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A Problem on the Filter Blank of Particulate Organic Carbon

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The adsorption blank on the determination of particulate organic carbon in the sea have been discussed by Menzel *et al.* However, the study about it's quantitative and qualitative problem of water sample have been neglected. The author examined the adsorbed carbon value with small volume of water sample. The adsorbed carbon increased with the volume of filtered water and gave the smallest value in the recent works. These results indicated the difficulty of the determination of adsorption blank.

Introduction

On the analysis of particulate organic matter in sea water using a glass fiber filter, it is commonly recognized that the extrapolated blank on varying volumes of water filtered clearly exceeds the filter blank (no used filter) only. Firstly, Menzel (1966) pointed out this problem and discussed. He thought the reason adsorption of dissolved organic matter by filter paper. The correction of adsorption blank by this method have been adopted usually.

At the point of this, the author reexamined the adsorption blank by using 25mm Whatman GF/C glass fiber filter for the purpose of a check of the blank value on the small (25mm diameter) filter and small volume (10-20*ml*) of sample, which was used for the determination of organic carbon content in cultured diatom.

Method

The sample water was the culture medium of *Skeletonema costatum* that was enriched inorganic nutrient salts to natural sea water in Exp.I, and was natural sea water pre-filtered through a Whatman GF/C (45mm) glass fiber filter and through a Whatman GF/C and a Millipore HAWP (45mm) filter, which was settled uder the former, in Exp.II and in Exp. III respectively. All natural sea water was obtained on Tsugaru-Strait. Usually it was almost clear.

In these adsorption experiments, only the Whatman GF/C glass fiber filters (25mm) were used. They were ignitioned by electric furnace at 450-500 °C for more than 1 hour.

Water volume was measured by using one to three combined pipettes in Exp. I and Exp. III (the series over 30*ml*), and a piston bulette in Exp. II and Exp. III

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(the series of 0.1-30*ml*). Moreover, in Exp .III, measuring cylinder was used on the series over 100*ml*.

The filtration was operated succssively in less than 4 hours using 25mm Millipore filter holder and a 300*ml* filtering flask, which was made vacuous by water aspirator. The water was continuously filtered in each sample without regard to water volume. The sample filters were kept for 2 or 3 days in a desicator with Silica-gel at room temperature and finally supplied to analyze organic carbon contents by Hitachi 026 CHN Analyzer.

Results

The organic carbon contents of living diatom *Skeletonema costatum* were plotted on 1, 2, 5, and 10*ml* sample water volume. They were linear to the sample volme and their extrapolated value to 0 point of the volume was 5.47μgC. This is the

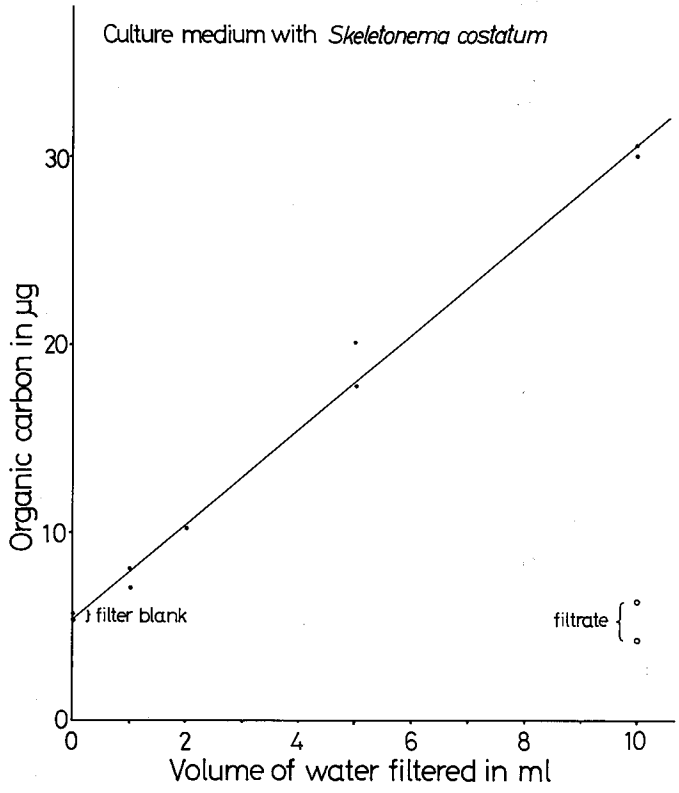

Fig. 1. Blank determination by the method of Menzel (1966) with *Skeletonema costatum* culture sample. The "filter blank" means non filtered sample, of which value is thought to be higher compared with later experiments, and the "filtrate" means the sample which 10*ml* filtrate was passed.

