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Full Length Research Paper

Phosphorus, copper and zinc leached in lysimeters with red-yellow latosol subjected to different rates of reused swine water and irrigation water

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This study evaluates some micro- elements, phosphorus, copper and zinc leached in lysimeters with red-yellow Latosol under different rates of reused water and irrigation water. This was done for a period of 40 days (August to October 2014) at the initial cycle of cauliflower cultivar 'Verona CMS', in Sinop/Mato Grosso. Reused swine water (0, 50 and 150 m³ ha-1) was applied in one portion before transplanting. Irrigation water of 100, 125 and 150% with crop evapotranspiration potential (ETc) was used in a drip irrigation system daily. Leachate samples were taken at 10, 20, 30 and 40 days after applying the reused water. With balanced leached phosphorus (P), a higher percentage of P retained in the soil was observed, indicating low mobility of this element. The concentrations of copper in the leachate were low at 150 m³ ha-1 rate after the reuse of swine water, at day 20. 150 m³ ha-1 used in the irrigated lysimeters with 100% ETc is a good alternative for vegetable crops with a short cycle (less than 40 days), in Sinop/Mato Grosso, as it does not exceed the limits of the Conama Resolution No. 396/2008.

Key words: Cauliflower, evapotranspiration potential, lysimeters, irrigation.

INTRODUCTION

The use of swine wastewater in agriculture is an alternative source of nutrients and organic matter (Bertol et al., 2010); it grows combined with available elements such as phosphorus (P), copper (Cu) and zinc (Zn) (Smanhotto et al., 2010). Although these elements are essential for the growth and development of plants, when applied in excess, they can become sources of surface and groundwater pollution.

Phosphorus losses can occur via soil surface and subsurface, being potentially greater in sandy soils when subjected to high mineral or organic fertilizers. Another problem associated with P is the eutrophication of surface water that results from superficial runoff and leaching. When leaching occurs in groundwater it may

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affect surface waters (rivers and lakes) due to percolation.

However, the soil has a high phosphate adsorption capacity, and its mobility is lower compared to other nutrients; in some cases, phosphorus loss by percolation in croplands is considered insignificant. Bertoli et al. (2010) showed that phosphorus can be lost with greater sensitivity under reused swine water compared to fertilization with NPK formulation, thus demonstrating that the transport of P is higher under organic sources.

According to Campos (2010), the movement of Cu and Zn in the soil profile depends on the physical and chemical properties of each type of soil and the physicochemical properties of the metal ion. Cu and Zn metals have low mobility in soil profiles and therefore tend to accumulate on the ground surface, reducing its leaching potential. However, excessive use of wastewater can cause losses in the subsurface (Sistani et al., 2008). Campos (2010) emphasizes that pH variation, biological processes, and chemical toxicity of the element and environment also play a fundamental role in the availability and mobility of these metals.

According to Rieuwerts et al. (2006), pH has an influence on cationic metal ions, as these ions are more mobile in acid pH conditions. However, in pH higher than six, these would possibly lead to the dissociation of H^+ of OH groups of the organic matter and Fe and Al oxides. This would thus increase the absorption of the metals with subsequent precipitation, resulting in the reduction of its bioavailabilities.

In this sense, this study aims to evaluate phosphorus, copper and zinc transported in lysimeters with red-yellow Latosol, after the application of swine reused water and irrigation water at different rates.

MATERIALS AND METHODS

Experiment location

The research was conducted at the Federal University of Mato Grosso, Sinop University Campus, located in 11°51'S and 55°29'W, from August to October 2014.

Precipitation occurred during the experiment. The soil of the experimental area is classified as red-yellow Latosol. By the Köppen climate classification, the prevailing climate of the North Central region is Aw (hot and humid tropical). It is characterized by the presence of two well defined seasons: rainy (from October to April) and dry (from May to September); with low annual temperature range (between 24 and 27°C) and average annual rainfall of 1974 mm (Souza et al., 2013).

Lysimeters

For the leaching study, twenty-seven lysimeters were built, and arranged in plate. The distance between each lysimeter was 0.50 m; they were inserted in trenches of approximately 1.20 m depth and 0.30 m diameter (Figure 1). The structure of the lysimeters was hard PVC filled with soil, keeping the same sequence as in the original profile. The chemical and physical analysis of the soils was performed at two depths (0 to 20 cm and 20 to 40 cm) for subsequent filling of the lysimeters.

