Environmental Pollution 227 (2017) 252–262

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

# The role of algae and cyanobacteria in the production and release of odorants in water☆

Jechan Lee [a], Prabhat Kumar Rai [b], Young Jae Jeon [c], Ki-Hyun Kim [d, *], Eilhann E. Kwon [a, **]

[a] Department of Environment and Energy, Sejong University, Seoul 05006, Republic of Korea
[b] Department of Environmental Science, Mizoram University, Aizawl 796004, India
[c] Department of Microbiology, Pukyong National University, Busan 48513, Republic of Korea
[d] Department of Civil and Environmental Engineering, Hanyang University, Seoul 04763, Republic of Korea

ARTICLE INFO

*Article history:*
Received 21 January 2017
Received in revised form
19 April 2017
Accepted 21 April 2017

*Keywords:*
Algae
Water
Odor
Volatile organic compound
Drinking-water quality
Contents

ABSTRACT

This review covers literatures pertaining to algal and cyanobacterial odor problems that have been published over the last five decades. Proper evaluation of algal and cyanobacterial odors may help establish removal strategies for hazardous metabolites while enhancing the recyclability of water. A bloom of microalgae is a sign of an anthropogenic disturbance in aquatic systems and can lead to diverse changes in ecosystems along with increased production of odorants. In general, because algal and cyanobacterial odors vary in chemistry and intensity according to blooming pattern, it is necessary to learn more about the related factors and processes (*e.g.*, changes due to differences in taxa). This necessitates systematic and transdisciplinary approaches that require the cooperation of chemists, biologists, engineers, and policy makers.



## 1. Introduction

Water is an integral component of the environment for the persistence of life on this planet. Rapid urbanization, industrialization, excessive agricultural practices, and increasing consumption of domestic water have led to the deterioration of water quality. A significant shortage of water resources is predicted in the near future due to rapid changes in water quality and the growing demand for clean water. As less than 1% of fresh water is available for human use, its proper conservation and management are necessary for sustainable use.

Progressive eutrophication and pollution of surface water have caused a steady increase in odor incidents related to the blooming of aquatic microorganisms in various aquatic environments (Bláha et al., 2009; Hayes and Burch, 1989; Paerl, 1988; Steffensen, 2008; Yoo, 1995). The microorganisms in these blooms produce various terpenoids, carotenoid derivatives, sulfur compounds, and other volatile organic compounds (VOCs) by algae and cyanobacteria most of which can contribute to odor problems (Fink, 2007; Satchwill, 2001; Van Durme et al., 2013). Aquaculture and fisheries are also affected by odor problems such as the presence of various VOCs like geosmin (Wnorowski, 1992). Algae-derived organic matter includes both intracellular and extracellular types with the potential to cause numerous water quality issues, especially the formation of disinfection byproducts and odorous compounds (Li et al., 2012a). These problems are complicated enough to cause profound socio-economic effects (Watson, 2004).

Herein, we provide a review of the multifaceted aspects of odors derived from algal and cyanobacterial species. The production of such unwanted pollutants can pose serious threats to human health and deteriorate the aesthetic quality of drinking water. Other aquatic microorganisms, such as actinomycetes, can also contribute to odor generation in various aquatic environments; however, in this review, the emphasis has been laid mainly on algal and cyanobacterial species. To this end, we attempt to describe the basic factors that exert controls on various types of algal and cyanobacterial odors and their generation. We also discuss the technical approaches required for the proper treatment of algal and cyanobacterial odors in light of potential risks associated with a number of metabolites released in the form of VOCs.

☆ This paper has been recommended for acceptance by Maria Cristina Fossi.

