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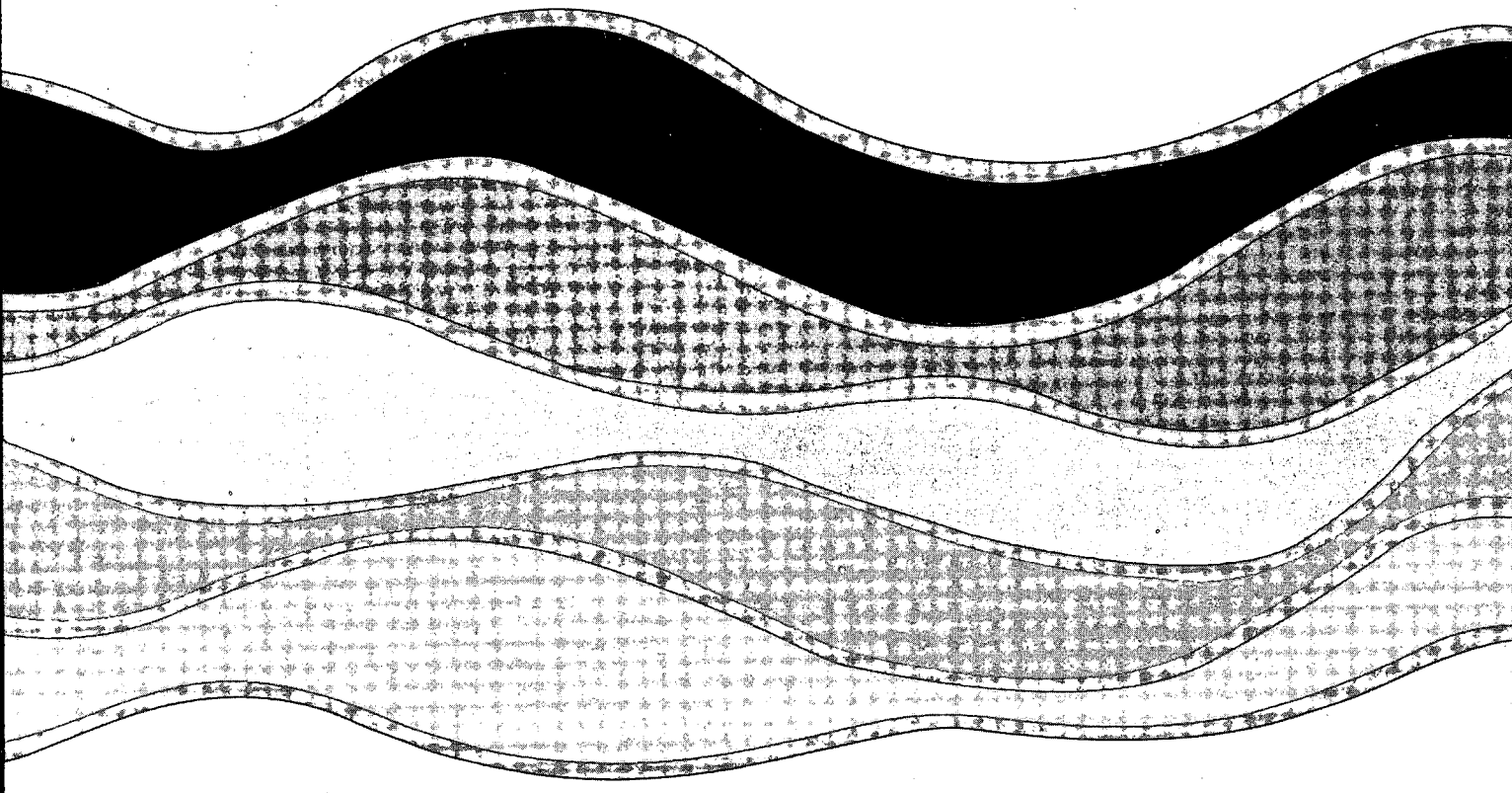

STATISTICAL ANALYSIS OF THE 1985 THREE-AGENCY INTERCOMPARISON STUDY ON LAKE ERIE

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STATISTICAL ANALYSIS OF THE 1985 THREE-AGENCY INTERCOMPARISON STUDY ON LAKE ERIE

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MANAGEMENT PERSPECTIVE

The Great Lakes Water Quality Agreement of 1978 between Canada and the United States specifies that a joint surveillance and monitoring program for the Great Lakes is necessary in order to evaluate water quality trends and the effectiveness of pollution control measures. To update the information concerning data intercomparability from Great Lakes monitoring programs, a three-ship laboratory comparison was conducted on the central basin (mid-lake) of Lake Erie in August 1985. Differences in the results reported by the agencies were shown to be due to laboratory procedures, not ship sampling procedures, and for most parameters were 30 to 50 percent of the mean. For total phosphours, the laboratory differences were as large as expected for the lake in a two- to three-year period, based on a conservative estimate of the rate of decline over time. Thus the magnitude of the differences between laboratories is large enough to conclude that careful consideration is necessary before combining results from the monitoring programs of different agencies.

PERSPECTIVES DE LA DIRECTION

L'Accord relatif à la qualité de l'eau dans les Grands Lacs, signé en 1978 entre le Canada et les États-Unis, stipule qu'un programme conjoint de surveillance et de suivi des Grands Lacs est nécessaire afin d'évaluer les tendances au niveau de la qualité de l'eau et l'efficacité des mesures de lutte contre la pollution. Afin de mettre à jour les informations relatives à la comparabilité des données des programmes de suivi des Grands Lacs, une comparaison des données fournies par les laboratoires à bord de trois bateaux a été effectuée en août 1985, et portait sur le bassin central (milieu du lac) du lac Érié. Les différences au niveau des résultats consignés par les organismes étaient attribuables aux techniques de laboratoire et non pas aux méthodes d'échantillonnage à bord des bateaux, et pour la plupart des paramètres, elles s'écartaient de 30 à 50 pour cent de la moyenne. Dans le cas du phosphore total, les différences expérimentales étaient aussi importantes que celles prévues pour le lac sur une période de deux à trois ans, d'après une estimation prudente du taux de diminution au cours des années. L'ampleur des écarts entre les laboratoires est donc suffisamment importante pour conclure qu'il faut examiner soigneusement les données avant de jumeler les résultats des programmes de suivi des différents organismes.

ABSTRACT

To update the information concerning data intercomparability from Great Lakes monitoring programs, a three-ship laboratory comparison was conducted on the central basin (mid-lake) of Lake Erie in August 1985, in which eight water quality parameters were measured: total phosphorus, total filtered phosphorus, soluble reactive phosphorus, nitrate plus nitrite, ammonia, soluble reactive silica, chloride, and chlorophyll-a. Participating were the R/V Roger R. Simons, operated by the U.S. Environmental Protection Agency; the R/V Hydra, operated by the Ohio State University; and CSS Limnos, utilized by Environment Canada. Two separate comparison studies were conducted. The first study provided data to identify that portion of the variability in measured concentrations that could be attributed to laboratory procedures, i.e., the analytical variability (AV). The second study provided data to assess the overall variability (OV) in whole-ship operations, including water sampling procedures at two depths, epilimnion and hypolimnion. In general, differences in mean levels were due primarily to laboratory procedures, with significant differences occurring between at least one pair of laboratories for every parameter. For all parameters, except chloride and nitrate plus nitrite, these differences ranged from 30 to nearly 100 percent of the mean in the water layer with the lower concentration and from 12 to 95 percent in the layer with higher concentration. The results for some parameters were overly precise for one or more laboratories, which lead to differences as small as 3 to 6 percent of the mean being significant (nitrate plus nitrite and chloride). However, large laboratory differences were observed for soluble reactive silica even though laboratory precision was high. These results are discussed in view of the quality assurance program of the Simons laboratory, the August 1985 monitoring of Central Basin stations by the three agencies, and the magnitude of changes in total phosphorus in Lake Erie

over time. It is concluded that, although at least one laboratory exhibited precision better than that of the 1985 monitoring program, the differences between laboratories estimated from the intercomparison study are large enough to be of practical significance and thus careful consideration is necessary before combining results from monitoring programs of the different agencies.

RÉSUMÉ

Dans le but de mettre à jour les informations relatives à la comparabilité des données des programmes de suivi des Grands Lacs, une comparaison des données de laboratoire à bord de trois bateaux a été menée en août 1985, et portait sur le bassin central (milieu du lac) du lac Érié; huit paramètres portant sur la qualité de l'eau ont été évalués, soit le phosphore total, le phosphore total filtré, le phosphore réactif soluble, les nitrates plus les nitrites, l'ammoniac, les silices réactives solubles, le chlorure, et la chlorophylle a. Les navires qui ont participé à ces travaux étaient le R/V Roger R. Simons, exploité par la U.S. Environmental Protection Agency; le R/V Hydra, exploité par l'université d'état de l'Ohio, et le nsc Limnos, utilisé par Environnement Canada. Deux études comparatives distinctes ont été menées. La première étude a fourni des données permettant de déterminer la fraction de la variabilité des concentrations mesurées qui pouvait être attribuée aux techniques de laboratoire, c'est-à-dire la variabilité analytique (VA). La deuxième étude a fourni les données pour évaluer la variabilité globale (VG) des activités de tout le bateau, notamment des techniques d'échantillonnage de l'eau à deux profondeurs, au niveau de l'épilimnion et de l'hypolimnion. En général, les écarts au niveau des teneurs moyennes étaient attribuables surtout à des techniques de laboratoire, avec des différences importantes entre au moins une paire de laboratoires pour chacun des paramètres. En ce qui concerne tous les paramètres, à l'exception du chlorure et des nitrates plus les nitrites, ces écarts s'écartaient de 30 à près de 100 pour cent de la moyenne dans la couche d'eau ayant la plus faible concentration, et de 12 à 95 pour cent, dans la couche à concentration plus élevée. Les résultats concernant certains paramètres étaient trop précis dans le cas d'un ou de plusieurs laboratoires, ce qui a eu pour résultat que des écarts s'écartant d'à peine 3 à 6 pour cent de la moyenne ont été jugés significatifs (nitrates plus nitrites et chlorure). Toutefois, des écarts importants ont été relevés dans le cas des silices réactives solubles même si la

précision expérimentale était élevée. Ces résultats sont examinés dans le cadre du programme d'assurance de la qualité du laboratoire Simons, le suivi du mois d'août 1985 des stations du bassin central par les trois organismes, et l'importance des variations du phosphore total dans le lac Érié au cours des années. Les chercheurs ont conclu que, même si la précision enregistrée par au moins un laboratoire était supérieure à celle du programme de suivi de 1985, les écarts entre les laboratoires, calculés à partir de l'étude de comparabilité, sont suffisamment grands pour avoir une signification pratique, et que les données doivent donc être examinées attentivement avant de combiner les résultats des programmes de suivi des différents organismes.

INTRODUCTION

The Great Lakes Water Quality Agreement of 1978 between Canada and the United States of America specifies that a joint surveillance and monitoring program of the waters of the Great Lakes is necessary, in part, for the evaluation of water quality trends and the effectiveness of pollution control measures, for the development of predictive techniques to assess the impact of new developments and pollution sources and for the identification of emerging problems. One implicit requirement of joint programs is that the data collected be directly comparable and compatible. A more complete understanding of water quality status and changes would be available if the data obtained by different agencies could be combined than is available from separate analyses of these data sets.

Previous intercomparisons of the laboratories of Great Lakes research ships have been conducted. The most recent was a decade ago between research vessels on Lake Erie (Feder and Zapotosky 1978). A comparison was also made between research vessels and environmental laboratories participating in the IFYGL studies of Lake Ontario (Robertson, Elder and Davies 1974). In both studies, significant differences were found, but the variance due to sampling procedures was less important than that due to the laboratory procedures.

To readdress the question of intercomparability of data from Great Lakes monitoring programs, a three-agency comparison was conducted on Lake Erie in August, 1985. Participating were the R/V Roger R. Simons, operated by the U.S. Environmental Protection Agency; the R/V Hydra, operated by the Ohio State University; and the CSS Limnos, utilized by Environment Canada. The study was designed to determine the sources and magnitude of variation in selected water

quality parameters as measured and reported by the participating agencies. Two comparisons were conducted. One provided data to assess analytical variability and the second provided data to assess overall variability, including water sampling procedures.

The objective of the analytical variability study (AV) was to identify that portion of the variability in parameter concentrations or measured values that could be attributed to laboratory procedures, variability due to different ship sampling procedures being eliminated by using one vessel as the collection source. The objective of the overall variability (OV) study was to assess the variability from the three independent monitoring programs sampling a single water mass simultaneously by determining the contribution to the variation that could be attributed to sampling procedures or laboratory effects. In the latter study, the influence of different parameter concentrations or values and of depth on sampling procedures were assessed by inclusion of two depths that represented epilimnetic and hypolimnetic waters.

STUDY DESIGN AND METHODS

Throughout this report, the abbreviated name of the ship (i.e., Limnos, Hydra and Simons), will be used to refer to the ship itself, to the laboratories associated with the ship, or to the agency that operated the ship. Ship samples will refer to water collected by a designated ship. Laboratory subsamples will refer to samples of water from a single ship sample.

The three ships met at the Canada Centre for Inland Waters (CCIW) station number 84 in the Central Basin of Lake Erie during the

early morning of 27 August, 1985 and anchored within 0.5 km of each other. During the sampling and analytical operations, skies were overcast, air temperature was 21 to 23°C, winds were from 270° at 10 knots, and waves were 0.3 to 1 m.