To fill the lysimeters, an isolated trench was opened at approximately 1.0 m depth; undisturbed samples were taken from every trench at a distance of 10 cm to determine the soil density. The soil profile in the lysimeter was rebuilt to keep the densities of the respective layers. The lysimeter was provided with a collection system (funnel and bottle) positioned at the bottom of the trench, and wherein leachate was stored for later collection.

Chemical and physical soil analysis

In the chemical analysis performed at soil layer of 0 to 20 cm, 2.46 to 32.00 mg dm⁻³ was determined for phosphorus and potassium, and 2.03 and 1.72 cmol dm⁻³ for calcium and magnesium, respectively. The micronutrients, zinc and copper concentrations were 3.90 and 0.59 mg dm⁻³, respectively; the concentration of aluminum was zero, the pH of $H₂O$ was 5.4; cation exchange capacity (CEC - $pH7.0$) was 6.98 cmol dm⁻³ and organic matter content was 38.22 g dm⁻³; for the textural analysis, 462, 250 and 288 g dm⁻³ was identified for the clay, silt and sand, respectively.

At 20 to 40 cm layer, for the same aforementioned variables, 4.61 and 55.00 mg dm⁻³ was obtained; 3.75 and 1.30 cmol dm⁻³, 85 and 0.84 mg dm³ was obtained for P, K, Ca, Mg, Cu and Zn, respectively; pH (H₂O) was 5.9; cation exchange capacity (CEC $pH7.0$) was 8.01 cmol dm⁻³ and organic matter content was 43.00 g dm⁻³; for the physical analysis of the clay, silt, and sand contents, 483, 167 and 350 g dm 3 respectively was obtained.

Chemical and physical characterization of reused water

Swine reused water was collected from a farm in the municipality of Vera/Mato Grosso, after treating with biodigesters.

The chemical and physical characteristics of the waste (reused water) were determined. The following was obtained: 6.85 pH, 4.970 NTU turbidity, electrical conductivity of 1.1 S m^{-1} , total dissolved solids concentration of 7.0 g L^1 , biochemical oxygen demand (BOD) of 283.3, total Kjeldahl nitrogen (TKN) of 308.7, nitrite (NO₂) of 154.7, nitrate (NO₃) of 811.36, total phosphorus (P) of 150.29, zinc (Zn) of 35,90 and copper concentration (Cu) of 10.88 mg L^{-1} .

Implementation of cultivation

After the chemical and physical soil characterization, the supplement chemical fertilizer was calculated following the technical recommendations of Zanuzo et al. (2013) for cauliflower cv. Verona.

In this context, the fertilizer used for cultivation corresponded with 10 g of urea, 15 g of potassium chloride, 20 g of simple superphosphate and 12.5 g of dolomite lime added to the surface of each of the lysimeter before transplanting the seedlings. Transplanting of cauliflower seedlings was performed in (*Brassica oleracea* L.) Verona CMS variety, manually in each lysimeter, in 08/03/2014. The spacing was set at 0.50 x 0.50 m (between plants and rows).

After transplanting, drip irrigation system was installed. Daily irrigation was done for 40 days by using dripped polyethylene hose with 25 cm space between emitters, outflow rate of 7.5 L h^{-1} m⁻¹ and 10 mwc working pressure.

Reused water and water irrigation rates

The reused water was applied once on the surface of the lysimeters, before transplanting the seedlings at three application rates of 0, 50 and 150 m^3 ha⁻¹ yr⁻¹. The percentage rates of water

Figure 1. Construction scheme of the lysimeters and disposal in plat with a variation of water irrigation rates and reuse water rates.

used for irrigation were 100, 125 and 150% of crop evapotranspiration (ETc), obtained from Equation 2.

