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Application of Optimum Multiparameter Analysis on Seawater Mixing in the South Sea of Korea Using Ra Isotopes

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Assuming that summer surface waters in the South Sea (northern East China Sea) are formed mostly by a mixing of three source water (Changjiang Discharge Water; Kuroshio Water and Yellow Sea Surface Water) we apply optimum multiparameter (OMP) analysis to calculate the mixing ratio of each source water to a given surface water. Since OMP requires more parameters than the number of water types (three in this study), we utilize two radium isotopes of dissolved ^{226}Ra and ^{228}Ra along with temperature and salinity. Parameter values of each source water are deduced from in situ and historical data. Results with three source of waters on the surface waters are quite promising with less than 1% of unanswered portions. Results not only reproduce the measured temperature and salinity faithfully but also discern the water masses of similar T and S according to their source water mixing. Extending OMP analysis to a whole water column obviously requires more parameters because more source waters are involved in the water mass formation. Original OMP routine utilized dissolved oxygen and nutrients. However, they seem to be perturbed too much by biological activities in the case of shallow waters. We discussed the use of other potential parameters. Also the benefit of parameter substitution is briefly introduced for the future OMP application on shallow waters.

Key words: OMP, Ra istopes, South Sea

Introduction

Epicontinental seas of Korea are unique in that the horizontal gradients of oceanic parameter are comparable or exceed vertical ones unlike other deep open oceans. Despite the small physical dimension and numerous previous efforts (Go, 1988; KORDI, 1993) the system is not well understood due to complex physiography and short term change in external forcing such as monsoon, intrusion of strong western boundary current (Kuroshio) and its extensions, short but intensive freshwater input, and winter overturning. This certainly gives an impression that seasonal signal is predominant as evidenced by frequent red tide out break offshore and salinity shock followed by mass mortality (Yang et al., 2000). However, recent investigations on South Sea ecosystem point out that annual variation is also noticeable such as coral bleaching and whitening (Chung et al., 1988). This leads to a speculation that the South Sea is experiencing the previously undocumented dynamic changes caused by not only local perturbations but global change related external forcing.

Characterizing waters in terms of the origin and subsequent mixing helps one to understand the circulation and biogeochemical processes on months and regional spatiotime scale. Two major tasks are involved for this. One is to define source waters and the other is to develop a suitable algorithm to calculate mixing ratio. The former may be deduced from the historical data and the latter is the scope of this study. In this paper we applied and modified the exiting method to quantify the formation of local water masses by mixing of source waters.

Origin and mixing of seawater can be, at least, semi-quantified by a number of existing methods. Various graphic analysis algorithms of T-S diagram were dated back to early modern oceanography era (Helland-Hansen, 1918; Jacobson, 1927; Defant, 19 29 cited in Tomczak 1981), and the latest addition to this family is the model by Chen et al. (1995).

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These methods rely on two most conservative parameters of temperature and salinity, which exceed in precision and availability over any other parameters. Although other parameters suffer from inherent poor conservativeness and lower precision compared to temperature and salinity, theoretically any two parameters are acceptable for graphic analyses. When source waters are few two-dimensional graphic analyses are straightforward and reproduces in situ data faithfully as demonstrated by Kim (2000). However, as the number of source water type increases, reliability of the solution by only two variables is weakened are be to based on necessary assumptions to overcome underdetermination. For more precise mixing ratio calculation, especially when multiple source waters are involved in sea-water formation like most Korea waters, utilizing multiple parameters as suggested by Tomczak and his colleagues seems mandatory.

Multiparameter analysis algorithm has been refined for more than a decade (Tomczak, 1981). Recently the source code of the latest optimum multiparameter (OMP) method is released for public use by developers (http://www.ifm.uni-hamburg.de/~wwwro/omp std/omp toc.html). Since it solves mixing ratio of source waters based on least square fitting that goodness-of-fit is provided as a proofing tool. Aiming for a universal application it is written to accommodate routinely measured oceanographic parameters i.e. temperature, salinity, dissolved oxygen and nutrients. Since each parameter has different unit, scale, variance, precision and accuracy, this method takes advantage of overdetermination, i.e. it uses more parameters than the number of source water types. Because of this one can use less conservative and precise parameters to solve mixing ratio of water types.

