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DEVELOPMENT OF UV SENSOR FOR THE RESERVOIR WATER QUALITY EVALUATION AND IT'S APPLICATION

貯水池水質評価のためのＵＶセンサーの開発とその適用

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Abstract, Thus far the pollution of closed waters has been pointed out all over the world. In this study, especially, the changing volumes of chlorophyll a and phosphate-phosphorus $(PO_4)^{3-}$ were examined with the observation of both sunlight UV-rays volume and water temperature in the reservoirs. And constructed simple water quality estimation model on the basis of the observation data was tried, and the closed water environment viewed from sunlight UV-rays by using this model was estimated As a result, it has turned out that we could obtain the related equation, viz., $D^{\lambda}=D^{\alpha}$ on the assumption that a related equation, viz., $D^{\lambda}=D^{\alpha}D^{\beta}D^{\gamma}$ (where, D: elapsed time, λ : quantity of chlorophyll a, α : UV-rays volume, β : water temperature, γ : quantity of $(PO_4)^{3-}$) would be applicable It is therefore considered that the specific characteristic of closed water environment such as a lake, a marsh or a reservoir etc. could be decided from the coefficient of observation value

Key words, sunlight UV, UV-rays volume, water quality, chlorophyll a, TLD

1 INTRODUCTION

As one of the global environmental problems, the destruction of the ozonosphere (the formation of ozone holes) has recently been noticed internationally. The increase of the ozone holes brings about the increase of the volume of the UV-rays pouring on the surface of the earth. It is said that the increase of the volume has a bad influence on cells and genes of the blue-green algae and also becomes a factor which brings about the inhibition of the growth of phytoplankton Therefore, at present a countermeasure must be taken in a great hurry[1].

In Japan, the Meteorological Agency has been observing ultraviolet radiation in sunlight since April, 1993. Similarly, personal monitoring of ultraviolet radiation is also necessary for the safety of water environment.

In the previous paper[2], we reported a sensitive thermoluminescence dosimeter (TLD) for sunlight as a sensor for estimating the reservoir water quality. At that time, we used CaF_2 : Tb_4O_7 as a TLD sensor material improved for estimating UV-rays volume

Now, it is firstly necessary to evaluate the construction of simple water quality estimation model in order to estimate the closed water environment by sunlight UV-rays volume as an environmental indicator. This model is very rough However, if the simple model is constructed by sunlight UV-rays volume, the evaluation of the closed water environment such as a pond or a reservoir can be conducted, and then the conservation of water environment will be possible It is secondly necessary to clear the relationship between sunlight UV-rays volume and two main factors which are connected with the occurrence of phytoplankton when we consider the sunlight UV-rays as an environmental indicator. One is the relationship between sunlight UV-rays volume and chlorophyll a, and the other, between sunlight UV-rays and pollutant in the water.

It is thirdly necessary to examine whether the changing volume of chlorophyll a in the reservoir by the three factors such as sunlight UV-rays volume, phosphate-phosphorus $(PO_4)^{3-}$ as a matter of cause of eutrophication and water temperature can be expressed or not in order to use the sunlight UV-rays as an envi-

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ronmental indicator. In this study, we select the two reservoirs in which the pollution conditions differ to construct the standard & simple model for estimating reservoir water quality which is in accord with the actual observation value Especially, changing volume of chlorophyll a and phosphate-phosphorus $(PO_4)^{3-}$ were examined with the observation of both *sunlight* UV-rays volume and water temperature And a construction of simple water quality estimation model on the basis of the observation data was tried, and the closed water environment viewed from sunlight UV-rays by using this model was estimated The examination on the related equation which is in agreement with actually observed value is carried out under the assumption that a related equation, viz., $D^{\lambda} = D^{\alpha} D^{\beta} D^{\gamma}$ (where, D elapsed time, λ : quantity of chlorophyll a, α · UV-rays volume, β water temperature, γ · quantity of $(PO_4)^{3-}$) would be applicable.

