Deliverable 8.4

Methodological guide for end users

SecurEau methodological achievements which could be used by stakeholders

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GLOSSARY

LoD	Limit of detection
DNA	deoxyribonucleic acid
DVC	direct viable count
FISH	fluorescence *in situ* hybridisation
PCR	polymerase chain reaction
PNA	peptide nucleic acid
qPCR	real-time PCR

Introduction

The importance of water and of water infrastructures to human health and to the running of our economy makes water systems likely targets for terrorism and CBRN (chemical, biological and radionuclide) contamination. Reducing the vulnerability of drinking water systems to deliberate attacks is one of the main security challenges. Rapidly restoring the functionality of drinking water infrastructures (catchment areas, raw water transfer systems, treatment facilities, treated water reservoirs and distribution networks), and the access to safe drinking water represents another major concern for regulatory agencies and water utilities. Indeed, the damage resulting from impairment of drinking water services would seriously impact the quality of life of many people not only by directly harming them but also making water systems unusable for a long period of time with a risk of societal disorder (similar situation as with any accidental contamination events or natural disasters).

Such accidental or malevolent contamination events determine a crisis situation, which affects or is likely to affect a water utility or its provided services, and require more than the usual means of operation and / or organisational structures to deal with it. The future ISO 11830 standard on crisis management will describe the fundamentals of a crisis management system (ISO, 2011). ISO 11830 will provide general guidance on how a crisis should be dealt with ("crisis phase"), on how to re-establish services (post-crisis phase) and on the best way to draw conclusions and revise procedures for future events. As shown in Figure 1, a large number of "preventive" actions have to be taken / implemented on a routine basis before the crisis, and recovery activities can start during the crisis phase. At the same time, specific scenarios for supplying potable waters (distribution of bottled waters, water tankers, emergency water treatment mobile systems, and so on) also have to be developed (Loo et al. 2012).

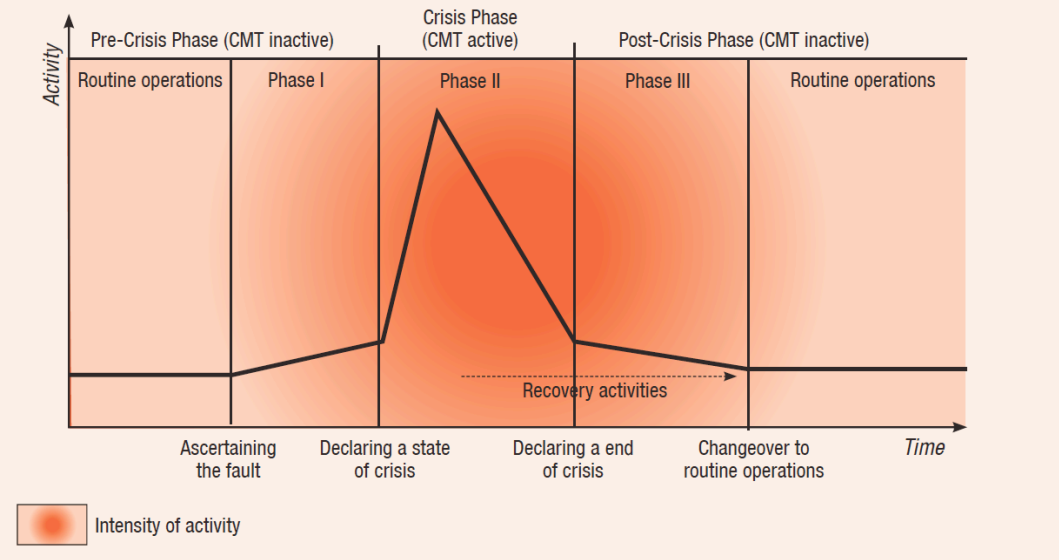

Figure 1: Management activities over the course of a crisis (ISO 2011).

In this context, SecurEau (a European project for restoring distribution systems after deliberate CBRN attacks involving 12 partners from 6 countries) has defined four research and development objectives:

(1) tools for detecting water quality changes by combining generic non-specific and specific sensors for measuring unexpected / abnormal signal variations (and to be integrated in an early warning system); methods for identifying the best locations for sensors for full coverage monitoring;

(2) methods for rapidly identifying the source(s) of intentional contamination thanks to accurate procedures and software;

(3) multi-step strategies for cleaning distribution systems: pipe walls / biofilms / deposits and waste (water bulk and deposits extracted from the network).

(4) analytical methods for confirming cleaning procedure efficiency.

The Deliverable 8.4 "Methodological guide for end users" aims to highlight, along with Deliverable 6.8 (*Decision tool Suitable for Assessment to Approval of Successful decontamination*), some of the methods

selected in SecurEau for each phase defined above, i.e. pre-crisis, crisis and post-crisis. Their main interests or novelty and their limits are also discussed hereafter.

During the pre-crisis phase, besides daily routine tasks and usual network management procedures, specific devices (e.g., reliable and robust sensors) should be dedicated to monitoring water quality. Any abnormal change in water quality (unexpected changes, taking into account historical data) should raise an alarm and determine the course of actions to be undertaken. Traditionally, an "abnormal situation" corresponds to a change three times greater than the standard deviation of the baseline, for the parameters measured (as usually done in analytical chemistry).

Insofar as specific sensors of any potential contaminants could not be developed, the aim of SecurEau was to develop sensors taking into consideration "classical" parameters for monitoring water quality, as well as some specific parameters such as radionuclides. Sensor positioning was optimised by modelling, taking account of both the hydraulics of the network and specific assumptions made by operators (protection of the population at risk, economic situation to minimise the number of sensors, and so on).

Besides, installation of dormant sentinel coupons was considered. The coupons would be installed in the water supply system and get colonised by biofilms and deposits just like pipe walls. They would then be used to validate the cleaning procedures applied throughout the network during the crisis phase but also during "normal" operation of the network (pre-crisis).

During the crisis, actions should be taken in order to identify the contaminant, the contaminated area and the source(s) of contamination. Obviously, decontamination strategies are needed for both the water bulk and the pipe walls, which represent a challenging objective. In order to bring to an end to the crisis phase, analytical methods - again adapted to pipe wall analysis – should be carried out.