* Corresponding author.
** Corresponding author.
*E-mail addresses:* kkim61@hanyang.ac.kr (K.-H. Kim), ekwon74@sejong.ac.kr (E.E. Kwon).

http://dx.doi.org/10.1016/j.envpol.2017.04.058
0269-7491/

## 2. Types of odors from algae and cyanobacteria

Most problems associated with odor are anthropogenic in nature, although some naturally occurring mineral salts (*e.g.*, sulfates and hydrogen sulfide) can also contribute to the production of such components. It was previously reported that more than 35,000 algal species have been demonstrated to cause aquatic odors, although many of them have yet to be characterized in terms of their effects on human health (Watson et al., 2000).

The types of odor vary in chemistry, intensity, and production patterns for different taxa. It has been indicated that odor problems in water supplies can be caused by algae (Dodds et al., 2009; Pretty et al., 2003). Therefore, it is critical to learn more about the type of algal species that are responsible for releasing odors or VOCs.

The major odorous components derived from most algae and cyanobacteria are commonly identified as terpenoids, carotenoid derivatives, fatty acid derivatives, and sulfur compounds (Watson, 2004). Among numerous algal and cyanobacterial odorants, geosmin and 2-methylisoborneol (MIB) with earthy/musty odors have been widely studied (Watson et al., 2008; Zaitlin and Watson, 2006). Geosmin is known to be produced by a variety of cyanobacteria species such as *Oscillatoria*, *Lyngbya, Symploca*, and *Anabaena* (Smith et al., 2008). Geosmin-producing *Anabaena solitaria* caused earthy odors (Wnorowski and Scott, 1990). Geosmin was also produced by *Oscillatoria simplicissima* (recently renamed *Planktothrix pseudagardhii*) and *Anabaena scheremetievi*, causing earthy/musty odors in water (Conradie et al., 2008). It was demonstrated that cyclization of farnesyl diphosphate to geosmin is catalyzed by geosmin synthase via three steps (farnesyl diphosphate to germacradienol, germacradienol to 8,10-dimethyl-1-octalin, and 8,10-dimethyl-1-octalin to geosmin) in cyanobacteria (Giglio et al., 2008). Incidents involving geosmin were noted in Vaal Dam, Klipvoor Dam, Bospoort Dam, and Wentzel Dam in the northern part of the Republic of South Africa. In all of these cases, *Microcystis aeruginosa* was found to be the most prominent microorganism present at the time of odor formation (Wnorowski and Scott, 1990). Three *Oscillatoria* strains and one *Anabaena* species were isolated from three different water supply systems in California that had experienced earthy/musty odor problems in their drinking water (Izaguirre et al., 1982).

MIB was known to be a metabolite of only certain actinomycetes until 1975, when different species (*e.g.*, *Hyella* sp., *Jagerinema genimatum*, and *Oscillatoria variabilis*) that were capable of releasing MIB were identified (Smith et al., 2008). The MIB synthesis in cyanobacteria consist of two important reactions (Giglio et al., 2011). First, geranyl diphosphate 2-C-methyltransferase catalyzed methylation of geranyl diphosphate, C10 monoterpene precursor, into 2-methylgeranyl diphosphate. Second, MIB synthase catalyzed cyclization of the 2-methylgeranyl diphosphate to MIB. Odors of biological origin were first noted in 1969 in the Yodo River basin, which includes Lake Biwa, Japan (Toui, 1991). Initially, these incidents were caused by the MIB-producing strain of *Phormidium tenue*, but the geosmin-producing strain of *Anabaena macrospora* was also isolated in 1981 (Yagi et al., 1983). Later, a strain of *Oscillatoria tenuis*, possessing significant MIB production, was identified (Negoro et al., 1988). Geosmin concentrations decreased along the river course, while the MIB level was not affected, probably due to its resistance to biodegradation (Hishida et al., 1988). Two MIB-producing cyanobacteria (*Oscillatoria germinate* and *Oscillatoria limnetica*) and three geosmin-producing cyanobacteria (*Oscillatoria amoena*, *Oscillatoria splendid*, and *Aphanizomenon flos-aquae*) were identified as sources of undesirable odor in these cases. In addition, benthic *Oscillatoria chalybea* was found to induce earthy smells (Tucker, 2000). *Oscillatoria curviceps* and *Oscillatoria tenuis*, also produce MIB resulting in earthy/musty odors in water (Conradie et al., 2008).

