

Estimates of wintertime mixed layer nutrient concentrations in the North Atlantic

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Abstract—Nonlinear, time-dependent model sensitivity to initial conditions poses a challenging problem when attempting to initialize such a model. In order to initialize a chemical–physical model of the upper several hundred meters of the North Atlantic, we have calculated the initial concentrations of several chemical species from three estimation methods by a combination of the *Climatological Atlas of the World Ocean* (LEVITUS, 1982) and the TTO north, and tropical, Atlantic study data bases. A $1^\circ \times 1^\circ$ grid of the average initial concentrations over the mixed layer depth was generated for the method of preference and added to the initialization data base of the model. Contour maps of this calculated initial concentration set are presented and comparisons with the other methods and actual data are made.

INTRODUCTION

KNOWLEDGE of the distribution of chemical variables in the sea is a principal goal of ocean chemists. For many years problems of technique, whether in analysis or in sampling, hampered progress. This, and the continuous challenge of determining new chemical species, has resulted in a fragmented data set which only recently has become in any way assimilable in the manner that large-scale physical data sets are commonly treated.

Within the deep ocean the chemical conditions are, with the exception of the artifacts introduced by man, in approximate steady state, so that a simple compilation of data laboriously produced over many years would eventually yield a map or atlas of chemical properties. In the upper ocean, however (viewed here as approximately extending to the maximum depth of wintertime mixing), steady-state conditions can not apply and chemical data obtained from diverse cruises are badly biased in time. It is quite unlikely that we will ever achieve synoptic sampling of the entire ocean, so that some kind of model or data treatment will have to be applied in order to uncover realistic seasonal chemical signals. In this paper we explore the problem further, and attempt to compute some wintertime surface chemical properties for the North Atlantic Ocean by manipulating expedition data greatly biased in time and comparing them, where possible, to actual winter observations.

The choice of a late wintertime signal is significant. Operationally winter cruises are difficult to conduct, so that data sets generally result from fair-weather seasons. More importantly, winter forcing sets chemical boundary conditions for the upper ocean that are critical in the initialization of seasonal models. JENSEN (1987) provides a review of how sensitive even simple nonlinear systems are to initial conditions.

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The data sets we choose cover the distributions of PO_4 , NO_3 , SiO_3 and alkalinity, since these are master variables of ocean chemistry. The rapidly exchanging gases (such as O_2 , etc.) are normally set close to atmospheric equilibrium in winter. However, the exceptionally slow exchange time for CO_2 (BOLIN, 1960; BROECKER and PENG, 1982) raises the possibility of treatment similar to that proposed here for the nutrient species; we plan to address this in a later paper. The strategy for non-gaseous species is quite general and many other chemical properties (e.g. trace metals) are potentially treatable in the same way.

Most ocean chemists have a general belief that wintertime properties can be estimated in some way from wintertime mixed layer depths and chemical profiles, but there appears to be a distinct lack of formalism in the concept. WOODS (1985) gives one expression of this process by developing a theory explaining the regional variation of the annual maximum depth of the mixed layer. Following from this, WOODS (1985) gives an equation for the nutrient balance within the seasonally varying mixed layer depth.

In this paper estimated winter surface concentrations were obtained by three methods applied to each station profile considered. The first method was by interpolation to the base of the average wintertime mixed layer depth (MLD) (extrapolation method). The second method involved integrating and averaging over this same depth interval (integral method). The third method was employed largely to demonstrate the necessity of information about the wintertime MLD, by interpolation to the base of the seasonal mixed layer (seasonal method) at the time of observation. The first two methods require some *a priori* knowledge of physical forcing while the last is a worst case example, applying to situations when only the fair-weather station data are available. Analysis of some limited time series data and comparisons with actual wintertime cruise data (also limited) provided a means to choose a preferred method.

Aside from the motivation we received from the initialization problem of our model, additional incentives exist. The Global Ocean Flux Study (GOFS) is currently in the process of planning time series stations and cruise tracks for the world oceans (U.S. GOFS Report 2, 1986). Maps of the sort derived in this paper provided an important insight into the structure and variability of the biologically active upper several hundred meters of the ocean. Knowledge of what the ocean looks like during the summer (fair weather) can be contrasted with estimates of its condition during the winter (foul weather). Another incentive is the sensitivity of inverse methods to initial conditions. WUNSCH (1987) shows that, while solving the governing equations backwards in time and upstream in space, one is moving in an inherently unstable direction; the end point of these calculations (the initial conditions) can have a strong effect on the outcome of the model. Although WUNSCH (1987) deals with the problems stemming from the initialization of an inverse model applied to transient tracers, the success we experienced in finding the initial conditions of tracers, that admittedly are in steady state on an annual time scale, leads us to believe that a similar treatment of transient tracer data also may be successful.

Existing compilations and databases

Although many oceanic atlases have been compiled by various workers, the climatological atlas prepared by LEVITUS (1982) was of primary use in this study. At standard depths he mapped temperature, salinity, dissolved oxygen and several derived quantities (e.g. potential density) via an objective analysis, to a $1^\circ \times 1^\circ$ grid. Our analysis used the

temperature (T), salinity (S) and sigma- t (σ_t) profiles to compute the MLD. In addition to this explicitly three-dimensional atlas, other implicitly three-dimensional atlases are also of some relevance. ISEMER and HASSE (1985) provide, to our model, the necessary latitudinal and longitudinal distributions of important air-sea heat fluxes as well as the averaged wind speeds with standard deviations. SIMONOT and LE TREUT (1986) have prepared an atlas of optical water types for the world oceans, though this compilation is aseasonal. These optical water types, in conjunction with the heat flux values from ISEMER and HASSE (1985), yield sufficient information to model the heat balance of the upper 500 m of water and thereby provide a physical template on which to construct chemical models. What is missing is information, either implicitly or explicitly three-dimensional in nature, of the chemical constituents within the upper 500 m at the time our model is initialized.

Nevertheless, previously prepared atlases of nutrient concentrations do not address the problem of finding the initial conditions (concentrations) directly. KAMYKOWSKI and ZENTARA (1986) provide cubic regressions of NO_3 , PO_4 and SiO_3 against temperature and σ_t based on a very large National Oceanographic Data Center (NODC) database. From LEVITUS's (1982) work we could have calculated these three nutrients at the model's initialization time, but we would not have obtained any information about the initial conditions of the CO_2 system (alkalinity). KAWASE and SARMIENTO (1985, 1986) performed isopycnal analyses on several nutrients and related properties from the TTO plus assorted cruises database; however, they restricted themselves to either the permanent thermocline (KAWASE and SARMIENTO, 1985) or a depth range of 800–3000 m (KAWASE and SARMIENTO, 1986). Our study provides another look at the chemical data of the North Atlantic from an initial condition point of view.

Basis of chemical variability

The basis of chemical variability in the ocean is due to both physical changes (mostly in heat flux) and biological changes (the growth and decay of organism populations). Purely chemical processes of adsorption, hydration, radioactive decay etc. are not addressed here. Much of chemical oceanographic modeling deals with an attempt to separate and characterize the above two classes of processes; here we seek the combination of these classes that yield an estimate of the average wintertime conditions within the mixed layer. GILL and NILER (1973) concluded that the main cause of seasonal changes in temperature, salinity, sea level and velocities is due to changes in the heat flux through the surface. They showed that, on the scales considered, heat storage is local and horizontal advection is not important to the ocean interior. GILL and TURNER (1976) developed a model that provides the mechanism of the MLD response to heat-derived buoyancy flux and wind-derived momentum flux. Through the use of hysteresis loops of sea surface temperature, water column heat storage and potential energy they determined that convective mixing is essentially non-penetrative. KIEFER and KREMER (1981) used this physical model of seasonal thermocline development and coupled it with a biological model of phytoplankton response to light and nutrients. For this model the response of water column constituents is largely stratigraphic with respect to the development of the seasonal thermocline; thus water column chemical properties become trapped relics within seasonally stratified layers awaiting wintertime deep mixing to release them back into the mixed layer. WOODS (1985) describes the balance between biological removal of nutrients from the mixed layer due to particulant loss, and nutrient

replacement in the average wintertime mixed layer due to changes in the MLD with circulation by the following equation.

$$N_0 = \frac{N_p(D - \mathbf{U} \cdot \nabla D \Delta t)}{bH_N + (D - \mathbf{U} \cdot \nabla D \Delta t)}. \quad (1)$$

Following Woods notation: N_0 is the uniform nutrient concentration within the mixed layer, N_p is the concentration of the nutrient-rich waters from below the permanent pycnocline, D is the annual maximum depth of the mixed layer, \mathbf{U} is the Lagrangian velocity vector of the water parcel under consideration, Δt is approximately 12 months, b is the fraction of nutrients lost from the mixed layer due to particles that settle into the permanent pycnocline, and H_N is the depth of the nutricline at, say, the end of the summer.

In this paper we test methods of estimating the product of this resupply of nutrients to the average wintertime MLD without dealing directly with either biological processes or horizontal circulation.