The rates were determined according to the daily reference evapotranspiration (ET_0) , obtained by the method of Class A Tank. It considers the product between the evaporation of Class A Tank (ECA) and the tank coefficient (Kp), depending on the tank type, weather conditions and its location. With an average value, Kp (0.7795) was estimated for the municipality of Sinop/Mato Gross. The value of the crop coefficient Kc (0.65) was used in the ETc calculation.

$$
ET_0 = ECA * Kp \tag{1}
$$

$$
ET_c = ET_0 * Kc \tag{2}
$$

Where, ET₀ is the daily reference evapotranspiration (L m⁻²); ETc is the evapotranspiration of daily culture $(L \ m^2)$; ECA is the evaporation of the daily class A tank $(L m^2)$; Kp is the coefficient of the tank; Kc is the crop coefficient depending on the development stage.

Collection and samples analysis

Four leachate collections were done (10, 20, 30 and 40 days after application of the wastewater) with the experiment. The leached elements evaluated were P, Cu, Zn ions and H⁺ concentration, and the volume of water applied and collected was monitored. The analyses were carried out in the waste treatment and integrated laboratory for research in chemical sciences, following the methodology described in standard Methods of Water and Wastewater (APHA, 2012).

Evaluation and statistical analysis of data

The experimental design is a randomized block subdivided into a factorial plot of 3 x 3 x 4 (application rates x irrigation water rates x collection times), with three repetitions. The results obtained were statistically evaluated and submitted to analysis of variance and F test; the means were compared by the Scott Knott test at 5% significance. The statistical package used was Sisvar 5.5 Build 82.

RESULTS AND DISCUSSION

Volume of water applied and collected

The highest percentage of ETc generated higher volumes of water used for irrigation, regardless of the season; total volume of 179.73, 224.67, 269.61 L of water led to increments of 0.25 and 50% ETc. However, there was a tendency to reduce the volume applied daily throughout the experimental time for all slides due to the reduction of $ET₀$ (Table 1).

This research was conducted in an area with annual rainfalls of 2,000 mm yr^{-1} , in seven months, from October to April (Souza et al., 2013). Thus, using irrigation water rates (125 and 150%) higher than the 100% ETc is fundamental for the generation of leachate and understanding the movement of P, Cu and Zn, in periods of rainfalls higher than the demand for cauliflower.

As for the volume of water collected, the data showed a significant interaction between the irrigation rate and time, and also between water reuse rate and irrigation rate. In Table 2, it was observed that, the collection volume was greater with higher supply of water for irrigation. In all the collection times, there was a reduction in the volume collected at 125 and 150% ETc rates. This reduction is caused by irrigation since excess water promotes translocation of solid particles of soil (mainly clays), which in turn favors the process of soil storage within the lysimeters, reducing its permeability over time. However, even with the replacement of 100% ETc, the formation of leachate lysimeters was observed.

According to Barros et al. (2009), the determination of the reference evapotranspiration ($ET₀$) by Class A tank provides overestimation even when Kp is regionally calibrated. The total volume collected at 100, 125 and 150 ETc was 8.86, 10.72 and 12.72% of the applied volume, respectively.

	Water irrigation rates (% ETc)*		
Time (days)	100	125	150
10	59.85 ^{Ca}	74.81 ^{Ba}	89.78 ^{Aa}
20	55.18 ^{Cb}	68.98 ^{Bb}	82.77 ^{Ab}
30	30.91 ^{Cd}	38.64 ^{Bd}	46.37Ad
40	33.79 Cc	42.24^{Bc}	50.69 ^{Ac}
Total (L)	179.73	224.67	269.61

Table 1. Volume of irrigation in liters subjected to different water irrigation rates and collection times.

*Means followed by the same lowercase letter in the columns and capitals in rows do not differ by the Scott Knott test at 5% probability.

Table 3. The volume of water collected in liters, submitted to different water irrigation rates and water reuse application rates.

*Means followed by the same lowercase letter in the columns and capitals in rows do not differ by the Scott Knott test at 5% probability.

Table 3 shows the interactions of irrigation water rates and reused water rates, observing that the leached volume increased with an increase rate, regardless of the wastewater percentages applied. In the highest irrigated rate without wastewater, higher leached volumes occurred (10.34 L). The variation of the rates was significant only at 150%. In this case, there was a reduction in the volume collected with increased rates. The total collected volume was also higher for the greater rate (25.72 L).

The difference between the volume of water applied and collected indicates that the rest of the remaining water content was required by the atmosphere for evaporation and/or was stored in the soil pores.

pH

The pH of the samples was assessed by the concentration of H⁺ ions. The transport of ions showed a significant interaction for rate x time and residual water rate x rate. The transport of H^+ ions was significant only for 40 days after the application of wastewaters; it was the highest concentration observed at 150% ETc rate (Table 4).

