

## DOC subgroup report

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### INTRODUCTION

The organic pool in the oceans is measured in terratons ( $10^{18}$  g) of carbon. It is a heterogeneous assemblage of an unknown mixture of components with a continuum of sizes ranging from simple molecules to complex organisms. Although the boundary between the dissolved and particulate states is hazy in natural waters, dissolved organic carbon (DOC) dominates over the particulate state (Sharp, 1973). A major proportion of the DOC in seawater consists of material of relatively resistant nature — the mean residence time of the DOC being measured in several oceanic circulation times (Williams and Druffel, 1987).

It is possible that the DOC pool, in common with the dissolved inorganic carbon (DIC) pool, will be a temporary residence for carbon produced as a consequence of anthropogenic activities. Along with other motivations, this has given rise to a need to establish more accurately the size of this carbon reservoir. The growing awareness of the major role played by the microheterotrophs in the marine food web has also focused attention on the flux rate of material through the DOC pool (Williams, 1981; Azam et al., 1983; Kirchman et al., 1991).

Various oxidation procedures have been used to obtain DOC measurements for natural waters from which estimates of pool size and flux have been derived (Williams, 1975; Cauwet, 1984). Our certainties over what we had believed to be the state and flux of the DOC pool were pro-

foundly upset by reports that high-temperature catalytic oxidation (HTCO) procedures gave markedly higher values than the earlier wet-chemical oxidation procedures (Sugimura and Suzuki, 1988). Furthermore, there were indications that this previously overlooked material was biologically labile. We could interpret these reports as evidence that we had seriously underestimated the size and the flux of the DOC pool or we could treat them as a false alarm. These uncertainties prompted a hard look at the current status of certain aspects of the DOC analysis of seawater. An array of questions were found in need of answering. We defined a number of pressing questions:

- (1) In terms of analytical precision what are our requirements of DOC analysis?
- (2) How can we estimate the accuracy of DOC analyses?
- (3) What are the appropriate procedures for:  
(a) obtaining analytical blanks; (b) the preparation of standards; (c) the production of reference materials?
- (4) What procedures should be adopted for quality assurance?
- (5) Is there evidence that a major component of the DOC pool was missed in past analyses?
- (6) If so, can we reconcile the earlier data with the new analyses?

We consolidated these into three questions which we felt we must address:

- (1) What are the requirements for the accuracy and precision of DOC analysis?
- (2) What are appropriate procedures for obtaining: (a) analytical blanks; (b) standards;

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(c) reference DOC materials, and what protocols should be set up for the quality assurance?

(3) Is there compelling evidence that high-temperature combustion methods give DOC concentrations which are greater than those determined by previously employed wet-chemical and photochemical oxidation methods? If so, can we adjust previously collected DOC data to any advantage?

QUESTION 1: WHAT ARE THE REQUIREMENTS FOR THE ACCURACY AND PRECISION OF DOC ANALYSIS?

#### *Accuracy*

The requirement for accuracy is absolute. If we are to determine the size of the oceanic DOC pool, nothing less is acceptable. If we need to establish the DOC pools to 1% then our accuracy must be 99% or better. It has to be recognized, however, that the 'real' accuracy of the DOC technique is unknown (see below) and philosophically can never be established with absolute certainty. For DOC analysis, the definition of absolute accuracy is that all types of dissolved carbon are oxidized and measured. A fundamental problem with determining accuracy is that we have no expectation in the foreseeable future of a comprehensive description of the composition of the DOC pool. Nor do we know which fraction of the DOC pool is difficult to oxidize with the present methods and to what extent its composition (and the 'refractivity') varies in time and space.

None of the present methods for DOC analysis (involving either HTCO or WCO) fulfil the criteria for setting the accuracy, for a method cannot assess itself. Thus referee methods are needed, based, for example, on sealed tube combustion (STC) (Alperin and Martens, 1993; Fry et al., 1993) and elemental analysis of isolated material using CHN analyzers. These methods are variants of dry combustion and it could therefore be argued that one of the potential problems with DOC analysis in seawater, the matrix effect, is by-passed. It is known that very 'refractory' sub-

stances (e.g. graphite, diamonds) can be measured with STC, and this is taken as a justification for its use as a referee method. The STC analysis allows the stable isotope ratio of the combusted material to be determined, which provides a further check on the completeness of oxidation.

