

THE STUDY OF SURFACE WATER QUALITY IN BUYUK MENDERES RIVER (TURKEY): DETERMINATION OF ANIONIC DETERGENT, PHOSPHATE, BORON AND SOME HEAVY METAL CONTENTS

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(Received 14th Jun 2018; accepted 1st Aug 2018)

Abstract. The Buyuk Menderes basin is very wide and the people living here deal with farming, which increases the importance of the river to the region. The pollution of the river increases because the industry, urbanization and agricultural activities are very intense in the river basin. For this reason, the aim of this study is to map the extent of pollution of Buyuk Menderes River, to detect sources causing pollution in the river and also to suggest solutions for taking necessary precautions. Anionic detergent, phosphate, boron and heavy metal concentrations were determined in water samples taken from Buyuk Menderes River in this study. Mean concentrations of anionic detergent, phosphate, boron, copper, chrome, nickel and lead were found 0.2345 mg l⁻¹, 0.0181 mg l⁻¹, 0.8352 mg l⁻¹, 0.0035 mg l⁻¹, 0.0045 mg l⁻¹, 0.0247 mg l⁻¹, 0.0002 mg l⁻¹, respectively.

Keywords: *surfactant, freshwater, nickel, pollution, water quality classes*

Introduction

Rapid population growth, the spreading of industrialization and mechanization of agriculture, cause pollution of the environment and the waters. Pollution is caused by the inability of people to perceive the importance of environmental conditions for life. Due to uncontrolled domestic and industrial wastes and agricultural activities, it is known that pollution reaches important dimensions in many water resources today (Akın and Akın, 2007). Büyük Menderes River is one of Turkey's important and large river. The River has been polluted by factors such as domestic wastewater, industrial wastewater, excessive, untimely and incorrect use of fertilizer and pesticide. These incidents require investigating pollution levels of the river. For this reason, the aim of this study is to map the extent of pollution of Buyuk Menderes River, to detect sources causing pollution in the river and also to suggest solutions for taking necessary precautions.

There are also detergents among pollutants coming from domestic and industrial wastes to aquatic environments. Detergents are used in general cleaning work. The detergents contain anionic surfactants such as alkyl sulphate or alkyl aryl sulphonate as the main cleaner and other materials that help the cleaning process. Detergents are mixtures of powder, granule, soft consistency or liquid. The detergents cause problems

like disturbing the taste of drinking water, making foam, preventing the water cleaning process, damaging the aquatic organisms by reducing the amount of dissolved oxygen, shortening the aging process of lakes by eutrophication due to phosphate content and damaging the aquatic life (Egemen, 2011).

Approximately half of phosphorus comes from the phosphate in the composition of detergents used in domestic wastewater. 91% of the phosphorus comes from domestic and industrial wastes and 9% from agricultural areas to water resources (Egemen, 2011).

Boron compounds are commonly found in surface and ground waters. The toxic limit value of the boron element is 1.0 mg l^{-1} . This value is determined for plants, animals and humans. Also this value is an acceptable for drinking and irrigation waters and wastewater (Kabay et al., 2006).

Elements like selenium, iron, manganese and cobalt are mixed from the soil to the water. Magnesium, potassium and cobalt are passed from the sea to the air. Toxic elements such as zinc, copper, cadmium, mercury, antimony, arsenic, argon, lead, chromium, selenium mix to the air, water and soil by anthropogenic activities (Samsunlu, 1999).

Materials and methods

The cities of Aydın and Denizli are located in the Aegean region. These cities are important industrial and agricultural centers of Turkey.

The Buyuk Menderes River comes from Afyon, passes through Usak, Denizli and Aydın, reaches to the Aegean Sea. The total length of the Buyuk Menderes is about 584 km and its basin covers $25\,000 \text{ km}^2$ (Boyacioglu et al., 2004).

In this research, six stations were determined in the discharge regions in Buyuk Menderes River (Fig. 1). The coordinates of the stations were showed in the Table 1.

