

Effect of Turbulence on Phosphorus Release from Estuarine Sediment

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Abstract

Phosphorus (P) is an essential element for growth in aquatic ecosystems but the dynamics of phosphorus cycling within catchments is poorly constrained. The aim of this study was therefore to develop analytical tools to investigate the release of inorganic and organic phosphorus species in rivers and estuaries during resuspension events such as storm, wind and tidal induced turbulence. To achieve this aim, laboratory simulations using a mini-annular flume coupled with segmented flow analyser detection were performed. To collect SPM (suspended particulate matter), a specially designed specimen box was deployed in the River Tamar (Devon, UK). Inorganic and total phosphorus were determined using segmented flow analyser methods adapted for use with acidified persulfate digests. The segmented flow analyser had a detection limit (3 s.d.) of $0.53 \mu\text{g P L}^{-1}$ for inorganic P and $1.5 \mu\text{g P L}^{-1}$ for total P. The mini-annular flume provides a suitable method for laboratory simulations, e.g. we managed to get low blanks and good experimental reproducibility, and are also able to see changes in P species within analytical precision. Results showed that increase of shear stress (or SPM) caused release of inorganic P from sediment. This could be used as a fact to build a model to study P dynamics during resuspension events in the river and estuaries environment.

Keywords

Phosphorus, Sediment-Water Interface, Transformation

1. Introduction

Phosphorus is an essential element for growth in aquatic systems and is fre-

quently the limiting nutrient in freshwaters and some marine waters. Although the effects of eutrophication are well known, the processes and mechanisms of phosphorus release from different reservoirs are poorly understood [1]. Dissolved inorganic phosphorus (DIP) is the most important form of phosphorus because it can be directly taken up by phytoplankton; dissolved organic phosphorus (DOP) (e.g. phospholipids, phytic acid, ATP) usually cannot be directly utilized by phytoplankton, but can be transformed into a bioavailable inorganic form by physical, chemical or biological processes [2]. Sediment represents both the largest sink and the largest source of P in aquatic systems [3] and the behavior of particle-associated molecules is closely linked with particle dynamics. Therefore, increased suspended particulate matter (SPM) concentrations during turbulent episodes in rivers and estuaries could enhance the release of DIP and DOP into the water column.

The aim of the work described in this paper was to use a mini-annular flume to investigate the effect of turbulent resuspension events (e.g. wind, storm and tidal induced turbulence) on the release of phosphorus species from sediment under controlled laboratory conditions. The specific objectives were to: apply an *in situ* sedimentation basin sampler in the Tamar Estuary to collect SPM; physically and chemically characterize Gunnislake SPM and Calstock surface sediment; determine the concentrations of DIP and DOP released by resuspended Tamar Estuary sediments under different shear stresses (turbulence) and in different water bodies; assess the environmental factors affecting P transfer between sediment and the water column in rivers and estuaries.

2. Experimental

Surface sediment, suspended particulate matter and water were collected from the Tamar Estuary which is a typical, turbid macrotidal estuary for which extensive background water quality data are available. The Tamar Estuary drains an area of 590 km². The length of the estuary, from Gunnislake (the tidal limit) to the mouth of the estuary in Plymouth Sound is 31.5 km. The geology of the region is mainly composed of underlying slate, limestone and grit [4]. Estuarine flushing time is typically one day in winter, when instantaneous flow can exceed 38 m³·s⁻¹ [5], increasing to one week in summer when flows can be as low as 5 m³·s⁻¹. Classification of the Tamar Estuary based on the type of mudflats shows that the system can be sub-divided into two areas: Calstock to Gunnislake (macro with very steep slope) and South Hooe-Weir Quay near river Tavy (macro with low slope) [6].

A 1 kg scrape sample of deposited surface sediment (top 10 mm) was collected from the Tamar Estuary bed at low tide (15:45, 17th October 2007) off a slipway at Calstock, Devon (SX 436 684). An acid-washed plastic scoop was used and the sample was transferred into a high density polyethylene (HDPE) container and stored frozen at -20°C until use.