Deliverable 8.4 gathers some of the key tools developed for pre-crisis and crisis phases. Obviously, it does not cover the complete range of situations which could occur as a result of malevolent contamination events. Moreover, we do not aim to provide here a handbook for end users or laboratory technicians, but a general framework for a new toolbox to be used in emergency situations.

1. Pre-Crisis Phase

The Pre-Crisis Phase is carried out with routine operations and normal management. It includes, for example, decisions on the structure of the crisis management team and training for the designated personnel (ISO, 2011)

The research under the SecurEau project has been conducted in three directions, being relevant to the pre-crisis phase:

- development of sensors, both specific and non specific. Respectively, they measure the radionuclide content in water and, thanks to the determination of traditional parameters (conductivity, chlorine, pressure, etc.), they may indicate any abrupt change in water quality; other sensors (OptiQuad, FS-900 and SkidSens) are able to monitor the deposits on the surface of the pipes.
- use of sentinel coupons. Sentinel coupons of polymeric materials (HDPE, EDPME, etc.) are to be installed in water distribution systems for deposits and biofilms to form on their inner surface. The extraction and analysis of these coupons, carried out without the water flow being interrupted, allow the concentration of contaminants associated with deposits to be estimated. At a later stage during the crisis phase, such coupons allow contaminant accumulation and cleaning procedure efficiency to be measured.
- optimal positioning of the sensors and coupons thanks to new models taking into account economic, strategic and technical assumptions made by the operators.

1.1 Sensors and sentinel coupons

Fourteen commercial non-specific sensors have been evaluated regarding 12 technical criteria (Deliverable 2.1.1, version 03, June 2012 and Deliverable 6.4, version 2, June 2012). Six of them were selected and their strengths and weaknesses are described below. Among the six sensors, three are devoted to water analysis (free chlorine, pressure, temperature, conductivity, organic matter, turbidity and radionuclides) while the other three are used for assessing the accumulation of deposits on the surface of the pipes (Table 1).

Sensors devoted to water analysis have two purposes. The first is to rapidly detect any abnormal changes in water quality, and the second is to provide assistance to the operator to manage the drinking water network under normal operational conditions.

Sentinel coupons have three main objectives: (i) characterise deposits on the coupon, (ii) identify the adsorbed contaminants and (iii) validate the cleaning and / or decontamination procedures.

These devices (sensors and sentinel coupons) should be installed during the pre-crisis phase in drinking water distribution networks. Nevertheless, the drawback is that it creates more access points to the distribution system, and hence could weaken it (i.e. more points that can be tampered with).

Table 1: General information on water quality sensors and on deposit accumulation devices

Sensor	Manufacturer	Status	Price in € (*)	Maintenance	Application
Kapta™ 3000 AC4	Endetec (http://www.endetec.com/en/)	Commercial	3,500	Low (every 12 months). Probe and Communication	Water
Kapta™ 3000 OT3	Endetec (http://www.endetec.com/en/)	Prototype	Not defined	Low (every 12 months)	Water
Kapta™ 3000 RAD1	Endetec & CEA	Prototype	Not defined		Water
OptiQuad	Krohne Optosens GmbH	Prototype	Approx. 30,000	Not self washing. Low (every 12 months)	Surface
FS-900	NeoSens S.A.	Commercial	Approx. 5,000	Not necessary	Surface
SkidSens	NeoSens S.A.	Commercial	Approx. 2,000	Not necessary	Surface
MSS	Enkrott Quimica	Prototype	3,000-4,000	Low. Does not need washing	Surface
Sentinel coupons	Home made	Not commercialised	Approx. 1,000 (**)	None	Surface

(*) Prices are approximate for 2012 and are subject to change. Prices are for the sensors only, and do not include the cost of installation and consumables.
(**) Price is for a device with 5 holders of 6 coupons. It is approximate for 2012 and is subject to change.

The development and design of Kapta™ 3000 AC4, Kapta™ 3000 OT3 and Kapta™ 3000 RAD1 were carried out during the SecurEau project with technical specifications meant for allowing rapid installation in drinking water networks.

The development of MSS (Mechatronic Surface Sensor) was mainly carried out during the SAFER project (FP5 project EVK1-CT-2002-00108). Its design and adaptation to drinking water networks were carried out during the SecurEau project.

The other three sensors (OptiQuad, FS-900 and SkidSens) are prototypes or commercial products elaborated by private companies outside of the framework of the SecurEau project.

1.1.1 Non-specific sensors (Kapta 3000 AC4 and Kapta 3000 OT3)

The Kapta™ 3000 AC4 sensor measures free chlorine, pressure, temperature and conductivity (Deliverable 2.1.2, version 2, June 2012) (Table 2). In the context of SecurEau, two European drinking water systems were equipped with 80 sensors each which measure water quality online and send results every two hours to operational control centres.

Table 2: Kapta™ 3000 AC4 specifications (product finalised, available on the market)

Parameter	Range	Resolution	Fidelity	Maintenance	Precision	Response time
Active chlorine	0–2.5 mg/L	0.01	± 5%	The multi-parameter probe should be replaced once a year.	± 10%	<30 s
Conductivity (µS/cm)	100–1,000	1	± 5%		± 5%	
Pressure	1–10 bars	1 mbar	± 2%		± 10%	
Temperature	0–40°C	0.1°C	± 5%		± 5%	<15 s/°C

The Kapta™ 3000 OT3 sensor, thanks to two LEDs, measures transmission at two wavelengths: 254 nm for organic matter and 625 nm for turbidity measurement. Two optic paths are used for each wavelength in order to compensate for fouling (Table 3). Two European drinking water systems are currently equipped

with 40 sensors each which measure water quality online and send results every two hours to operational control centres. The Kapta 3000 OT3 probe is currently under development and all its specifications are being evaluated.

Figure 2 : Kapta™ 3000 AC4 (left) and Kapta™ 3000 OT3 (right) (Courtesy from VERI)

Table 3: Kapta™ 3000 OT3 specifications (prototype, not available on the market)

Parameter	Range	Resolution	Fidelity	Maintenance	Precision	Response time
Organic matter TOC equivalent	0.1-10 mgC/L	0.1 mgC/L	± 5%	The multi-parameter probe should be replaced once a year.	± 10%	<6 s
UV absorbance (254 nm)	0.01-0.3 AU/cm	0.01 UA/cm	± 5%		± 10%	<6 s
Turbidity equivalent	2-50 NTU	1 NTU	*Not evaluated*		*Not evaluated*	<6 s

Both sensors are designed to be easily and quickly installed in drinking water distribution networks. The number of sensors to be installed and their optimal positioning is discussed in paragraph 1.2.

