Understanding the Impact of Extracellular Polymeric Substances on Lead Release in Drinking Water Systems

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Supporting Information

ABSTRACT: Lead release in a lead (Pb, anode)—iron oxide ($\alpha$-Fe$_2$O$_3$, cathode) galvanic system was studied under the influence of synthetic extracellular polymeric substances (sEPS). Sodium alginate, bovine serum albumin (BSA), and cytochrome c represented extracellular polysaccharides, proteins, and electrochemically active components, respectively. Microbiologically influenced corrosion was investigated using sEPS and pelleted and resuspended Pseudomonas aeruginosa cells. Relative to the anaerobic inorganic control, Pb release increased by 156, 202, and 198 $\mu$g/L when sEPS was present on the cathode side at 200 mg/L (100 mg/L alginate + 100 mg/L BSA), 400 mg/L (200 mg/L alginate + 200 mg/L BSA), and 200 mg/L with 123.84 mg/L cytochrome c, respectively, under anaerobic conditions. When the cathode was aerated, Pb release increased by 75, 260, and $71 \mu$g/L under the aforementioned conditions, all relative to the aerated inorganic control. When sEPS was instead present on the anode side, sEPS caused localized corrosion on Pb and resulted in higher Pb release than predicted by electric current. P. aeruginosa generally enhanced corrosion; when cells were dosed in the anode side, part of the oxidized Pb was immobilized by cells or organic compounds adhered to the electrodes.

INTRODUCTION

Environmental lead exposure is strongly linked to cognitive deficits in children and cardiovascular disease mortality in adults. While exposure has declined dramatically over the past 50 years due to public health interventions, tap water remains an important mode of exposure. Significantly sources of lead in this context include legacy lead pipes, leaded solder, leaded brass, and galvanized steel pipe. Lead release to drinking water is a complex and dynamic process influenced by water chemistry variables, such as disinfectant type, the availability of orthophosphate or other corrosion inhibitors, the concentration of corrosive anions, and the composition of natural organic matter (NOM). Additionally, galvanic lead corrosion is a significant cause of elevated lead levels in drinking water. Galvanic reactions between lead and other metals, including copper—brass following partial lead service line replacement, have been reported. Corrosion products may also induce galvanic corrosion: one possibility is galvanic interaction between colloidal/particulate iron oxides and the surfaces of lead service lines. These reactions might be prevalent in systems with both lead service lines and corroded upstream iron mains.

Microbiologically influenced corrosion (MIC) is often an important corrosion pathway of iron and copper pipelines, but biofilm has received comparatively little attention as a driver of lead release from lead service lines. In one study of biofilm in lead service lines, bacteria from multiple genera such as Massilia, Bacillus, Sphingomonas, Arthrobacter, Brevundimonas, Microbacterium, Pseudomonas, and Exiguobacterium were detected, and these bacteria are either heavy metal tolerant or capable of surviving in heavy-metal-rich environments; an earlier study of lead pipes recovered from the city of Rochester in NY simply reported the detection of coliform bacteria in the scales. Generally, biofilms in drinking water distribution systems may induce biological corrosion and harbor opportunistic human pathogens such as Legionella pneumophila, Mycobacterium avium, and Pseudomonas aeruginosa. During the Flint water crisis, interruption of corrosion control accompanied the occurrence of Legionella at points of use within the system. These observations suggest that corrosion may promote biofilm growth by depleting disinfectant residuals, and biofilm can in turn influence corrosion by altering the localized conditions at the metal—water interface.

Conventional studies of MIC often focus on microbial metabolisms such as [H] consumption and H$_2$S generation by sulfate-reducing bacteria. However, biofilms are largely composed of extracellular polymeric substances (EPS), including polysaccharides, proteins, lipids, and nucleic acids. EPS can substantially exceed cell volume in drinking water distribution systems. At the interface of metallic pipe/
corrosion products and water, polymeric substances act as the medium through which mass transfer between the sessile microorganisms and their surroundings occurs.\textsuperscript{21} Previously, the functions of EPS have generally been explored in the context of iron corrosion.\textsuperscript{21,22} With regard to lead corrosion, EPS components may form complexes with lead.\textsuperscript{23} It is plausible that EPS components may also be active in a colloidal dispersion of insoluble corrosion products although this is relatively unknown. Since the role of EPS in the corrosion of lead pipelines has not been extensively evaluated, this study aimed to understand the effects of EPS in galvanic corrosion of lead. The influence of model polymeric substances as synthetic EPS (sEPS) and cells of a model opportunistic plumbing pathogen—\textit{P. aeruginosa}—on the galvanic corrosion of lead by hematite was investigated.