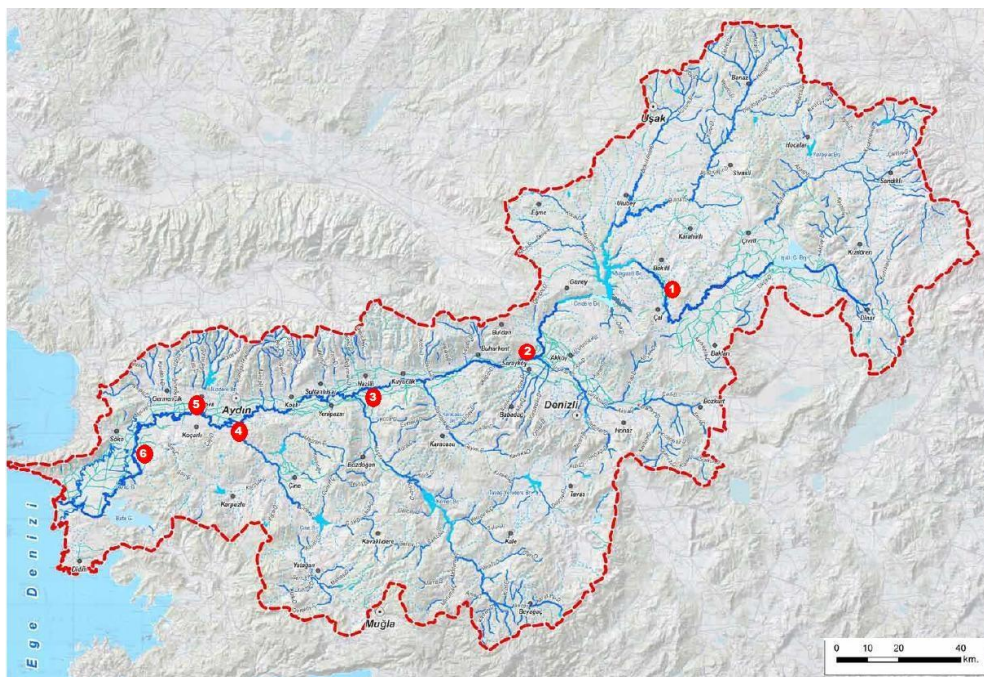


Figure 1. Sampling points

Table 1. *Coordinates of stations*

	Stations	Coordinates
1	Kumralli	38° 6' 1.62" N, 29° 25' 22.26" E
2	Saraykoy	37° 57' 5.73" N, 28° 54' 58.00" E
3	Nazilli	37°52'33.28" N, 28°19'39.26" E
4	Aydın	37°46'56.76" N, 27°50'22.99" E
5	Kocarlı	37°48'36.57" N, 27°42'47.00" E
6	Soke	37°42'26.93" N, 27°28'36.62" E

As a research material, water samples taken from six stations were selected. The water samples were taken on a monthly basis. They were collected between July 2012–June 2013. pH, temperature, dissolved oxygen, total dissolved substance and conductivity parameters were measured by TOA WQC (Water Quality Checker) – 20A.

The method in the determination of anionic detergent is based on the spectrophotometric measurement of methylene blue by being dissolved in the chloroform of the blue colored salt resulting from the anionic surfactant reaction (Anonymous, 1995). Orthophosphate phosphorus is determined by measuring the blue-colored phosphomolybdic acid in the spectrophotometer resulting from the reaction with ascorbic acid, ammonium molybdate and potassium antimony tartrate in acidic environment (Parsons et al., 1984). Determination of the amount of boron is based on the spectrophotometer measurement of the color compound formed with the carmin, a specific reagent of the tube (Hatcher and Wilcox, 1950; Anonymous, 2005). Heavy metal analysis of prepared water samples were made in ICP-MS (Inductively Coupled Plasma – Mass Spectrophotometer).

Statistical analyzes were performed using Windows, Graphpad Prism software package. “One-way Anova” variance analysis was applied to detect whether the amounts of anionic detergent, phosphorus, boron and heavy metals showed significant difference among months and stations. “Tukey test” was applied to detect in which stations and months the significant differences.

Result and discussion

In this study, anionic detergent, phosphate, boron and heavy metal concentrations were detected in the water samples from Buyuk Menderes River that flows from Denizli and Aydın cities centers. pH, temperature, dissolved oxygen, total soluble substance and conductivity parameters were measured. On average, pH 8.24, temperature 15.6 °C, dissolved oxygen 6.04 mg l⁻¹, total soluble substance 426 mg l⁻¹ and conductivity 470 µS/cm were found. The river water in terms of pH and dissolved oxygen parameters 2nd quality and in terms of all other parameters 1st quality in water class were found, according to the Water Pollution Control Regulation (Official Gazette, 2004) (*Table 2*).

