

Characterization of Atmospheric Organic Carbon and Element Carbon of PM_{2.5} during the Long Dry Period in Cotonou, Benin

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Abstract

In the African countries, air pollution appears as a public health problem. The health consequences of this pollution are currently causing concern among the population and decision-makers. Air quality degradation is a major issue in the large conurbations on the shore of the Gulf of Guinea. In this study, daily atmospheric PM_{2.5} and carbonaceous aerosol (organic carbon (OC) and elemental carbon (EC)) concentrations were measured at Dantokpa site in Cotonou, Benin, Southern West Africa during the long dry period (December 2016 to March 2017). We analyzed the mass concentrations and carbonaceous species of PM_{2.5}. The average PM_{2.5} concentration was 69.20 $\mu\text{g}\cdot\text{m}^{-3}$, while OC and EC concentrations were $34.39 \pm 12.62 \mu\text{g}\cdot\text{m}^{-3}$ and $10.82 \pm 7.89 \mu\text{g}\cdot\text{m}^{-3}$, respectively. Total carbon (TC) accounted for 65.35% of the PM_{2.5}. Strong correlation between OC and EC was found during the long dry period, suggesting the contributions of similar sources. We have also studied the correlations between OC-EC and PM_{2.5}. We found that OC was highly correlated with PM_{2.5} ($R = 0.94$) while EC was moderately correlated with PM_{2.5} ($R = 0.77$), suggesting that carbonaceous aerosols and PM_{2.5} shared major sources at Dantokpa site during the long dry seasons.

Keywords

Aerosol, PM_{2.5}, Concentration, Carbonaceous, Organic, Elemental Carbon

1. Introduction

The already densely populated southern West Africa (SWA hereafter) experiences strong population growth and urbanization [1]. According to [2], Southern West Africa has one of the fastest growing populations worldwide. This has led to a higher water demand and lower air quality. Air pollution is a concern in the West Africa region where it is known that meteorological parameters such as ambient temperature and humidity can affect the particulate matter loading through atmospheric convection and dry deposition [3]. According to [4], air pollution is a major environmental health problem affecting large populations around the world. Epidemiological and toxicological research has shown the relationship between particulate matter exposure and human health effects such as cardiovascular diseases [5] [6], mortality and morbidity [7] [8] and lung cancer [9] [10]. According to [11], exposure to air pollutants causes respiratory infections, cardiovascular diseases and lung cancer.

Atmospheric pollution plays an important role in regional air quality, public health, atmospheric chemistry and climate change in West Africa. Particulate Matter (PM), especially in urban areas, contains an important fraction of carbonaceous materials [12] [13]. Much of the air pollution that has adverse impacts on human health and the environment today is the result of anthropogenic activities [14]. Road traffic has led to increase in many air pollutants to levels around the world. Air pollutants can be classed as primary (e.g., particulate matter (PM)), or as secondary if they are as consequences of chemical reactions in the lower atmosphere (e.g., ozone (O₃)) [15]. PM is described in the literature as a mixture of metals, salts, organic compounds from combustion and elemental carbon [16]. The concentration measured at ground level is a common way to quantify the amount of aerosol particles in the atmosphere and is used as a standard in air quality assessment [17]. Atmospheric pollutants can have a harmful influence on the atmosphere in different ways [18]. According to [19], particles from combustion sources are more relevant to human health than are particles from other sources. Epidemiological studies showed that particles smaller than 2.5 µm in diameter (PM_{2.5}) penetrating deep in the respiratory system, are associated with an important health burden including the aforementioned pathologies, the development of asthma especially in children and chronic respiratory diseases such as Chronic Obstructive Pulmonary Disease (COPD) affecting both children and adults [14] and furthermore neurodevelopmental disorders in both the very young and the very old. According to [9], excessive PM_{2.5} concentrations affect negatively human respiratory and cardiac health. PM_{2.5} was considered more toxic than the coarse particles [20]. The spatially continuous mapping of PM_{2.5} is substantially required for determining the population exposure to PM_{2.5} [21] [22]. The high concentrations of fine particles originate mainly from automobile combustion and biomass burning also under the influence of the Sahara Desert [23]. According to [24] [25], high aerosol concentration levels in West African cities may have strong implications for the population's health. In four West

African cities, Abidjan (Ivory Coast), Cotonou (Benin), Dakar (Senegal), and Ouagadougou (Burkina Faso), the International Development Research Center of Canada is founding research that aims at improving the understanding of urban air pollution and its impacts on non-transmittable breathing diseases [26]. This project is a collaboration between four African universities and is under the auspices of the Community of Practice in Ecohealth-West and Central Africa (CoPES-AOC). The CoPES-AOC has been very active in the region to promote an ecosystem approach to health (ecohealth), to foster collaboration between scholars and practitioners, and to train a new generation of African scholars since 2006.