Result of OMP application by Mackas et al. (1987) was satisfactory for deeper waters of lesser variability but erroneous for surface waters, which are more specific concern in terms of weather and fisheries. This is an expected result since all parameters except temperature and salinity are not conservative in biologically active surface layer. Even temperature and salinity near land are not conservative enough in summer due to short-term local weather variability. In such a case overdetermination alone cannot overcome nonconservative nature of most parameters.

Our primary concern is the epicontinental waters where strictly speaking no parameters are conservative. Overdeterministic feature of OMP seems adequate to study epicontinental water mixing. However, it requires evaluation of parameters before applying to surface waters. The aim of this study is to demonstrate that surface water can be handled properly by substituting original parameters with others, for example, radium isotopes in this study. Based on previous studies (Moore, 1969; Nozaki et al., 1989; Lee and Kim, 1997), dissolved Ra isotope activities are water type specific and more conservative than other parameters available for the South Sea to date. We assumes from previous studies that in summer surface water type of the South Sea can be simplified to three major types; Kuroshio Water or Tsushima Current, Changjiang Discharge or Changjiang Dilute Water and Yellow Sea Surface Water. Although we utilized four parameters for three water types, results were not the typical overdetermined case as it looked because the pattern of temperature distribution showed quite close to randomness. For the future generalization, an extension of OMP method to a whole column and addition of parameters are discussed.

Method

Mixing ratio calculation by OMP analysis requires a definition of several source waters (water types hereafter). Water masses are the products of mixing among several water types. Hydrographic properties of an ideal water type would be presented as an end point in the parameter space, such as TS diagram with own set of dispersion mode (standard deviation). In reality, each water type can be included in measured data or invisible due to its remote origin. For the latter case one should refer to historical data. The basic assumptions of OMP analysis are that all water masses are produced by mixing of a few water types and as a result of mixing hydrographic characteristics are altered linearly.

The framework of OMP analysis is to solve linear mixing equations which is expressed as a linear equations

$$Gx - d = R \qquad (1)$$

where G is a matrix representing the water type hydrographic parameters of concern, d is a measured data vector arranged in accordance to water type parameters, x is a vector consisting of mixing ratios which is to be solved and R is a vector of residuals. OMP analysis solves x vector which minimizes residual sum of square i.e. R^TR. Residual sum of square reflects the degree of uncertainty: measurement error, water type parameter variance, nonlinear mixing nature, etc.

If we do not impose any constraint on mixing ratio, it can be given as either positive or negative. Since physical mixing explicitly means addition, nonnegativity constraint on solution vector is essential. According to Kuhn-Tucker theory, nonnegative x that minimize R^TR exists and details are discussed in Menke (1984). Since OMP analysis relies multiple parameters, differences in data quality, accuracy, degree of conservativeness should be considered. To reflect the overall data quality, OMP analysis introduces weight matrix W, which are generated from each parameter data set. The nature of data scatter from the mean is commonly described by variance. Previously Thompson and Edward (1981) utilized variance due to measurement error for weighting, later Mackas et al (1987) derived W from historical data. It would be better if W can be calculated from real data set. In this context Tomczak and Large (1989) proposed that inverse of variance was logically preferred. Since accurate and precise parameters, such as T and S, carry small variance, their weighting score is assigned higher than others with lower data quality and conservativeness such as nutrients data. Mathematical form of residual sum of square introducing weighting matrix is given as follows.

$$R^TR=(Gx-d)^TW^TW(Gx-d)$$
$$=\sum_{j=1}^{m}W_j^2\left(\sum_{j=1}^{m}G_{ji}x_i-d_j\right)^2 \quad (2)$$

where, m is a number of parameter used and n is a number of water type. Typically OMP analysis accommodates $n \geq 2$, and $m \geq n$.

Above mathematical form is still impractical because it carries an incommensurable unit of each parameters. In order to make comparable each elements of G need to be normalized such that

$$G'_{ji}=(G_{ji}-G_j)/\sigma_j \quad (3)$$

where G_j and σ_j are the mean and standard deviation of j-th parameter in G matrix. Tomczak and Large (1989) assigned the weight of each parameter from the data subsets having well defined linearity as

$$W_j=\sigma^2{}_j/\delta_{jmax} \quad (4)$$

where δ_{jmax} is the largest of the water mass variances for parameter j. When measurement error is small enough as in the case of temperature and salinity acquired by CTD, variance (degree of dispersion from mean) is a good measure of resolving power to discern different water masses whereas magnitude of inherent variability sets limit the resolution of parameter.