These mean values were compared with the Aboveground Water Quality Regulation “Quality Criteria According to Classes in Terms of General Chemical and Physicochemical Parameters of Coastal Waters” (Official Gazette, 2012). The river water was determined as the 2nd quality in terms of pH and conductivity parameters and the 3rd quality in terms of dissolved oxygen parameter (*Table 3*).

Table 2. Quality criteria (Official Gazette, 2004)

Water quality parameters	Water quality classes				This study
	1 st	2 nd	3 rd	4 th	
Temperature (°C)	25	25	30	>30	15.6
pH	6.5-8.5	6.5-8.5	6.0-9.0	6.0-9.0 except	8.24
Dissolved oxygen (mg l ⁻¹)	8	6	3	< 3	6.04
Total soluble substance (mg l ⁻¹)	500	1500	5000	>5000	426
Surfactant (mg l ⁻¹)	0.05	0.2	1	>1.5	0.2345
Boron (mg l ⁻¹)	1	1	1	>1	0.8352
Total phosphorus (mg l ⁻¹)	0.02	0.16	0.65	>0.65	0.0181
Copper (µg l ⁻¹)	20	50	200	>200	3.5
Chrome (µg l ⁻¹)	20	50	200	>200	4.5
Nickel (µg l ⁻¹)	20	50	200	>200	24.7
Lead (µg l ⁻¹)	10	20	50	>50	0.2

Table 3. Quality criteria (Official Gazette, 2012)

Water quality parameters	Water quality classes				This study
	1 st	2 nd	3 rd	4 th	
pH	6-9	6-9	6-9	6-9	8.24
Conductivity (µs)	< 400	1000	3000	> 3000	470
Dissolved oxygen (mg l ⁻¹)	> 8	6	3	< 3	4.94

Mean concentrations of anionic detergent, phosphate, boron, copper, chrome, nickel and lead were found 0.2345 mg l⁻¹, 0.0181 mg l⁻¹, 0.8352 mg l⁻¹, 0.0035 mg l⁻¹, 0.0045 mg l⁻¹, 0.0247 mg l⁻¹, 0.0002 mg l⁻¹, respectively. Anionic detergent, phosphate, boron and heavy metal concentrations mean values were presented in *Table 4*. These concentrations were compared with the Water Pollution Control Regulation (Official Gazette, 2004). Buyuk Menderes River is in the class of less polluted water (2nd class) in terms of anionic surfactant and nickel (*Table 2*). Because the Buyuk Menderes River is close to the settlements, it is thought that the discharges are reaching to the river. Due to domestic waste load, the anionic detergent load increases. The average anionic detergent concentration (0.2345 mg l⁻¹) is below the surfactant concentration, which is considered to be ≤ 0.3 mg l⁻¹ in European Union quality criteria. The average heavy metal values were compared with the heavy metal concentrations allowed in the irrigation waters specified in the Water Pollution Control Regulation Technical Procedures Bulletin (Official Gazette, 1991) and the metal concentrations were found to be low.

According to the One Way ANOVA test, statistically significant differences were not found for heavy metals, pH, dissolved oxygen, total soluble substance and conductivity (p > 0.05) and differences were found for phosphate (p < 0.05). Also the difference among the stations was statistically insignificant (p > 0.05) and the difference among the months was statistically significant (p < 0.05) for anionic detergent and boron amounts (*Table 5*).

Table 4. Monthly average concentrations of detergent, phosphate, boron, copper, chromium, nickel and lead in water samples of Buyuk Menderes River (mg l^{-1} , $\pm \text{SD} < 0.001$)

