Monitoring and Assessment of Chemical Quality

Session Objectives

- To highlight the relative priority for microbiological and chemical water quality monitoring and emphasis the need for a rational, health-based approach to monitoring of water quality.

- To outline the key characteristics of monitoring programmes which may be implemented for chemical water quality.

- To describe the analytical ranges commonly employed in chemical water quality monitoring, highlight key constraints in chemical analysis and stress the need for quality control.

- To emphasis the value of risk assessment as a key supporting activity of chemical analysis and in planning monitoring programmes.

Monitoring and Assessment of Chemical Quality

Introduction

Chemical testing is generally not undertaken as frequently as microbiological analysis because, in general, the health risks posed by chemicals are chronic rather than acute and because changes in water chemistry tend to be longer-term unless a specific pollution event has occurred. It should be stressed that monitoring the microbiological quality of water is much more important than monitoring of chemical quality and chemical testing should generally be a lower priority.

However, where resources permit, routine testing of the chemical quality of water should be undertaken. Priority should be given to those substances which are known to be of importance to health and which are known to be present in significant concentrations in drinking-water. For instance, the monitoring of nitrate is recommended in many water supplies and in particular those which are located in rural areas, or where recharge occurs in an agricultural area. In these circumstances, regular monitoring is recommended to ensure that early warning of increases is noted or when nitrate releases are highly seasonal in nature.

An assessment of the chemical quality of water should be undertaken during source selection and this should relate to known activities within the catchment of the source and possible natural pollutants. This should be as comprehensive as possible and cover a wide range of pollutants.

In areas where toxic chemicals are released into the aquatic environment, routine monitoring should be undertaken and closely linked with an emergencies warning procedure which should function to alert water suppliers, surveillance agencies and health bodies of any accidental releases of substances into water sources.

Types of monitoring programme

As with any form of monitoring, it is important that clear objectives are set before the start of data collection activities and that sample sites and frequency of analysis are determined to meet the objectives and not vice versa. In the past, some water quality assessments have worked from the other way round and monitoring programmes have been designed to fit existing infrastructure. The problem with this approach is that it very often results in a failure to address the most pressing problems and also a failure to provide a full picture of the problem being monitored.

In general, monitoring of the chemical quality of water may be undertaken in two ways.

1. *Routine monitoring of known problem substances*: this type of programme is designed to keep a continuous watch on substances which are known to have a health impact or compromise treatment efficiency and which are known or suspected to be in the water supply to be monitored. It is important that substances whose concentration is likely to change are monitored more regularly than those where concentrations are essentially stable. This is largely determined by the source of the contamination. Contaminants from essentially natural sources, such as fluoride, are unlikely to vary significantly over time and therefore do not

require frequent analysis. Although there may be exceptions to this such as the raised arsenic levels in some groundwaters in West Bengal, India. Contaminants deriving from anthropogenic sources of pollution may require more frequent analysis, for instance heavy metals in water sources downstream of tannery waste discharges. Equally, where treatment is employed to remove or control specific substances (e.g. nitrate or phosphorous), these should be routinely monitored at the plant to ensure that treatment is effective.

2. *Periodic quality assessment*: this type of monitoring is either routine or non-routine assessment of water quality done on a relatively infrequent basis (annual or greater). Such assessments will certainly be done during the source selection procedure and may involve periodic evaluations of trends in water quality over time. Such assessments are likely to include a wider analytical range and be used to provide regular comprehensive assessments of water quality to assist in long-term water source and supply management and for long-term trend analysis.

Both approaches will concentrate on water quality in the source and as it leaves the treatment works or borehole, with a limited number of samples taken from within the distribution system, unless the materials used in the distribution system are suspected of providing a significant proportion of a harmful substance. In these circumstances it is usually more effective to monitor and control the quality of materials and chemicals used in water treatment during their production and prior to their use. However, where materials or chemicals have been used without quality control during manufacture, some monitoring of specific chemicals may be required by the public health agency. For instance, where lead pipes or lead-based solders are used, regular monitoring of lead may be recommended.

