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Source: Environmental Health Insights, 9(s2)

Published By: SAGE Publishing

URL: https://doi.org/10.1177/EHI.S19588

Using Caffeine as a Water Quality Indicator in the Ambient Monitoring Program for Third Fork Creek Watershed, Durham, North Carolina

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Supplementary Issue: Ecosystem Services and Environmental Health

ABSTRACT: Caffeine has been suggested as a chemical indicator for domestic wastewater in freshwater systems, although it is not included in water quality monitoring programs. The Third Fork Creek watershed in Durham, NC, is highly urbanized, with a history of receiving untreated wastewater from leaking and overflowing sanitary sewers. The poor water quality originating in the Third Fork Creek watershed threatens its intended uses and jeopardizes drinking water, aquatic life, and recreational activities provided by Jordan Lake. Organic waste contaminants have been detected in both Third Fork Creek watershed and Jordan Lake; however, the sampling periods were temporary, resulting in a few samples collected during nonstorm periods. It is recommended that (1) the concentration of caffeine and other organic waste contaminants are determined during storm and nonstorm periods and (2) caffeine is monitored regularly with traditional water quality indicators to evaluate the health of Third Fork Creek watershed.

KEYWORDS: caffeine, ecosystems services, fecal coliform, stormwater, urban watersheds

SUPPLEMENT: Ecosystem Services and Environmental Health

CITATION: Spence. Using Caffeine as a Water Quality Indicator in the Ambient Monitoring Program for Third Fork Creek Watershed, Durham, North Carolina. *Environmental Health Insights* 2015:9(S2) 29–34 doi: 10.4137/EHI.S19588.

RECEIVED: November 27, 2015. **RESUBMITTED:** April 16, 2015. **ACCEPTED FOR PUBLICATION:** April 21, 2015.

ACADEMIC EDITOR: Timothy Kelley, Editor in Chief

TYPE: Perspective

FUNDING: Author discloses no funding sources.

COMPETING INTERESTS: Author discloses no potential conflicts of interest.

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Introduction

Clean streams are essential for providing ecosystem services to sustain thriving communities and healthy ecosystems. The City of Durham Stormwater Services Division publishes an annual report to inform the citizens of Durham County about the water quality conditions of their local watersheds. The intent of these reports is to encourage residents to become aware of the water quality issues and to help eliminate the sources of pollution. Untreated human waste from (1) leaking and overflowing sanitary sewers and (2) failing septic tanks during storms is the main source of nutrients and bacteria entering streams located in the City of Durham, NC,[1] and other cities with aging sewer systems.[2,3]

Pharmaceuticals, such as caffeine, frequently co-occur with nutrients[4] and bacteria[5] in surface waters contaminated with domestic wastewaters.[6] Caffeine is classified as a nonprescription stimulant and is one of the 10 most frequently detected organic waste contaminants (OWCs) in the water samples collected from eight drinking water sources located in the Raleigh–Durham–Chapel Hill metropolitan area of North Carolina.[7] Caffeine has been detected often in surface water systems throughout the United States[8] but has not been examined in urban watersheds located within the city of Durham, NC, such as Third Fork Creek watershed.

Buerge et al.[6] stated that caffeine should not be used as a chemical indicator in areas with considerable natural and industrial sources. Even though there are at least 60 plant species worldwide that naturally contain caffeine,[9] the Yaupon is the only indigenous caffeine-producing plant in the United States.[10] The Yaupon is found naturally in coastal areas, extending from Virginia to Texas.[10] Native Americans in the southeastern region of the United States used the leaves and shoots of the Yaupon to make a tea-like drink known as the "black drink" for purification rituals.[10] Average caffeine consumption in the United States is 210 mg per person per day.[6] Ingested caffeine is metabolized; however, a small percentage (approximately 3%) is excreted in the urine.[11] Unconsumed caffeinated drinks, such as coffee, tea, soft drinks, cocoa, as well as chocolate drinks and energy drinks, disposed down the drain enter streams via domestic wastewater.[12]

