A NOVEL APPROACH FOR EARLY WARNING OF DRINKING WATER CONTAMINATION EVENTS

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1 INTRODUCTION

Quality and safety of drinking water is intensively guarded by water companies and authorities, but a 100% safeguard against accidental or intentional contamination is virtually impossible. In case of a public health threatening contamination event in the distribution network, early warning is essential. The relatively fast spreading of contaminants throughout the distribution system implies that the processing time of traditional sampling is often too long. Water companies are looking for ways to continuously monitor, either in-line or on-line, the quality and safety of water in their distribution networks. Such an early warning system is supplementary to the spot sampling and continuous monitoring of the treatment process. A sensor as part of an early warning system should be generic, it should alert on harmful contaminants and it should distinguish between accidents and normal quality fluctuations.

The research presented in this paper has been executed in the project ‘Aqua Vitaal: online sensor for the detection of drinking water incidents’. Aqua Vitaal is a consortium of knowledge institute RIVM (The Netherlands), research company Philips Research (The Netherlands), drinking water company Vitens (The Netherlands) and sensor developer Optiqua (Singapore and The Netherlands).

The assessment and validation of sensors for deployment in an early warning system is driven by the ability to detect concentration levels of contaminants down to threshold levels that do not pose short term public health effects. For many substances, standards for long term exposure (lifetime) are available, for instance the drinking-water guidelines of the World Health Organization (WHO) and the drinking-water standards of the European Union. However, specific guideline threshold values for acute exposure in case of an
incident are lacking. In the 3rd edition of the WHO Guidelines for Drinking-water Quality\(^1\) this need for emergency values is explicitly noted. On the basis of toxicological literature, short term exposure limits have been derived, denoted as Drinking water Alert Levels (DALs). In accordance with the method as used for deriving US Environmental Protection Agency (EPA) Acute Exposure Guideline Levels for air (AEGLs), the DALs have been derived for three health effect categories: ‘no adverse effects’, ‘serious effects’ and ‘lethal effects’.

The DALs are used in the evaluation of a new sensor platform based on a Mach Zehnder Interferometer (MZI) concept as developed by Optiqua (chapter 3). This sensor has been tested in laboratory batch experiments. The response to target contaminants for which DALs are derived is analyzed (chapter 4). Data interpretation software has been developed and applied to distinguish contamination events from ‘normal’ quality changing patterns (chapter 5). The data algorithm and its application to measured data will be discussed.

2 DERIVATION OF DRINKING WATER ALERT LEVELS

2.1 Background and definition

‘Alert levels’ as required for the Aqua Vitaal project, represent the range of concentrations in drinking-water that are relevant from a health-based point of view. To optimally meet this requirement, the templates as used for the Dutch Intervention Values (DIVs) and the US-EPA Acute Exposure Guideline Levels (AEGLs) for inhalation exposure are used\(^2\). These templates involve deriving estimates of the thresholds above which toxic effects of pre-defined severity can be expected upon single exposure. Thus the whole range of possible toxic effects for any chemical due to its presence in drinking-water is covered, from the first minor signs of exposure up to lethality. As with the DIVs and AEGLs, the Drinking water Alert Levels (DALs) indicate at which levels acute toxic effects in three pre-defined severity categories are to be expected. Similarly like the DIV and AEGL values, the DALs represent an estimate, as precise as possible, of the threshold for acute toxic effects of the specified category in humans. This notion of DALs being predicted thresholds applies in particular to the two highest pre-defined effect severity categories, DAL-2 and DAL-3. As with DIVs and AEGLs, for these two values assessment factors used in their derivation should not be higher than strictly necessary. Like the DIVs and AEGLs, these values are intended to be predictive rather than preventive. The lowest category (DAL-1) is bases on the concept of the Acute Reference Dose (ARfD). The ARfD was chosen here because it is accepted and well known\(^3\).

Deriving DALs requires a review of all available information on acute toxicity of a chemical via the drinking water route. Ideally, this yields an estimate of the threshold for humans, including sensitive subpopulations, for toxic effects in each of the three pre-defined severity categories. As is usual within toxicology, this threshold is expressed as the dose in mg/kg body weight. To convert this body dose to DALs as concentrations in drinking-water, scenarios are used covering single-day exposure (24 hours) via ingestion and showering (inhalation) for an adult and ingestion and bathing (dermal uptake) for a bottle-fed infant.

At present the methodology of DAL derivation as presented in this paper is not widely accepted. One programme where a similar approach already has been applied for drinking water, is the development of ‘Provisional Advisory Levels’ (PALs) for priority toxic
industrial chemicals, chemical warfare agents and pesticides in air and drinking-water, as carried out within US-EPA’s National Homeland Security Research Center (NHSRC).

