

## Distribution of Dissolved and Particulate Organic Carbon in the Setiu River Basin, Malaysia

<sup>1</sup>S. Suratman, <sup>1</sup>Y. Y. Hee, <sup>1</sup>N. Mohd Tahir and <sup>2</sup>N. Mohd Tahir

<sup>1</sup>Institute of Oceanography and Environment,

<sup>2</sup>School of Marine Science and Environment, Universiti Malaysia Terengganu,  
21030 Kuala Terengganu, Terengganu, Malaysia

**Abstract:** Mean concentrations of Dissolved Organic Carbon (DOC) and Particulate Organic Carbon (POC) were in the ranges of 180-5390 and 1310-2610 µg/LC, respectively. Generally, higher concentrations of DOC and POC were recorded in downstream areas as a result of inputs from anthropogenic activities. DOC was size fractionated into high molecular weight (HMW, <100 kDa) and low molecular weight (LMW, <30 kDa). The HMW DOC fraction generally dominated the total DOC. The HMW DOC dominance was associated with agricultural, aquaculture and urban areas inputs. Resuspension of river sediment may also have played an important role in controlling the HMW DOC distribution. The LMW DOC was significantly correlated with chlorophyll-a (chl-a) suggesting processes related to phytoplankton may influence LMW DOC in the water column. The DOC and POC concentrations were also influenced by climatological factors with high values occurring during the monsoon season and lower values during non-monsoon season. In conclusion, the results from this study aim to improve understanding of the dynamics of DOC and POC concentrations in the tropical region.

**Key words:** Surface water, dissolved and particulate organic carbon, fractionation, chlorophyll-a, Southern South China Sea (Malaysia)

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### INTRODUCTION

The Organic Matter (OM) found in surface waters is a heterogeneous matrix of organic compounds. OM is further divisible into two broad categories based on physical state Dissolved Organic Matter (DOM) and Particulate Organic Matter (POM). The term “dissolved” is operationally defined as compounds that will pass through a filter while “particulate” corresponds to compounds that are retained by this filter. DOM is a vital component of and an intermediary substance in global carbon cycles (Hedges *et al.*, 1997). DOM is a complex and heterogeneous mixture of components originating from the degradation of plants, animals and microorganisms. A study by Gobler and Wilhelm (2003) suggested that phytoplankton are the primary source of OM to the world's oceans. A further DOM source might include terrestrial allochthonous matter (Lonborg *et al.*, 2009).

In most studies concerning DOM, the DOC component is quantified. Concentrations of DOC in natural waters vary widely with the lowest values normally observed in the oceans, groundwater and

“clearwater” lakes and rivers draining bare rock or thin organic-poor soils. Concentrations are highest in organic soil porewaters and freshwaters draining wetlands and peatlands, especially where run-off is low (Evans *et al.*, 2005). Heavy anthropogenic activities within and next to rivers could also generate large amounts of organic pollutants (Ni *et al.*, 2008).

DOM can be divided into two groups: High Molecular Weight Dissolved Organic Matter (HWM DOM) and Low Molecular Weight Dissolved Organic Matter (LWM DOM), operationally defined by ultrafiltration membrane cut-off. Over the past few years, the study of DOM molecular weight fractionation in natural waters has received increasing attention (Wang *et al.*, 2004; Suratman *et al.*, 2008). The size-based distinction between HWM and LWM DOC is useful in understanding the sources and transformations of DOC. In general, HMW DOC is considered to be of terrigenous origin and sediment resuspension (Wang *et al.*, 2004; Guo and Santschi, 2000) while LMW DOC is considered to be of biological origin (Suratman *et al.*, 2009). In order to determine the seasonal and spatial variations of organic carbon, surveys of both dissolved and particulate organic

carbon were undertaken in the Setiu River Basin, Malaysia. A size fractionation study was also carried out in order to identify the possible sources of organic matter. The study aims to understand the dynamics of OM in the aquatic system. In addition, in areas such as the Setiu River Basin where land areas within the basin have been developed for housing, agricultural and aquaculture activities in recent years, information on DOC is essential.