MIXED LAYER DEPTH CALCULATION

The MLD was calculated from Levitus's climatological atlas (LEVITUS, 1982) or taken directly from the station profile. Where the MLD values came from the atlas, the Transient Tracers in the Oceans (TTO) stations (both the north and tropical Atlantic studies) were navigated to this $1^\circ \times 1^\circ$ grid. Levitus's average wintertime database was used to calculate the MLD's because it already exists on a grid, has a three-dimensional distribution of T , salinity and σ_t at the right time of year for initialization, and has been previously analysed for MLD for comparison (LEVITUS, 1982, Fig. 95). Each station on the Levitus grid (extrapolation and integral methods) or each TTO station profile (seasonal method) was subjected to the following algorithm to find the MLD by a variable σ_t criterion. The surface values of temperature and salinity were taken as starting values, and a $\Delta\sigma_t$ due to a lowering of the temperature of this parcel of water by 0.5°C was calculated to allow comparison with LEVITUS's (1982) results. Subsequent subsurface σ_t values were checked against the surface σ_t until the difference was greater than the calculated $\Delta\sigma_t$. A linear interpolation between the last depth interrogated and the one directly above was performed to find the precise depth at which the density profile reaches its target value. At certain grid points this algorithm failed to calculate a value. These occurrences fell into two distinct categories. The first happened when the algorithm estimated a MLD greater than the last depth of the reported profile. Since there were no data to support this contention, this grid point was set to the previously designated 'undefined' value. Additionally, the calculation of the MLD was based on the assumption that the σ_t profile monotonically increased with depth. Whenever this assumption was violated, that grid point also was set to the 'undefined' value for that station. These 'undefined' values (1049 out of 5227 grid points) were later replaced by a spline/relaxation interpolation performed by the mapping software package ATLAS (SGOUROS and KEFFER, 1983). The MLD's and their grid latitude and longitude were then written out to a data file for later use, both for initializing our model and for interpolating/integrating the TTO database. Maps of the MLD are shown (Fig. 1) for

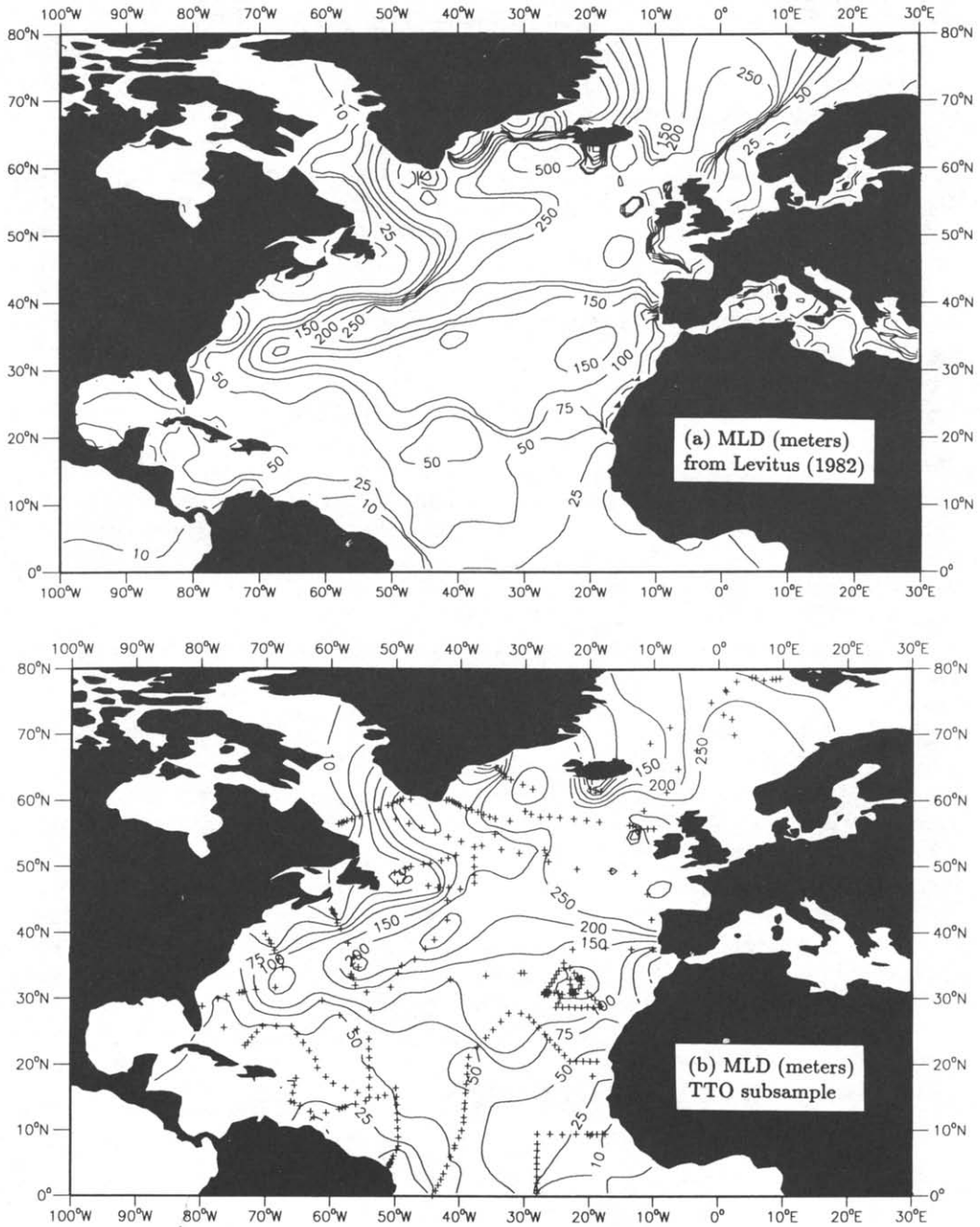


Fig. 1. Mixed layer depth (m) as determined by a variable $\Delta\sigma_t$ criterion. (a) Map based on a $1^\circ \times 1^\circ$ grid of average wintertime profiles (LEVITUS, 1982). (b) The same surface subsampled at the TTO station locations (crosses). Contour levels are 10, 25, 50, 100, 150, 200, 250 and 500 m. See text for further remarks.

comparison of the MLD derived from the Levitus and TTO databases. Figure 1b was created by extracting the MLD's from Fig. 1a at only the TTO station locations.

A great reduction in the complexity of our results was achieved by having only one MLD criterion. Alternate techniques for calculation of MLD were considered, including a simple ΔT criterion. We chose the variable $\Delta\sigma_t$ approach to include nonlinear effects. For example, a $\Delta\sigma_t$ criterion was calculated for each station based on the effect of a 0.5°C change; since the density response is nonlinear this created different $\Delta\sigma_t$ values depending on the surface water T and S [e.g. a 0.5°C change in waters with $T = 6\text{--}10^\circ\text{C}$ and $S = 35\text{‰}$ would yield a $\Delta\sigma_t$ criterion of 0.075, while for waters of the same salinity but with $T = 24\text{--}26^\circ\text{C}$ a $\Delta\sigma_t = 0.15$ would be found (LEVITUS, 1982)]. The inclusion of this nonlinear dependency of σ_t on temperature into our analysis allows us to show only one map for each property analysed, instead of one for an *a priori* ΔT criterion and one for an *a priori* $\Delta\sigma_t$ criterion as conventionally done [LEVITUS (1982) used 0.5°C and 0.125 units, respectively].

Comparison of the distribution of the wintertime MLD (Fig. 1) was made with those published by LEVITUS (1982, Fig. 95). Levitus's MLD's are based on either a ΔT or a $\Delta\sigma_t$ differential restricted to the month of March and are frequently thought of as *dead-of-winter* MLD's. We have used the *average wintertime* MLD's (Fig. 1a) as a more robust indicator of the upper ocean preconditioning during the *entire* winter (February, March and April). By so doing we have used a broader band filter than Levitus to average out the anomalous behavior of the MLD from year to year because this technique must work equally well everywhere in the North Atlantic regardless of the year or month the chemical profile was collected [LEETMAA (1977) reports a MLD of over 500 m in the northern Sargasso Sea]. Nevertheless, some differences and similarities exist. The ridge of shallow MLD extending along the Gulf Stream can be seen in the Levitus atlas, Fig. 95a (ΔT), but not in Fig. 95b ($\Delta\sigma_t$), nor here in our Fig. 1 (variable $\Delta\sigma_t$). The local minimum in MLD located at $\sim 38^\circ\text{W}$ and $\sim 50^\circ\text{N}$ on Levitus's ΔT map is apparent here only as a plateau in Fig. 1a and b. The strong trough of deep MLD just south of the Gulf Stream apparent in the Levitus atlas is also a strong feature in Fig. 1a and b. The MLD north of the British Isles and east of Iceland is not the same in detail as Levitus's maps, but in general was similar. Even though a great deal of smoothing was introduced into the data in the compilation of the average wintertime database, some of the noise noted by LEVITUS (1982) was still apparent in Fig. 1a and b. Although the chemical database has only 338 station locations (Fig. 1b) compared to the Levitus grid of 5227 locations (Fig. 1a), the reduced χ^2 (BEVINGTON, 1969) between the two interpolated grids is statistically significant ($\chi^2_v = 0.51$, $v = 5306$, the spline/relaxation algorithm produced 5307 grid points from both data sets). This implies the TTO station locations were an adequate subsample of the original Levitus grid.

