Emerging methods to monitor emerging chemicals in the drinking water production chain

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Titel
Emerging methods to monitor emerging chemicals in the drinking water production chain

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Inhoud

1 Abstract

New monitoring techniques enable a shift in monitoring chemical quality from mainly at the end product tap water, towards monitoring during the whole process in the production chain. This is congruent with the 'HACCP' system (Hazard analysis critical control points) that is fairly integrated in food production but still less in drinking water production. This shift brings about more knowledge of source quality, the efficiency of treatment and distribution and understanding of processes within the production chain, and therefore can lead to a more pro-active management of drinking water production. At present, monitoring is focused neither on emerging chemicals, nor on detection of chronic toxicity. We discuss techniques to be used, detection limits compared to quality criteria, data interpretation and possible interventions in the production.

Key words:
drinking water, HACCP, emerging chemical, effect assays, sensors, screening and identification

2 Introduction: Emerging chemicals and interpreting their significance to human health

2.1 Pressure of emerging chemicals on drinking water sources

In sources for drinking water, thousands of industrial chemicals can be present (Schwarzenbach *et al*., 2006). Due to global trends such as a growing and older population and thus a higher use of eg. pharmaceuticals, increasing prosperity and thus more consumption and emission of chemicals, and urbanization and more extreme events leading to faster transport rates between environmental compartments (Diamond and Hodge, 2007), there is an increasing chemical pressure on drinking water sources. For example, only about 10% of European river water samples could be classified as 'very clean' (Loos *et al*., 2009). Pharmaceuticals, perfluorinated compounds, personal care products, detergents and endocrine disruptors could be found throughout Europe up to high ng/L median concentrations (Loos *et al*., 2009), many entering the water cycle via wastewater (Reemtsma *et al*, 2006). This occurrence in sources of drinking water is, depending on the treatment processes, sometimes reflected in (much lower) occurrence of these chemicals in finished drinking water (Benotti *et al*., 2009).
As analytical techniques evolve more and more chemicals are measured, often at low concentrations. The majority of the chemicals found are not covered by actual directives on (drinking) water quality, and are not monitored on a routine basis.
Especially the presence of so-called 'emerging chemicals' such as pharmaceuticals, personal-care products, drugs-of-abuse, endocrine disruptors and nanochemicals may lead to consumers concern (e.g. Bound *et al*., 2006, Proulx et al, 2007, Turgeon et al, 2004, Jardine et al. 1999, Owen et al., 1999). Emerging chemicals can be defined as chemicals which are not covered by existing water quality legislation, and for which relatively little information is available on their environmental behavior and toxicological properties. Current risk assessment models are based on our understanding of processes for 'classic' chemicals such as hydrophobic chlorinated hydrocarbons, and it is not always clear how well they apply to chemicals with other physico-chemical characteristics. Emerging diseases -such as ADHD, breast cancer, obesity or infertility- are sometimes brought in relation to the ubiquitous presence of low concentrations of a variety of emerging chemicals especially during prenatal exposure (eg. Johnson *et al*., 2008, Silva *et al*., 2002, Codru *et al*., 2007, Christiansen *et al*., 2007, Olesen *et al*., 2007, Courant *et al*., 2007, Harnley *et al*., 2005, Roberts *et al*., 2007, Codru *et al*., 2007, Petersen *et al*., in press). However, a strong causal evidence for a possible relation between these emerging diseases and the chemical pressure has not been proven.

2.2 Treshold of toxicological concern to interpret analytical data

For unregulated chemicals the concept of 'threshold of toxicological concern' or TTC (Kroes *et al*. 2004, 2005) can be applied to drinking water (Mons *et al*., in prep), to interpret the toxicological significance of low concentrations of emerging chemicals as found in (sources for) drinking water. The TTC concept was developed in the context of food safety, for a first clue on risks of unregulated chemicals present at low levels. The TTC is derived based on the chemical structure of the chemical involved, and its related mode of toxic action (Munro *et al*., 1996, Cramer *et al*., 1978). Assuming a daily intake of 2 L/d of drinking water, and a maximum allocation of 10% of the total exposure towards consumption of drinking water – both of which are standard assumptions for deriving drinking water quality guidelines (WHO, 2006) - TTCs derived for drinking water are 0,1 µg/L for non-genotoxic compounds and 0,01 µg/L for genotoxicants. For mixtures, summed concentrations of 1 and 0,05 µg/L are proposed (Mons *et al*., in prep.). Contrary to the original papers where Kroes *et al.* derived higher TTC-values for organophosphates and compounds in Cramer structural classes II and III, these less conservative TTCs were not taken into account in deriving TTCs for drinking water. The TTCs for drinking water are indicative values and have no legislative purpose. As TTCs for food safety, they must be considered as

conservative values which can be derived in the absence of toxicological data. If (provisional) drinking water guideline values are derived based upon available toxicological data, these are often less conservative than the TTC (Schriks *et al*., submitted).

