Chapter 19

Risk assessment and risk management in Managed Aquifer Recharge

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This chapter presents the methodologies used for risk assessment (RA) and risk management (RM) in MAR in Australia and within the European Union, qualitative and quantitative approaches adopted within the RECLAIM Water project and case studies where the outcomes of these approaches are presented.

19.1 METHODOLOGIES FOR RISK ASSESSMENT AND MANAGEMENT

Risks to human health and the environment are dealt with in each country based on the particular legislative environment. General methodologies for risk assessment in Australia and in the European Union associated with MAR are summarised in this section.

19.1.1 European Union

While there are no provisions in European Union (EU) wide legislation focussed explicitly on RA and RM for MAR, there are many pieces of legislation and policy affecting them. Key Union wide regulatory elements having a strong impact on RA/RM for MAR include the Water Framework Directive 2000/60/EC (WFD), the Ground Water Daughter Directive 2006/18/EC (GWD), the Environmental Impact Assessment Directive 85/337/EEC (EIAD), the Nitrate Directive 91/676/EEC (ND) and for water to be intended for human consumption, the Drinking Water Directive 98/83/EC (DWD).

The WFD reinforces the well established requirement of taking into account the precautionary principle, relying in particular on the determination of any potentially adverse effects of the reclaimed water and on a scientific assessment of the risk. It recognises that preventative measures or treatment shall have to be employed in each case consistent with the perceived level of risk. Whilst specifying preventative measures to be employed, the WFD consents also case-by-case assessment where field data or model ecosystems would allow more precise preventative measures to be calculated and applied.

Article 16 (2) of the WFD prescribes that risk assessment for chemical contaminants should be performed under Council Regulation (EEC) No 793/93, Council Directive 91/414/EEC (both repealed by Regulation (EC) 1907/2006), and Directive 98/8/EC, or targeted risk-based assessment focusing solely on aquatic eco-toxicity and on human toxicity via the aquatic environment. This simplified risk-based assessment procedure based on scientific principles should take particular account of:

- Evidence regarding the intrinsic hazard of the substance concerned, and in particular its aquatic eco-toxicity and human toxicity via aquatic exposure routes, and
- Evidence from monitoring of widespread environmental contamination, and
- Other proven factors which may indicate the possibility of widespread environmental contamination, such as production or use volume of the substance concerned, and use patterns.

Other specific actions for the protection of the groundwater resources connected to the WFD are included in the ND and in the GWD. In particular, Annex I of the GWD prescribes that the results of the application of the quality standards for

pesticides in the manner specified for the purposes of the GWD will be without prejudice to the results of the risk assessment procedures required by the above mentioned Directive 91/414/EEC (repealed by Regulation (EC) 1907/2006) or Directive 98/8/EC.

If recovered water is intended for use as a drinking water supply, then the main legal instruments for the control of drinking water quality is the DWD. The existing DWD focuses on compliance monitoring of the final product. In light of the precautionary principle, however, parametric indicators set out in the DWD are not sufficient to say that recovered water from MAR sites is safe. The water supplier is requested to perform analyses on the chemicals and microorganisms not covered by the limits but that can be present in the water and that can pose a risk to public health. Reclaimed water can possibly contain microbiological and chemical contamination of a much larger number of compounds than the minimum set included in the DWD, which refers to pristine catchments. The starting point for risk assessment is provided by the Decision 2455/2001/CE of the European Parliament and of the Council establishing a first list of priority substances ubiquitously present in wastewater, based on a procedure for the definition of the priorities based on the principles of monitoring and modelling.

The European Commission is considering further development of preventive risk management to update/revise DWD. Areas of intervention should include the introduction of the principles of RA/RM, and of the basis of those principles, revision of microbiological and chemical parameters with an increasing decision making role of the single water utility. Several EU member states and federal regions have already adopted their own standards and regulations in this sense, while others are reportedly waiting for revision of the DWD to introduce such concepts. For example, in France, Article 18 of the Decree 2001-1220 shifts emphasis in national drinking water legislation towards a preventative quality assurance approach that encompasses RA and RM strategies. RA/RM principles and methods used in drinking water draw on other methods, particularly on Hazard Analysis and Critical Control Points (HACCP). As the HACCP approach is compulsory in the food sector, in EU member states where water utilities fall under the provisions of Food Safety Acts, such as for instance in Lithuania and in Austria, development and implementation of a HACCP is already an obligation.

Similarly, in Spain, the central water authority is evaluating the implementation of WHO style water safety plans (WSPs), see also the section below specific to Spain. The WSP can be defined as the adaptation of HACCP to the specific requirements of the drinking water sector. Although some MAR projects are under way in Spain, with experience being gained through pilot studies, a specific regulation is still lacking in the country. Every MAR project is regarded as a different case, and different authorisations are required, depending on the environmental matrices involved.