DATA MANIPULATION METHODS

The data manipulation methods employed in this study were straightforward; nevertheless, simple examples will be given here to illustrate the basic ideas. Chemical databases, such as the TTO database, typically consist of many profiles measured at different times of the year. We wished to approximate the appearance of the profiles under average wintertime conditions. Figure 2a shows TTO Sta. 117 (49.51°N , 16.71°W) as an example of some property measured at an arbitrary time of year (in this case PO_4

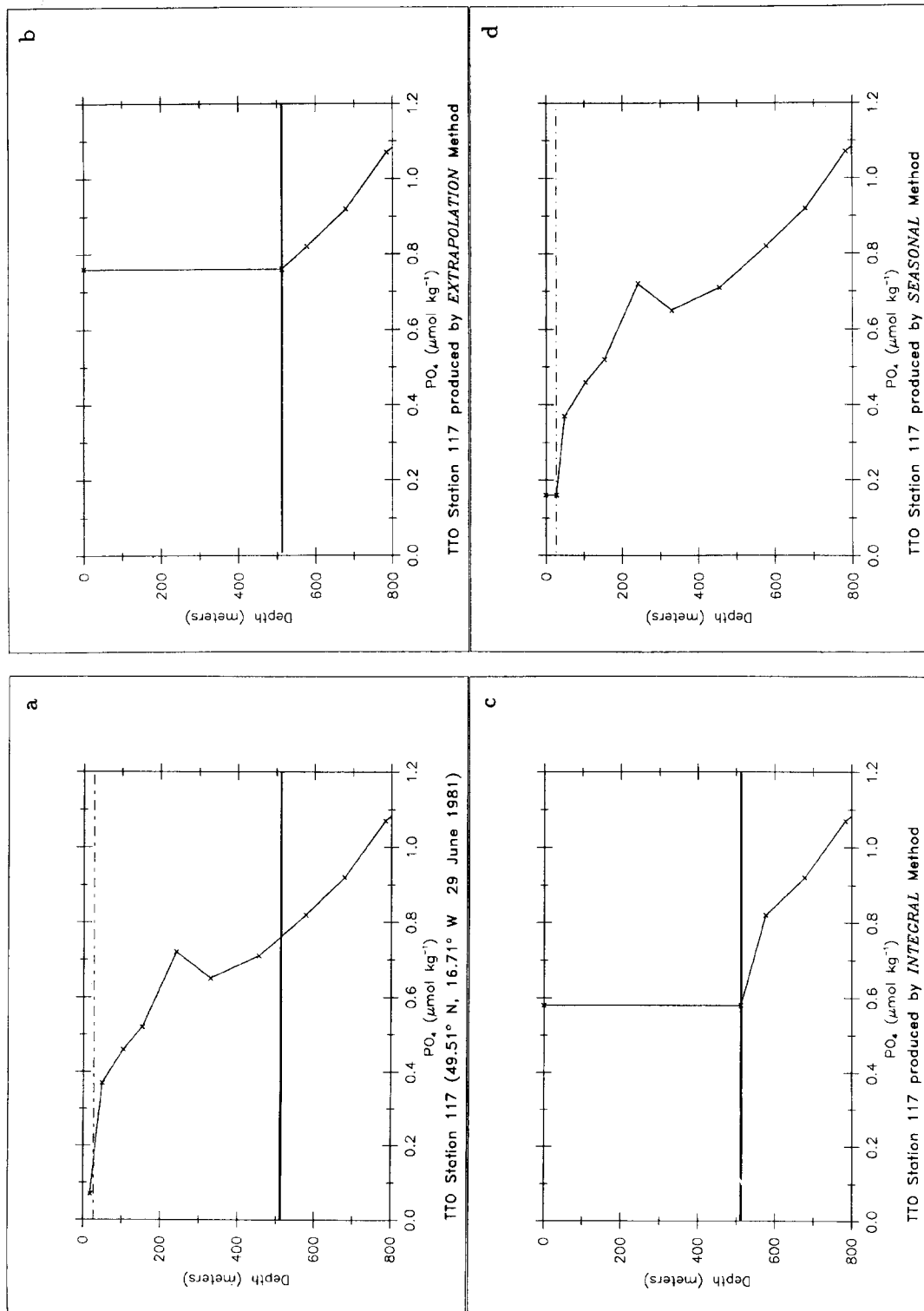


Fig. 2. Four views of the PO_4 profile ($\mu\text{mol kg}^{-1}$) from the TTO NAS Sta. 117 (49.51°N, 16.71°W, 29 June 1981). In all plots the heavy line is the base of the average wintertime mixed layer at this location (512 m), the dot-dashed line the base of the mixed layer at the time the station was occupied (27.7 m) both determined using a variable $\Delta\sigma_t$ criterion. (a) The profile as it appeared at time of collection. The wintertime estimates are based on: (b) interpolation to the base of the wintertime mixed layer (extrapolation), (c) integration and averaging over the wintertime mixed layer (integral) and (d) interpolation to the base of the seasonal mixed layer (seasonal). See text for further explanation.

on 29 June 1981). Also shown in Fig. 2 is the average wintertime MLD and the seasonal MLD. In the extrapolation method we merely interpolated the concentration at the base of this average wintertime mixed layer and applied that concentration over this depth uniformly (Fig. 2b). We derived the integral method estimate of the initial condition profile by integrating Fig. 2a down to the average wintertime MLD and then averaged the integral over this MLD as in Fig. 2c. In the worst case scenario, assuming nothing was known about the wintertime conditions, we derived a seasonal method by interpolating to the base of the observed seasonal mixed layer as in the extrapolation method (Fig. 2d).

Several assumptions were implicit in these operations; for instance, general circulation and upwelling were ignored in each case. Most of the property mass was assumed to stay within reach of the wintertime MLD in the integral method. Deviations from the average wintertime MLD were assumed to be of short enough duration to have an insignificant effect on the initial concentrations (extrapolation and integral methods). In the extrapolation and seasonal methods the water beneath the MLD was assumed to be sufficiently isolated, in time, from the changes that have occurred in the MLD. Finally, loss due to sinking of biologically produced particles below the maximum depth of wintertime mixing was also assumed negligible (in all cases), the integral method ignored any particulate matter within the water column being integrated, and the rate of utilization of nutrients in winter was assumed to proceed negligibly slowly compared to the rate of supply by mixing processes.

Chemical data interpolation

Similar to the calculation of the MLD was the interpolation routine used in the extrapolation and seasonal methods. The chemical database was first navigated to the MLD grid by finding the nearest neighbor grid point to each station location (i.e. within a 1° square). Once the MLD was calculated, the profile was interrogated to find the two depths that most closely bracketed the MLD. A linear interpolation between these two depths (on the average 93 ± 85 m, with a median of 69 m, apart) to the MLD was performed to find the concentration of the property at the MLD. The extrapolation of these values to the surface as an approximation of wintertime conditions is similar to the approach used by JENNINGS *et al.* (1984). These concentrations were written out to a data file with the original TTO station latitude and longitude. We used the mapping software package ATLAS (SGOUROS and KEFFER, 1983) as before to generate another $1^\circ \times 1^\circ$ grid by a spline/relaxation algorithm with a moderate 'stiffness' and a radius of influence that extended equally in all directions. Failures to extrapolate were set to the 'undefined' value and not used in the grid generation. Contour maps of the distribution of these MLD concentrations were made and the grid retained for future model initialization.

Figures 3–6 show maps of PO_4 , NO_3 , SiO_3 and alkalinity yielded by the extrapolation method. Many features were seen in these maps and, no doubt, others will be discovered with further study. The influence of the Gulf Stream upon the distribution of PO_4 , NO_3 , SiO_3 and alkalinity is apparent in Figs 3–6. Concentrations were, as expected, lower in regions thought of as oligotrophic and higher at northern latitudes, due both to deep wintertime mixing and advective replacement from the Gulf Stream source. As an example of the distortion of nutrient concentrations introduced by neglecting seasonality compare Figs 3 and 7.