Months	Detergent	Phosphate	Boron	Copper	Chrome	Nickel	Lead
July	0.1812	0.0117	0.6397	0.0203	0.0010	0.0277	0.0000
August	0.1615	0.0102	0.6733	0.0032	0.0014	0.0317	0.0003
September	0.0583	0.0087	0.3215	0.0012	0.0017	0.0283	0.0004
October	0.2297	0.0228	0.8938	0.0018	0.0009	0.0320	0.0004
November	0.3345	0.0207	1.0681	0.0025	0.0010	0.0557	0.0002
December	0.3260	0.0173	0.3407	0.0037	0.0004	0.0637	0.0001
January	0.1442	0.0182	0.7017	0.0012	0.0008	0.0310	0.0000
February	0.3385	0.0237	0.6259	0.0032	0.0015	0.0051	0.0001
March	0.2227	0.0153	0.8025	0.0018	0.0094	0.0081	0.0002
April	0.2442	0.0245	1.1856	0.0008	0.0169	0.0070	0.0002
May	0.3200	0.0228	1.3985	0.0010	0.0123	0.0036	0.0002
June	0.2528	0.0208	1.3715	0.0019	0.0070	0.0034	0.0002
MEAN	0.2345	0.0181	0.8352	0.0035	0.0045	0.0247	0.0002

Each value is the average of 3 samples from 6 stations with three repetitions (n = 54)

Table 5. The result of the one-way ANOVA test between months and stations

Table analyzed	Between months			Between stations		
	Detergent	Phosphate	Boron	Detergent	Phosphate	Boron
One-way analysis of variance						
P value	P<0.0001	0.0002	P<0.0001		0.0067	
P value summary	***	***	***		**	
Are means signif. different? (p < 0.05)	Yes	Yes	Yes	No	Yes	No
Number of groups	12	12	12		6	
F	8.752	4.071	4.233		3.549	
R squared	0.6161	0.4274	0.437		0.2119	

The differences among the months and stations were determined by the Tukey test. Tukey test results are shown in Tables 6, 7 and 8. Especially in summer, the decline in detergent quantities can be attributed to the decline in population at residential areas as well as the decline in domestic waste loads in these months (Table 6). 50% of the amount of phosphorus in domestic wastewater is caused by the detergent-based phosphates used in houses. As a result, the amount of phosphate has decreased in parallel with the decrease in the amount of detergent (Table 7). Increase in detergent values in winter months, can be considered as an increase of domestic waste load transport to river with the increase of rainfall. Significant boron differences were showed in May and June (Table 8). Boron concentrations were high in May and June. Especially in May and June, together with agricultural irrigation using groundwater resources, abundant amounts of boron in underground waters are mixed in to Buyuk Menderes River.

Table 6. The result of the Tukey test among the months (anionic detergent) (only significant values)

	Jul	Aug	Sep	Oct	Nov	Dec	Jan
Jun			0.0011				
May		0.017	<0.0001				0.0047
Apr			0.0022				
Mar			0.0112				
Feb	0.0185	0.0043	<0.0001				0.0011
Jan					0.0015	0.003	
Dec	0.0428	0.0111	<0.0001				
Nov	0.0244	0.0059	<0.0001				
Oct			0.0067				

Table 7. The result of the Tukey test between months and stations (phosphate) (only significant values)

	Aug	Sep	St 1	
May		0.0232	St 6	0.0182
Apr	0.0205	0.0063	St 5	0.0445
Feb	0.0378	0.0123	St 3	0.0058
Oct		0.0232		

Table 8. The result of the Tukey test among the months (boron) (only significant values)

	Sep	Dec
Jun	0.004	0.0051
May	0.0028	0.0036
Apr	0.0384	0.0474

When we compared the values with the results of other studies which investigated anionic detergent, phosphate, boron and heavy metal levels of Buyuk Menderes, we measured similar values in present study. In the study in Buyuk Menderes River, average copper 0.011 ppm, chromium 0.012 ppm, nickel 0.01 ppm, lead 0.011 ppm, iron 0.006 ppm, mangan 0.09 ppm, zinc 0.051 ppm, cobalt 0.08 ppm were found (Akçay et al., 2003). The average boron value of the Buyuk Menderes River was determined as 0.6 mg l⁻¹ in another study. According to all parameters, it was stated that the water was mostly polluted in Saraykoy and Nazilli regions (Kucuk, 2007). Boron content was found to be between 0.33 and 6.41 mg l⁻¹. The boron concentration is high especially in the regions of under ground thermal water resources (Aydın and Seferoglu, 2000). And the boron concentration was found to be 1.1 mg l⁻¹ due to geothermal wastewater discharges to the river and river water used for agricultural irrigation affected the production of agricultural products (Akar, 2007). Buyuk Menderes River is

in the third class pollution level due to domestic and industrial wastes and agricultural activities (Akın and Akın, 2007).