The definition of DALs is as follows:

**DAL-1**: The DAL-1 is the estimated concentration in drinking-water that can be ingested over a period of 24 h or less without any appreciable health risk to the consumer on the basis of all known facts at the time of the evaluation. The DAL-1 is based on the concept of the ARfD (Acute Reference Dose), which has been developed for pesticides. As is the case for the ARfD, the DAL-1 is based on the most sensitive acute toxic effect for the chemical in question. All adverse effects are taken into account. Thus the critical effect (the adverse effect seen at the lowest dose) may occur in any organ: e.g. in the blood, immune system, nervous system, liver, kidneys or endocrine system. The DAL-1 is a preventive value, incorporating a larger safety margin than DAL-2 and DAL-3.

**DAL-2**: The DAL-2 is the estimated concentration in drinking-water that can be ingested over a period of 24 h above which serious, irreversible or other serious health effects could result among the general population (including all ages and sensitive subpopulations). Examples of severe or irreversible effects possibly occurring above DAL-2 include ocular damage, gastrointestinal irritation/bleeding, organ injury, clinically relevant haemolysis, ocular or dermal effects and pulmonary damage. If toxicity data are insufficient for a chemical, a DAL-2 can sometimes be estimated by a reduction of the respective DAL-3 (depending on the steepness of the dose-response curve).

As follows from the definitions, for concentrations above DAL-1 but below DAL-2 minor and reversible health effects are expected (headache, minor intestinal complaints).

**DAL-3**: The DAL-3 is the estimated concentration in drinking-water that can be ingested over a period of 24 h above which life-threatening health effects or lethality in the general population, including all ages and sensitive subpopulations, could occur.

### 2.2 Toxicological evaluation

For many chemicals only limited acute oral toxicity data are available, which impacts the derivability of DALs. Ideally, acute toxicity studies with multiple dose levels should be available from which No Observed Adverse Effect Levels (NOAELs) can be derived for DAL-1, -2 and -3 effects, respectively. However, such acute studies are available for relatively few chemicals. Such studies are only routinely carried out for pesticides that are acutely toxic. From these studies, relevant no-effect-levels for DAL-1 and DAL-2 effects can be selected. For many other chemicals however acute oral toxicity has been examined only for the endpoint of lethality. Mostly, this involves determination of the LD₅₀, the dose at which 50% of the animals die. Traditionally, this has been the acute toxicity study carried out routinely in chemical safety testing. In recent years more attention has been given to dose response for the various acute toxic effects a chemical may produce. When limitations exist in the database of information on acute toxicity, useful surrogate information may be derived from oral studies of longer duration (sub-acute, semi-chronic) carried out with the chemical in question. These studies sometimes provide relevant information concerning acute thresholds of toxicity or they can be used as a cap to delimit the range at which certain acute effects are unlikely to occur. Additionally, acute toxicity

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* The ARfD is intended as a preventive limit value to be used as a screening tool for possible health risk due to inadvertently high pesticide residues on individual food crops and as such, incorporates a relatively wide safety margin.
via other exposure routes than orally may have been studied more extensively. The results of these studies may be extrapolated to the oral route (see also Solecki et al.\(^3\)). Important toxicological effects used for the DAL-2 and DAL-3 derivation are:

- Cholinesterase inhibition
- Carcinogenicity
- Reproductive toxicity
- Lethality

The outcome of the evaluation of acute oral toxicity for animals or humans is the dose that can be used as Point Of Departure (POD) for the three pre-defined effect categories. This POD should quantify the threshold for the selected critical effect. The POD selected refers to the specific sample of healthy laboratory animals or the healthy human volunteers studied in the underlying experiment. For estimating the desired threshold for the entire human population, including potentially sensitive subpopulations, the POD has to be extrapolated to the latter population; this is done by dividing it by one or more assessment factors. This procedure is in agreement with the method used for DIVs and AEGLs. Separate assessment factors are applied for extrapolation from animals to humans (interspecies) and for extrapolation to sensitive (but not hyper susceptible) humans (intraspecies). Since the aim is to estimate thresholds for effects, assessment factors should not be higher than strictly needed. In agreement with guidelines for the derivation of DIVs, two extrapolation factors, each ranging from 1 to 10, are used for inter- and intraspecies extrapolation, respectively. As a default, a factor of 3 will be used. Higher or lower factors are used (case-by-case) depending on the available data. Lower factors than the default may be warranted based on considerations concerning inter/intraspecies differences in the mechanism of action for the chemical in question. Additional assessment factors may be included for extrapolation to a NOAEL when a NOAEL has not been identified (up to 10, depending on the steepness of the dose response curve), for the use of sub-acute/sub-chronic data (<1, with reservations, since it is not known how much lower than 1 may be justified) or for uncertainty in the database (up to 10). If factors move estimated thresholds to implausibly low levels when judged against other evidence from the available database, this indicates that lower factors are warranted. On the whole, the DAL-1, -2 and -3 derived for any compound should credibly reflect available dose response information for that compound, including a reasonable spacing between the estimated thresholds for the three effect categories.

