Expanded Summary: Real-time detection of intentional chemical contamination IN THE DISTRIBUTION SYSTEM

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Source: *Journal (American Water Works Association)*, Vol. 97, No. 7 (July 2005), pp. 130-133
Published by: Wiley
Stable URL: https://www.jstor.org/stable/41312212
Accessed: 01-09-2020 22:23 UTC

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ROUTINE, REAL-TIME MONITORING OF WATER DISTRIBUTION SYSTEMS CAN HELP PROVIDE EARLY WARNING OF INTENTIONAL THREAT CONTAMINATION AS WELL AS COMMON WATER QUALITY COMPROMISES.

Because 80% of the US population is served by 14% of the utilities (Clark et al, 2002), an act of sabotage could have a significant effect on a large drinking water system. A water distribution system has been identified as a major vulnerability because of its accessibility to those it serves and its geographic span. Khan et al (2001) highlight the fact that except in the case of aerosols, food or water contamination is the easiest way to distribute chemical and biological agents. Because of the size of the population that a water distribution system serves, a large number of casualties could occur over a wide geographic area. That as much time as three weeks could pass before a source of contamination could be identified—as happened during the cryptosporidiosis outbreak in Milwaukee, Wis., during 1993—is alarming. This outbreak in itself demonstrated the potential for drinking water to serve as a conveyance for the spread of disease.

Early detection of a chemical or biological contamination event is crucial and could save lives. The use of new agents, combinations of agents, or contaminants that haven't been seriously considered in the past is a plausible terrorist approach, and thus the use of surrogates for detection—to cast a broader net—is one approach that needs investigation. Early detection is absolutely essential.

This view was highlighted by the National Research Council (2002), which recognized that forced entry of a highly toxic contaminant into the distribution system could have serious consequences. The council further declared that monitoring and identification of biological and chemical agents are among the four highest-priority areas for research on water security. Similarly, Luthy (2002) emphasized the importance of protecting water quality by expediting the detection of contaminants to minimize effects on human health. Online detection using water quality surrogates for contaminant detection may be considered an additional barrier in the distribution system.

Development and use of real-time monitoring was also recommended by Parmelee (2002) and States et al (2003) to protect against terrorism in water systems. This recommendation was validated when the US Environmental Protection Agency (USEPA) awarded a $500,000 project to the US Geological Survey to set up real-time monitoring equipment at two drinking water systems in New Jersey (USEPA, 2002). The significance of this effort is best captured in USEPA's quote at the onset of the project: "Whether a contaminant enters a water supply system by terrorist action or by accident, it is vital that we have the information to respond quickly. That's why real-time monitoring offers such great promise." In addition, it was emphasized that real-time monitoring would allow water system operators to be aware of potentially dangerous situations before contaminated water could reach consumer taps. Deininger et al (2000) summarize it best: "Strategically placed monitors in a distribution system are the obvious solution for the protection of a water supply system."

The threat of chemical or microbiological contamination to drinking water is well-established and would be an effective way of causing serious public health consequences. The technology to detect these contaminants is currently lacking. Early detection of these contaminants via online or real-time monitoring has been identified as a feasible way to provide early warning to protect public health. This research is a first step to address the challenge of detecting a large number of potential contaminants in a drinking water distribution system in real time. The basic premise of this research is that readily available and relatively inexpensive equipment can be used to determine in real time when contamination has occurred in a distribution system, with the intent being to provide an early warning so that public health may be protected.

Experiments were conducted with actual distribution system water using both batch and continuous-flow data collection. After determining the baseline water quality in real-time online instruments, model contaminants were added to batch- and pilot-scale distribution systems to determine the level of detection with different water quality parameters. A 1-in. (25-mm) polyvinyl chloride pipe loop fed running tap water to two online water quality panels—a multi-instrument panel[1] that measured pH, turbidity, conductivity, and chlorine residual and a panel[2] that measured total organic carbon (TOC). Data were collected once per minute using datalogger software, collecting more than 16,000 data points. These data were used to determine what represents "normal" water quality in the distribution system and to estimate the population standard deviation. In addition, some general information about the distribution of the data was provided as well as summary statistics.

Miller and Miller (2000) defined the limit of detection as being equal to the blank signal, y_B, plus three standard deviations of the blank, or

$$\text{Limit of detection} = y_B + 3\sigma_B \qquad (1)$$

In this case, the "blank" signal is zero because the difference between baseline conditions and the addition of a contaminant is what is being measured, leaving three standard deviations as the limit of detection.

The baseline is key to determining the normal signal variation. Normally distributed data will result in 99.96% of the points falling within three standard deviations from the mean ($\bar{x} \pm 3\sigma$) when only considering random variability. Anything outside three standard deviations (3 σ) represents an anomaly and should be addressed accordingly (there is a 4-in-10,000 chance that the anomaly is a *false-positive*). The standard deviation in the baseline data was used to compare beaker test data to the 3σ values to determine a limit of detection. This provides the first indication of the potential of using water quality parameters as surrogates to detect a contamination event. Similarly, baseline data were collected for 100 minutes, immediately before the introduction of contaminants into the distribution system. This ensures that the baseline data are representative of system conditions when the experiments were conducted.