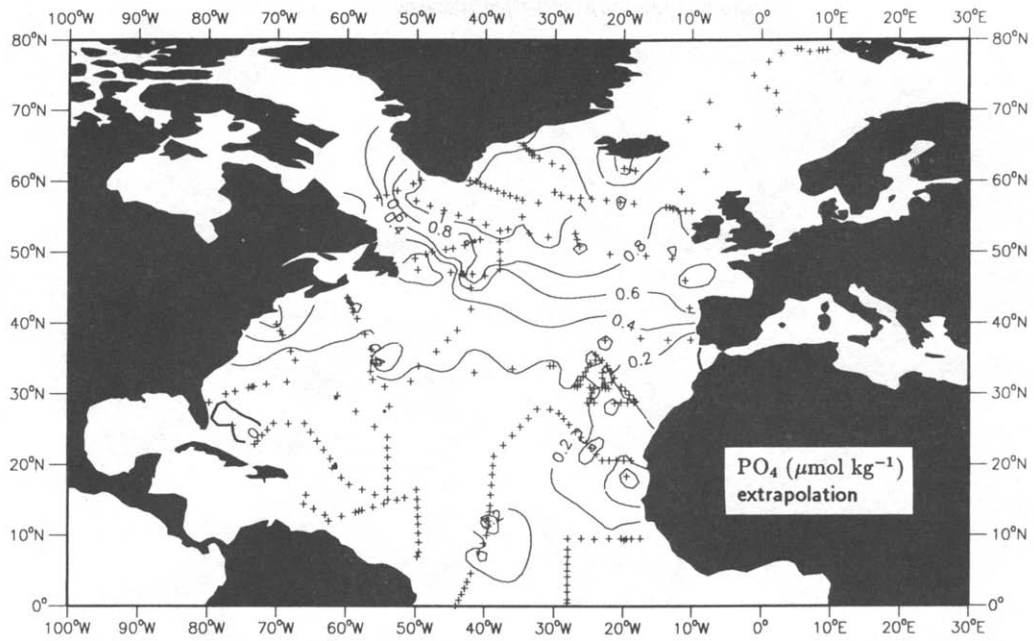


Fig. 3. Estimate of the average wintertime mixed layer PO_4 concentration ($\mu\text{mol kg}^{-1}$) as determined by the extrapolation method.

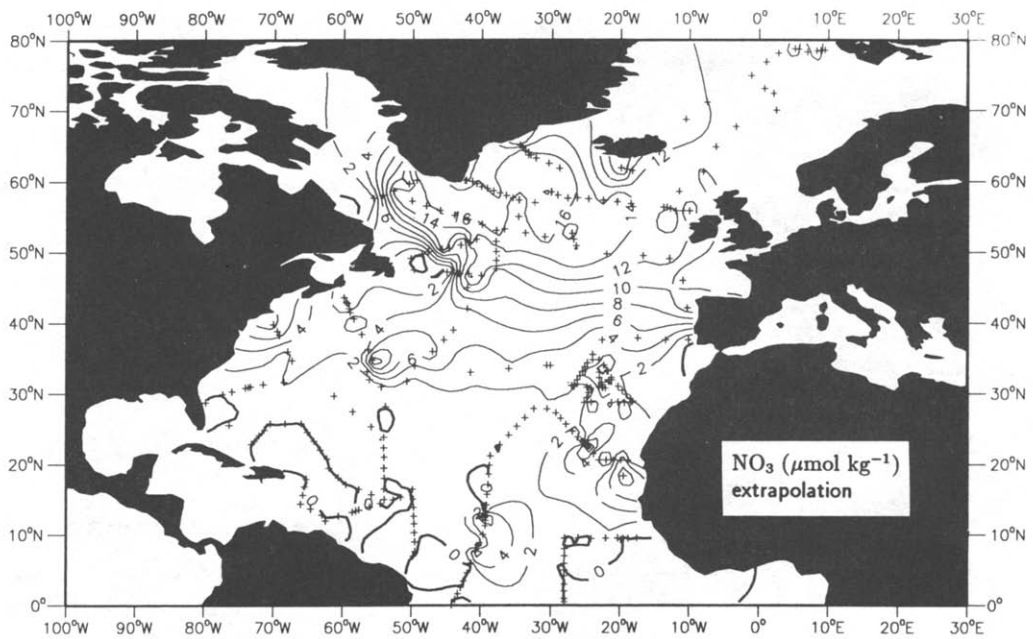


Fig. 4. Estimate of the average wintertime mixed layer NO_3 concentration ($\mu\text{mol kg}^{-1}$) as determined by the extrapolation method.

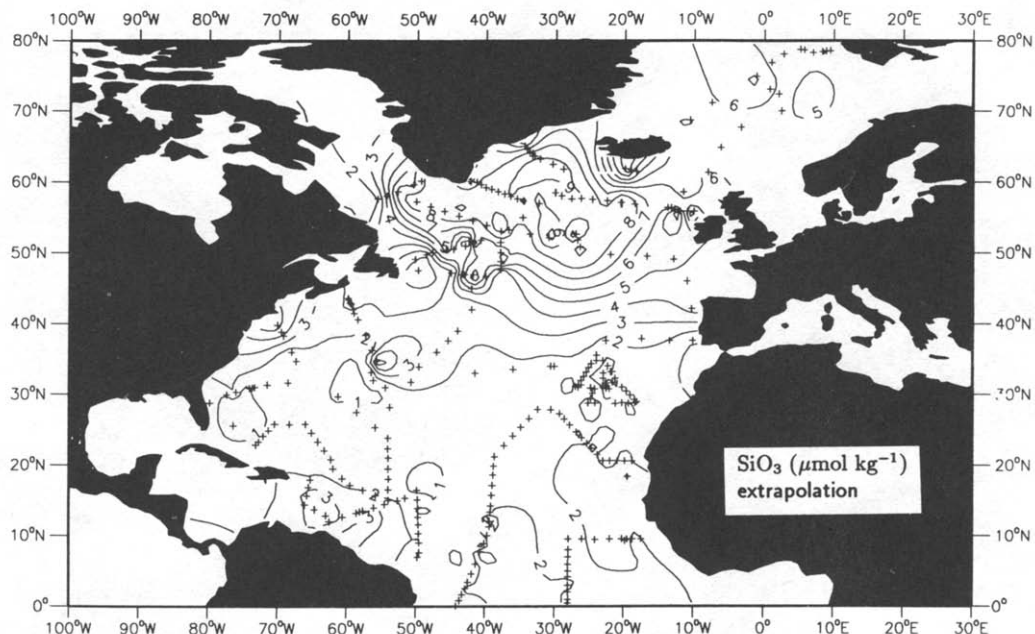


Fig. 5. Estimate of the average wintertime mixed layer SiO_3 concentration ($\mu\text{mol kg}^{-1}$) as determined by the extrapolation method.

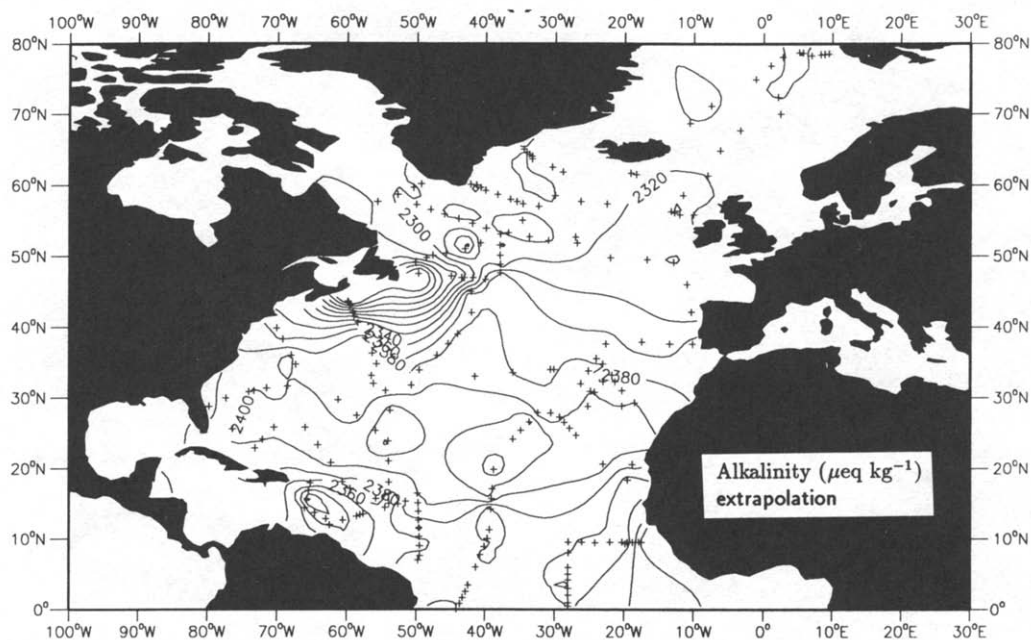


Fig. 6. Estimate of the average wintertime mixed layer alkalinity ($\mu\text{eq kg}^{-1}$) as determined by the extrapolation method.