Exp. I and shown in Fig. 1. The adsorption blank values have been required in such a way on sample volume from 0.25 to 4.0*l* (Menzel 1966) or from 0.5 to 2.0*l* (Nishizawa 1969). It will be convincing, if the extrapolated line is rectilinear. But there are no solid foundations for the line to be rectilinear in the case of small sample volume. The value of 5.47 is too low compared with the data of Menzel (1966) and Nishizawa (1969). If the adsorbed organic carbon grows sigmoidally, this low value of adsorption blank is quite reasonable in such a experiment of small sample volume. And then it is required to attempt a more closed experiment. While the filter blank values (Mean: 5.59) which is determined by no used filters exceed the adsorption blank value in the Exp. I. They are obviously unreasonadle excess for the data obtained in later experiments (II and III) that shows 3.5 and 3.8μgC respectively, and for the filtrate blank values (Mean: 5.32) determined by the filters which 10*ml* filtrate passed in. It is thought that there are a little error on the filter blanks.

A more detailed adsorption experiment (Exp. II) was done with natural sea water pre-filtered by Whatman GF/C filter, which is shown in Fig. 2. This experiment has the data on 33 sample filters in the range of 0.1-25*ml* water sample volume. The "Filter Blank" value is 3.5μgC per sheet and organic carbon contents increase rapidly with it's sample water volume to 0.5*ml*, and then gradually from 0.5 to 25*ml*. They should so increase with the volume after 25*ml*. However, it is unknown whether the organic carbon contents increase

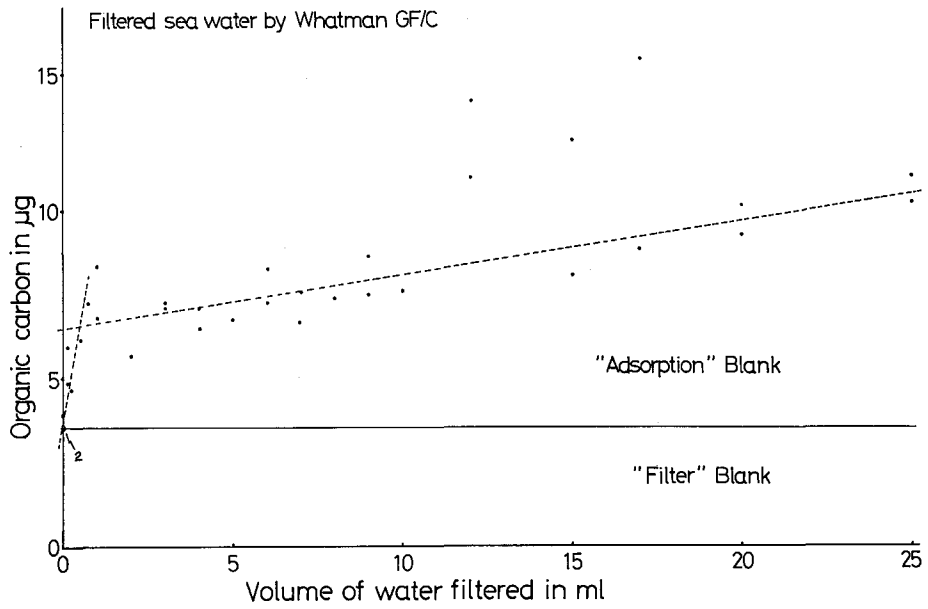

Fig. 2. Organic carbon contents of filters in which pre-filtered (by Whatman GF/C filter) sea water was passed.