In order to figure out chemical composition of atmospheric particles and to establish emission control policies at Dantokpa market in Cotonou, an observation of both OC and EC PM_{2.5} fractions was conducted. Carbonaceous material constitutes a large portion of suspended particulate matter (PM). According to [27] [28], the carbonaceous aerosols consist of highly polymerized organic material with a low hydrogen and oxygen content. Particle is usually divided into two fractions, organic carbon (OC) and elemental carbon (EC) [29]. Carbonaceous particles can play an important role in climate processes [30] [31]. Elemental carbon (EC) generally refers to the portion of ambient particles that absorb strongly in the visible and near infrared light [32]. According to [28], OC represents only a fraction of the total organic matter present in the aerosol because OC is a measure of the carbon mass.

Several studies have shown the clear relationship between automobile traffic density, the use of leaded gasoline and lead content in the air and soil in urban zones [14] [33]-[37]. In Cotonou, the economic capital of Benin, poor air quality has been reported by [38]. The increase in recorded air pollution is mainly due to urbanization [39]. It is in this perspective, that we performed a study on Characterization of the air pollution in Cotonou. For this purpose, we propose to base our research work on aerosol measurements during the long dry period at Dantokpa site in Cotonou, Benin in southern West Africa. PM_{2.5} and carbonaceous measurements were collected during the long dry period (December 2016 to March 2017). This long dry season coincides with the Harmattan dust period in West Africa, along with dust storm episodes [40]-[42]. Furthermore, in addition to Saharan dust and biomass burning events, anthropogenic particulate pollution sources are still the main PM anthropogenic sources which are quite different over this site. Note that biomass burning occurring around West Africa may also impact our site [34].

This paper focuses on fine-particle mass and particulate carbon species measurements performed at the Dantokpa market. The objective of this paper is to evaluate the PM_{2.5} particle exposure of vendors at Dantokpa market and to study the relationship between OC, EC and PM_{2.5} mass concentrations in order to assess if they share major sources during the long dry period.

2. Materials and Methods

2.1. Site Description

The 08-h (09:00 to 17:00 local time) PM_{2.5} sample was collected at an urban

sampling site (Dantokpa market) (**Figure 1**). This site is located in Cotonou, it is one of the biggest markets in western Africa. Cotonou ($6^{\circ}21'N$, $2^{\circ}26'E$) as an economic capital, political and administrative center [18] is the most important city in Benin (**Figure 1**). The city has a subequatorial climate characterized by two dry periods that extend from December to March and from August to September [43]-[45]. Seasonal average precipitations and wind speed, for Cotonou, have been determined in previous paper from [34] during our study period. The average precipitation and wind speed was 80 mm and $3.6 \text{ m}\cdot\text{s}^{-1}$ in long dry season. Cotonou is a coastal city dominated by winds from the southwestern part of the African Gulf of Guinea monsoon [46].