Sankararamakrishnan and Guo[2] report that fecal coiform bacteria levels and caffeine concentrations measured from stormwater outfalls located around Deal Lake in New Jersey are higher during storm events than during nonstorm periods, indicating leaking or overflowing sanitary sewers. The stormwater outfall site with the highest caffeine concentrations is connected to one of the oldest public sanitary sewer lines in the United States.[2] Correlations between caffeine concentrations and fecal coliform bacteria levels measured in urban streams, stormwater collection pipes, and stormwater discharge points located in Montreal, Canada, suggest that caffeine can be used as a tracer for human waste.[5] Several studies have reported correlations between caffeine and fecal coliform bacteria in watersheds with urban, mixed, or rural land uses (Table 1). Reported correlations suggest that caffeine is a good indicator for domestic wastewater in urban streams impacted by human activities.[2,5,10] Furthermore, freshwater systems located in rural areas with limited to no human activity do not contain measurable concentrations of caffeine.[3,13]

Currently, fecal coliform bacteria is used as a water quality indicator to determine whether freshwater systems are contaminated with domestic waste and pose a potential risk to human health. Young and Thackston[14] find that fecal coliform bacteria levels are higher in watersheds containing sewer systems than watersheds without sewer systems and the levels are influenced by the density of housing, population, development, and domestic animals.[14] Fecal coliform levels in raw sewage (6.4×10^6) are higher than combined sewer overflows (10^4–10^6) and urban stormwater runoff (2.0×10^4).[15] The majority of fecal coliform bacteria in stormwater runoff are presumed to be of nonhuman origin. Dogs, cats, raccoons, rats, beavers, and geese are sources of nonhuman fecal coliform in urban watersheds.[15] Fecal coliform is considered an imperfect water quality indicator because it is challenging to distinguish between human and nonhuman sources.[6,15,16] Microbial source tracking methods for aquatic environments have been developed to differentiate human from nonhuman sources. These methods have their advantages and disadvantages, but there is not a single method capable of identifying the source of fecal bacteria in aquatic environments with absolute certainty.[16]

Caffeine has been suggested as a chemical tracer for domestic wastewater contamination in urban streams because it is regularly consumed and excreted by humans, which makes caffeine anthropogenic in origin and predominantly associated with domestic wastewater contamination.[5,6,12] Ferreira et al.[12] denote caffeine to be an excellent indicator for the presence of OWCs and pathogens in urban streams frequently affected by raw sewage in Brazil. Furthermore, a recent study conducted by Montagner et al.[17] suggests that caffeine can be used as an indicator for estrogenic activity in streams located in Sao Paulo, Brazil.[17] Currently, caffeine is not routinely measured with other water quality indicators in urban stream monitoring programs.[7]

Ambient Water Quality Monitoring Program

The City of Durham Stormwater Division established an ambient water quality monitoring program to comply with federal permitting regulations by improving the water quality conditions of their local streams.[18] Their monitoring program consists of 12 watersheds, including Third Fork Creek,[19] with approximately 40 monitoring sites located within and around the city of Durham.[20] Monitoring locations are generally located in areas frequently affected by sanitary sewer overflows and spills or areas presumed to be affected by pollution sources.[21] These watersheds are monitored monthly for water quality indicators, such as fecal coliform bacteria, nutrients, turbidity, aquatic life, metals, and biological oxygen demand.[18] Fecal coliform bacteria levels suggest whether streams can be used for recreational activities without posing a threat to human health. Nitrogen and phosphorus are used to manage

Table 1. Freshwater system locations, land use, wastewater treatment plant (WWTP) discharge, and correlations between fecal coliform levels and caffeine concentrations.

FRESHWATER SYSTEM	LOCATION	COUNTRY	LAND USE	WWTP DISCHARGE	R^2 FECAL COLIFORM AND CAFFEINE	REFERENCE
Ochlocknee watershed	Georgia/Florida	United States	Rural	Yes	0.38	Peeler et al (2006)
Chickasawhatchee watershed	Georgia	United States	Rural	No		Peeler et al (2006)
Deal lake	New Jersey	United States			1.00	Sankararamakrishnan and Guo (2005)
Small streams*	Montreal	Canada	Urban		0.56	Sauve et al (2012)
Brooks collectors*	Montreal	Canada	Urban		0.56	Sauve et al (2012)
Storm sewer* Outfall pipes	Montreal	Canada	Urban		0.56	Sauve et al (2012)
Gwynns falls*	Maryland	United States	Mixed	No	0.31	Young et al (2008)
Jones falls*	Maryland	United States	Mixed	No	0.31	Young et al (2008)
Herring run*	Maryland	United States	Mixed	No	0.31	Young et al (2008)