In the new hydrological plan developed by the Spanish Environment Department, MAR is included in only those using the riverbed of main rivers to recharge, and only two, the Llobregat River and Pla de Palma, use a recycled water source. However, there are many more pilot studies using reclaimed water as a source. In most of the cases, MAR is considered as a treated wastewater reuse case, thus it has to attain the Royal Decree concerning water reuse (R. D. 1620/2007 of 7th September 2007). This Royal Decree defines the quality that the reclaimed water must have depending on its final reuse purpose, considering MAR as one of them. Besides, and in view of the lack of regulations, a groundwater law is being prepared by the Spanish Environmental Department, which will also consider MAR.

The Spanish case study involved in the RECLAIM Water project, Sabadell, uses a riverbed as a means of recharging the underlying alluvial aquifer. To date, no authorisation procedure for the recharge of the aquifer is required, as the system is not interpreted as a "pure" artificial recharge scheme by the administration. It is considered that the WWTP discharges the effluent in the Ripoll River, hence contributing to the preservation of its ecological flow, and as such is not constrained to discharge regulations. It is not considered as an indirect artificial recharge site but specifically as an "ecological river flow maintenance" site. For this type of reuse application, the water quality or sampling routine required have not been specifically defined yet, the decree only indicates that "the minimum quality required will be studied case by case".

In the UK, impetus for WSP implementation was given by the regulator stating that drinking-water improvement schemes for the next five year investment programme would only receive regulator support if they were identified through WSP methodology. Compliance monitoring was initially viewed as the main WSP verification stage. However, additionally from the beginning of 2008, the hazard identification and risk assessment elements of the WSP framework were made regulatory requirements and WSPs began to feature in the regulator's audit programme. Drinking-water improvement programmes from 2009 onward must be identified through the water safety plan approach.

Furthermore, other incentives for implementation of preventive risk management are the provisions of the European Council Directive 2004/35/CE on Environmental Liability. This Directive prescribes that it is incumbent on the operator to demonstrate that he is not negligent/at fault. Another strong incentive to operate with state of the art risk management procedures is the requirement for the development of financial security instruments and markets.

HACCP methodology

HACCP is a tool which evaluates the hazards and establishes control systems which focuses on prevention rather than on the final product. The tool can be applied to the whole water treatment train and to the environment where water is disposed.

Initially, seven basic principles of the HACCP system were stated, namely (Codex Alimentarius, 1997):

(1) Hazard analysis and determination of preventive measures – conduct a hazard analysis by indentifying each hazard, assess the likelihood of occurrence and severity and identify the preventive control measures in place to control that hazard. Hazards are usually described as any biological/microbiological, chemical or physical agent that may contaminate the product (in our case groundwater).
(2) Identification of the Critical Control Points (CCP) – determine the Critical Control Points (CCPs) in the process and operational procedures that can be controlled to minimise the likelihood of each hazard occurring.
(3) Determination of the critical limits for every CCP – establish critical limit(s) for each CCP which must be met to ensure that the CCP is under control.
(4) Monitoring of the CCP – establish a system to monitor the control of the CCP, which is a planned sequence of events, observations, measurements and records needed for assessment whether a CCP is under control.
(5) Corrective measures – implements the corrective action to be taken in case of monitoring indicating that a particular CCP is not under control.
(6) Verification/validation – establish procedures for verification, including supplementary tests to ensure that the HACCP system is working effectively.
(7) Registers – establish documentation concerning all relevant procedures and records to meet these principles and their application.

The seven principles are necessary elements for developing a self-controlled procedure based on the HACCP system in order to ensure the control of the risks which are significant for the safety of the reclaimed water. The water-related authorities – like other authorities – adopt the concept that self-control is a necessity in order to not oversize the bodies of the administration and to incorporate the stakeholders in the important task to ensure public health and success of any environmental or agrofood project. Additional examples of adaption of the HACCP methodology are given the following section on Australia.

19.1.2 Australia

The Australian Guidelines for Water Recycling (Phase 2): Managed Aquifer Recharge (called the MAR guidelines) are the foundational document which describe the approach adopted to risk assessment and management for MAR in Australia. The MAR guidelines form an integral part of the National Water Quality Management Strategy (NWQMS), upon which contemporary water resource management in Australia is based. The MAR guidelines build on the policies and principles of the strategy, and on other key NWQMS guidelines, such as drinking water. The MAR guidelines include assessment of the aquifer which is what sets them apart from the other water recycling examples in the Phase 1 guidelines (NHMRC–EPHC–AHMC, 2006).

Although the subsurface component provides water storage and treatment functions, it may add hazards to stored water and create other environmental problems. The Australian MAR guidelines aim to provide a sound and consistent basis for protecting human health and the environment for MAR operations. The guidelines focus on the protection of aquifers and the quality of recovered water in managed aquifer recharge projects. Where managed aquifer recharge is part of water recycling projects, the MAR guidelines are used in conjunction with the Australian Guidelines for Water Recycling (Phase 1) (NHMRC– EPHC–AHMC, 2006). If stormwater is the source of the water to be recharged, then Australian Guidelines for Water Recycling: Stormwater Harvesting and Reuse (NRMMC-EPHC–NHMRC, 2009a) should be used. If recovered water is intended for use as a drinking water supply, then Australian Guidelines for Water Recycling: Augmentation of Drinking Water should also be used.