#### *Precision*

In the case of precision the matter is more subtle, the needs depending upon the goals. We can assess this need for several cases, for example, that of geochemical budgeting and modeling. The oceanic inorganic and organic pools of carbon are among the largest on the planet and as such may be temporary repositories for the carbon arising from the combustion of fossil fuels. At some stage we will most likely need to assess the DOC pool as a sink for anthropogenic CO<sub>2</sub>, and this raises the question of the analytical requirement needed to achieve this. We may arrive at an estimate for the required precision in two ways. Present estimates of the DOC pool are  $1-2 \times 10^{18}$  g C (Williams and Druffel, 1987). The anthropogenic fluxes are estimated at  $6 \times 10^{15}$  g C year<sup>-1</sup>, of which  $1-2$  Gt C year<sup>-1</sup> enters the ocean (Bolin, 1986). If this material were to accumulate in the DOC pool it would give rise to an annual increase of the order of 0.1%. If we need to look for changes in the DOC pool over reasonable periods of time (i.e. decades) then we would need a precision of the order of 1% (i.e. around  $1 \mu\text{mol l}^{-1}$ ).

Another approach is to argue that, if we need to assess the size of the DOC pool with the same absolute precision as the DIC pool, then we need DOC methods with the same analytical precision as the DIC methods, i.e. of the order of  $1 \mu\text{mol l}^{-1}$  (Robinson and Williams, 1991). However, if the goal is only to determine the actual pool size, the precision needed is lower.

To determine the precision needs for measuring biological processes, we can consider that fluxes of carbon (as a result of primary production and heterotrophic consumption) range from  $1$  to  $20 \mu\text{mol l}^{-1} \text{ day}^{-1}$ . To determine such

changes against a background of  $100 \mu\text{mol l}^{-1}$ , we require a minimum precision of  $1 \mu\text{mol l}^{-1}$ . In the particular cases of time series and flux studies, the stability of the analysis is often more critical than accuracy, as changes are characteristically more important than the absolute value.

It is a common procedure to normalize or reference analyses of individual components of the DOC pool against total DOC. In such a case one might argue that the precision of the total DOC measurement needs to be compatible with that of the analysis of the component, which in most cases would be no better than 10%; thus 5% precision in the DOC analysis is probably adequate.

The analytical precision has been reported for the various methods. For the wet-chemical methods, the precision is about  $2\text{--}5 \mu\text{mol l}^{-1}$ . The analytical precision of HTCO instruments, based on replicate injections of the same sample, is reported to be 3–5%, i.e.  $5\text{--}8 \mu\text{mol l}^{-1}$  (Peltzer and Brewer, 1993), falling to  $8\text{--}16 \mu\text{mol l}^{-1}$  at sea. In the intercalibration study, the analytical precision (using ideal replicate samples) was  $3\text{--}5 \mu\text{mol l}^{-1}$ . The instrument stability (variation during the day and from day to day) is normally not reported. In the future with the growth of major international programs such as the Joint Global Ocean Flux Study (JGOFS) and the World Ocean Circulation Experiment (WOCE), there will be considerable pressure to sustain a high degree of precision and accuracy over extended periods and to have a consistent minimum performance from various participating countries and laboratories. The only answer to this problem would appear to be the preparation by the oceanographic community of a reference DOC standard, following the route taken for another heterogeneous seawater property: salinity.

### *Recommendations*

(1) Targets for analytical precision and accuracy need to be agreed upon.

(2) The accuracy of DOC measurements by currently used techniques, such as persulfate, UV and HTCO methods, should be directly addressed using referee analytical techniques, such as sealed tube combustions. This is seen as a high priority.

QUESTION 2: WHAT ARE APPROPRIATE PROCEDURES FOR OBTAINING ANALYTICAL BLANKS, USING CALIBRATION AND REFERENCE STANDARDS AND WHAT PROTOCOLS SHOULD BE SET UP FOR QUALITY ASSURANCE?