Note: *The results from the sampling locations within a given study were combined to determine the correlation between fecal coliform levels and caffeine concentrations. Therefore, the R^2 values for the sampling locations within a given study were identical.

excessive algae growth, which can lead to low oxygen levels, fish kills, and problems with the drinking water treatment process. Turbidity levels and aquatic life measure the ecological health of the watershed. Prior to 2011, these watersheds were monitored each year. Currently, these watersheds are monitored every 2 years to accommodate the increase in field time needed to comply with the modified collection methods for copper and zinc samples.[21] The City of Durham Stormwater Services Division does not monitor its watersheds for OWCs[20] perhaps due to limited staff and resources.[1]

The North Carolina fresh surface water quality standard for fecal coliform bacteria applicable for class C waters is as follows:

> Fecal coliform shall not exceed a geometric mean of 200 colony forming units (cfu)/100 mL based upon least five consecutive samples examined during any 30 day period, nor exceed 400 cfu/100 mL in more than 20% of the samples examined during such period; violations of the fecal coliform standard are expected during rainfall events and, in some cases, this violation is expected to be caused by uncontrollable nonpoint source pollution. (15 A NCAC 02B.0211)[22]

The City of Durham Stormwater Division does not examine fecal coliform levels in its watersheds by collecting five consecutive samples during a 30-day sampling period but by collecting grab samples each month. Therefore, a 30-day geometric mean is not calculated, which prevents the city of Durham from determining whether their watersheds are meeting water quality standard. The fecal coliform concentrations from the monthly grab samples can be compared to the benchmark in the water quality standard (ie, not exceeding 400 colony-forming units [cfu]/100 mL in >20% of the samples analyzed during such a period).[23] Therefore, the City of Durham Stormwater Division evaluates the health of their watersheds by determining whether 20% of the monthly fecal coliform samples collected during the monitoring year exceed 400 cfu/100 mL.[23]

Why Third Fork Creek Watershed?

Third Fork Creek watershed is located entirely in the city of Durham, NC (Fig. 1). Third Fork Creek watershed contains the second highest population density of the Durham County watersheds, the oldest developed areas in the city of Durham, several educational institutions such as North Carolina Central University and Durham Technical Community College, and several parks and preserved lands.[24] This watershed does not receive treated effluent from wastewater treatment but has a history of suffering from overflowing sanitary sewers[1,18,19,24–29] and stormwater runoff that transport pollutants from lawns, driveways, roofs, parking lots, streets, gutters, and chemicals

