Security approaches against intentional contamination of water supply systems

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Abstract

The rational and sustainable use of water resources perhaps constitutes the most important topic of the XXI century: water undoubtedly symbolizes the blue gold of the future. Therefore it is very important, with reference to water supply systems, to have an effective prevention, control and mitigation of ordinary and extraordinary risks. With special reference to intentional contamination of water resources, this paper presents the problems that must be taken into account for a water system in order to develop an effective vulnerability assessment. The paper also presents a detailed picture of the preliminary tests of a wide-ranging experimental investigation to examine analytical methods for identification and quantification of contaminants. The experiments, even though until now only carried out for an irritating agent (Capsaicin), allowed us to define analytical test procedures in order to detect the various contaminants and to value subsequently the concentration. Other experiments are in progress with reference to Ricina which is one of the more dangerous pollutant agents.

Keywords: water supply systems, drinking water, intentional contamination, analytical test procedures, risk management.

1 Introduction

The water sector is critical from both a public health and economic standpoint. It consists of two basic components: water supply and wastewater collection and
treatment. Water supply systems play a major role in our society, granting water supply during the ordinary management. Therefore, it is fundamental for the water management agencies to assure the functionality of waterworks and to grant the quality standards of the stored and distributed water. Within water systems the rule of storage waterworks and of small water capacities has great relevance: particular care is necessary to prevent intentional water contamination.

The potential contamination of the water reserves in the storage waterworks is a problem that has a large relevance for the fear of terrorist attacks, both with chemical or biological or radiological agents (CBR Attack). The danger represented by the use of chemical and biological substances is determined by the circumstance that, from a technical point of view, these agents are easy to produce and relatively inexpensive, when compared to other conventional or nuclear weapons. Moreover, in the perspective of the control of the chemical agents, in spite of the good knowledge of the main physical mechanisms ruling their movement in water bodies, it is difficult in many cases to make an analytical or numerical assessment of contaminants spreading because of the complexity of the flow field (for example, in storage tanks having small dimension and/or in the presence of chemical input presenting strong mixing).

Therefore the constant control of the contamination of drinking water and the provision of decontamination programs to be executed in case of contamination, in order to prevent catastrophic effects, have a fundamental relevance.

2 Water systems vulnerability assessment

In general, there are four areas of primary concentration of threats to water infrastructures:

- physical damage or destruction of critical assets;
- actual or threatened contamination of the water supply;
- cyber attack on information management systems or other electronic systems;
- interruption of services from another infrastructure.

A suitable vulnerability assessment helps the evaluation of the water system’s overall susceptibility to potential threats (e.g. vandalism, insider sabotages, terrorist attacks, etc) and identifies corrective actions that can reduce or mitigate the risk of serious consequences [4].

Such an assessment for water systems must take into account the vulnerability of the water supplies (both ground and surface waters) and the transmission, treatment, storage and distribution systems. It also must consider risks posed to the surrounding community related to attacks on the water system.

Therefore an effective vulnerability assessment serves as a guide to the water utility by providing a plan to mitigate the risks and provides a framework for developing risk reduction options and for estimating associated costs.
The basic elements of vulnerability assessments are:

- characterization of the water system (defining the highest priority services);
- determination of critical facilities, processes and assets of the water system, assessing also the dependence on other infrastructures (e.g., electricity, transportation, other water utilities) and the malevolent acts that could result in undesired consequences (physical damages, contamination of water, intentional release of stored chemicals, interruption of electricity or other infrastructure interdependencies);
- identification and prioritization of adverse consequences to avoid. Factors to be considered may include: magnitude of service disruption; economic impact (replacement and installation costs for damaged critical assets or losses due to service outage); number of illnesses or deaths resulting from an event; impact on public confidence in the water supply. Obviously risk reduction recommendations at the conclusion of the vulnerability assessment should aim to prevent or reduce these consequences;
- assessment of the likelihood of particular “attack scenarios”: this is a very difficult task as there is often insufficient information to determine the likelihood of a particular event with any degree of probability;
- evaluation of existing countermeasures: this step will aid in identification of the areas of greatest concern, and help to focus priorities for risk reduction;
- information gathered on threats, critical assets, water utility operations, consequences and existing countermeasures should be analyzed to determine the current level of risk. The utility should then determine whether current risks are acceptable or a prioritized plan for risk reduction should be developed. For example, the infrastructure risk analysis model (IRAM) can be used for complex, interconnected infrastructures (electric power generation and distribution, water distribution, etc.) [3]. Recommended actions should measurably reduce risks by reducing vulnerabilities and/or consequences; some actions can both reduce vulnerabilities and enhance day-to-day operation. Selection of specific risk reducing actions should be completed considering both short- and long-term costs.

