

# Radiation-induced degradation products of 2-methyl isoborneol and geosmin: the role of different reactive species

Christophoridis C.<sup>1</sup>, Pestana C.J.<sup>2</sup>, Kaloudis T.<sup>1,3</sup>, Lawton L.<sup>2</sup>, Hiskia A.<sup>1,\*</sup>

<sup>1</sup> Institute of Nanoscience and Nanotechnology, NCSR “Demokritos”, Athens, Greece.

<sup>2</sup> School of Pharmacy and Life Sciences, Robert Gordon University, Aberdeen, UK

<sup>3</sup> Athens Water Supply and Sewerage Company (EYDAP SA), Athens, Greece

\*corresponding author: e-mail: a.hiskia@inn.demokritos.gr

## Abstract

Gamma radiolysis can serve as an effective method for the degradation of organic water pollutants, due to the production of reactive species, oxidative (OH•, OOH•, O<sub>2</sub>•<sup>-</sup>) or reductive (e<sub>aq</sub><sup>-</sup>, H•). The application of scavengers enables the selective production of these species. Our aim was to explore the effects of the radiolytically produced reactive species, on commonly occurring water taste and odour compounds (T&O), 2-methyl isoborneol (MIB) and geosmin (GSM). Transformation products (TPs) were identified using liquid extraction followed by GC-MS/MS and confirmed with Linear Retention Indexes (LRI). The diversity and proposed structure of the TPs depend on the reactive species present in the solution. Structure elucidation of TPs revealed that reaction pathways are strongly dependent on the presence of individual reactive species. The oxidative degradation of MIB via OH• proceeds with the production of carbonyl- (camphor) and hydroxyl-containing TPs, a subsequent ring opening, arriving to linear structured products. Fewer TPs are produced upon the effect of OOH•, starting with a ring opening and addition of one hydroxyl group. The oxidative pathway of GSM via OH• occurs with an initial ring opening, formation of carboxyl-group and subsequent second ring opening. The reductive pathway is currently under study.

**Keywords:** gamma-radiolysis, water treatment, taste & odour compounds, transformation products

## 1. Introduction

A large number of diverse T&O compounds in water can be produced in source waters by prokaryotic and eukaryotic microorganisms commonly known as “algae” (Watson 2004). T&O compounds present extremely low odor threshold concentrations, which makes them detectable at extremely low concentrations, therefore their presence is a frequent cause of consumer complaints (McGuire 1995). Although T&O compounds are generally nontoxic, they are easily detected by consumers, which can make water unacceptable for aesthetic reasons and have serious negative socioeconomic impacts, affecting consumer confidence of a water supply or induce substantial costs to water, aquaculture and tourism industries, related to contaminated surface waters. The most widely known and frequently occurring T&Os, are terpenoids produced by

algae, including geosmin (GSM) and 2-methylisoborneol (MIB), having strong “earthy” and “musty” odours, and odour thresholds at 4 and 6 ng/L, respectively (Young et al. 1996). Although T&O compounds are generally nontoxic, their presence is a frequent cause of consumer complaints since they present extremely low odor threshold (McGuire 1995), which can make water unacceptable for aesthetic reasons and have serious negative socioeconomic impacts, affecting consumer confidence of a water causing additional cost for treatment to contaminated surface waters. For the removal of T&O, several conventional treatment processes, have been proven generally ineffective, while advanced oxidation processes (AOPs) could present effective alternatives (Antonopoulou et al., 2014). AOPs are commonly driven by the production of reactive oxygen species (ROS), i.e. the hydroxyl radical - HO•, superoxide anion - O<sub>2</sub>•<sup>-</sup>, hydroperoxyl radical - HOO• as well as hydrogen peroxide - H<sub>2</sub>O<sub>2</sub>. Among others, several studies have been carried out, related to the removal of T&O using UV/H<sub>2</sub>O<sub>2</sub> (Peter & von Gunten, 2007), O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (Mizuno et al., 2011), TiO<sub>2</sub>- photocatalysis (Fotiou et al., 2015), and sonolysis (Song & O’Shea, 2007).

High energy irradiation of water with gamma rays or electron beams produces instantaneous transformation of water molecules, resulting in the breakage of interatomic bonds and the formation of highly reactive products (water radiolysis (Buxton et al. 1988). Among the products of the process (HO•, H•, e<sub>aq</sub><sup>-</sup>, H<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, H<sup>+</sup>), HO• is the predominant oxidative species, by virtue of its high yield as well as of its high oxidation potential. Reducing species (e<sub>aq</sub><sup>-</sup>) are also formed. The highly reactive products of water radiolysis can rapidly react with organic compounds dissolved in water and lead to their degradation. As a result, several applications of radiation treatment of polluted water and wastewater have been reported in the literature (Son 2017). Radiation chemistry of water (also known as water radiolysis) provides a useful tool to study the effects of ROS on organic compounds in water, as these systems can be chemically manipulated to produce selected ROS species with known yields.

