odour (OTC* 4 ng L^{-1})
- Mainly produced by *Oscillatoria, Anabaena* and actinomycetes.



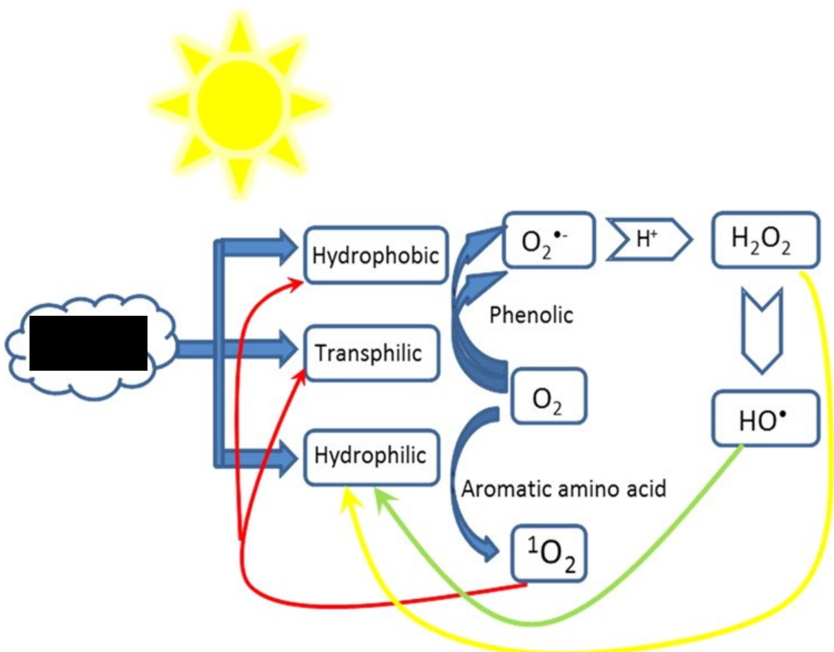
- **2-methylisoborneol** (MIB)
- Semi-volatile
- Musty odour (OTC 5 ng L^{-1})
- Mainly produced by *Oscillatoria, Phormidium* and actinomycetes



*OTC: odor threshold concentration

Natural processes and pollutant degradation

It has been shown that the interaction of solar radiation in natural systems with organic matter of natural origin, results in the production of Reactive Oxygen Species (ROS), capable of breaking down organic pollutants.



Zhang et al. (2014) ES&T 48 (21), pp 12645–12653
Cottrell et. al. (2013) Water Research 47(14), pp. 5189-5199
Zafiriou et. Al. (1984) ES&T 18(12), pp. 358A-371A

Advanced Oxidation Processes (AOPs)

⬇

Reactive Oxygen Species (ROS) production

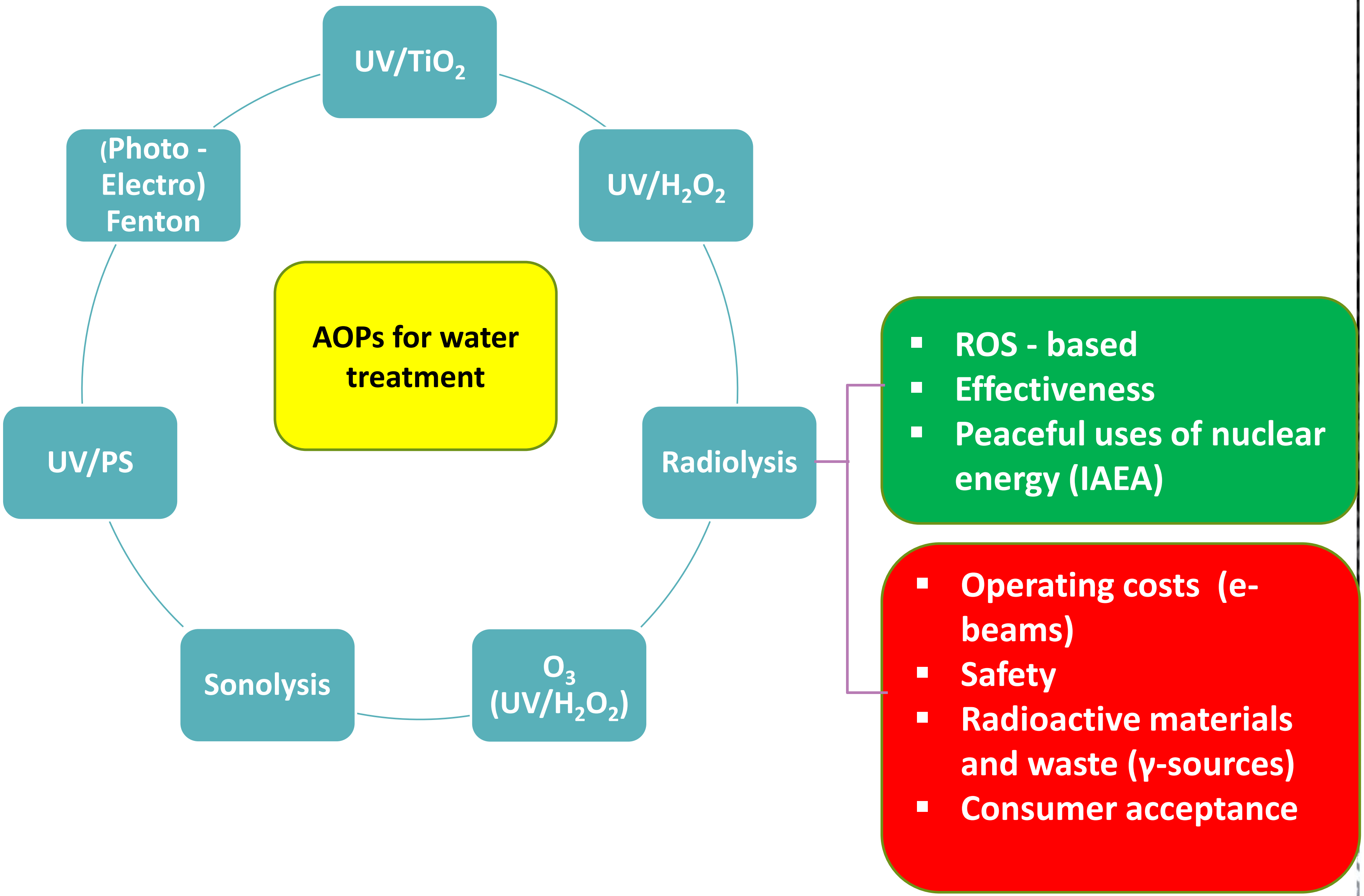
⬇

(transformation products TPs)