\section*{RESULTS AND DISCUSSION}

In drinking water supply systems that contain lead pipes, microbial corrosion on lead surfaces may cause breakdown of the passive corrosion product layer, resulting in lead release.\textsuperscript{15a} With active microbial metabolism, dissolved oxygen (DO) may be gradually depleted at the biofilm and metal interface, leaving a more anaerobic condition close to the lead metal surfaces and a more aerobic condition at the biofilm surfaces. Deposition of corrosion products, such as metal oxides, from the bulk water on or near this corrosion site may lead to complicated galvanic corrosion processes, which were simulated in this study.

\textbf{Effects of Polymeric Substances and Dissolved Oxygen. Polymeric Substances on the Cathode Side.} In the absence of bacterial cells and cytochrome c (Cyto. c), sEPS was a significant predictor of galvanic corrosion, based on a two-way analysis of variance (ANOVA) with DO and sEPS as predictors and theoretically oxidized lead as the response (i.e., Pb\textsuperscript{2+} concentrations equivalent to accumulated coulombs) (Figure S2-A1; sEPS on Fe\textsubscript{2}O\textsubscript{3}: $F_{2,15} = 36.10$, $p < 0.0001$). Compared to their respective inorganic control conditions, sEPS1 on the cathode enhanced average theoretically oxidized lead by 20 and 140\% under aerobic and anaerobic conditions, respectively (Figure 2A,C; sEPS on Fe\textsubscript{2}O\textsubscript{3}). sEPS2 increased average theoretically oxidized lead by 9\% under aerobic conditions but decreased the same parameter by 41\% under anaerobic conditions.
anaerobic conditions. The same ANOVA showed significant interaction of sEPS and DO (Figure S2-A1; sEPS on Fe₂O₃: F₂,15 = 20.00, p < 0.0001), whereas an analysis based on measured lead concentrations showed insignificant interaction (Figure S2-A1; sEPS on Fe₂O₃: F₁,14 = 0.42, p > 0.05). This, the selected levels of sEPS may have affected oxygen diffusion, as described in the next paragraph. Only a fraction of the oxidized lead was recovered from the aqueous phase at pH 7.5−8.5 (Figure 2A,B: sEPS on Fe₂O₃), presumably due to the formation of lead carbonate compounds on lead coupon surfaces. For this reason, electric current more accurately estimates total oxidized lead (blue rings in Figure 2) as compared with total detected aqueous lead (orange rings in Figure 2) in the absence of localized corrosion at the anode.

Previous studies on the effect of EPS on the corrosion of iron or steel often report divergent findings: both corrosion induction and inhibition by EPS have been documented. Corrosion induced by EPS is usually attributed to (1) the formation of a differential aeration cell caused by the uneven distribution of EPS on metal surfaces and (2) encouraged anodic reaction via complexation of oxidized iron. The passivation caused by EPS is often explained by (1) the reduced diffusivity of DO in a viscous organic matrix and (2) stabilization of corrosion products. In this study, lead oxidation was not proportional to the concentration of sEPS under aerobic conditions. This may be explained by restricted diffusion of oxygen at the higher level of sEPS. Observations under anaerobic conditions may be explained by two other interacting processes: reduction of BSA and restricted diffusion of reduced iron species. The measured potential of the cathode in the presence of sEPS1 was between −0.47 and −0.73 V (Figure S3). This overlaps with the potential range for the reduction of disulfide bonds from BSA, −0.45 to −0.65 V, indicating possible breakage of the disulfide bonds on the cathode. The negative current upon contact of sEPS2 with iron oxide during a hematite−hematite galvanic test supports this speculation (Figure 3): the side dosed with sEPS2 accepted electrons from the other side. Although BSA is different from microbial extracellular proteins, disulfide bonds may be prevalent in EPS. Proteins are known to form disulfide bonds through the oxidation of cysteine thiols under the oxidative stress of chlorine species, which are common in water distribution systems. In the presence of sEPS2, the reduction of disulfide bonds was still likely, but binding and accumulation of reduced iron on the cathode surfaces at higher viscosity may have caused an early termination of the cathodic reaction.