Generally, strategies for reducing vulnerabilities fall into three broad categories:

- sound business practices: affect policies, procedures and training to improve the overall security-related culture at the drinking water facilities. For example, it is important to ensure quick communication capabilities between public health authorities and local enforcement and emergency responders;
- water system upgrades: include changes in operations, equipment processes and infrastructures itself in order to make the system fundamentally safer;
- security upgrades: improve capabilities for detection, delay or response.
3 Intentional contamination of water resources

With particular reference to intentional contamination of water resources, we must be afraid of:

- contamination of groundwater aquifers: these facilities are dispersed across the landscape and generally little protected. Better surveillance, use of locks on valves, entry points to inhibit intrusion and water testing would be immediate steps towards prevention;

- contamination of water transmission and distribution networks and storage facilities by chemical, biological or radiological agents (CBR attack). Even if the mortality or morbidity caused by such contamination was minimal, the psychological effect of a credible threat could be significant. There are several locations where the water supply systems could be effectively contaminated, but some remarks can be done:
  - the threat of contamination in storage facilities generally is considered limited, by the large volumes of water and thus dilution involved at that stage. Conventional wisdom holds that because of dilution effects, large quantities of contaminants would be required to pose health problems in the water supply. But this conjecture is poorly supported by research and experimental data. More careful analysis is needed in order to determine precisely what agents in what quantities pose a serious threat in a potable water supply system [4];
  - the effects of filtering and disinfection (chlorination) at the treatment plants could be neutralization agents for at least some contaminants;
  - a scenario of concern to many water districts is the potential for “backflow” contamination. Contaminating agents introduced by produced backflow could arrive in concentrations high enough to be harmful or even deadly, subject only to the effects of the residual levels of chlorine in the water. Such an attack could be targeted to specific populations, such as those in a government building (e.g., the U.S. Embassy in Rome) [2];
  - protection from attack on control systems need urgent attention. The manner in which data are transmitted between control points and Supervisory Control And Data Acquisition (SCADA) systems needs review to improve security and reduce the potential for hacking or disruption.

Therefore with particular reference to the intentional contamination of water resources, a number of near-terms actions to improve protection, response and recovery from terrorist attacks can be identified by water supply systems:

**Risk prevention**

- determining the base threats (CBR attack), considering these factors:
  - volume of water that needs to be protected;
  - organoleptic properties and toxicity of contaminants;
  - accessibility of contaminants;
• solubility of contaminants in the water and their behaviour;
• amount of each contaminant that must be taken into account for an attack;
• reaction of contaminants to chlorine and other disinfectants;

• implementing physical barriers and hardening water supply systems (electronic alarms, cameras, backflow preventers, remote controlled valves, etc).

Risk control
• preparing laboratories that are capable of detecting the various contaminants;
• defining standard sampling and analytical test procedures.

A research unit of University of Naples Federico II is working with particular reference to these problems [1]: in the next paragraph the first results of the laboratory tests carried out until now will be discussed.

Risk mitigation
• after initial detection, responding immediately while verifying afterwards (for example, enabling the complete drainage of the system);
• defining minimum water consumption demands in relation to various conditions;
• preparing alternative means for water supply (for example, portable chlorinators);
• defining techniques for water renovation after shut down;
• defining procedures for the depuration of water system.

Public notification, however, is very important. The public should be made aware of dangerous situations, focusing on specific instructions for water use (what is allowed and what is forbidden).