1.1.2 Specific sensor (Kapta™ 3000 RAD1)

The design procedure and prototype development of a new type of online sensors for measurement of traces of gamma emitters in solution are described in Deliverable 2.1.3 (version 3, June 2012) and shown in Figure 3.

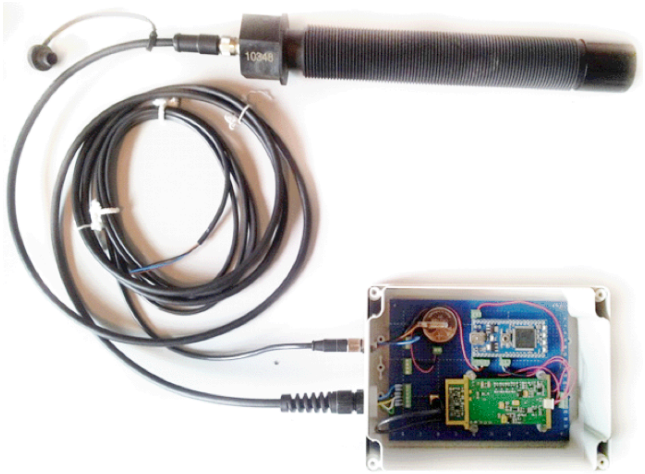

Figure 3: Picture of the Kapta™ 3000 RAD1 (Courtesy from CEA List)

Table 4: Kapta™ 3000 RAD1 specifications (prototype, not available on the market)

Radionuclide	LoD	Precision	Maintenance	Response time
241 Am	984		Not evaluated	Not evaluated
137 Cs	492		Not evaluated	Not evaluated
60 Co	25		Not evaluated	Not evaluated

The detection limits (Bq/kg, measurement for 10 seconds) with the NaI(Tl) detector are presented in the Table 4.

Using an integration time of 10 s, the sensor allows an alarm to be raised before the maximum permitted levels of radioactive ^{60}Co and ^{137}Cs are reached. On the other hand, the limit of detection is too high for ^{241}Am. In order not to exceed the maximum value of 10 Bq L^{-1}, the integration time should be around 90 min (^{241}Am is essentially an alpha emitter and the system is not well adapted). This sensor is designed to be easily and quickly installed in drinking water distribution networks.

1.1.3 Biofilm sensors (MSS, Optiquad and Neosens FS-900 / SkidSens)

Allowing deposits to be monitored is to be seen as a key aspect as contaminants, depending on their nature, may adsorb onto pipe walls. Biofilm sensors appear very useful for evaluating the effectiveness of a cleaning procedure throughout the network. However, their interest is quite limited in a drinking water distribution system for two main reasons:

- First, their high cost does not allow them to be used in large numbers in a network (Table 5),
- Secondly, the low sensitivity of FS-900 and SkidSens does not allow them to be used in drinking water systems (Deliverable 6.4, version 2, June 2012). The OptiQuad sensor can only detect the first deposition events. The latter act as a screen and inhibit the spread of the signal, thus preventing the sensor from distinguishing between thin and thick deposits.

Three commercially available sensors - MSS, FS-900 and SkidSens – and one prototype - Optiquad - were tested over a relatively short time period of one month to monitor the deposits formed on the pipe surfaces in a drinking water distribution network.

The four systems need a power supply (Optiquad: 230 V, FS-900 and SkidSens: 24 V or 230 V) and calibration step (to convert the signal to cell counts or deposit thickness, for example).

Table 5: Specifications for biofilm sensors (assays done over a short time period of about one month)

Sensor	Parameter measured	Resolution	Accuracy	Maintenance	Response time	Price in € (*)
OptiQuad	Fluorescence, scattering, reflection and transmission	Early events	Not appropriate	Once a year.	<1 min	Approx. 30,000
FS-900	Heat transfer resistance	10-1,000 µm	Not appropriate	Once a year	2-4 h	Approx. 5,000
SkidSens	Heat transfer resistance	10-5,000 µm	Not appropriate	Once a year	1 h	Approx. 2,000
MSS	Amplitude and damping of propagated wave	0.076 mV	± 2%		Instantaneous (30 ms)	3,000

(*) Prices are approximate for 2012 and are subject to change.

1.1.4 Sentinel coupons

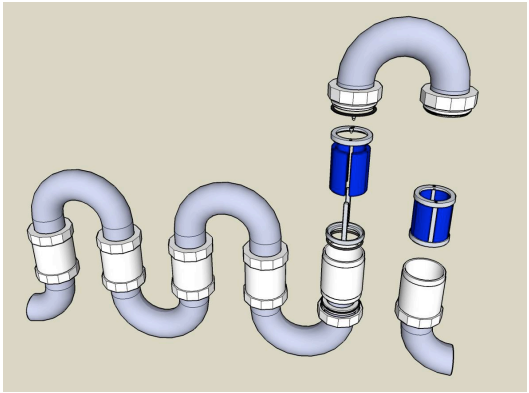

Figure 4 : Drawing of sentinel coupons (Courtesy of Martin Strathmann, IWW Water Centre).

Sentinel coupons (Table 1 and Figure 4) should be installed during the pre-crisis phase in drinking water distribution networks so as to allow, during and after the crisis period, (i) the deposits on the coupons to be analysed, (ii) the adsorbed contaminants to be identified and (iii) the efficiency of the decontamination

procedures to be assessed. The materials used for the coupons should not be corrodible as they will be in the pipes for years.

Our experiments (Deliverable 6.6, January 2012) show that coupon-monitoring devices are suited to follow deposit / biofilm formation in drinking water distribution systems as well as to investigate and confirm the successful removal of deposits from surfaces..

The "sentinel coupons" approach is a new tool developed in the SecurEau project. Such devices have to be installed proactively on bursts / leaks (in specific chambers) during pipe repair or installed in each district meter area in meter / pressure reducing valve chambers. They can also be fitted in a chamber equipped with other sensors.

A major downside of sentinel coupons is that they need to be installed in a chamber in advance, which implies additional expenses (see 1.1.5), while pipe sampling can be done in various places at any time.

