

## COMPARISON OF 1980 AND 1989 ANALYSES OF 101 MISSOURI DRINKING WATER SUPPLIES FOR TOTAL ORGANIC CARBON

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A comparison of data from the two samplings for total organic carbon taken from 101 drinking water distribution systems nearly a decade apart shows a most remarkable consistency. Changes in water quality over this period might have been attributed to many diverse factors, including natural fluctuations in water quality, seasonal trends, progressive human contamination of the water supply, modifications in water treatment practice, changes in water sources, increased rates of water withdrawal, drought, lowered rates of ground water infiltration and many other natural or anthropogenic factors. There would be many explanations for an entirely random series of results. Instead, the results, summarized in Tables 4 and 5, indicate a degree of consistency that, initially, would have been considered a remote possibility.

Seventy-five out of 84 communities for which comparative data is currently available showed that TOC values remained within a factor of approximately two. Of those showing major changes, two supplies are presently known to have been exchanged between ground water and surface water. Most often, those with initially high TOC remained high while those which were low in 1980 remained low in 1989, indicating maintenance of a stable pristine condition. Comparisons of the averages for high and low TOC water indicate virtually no systematic change over nearly a decade.

The results are both surprising and gratifying news for a number of reasons. Most important, many observers, including the authors, have anticipated a progressive worsening of drinking water quality owing to increasing source water contamination with the organic compounds used in agriculture, drained from landfills, leaked from septic tanks or underground storage tanks or draining from other controlled and uncontrolled sources of liquid and solid waste. The cumulative effect of the increasing pace of human activity should be reflected in the gradual deterioration of drinking water quality. With progressively sensitive analytical equipment, it should be possible to detail the progress of this water quality deterioration.

The present study offered a *unique* opportunity to detect and quantify the progressive contamination of drinking water supplies. This was possible because the University of Missouri-Columbia, utilizing a grant from the Monsanto Charitable Trust Fund to Professor John T. O'Connor for the study of drinking water quality, was the first university to obtain the newest, most sensitive and, at the time, untried analytic equipment for the detection of ultra-low concentrations of organic substances in water. At the time of purchase (1979) it was not known whether the equipment would perform as anticipated on drinking water samples. In addition to reliable equipment performance, much of the success of the analytical program depended on the sample collection, handling and preparation techniques. It was necessary to avoid losses of organic compounds due to volatilization, adsorption on glass or deterioration in storage. Alternately, contamination of samples from solvents adsorbed from the laboratory atmosphere needed to be overcome, since these were detected by the sensitive new equipment.

The initial (1980) survey was conducted, primarily, to test the equipment and develop the methodology which was not "*standard*" at that time and would not, universally, be considered as "*acceptable*" or verifiable. In addition, the survey was broadly based in an effort to obtain preliminary data from as wide a variety of drinking water sources as were available in the State. Therefore, the 1980 sampling of Missouri drinking water was carried out in conjunction with the Missouri Department of Natural Resources (MDNR). The significant contribution of MDNR in blanketing the State and expediting the transport of the drinking water samples to the Department of Civil Engineering, Environmental Engineering Laboratories, made it possible to conduct a timely study which would provide this subsequent opportunity to observe changes in drinking water quality on a scale which is large enough to have significant statistical reliability.

The 1980 study did not receive direct financial support. Because the analytical methods development was proceeding simultaneously with the arrival and analysis of the samples, the analysts consistently challenged the accuracy and validity of their results. Numerous extra precautions were taken and all samples were replicated a minimum of three times in an effort to ensure reproducibility. Ultimately, the results of this initial sampling program were shared with the MDNR for advisory purposes only.