In our case coincident mixing of three water masses scatters data in triangular shapes in 2-D plot. Since OMP weighting method relies on linear relationship it is not applicable to our case. We did semi-quantitative weighting considering the characteristics of parameters. Usually quality of temperature data excels salinity by one order of magnitude. This is the reason why OMP analysis takes temperature as a master parameter. However, in summer sea surface temperature varies due to local perturbations. Heating, precipitations, winds and cloud cover easily change surface temperature more than 1℃ that precision of temperature is weakened where local variation is merely about 3℃. Thus we choose salinity as a master parameters (98%) and weight of temperature is assigned as a coefficient of determination for a linear correlation (R^2) against salinity. Weights of two radium isotopes concentration are given as a coefficient of determination for a multiple correlation against salinity and temperature.

Finalized equation representing OMP analysis algorithm is expressed as a matrix form

$$W(G'x-d')=R \quad (5)$$

and solving for vector x of nonnegative elements minimizing the residuals using equation (2) according to Kuhn-Tucker theory.

Data

The study area covers northwestern part of the East China Sea and western South Sea of Korea.

The area extends from 30′ to 34′N and from 124′ to 127′W. A total of 24 surface radium samples were taken from Aug. 25 to Sep. 1, 1997 along with temperature and salinity using SBE 911 plus CTD. About 60 L of seawater was passed through Mn-impregnated fiber with a flow control of less than 2 L/min. Radiochemical purification was made following the methods of Yamada and Nozaki (19 86). Activities of $^{226,228}Ra$ were counted with a high purity germanium detector with well geometry.

Results

OMP analysis of surface waters was made based on three water types: Tsushima Current Surface Water assuming it stems from Kuroshio, Changjiang Discharge Water and Yellow Sea Surface Water. Since study area does not include the regions of pure water type, parameter values of water type are extracted from available historical data as shown in Table 1. Water type values of radium isotopes are deduced from the salinity vs. Ra activity diagram (Fig. 1). The vertices of the triangles shown in Fig. 1 were drawn to include the data including historical ones while keeping the area as small as possible. End-member values of radium isotopes for three water types are available from the previous studies (Elsinger and Moore, 1984; Nozaki et al., 1989). Major sources of radium in seawater are the terrestrial input and diffusion from bottom sediment. Oceanic waters such as KW contain least Ra due to remoteness from the sources and *vice versa* in the case of YSSW which show highest Ra concentration in the study area.

Table 1. Parameter values of three water types and weights used for OMP analysis.

Water Type / Parameter	Changjiang Discharge Water	Kuroshio Water	Yellow Sea Surface Water	Weight
Temperature (℃)	28.0*	27.5	28.0	9
Salinity	0.0	34.688§	32.0	98
^{226}Ra (dpm/1000 L)	113.5‡	65.2§	315	39
^{228}Ra (dpm/1000 L)	165.0‡	16.5§	740	20

* No data available, arbitrary value is assigned to initialize G matrix. Due to low weight of temperature calculated results are not sensitive to this value.
§ Nozaki et al. (1989)
‡ Elsinger and Moore (1984)

Each element of G matrix (parameter values of water types) is summarized in Table 1 with remark on its source when references are made. Last column of Table 1 is a weight vector calculated as discussed in previous section. Weight of temperature is given very low implying poor information content. It is expected from the absence of real temperature data of the Changjiang discharge, relatively large short-term variation of temperature at surface as described in previous section, and weak zonal differences in summer.

Results of calculated mixing ratio are given in Fig.2 for each water type along with residuals (Fig. 3), which designate the unexplained portion of water mass in percent with currently defined water type parameters. Residuals fall within fairly satisfactory margin of less than 1% of total mass. Here it should be emphasized that OMP analysis is the only kind that reports the error of the solution in quantitative manner. Contour diagrams show smooth fractional changes with only two isolated isopleths at stations B7 and C7. Overall characteristics of mixing ratio diagram (Fig. 2a~c) look quite similar to the combined feature of temperature and salinity distribution diagram (Fig. 4). From this point of view we judge that OMP analyze results are convincing.