1.1.5 Cost of sensor and coupon installation

The main cost when installing coupons or sensors is building an access chamber. It can cost from 1,500 to 15,000 €, depending on its location (rural area without road-works or urban area with traffic interruptions and road-works), the availability of power, the availability of maps for the network, and so on. Various sensors (incl. sentinel coupons) can be installed in the same chamber.

There are at least two possible strategies for installing an access chamber:

- either planned in advance and performed as part of a mains renewal programme,
- or taking advantage of works being undertaken (maintenance, leak repair, sampling, etc.).

Both strategies should be crossed with mathematical models which will define the best locations for their implementation (see 1.2).

The cost for installing and retrieving coupons is estimated to average 200 € (cost for the staff to get to the chamber, close valves, take coupons out, open valves, etc.). By comparison, the cost for taking a pipe sample ranges from 600 € for a 'coupon' and clamp repair to 2,000 € for a one-metre cut-out. Therefore, coupons can only be cost effective if they are used on a regular basis.

1.2 Optimal location of water quality sensors

The installation of water quality sensors in a drinking water system allows an alert to be issued rapidly when abrupt changes in the quality of water are detected. It is necessary to ideally distribute these sensors taking into account a number of considerations. Indeed, water supply providers may consider expenses (limited budgets), efficiency (willingness to detect a contamination event within less than *x* hours), protection of specific groups of consumers (e.g., children, hospital patients or retirement home residents,), etc. These considerations can of course be combined, always with the same purpose in mind: to alert as quickly as possible (early warning concept).

Objectives and constraints need to be defined to ensure that sensors are distributed in the best possible way: some are sensor specific (technical considerations for installation), others are to be considered when it comes to cleaning, while others are peculiar to population vulnerability and financial costs (Deliverable 2.2.2, June 2012).

Table 6: Availability and additional work to adapt models for partners outside of SecurEau consortium

Mathematical treatment	Availability	Work to be done for the models to be used in other distribution systems	Status
Generation of contamination events by a Monte Carlo process, to train the model	C source code + executable + link with the Epanet DLL (***)	Need an INP (**) file for the network model and the accurate hydraulics	The software is free of charge. No access right for the source code. Contact: Irstea (see page 2)
Formulation of a multi-stage INLP (*) problem	Executable available	Need the generation of contamination events described previously	The software is free of charge. No access right for the source code. Contact: Irstea (see page 2)

* INLP Integer Non-Linear Programming ---- ** INP is an Epanet ASCII format file ---- *** DLL Dynamic Link Library

The models Irstea has developed so far under SecurEau cannot be transferred to partners outside of the project in their current state. To do so, additional work would be required as described in Table 6.

1.3 Optimal distribution of sentinel coupons

Sentinel coupons are simple tools which can be used to control the efficiency of decontamination and to identify the composition of deposits throughout the network under normal operational conditions. The coupons must be positioned optimally throughout the network so as to be representative of water quality interaction with pipe surfaces while minimizing costs (Deliverable 6.5, April 2012). Consequently, the mathematical models dedicated to the spatial optimisation of sentinel coupons differ from those dedicated to the spatial optimisation of generic water quality sensors, because the objectives and constraints are not the same.

The design relies on the principle that a downstream sensor gives indirect indications of the quality of the water upstream. Moreover, the areas where contaminant concentration is higher and the shear stress is lower are considered as ideal candidates. This concept is very simple to implement and has, as a one and only prerequisite, the existence of a network model for hydraulic solving. Application of the methods developed here to large networks requires optimisations. The models Irstea has developed so far under SecurEau cannot be transferred to partners outside of the project in their current state. To do so, additional work would be required as described in Table 7.

Table 7: Availability and additional work to adapt models for partners outside of SecurEau consortium

Mathematical treatment	Availability	Work to be done for the models to be used in other distribution systems	Status
ILP (*) formulation that is a maximum coverage problem	A C- code preparing the objective and constraint description ready to use with GLPK (***)	Need an INP (**) file for the network model (network topology) and the accurate hydraulics (node demand calibrated)	The software is free of charge. No access right for the source code. Contact: Irstea (see page 2)

* ILP Integer Linear Programming
** INP is an Epanet ASCII format file
*** GLPK Gnu Linear Programming Kit

1.4 Conclusions

The sensors and sentinel coupons described herein need to be installed during the pre-crisis phase. Water quality sensors should be used, during normal operation of the drinking water network, for routine water quality monitoring. Expected fluctuations (daily, weekly, seasonal variations or large predictable events such as festivals and sporting events) should be monitored to better understand the network and its operating profile under normal conditions on the one hand, and to be able to better detect any abnormal changes during normal operation of the network on the other hand.

2. Crisis Phase

The crisis phase begins by declaring a state of crisis (ISO 2011 and Deliverable 6.8) and assembling the crisis management team. It comprises crisis control activities. It is terminated when the end of a crisis is declared and the crisis management team is dissolved. At this stage, the normal management team begins the post-crisis phase. The crisis phase is characterised by a high level of activity.

During the crisis phase, some tools developed in SecurEau should be used:

- water quality sensors to continue monitoring water quality and to measure the extent of contamination (if the water flow has not been interrupted),
- sentinel coupons to monitor the concentration of the pollutant adsorbed onto the pipe walls,
- mathematical models to determine, thanks to measurements carried out throughout the network, the areas which have been contaminated and the sources of contamination,
- various cleaning methods, both traditional and new ones, are to be applied to decontaminate the network, especially pipe walls.

2.1 Identification of the sources of contamination and the contaminated areas

If a contamination event (accidental or deliberate) occurs in a drinking water network, it is essential to identify the sources of contamination and to determine the area which is likely to be contaminated, in order to isolate and decontaminate the affected area only, as well as keep supplying drinking water in non-affected areas.

Different mathematical approaches combined with hydraulic models were applied within the SecurEau project to determine, as quickly as possible, the possible contamination sources and the respective probable contaminated areas. Such determination is made possible thanks to information provided by the water quality sensors installed during normal management of the networks. The precision and rapidity of the determination are directly correlated with the number of sensors installed. The models Irstea has developed so far under SecurEau cannot be transferred to partners outside of the project in their current state. To do so, additional work would be required as described in Table 8.

Table 8: Availability and additional work to adapt models for partners outside of SecurEau consortium.