Australian approach to risk management in MAR

In Australia, the risks to human health and the environment, including the receiving aquifer, are managed through the development of a risk management plan for MAR. This plan involves the 12 fundamental elements (developed on the 7 HACCP principals) adopted in Phase 1 of Australia's guidelines for water recycling (NRMMC–EPHC–AHMC 2006); these elements are shown in Figure 19.1.

The 12 elements of the framework presented in the Phase 1 Australian guidelines for Water Recycling apply as much to MAR as to other applications of recycled or drinking water management. The 12 elements are not sequential; they should all be followed to ensure that the risk management plan is comprehensive. The resulting 'managed aquifer recharge risk management plan' is a documented system for the management of aquifer recharge. The central philosophy of the MAR guidelines is that it is better to prevent hazardous events from occurring than to clean up their effects afterwards. The multiple barrier approach is a key concept in the management of risks in aquifer recharge. This same approach is well established as a means of protecting drinking water quality in Australia (NHMRC–NRMMC, 2004), and internationally by the WSP approach described above (WHO, 2006). The application of the multiple barrier approach through the MAR risk management plan should encompass every component of the MAR system.

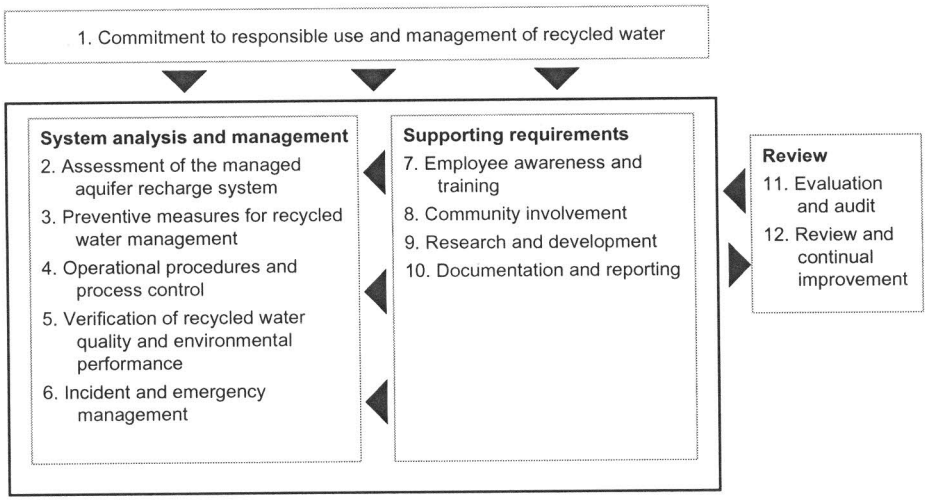

Figure 19.1. Elements of the framework used in Australia for managing water quality and use

Australian approach to stage project development in Managed Aquifer Recharge

MAR risk assessments are interspersed between the various project development stages to address catchment and groundwater plans as well as local government requirements. Figure 19.2 shows a series of risk assessments that are designed to ensure protection of human health and the environment, as in the Phase 1 guidelines (NRMMC–EPHC–AHMC 2006). These risk assessments allow staged decision points for investment, based on an informed understanding of the next required level of investigations.