A sedimentation basin particle sampler (SBPS), supplied by Dr Matthias

Ricking from the Free University of Berlin, was used to collect resuspended particles (kg amounts) for characterisation and experimentation. Before deployment the SBPS sampler was soaked in 0.5% m/v detergent (Nutricon), rinsed thoroughly with ultra high purity (UHP) water and air dried. The SBPS was deployed with the inlets facing upstream at a depth of ~1 m at a riverine sampling station near Gunnislake (SX 426 725) for 2 - 4 week periods during the winter. Samples were then transferred from the SBPS into HDPE bottles using an acid washed plastic scoop. The sample slurries were then frozen at -20°C until use. The sedimentation basin system consisted of a sedimentation unit and a filtration unit. River water was routed into the sedimentation basin via inlet holes and slowed down by the blades and SPM was deposited in the sedimentation basin by gravitational settling.

Experiments were performed in a turbulent water column [7] created by a mini-annular flume (Figure 1). The annular flume was specifically constructed to enable rapid sample removal for chemical analysis and has been used previously in physical cohesive sediment experiments [8]. It was fabricated from gel-coated fibreglass with an outer diameter of 1.2 m, a channel width of 0.1 m and a maximum depth of 0.15 m. The channel section holds a nominal fluid volume of 45 L. The detachable roof and ring components were machined from 10 mm thick Perspex sheets.

The annular ring was suspended from the roof section by six M8 stainless steel threaded rods. The motor configuration to drive the flume annular ring comprised a 370 W single-phase electronic 230 V 2-pole AC motor with a maximum rotational rate of 3000 rpm. The motor was mounted vertically with the drive-shaft connecting into a specialist reduction gear box, to which the flume roof could be attached.

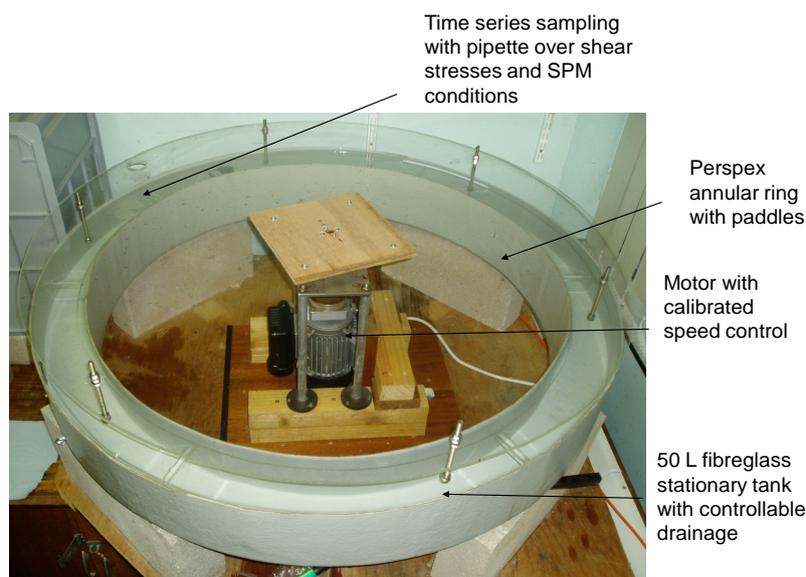


Figure 1. Mini-annular flume.

In each experiment, slurry (Calstock and Gunnislake) was added to the flume channel and incrementally increased levels of shear stress were applied. Both the shear stresses and slurry concentrations applied were within the ranges observed in the Tamar Estuary [4]. The following sequence of events was then performed to simulate the varying physico-chemical conditions (resulting from changes in shear stress) in a macrotidal estuary within the timescale of one complete tidal cycle:

- 1) Take T_0 sample with syringe, add sediment, stir for 30 s (shear stress 0.91 N m^{-2}), equilibrate for 1 h and take T_1 sample.
- 2) Apply a shear stress of 0.06 N m^{-2} for 30 min, turn off motor, immediately take T_2 sample.
- 3) Repeat step 2 for three more shear stresses ($0.35, 0.60, 0.91 \text{ N m}^{-2}$, $T_3 - T_5$ samples).
- 4) Turn off the motor and leave for 18 - 24 h to equilibrate, then take T_6 sample.
- 5) Repeat step 2 for the four shear stresses ($T_7 - T_{10}$ samples).

Water was sub-sampled throughout each run to measure changes in DIP and DOP in filtered water column samples. Two matrices were chosen for the mini-flume experiments. UHP water and artificial seawater (ASW), to mimic DIP and DOP release into pristine end members of an estuarine system.