“Pollution of the Buyuk Menderes is to pollute the future” in the project final report, the mean values were compared with the Water Pollution Control Regulation. Buyuk Menderes River is 2nd class, namely in the class of less polluted water in terms of lead and 1st class, namely it is high quality water in terms of copper, chrome and zinc. It is below the permissible limits when compared with the maximum allowable concentrations of heavy metals and toxic elements in irrigation waters (Durdu et al., 2012).

It is stated that the most serious problems in terms of water quality in rivers in Buyuk Menderes basin are excessive organic matter, nitrogen, pH, boron and heavy metal pollution (Tubitak Mam, 2013).

Isıklı Lake is on resources that feed the Buyuk Menderes River. Isıklı Stream is a branch of the Buyuk Menderes River. Isıklı Lake and Isıklı Stream were determined to be as 2nd class (less contaminated water) in terms of anionic detergent parameter (Cakir and Minareci, 2015). Also in Isıklı Lake, it was found that organic pollution significantly increased and the amount of dissolved oxygen decreased in summer in some stations of the lake. It is stated that the important source that pollutes the lake is Buyuk Menderes River (Bulut et al., 2012). Adıguzel Dam Lake is on the Buyuk Menderes River. Adıguzel Dam Lake was categorized as less contaminated water in terms of anionic detergent parameter (Minareci and Cakir, 2018).

The measured values in the different rivers in the same region are higher than the measured values in our study. The Gediz River is highly polluted surface water in the Gediz Basin. Due to domestic and industrial wastes and agricultural activities, the river is determined as IV. class water quality in terms of nitrogen, organic matter and heavy metals (Akın and Akın, 2007). In the study carried out in Gediz River, copper 0.034 ppm, chromium 0.099 ppm, nickel 0.062 ppm, lead 0.218 ppm, iron 0.121 ppm, manganese 0.053 ppm, zinc 1.181 ppm, cobalt 0.006 ppm, cadmium 0.0036 ppm were found. The river was found dirty in terms of chrome and lead (Minareci et al., 2009a). In another study in Gediz River, boron concentrations are found between 0.19–2.25 mg l⁻¹ (Demirbas and Orhun, 2008). The average boron value was 2.428 mg l⁻¹ in Gediz River and Gediz River was determined as very polluted water for boron parameter (Minareci, 2014).

In Kucuk Menderes River, copper concentrations 0.01–0.02 ppm, chrome concentrations 0.01–0.02 ppm, nickel concentrations 0.03–0.08 ppm and lead concentrations 0.08–0.12 ppm were found between these amounts (Egemen et al., 2005). In the study conducted by Gundogdu and Ozkan (2006) in Kucuk Menderes River in 2006, it was determined that the iron value is 3rd class water quality. In another study, it has been reported that the Kucuk Menderes River is in the 4th class pollution level in terms of nitrogen, organic matter and heavy metals from domestic and industrial wastes and agricultural activities (Akın and Akın, 2007). It was determined that other heavy metal concentrations except Ni, Cu and Zn were low in surface water of Kucuk Menderes River (Turgut, 2003).

Anionic detergent and heavy metal levels of Berdan Stream have been found higher than the standard levels (Kumbur and Vural, 1989).

The anionic detergent values are shown comparatively in *Table 9*. The obtained phosphate values from Buyuk Menderes River were lower than the obtained values from many other rivers (*Table 10*).