### *Quality assurance*

This has become a critical issue in the development of methods for the measurement of DOC content of seawater. In the past, the major concern has been the consistency of the analyses performed by individual analysts; data produced have largely been used by the individuals or groups for the solution of problems put forward by them. As a consequence, the scientific community concerned with the measurement of DOC has been effectively operating as individual analysts, each developing individual methodologies. With notable exceptions (Gershey et al., 1979), comparison between analysts was of secondary consideration, and was usually done with the knowledge that differences between analysts were common for even the most routine analyses using most standard methods. This philosophy cannot be adopted in programs examining problems on a global scale, which will involve many analysts, from a number of countries, over time spans of many years. Data used in such programs must be compatible and for this the methods have to be described in sufficient detail; the standards of data- and record-taking must be such that the user of the data in the future must be able to reconstruct what was actually done. Where the data may be used for intercomparisons over periods of decades or longer, as in the tracking of global warming, the requirements become even more stringent.

In the field of commercial analysis, it is now common practice to expect or require that an

accreditation procedure be adopted. This may entail the independent checking of the calibration and certification of instruments and the attainment of certain criteria concerning the level of the blank, the precision of the analysis and the signal from the reference standard before analysis of unknowns is to proceed. We shall need to adopt this rigor in oceanographic work. Whereas we did not feel that the time available to us at the Workshop was sufficient to undertake the development of such a protocol, we saw this to be a matter of some urgency. We have in Appendix 1 given our preliminary thoughts on the matter.

The JGOFS program has brought home to us the importance of attaining consistency in analytical technique. Investigators making high-precision measurements of the carbonate system are developing recommended protocols for the collection and reporting of data and the preparation of reference material, as have the community of trace metals analysts. In this section we will consider procedures and offer recommendations for the analysis of DOC in natural waters that we would expect to increase the usefulness of the data.

#### *Analytical blanks*

These must be carefully assessed in all future studies. During our evaluation of the workshop intercomparison data and previously published data on DOC in seawater, it has become apparent that the methods used to assess analytical blanks vary widely and are often incompletely reported in the literature. The potential significance of blank corrections is dependent on the analytical technique used but it can be a substantial fraction of the total instrument response in waters that contain low concentrations of DOC. It was observed in our evaluation of the Workshop intercomparison data that the simple subtraction of a constant assumed value (that was similar in magnitude to those analytical blanks measured) could bring most of the reported values to within 15% of the mean value. The magnitude of this correction (approximately

$30 \mu\text{mol C l}^{-1}$ ) was similar to that often measured as an analytical blank in the HTCO method, and led to our development of this discussion of methods and protocol for determination of an analytical blank.

There are three basic components that give rise to the analytical blanks measured in most DOC analyzers: (1) the reagents used in the analysis, the 'reagent blank'; (2) the water to which the reagents are added (we shall refer to this as the 'water blank'); (3) the components of the system itself (the so-called 'system blank'). The last, in reality, comprises a mixture of signals contributing to the blank: sample contamination, steam-induced pressure effects on the detector, matrix effects, release of  $\text{CO}_2$  from components of the system, etc. Methods for the establishment of blank values for the standard wet-chemical and UV oxidation techniques have been evolved over the past two decades, and the ensuing discussion is directed primarily at the establishment of blank values for the HTCO method. Blank values are variable, and may be dependent upon the type of catalyst and support used in the instrument, and upon the volume of sample analyzed. Accordingly, it is important that individual investigators report the exact protocol used for blank evaluations, and that system and water blanks be included in the evaluation of the overall analytical blank.

Of the various components comprising the analytical blank of HTCO systems, the 'water' and 'reagent acid' blanks are most easily controlled, and can be minor components relative to the system blank. High-purity (carbon-free) phosphoric acid is commercially available and does not contribute significantly to the analytical blank. High-purity water containing low concentrations of DOC ( $4\text{--}5 \mu\text{mol C l}^{-1}$ ) is also commercially available. Many investigators produce low-DOC water in their laboratories, and a variety of methods has been used successfully, including: distillation from persulfate, UV irradiation, HT combustion, reverse osmosis, and other commercially available water treatment units. It should be noted that the microelec-

tronics industry has made considerable progress in producing low organic content water on an industrial scale, and it may be that the oceanographic community could profit from pursuing this potential resource for DOC analyses. It is important to establish by independent analytical methods the level of organic carbon contamination in this blank water.