4 Standard sampling and analytical test procedures

Experimental tests have been carried out at the Laboratory of Pharmaceutical and Toxicological Chemistry of the Faculty of Pharmacy (University of Naples Federico II). The analysis aims to develop analytical methodologies to identify and quantify contamination threat, in order to define procedures and protocols which should be submitted to drinking water system agencies. The Response Guidelines should be economically sustainable and will support staff in the field or decision officials during management of a crisis. To this end, in the first part of the research analysis has been turned to develop a procedure protocol with reference to Capsaicin, an irritating agent (but not lethal in small doses for human health), for the preliminary identification of the contaminant and the consequent quantification of its concentration.

The main tasks analyzed in the experiments are listed below:

a) Contaminant identification. Many methodologies can be adopted for rapid field testing of the potentially contaminated water. The most common ones are based on:
biosensors: a Biological Early Warning System allows a constant monitoring of physical and chemical properties of water, so that contamination by toxic agents can be detected by means of the movement or the oxygenation of aquatic species (fishes, algae, mussels). For instance, US Army Center for Environment Health Research (USACEHR) uses as biosensor a freshwater fish (Lepomis Macrochirus), analyzing through special sensors ventilatory, coughs, ventilatory depth and body movement. Other biosensors are the Dynamic Daphnia Test, Mussel Monitor, Delayed Algal fluorescence, Luminescent Bacteria [5];

detect papers, which are special papers subjected to an almost instantaneous pigmentation when some chemical agents are present in the water. Anyway, they should be used by experienced users, given that other common substances (for example solvents, oils, fats, etc.) can cause a similar effect;

spot tests, which allow a visible and instantaneous chromatic change of the solution.

b) Contaminant quantification. It has been achieved by means of chromatography, in order to obtain the calibration curve of the contaminant.

c) Contaminant reaction with disinfectants. Italian laws prescribe a minimum concentration of chlorine in drinking water of 0.2 mg/l: if lower values are measured in a section of a drinking water system it must be determined whether these levels represent typical background or result from intentional contamination (for instance the tail of transient contaminant slug or a low-level contamination incident). This uncertainty in the source of the detected contaminant would likely lead to additional sampling and analysis to support the threat evaluation process [6].

As reported above, the Capsaicin contamination threat has been analyzed in the experiments. Capsaicin (C_{18}H_{27}NO_{3} – trans-8-methyl-N-vanillyl-6-nonenamide, see Figure 1) is a crystalline alkaloid derived from chilli (Capsicum annuum) with a molecular weight of 304.42. It was first synthesized in 1930, has no odour or flavour, but it is one of the most pungent compounds known, and it is able to stimulate the mucous membrane of the mouth and stomach, increasing the secretion of gastric juices. Moreover, Capsaicin is slightly soluble in water, but very soluble in alcohol, fats and oils.

Scientists have identified and isolated six naturally occurring members of the family and one synthetic compound, which is used as a reference gauge for determining the relative pungency of the others. The major capsaicinoids contained in the crystalline extract and their percentages are capsaicin (69%), dihydrocapsaicin (22%), and three minor related components: nordihydrocapsaicin (7%), homocapsaicin (1%) and homodihydrocapsaicin (1%).

The lethal toxic dose of capsaicin, measured in mg/kg of animal weight, ranges from 0.56-190 mg when administered intravenously; when consumed, LD_{50} ranges from 119-97 mg for a mouse, 161-148 mg for a rat, 120 mg for a
hamster. The most probable cause of death is presumed to be respiratory paralysis.

![Figure 1: Structure formula of Capsaicin.](image)

Spot tests have been adopted for a rapid detection of Capsaicin in water. After many non satisfactory attempts (Bromothymol blue, Bromophenol blue, Phenol red, Malachite green, Iron (III) chloride), good results have been obtained with Diazonium salts, which cause a chromatic change of the solution, ranging from violet to red as Capsaicin concentration varies.

Chromatography has been adopted to quantify the concentration of Capsaicin. Chromatography is a laboratory analytical technique with many applications, including separation, identification, purification and quantification of chemical compounds in complex mixtures. The most common chromatographic techniques are:

- Column chromatography, with packed columns usually containing a granular adsorbent or a granular support material coated with a thin layer of high-boiling solvent (partitioning liquid) or open-tubular columns containing a thin film or partitioning liquid on the column walls and having an opening so that gas can pass throw the column;
- Thin-layer chromatography, with the progressive absorption (by gravity or capillarity) of the components of the unknown sample on thin layers of adsorbents or on a special grade of paper rather than in columns.