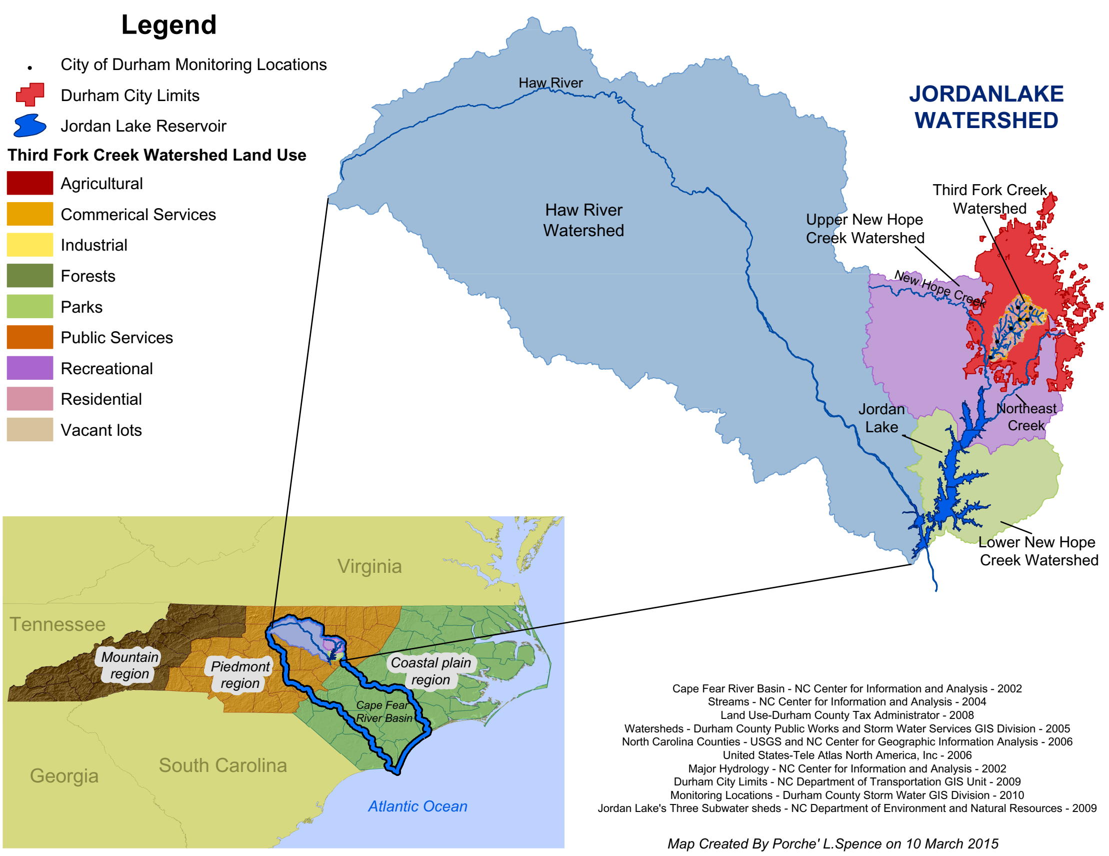

Figure 1. Geographical location of Third Fork Creek watershed and Jordan Lake.

washing off vehicles. Runoff entering storm drains empties directly into the nearest stream.[18]

The City of Durham Stormwater Services Division monitors six locations within the Third Fork Creek watershed biannually and two locations annually.[21] Third Fork Creek watershed has been impaired due to high fecal coliform levels, excessive nutrient concentrations, high turbidity, elevated zinc and copper levels, low dissolved oxygen levels, and poor biological conditions.[30] Fecal coliform bacteria levels are generally higher in the section of Third Fork Creek watershed with the oldest infrastructure.[27] Fecal coliform bacteria levels should not exceed 400 cfu/100 mL in >20% of the samples collected from freshwater systems classified as secondary recreational activities.[22] Figure 2 illustrates the monitoring sites in Third Fork Creek watershed with fecal coliform concentrations exceeding 400 cfu/100 mL in >20% of the samples collected during 2010, 2012, and 2014. Even though the city of Durham has been efficient in locating and repairing sanitary sewer collection systems, untreated human waste from leaking and overflowing sanitary sewers and failing septic tanks continues to pollute this watershed.[1] Figure 2 also indicates that fecal coliform bacteria levels exceeding 400 cfu/100 mL in 20% of the samples persist throughout this watershed.

Third Fork Creek drains into Upper New Hope Creek subwatershed prior to entering into Jordan Lake (Fig. 1). Jordan Lake supplies drinking water to several communities in the Piedmont region of North Carolina. The Upper New Hope Creek subwatershed, including Third Fork Creek watershed, is a contributor to the water quality impairment of Jordan Lake.[31] Third Fork Creek watershed has to abide by the Jordan Lake nutrient management strategy, which is designed to reduce the quantity of nutrients and algae growth in order to meet the chlorophyll A water quality standard set by the State of North Carolina Division of Water Resources.[1] Therefore, a water quality management plan has been developed for the Third Fork Creek watershed to prevent future pollution, identify strategies to improve the water quality conditions, and reduce the quantity of nutrients entering Jordan Lake.[1] The water management plan objectives for stream and drinking water quality are as follows: (1) to improve the water quality and to protect human health and aquatic ecosystems by locating and preventing illicit discharges and preventing sanitary sewers from overflowing during storm events; (2) to reduce the effects of pathogens, nutrients, and toxins transported in storm water runoff on drinking water sources; and (3) to ensure that the Jordan Lake remains in compliance with the water quality