Polymeric Substances on the Anode Side. sEPS on the anode significantly affected theoretically oxidized lead, but to a lesser extent than in the corresponding cathode experiments (Figure S2-A1; sEPS on Pb: F₁,14 = 7.14, p < 0.005). When the average theoretically oxidized lead concentrations of the tested conditions and the corresponding control conditions were compared, sEPS1 depressed corrosion by 22 and 29% under aerobic and anaerobic conditions, respectively; sEPS2 had little effect (Figures 1A,C,E and 2A,C: sEPS on Pb). However, some of the measured aqueous lead concentrations were higher than the theoretical values (Figure 2A,C: sEPS on Pb). For example, the measured lead concentrations, 0.82−1.01 mg/L, were approximately twice the theoretical lead level, 0.40−0.62 mg/L, when the cathode was in an anaerobic condition and sEPS2 contacted the anode. This discrepancy suggests the occurrence of localized or non-galvanic corrosion. In a previous work, lead concentrations in excess of predictions based on galvanic current were observed and attributed to localized non-galvanic corrosion. In the presence of free chlorine under continuous flow, the excess lead concentrations that were observed by the authors may be attributed to redox reaction between PbO₂, a
corrosion product, and lead metal. In another study, extracellular polysaccharides from sulfate-reducing bacteria were hypothesized to be responsible for the localized oxidation of steel, though bacterial extracellular polysaccharides are rarely reported as redox active unless they bind redox-active ions, such as Fe (II) or U (VI). Since the lead coupons in this study were acid-washed and alginate is inert to common electron transfer reactions involving metals and metal oxides, the much-higher lead recovery indicates that a distinct non-galvanic corrosion occurred. Size-exclusion chromatography and inductively coupled plasma mass spectrometry (SEC ICP-MS) chromatograms (Figure 4) show that alginate was the major complexing agent of lead in the sEPS mixture of alginate and BSA. Considering the oxidative property of BSA, the observed non-galvanic reaction could stem from the reduction of BSA and the complexation of oxidized lead by alginate. Whether the two reactions occurred simultaneously or sequentially is unknown, but the lead--lead galvanic test suggests that the sEPS demonstrate a strong ability to bind or withdraw Pb (II) from the anode surfaces as opposed to accepting electrons from the anode (Figure 3)—electrons flowed away from the lead electrode that was in contact with sEPS2, indicating the generation of excessive electrons on that electrode through complexation of lead.

Figure 3. Representative chromatograms and UV–vis absorption spectra showing the complexation of metal ions and reduction of cytochrome c. Panel (A) shows the complexation of Pb by sEPS1 (alginate and BSA) on the anode (orange), the complexation of Fe by sEPS1 on the cathode (blue), and the complexation of Pb when Cyto. c (alginate, BSA, and cytochrome c) was on the anode (red). Panel (B) shows the contrast of UV–vis absorption spectra from cytochrome c before and after corrosion tests on the anode and cathode in which anaerobic or aerobic states the condition on the cathode side and those after the colon indicate the location of Cyto. c.

Effect of Dissolved Oxygen. When the corrosion under aerobic and anaerobic conditions is compared in terms of the theoretically oxidized lead, the effect of DO was positive and statistically significant (Figures 2A, C and S2; sEPS on Fe (II), F(1,15) = 124.21, p < 0.0001 and sEPS on Pb, F(1,14) = 156.60, p < 0.0001). An ANOVA on measured aqueous lead concentrations reached the same conclusion. For instance, when the sEPS contacted the cathode, the aerobic condition yielded oxidized lead ranging from 0.36 to 0.74 mg/L, while the anaerobic condition generated 0.27–0.40 mg/L lead. The measured potential of the cathode was approximately −0.47 V with DO and declined to approximately −0.66 V under anaerobic conditions, bringing a dramatic drop, from 0.28 to 0.09 V, in the driving force of the galvanic corrosion (Figure S3). Oxygen is one of the main electron acceptors in the corrosion of metallic piping materials. In this study, DO reduction was expected on the cathode surfaces by electrons originating from lead oxidation. The stepwise transfer of electrons from lead to iron oxide and finally to oxygen is in line with the electron-conducting activity of iron–sulfur compounds in sulfate-induced iron corrosion, as both iron compounds are semiconductive.