## MATERIALS AND METHODS

**Study area:** The study was carried out in the Setiu River Basin in Terengganu on the east coast of Peninsular Malaysia. Ten sampling stations were chosen as shown in Fig. 1. The river is approximately 60 km in length and receives run-off from its main tributaries: the Guntung River, the Tarum River and the Caluk River. Land use

within the river basin is expanding and is primarily associated with aquaculture at the lower reaches of the river. The aquaculture consists of brackish water cage culture, pond culture, pen culture, oyster farming and prawn farming. Population density is concentrated at the middle and lower reaches of the river. This river basin is economically important since it provides water for irrigation as well as services related to aquaculture, municipal water supply and wastewater dilution. There are two distinct monsoon seasons a wet North East (NE) monsoon from November-March and a dry South West (SW) monsoon from May-September. October is an intermonsoon season or transition period preceding the NE monsoon as is April which proceeds the SW monsoon. The annual rainfall within the basin ranges from 1800-2000 mm with the highest rainfall occurring in November-December.

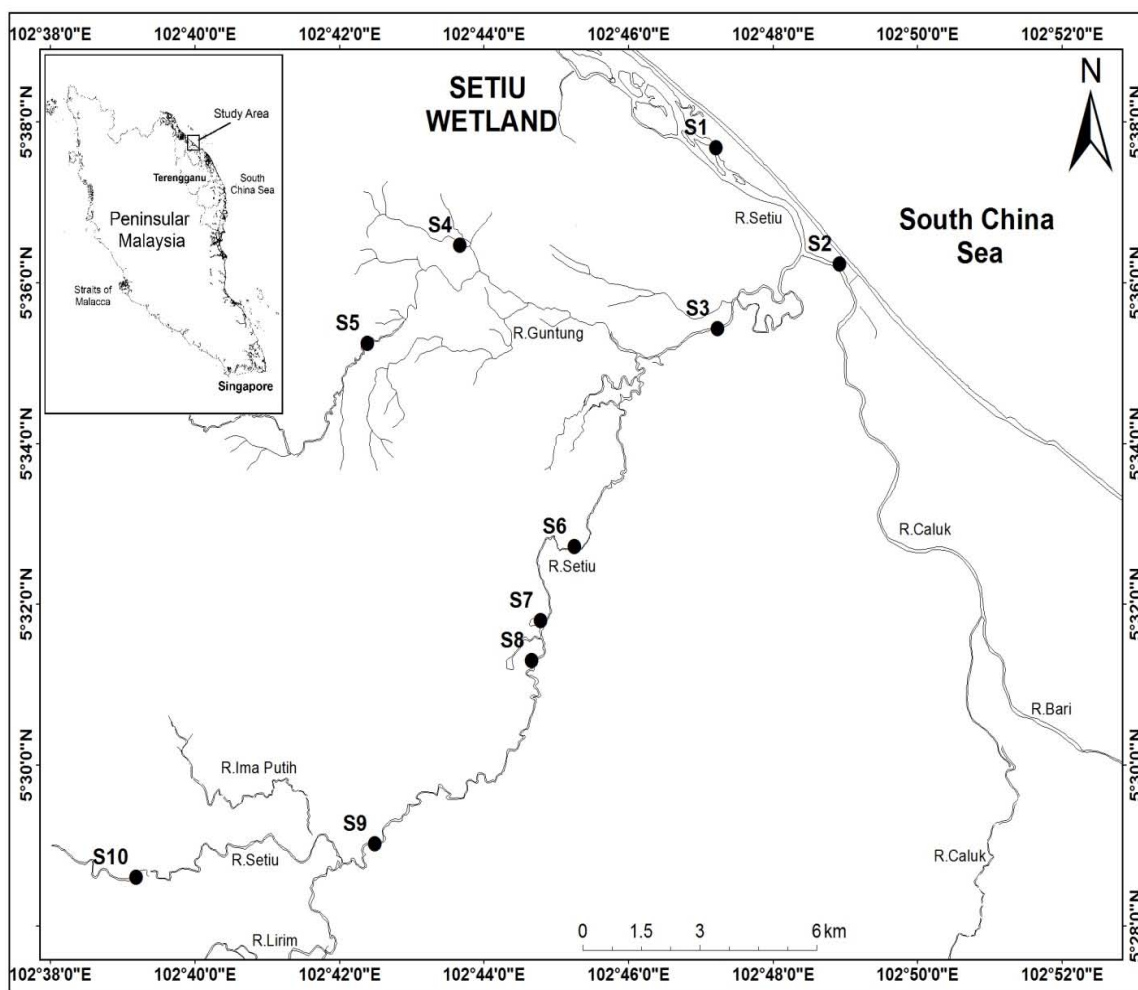


Fig. 1: Locations of sampling sites in Setiu River Basin

**Samples collection:** Surface water samples were collected at monthly intervals over a 1 year period (July 2010 to June 2011). The water samples were collected at a depth of 0.5 m directly into Polyethylene (PE) bottles. All PE bottles used for sample storage were acid-washed for 24 h in 10% HCl, rinsed with Deionized (DI) water and dried before use. Immediately after sampling, bottles were stored in an icebox filled with ice. Samples for DOC and POC determination were filtered as soon as possible after sampling through pre-combusted (450°C for 5 h) GF/F glass filters (pore size 0.7 µm). Samples were stored frozen at -20°C until analysis.

**Samples collection:** The DOC in the samples was analysed using High-Temperature Catalytic Oxidation (HTCO) using a Shimadzu TOC-V analyzer fitted with a Non-Dispersive Infrared (NDIR) detector. The filtered samples for DOC analysis were acidified to a pH of ≤2. The acidified samples were then sparged to eliminate all dissolved inorganic carbon. To evaluate the performance of the analysis system for DOC, a Certified Reference Material (CRM) was also analysed. A CRM of deep seawater was obtained from the Hansell Laboratory, University of Miami. The CRM is certified for a DOC concentration of 41-44 µM (492-528 µg/LC). When analysed in this study, the CRM gave an average value of 497 µg/LC which is within its certified values.