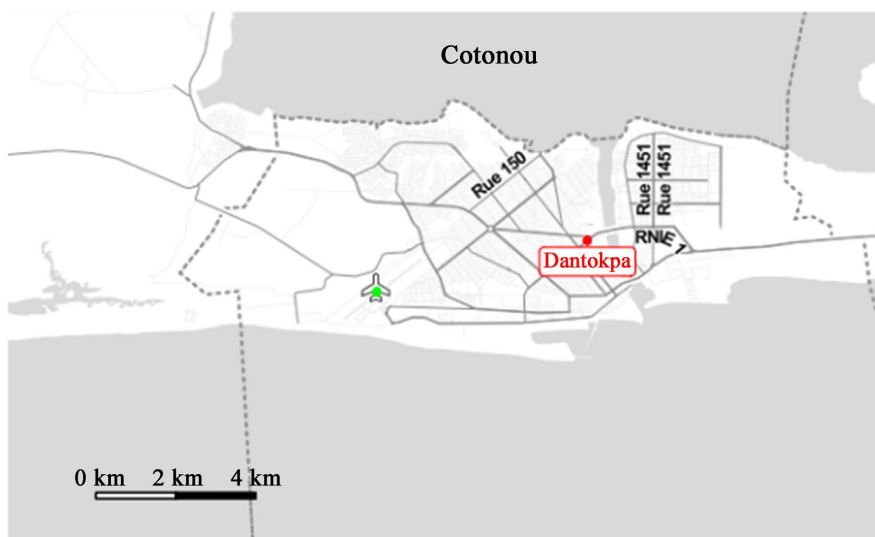


Figure 1. Map of the city of Cotonou reporting the location of the PM_{2.5} sampling Dantokpa site.

2.2. Sampling and Analysis

2.2.1. Sample Collection

The device adopted is the EVM-7 environmental monitor. The EVM-7 (version 1.05 Quest Technologies) is a compact environmental monitor for the measurement of the airborne concentrations [47].

The campaign of the PM_{2.5} and carbonaceous aerosols was collected on 37 mm diameter filters at Dantokpa, Cotonou from December 2016 to March 2017, using the EVM-7. Quartz fibre filters were used for gravimetric measurements and carbonaceous aerosol analysis only. The filters had been stored in packs before sampling, then individually in Petri dishes and covered with aluminium foil once the sample has been collected. Then they are returned to the Laboratoire d'Aérogologie in Toulouse, France for different analyses.

This measuring device was placed 6 meters from the road, in a metallic cage, at 1.20 m from the ground, representing the average human respiratory level. The measurements have been made daily from 9:00 to 17:00. During this period of time, the market very is animated with the presence of a large crowd of vendors.

2.2.2. Gravimetric Analysis

Quartz filter was weighted before and after sampling for mass determination using a Mettler microbalance MC21S with 1 µg sensitivity in Toulouse, France, at Laboratoire d'Aérogologie. Before weighing, the samples were kept for about 24 h in the weighing room at an ambient relative humidity of 30% ± 15% [34].

2.2.3. Carbonaceous Aerosols

Quartz filters were analyzed with a DRI analyzer using the Improve methods [48]-[51] (for EC and OC measurements). Briefly, carbonaceous materials are volatilized, pyrolyzed, and combusted to gas-phase compounds that leave the sample and are converted to carbon dioxide (CO₂). Temperature atmosphere fractions in pure He are 120°C, 250°C, 450°C, and 550°C and the corresponding carbon fractions are called OC1, OC2, OC3 and OC4. In an oxidizing atmosphere, temperature plateaus are 550°C (EC1), 700°C (EC2), and 800°C (EC3). The carbon measured after the introduction of the He/O₂ atmosphere at 550°C is defined as organic pyrolysis char (OP). The detection limit estimated by the DRI analyser based on the instrument blank is 0.4, 0.1 and 0.3 µgC·cm⁻² for TC, EC and OC. The accuracy estimated from our measurements is 5% for TC and 10% for EC and OC [34].

3. Results and Discussion

3.1. PM2.5 and Carbonaceous Aerosols

3.1.1. PM2.5, OC and EC Variations

Daily concentrations of PM2.5 and carbonaceous aerosols (OC and EC) in atmospheric particles were measured at Dantokpa site during the long dry seasons. In this month, the daily concentration varied from 29.71 to 81.7 µg·m⁻³ for PM2.5, 27.13 to 48.52 µg·m⁻³ for OC and 1.75 to 23.13 µg·m⁻³ for EC, respectively. Average concentration was 69.20 ± 20.41 µg·m⁻³ for PM2.5, 34.39 ± 12.62 µg·m⁻³ for OC and 10.82 ± 7.89 µg·m⁻³ for EC, respectively. The analysis of carbonaceous aerosol composition shows that EC and OC concentrations constitute 24% and 76% of TC, respectively. Among the carbonaceous components, OC was the most abundant.

