Effects of radiolytically produced reactive species on 2-methylisoborneol and geosmin in water

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Abstract

Water radiolysis is known as an Advanced Oxidation Process (AOP) for treatment of organic pollutants but it can also serve as a useful tool to study the effects of highly reactive species that are commonly present in AOPs. Such studies are carried out in simpler homogeneous systems that can be manipulated with use of scavengers to selectively produce different oxidative ($OH^.$, $OOH^.$, O_2^-, $H^.$) or reductive species (e_{aq}^-, $H^.$), at known yields that are proportional to irradiation dose. The aim of this study was to investigate the effects of the above reactive species on two commonly occurring, cyanobacterial taste and odour compounds, 2-methylisoborneol (MIB) and geosmin (GSM), upon steady-state radiolysis using ^{60}Co gamma rays. Degradation processes and products were monitored using headspace (HS) solid phase micro extraction (SPME), followed by GC-MS. Results showed that degradation of both MIB and GSM was faster when hydroxyl radical ($OH^.$) is the reactive species and slower with hydroperoxyl radicals/superoxide ($OOH^./O_2^-$) or hydrated electrons (e_{aq}^-). Degradation products indicated different reaction pathways that depend on reactive species, i.e. oxidative ($OH^.$) versus reductive (e_{aq}^-), as well as on chemical structure of the initial compound. Those results can be valuable in understanding and evaluating the role of reactive species in AOPs for water treatment.

Keywords: Radiation chemistry, Advanced Oxidation Processes (AOPs), 2-methyl-isoborneol (MIB), geosmin, Reactive Oxygen Species (ROS)

1. Introduction

Taste and Odour (T&O) is a key aesthetic parameter influencing the consumers' perception of drinking water quality. Occurrence of T&O compounds in water can result in unacceptability by consumers, regardless to their association with possible health hazards. A large number of diverse T&O compounds in water are produced in source waters by prokaryotic and eukaryotic microorganisms commonly known as "algae" (Watson, 2004). Among those, the most frequent causes of T&O incidents in water are associated with 2-methylisoborneol (MIB) and geosmin (GSM). MIB is a bicyclic terpenoid with a strong musty odour that can be sensed by the human nose at concentrations as low as 6 ng/L (Young *et al*.,

1996). GSM is a bicyclic sesquiterpene with an intense earthy smell (from Greek geo:earth, osme:odour) with an odour threshold concentration of 4 ng/L. The chemical structures of MIB and GSM are shown in Figure 1. The occurrence of both MIB and GSM in aquatic systems and water supplies is mainly associated with cyanobacterial metabolism, although they can be produced by other microorganisms such as terrestrial actinomycetes (Zeitlin and Watson, 2006).

2-methylisoborneol (MIB)   geosmin (GSM)
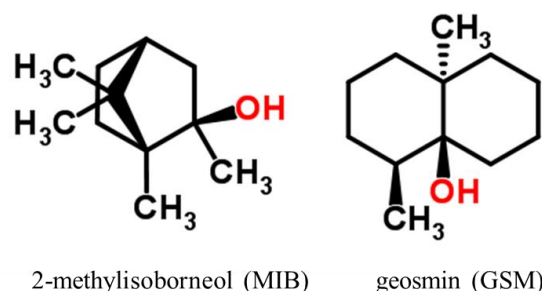
Figure 1. Chemical structures of MIB and GSM