The aims of this study were a) to demonstrate the effects of various radiolytically produced ROS, on MIB and GSM and b) to detect and identify the various TPs

produced, in order to clarify degradation mechanisms of these compounds by AOPs.

## 2. Experimental

Steady-state gamma radiolysis experiments were carried out in a  $^{60}\text{Co}$  Gamma Chamber source (model 4000A, Bhabha Atomic Research Centre, India). The dose rate ( $0.064 \text{ Gy s}^{-1}$ ) was determined with use of the Fricke dosimeter (Olszanski et al., 2002). Solutions (10 ml) for irradiation were prepared by adding chemical scavengers and/or purging with gases and then spiking with concentrated aqueous solutions of MIB/GSM. Samples were obtained for analysis at various time intervals. Standard compounds 2-MIB (>98%) and GSM (>97%), tert-butyl alcohol (TBA, anhydrous, >99,5%), sodium formate (>99%) and dichloromethane (>99,8%) were purchased from Sigma-Aldrich. Determination of MIB and GSM was carried out with HS-SPME-GC/MS (Fotiou et al., 2014). Transformation products (TPs) were identified using liquid extraction followed by GC-MS/MS and confirmed with Linear Retention Indexes (LRI).

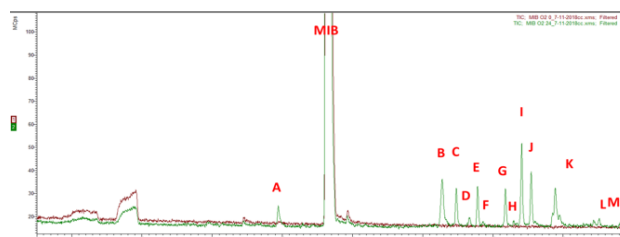
## 3. Results

The production of single reactive species was manipulated using chemical scavengers (Richter, 1998) as shown in Table 1. Results demonstrated that degradation is faster for both MIB and GSM, when hydroxyl radicals ( $\text{HO}^\bullet$ ) are the dominant reactive species. The degradation caused by superoxide/hydroperoxyl radicals ( $\text{O}_2^{\bullet-}/\text{HOO}^\bullet$ ) is a much slower process, since they are known to exhibit slower reaction rates with organic substrates (Buxton et al., 1988). These results are relevant to AOPs, such as visible-light photocatalysis, where they are formed as major reactive species (Fotiou et al., 2016). Hydrated electrons ( $e_{\text{aq}}^-$ ) are also able to degrade MIB and GSM. Hydrogen atoms ( $\text{H}^\bullet$ ) promote degradation, since they can act as oxidants, through hydrogen abstraction.

Identification of TPs revealed that reaction pathways are strongly dependent on the presence of individual reactive species (Figure 1). Degradation of MIB and GSM in the presence of  $\text{OH}^\bullet$  proceeds with the production of numerous TPs, including carbonyl- (camphor) and hydroxyl-containing TPs, proceeding with a subsequent ring opening, until linear structured products. Upon the effect of  $\text{OOH}^\bullet$  less TPs are produced, starting with a ring opening and addition of one hydroxyl group. In the case of GSM, in the presence of  $\text{OH}^\bullet$ , degradation occurs with an initial ring opening, formation of carboxyl-group and subsequent second ring opening. For confirmation purposes, LRIs of eluting compounds were finally compared to LRIs reported for the same chromatographic column in databases (e.g. NIST webbook) or publications.

**Table 1.** Production of single radical species under controlled conditions

Conditions	Scavenged species	Produced species ( $\mu\text{mol J}^{-1}$ )
<b><math>\text{N}_2\text{O}</math> saturated</b>	$e_{\text{aq}}^-$	$\text{HO}^\bullet(0,55)$ $\text{H}^\bullet(0,06)$
<b><math>\text{O}_2</math> sat.- formate</b>	$e_{\text{aq}}^-$ , $\text{H}^\bullet$ , $\text{HO}^\bullet$	$\text{O}_2^{\bullet-}/\text{HOO}^\bullet$ (0,33)
<b>Deaerated - TBA</b>	$\text{HO}^\bullet$	$e_{\text{aq}}^-$ (0,27) $\text{H}^\bullet$ (0,06)
<b>Same as C, pH1</b>	$\text{HO}^\bullet$	$\text{H}^\bullet$ (0,33)
<b>No addition of scavengers – “Uncontrolled” experiment</b>		



**Figure 1.** TPs produced by MIB oxidation in the presence of  $\text{HO}^\bullet$

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