4. Observational results and remarks on system improvements

The dominant feature revealed from the observed temporal-spatial variations is that the temperature variability of in the upper layer is larger in the region of relatively low salinity suggesting that both heating and cooling from above readily transfer or remove heat from the mixed layer above the pycnocline, which is enhanced by the vertical salinity gradient. The temperature is important because it affects the rates of most reactions. As shown below, T is one of the factors that determine the solubility of carbon dioxide in sea water.

Salinity is useful as a tracer of fresh water inputs. The seasonal variability of salinity in the Tsushima Strait is remarkable in Fig.6. The Tsushima Current was believed to be a branch of the Kuroshio, the western boundary current of the North Pacific subtropical gyre. However, the salinity decline observed in summer implies a considerable amount of entrainment of water from the East China Sea, which is affected by the fresh water inputs of the Changjiang (Yangtze) and the Huan Ho (Yellow) Rivers. The importance of major rivers on the ecosystems of marginal seas has been pointed out (Milliman, 1991). In the monsoonal areas, where river runoff is characterized by extensive seasonal change, the yearly cycle of ecological factors in marginal seas should be studied. The S sensor output was interupted several times, especially during summer. The salinity data deficit shown as black in Fig. 5 is attributed to particulate contaminants that stuck to the sensor. We have subsequently improved the arrangement of sensors in the overflow tank so that sea water flows relatively strongly against the salinity sensors to prevent fouling.

The *in vivo* fluorescence data has revealed the occurrence of spring and autumn blooms and the spatial variations within them. *In vivo* fluorescence was higher in the eastern Seto Inland Sea and lower in the Tsushima Strait (Fig.8).

To make rough estimate of pigment concentrations from fluorescence, following analysis was performed. The output of the fluorometer is thought to contain the informations not only of the photosynthetic pigments concentration but also of dissolved organic matters. Furthermore, the *in vivo* fluorescence depends on the physiological states and species of phytoplankton.

Therefore, the sum of concentrations of analysis-based pigments concentration seems to be appropriate as the independent variable for regression regarding the fluorescence as a dependent variable.

Assuming that the *in vivo* fluorescence intensity f is a linear function of the directly measured (analysis-based) chlorophyll-a and the pheopigments, (hereafter denoted by *Chla* and *Pheo*, respectively), fitting to the data pairs from the 668 filter samples from 22 cruises yields

$$f = 2.35(\ Chla + Pheo\ ) + 2.43. \qquad (4\text{-}1)$$

The assumption on which (4-1) is based implies that only f, the dependent variable, contains errors. However *Chla* and *Pheo* are not controllable variables and they also contains measurement errors. In such a case, it would be more appropriate to use the geometrical mean Model II regression (Ricker, 1972 and Laws *et al.* , 1981), which yields,

$$f = 2.82(Chla + Pheo) + 1.60 \quad (4\text{-}2)$$

The inverse function

$$Chla + Pheo = 0.355f - 0.564 \quad (4\text{-}3)$$

allows us to estimate the concentration of pigments from the fluorescence. Considering that the *Chla /Pheo* ratio is around 4 in most of the samples, the value of chlorophyll-a concentration can independently be estimated as $0.28f$ -0.45.

Both the fluorescence-derived and directly measured chlorophyll-a indicate a decline of phytoplankton biomass in mid-summer. The yearly cycle of phytoplankton blooms and declines was closely connected to the behavior of nutrients. The following discussion is possible although it is confined to the conditions in the upper layer near the ferry's sampling depth.

The nutrient concentrations were generally higher in the eastern part of the Seto Inland Sea than in the Tsushima Current area. Concentrations of PO_4-P, NO_2-N and NO_3-N showed similar variations, *i.e.*, decreasing during phytoplankton blooms, becoming depleted in mid-summer, and recovering when vertical mixing began to entrain deeper, nutrient-rich water. NH_4-N concentrations were low throughout the year except in the area of the Kanmon Strait, where phytoplankton biomass was relatively high and vertical mixing was strong throughout the year. Dissolved-Si also varied in parallel with phytoplankton biomass concentration, however the Si recovery occurred before those of N and P because of summer runoff in the eastern part of the Seto Inland Sea. There, N or P limited the phytoplankton growth preventing the complete depletion of dissolved Si.

Examination of PO_4-P and NO_3-N data for the period during phytoplankton blooms in the Tsushima Strait showed that about 0.1μM of PO_4-P remained when NO_3-N was completely depleted by phytoplankton uptake, *i.e.*, N-limitation rather than the other factors presumably terminated the blooming the blooms. The depletion of N continued throughout the five months from early summer until vertical mixing began in October. Si did not vanish in mid-summer and was presumably not the limiting factor for the growth of the phytoplankton, particularly diatoms, although the Si concentration threshold for diatom growth is not clearly defined. The persistance of Si in the mixed layer may be due to the entrainment of East China Sea Water containing Si of terrestrial origin.

N and P in the Eastern Seto Inland Sea were not completely depleted although they decreased during the phytoplankton blooms in which concentration of chlorophyll-a remained near or above 1μg/l throughout the summer. N and P were probably resupplied by both remineralization from sediment organic matter, which increasess with increasing water temperature and river runoff.

Two unusual blooms occurred in autumn of 1991 after the passage of two typhoons(see around 260th and 280th day of year in Fig.8). Perhaps the wind stress mixed nutrients to the upper layer thus initiating the bloom. On the other hand, the autumn bloom of 1992 was not characterized as storm-induced, although atmospheric lows of moderate magnitude did pass

through the area. This difference implies a threshold for the occurrence of storm-induced blooms. The parameters of this threshold, wind stress and the stability of stratification, must be somewhat higher than the regular atmospheric lows which pass through this area in most autumns.