3.1.2. OC and EC Ratio

The daily average OC/EC ratios during the long dry period is 3 ± 1. Such high OC/EC value could indicate the presence of secondary organic carbon at Dantokpa. Moreover, the large OC/EC range also suggests that carbonaceous aerosols measured at Dantokpa are linked to a mixture of sources.

The correlation between OC and EC can reflect sources common to both elements. **Figure 2** shows the relationship between the daily concentrations of OC and EC in PM2.5 at Dantokpa site during the long dry period. The correlation between OC and EC Concentrations is 0.97. This value observed shows a good correlation between these elements (OC and EC). Such a correlation means that OC and EC share the same sources of pollution at Dantokpa site during the long dry period.

3.1.3. OC, EC and TC Contributions to PM2.5

The average mass ratio showed that TC accounted for 65% of PM2.5 during the long dry period. On average, the daily average OC and EC accounted for 49.71% and 15.64% of PM2.5 during the long dry period. We have also studied the correlations between OC, EC and PM2.5 concentrations. **Figure 3** shows the relationship between OC, EC and PM2.5 mass concentrations. OC concentration was highly correlated with PM2.5 mass concentration ($R = 0.94$), suggesting that OC and PM2.5 shared major sources. On the other hand, EC was moderately correlated with PM2.5 ($r = 0.77$), suggesting that EC share also major sources. Finally, we can say that carbonaceous aerosol and PM2.5 shared major sources at Dantokpa site during the long dry period.

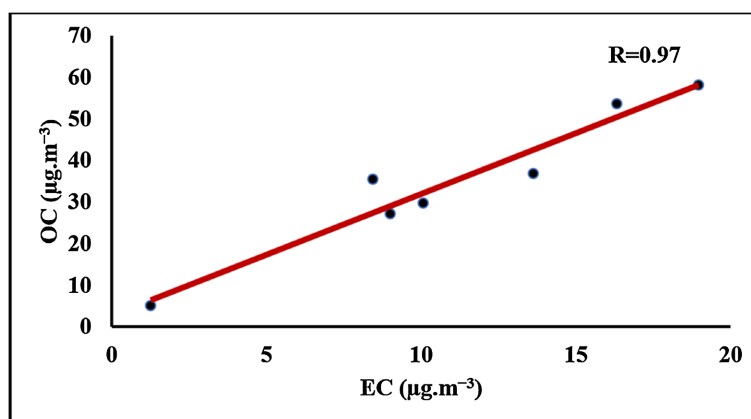


Figure 2. Correlation between OC and EC in PM2.5.

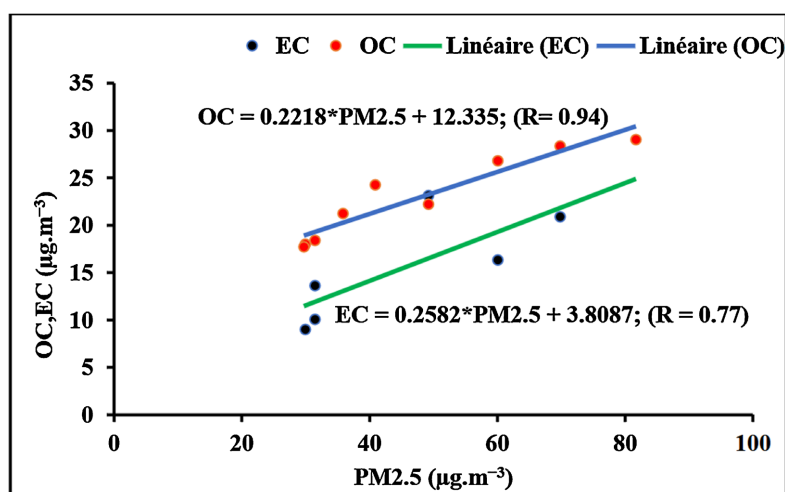


Figure 3. Correlations between carbonaceous aerosol and PM2.5 mass concentrations.