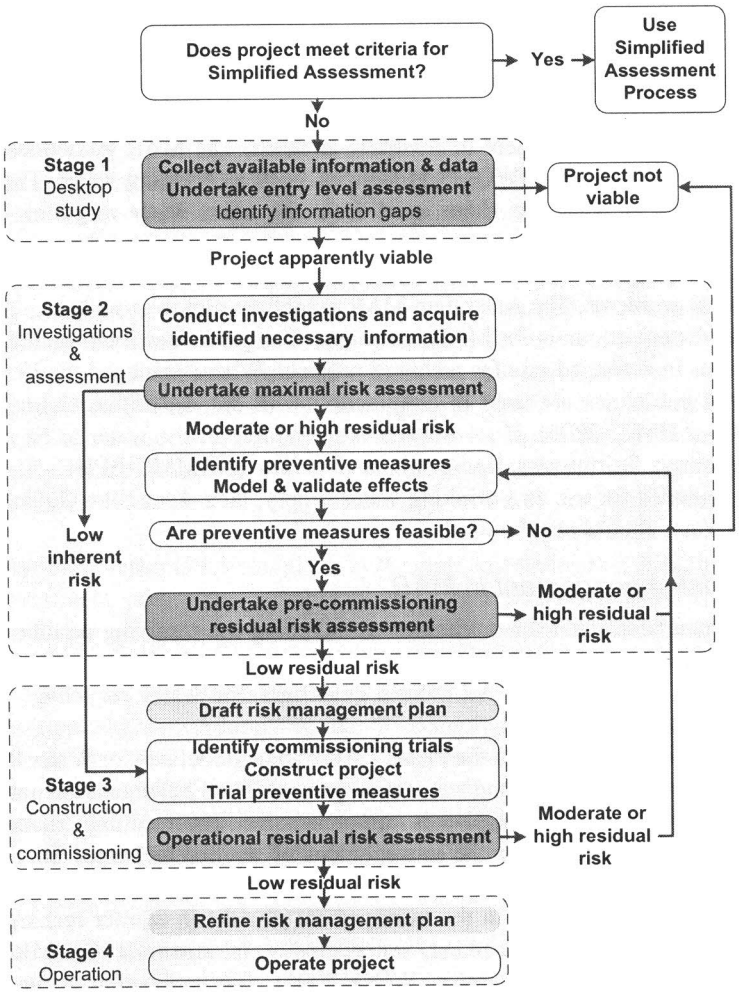

Figure 19.2. Risk assessment stages in managed aquifer recharge project development

New MAR projects begin with the Stage 1 entry level risk assessment which largely address water allocation issues that are usually adequately determined without detailed site-specific information. Governance of these issues will generally be in the hands of a state or regional water resources management agency. The entry level assessment gives an indication of the effort likely to be required to demonstrate low risks to human health and the environment. The Stage 1 entry level assessment is intended to inform on the likely degree of difficulty of the MAR project, and hence inform proponents of the extent of field investigations needed in Stage 2.

Stage 1 is the most cost-effective stage at which to abandon MAR projects for which the potential rewards do not justify the high degree of difficulty. If the potential value of recycled water generated is large, an investment in Stage 2 investigations can focus on the highest risk issues. Causes of the high degree of difficulty may be resolved with determination of viable preventive measures, such as pre- or post-MAR treatment.

At Stage 2, risk is assessed at two levels – maximal risk and residual risk. The maximal risk (also referred to as unmitigated or inherent risk) is risk in the absence of any preventive measures. Whereas, the residual risk is the risk after consideration of preventive measures, including potential aquifer treatment. A residual risk assessment provides an indication of the safety and sustainability of the MAR scheme and must be less than the upper limits of tolerable risk.

Following investigations in Stage 2 maximal risk is determined for each hazard. If the responsible authority in the jurisdiction assesses the maximal risk to be low for all hazards the MAR project may then proceed directly to construction. The more usual case will require preventive measures related to some hazards to reduce risk and reassessment of residual risk at pre-commissioning stage. This step estimates the residual risk of commissioning the project. Preventive measures, operational procedures and incident and emergency management plans are intended to give confidence that the project will be safe during commissioning trials (Stage 3). If residual risks fail to reach acceptance criteria, preventive measures are added and residual risks reassessed until residual risks are determined to be low, or the project proponent determines that the expense of these measures makes the project unviable.

The risks for each MAR project will depend on the quality of the source of water, the intended uses of recovered water and the environmental values of the aquifer. While all projects follow the same risk assessment pathway, the level of effort required in risk assessment and management can vary markedly between projects based on the specific risk profile of the project. For example, MAR projects intending to produce drinking water supplies (e.g. the Parafield case study site) will in general require substantially more effort than those producing irrigation supplies. For many MAR projects, the level of some risks can only be approximated before full-scale implementation and validation monitoring.

Following construction of the MAR scheme, commissioning trials are run to enable validation of processes that could not be measured until recharge occurs, and to allow verification of the efficacy of the preventive measures. At this stage, Stage 3 (Figure 19.2), an accurate calculation of residual risk, an operational residual risk assessment, can be made. A low residual risk assessed at Stage 3 provides a basis for ongoing operation of the site and development of risk management plans (including verification and operational monitoring and reporting) (Stage 4). The risk management plans may be subject to periodic review subject to monitoring results. In the event that the forecast low risks are not achieved, the proponent needs to identify and adopt additional preventive measures and perform further commissioning trials to proceed with the project.

Examples of the application of this risk assessment methodology to Australian MAR sites has been documented in a recent studies by Page *et al.* (2010a; 2010d).

19.2 CHEMICAL RISK ASSESSMENT METHODOLOGY

Many chemical hazards (both inorganic and organic) found in wastewater have human health guideline values which indicate the acceptable level if found in a drinking water supply. The term 'trace organics' more specifically refers to a range of emerging chemicals, such as: pharmaceuticals, endocrine disrupters, disinfection by-products and flame retardants. These emerging contaminants pose a challenge to public health regulation as in many cases there is no toxicological data or guideline value from which to derive the potential human health risk.

A chemical risk assessment was conducted on the case study sites to assess which organic chemicals had potential to be a human health risk. The approach selected in the framework of the RECLAIM WATER project was based on the USEPA guidelines for chemical risk assessment (USEPA, 1987, 1998, 2002), also adopted by the Australian Guidelines for Water Recycling (NRMMC EPHC & NHMRC, 2008). A preliminary work applying these concepts appears in Ayuso-Gabella *et al.* (2007). The methodology is based on comparing the amount of a certain chemical compound with a reference value or daily dose intake reported within the USEPA guidelines (USEPA, 1987, 1998, 2002), WHO drinking water guidelines (WHO, 2004) or other sources of data. Lower exposure to recycled water through irrigation (e.g. at the Nardò, Sabadell and Shafdan case study sites) is unlikely to result in any significant risk to human health from chemicals; however, the risk quotient approach using drinking water guidelines allows comparison of risk associated with different chemicals.