A summary of operational details, including the water quality parameters measured and the analytical methods used, is presented in Table 1. Each ship was requested to process samples through the analytical runstream in the manner normal for that ship. Parameters that are normally analyzed onboard were done so, and likewise, those that are normally analyzed at a shore-based laboratory were returned to shore for later analysis.

For that portion of the study requiring the collection of water samples by each ship (OV), procedures normal for each ship were used. To avoid problems of logistics and potential variance due to differing transfer bottles, all ships emptied water from the collection device (water bottles or submersible pump) into new 4-L unwashed Cubitainer (brand) plastic bottles. The bottles were then distributed to other ships or retained for analysis as per study design.

For the dissolved chemical constituents, a single filtration of water from each Cubitainer was made, and laboratory subsamples were taken from the filtered source. For total phosphorus, separate digestions of unfiltered water were performed for each laboratory subsample; for total filtered phosphorus, separate digestions were performed for laboratory subsamples drawn from the same filtered water source; and for soluble reactive phosphorus, separate analyses were performed for laboratory subsamples drawn from the same filtered water source.

Analytical Variability

Each ship laboratory was provided with samples from a homogeneous water source that was obtained by pumping water from the 5 m depth into a holding tank on board the Limnos (Figure 1). While the water in the holding tank was being continually mixed, it was sampled by being pumped into Cubitainers. Three such samples were prepared for and delivered to each ship for water chemistry analysis at 0900 local time. Three laboratory subsamples were taken from each of the Cubitainer samples and analyzed, yielding a total of nine analyses per parameter per ship. The Limnos and the Hydra laboratories were each supplied with three additional samples for analysis of chlorophyll-a, while the Simons laboratory, requiring a smaller volume for analysis, used the samples supplied for the water chemistry analyses.

Overall Variability

The depths chosen to represent epilimnetic and hypolimnetic waters were 5 and 24 m (1 m above the bottom). At both depths, each ship collected enough water to provide each of the three laboratories with three ship samples. Two laboratory subsamples were analyzed for water chemistry parameters from each ship sample, resulting in a total of 18 measurements of a parameter per laboratory per depth. As for the analytical variance comparison, the Limnos and the Hydra were each supplied with three additional samples for analysis of chlorophyll-a. Samples were taken by the Simons and the Hydra at 1445 hrs, and by the Limnos at approximately 1600 hrs. All samples were exchanged between 1630 and 1700 hrs.

Routine Agency QC Programs

As part of the normal QC program onboard the Simons, analyses for water chemistry parameters were performed for standard solutions approximately every 20 samples on the AutoAnalyzer systems. These check standards were independent of the standards used to define the calibration curves, and thereby were used to assess satisfactory performance for each analytical run. Based on the previous year's QC data, a current run was considered in control unless one or more of the following conditions applied:

1) a single measurement of more than three standard deviations from the mean;

2) two consecutive measurements of more than two standard deviations from the mean; or

3) seven consecutive measurements all either greater than or less than the mean.

STATISTICAL METHODS

For a given water quality parameter, the partially nested design for the analytical variability study can be described by the following model:

$$y_{ijk} = \mu + l_i + b_{j(i)} + \epsilon_{k(ij)} \quad (i=1,2,3;\ j=1,2,3;\ k=1,2,3) \qquad (1)$$

where y_{ijk} = parameter value for the kth laboratory subsample of jth ship sample analyzed by the ith laboratory;

μ = holding tank concentration;

l_i = laboratory effect;

$b_{j(i)}$ = sampling effect due to the jth ship sample allotted to laboratory i, variance = σ_b^2;

$\varepsilon_{k(ij)}$ = analytical error, variance σ^2.

The concentration for laboratory subsample y_{ijk} is assumed to be the sum of the holding tank concentration, a fixed quantity due to laboratory i, and a random component with two parts: (1) variability among the ship samples, and (2) variability among the laboratory subsamples from a ship sample, which will also be called analytical variability. The difference between the mean of the results for the three laboratory subsamples obtained from one ship sample and the mean over all ship samples analyzed by one laboratory contributes to the estimate of the ship sampling variance, σ_b^2. The difference between the result for one laboratory subsample and the mean of the results for all laboratory subsamples for a particular ship sample and laboratory contributes to the estimate of the analytical variance, σ^2.

Using normal theory analysis of variance techniques, the fixed laboratory effect and the components of variance can be estimated. An analysis of variance was performed for each parameter on the data as a whole and separately for each laboratory. Residual analyses were performed and the studentized range was used to test the differences between all pairs of laboratory means.

Similarly for the overall variability study, the partially nested design can be described by the model:

$$y_{ijkmr} = \mu + d_i + s_j + l_k + ds_{ij} + dl_{ik} + sl_{jk} + dsl_{ijk} + b_{m(ijk)} + \varepsilon_{r(ijkm)} \quad (2)$$

where μ, d_i, s_j and l_k represent the overall mean, and the effects due to the ith depth, the jth ship, and the kth laboratory, respectively. The terms consisting of two or three letters represent the interactions of the respective effects and $b_{m(ijk)}$ represents the ship samping effect, with variance σ_b^2. The difference between ship sample means and the mean over all ship samples for samples analyzed by one laboratory and collected by one ship at one depth contributes to the estimate of σ_b^2, whereas the difference between the results on the two laboratory subsamples of one particular ship sample contributes to the estimate of the analytical variance, σ^2. As for the analytical variability results, the analysis of variance, residual analyses and studentized range tests were performed. For both parts, single missing observations were estimated by the mean of the other laboratory subsamples or the other subsample for that particular ship sample and the degrees of freedom for error were adjusted accordingly.

The conclusions from the analysis of variance were confirmed for the analytical variability data as follows. The Kruskal-Wallis statistic was used for all parameters to test the hypotheses of no differences between laboratories and no differences between ship samples for all laboratories together and for each laboratory separately. The hypothesis for no differences between laboratories was also tested (1) pair-wise, using the Wilcoxon rank sum statistic and (2) overall using a weighted analysis of variance assuming different levels of analytical variability for each laboratory.

RESULTS

Analytical Variability Study

The nature of the differences in level and variability can be seen from the plots of the concentrations of the nine water quality parameters for the nine samples analyzed by each laboratory (Figure 2) and their means and standard deviations (Table 2). The mean concentration reported by the Simons laboratory was lower than those of the other two laboratories for four of the nine parameters, with the Limnos laboratory lowest for soluble reactive silica and uncorrected and corrected chlorophyll-a and the Hydra laboratory lowest for total phosphorus and ammonia. As well as apparent differences in the level of concentration between laboratories, there are differences in variability between laboratories, with no analytical variation in some instances (Table 2). The Hydra results are most variable for seven of the nine parameters and the Simons results least variable for six of the nine parameters, with the Simons laboratory reporting the same value for all nine laboratory subsamples for nitrate plus nitrite, soluble reactive silica and chloride, and the Limnos and Simons laboratories reporting only two values for soluble reactive silica and ammonia, respectively.

These observations are of concern, since the study was designed with the intention of comparing the differences between laboratories to sampling and analytical variability, and in several cases the estimate of the analytical variance is zero for one laboratory. Because the other two laboratories had analytical variances near zero for these parameters, and the effect of inequality of variances on inferences about means is slight for equal group sizes (Scheffé, 1959), the results of the analysis of variance have been

reported. Non-parametric analyses and a weighted analysis of variance were performed to confirm the conclusions from the analysis of variance.

The results of the analysis of variance based on model (1) are summarized in columns two to five of Table 3. For all water quality parameters except total phosphorus, the conclusion is that the three laboratories are not reporting the same mean concentrations. The differences are significant at levels of 0.005 or less, whereas the significance level for total phosphorus is 0.07. The component of variance due to the ship sampling procedure was found to be significantly different from zero at a level of 0.02 or less (columns 4 and 5 of Table 3) for total phosphorus, total filtered phosphorus, nitrate plus nitrite and chloride. A non-zero component of variance due to ship sampling would appear to show that the nine samples prepared on the Limnos were not from a homogeneous water volume or that some of the samples were altered during transfer or storage in the Cubitainer. However, since the ship sampling procedure was found to contribute to the variability for some, but not all parameters (in particular, total and total filtered phosphorus, but not soluble reactive phosphorus), this was examined further. When possible, an analysis of variance was performed separately for each laboratory (Table 4), and the component of variance due to ship sampling was found to be significantly different from 0 for the Simons laboratory for chlorophyll-a, uncorrected and corrected, and for the Hydra laboratory for five of the other seven parameters. This suggests that the observed differences between ship samples are due to laboratory procedures or to only one of the laboratories receiving a set of ship samples with differences between the samples for some of the parameters. A hypothetical laboratory practice that could produce the

observed effect is one of unstable analytical conditions combined with all the subsamples of a ship sample being analyzed consecutively.

To obtain an analysis of variance for which a corresponding non-parametric analysis can be performed, the between-laboratory mean square can be compared to the within-laboratory mean square instead of the ship sampling mean square. This corresponds either to treating the ship sampling effect as fixed or to ignoring ship sample identity. If the within-laboratory mean square is used, the difference between laboratories becomes highly significant for total phosphorus and remains highly significant for all other parameters (columns 6 and 7, Table 3). An analogous non-parametric analysis can be obtained using the Kruskal-Wallis statistic, and the same conclusion, that laboratory differences are significant for all parameters (columns 8 and 9, Table 3), is reached. To confirm that the overly precise values reported by one laboratory were not leading to faulty conclusions, the weighted and unweighted analysis of variance for total phosphorus, the parameter with the largest observed significance level, was performed. The weights were estimated by the inverses of the standard deviations for each laboratory and the difference between laboratories was again found significant (columns 6 and 7 of Table 3). The analysis of variance for all parameters was also performed using only the Limnos and Hydra data to estimate the error variance and the conclusions were the same, except for TFP with a change from a significance level of 0.002 to 0.025. The differences between laboratories for TP remained non-significant and those for all the other parameters highly significant ($p<0.005$).

Using the studentized range and the within-laboratory mean square (ship samples not identified) to estimate analytical variance, the pair-wise differences between laboratories was found significant

at the 5% level for all three pairs of laboratories for all parameters except total phosphorus, soluble reactive silica, chloride and chlorophyll-a, uncorrected (Table 5). The mean total phosphorus concentrations of the Simons and Hydra laboratories, the mean soluble reactive silica concentrations for the Limnos and Simons laboratories and the mean chloride and uncorrected chlorophyll-a concentrations of the Limnos and Hydra laboratories were found not to differ significantly. For purposes of comparison, the pair-wise non-parametric test, based on the Wilcoxon rank sum and an experiment-wise error rate, was performed for total phosphorus. The same conclusion, that only the Simons and Hydra concentrations do not differ significantly at the 5% level, was found.

Overall Variability Study

As for the analytical variability study, plots and summary statistics are presented. The data for each parameter is displayed in a plot (Figure 3) which includes all the levels of the design. The ship and laboratory means and standard deviations for each depth are given in Table 6.

The inclusion of the term d_i in equation (2) may give the impression that one of the objectives of the study was to test whether concentrations at the two depths are different. On the contrary, as mentioned in the introduction, the depths were chosen to provide different concentrations so that the effect of level of concentration could be evaluated. Nonetheless, if the model is to reflect the design, as it should for proper analysis, depth terms must be included. Further, although testing the main depth effect may not be of much interest (provided the results are as expected), clearly

interactions with depth are of interest since we would like to know if the ships can sample at depth as well as they can near the surface and if laboratories can determine high and low concentrations equally as well.

The means that correspond to the first three subscripted terms of equation (2) are given for all nine parameters in Table 7a and, as an example, the complete set of means for terms involving depth, ship or laboratory in equation (2) is given for total phosphorus in Table 7b. This latter set of means has been plotted for all parameters in Figure 4. From the analysis of variance (Table 8), interaction terms which include depth are seen to be significant for seven of the nine parameters. The results of the analysis of variance performed separately for each depth is shown in Table 9, and of the test of the hypothesis that the ship sampling variance, σ_b^2, is zero, separately for each laboratory in Table 10. To understand the interactions, refer to the laboratory means by depth and ship which have been plotted in Figure 4.

The lower variability reported by the Simons laboratory for six of the nine parameters in the analytical variability study, is not present in the overall variability study, as can be seen by ranking the within ship sample standard deviations (Table 11a). However, the ship sampling variance was again found to be significantly different from zero for some of the parameters (Table 8). When the analysis is separated for the two depths, the ship sample variance is significantly different from zero at a level of 0.05 or less for four of the nine parameters at 5 m, and for an additional two parameters at 24 m (Table 9). At 5 m this is due primarily to the results of the Hydra laboratory (Table 10), in agreement with the analytical variability results. At 24 m this no longer holds, and it is not clear whether

the between ship sample variability is introduced at the ship level, laboratory level or both.

The results for the fixed effects in equation (2) are also more complicated than those from the analytical variability study due to significant interaction terms (Tables 8 and 9). Chloride is the only parameter showing no significant differences between depths, ships or laboratories and no significant interactions. Total phosphorus is the only other parameter showing no significant interactions, but concentrations are different at 5 and 24 m and are reported to be different by all three laboratories. Nitrate plus nitrite is the only other parameter for which the depth by laboratory interaction is not significant. Despite these depth by laboratory interactions, it is clear that the concentrations are different at the two depths. The interaction takes the form either of a different ranking in the laboratory concentrations at the two depths or a change in the size of relative differences but the same order.