Mathematical treatment	Availability	Work to be done for the models to be used in other distribution systems	Status
1. Solves the inverse transport equations on the network graph by a method of characteristics	A C-code that solves the inverse transport problem and assembles the Input / Output transport matrix and gives a potential contamination list (location + starting time + duration)	Pre-requirement binary positive sensor responses. Need an INP (*) file for the network model and the accurate hydraulics	The software is free of charge. No access right for the source code. Contact: Irstea (see page 2)
2. Solves a Minimum Relative Entropy problem in order to get a stochastic estimation	A Matlab code that solves the minimization problem	Need the Input / Output transport and the potential contamination list described previously	The software is free of charge. Access right for the source code with Irstea agreement.
Evaluates which contamination sources could be responsible for each detection and crosses that information to determine the possible contamination sources (determinist estimation, very high calculation time)	Matlab routine that identifies contamination sources based on the information given by positive readings of the sensors.	Need an INP file for the network model and the accurate hydraulics to create the input files to the Matlab routine.	The software is free of use. Access right for the source code. Contact: UPORTO (see page 2)
Application of artificial neural networks (ANN). (acceleration of the mathematical treatment compared to the determinist estimation)	Matlab routine that identifies contamination sources + Matlab routine that trains the ANN to estimate the time of contamination at each node from the time of detection at each sensor.	Need an INP file for the network model and the accurate hydraulics to create a database of contamination scenarios. This database is used to train the ANN for new distribution systems.	The software is free of use. Access right for the source code. Contact: UPORTO (see page 2)
Online – Divides the network into a series of nodes and tracks changes in concentration at the nodes. Movement of contaminant is tracked using data from flow direction sensors. **Offline** – Uses Lagrangian transport mechanism. Tracks movement of contaminant along with flow and interaction with walls in discrete water volumes. **Combined model** – Applies the online algorithm to the sections of the network fitted with flow direction sensors, and the offline algorithm to the other sections.	**Online** – A Delphi code that uses data provided by flow direction sensors to track contamination travelling from node to node. **Offline** – A C-code that solves a system of equations representing mass conservation and reactions.	**Online** – Need an INP file for the network model. Flow direction sensor locations must be entered by an operator. Need data from the sensors. **Offline** – Need an INP file for the network model.	The software is free of use. Access right for the source code. Contact: RTU (see page 2)

* INP is an Epanet ASCII format file

2.2 CBRN analysis

In the event of a terrorist attack resulting in the contamination of drinking water supplies, rapid response techniques are required that will allow any potential CBRN contamination events to be detected and quantified taking into account an even negligibly small risk of false-negative or false-positive results.

Analytical methods were developed or improved in the SecurEau project for a number of typical CBRN pollutants. Some of them were developed for SecurEau teams' own purposes while others could be used in the case of contamination. All the methods used provided accurate results when determining the nature and / or concentration of a contaminant in water. However, determining the nature and / or concentration of a pollutant adsorbed onto the walls of the network was systematically found to be a major difficulty.

2.2.1 Chemicals

Quantitative and qualitative methods developed for chemical measurements were for the own purpose of the SecurEau project. They were first developed for measurements in the water phase (Deliverable 3.4, version 2, July 2012) and analytical methods (Table 9).

Table 9: Chemicals tested, methods of analysis **in water**, limit of detection

Contaminant	**Method**	**Linearity range**	**Limit of detection**	**Time needed for analysis**	**Precision**	**Accuracy**
Paraquat	DI-HPLC-DAD	0.1-80 mg L^{-1}	0.01 mg L^{-1}	4 min	21%	98-101%
Paraquat	SPE-HPLC-DAD	0.1- 100 µg L^{-1}	0.05 µg L^{-1}	8 h	3% (repeatability)	To be concluded
Chlorfenvinphos	DLLME + GC-MS	0.01–10 µg L^{-1}	0.0014 µg L^{-1}	30 min	10%	74%
Carbofuran	DLLME + GC-MS	0.01-10 µg L^{-1}	0.0023 µg L^{-1}	30 min	15%	83%
BDE-100	DLLME + GC-MS/MS	0.1-10 µg L^{-1}	0.018 µg L^{-1}	30 min	21%	116%
Methylmercury	LLE + derivatization + GC-HRMS	1- 50 ng L^{-1}	0.21 ng L^{-1}	150 min	10%	103%

BDE-100: 2,2',4,4',6- pentabromodiphenyl ether; DLLME: Dispersive liquid-liquid micro extraction

The analytical procedures developed are too complex for a rapid response in emergency situations. Nevertheless, quantifying the chemicals adsorbed onto deposits and biofilms is not a matter of emergency, but is needed for waste disposal purposes after an event is detected. In that sense, the developed methodologies are in accordance with the objectives of the project (Deliverable 3.5, December 2011).

Table 10: Chemicals tested, methods of analysis in **biofilms / deposits**, limit of detection

Contaminant	**Adsorption**	**Desorption method**	**Extraction rate**	**Method**	**Limit of detection**
Paraquat	Very high	hot acidic reflux with concentrated sulphuric acid	70%	EAM	0.13 mg/g of kaolin
Chlorfenvinphos	75%	acetonitrile	93%	HPLC-DAD	4.30 µg/g of kaolin
Carbofuran	50%	Not available yet	Not available yet	HPLC-DAD	Not available yet
BDE-100	Not available yet				
Methylmercury	High with some deposits	Dichlromethane-hexane from acidified deposit leachate	15-66%	GC-HRMS	Biofilm 8 ng/L. Ferrous deposits 1.7-2.9 ng/g dws

As some chemicals will strongly attach to the deposits (depending on the nature of the contaminant and deposit), extraction techniques are required (e.g., hot acidic reflux with concentrated sulphuric acid for Paraquat) (Table 10). The extraction yields will greatly depend on the contaminant / deposit pair, making any *a priori* predictions impossible. In addition to extraction, deposit-specific derivatization problems may also appear, as was most likely the case for methylmercury, with a calcium-rich deposit. As shown in Table

10, the detection limits of analytical methods applied to molecules adsorbed on deposits are much higher than when analysis is performed in the water phase.

2.2.2 Biological agents

Analyses of biological contaminants must allow low levels of bacterial pathogens to be detected, including non-spore forming and spore forming species, and provide a measure of their infectivity so that the public health risk can be accurately assessed.