The 'system' blank is a much more difficult property to establish, because it is a complex of spurious signals, both instrumental and operational. If contamination during handling can be separated out and if there is no matrix effect, then once the reagent and water blanks have been established, calibration standards made using high-purity water and acid can be used to establish the system blank. In some analyzers high-purity water is available from the condensates from the combustion column or it can be obtained from an oxihydrogen flame. The 'system' blank may be dependent upon the volume of sample (i.e. steam pressure) but given pure water this can be determined. If, however, there is a seawater salts matrix effect then the determination of the 'system' blank for an HTOCO instrument is a nontrivial problem. Although in principle this can be investigated using low-DOC artificial seawater, experience in making up these solutions is not encouraging; in the case of the persulfate and UV methods, UV-irradiated seawater may be used. This could not be recommended for the HTOCO methods, as residual DOC in the irradiated water would give an erroneously high blank for the HTOCO analysis and result in an underestimate of the DOC content of the sample.

#### *Calibration and check standards*

These are required to obtain reproducible and comparable DOC data. Calibration standards provide a procedure for the calibration of the signal from the detector. Typically, organic compounds that are easily oxidized, such as potassium phthalate, oxalic acid, or caffeine, are used. The detector may also be calibrated with a standard injection of CO<sub>2</sub> gas as in the analysis of DIC

(Johnson et al., 1987). Standard solutions are usually prepared using the same high-purity water with which the water blank is determined. The standard solution can be stored in a refrigerator, but the period over which a working standard remains constant, and therefore usable, needs to be checked, as it will vary with choice of compound and conditions of use.

The check standard is used to ensure that the instrument is giving a proper response to a known amount of DOC in a natural seawater matrix. At the present time, the only appropriate check standard that we can recommend is deep-sea water. Even in this case we must caution that if it is confirmed that a DOC fraction is missed by the earlier method and if that fraction is labile and more abundant in the upper water column (Sugimura and Suzuki, 1988), then we may need to revise this recommendation. A procedure for preparing the check standard might take the following form. A deep-sea water sample is collected using a clean sampler, and transferred into a 'clean' bottle affording a minimum contribution of organic compounds. Glass, polycarbonate, or polysulfonate bottles are recommended. The seawater should be filtered through a pre-rinsed 0.2  $\mu\text{m}$  Nuclepore filter using a closed system which excludes ambient air. The standard should be made up into 50–100 cm<sup>3</sup> aliquots in glass ampules or perhaps polycarbonate containers and stored under refrigeration. The same check standard seawater should be used throughout a cruise or a laboratory experiment (about 2–4 weeks). At this time, we do not know how long a check standard can be stored without significant change in DOC; to some extent, this is a function of the practices of the particular laboratory and the source of the sample. Each laboratory will need to determine the working life of its check standards. The frequency of use of check standards depends upon the number of water samples normally run by the laboratory. Every 100 injections might, for example, be a working norm. If samples are run only infrequently, the check standards need to be used more often, and at least once with every sample group.

### *Reference standard materials*

These must be developed to assess accuracy of measurements. During the next decade, a large number of DOC measurements will be made by the various laboratories from countries participating in the JGOFS program. The intention is that data sets are to be shared among the participating groups. Accordingly, it is vital to have criteria to evaluate the quality of the various data sets. To achieve this, two things are required. First, an agreed protocol needs to be devised and adopted; second, reference standards have to be available.

A reference material is required to compare the performance of the different laboratories, to allow the laboratories to keep track of their own performance, and for accreditation of analyses and instrumentation. In other contexts, such as the analysis of polychlorinated biphenyls (PCBs), this reference material is often a specific organic compound. At this point in time, we cannot specify any single organic compound as being typically marine, and thus useful as a reference material. There was a strong consensus that this reference material would need to be seawater. It was felt that no single compound or mixture could serve as an adequate proxy for seawater.

Along with the problem of preparing reference (as well as check) standards goes the issue of preservation: if we are not able to preserve the standards, then they are useless. We know little about preserving seawater for organic analysis, and this problem is shared with our colleagues concerned with inorganic carbon analysis. A number of options are available to us: mercuric chloride, acidification, and heat and radiation sterilization.

### *Recommendations*

(1) There is an immediate need for reference DOC material for use by the oceanographic community.

(2) Associated with this is a pressing need to

determine satisfactory procedures to preserve seawater for organic analysis.

(3) A protocol for the measurement and reporting of DOC should be developed for use by the oceanographic community.

QUESTION 3: IS THERE COMPELLING EVIDENCE THAT HIGH-TEMPERATURE COMBUSTION METHODS GIVE DOC CONCENTRATIONS GREATER THAN THOSE DETERMINED BY THE WET-CHEMICAL AND PHOTOCHEMICAL OXIDATION METHODS? IF SO, CAN WE ADJUST PREVIOUSLY COLLECTED DOC DATA TO ANY ADVANTAGE?