The pH is acidic throughout the experimental period, although it has been observed that the unfolding time results were only significant at 150% ETc rate. In this case, the mineralization of organic matter and nitrogen, as well as the reduction of soil CEC can cause

Table 4. Concentration of ion H^* (L⁻¹ mg) and pH values (in parentheses) submitted to different water irrigation rates and collection times.

*Means followed by the same lowercase letter in the columns and capitals in rows do not differ by the Scott Knott test at 5% probability. Note: pH values were transformed into H⁺ ions using [H⁺] = 10 γ -pH).

Table 5. Concentration of H⁺ ions (mg L⁻¹) and pH values (in parentheses) submitted to different water irrigation rates and reuse water application rate.

	Reuse water rates (m ³ ha ⁻¹)*			
Water irrigation rates (% ETc)		50	150	
100	0.81 x10 ^{-06 Ab} (6.25)	$0.78x10^{-06}$ Aa (6.18)	4.64x10 ^{-07 Aa} (6.50)	
125	0.67 x10 ^{-06 Ab} (6.31)	$1.70x10^{-06}$ Aa (5.90)	$8.21x10^{-07}$ Aa (6.19)	
150	$2.66x10^{-06}$ Aa (6.06)	1.49x10 ^{-06 Ba} (6.26)	7.57 x10 ^{-07 Ba} (6.40)	

*Means followed by the same lowercase letter in the columns and capitals in rows do not differ by the Scott Knott test at 5% probability. Note: pH values were transformed into H⁺ ions using $[H^+] = 10 \gamma - pH$).

solubilization of H^+ ions, causing its increase in leachate and reducing the pH over time. At 40 days, after the reuse of swine water it was observed that at 125 and 150% there was a higher concentration of H^+ ions.

Table 5 shows the data of the interaction rate x rate, corroborating the fact that the transport of H^+ ions was significant only at 150%, with higher and lower concentrations in the lysimeters that did not receive wastewater and with the highest rates, respectively $(2.66x10^{-6}$ pH value 6.06; 1.49x10⁻⁶ pH value 6.26, and $7.57x10^{-6}$ pH value 6.40). The evaluation of the H⁺ ion transport in the rate x rate interaction indicates it was significant only in the lysimeters withot waste water, which increased with increased rates.

Soil acids interfere with the proper development of roots; being necessary to carry out liming for acidity correction. Thus, acid in soils can be a concern considering that productivity can be affected. In this sense, the rate that provided higher transport of ions out of the zone of the root system of the plant was 150% ETc, observed in 0 rate, with a concentration of H⁺ ions of 2.66x10⁻⁶. Therefore, 50 and 150 m^3 h⁻¹ rates were similar to the effect observed in this interaction with 150% ETc.

Phosphorus

Table 6 shows that phosphorus leached in irrigation water at days 10 and 30, after application of wastewater did not differ statistically. However, P leached significantly increased after 20 days with increased irrigation water percent. At day 40, this behavior differed from other samplings since there was an increase in the leaching of P between 100 and 125% ETc, with a further reduction from 125 to 150% ETc.

P mobility in soil is very low, thus justifying the fact that the losses caused by leaching in arable soils are considered insignificant. The available phosphorus content usually tends to decrease with depth, following the content of soil organic matter. P applied at concentration exceeding the culture of demand can lead to leaching of this element in soil profile.

According to Maggi et al. (2011), evaluating the leachate impacts on drainage lysimeters at different times of collection, under different swine wastewater rates during the soy crop cycle observed quadratic regression models for phosphorus concentrations in the leachate over time. This approach confirms the data found in this work, which despite not having adjusted regression models showed that the P concentrations in the leachate increased and soon after decreased.

At 100 and 125% ETc, after the application of wastewaters at day 20, there were lower concentrations of P in the leachate over 150% ETc. This result indicates that P concentrations subjected with diiferent rates were very heterogeneous with respect to the various collection times.