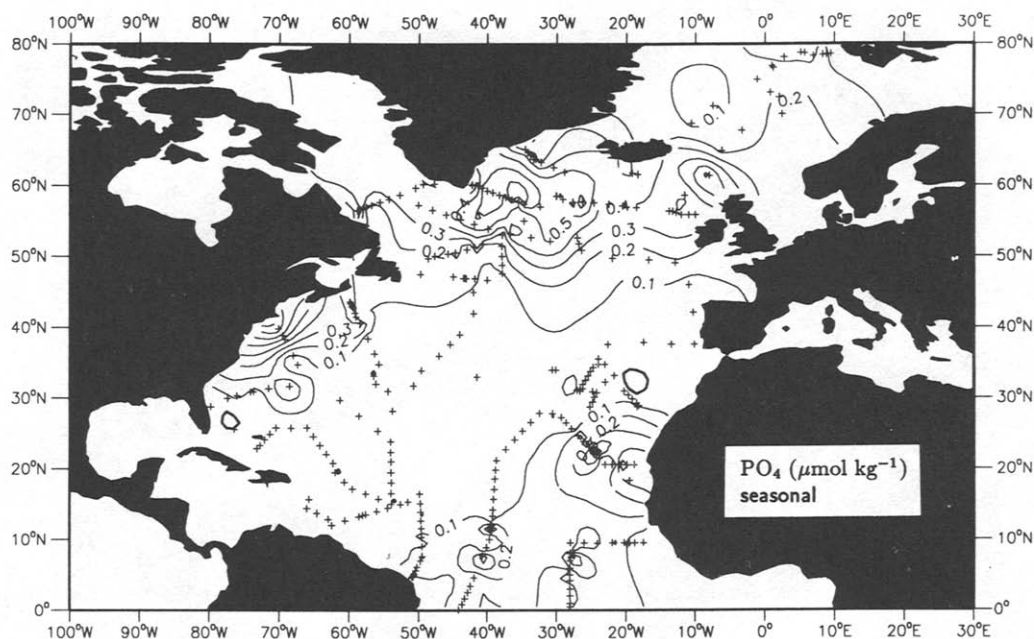


Fig. 7. Estimate of the mixed layer PO_4 concentration ($\mu\text{mol kg}^{-1}$) as determined by the seasonal method. Note the lower concentrations when compared to Fig. 3.

Chemical data integration

Additional maps were prepared by our integral technique as follows. On a station-by-station basis each property profile was integrated down to the corresponding MLD using the trapezoidal rule:

$$I_C = \sum_{i=2}^{\text{MLD}} \frac{1}{2} (C_i + C_{i+1}) (z_{i+1} - z_i), \quad (2)$$

where I_C is the integral of the property C (e.g. $\mu\text{mol m kg}^{-1}$); C_i is the concentration at depth i ($\mu\text{mol kg}^{-1}$); and z_i is depth i (m). The first depth was extrapolated to the surface, multiplied by its depth and added to the integral. The final integration depth was linearly interpolated from data points bracketing the MLD. The average concentration was then obtained by dividing by the MLD, a procedure similar to one utilized by SPENCER *et al.* (1980). Replicate data points were averaged where they existed and missing data points were ignored. The gridding of the results was handled in the same manner as in the method discussed above.

At one time or another each property presented a profile for which it was impossible to accurately estimate the wintertime MLD concentration. One of the most common problems dealt with 'missing' data. When all of the data within the MLD were missing, that station's value was simply set to 'undefined'; when some of the data within the MLD were 'missing', under certain circumstances it was impossible to be sure the algorithm, as outlined, gave a reliable estimate; again the value was set to 'undefined'. At best, an accepted station would have two data points that bracketed the MLD, at worst, all the data would be above the MLD.

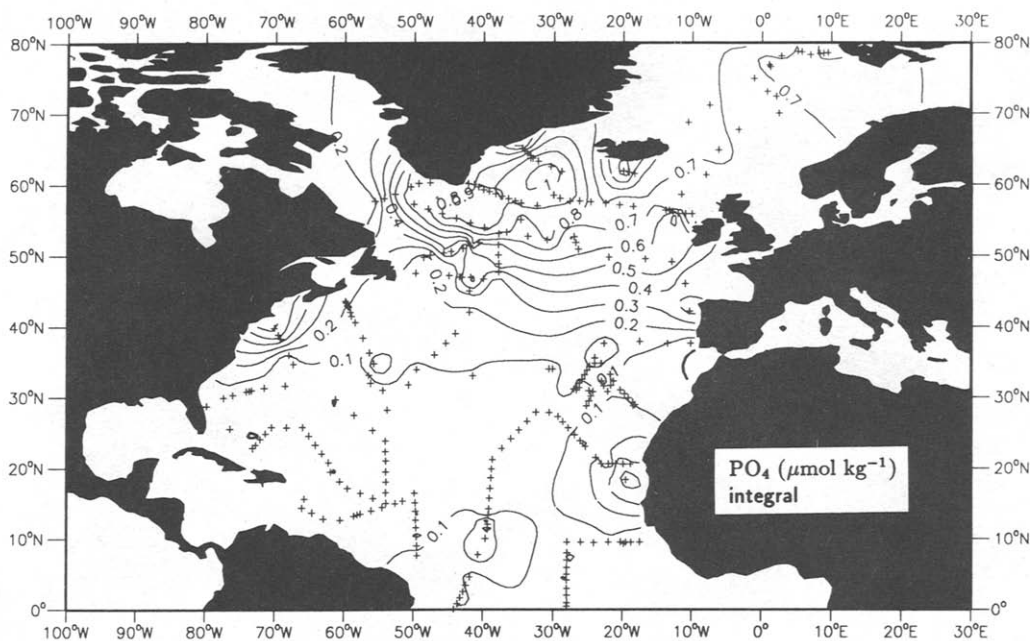


Fig. 8. Estimate of the average wintertime mixed layer PO_4 concentration ($\mu\text{mol kg}^{-1}$) as determined by the integral method. Note the general similarity with Fig. 3, see text for details of the differences.

Figure 8 presents averaged, integrated PO_4 concentrations yielded by the integral method. A comparison to Fig. 3 shows that the concentrations and their patterns are remarkably similar. Nevertheless, the concentrations of PO_4 (and NO_3 , SiO_3 but not alkalinity) are lower in the northern regions and higher in the oligotrophic regions when compared to the results of the extrapolation method. The insensitivity of alkalinity is discussed below in the sensitivity section of this report.

Implications

Intrinsic to these methods are certain implications due to the inherent assumptions behind the algorithms. The assumptions that horizontal advection and upwelling were negligible broke down in certain areas of the North Atlantic. To evaluate the effect of this collapse, the distribution of the TTO stations in time as well as in space needed to be considered. Stations located in the Gulf Stream provided a good example; stations located in equatorial upwelling areas are similarly affected. SARMIENTO (1983) provides a map of the annual displacement of a water parcel caused by the general circulation of the North Atlantic at 159 m (approximately the mean of the MLD's). From this map (SARMIENTO, 1983, Fig. 3b) and the appearance of the chemical data provided in this report, it is apparent that only water parcels that traverse a considerable meridional distance strongly effect the validity of our argument. Stations located in the Gulf Stream, that travel considerable distances meridionally, were collected in April (Fig. 9). April stations, while admittedly affected by early spring stratification, are close (in time) to the wintertime conditions we wished to estimate; we believe that this did not compromise our estimation significantly.

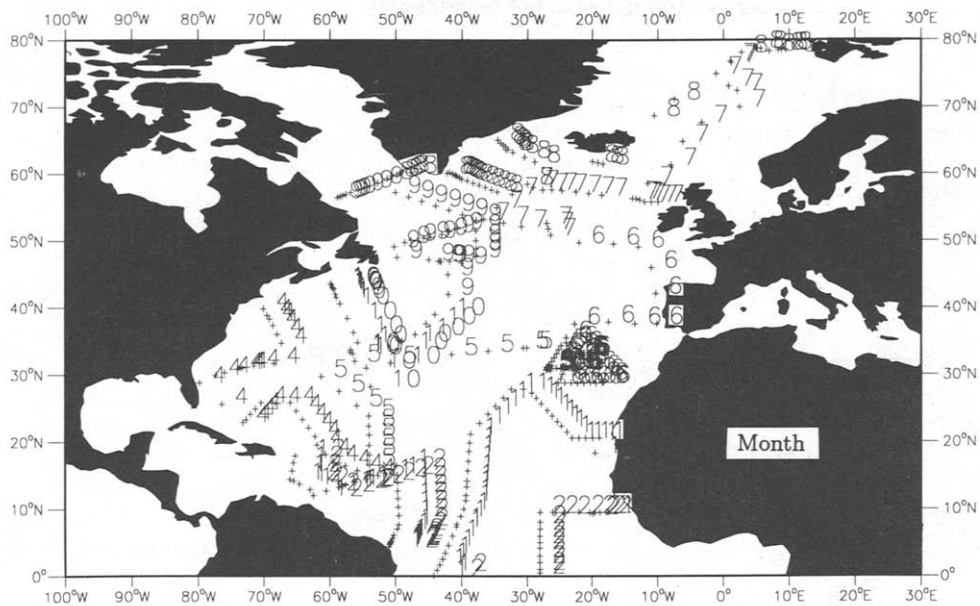


Fig. 9. TTO station locations (NAS and TAS) and the month they were occupied.