In the analysis High Performance Liquid Chromatography (HPLC) has been adopted, in which the solvent passes through the column under pressure. After selecting a detector (the component that emits a response due to the eluting sample compound and subsequently signals a peak on the chromatogram), a separation assay must be developed. The parameters of this assay should give a clean peak of the known sample, which should have a reasonable retention time and should be well separated from extraneous peaks. Several parameters can be manipulated to alter the retention time of a compound (e.g. the temperature, the choice of column and mobile phase or the choice in flow rate). A chromatogram is characterized by several symmetrical peaks. The position of the peaks (and so the retention times) identifies each compound of the sample, while the area under the peak can be correlate to the concentration of the compound injected.

In the tests we used a solution of Capsaicin standard solved in methanol. HPLC analysis was performed at ambient temperature injecting 40 µl of methanolic solution in the HPLC apparatus (SunicomOy, U.S.A.) equipped with
UV/VIS detector, using a column C\textsubscript{18} Ultracarb 5µ ODS (20) 250 mm x 4.6 i.d. (Phenomenex, U.S.A.). An isocratic system of acetonitrile: water (70:30 v/v) was used as mobile phase with a flow of 1 ml/min setting the spectrophotometer at 281 nm. The Capsaicin peak shows a retention time of 8.2 minutes.

By way of example, Figure 2 shows the chromatogram of a solution of Capsaicin in methanol (V: 40 µl, C: 5 mg/10 ml).

![HPLC Chromatogram of Capsaicin in methanol](image)

Figure 2: HPLC Chromatogram of Capsaicin in methanol (V: 40 µl, C: 5 mg/10 ml): (a) Capsaicin, (b) dihydrocapsaicin.

Figure 2 shows two peaks: peak (a) represents Capsaicin, peak (b) represents dihydrocapsaicin. In the first series of tests, the correlation between the peak area and the volume of the compound injected has been investigated. A solution of 5 mg of Capsaicin in 10 ml of methanol has been adopted, injecting 5 samples at rising volume, and every test repeated three times, assuming the mean value of the recorded peak area. The main results of the tests (injected volume and peak area) are reported in Table 1.

<table>
<thead>
<tr>
<th>Test</th>
<th>Injected volume (µl)</th>
<th>Area (units \cdot 10^6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>st_1</td>
<td>10</td>
<td>1.57</td>
</tr>
<tr>
<td>st_2</td>
<td>20</td>
<td>3.80</td>
</tr>
<tr>
<td>st_3</td>
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<td>6.87</td>
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<tr>
<td>st_4</td>
<td>40</td>
<td>10.24</td>
</tr>
<tr>
<td>st_5</td>
<td>50</td>
<td>12.85</td>
</tr>
</tbody>
</table>

Similarly, Figure 3 reports the graph peak area vs injected volume and the corresponding best fit line.
Figure 3: Graph peak area vs injected volume.

Figure 4: Calibration curve of Capsaicin.

In the next task the calibration curve of Capsaicin has been derived, on the basis of five samples with concentration ranging from 0.83 mg/l to 2.50 mg/l. Every test has been repeated three times (with a standard deviation always less than 1%) and the main results are summarized in Table 2. Figure 4, moreover, shows experimental values and the corresponding calibration curve.

The calibration curve allows for calculation of the solubility of Capsaicin in water, which is estimated to be around 6%.
Concerning the reactivity of Capsaicin with chlorine, several tests have shown that no interaction happens when Capsaicin is dissolved in drinking water, and so no variation in disinfection by-product is produced.

5 Further analysis required

In actual fact, other experiments have been programmed with reference to Ricina that is one of the more dangerous pollutant agents, a draft of a toxin derived from seeds of common ricino, a plant that grows easy all over the world.

The goal of researchers is, therefore, to define an adequate program of identification and quantification of contaminants in water supply systems, which could be applied to a simplified installation at the Laboratory of the Hydraulic and Environmental Engineering Department at Naples University.

References