Table 7 shows the total average concentrations of the phosphorus obtained from the reused water and collected

	Water irrigation rates (% ETc)*			
Time (days)	100	125	150	
10	0.12^{Ab}	0.10^{Ac}	0.28^{Ab}	
20	1.30 ^{Ba}	1.57 ^{Ba}	2.32^{Aa}	
30	0.30^{Ab}	0.31^{Ac}	0.42^{Ab}	
	אח ר'	0.96^{Ab}	0.01^{Bb}	

Table 6. Concentration of P (mg L^{-1}) submitted to different water irrigation rates and collection times.

Table 7. Total P average concentration applied and leached (in 4 collections) and the average nutrient retained in the soil.

Li: water irrigation rate; Ti: reuse water rates; P: phosphorus.

in lysimeters and average nutrient retained in the soil. From the results, a higher concentration of P was leached at 150% ETc; at 0 m^3 h⁻¹ rate, there was a concentration of 8.37 mg L^{-1} and at 100 and 125% ETc, there was an increase of P rates in the leachate. At 150% ETc, a decrease was observed in P leachate concentration due to increased concentration of P.

The P concentration in the leachate was lower than the concentration applied, at a rate of 50 to 150 m^3 h⁻¹ for the three evaluated rates. In the treatment without wastewater, P concentrations in the leachate were observed at the three irrigation water rates, resulting from leaching of existing sources in soil and additional chemical fertilization performed with superphosphate in the experiment.

The balanced P applied and leached in lysimeters showed that most of the nutrient was retained in the soil and, therefore, available for the culture and various irrigation water rates L2 to L3. This led to a reduction of the P leached only in T150, ranging from 5.87 to 4.48 mg, respectively. The results found by Chahal et al. (2011) corroborate with this research since phosphorus and potassium concentrations were observed in the leachate, and are lower than the wastewater concentrations used.

Copper

Table 8 shows Cu concentration in the leachate under various wastewater rates and collection times. Changes were observed in Cu concentration in the leachate only at 20 and 40 days after the application of wastewater. The mobility of Cu in this study was much reduced because the leachable concentrations did not exceed 0.044 mg L⁻ 1 , indicating that part of the metal applied by the effluent was retained in the soil particles inside the lysimeters and/or was absorbed by the used culture.

The copper concentrations obtained were lower as observed by Barros et al. (2003), in which swine effluents subjected to integrated treatment under soil deformed columns were applied. From their study, a leached maximum concentration of Cu with value around 0.06 mg L⁻¹ was obtained. Messias et al. (2007) observed low movement of Fe, Zn and Cu with sewage sludge contents, and Cu concentrations observed in soil without wastewater proved to be uniform in depth. However, in the soils containing swine waste, the authors observed higher metal concentrations in surface layers (0 to 5.0 cm). According to Oliveira and Mattiazzo (2001), low movement may be related to mechanisms of

	Reuse water rates $(m^3 \text{ ha}^{-1})^*$		
Time (days)		50	150
10	0.012 Ab	0.013^{Ac}	0.014^{Ab}
20	0.015 ^{Bb}	0.028^{Ab}	0.021^{Bb}
30	0.015 Ab	0.017^{Ac}	0.012^{Ab}
	0.031 ^{Ba}	0.039^{Aa}	0.044^{Aa}

Table 8. Concentration of Cu (mg L^{-1}) submitted under different reuse water rates and collection times.

Table 9. Zn concentration (mg L^{-1}) submitted to different water rates reuse and water irrigation rates.

	Reuse water rates $(m^3 \text{ ha}^{-1})^*$		
Water irrigation rates (% ETc)		50	150
100	$0.139 B_{\text{bb}}$	0.322 Aa	0.228 ^{Bb}
125	0.201 ^{Bb}	0.306 Aa	0.376 Aa
150	0.486 ^{Aa}	0.385 ^{Ba}	0.349^{Ba}

*Means followed by the same lowercase letter in the columns and capitals in rows do not differ by the Scott Knott test at 5% probability.

adsorption/desorption, precipitation/dissolution, complexation, and redox.

The collection done at day 20 showed an increased concentration of the element at 50 m^3 ha⁻¹, while at day 40, the highest Cu concentrations occurred in soils containing wastewater. There was a noted trend of increased Cu concentration in all the three evaluated rates over time. In this case, the presence of Cu metal regardless of the rate was increased by fertilization cultivation.