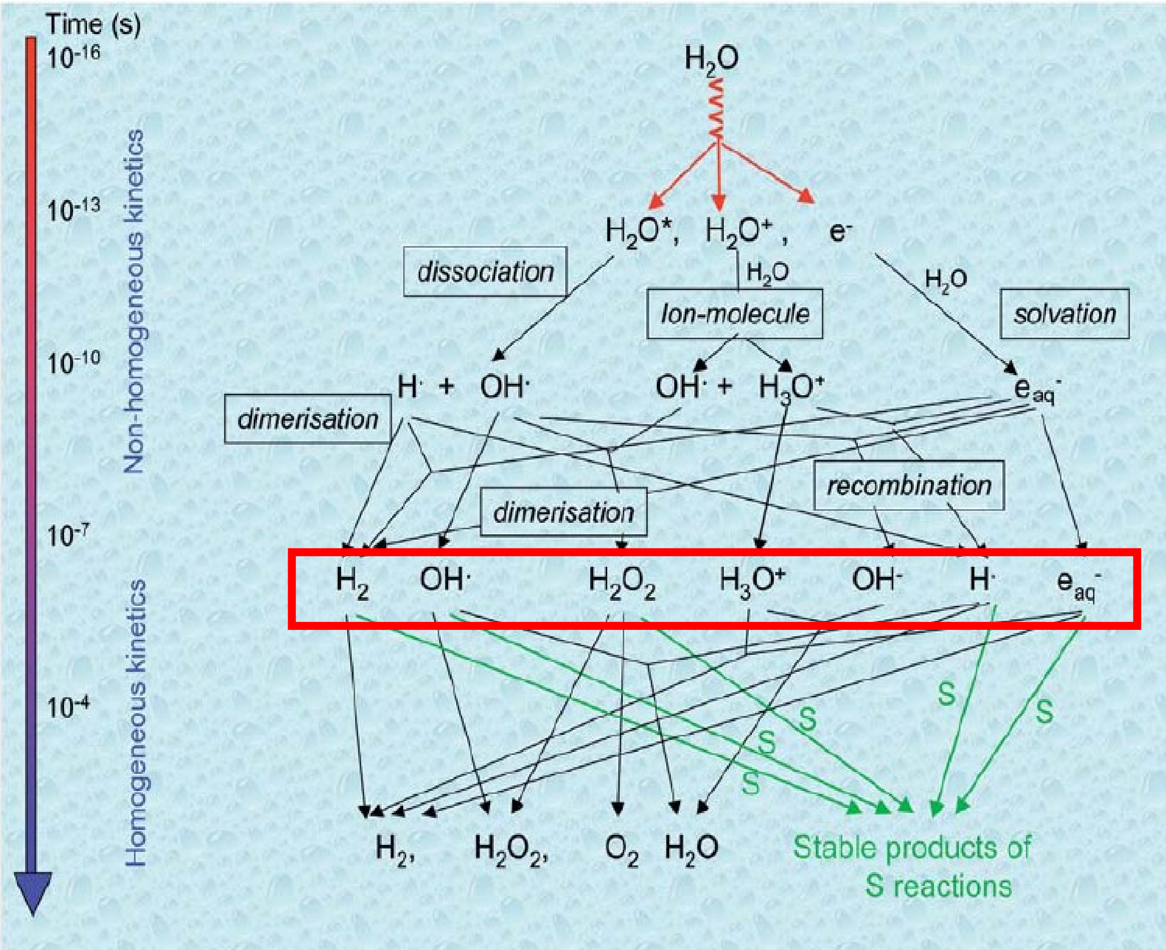
⬇

Simulation of natural degradation processes

Advanced Oxidation Processes (AOPs)



Water Radiolysis



Reactions of transient species formed during radiolysis of water with low LET radiation (^{60}Co, electron beams). S=solutes. From Buxton (2008), Chapter 1, in "Radiation Chemistry", EDP Sciences.

direct transformation of water molecules through energy transfer to orbital electrons, resulting in the breaking of bonds and the creation of very active products (radiolysis of water)

Reactive Species (RS) :
(HO•, H•, e^-_{aq}, HOO• /O_2^-, H_2, H_2O_2, H^+)

Oxidative / Reductive Species

RS could readily react with dissolved organic compounds and degrade them

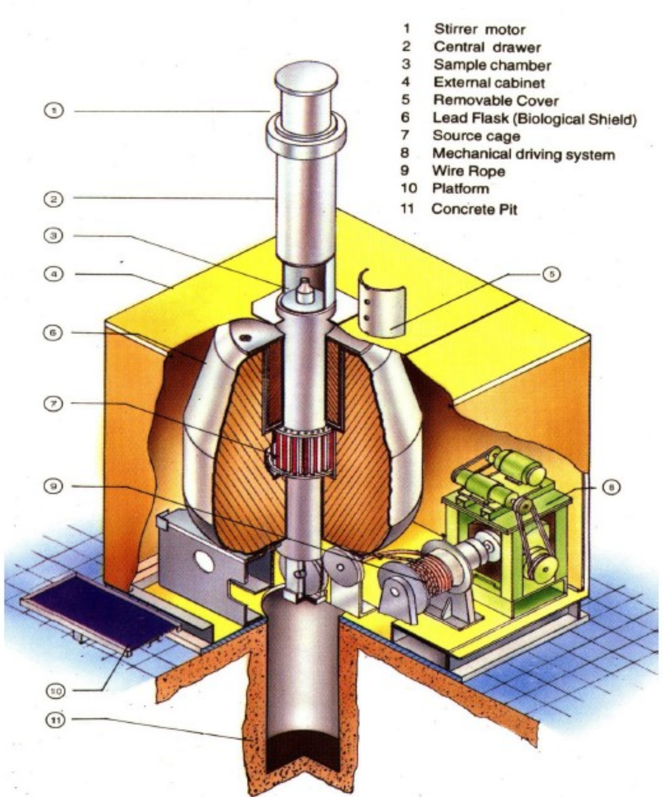
Radiolysis as an AOP - Characteristics

- Non-selective absorption of energy
- Production of Reactive Species (RS)

  (HO•, H•, e^-_{aq}, HOO• /O_2^-, H_2, H_2O_2, H^+)
- Homogeneous system
- Known yields of RS (G-values), i.e. species produced per unit of absorbed energy
- Simple determination of absorbed energy using chemical dosimetry (Fricke)
- System can be manipulated with scavengers to produce specific/single ROS

Dominant Species	System
e^-_{aq}	Deaeration + Tert-butyl alcohol
H•	Deaeration + Tert-butyl alcohol pH1
HO•	N_2O
HOO•/O_2^-	O_2 / formate

Gamma radiation source at NCSR Demokritos



Gamma chamber 4000, Bhabha Atomic Research Center, India (at NCSR Demokritos)

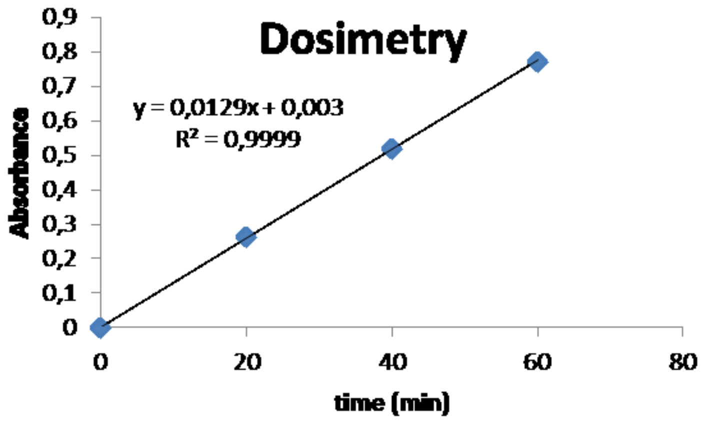
- ^{60}Co is produced by neutron activation of ^{59}Co. It decays to the stable ^{60}Ni, with emission of two gamma rays (1.17 and 1.33 MeV).
- ^{60}Co has a half-life of 5.27 years.
- ^{60}Co gamma rays and electron beams below 10 MeV do not produce radioactive isotopes by nuclear activation, i.e. the irradiated materials do not become radioactive.

Chemical dosimetry: The Fricke dosimeter

The Fricke dosimeter is:

- an aqueous solution of Ferrous sulfate, $FeSO_4$ (0.001M), Sulfuric acid, H_2SO_4 (0.4 M), Sodium chloride, NaCl (0.001 M)
- Upon irradiation Fe^{2+} is oxidized to Fe^{3+}.
- The concentration of Fe^{3+} is measured by photometry at 304 nm.

- $Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$
- $H\bullet + O_2 \rightarrow \bullet HO_2$
- $Fe^{2+} + \bullet HO_2 \rightarrow Fe^{3+} + HO_2^-$
- $HO_2^- + H^+ \rightarrow H_2O_2$
- $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$
- $Fe^{2+} + HO\bullet \rightarrow Fe^{3+} + OH^-$



$G(Fe^{3+})$=15.6 (species per 100 eV) = 1,616 µmol J^{-1}

Olszanski et al. (2002), Ionizing Radiation Standards, NRC, Canada

Determined dose rate: 0,064 Gy s^{-1}

(1 Gy = 1 J kg^{-1} = 100 rad)

Manipulation of the system with scavengers

Είδος	G* value (100 eV)	G value (μmol J^{-1})					
	-	-	N_2O	TBA	TBA pH 1	O_2	O_2/ HCOOH
e^-_{aq}	**2.7**	**0.28**	0	**0.28**	0	0	0
H·	0.6	0.06	0,06	0.06	**0.34**	0	0
OH·	**2.7**	**0.28**	**0.56**	0	0	**0.28**	0
H_2O_2	0.7	0.07	0.09	0.07	0.07	0.05	0.005
HOO· /O_2^-	0	0	0	0	0	**0.33**	**0.62**

* G-value: Moles of species produced / Joule of adsorbed energy

Scavenging reactions

$$e^-_{aq} + H^+ \rightarrow H\cdot$$

$$e^-_{aq} + O_2 \rightarrow O_2^-$$

$$H\cdot + O_2 \rightarrow HOO\cdot$$

$$HO^\cdot + HCO_2^- \rightarrow H_2O + CO_2^{\cdot -}$$

$$CO_2^{\cdot -} + O_2 \rightarrow CO_2 + O_2^{\cdot -}$$

$$e^-_{aq} + N_2O \rightarrow N_2 + HO^- + HO^\cdot$$

$$HO^\cdot + (CH_3)_3COH \rightarrow H_2O + (CH_2^\cdot)(CH_3)_2COH$$

Objectives of the study:

- ✓ to demonstrate the effects of various radiolytically produced RS, on the degradation of and MIB and GSM.
- ✓ to detect and identify the various Transformation Products (TPs) generated under the presence of various reactive species, in order to clarify the degradation mechanisms of these compounds.