unlimitedly or not, and on what volume of sample they are saturated, if limited. On the other hand, are they not saturated, the carbon contents of the rising fraction in Fig. 2 will be occupied by the small particulate matter which passed through a Whatman GF/C filter in pre-filtering, and the adsorpton blank value is devided to two parts; true filter blank and true adsorption blank including small particle fraction. We have defined the particulate and the dissolved matter in sea water by whether they can pass or not the 0.45μm pore size (cf: Millipore HAWP). And Ogura (1970) gave that many dissolved organic carbon exists below 0.1μm. As the Whatman GF/C filter have larger and unequal pore size than the Millipore HA filter, if there are many small particles which can pass through the whatman GF/C filter on one occasion and can not pass through it on another occasion, the adsorption blank value should be too difficult to be determine.

The results of the last experiment (Exp. III) is shown in Fig. 3. The sample water was natural sea water pre-filtered by Whatman GF/C and Millipore HAWP

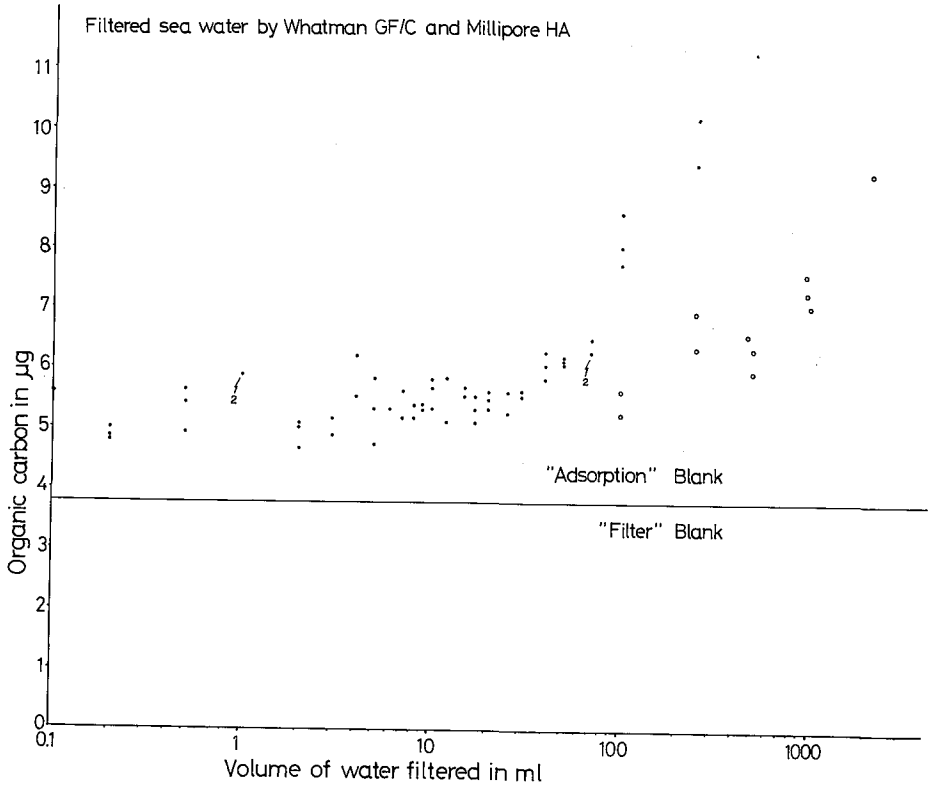

Fig. 3. Organic carbon conrents of filters in which pre-filtered (by Whatman GF/C filter+Millipore HA filter) sea water was passed. Closed circles: Series A (from 0.1*ml* to 500*ml*), Open circles: Series B (from 100*ml* to 2100*ml*).

filters. From 0.1*ml* to 2,000*ml*, the sample of 27 stages was analyzed for double or triplicate on two kind of sea water, the series A was sooner filtered after pre-filtering, the series B was done 1 week later after the pre-filtering. The organic carbon content in the filter gradually increased with the volume to 70*ml*, and it's growth pattern is simple to Exp. II. But it's quantity is about 20 % lower than the data from Exp. II. However, from 100*ml* of sample volume, the carbon contents are rapidly rising with the volume. The lowering of carbon contents in Exp. III is considered to be caused by the decreasing of dissolved organic carbon in the sample water, which depends on following two affaires ; the one is falling of small particles by filtering with Millipore HAWP and the another is adsorption of dissolved organic carbon by Millipore HAWP and Whatman GF/C filters. Quinn and Meyers (1971) suggested 86 and 48 per cent decrease of dissolved organic carbon (heptadecanoic acid) by filtering with Millipore HAWP and Whatman GF/C respectively.