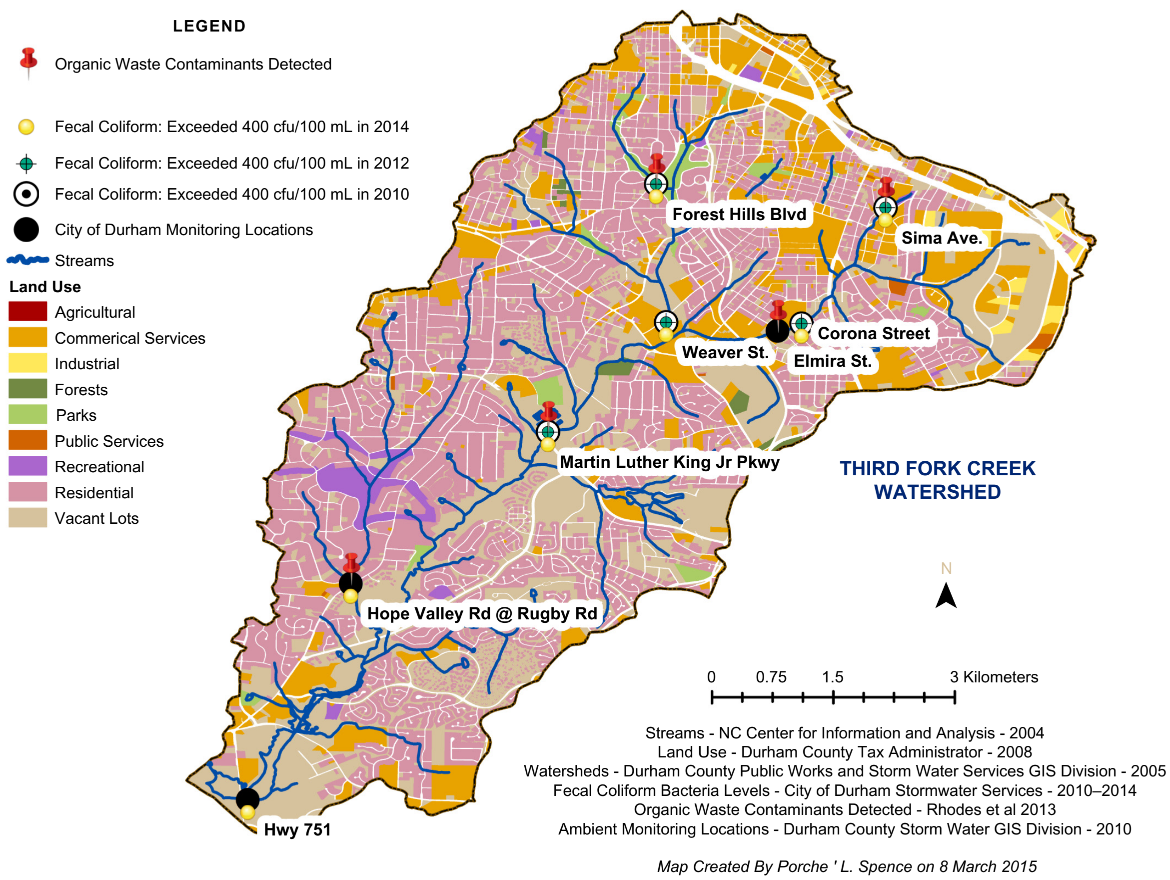

Figure 2. The organic waste contaminants detected sites represent the sampling locations where OWCs were detected in Third Fork Creek Watershed by Rhodes et al (2013).[32] The fecal coliform: exceeded 400 cfu/100 mL sites indicate the city of Durham Stormwater monitoring locations with fecal coliform levels exceeding 400 cfu/100 mL during 2010, 2012, and 2014, respectfully.

regulations and standards set by the State of North Carolina.[31] The Third Fork Creek water management plan did not discuss monitoring OWCs.

OWCs Detected in Third Fork Creek Watershed and Jordan Lake

Rhodes et al.[32] detected a select number of OWCs (stimulants, antioxidants, and steroid hormones) in stream samples collected between June and July of 2010 from the Third Fork Creek. Five of the monitoring locations established by the City of Durham Stormwater Services were used in the study of Rhodes et al.[32] (Fig. 2). The concentrations of OWCs in Third Fork Creek remain unknown because the selected OWCs detected were not quantified.[32] Pharmaceuticals (caffeine, cotinine, and acetaminophen), antibiotics, fire retardants, plasticizers, and pesticides have been detected in Jordan Lake.[7] However, only two samples were collected between April 2004 and April 2005, providing limited information regarding the number of OWCs detected in Jordan Lake.[7]