Methods

g-irradiation source

- ^{60}Co Gamma Chamber source (model 4000A, Bhabha Atomic Research Centre, India).
  - 0.064 Gy s^{-1}
  - 10mL glass tubes
  - t_{irrad} 0-8h

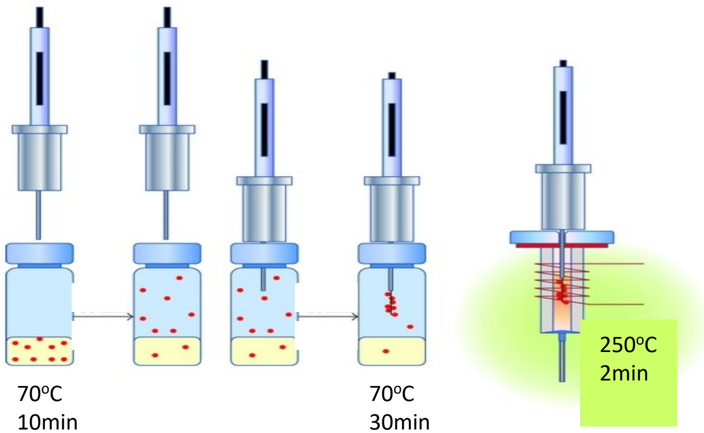
Selective production of RS

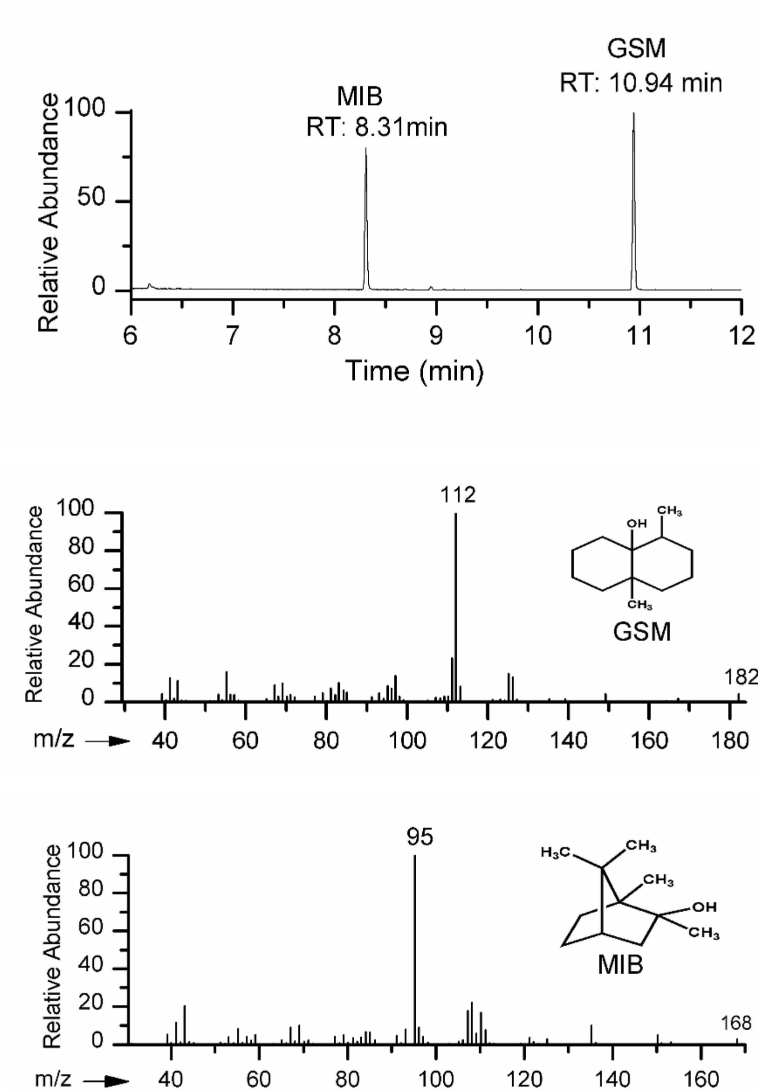
Dominant Species	System
e^-_{aq}	Deaeration + Tert-butyl alcohol
H•	Deaeration + Tert-butyl alcohol pH1
HO•	N_2O
$HOO•/O_2^-$	O_2 / formate

Methods

Monitoring of compound degradation

- Headspace Solid-Phase Microextraction (HS-SPME) coupled with Agilent 6890 Series GC





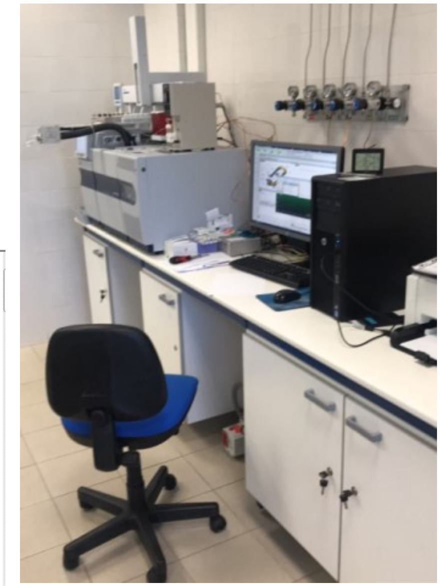
- NaCl saturated solutions.
- Fiber: DVB/CAR/PDMS 50/30µm
- Extraction: 70°C for 30min

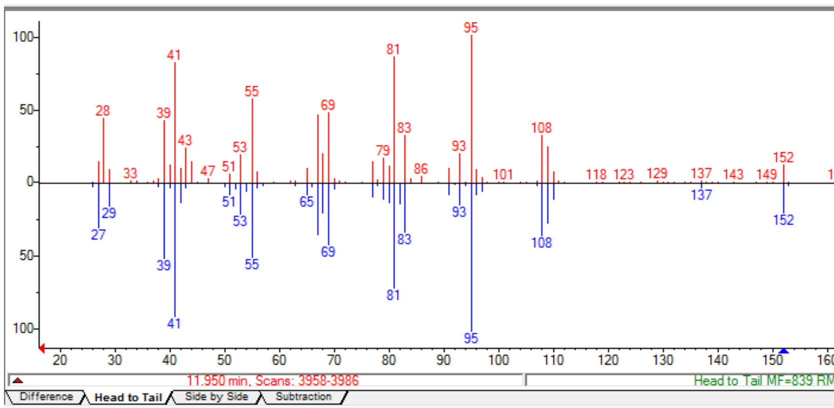
- Fotiou et al. (2014) J. Photochem. Photobiol.
- Kaloudis et al. (2017), Handbook of Cyanobacterial Monitoring & Cyanotoxin Analysis