Four chemical contaminants were chosen for the study using the criteria of (1) toxicity, (2) water solubility, (3) chemical and physical stability, (4) a lack of taste, color, and odor, (5) ability to be used as a weapon, and (6) a low chance of detection with normal analytical methods. After the baseline was established

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using online equipment, tap water was added to a beaker, and the bulk parameters were measured using bench-top analytical equipment. The four contaminants were then added to the beakers in specified concentrations, and the water quality parameters were measured again, using the same analytical equipment. Finally, the difference was taken between the tap-water-only measurements and the tap-water-plus-contaminant measurements, and a change in the water quality parameters was determined.

The bench-scale distribution system provided flexibility for conducting controlled experiments to determine online contaminant instrument response in a distribution system.

The bench-scale distribution system provided flexibility for conducting controlled experiments to determine online contaminant instrument response in a distribution system. This was accomplished without compromising simulation of real-world distribution system parameters, including water quality, dilution, flow, and pipe materials. The bench-scale distribution system was built around a ventilation hood to accommodate the safe introduction of highly toxic and volatile hazardous materials into the distribution system. In addition, the system was designed to discharge hazardous waste under the ventilation hood to ensure safe handling.

The objective of this research was to detect contamination events in the distribution system in real time using water quality parameters. The parameters that were used in this study to detect changes in drinking water quality included chlorine residual, turbidity, pH, conductivity, and TOC.

Chlorine residual, turbidity, pH, and conductivity are all referenced in the literature as good choices of surrogates for detecting distribution system contamination. TOC is not cited but is an obvious choice to detect organic contaminants. The drawback to online TOC analysis is its high relative cost. Further work may be directed at how effective the other water quality surrogates (chlorine residual, turbidity, pH, conductivity) are at detecting organics without the use of TOC to eliminate this costly equipment from the suite of instruments required to provide robust early warning in the distribution system.

The baseline provided information to determine what is "normal" in the distribution system relative to the time that the data were collected. The standard deviation in the on-line baseline data was used in conjunction with the beaker test data to determine a limit of detection. This limit provides an indication of the potential of using water quality parameters as surrogates to detect a contamination event. Time-series plots indicated that every parameter behaves differently with respect to time and that the values of the parameters are in a constant state of flux.

Results from this study indicate that routine water quality instruments can detect chemical disturbances in drinking water distribution systems at relatively low concentrations.

Beaker tests were conducted before the contaminants were introduced into the bench-scale distribution system. There were three primary objectives behind conducting the beaker tests: (1) to determine which parameters would be directly influenced by specific contaminants, (2) to determine the approximate minimal concentration at which contaminants in a controlled environment would affect water quality, and (3) to anticipate concentrations that should be pumped into the bench-scale distribution system.

In addition, the beaker tests served as indicators of the actual concentration that the on-line instruments measured. The contaminants were pumped into the bench-scale distribution system at known concentrations and were then diluted as a result of mixing within the system before flowing through the instrument panels. At this point, the contaminant concentration flowing through the panels was an unknown. The beaker tests provide an indication of the concentration flowing through the online panels, much like a calibration curve.

The 3σ line represents an estimate for the limit of detection for a contamination event using the water quality surrogate specified. Theoretically, 99.96% of the data points under "normal" conditions will fall within three standard deviations and anything outside the 3σ limit will represent a nonrandom deviation in the signal. More important, the limit of detection is lower than the corresponding dangerous contaminant concentrations.

All four contaminants were detected at relatively low concentrations using the online equipment, whereas only three of the four were detected at low enough concentrations using the beaker tests and bench-top analytical equipment. The key difference is using the online turbidimeters to detect the arsenic compound. Online data suggest that the arsenic compound may be detected at concentrations below 15 mg/L or much closer to the concentration of concern than could be detected with conductivity (~27 mg/L).

Conductivity showed the most significant instrument response for arsenic. Cyanide and one of the pesticides also had measurable instrument responses for conductivity. Cyanide significantly changed all of the water quality parameters at relatively low concentrations. It was the only contaminant that significantly changed pH. One pesticide quickly affected the chlorine residual, as did cyanide. Both pesticides increased the TOC as would be expected, because each has a high fraction of organic carbon.

Results from this study indicate that routine water quality instruments can detect chemical disturbances in drinking water distribution systems at relatively low concentrations. Three of the four contaminants were detected well below concentrations of concern. The fourth was detected near the "life-threatening toxicity" concentration using online monitoring of turbidity.

In an effort to further reduce the limit of detection, potential may lie in applying statistical pattern recognition or artificial neural networks to the large data sets available from online monitors. Online TOC analysis has proven helpful in reducing the limit of detection for organic contaminants. If the cost of online TOC analyzers proves prohibitive for some utilities, an effort to quantify changes in other water quality parameters (e.g., ultraviolet absorbance) when organic contaminants are added to drinking water may offer a viable option.

The results of this research indicate that routine monitoring can be used in the distribution system to detect a range of contaminants in real time, potentially providing adequate early warning to take appropriate action and protect public health. In addition to detecting intentional threat contaminants in a distribution system, real-time monitoring offers the secondary benefit of providing valuable water quality data that may be key to detecting routine water quality compromises associated with line breaks, backflow events, treatment plant failures, or seasonal biofilm sloughing.

ACKNOWLEDGMENT

The opinions and conclusions in this article are the authors' alone and do not necessarily reflect those of the US Air Force or the federal government.

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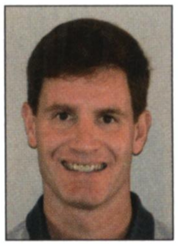

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FOOTNOTES

[1]Distribution monitoring panel, Hach Co., Loveland, Colo.

[2]Astro AutoTOC 1950plus process TOC analyzer, Hach Co., Loveland, Colo.

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