Selection of variables for monitoring and assessment

As mentioned above, during source selection, a comprehensive assessment should be made of water quality to ensure that any likely risks to health are identified and appropriate action taken with regard to source protection, treatment requirements and blending of water. Thus analysis of the major ions and nutrients should be done on all water supplies as well as any other substances deemed likely to be present on the basis of land-use within the catchment of the source. However, whilst it is preferable to have a complete and comprehensive description of water quality before a water supply is commissioned, there are a number of constraints in trying to achieve this.

Many analyses are expensive to carry out, both in terms of the equipment required to perform the analysis and in terms of the consumable required. This means that if analysis is required for a particular analyte which uses sophisticated equipment, this may only be done occasionally when the laboratory has enough samples to make it economic to start up the equipment and run the analysis. It is never economic to start equipment such HPLC or a flame photometer to carry out a single analysis. Therefore appropriate storage facilities are required for the sample and appropriate preservatives must be available to prevent sample deterioration. This will further increase the costs of analysis.

Thus for some parameters, there may be a considerable time to wait before the results of analysis are known. However, the delay in opening the water supply, particularly in droughtprone areas, may be unacceptable. Therefore during source selection, parameters should be divided into essential and desirable. This should be done based on the risk to health, potential to cause consumer rejection, likelihood of causing operational problems, cost and ease of analysis, likelihood of presence in drinking-water.

The net result is likely to be a range of parameters which are analysed rapidly and perhaps on-site and before the source is commissioned (for instance, nitrate, fluoride, iron etc.) and those which will be done, but possibly after the source has been commissioned.

There are a number of parameters which, when used in conjunction with a pollution source assessment, provide a good overall indication of chemical water quality and others whose impact on human health or the environment are great and should be included in initial testing. The presence at high levels of these parameters in the source water may indicate that other analyses are required. These include: nitrate, pH, Eh, fluoride, dissolved oxygen and chloride.

The presence of elevated levels of nitrate in water indicates pollution of the source and it is important that the type and source of the pollution is identified. Nitrate pollution may occur from agricultural source, sewage disposal and urban runoff. Agricultural sources may indicate that there will also be a problem with other agricultural pollutants such as pesticides. It is important that a survey is carried out to identify whether there is use of pesticides in the area and to find out application rates and time of application. Pesticide analysis is difficult and expensive, indeed there are a number of pesticides for which no analytical methods exists for detection in water, therefore routine analysis of pesticides will not be carried out at the start of a programme and is rarely fully developed. Nitrate contamination which can be linked to a sewage outfall may also indicate unacceptably high levels of microbiological contamination which should be addressed as a matter of priority.

For routine analysis, both the monitoring agency and the supplier should aim to concentrate on those chemical parameters which are of greatest health significance or provide a general description of water quality and for which analysis is inexpensive, quick and may be done on-site. There are variables such as pH and Eh (redox potential) which should, by preference, be done on-site as the sample may deteriorate during transport.

Risk assessment

As with microbiological monitoring, it is important that monitoring of chemical water quality is linked to a process of hazard identification and risk assessment. Thus when designing a monitoring programme, an inventory of likely sources of pollution and the likely vulnerability of a water source or distribution system to contamination should be made. This means that information will be required on the following:

- geographical features, including topography, relief, lithology, climate, land-use, hydrology;
- other water uses from the source; and
- pollution sources, treatment of wastes and discharge consents in operation.

Risk assessment should be a dynamic process which is conducted or updated routinely by suppliers and surveillance bodies to ensure that no new risks are developing for which remedial or preventative action is required. Thus, for each new activity established within the catchment of the water source used for drinking purposes, a detailed description of likely pollutants that may be discharged, wastewater treatment arrangements, recycling and discharge consents must be obtained. These should be used to allow water suppliers and surveillance bodies to object to developments which will compromise public health through likely discharges and to establish monitoring programmes which are focused on health-based risk assessment.

Chemical testing of drinking-water supplies is often linked to source quality monitoring and thus it is very important that hydrological data are collected at the same time as quality data as this has a profound influence on water quality. Flows in rivers will determine the concentration of pollutants in the aquatic environment. For instance, in the UK at low flows, up to 95 per cent of the flow of many rivers which pass through urban areas is municipal effluent, whilst at high flows this percentage will be greatly decreased and effluent may only account for 30% of the flow.