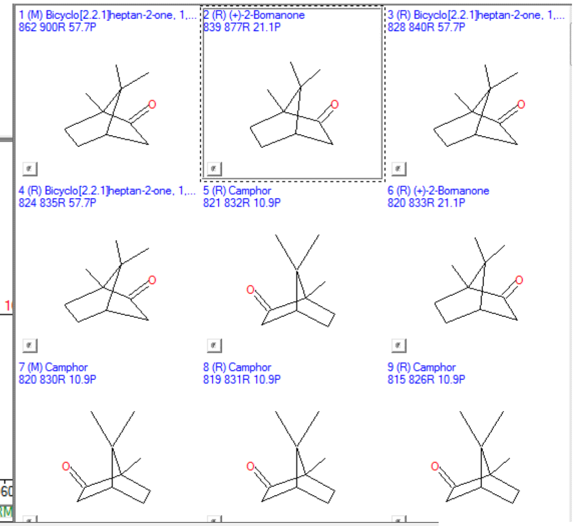
Methods

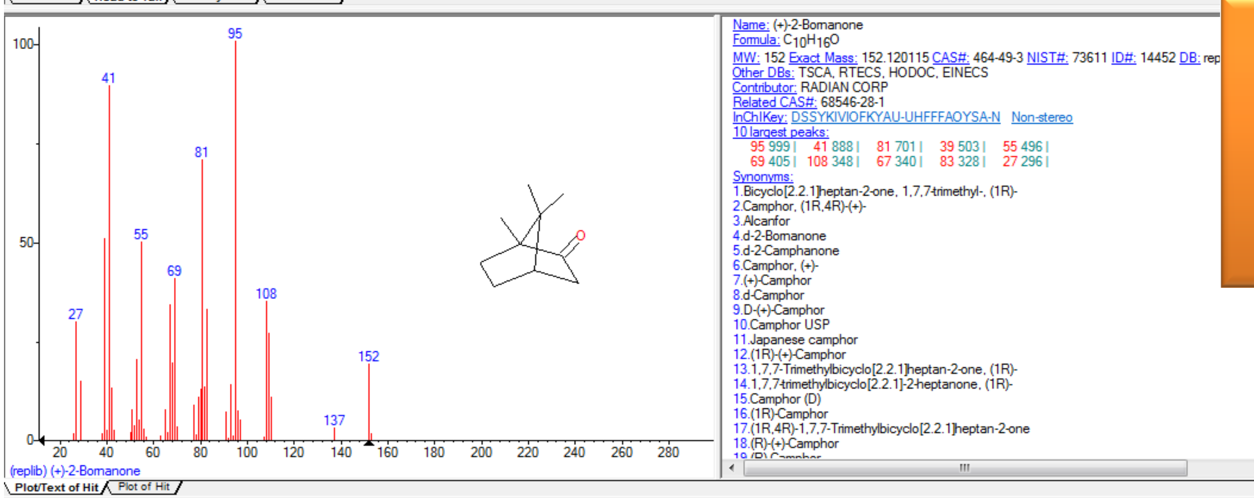
Identification of TPs

Liquid extraction followed by GC-MS/MS (Bruker, Germany) and confirmed with Linear Retention Indexes (LRI)









Retention Index median±deviation

Semi-standard non-polar: 1142±3 (2)

Standard non-polar: 1146±N/A (1)

Polar: 1520±13 (2)

Estimated non-polar retention index (n-alkane scale):

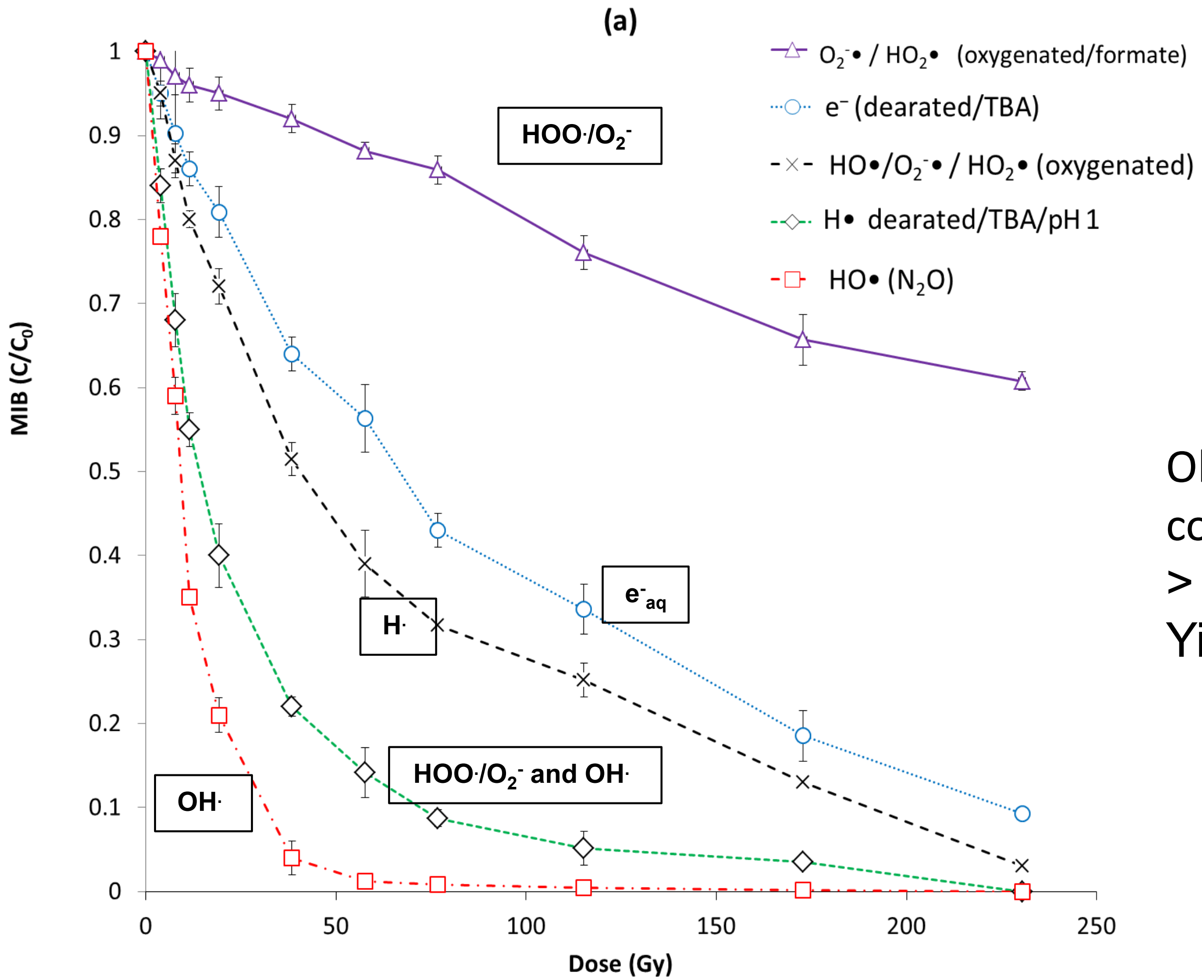
Value: 1121 iu

Estimated t_R based on RI

11.73min

ACCEPTED

Results – MIB degradation

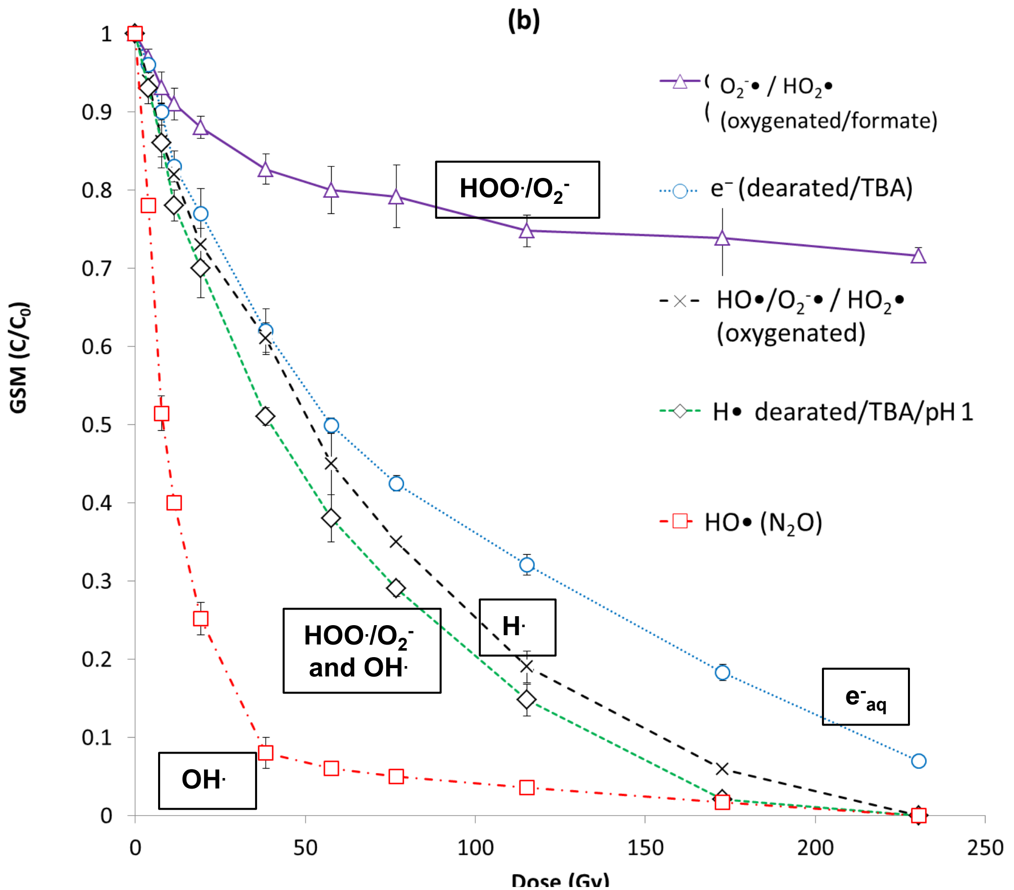


Observed Degradation rate constants (HO• > H• >> e^-_{aq} > HOO• /O_2^-)
Yields

Parameters extracted from the assessment of the first order kinetic reaction model for the degradation of MIB.