Primary interest on the summer surface water in the study area is the behavior of the Changjiang Discharge Water due to its detrimental ecological impacts. Results show that water mass consists of more than 10% of CDW resided at the south-western part of Jeju Island and disconnected from the low saline water body at the Chinese side (Fig. 2a). On the other hand considerable amount of oceanic water (Kuroshio origin) intercepted two low salinity water masses (Fig. 2b). Considering its distribution pattern CDW seems to be at its waning stage at that time and saline oceanic waters were expanding westward.

The Yellow Sea Surface Water extended far south and near to Chinese coast (Fig. 2c) but its eastward expansion was hindered by oceanic water mass resided near the Jeju Island and southern coast of Korea. According to out result, flow of YSSW along the southern coastline seems to be blocked. To understand the material transport from the Yellow

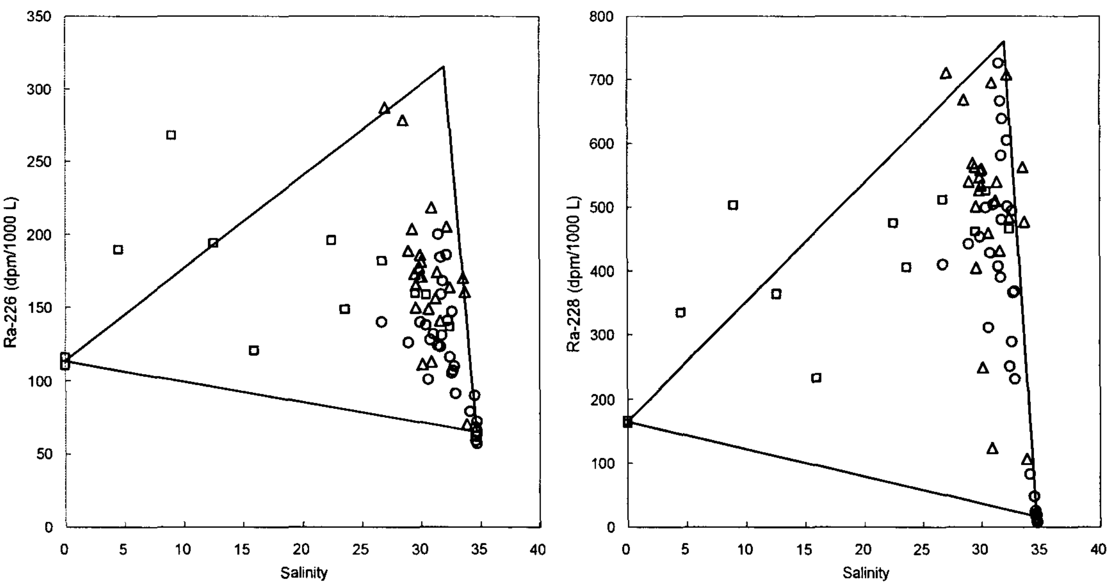

Fig. 1. Scatter diagram of surface seawater ^{226}Ra (left panel) and ^{228}Ra (right panel) activities (dmp/1000 L) against salinity measured in the South Sea from Aug. 25 to Sep. 1, 1997 (triangles). Data sets of Elsinger and Moore (1984) and Nozaki et al. (1989) are shown together as squares and circles, respectively. Lines of triangles are inferred from the result of linear regression analysis of data located outer margins. Each coordinate value of vertices is assigned as water type value.

Sea to the East Sea (Japan Sea) possible existence and the role of salt front and its location subject to future examination. Another aspect worthy of mentioning is the absence of pure water types in the study area. Results point out that all the waters are more or less modified by mixing of all three water types.

Discussion

Both the South Sea and the East China Sea lie on the vast continental shelf and receives huge amount of fresh water and oceanic waters at the same time. Unlike to other epicontinental seas over large shelf, they border land masses and islands arc, and supply materials to the semi-enclosed seas downstream. As a result waters in the South Sea significantly affect other Korean waters directly or indirectly. Also a short spatiotime scale of environmental variability in these seas needs to be considered more seriously. This is the main reason we need to trace the mixing process in detail. Methods other than OMP analysis are two-dimensional in nature. Familiar examples are the classical T-S analysis and its varieties as mentioned earlier. Considering its multidimensional nature and provided with suitable parameter set OMP method should be able to trace more realistic mixing history of water mass than 2-D analogues. In this respect a potential of OMP analysis is tested though in a reduced scale, i.e. confined to surface waters and the result is quite affirmative.

