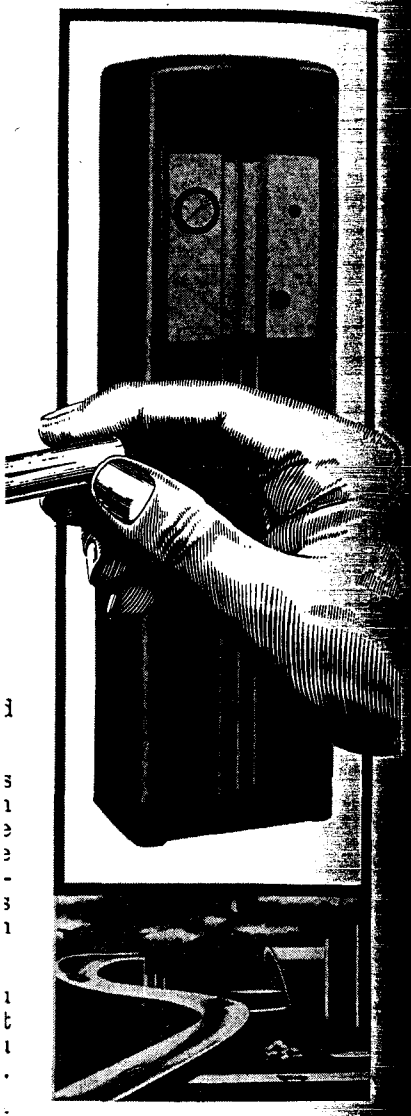


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Journal

AMERICAN WATER WORKS ASSOCIATION

VOL. 52 • JUNE 1960 • NO. 6

Proposed Toxicity Screening Procedure for Use in Protecting Drinking-Water Quality

M. B. Ettinger

A contribution to the Journal by M. B. Ettinger, Chief, Chemistry & Physics, Water Supply & Water Pollution Research, Robert A. Taft San. Eng. Center, USPHS, Cincinnati, Ohio. The procedure described here is under consideration by the USPHS Advisory Committee on Revision of the Drinking Water Standards, which has AWWA representation. Suggestions or comments concerning this proposal or other related matters should be directed to the author or to the AWWA representative, Oscar Gullans, 3300 E. Cheltenham Place, Chicago, Ill.

MORE than 500,000 organic chemicals are known and have been synthesized and described. A few dozen of them are accepted by the Food and Drug Administration as being safe for addition to food and beverages. Tolerance levels, varying according to the food, have been established for a few pesticides.[1] The zero tolerance is relatively common, and is directed by law in some instances.

There is a vast area of ignorance concerning the toxicology and pharmacology of both synthetic and naturally occurring organic materials, and new materials are being made much faster than the toxicology of known materials is being studied.

Most surface waters receive a large, variable, and anonymous load of organic chemicals. Only a minute fraction of the materials dumped or washed into surface waters could hope to qualify with the Food and Drug Administration as acceptable for addition to food and beverages, and the water utility operator can usually be confident that his surface water is subject to pollution by chemical pesticides which have been assigned low tolerances or even a zero tolerance by the Food and Drug Administration. The responsible water producer must feel some concern about how wholesome the water he furnishes the consumer may be.

The problem of keeping toxic material out of drinking water parallels that of keeping pathogenic material out. It is difficult to detail all pathogens which may conceivably be waterborne, and it

is absurd to ask water utilities to check treated water for each specific organism or virus to insure that it is not present. The same is true of toxic materials. Fortunately, the relatively simple observation of coliform organisms has served as a theoretically imperfect but practically workable measure for protecting water from pathogens. Assuming that some similar blanket safeguard against exposure to toxicants is desirable, how can it be provided?

Only a few micrograms per liter is the minimum concentration of some organic materials that can produce toxic reactions in man. There is, however, little likelihood that material of such extreme physiological effect is introduced into water supplies by the ordinary industrial activities of man.

Toxicity Index Requirements

A nonspecific analytic criterion to serve as a toxicity warning should:

1. Be suitable for execution by the water utility at a reasonable cost
2. Afford the maximum possible protection against the intrusion of unknown or undetected toxic materials
3. Be a criterion that all or almost all safe and acceptable water supplies can meet
4. Be based upon examination of an integrated or composite sample, as the problem is primarily one of chronic toxicity rather than acute toxicity
5. Have further value in promoting good water utility operation.