3 Current monitoring practices and legal requirements

3.1 Monitoring requirements of chemicals in the drinking water production chain

Chemical (drinking) water quality monitoring is needed to evaluate if quality standards are met, to assess temporal and spatial trends and to guarantee the reliability of drinking water to consumers. Drinking water can be produced from various sources, such as surface water, groundwater affected by anthropogenic pressure or stable groundwater. Dependent on the quality of the source used, simple treatment suffices or a more intensive treatment is necessary. After treatment, the drinking water is distributed and delivered at the tap. The whole process is referred to as the drinking water production chain. In Europe, a minimum of monitoring obligations within the drinking water production chain is set by three European directives on water quality, i.e. the Drinking Water Directive, the Water Framework Directive and the Groundwater Directive (Figure 1a).

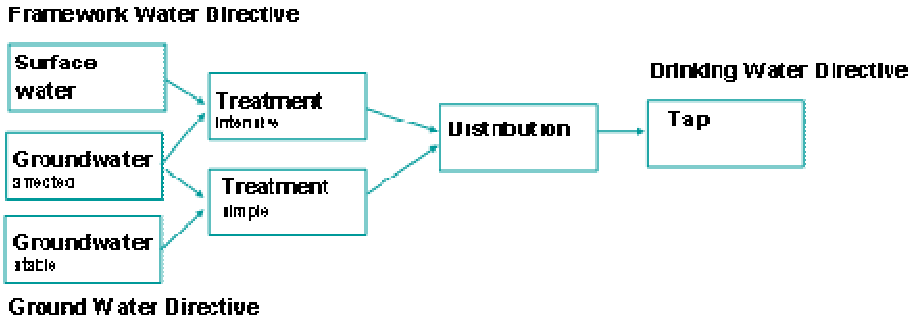

Figure 1a. Minimum monitoring requirements in the drinking water production chain as set by the various EU Directives.

The Drinking Water Directive (98/93/EC, EU, 1998) specifies a minimum set of drinking water quality guidelines for 23 chemical compounds or groups of compounds. Compliance to the drinking water directive is to be monitored at the tap with a defined frequency. For sources of drinking water, surface water or groundwater, monitoring requirements are given by the Water Framework Directive and the Groundwater Directive. The Water Framework Directive proposes environmental quality criteria for over 30 priority substances (2455/2001/EC, EU 2001; COM (2006) 397, EU 2006), mainly pesticides, PAHs, heavy metals, halogenated benzenes, alkanes, phenols or diphenylethers. Per catchment area, additional environmental quality guidelines are established. The Groundwater Directive (2006/118/EC, EU, 2006) prescribes the requirements for groundwater. Table 1 gives an overview of monitoring requirements for chemicals considered in the three described European directives on water quality.

Next to these requirements there is obviously room for member states to perform additional investigative monitoring (EU, 2007), however the prescribed monitoring requirements strongly influence actual monitoring programs. The Table shows that the directives focus on classical, well-known chemicals. There is a very limited overlap between the three mentioned EU water quality directives which prescribe monitoring obligations in different parts of the drinking water production chain.

Table 1. Chemicals involved in various EU Directives, resulting in monitoring obligations.