3.2. Discussion

Our result shows that the average PM2.5 concentration at our urban site is 69.20 µg.m⁻³. For comparison, the World Health Organization recommends of the threshold values of 25 µg/m³ and 10 µg/m³ as a guideline for daily and annual PM2.5 respectively. Level observed at our site is higher than WHO daily and

annual standards. Red (annual) and yellow (daily) Horizontal lines illustrate current WHO guidelines (**Figure 4**). The mean daily concentration of PM_{2.5} during the measurement period exceeded the standard of WHO by 2.77 times. Finally, we can say that Dantokpa market vendors are exposed to PM_{2.5} particles because of their high concentrations at the respiratory level. According to [52], 80% of the world's population lives in areas where average annual concentrations of PM_{2.5} exceed highly the WHO guideline's (10 µg·m⁻³). In Africa, the regions most exposed to fine particles (PM_{2.5}) are found in Ghana (50 µg·m⁻³, Accra), Madagascar (59 µg·m⁻³, Antananarivo) and Senegal (38 µg·m⁻³, Dakar) [53].

Table 1 shows the range of mean PM_{2.5} level obtained on the traffic site with other measurements existing in Africa on the traffic site for cities.

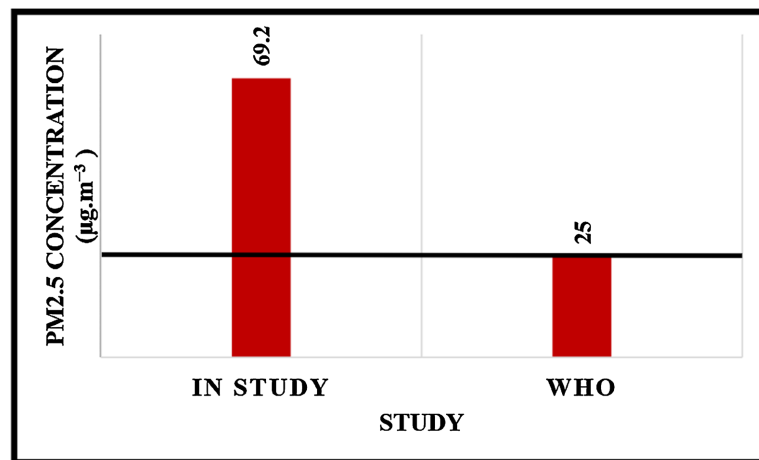


Figure 4. Comparison of daily PM_{2.5} mass concentration at our site and WHO guideline (daily).

Table 1. Mean PM_{2.5} level obtained on the traffic site with other measurements existing in Africa on the traffic site for cities.

Location	Periods	Mean Concentrations (µg·m ⁻³)	Site description	References
Cotonou, Benin	Long dry period (December 2016 to March 2017)	69.2	Traffic site	In study
Constantine, Algeria	23 December 2011 and 8 January 2013	57.8	Traffic site	[54]
Kenitra, Morocco	June 2007 and May 2008	51.32	Traffic site	[55]
Dakar, Senegal		80.7	Traffic site	[25]

In **Table 1**, PM_{2.5} concentrations vary from 51.32 to 80.7 µg·m⁻³. The daily PM_{2.5} levels recorded in Constantine, Algeria, between 23 December 2011 to 8 January 2013 were reported by [54] at 57.8 µg·m⁻³. In another sampling campaign

during 23 December 2011 to 8 January 2013, average concentration of PM_{2.5} (57.8 $\mu\text{g}\cdot\text{m}^{-3}$) greatly exceeded the WHO guideline values. According to study carried out by [55] during the period between June 2007 and May 2008, in Kenitra city which is located 50 km north of Rabat, the average PM_{2.5} concentration was 51.32 $\mu\text{g}\cdot\text{m}^{-3}$. The major sources of pollution in this region were attributed to road traffic and dust resuspension [14]. [25] reported that daily PM mean level Dakar city reached 80.7 $\mu\text{g}\cdot\text{m}^{-3}$; this high concentration is mainly due to traffic emissions and biomass burning used for cooking and heating purposes. After analyzing the table, we can say that the PM_{2.5} concentration measured on our traffic site agrees with those measured on other traffic sites in certain African cities.

Atmospheric EC is emitted directly by incomplete combustion sources such as biomass burning [28] [56]. Part of OC (primary organic carbon) is also emitted as primary particles directly from sources, whereas secondary organic carbon is formed in the atmosphere from the low vapor pressure products of atmospheric chemical reactions [56] [57]. The relationship between OC and EC and the mass ratio of OC to EC have been used to identify origins, emission and transformation characteristics of carbonaceous aerosols [34] [56] [58]. According to [57] [59] [60], the OC/EC ratio exceeding 2.0 has been used to indicate the presence of secondary organic aerosols. The variation of the OC/EC ratio can be used as an indicator of changes in emission sources, source processes or source regions [61].