The intercomparison of DOC measurements which was conducted as part of the DOC/DON Workshop gave no clear answer to this question. It was postulated that an assumed blank correction could explain a major part of the variability in reported DOC values. Accordingly, in attempting to answer the above question, we examined other comparisons of the HTOCO method with either persulfate or UV oxidations to determine whether or not a pattern existed.

DOC measurements performed on common samples using different methods provide a means of comparison. The limited data sets which exist for DOC measurements conducted by both the HTOCO and persulfate or UV methods are assembled in Table 1. We start by noting that in all cases the HTOCO method gave estimates of DOC concentrations equal to or higher than those obtained by the wet-chemical or photochemical methods (never vice versa).

In trying to undertake an analysis of the data sets, we considered the existence of two different patterns of analytical discrepancy. If the purported previously overlooked material is of long residence time, then it should tend towards a uniform concentration with depth and thus a constant offset should be observed. We have termed this a Type 1 offset. It should be noted that an underestimate of the HTOCO blank would give the same pattern. An alternative situation is that the material is ephemeral and as such will only be present in significant amounts in the surface ocean where biologically mediated carbon

TABLE 1

Paired analyses of DOC determined by HTCO and either wet-chemical or photochemical oxidation methods

Reference	Methods compared	Sample location	Discrepancy (fM)	Offset type
1. Bauer et al. (1990)	HTCO vs. UV	Sargasso Sea	60–70	1
2. Sharp et al. (1993)	HTCO vs. Pers. (MRI instrument) (Shimadzu instrument)	Coastal Atlantic	140–180 50	1 1
3. Druffel et al. (1989)	HTCO vs. UV	N. Pacific	50–100	2
4. Cauwet et al. (1990)	HTCO vs. UV & Pers.	Gulf of Lions	0–40	2
5. Martin and Fitzwater (1992)	HTCO vs. UV	N. Pacific	40–130	2
6. Suzuki and Tanoue (1991)	HTCO vs. Pers.	E. China Sea	20–180	2
7. Cauwet et al. (1990)	HTCO vs. UV	Mediterranean	20–40	2
8. Goulden and Brooksbank (1975)	HTCO vs. UV & Pers.	Greek Lakes (freshwater)	0	NA
9. Benner and Hedges (1993)	HTCO vs. Pers.	Amazon River (freshwater)	0	NA
10. Sharp et al. (1993)	HTCO vs. Pers.	Delaware River Estuary	200 0–30	1 2
11. Miller et al. (1993)	HTCO vs. UV & Pers.	Tamar River Estuary	0–110	NA
12. Chen and Wangersky (1993)	HTCO vs. UV	Diatom culture	0–40	2
13. Alperin and Martens (1993)	HTCO vs. Pers.	Sediment porewaters	< 10%	NA
14. Tugrul (1993)	HTCO vs. Pers.	Black Sea	10–60	2

NA–Not applicable.

transformations are significant in relation to the standing level of DOC and thus a significant concentration of shortlived material is sustained. This is termed a Type 2 offset. There is, of course, no reason to expect that situations intermediate to these two will not occur. However, the separation of these two general patterns was thought to be a useful initial formalism. An issue that arose when producing this compilation of data was whether we were able to assess the characteristic blank of the method to scale it against the observed discrepancies. In all but few cases the blank is not reported in the original publication.

Although we were able to obtain some values by ‘word of mouth’ or hearsay, in view of all the current uncertainties surrounding DOC methodologies it was decided not to report informal unconfirmed values.

For the Type 1 pattern, we need to examine critically the simple explanation that a correct blank value has not been subtracted. It can be seen, for example, that part of the difference in concentrations in some cases (e.g. No. 1) could potentially be accounted for by blanks. In others (e.g. No. 2) it is not easy, with the information available to us at the time of working, to argue

for a blank large enough to account for up to a 180  $\mu\text{M}$  offset.

For Type 2 offsets, which comprise the majority of the cases, it is not possible to account for the differences with a simple blank correction. In numerous cases involving oceanic profiles, the DOC profiles determined by both methods were discrepant at the surface, converged at mid-depth, and on occasions diverged again at depth. If we attempt to reconcile the measurements by invoking a simple blank correction, we need also, for logical consistency, to accept that in the previous zones of 'agreement' the HTCO method is giving 'blank corrected' values less than the wet-chemical or photochemical methods. Although this is not impossible, it presents problems in the explanation.