### 2.3 Exposure scenarios

For the 24 hours exposure to drinking water three uptake routes are distinguished: drinking, showering (inhalation) and bathing (dermal exposure). These scenarios are summarized in Table 1. Because young infants, particularly bottle-fed infants, consume much more drinking-water on a body weight basis than adults, we use a different exposure scenario for this group. Thus, we calculate DALs from the relevant toxicity thresholds expressed as mg/kg body weight for:

- a 70 kg adult drinking 2 litres of water and showering for 10 minutes;
- a 4.5-month old infant of 6.75 kg drinking 1 litre of water and bathing once per exposure day.

Showering will only be included in the formula when it contributes \( \geq 20\% \) to the exposure of adults. For bathing the same figure is applied in the calculation of the exposure of infants.
Table 1 Exposure scenarios

<table>
<thead>
<tr>
<th></th>
<th>Drinking (oral exposure)</th>
<th>Showering (inhalation exposure)</th>
<th>Bathing (dermal exposure)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adult (70 kg)</td>
<td>2 litres per day</td>
<td>10 minutes with ventilation</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>volume of 1.5 m$^3$/hour</td>
<td></td>
</tr>
<tr>
<td>Infant (6.75 kg)</td>
<td>1 litre per day</td>
<td>-</td>
<td>0.346 litres making contact</td>
</tr>
<tr>
<td></td>
<td></td>
<td>with the skin</td>
<td></td>
</tr>
</tbody>
</table>

2.4 Results

In Figure 1 the DAL-values for four substances are presented. They represent three pesticides (aldicarb, azinphosmethyl, fenamiphos) and one toxic chemical (sodium cyanide). The values are given on a logarithmic scale for easy comparison between dose levels of different substances. As expected the DAL-values for adults are higher than for infants. In most cases DAL-1 values are more than a magnitude lower than DAL-2 or DAL-3 values which reflects the preventive nature of the underlying limit value for DAL-1, the ARfD. The DAL-values are typically in the order of magnitude of milligrams per liter. Long-term exposure values typically correspond to concentrations in the order of magnitude of micrograms per litre. Hence, acute health hazards typically correspond to concentrations approximately a factor 1,000 higher than long-term exposure limits. For sodium cyanide the toxicological information was insufficient to derive DAL-3 values.

![Figure 1 DAL-values for four target substances](image-url)

* This figure is based on a 0.1 cm layer of water around the exposed skin of a 4.5 month old infant with a body surface of 3460 cm$^2$. 
3 THE OPTIQUA SENSOR

3.1 Characteristics of the sensor

Optiqua has a generic optical sensor concept that measures minute refractive index changes in water flowing over the surface of the sensor. The Optiqua optical sensor meets four key requirements imposed by an early warning system: rapid detection, generic detection, high sensitivity and low-cost.

Firstly, the sensor’s fully continuous measurements allow for instant event detection. In this case an event is defined as an abnormal change in water quality that manifests itself as a change in the water refractive index in a predefined time window.

Secondly, the sensor is responsive to an extensive spectrum of possible contaminants and other substances. The Refractive Index (RI) is a useful generic indicator of water quality. RI is a physical quantity of every substance, defined by the speed of light through that substance, relative to the theoretical speed of light in a vacuum. Any substance, when dissolved in water, will change the refractive index of the water matrix. The change in refractive index is proportional to the concentration and the refractive index of the substance. Virtually all relevant substances have refractive indices that are clearly higher than water. As an example, Figure 2 depicts the concentration of lithium chloride in pure water and the resulting change in refractive index.

![Figure 2](image)

**Figure 2** Index of refractive increment of pure water as a function of the concentration of LiCl (in g per litre). Data taken from the Handbook of Chemistry and Physics.

As can be seen, the relationship between refractive index and concentration is linear. This linearity is maintained when a substance is dissolved in a water mixture containing various elements provided that there is no chemical interaction between the added substance and the elements already present in the initial water solution.

