



Acute toxicity of emerging atmospheric pollutants from wood lignin due to biomass burning



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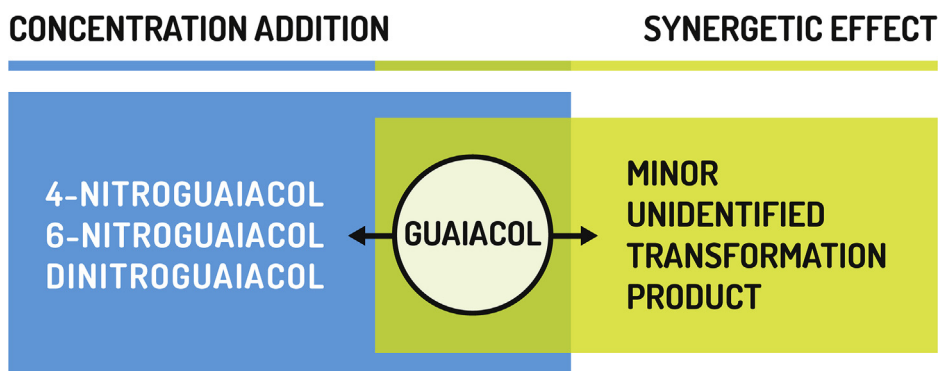
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HIGHLIGHTS

- The first toxicity data of guaiacol and its nitrated products are presented.
- All studied compounds are considered harmful according to the European legislation.
- This study revealed similar harmful potential of studied compounds to nitrophenols.
- No significant joint actions between the four studied compounds were observed.
- A synergistic effect between guaiacol and minor unidentified products is suggested.

GRAPHICAL ABSTRACT



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ABSTRACT

Guaiacol (2-methoxyphenol) is an important atmospheric pollutant. It is the major component of wood lignin and is essentially emitted to the atmosphere during biomass burning. Its aging in the tropospheric aqueous phase leads to the generation of the following ring-retaining transformation products, also during nighttime: 4-nitroguaiacol, 6-nitroguaiacol, and dinitroguaiacol. This study presents the first toxicological data of guaiacol and its nitro derivatives and reveals their harmful potential for the ecosystem. Applying *V. fischeri* bioluminescence acute toxicity test, EC50 values range from 16.7 to 103 mg L⁻¹ after a 30-min incubation period, which classifies all investigated compounds as 'harmful' according to the European legislation. The investigation of environmentally relevant mixtures did not show significant joint actions between the four studied compounds. Therefore, their concentration addition can be considered for ecotoxicological purposes. However, a synergistic effect between guaiacol and a minor unidentified first-generation product of its aqueous-phase aging was observed and should be taken into account when assessing the reaction mixture toxicity. These results stress the need for further toxicological testing, including organisms of different trophic levels, to better evaluate the environmental hazard of guaiacol and especially its nitro derivatives.

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1. Introduction

Guaiacol (2-methoxyphenol, GUA), the main component of the most abundant natural aromatic polymer lignin, is ubiquitous in the environment. Wood biomass is by far the most important source of this semi-volatile pollutant in the atmosphere. Emission factors of

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GUA have been reported for several types of biomass combusted (from natural wildfires and prescribed burns to domestic heating and cooking, crop residue and peat burning) under different burning conditions and range up to 1.4 g/kg fuel burned [1–3]. Taking into account 5130 Tg vegetation burned each year [4], several hundred tons of GUA are annually released into the atmosphere by biomass burning (BB). Industrial sewages can also contribute substantially to the burden of GUA on a local level [5], as well as vegetation, which has recently been reported to globally emit up to 0.1 Tg/year coniferyl alcohol, an analogue of GUA [6]. Due to the nature of its emission sources, GUA is not expected to be evenly distributed in the environment. However, GUA and its transformation products have already been determined in the tropospheric gaseous, aqueous, and particulate phases, in surface rivers and even in drinking water [2,5,7–11].

After being emitted into the troposphere, GUA partitions between the atmospheric gaseous and aqueous phases and is involved in diverse aging processes. Many studies report on its transformation products. They can be colored, absorb solar irradiation in a (sub)visible range, and are thus considered constituents of atmospheric brown carbon, which influences the Earth's radiative balance and critically contributes to climate forcing [12–15]. Being less volatile than their precursor compound, oxidized products also bear a potential to form secondary organic aerosols (SOA) that scatter light, often affect CNN activity, and can penetrate deep into the human lungs where they can exert a substantial damage [16–20]. Moreover, transformation products of GUA can become particularly toxic for living organisms, especially when nitrogen-containing reactive species are involved in the chemistry of the troposphere [21,22]; noteworthy, airborne nitrophenols (NPs) have long been speculated co-responsible for forest decline [23]. Although nitroguaiacols (NGs) are usually regarded as products of aging of GUA in the atmosphere, they can also form during lignocellulosic biomass combustion and are directly emitted into the troposphere with a BB smoke. Primary and secondary atmospheric pollutants are usually deposited onto the Earth's surface with precipitation (when dissolved in rain drops, snowflakes etc.) or by dry deposition as components of atmospheric aerosols and are considered a relevant input vector of toxic compounds [24]. Representing a water-soluble fraction of atmospheric particulate matter (PM), NGs can also accumulate on the surface if deposited by snow or dry particles and are only washed in the ground by rain or when the snow melts, resulting in high concentration of toxicants locally.