The status of rivers with regard to groundwater is also important as this will influence water quality. Hydrogeological data are also important as water level, flow patterns and water movement rates will all affect water quality. For example, changes in water level may significantly alter water quality as pollutants removed from infiltrating water in the unsaturated zone by sorption may be eluted (de-sorbed) if the groundwater level later rises.

Quality control

It is important that data generated in chemical testing programmes in different regions are comparable and that time series of data are also comparable. Therefore: standard operating procedures are required for sampling, field testing and data reporting; AQC schemes should be carried out for all laboratories carrying out analysis; field equipment should be regularly checked and calibrated; staff should be adequately trained and supervised.

Provided the same analytical techniques are used over the time period to be studied and the above are implemented, data time series should be comparable. However, as analytical techniques are continually improving and changing, it is common to find that techniques for analysing particular variables change and that the results produced are not directly comparable to previous methods. When this happens, it is important that both the new and old technique are used to analyse samples for a hand-over period to allow a conversion graph to be prepared to allow comparison of the results of both methods.

Where there are a number of laboratories involved in water quality analysis, there should, preferably be some form of inter-laboratory comparison. This may take the form of a reference laboratory provided spiked samples to laboratories in which the concentrations of chemical constituents is not known by the participating laboratories. Alternatively, laboratories can rotate quality assurance sample preparation. The purpose of such procedures is to improve the overall reliability of the data produced in water quality analysis.

Conclusion

Chemical monitoring is a lower priority than microbiological monitoring. As monitoring of chemical water quality is developed, a clear priority should be given to substances of known health impact and which are known or suspected to be in the water supply. Monitoring may be carried out routinely for some chemicals whose presence in water is likely to change over time, for which treatment is applied, or which have highly seasonal profiles. For most chemicals, and for all contaminants which have a natural source in the environment, monitoring may be done through periodic assessment of water quality.

Monitoring of chemical water quality should incorporate hazard identification and risk assessment as a key tool for managing risks. Thus, water suppliers and surveillance bodies should be aware of all potentially polluting activities within the catchment of a water source and use this information to help design monitoring programmes. Where activities involving the use or production of toxic chemicals, adequate emergency warning procedures must be established which will ensure that water suppliers and surveillance bodies are kept informed of any accidental spill into water sources.

References

Chapman, D. (ed) (1996) Water Quality Assessments. 2nd edition. Chapman and Hall.

Anon. (1993) WHO Guidelines for Drinking-water Quality, Volume 1. WHO, Geneva.

Howard, G and Simonds, A, (1995) Where there is no training - pollution risk assessment for field staff. Waterlines, Vol 14, No. 1. July 1995.

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Presentation Plan

Section	Key points	OHP
Introduction	• chemicals evaluated during the preparation of the 2nd edition of the Guidelines • many chemicals, such as nitrate, lead and arsenic, can be toxic to humans and may come from natural and anthropogenic sources • chemical testing not undertaken as often as microbiological testing because most health risks are chronic not acute • changes in water chemistry also tend to be long-term unless specific pollution event occurs • where possible do routine monitoring of chemicals of health concern and known to be in drinking-water - e.g. nitrate • comprehensive assessment of chemical water quality should be done during source selection • early warning procedures essential and should link resource managers, water suppliers, surveillance agency and health bodies	**1,2,3**
Types of monitoring programme	• need to have clear objectives before data collection starts and monitoring network should be designed to match objectives not vice versa • where objectives are set to match monitoring programmes may fail to meet most pressing needs • two key approaches to chemical monitoring *1 routine monitoring of known problem substances* - designed for continuous surveillance of substances of health concern and which are in water supply - only routinely monitor substances where concentration likely to change because of a pollution event or treatment failure *2 periodic quality assessment* - either routine or non-routine assessment of water quality on relatively infrequent basis - assessment certainly done during source selection and subsequent occasional evaluations - such assessments likely to have a broader analytical range than routine monitoring	**4,5**