Thirdly, the sensor is highly sensitive. The refractive index as a generic quality indicator for drinking water has been proposed before. However, the sensitivity levels needed for
application in drinking water control have not been achieved with commercially available technologies. The Optiqua sensor accurately measures a minimal change in refractive index in the order of magnitude of $10^{-7}$ RI. Changes of RI in that order of magnitude typically correspond to detection limits of concentration levels in or under the single-digit milligrams-per-liter concentration range. In the example of lithium chloride, the Optiqua sensor has a detection limit that is a factor 1000 smaller than the refractive index of the lowest concentration reported in the Handbook of Chemistry and Physics. Therefore it is important to validate via spiking experiments that the linear relationship between concentration and refractive index still holds for the tested compounds in these low concentration experimental windows.

The practical sensitivity to detect events is not only driven by the detection limit of the sensor, but also by the natural variation present in drinking water. Therefore, in chapter 5 the response is analyzed in relation to a baseline of continuous measurement in regular drinking water flowing from the tap.

Finally, the sensor offers a low cost platform. The sensor is developed in a dipstick probe format (no moving parts) and does not require any reagents. The sensor is suitable for operation in a network at locations with limited or no direct supervision.

### 3.2 Sensor design

Optiqua’s sensor is based on an integrated optical version of the Mach-Zehnder Interferometer (MZI). The MZI works as an optical scale, measuring differences in refractive index as seen by the sensing arm versus the reference arm.

The basic layout of the MZI consists of an input channel wave-guide that splits up into two identical branches (see Figure 3). After a well-defined length, these two branches are combined again to form the output wave-guide. Light that enters the input wave-guide splits equally over the two branches and combines again at the output wave-guide. The wave-guides are so called buried wave-guides in which the light travelling through the wave-guide is shielded from the environment via a top cladding. By using etching techniques, the top cladding is locally removed at a well-defined position above the wave-guide in the sensing branch. In this so-called sensing window, the evanescent field of the light that travels through the under-lying channel wave-guide, extents into the environment above the sensor and becomes susceptible to changes in refractive index of the water sample on top of the sensor. The resulting change of the effective refractive index leads to a change of the speed of the light in the sensing branch and a change in the relative phase between light that has travelled through the sensing branch as compared to the reference branch. This change in relative phase leads to a change in the interference between light coming from the sensing and reference branch at the combining section and manifests itself as change in the output intensity of the MZI.

The patented Optiqua sensor is an adaptation of the basic MZI design to improve the overall performance in terms of sensitivity, robustness and temperature dependence. By incorporating a modulator section and utilizing a serrodyne modulation concept (see Heideman\(^7\)) an unambiguous phase determination can be performed using Fourier analysis. In addition this concept is robust against laser intensity variations. The integrated optical design with no moving parts further enhances the overall sensitivity and robustness.

The configuration with one sensing window results in a reading that is sensitive for temperature changes. This is explained by both the temperature sensitivity of the bulk refractive index of water and the materials of which the sensor is constructed. In the Optiqua MZI design, the temperature sensitivity is well predictable. Combing the sensor
with an independent temperature reading allows for effective compensation for temperature effects. For a more elaborate description of the technological principle, please refer to Heideman\textsuperscript{7} and Lambeck\textsuperscript{8}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure3.png}
\caption{Basic layout of the Optiqua MZI sensor}
\end{figure}

Changes in refractive index of the water sample on top of the sensor are measured by phase changes of the light propagating over the interaction window. The primary output signal of the sensor is the phase shift of light $\Delta \Phi_m$ (measured):

$$\Delta \Phi_m = \left(\frac{2\pi}{\lambda}\right) L_{\text{int}} \left(\frac{\partial n_{\text{eff}}}{\partial n_{\text{water}}}\right) \Delta n_{\text{water}} \text{ [radians]}$$

where $\lambda$ is the wavelength of the light in vacuum, $L_{\text{int}}$ is the interaction length of the sensing window, $\frac{\partial n_{\text{eff}}}{\partial n_{\text{water}}} \approx 0.21$ and indicates how sensitive the light travelling through the sensing window is for refractive index changes of the water, and $\Delta n_{\text{water}}$ is the refractive index change in the water flowing over the sensing window.