Chemical	**Drinking Water Directive (98/93/EC)**	**Water Framework Directive (2455/2001/EC)**	**Groundwater Directive (2006/118/EC)**
Acrylamide	x		
Alachlor		x	
Anthracene		x	
Antimony	x		
Arsenic	x		x
Atrazine		x	
Benzene	x	x	
Benzo(a)pyrene	x		
Boron	x		
Bromate	x		
Brominated diphenylethers		x	
Cadmium	x	x (and cadmium compounds)	x
C_{10-13}-chloroalkanes		x	
Chlorfenvinphos		x	
Chlorpyrifos		x	
Chromium	x		
Copper	x		
Cyanide	x		
1,2-dichloroethane	x	x	
Dichloromethane		x	
Di(2-ethylhexyl)phtalate		x	
Diuron		x	
Endosulfan		x	
A- Endosulfan		x	
Epichlorohydrin	x		
Fluoranthene		x	
Fluoride	x		
Hexachlorobenzene		x	
Hexachlorobutadiene		x	
Hexachlorocyclohexane		x	
Isoproturon		x	
Lead	x	x (and its compounds)	x
Lindane		x	
Mercury	x	x (and its compounds)	x
Naphthalene		x	

Chemical	Drinking Water Directive (98/93/EC)	Water Framework Directive (2455/2001/EC)	Groundwater Directive (2006/118/EC)
Nickel	x	x (and its compounds)	
Nonylphenols		x	
4-para-nonylphenol		x	
Octylphenols		x	
Para-tert-octylphenol		x	
Pentachlorobenzene		x	
Pentachlorophenol		x	
Pesticides	x		
Polycyclic aromatic hydrocarbons	x	x[a]	
Selenium	x		
Simazine		x	
Tetrachloroethene and trichloroethene	x		
Tributyltin compounds		x	
Trichlorobenzenes		x	
1,2,4-trichlorobenzene		x	
Trichloroethylene			x
Trichloromethane		x	
Trihalomethanes	x		
Trifluralin		x	
Tetrachloroethylene			x
Vinyl chloride	x		

[a]Specifically mentioned are benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, indeno(1,2,3-cd)pyrene.

3.2 Current practice on monitoring in the Dutch drinking water production chain

In the Netherlands, about 60% of the drinking water is produced from groundwater. Shallow groundwaters interacting with aboveground land-use, groundwaters influenced by soil contamination or aquifers covered by porous soil layers are affected by anthropogenic pressure. The remaining 40% of Dutch drinking water is produced from surface water. In densely populated deltas such as the Netherlands, surface waters are obviously strongly influenced by human activities.
At all drinking water production locations, weekly off-line laboratory analyses of legally prescribed classical toxicants are performed in raw water and the treated water leaving the production plant. In the distribution network, further monitoring focuses on physical parameters (eg. turbity, pressure, pH, UV adsorption), which are not sensitive to changes in toxicant concentration but can be able to detect large changes in water quality (Hall *et al*., 2007). Monitoring of tap quality and its frequency is performed as prescribed by the EU Drinking Water Directive.
On-line monitoring is used at nine locations in Dutch surface water, seven of which are intake points of surface water for the production of drinking water. The effect-based biomonitoring systems use algae, daphnia, mussels, fish or bacteria, focusing on acute ecotoxicological effects. Biomonitors determine the overall biological effect of the mixture of (partly unidentified) substances present (De Hoogh *et al*., 2006). In case of significant behavioral changes, an alarm is generated upon which adequate measures can be taken to prevent the chemicals enter a drinking water treatment plant or a storage reservoir. Despite recent technological developments, detection limits of these event biomonitors do not meet the aforementioned toxicologically relevant thresholds or TTCs and are therefore not useful as a predictor for human health effects (Table 2).

At few locations biomonitoring is combined with on-line analytical chemical monitoring using HPLC-UV for relatively polar chemicals or GC-MS for the more apolar and thermostable compounds. Though technically on-line monitoring of a whole series of classical and emerging toxicants is feasible, the existing on-line chemical monitoring is directed towards a limited series of pesticides. Detection limits do not yet fully meet the aforementioned toxicologically relevant thresholds or TTCs (ng/L to µg/L, Table 3). However, the sensitivity is enough to cover existing drinking water limits.
In general, drinking water limits are exceeded only rarely in the Netherlands (eg. Versteegh and Dik, 2007).

Table 2. Sensitivity of currently used on-line biomonitors, for various substance classes and detection principles.