2 PRINCIPLE OF MEASUREMENT AND DOSIMETER WITH RESPECT TO ULTRAVIOLET RAYS VOLUME

In general, radiation is divided into two kinds of rays, that is, charged particle rays (α , β rays etc.) and electromagnetic waves (X, γ rays). Its fundamental characteristic is to ionize materials (ioning radiation) In this parameter, in order to examine the relationship between theUV-rays volume and the ozone holes, we pay attention to X rays (γ rays) in the radiation mentioned above, and then take up UV-rays which is longer than X rays in wavelength

At present, in facilities where radiation is used, for example, nuclear power plants, the film dosimeter is used for measuring volume for personal dosimetry. One of the dosimeters for that purpose is the TLD. At that time we tried the measurement of ultraviolet rays by using the TLD. **Fig. 1** shows the principle of TL phenomenon[3),4)] First, by irradiating radiation (X, or UV-rays), impurity ions trap electron or hole, and by the trap irradiation volume is memorized And, by recombination of electron (or hole) trapped impurities and hole (or electron), emission peculiar to impurity ion, appears

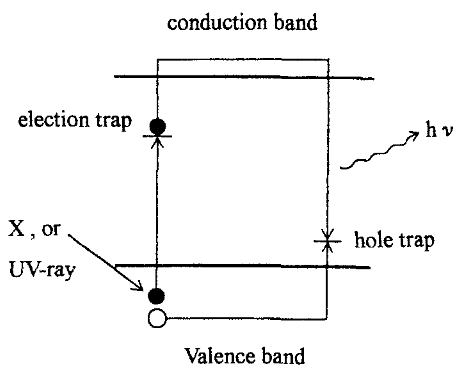

Fig. 1 Principle of TL phenomenon

3 MEASUREMENT OF ULTRAVIOLET RAYS VOLUME

This time we made the sintered CaF_2 with Tb ion as impurities, and used it as a TLD device. **Fig.2** shows an example of glow curve The area written with a slant line is in proportion to doses of Tb. As is seen in **Fig.3** (the relationship between the temperature and TL intensity), after irradiating the UV-rays (low pressure Hg-lamp) to the sintered CaF_2 : Tb_4O_7 (0 06 wt %), the observed TL glow curve has a peak which is observed in the vicinity of 100℃ and 175 ℃. However, the TL peak in the low temperature side (100 ℃) may fade by such kinds of heat as room temperature and sunlight Therefore, we have to be careful about the treatment of data Consequently, we need to consider the other TL peak in the vicinity of 175℃, which is not influenced by those kinds of heat If we take the TL in the vicinity of 175℃ the value is proportional to the UV-rays volume The proper area of TL glow curve having the peak in the vicinity of 175℃ is taken to range from 153-242℃ for the present And then by the radiation of Hg-lamp (13.5 W of low pressure Hg-lamp), we examined the relationship between the area and UV-rays volume. As a result, it is confirmed that this range is appropriate. It is generally considered that UV-A & UV-B reach the surface of the earth. We can perceive UV-B & UV-C which has been spoken of as not reaching the surface of the earth with the sensor which we have lately developed. Even if the UV-C volume is mall, the light energy of UV- C is extremely large because of short wavelength (Light energy is inversely proportional to the wavelength.) Then, it brings about a serious action for the life of the earth. There fore, the features of this study are the development of UV sensor (UV- B & UV-C) and the examination of the relationship between UV-rays volume and chlorophyll a

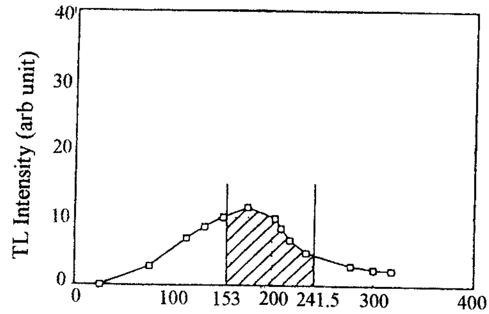

Fig. 2 Dose measurement of the sunlight

4 EXPERIMENTAL PROCEDURE

4.1 Preparation of TLD as a sensor

In the present paper, the dose of ultraviolet radiation in sunlight was estimated by using terbium-doped calcium fluorite as a TLD

The sample was prepared by solid-state reaction The starting materials, CaF_2 (purity 99 99%) and Tb_4O_7(99 99%) were mixed in the desired ratio and pressed into pellets. The mixture was heated at 1,100℃ for 5 hours in air. UV-rays were obtained by using a low pressure Hg or Xe lamp The TL glow curves were measured by using a Hamamatsu HTV-R212 photomultiplier The heating rate was 20℃/min. The samples were annealed at 400℃ for 30 min and cooled slowly to room temperature after the TL measurement As a result, CaF_2 : Tb_4O_7 was found to be a promising candidate as a TLD in the UV range, especially UV-C range When estimating the UV radiation in sunlight, it should be noticed that the appropriate filters are needed to avoid optical or thermal bleaching