Both geosmin and MIB exhibit strong resistance to oxidation, which is a process routinely applied in water purification. This, combined with their extremely low odor threshold values, makes them the foremost nuisance substances in odor incidents. Numerous cases of these odor incidents have been reported in North America, Japan, Australia, Europe, and China (Su et al., 2015).

The cyanobacteria synthesize geosmin/MIB through their isopernoid pathways via either mavelonic or non-mavelonic pathways during growth. These cyanobacterial cells release or store odorants depending on the growth phase and environmental factors (Watson et al., 2016). Most of the geosmin/MIB is released during the death and biodegradation of these cells. However, there has been immense difficulty in identifying these materials from environmental samples due to difficulties in isolating and maintaining pure strains of cyanobacteria. Some of the geosmin/MIB-producing cyanobacteria can be used to generate axenic cultures. As geosmin/MIB production is not species-specific, genetic markers (*e.g.*, 16S rRNA regions) are not useful in discriminating between potential producers and non-producers. In order to overcome these problems, intensive researches in next-generation sequencing technologies have been performed to elucidate the genes and enzymes involved in the metabolic routes of geosmin and MIB production. This bioinformatic information can be used to quantify the geosmin/MIB production potential in various aquatic environments as well as the chemical synthetic mechanisms responsible for the generation of odorous chemicals (Otten et al., 2016). Polymerase chain reaction (PCR) methods used to target the genes coding for geosmin synthase and MIB synthase involved in geosmin and MIB syntheses, respectively, have been useful for identifying geosmin/MIB-producing cyanobacteria (Kim et al., 2014; Suurnäkki et al., 2015; Wang et al., 2015b).

Algal cells store and/or release geosmin and MIB, producing variable, often prolonged odor dynamics that depend on the algal strain, the environment, and the growth phase (Rashash et al., 1995, 1996). Cell lysis through senescence, death, or treatment can also increase source-water geosmin and/or MIB via the release of preformed cell metabolites (Peterson et al., 1995). The production of VOCs in Lake Ontario was investigated by Watson (2004), who emphasized that there may be a complex interrelationship among physical, hydrological, and climatic factors. Geosmin and MIB serve as important signals, but they are not indicative of cyanobacteria species composition. In addition, they are not necessarily linked to toxin-producing taxa (Watson, 2003a). Therefore, metabolites may not act as a proxy for algal composition.

β-Cyclocitral (a tobacco-smelling substance of the norcarotenoid group) is often found in eutrophic waters, which is the most dominant VOC of all species of *Microcystis* (a genus of cyanobacteria in freshwater) (Jüttner et al., 2010; Ozaki et al., 2008). In addition, β-cyclocitral is involved in the blue-color formation caused by the lysis of cyanobacteria in natural environments. This chemical has been confirmed to originate from *Microcystis* while exhibiting lytic activity against *Microcystis* itself but not for other algae (Arii et al., 2015; Tomita et al., 2016). Also, it is known that *Microcystis aeruginosa* causes a fruity odor resulting from β-ionone (Zhang et al., 2016). Alkyl sulfides and the β-carotene derivative β-cyclocitral often produce these odors in surface waters; certain noxious cyanobacteria species are the major sources of these compounds (Jüttner, 1984b). Also, β-cyclocitral causing musty/tobacco smell was generated during the death of *Microcystis* spp. via enzyme-mediated catalysis (Jüttner, 1984a). It was also reported that β-cyclocitral and β-ionone are released by green algae (*e.g.*, *Ulothrix fimbriata*) (Fink et al., 2006b).

Algal polyunsaturated fatty acid (PUFA) derivatives have been