European Environmental Agency (EEA) and other regulatory agencies such as World Health Organisation (WHO) and U. S. Environmental Protection Agency (EPA) recognize both PM and volatile organic compounds (VOCs) as harmful for human health [25]. As BB is estimated to be the second largest global source of atmospheric gas-phase non-methane organic compounds and a major source of tropospheric organic aerosol (OA) [18,26], it is not surprising that, in the beginning of 2015, EPA strengthened the existing standards for residential wood heaters originating from the 1988 [27]. However, new standards for emission factors are still missing and GUA, as a common constituent of BB smoke, is not yet included on any of the EPA's pollutant lists [28,29]. Conversely—although not explicitly addressed in the document—corresponding to the group of NPs, NGs are ranked among Toxic Pollutants in Clean Water Act [30]. GUA and its nitro-derivatives could be evaluated by use of EPI Suite [31], ETX [32], and Toxtree [33] software for their toxic potential and mode of action, whereas our scientific literature survey did not result in any experimental ecotoxicological data for GUA or NGs so far.

This study aims to provide the first toxicological data for GUA, 4-nitroguaiacol (4NG), 6-nitroguaiacol (6NG), and 4,6-dinitroguaiacol (DNG). The investigated compounds have already been detected in different environmental compartments and pos-

sess potentially toxic structural characteristics. Besides, they are believed to share a common biogenic cycle, which often makes them coexist in the environment, therefore it is important to also evaluate their possible joint actions [34]. Acute aquatic toxicities of individual compounds as well as of their environmentally relevant mixtures will be determined by use of marine bioluminescent bacterium *Vibrio fischeri*. *V. fischeri* is the most commonly utilized biosensor in risk assessment because it allows rapid toxicological screening, is standardized for single substances and complex eluates (ISO 11348), and has been shown to correlate well with other toxicity tests [35,36]. Obtained toxicological parameters will be used for assessing the risk posed by the investigated group of compounds to the environment. Acute toxicity of GUA, 4NG, 6NG, and DNG will be compared with the available toxicological data of phenol (P) and its nitrated derivatives (NP), which are regulated by the EPA's standards for aquatic and air pollutants [37–42]. Additionally, eventual joint actions, synergism or antagonism, between the investigated compounds will be studied and discussed in a sense of potentiated environmental hazard. As the complexity of toxicological evaluation substantially increases when considering real environmental mixtures [43–45], the reader should be aware, that exact ecotoxicological screening is out of the scope of the present study. This toxicological testing was oriented towards the assessment of evolving hazardous potential during the nitration of biomass burning pollutant GUA in the atmospheric aqueous phase.

2. Experimental

2.1. Materials

The purity of tested standard compounds, guaiacol (GUA), 4-nitroguaiacol (4NG), 6-nitroguaiacol (6NG, BIONET, Key Organics Ltd, United Kingdom), and 4,6-dinitroguaiacol (DNG, provided by AKos GmbH, Germany) was $\geq 97\%$; they were used without further purification. Sodium chloride (NaCl, ACS reagent, $\geq 99.8\%$), hydrochloric acid (HCl, 1, 0.1, and 0.01 M, $\geq 30\%$), sodium hydroxide (NaOH, 1, 0.1, and 0.01 M, $\geq 98\%$) and potassium dichromate ($K_2Cr_2O_7$, ACS reagent, $\geq 99.0\%$) were used for the LUMISTox testing with bioluminescent *V. fischeri* (NRRL B-111777, Hach Dr. Lange GmbH, Germany). Liquid-dried *V. fischeri* aliquots were stored at $-20^\circ C$ and rehydrated before each testing. Sulfuric acid 98% (H_2SO_4 , analysis grade), sodium nitrite ($NaNO_2$, ACS reagent, $\geq 97.0\%$), and vitamin C (ascorbic acid, puriss *p.a.*, $\geq 99.0\%$) were used for the preparation of reaction mixture and reaction quenching. For the mobile phase preparation, acetonitrile (Chromasolv gradient grade, for HPLC, $\geq 99.9\%$), tetrahydrofuran (Chromasolv Plus, for HPLC, $\geq 99.9\%$, inhibitor-free), ammonium formate (Puriss *p.a.*, eluent additive for LC/MS), formic acid (Puriss *p.a.*, eluent additive for LC/MS), and high purity water (18.2 M Ω cm), supplied by a Milli-Q water purification system, were used.

2.2. Bioluminescence test

Acute toxicities of individual compounds (GUA, 4NG, 6NG, and DNG) and their mixtures were determined according to the international standard ISO 11348-2:2007. Inhibition of luminescence emitted by marine bacteria *V. fischeri* was determined. The luminescence produced by the bacteria, being proportional to its metabolic activity, was measured with a photomultiplier (LUMISTox 300 luminometer, Hach Dr. Lange GmbH, Germany) equipped with a thermoblock (LUMISTherm, Hach Dr. Lange GmbH, Germany). The inhibition of a natural light emission in the presence of a sample, i.e. aqueous solution of a single standard component or a mixture, was determined against a non-toxic control (2% NaCl with adjusted pH, see below) after 15 and 30 min incubation times at

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