Organism	**Detection principle**	**Substance class**	**Detection limit**
Algae (Chlorella, Scenedesmus)	Fluorescence	Herbicides	Low µg/L
Daphnia	Movement	Pesticides, cholinesterase inhibitors	Low µg/L
Mussel (Dreissena polymorpha)	Valve opening	Chlorinated organics, metals, antifoulants	µg/L
Bacteria (Vibrio fischeri)	Fluorescence	Aromates, chlorobenzenes, pesticides, halogenated organics	µg-mg/L

Table 3. Sensitivity of currently used on-line chemical monitors for various substances

HPLC-UV			
Compound	**Detection limit (µg/L)**	**Compound**	**Detection limit (µg/L)**
Phenylureum pesticides	0.2	Triazines	0.1
Carbendazim	0.2	Barban	0.2
Carbamazepine	1	Phoxime	0.2
TAED	1	3,3-dichlorobenzidine	1
N-butylbenzene sulfonamide	1	2,4,5-trichlooraniline	0.2
Triphenylphosphine oxide	1		
GC-MS			
Compound	**Detection limit (µg/L)**	**Compound**	**Detection limit (µg/L)**
1,1-biphenyl	0.2	N-butylbenzenesulfonamide	0.2
Bis(2-chloroethyl)ether	1	Phenanthrene	0.2
Dibenzofuran	0.2	Pirimicarb	0.2
2,6-dimethylpyridine	1	Cafeïn	0.2
BAM	0.2	Triphenylphosphine oxide	0.2
Phtalates	0.2 – 1	Triazines	0.2
Organophosphates	0.2		

4 HACCP combined with emerging techniques to optimize water quality monitoring

In the early nineties 'Hazard Analysis Critical Control Points' (HACCP) was developed to manage and control food safety for microbiological, chemical and physical risks (eg. Ropkins and Beck, 2007, Hoornstra *et al*., 2001). HACCP is currently well-established for food safety, and incorporated in various EU directives and regulations related to food safety (93/43/EEC, 852/2004).
HACCP consists of risk analysis and risk management in the whole production process:

- possible risks are discerned in the production process
- measures to control risks at critical control points (CCP) are established
- critical quality limits are set per CCP
- these are monitored at the CCP
- possible corrective actions per CCP are established.

The HACCP concept is equally valid for drinking water production, however this application is less well-established and not yet incorporated in legislation (Damikouka *et al*., 2007). Recent developments adjacent to the European Drinking Water Directive, such as the Water Safety Plans (WHO, 2006) and the 'Bonn Charter' (IWA, 2004) are in accordance with HACPP and have been worked out primarily for microbiological risks. In some individual European member states, Water Safety Plans on microbial risks are set as an obligation for drinking water producers.

HACCP and Water Safety Plans give clues for optimizing the monitoring of the chemical quality in the drinking water production chain. Emerging monitoring techniques enable a shift towards a more intensive and frequent monitoring during the whole process in the production chain (Figure 1b). Next, emerging techniques enable a regular monitoring of a broad set of chemicals, which are partly not regulated by drinking water or water quality legislation. This shift brings more knowledge and understanding of processes within the production chain (on source quality, efficiency of measures at critical control points such as treatment and distribution), and hence can lead to a more pro-active management of drinking water production.

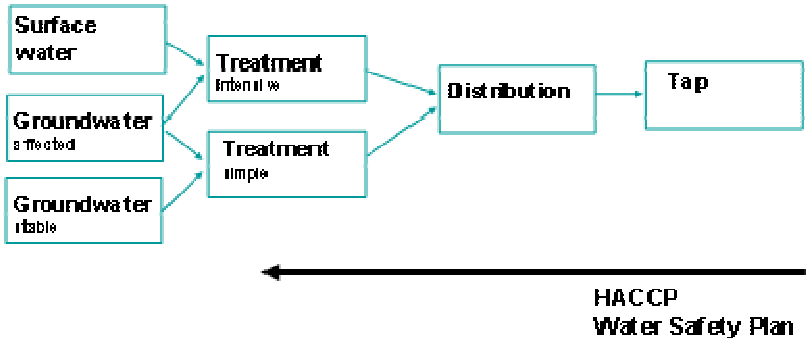

Figure 1b. HACCP enables a shift in monitoring chemical quality mainly in the end product (tap water) towards monitoring during the whole drinking water production chain.