Reconstruction of water type mixing ratio of epicontinental water is difficult due to its multiple origin and precarious nature but rewarding. Northern East China Sea and the South Sea surface waters are cooled once every winter so that waters are mixed vertically and acquire homogeneous characteristics. If we have data of winter condition and subsequent stratified seasons, behavior of biogeochemically active elements can be deduced without further efforts. For example, the discrepancy between *in situ* nutrient concentrations and those estimated from OMP analysis result and end-member values implicitly contain the information about the size of a new production. For that purpose we excluded nutrients deliberately from OMP analysis initialization unlike to Tomczak and Large (1989). They wanted to utilize routinely measured parameters of 80's to solve the water type

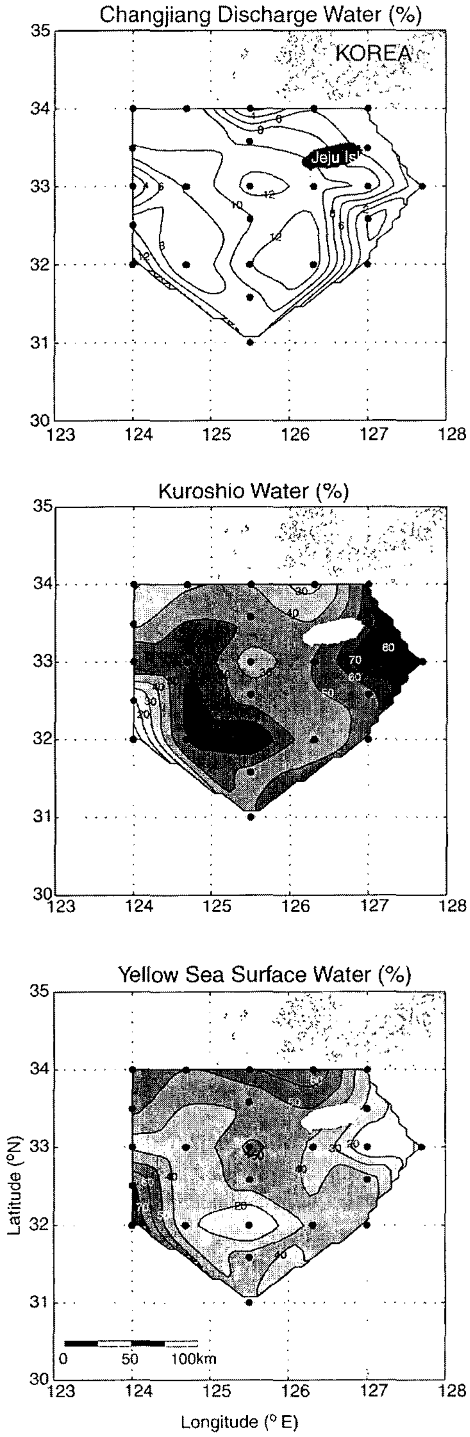

Fig. 2. Results of OMP analysis shown as water type mixing ratio (%) for the surface water observed from Aug. 25 to Sep. 1, 1997: Changjiang Discharge Water (top), Kuroshio Water (middle) and Yellow Sea Surface Water (bottom).

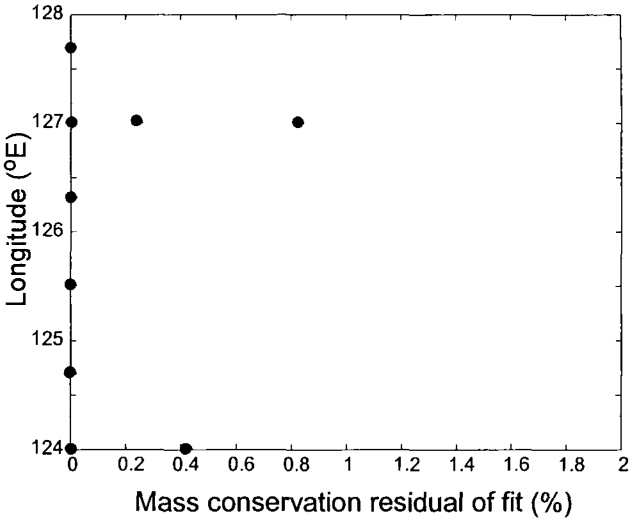

Fig. 3. Mass balance residuals of fit (in %) arranged by the longitude of sampling stations (n=24).

mixing and chosen nutrients as important input variables. By omitting nutrients we need multiple parameters instead to initialize OMP analysis.