Total filtered phosphorus and soluble reactive phosphorus present the most complex picture with all main effects and interactions of depths, ships and laboratories being significant. When the analysis is done separately for the two depths, there is no interaction between ship and laboratory at 5 m but there are significant differences between ships for soluble reactive phosphorus and between laboratories for total filtered phosphorus (Figure 4 and Table 9). At 24 m, the ship by laboratory interaction is significant due to higher values reported for total filtered phosphorus for samples both collected and analyzed by the same agency, and to lower values reported for soluble reactive phosphorus by the Hydra laboratory when samples from the Limnos and Simons ships were analyzed.

The ship by laboratory interactions are significant at both depths for nitrate plus nitrite due to the Simons laboratory reporting higher values for Simons samples than for samples from the other two ships. For ammonia, although interaction terms are significant, they are small relative to the differences between laboratories. The depth by laboratory interaction for chlorophyll-a, corrected and uncorrected, best described as an inconsistency between the two depths, accounts for nearly as much variability as the differences between laboratories. For soluble reactive silica, the very strong depth by laboratory interaction results from the Hydra laboratory reporting higher concentrations than the Limnos and Simons laboratories for 5 m samples but not for 24 m samples.

A summary of the pair-wise tests for ships and/or laboratories, in cases where the ship by laboratory interaction was not significant are given in Table 12. The situation in the other cases can be seen from Figure 4, where the differences required between pairs of laboratories for significance at the 5% level has been plotted. Pair-wise comparisons using subsets of the data will be considered in the next section.

Further comparisons can be made from Figure 4 since the laboratory means at both depths in the OV study and in the AV study are plotted as L, S and H on the right side of each plot. The ship means appear as horizontal lines in Figure 4. See also Table 13 for comparison of the 5 m means.

Because the water analyzed for both analytical runstream evaluation and the overall sampling plus runstream evaluation was taken from the 5 m depth at the same station on the same day, a direct comparison of the mean results by parameter and analyst will help

identify inconsistencies within each laboratory. The mean concentrations for seven parameters for both parts of the study are presented in Table 13, along with the difference between the two results. For every parameter, the sign of the difference was the same for all three ships, thereby indicating that the water mass represented by the composite of three ship sampling efforts was different from the homogeneous water mass used for the analytical runstream evaluation, and that each ship laboratory was able to detect the direction of the difference for each parameter. The magnitude of the change between the two reported results also appeared consistent, with the exception of Limnos results for ammonia, Hydra results for total filtered phosphorus, and Simons results for nitrate plus nitrite.

Results from the normal QC program on board the Simons are given in Table 14. The mean, standard deviation, number of analyses and target concentration for each check standard for the 1985 summer surveillance season of the Simons are presented in the table. Also presented are the summary statistics for the check standards as analyzed during the intercomparison study.

On the day prior to the intercomparison study, eight stations in the open waters of the Central Basin of Lake Erie were sampled and the water analyzed for nutrients by EPA onboard the Simons as part of the summer surveillance survey. A summary of the results for the surface water samples is presented in Table 15. Nearly all the average results by analyst of the overall comparison for the 5 m depth were within the range of Central Basin values reported by the Simons. The exceptions included Limnos TP, Hydra NH_3 and SiO_2, and Limnos + Hydra Cl^-.

DISCUSSION

Significant differences have been demonstrated between the results reported by the three laboratories for most of the parameters for both parts of the study. Unexpected results were obtained which appear to be due to ship and laboratory procedures. Since these are also of consequence to surveillance programs, the conclusions will include explanations in terms of operational procedures when possible. The relevance of the results of these studies to routine surveillance programs will then be examined.

Some of the conclusions have been drawn on small numbers of observations, particularly when analyses have been done separately on the samples from one ship. This is the case in the AV study, Table 4. However, the large differences in the F ratios for the three laboratories leave little doubt that there are differences between the laboratories. The number of observations is reasonable for the present design because the replication is within one day and one sampling location. It is the result of the intentional limitation of the scope of the studies and this is acknowledged and discussed below. Also worth noting is that the apparent redundancy of a separate analytical variability study, redundant in that the analytical variability component also appears in the overall variability study, provided information on analytical variability not available in the overall variability study due to operational complications.

Analytical Variability

The unexpected results from the analytical variability study were that (1) ship sample heterogeneity occurred in the samples for

only one laboratory (Hydra for five parameters and Simons for two) and (2) that the Simons laboratory reported overly precise results. To assess the effects of these observations on the conclusions, the analysis was performed in several ways. The concensus is that laboratories are reporting different concentrations for most of the parameters, but there are some for which the conclusions are much stronger. The most important point is that the differences between the laboratories is one of bias. The results from a given laboratory may be very precise but different than the results from another laboratory. See for example the plot of nitrate plus nitrite in Figure 2. From this study it cannot be determined if all laboratories are biased since no reference samples were included. Also, since samples in this study would all be analyzed on one day, it is not known whether the bias is fixed from day to day or appears as a random component in routine surveillance programs when samples are collected and analyzed on different days.

Overall Variability Study

The many significant interaction terms made it difficult to draw conclusions from this study. There are a number of operational details that may have contributed to this. The Limnos water samples were taken later than those of the Simons and Hydra ships, and the samples were transferred after the Limnos sampling. Thus different water masses were sampled and ship-board analyses of the Simons and Hydra samples may have been performed later by other laboratories than by the laboratory of the ship collecting the sample. The sampling devices differed, being 4- and 8-L bottles on rosettes for the Limnos and Simons, respectively, and a submersible pump for the Hydra. The procedures used for positioning the sampler 1 m above the bottom also

varied. The method for chlorophyll-a used by the Simons laboratory was not the same as that used by the Limnos and Hydra laboratories, and the Limnos laboratory filtered ship subsamples separately whereas the other laboratories filtered at the ship sample level.

The different times of sampling and different sampling procedures might lead to ship differences, in either level or variability. Comparison of the 5 m samples from the analytical and overall variability studies showed that at least one laboratory detected differences in five of the nine parameters (Table 13). However, for parameters with no ship by laboratory interaction, significant differences between ship means were found only for soluble reactive phosphorus at 5 m (Hydra > Limnos and Simons). Thus the only ship effect appears to be greater sampling variability for the Limnos and Simons ships at 24 m than at 5 m (Table 10).

The significant interaction terms which may be attributable to different waiting times between collection and analysis for different laboratories are (Table 9 and Figure 4): (1) for total filtered phosphorus at 24 m, results were higher when collector and analyst were the same, (2) for soluble reactive phosphorus at 24 m, the Hydra laboratory's results were low for the Limnos and Simons samples relative to the Hydra samples, and (3) for nitrate plus nitrite at both 5 and 24 m, the Simons laboratory results were higher for Simons samples than for those of the Limnos and Hydra. The question arises as to why the interactions given in points (1) and (2) above were not also present for 5 m samples. This may be related to the larger concentration differences between depths (Table 7a) for total filtered phosphorus and soluble reactive phosphorus than for nitrate plus nitrite. The significant interaction terms for soluble reactive silica result from the higher concentrations reported by the

Hydra for 5 m samples but not for 24 m samples (Figure 3). One could speculate that this is due either to contamination or a bias at low levels of concentration only.

Summary of Laboratory Differences in AV and OV Studies

Pair-wise differences between laboratory means for all water quality parameters and both studies are given in Table 16. For the overall variability study, most of these differences were not given previously because, in the presence of significant ship by laboratory interactions, the difference between a pair of laboratories will depend upon which ship collected the samples. The differences in Table 16 fall into three groups: (1) differences previously given in Table 12, (2) differences calculated on a subset of the data because of the above described interactions or extreme values, and (3) cases where signficant ship by laboratory interactions still exist, but useful observations can be made even if tests of significance are not appropriate.

The conclusions to be drawn from the TP data are unambiguous. The Limnos laboratory means ranged from 2.3 to 4.1 µg/L higher than those of the Simons and Hydra laboratories (Table 16). The TFP and SRP data are more difficult to interpret because of the cases where higher concentrations were reported when the same agency collected and analyzed the samples. In the AV comparison, the Simons laboratory means for TFP were 1.8 and 2.6 µg/L lower (significant at 0.05 level) than those of the Limnos and Hydra laboratories. If differences between laboratory means are calculated from only the samples collected and analyzed by the same agency (OV comparison), then the Simons TFP means are lower than those of the Limnos and

Hydra, as in the AV comparison (Table 16). Even more limited conclusions can be drawn from the SRP data because of the problems with the 24 m data. The Limnos laboratory means ranged from 0.2 to 0.4 µg/L higher than those of the Simons laboratory (AV and OV). Only 5 m samples could be used for comparing the other two pairs of laboratories with consistency of the direction of difference being the only conclusion.

In the AV comparison, the differences between NO_3NO_2 concentrations were significant for all laboratory pairs (3 to 6 µg/L), despite good laboratory precision. In the OV comparison the Simons laboratory reported higher concentrations for samples collected by the Simons ship. If, as was done for TFP and SRP, means are calculated only from samples collected and analyzed by the same agency, differences in means are in good agreement with the AV results (Table 16). This appears to be the appropriate subset for removal of the effect of the anomalously high values, since differences calculated from Limnos and Hydra ship samples only are much higher than differences found in the AV comparison (Table 16).

The largest and most consistent difference between laboratories is that for ammonia, with the Hydra means always lower than those of the Limnos and Simons (Table 2 and 6) by at least 45%. Significant differences of 6 µg/L between the Limnos and Simons and Simons and Hydra laboratories were reported for NH_3 (AV, Table 16), despite good laboratory precision, particularly for the Simons laboratories (Table 11). In the OV part of the study, the Limnos and Simons concentrations were closer, with the Hydra laboratory still reporting the lowest values. These differences have not been tested for significance because of the conclusion that the size of the difference between laboratories depends upon which ship collected the samples

(significant ship by laboratory interaction, Table 9). However, it is clear from Figure 4 that the same relative order (Limnos > Simons > Hydra) holds for the samples from all three ships at both depths.

The Hydra laboratory SRS concentrations were 0.2 mg/L higher than those of the other two laboratories for the 5 m samples (concentrations 0.3 to 0.4 mg/L), but not for the higher concentrations of the 24 m samples. The Simons and Limnos laboratories appear to be reporting concentrations to too few digits since the same value or few values were reported for replicates (Table 11). As for ammonia, mean differences in the OV comparison were not tested for significance due to significant interactions (Table 9).

Also of consequence to routine surveillance programs, in which replication of sampling at a particular location and time and replication of laboratory analyses of a sample are not common, are the occasional high or low values reported in these studies. Although the variance for chloride due to laboratory subsamples did not exceed about 2% of mean values in these studies, extreme values (Figure 4) were reported four times by the Hydra laboratory and one value, exceeding the mean for the other five results on the three samples from the same ship by more than five standard deviations, was reported by the Limnos laboratory. Removal of the two most extreme results reduces the estimate of σ_b^2 substantially and results in the conclusion that the mean chloride concentration reported by the Simons laboratory was significantly less than those reported by the Limnos and Hydra laboratories, in agreement with the conclusions of the analytical variability study (Table 16). Note that this is different from the conclusion based on the analysis of all the OV data (Table 9), where no significant differences were found between laboratories. Thus the observations relevant to the surveillance programs

are that the Simons laboratory means for chloride were significantly lower than those of the Limnos and Hydra laboratories (0.3 to 0.9 mg/L) and that occasional extreme values were obtained.

Although the parameter of interest is corrected chlorophyll-a, the results of both corrected and uncorrected chlorophyll-a have been reported since the conclusions regarding significant differences do not completely agree (Tables 5, 9 and 12). Thus it seems of importance to note that differences occur not only in determining uncorrected chlorophyll-a but also in the correction factor. The procedural differences mentioned above do not seem to have affected results since the between ship sample variability for the Limnos laboratory is not significant and there were not consistent differences between the Simons laboratory and the other two laboratories. Corrected chlorophyll-a concentrations, in the AV comparison, differed significantly between all three laboratories and, at 24 m in the OV comparison, the Limnos laboratory concentrations were lower than those of the Simons and Hydra laoratories. The high variability in this parameter and inconsistent relative differences between laboratories for depths, ship and corrected and uncorrected chlorophyll make any further conclusions impossible.

There are several types of information which might help to further explain the results. Details of whether each laboratory processes all samples for a given parameter within a single analytical run or in two or more runs are not available. If two or more runs were involved within a given laboratory, the problem of inconsistent ship-by-laboratory results could be due to variance within an analytical run being smaller than the bias between runs. If single analytical runs were involved for any given parameter, then other sources of variance were operating. Factors such as different batches of

filters, processing order, and holding times could be considered for further investigation. In order to document the variability within each analytical run, each monitoring program must continue a strong quality control program that includes the analysis of stable reference materials that are independent of the standards used to establish calibration curves.

Importance of Laboratory Differences to Surveillance Program

The study protocol required that laboratories process samples in the usual manner, since the objective was to draw inferences about comparability of routine surveillance data produced by the different agencies. However, as can be seen from the Simons check standards, the small number of samples being processed in the present studies led to nonstandard conditions in the Simons laboratory. The variances associated with the Simons for all water chemistry parameters from the analytical runstream part of the study were significantly less (F test significance $<< 0.005$) than those reported for the check standards from the Simons' 1985 surveillance program (Table 14). Even for the overall intercomparison data, in which two-thirds of the samples analyzed by the Simons contained an uncontrollable source of variance (ship sampling procedures), only the variance associated with SRP (5 m), $NO_3 + NO_2$ (5 m + 24 m), and SiO_2 (24 m) exceeded that of the appropriate check standard.