With $\lambda$=850nm and $L_{\text{int}}$=10mm and using equation (1) the change in refractive index of the water $\Delta n_{\text{water}}$ is given by:

$$\Delta n_{\text{water}} \approx 4 \times 10^{-4} \left(\frac{\Delta \Phi_m}{2\pi}\right)$$

\section{SPIKING EXPERIMENTS}

\subsection{Test setup}

The test setup was built around the Optiqua MZI sensor in combination with a flow-through cell (Figure 4). To prevent a surplus of waste, a relatively small volume (1 ml) of test medium was used to test for a change of refractive index. Milli-Q purified water was pumped over the sensor using a micro dialysis syringe pump with a flow rate of 100 $\mu$l/minute. The volume of the sample loop was 100 $\mu$l. It was loaded using a syringe containing a total volume of 1 ml of the spiked solution. Loading the sample loop with a tenfold higher volume guarantees that the final concentration in the sample loop corresponds to the actual concentration of the prepared spiked test solution. The internal volume of the flow container was 40 $\mu$l.
The total duration of one test run was 6 minutes. During the first three minutes Milli-Q water was pumped over the sensor, thereafter the 6-way sample injector was automatically switched to the sample loop that was pre-loaded with the spiked test solution. After the plug of spiked test solution had passed the flow-cell (approx. 1 minute), purified Milli-Q water flushed again through the flow-cell for another 2 minutes. At the end of the test cycle the 6-way valve was switched to the LOAD position for running the next test in the series.

4.2 Test compounds and preparation of test solutions

Because the tested compounds are highly toxic, the measurements were performed in a BSL2 cabinet for safety reasons. Room temperature was maintained at 22°C. Chemical characteristics of the test compounds are given in Table 2; the compounds are the same as for the derivation of DAL values.

<table>
<thead>
<tr>
<th>Chemical</th>
<th>CAS number</th>
<th>Water solubility at 25°C in mg/l</th>
<th>Log K_{ow}</th>
<th>Concentration to be tested (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldicarb</td>
<td>116-06-3</td>
<td>6030</td>
<td>1.13</td>
<td>0-1.56-3.125-6.25-12.5-25</td>
</tr>
<tr>
<td>Azinphos-methyl</td>
<td>86-50-0</td>
<td>2604</td>
<td>0.78</td>
<td>0-1.56-3.125-6.25-12.5-25</td>
</tr>
<tr>
<td>Fenamiphos</td>
<td>22224-92-6</td>
<td>20.47</td>
<td>3.23</td>
<td>0-0.625-1.25-2.5-5-10-20</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>143-33-9</td>
<td>1000000</td>
<td>-1.69</td>
<td>0-1.95-3.91-7.81-15.63-31.25-62.5-125-250-500-1000</td>
</tr>
</tbody>
</table>

1. prepared in Milli-Q purified water

Stock solutions were prepared in Milli-Q water. Test concentrations were prepared at least 24 hours before actual measurement to acclimatize to room temperature. Measurements were done from low to high concentrations. The prepared dilutions were gently homogenized shortly before measurement. The samples to fill the sample loop were drawn about 1 cm under the fluid surface. If the test solutions were measured at different days, they were stored in the dark and at room temperature in between.

The spike test solutions were prepared as follows:
Aldicarb: 6.1 mg was weighted and dissolved in 100 ml Milli-Q water. From this stock the dilutions were prepared with Milli-Q water.

Azinfos-methyl: 5.1 mg was weighted and after 5 minutes of ultra-sonification the chemical compound was completely dissolved in 100 ml Milli-Q water. From this stock the dilutions were prepared with Milli-Q water.

Fenamiphos: 4 mg was weighted and after 2 minutes of ultra-sonification the chemical compound was completely dissolved in 200 ml Milli-Q water. The stock solution had a light yellow color. The color was less profound after 24 hours. This may indicate breakdown of the chemical.

Sodium cyanide: 40 mg was weighted and dissolved in 20 ml Milli-Q water. From this stock the dilutions were prepared with Milli-Q water.

4.3 Data evaluation and results

In Figure 5 the sensor output is given for the complete 6 minutes test runs with different concentrations of Azinphos-methyl. The first 3 minutes of continuous flowing Milli-Q water provide a stable sensor response. The insertion of the spiked sample at levels at 180 seconds leads to a sensor response that is clearly visible in the graph. Higher concentrations of the spiked solution result into a higher response of the sensor. The step change was quantified by taking the value of the plateau of the sensor response caused by the spiked test sample and subtract the value of the baseline before the spike injection.

![Spiking experiments Azinphos-methyl](image)

**Figure 5** Sensor response during azinphos-methyl spiking experiment

Figure 6 depicts the different concentrations included in the experiment and the related step change of the events in Refractive Index (RI) units.

A regression was run to determine the calibration factor:

\[ \Delta R_I = \beta C \]  

with C the concentration of the spiked test solution in mg/l. The linear regression model provides a strong fit with the experimental results (R² of 99%). The slope \( \beta \) of the regression line can be interpreted as the calibration factor of the sensor response for each mg of the target solution in 1 liter of reference water. For azinphos-methyl the obtained calibration factor is \( 1.54 \times 10^{-6} \text{ (mg/l)}^{-1} \). We followed the same methodology for the other
tested compounds. Table 3 provides an overview of the experimentally derived calibration factors for each of the tested compounds.