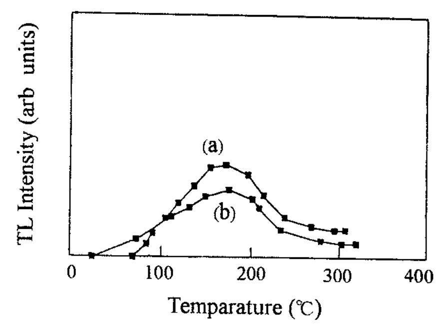

Fig 3 TL glow curves of CaF2 : Tb4O7 (0.06 wt %) after sunlight exposure for (a) 1.5 h, (b) 1 0 h

4.2 Experimental condition

We selected the two reservoirs (A & B) as objective ponds at the eastern & southern parts in Osaka prefecture in order to examine the difference of experimental result due to pollution conditions The reservoir A is a pond which is located in the mountain area, and the elevation is 270m, and the area of the reservoir is 5250m^2. The treated water from the neighboring treatment plant flows in that reservoir slightly. On the other hand, the area of the reservoir B is 3000m^2, and it is considered that the pollution of the reservoir has been progressing because of the neighboring factory. The exposure of the samples to sunlight was carried out without any filters in Osaka prefecture, Japan in May - Oct., 2000

We fundamentally tried to expose TLD to the sunlight indirectly to examine the influence of UV-rays included in sunlight. Therefore, the two TLDs are set up, and then we tried to measure the UV-rays volume Other experimental conditions are : in or out of use of filters, and two exposure time (1.5 & 1.0 hrs)

The sampling of water for analyzing the water quality was carried out every one month at the each one point in the two reservoirs The time and depth of the sampling of water are 14.00 and 10cm below the surface, respectively The time of measurement of sunlight UV-rays volume by TLD is from 13:00 to 15:00. And we measured UV-rays volume, chlorophyll a, phosphate-phosphorus $(PO_4)^{3-}$ and water temperature at the reservoirs

5 RESULTS AND DISCUSSION

Fig.4 shows the relationship between the exposure time and irradiation volume of sunlight. It can be seen from the **Fig.2** that the clear proportional relationship is obtained. **Fig.5** shows the dependence of the irradiation wavelength on TL intensity[2]

The TL excitation peak was located near 235nm, and TL was not observed when the excitation wavelength was longer than 320nm The TL excitation seems to be related to the optical excitation band near 240nm. Therefore, the materials (CaF_2 Tb_4O_7) we used as a sensor for measuring the UV-rays volume may be used for UV-C and UV-B dosimeters The difference between UV-B and C is wavelength. The wavelength of UV-C is short in comparison with that of UV-B. However, the sensitivity of TLD in UV-B region is very weak compared with that of TLD in UV-C region. In actual measurement, therefore, it may be necessary to expose the material to the sunlight UV-rays more than 0.5hr[5]

As noted above, even if the UV-C volume is small, the light energy is extremely large because of short wavelength. Then, it brings about a serious action for the life of the earth.

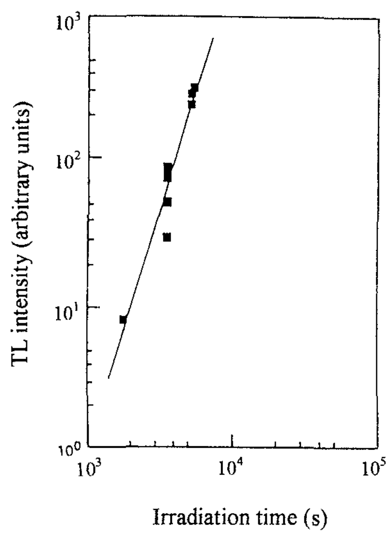

Fig 4 Relationship between TL intensity and sunlight Exposure time TL intensity was integrated from 152 to 242℃

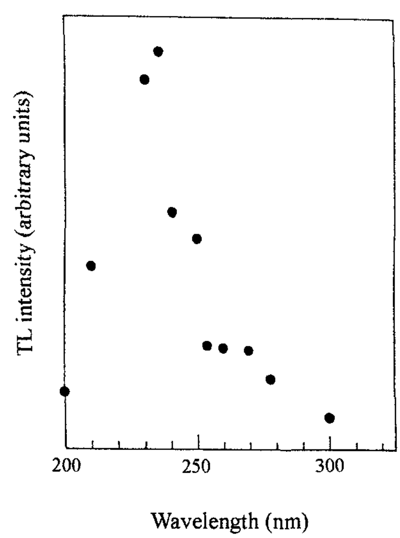

Fig 5 TL excitation spectrum of CaF_2:Tb_4O_7 (0 06 wt %)