The change in a water quality parameter over time can be assessed from the analysis of yearly means, where the mean for each year is for some defined region, thermal layer and time period. The variance corresponding to one such mean includes spatial variability and sampling and analytical variability. The present study provided

estimates of the latter sources of variability. However, all of the intercomparison analyses were completed with one or two runs of an Autoanalyzer, and all within the same day. Over the duration of a survey, several runs may be initiated daily for a period of three weeks or so. Therefore, a source of variance not included in the intercomparison study is that of items associated with the startup of a chemistry analytical run. Sets of data were sought which would provide estimates of laboratory variability over a longer time and estimates of laboratory differences and variablity in the presence of a spatial component.

Two sets of data from the Simons surveillance program (Tables 14 and 15) were compared with the Simons laboratory results in the three ships study. Standard deviations obtained from repeated measurements of check standards during the Simons' 1985 surveillance program were larger than standard deviations obtained from samples analyzed by the Simons laboratory in both the AV and OV comparisons. However, the standard deviations of the check standards were much closer to those calculated for surface samples from eight open lake stations in the Central Basin of Lake Erie by the Simons on the day before the intercomparison study, with the exception of $NO_3 + NO_2$. The standard deviations for the check standards contain both of the above-mentioned types of laboratory variability, while those from the eight stations contain spatial and within-day laboratory variabiltiy. This suggests that, for these two sets of data from the Simons laboratory, day to day laboratory variablity is similar in size to the spatial variability.

Each of the three ships sampled open lake stations of the Central Basin in August 1985, with the Hydra and Simons conducting surveys and the Limnos sampling for research studies. The same

summary statistics, as available for the Simons and Hydra data, have been calculated for the Limnos samples (see footnotes Table 17), where all are restricted to depths within the epilimnion. Comparison of the standard deviations from the three-ship study with those from the Central Basin sampling programs show that the latter are larger for the Limnos and Hydra samples as well, with the difference greatest for $NO_3 + NO_2$. The difference between agency means, for at least one pair of means, are significant at a level of 0.025 or lower, relative to the variance of these samples, and differences are of similar size to those between laboratories in the three-ship study, except for the $NO_3 + NO_2$ differences which are larger. Although differences between means are comparable to those in the three-ship study, significant differences for a particular water quality parameter are not always between the same pair of laboratories as found in the three-ship study. This same lack of consistency was observed for the AV and OV comparison for some parameters. The high bias for SRS and low bias for NH_3 of the Hydra laboratory in the AV and OV comparison is again evident in Central Basin means (Table 17). The larger variablity and larger differences between means for $NO_3 + NO_2$ concentrations obtained from the sampling programs relative to the three-ship study are consistent with larger spatial heterogeneity for $NO_3 + NO_2$ than the other water quality parameters.

Thus, on the basis of this comparison with limited survey data, it appears that laboratory differences contribute to differences between Central Basin means reported by the three agencies and may contribute to the associated estimates of variance. However, a study designed for the specific purpose would be required to estimate the components due to spatial heterogeneity and sampling and laboratory variability.

The laboratory differences obtained from the three-ships study can be compared with estimates of the decrease in concentrations in the Central Basin of Lake Erie over time. Two examples of such estimates are considered. Rosa (1987), using CCIW and CLEAR data for stations within a consistent and limited region, depths within the epilimnion and dates between mid-June to mid-August, estimated a rate of decrease of 0.51 $\mu g\ L^{-1}\ yr^{-1}$ over the period 1968 to 1982. Instead of estimating a slope from the data of two agencies, the change in TP concentrations can be calculated for intervals between the years in which one agency sampled the lake (means and standard deviations were provided by F. Rosa). Assuming a constant level between 1968 and 1972 and another between 1977 and 1979, the two periods in which CCIW conducted surveys, the change in mean level is 3.3 µg/L. From the analogous calculation for the difference between the periods in which CLEAR was involved in the data collection, 1974 to 1975 and 1980 to 1982, the change in mean level is 3.1 µg/L. Comparison with the significant differences between laboratories (Table 16), which range from 2.3 to 4.1 µg/L, shows that laboratory differences are of the size of the change estimated to occur over six to eight years. El-Shaarawi (1984), using CCIW data for surface samples from all stations sampled in the Central Basin and all available surveys in a year, accounted for the seasonality in the model upon which the analyses was based and estimated yearly levels adjusted for different seasonal cycles. The change in these yearly levels between 1970 and 1972 and between 1977 and 1980 were 3.5 and 3.1 µg/L, respectively, which give higher estimates of rates of change, i.e., 1.75 and 1.03 $\mu g\ L^{-1}\ yr^{-1}$, than obtained by Rosa (1987). Based upon these rates, laboratory differences are of the size estimated to occur in two to three years.

The effect of the combination of data from different agencies depends upon how the data is combined. A simple example, involving the estimation of the mean concentration by combining data from two laboratories, will illustrate the point. Suppose the first laboratory determines the concentration, c, without bias but the second laboratory has a bias, δ, and both have a variance of σ^2. If n_1 and n_2 samples ($n = n_1 + n_2$) from laboratories one and two, respectively, are used to estimate the mean concentration, then the expected mean concentration is $c + (n_2\delta/n)$ with the standard error of the mean equal to $\sigma/\sqrt{n}$. Thus if thirty samples were used to calculate the mean where c = 11 µg/L and the bias of laboratory two was 2 µg/L, the mean would be expected to be 11.6 and 12.0 and 12.4 if 9, 15 and 21 of the samples were analyzed by laboratory two. The latter two values would be obtained with probability less than 0.05 for σ = 2 if all samples were analyzed by the laboratory without bias. The values of c, δ and σ are consistent with the TP data from the three ships study.

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TABLE 1 Operational details of three-ship intercomparison study on Lake Erie. (a)

Date: 27 August, 1985

Location: Lake Erie, CCIW Station #84
Latitute 41 55 66
Longitude 81 39 39

Ships: R/V Roger R. Simons at Loran 43975.3, 57612.3
R/V Hydra at Loran 43974.3, 57614.3
CSS Limnos at Loran 43975.6, 57615.0

Parameters measured and analytical methods used:

Temperautre profile[d]

Secchi disc dapth[d]
L: 30 cm white disk
H: 30 cm Whipple disk
S: 30 cm white disk

Specific conductance
L: ambient temperature plus correction
H: ambient temperature plus correction
S: heated to 25°C before determination

pH[e]

Chlorophyll-a (CHla)
L: spectrophotometric[b], separate filtration for replicates
H: spectrophotometric[b]
S: fluorometric[b]

Particulate organic carbon (POC)[d]
L: CHN analyzer[b]
H: CHN analyzer[b]

Particulate organic nitrogen (PON)[d]
L: CHN analyzer[b]
H: CHN analyzer[b]

TABLE 1 Operational details of three-ship intercomparison study on Lake Erie (continued). (a)

Technicon Autoanalyzer Analyses:

Total phosphorus (TP)
- L: ammonium molybdate - stannous chloride[b]
- H: ammonium molybdate - stannous chloride[b]
- S: ammonium molybdate - absorbic acid
  ammonium molybdate - stannous chloride[c]

Total Filtered Phosphorus (TFP)
- Same as TP

Soluble reactive phosphorus (SRP)
- Same as TP, except run onboard for all three ships

Nitrate plus nitrite, filtered ($NO_3 + NO_2$)
- L: cadium reduction - sulfanilamide
- H: cadium reduction - sulfanilamide
- S: cadium reduction - sulfanilamide

Ammonia (NH_3)
- L: filtered, sodium hypochlorite - o-tolidine
- H: filtered, alkaline phenol - hypochlorite - nitroprusside
- S: unfiltered, alkaline phenol - hypochlorite - nitroprusside

Soluble reactive silica (SRS)
- L: ammonium molybdate - ANSA/heterpoly blue
- H: ammonium molybdate - ascorbic acid/molybdenum blue
- S: ammonium molybdate - ascorbic acid/molybdenum blue

Chloride (Cl)
- L: filtered, mercuric thiocyanate - ferric ammonium sulphate
- H: filtered, mercuric thiocyanate - ferric nitrate
- S: unfiltered, mercuric thiocyanate - ferric nitrate

Sampling methods:
- L: 4-Litre Niskin bottles on a rosette
- H: submerged pump
- S: 8-Litre Niskin bottles on a rosette

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[a] Abbreviations used: L = CSS Limnos, H = R/V Hydra, S = R/V Roger R. Simons.

[b] Samples processed or preserved onboard, then returned to shore-based laboratory for analysis.

[c] Normally the R/V Roger R. Simons uses the ascorbic acid method. A split sample comparison was performed for this study using stannous chloride.

[d] Measured for whole-ship comparison study only.

[e] Measured for analytical runstream study only.

TABLE 2 **Summary statistics by laboratory for the nine water quality parameters**

Parameter	Mean			Standard Deviation			Number of Ship Samples With All Replicates the Same		
	Limnos	Simons	Hydra	Limnos	Simons	Hydra	Limnos	Simons	Hydra
Total phosphorus	14.6	12.3	11.7	1.52	0.88	1.68	0	1	0
Total phosphorus, filtered	6.9	5.1	7.7	0.44	0.26	0.74	0	0	0
Soluble reactive phosphorus	1.5	1.1	1.8	0.14	0.23	0.31	0	0	0
Nitrate + nitrite	196	190	193	0.50	0.00	1.32	0	3[a]	0
Ammonia	18.6	12.2	6.6	1.67	0.44	0.33	0	1[b]	0
Soluble reactive silica	0.338	0.354	0.553	0.0667	0.0000	0.0259	2[c]	3[a]	1
Chloride	15.0	14.1	15.0	0.11	0.00	0.16	1	3[a]	0
Chlorophyll-a, uncorrected	3.24	4.77	3.59	0.65	0.46	0.65	0	0	0
Chlorophyll-a, corrected	2.41	3.73	3.14	0.46	0.24	0.63	0	0	0

[a] The same concentration was reported for all nine laboratory subsamples.
[b] Only two concentrations, 12 and 13, were reported for all nine values.
[c] One value of 0.160 was reported and the other eight were 0.360.

TABLE 3 Results of analyses to test the hypotheses of no laboratory differences and zero ship subsampling variance

Water Quality Parameter	Ship Samples Identified				Ship Samples Not Identified			
	Analysis of Variance				Analysis of Variance		Non Parametric Analysis	
	Laboratory		Ship		Laboratory		Laboratory	
	F	s.l.	F	s.l.	F	s.l.	K	s.l.
Total phosphorus	4.25	0.07	5.39	0.003	10.92 9.62w	0.001 0.001w	10.3	0.003
Total phosphorus, filtered	23.8	0.002	4.81	0.004	58.6	<0.001	19.3	<0.001
Soluble reactive phosporus	42.9	0.001	0.41	0.86	20.6	< 0.001	18.7	<0.001
Nitrate + nitrite	62.5	<0.001	3.55	0.02	135	< 0.001	23.7	<0.001
Ammonia	383	<0.001	0.73	0.63	301	< 0.001	22.8	<0.001
Soluble reactive silica	54.6	<0.001	1.60	0.20	76.1 487°	< 0.001 < 0.001	22.3	<0.001
Chloride	81.1	<0.001	4.00	0.01	186	<0.001	18.4	<0.001
Chlorophyll-a, uncorrected	14.9	0.005	1.14	0.38	16.4	< 0.001	15.0	<0.001
Chlorophyll-a, corrected	30.3	0.001	0.51	0.79	17.5	<0.001	14.8	0.001

F is the ratio of mean squares, s.l. the observed significance level and K the Kruskal-Wallis statistic.

w Weighted analysis of variance.

o Single value 0.160 from Limnos laboratory removed.

TABLE 4 Test of the hypothesis that the ship sampling variance is zero performed separately for each laboratory

Water Quality Parameter	F Ratio, (s.l.)			Kruskal-Wallis Statistic (s.l.)		
	Limons	Simons	Hydra	Limnos	Simons	Hydra
Total phosphorus	2.30	0.24	91.00 (<0.001)	2.76	0.11	6.71 (0.007)
Total phosphorus, filtered	0.70	1.50	12.26 (0.008)	1.90	2.04	5.85 (0.03)
Soluble reactive phosphorus	0.04	0.67	0.36	0.22	1.55	1.48
Nitrate + nitrite	0.00	na	4.87 (0.06)	0.00	I	5.93 (0.02)
Ammonia	0.70	0.50	5.74 (0.05)	0.74	1.14	5.12 (0.05)
Soluble reactive silica	1.00	na	705. (<0.001)	2.00	I	7.58 (<0.001)
Chloride	1.30	na	7.00 (0.03)	2.94	I	5.90 (0.03)
Chlorophyll-a, uncorrected	0.85	19.1 (0.003)	0.08	1.45	6.01 (0.02)	0.09
Chlorophyll-a, corrected	0.73	22.9 (0.002)	0.04	0.69	5.78 (0.03)	0.09

na Both numerator and denominator are zero.
(s.l.) Bracketed values are observed significance levels which have been reported only when they are ≤0.10.
I Indefinite since all values are the same.