The POC concentrations of the samples were determined using a flash EA 1112 CHNS-O elemental analyser, calibrated with acetanilide, C<sub>8</sub>H<sub>9</sub>NO. In the system, the temperature was raised to approximately 1800°C causing instant combustion of the samples and the production of CO<sub>2</sub> for measurement by a thermal conductivity detector. Prior to analysis, samples for POC determination were collected on pre-combusted (450°C; 5 h) 0.7 µm diameter GF/F filters that were then dried at 60°C for 24 h. Afterwards the filters were fumed with concentrated HCl in a closed container for half an hour to eliminate carbonates. For chlorophyll a (chl-a) determination method was employed.

Five selected stations, i.e., S1, S2, S5 and S8 were chosen for the size fractionation study. Size fractionation of DOC was undertaken using membrane ultrafiltration in a stirred cell (Amicon) under nitrogen pressure. The HMW DOC and LMW DOC in this study were operationally defined as the fractions with sizes <100 kDa and <30 kDa, respectively. Each DOC fraction was then analysed using the HTCO method as described previously.

## RESULTS AND DISCUSSION

**Distribution of DOC and POC:** The mean DOC concentrations measured in the surface water samples from the Setiu River Basin ranged from 1782-5388 µg/LC

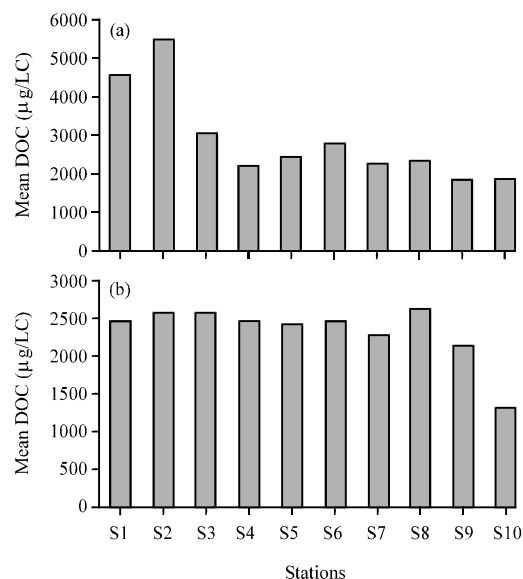


Fig. 2: Variation of mean organic C-based nutrient concentrations in the Setiu River Basin

(Fig. 2). The lowest mean value was observed at an upstream station (station S9) and the highest mean value was observed at a downstream station (station S2). In general, the lower DOC mean values were observed at upstream stations (stations S9 and S10) and the values increased slightly at urban stations (stations S8 and S6). Lower mean concentrations were also observed at stations S7, S5 and S4 whilst higher mean concentrations were observed at the downstream stations (S3 and S1). A two-factor without replication ANOVA test indicated that there was a significant difference between sampling sites ( $p < 0.05$ ) reflecting the marked variation of DOC concentrations across the area.

