

# AN OVERVIEW ON NON-SPECIFIC METHODS OF ORGANIC MATTER IN MARINE MORTALITY INVESTIGATION TECHNIQUES

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The selection of variables for any water quality assessment programme depends upon the objectives of the programme. Appropriate selection of variables will help the objectives to be met, efficiently and in the most cost effective way. The purpose of this paper is to give good insight on non-specific methods of organic determination (BOD, COD and TOC) and their relationship to provide information. Also, Humic and fulvic acids will be considered. Each variable is discussed with respect to its origins, sources, behaviour and transformations in the aquatic system, the role of the variable in assessment programmes, and any special handling or treatment of samples that is required. The methods employed to measure the selected variables depend on access to equipment and reagents, availability of technical staff and their degree of expertise, and the level of accuracy required by the objectives of the programme. Finally, this paper suggests a combination of two of the three variables in mathematical equation, which might be used for specific water, especially if the three parameters were not available. This can be used as a basis for developing individual programmes.

## 1. Organic matter

Most freshwaters contain organic matter which can be measured as total organic carbon (TOC). For comparative purposes an indication of the amount of organic matter present can be obtained by measuring related properties, principally the biochemical oxygen demand (BOD) or the chemical oxygen demand (COD). The COD usually includes all, or most, of the BOD as well as some other chemical demands. In most samples, COD > BOD > TOC. However, in some situations this relationship may not be true, such as when the sample contains toxic substances.

### 1.1. Total organic carbon

The total organic matter in the water can be a useful indication of the degree of pollution, particularly when concentrations can be compared upstream and downstream of potential sources of pollution, such as sewage or industrial discharges or urban areas. In surface waters, TOC concentrations are generally less than 10 mg l<sup>-1</sup>, and in groundwater less than 2 mg l<sup>-1</sup>, unless the water receives municipal or industrial wastes, or is highly coloured due to natural organic material, as in swamps. In such situations, TOC concentrations may exceed 100 mg l<sup>-1</sup> (TOC concentrations in municipal wastewaters range from 10 to > 100 mg l<sup>-1</sup>, depending on the level of wastewater treatment). Total organic carbon consists of dissolved and particulate material and is, therefore, affected by fluctuations in suspended solids. Total organic carbon is determined without filtration of the sample. Samples for TOC determination should be stored in dark glass bottles, with minimum exposure to light or air, at 3-4° C for no more than seven days prior to analysis. Alternatively, samples can be acidified with sulphuric acid to pH 2 or less. There are various methods available for determining organic carbon depending on the type of sample to be analysed. Methods are based on the principle of oxidation of the carbon in the sample to carbon dioxide (e.g. by combustion, chemical reaction or ultra violet irradiation) which is then determined by one of several methods (e.g. volumetric determination, thermal conductivity or specific CO<sub>2</sub> electrode).

## 1.2. Chemical oxygen demand

The chemical oxygen demand (COD) is a measure of the oxygen equivalent of the organic matter in a water sample that is susceptible to oxidation by a strong chemical oxidant, such as dichromate. The test for COD is non-specific, in that it does not identify the oxidisable material or differentiate between the organic and inorganic material present. Similarly, it does not indicate the total organic carbon present since some organic compounds are not oxidised by the dichromate method whereas some inorganic compounds are oxidised. Nevertheless, COD is a useful, rapidly measured, variable for many industrial wastes and has been in use for several decades. The concentrations of COD observed in surface waters range from 20 mg l<sup>-1</sup> O<sub>2</sub> or less in unpolluted waters to greater than 200 mg l<sup>-1</sup> O<sub>2</sub> in waters receiving effluents. Samples for COD analysis should be collected in bottles which do not release organic substances into the water, such as glass-stoppered glass bottles. Ideally samples should be analysed immediately, or if unpolluted, within 24 hours provided they are stored cold. If analysis cannot be carried out immediately, the samples should be preserved with sulphuric acid. For prolonged storage samples should be deep frozen. If appropriate, samples can be filtered prior to analysis using glass fibre filters. Unfiltered samples containing settleable solids should be homogenised prior to sub-sampling. The standard method for measurement of COD is oxidation of the sample with potassium dichromate in a sulphuric acid solution (although other oxidants can be used which may have different oxidation characteristics) followed by a titration. It is extremely important that the same method is followed each time during a series of measurements so that the results are comparable.