Galvanic Corrosion in the Presence of P. aeruginosa. P. aeruginosa was employed to investigate corrosion with cell adhesion on the electrodes. The duration of tests here allows cell adhesion, which often requires 20–40 min, but is short enough that biofilm formation via the consumption of sEPS was minimized. When bacterial cells were dosed with sEPS (Figure 1B,D), the interaction between sEPS and DO was not significant in ANOVA with either predicted or observed lead release as the response (Figure S2A). The main effects of DO and sEPS on lead corrosion were significant, except in the ANOVA with measured lead concentrations and sEPS on the cathode (DO: F(1,13) = 4.02, p > 0.05; sEPS: F(1,13) = 1.82, p > 0.1). Here as well, theoretically oxidized lead was considered a better metric of galvanic reactions. Cell lysis occurred during the test: the optical density at 600 nm (OD600) of the cell suspensions before and after the tests showed decreased cell density at the end (average 2 × 10⁸ CFU/mL), while soluble chemical oxygen demand (sCOD) measurement showed 51–119% increase in soluble organics. The released intracellular compounds during cell lysis, an essential part of natural EPS, may have affected the corrosion process.

Generally, corrosion current in the presence of P. aeruginosa was slightly higher and more sustained as compared against tests without the bacterium (Figure 1). When P. aeruginosa cells were on the cathode, theoretical lead oxidation was significantly increased in both aerobic and anaerobic conditions (10–220% increase, Figure 2). Hence, certain intracellular materials, including ions and small molecules, might have facilitated (1) the transfer of electrons on the cathode surfaces to DO or other oxidative compounds and/or (2) the diffusion of reduced iron away from the cathode. When P. aeruginosa cells were on the anode, the corrosion current was similar to those cases when there were no cells; however, the detected aqueous lead concentrations were lower than those cases when cells were absent (sEPS on Pb in Figure 2B,D compared with sEPS on Pb in Figure 2A,C). This was not expected because the pH slightly shifted to the acidic range (7.2–7.6) at the end of test runs, and the decreased pH encourages lead dissolution. This discrepancy implies that more lead ions were immobilized on the anode via complexation with organic compounds/cells adsorbed on the anode. Nevertheless, a conclusion that sessile P. aeruginosa on lead surfaces is capable of impeding lead corrosion and release may not be valid because the P. aeruginosa in this study was not expected to have formed a mature biofilm on the anode. In an active biofilm-covered corrosion site, various other proteins or enzyme cofactors can potentially affect the reaction, and some of them are redox active around the potentials that are relevant to corrosion. Some have been demonstrated to conduct...
electrons in extracellular spaces, such as extracellular redox-active iron–sulfur proteins and extracellular flavins/riboflavins. These observations warrant more studies on the interaction between EPS and cells in lead corrosion.