In the present section, a systematic desktop assessment of potential adverse health effects of organic chemicals at the concentrations observed at the case study sites assuming that recovered water were available for drinking is presented. The assessment requires the quantification of trace organic chemical. Full details on the methodology are shown in Ayuso-Gabella *et al.* (2009).

The risk quotients (RQ) method is the most widely used method of assessing risk from trace organic chemicals by comparing the measured chemical concentrations as a ratio for guideline values. Health values are concentrations below which no adverse health effects are expected if the water is consumed over a lifetime. The health values are calculated assuming an average daily intake of 2 litres of water for an individual with a 70 kg body weight over 70 years of water consumption. All values were calculated using the equations used in the Australian Guidelines for Water Recycling phase 2: Augmentation of Drinking Water Supplies (NRMMC EPHC & NHMRC, 2008).

19.3 CHEMICAL RISK ASSESSMENT OF THE CASE STUDY SITES

19.3.1 Source waters

A selection of organic chemicals were analysed for at the case study site source waters. The list of chemicals tested for is detailed in the risk assessment work package (Ayuso-Gabella *et al.* 2009) and also in the work package devoted to the detection of organic chemicals (Ernst *et al.* 2009). The Australian case study site analysed a larger set of organic chemicals that were more likely to be found in stormwater such as herbicides and petroleum products. The results of the chemicals assessed and the risks to human health are detailed below.

Of the organic chemicals tested for in the source waters, most were detected in at least one of the seven case study sites. The total number of chemicals analysed for each case study site source waters and the percentage of detections at each site is given in Table 19.1. The list of chemical groups analysed for includes a broad range of chemical groups with different physico-chemical characteristics and toxic effects (see Table 19.2). Table 19.2 summarizes the number of samples, median and max results for each compound analyzed in source waters at each site, as well as the RQ value for each compound (using the median value to calculate it). The compounds that were not detected in any of the case studies do not appear in Table 19.2 and include the following: NDPhA (N-Nitrosodiphenylamine), NMEA (N-Nitrosomethylethylamine), florfenicole, sulfadiazine, sulfadimethoxine, sulfadoxine, sulfamerazine, sulfisoxazole, tiamulin, ioxitalamic acid, ethinylestradiol EE2, mefenamic acid, methadon, morphine, nordiazepam, oxazepam and paracetamol.

Table 19.1 Total number of chemicals analysed for each case study site in the source waters and the percentage of detections.

Compound detection in source water at each site	Atlantis		Gaobeidian		Nardò		Parafield		Sabadell		Shafdan		Torreele	
	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)
DBPs														
THMS							11	9						
HAAs							*							
N-nitrosamines					9	50	*		5	40	9	72	7	62
Pharmaceuticals														
Antibiotics	5	80	6	73	11	55	2	0	9	50	6	79	13	29
Contrast media	5	30	5	80	6	56	2	0	5	73	5	95	5	60
Hormones					1	0	2	0	3	33	3	33	3	33
Other	14	50	4	47	7	50	2	0	7	69	4	100	6	86
VOC's							11	0						
PAH's							11	0						
Dioxin and Furans							11	0						
PCB's							11	0						
Complexing agents			3	100	3	33	11	0	3	100	3	100	3	56
Pesticides and herbicides	1	0	1	75	1	0	11	63	1	100	1	0	1	0
Other chemicals					1	50	11	45	1	0			1	100

*monitored as disinfection by product formation potential.

Table 19.2 Endocrine disruptor and personal care products chemical risk quotients in the case study source waters.