Removal of MIB and GSM from drinking water in order to preserve its aesthetic quality is a challenging task, as even traces of residual compounds (e.g. ng/L) impart off-odours. Also, competition with natural organic matter (NOM) or other compounds present in water generally decreases the efficiency of MIB/GSM removal processes. Adsorption with granular or powdered activated carbon (GAC or PAC), is commonly applied by water utilities for treatment of T&O, however, removal of MIB/GSM depends on competitive adsorption (Newcombe *et al*., 2002). While conventional treatment processes, such as coagulation, sedimentation and chlorination are generally ineffective, advanced oxidation processes (AOPs) are currently considered as prospective alternatives (Antonopoulou *et al*., 2014). Studies have been conducted using UV/H_2O_2 (Peter & von Gunten, 2007), O_3/H_2O_2 (Mizuno *et al*., 2011), O_3/UV (Collivignarelli & Sorlini, 2004), TiO_2-photocatalysis (Fotiou *et al*., 2015, Pestana *et al*., 2014), and sonolysis (Song & O'Shea, 2007) among others. Degradation mechanisms in AOPs are commonly driven by reactive oxygen species (ROS), such as the hydroxyl radical - $HO^.$, superoxide anion - $O_2^{.-}$, hydroperoxyl radical

- HOO$^\bullet$, hydrogen peroxide - H_2O_2. Nevertheless, in AOPs various ROS usually co-occur, whereas determination of their yield is generally difficult or problematic. 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 the radiolytic systems can be chemically manipulated to produce only certain ROS species with known yields. This enables the qualitative and quantitative study of ROS effects on target compounds, that can be useful for interpretation of mechanisms in common AOPs. The objective of this study was to investigate the effects of ROS species on MIB/GSM in water, using controlled radiolytic systems, in order to contribute to basic understanding of the mechanisms that drive degradation and removal of those compounds by common AOPs.

2. Experimental

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. High-purity nitrous oxide (N_2O), Ar, O_2 and He gases were from AirLiquide. Solutions of MIB/GSM for radiolysis experiments were prepared in ultrapure (18,2 MΩ) water (TEMAK SA TSDW21 ultrapure water system). Steady-state gamma radiolysis experiments were carried out in a ^{60}Co Gamma Chamber source (model 4000A, Bhabha Atomic Research Centre, India). The dose rate was determined with use of the Fricke dosimeter that is based on the oxidation of ferrous ions in acidic aqueous solutions and measurement of the absorbance of Fe^{3+} at 304 nm (Olszanski *et al.*, 2002). The dose rate was 0.064 Gy s^{-1} in all experiments. Solutions (10 ml) for irradiation were prepared by adding chemical scavengers and/or purging with gasses and then spiking with concentrated aqueous solutions of MIB/GSM. Samples for analysis were taken at standard time intervals. Determination of MIB and GSM was carried out with HS-SPME-GC/MS as described before (Fotiou *et al.*, 2014). Detection and identification of degradation products was carried out by HS-SPME or after extraction with dichloromethane and analysis by GC-MS.

3. Results and discussion

The primary reactive species formed in the radiolysis of water and dilute aqueous solutions are shown in Table 1, together with their respective G values (compiled from Buxton *et al.*,1988). G values refer to the micromoles of species produced per Joule of absorbed energy. Degradation driven by superoxide/hydroperoxyl radicals ($O_2^{\bullet-}$/ HOO$^\bullet$) is a much slower process, as expected from the generally slow rates of reactions of $O_2^{\bullet-}$/HOO$^\bullet$ with organic substrates (Buxton *et al.*, 1988). Those results can shed light on AOP mechanisms where $O_2^{\bullet-}$/HOO$^\bullet$ are likely to be the major species formed, e.g. in visible-light photocatalysis (Fotiou *et al.*, 2016). In this study the system was manipulated with addition of chemical scavengers in order to create conditions where largely single reactive species are produced (Richter, 1998).

Conditions of those controlled experiments, together with the scavenged and produced species are shown in Table 2.