TABLE 5 Pair-wise comparison of laboratory means based on studentized range test at the 5% level

Water Quality Parameter	Difference Between Laboratory Means Significant Difference (a,b)			Critical Absolute Value for Difference Model with Ship Samples	
	Limnos-Simons	Limnos-Hydra	Simons-Hydra	(a) Identified	(b) Not Identified
Total phosphorus	2.3b	2.9b	0.7	3.3	1.6
Total phosphorus, filtered	1.8a,b	-0.8b	-2.6a,b	1.2	0.6
Soluble reactive phosphorus	0.4a,b	-0.3a,b	-0.7a,b	0.2	0.3
Nitrate + nitrite	6a,b	3a,b	-3a,b	2	1
Ammonia	6.3a,b	12.0a,b	5.6a,b	1.3	1.2
Soluble reactive silica	0.016	-0.215a,b	-0.199a,b	0.070	0.049
Chloride	0.88a,b	0.01	-0.87a,b	0.24	0.13
Chlorophyll-a uncorrected	-1.52a,b	-0.35	1.17a,b	0.90	0.70
Chlorophyll-a corrected	-1.32a,b	-0.73a,b	0.59a,b	0.52	0.56

The a or b indicates that the difference between means is significantly different from zero when the analysis was based on the model with or without ship samples identified, respectively.

Compare with results for total phosphorous obtained from the Wilcoxon rank sum statistic.

Larger Rank Sum			
Limnos-Simons	Limnos-Hydra	Simons-Hydra	Critical Value at 5% Level
116	116	96	113

TABLE 6 Laboratory and ship means (standard deviations) for each water quality parameter at each depth

Water Quality Parameter	Laboratory			Ship		
	Limnos	Simons	Hydra	Limnos	Simons	Hydra
5 meters						
Total phosphorus, µg/L	12.5 (1.1)	9.8 (0.6)	10.2 (0.8)	10.7 (1.4)	10.7 (1.7)	11.0 (1.2)
Total filtered phosphorus, µg/L	6.0 (0.3)	4.3 (0.5)	5.0 (1.0)	5.2 (1.1)	4.7 (0.9)	5.4 (0.7)
Soluble reactive phosphorus, µg/L	1.1 (0.1)	0.9 (0.8)	1.3 (0.4)	1.0 (0.3)	0.8 (0.3)	1.5 (0.7)
Nitrate + nitrite, µg/L	190 (1)	170 (10)	188 (2)	182 (11)	187 (3)	180 (14)
Ammonia, µg/L	14.3 (1.1)	12.1 (0.9)	5.6 (1.0)	11.2 (4.4)	10.5 (3.1)	10.4 (3.9)
Soluble reactive silica, mg/L	0.367 (0.048)	0.354 (0.005)	0.598 (0.066)	0.469 (0.152)	0.428 (0.111)	0.423 (0.086)
Chloride, mg/L	15.0 (0.3)	14.6 (0.2)	15.8 (2.6)	15.2 (0.2)	14.8 (0.2)	15.5 (2.6)
Chlorophyll-a, µg/L	3.2 (0.6)	4.8 (1.0)	4.0 (0.3)	4.2 (0.8)	3.9 (1.1)	3.8 (0.9)

TABLE 6 Laboratory and ship means (standard deviations) for each water quality parameter at each depth, continued

Water Quality Parameter	Laboratory			Ship		
	Limnos	Simons	Hydra	Limnos	Simons	Hydra
24 meters						
Total phosphorus, µg/L	34.5 (1.1)	30.5 (0.9)	31.9 (0.4)	32.2 (1.8)	32.3 (2.3)	32.5 (1.5)
Total filtered phosphorus, µg/L	21.5 (3.4)	19.6 (2.0)	21.7 (2.5)	23.3 (2.3)	19.4 (1.1)	20.3 (3.1)
Soluble reactive phosphorus, µg/L	15.7 (2.6)	15.8 (2.0)	12.2 (1.7)	16.4 (3.3)	13.0 (2.2)	14.2 (0.9)
Nitrate + nitrite, µg/L	181 (2)	160 (11)	178 (4)	171 (11)	170 (4)	168 (14)
Ammonia, µg/L	45.8 (2.1)	41.1 (0.9)	26.5 (0.9)	38.3 (8.5)	37.1 (7.8)	38.0 (8.6)
Soluble reactive silica, mg/L	3.10 (0.11)	3.13 (0.04)	3.16 (0.03)	3.09 (0.12)	3.16 (0.03)	3.14 (0.02)
Chloride, mg/L	15.2 (0.1)	14.8 (0.1)	15.5 (1.0)	15.0 (0.1)	15.4 (0.3)	15.1 (1.0)
Chlorophyll-a, µg/L	0.48 (0.13)	1.15 (0.18)	1.05 (0.26)	0.99 (0.34)	0.84 (0.34)	0.86 (0.36)

TABLE 7a **Laboratory, ship and depth means for each water quality parameter**

Water Quality Parameter	Laboratory			Ship			Depth	
	Limnos	Simons	Hydra	Limnos	Simons	Hydra	5 m	24 m
Total phosphorus	23.5	20.1	21.0	21.5	21.5	21.7	10.8	32.4
Total phosphorus, filtered	13.7	12.0	13.4	14.1	12.1	12.9	5.1	20.9
Soluble reactive phosphorus	8.4	8.4	6.7	8.7	6.9	7.8	1.1	14.5
Nitrate + nitrite	185	165	183	176	183	174	183	173
Ammonia	30.1	26.6	16.1	24.8	23.8	24.2	10.7	37.8
Soluble reactive silica	1.735	1.790	1.877	1.797	1.807	1.799	0.443	3.158
Chloride	15.1	14.7	15.6	14.9	15.6	15.0	15.1	15.2
Chlorophyll-a, uncorrected	2.86	4.06	3.34	3.71	3.32	3.23	4.89	1.95
Chlorophyll-a, corrected	1.82	2.97	2.52	2.59	2.37	2.35	3.98	0.90

TABLE 7b Means by laboratory, ship and depth for total phosphorus

Depth	Laboratory	Ship			Laboratory Mean
		Limnos	Simons	Hydra	
5 m	Limnos	12.3	12.6	12.5	12.5
	Simons	9.8	9.2	10.0	9.7
	Hydra	10.0	10.1	10.4	10.2
Ship Mean		10.7	10.6	11.0	
24 m	Limnos	34.4	35.2	34.3	34.6
	Simons	30.4	30.1	31.0	30.5
	Hydra	32.2	31.5	32.1	31.9
Ship Mean		32.3	32.3	32.5	

TABLE 8 Analysis of variance under the model given by equation 2

Water Quality Parameter	Observed Significance Level							
	D	S	L	DxS	DxL	SxL	DxSxL	σ_b^2
Total phosphorus	*	0.66	*	0.93	0.06	0.36	0.81	*
Total filtered phosphorus	*	*	*	*	0.03	*	*	*
Soluble reactive phosphorus	*	*	*	*	*	*	*	*
Nitrate + nitrite	*	*	*	0.02	0.55	*	0.51	*
Ammonia	*	*	*	0.09	*	0.005	0.001	0.95
Soluble reactive silica	*	0.79	*	0.003	*	*	0.23	*
Chloride	0.86	0.20	0.09	0.79	0.72	0.32	0.86	*
Chlorophyll-a, uncorrected	*	0.003	*	0.66	*	0.52	0.006	0.89
Chlorophyll-a, corrected	*	0.04	*	0.54	*	0.07	0.01	0.93

* Observed significance level less than 0.001.
D,S,L stand for depth, ship and laboratory, respectively.

TABLE 9 Analysis of variance performed for each depth

Water Quality Parameter	Observed Significance Level							
	5 m				24 m			
	S	L	SxL	σ_b^2	S	L	SxL	σ_b^2
Total phosphorus	0.65	*	0.86	0.04	0.92	*	0.39	*
Total phosphorus filtered	0.06	*	0.63	*	*	*	*	*
Soluble reactive phosphorus	0.002	0.08	0.26	0.59	*	*	*	*
Nitrate + nitrite	*	*	*	0.008	*	*	*	*
Ammonia	0.04	*	0.01	0.18	0.003	*	0.004	0.99
Soluble reactive silica	0.001	*	*	0.57	0.10	0.005	0.05	*
Chloride	0.43	0.28	0.54	*	0.29	0.17	0.69	*
Chlorophyll-a, uncorrected	0.17	*	0.11	0.79	*	*	0.01	0.87
Chlorophyll-a, corrected	0.17	*	0.03	0.87	0.08	*	0.59	0.34

* Observed significance level less than 0.001.
D,S,L stand for depth, ship and laboratory, respectively.

TABLE 10 Observed significance levels from testing $\sigma_b^2 = 0$

Water Quality Parameter	5 m			24 m		
	Laboratory			Laboratory		
	Limnos	Simons	Hydra	Limnos	Simons	Hydra
Total phosphorus	0.50	0.20	< 0.001	0.01	0.02	0.29
Total phosphorus filtered	0.39	0.24	< 0.001	< 0.001	< 0.001	< 0.001
Soluble reactive phosphorus	0.19	0.56	0.39	0.002	0.07	0.003
Nitrate + nitrite	0.40	0.21	0.01	0.40	a	0.01
Ammonia	0.70	0.20	0.13	0.94	0.37	0.69
Soluble reactive silica	0.81	< 0.001	0.006	< 0.001	< 0.001	0.18
Chloride	0.14	0.84	< 0.001	0.64	0.79	< 0.001
Chlorophyll-a, uncorrected	0.99	0.59	0.14	0.27	0.56	0.86
Chlorophyll-a, corrected	0.97	0.70	0.41	0.16	0.48	0.41

a The same value was reported for all ship subsamples and thus the test could not be performed.

TABLE 11a Variability due to laboratory analysis of subsamples of ship samples, expressed as the standard deviation, by study, depth and laboratory

Water Quality Parameter	Analytical Variability			Overall Variability					
	5 m			5 m			24 m		
	Limnos	Simons	Hydra	Limnos	Simons	Hydra	Limnos	Simons	Hydra
Total phosphorus	1.32	0.97	0.35	1.21	0.58	0.16	0.71	0.62	0.21
Total phosphorus filtered	0.46	0.24	0.38	0.27	0.31	0.12	0.24	0.25	0.27
Soluble reactive phosphorus	0.16	0.24	0.34	0.11	0.82	0.25	0.51	0.79	0.14
Nitrate + nitrite	0.58	0[1]	0.94	0.58	1.91	1.25	1.37	0[1]	1.75
Ammonia	1.73	0.47[2]	0.23	0.88	0.58	0.81	2.35	0.47	1.05
Soluble reactive silica	0.0667[3]	0[1]	0.0020	0.0574	0.0007	0.0148	0.0210	0.0047	0.0173
Chloride	0.11	0[1]	0.10	0.22	0.20	0.31	0.09	0.07	0.13
Chlorophyll-a, uncorrected	0.66	0.20	0.74	0.67	1.40	0.13	0.10	0.44	0.53
Chlorophyll-a, corrected	0.48	0.09	0.73	0.47	1.16	0.23	0.10	0.19	0.25

[1] The same value was reported for all laboratory subsamples.
[2] Only two concentrations, 12 and 13, were reported for all nine values.
[3] One value of 0.160 was reported and the other eight were 0.360.

TABLE 11b Variability due to ship sampling, expressed as the standard deviation, by study, depth and laboratory

Water Quality Parameter	Analytical Variability			Overall Variability					
	5 m			5 m			24 m		
	Limnos	Simons	Hydra	Limnos	Simons	Hydra	Limnos	Simons	Hydra
Total phosphorus	2.00	0.47	3.30	1.18	0.79	1.33	1.71	1.31	0.26
Total phosphorus filtered	0.38	0.30	1.32	0.29	0.40	1.45	1.60	1.19	1.31
Soluble reactive phosphorus	0.03	0.20	0.20	0.15	0.75	0.27	2.32	1.36	0.42
Nitrate + nitrite	0[2]	0[1]	2.08	0.62	2.54	2.96	1.49	3.33	4.10
Ammonia	1.45	0.33	0.56	0.71	0.78	1.23	1.20	0.53	0.86
Soluble reactive silica	0.0667	0[1]	0.0516	0.0394	0.0071	0.0398	0.1355	0.0666	0.0242
Chloride	0.12	0[1]	0.26	0.33	0.13	3.94	0.08	0.05	1.61
Chlorophyll-a, uncorrected	0.61	0.86	0.21	0.25	1.26	0.19	0.13	0.40	0.33
Chlorophyll-a, corrected	0.41	0.45	0.14	0.20	0.92	0.24	0.14	0.19	0.27

[1] The same value was reported for all laboratory subsamples.
[2] The ship means were the same.

TABLE 12 Pair-wise comparison of means based on the Studentized range test for parameters and depths with no significant ship by laboratory interactions

Water Quality Parameter	Depth	Laboratory Differences			Ship Differences			Critical Value D
		Limnos-Simons	Limnos-Hydra	Simons-Hydra	Limnos-Simons	Limnos-Hydra	Simons-Hydra	
Total phosphorus	5	2.8*	2.3*	-0.5	0.1	-0.3	-0.4	1.0
	24	4.1*	2.7*	-1.4*	0.0	-0.2	-0.2	1.1
Total filtered phosphorus	5	1.7*	1.0*	-0.7	0.4	-0.3	-0.7	0.9
Soluble reactive phosphorus	5	0.2	-0.2	-0.4*	0.2	-0.5*	-0.7*	0.4
Nitrate + nitrite	5	26*	1	-25*		2		4.1 ℓ 2.7 s
(Limnos + Hydra ships only)	24	27*	2	-25*		2		5.8 ℓ 3.9 s
Chlorophyll-a, uncorrected	5	-1.84*	-0.19	1.65*	0.28	0.48	0.20	0.64
Chlorophyll-a, corrected	24	-0.66*	-0.56*	0.10	0.15	0.13	-0.02	0.18

* Differences between either ship or laboratory means larger than D in absolute value are significant at the 0.05 level.