No test or criterion that has yet been devised can satisfy all these requirements. This is not, however, a good reason for failing to adopt the closest possible approach to the ideal criterion. Such a practical criterion obviously should relate to finished drinking water and be an index principally to the organic toxicants of greatest public health concern. As a standard it should be a value measurable by some well defined technique and reducible to a simple number.

Proposed Criterion

The carbon filter technique has been described previously in some detail.[2] The criterion proposed relates to the material concentrated by activated carbon in the filter from about 5,000 gal of water, and subsequently eluted from the dried carbon by repeated extraction with chloroform in a very large Soxhlet-type extractor.

In the carbon filter technique, as it is now used, a second series of extractions is usually made with ethyl alcohol to recover a further extract. The total carbon filter extract provides a variable and incomplete recovery of the organic materials present. It is not more than a substantial fraction of the total organic material present in a sample of surface water.

Limitations of Method

The mechanics of the carbon filter process for sampling the water cause a first series of restrictions. If a substance cannot be adsorbed from the water sampled by the carbon filter, then it is not available for extraction by chloroform. Chloroform extraction obviously recovers only material soluble in chloroform and extractable by the solvent from the carbon. Knowledge of precisely which compounds can be collected by the procedure is limited.

Some materials, such as simple hydrocarbons and chlorinated insecticides, can be recovered almost quantitatively. Other compounds, such as the alkyl benzene sulfonates, may be quantitatively collected but will not be removed

the chloroform, although they can be removed almost quantitatively by other solvents. About 60–70 per cent of some substances, such as simple phenols, are recovered by chloroform extraction even though they are adsorbed quantitatively from the water originally put through the carbon filter. Materials such as sugars, polysaccharides, proteins, and tannins, have not been observed in chloroform extracts. These materials are either insoluble in chloroform or not extractable by chloroform from carbon, or the carbon column is unable to remove them from water.

It might be thought that the carbon filter would readily develop into an efficient device for biological attrition of the material dissolved in the water submitted to it. This apparently is not the case, and with reasonable precautions in handling, losses as a result of biological destruction are believed to be small or negligible. The quantity of extract recovered is affected by the pH of the water submitted to the carbon. Variations in the pH of satisfactory waters are believed to have little effect, as most of the extract is ordinarily neutral or only very weakly acidic or basic.

Characteristics of Samples

Carbon filter sampling of waters remote from concentrated industrial areas or heavily populated regions invariably yields a small chloroform-soluble extract, usually less than 50 ppb. Large amounts of chloroform-soluble extract appear in industrial effluents, especially if they have not been given much treatment. Values as high as 3,000 ppb have been observed in a raw municipal supply during a period of exceptionally heavy industrial pollution.[4]

Figure 1 shows the distribution of the data on concentrations of chloroform extractables yielded during the first 2 years of the USPHS program to collect basic data on water quality.[5] Principal streams all over the United States were sampled at approximately 50 points. Analytical data were pooled to make up the "total" curve presented. The median concentration of chloroform-soluble extract recovered was 47 ppb and only 19 samples of 750 showed values in excess of 200 ppb. In addition to the distribution of the chloroform-soluble carbon filter extracts in the total data, curves are presented showing the data on the Mississippi, Missouri, and Ohio rivers.

The stations of the national data collection network active during the period reported represent a reasonable cross section of the surface water available in the United States.[6] A detailed breakdown of the 19 samples in which the concentration of chloroform extractables exceeded 200 ppb is instructive. Of the 19 samples, only 9 were taken from a city water inlet; 10 were secured at points where the city uses well water, or where the municipal water inlet has been placed in another location for good reasons. For instance, at Lowell, Mass., the samples were taken from a site on the Merrimack River abandoned when the city changed to a well supply; at Poughkeepsie, N.Y., samples were taken below the town from an industrial water inlet which is relatively close to the river bank.

Experience has shown that there is a rough correlation between taste and odor problems and the amount of chloroform-soluble material present. The 200-ppb value cited above has never been exceeded in treated water

where the population served was satisfied with the water delivered. According to data covering a period of 4 years,[3] the 200-ppb concentration was exceeded for a sustained period at Cincinnati for only a few months in 1953, and this period was coincident with particularly low flow in the river and

have been found in which the concentration sometimes exceeded 200 ppb in both raw and finished water. Specifically, the cities involved were Wyandotte and Mt. Clemens, Mich.[7]

Water containing less than 200 ppb chloroform extractables is not necessarily of good taste and odor quality.