3. Results and Discussion

The Calstock surface sediment and Gunnislake SPM had similar particle size distributions but the Calstock surface sediment had a higher percentage of particles in the larger size range ($>60 \mu\text{m}$) as would be expected for surface sediment compared with SPM. The Calstock surface sediment also had a higher density than Gunnislake SPM ($326 \text{ g}\cdot\text{L}^{-1}$ compared with $141 \text{ g}\cdot\text{L}^{-1}$). The organic content of Gunnislake SPM was 16% (m/m) and the IP and OP content were $830 \mu\text{g}\cdot\text{g}^{-1}$ and $690 \mu\text{g}\cdot\text{g}^{-1}$ respectively. 160 mL of the Gunnislake SPM slurry were added to the flume to give an overall particle concentration of $0.5 \text{ g}\cdot\text{L}^{-1}$. The SPM concentrations were in the range $0 - 400 \text{ mg}\cdot\text{L}^{-1}$, which are typical of concentrations found in the Tamar Estuary ($40 - 300 \text{ mg}\cdot\text{L}^{-1}$ Langston *et al.*, 2003), and the SPM concentration increased linearly with shear stress ($R^2 = 0.97$). A t-test showed no significant difference of SPM concentration at each sample time among experiments ($P = 0.24$), thus there was broadly no significant difference among the suspension of the SPM used in each experiment and hence the flume experiments were comparable. The SPM concentration in the water column was therefore directly related to the shear stress applied. During the 18-hour rest period the SPM concentration decreased to $<10 \text{ mg}\cdot\text{L}^{-1}$ in each experiment.

3.1. Phosphorus Release from Sediment and SPM to UHP Water

Figure 2(a) and Figure 2(d) show the SPM concentrations at each sampling

time throughout each experiment. **Figure 2(b)** and e show the release of DIP from both Calstock surface sediment and Gunnislake SPM. The highest release was approximately $35 \mu\text{g P L}^{-1}$ from both sediments, but the initial release (T_0 to T_1) from Calstock surface sediment contributed 66% of the total DIP released, compared with 31% for Gunnislake SPM. Since DIP contributions from the pore waters were $<0.6 \mu\text{g P L}^{-1}$ in the 45 L flume volume, the initial P release was due to desorption from the sediment/SPM [9]. Therefore the sediment type can influence the initial DIP release within a time of 30 s. There was a linear correlation between the DIP and SPM concentrations in both the Calstock and Gunnislake experiments from $T_1 - T_5$ ($Y = 3.198X + 21.34$, $R^2 = 0.99$ and $Y = 4.979X + 6.592$, $R^2 = 0.98$ respectively), which indicates a simple desorption process based on sediment suspension [10]. The sensitivity (slope) decreased on the second day ($T_6 - T_{10}$) of each experiment because at T_6 there was a higher starting DIP concentration than at T_0 . Therefore, a general conclusion is that more DIP becomes available during and following turbulent events.

From T_5 to T_6 , the flume system was left unstirred for 18 h to allow re-equilibration of the system. The majority of the sediment/SPM resettled during this period but the DIP concentration only decreased by approximately 8% in the water column in both systems (**Figure 2(b)** and **Figure 2(e)**). Therefore, re-adsorption of DIP was limited. It is possible that the 8% loss of P was due to biological uptake, rather than re-adsorption, but this is less likely because of the