Table 3  Calibration factors and limit of detections

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Calibration factor [(\text{ARI}/(\text{mg/l}))]</th>
<th>Limit of detection [mg/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldicarb</td>
<td>(2.0 \times 10^{-7})</td>
<td>1.0</td>
</tr>
<tr>
<td>Azinphos-methyl</td>
<td>(1.5 \times 10^{-6})</td>
<td>0.2</td>
</tr>
<tr>
<td>Fenamifos</td>
<td>(6.5 \times 10^{-7})</td>
<td>0.3</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>(1.2 \times 10^{-7})</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Figure 6  Calibration curve azinphos-methyl spiking experiment

Figure 7 depicts the detection limit for the different compounds and compares to the DAL-values. The detection limit was clearly below the DAL-2 values for all these compounds. For azinphos-methyl and sodium cyanide the detection limit was below the DAL-1 value. The results indicate that the Optiqua sensor is well suited to prevent major health damage from a contamination event by detecting concentrations below the levels of serious and irreversible health damage (DAL-2).
5 DATA ANALYSIS

5.1 Background

The data collected by the generic sensor needs to be interpreted to distinguish contamination events from ‘normal’ water quality changing patterns. The ‘normal’ quality changes were collected by monitoring the tap water in an office building in The Netherlands and the events by means of the spiking experiments in the lab. The direct observation of the data indicated that the natural variations tend to be smoother than the contamination which generates a sudden change in the sensor response. Although this might not be true if the contamination happens very far from the sensor location, we began developing the event detection algorithms by exploiting this key difference.

From the algorithm perspective, the sensor data are simply a series of digital data. The event detection problem can then be expressed as the detection of a sudden change in a digital data series. This is a well investigated topic in the signal processing community since it can have a multiplicity of applications ranging from modeling of biological phenomena to enhancing picture quality in TV. Quite recently, event detection algorithms have been used to detect contamination events in drinking water distribution systems\(^9\). The authors present an extensive investigation and provide a rich reference. They apply event detection algorithms to standard water quality indicators such as pH, free chlorine, total organic carbon and specific conductivity. They design event detection algorithms to interpret these sensor readings and provide a way of detecting the contamination event. In this work, we do not apply the detection algorithms to the data of a conventional sensor, but on the data obtained from the new sensor presented in chapter 3 which reacts to a broad spectrum of contaminants. At the same time, this also means that the sensor will be more sensitive to natural variations of water characteristics, thus requiring a proper signal processing stage to distinguish between the contamination events and the natural variations.

We propose to use almost conventional edge detection algorithms\(^10\), after having conditioned the sensor signal to improve the quality of the sensor data. The signal conditioning includes a temperature compensation algorithm.
5.2 Temperature compensation

Since the first sensor data became available, it has been evident that there was a close relationship between the temperature variations of the water and the sensor response. As we have access to the temperature measurement we can make use of this information and properly compensate for the changes due to temperature variations. By compensating the effects of the temperature, we also limit the detection of events that generates a temperature change. In case of a contamination, the volume of the contaminant is going to be significantly smaller than the volume of the water in the pipes. Therefore, we can reasonably assume that the thermal mass of the contaminant is much smaller than the thermal mass of the water and that compensating for the temperature variations does not remove the contamination events.

Abbate et al\textsuperscript{11} propose a model for the dependency of the water refractive index on temperature. The model is richer than we need in this context, thus we truncate the model at the first linear terms. With \( n(T) \) the water refractive index, \( T \) the temperature, \( T_0 \) a reference temperature and \( B \) a given constant, we obtain:

\[
n(T) = n(T_0) + B \times (T - T_0) .
\]  \( 4 \)

They estimate the factor \( B \) on basis of measurements and derived it as a general constant for large temperature variations. However, we are interested in a much smaller temperature scale and we also need to take into account the temperature dependency of the sensor itself. We propose to nevertheless apply the model in (4), but to locally estimate \( B \) and remove the temperature variations from the water refractive index. With this aim, we select a window of data of size \( W \) and for each time instant \( k \) we collect \( W \) samples of the water refractive index to build the vector

\[
\mathbf{n}(k) = \begin{bmatrix} n(k-W+1) & n(k-W+2) & \cdots & n(k) \end{bmatrix}^T
\]  \( 5 \)

where \( \begin{bmatrix} \cdot \end{bmatrix}^T \) indicates the transpose. With a similar procedure we define the temperature vector as

\[
\mathbf{T}(k) = \begin{bmatrix} T(k-W+1) & T(k-W+2) & \cdots & T(k) \end{bmatrix}^T .
\]  \( 6 \)