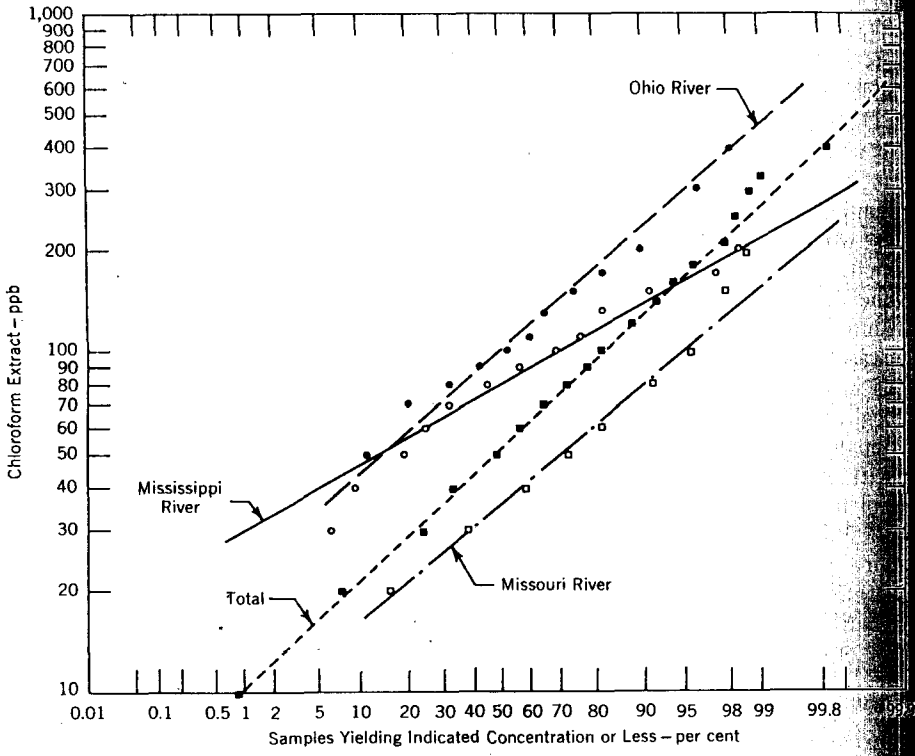


Fig. 1. Distribution of Chloroform Extractables in Major United States Streams, 1957–59

Shown are data on three major streams as well as a "total" curve for carbon filter data from approximately 50 points on principal streams all over the United States.

sustained consumer distress with the water supply. This concentration is also reported to have been exceeded a number of times at Nitro, W.Va.[4]

In studies of the boundary waters in the general area around Detroit and Windsor, Ont., a number of samples and samples that are relatively low in chloroform extractables can sometimes show surprisingly high odor and taste. It would be easy to suggest compositions of water pollutants which would have no odor and would nevertheless greatly exceed the 200 ppb value. In actual practice, however, this condition seems to be encountered infrequently, and it is usually followed or preceded by water of an inferior taste and odor quality.

Further Investigations

At the Robert A. Taft Sanitary Engineering Center, Cincinnati, Ohio, chloroform-soluble carbon filter extract has been subjected to further analysis and separation. This work has shown the presence of toxic materials in various waters. Materials recovered include chlorinated insecticides, nitriles, substituted nitrobenzene, aromatic ethers, and the like. These materials have yet to be found in dangerous concentrations, but all those that have been found so far have been recovered with the chloroform extract. This does not mean that the chloroform-soluble carbon filter extract provides a complete sample of toxicants in water; the finding of toxic materials in the chloroform-soluble carbon filter extract may be the natural result of concentration of efforts on examination of this material. The technique does, however, appear to be valuable for collecting material of industrial origin likely to have toxic properties, and it has the additional advantage of giving a clear and objective indication of whether or not a water supply has been unreasonably burdened with the wastes from industry, humanity, or agricultural practice.

Adequacy of Proposed Technique

The proposed technique is quite suitable for execution by water utility personnel at a reasonable cost, or it can be easily handled by an outside laboratory with only the sampling done by the water utility. The procedure has been used by personnel in both large and small water utilities. In the Taft Center operations of the National Water Quality Network it is routinely executed on shipped carbon filters by subprofessional personnel. The cost is relatively small. Most water utilities should be able to do it for approximately $15 in labor and materials.

Although application of the carbon filter technique has already resulted in the detection of a number of toxic materials in water, there are toxic materials that the proposed test cannot recover. For example, it affords little protection against some of the commercial poisons which are sometimes used in large agricultural fumigation or insect control operations. The test is, however, likely to be at least a good indicator of large amounts of potentially toxic materials released as the result of industrial operations, and it is possible that it will actually collect toxic materials. The proposed measurement could give a substantial amount of protection if used as a standard, and it would afford more protection than could be obtained from any other technically simple and administratively feasible test devised thus far.