The 1989 study was conceived largely because of the existence of the earlier data base. By this date, other laboratories had similar equipment and the analytic methods had become standardized. Piecemeal, similar data was being published. However, no study on the scale of Missouri's 1980 survey has been reported to date. Even if a similar study were to be undertaken today, another decade would have to pass before similar comparisons could be made. Therefore, owing to the fact that the 1980 data would have to be considered pioneering, a repeat survey was proposed to the University of Missouri–Columbia Extension Division by Professor Cyrus Harbourt, Director of Engineering Extension. In the present survey, University Extension field personnel from throughout the State were organized to assist in the collection of samples and expedite their return to the laboratory.

### **Elemental Analysis**

Recognizing the opportunity this extensive sampling effort provided, other University researchers offered to contribute to the results of the present study. Dr. Thomas Clevenger, Director of the Missouri Water Resources Research Center and former Director of the Environmental Trace Substances Research Center (ETSRC), offered to conduct elemental analysis on the samples. These supplemental analyses included the major water constituents plus those of health concern (Ca, Mg, Na, K, Sr, Fe, Mn, Ag, As, Ba, Cd, Cr, Pb, Se, Al, Cu and Zn). In addition, the elemental analyses, which were conducted at the Environmental Trace Substances Research Laboratory, yielded B, Be, Bi, Co, W, Li, Mo, Ni, P, Sb, Si, Sn, Ti, Th and V for future reference. The results of the analyses conducted by the Environmental Trace Substances Research Center are presented in Table 6 and summarized in Table 7.

### **Total Bacterial Cell Count**

Another feature of the present study was the first systematic enumeration of the *total* bacteria in drinking water supplies. This added feature of the study was provided by Blaise J. Brazos, Research Associate in Civil Engineering, who has developed advanced microbiological methods for assessing drinking water quality over the past seven years. As principal analyst for the 1989 project, he conducted or supervised the overall testing program and added the microbiological component out of his special interest. As a result of these efforts, the State of Missouri has not only the first comparative TOC data but the first data on total bacterial populations in drinking water. The microbiological data, ranked in Table 8 by decreasing bacterial population, ranges from over  $2.5 \times 10^6$  to less than  $10^3$  cells/ml.

### **REPRODUCIBILITY OF TOC DATA**

The comparative data on total organic carbon has indicated six different conditions, all of which would have to exist if the analytical results were to be comparable in 1980 and 1989. First, the developmental efforts of 1980 had to have been successful in providing the correct results. Secondly, the 1989 analyses similarly had to be performed with accuracy and precision. Again, all TOC analyses were performed in triplicate as a minimum.

It should be noted that the same equipment was used for TOC analysis in 1989 as in the earlier test program. While this is desirable for reproducibility, the well-used equipment was in continuous need of repair. The analytic program was plagued with repetitive breakdowns. Fortunately, the previous studies had demonstrated that the organic material present was extremely stable and could withstand storage under refrigeration for prolonged periods. Analyses for chlorine residual and microbiological parameters, however, had to be conducted immediately upon sample arrival.

### **SAMPLING PROTOCOLS**

In addition to reliable analytical techniques, the results depended heavily on correct sampling protocols. Field personnel were trained in sample collection. Five different samples were collected at each sampling site, each with a different objective. One sample was to preserve the chlorine residual. Another was dechlorinated to preserve the microbial population. In this case, the bottle could not be rinsed of its dechlorinating agent. The samples for organic analysis had to be collected *head space free*, i.e., no air bubbles. This is a difficult and unusual sampling task. Finally, samples for elemental (and metals) analysis required acidification to keep the metals in solution and minimize adsorption of the trace elements to the glassware. Far from being a trivial matter, the collection and transport of reliable, representative samples to the laboratory must be considered to be half of the effort and cost of any comprehensive analytical program. The results indicate that the care taken over the collection methods in both sampling programs yielded reliable samples.

Since the samples were taken from water distribution systems by different sampling personnel, it is unlikely that the samples were taken at the same location in a given distribution system. However, TOC, does not seem to be sensitive to the distribution system sampling location possibly because it is a stable characteristic of the water source. This is yet another condition necessary in order for the results to be comparable.