Furthermore, the assumption that most of the mass of the property being analysed remained within reach of the average wintertime MLD overlooks the possibility of losing mass due to deep water formation and particle sinking. At this level of approximation we can only state that the magnitude of this loss is compensated, to some degree, by the resupply of nutrients due to horizontal advection, which we also ignore.

PREFERRED METHOD SELECTION

Given that three different estimation methods provided a bewildering selection of maps (all at least slightly different), some sort of objective selection has to be made between them to select a best estimate. Although data necessary to make this sort of decision are scarce, we examined selected time series data, made direct comparisons with one wintertime data set, and carried out an examination of the sensitivity of the three methods.

Time series analysis

The time series data available from the Bermuda *Panulirus* site (32°N, 64°W) contain some limited nutrient data for PO_4 , NO_3 , and SiO_3 from approximately 1958 to 1965, inclusive. By applying our three different methods to this time series we were able to observe the variability in time of each method. We felt that the method with the smallest variability should probably be considered the best estimate. Figure 10a–c shows the time series of the *Panulirus* site rendered by the extrapolation, integral and seasonal methods for the nutrient PO_4 . The MLD was the same for all years at the *Panulirus* site for the extrapolation and integral methods (Fig. 10a,b); however, for the seasonal method the MLD varied with the time the station was collected (Fig. 10c). Immediately apparent

was the high level of noise in the 'seasonal' treatment, which was also obvious in analysis of NO_3 and SiO_3 (not presented here).

Further analysis of this time series was done to determine if the time of year the profile was collected had any effect on the estimate of average wintertime concentrations. Figure 10d–f presents the same kind of analysis as in Fig. 10a–c, but the results were binned and averaged by the month the station profile was collected, producing average monthly results for the period 1958–1965. Averaging the monthly data produced annual mean PO_4 concentrations with relative standard deviations (RSD) of 12.0, 14.6 and 50.0% for the extrapolation, integral, and seasonal methods, respectively. These results indicate that the seasonal method was not the best estimator due to the large variances (Fig. 10c,f).

To assess the statistical significance of perceived differences between the three methods a two-way analysis of variance (ANOVA) was performed. The structure of the analysis had, as treatments, the three different methods (extrapolation, integral and seasonal), and as samples, the 12 monthly averages [see DAVIS (1973) for terminology]. When all treatments were considered, there was a statistically significant difference between the treatments but not among the monthly means at the 95% confidence level. Separating the treatments by pairs yielded results indicating a significant difference between the extrapolation method and all other methods, but no significant difference between the integral and seasonal methods. The results of this two-way analysis of variance are shown in Table 1 (for PO_4 only) with the upper right half the F -ratios for variance among monthly means and the lower left half among methods (treatments).

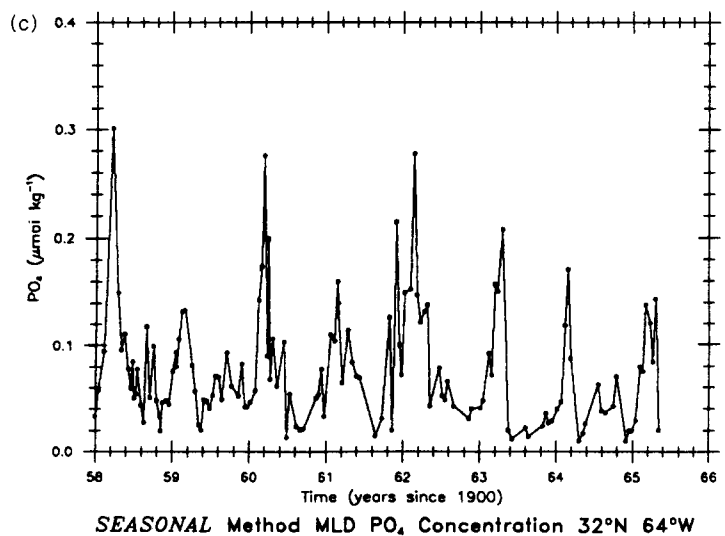
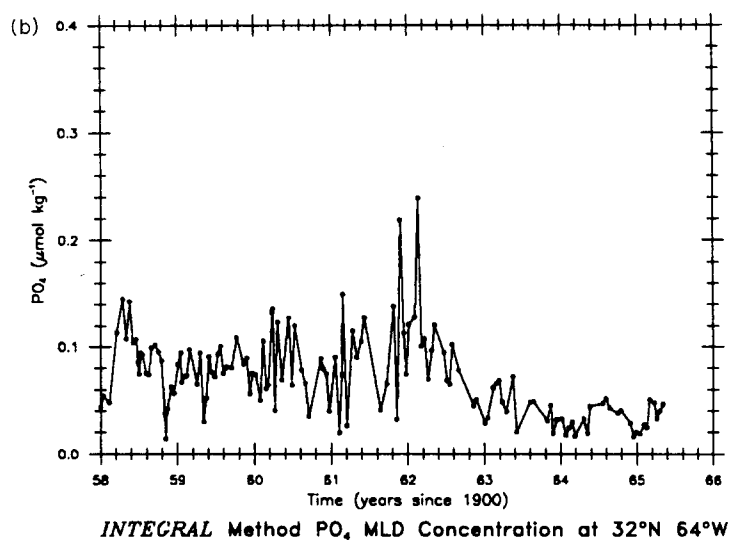
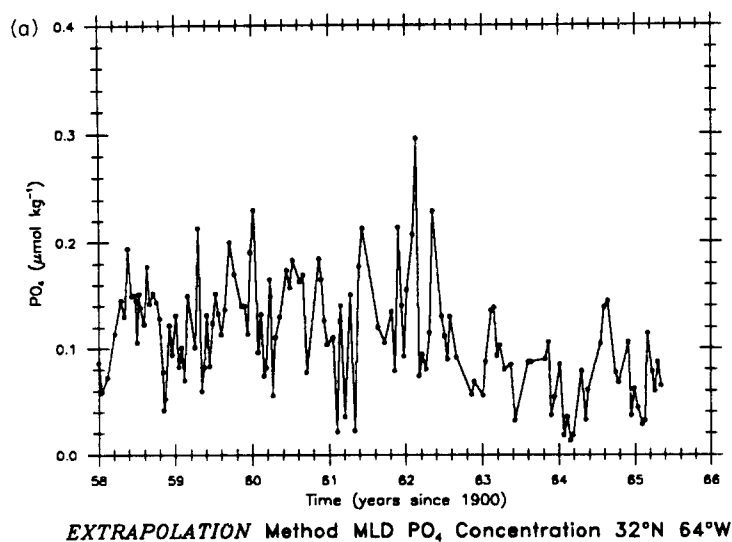
This ANOVA did not provide a definitive answer; we feel that interannual variations could well account for the slight difference between the monthly means but not between the methods. The choice, then, seemed to be between the statistically different extrapolation and integral methods, since the seasonal method had a large RSD for all properties analysed. Nevertheless, the analysis of the time series from one site located in the Sargasso Sea could not indicate which was better.

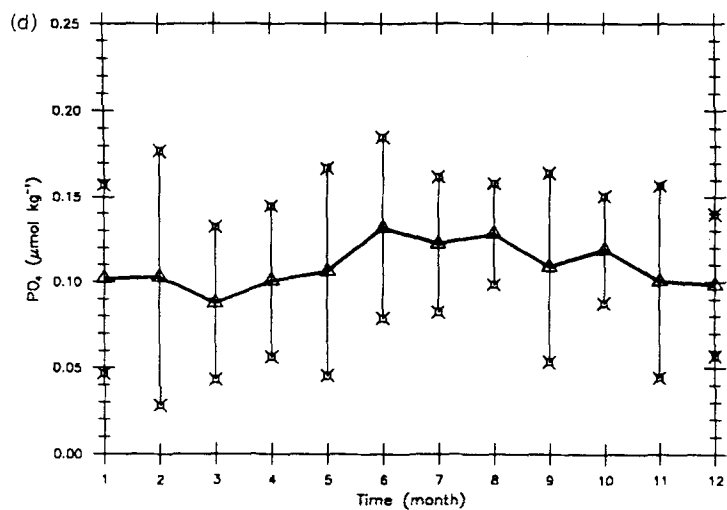
Wintertime cruise vs estimations

Further analysis was accomplished by a comparison of the two methods (extrapolation and integral) to data collected on a wintertime cruise further to the north. One excellent winter data set for comparison is that of the C.S.S. *Hudson* (cruise 82–001) expedition in the area bounded by 60°N , 10°W and 80°N , 20°E . These results (SIO, 1984) are examined here in comparison with our computed properties.