In terms of carbonaceous aerosol, the concentration measured during the long dry period at Dantokpa site is 10.82 $\mu\text{g}\cdot\text{m}^{-3}$ for EC and 34.39 $\mu\text{g}\cdot\text{m}^{-3}$ for OC. We compared our aerosol values with those measured at the same period (dry season). The OC and EC concentrations are higher than the ones found during the great dry season for two traffic sites in Abidjan, Côte d'Ivoire (OC: 20 $\mu\text{g}\cdot\text{m}^{-3}$; EC: 8.5 $\mu\text{g}\cdot\text{m}^{-3}$) and Cotonou, Benin (OC: 10 $\mu\text{g}\cdot\text{m}^{-3}$; EC: 3 $\mu\text{g}\cdot\text{m}^{-3}$) [34]. To identify the possible sources of atmospheric PM_{2.5} aerosole in this study, we used OC/EC ratio. This ratio obtained at our site is 3, exceeded 2. It is higher than the one found at Abidjan (OC/EC: 2.5) but lower than the one found at a different location than the Dantokpa market at Cotonou (OC/EC: 3.5) [34]. In our study, this value (OC/EC: 3) found is due to the predominant influence of sources with incomplete combustion such as biomass fires and vehicle traffic [62].

According to [59], the good correlation between OC and EC indicates one or more common sources. In other words, the correlation between OC and EC was 0.97. Our correlation is similar and higher than the one (0.98) found by [56] and (0.89) [63], respectively. The strong correlation ($R > 0.8$) between OC and EC concentrations, indicates that similar emission sources might contribute to atmospheric fine particles and secondary organic aerosol (SOA) formation might be minor during this season [56]. However, the OC/EC-PM_{2.5} correlations (R (OC-PM_{2.5}) = 0.94 and R (EC-PM_{2.5}) = 0.77) have been studied during the long dry period. The strong correlation between OC and PM_{2.5} suggests that both elements shared major sources [56].

4. Conclusions

This study reports observations of daily PM_{2.5} mass and carbonaceous aerosol concentrations on the traffic site in coastal city of southern West Africa. Traffic emissions were investigated at Dantokpa market Cotonou in Benin. The period of observations spans from December 2016 to March 2017. Our findings can be summarized as follows.

The average daily PM_{2.5} concentrations for our urban traffic site is about 69.2 $\mu\text{g}\cdot\text{m}^{-3}$ and in the range of those of previous studies in sub-Saharan western Africa. It is 2.77 times higher than the concentrations recommended by the World Health Organization.

Average daily concentrations were 10.82 $\mu\text{g}\cdot\text{m}^{-3}$ for EC and 34.39 $\mu\text{g}\cdot\text{m}^{-3}$ for OC, respectively. The average OC/EC ratio is 3, clearly indicating the larger contribution of emissions related to human activities, motorcycles and vehicles at Dantokpa site. The highest correlation between OC and EC is found during the long dry period, suggesting the contributions of similar sources. We have also studied the correlations between OC-EC and PM_{2.5}. The OC was highly correlated with PM_{2.5} ($R = 0.94$) while the EC was moderately correlated with PM_{2.5} ($R = 0.77$). We can say that the carbonaceous aerosols and PM_{2.5} particles share the major sources at Dantokpa site.

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Author Contributions

Conceptualization, data curation, formal analysis, investigation, methodology, software, writing original draft and writing review and editing preparations, J. Djossou; writing review and editing, K. P. Mathos and S. P. Lamah; supervision, J. Djossou. All authors have read and agreed to the published version of the manuscript.

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Institutional Review Board Statement

Not applicable.

Informed Consent Statement

Not applicable.

Data Availability Statement

The PMs concentrations data used in this study are not available online in any database so we cannot provide a link to reach them. However, the datasets are available from the International Development Research Center (IDRC) via the “Chairpol” project (IDRC project 107347) of the Ecohealth Community of Practice - West and Central Africa (CoPEH-WCA) on reasonable request.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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