Experimental Conditions	Prominent RS	k_{obs} (Gy^{-1})	R^2	Initial rate (μmol J^{-1})	Y (MIB)	G (RS) (μmol J^{-1})
N_2O	$HO^•$	0.083	0.996	0.49	1.14	$HO^•$ (0.56)
Deaerated / TBA	e_{aq}^-	0.012	0.995	0.07	4.03	e_{aq}^- (0.28)
Deaerated / TBA /pH 1	$H^•$	0.042	0.974	0.25	1.36	$H^•$ (0.34)
O_2	$HO^•$ / $O_2^{-•}$ / $HO_2^•$	0.017	0.997	0.10	5.92	$HO^•$ (0.28) $O_2^{-•}$/$HO_2^•$ (0.33)
O_2/HCOOH	$O_2^{-•}$ / $HO_2^•$	0.002	0.960	0.01	43.48	$O_2^{-•}$/$HO_2^•$ (0.62)

Results – GSM degradation



Observed Degradation rate constants (HO• > H• >> e^-_{aq} > HOO• /O_2^-)
Yields

- Similar degradation pattern for both compounds
- Degradation is faster for both MIB and GSM, when hydroxyl radicals (HO•) are the dominant reactive species
- Slowest degradation through oxidation with HOO•/O_2^-

Parameters extracted from the assessment of the first order kinetic model for the degradation of GSM.

Experimental Conditions	Prominent RS	k_{obs} (Gy^{-1})	R^2	Initial rate (µmol J^{-1})	Y (GSM)
N_2O	$HO^•$	0.068	0.988	0.38	1.49
Deaerated / TBA	e_{aq}^-	0.013	0.997	0.07	4.02
Deaerated / TBA / pH 1	$H^•$	0.018	0.922	0.10	3.42
O_2	$HO^•$ / $O_2^{-•}$ / $HO_2^•$	0.014	0.956	0.08	7.94
O_2/HCOOH	$O_2^{-•}$ / $HO_2^•$	0.006	0.880	0.03	20.0

Main RS reactions with organic molecules

Reactions with $OH^{\cdot}$:
With saturated compounds such as GSM and MIB, $OH^{\cdot}$ reacts mainly by hydrogen abstraction: $OH^{\cdot} + RCH(OH)CH_3 \rightarrow R^{\cdot}C(OH)CH_3 + H_2O$

Reactions with the hydroperoxyl ($HOO^{\cdot}$) and superoxide (O_2-) radicals:
Hydroperoxyl and superoxide radicals can react as reductants or oxidants. Reactions with organic compounds are generally slower (Buxton et al. 1988).
Similar to vis-TiO_2 photocatalysis of GSM and MIB (Fotiou et al. 2016).

Reactions with the hydrated electron, e^-_{aq} and hydrogen atom, $H^{\cdot}$:
e^-_{aq} is a powerful reducing agent, E=-2.87 V
In acidic conditions, it is converted to hydrogen atom, $H^{\cdot}$ (E=-2.1 V):

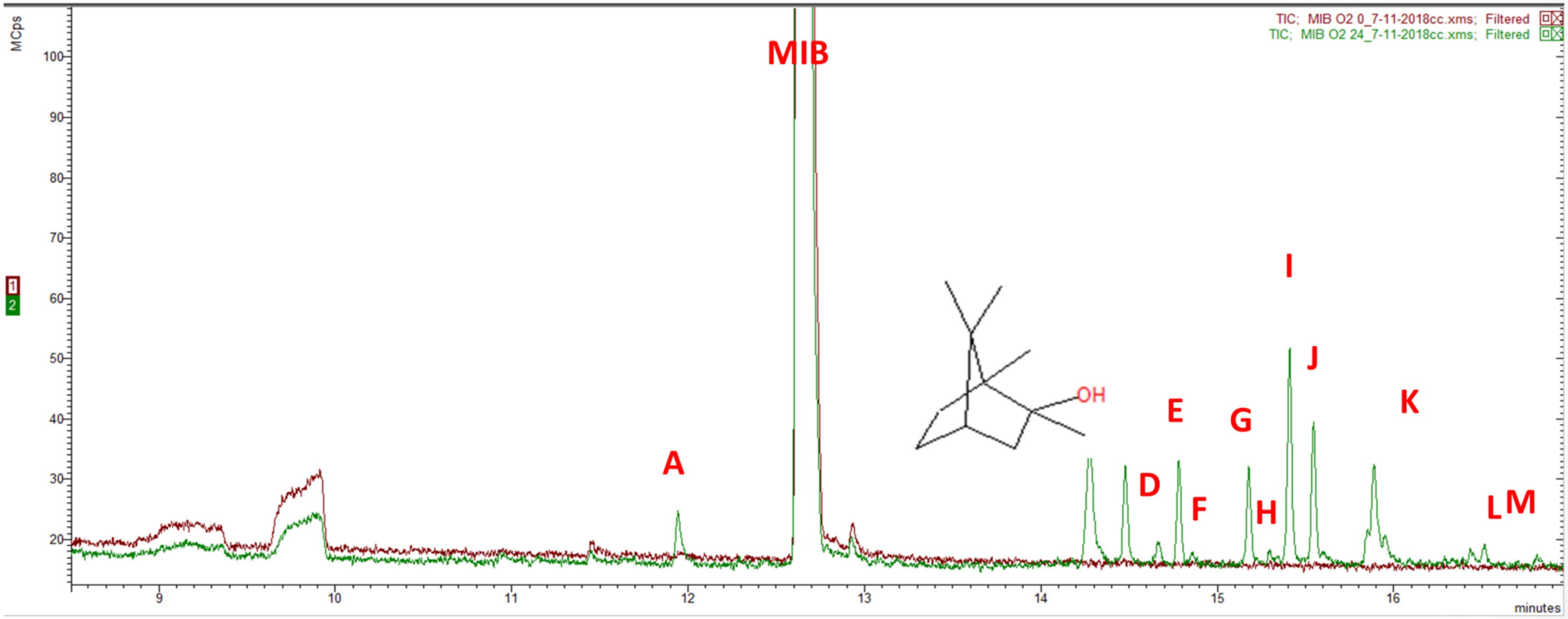
$$e^-_{aq} + H^+ \rightarrow H^{\cdot}\ ,\ k=2.3 \times 10^{10}\ L\ mol^{-1}\ s^{-1}$$

With organic compounds, **$H^{\cdot}$** reacts as reductant or oxidant with abstraction of H atoms from saturated compounds : $\mathbf{H^{\cdot} + CH_3OH \rightarrow H_2 + {}^{\cdot}CH_2OH}$

Transformation Products - MIB

- Reaction in the presence of HO•
- 48 min of reaction
- 13 different transformation products
- Use of NIST mass spectral library
- Confirmation with Linear Retention Indices (LRI) using the standardized n-alkane method

B.d.A. Zellner, C. Bicchi, P. Dugo, P. Rubiolo, G. Dugo, L. Mondello, Linear retention indices in gas chromatographic analysis: a review, Flavour Fragr J. 23 (2008) 297–314.