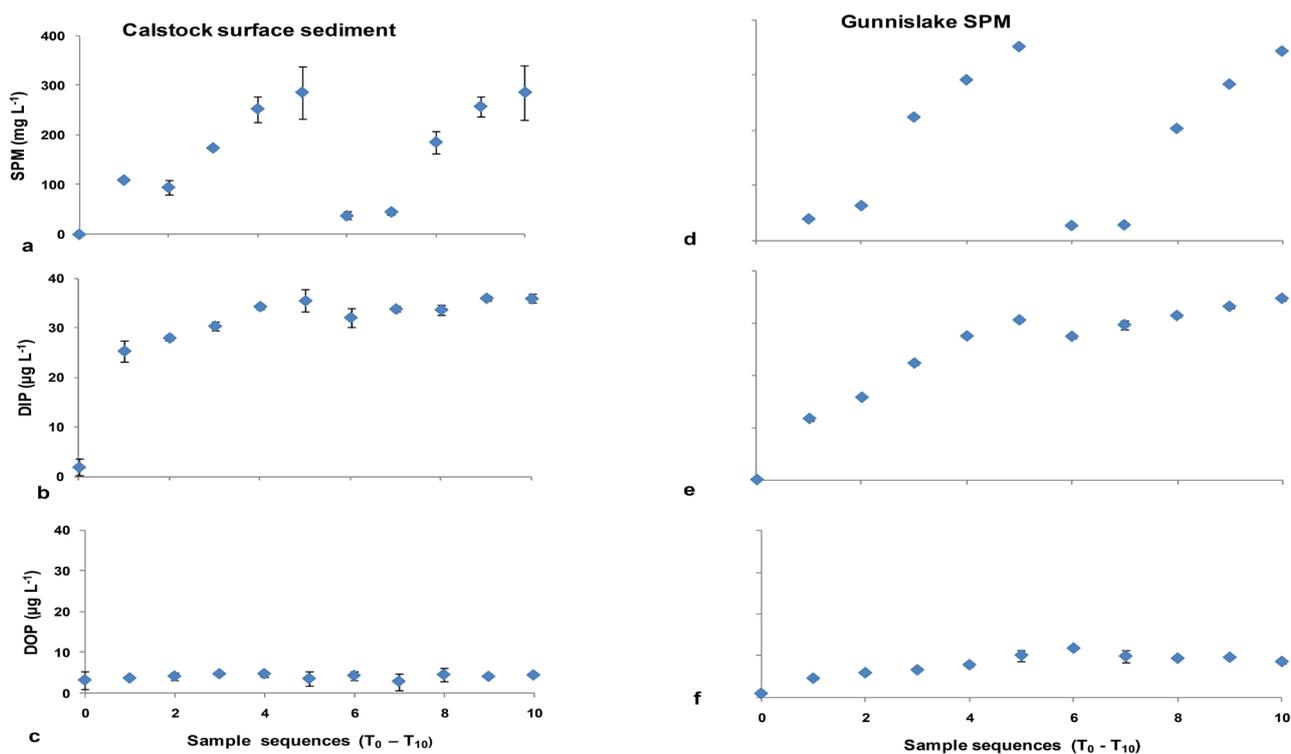


Figure 2. P release from sediment to salinity 0 UHP water. (a)-(c) show SPM, DIP released and DOP released respectively, from $0.5 \text{ g}\cdot\text{L}^{-1}$ Calstock sediment. Error bars represent ± 1 s.d. for duplicate experiments, samples analysed in triplicate ($n = 6$). (d)-(f) show SPM, DIP released and DOP released respectively, from $0.5 \text{ g}\cdot\text{L}^{-1}$ Gunnislake SPM. Error bars represent ± 1 s.d. ($n = 3$).

experimental conditions used. The results suggest that P released from sediment/SPM during turbulent events will remain in the water column for a significant (>18 h) period in a bioavailable form, which has important implications for biomass uptake and growth.

Figure 2(c) shows that there was negligible DOP release from the Calstock surface sediment. Therefore, DOP release from this sediment was not significant over the timescale of a tidal cycle. However, **Figure 2(f)** shows that there was a rapid initial release of DOP into the water column from Gunnislake SPM and release continued up to the maximum concentration observed of $11.8 \mu\text{g}\cdot\text{L}^{-1}$ at T_6 . The pore water contained negligible DOP, thus it can be concluded that the DOP desorbed from the SPM. From $T_6 - T_{10}$ the DOP gradually decreased to $8 \mu\text{g}\cdot\text{L}^{-1}$, possibly due to re-adsorption onto SPM [11], precipitation (e.g. with Fe [12], and/or Mg and Ca [13]; ligand exchange and/or hydrolysis [12] [14] [15] [16]. These contrasting results show that the nature of the sediment/SPM is a key factor that determines DOP release into the water column as a function of shear stress. Gunnislake SPM had a higher OP content than Calstock sediment, which was an important factor in the release of DOP.