5 Emerging techniques for chemical monitoring of water quality

5.1 Chemical screening

Analytical chemical techniques are often used for quantitative measurements of target chemicals. Chemical screening of a broad spectrum of chemicals is another possibility. Identification an quantification of the most important peaks is then possible afterwards. Recently advanced techniques have become available to identify unknown organic contaminants with higher sensitivity, such as GC/LC-UV(DAD)-Quadrupole time-of-flight mass spectrometry (LC-QTOF MS) and LC-LTQ FT Orbitrap MS, which can identify molecular weights very accurately (e.g. Hogenboom et al., 2009; Hernandez et al., 2007, Richardson 2008). Complementary techniques such as infra red spectra or nuclear magnetic resonance (NMR) can also provide structure specific information to help identify unknown structures. An example of LC-LTQ FT Orbitrap MS spectrum in influenced groundwater is given in Figure 2.

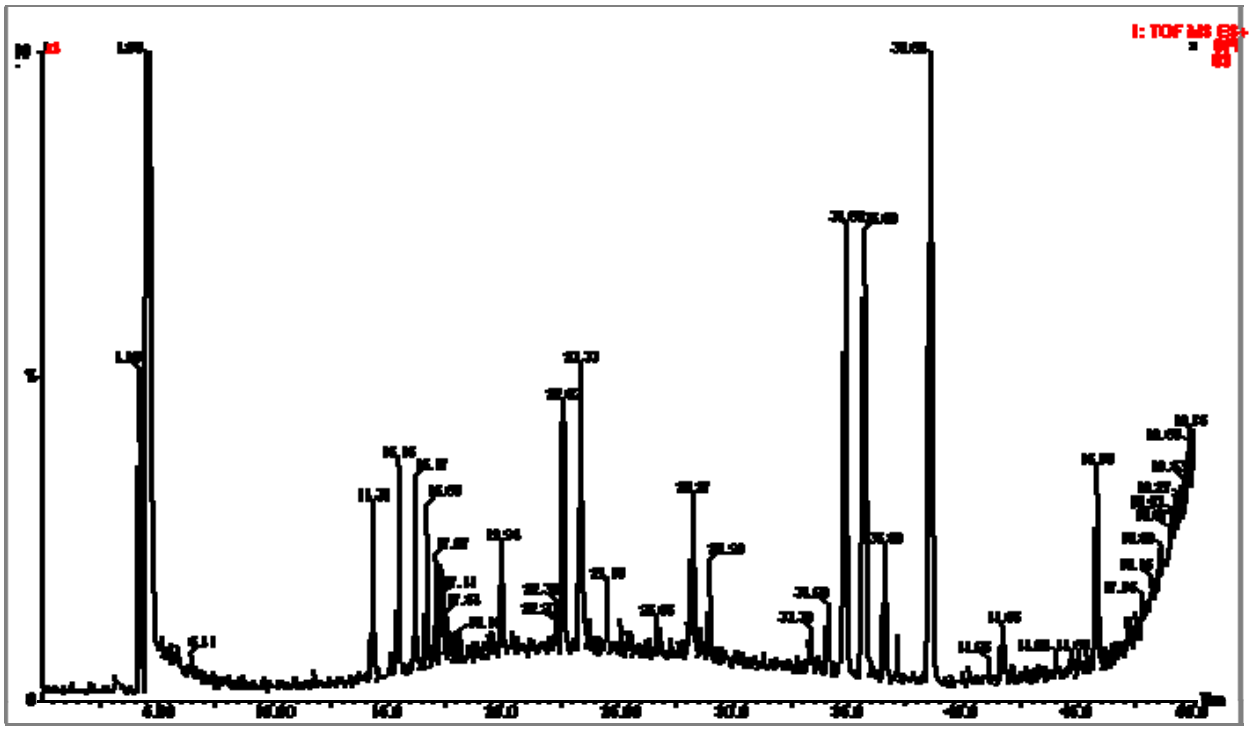

Figure 2. Example of an LC-LTQ FT Orbitrap MS spectrum in influenced groundwater.

The unknown chemicals observed in the spectra can be identified with help of exact mass. A library of approximately three thousand contaminants has been created thus far based upon field measurements in groundwater and surface water samples (Hogenboom et al., 2009). The LC-Orbitrap MS-MS has been applied in 25 Dutch groundwater abstraction wells, and various unknown polar organics have been observed in raw water (up to 20 compounds >0,5 µg/L, total concentration of 10 to 100 mg/l). An – incomplete- list of compounds that were found in groundwater is given in Table 4 (KWR Watercycle Research Institute, unpublished data). Some compounds were also identified in drinking water, in much lower concentrations. Further development is needed on sample clean-up procedures (isolation, concentration, solid phase extraction) for these polar compounds (Geiss et al, 2006; Fontanals et al, 2007).