The trend of POC (Fig. 2) across the sampling sites from stations S1-S10 differed from that of DOC. Station 10 showed the lowest mean concentration of POC (1307 µg/LC), similar to DOC but the urban station (station S8) showed the highest mean concentration of POC with a mean value of 2611 µg/LC. As can be seen from Fig. 2, dramatically increasing or decreasing of POC generally was not observed among the stations in the study area. It is of note that stations S4 and S5 showed the same level of POC as downstream stations. The ANOVA test revealed no significant difference in POC concentrations ( $p > 0.05$ ) between stations.

**Weight fractionation of DOC:** The results showed that the concentrations of LMW DOC varied from 374-6951 µg/LC with LMW DOC contributing to 34-91% of the total DOC. The concentrations of HMW DOC

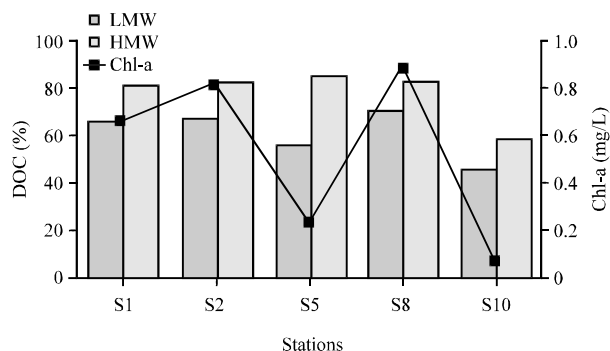


Fig. 3: Variation of mean LMW and HMW DOC (%) with mean concentrations of chl-a

varied from 427-10249  $\mu\text{g/LC}$  and contributed to 45-97% of the total DOC. Overall, the highest mean percentage of LMW DOC was related to urban areas (station S8; 69.72%) and the lowest mean percentage of LMW DOC occurred at an upstream station (station S10; 44.68%) (Fig. 3). The trend of HMW DOC was similar to LMW DOC with highest and lowest concentrations of HMW DOC at the same stations (Fig. 3). In general, stations with a high percentage of LMW DOC also exhibited high chl-a concentrations (Fig. 3).

**Seasonal variation of organic C:** Statistical analysis (ANOVA test) indicated that there was a significant difference in DOC and POC dependent on the time of year ( $p < 0.05$ ). DOC concentrations in the Setiu River Basin were responsive to the rainfall with DOC generally increasing during periods of high rainfall, i.e., the NE monsoon season (November-March) (Fig. 4). This observation suggests that the variation of the DOC in the river is dependent on the season. The POC concentrations in the water column were also seasonal and related to rainfall pattern with higher POC concentrations during the NE monsoon (Fig. 4). The maximum concentration of POC (5800  $\mu\text{g/LC}$ ) occurred in December during a period of high rainfall (704 mm/month) considerably higher than a non-monsoon period, e.g., June (2080  $\mu\text{g/LC}$ ; 390 mm/month). However, POC concentrations were not consistently higher in the monsoon; low POC concentrations were recorded in March which was also the month with maximum rainfall (1057 mm/month). The weight fractions of DOC generally followed the same pattern as total DOC, showing a good relationship with season (Fig. 5). An ANOVA test revealed that both LMW and HMW DOC were varied significantly with sampling month ( $p < 0.05$ ).

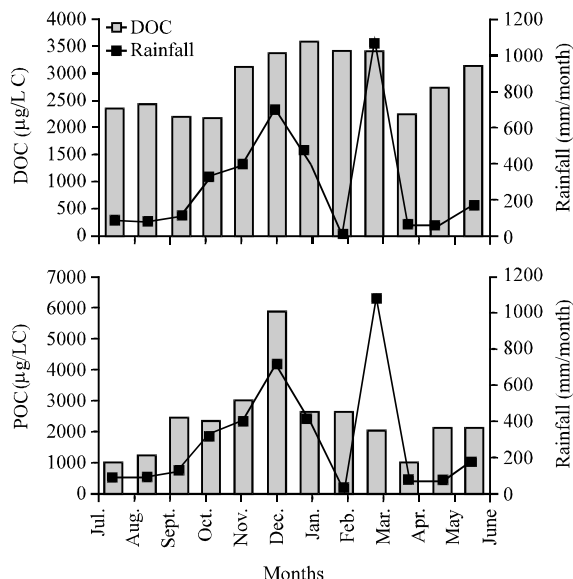


Fig. 4: Variation of mean organic C-based nutrient concentrations for each month with monthly rainfall