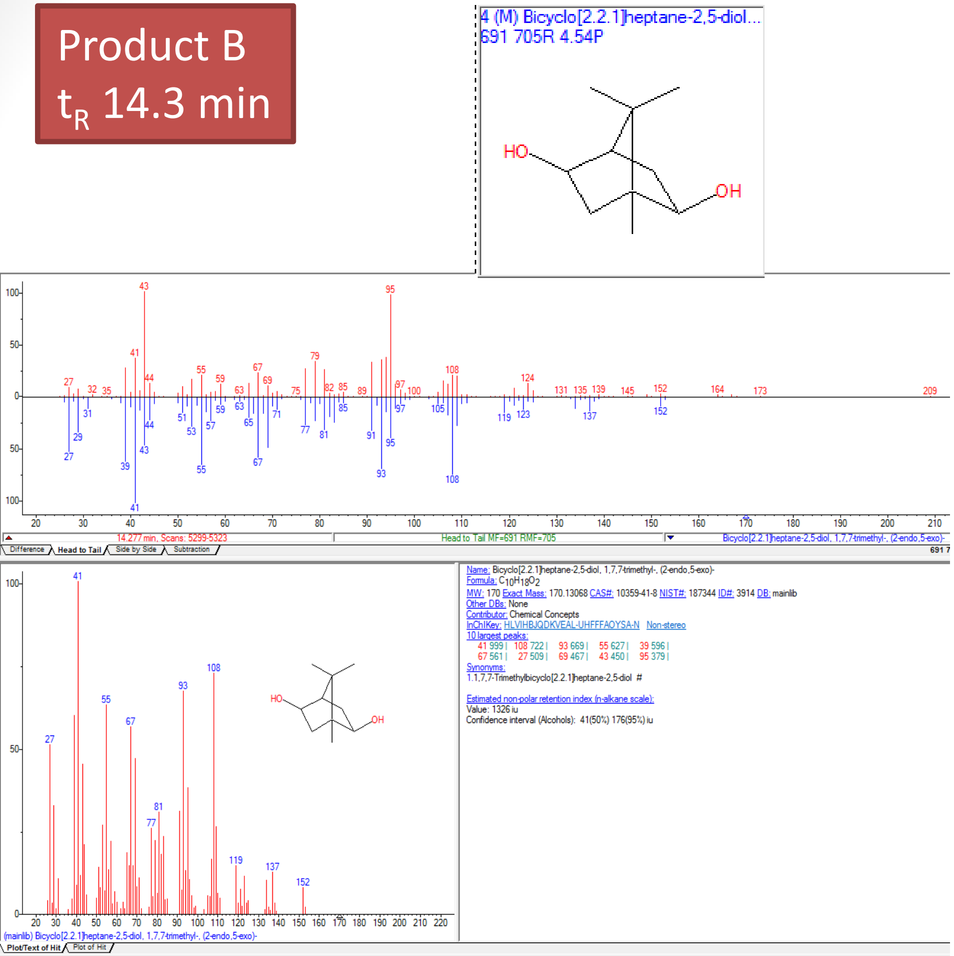


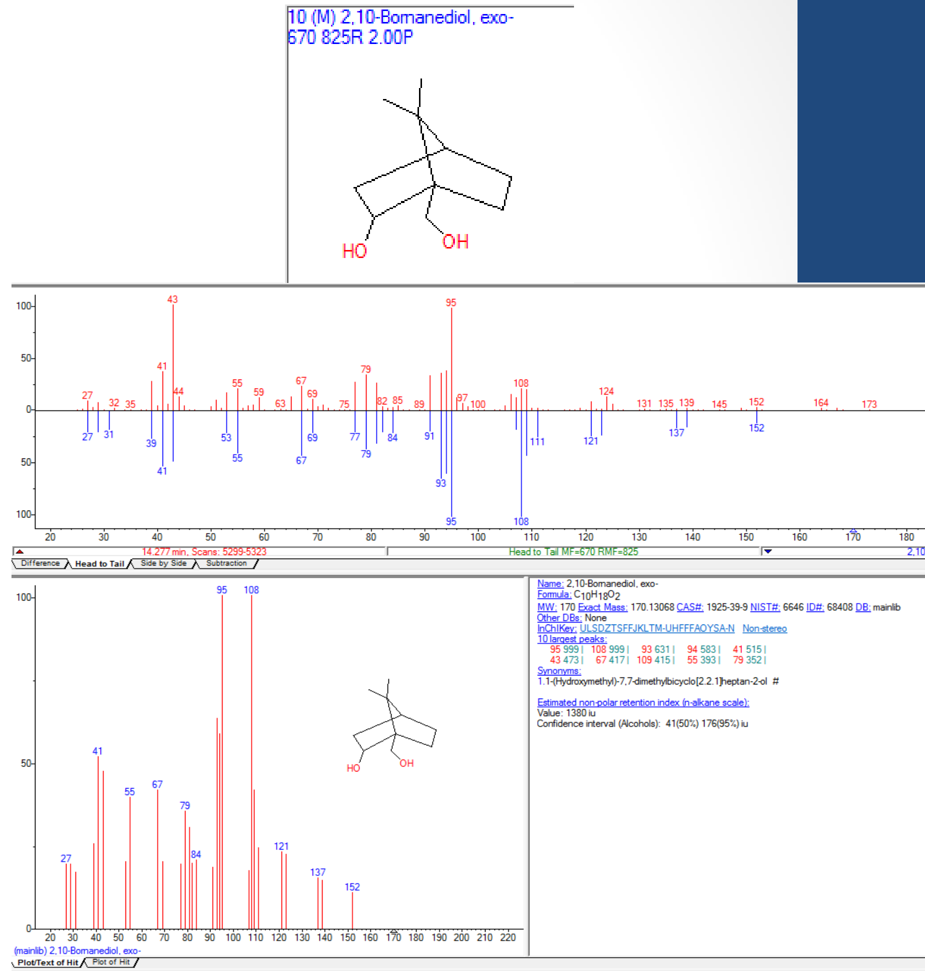
Levels of certainty

- Retention time
- NIST mass spectral match (score based on spectra characteristics)
- LRI confirmation