Disccusion

For the purpose of blank correction for particulate organic carbon, a few method have been made. Newell and Kerr (1968) used 17μgC of filter blank, and does not used adsorption correction. Menzel (1967) carried out periodical filtering a series of samples of varing volume for the blank of surface samples and obtained 20-40μgC of "filter" plus "adsorption" blank by the positive intercept on the carbon axis. On the other hand, deep water values of particulate organic carbon were determined by the differences between 3 and 6*l* samples of filtered material. These methods are more fittable in field observations for the reason why the adsorption blank varies with each sample water. However, there are no solid foundations that the adsorption blank value increase rectilinearlly with sample water volume. Uno (1971) adopted 14.8μgC of "filter" plus "adsorption" blank in all his experiments of cultured phytoplankton. The blank value was converted from 45mm diameter filter's blank which was the mean value of natural seawater sample by the interception method. It is satisfied to have been used it's blank value throughout the experiments because of their uniformity of the quantity and the quality of sample water, but is not suitable for the difference of the water quality and the water volume between the samples and blank. Recently, Loder (1971) determined the particulate organic carbon value by the difference between two filters placed in single filter holder, so he gave the blank value 14-40μgC/*l*. This layering method is very practical, but in the case of small sample volume it is not so better because 48% of dissolved organic carbon (heptadecanoic acid) is adsorbed by glass filter as shown by Quinn and Meyers (1971).

In this study, the lowest adsorption blank values in the recent works were obtained with small sample volume. We have had no data on the blank value about small sample volume and on the increasing of the blank value with the sample volume. And if there were data on more than 1*l* sample volume in these experiments, the adsorption blank value would get closer to the data from recent works.

While the accuracy on these carbon determination is satisfactory, and the range of analyzing error was far smaller than the adsorbed carbon value. As the containable water volume in a 25mm Whatman GF/C filter is only 0.060*ml*, dissolved organic carbon of contained water in the filter is neligeble.

The difficulty of the determination of adsorption blank value depends upon it's unstableness; adsorbed carbon value obviously increases with sample volume and changes by each sample water as shown in Fig. 3. And the determination of dissolved and particulate organic matter have been ambiguous. In fact, the filtering process always does not means the selection of particles by it's size (Sheldon and Sutcliffe 1969). It is very difficult to determine the adsorption blank correctly, and necessary to do it about same quality and quantity to used sample water at least.

Summary

1. The adsorption blank value was checked using 25 mm Whatman GF/C glass fiber filters with small sample water volume.
2. Culture medium with *Skaletonema costatum,* filtered sea water by GF/C filter and by GF/C and Millipore HA filters were supplied to the experiments.
3. Adsorbed carbon values in the filter were obviously increased with the sample water volume and gave the lowest blank value in the recent works.
4. For the blank correction, it is necessary to determine the blank value with same water on quality and quantity to the sample water for particulate carbon.

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粒状有機炭素測定におけるフィルターブランクの問題

宇　野　史　郎

海水中の粒状有機物をガラス繊維沪紙に沪して定量する際に，溶存有機物の沪紙による吸着の問題が以前より Menzel らによって指摘されており，この値をブランク値として差し引く事が行われている。著者はこのブランク値についてこれまで行われていなかった量的，質的な検討を試みた。溶存有機物の吸着によると考えられるブランク値は一定ではなく沪水量と共に増加し，また試水の質によって異る事が明らかとなった。本研究では特に培養植物プランクトン試料についての有機炭素量測定におけるブランク補正値を求めるというねらいから，少量の試水について詳細な検討が行われたが，これまで報告されているブランク値のうち最も低い値が得られた。