Less information is available for assessment of discrepancies in freshwater and estuarine systems (Nos. 8–11). In No. 8, no difference was observed in lake water samples between the HTCO and persulfate methods of oxidation, and in No. 9 no differences were observed between HTCO and persulfate or UV methods of oxidation and in the extent of oxidation of the high molecular weight fraction of DOC from riverine samples. In samples from estuarine environments (Nos. 10 and 11), up to 200  $\mu\text{M}$  differences in DOC concentration have been observed between the HTCO and the wet combustion methods. The lack of clear correlation between salinity and the extent of discrepancy between the wet and HTCO methods appear to argue less for factors such as chloride inhibition of DOC oxidation and more for qualitative differences in the nature of the DOC in different environments or an undetermined matrix effect on the blank. Unfortunately, possible differences in the exact form of the persulfate method used add yet another variable and preclude a rigorous intercomparison of these offsets in both marine and freshwater environments. Interesting differences have recently been noted when both HTCO and wet-chemical methods were applied to plankton cultures (No. 12) and sediment porewaters (No. 13). In cultures, the difference in DOC concentration as determined by the two methods increased with

increasing age of the culture, whereas in sediment porewaters the discrepancy was always less than 10%. Findings such as these from other environments may lead to important insights into the potential reasons for the frequently observed differences between these two methods of oxidation.

Differences of 5–10% between DOC values determined by HTCO and wet-chemical or photochemical methods may, in part, result from systematic problems in correctly applying appropriate blank corrections, subtle differences in signal detection and processing, and other operator-related factors. It is not these low-order discrepancies that are of concern at this stage in the discussion. Discrepancies as high as 100–200%, however, are a matter for concern. These large differences can only be the result of one or more of the following: (1) some procedural inadequacy in previously used methodologies; (2) the inability of previously employed methods to oxidize all forms of DOC; (3) erroneously high results from the HTCO method, because of an as yet unrecognized or underassessed blank or other undetermined instrumental artifacts: pressure effects, desorption of  $\text{CO}_2$  from the catalyst, etc.

Whereas (1) may be evaluated by conducting appropriate experimental examinations of the methodological problems, (2) and (3) are not so readily resolved and are directly concerned in the various issues of measurement accuracy. All too often, one ends up resorting to comparing the results of methods; the difficulties associated with this were discussed in some detail by Gershey et al. (1979).

Recovery of residual DOC in previously oxidized seawater samples has been observed. There are, to our knowledge, three instances in which seawater samples which were initially oxidized by either wet-chemical or photochemical methods were subsequently re-oxidized by HTCO methods: those reported by Sugimura and Suzuki (1988), Druffel et al. (1989) and Suzuki and Tanoue (1991). In all cases, an additional amount of carbon was extracted which was equal to the difference in the amount of carbon obtained by the HTCO and photochemical methods. The

possibility of such findings being due to random error alone are remote. Further determinations of residual DOC remaining after wet-chemical or photochemical oxidation should be made to help establish whether DOC exists which is not revealed by these methods and if this DOC is in any way 'geochemically distinct'.

During the NSF/Seattle intercomparison, the precision of replicate analyses for an individual analyst was high, suggesting that 'random' contamination/error in analytical procedures is not a significant problem. Accepting therefore that the errors are systematic and accordingly probably persistent, the source of the error(s) was examined. Wide variability of DOC concentration between analysts could be attributed to two sources: (1) genuine differences in the oxidation efficiencies of individual analyzers, and/or (2) inadequate correction of results for the overall or 'procedural' blank — defined as the signal attributable to the combination of sample handling, through injection and oxidation, to detection.

Grouping of intercomparison data according to analyzer type leads to the conclusion that this was certainly not the sole, perhaps not even the major cause of the variation. Background and scaling adjustment can be used to produce a considerable reduction in the variation of results between analysts, suggesting 'systematic' differences between data sets, as opposed to random combustion inefficiency or contamination.

This particular intercomparison did not provide systematic and compelling evidence that, for the specific samples analyzed, significant differences in DOC concentrations existed across the entire range of analyzers used. The great majority of the results fell on a continuous line once the data were corrected for assumed background and scaling adjustments.