3.2. Phosphorus Release from Sediment and SPM to Artificial Sea Water

Calstock SPM increased to $380 \pm 21 \text{ mg}\cdot\text{L}^{-1}$ at the maximum shear stress, whilst Gunnislake SPM increased to $350 \text{ mg}\cdot\text{L}^{-1}$. The SPM concentration from both experiments decreased to $0 - 10 \text{ mg}\cdot\text{L}^{-1}$ after 18 h resting time and there was negligible difference ($T_0 - T_5$, $P = 0.93$; $T_6 - T_{10}$, $P = 0.90$) between Calstock and Gunnislake SPM concentrations.

Calstock surface sediment and Gunnislake SPM released 27 and $29 \mu\text{g P L}^{-1}$ of DIP, respectively, over the course of the experiment (from 33 to $60 \mu\text{g P L}^{-1}$ in the Calstock experiment and from 37 to $66 \mu\text{g P L}^{-1}$ in the Gunnislake experiment). Unlike the UHP water experiment, the initial release after 30 s of shear stress applied was small and represented only about 11% of the total DIP release from Calstock surface sediment and 12% from Gunnislake SPM. The DIP concentration did not change significantly (Calstock: $P = 0.43$; Gunnislake: $P = 0.52$) during the 18 h rest period from T_5 to T_6 , possibly because the high ionic strength of the ASW did not favour re-adsorption of DIP onto SPM, *i.e.* [DIP] released > [DIP] re-adsorbed under saline conditions [17]. The initial releases of DIP and DOP from Calstock surface sediment were smaller as a % of sediment IP and OP concentration than from Gunnislake SPM, which suggests that the sediment type influences the initial DIP and DOP release.

Interpretation of the DOP data (**Figure 3(c)** and **Figure 3(f)**) is complicated by a very high DOP background signal in the ASW; about $40 \pm 3 \mu\text{g}\cdot\text{L}^{-1}$ in the Calstock experiments and $27 \pm 1.2 \mu\text{g}\cdot\text{L}^{-1}$ in the Gunnislake experiments. The different DOP concentrations in these experiments were due to the use of different salts. Despite a significant initial release of DOP from the Gunnislake SPM (from 27 to $37 \mu\text{g}\cdot\text{L}^{-1}$), there was no significant release of DOP from either