TP identification - NIST and LRI contribution

Product B
t_R 14.3 min



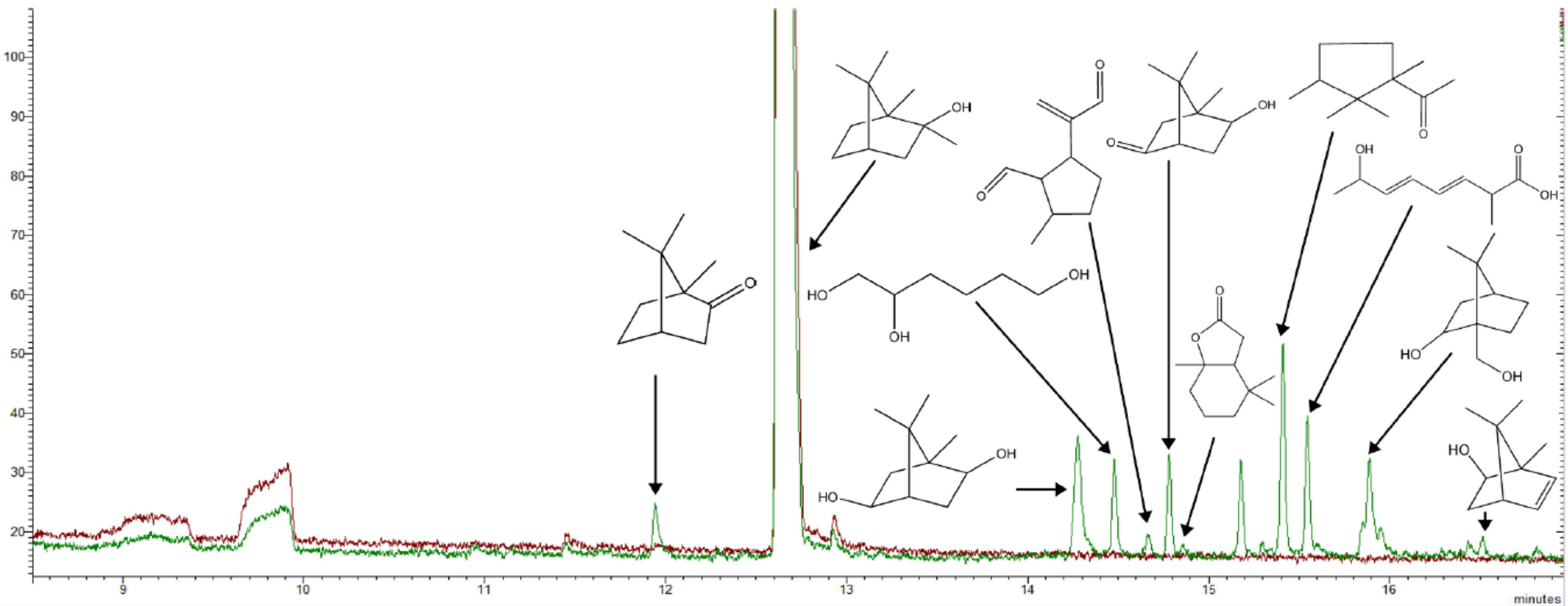


Retention Index
Standard non-polar: 1326
Estimated t_R 14.33
ACCEPTED

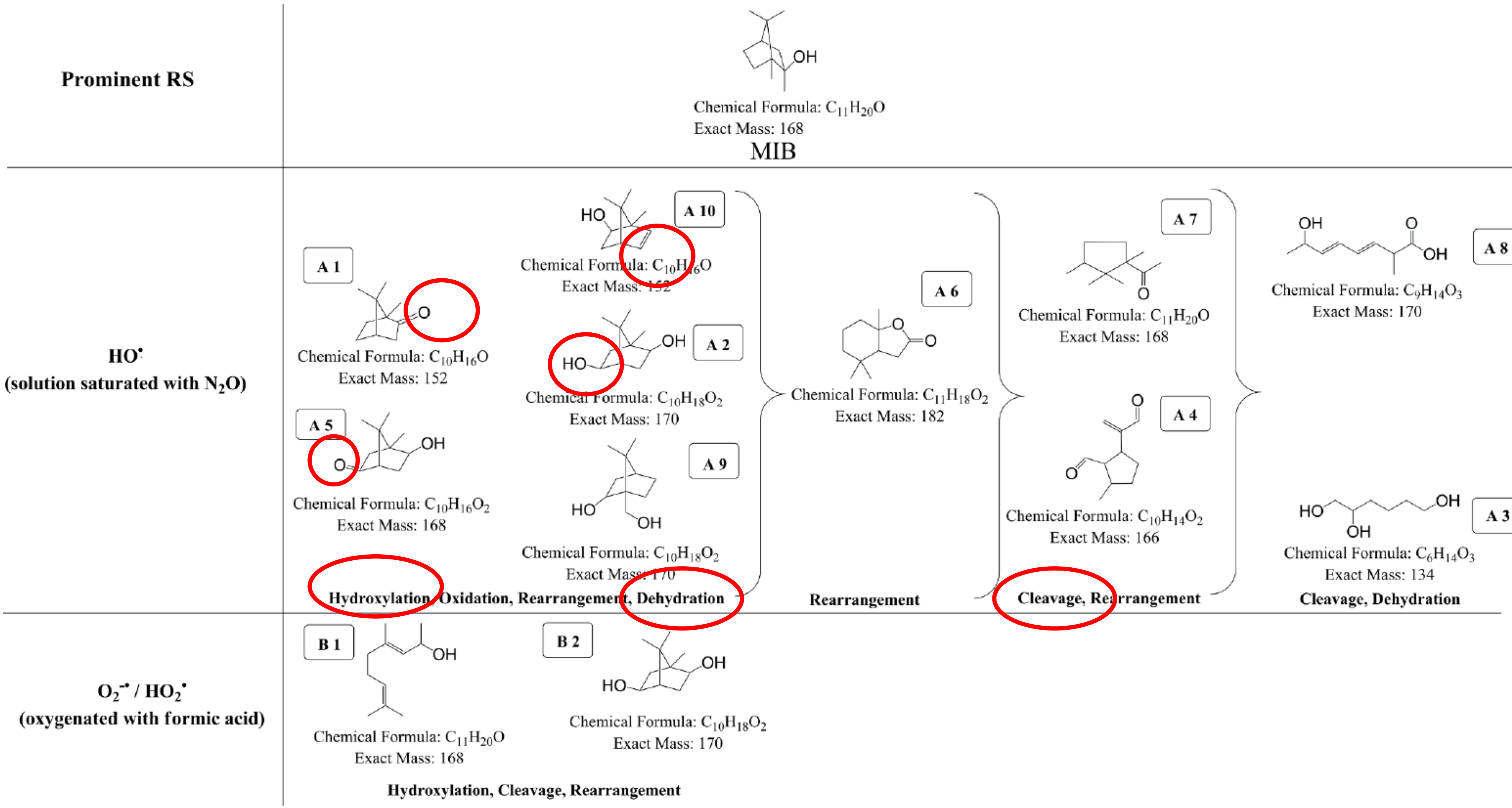
Retention Index
Standard non-polar: 1380
Estimated t_R 15.28

B.d.A. Zellner, C. Bicchi, P. Dugo, P. Rubiolo, G. Dugo, L. Mondello, Linear retention indices in gas chromatographic analysis: a review, Flavour Fragr J. 23 (2008) 297–314.