**Distribution of DOC and POC:** The results reveal that a sharply increase in DOC concentration at station S2 which is located in a downstream area and has concentrated agricultural and aquaculture activities nearby. This increase could be attributed to the anthropogenic inputs, such as fertilizers used in the areas that runoff towards the adjacent river. Royer and David (2005) assert that DOC from agricultural area run-off to rivers was proportional to the pool of organic C in the soil. In their study, they hypothesise that the fraction of the DOC could be loaded during late summer and autumn when agricultural drainage has ceased. Station S1 also had dramatically elevated DOC concentrations; this may be due to its location in the Setiu Wetland. A study by Aitkenhead and McDowell (2000) cited the rates of DOC production in organic soils, the infiltration of the mineral soils and the flow path of water through different soil horizons to streams as influences on stream water DOC concentrations. Their study found that wetlands are more likely to produce large amounts of total organic C. In the present study, the saturated soils at station S1 (in the Setiu Wetland) are likely to retain organic C, therefore contributing to higher DOC concentrations at S1.

The relatively constant value of POC along the sampling transect may be a result of a number of point sources contributing to the POC concentrations in the water column. Krusche *et al.* (2002) have shown that an important contributor of particulate organic matter was urban and industrial effluents. This may explain the high POC concentrations at urban stations (stations S6 and S8). Findlay *et al.* (1991) found a link between POC and

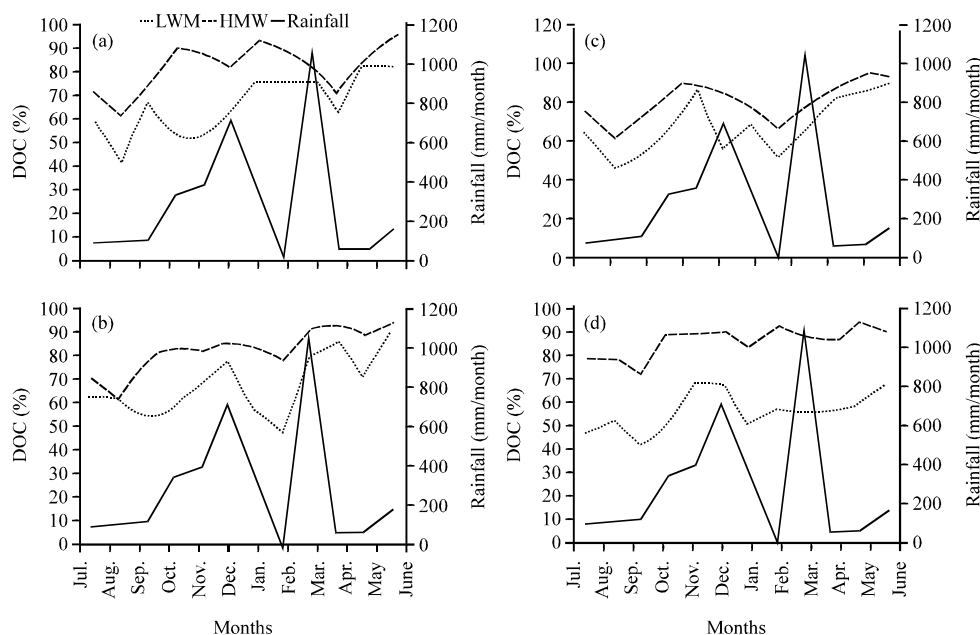


Fig. 5: Variation of LMW and HMW DOC (%) with monthly rainfall

the resuspension of benthic organic matter. This link may explain the higher POC concentrations at station S5, especially during December sampling due to construction work taking place at this time. Another point source of POC may be the construction activities associated with shrimp aquaculture. Downstream stations, especially station S3 which is located near to the project have been impacted during the aquaculture project's construction phase. During this project, a large tract of the Gelam forest was cleared to make way for phase one of the 1000 ha integrated shrimp aquaculture park (i-SHARP). There has been soil erosion associated with this project that is likely to account for the elevated POC concentrations at downstream stations.