**Effects of Electrochemically Active Small-Sized Proteins.** Microorganisms secrete electrochemically active molecules during extracellular respiration on insoluble electron acceptors such as iron oxides and manganese dioxide. These oxidized forms of metals are commonly found in the corrosion scales inside lead service pipelines. Therefore, local biofilm-covered anaerobic spots on lead service lines may encourage the growth of microorganisms that are actively involved in the reductive dissolution of oxidized iron, manganese, or even lead. Furthermore, direct oxidation of reduced metal–metal ions by some lithoautotrophic and acetogenic microorganisms has been reported, and these reactions may also occur in some lithoautotrophic and acetogenic microorganisms has been reported, and these reactions may also occur in aqueous lead levels were high, in the range of 1–2.5 mg/L, and exceeded the predicted levels from corrosion current. These observations indicate that 1) galvanic current cannot reveal the effect of cytochrome c and its interaction with DO/cells on the anode and 2) when cytochrome c is in contact with lead, it encourages non-galvanic corrosion. The lead–lead galvanic test with cytochrome c supports the idea that cytochrome c can accept electrons from lead (Figure 3). Although an environmental biofilm actively conducting dissimilatory metal oxide reduction usually contains a fraction of oxidized cytochrome c, microorganisms involved in a corrosion reaction may directly oxidize metal surfaces with the assistance of oxidized cytochrome c. Together with its lead-binding ability (Figure 4A), the current work suggests that electrochemically active proteins, such as cytochrome c, may result in localized non-galvanic corrosion of lead. While a system that is composed of model compounds is less complex than natural biofilm matrices, the results presented here nevertheless imply that biofilm EPS may participate in the corrosion process of lead-made materials. This can happen via complexation of metal ions as well as redox reactions with corrosion products or metal surfaces. These implications, especially the latter, accord with findings from recent microbial corrosion and bioelectrochemical studies. Despite the well-accepted hypothesis of cathodic depolarization or [H]/H2 utilization during the sulfate-driven MIC, direct electron transfer from metal atoms to bacteria through iron and iron–sulfur compounds may occur. These studies showed that sulfate-reducing and methane-generating microorganisms directly extracted electrons from the surfaces of metals or corrosion products. This direct electron transfer might have relied on either cytoplasmic membrane-associated or extracellular cytochrome c. In another case, extracellular hydrogenase or formate dehydrogenase from *Methanococcus*...
maripaludis catalyzed the formation of H₂ or formate on iron surfaces in the absence of cells, and the formation of these reducing equivalents was well correlated to the corrosion process. Additionally, biofilms may trap and accumulate trace amounts of NOM containing redox-active functional groups that resemble quinones; some of these are still oxidative following disinfection and may act as an electron sink in a corrosion reaction. Therefore, during MIC of lead pipelines, commonly observed binding or complexing of metal ions probably takes place in concert with redox reactions between redox-active molecules in EPS and the solid surfaces, especially in a local anaerobic environment away from the bulk liquid. These reactions are relatively independent of traditionally reported galvanic reactions and may significantly influence the dynamics of lead corrosion and release. Future studies on the corrosion of lead pipes at pilot- or full-scale could be designed to address some of the limitations of this study. In particular, the role of biofilm under more representative drinking water conditions that include elements related to a well-developed corrosion scale, corrosion control agent, and a disinfectant residual should be examined. In this way, the synergies observed here between EPS and lead release can have greater application context.

### MATERIALS AND METHODS

#### Experimental Design.

Scanning electron microscopy images from previous studies show that the corrosion scales on lead service line corrosion scales may trap and accumulate trace concentrations of EPS in biofilm or at the biofilm and water interface. Since heavy-metal-resistant microorganisms mostly inhabit copper and lead pipelines, the lower end of a commonly studied EPS concentration range (a few hundreds to 10 000 mg/L) was selected. The concentration of cytochrome c was determined according to a previous study on Geobacter spp. Microorganisms have been shown to occur both on top and beneath corrosion scales and to induce pitting corrosion in copper and iron pipelines. Since MIC in lead corrosion has rarely been reported, MIC of copper was deemed analogous to MIC of lead. Therefore, bare lead coupons were applied in this preliminary study of the effect of EPS on lead corrosion; corrosion scale was allowed to develop over the 8 h test period. The control tests in the base electrolyte with either aerobic cathode or anaerobic cathode were labeled sEPS0 (i.e., no sEPS), and the tests carried out with bacterial cells were denoted XX + cells.

Two-way ANOVA was conducted to compare the main effects of DO (anaerobic and aerobic) and sEPS (sEPS0, sEPS1, and sEPS2) and the interaction effect between DO and sEPS on galvanic corrosion. In the presence of cytochrome c and cells, three-way ANOVA was applied to examine the main effects of DO (anaerobic and aerobic), cytochrome c (sEPS1 and Cyto. c), and bacterial cells (with and without cells) plus the interactions among these three factors; all tests were conducted at a significance level of 0.05. Two sets of data were analyzed by ANOVA: the measured total aqueous lead concentrations and the theoretical lead release as predicted by Faraday’s law from galvanic current (eq 1). Wolfram Mathematica 11.3 was used for comparisons and for figure preparation.

\[
C = \frac{M \times \int I \, dt}{z \times F \times V}
\]

where C is the equivalent (or theoretical total released) lead concentration in g/L; M is the molar mass of lead, 207.2 g/mol; I is current in Ampere; t is the elapsed time in second; z is the charges of lead ions, which is 2 here; F is the Faraday constant, 96 485 C/mol; and V is the volume of the base electrolyte in each chamber, 0.175 L.