## 1.3. Biochemical oxygen demand

The biochemical oxygen demand (BOD) is an approximate measure of the amount of biochemically degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic micro-organisms present in the sample to oxidise the organic matter to a stable inorganic form. The method is subject to various complicating factors such as the oxygen demand resulting from the respiration of algae in the sample and the possible oxidation of ammonia (if nitrifying bacteria are also present). The presence of toxic substances in a sample may affect microbial activity leading to a reduction in the measured BOD. The conditions in a BOD bottle usually differ from those in a sea. Therefore, interpretation of BOD results and their implications must be done with great care and by experienced personnel.

Standardised laboratory procedures are used to determine BOD by measuring the amount of oxygen consumed after incubating the sample in the dark at a specified temperature, which is usually 20° C, for a specific period of time, usually five days. This gives rise to the commonly used term “BOD<sub>5</sub>”. The oxygen consumption is determined from the difference between the dissolved oxygen concentrations in the sample before and after the incubation period. If the concentration of organic material in the samples is very high, samples may require dilution with distilled water prior to incubation so that the oxygen is not totally depleted.

The BOD measurements are usually lower than COD measurements. Unpolluted waters typically have BOD values of 2 mg l<sup>-1</sup> O<sub>2</sub> or less, whereas those receiving wastewaters may have values up to 10 mg l<sup>-1</sup> O<sub>2</sub> or more, particularly near to the point of wastewater discharge. Water samples collected for BOD measurement must not contain any added preservatives and must be stored in glass bottles. Ideally the sample should be tested immediately since any form of storage at room temperature can cause changes in the BOD (increase or decrease depending on the character of the sample) by as much as 40 per cent. Storage should be at 5° C and only when absolutely necessary.

## 1.4. Humic and fulvic acids

Organic matter arising from living organisms makes an important contribution to the natural quality of surface waters. The composition of this organic matter is extremely diverse. Natural organic compounds are not usually toxic, but exert major controlling effects on the hydrochemical and biochemical processes in a water body. Some natural organic compounds significantly affect the quality of water for certain uses, especially those which depend on organoleptic properties (taste and smell). During chlorination for drinking water disinfection, humic and fulvic acids act as precursor substances in the formation of trihalomethanes such as chloroform. In addition, substances included in aquatic humus determine the

speciation of heavy metals and some other pollutants because of their high complexing ability. As a result, humic substances affect the toxicity and mobility of metal complexes. Therefore, measurement of the concentrations of these substances can be important for determining anthropogenic impacts on water bodies.

Humus is formed by the chemical and biochemical decomposition of vegetative residues and from the synthetic activity of micro-organisms. Humus enters water bodies from the soil and from peat bogs, or it can be formed directly within water bodies as a result of biochemical transformations. It is operationally separated into fulvic and humic acid fractions, each being an aggregate of many organic compounds of different masses. Humic and fulvic acids are fairly stable (i.e. their BOD is low). However, these substances are chemically oxidisable and, therefore, can readily affect the results of COD determinations. Fulvic and humic acid concentrations in waters are highly dependent on the physico-geographical conditions and are usually in the range of tens and hundreds of micrograms of carbon per litre. However, concentrations can reach milligrams of carbon per litre in waters of marshy and woodland areas. In natural conditions fulvic and humic acids can comprise up to 80 per cent of the DOC, which can be used as an approximate estimate of their concentrations. Samples for fulvic and humic acid determination are not usually filtered or preserved. They can be stored for some months in a refrigerator (3-4° C). Total fulvic and humic acid content can be determined photometrically and their separate determination can be made with spectrophotometric methods.