A frequent screening of sources for drinking water, surface water as well as groundwater, improves the knowledge on the presence of unknown compounds and their sources. This information can feed possible policy actions on new priority substances. Currently however, advanced chemical screening is not performed on a routine basis and only takes place on a limited scale in research projects.

Table 4. Identified chemicals of different chemical classes found by chemical screening in Dutch groundwater wells for drinking water abstraction.

Chemical class	Chemical
pesticides	bentazon[a], metolachor[a], metazachlor, carbendazim, DEET[a], 2,6-dichlorobenzamide[a]
industrial chemicals	triethylphosphate[a], tributylphosphate[a], trifenylphosphine-oxide, bis(chloro-isopropyl)ether, bis(chloro-n-propyl)ether
pharmaceuticals	phenazon[a], propylphenazon[a], barbital[a], phenobarbital[a], meprobamate[a], aphetamine-derivate, oxymethazoline
sulfonamides	4-methylbenzenesulfonamide, n-methylsulfonamide, n-butylbenzenesulfonamide, other alkylbenzenesulfonamides
Others	various carbonic acids, ethers, tertbutylphenol, bisphenol-A, 3-cyclohexyl-1,1-dimethylureum, dicyclohexylureum, 2,3-dimethylphenylisocyanate, benzothiazolinone

[a]chemical was also found in drinking water

5.2 In vitro effect-directed bioassays

In vitro effect-directed bioassays do not determine the presence of a (group of) compound directly, but determine their effect in a biological system – often cultured cells. The identity of the compounds responsible for the toxicological effect remains unraveled, unless the effect directed bioassays are combined with analytical chemical techniques in a toxicity identification evaluation (e.g. Houtman *et al.*, 2006, Kay *et al.*, 2008). Chemicals that cannot be revealed by analytical techniques but do attribute to the toxicological effects are included in the effect directed bioassays, and the bioassays give a clue of the toxicity of the total mixture of chemicals present in environmental samples (e.g. Legler *et al.*, 2003).
For quality assessment of the drinking water production chain, relevant effect-directed bioassays are related to carcinogenicity and genotoxicity, hormonal disruption or developmental effects. These end-points are relevant human health effects which can occur after chronic exposure to relatively low concentrations. Toxicity assays that focus on acute effects are considered as less relevant; human health effects after acute exposure are not expected given the drinking water quality in developed countries.
For hormonal disruption, several effect-directed bioassays are available to measure estrogen, androgen, progesteron, glucocorticoid and thyroid activity of contaminants in human and yeast cells (Thomas *et al.*, 2002, Jin *et al.*, 1997, Sonneveld *et al.*, 2005; Marchesini *et al.*, 2006; Van der Linden *et al.*, 2008). Detection limits of the *in vitro* effect directed bioassays, including the techniques for sample preparation, are sufficiently low to meet TTC levels for the hormonal disruption tests (Table 5).

Table 5. Detection limits of various CALUX assays in water (ng/L).

Bioassay	**LOD (ng/L)**	**Reference compound**
ER (T47D)	0.004	Estradiol (E2)
Erα (U2OS)	0.01	Estradiol (E2)
AR (U2OS)	0.1	Dihydrotestosterone (DHT)
PR (U2OS)	0.05	Org2058
GR (U2OS)	0.3	Dexamethasone (Dex)
TRβ (U2OS)	0.4	Tri-iodium-thyronine (T3)