We then apply a conventional linear regression approach to estimate the linear factor as

\[
\hat{B}(k) = \frac{\mathbf{n}^T(k) \bar{\mathbf{T}}(k)}{\bar{\mathbf{T}}^T(k) \bar{\mathbf{T}}(k)} ,
\]  \( 7 \)

where \( \bar{\mathbf{T}}(k) \) is the zero-mean version normalization of \( \mathbf{T}(k) \) of (7). Equation (7) can be then used to obtain the temperature compensated water refractive index vector as

\[
\tilde{\mathbf{n}}(k) = \mathbf{n}(k) - \hat{B}(k) \mathbf{T}(k) .
\]  \( 8 \)

Equation (7) shows that the compensated water refractive index \( \tilde{\mathbf{n}}(k) \) is obtained by subtracting a properly scaled version of the temperature, i.e. \( \hat{B}(k) \mathbf{T}(k) \), from the original
water refractive index. Event detection algorithms can be applied to the compensated water refractive index \( \tilde{n}(k) \).

As an example, we depict in Figure 8 the change in refractive index, the temperature as collected during an experiment and the resulting signal after temperature compensation. The change in refractive index \( \Delta n \) is composed of a default index difference \( \Delta n_0 \) between sensing and reference branch and varying term \( \Delta n_{\text{water}} \) that represents the change in water refractive index: \( \Delta n = \Delta n_0 + \Delta n_{\text{water}} \). The correlation between phase and temperature can be clearly noticed. The resulting \( \Delta n \) of the temperature compensation algorithm shows ‘white noise’.

![Figure 8](image)

**Figure 8.** Variations in the change in refractive index \( \Delta n \) and temperature as a function of time. Note that the scale in y-axis is reduced by two orders of magnitude.

### 5.3 Event detection algorithm

We propose to use an event detection algorithm similar to the one presented by Smith\(^{12}\), the so called edge detector. The basic idea is to compare the average value of the sensor output estimated in two separated windows. The difference between the two averages is the decision variable that is then compared to a threshold. The basic idea is illustrated in Figure 9 where we indicate with \( B \) the backward window, with \( F \) the forward window and with \( D \) a delay window. The averaged value in the backward and forward windows are indicated with \( m_B \) and \( m_F \), respectively. The variable \( S \) is the standard deviation.

![Diagram](image)
Figure 9 *Graphic description of the proposed edge detector*

The output of the event detector is the decision variable \( y(i) \). We estimate the averages as

\[
m_{B,F} = \frac{1}{\# B,F} \sum_{k \in B,F} x(k)
\]

and the variance as

\[
S^2_{B,F} = \frac{1}{\# B,F - 1} \sum_{k \in B,F} (x(k) - m_{B,F})^2,
\]

where the symbol \( \# \) indicates the cardinality of the set, i.e. the size in sample of the windows. The decision variable is then

\[
y(i) = \frac{m_F - m_B}{S}.
\]

The approach proposed by Smith\(^{12}\) suggests calculating the variance \( S^2 \) in such a way to limit the impact of the edge size on the estimation of the variance itself. We do not directly apply the solution presented by Smith. Actually, we propose to apply equation (9)-(11) twice on the same set of data. This means that the output \( y(i) \) of (11) is used as the input \( x(k) \) of (9) and (10). The reason for this choice is related to the characteristics of the background noise. In the data collected via experiments, there were some cases in which the variations in the background water refractive index were quite sharp. If an event happens during these sharp variations, the detection algorithm could not detect it. By applying twice (9)-(11), we could identify also those cases, thus improving the performance of the detection algorithms.

5.4 Simulation results

We consider the water refractive index collected by the sensor in a real environment to evaluate the performance of the event detection algorithm. The data were collected by monitoring the tap water in an office building in the Netherlands. The events were added via software. The shape of the events has been determined by the spiking experiments with the contaminants, see chapter 4, and the amplitude has been properly normalized to a DAL level. The performance is showed in terms of receiver operator characteristic (ROC) curves that plot the true positive rate (TP) versus the false positive rate (FP)\(^{12}\). The ROC curve shows how the trade-off between the true positives and the false positives changes depending on the threshold. Each point of the ROC curve is obtained for a fixed threshold. For instance, assume that the decision variable is strictly larger than zero and that there is no noise. Then, if we set the threshold value to zero, the algorithm must detect all events and it must return a true positive rate of 1. For the same threshold value, the false positive rate is also equal to 1 because all false positives are detected. By increasing the threshold the algorithm will return a different balance between true positive and false positives.