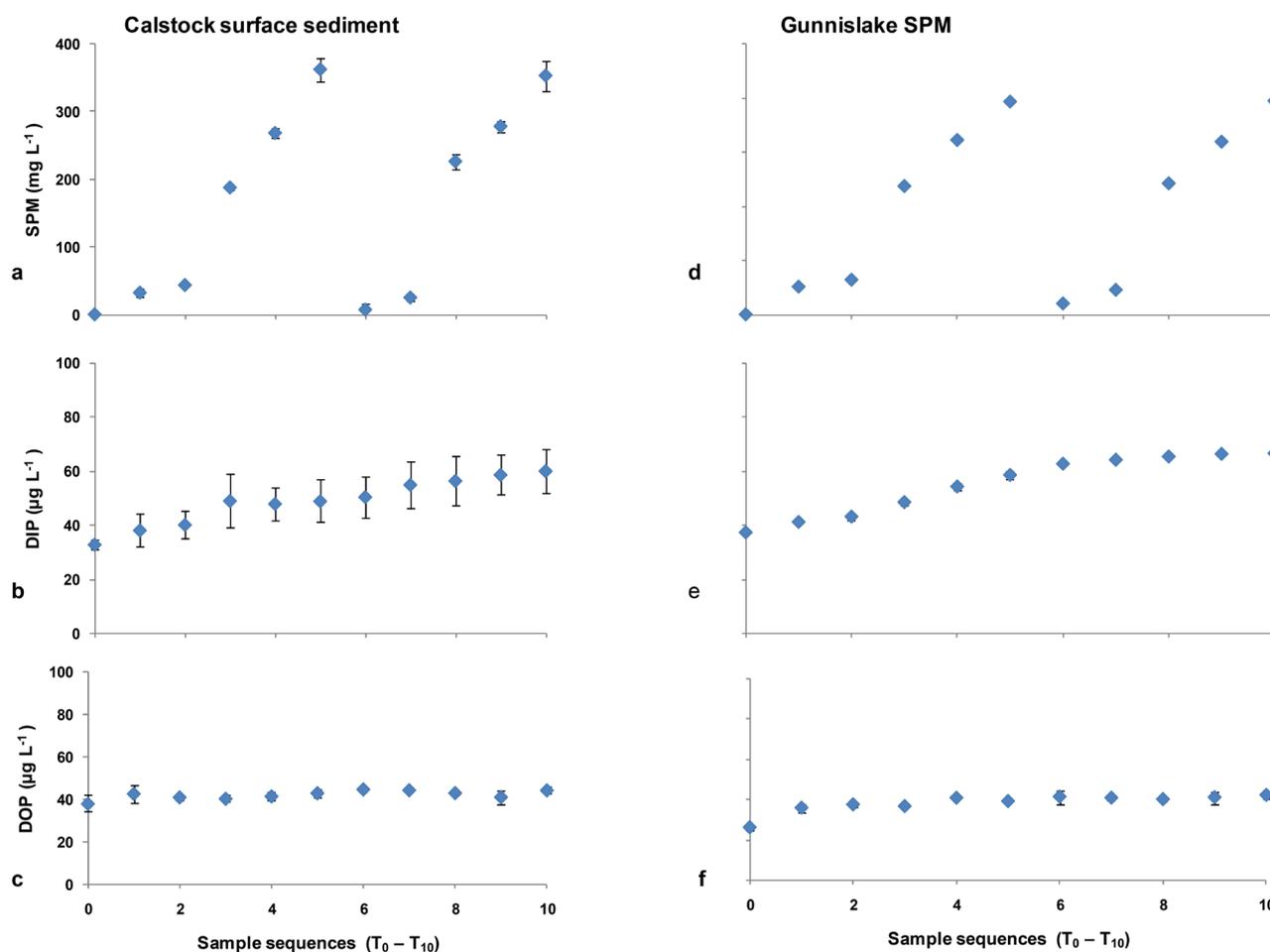


Figure 3. P release from sediment to salinity 35 UHP water. (a)-(c) show released SPM, DIP and DOP concentrations respectively, from $0.5 \text{ g}\cdot\text{L}^{-1}$ Calstock sediment in 45 L of salinity 35 UHP water. Error bars represent ± 1 s.d. for duplicate experiments, samples analysed in triplicate ($n = 6$). (d)-(f) show SPM, released DIP and DOP concentrations in ASW water during mini-flume experiment. Error bars represent ± 1 s.d analysed in triplicate ($n = 3$).

sediment in response to shear stress. There is no evidence ($P = 0.33$) that the DOP concentration decreased after 18 h resting time from $T_5 - T_6$. Again this may be due to the increased ionic strength which reduced the ability of DOP to re-adsorb onto SPM. A t-test shows that the release of DOP was significantly different between Calstock surface sediment and Gunnislake SPM ($P < 0.001$). This suggests that the characteristics of the sediment, *i.e.* particle size and sediment organic phosphorus content play an important role in the capacity of the sediment to release P to the water column. Similar observations have been reported from benthic sea and lake sediment studies [18] [19] [20]. This means that under the same conditions, sediments with smaller particle sizes, higher sediment P concentrations and higher organic content would be expected to release more DIP and DOP into the water column.

4. Conclusion

An *in-situ* sampler has been successfully deployed in the Tamar Estuary to col-

lect SPM and a mini-annular flume has been used to simulate the physicochemical conditions in a macro-tidal estuary over the timescale of one tidal cycle. The results from the flume showed that a high initial release of DIP depended on the nature of the sediment (high IP content) and the low background concentration of DIP in the water column. The applied shear stress had a strong linear relationship with DIP release. High salinity (35) reduced the ability of DIP to be re-adsorbed onto particles, prolonging its bioavailability in the water column. The initial release of DOP was related to the type of sediment, with the sediment containing high OP having a greater initial ability to release DOP. The applied shear stress had no relationship with DOP release. Therefore, in the context of estuarine mixing, turbulence and/or tidal action are/is likely to promote the release of DIP from the sediment, particularly when the sediment has a high IP content and the water column DIP is low, but very little DOP will initially be released to the water body. Any phosphorus released from the sediment is likely to have a long water column residence time as very little re-adsorption back onto the SPM was observed.

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Conflicts of Interest

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

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