In mid-February of 1992 (see data missing in Fig.8(b)), the fluorometer lamp burned out after working for seven months. In the week before the burn out, the baseline of the fluorescence output showed abnormally high values. These signals could be distinguished from the signal of a real bloom outbreak because they were high regardless of ship position. This high background is attributed to the compensating circuit which raised the baseline corresponding to the decline in lamp output before the burnout. Thus changing the lamp every few months, which is possibly shorter than lamp lifetime, is crucial.

Several papers concerning the efficiency of chlorophyll as an indicator of marine environmental change have appeared in various forms of expressions from simple to the sophisticated after our ferry monitoring scheme was designed. Falkowski and Wilson (1992) analyzed historical Secchi depth data, which depended on the chlorophyll concentration, to investigate whether the phytoplankton biomass has increased in the past 70 years as a result of atmospheric CO_2 increase. On the other hand, the use of a dual-flash fluorometer has been proposed as a sophisticated method to measure the photosynthetic efficiency (Falkowski and Kolber, 1992). So far as our automated monitoring program is concerned, the present setup of *in vivo* fluorescence measurements by a typical fluorometer seems the most appropriate, because laboratory-quality space cannot always be provided aboard volunteer observation ships. However, sophisticated sensors can be installed on the sea water intake system of ferries provided that the sensor system is somewhat robust.

HPLC has recently been recommended as a standard method for the analysis of photosynthetic pigments. However, before switching to this new standard, a certain period should be provided for the parallel use of HPLC and the traditional fluorescent or spectrophotometric chlorophyll-a and pheopigments analyses. Such a transition period would permit better utilization of the extensive historical pigment data set, for the assessment of long-term environmental change. Thus it may be necessary to continue cross-checking the results of the HPLC and the fluorescent and spectrophotometric chlorophyll-pheopigment methods for a certain period. In the present configuration of automated filtration sampler, the sea water quantity for each filtration is around 450ml, which is insufficient for analysis by HPLC. One possible procedure would be to use *in vivo* fluorescence for the temporal-spatial survey with co-use of limited number of HPLC sampling on the manned cruises.

The importance of measuring pH has been recognized and the available methods have been improved (Dickson, 1993a, 1993b, Millero, 1986, Millero *et al.*, 1993). From the requirements of the recent carbon dioxide problem, pH is a suitable variable with which to evaluate the sea water carbonate system. The measurement of any two of the four carbonate system variables, At (total alkalinity), Ct (total inorganic carbon), pCO_2 (partial pressure of dissolved carbon dioxide), and pH, permits the calculation of the other two quantities using equilibrium relationships (DOE, 1994). The desired pH measurement accuracy for this purpose is 0.002 and the colorimetric technique is expected to fulfill it. The pH electrode

sensor installed on the ferry does not fulfill this requirement. However, it is suitable for visualizing temporal and spatial patterns to explore related processes.

Indeed, the pH observed in both 1991 and 1992 in the eastern Seto Inland Sea (See Fig. 7) was lower by 0.2 pH unit relative to other areas. Generally speaking, the spatial variations of pH should be small because of the large buffering capacity of the sea water carbonate system. This pH-low was not due to rainfall or the consequent river runoff characterized by lower pH because the salinity in this area was not remarkably lower than those of other areas. It was therefore attributed to the mixing of benthic water, in which the decomposition of organic matter lowers pH, into the surface layer.

It was found that phytoplankton biomass was correlated with pH implying that photosynthesis consumed CO_2 and therefore raised pH. pCO_2 measurements (Kimoto and Harashima, 1993), particularly those made during the manned investigation on the March 1992 cruise, supported this explanation. This cruise took place during the initiation phase of a phytoplankton bloom characterized by intense photosynthetic activity. pCO_2 was low and pH was high in an area of high fluorometric chlorophyll.

On the other hand, the data of the July 1992 Cruise did not reveal a similar trend. This cruise took place when a phytoplankton bloom had terminated and therefore pCO_2 was rather higher in the area where phytoplankton had peaked in early spring than the other area. This contrast may be partly due to the fact that the higher production in the past contributed to the current high pCO_2 via a high rate of respiration or biodecomposition of organic matter. It is also true that higher water temperature increased the pCO_2 as supposed from the reduced solubility of gases.

Several problems in the process of calibrating the output from pH electrode have become clear. From October to December of 1991, the baseline of the pH signal was anomalously elevated compared to that in other seasons by about 0.3 pH unit. This difference is attributed to a change in the quality of the pH buffers. It is also became apparent that the use of freshwater-based calibration buffers could lead to a substantial offset error due to the difference in ionic strength between the buffers and sea water. In the new program beginning in 1994, sea water-based buffer solution (Smith, 1968) has been used to calibrate the intercept of the pH electrode output after measuring the slope with two freshwater-based buffer solutions.

Apart from the specific procedures for each measurement, the way of the sea water supply from the engine cooling pipe for the monitoring system is crucial. To minimize the time taken for the water to reach the measurement system from the entrance of the intake pipe and to keep the response of measurement, the flow rate should be as much as possible. This is particularly important in the measurement of dissolved pCO_2 because the carbonate equilibrium depends on the *in situ* water temperature. From these requirements, a pipe water pressure was adjusted to around 1 kgW/cm^2, which produced flow rate of around 10 l/min. On the other hand, we should consider avoidance of accidents due to the leakage of sea water and damages of the flow cells of the measurement system. To set up an overflow tank with open surface (see Fig.2 of the Harashima (1993c), in which the sensors are dipped, was found to be crucial to solve the pressure/flowrate problem. As we could not find a pressure regulator for