ℓ,s indicate critical absolute value for laboratory and ship difference, respectively.

TABLE 13 Average water chemistry results, presented by analyst, from the analytical variance comparison (AV) and from the overall variance comparison (OV) at 5 m

Analyst	Comparison	TP µg/L	TFP µg/L	SRP µg/L	NO_3 µg/L	NH_3 µg/L	SiO_2 µg/L	Cl^- µg/L	$Chla_u$	$Chla_c$
Limnos	AV	14.6	6.9	1.6	196	18.6	338	15.0	3.24	2.41
	OV	12.5	6.03	1.06	190	14.3	367	15.01	4.21	3.16
	Difference	-2.1	-0.87	-0.44	-6	-4.3	+29	+0.01	+0.97	+0.75
Simons	AV	12.3	5.1	1.1	190	12.2	354	14.1	4.77	3.73
	OV	9.8	4.3	0.9	170	12.1	355	14.6	6.05	4.79
	Difference	-2.5	-0.8	-0.2	-20	-0.1	+1	+0.5	+1.28	+1.06
Hydra	AV	11.7	7.7	1.8	193	6.6	553	15.0	3.59	3.14
	OV	10.2	5.0	1.3	188	5.6	598	15.8	4.40	4.00
	Difference	-1.5	-2.7	-0.5	-5	-1.0	+45	+0.8	+0.81	+0.86

TABLE 14. Summary of quality control check samples on board the R/V Roger R. Simons during the 1985 summer surveillance season (measured), and during the intercomparison study (3-ship): mean of measured concentration, ± standard deviation (number of analyses), nominal concentration

	Low Standard			High Standard		
Parameter	Nominal	Measured	3-Ship	Nominal	Measured	3-Ship
Total phosphorus µg/L	5.6	5.3±2.1 (118)	5.0±1.1 (7)	28	27.5±2.7 (118)	25.7±2.2 (7)
Total filtered phosphorus µg/L	5.6	4.9±1.4 (116)	4.8±0.4 (7)	28	27.7±3.3 (116)	27.4±0.9 (7)
Soluble reactive phosphorus µg/L	4.2	4.7±0.7 (116)	4.9±0.5 (13)	21	23.8±2.0 (116)	24.8±0.3 (13)
Nitrate + nitrite µg/L	70	65±6 (116)	56±7 (13)	720	729±25 (116)	720±8 (12)
Ammonia µg/L	4.4	8±3 (118)	7 (1)	44	46±5 (118)	40 (1)
Soluble reactive silica mg/L	0.199	0.201±0.006 (116)	0.202±0.005 (13)	0.999	1.008±0.011 (116)	1.013±0.005 (13)
Chloride mg/L	5.6	5.4±0.2 (118)	5.2 (1)	17.3	17.4±0.3 (118)	17 (1)

TABLE 15 Concentrations of nutrients in open surface waters of the Central Basin of Lake Erie, August 26, 1985. (a)

Parameter	Average	Standard Deviation	Minimum	Maximum
Total phosphorus µg/L	8.43	2.42	4.0	12.3
Total filtered phosphorus µg/L	4.33	1.29	3.2	6.7
Soluble reactive phosphorus µg/L	1.1	0.7	0.5	2.7
Nitrate + nitrite µg/L	180	34	135	221
Ammonia µg/L	13	5	8	23
Soluble reactive silica mg/L	0.310	0.054	0.240	0.400
Chloride mg/L	14.4	0.28	13.9	14.8

[a] Eight stations were sampled and analyzed by EPA onboard the R/V Roger R. Simons as part of the summer surveillance cruise immediately prior to the three-ship intercomparison study.

TABLE 16 Pair-wise comparison of laboratory means under the original analyses and for subsets of the data

Water Quality Parameter	Study Depth (m)	Subset of data used, if some was omitted[1]	Laboratory Difference			Critical Absolute Value, D[1]
			Limnos-Simons	Limnos-Hydra	Simons-Hydra	
Total phosphorus µg/L	AV,5		2.3	2.9	0.7	3.3[2]
	OV,5		2.8*	2.3*	-0.5	1.0
	OV,24		4.1*	2.7*	-1.4*	1.1
Total filtered phosphorus µg/L	AV,5		1.8*	-0.8	-2.6*	1.2
	OV,5		1.7*	1.0*	-0.7	0.9
	OV,5	Same ship as laboratory	2.1	0.7	-1.4	
	OV,24		5.0	1.5	-3.5	
Soluble reactive phosphorus µg/L	AV,5		0.4*	-0.3*	-0.7*	0.2
	OV,5		0.2	-0.2	-0.4*	0.4
	OV,24	Limnos + Simons ships	0.3			
Nitrate + nitrite µg/L	AV,5		6*	3*	-3*	2
	OV,5	Same ship as laboratory	6	1	-5	
	OV,24		6	2	-4	
	OV,5	Limnos + Hydra only	26	1	-25	
	OV,24		27	2	-25	
Ammonia µg/L	AV,5		6.3*	12.0*	5.6*	1.3
	OV,5		2.2	8.7	6.5	
	OV,24		4.7	19.3	14.6	
Soluble reactive silica mg/L	AV,5		0.016	-0.215*	-0.199*	0.070
	OV,5		0.003	-0.231	-0.234	
	OV,24		-0.112	-0.053	0.059	
Chloride mg/L	AV,5		0.9*	0.01	-0.9*	0.2
	OV,5	2 extremes removed at each depth*	0.4*	0.1	-0.3*	0.2
	OV,24		0.4*	0.1	-0.3*	0.2
Chlorophyll-a uncorrected µg/L	AV,5		-1.52*	-0.35	1.17*	0.90
	OV,5		-1.84*	-0.19	1.65*	0.64
	OV,24		-0.54	-0.76	-0.22	
Chlorophyll-a corrected µg/L	AV,5		-1.32*	-0.73*	0.59*	0.52
	OV,5		-1.63	-0.84	0.79	
	OV,24		-0.66*	-0.56*	0.10	0.18

cont'd.../

TABLE 16 (cont'd)

* Indicates that the difference is significant at the 0.05 level, in that the magnitude of the difference is larger than D, the critical value for the studentized range test.

[1] Critical values were not calculated when either subsets of the data were chosen after the original analysis or interactions were significant. An indication of the importance of the difference can be obtained by comparison with a value of D for another case of that parameter.

[2] The lack of significance is due to the large ship sampling variance of the Hydra laboratory.

TABLE 17 **Comparison of summary statistics on epilimnion water quality parameters from the three-ship study and from Central Basin open lake stations sampled by the three agencies during August, 1985.**

Water Quality Parameter	Agency[1]	Three-Ship Study				August Monitoring or Research Programs							
		Mean		Standard Deviation[2]									
		AV	OV	AV	OV	n	Mean	Standard Deviation[3]	Median	Minimum	Maximum	Q_1	Q_3
Total phosphorus µg/L	Limnos	14.6	12.5	2.00	1.18	19	11.1	3.06	10.7	4.5	15.5	9.6	14.1
	Simons	12.3	9.8	0.47	0.79	23	9.2	2.20	8.8	4.0	15.6	8.3	9.3
	Hydra	11.7	10.2	3.30	1.33	30	12.7	2.80	12.2	8.2	20.1	11.1	13.6
Total filtered phosphorus µg/L	Limnos	6.9	6.0	0.38	0.29	21	5.2	1.86	4.9	1.4	9.7	4.8	5.5
	Simons	5.1	4.3	0.30	0.40	23	5.2	3.10	4.4	3.2	17.9	3.6	4.9
	Hydra	7.7	5.0	1.32	1.45	30	7.4	1.72	7.3	5.1	12.0	5.8	8.4
Soluble reactive phosphorus µg/L	Limnos	1.5	1.1	0.03	0.15	21	0.7	0.40	0.5	0.3	1.8	0.4	0.9
	Simons	1.1	0.9	0.20	0.75	22	1.3	1.30	0.8	0.3	6.5	0.5	1.1
	Hydra	1.8	1.3	0.20	0.27	30	2.3	0.58	2.1	1.5	4.3	2.0	2.5
Nitrate + nitrite µg/L	Limnos	196	190	0[4]	0.6	21	213	17.3	212	193	248	195	228
	Simons	190	170	0[5]	2.5	23	180	32.0	192	135	221	155	206
	Hydra	193	188	2.1	3.0	30	179	24.1	182	137	215	165	200
Ammonia µg/L	Limnos	18.6	14.3	1.45	0.71	8	13.9	5.00	14.5	7.0	19.0	9.0	19.0
	Simons	12.2	12.1	0.33	0.78	23	16.9	5.00	15.0	8.0	32.0	13.0	16.0
	Hydra	6.6	5.6	0.56	1.23	30	8.7	4.48	7.5	3.2	26.8	5.5	10.2

cont'd.../

TABLE 17 (cont'd)

Water Quality Parameter	Agency[1]	Three-Ship Study: Mean AV	Three-Ship Study: Mean OV	Three-Ship Study: Standard Deviation[2] AV	Three-Ship Study: Standard Deviation[2] OV	August Monitoring or Research Programs: n	Mean	Standard Deviation[3]	Median	Minimum	Maximum	Q_1	Q_3
Soluble reactive silica mg/L	Limnos	0.338	0.367	0.0667	0.0394	4	0.4[1]	-	0.40	0.39	0.43	-	-
	Simons	0.354	0.354	0[5]	0.0071	23	0.372	0.154	0.336	0.240	0.965	0.310	0.385
	Hydra	0.553	0.598	0.0516	0.0398	30	0.588	0.123	0.578	0.380	0.890	0.500	0.625
Chloride mg/L	Limnos	15.0	15.0	0.12	0.33	nm	nm	nm	nm	nm	nm	nm	nm
	Simons	14.1	14.6	0[5]	0.13	23	14.6	0.50	14.6	13.7	15.4	14.4	15.0
	Hydra	15.0	15.8	0.26	0.16[6]	30	15.3	0.30	15.2	14.8	16.1	15.0	15.5
Chlorophyll-a corrected µg/L	Limnos	2.41	3.16	0.41	0.20	21	2.19	0.93	2.30	0.70	3.70	1.35	2.88
	Simons	3.73	4.79	0.45	0.92	23	3.30	0.90	3.20	1.70	5.70	2.80	3.70
	Hydra	3.14	4.00	0.14	0.24	30	2.70	0.77	2.68	1.29	4.40	2.31	3.14

[1] The summary statistics for the three ships study are based on samples analyzed by the indicated laboratory. The statistics given in the eight right-most columns were obtained as follows: (1) Limnos - quantities were calculated from NWRI data, collected during cruises August 12 to 16 and August 26 to 29 from eight stations, including data from repeated sampling of the same station at different times. (2) Simons - summary statistics for surface water samples from eight open lake stations collected August 26 as part of the summer surveillance cruise immediately prior to the three-ship study (Rockwell et al., 1989). (3) Hydra - summary statistics from ten stations during the August 28 to 29 monitoring cruise conducted by CLEAR (Fay and Rathke, 1986).

[2] Standard deviation due to differences between ship samples.

[3] Hydra standard deviation was calculated from n and standard error reported by Fay and Rathke (1986).

[4] All ship means were the same.

[5] All nine results were the same.

[6] Extreme values deleted. Standard deviation is 3.94 with extreme.

nm Not measured.

- Not calculated becuase n is too small.

FIGURE CAPTIONS

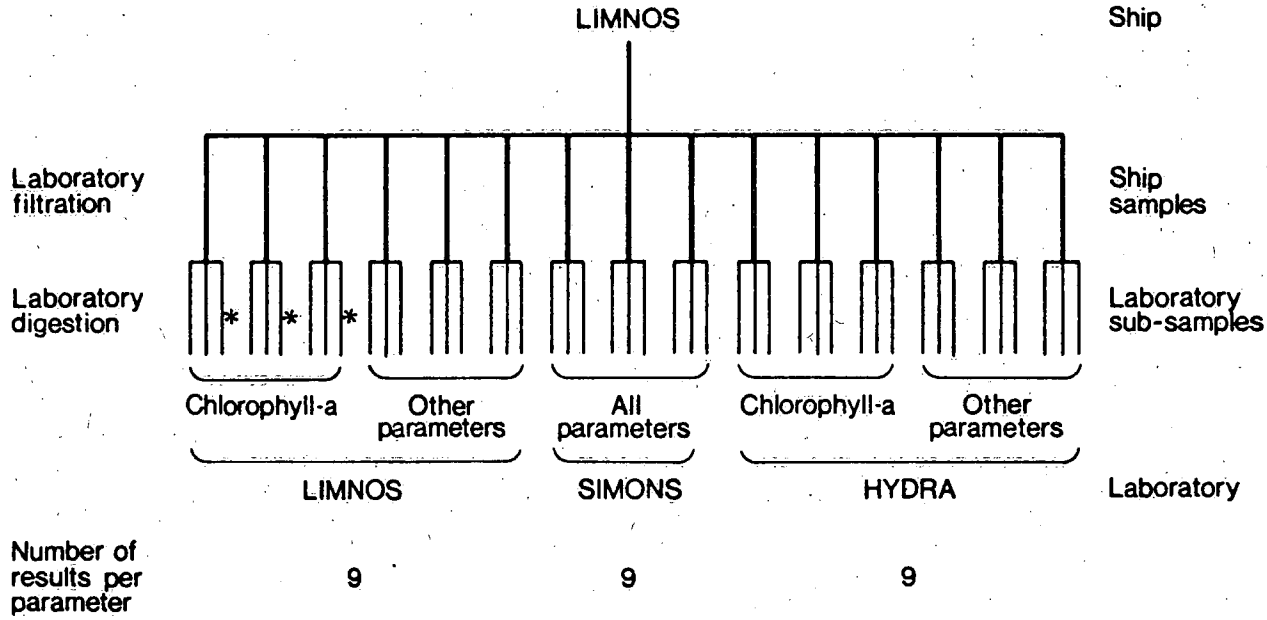
Figure 1 Design of the analytical variability study. In the overall variability study this was repeated for each ship with the exception that two laboratory subsamples were taken from each ship sample yielding six results per parameter instead of nine.