We consider the event obtained with aldicarb scaled down to a concentration of 3.6 mg/L, which corresponds to a DAL-2 level for adults, see Figure 1. The algorithm does not need to know which contaminant generated the event; it is designed to detect abrupt changes.
The amplitude of these changes is determined by the experimental results. The ROCs are obtained by software simulations which randomly select a chunk of sensor data, sum up an event, run the algorithm and collect the true positives and false positives. This procedure is iterated many times (about 10000 times). Figure 10 shows a zoomed version of the ROC curves for aldicarb DAL-2 when the edge detector is applied once and twice. The performance is good: For a 1% of false positive all methods provide more than 98% of true positives. We can also observe the effect of the temperature compensation algorithm as we switch it ON or OFF. It appears that the temperature compensation provides a significant improvement. It also appears that the temperature compensation boost the performance of the single edge detector to the same performance as the double edge detector.

![Figure 10](image)

**Figure 10** ROC curve, aldicarb DAL-2 for adults (3.6 mg/L). B=F=20. D=5. The units of B,F and D are in samples and each sample corresponds to 1s. Four cases are shown: 1 time T:OFF, corresponds to one application of the edge detector with the temperature compensation algorithm switched OFF.

To better appreciate the differences between the application of the edge detector once or twice, we run the same simulations but with a much lower concentration of 0.6 mg/L corresponding to a DAL-2 for an infant. This means that the events added to the simulation are six times smaller than the one used in Figure 10. The results are shown in Figure 11 and they are worse than those in Figure 10, as expected.
However, in this case we can clearly appreciate the improvement of applying the edge detector twice while in Figure 10 it seems that the temperature compensation and the application of the edge detector twice provided the same improvement. We can also notice the different scale and the reduced performance due to the much smaller events.

6 CONCLUSIONS

Based on the template of Acute Exposure Guidelines Levels it is feasible to derive short time exposure levels (Drinking water Alert Levels) for drinking water contaminants. In accordance with the AEGLs three severity categories for public health effects can be distinguished (DAL-1, DAL-2 and DAL-3). DAL values can be derived for adults and infants separately, with reference to the differences in drinking water uptake on a body weight basis.

In order to evaluate the short time exposure to drinking water contaminants the Drinking water Alert Levels are useful. Comparison of these alert levels with the detection limit of Optiqua’s Mach Zehnder interferometer shows that for the selected substances detection is possible in a concentration range where no severe health effects are expected.

Temperature variations have a large impact on the sensor response. With a model of temperature dependence of the refractive index an algorithm for temperature compensation has been applied.

Application of the edge detecting algorithm on time series of natural drinking water quality, superimposed with spiking signals, shows that contamination events can be detected. These results suggest that the Optiqua sensor can be used as an early warning monitor in a drinking water network to detect harmful contaminants.

7 FURTHER RESEARCH
The promising results of the Aqua Vitaal project are now followed up with further development and testing. There are four areas of further research that are now actively worked on:

- **Event simulation in drinking water instead of MQ water**
  Vitens is working together with Optiqua to simulate contamination events in a continuous flow test system using regular drinking water as running medium. In addition to the Optiqua sensor, the test system contains a spectrum of other sensors to monitor regular process parameters (pH, conductivity). Vitens and Optiqua are deriving detection limits for a wide range of substances, and are validating and refining calibration factors and detection limits in real drinking water for the substances investigated in this paper.

- **Analysis of normal water quality fluctuation in a real distribution network**
  The fundamental driver for practical effectiveness of an early warning system is the ability to discriminate the signal of an event from the background signal. Vitens and PUB in Singapore are currently collecting continuous data on various strategic locations in the network, using the Optiqua sensor. Long time series of continuous data at different locations will provide the opportunity to validate the robustness of the sensor in different water sources against a background of natural variation including seasonal patterns. Also the effect of a slowly varying contamination will be investigated.

- **Duration testing in a real distribution network**
  Optiqua will use the results from the testing at the Vitens and PUB locations to evaluate the durability and long-term performance of the sensor.

- **Analysis of locations for sensor placement**
  An important area of research is into the question on where to locate sensors within the distribution grid. A dense network of sensors in the distribution grid would have the benefit of detection of a contamination close to the source. Contamination of a relatively large area above the DAL values would mean that at the source the concentrations are much higher due to the effect of mixing and diluting. The location of the sensor is likely to have an important impact on the performance of the sensor. Best locations for optimal benefits will depend on characteristics of the network (e.g. number of crossing pipes, flow rate, numbers of end-points).
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