Figs. 6-9 show the seasonal changes (water depth 10 cm) concerning the chlorophyll a, UV-rays volume, T-N (only this item is the data in 1997) and $(PO_4)^{3-}$ for the past three years (Apr -Aug , 1995-1997) at the reservoir A It can be seen from the Figures that the peak of each value of three other items besides the UV-rays volume exist at about 80 days (July) from the starting day of measuring in each year First, the certain correlation between the chlorophyll a and UV-rays volume is indicated by the data plotted in **Figs 6 & 7** And, this indicates that the certain correlation between the sunlight and chlorophyll a exists at the same time That is to say, it is understood that the photosynthesis is conducted Second, although the certain correlation between the UV-rays volume included in the sunlight and nutrient $(PO_4)^{3-}$ under water is indicated by the data plotted in **Fig 8**, the certain correlation between the UV-rays volume and T-N is hardly found as shown in **Fig 9** From the consideration mentioned above, as the volume of chlorophyll a (a substitute of photosynthetic speed) increases in proportion to the concentration of $(PO_4)^{3-}$, the chlorophyll a in the reservoir seems to be P rate-determining.

By using the TLD sensor mentioned above, the measurements on UV-rays, chlorophyll a, phosphate-phosphorus $(PO_4)^{3-}$ and water temperature were carried out. And the examination of related equation mentioned above was conducted referencing the equation ($D^{\lambda} = D^{\alpha} D^{\beta} D^{\gamma}$, where, D elapsed time (day), λ

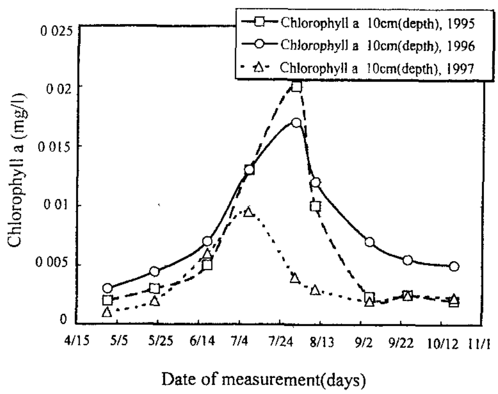

Fig. 6 Seasonal change of chlorophyll a

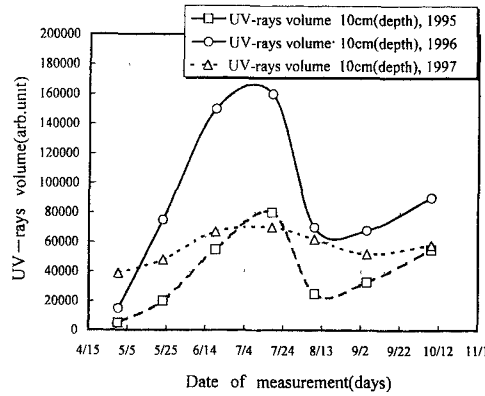

Fig.7 Seasonal change of UV-rays volume included in the sunlight

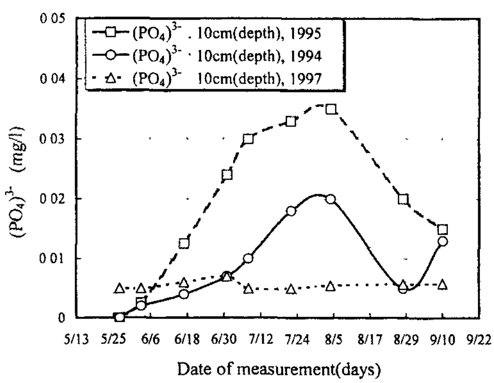

Fig.8 Seasonal change of $(PO_4)^{3-}$

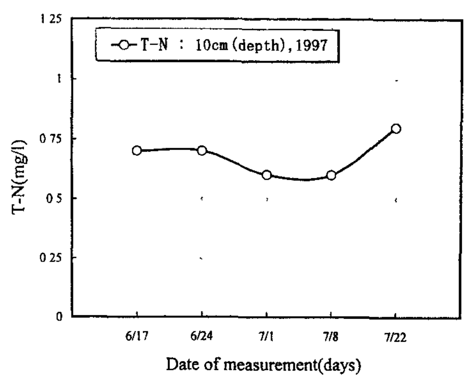

Fig. 9 Seasonal change of T-N

quantity of chlorophyll a (mg/l), α . UV-rays volume (arb unit), β : water temperature (℃), γ · quantity of $(PO_4)^{3-}$(mg/l)) we defined before[6].