**Weight fractionation of DOC:** The weight distribution of DOC was used to aid source discrimination of the organic matter and to help understanding of the functional role of DOC in aquatic systems. Chl-a concentrations are typically used as a proxy for primary production. DOC may also be associated with chl-a (Kragh and Sondergaard, 2009), since DOC can result from phytoplankton exudation or decomposition (Lonborg *et al.*, 2009). Suratman *et al.* (2009) found that LMW DOM was correlated with phytoplankton DOM release. They suggest that LMW DOC could be directly released by phytoplankton, especially if nutrients in the water column are not limited or during the exponential growth of certain diatom species. These findings are similar to those of the present study which suggests that LMW DOC was highly influenced by phytoplankton.

Of the five stations with high percentages of HMW DOC, three were associated with agriculture and urban areas (S1, S2 and S8). This relationship suggests that there may have been anthropogenic sources of the HMW DOC. This is in agreement with Wang *et al.* (2004) who found that terrestrial and local anthropogenic inputs played an important role as sources of DOM and in the formation and transport of HMW DOM in estuarine waters. In this study area, agricultural land use is of growing importance with agricultural activities at the lower reaches of the river and urban areas in the middle and lower reaches of the river. Thus, the agricultural area and urban centre are sites that have been consistently contaminated with input from sewage and fertilizer run-off. This could be contributing to the high HMW DOC at stations S1, S2 and S8.

The higher percentages of HMW DOC in the samples could also come from other sources for example sedimentary organic carbon. The higher percentages of HMW DOC at station S5 may be caused by the resuspension of sediments and the release of organic carbon into water column, due to an on-going construction project occurring during the December sampling period. A mechanism for this input may be due to activities related to the construction project stirring up older Colloidal Organic Carbon (COC, i.e., high molecular weight DOC) from the sedimentary organic carbon pool. A similar phenomenon was demonstrated by Guo and Santschi (2000).

**Seasonal variation of organic C:** Saunders and Lewis (1988) described how the alternation of wet and dry seasons influence the retention and loss of nutrient compounds. For example, agricultural run-off, a non-point source of excess organic C and N is increased during periods of increased rainfall through wash out into rivers and leaching through the soil. This run-off could explain the high levels of organic C observed in the present study. Romani *et al.* (2006) found large and rapid DOC inputs entering an intermittent river system during the transition from drought to precipitation and which reached its maximum value of DOC after the initial rains. The seasonal pattern in the concentration of POC can be explained by following mechanism. As rainfall increases, an increase in soil erosion and resuspension of deposited solids occurs. Together these processes result in the wash out of POM and DOM from the land into rivers. The concentrations of particulate matter are also sensitive to the initial rise in the stage height of the water body. As soon as the stage height rises sharply, there can be a marked rise in concentrations of particulate material (Saunders and Lewis, 1988). When the rainfall reached its maximum in March, there was a decrease in concentration of POC relative to December. This decrease in POC might be caused by the depletion of POC from the adjacent soil in previous rainfall events.

### CONCLUSION

This study in the Setiu River Basin shows that DOC and POC in surface waters were relatively high in agricultural, aquaculture and town centre areas, indicating some anthropogenic inputs. Most of the organic matter was linked to the discharge of domestic and aquaculture waste and run-off from agricultural areas. The DOC pool was dominated by HMW DOC fractions which may be driven by the anthropogenic inputs and also resuspension of organic matter from sediment due to construction activities. Significant association of LMW DOC with chl-a suggests that the LMW DOC seen in the present study was in part a result of phytoplankton exudation or degradation. The organic carbon concentrations were also linked to the season with higher concentrations during monsoon season (November-March) and lower during non-monsoon season (May-September). This relationship is hypothesised to be driven by the higher run-off of nutrients into the river and resuspension of sediment caused by increased river flow.

### ACKNOWLEDGEMENTS

The financial support from the Ministry of Science, Technology and Innovation, Malaysia (Grant No. 04-01-12-SF0085) is very much appreciated. Thanks to Dr. Rose Norman for assistance with proof reading of the manuscript.

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