**Galvanic Cells.** A double-chamber electrochemical reactor (Figure S1) was used in this study. Spark plasma sintered α-Fe₂O₃ disks and lead coupons (Ames Metal Products Co.) served as the cathode and anode, respectively. For each test run, a pair comprising one Fe₂O₃ disk and one lead coupon was randomly selected from four identical Fe₂O₃ disks and

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**Table 1. Experimental Design of the Lead—Iron Oxide Galvanic Corrosion**

| Control Tests* (Inorganic Controls) | Cathode (Fe₂O₃) | Anode (Pb) |
|-------------------------------------|-----------------|------------|
| Control tests*                     | Anaerobic       | Anaerobic  |
| Tests on sEPS*                      | Anaerobic       | Anaerobic  |
| Tests on sEPS in the Presence of Bacterial Cells* | Anaerobic       | Anaerobic  |

*Note: each side contains 175 mL of base electrolyte; *triplicate or more; # duplicate.

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three identical lead coupons. The half-cells (250 mL/side) were each made from a media bottle, and they were connected via a salt bridge (2.5% of agar and 3 mol/L KCl). The body of the salt bridge was a 32.5 cm-long MasterFlex #16 silicone tube. The electrode and the external measurement circuit were connected using an alligator clip and titanium wires (0.051 in. diameter, McMaster Carr). The base electrolyte (pH ≥ 7.5) was 60 mg/L sodium bicarbonate in ultrapure water; the pH in the anode chamber increased after test runs but was always below 8.5, while the pH in the cathode chamber varied little. When cells were present in the electrolyte, the pH at the end of the reactions was in the range of 7.2−7.6. Two extra lines made of MasterFlex #14 pump tubing were added to allow gas exchange. Nitrogen sparging (Air Liquide, 2 L/min, ≥30 min) was applied to create the anaerobic condition. The corrosion current was recorded by a digital multimeter (PeakMeter MS8236). Electrode potentials were measured against Ag/AgCl electrodes (BME 8 W, BioMed Products Inc), and details are available in the Supporting Information (Figure S3). Fresh stock solutions of sEPS (100× concentrated) were prepared every 2 weeks and stored at 4 °C. Before a test run, the sEPS were added by mixing the stock solutions with the base electrolyte. Flakes of cytochrome c were dissolved in the base electrolyte when needed. Thin films of polymeric substances were allowed to form through the partitioning of sEPS components between the liquid and solid phases. As a control, the effect of chloride on galvanic corrosion was also evaluated (Figure S4).

To oxidize the reduced portion of the Fe₂O₃ disks after each test, the disks were thoroughly rinsed with water, dried at 102 °C, and then baked at 750 °C for 3 h.⁴⁹ Lead coupons were immersed in dilute nitric acid for 10 min and then rinsed with ultrapure water before each test. Lead is known not to form corrosion scales in dilute nitric acid.⁵⁰ When necessary, the coupons were polished with 320-grit sandpaper. After each test, the electrodes were removed from the solutions, and 4 mL of trace-metal-grade nitric acid was added to desorb lead from the glass bottle surfaces; the bottles were sealed and stored at 4 °C for at least 24 h before analysis. When sEPS were present, nitric acid digestion (2 mL HNO₃ + 2 mL 30% H₂O₂ + 15 mL sample, 105 °C and 2 h) was applied to disintegrate the alginate flocs. For electrolytes with suspended cells, sCOD and OD600 were measured before and after the test run were quantified by OD600. Average cell density in the electrolyte at the beginning of the tests was 4 × 10⁸ CFU/mL according to a correlation between the OD600 and the heterotrophic plate count.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02363.

Corrosion cell used in this study, interaction plots of ANOVA tests, redox potentials of anode and cathode at various conditions, a control test, and UV204 absorption spectrum for peak identification in SEC ICP-MS (PDF)

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Notes

The authors declare no competing financial interest.

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