Table 1. Primary reactive species in radiolysis of water

Primary active species	G (μmol J^{-1})
Solvated electron (e_{aq}^-)	0,27
Hydroxyl radical (HO$^\bullet$)	0,28
Hydrogen atom (H$^\bullet$)	0,06
Hydrogen peroxide (H_2O_2)	0,07

**Table 2.** Controlled conditions for production of single radical species

	Conditions	Scavenged species	Produced species (μmol J^{-1})
A	N_2O sat.	e_{aq}^-	HO$^\bullet$(0,55) H$^\bullet$(0,06)
B	O_2 sat.- formate	e_{aq}^-, H$^\bullet$, HO$^\bullet$	$O_2^{\bullet-}$/ HOO$^\bullet$ (0,33)
C	Deaerated - TBA	HO$^\bullet$	e_{aq}^-(0,27) H$^\bullet$ (0,06)
D	Same as C, pH1	HO$^\bullet$	H$^\bullet$ (0,33)
U	No addition of scavengers – "Uncontrolled" experiment		

Degradation curves of MIB and GSM vs absorbed dose under the conditions described in Table 2 are shown in Figures 1 and 2.
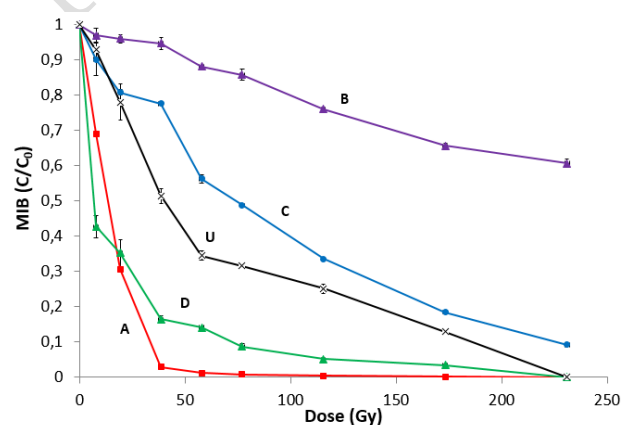
Figure 1. Degradation of MIB vs absorbed dose under conditions presented in Table 2.

Results show that for both MIB and GSM degradation is faster when it is driven by hydroxyl radicals (HO$^\bullet$), as anticipated from the high reactivity and reaction rate constants of HO$^\bullet$ with those compounds (Westerhoff *et al.*, 2006). The hydroxyl radical can rapidly oxidize saturated compounds mainly via hydrogen abstraction while the faster kinetics observed with MIB vs GSM can be attributed the availability of more sites for hydrogen abstraction in MIB (Figure 1).
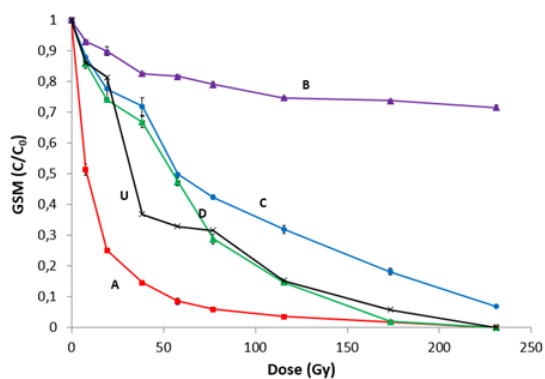
Figure 2. Degradation of GSM vs absorbed dose under conditions presented in Table 2.

Interestingly, hydrated electrons (e_{aq}^-) lead to reductive degradation pathways for both MIB and GSM (curves C) while upon conversion to hydrogen atoms (H·) degradation is faster, especially for MIB (curves D). Although e_{aq}^- is a stronger reducing species (E=-2,77 V) than H·(E=-2,1 V), the hydrogen atom can also react as an oxidant by hydrogen abstraction similarly to HO·, therefore its effect is most prominent with MIB. The e_{aq}^- - H· equilibrium is controlled by pH and pKa of H· is 9,6 (Buxton *et al.*, 1988). The e_{aq}^- - H· system can play a significant role in reductive or oxidative degradation pathways in AOPs where those species are produced (e.g. UV, photocatalytic systems, sonolysis).Degradation products identified during the processes described in Table 2 indicate the different pathways followed by single reactive species as well as the different reductive-oxidative pathways (not discussed further in this short paper). Overall results of this study show that controlled radiolysis of aqueous solutions can be a useful tool to study the effects of single reactive species that are common in AOPs.

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