The form of the function is based on the assumption that the related equation ($D^{\lambda} = D^{\alpha} D^{\beta} D^{\gamma}$) would be applicable for expressing the relationship between UV-rays volume and water qualities (chlorophyll a, $(PO_4)^{3-}$ and water temperature). This form of product is derived from the experimental data we obtained so far It seems that the examination due to the other workers is rarely found in this field.

Figs. 10 and **11** show the seasonal change of chlorophyll a and **Figs.12** and **13,** the seasonal change of UV-rays volume, respectively , at the reservoirs A and B. Furthermore, **Figs 14** and **15** show that of water temperature and **Figs 16** and **17** show that of $(PO_4)^{3-}$, respectively, at the reservoirs The following points are introduced from **Figs.10 -17**

At the reservoir A, the coefficient λ of involution curve from the rise of seasonal change of chlorophyll a is 0.29 (**Fig.10**), and then 0.29 for the coefficient α of that of UV (**Fig.12**) Furthermore, the coefficients β for water temperature and γ for phosphate-phosphorus $(PO_4)^{3-}$, 0 06 and 1 33, respectively (**Figs.14 & 16**).

At the reservoir B on the other hand, the coefficient λ for the chlorophyll a is 0 58 (**Fig.11**), and 0 58 for the

UV (**Fig.13**). Furthermore, the coefficients β and γ, 0.26 (**Fig.15**) and 0.01(**Fig.17**), respectively. It has turned out from the results that the seasonal change of chlorophyll a (D^{λ}) can be expressed by the related equation of only UV-rays volume (D^{α}) from the standpoint of the same value of coefficient, and chlorophyll a (D^{λ}) has not been directly concerned with the water temperature (D^{β}) and phosphate-phosphorus $(PO_4)^{3-}$ (D^{γ}). And, in the area in which the value of chlorophyll a is large the value of phosphate-phosphorus $(PO_4)^{3-}$ is also large.

Therefore, we consider that UV-rays volume may be useful as a simple indicator of closed water environment such as a lake, a marsh, or a reservoir etc. in place of chlorophyll a, and from the coefficient λ of observed value, the characteristics of each of the closed water environment could be decided.