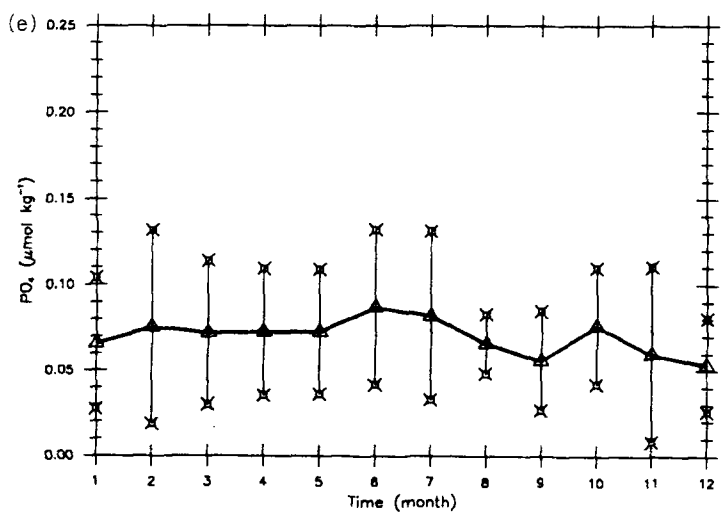
Tables 2 and 3 summarize the mean sum of squares and the total residuals for 18 TTO stations that fell into the same locality as the C.S.S. *Hudson* cruise stations. From these tables two facts emerge: the extrapolation method slightly overestimates the actual wintertime concentrations since it is a straightforward projection of a single, deep, enriched point value to the surface; the integral method consistently underestimates the wintertime concentrations due to the loss of material from the upper water column. The

Fig. 10. Time series and monthly means of the PO_4 concentration data from the *Panulirus* site (32°N , 64°W). The time series concentrations were (a) interpolated to the base of the wintertime mixed layer (extrapolation), (b) integrated and averaged over the wintertime MLD (integral), and (c) interpolated to the base of the seasonal MLD based on a variable $\Delta\sigma$ criterion. The monthly means, (d) the extrapolation method, (e) the integral method and (f) the seasonal method, were created from the time series by binning and averaging by month, the error bars are ± 1 S.D. of the means.

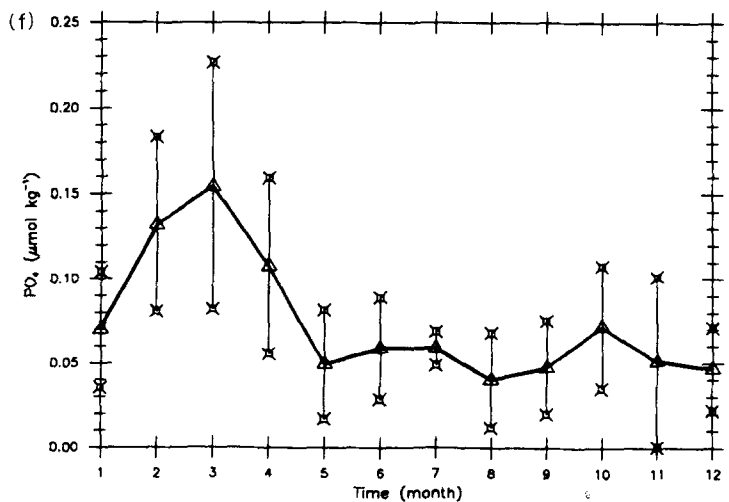




Monthly Averaged *EXTRAPOLATION* PO₄ Conc. at 32°N 64°W



Monthly Averaged *INTEGRAL* PO₄ MLD Conc. at 32°N 64°W



Monthly Averaged *SEASONAL* PO₄ Conc. at 32°N 64°W

Table 1. Two-way ANOVA of *Panulirus* PO₄ data

Methods*	Extrapolation	Integral	Seasonal
Extrapolation	—	2.8148†	0.4839
Integral	125.5437‡	—	1.3621
Seasonal	7.0895‡	0.1740	—

* Upper diagonal half $v_1 = 11$, $v_2 = 11$, i.e. variance among monthly means; lower diagonal half $v_1 = 1$, $v_2 = 11$, i.e. variance among methods.

† *F*-ratio statistically significant at $\alpha = 0.10$.

‡ *F*-ratio statistically significant at $\alpha = 0.05$.

Table 2. Mean sum of squares between Hudson profiles and extrapolation and integral methods

Property	Methods	
	Extrapolation	Integral
Alkalinity	29.8	64.9
PO ₄	0.00218	0.0238
NO ₃	0.956	13.2
SiO ₃	0.497	2.50

Table 3. Total residuals between Hudson profiles and extrapolation and integral methods

Property	Methods	
	Extrapolation	Integral
Alkalinity	1.19	-0.854
PO ₄	0.017	-0.139
NO ₃	0.0973	-3.17
SiO ₃	-0.00264	-1.36

implication of this analysis is that the *Hudson* cruise was located in a part of the ocean where information (material) undoubtedly has been lost during the course of the summer via particulate flux, and extrapolation to the surface ignores dilution effects, while re-integrating the water column cannot entirely restore the lost information. Nonetheless, each approach yields a remarkably good approximation to the observed conditions.

Figure 11 shows a comparison of the extrapolation and integral methods applied to the PO₄ profiles of the TTO NAS Sta. 149 (76.88°N, 1.04°E, 31 July 1981) with the *Hudson* Sta. 37 (76.90°N, 1.00°E, 11 March 1982). The sum of squares (covariances) between the profiles, down to the average wintertime MLD, was used as the objective selection criterion. The sum of squares between the extrapolation method and the *Hudson* profile (Fig. 11a) was 0.0000439. In the comparison of the integral method with the *Hudson* profile, the mean sum of squares was 0.011 (Fig. 11b). These two stations were chosen because the *Hudson* cruise very nearly exactly reoccupied the earlier TTO station (the spatial distance between the two stations was 2.76 km). Although the coordinates of other near repeats are not as close, similar results were obtained. The integral method consistently underestimates the actual wintertime property concentrations due to loss of these properties from the upper water column. This closer agreement between TTO profiles treated with the extrapolation method and C.S.S. *Hudson* profiles, actually measured during the winter, provides the final evidence needed to choose the extrapolation method as the preferred method of estimation.

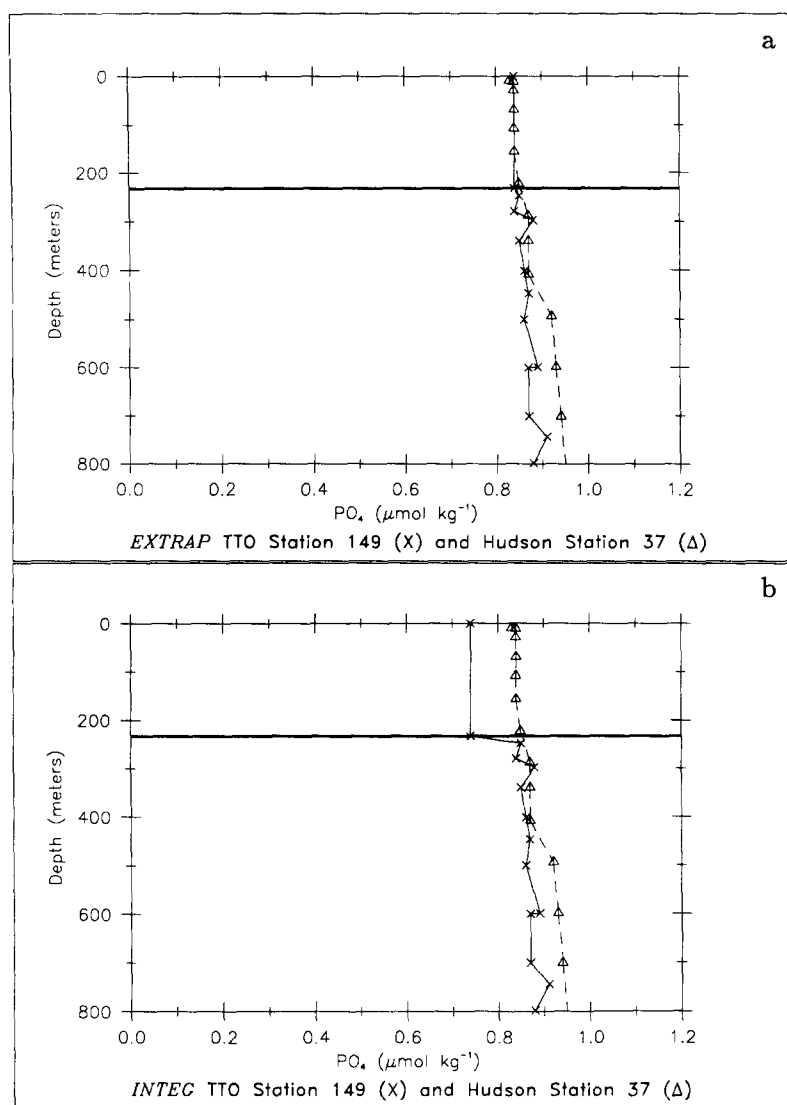


Fig. 11. Comparison of PO_4 profiles ($\mu\text{mol kg}^{-1}$) from a station where the C.S.S. *Hudson* cruise very nearly reoccupied a previous TTO station. The manipulated profiles from the TTO station are represented by solid lines, the average wintertime MLD (233 m) by heavy lines and the *Hudson* profiles by dot-dashed lines. TTO NAS Sta. 149 (76.88°N , 10.4°E 31 July 1981) and *Hudson* cruise 82-001 Sta. 37 (76.90°N , 1.00°E , 11 March 1982). (a) The extrapolation method; (b) the integral method.