The final condition necessary for comparable results in 1980 and 1989 seems the least probable. There must be little or no significant change in the total content of organic substances in the water sources. Seemingly, there are an almost endless list of possibilities which would make such a postulate untrue.

Because the results were comparable over so long a time, the value of TOC as an organic pollution indicator is enormously enhanced. The results indicate that infrequent sampling might be adequate to confirm pristine conditions or observe trends in progressive pollution of groundwaters. Readily detectable increases, such as by a factor of two, would have to be considered as a significant indicator of potential aquifer contamination.

The TOC of surface waters are more variable since they are strongly influenced by seasonality (algal growth), bacterial nutrients from waste discharges, rainfall and drought. For these supplies, TOC analysis is more useful in evaluating treatment plant performance with respect to the effectiveness of treatment (coagulation, filtration) in reducing the gross quantity of organic material in finished drinking water. In surface waters, a considerable amount of the TOC may be due to bacterial cell mass. As a result, large TOC reductions during treatment may represent effective removal of bacterial cells.

### **TOTAL BACTERIAL CELL COUNT**

As shown in Table 8, the total bacterial cell count in the drinking waters samples ranged from over 2,500,000 to less than 1,000 per milliliter. This number was determined by direct microscopic count rather than by conventional plate count techniques which enumerate only a small fraction of the total bacteria present. However, the direct count does not distinguish dead from living organisms. Presumably, many of the cells observed have been destroyed and are in the process of lysing (decomposing). Since the samples were taken at locations in the distribution system which were remote from the point of entry, the cells have been in contact with the disinfecting agent (generally, chlorine) for some time and have still not lysed. This may indicate that many of the cells observed are viable.

While most of the bacteria found in nature do not cause disease, food spoilage or undesirable changes, such as corrosion, in household plumbing, water supplies having large numbers of bacteria in their source water have also been found to have large numbers entering the household and colonizing the household plumbing. As chlorine is lost during periods of low water use, the number of both total bacteria and plate count organisms is observed to increase substantially.

Alternately, water supplies which have low bacterial populations appear to be supplies which, intrinsically, have little ability (nutrient) to support bacterial growth. Data from this study shows that these are likely to be waters which are also low in TOC. As a result, high quality drinking waters may be characterized by both low total bacterial populations and low TOC. If such waters were to be infiltrated by sources of wastewater, such as septic tank drainage, even a small amount of degradable organic matter would result in an enormous increase in total bacterial population even if other indicator organisms did not penetrate into the supply. Increases in total bacterial cell count would, therefore, be a very inexpensive, rapid, readily observable early-warning indicator of the migration of dissolved organic matter from wastewater systems.

Based on the results of this survey, it appears that groundwater drinking water supplies which are exempted from chlorination should be routinely monitored to ensure that significant increases in total bacterial populations, whether pathogenic (disease-causing) or not, are occurring. Presently, analyses are only conducted for surrogates for bacterial pathogens (coliform organisms). While analysis for coliform is useful and important, the additional information provided by the enumeration of the total bacterial population may prove to be decisive regarding the award of variances for communities which are not practicing disinfection. Conventional total coliform data generally provides negative data indicating the absence of direct contamination by human feces. Total bacteria cell counts can provide positive data on increases in bacterial populations. This is a far more scientifically valid and useful monitoring approach, particularly since coliform organisms are more sensitive to adverse environmental conditions than many organisms of health concern. In many instances of disease outbreaks due to contaminated groundwater, coliform organisms have not been isolated and did not serve as an indication of gross well water contamination.

## RESULTS OF ANALYSIS FOR INORGANIC CONSTITUENTS

Because of extensive limestone geology, most of Missouri's surface and ground waters are classified as "hard". Hardness, the ability to consume soap, is primarily due to the presence of the divalent ions,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . While there are regions of high sodium ion ( $\text{Na}^+$ ) near natural salt and brine deposits, Missouri waters are not generally high in sodium. Potassium, strontium, iron and manganese are generally very low. These analyses confirm the fact that Missouri waters are dominated by the hardness-producing cations, calcium and magnesium.