TP structure assignment - MIB

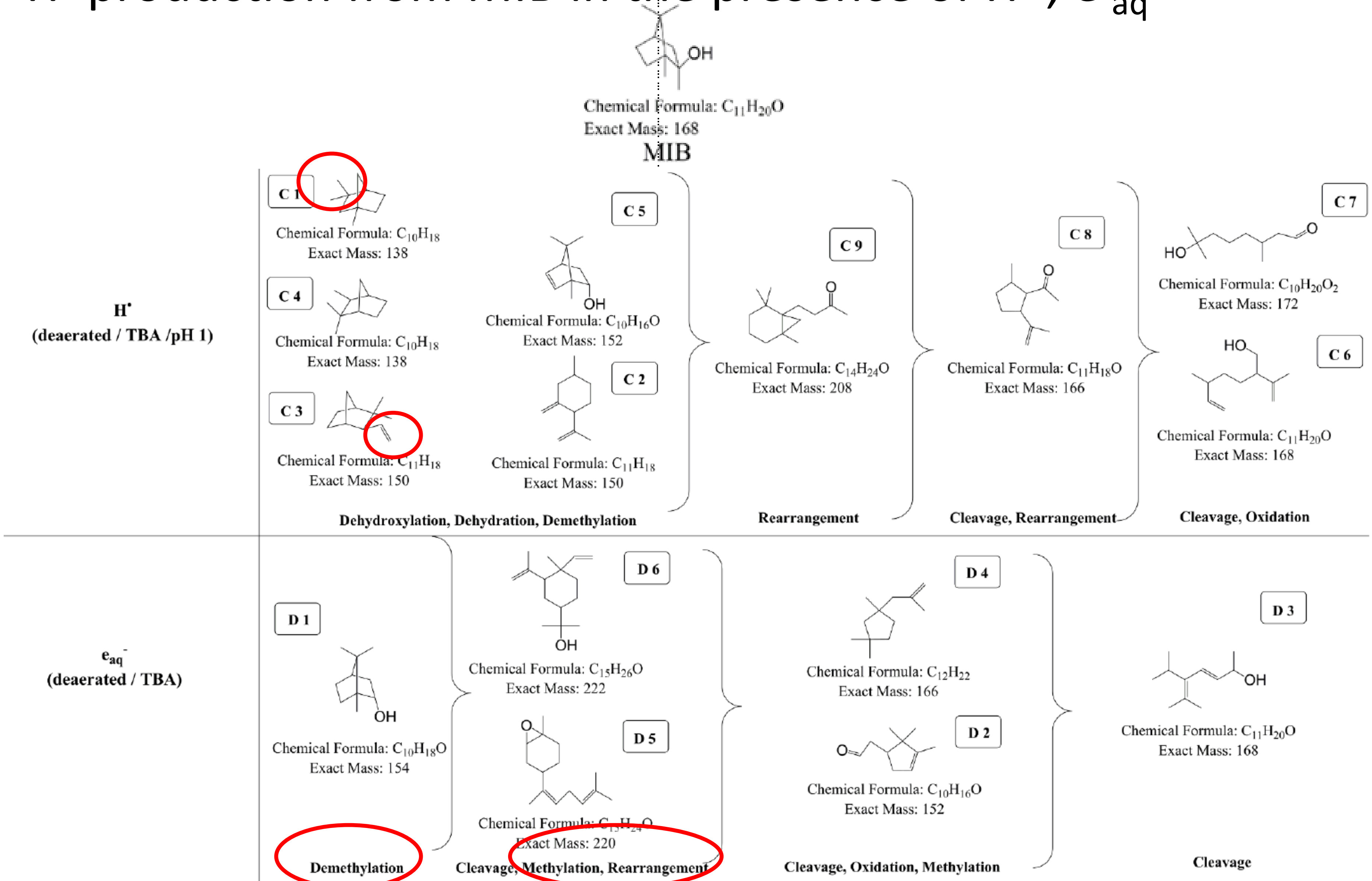


TP production from MIB – oxidative pathway



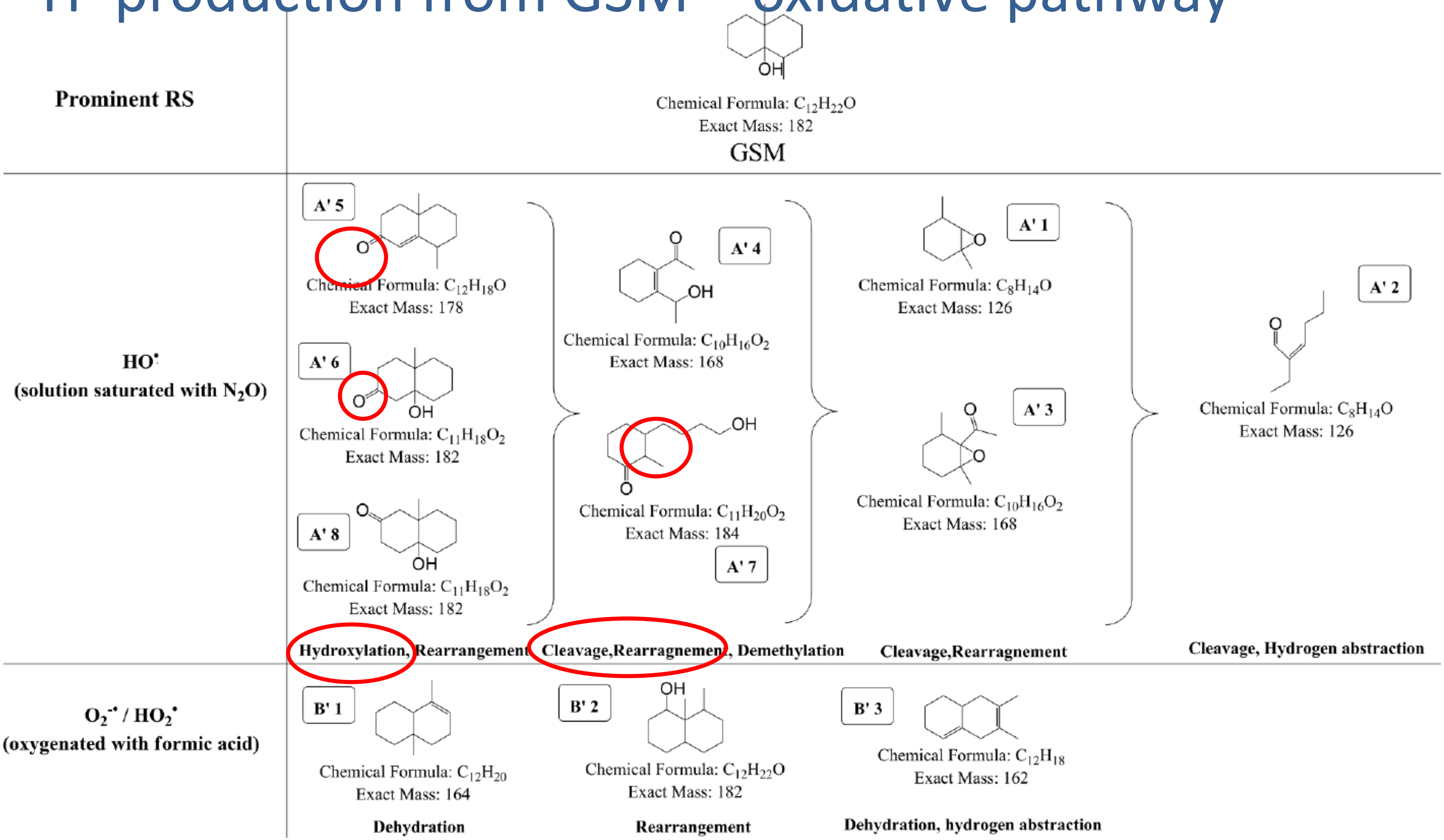
- the reaction of HO• with MIB, seems to lead to formation of hydroxylated TPs, oxidized ketone and aldehyde products and further production of smaller derivatives and linear oxidized carbon chains.
- HOO• /O_2^- generate far less TPs, mainly via hydroxylation.

TP production from MIB in the presence of H•, e^-_{aq}



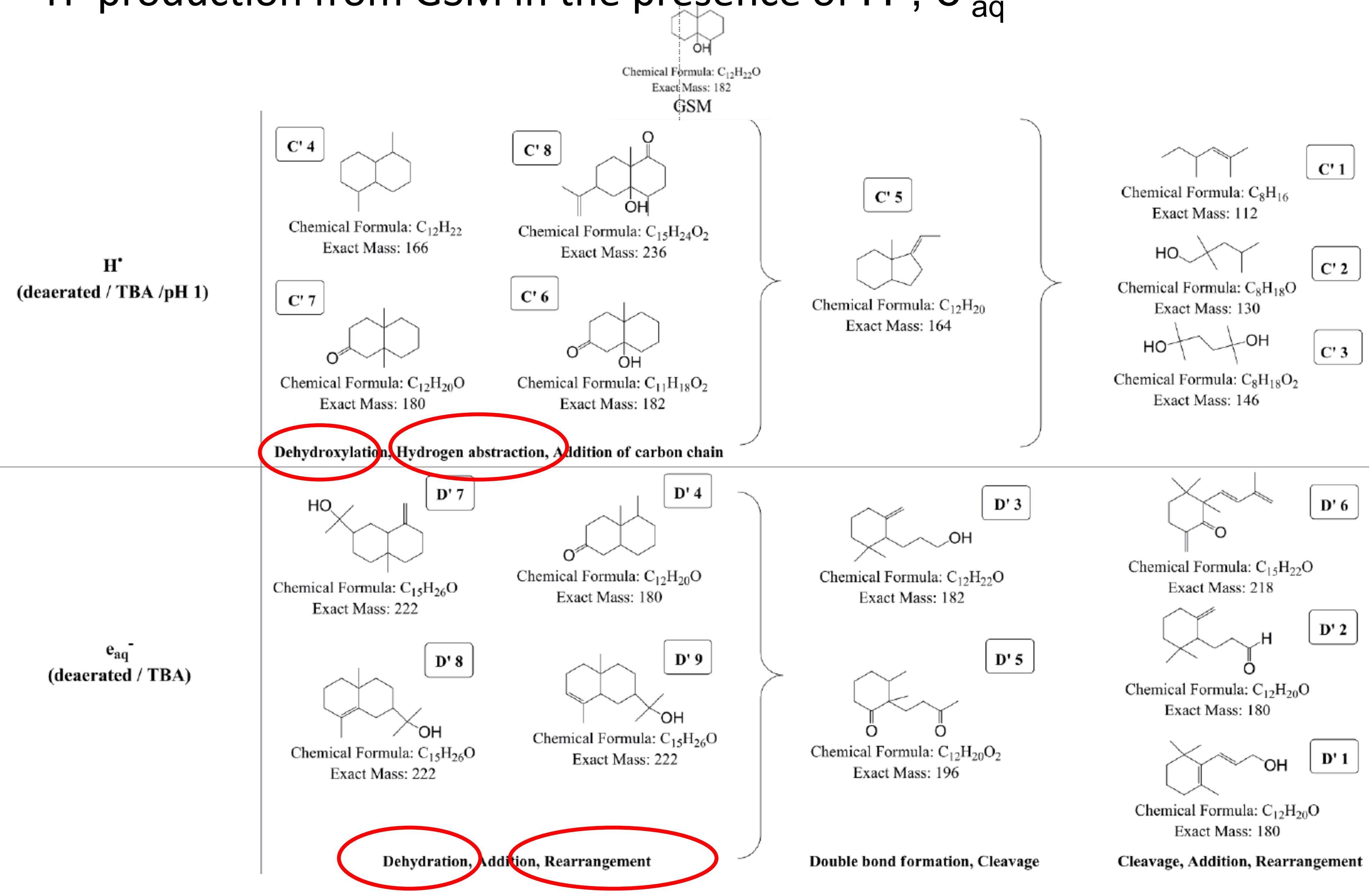
MIB is effectively degraded by H•, with numerous TPs, including dehydroxylated and demethylated products, as well as products of carbon chain addition and hydrogen abstraction to form alkene or aldehyde structures

TP production from GSM – oxidative pathway



- degradation of GSM by HO•, gave rise to hydroxylated TPs, oxidated ketone products and further ring opening of the bicyclic structure, with final formation of smaller linear aldehyde chain products.
- HOO• /O_2^- generated far less TPs, mainly via hydroxylation.

TP production from GSM in the presence of H•, e^-_{aq}



- H• led to numerous TPs via dehydroxylation and hydrogen abstraction, producing ketones with double bonds, leading to alkenes or smaller oxidized carbon chains.

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Radiolytic degradation of 2-methylisoborneol and geosmin in water: Reactive radical species and transformation pathways

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CONCLUSIONS

- Water radiolysis is a useful tool to study the role of RS commonly produced in AOPs
- It is possible to calculate the kinetics of each reaction
- With the use of scavengers it is possible to control the production of specific RS
- Radiolytic degradation of GSM and MIB proceeds via oxidative (HO•) and reductive pathway (e^-_{aq})
- The reaction of GSM / MIB with HOO• /O_2^- is much slower and produces fewer TPs resembling photocatalysis using visible spectrum radiation
- Reaction pathways are strongly dependent on the presence of individual reactive species
- LRIs of eluting compounds proved a powerful tool for structure confirmation

NATIONAL CENTRE FOR SCIENTIFIC RESEARCH "DEMOKRITOS"

Thank you for your attention!

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