Table 9. Anionic detergent concentrations of studies

Rivers name	Detergent concentrations	References
Gediz River	0.023–4.48 mg l ⁻¹	Tugrul, 1992
Yuvarlak Stream	0.12 mg l ⁻¹	Balik et al., 2002
Bakircay River	0.01–0.29 mg l ⁻¹	Basaran, 2004
Kucuk Menderes River	0–0.93 mg l ⁻¹	Egemen et al., 2005
Gediz River	0.951 mg l ⁻¹	Minareci et al., 2009b
Karacay Stream	0.071–1.122 mg l ⁻¹	Minareci et al., 2009b
Halifax Harbour River	0.001–mg l ⁻¹	Gagnon, 1983
Tama River	0.035–0.219 mg l ⁻¹	Yoshikawa et al., 1984
Hyogo River	0.004–2.5 mg l ⁻¹	Kobuke, 1985
Tsurumi River	0.01–0.29 mg l ⁻¹	Yoshikawa et al., 1985
Sumida River	0.005–0.01 mg l ⁻¹	Kikuchi et al., 1986
Saar River	0.01–0.09 mg l ⁻¹	Matthijs and De Henau, 1987
Teshiro River	0.01–0.27 mg l ⁻¹	Kojima, 1989
Teganuma River	0.019–1.4 mg l ⁻¹	Nonaka et al., 1989
Yodo River	0.043–0.089 mg l ⁻¹	Nonaka et al., 1990
Miami River	< 0.05 mg l ⁻¹	Hand et al., 1990
Oohori River	0.5–1.6 mg l ⁻¹	Amano et al., 1991
Mississippi River	0.01–0.3 mg l ⁻¹	McAvoy et al., 1993
Litheos River	0.1 mg l ⁻¹	Dassenakis et al., 1998
Yorkshire River	0.05–0.25 mg l ⁻¹	Fox et al., 2000
Itter River	0.007–0.011 mg l ⁻¹	Wind et al., 2004
Buyuk Menderes River	0.0583–0.3385 mg l⁻¹ (mean 0.2345 mg l⁻¹)	This study

Table 10. Phosphate concentrations of studies

Rivers name	Phosphate concentrations	References
MericRiver	0.0001–0.02 mg l ⁻¹	Kontas, 1990
Gediz River	0.016–4.054 mg l ⁻¹	Tugrul, 1992
Gediz River	0.02–7.41 mg l ⁻¹	Okur et al., 1997
Asi River	0.002–2.44 mg l ⁻¹	Tasdemir and Goksu, 2001
Bakircay River	0.0018–0.0229 mg l ⁻¹	Basaran, 2004
Bakircay River	0–0.7 mg l ⁻¹	Gundogdu and Turhan, 2004
Karacay Stream	0.22– 6.82 mg l ⁻¹	Kara and Comlekcioglu, 2004
Kucuk Menderes River	0–1.88 mg l ⁻¹	Egemen et al., 2005
Gediz River	0.0044–0.2481 mg l ⁻¹	Minareci et al., 2009b
Karacay Stream	0.002–0.225 mg l ⁻¹	Minareci et al., 2009b
Rheraya River	0.043–1.286 mg l ⁻¹	Khebiza et al., 2006
Nhue River	3.5 mg l ⁻¹	Duc et al., 2006
Dun River	0.086 mg l ⁻¹	Neal et al., 2006
Kenet River	0.083 mg l ⁻¹	Neal et al., 2006
Fuji River	0.01–0.13 mg l ⁻¹	Shrestha and Kazama, 2007
Yangtze River	0.64–1.31 mg l ⁻¹	Zhang et al., 2007
Buyuk Menderes River	0.0087–0.0245 mg l⁻¹ (mean 0.0181 mg l⁻¹)	This study

Conclusions and recommendations

The Buyuk Menderes River water is 2nd quality in terms of pH, conductivity, anionic surfactant and nickel parameters. Also the river water is 3rd quality in terms of dissolved oxygen parameter. Because the Buyuk Menderes River is close to the settlements, the discharges reach to the river. Due to domestic and industrial waste load, pollution load increases.

For the sustainable productivity of the Buyuk Menderes Basin lands and the protection of all aboveground and underground waters from pollution,

- The protection of the Buyuk Menderes River from all kinds of pollution (especially domestic and industrial wastes),
- Analysis of surface and groundwater should be done periodically,
- The water not suitable for irrigation should not be used,
- Fertilizer should be used as much as necessary,
- The farmers are directed to organic farming,
- Use of pesticides should be minimized,
- Industrial facilities and local governments should establish and use wastewater treatment facilities,
- The chemical fertilizers and agrochemicals must be controlled by authorized institutions.

As a result, the investigation of the underground and surface water quality of Buyuk Menderes Basin should be continued periodically, the factors that decrease the quality should be revealed and necessary precautions should be taken.

Acknowledgements. This study is supported by Manisa Celal Bayar University Scientific Research Projects Coordination Unit within the frame of the projects numbers FEF 2012-099 and FEF 2013-139. We are indebted to MCBU-BAP fund for providing financial support to this study.

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