### *Recommendations*

(1) Further DOC measurements performed on common samples using different methods and with close attention to analytical blanks and

standards are necessary to determine the source of discrepancies between measurements.

(2) The residual DOC remaining after wet-chemical or photochemical oxidation should be systematically investigated.

### GENERAL CONCLUSIONS

The formal position of the DOC Subgroup was that, on close examination of the paired analyses in Table 1, it was not possible in all cases to argue for significant differences in reported DOC concentrations between the HTOCO and wet-chemical or photochemical oxidation methods, given the information available to us at the Workshop. In a number of cases, however, it seemed one can only conclude that there are observed differences between the methods. Why this should be seen in some cases and not in others is not known. Whether the observed differences in DOC concentrations obtained by different methods are due to qualitative differences in the organic composition of waters sampled or to problems in the analytical methods employed we were unable to determine. Furthermore, until the current problems are resolved, it is simply not possible to evaluate the accuracy and/or 'recoverability' of past data sets on DOC distributions.

Until and unless a resolution between the different methods is obtained it would seem prudent that measurements of DOC be continued using both the HTOCO and the wet oxidation methods.

That there should be such striking patterns of variation in the differences of DOC concentrations is profoundly disturbing to the analyst as much as to the users of the information. We are left unable to estimate one of the planet's major organic pools to within a factor of two. The apparently contradictory evidence from the very limited set of data from freshwater environments emphasizes the need for further work along the lines of methodological problems before operational definitions of the 'quality' of DOC (i.e. 'new' or 'extra' DOC) can be justifiably adopted.

## GENERAL RECOMMENDATIONS

(1) To resolve the above uncertainties there is a need to undertake intercomparisons in both marine and fresh waters which address the issues raised in this report, in particular: (i) potential deficiencies resulting from methodological, procedural and/or matrix problems; (ii) to what extent the discrepancies in DOC concentrations determined by the different methods are due to material of recent biological origin and thus due to marked temporal variation; (iii) whether we can resolve the problem of assessing the validity of past measurements of DOC concentrations by means of an adequate knowledge of the instrumentation used, analytical conditions, blank evaluations, etc.

(2) We need in addition, and with some urgency, to set in motion the following: (i) the development of protocols to assure data quality and provide accreditation for DOC analyses that will come from major international programs such as JGOFS; (ii) the commissioning of a laboratory or agency with the task of preparing and certifying a stable reference standard(s) of DOC.

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#### APPENDIX 1: SOME CONSIDERATION CONCERNING AN EXPERIMENTAL PROTOCOL FOR DOC

##### 1. *Accreditation of analyses*

In the field of commercial analytical chemistry it is now normal procedure to lay down protocols for the accreditation of analyses and instrumentation. Before undertaking the analysis of unknowns, instruments themselves have to be certified and on a daily basis certain performance criteria have to be met. In the case of DOC the latter might take the following form:

- (i) the blank value must be below a specified value.
- (ii) the precision must reach a prescribed level.
- (iii) the blank analysis of a reference or check standard must fall within certain limits.

The important point is that if these criteria cannot be met then the analysis need not be abandoned but the data will not be recorded as accredited data in international data sets.

##### 2. *Information which might be reported with each analysis*

- (i) Blank value: the value (in concentration

units) subtracted from the raw instrument signal. In addition, the apparent DOC content of water used for making up calibration standards should be reported for each day on which analyses are made.

- (ii) Daily precision: the analytical precision, determined from a standard calibration.

- (iii) Check standard value: the value of the check standard, relative to its long-term average, should be reported for each day on which analyses are made. Also noted should be (a) origin of check standard, (b) manner of preservation of check standard, (c) when and how DOC content of check standard was established.

- (iv) Reference standard: the value obtained for a community-wide reference standard at the beginning of a set of analyses.

##### 3. *Topics which warrant further consideration*

- (i) Archiving of samples: in the interest of establishing a data base useful in the examination of decade-scale ocean changes, it may be imperative to archive subsamples from major oceanographic initiatives.

- (ii) Instrument parameters to be reported: a list of instrumental parameters reported with each analysis (for a given instrument type) should also be developed. These parameters need to be chosen to allow the sort of 'post mortem' comparison of analyses discussed in the text above.

- (iii) Details of data work-up: the potential effects of using varying individual data treatments must be addressed. If the effects of inconsistent data treatment are judged to be significant, appropriate protocols must be developed.