OWCs have been detected in Third Fork Creek and Jordan Lake; however, these studies consisted of temporary sampling periods, resulting in only a few samples collected during nonstorm event periods. Because Third Fork Creek watershed suffers from overflowing sanitary sewers during storm events, this watershed should be monitored for at least 1 complete year (1) to screen for caffeine and other OWCs and (2) to determine the concentration of OWCs in these watersheds during storm events and dry normal-flow conditions. Using caffeine as a water quality indicator for human waste contamination, OWCs, pathogens,[5,12] and estrogenic activity,[17] as part of the stream monitoring program, would be simple to execute, helpful in identifying sources of contamination, and potentially reduce pollution in urban watersheds.[5] It is recommended that caffeine is monitored regularly along with fecal coliform bacteria levels, nutrients, turbidity, aquatic life, metals, and biological oxygen demand to assess the health of the Third Fork Creek watershed.

Effects of Pharmaceuticals on Aquatic Ecosystems and Potentially on Ecosystem Services

Ecosystem services are goods and services provided by ecosystems that are free of charge to society, but essential for sustaining healthy communities.[33] In urbanized areas, the quality of ecosystem services is influenced by the land use.[34] Urban development jeopardizes water quality and availability, waste processing, recycling, air quality, and other ecosystem services that influence human well-being.[35] Streams provide provisional (clean freshwater and food), cultural (recreation), and supporting (nutrient fluxes and biodiversity) ecosystem services.[34] Recreation is one of the most important urban ecosystem services because it provides residents with a means of relaxation.[34]

Third Fork Creek watershed is classified as an upstream nutrient-sensitive water supply located in a highly developed area that is protected for secondary recreation (boating, wading, and swimming), wildlife, fishing, fish consumption, and aquatic life processes.[36,37] Third Fork Creek's poor water quality condition threatens its intended uses as well as jeopardizes drinking water, aquatic life, and recreation activities provided by Jordan Lake.[1,26] Many residents use Jordan Lake for many recreational activities, such as swimming, kayaking, boating, and fishing. Ecosystem services provided by local streams can have a regional impact by affecting human health and aquatic ecosystems downstream and throughout the watershed.[38]

Moore et al.[39] find that caffeine does not pose an immediate threat to aquatic vertebrates and invertebrates given the concentrations currently detected in streams.[39] However, Rosi-Marshall et al.[4] find that caffeine adversely affected the respiration and function of heterotrophic microbial biofilms found in streams located in Maryland, New York, and Indiana. Stream biofilms, complex communities of algae, fungi, and bacteria interacting and residing on stream rocks serve as the basis for aquatic food chains and as the interface between the physiochemical environment and the biological community. The occurrence of ubiquitous pharmaceuticals in streams can suppress algal growth as well as microbial respiration and function, which potentially leads to negative consequences for aquatic species, such as invertebrates and fish, and vital ecosystem processes.[4] These findings could indicate that pharmaceuticals have the potential to negatively influence provisioning and supporting ecosystem services. Additional research is needed to determine the occurrence and concentrations of caffeine in streams during longer sampling periods,[5] the effect of pharmaceuticals on aquatic organisms, and the interaction between nutrients and pharmaceuticals.[4]

Potential Collaborative Efforts for Monitoring Caffeine

Citizens are encouraged to get involved with finding and eliminating pollution sources. The City of Durham Stormwater Division established a water pollution hotline for citizens to report pollution sources[18] and held public education and outreach activities.[21,30] If the city of Durham does not have the staff or resources to monitor OWCs with traditional water quality indicators, maybe collaborations with citizen volunteer groups, scientists from the US Geological Survey or the US Environmental Protection Agency, and professors and graduate students from local universities can assist with monitoring the Third Fork Creek Watershed for caffeine and other OWCs. Becoming informed about the presence and frequency of OWCs in the Third Fork Creek watershed is important for protecting public health, aquatic ecosystems, and ecosystem services.

Author Contributions

Conceived and designed the experiments: PLS. Analyzed the data: PLS. Wrote the first draft of the manuscript: PLS. Contributed to the writing of the manuscript: PLS. Agree with manuscript results and conclusions: PLS. Jointly developed the structure and arguments for the paper: PLS. Made critical revisions and approved final version: PLS. The author reviewed and approved of the final manuscript.

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