	Units	LOQ	Atlantis				Gaobeidian				Nardò				Parafield				Sabadell				Shafdan				Torreele				Hth. v.	Reference
			n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med		
DBPs																																
N-nitrosamines																																
N-Nitrosodibutylamine (NDBA)	ng/L	3									2	<LOQ	<LOQ	–					1	<LOQ	–	–	4	8.2	45	**1.4**	1	<LOQ	–	–	6	USEPA
N-Nitrosodiethylamine (NDEA)	ng/L	0.3									2	4.1	4.6	0.41					1	<LOQ	–	–	4	13	32	**1.3**	2	0.81	1.3	0.08	10	AGADWS
N-Nitrosodimethylamine (NDMA)	ng/L	0.7									2	3.5	4.7	0.35					1	17	–	**1.7**	4	9.8	53	0.98	3	5.8	6.3	0.58	10	AGADWS
N-Nitrosodipropylamine (NDPA)	ng/L	1.1									1	<LOQ	–	–									4	1.2	2.4	0.24	1	<LOQ	–	–	5	USEPA
N-Nitrosomorpholine (NMOR)	ng/L	1.3									2	11	20	**11**					1	9.6	–	**9.6**	4	11	53	**11**	2	3.5	3.8	**3.5**	1	AGADWS
N-Nitrosopiperidine (NPIP)	ng/L	3.2									2	<LOQ	<LOQ	–					1	<LOQ	–	–	4	3.2	6.9	0.86	2	1.1	1.4	0.29	3.7	OEHHA
N-Nitrosopyrrolidine (NPYR)	ng/L	3									2	<LOQ	<LOQ	–									3	2.4	3.7	0.12	2	<LOQ	<LOQ	–	20	USEPA
Pharmaceuticals																																
Azithromycin	µg/L	0.01									1	0.32	–	0.08																	3.9	AGADWS
Clarithromycin	µg/L	0.02	2	0.03	0.04	0.00	5	0.02	0.06	0.00	4	0.15	0.31	0.00					2	0.21	0.22	0.00	4	0.03	0.13	0.00	3	0.05	0.23	0.00	250	AGADWS
Erythromycin	µg/L	0.01	2	0.18	0.23	0.01	5	0.02	0.06	0.00	4	0.02	0.05	0.00					2	0.35	0.46	0.02	4	0.16	0.22	0.01	3	<LOQ	<LOQ	–	17.5	AGADWS
N-Acetilsulfamethoxazole	µg/L	0.01									4	0.07	0.09	0.00					2	0.08	0.08	0.00					1	0.06	–	0.00	35	AGADWS
Roxythromycin	µg/L	0.02	2	<LOQ	<LOQ	–	5	0.05	0.19	0.00	4	0.02	0.03	0.00					2	<LOQ	<LOQ	–	4	0.11	0.23	0.00	3	<LOQ	<LOQ	–	150	AGADWS
Sulfamethoxazole	µg/L	0.01	2	3.4	3.7	0.10	5	0.45	0.65	0.01	4	0.10	0.48	0.00					2	0.32	0.47	0.01	4	0.15	0.73	0.00	3	0.05	0.18	0.00	35	AGADWS
Sulfamethazine	µg/L	0.01					5	0.04	0.14	0.00	4	<LOQ	<LOQ	–					2	<LOQ	<LOQ	–	4	0.01	0.01	0.00	3	<LOQ	<LOQ	–	35	AGADWS
Sulfapyridine	µg/L	0.01									1	0.06	–	0.00																	35	AGADWS
Trimethoprim	µg/L	0.01	2	0.76	0.94	0.01	5	0.01	0.03	0.00	2	<LOQ	<LOQ	–					3	0.01	0.26	0.00	4	0.05	0.07	0.00	3	0.11	0.15	0.00	70	AGADWS
Contrast media																																
Diatrizoate	µg/L	0.01	2	<LOQ	<LOQ	–	4	1.2	1.8	0.00	4	1.0	1.7	0.00					3	11	28	0.02	4	0.31	0.84	0.00	3	3.0	6.9	0.00	600	LTD
Iohexol	µg/L	0.02	2	<LOQ	<LOQ	–	4	1.7	2.2	0.00	2	<LOQ	<LOQ	–					3	0.02	0.64	0.00	4	4.0	4.7	0.01	3	<LOQ	<LOQ	–	720	AGADWS
Iomeprol	µg/L	0.02	2	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	4	0.56	1.1	0.00					3	0.22	0.34	0.00	4	0.15	0.30	0.00	3	0.60	1.4	0.00	375	LTD
Iopamidol	µg/L	0.02	2	0.84	1.7	0.00	4	3.7	6.5	0.01	3	0.05	0.87	0.00					3	0.25	0.29	0.00	4	5.1	7.7	0.01	3	<LOQ	<LOQ	–	400	AGADWS
Iopromide	µg/L	0.02	2	0.09	0.15	0.00	4	1.0	1.6	0.00	4	<LOQ	<LOQ	–					3	6.6	10.1	0.01	4	6.8	7.8	0.01	3	0.38	3.8	0.00	750	AGADWS
Hormones																																
Estradiol E2	ng/L	1																	1	<LOQ	–	–	4	<LOQ	<LOQ	–	3	1.0	1.9	0.01	175	AGADWS
Estrone E1	ng/L	0.5									2	<LOQ	<LOQ	–					1	64	–	**2.1**	4	<LOQ	<LOQ	–	3	4.5	6.4	0.15	30	AGADWS
Other																																
Benzoylegconine	µg/L	0.02	2	0.10	0.16	0.01																									20	LTD
Bezafibrate	µg/L	0.01	2	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–					3	0.06	0.13	0.00	4	0.68	0.80	0.00	2	<LOQ	<LOQ	–	300	AGADWS

(*Continued*)

Table 19.2 Endocrine disruptor and personal care products chemical risk quotients in the case study source waters (*Continued*).