Figure 2 Concentrations of the nine water quality parameters obtained from the analytical variability study with the three laboratory subsamples plotted at the same point on the abscissa and ship samples (1,2,3) and laboratories (L,S,H) identified. The numbers on the plot indicate identical values for laboratory subsamples or differences smaller than the resolution of the plotter.

Figure 3 Concentrations of the nine water quality parameters obtained from the overall variability study with the two laboratory subsamples plotted at the same point on the abscissa. Ship samples (1,2,3), laboratory (L,S,H), ship (L,S,H), and sampling depth are identified.

Figure 4 The complete set of means for the AV and OV comparison for the nine water quality parameters.

The laboratory means for samples from one ship, taken at one depth are joined by lines (_____ 5 m and ----- 24 m). Ship means over all three laboratories for samples from one depth are shown as horizontal lines (_____ 5 m and ----- 24 m). The laboratory means over all ship samples from one depth are shown as letters (L,S,H) to the right of each plot as indicated by LABII, and the laboratory means for the AV comparison are shown as letters (L,S,H) as indicated by LAB I. Also on the right side of each plot are vertical lines which give the smallest difference between OV means significant at the 0.05 level, where D_1 is for the difference between laboratory or ship means at one depth and D_2 is for the difference between laboratory means for samples collected by one ship.



*filtration here for Limnos chlorophyll-a only

FIGURE 1

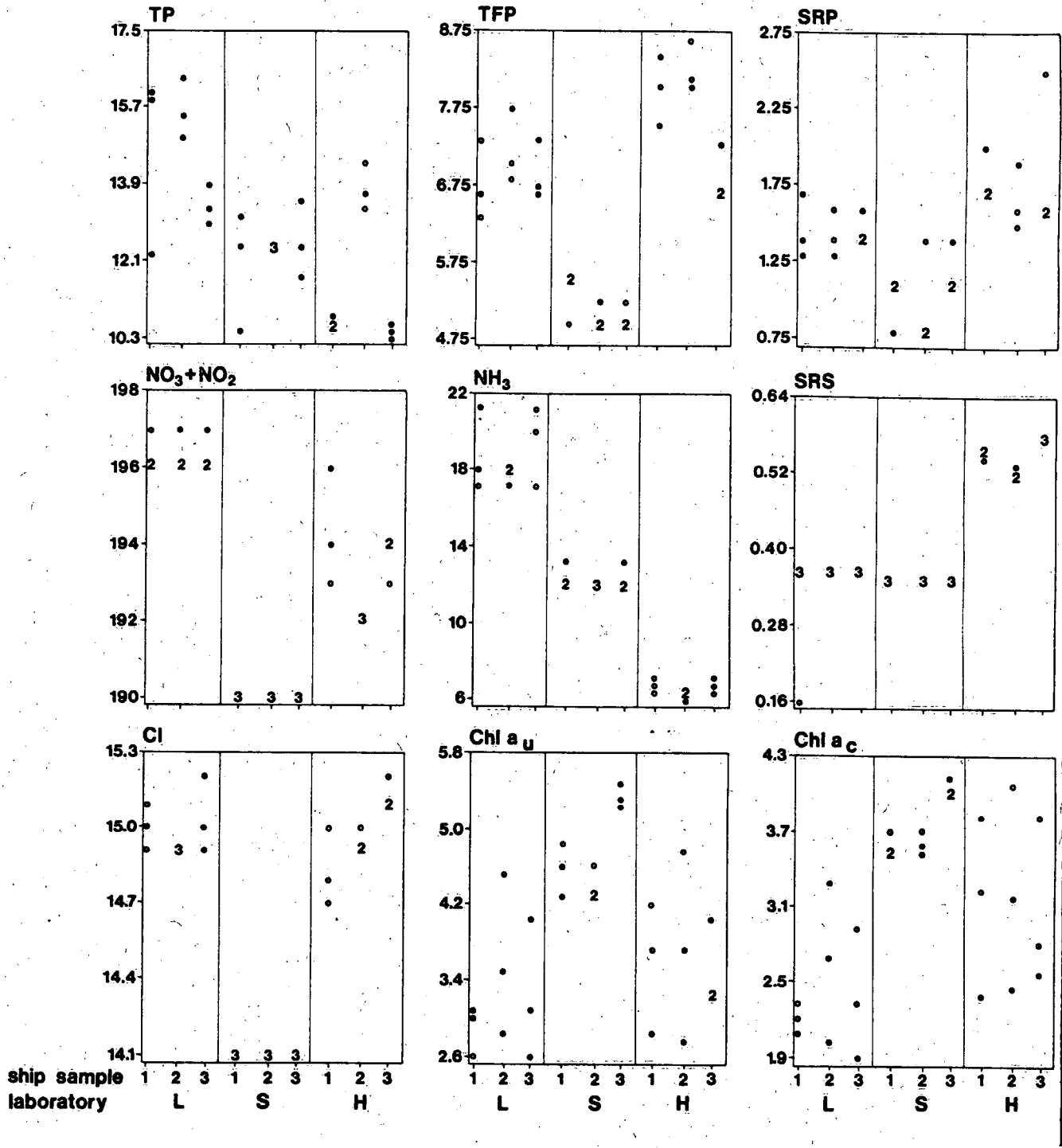

TP
17.5
15.7
13.9
12.1
10.3
TFP
8.75
7.75
6.75
5.75
4.75
SRP
2.75
2.25
1.75
1.25
0.75
NO3+NO2
198
196
194
192
190
NH3
22
18
14
10
6
SRS
0.64
0.52
0.40
0.28
0.16
Cl
15.3
15.0
14.7
14.4
14.1
Chl a u
5.8
5.0
4.2
3.4
2.6
Chl a c
4.3
3.7
3.1
2.5
1.9
ship sample 1 2 3 1 2 3 1 2 3
laboratory L S H

FIGURE 2

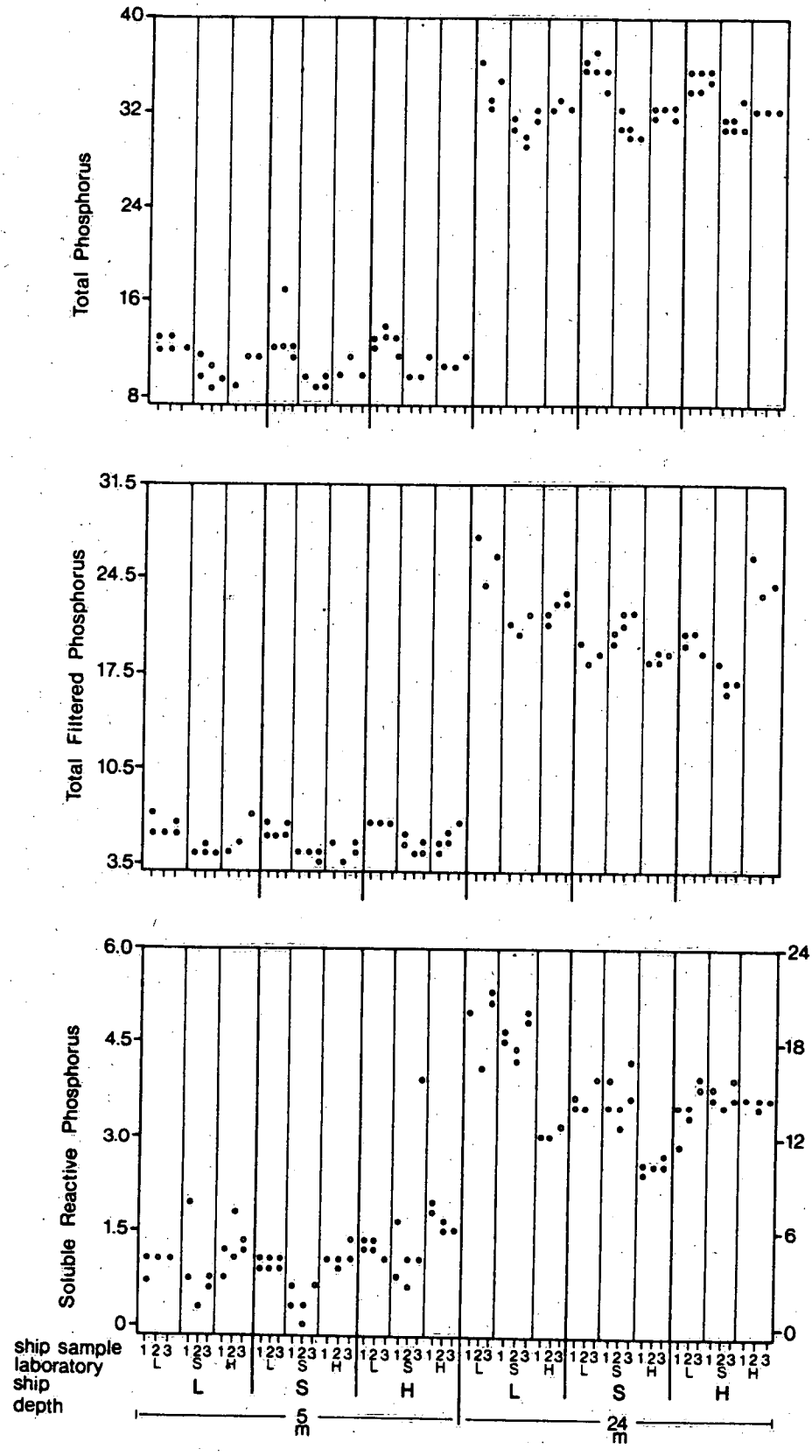

Total Phosphorus
40
32
24
16
8
Total Filtered Phosphorus
31.5
24.5
17.5
10.5
3.5
Soluble Reactive Phosphorus
6.0
4.5
3.0
1.5
0
24
18
12
6
0
ship sample
laboratory
ship
depth
1 2 3 L
1 2 3 S
1 2 3 H
L
S
H
5 m
24 m

FIGURE 3

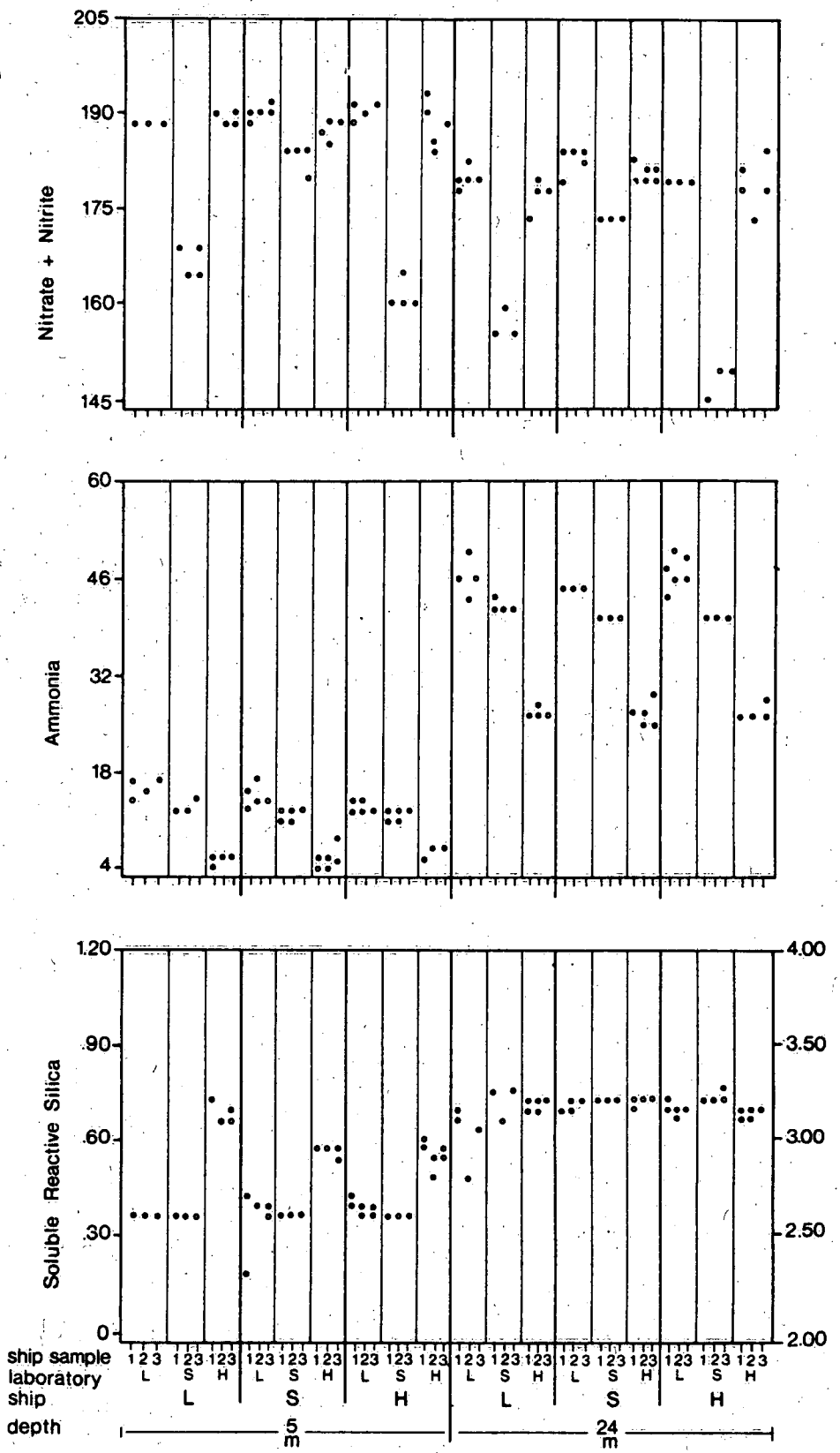


FIGURE 3 (continued)