For detection of genotoxicity, various tests are available. The genotoxicity tests are classically performed with and without metabolic activation, by means of addition of S9- liver enzyme mix. Genotoxicity can be tested by measuring the induction of DNA damage itself (gene mutations, chromosomal aberrations) or by measuring the induction of the various DNA repair enzymes. As DNA damage can occur through different mechanisms, a battery of tests is necessary in both cases. However, no full battery covering all repair types for the different types of damage is available. Therefore, a battery consisting of a gene mutation test and a chromosomal aberration test is recommended (Heringa, 2005; Pfuhler *et al*., 2007). Such a combination has been shown to have good sensitivity (i.e. degree of correct positives) for rodent carcinogenicity, but poor specificity (i.e. degree of correct negatives) (Kirkland et al., 2005). To assess genotoxicity in surface water a combination of the Comet assay with human lymphocytes next to the Ames or umu-test was proven useful (Grummt, 2001; Minnear and Plewa, 2003). If one of the tests is positive, a third assay should be performed preferably using an assay based on mammalian cells. If a genotoxic sample remains genotoxic after conventional water treatment, additional research including unraveling of responsible chemicals and risk assessment will be necessary.
Finally, there are several assays to cover adverse developmental effects using Daphnia, fish or tadpole as model systems (eg Abe *et al*. 2000; McGrath & Li, 2008, Gutleb *et al*., 2007). These are at the moment not used in screening of drinking water quality, but seem promising and relevant tools also as model systems for humans (Schmale *et al*. 2006, Berry *et al*., 2007). Many of the emerging diseases mentioned in the introduction which are sometimes suggested to be related to exposure to chemicals can originate during the fetal development.
Because of the detection limits of the assays, often sample preparation and concentration will be needed to test aqueous samples in effect-directed bioassays. During this sample preparation, the original chemical mixture should be modified due to eg. volatilization or sorption as least as possible.
Currently, the significance of test results in the effect-directed bioassays in terms of human health risks is still in debate. Adsorption, distribution, metabolism and elimination of contaminants by the human body influence their toxicity, and these processes are only partly mimicked in the bioassays. At the moment, water quality limits expressed in terms of acceptable effects in *in vitro* bioassays are still to be developed. In *in vivo* assays adsorption, distribution, metabolism and elimination (ADME) will influence toxicokinetics. These factors will not always be well mimicked in *in vitro* assays. In order to come to effect-directed quality limits, it is proposed to base these on the Acceptable Daily Intake value (ADI) of a highly potent reference compound, and to translate this value into effect-based limits using worst case assumptions for ADME (Van der Oost, 2008).

5.3 Sensoring

During the past decades there has been much scientific progress in the development of on-line detectors and –sensors for the monitoring of chemical water quality (eg Allan *et al*, 2006ab, Rodriguez-Mozaz *et al*., 2007, Greenwood *et al*., 2007, Lambeck 2006). For many chemicals or chemical classes, on-line sensor systems are not yet available.
A promising development are on-line biosensors, using the (specific) binding of chemicals to receptors in genetically engineered luminescent bacteria. Pilot experiments are carried out with these biosensors (e.g. Gu *et al*, 2004; Lee and Gu, 2005; Popovtzer *et al*, 2005; Polyak *et al* 2001; Pedahzur *et al* 2004; Stolper *et al* 2008, Daniel *et al* 2008). More general measurements can also be useful for event detection. An example is the use of UV or fluorescence sensors or probes to detect contamination events (Henderson *et al*., in press).
A recent survey at various waterworks over the world showed that sensors for chemical water quality are not commonly used yet (van der Gaag and Volz, 2008). Suggestions to explain the lack of chemical sensor implementation included a poor link between available sensor technologies and water quality regulations, and the challenge for management of the data quantities and translating them into meaningful operational information. The main benefits of using sensors are their low costs and their speed, thus enabling a fast reaction on possible disturbances of water quality due to calamities. To make fast corrective action possible, intelligent data handling systems integrating available sensor data in time and space are still to be developed.
At the moment the available sensors do not yet compete with on-line SPE LC-MS methods concerning sensitivity, reproducibility and suitability for multi-chemical analysis (Rodriguez-Mozaz *et al*., 2007).

5.4 Integration of different monitoring techniques

The different monitoring techniques available can yield complementary information. For example, on-line sensoring and biomonitoting techniques can provide a first tier. For further assessment, a combination of a toolbox of effect-directed bioassays is useful. To unravel the identity of the responsible toxic compounds chemical screening techniques are very helpful. A further automation of monitoring techniques and developments to become more online and (semi-) continuous, will increase available information and integration possibilities.

6 Frequency of monitoring

The monitoring frequency at a location depends on the time-variability of the water quality and on the presence of local threats, such soil contamination, an aged distribution network or terror threats. At points where corrective actions are taken sometimes, (semi-) continuous monitoring makes sense. Automated, real-time and on-line monitoring systems are relevant in situations with a high time-variability at control points where corrective actions are taken relatively often. Table 6 works this out in more detail for the drinking water production chain.

Table 6. Monitoring in the drinking water production chain, coupled to management and incidental corrective actions.