	Units	LOQ	Atlantis			Gaobeidian				Nardò				Parafield				Sabadell				Shafdan				Torreele				Hth. v.	Reference
			n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med		
Carbamazepine	µg/L	0.01	2	2.7	3.5	0.03					4	0.71	0.85	0.01					2	0.18	0.30	0.00					3	1.4	1.4	0.01	100	AGADWS
Clofibric acid	µg/L	0.01	2	<LOQ	<LOQ	–	4	0.04	0.05	0.00	4	<LOQ	<LOQ	–					3	0.02	0.03	0.00	4	<LOQ	<LOQ	–	3	<LOQ	<LOQ	–	750	AGADWS
Codein	µg/L	0.02	2	1.4	1.8	0.03																									50	AGADWS
Diazepam	µg/L	0.02	2	0.03	0.04	0.01																									2.5	AGADWS
Diclofenac	µg/L	0.01	2	0.90	0.92	0.50	3	0.20	0.22	0.11	4	0.28	0.35	0.16					2	0.16	0.19	0.09	4	0.37	0.80	0.21	2	0.59	0.79	0.33	1.8	AGADWS
Ibuprofen	µg/L	0.02	2	9.6	11	0.02	4	0.04	0.21	0.00	4	<LOQ	<LOQ	–					3	<LOQ	<LOQ	–	3	0.31	0.41	0.00	2	0.21	0.26	0.00	400	AGADWS
Naproxen	µg/L	0.01	2	<LOQ	<LOQ	–	4	0.07	0.09	0.00	4	0.04	0.06	0.00					3	0.04	0.57	0.00	4	0.5	0.66	0.00	2	0.46	0.70	0.00	220	AGADWS
Primidone	µg/L	0.01	2	<LOQ	<LOQ	–					3	0.16	0.20	0.00					2	0.18	0.24	0.00					3	0.14	0.21	0.00	125	LTD
Temazepam	µg/L	0.02	2	0.07	0.08	0.01																									5	AGADWS
Complexing Agents																																
4-Tolyltriazole	µg/L	0.1					5	0.73	1.3	0.10	1	<LOQ	–	–					1	0.30	–	0.04	4	0.39	4.0	0.06	3	0.1	0.27	0.01	7	AGADWS
5-Tolyltriazole	µg/L	0.1					5	0.16	1.7	0.02	1	<LOQ	–	–					1	0.24	–	0.03	4	0.25	0.45	0.04	3	0.1	0.24	0.01	7	AGADWS
Benzotriazole	µg/L	0.1					5	2.3	3.2	0.33	1	0.24	–	0.03					1	2.5	–	0.36	4	2.2	3.3	0.32	3	5.4	6.0	0.77	7	AGADWS
Other chemicals																																
Adsorbable organic iodine	µg/L	0.5					5	11	39	0.18	1	11	–	0.18									4	21	32	0.36	3	21	30	0.35	60	ADWG
Bisphenol-A	µg/L	0.01									4	0.04	0.39	0.00					2	<LOQ	<LOQ	–					3	0.08	0.17	0.00	200	AGADWS

<LOQ: value below the limit of quantification; AGADWS: Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies; LTD: Lowest Terapeutic Dose; USEPA: United States Environmental Protection Agency (IRIS website); OEHHA: Office of Environmental Health Hazard Assessment (California Environmental Protection Agency).

Note: For those compounds were data included measured values and values <LOQ, the values <LOQ were substituted for the actual LOQ for the compound in order to calculate the median value.

Atlantis case study has two different source waters: the secondary effluent of Wesfleur WWTP and stormwater. Both source waters were monitored for herbicides, antibiotics, contrast media and other pharmaceuticals in two sampling campaigns. The results given in Table 19.2 correspond to the source water (secondary effluent or stormwater) with the highest values for the selected compound used to perform the risk assessment. Among the five antibiotics monitored, four could be detected, with sulfamethoxazole being detected in the highest concentration (3.7 μg/L). For contrast media, two out of five compounds could be detected, in 30% of the samples analyzed. Among the other pharmaceuticals, eight out of fifteen could be detected. Ibuprofen was the pharmaceutical detected in the highest concentration (10.6 μg/L). Carbamazepine could be detected with a maximum concentration of 3.5 μg/L. For the herbicides, only clofibric acid was monitored and it could not be detected in any of the sampling campaigns.

Gaobeidian uses secondary effluent of Gaobeidian WWTP as source water. Five samplings were performed on source waters at Gaobeidian, six antibiotics were monitored and all of them were detected, but in very low concentrations. The highest value detected corresponded to sulfamethoxazole, 0.65 μg/L. Four out of five contrast media compounds could be detected. The highest values corresponded to iopamidol (6.5 μg/L) and iohexol (2.2 μg/L). Other pharmaceuticals were also monitored, and three out of four could be detected: diclofenac, ibuprofen and naproxen. Three complexing agents were monitored at this site, and all of them could be detected. Benzotriazole was the complexing agent detected at the highest concentration, 3.2 μg/L. Clofibric acid was the only pesticide monitored, and it was detected at a low concentration. Absorbable organic iodine was also detected with a median value of 11.0 μg/L and the maximum value 39.0 μg/L.