Two main categories of methods were distinguished (Table 11):

- molecular biological methods: they will give information on the presence / absence of undesirable microorganisms but will give no information on viability and / or infectivity.
- viability determination, *via* methods such as PMA-qPCR and DVC-PNA-FISH: with acceptable limits of detection in water (Deliverable 3.2, version 2, July 2012), it could provide estimation of microorganism viability.

Table 11: Summary of method development findings for each target bacterial group in water ("-" denotes where the method did not work; "not tested" means the method was not used for the bacterial species considered)

Target bacteria	Limit of detection in water (cells/ml)			
	PNA-FISH	DVC-PNA-FISH	qPCR	PMA-qPCR
Escherichia coli O157:H7	2×10^4	2×10^4	1	1
Bacillus cereus E33L (surrogate for *B. anthracis*)	2×10^4	2×10^4	10	-
Francisella tularensis sups. novicida	-	-	5	5
Francisella philomiragia (surrogate for *F. tularensis)*	-	-	1	1
Yersinia pestis	quantity not tested	quantity not tested	5	5
Yersinia pseudotuberculosis (surrogate for *Y. pestis*)	2×10^4	2×10^4	20	20

It should be noted that the detection limits of microscopy-based methods (PNA-FISH and DVC-PNA-FISH) can be improved with larger sample volumes (the above values are based on 1 ml samples rather than on the 100 ml ones which are routinely used by water companies) or using an automated system which allows the entire filter membrane area to be assessed.

For measurements in biofilms / deposits, none of the methods developed allow the number of microorganisms to be determined with accuracy (Deliverable 3.3, March 2012) (Tables 12 and 13), just as shown with chemicals.

The content of deposit samples may affect the results of bacterial detection techniques. The DVC-FISH and PMA-PCR techniques could be used to estimate bacterial strain viability in water, biofilm and deposit samples.

Table 12: Summary of method development findings for each target bacterial group in deposits ("-" denotes where the method did not work; "not tested" means the method was not used for the bacterial species considered) ---- * The lowest concentration tested.

Target bacteria	Limit of detection in deposits (cells/g)			
	PNA-FISH	DVC-PNA-FISH	qPCR	PMA-qPCR
Escherichia coli O157:H7	2×10^4	2×10^4	2×10^1	3×10^2
Bacillus cereus E33L (surrogate for *B. anthracis*)	2×10^4	2×10^4	2×10^2	-
Francisella tularensis sups. novicida	-	-	1.1×10^3 *	1.1×10^3 *
Francisella philomiragia (surrogate for *F. tularensis)*	-	-	3.3×10^1	3.3×10^1
Yersinia pestis	not tested	not tested	1.1×10^4 *	1.1×10^4 *
Yersinia pseudotuberculosis (surrogate for *Y. pestis*)	1.7×10^6	1.7×10^6	5×10^3	5×10^3

As mentioned earlier, the limit of detection using PNA-FISH and DVC-PNA-FISH with water samples can be improved with larger volumes and the use of automated systems. However, in the case of deposit samples, care must be taken to allow for the effect of autofluorescence of deposit particles. The limit of detection will vary depending on deposit composition.

Additionally, it is difficult to set detection limits for qPCR methods due to differing compositions of deposits (e.g., DNA extraction may prove difficult with humic concentration). Therefore, care must be taken when selecting an extraction method.

Table 13: Summary of method development findings for each target bacterial group in biofilms ("-" denotes where the method did not work; "not tested" means the method was not used for the bacterial species considered)

Target bacteria	Limit of detection in biofilms (cells/cm^2)			
	PNA-FISH	DVC-PNA-FISH	qPCR	PMA-qPCR
Escherichia coli O157:H7	2×10^4	2×10^4	2×10^1	2×10^1
Bacillus cereus E33L (surrogate for *B. anthracis*)	2×10^4	2×10^4	2×10^2	-
Francisella tularensis sups. novicida	-	-	2	2
Francisella philomiragia (surrogate for *F. tularensis)*	-	-	4	4
Yersinia pestis	not tested	not tested	2	2
Yersinia pseudotuberculosis (surrogate for *Y. pestis*)	2×10^4	2×10^4	5.5×10^1	5.5×10^1

It thus appears that the only useful methods for detection of pathogenic microorganisms in deposits are molecular biology ones. However, many interferences lead to a high detection threshold for deposits, but PNA-FISH while appearing less sensitive was more reliable than qPCR.

Table 14 provides details about the amount of time needed for each type of analysis and whether the method can assess bacterial viability.

Table 14: Summary of the amount of time each analysis requires

Type of analysis:	Time delay before results:	Information provided:
PNA-FISH	2–3 h	Total target bacteria
PNA-DVC-FISH	16 h	Total and viable target bacteria
qPCR	2–3 h	Total target bacteria
PMA-qPCR	4 h	Total and viable target bacteria

In summary, total cells can be determined quickly, which is essential for rapid confirmation of an event. The determination of viable cells take longer: but this can be done at a more leisurely pace when it is more important to confirm successful decontamination efficacy.

2.2.3 Radionuclides

To confirm the intrusion or presence of radionuclides in a drinking water network, robust screening methods are required for detection and quantitation of alpha, beta and gamma emitting radionuclides, both in water (Deliverable 3.6, version 2, June 2012) and in biofilms / deposits (Deliverable 3.7, March 2012).

Liquid scintillation counting, coupled with spectral analysis and simple acid treatments of the biofilms and deposits which lead to dissolution / digestion / decolourisation, is shown to be effective. The technique enables the target radionuclides to be detected with limits of detection of 1 Bq/g or less with preparation and counting times taking less than three hours (Table 15)