Any water supply that would be unable to meet the proposed criterion would almost certainly be unacceptable to the consuming public, for it would have acute taste and odor periodically or continuously. Although it might be sufficient to maintain direct examination of waters for taste and odor, the criterion proposed here is nonsubjective. It does not depend on the judgment of one man or on other variables, such as proximity to heavy industrial operations which make it difficult to carry out reasonable taste and odor examinations because of the high background odor. It is the author's opinion that no high-quality water is likely to be in violation of the proposed crite-

rion for more than very short periods, if at all.

The carbon filter procedure represents a sample that is integrated over a period of approximately 2 weeks, and is therefore likely to reflect the average condition of the water put into the mains over the same period. The concern over the possible dangers of toxicants in public water supplies is largely related to chronic exposure. This means that average conditions are what should be observed rather than short-time exposures to materials that are temporarily present in insignificant amounts.

It is clear that the proposed test could be a valuable adjunct to water utility records. In time it could become a measure of long-time trends of finished-water quality and it would give an indication of the effectiveness of such procedures as carbon treatment.

Results of the chloroform-soluble carbon filter extract determination are likely to be available about 3 weeks after the beginning of the 2-week sampling period. It will report on an integrated average condition during the sampling period. Clearly, the determination relates more to long, sustained organic intrusions than to brief intervals when the water system is under stress.

The criterion serves as an integrated survey of chemical pollution of the watershed and of water system performance in coping with chemical pollutants. Measures that should be considered when chloroform-soluble carbon filter extract is high include improvement of the quality of raw water by a vigorous program of watershed pollution abatement, consideration of alternative sources of water, or development and adoption of treatment procedures designed to remove organic contaminants.

Recommended Limit

A recommended limit for chloroform-soluble carbon filter extract is being considered for incorporation into the next revision of the USPHS Drinking Water Standards. A recommended limit differs from a mandatory limit in that water exceeding a recommended limit may be certified by the USPHS for use on interstate carriers when a more desirable water supply is not available.

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Proposed Method for Examination of Water for Free-Living Nematodes

Shih L. Chang

A contribution to the Journal by Shih L. Chang, Medical Director, Robert A. Taft San. Eng. Center, USPHS, Cincinnati, Ohio.

BECAUSE of current interest in the subject, it has appeared desirable to develop a method of examining sizable quantities of water for free-living nematodes, including collection of water samples, concentration of samples, direct microscopic examination of concentrates, and general identification of nematodes. Such a method is presented below.

Laboratory Apparatus

1. *Sample bottles,* 1 gal, glass or plastic, with metal or plastic screw caps, thoroughly washed and rinsed three times with distilled water.
2. *Capillary pipets,* Pasteur type, 9 in. long, with rubber bulbs of 2-ml capacity.
3. *Filtration unit,* of any filter holder assembly type used in bacteriologic examination.[1] The funnel should be of at least 650-ml capacity and the filter flask of at least 2-liter capacity.
4. *Filter membranes,* of Millipore * HA (SS 047 MM) type or equivalent.
5. *Microscope,* binocular type with 10× eye piece, 4×, 10×, and 43× objectives, and mechanical stage.

Collection of Water Samples

Samples are collected in the same manner as samples for bacteriologic examination,[1] except that a dechlorinating agent is not needed. Samples of 0.5–1 gal are collected from raw water and 1-gal samples from tap water. Refrigeration is not essential, and samples may be transported without it unless examination is to be delayed for more than 5 days.

Concentration of Samples

A 1-gal sample of tap water can usually be filtered through a single membrane within 15 min, unless the water is turbid. At least 1 gal of sample should be used in a single examination. Immediately after the last of the water has disappeared through the membrane, the suction line should be disconnected and the membrane should be placed on the wall of a clean 50–100-ml beaker and flushed repeatedly with approximately 2 ml of sterile distilled water. A capillary pipet with a rubber bulb should be used for flushing. The concentrate should then be pipeted into a clean Sedgwick-Rafter counting cell, after which it is ready for examination.

In concentration of raw-water samples having visible turbidity, two to four membranes may be required per sample, with filtration through each membrane being limited to not more than 20 min. Samples ranging from 500 ml to 2 liters may be filtered, depending on whether turbidity is high or low. After filtration the membranes are placed on the walls of separate

* A product of Millipore Filter Corp., Watertown, Mass.