



# Removal of polycyclic synthetic musks and antineoplastic drugs in ozonated wastewater: Quantitation based on the data of differential spectroscopy



Wei Li<sup>a,\*</sup>, Venkateswarlu Nanaboina<sup>b</sup>, Fang Chen<sup>c</sup>, Gregory V. Korshin<sup>d</sup>

<sup>a</sup> Co-Innovation Center for Sustainable Forestry in Southern China, Nanjing Forestry University, Longpan Road 159, Nanjing 210037, China

<sup>b</sup> Sri Lakshmi Bhargavi Pharma Pvt. Ltd., 3GF & 3,4,5FF, SDF Block-2, EPIP, TSIIIC, Pashmylaram, Patancheru Mandal, Medak District, Telangana 502305, India

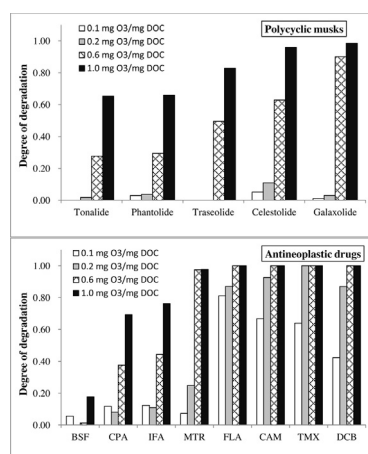
<sup>c</sup> School of Resources and Materials, Northeastern University at Qinhuangdao, 066004, China

<sup>d</sup> Department of Civil and Environmental Engineering Box 352700 University of Washington, Seattle, WA 98195-2700, United States

## HIGHLIGHTS

- Degradation of five polycyclic musks (PMs) by ozone was examined.
- Effects of ozonation on eight anti-neoplastic drugs (ADs) were determined as well.
- Strong correlations between  $\Delta A_{254}/A_{254}^0$  and removal of PMs and ADs were observed.
- PM compounds were degraded primarily via OH radical attack.
- Rate constants for reactions between selected ADs, PMs and OH radical were estimated.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study examined the degradation behavior of polycyclic musks (PMs) and antineoplastic drugs (ADs) and the absorbance spectra of effluent organic matter (EfOM) in municipal wastewater by ozone. Specific ozone doses used in the experiments ranged from 0 to 1 mg O<sub>3</sub>/mg dissolved organic matter (DOC). The examined PMs included galaxolide, tonalide, celestolide, traseolide and phantolide. ADs included busulfan, chlorambucil, cyclophosphamide, dacarbazine, flutamide, ifosfamide, tamoxifen and methotrexate. Strong monotonic albeit nonlinear correlations were found to exist between relative changes of EfOM absorbance at 254 nm (i.e.  $\Delta A_{254}/A_{254}^0$ ) and the degradation of the selected PMs and ADs. This result was interpreted based on the concept of the simultaneous oxidation of EfOM and, on the other hand, PMs and ADs. This interpretation showed that PMs were degraded primarily via OH radical attack, with tonalide and phantolide being less reactive compared with the other PMs. ADs such as cyclophosphamide, ifosfamide and busulfan were also determined to undergo oxidation by OH radicals. Comparison of the behavior of the radical probe para-chlorobenzoic acid and the examined ADs and PMs allowed evaluating corresponding reaction rate constants for reactions between these species and OH radicals.

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\* Corresponding author.

E-mail address: [uwliwei@163.com](mailto:uwliwei@163.com) (W. Li).

## 1. Introduction

The occurrence, fate, ecological risks and removal of pharmaceuticals and personal care products (PPCPs) have attracted increasing attention for more than two decades [1–4]. PPCPs that comprise human and veterinary drugs (e.g., antibiotics, steroid hormones etc.), synthetic musks and related compounds are continuously discharged into the influents of wastewater treatment plants (WWTP). Because many PPCPs tend to be hydrophilic and/or resistant to biodegradation, they are insufficiently, if at all, removed by conventional WWTP operations and remain in the discharged effluents together with effluent organic matter (EfOM) whose concentration is many orders of magnitude higher than those of individual PPCPs [5].

Polycyclic musks (PMs) constitute one of the most ubiquitous PPCP groups. Since their development in the 1950s, PMs have been extensively used as fragrance ingredients in cosmetics and detergents. Currently they account for 85% of the total synthetic musk production [6]. Of the individual compounds constituting the PM group, tonalide (AHTN) and galaxolide (HHCB) are the largest volume products contributing together to ca. 95% of the EU market and 90% of the US market for all PMs [7]. Other PMs such as celestolide (ADBI), phantolide (AHDI) and trasolide (ATII) comprise the remaining 5% of PM consumption.

The extensive use of PMs in consumer products has resulted in their occurrence in wastewater [6–8], surface water and sediments [9–11], air and biota [12] as well as in human milk, blood and adipose tissue [13–15]. Even at their environmental levels, these species have been shown to cause detectable adverse effects in the exposed organisms [16].