Table 15: Radionuclides considered in SecurEau

Nuclide	Half life	Main decay mode	Main emission energies (keV)	Max permitted activity conc. [Bq/L][2]	Rapid analytical technique	Typical LoD in water	Typical LoD in deposits Bq/g
Cobalt-60	5.27 years	Beta / gamma	β318 (99.89%) γ1,173 (99.86%) 1,333 (99.98%)	1,000	LSC	4	0.3
Strontium-90	28.64 years	Beta	β546 (100%)	125	LSC	2	0.1
+Yttrium-90	2.67 days	Beta	β2,279 (100%)		LSC		
Iodine-131	8.04 days	Beta / gamma	β606 (89.4%) 334 (7.36%) γ364 (81.2%)	500	LSC	4	0.3
Caesium-137	30.17 years	Beta	β512 (94.6%)	1,000	LSC	4	0.3
+Barium-137m	3.53 min	Gamma	γ661 (90.1%)		LSC		
Iridium-192	73.83 days	Beta / gamma	β536 (41.6%) β672 (48.1%) γ317 (83%)	1,000	LSC	4	0.3
Polonium-210	138.38 days	Alpha	α5,304 (100%)	1,000	LSC	3	0.3
Radium-226	1,600 years	Alpha / gamma	α4,602 (5.55%) 4,785 (94.45% γ186 (3.28%) (also multiple daughter progeny)	1,000	LSC	1	0.1
Americium-241	432.7 years	Alpha / gamma	α5,443 (12.8%) 5,486 (85.2%) γ59.5 (35.9%)	20	LSC	3	0.3
Californium-252	2.645 years	Alpha	α6,076 (15.2%) 6,118 (81.6%)	20	LSC	3	0.3

[2]Maximum permitted levels of radioactivity in drinking water supplies in the event of a radiological emergency. After Nisbet et al, 2008; Euratom 1989; [1]Warwick and Croudace (in preparation)

Euratom (1989) Council Regulation 2218/89 of 18th June 1989 amending regulation 3954/87 laying down maximum radioactive contamination in foodstuffs following a nuclear accident or any other case of radiological emergency. *Off. J Eur. Commun. L3211 22nd July 1989.*

Nisbet A., Jones A., Brown J., Mortimer K., Roberts G. & Mobbs S. (2008). UK Recovery Handbook for Radiation Incidents, 2008. HPA-RPD-042. Version 2. Health Protection Agency, Chilton, UK

Warwick P.E. & Croudace I.W. (SecurEau, manuscript in preparation) Rapid screening of drinking waters and pipeline deposits for radionuclide contamination using LSC combined with intrinsic spectral parameter corrections.

A simplified sample preparation method (a 0.5 mL water sample evaporated on a disk) followed by 10 min measurement and sophisticated alpha spectrometric analysis methods (the ADAM method) seems adequate when intending to identify pure alpha emitters in a mixture of radionuclides (radionuclides tested: Po-210 and Am-241). However, non-destructive radionuclide identification for biofilms and scales may prove difficult and using radiochemical sample processing cannot always be avoided. The reason is that alpha emissions from thick samples produce spectral complexity that prohibits radioelement identification.

2.3 Cleaning

Experience from contamination events in drinking water distribution systems showed that the procedure of decontamination is cumbersome and time-consuming when attempting to reach acceptable levels of safety. A number of challenges should be solved to make decontamination methods more efficient, among which are persistence of contaminants in pipes and deposits, recycling of contaminated water and exposure of emergency teams to contaminants. The following steps should be followed to ensure efficient cleaning:

1. Isolate the contaminated area of the network. The area is isolated to prevent the pollutant from spreading any further . Pollutants might accumulate in biofilms or in loose deposits.

2. Use a combination of different methods: first, deposits should be removed from the walls, and then specific treatments should be applied to remove any deposits still attached to the walls.

3. Apply a sludge and supernatant treatment. If the *in situ* treatment is not efficient enough, the pollutant is removed form the network by flushing or pigging and handled outside.

Tables 16, 17 and 18 list a few techniques available for decontaminating a drinking distribution system polluted with chemicals, biological agents and radionuclides, respectively.

Selecting the most suitable decontamination method is dependent on where the contaminant is located (the red cross on the picture on the right):

- at the surface, associated with loose deposits and / or biofilms. If such is the case, can traditional mechanical techniques allow this surface layer to be removed?
- deeper in the deposits, due to diffusion reactions. If such is the case, will the cleaning methods applied be less effective?

Traditional cleaning methods such as shock chlorination and flushing are not efficient enough to ensure a high safety margin when removing resistant bacterial agents such as spores; furthermore, loose deposits which have formed in water distribution networks also contribute to hindering efficiency. For example acidified potassium permanganate followed by flushing can be used as an effective decontamination method for the removal of arsenic and mercury from cement-lined ductile iron pipe surfaces.

Table 16: Techniques for decontaminating a drinking distribution system polluted with chemicals

Method	**Principle**	**Action on…**	**Efficiency**	**Limits**
Flushing with water then with 10 mg/l of mg L^{-1} chlorine for 1 hour	water flushing	Mercury sorbed on biofilm coated PEX plastic	Eighty-two percent mercury removal from the pipes	More concentrated chlorine and longer flushing time needed for better Hg^{2+} removal. Or acidic conditions.
Mechanical removal of contaminated corrosion layer	Mixing with ice cubes	Mercury sorbed on a piece of corroded cast iron pipe	Sixty percent mercury removal from the section of pipe	Mercury not removed from deeper parts of corroded surfaces. More shear stress needed.
Fenton's reaction	Advanced oxidation with iron salt as catalyst and hydrogen peroxide as oxidant	Chlorphenvinphos sorbed on deposits (kaolin)	One hour was required to completely oxidise the pesticide in the water phase.	Longer time is necessary for action in the fixed phase Acid pH improves the efficiency of degradation
Fenton's reaction	Advanced oxidation with real deposits/steel pipes or iron salt as catalyst and hydrogen peroxide as oxidant	Paraquat dichloride.	Steel pipes increases the oxidation process. The gradual addition of hydrogen peroxide showed to be the best option in the oxidation process. 8 hours were enough to degrade all the pesticide.	Acid pH improves the efficiency of degradation
Flushing with air-water / or with water / or mixture of water with crushed ice	Flushing and application of crushed ice, stones	Biofilms, layers and deposits from different type of pipe material	Air-water Comprex® flushing with velocity up to 15–20 m/s removed 99% of the biofilms and ice pigging 99,999%	The higher the shear force, the more efficient the removal of biofilms + sediments. Incrustations are difficult to remove

(1) Experimental conditions: $[FeSO_4] = 5 \times 10^{-4}$ M; $[H_2O_2] = 1.5 \times 10^{-2}$ M; $pH_0 = 3$; room temperature, [CFVP] = 2.78×10^{-4} M; (batch reactor; slurry system; lab scale)

(2) T ≈ 20 ºC; pH_0 = 3.0; [PQ] =3.98 × 10^{-4} M $[H2O2]_0$ =1.5 × 10^{-2} M; [Fe] =5.0 × 10^{-4} M; (recirculation reactor; pilot scale)