According to Messias et al. (2007), from the evaluation of iron, copper, zinc and cadmium movement in soil treated with sewage sludge, higher sludge dose increased the leachates elements concentration, except for copper. In short, the lower Cu concentrations found in the leachate were observed at 0 rates in all collection times. At day 20, there were no differences between the rates of 0 and 150 m3 ha⁻¹, being characterized as the period and rates that provided lower losses of Cu leaching. With observed low concentration of Cu under the experimental conditions and considering that the use of waste can occur for decades, it is necessary to monitor groundwater to ensure metals do not concentrate on the water resource.

Zinc

The zinc concentration showed an increased changes with increasing irrigation rate at 0 and 150 m^3 h⁻¹ (Table 9), ranging from 0.139 to 0.486 mg L⁻¹ and 0.228 to 0.349 $mg L^{-1}$, respectively.

The variation of reused water rates had a significant effect on metal leaching in any of the observed rates, and control plots. Zn leaching was also observed, which might be due to fertilizer incorporated in the soil. Since the plots did not receive an effluent and have a lower organic matter content compared to other lysimeters, the lowest content of organic matter may have provided greater leaching of Zn. The presence of organic matter provides negative charges to the ground, and this in turn acts to maintain the positively charged elements adsorbed (as Cu and Zn), which consequently reduces mobility in the soil profile.

The affinity of metals with soil varies according to the type, amount of organic matter, cation exchange capacity (CEC), pH, clay quantity, mineralogy, and other characteristics; and it is also influenced by characteristics of metals. According to Paganini et al. (2004), a large amount of Zn can be fixed in the organic fraction of the soil, and may be temporarily fixed in microorganisms after the addition of organic matter in the soil. In this context, it is evident that treatment with a replacement of 100% ETc, at 0 rates and 150 m^3 ha⁻¹ led to lower losses of Zn in the cauliflower.

Table 10 shows that the increase in reused water rates applied to the lysimeters was significant only for 40 days, with an increase in Zn losses in the lysimeters under effluent application. This behavior can be explained based on pH (Table 4), while Campos (2010) states that

	Reuse water rates $(m^3 \text{ ha}^{-1})^*$		
Time (days)		50	150
10	0.201^{Ac}	0.213^{Ac}	0.183^{Ac}
20	0.217^{Ac}	0.268^{Ac}	0.279^{Ab}
30	0.402^{Aa}	0.349^{Ab}	0.397^{Aa}
40	0.280^{Bb}	0.521^{Aa}	0.412^{Aa}

Table 10. Zn Concentration (mg L⁻¹) submitted to different water reuse rates and collection times.

low pH values favor lixiviation and availability of metals in the soil. Increase in pH increases the CEC which allows the formation of chelates from the organic material, decreasing its mobility in soil.

According to Messias et al. (2007), evaluating the mobility of micronutrients there were no observed variations in the leaching of Cu and Zn over time (60 days), even for soils with a higher concentration of sewage sludge (75 mg h⁻¹). In this sense, the rate of 150 m3 ha⁻¹ reused water was a good choice for nutrient supply of cauliflower until 30 days. The data evaluated at 40 days showed higher Zn concentrations compared to other evaluated periods. It is noteworthy that the continued application of reused water in the soil as a source of nutrients for crops can cause groundwater contamination, due mainly to changes in the concentrations of Cu and Zn based on the provisions of Conama resolution No. 396/2008 (maximum values of 2.0 and 5.0 mg L^{-1} for copper and zinc, respectively).

Conclusion

The volume of leaching increased with increasing amount of water supplied by irrigation; however, it decreased with increased swine wastewater rates. At 100 and 125% ETc, there were higher concentrations of H^+ ions at day 40, after the application of swine wastewater.

P leached concentrations were higher at day 20 after the wastewater application, regardless of the irrigation water rates. The smaller Cu concentrations found in the leachate were observed at 150 m^3 ha⁻¹ rates at 20 days after application of reused water.

The application of 150 m^3 ha⁻¹ and replacement of 100% ETc can be indicated as a good alternative for short cycled vegetables (less than 40 days), as the concentrations of Cu and Zn did not exceed the limits of Conama resolution No. 396/2008, at this interval, for redyellow Latosol.

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CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.