The occurrence and effects of antineoplastic drugs (ADs) (alternatively referred to as cytostatic or chemotherapeutic compounds) have attracted considerable attention due to the inherently high toxicity of these species [17–18]. Trace levels of ADs have been suggested to have a capacity to cause pronounced environmental effects because these drugs are designed to inhibit cell growth and have been associated with carcinogenic, teratogenic and mutagenic properties [19–21]. Although the total mass of ADs consumed in inpatient or outpatient cancer treatment procedures is lower than those of many more commonly used PPCPs, ADs have been frequently detected in hospital wastewater, WWTP effluents and surface water [4,22–23]. Predictions of their occurrence have also been made based on model estimates that took into account literature data on their consumption, rates of excretion and environmental fate [24]. Given the current trend of an increasing use of ADs in outpatient treatment of cancer patients, environmental concentration of ADs are likely to increase in the future [17].

Because PMs and AD can cause adverse effects in the affected ecosystems [4,16,19,25–27] and these compounds are incompletely removed from WWTP effluents, it is necessary to examine the performance of advanced methods to degrade these compounds in wastewater.

Ozonation is one such technique which is frequently used for drinking water disinfection [28] and for oxidative wastewater treatment [29]. Other conventional disinfection methods, for instance, chlorination are not effective for the removal of PMs [30,31]. Chlorine can remove only a narrow range of ADs, for instance methotrexate and 5-fluorouracil [32,33], and its reactions with these compounds tend to be slow. Ozonation is an efficient method to remove a wide range of PPCPs [34] and a limited number of prior studies have examined the removal of selected PMs (e.g., galaxolide, tonalide) and ADs (e.g., cyclophosphamide and ifosfamide) by ozone [35–38]. Because many other PM and AD compounds are discharged into aquatic environments, detailed information concerning the efficiency of ozonation and related

treatment methods in removing of a wider range PM and AD species and mechanism of their degradation needs to be obtained.

The use of ozonation or related methods can be optimized if the extent of degradation of the trace-level contaminants can be monitored and/or predicted in real time. This is difficult to achieve based solely on chromatographic determinations because, while extremely sensitive and precise, they remain labor- and time-intensive. To circumvent this complication, surrogate parameters, for instance changes of the absorbance or fluorescence of EfOM have been used to estimate the degradation of PPCPs [39–41]. The observed strong correlations between the degradation of PPCPs and concurrent changes of EfOM absorbance or fluorescence have been explained based on the concept that the oxidation of EfOM by ozone proceeds concurrently with and is indicative of the degradation of trace-level PPCPs present in the wastewater. Nanaboina and Korshin [41] used this approach to demonstrate that relative changes of EfOM absorbance denoted as  $\Delta A_{254}/A_{254}^0$  could be used to predict the degradation of selected PPCPs and derived a numerical approach that takes into account intrinsic rates of the oxidation of EfOM and PPCP compounds by ozone and hydroxyl radical.

More recent research showed the applicability of this approach to a wide range of ozonation and AOP conditions, individual PPCPs and products of their degradation and wastewater effluents of varying provenance [29,42]. However, this method has not been applied to quantify the degradation of any ADs or PMs while the examination of the applicability of this approach to other musks such as musk ketone (a synthetic aromatic nitro-musk) has been hindered by its volatility and resultant scatter in the analytical data [29,42].

Accordingly, the objectives of this study are: (1) to examine the degradation of a representative range of commonly used PM (galaxolide, tonalide, celestolide, phantolide, and traseolide) and AD compounds (busulfan, chlorambucil, cyclophosphamide, dacarbazine, flutamide, ifosfamide, tamoxifen and methotrexate) as function of ozone dose applied to municipal wastewater; (2) to compare and correlate the degradation of these species with concurrent changes of the absorbance spectra of ozonated wastewater, and (3) to examine the applicability of the previously developed approach to model correlations between the oxidation of EfOM and degradation of trace-level PPCPs to the ozonation of wastewater containing PM and AD species.

## 2. Materials and methods

### 2.1. Reagents and wastewater

Polycyclic musks tonalide, galaxolide, celestolide, phantolide and traseolide with the purity of 99%, 76%, 99%, 95% and 90%, respectively, were purchased from LGC Standards. Antineoplastic drugs including busulfan, chlorambucil, cyclophosphamide, dacarbazine, flutamide, ifosfamide, tamoxifen and methotrexate with the purity > 98% were purchased from Sigma–Aldrich. Their structures and selected physico-chemical characteristics are listed in Table 1. Stock solutions were prepared by weighing and dissolving requisite amount of each compound in ultrapure water and methanol mixture (50:50 v/v) to yield a 100 mg/L concentration. HPLC grade acetonitrile was obtained from Fisher Scientific Co. Potassium indigo trisulfonate used to determine ozone concentration was ACS grade and purchased from Sigma–Aldrich. All reagents were used as received without further purification. The ultrapure water (18.2 M $\Omega$ ) used in the experiment was produced by a Milli Q system (Millipore, USA).

Samples of secondary effluent (before disinfection) were collected from West Point Wastewater Treatment plant in Seattle. The collected wastewater was filtered through a 0.45  $\mu$ m filter immediately after it was transported to the research laboratory.

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