In 90's advances in analytical method made a few other parameters routinely measurable with reasonable precision. As exemplified in this paper, radium isotopes are the good candidates for water mixing studies. One shortcoming of radium is that it requires rather elaborate radiochemical analysis. Routine measurement is not impossible but not easily accommodated. Another promising parameters are the pH and alkalinity revised and upgraded for the oceanic carbon cycle studies recently (Clayton and Byrne, 1993; Yao and Byrne, 1998). Nowadays dissolved oxygen can be measured continuously using a sensor attached to CTD though accurate measurement is a little bit tricky. Apparent oxygen utilization seems to have more information on the water mass history than dissolved oxygen concentration itself. When two or more fresh water input is sizable, seawater $\delta^{18}O$ offers a solid background to discriminate the sources. Considering biological perturbation, those parameters mentioned above are at least equal or better than nutrients (nitrate, phosphate and silicate). Once nutrients are released from input variables then we can treat nutrient as dependent variables to take a glance at the local biogeochemical cycle. A simple model can give us a ball park number of biological process

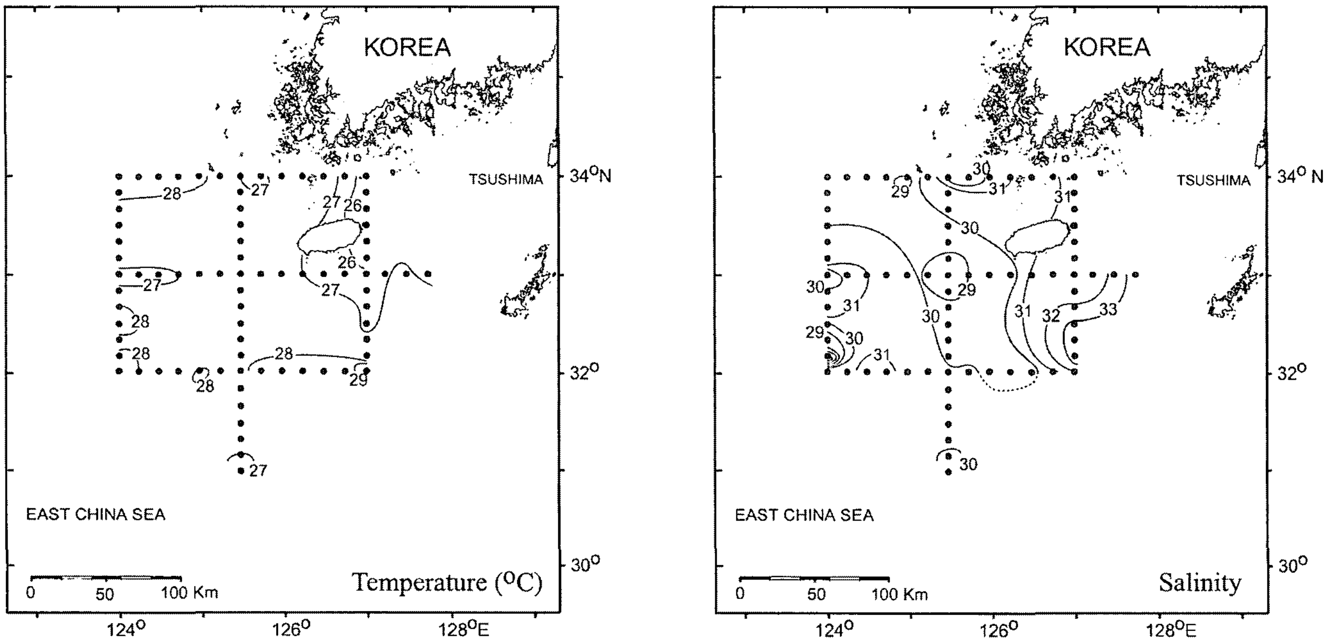

Fig. 4. Regional distribution of surface temperature (left) and salinity (right) measured from Aug. 25 to Sep. 1, 1997.

instantly.

In this paper we were not able to use none of the parameters mentioned above due to simply lack of a sufficient data. Also the OMP analysis was confined to surface waters due to limited number of radium isotope data. Studies on the South Sea/ East China Sea are still ongoing that we'll be able to extend OMP analysis to whole water column considering middle and bottom water types together in the near future.

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