Section	Key points	OHP
Types of monitoring programme *(continued)*	• both types of monitoring tend to focus on sources and where water leaves pumping station or treatment plant unless distribution system suspected of leaching substances into the water • where substances in water are derived from chemicals and materials used to treat and distribute water, it is often better to monitor and control manufacture than in drinking-water	
Variable selection	• preferable to have a complete description of quality of a water supply prior to commissioning, but may be problems in achieving this • many analytes expensive to analyse for and only economic for analysis of a limited number of samples, therefore may delay analysis • this has implications for source commission as unacceptable in many circumstances to wait until results available for commissioning • therefore need to identify a restricted range of analytes of health concern which can be used to indicate broader problems and which are relatively easy to analyse, e.g. nitrate and pH • nitrate is of particular concern and in many circumstances is routinely monitored and source identified as this may indicate other pollution • for routine analysis concentrate on chemicals of known health concern and can be easily monitored • some parameters should be done on-site to prevent sample deterioration	**6**
Risk assessment	• monitoring chemical quality should also be linked to risk assessment and hazard identification • when assessing vulnerability make sure collect information on geographical/geological features that may increase vulnerability • during risk assessment identify all likely sources of pollution • risk assessment is dynamic and should be routinely undertaken • both supplier and surveillance agency should be aware of new activities within the catchment to predict likely impacts on water supply • need to collect hydrological/hydrogeological data as well as quality data	**7**

Section	Key points	OHP
Quality control	• need to be able to compare data from different regions and time series of data • therefore quality control is essential and standard operating procedures are required for sampling, analysis and reporting • all equipment, including field kits, require calibration and staff trained • where techniques change over time, ensure that new techniques is calibrated against old technique to ensure comparability • inter-laboratory comparison is important for improving and maintaining analytical quality	
Conclusions	• chemical monitoring is a lower priority than microbiological monitoring • priority should be given to those parameters of known health concern • routine monitoring should be done for parameters whose concentration is likely to vary, for which treatment is carried out or which have seasonal profiles • hazard identification and risk assessment should also be carried out and an early warning system implemented	

Assessment of Health Risks of Chemicals in Drinking-Water

	Number of chemicals considered
Inorganics	34
Organics	
Chlorinated alkanes	5
Chlorinated ethenes	5
Aromatic hyrdocarbons	6
Chlorinated benzenes	5
Miscellaneous organics	9
Pesticides	35
Disinfectants	6
Disinfectant by-products	23
TOTAL	**128**

Chemical Monitoring

- Far lower priority than microbiological monitoring
- Comprehensive assessment of water quality recommended during source selection
- Must be linked to ongoing risk assessment
- Quality control and assurance are vital for compliance monitoring

Toxic Chemicals in Water

Nitrate:

- Causes acute health effect in infants
- May be pronounced seasonal variation
- Long-term levels increasing worldwide
- Nitrate often monitored routinely

Lead:

- Link to intellectual impairment
- Main source in water likely to be from pipes/solders
- Monitor lead in water *or* monitor use of lead pipes

Arsenic:

- Often natural source
- Release due to water table lowering (India) - arsenates are desorbed during recharge
- Release under urban areas related to waterlogging and raised pH from humic and fluvic acids

Monitoring Chemical Contaminants

- Chemicals are often difficult or expensive to remove
- Chemical pollutants from natural sources tend to vary slowly
- No universal indicator chemicals have been identified unlike indicator bacteria
- Therefore, monitoring at long intervals unless:
  - a health problem is identified
  - treatment is applied to remove substance
  - a pollution event is recorded which may affect supply
  - upgrading/expansion of system is planned

Monitoring Strategies for Physio-Chemical Monitoring

These vary according to parameter:

- Critical parameters (turbidity, pH, chlorine residual) routine analysis
- Known/suspected problem with particular substance (nitrate, THM, etc.) - routine analysis

Other parameters are analysed on an occasional basis:

- If their presence is suspected at harmful levels (e.g. fluoride)
- During source selection and infrequently afterwards
- Once problem and scale is identified there is no value in regular monitoring as levels unlikely to change quickly.

Physio-Chemical Monitoring

Parameters:

- Temperature
- pH
- Conductivity
- Redox potential (Eh)
- Turbidity
- Total suspended solids
- Total dissolved solids

Chemical compounds such as:

- Chlorine residual
- Nitrate
- Fluoride
- Arsenic
- Aluminum
- Lead
- THMs
- Some pesticides, etc..

Risk Assessment

- Risk assessment should be ongoing
- Initial assessment during source selection should identify potential sources of pollution
- Pollution risks assessment should be carried out whenever a new activity starts
- Regular assessment will support analytical work