Table 17: Techniques for decontaminating a drinking distribution system polluted with biological agents

Method	**Principle**	**Action on…**	**Efficiency**	**Limits**
Shock chlorination (Ct value = 30,000 mg·min/L)	Introduction of the agent for a selected contact time. Flushing of the system.	Spores of *Bacillus subtilis*	A 5 log_{10} decrease after a 3 hour chlorination period	Surface disinfection; 3× 10^3 spores/cm^2 attached to the surface of the pipes survived
Alternated chlorination and alkaline treatments	Introduction of the agent (NaOCl→NaOH→NaOCl) for a selected contact time. Flushing of the system.	Spores of *Bacillus subtilis* attached to the surface of the pipes	After first chlorination (3 h), the amount of spores able to form colonies on R2A agar decreased by 1 log_{10}. After the second chlorination (NaOH was used in between), the amount of spores decreased by 2 log_{10}.	
Fenton's reaction	Advanced oxidation with copper or iron salt as a transition metal and ascorbic acid as a catalyst	Spores of *Bacillus subtilis*	Not pH correction necessary (using copper and ascorbic acid). Presence of salt and surfactant benefit Fenton reaction.	
5 nM to 50 mM NO concentrations	Introduction of nitric oxide using the donor molecule, sodium nitroprusside (SNP), as a biofilm dispersal agent.	Drinking water biofilm. *E. coli* O157 and *Bacillus cereus* E33L spores (closest molecular surrogate for *B. anthracis*)	No significant effect was observed for either general biofilm release nor for the release of specific pathogens	Technique only tested at the lab scale. The SNP donor requires light activation.
Chlorination (10mg/L, 15 min)	Addition of hypochlorite solution	*Yersinia pestis*	Majority of the cells are dead, but some viable cells are detectable with qPCR	Only in vitro results available
Chlorination (6-8 mg/l)	Introduction of hypochlorite solution in to test pipeline	*Y.pseudotuberculosis* attached on the pipelines	Majority of bacteria (99%) removed from biofilms within 2 hours. Viability of bacteria (water/biofilms) lost completely within 1 hour	
Chlorination (10mg/L, 15 min)	Addition of hypochlorite solution	*Francisella tularensis*	Majority of the cells are dead, but some viable cells are detectable with qPCR	Only in vitro results available
Chlorination (10 mg/l)	Introduction of hypochlorite solution in to pipeline	*Francisella philomiragia*	All bacteria removed and inactivated from biofilms and water within few minutes	
Peracetic acid (5 mg/l)	Introduction of peracetic acid solution in to pipeline	*Y.pseudotuberculosis*	50% removal (qPCR) from biofilms within 2 hours. However all microbes were inactivated withing 2 hours. Total removal of bacteria from biofilms within 24 hours	

Chlorination 10 mg/l, 24 hours	Introduction of hypochorite solution in to pipeline	Adenoviruses	Complete removal of microbes from biofilms within 1 hour.	
Peracetic acid (2- 4 mg/l)	Introduction of peracetic acid solution in to pipeline	Adenoviruses	2.5 log removal from biofilms within 1 hour, total removal within 24 hours	

Table 18: Techniques for decontaminating a drinking distribution system polluted with radionuclides

Method	**Principle**	**Action on…**	**Efficiency**	**Limits**
Sodium bicarbonate	chelation	Americium, Polonium	++	Technique only tested at the lab scale
5 nM to 50 mM NO concentrations	Introduction of nitric oxide using the donor molecule, sodium nitroprusside (SNP), as a biofilm dispersal agent.	Americium, Polonium Nitric oxide has no significant effect on biofilms	-	Technique only tested at the lab scale

2.4 Conclusion

The application of cleaning procedures coupled with analytical methods in water and on deposits is used to decide if the network is back to a normal, "healthy" state, i.e. the water supply can be reopened to all consumers. A decision tool (Deliverable 6.8: *Decision tool Suitable for Assessment to Approval of Successful decontamination*) will help make that choice.

3. Post-Crisis Phase

The Post-Crisis Phase is the complete changeover from crisis management to normal management including normal supply of the water utility services. Part of this phase is carried out under crisis management and part under normal management (ISO 2011). No specific tools were developed for such a phase as it is a matter of management and restarting routine actions.

4. References

ISO 2011. ISO 11830: Activities related to drinking water and wastewater services – Crisis management of water utilities. ISO/TC 224/WG7, August 2011.

Loo, S.-L., Anthony, G.F., Krantz, W.B., Lim, T.-T., 2012. Emergency water supply: a review of potential technologies and selection criteria. Water Research 46, 3125-3151.

Public deliverables:

Deliverable 2.1.1, version 03, June 2012, State of the art report on chemical sensors for early warning systems

Non-public deliverables:

Deliverable 2.1.2, version 2, June 2012, Prototypes of chemical sensors adapted for EWS (low maintenance and calibration requirements, sensitivity, possibility of miniaturisation and large scale production) including specifications (sensitivity, detection limit, etc.)

Deliverable 2.1.3, version 3, June 2012, Prototype for radioactivity sensor and report on specifications

Deliverable 2.2.2, June 2012, Report on modelisation of the optimal location of sensors for the 2 selected sites

Deliverable 3.2, version 2, July 2012, Off-line sensitive, specific procedures for pathogens in water

Deliverable 3.3, March 2012, Off-line sensitive, specific procedures for pathogens in biofilms/deposits

Deliverable 3.4, version 2, July 2012, Off-line rapid analytical procedures for chemicals in water

Deliverable 3.5, December 2011, Off-line rapid analytical procedures for chemicals in biofilms/deposits

Deliverable 3.6, version 2, June 2012, Off-line sensitive, specific procedures for radionuclides in water

Deliverable 3.7, March 2012, Off-line sensitive, specific procedures for radionuclides in biofilms/deposits

Deliverable 6.4, version 2, June 2012, Protocol for successful application of devices in laboratory systems

Deliverable 6.5, April 2012, Concept for positioning the coupon systems and sensors at representative locations in the system

Deliverable 6.6, January 2012, Report on implementation of the coupon systems and sensors into an experimental loop system, generation of deposits and challenge with contaminants, optimization and verification of decontamination efficacy

Deliverable 6.8, Decision tool Suitable for Assessment to Approval of Successful decontamination