The analysis for the trace elements which are regulated by MDNR and USEPA show that all Missouri drinking waters sampled are well below the limits set for silver, barium, cadmium and chromium. The analyses for arsenic, lead and selenium were not sufficiently sensitive to determine whether these waters were within limits set for the protection of public health. However, the limit of detection for arsenic ( $60 \text{ mg/m}^3$ ) was sufficiently close to the maximum contaminant level (MCL) for arsenic ( $50 \text{ mg/m}^3$ ) to indicate that arsenic is not likely to constitute a health hazard. This result is important since arsenic is fairly abundant in natural waters and is known to be present in shallow private well water supplies in Missouri.

New regulations for lead have mandated its testing at the household tap and the MCL has been lowered to  $5 \text{ mg/m}^3$ . The present survey results ( $<40 \text{ mg/m}^3$ ) therefore represent only a coarse screening for lead concentration. Similarly, the detection limit for selenium was well above its MCL.

Presently, MCL's have not been set for aluminum and copper. However, a secondary regulation (SMCL) (addressing aesthetic concerns) has been set for copper at  $1000 \text{ mg/m}^3$  and a SMCL is proposed for aluminum at  $50 \text{ mg/m}^3$ . Whereas copper levels are well below the SMCL in the Missouri waters tested, the average for aluminum ( $128 \text{ mg/m}^3$ ) is well above the proposed SMCL. Half of the Missouri supplies contain less than  $50 \text{ mg Al/m}^3$  while 15 supplies contain in excess of  $300 \text{ mg Al/m}^3$ . Much of the aluminum present may be the residue from the use of aluminum sulfate as a coagulant in the treatment of surface waters.

### Statistical Analysis of TOC Data

The linear regression coefficient (0.834) for all 84 comparable data sets indicates a high degree of correlation between the 1980 and 1989 data. However, when the TOC data is divided into sub-sets, based on concentrations, correlations are found to vary markedly. For those drinking water supplies with TOC greater than  $2000 \text{ mg C/m}^3$  in 1989 ( $n=36$ ), the correlation coefficient declines to 0.169. This may reflect the variability of TOC in surface waters subject to the transient effects of rainfall and runoff on flow, sediment scour and waste dilution. These results would indicate that more frequent sampling would be required to establish mean values and long-term trends for surface water supplies.

For the waters having TOC concentrations in the range of  $500$  to  $2000 \text{ mg/m}^3$ , the correlation coefficient increases to 0.578 while for waters with TOC less than  $500 \text{ mg/m}^3$ , the correlation coefficient is 0.436. When all 84 comparable data sets are included to extend the full TOC range, the correlation coefficient increases to a strong 0.834. Finally, if the TOC range is restricted to include only those water supplies having TOC concentrations less than  $2000 \text{ mg C/m}^3$ , the correlation coefficient increases slightly to 0.854. These results indicate that TOC is a very stable and predictable chemical characteristic of a water supply. As a result, progressive contamination of water supplies with organic substances of unknown origin or composition should be detectable from TOC analysis.

The mean TOC values for all 84 comparable data sets were found to decline 7.5 percent, from  $2309 \text{ mg C/m}^3$  in 1980 to  $2136 \text{ mg C/m}^3$  in 1989. While this difference may not have real significance, at least, it tends to refute the contention of a progressive increase in organic contamination of Missouri drinking water sources. The TOC means for deep well waters with less than  $500 \text{ mg C/m}^3$  remained unchanged at  $212 \text{ mg C/m}^3$  in 1980 and  $210 \text{ mg C/m}^3$  in 1989.

A weak negative correlation ( $-0.11$ ) was found between total bacterial cell count and TOC when all data sets were compared. This result may have been due to the failure to separate the data from chlorinated and unchlorinated water supplies.