Point in production chain	Management measure	Frequency monitoring	Possible corrective action
Source: stable groundwater	Rely on relatively clean sources	Incidental	
Source: influenced groundwater	Rely on relatively clean sources	Low to frequent	Intake shift coupled to redundancy in sources
Source: surface water	Rely on relatively clean sources	High to (semi-) continuous	Intake stop coupled to reservoir
Treatment	Add extra treatment steps	Frequency depends on type of source and treatment[a]	Distributionstop, distribution from redundant facility, informing consumers
Distribution	Knowledge of distribution network and soil quality, threat of terror	Frequency depends on type of threats[b]	Distributionstop, distribution from redundant facility, informing consumers
Tap	Verification	Avarage	

[a]High frequency if source quality is variable and reactive treatment methods are applied, low frequency if sources are relatively clean and treatment methods are well-known (aeration, sand filtration, organic carbon)
[b]High frequency with aged distribution network, presence of serious soil contamination or threat of terror

Source quality is often highly variable for surface water, less variable for artificial infiltrates in soil, dunes or river banks and groundwaters influenced by human activities, and stable for pristine groundwaters. The intensity of the monitoring is coupled to this time-variability. Possible corrective actions are e.g. intake stops for surface water coupled to a redundant reservoir, and possibilities to shift between various sources. Depending on source quality, drinking water is treated with simple physical techniques (e.g. sand filtration and aeration) or more advanced and intensive treatment (e.g. ozonation, UV-radiation, peroxidation, reversed osmosis, ultrafiltration or keramic membranes, antiscalants etc.). The monitoring intensity of the treatment depends on the type of source and treatment techniques used. A higher frequency makes sense with a time-variable source quality and with reactive treatment techniques possibly resulting in toxic by-products (eg. Andrzejewski *et al*., 2008, Von Gunten, 2003, Toor & Mohseni, 2007, Wang *et al*., 2007, Ashbolt, 2004). Since drinking water distribution is a vital infrastructure for society, since the beginning of this decade the threat of terror is of relevance. Malicious acts will presumable include warfare chemicals such as vesicant agents, nerve agents, herbicides, cyanide or biotoxines (Bismuth *et al*., 2004, Szinicz 2005). As ultimate corrective actions, a distribution stop, distribution from a redundant facility or informing consumers on water use limitations can be mentioned. However, it is clear that corrective actions taken earlier in the drinking water production chain will in general be cheaper and less harmful towards consumers' trust in the quality of the drinking water.

7 Conclusions

Present routine monitoring in the drinking water production chain is mainly focused upon 'classical' chemicals such as heavy metals, PAHs, pesticides and chlorinated hydrocarbons, compounds which are also regulated by various EU Directives. The water quality monitoring is much less focused on emerging environmental contaminants which are often coupled to consumers' behavior, such as pharmaceuticals, drugs-of- abuse, endocrine disrupting compounds and perfluorinated chemicals, nor is it focused on detecting risks for chronic toxicity. However, many literature sources point to the relevance of these emerging contaminants and their possible chronic toxicological effects.

As analytical techniques evolve, more and more emerging chemicals are measured. For unregulated chemicals the concept of 'threshold of toxicological concern' or TTC can be applied to drinking water to interpret the significance for human health risks. Current on-line biomonitoring and on-line analytical methods do not meet the aforementioned TTCs.

The HACCP (Hazard Analysis Critical Control Points) is valid for drinking water production, but less well-established then in the context of food safety. HACCP gives clues for optimizing chemical monitoring in the drinking water production chain, and emerging monitoring techniques enable a shift to more intensive and frequent monitoring during the whole production process and for a broad set of chemicals. A shift in focus from monitoring water quality at the end of the drinking water production chain towards monitoring throughout the chain, coupled to process knowledge and possible corrective actions, can stimulate further process knowledge for example on the efficiency of various water treatment technologies and enables a more pro-active management for drinking water production. Examples of emerging monitoring techniques are chemical screening, sensoring and effect-directed assays for relevant human health endpoints (e.g. genotoxicity, endocrine disruption and developmental effects).

Combining various techniques, such as chemical target analysis, screening and identification, biomonitors, health-related effect assays and possibly sensor information will lead to the much needed complementary information.

The desirable monitoring frequency at a location depends on the time-variability of the water quality and on the presence of local threats.

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