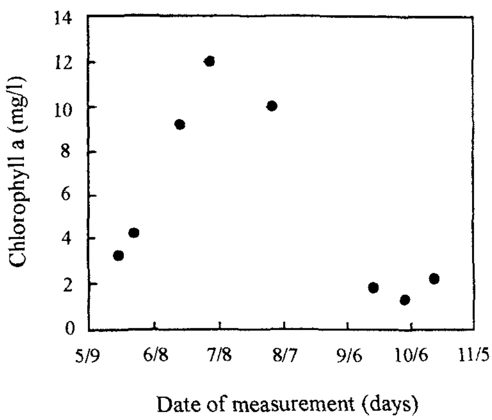

Fig 10 Seasonal change of Chlorophyll a at the reservoir A

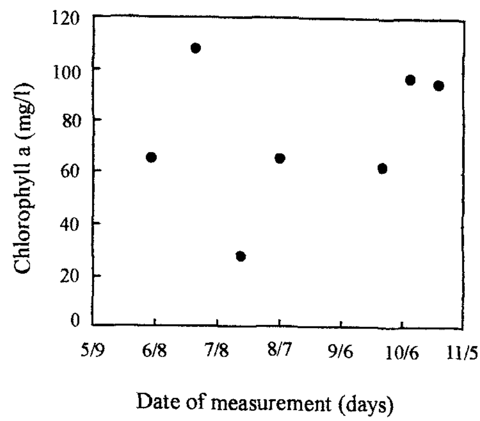

Fig 11 Seasonal change of Chlorophyll a at the reservoir B

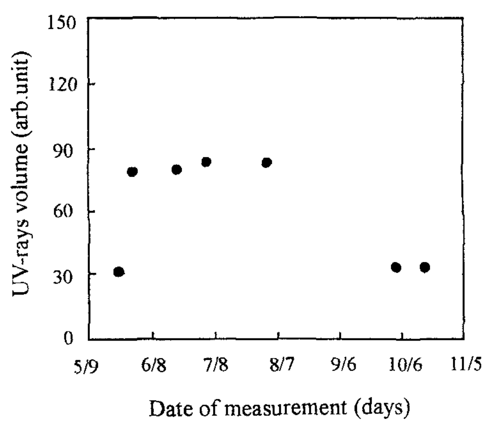

Fig 12 Seasonal change of UV-rays volume at the reservoir A

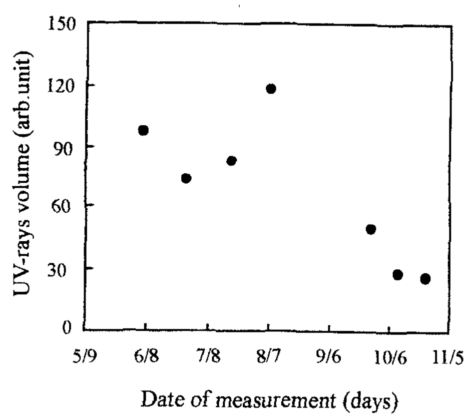

Fig 13 Seasonal change of UV-rays volume at the reservoir B

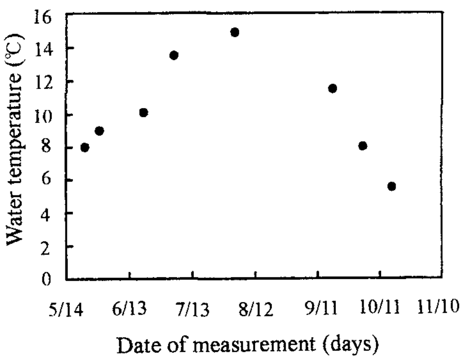

Fig 14 Seasonal change of water temperature at the reservoir A

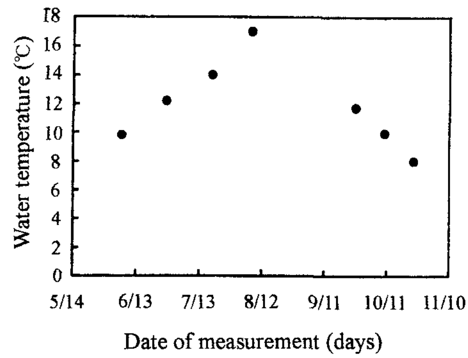

Fig 15 Seasonal change of water temperature at the reservoir B

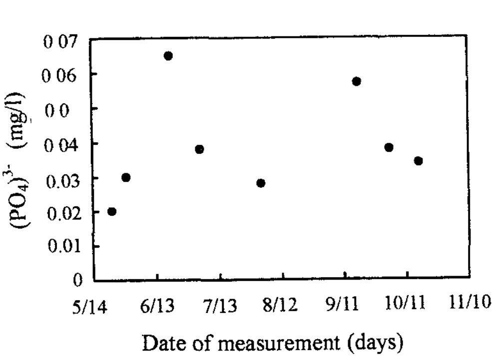

Fig 16 Seasonal change of $(PO_4)^{3-}$ at the reservoir A

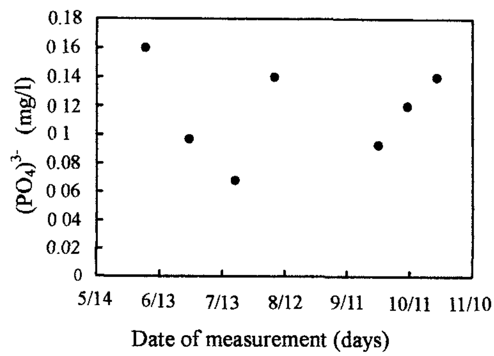

Fig.17 Seasonal change of $(PO_4)^{3-}$ at the reservoir B

6 CONCLUSION

In this study, the examination on the related equation which is in agreement with actually observed value is carried out under the assumption that a related equation, viz., $D^{\lambda} = D^{\alpha} D^{\beta} D^{\gamma}$ (where, D: elapsed time, λ : quantity of chlorophyll a, α . UV-rays volume, β . water temperature, γ . quantity of $(PO_4)^{3-}$) would be applicable. By using this model, the influence to the closed water environment viewed from sunlight UV-rays was estimated

As a result, it has turned out that the related equation, viz, $D^{\lambda} = D^{\alpha}$ which we could obtain would be applicable It is therefore considered that the specific characteristic of closed water environment such as a lake, a marsh or a reservoir etc could be decided from the coefficient λ of observed value.

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