Sensitivity analysis

An investigation into the sensitivity of these methods of estimation was done to determine the reliability of the initial conditions provided by the method of preference. Table 4 gives a summary of a sensitivity coefficient (S_a^B) similar to the one defined by HUSON (1984/1985). This coefficient shows what percentage of output variables (in our case MLD concentrations) change by more than $100 \times \alpha\%$ when the input variables (in

Table 4. $\Sigma S_{\alpha}^{\beta}$ Coefficients

α	β			
	0.05	0.10	0.20	0.50
Extrapolation method				
0.01	0.5337	0.6316	0.7091	0.8228
0.05	0.1879	0.3873	0.5262	0.7046
0.10	0.0646	0.1879	0.3937	0.6131
0.20	0.0074	0.0678	0.1913	0.4949
0.50	0.0013	0.0068	0.0487	0.2095
N^*	1486	1474	1458	1394
Integral method				
0.01	0.6831	0.7922	0.8254	0.8570
0.05	0.1651	0.3744	0.6093	0.7903
0.10	0.0546	0.1638	0.3785	0.6829
0.20	0.0144	0.0525	0.1696	0.4758
0.50	0.0014	0.0079	0.0324	0.1646
N	1392	1392	1392	1330
Seasonal method				
0.01	0.6855	0.7342	0.7610	0.7978
0.05	0.2855	0.4763	0.6441	0.7428
0.10	0.1312	0.2799	0.4730	0.6920
0.20	0.0602	0.1217	0.2652	0.5283
0.50	0.0239	0.0434	0.0870	0.2533
N	1380	1380	1380	1350

* N is the sum of all the PO_4 , NO_3 and SiO_3 stations after each was subjected to a $\pm\beta\%$ variation of MLD.

our case the individual station MLD estimations) are allowed to change by their maximum uncertainty ($\pm 100 \times \beta\%$). Since the uncertainty in the MLD estimation was difficult to ascertain, several MLD uncertainties are presented—from an optimistic $\pm 5\%$ to a pessimistic $\pm 50\%$. The numbers present are a composite value for PO_4 , NO_3 and SiO_3 for each case, weighted by the number of stations analysed (alkalinity was not sensitive to any uncertainty in MLD and will be discussed later). In a strict test of sensitivity ($S_{0.01}^{0.20}$) the extrapolation method had 70.91% of the station estimates of MLD concentration change by more than 1% when the MLD was varied by $\pm 20\%$. In comparison, the integral method, under the same conditions, had 82.54% of the station estimates change, the seasonal method 76.10%. At $S_{0.20}^{0.20}$ the extrapolation method had only 19.13% of the station estimates change by more than 20%. The sensitivity coefficient $S_{0.05}^{0.20}$ indicates that 52.62% of the station concentration estimates change by more than 5% when the MLD is varied by $\pm 20\%$, which may have profound implications for their usage in model initialization.

The distribution of this sensitivity among the various chemical species shows which are more sensitive than the others, with attendant implications for model initialization. Table

Table 5. Sensitivity coefficients of the extrapolation method

Property	$S_{\alpha}^{0.20}$				
	0.01	0.05	0.10	0.20	0.50
Alkalinity	0.0	0.0	0.0	0.0	0.0
PO_4	0.7700	0.5745	0.4510	0.1745	0.0468
NO_3	0.7620	0.6010	0.5315	0.3795	0.1130
SiO_3	0.6205	0.4320	0.2465	0.0682	0.0035

5 is compiled from one of many sensitivity runs for the extrapolation method to show how this sensitivity is distributed between the various properties. An examination of this table shows that for some there was virtually no sensitivity (alkalinity) while for others there was a significant difference (NO_3). The other properties, PO_4 and SiO_3 , fell in between these two extremes. The implication for alkalinity was that this method (extrapolation) was a robust estimator for this property regardless of the MLD; this was also seen to be true for the integral method while for the seasonal method there was some sensitivity to variations of $\pm 50\%$ in the MLD. This insensitivity is due to the large size of the alkalinity pool in comparison to the lower concentrations of the other properties. For NO_3 , many of the differences were seen to be located in the oligotrophic regions of the North Atlantic where the NO_3 values are ~ 0 ; any small increase would appear as a large percent increase. These differences did not occur where LEVITUS (1982) warns that the halocline influences different methods of MLD calculation, implying that the calculation of the MLD, *per se*, was not responsible.

To complete the examination of the sensitivity of these methods one should look at the response of one station and one variable to a specific MLD perturbation. A specific example can be given: were the MLD to increase by 20% at TTO NAS Sta. 117 (refer to Fig. 2) the PO_4 value would increase from 0.758 to 0.857 $\mu\text{mol kg}^{-1}$ in Fig. 2b (extrapolation), from 0.581 to 0.619 $\mu\text{mol kg}^{-1}$ in Fig. 2c (integral) and from 0.157 to 0.213 $\mu\text{mol kg}^{-1}$ in Fig. 2d (seasonal). The percent change in this specific example does not correspond directly to the values predicted in Tables 4 or 5 because these tables reflect the average change of all stations.

CONCLUSION

Although there are no similar maps to compare our results to, comparisons with KAMYKOWSKI and ZENTARA (1986) and KAWASE and SARMIENTO (1985) can be made. A comparison between our maps and those of KAMYKOWSKI and ZENTARA (1986) was difficult, since they only provide a spatial distribution of where the three nutrients investigated become unmeasurable at that temperature or density. Interestingly, KAWASE and SARMIENTO (1985) report increasing concentrations of NO_3 and SiO_3 as one travels southward along their isopycnal surfaces, whereas we report increasing concentration of those nutrients as one travels north in the wintertime MLD. These opposite trends are consistent if one remembers that the isopycnal surfaces curve surfaceward as one travels northward.

What appears here is that surface wintertime chemical conditions can be estimated and mapped reasonably well by very simple means. It is of interest to ask why this should be so, and to examine a little further the assumptions this is based upon. Local conservation of matter (i.e. nutrients) is probably violated at high latitudes where the term $N(D - U \cdot \nabla D \Delta t)$ is large [using WOODS (1985) notation again; see also SARMIENTO (1983) Fig. 3b]. Similarly the assumption, that particles formed in the surface layer are largely recycled within the MLD range considered here, can not always be true. MARTIN *et al.* (1987) present data on such fluxes in which the C flux change with depth is described by a power function $F = F_{100} (z/100)^G$, with $\geq 90\%$ of the particle flux regenerating within MLD's characteristic of the Atlantic north of 30°N . However, these data are exclusively from the northeast Pacific. In the Atlantic much greater particle penetration has been observed (BILLETT *et al.*, 1983) and a theoretical basis for this has been presented (FROST, 1984). Neglected also here is the question of conversion of C, N and P to dissolved

organic forms which show seasonal fluctuations in abundance (BUTLER *et al.*, 1979); the matter of the cycling of dissolved organic C and N in the ocean is currently of great controversy (SUZUKI *et al.*, 1985), and we suspect that such terms will eventually have to be included.

Overall it would appear that quite good estimates given here perhaps result from a fortunate compensation of positive and negative errors, rather than from the trivial nature of any one of the processes discussed above. Interestingly the ability to estimate initial conditions and the availability of seasonal numerical models of the upper ocean should lead very rapidly to the ability to predict the approximate chemical characteristics of the upper ocean over very large space and time scales. The challenge to observational programs to improve this knowledge will be formidable.

Here, for the first time as far as we know, the methods for estimating initial conditions from existing data for seasonal modeling are developed, explored and an attempt to objectively choose between them made. The following summary can be made. The three methods developed and explored were: extrapolation—an interpolation to the base of the wintertime mixed layer; integral—an integration to the base of the wintertime mixed layer followed by averaging over that depth; and seasonal—an interpolation to the base of the seasonal mixed layer. For the method of preference (extrapolation) a $1^\circ \times 1^\circ$ grid of average wintertime MLD's was derived from LEVITUS's (1982) average wintertime conditions, chemical data was obtained from the NAS and TAS TTO database. For each TTO station the preferred method of estimation of the average wintertime concentration was, in detail: the MLD was taken from a $1^\circ \times 1^\circ$ grid by a nearest neighbor search; four chemical properties were interpolated to the average wintertime MLD and this concentration applied to the entire MLD; these station MLD concentrations were fit to a $1^\circ \times 1^\circ$ grid with a spline/relaxation algorithm, contour maps were made and the grid retained for model initialization. The grid and other ancillary data can be obtained from the authors.

Our preferred method for reconstructing this wintertime mixed layer from biased seasonal profiles was to interpolate the property concentrations of interest to the average wintertime MLD and extend this value over the entire MLD. We have not yet discussed the important problem of CO_2 cycling; however, the slow exchange rate of CO_2 with the atmosphere suggests that it may be possible to treat this in a similar manner to the non-gaseous chemical species described here.

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