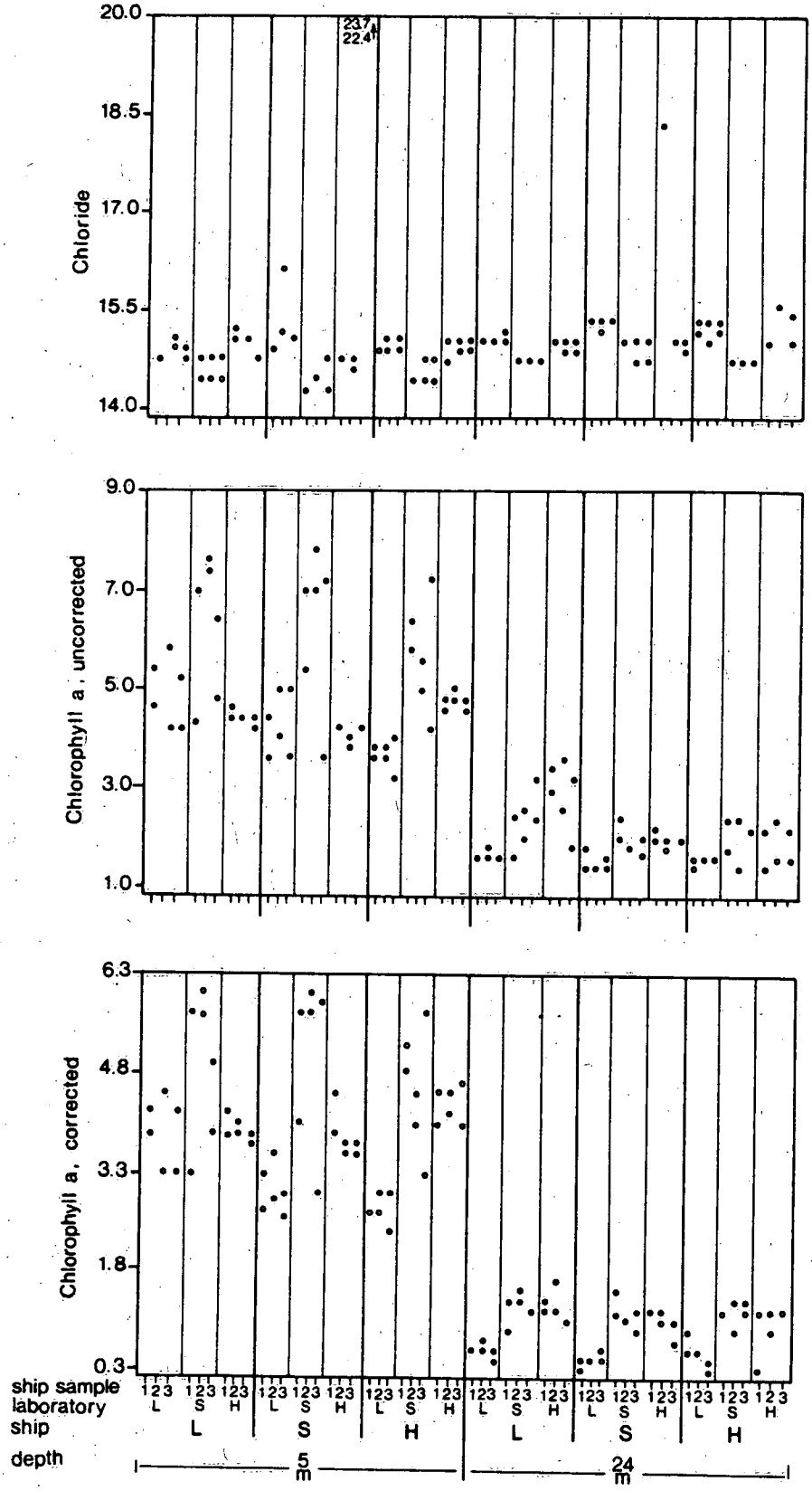


FIGURE 3 (continued)

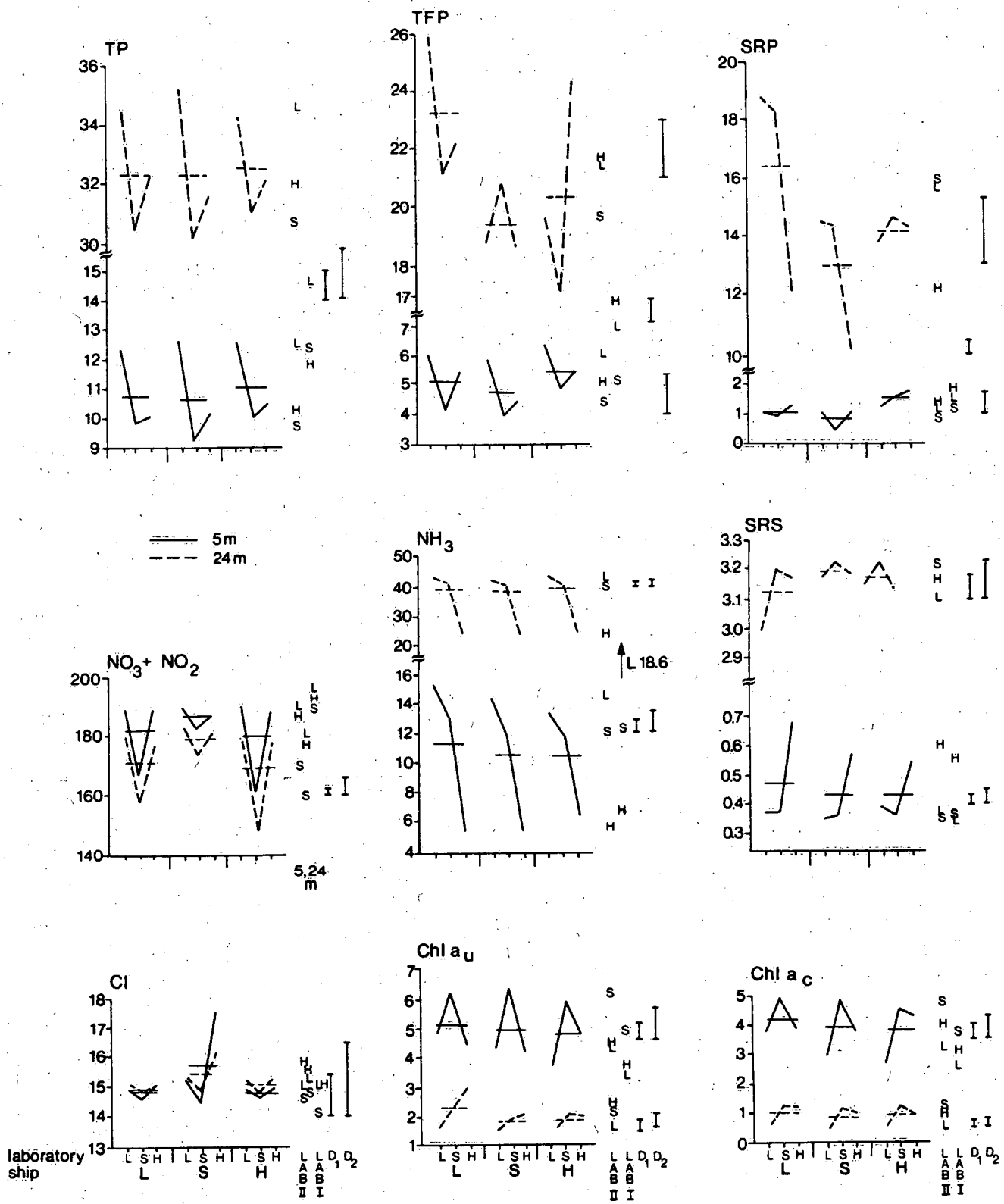
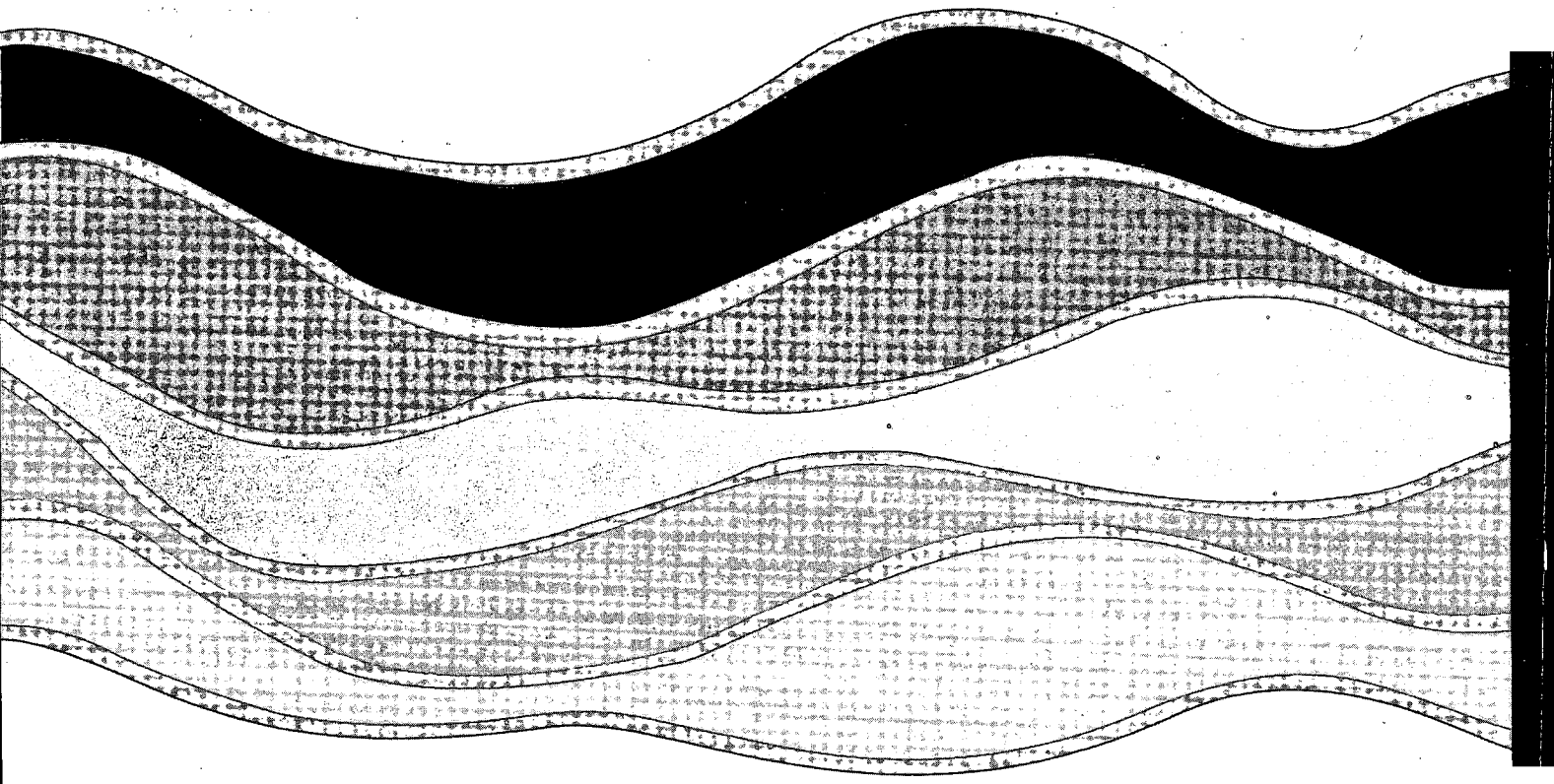

TP
TFP
SRP
5m
24m
NO_3+ NO_2
NH_3
SRS
Cl
Chl a_u
Chl a_c
laboratory
ship
L
S
H
5,24 m

FIGURE 4

Environment Canada Library, Burlington
3 9055 1017 0405 3



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