At the Nardò site, the effluents of three different WWTPs are gathered and transported in an open channel to the sinkhole, where they are infiltrated to the subsurface. The effluent from Galatone WWTP accounts for the highest volume of source water, and it was sampled in the four sampling campaigns. Nine nitrosamines were monitored but only three were detected. NMOR was the nitrosamine found at the highest concentrations, with a median value of 10.8 ng/L and a maximum value of 20 ng/L. Seven out of eleven antibiotics could be detected at Nardò. All of the antibiotics were detected in low concentrations. In this site, six contrast media were monitored, and half of them were detected. The highest concentration detected was for diatrizoate, 1.7 μg/L. Only one hormone was investigated at this site, estrone E1, but was not detected. Other pharmaceuticals were monitored included carbamazepine, diclofenac, naproxen and primidone were detected. One out of the three complexing agents monitored could be detected; benzotriazole. Clofibric acid was not detected. Adsorbable organic iodine was monitored in only one sample, and the concentration was 10.8 μg/L. Bisphenol A was also monitored, and the highest concentration detected was 0.39 μg/L.

For Parafield, the organic chemicals in the influent stormwater were monitored on 11 campaigns. The Parafield case study had a separate monitoring program of over 300 organic chemicals as described by Page *et al.* (2009; 2010d). There were no pharmaceuticals detected in the influent water, and a single THM (dichloromethane 1.4 μg/L) was detected. The most frequently detected pesticide was simazine with a maximum concentration of 0.86 μg/L. In addition, methyl blue active substances (a general class for detergents and surfactants) were detected with a maximum concentration of 120 μg/L. Additional sampling using passive samplers detected ng/L concentrations of other herbicides and chemicals as reported by Page *et al.* (2010d).

For Sabadell case study, the secondary treated effluent of the Ripoll River WWTP was sampled in 3 sampling campaigns.

Five N-nitrosamines were monitored in only one of the sampling campaigns performed. NDMA was detected at a concentration of 16.5 ng/L and NMOR 9.6 ng/L. Presence of pharmaceuticals was expected as the Taulí Hospital sends its wastewater to the Ripoll River WWTP. Five out of nine antibiotics monitored could be detected. Contrast media was detected in medium to high concentrations in all sampling campaigns, with peak values of 27.7 μg/L of diatrizoate and 10.1 μg/L of iopromide. Hormones were only monitored in one sampling campaign, and only estrone E1 was detected, at a concentration of 64 ng/L. Other pharmaceuticals detected were bezafibrate, carbamazepine, diclofenac, primidone and naproxen. All complexing agents monitored in the secondary effluent of the Ripoll River WWTP were detected in the only sampling campaign they were tested for, benzotriazole being the one detected at the highest concentration (2.5 μg/L). For the herbicides, only clofibric acid was monitored and it could be detected in all sampling campaigns at low concentrations. Bisphenol A could not be detected.

The Shafdan site also uses the secondary effluent of a WWTP as source water. Four sampling campaigns were performed. Nine nitrosamines were monitored and seven could be detected. NDBA, NDEA NDMA and NMOR were found at high concentrations, with median values of 8.2, 12.8, 9.8 and 10.9 ng/L respectively, and reaching peak values of 45.2, 32.4, 53.0 and 53.5 ng/L respectively. Six antibiotics were monitored at this site, and detected in 79% of the samples. Contrast media was detected at concentrations ranging from 0.15 μg/L (median value for iomeprol) to 6.8 μg/L (median value for iopromide). Hormones were not detected in any of the samplings. Other pharmaceuticals monitored were bezafibrate, diclofenac, ibuprofen and naproxen. Complexing agents were detected in all sampling campaigns, and benzotriazole was detected at the highest concentrations (median value of 2.2 μg/L and maximum value of 3.3 μg/L). Clofibric acid could not be detected, and absorbable organic ionic median value was 21.4 μg/L.

In Torreele case study the secondary effluent of the Wulpen WWTP was monitored in 3 sampling campaigns. Different N-nitrosamines were detected in all sampling campaigns, with NDMA being the most frequently detected and also in the highest concentration (maximum of 6.3 ng/L). NMOR concentrations were also high, with a median value of 3.5 ng/L and a maximum value of 3.8 ng/L. In Torreele, 13 antibiotics were monitored and only clarithromycin, sulfamethoxazole, N-Acetil-sulfamethoxazole and trimethoprim could be detected, at very low concentrations. Contrast media was detected in high concentrations in 60% of the samples, with peak values of 6.9 μg/L for diatrizoate and 3.8 μg/L for iopromide. Concentrations of hormones varied more than the antibiotics, contrast media or other pharmaceuticals, and varied between campaigns. Of the other pharmaceuticals analysed, carbamazepine was detected in the highest concentration (1.4 μg/L), followed by diclofenac and naproxen at trace levels. Other pharmaceuticals detected were primidone and ibuprofen at the limit of detection. All complexing agents monitored could be detected, with benzotrizole being the most abundant (6.0 μg/L, maximum concentration). For the herbicides, only clofibric acid was monitored and it could not be detected in any of the sampling campaigns. Bisphenol A had a maximum concentration was of 0.17 μg/L.

Table 19.2 summarises the organic chemical risk assessment performed for the detected chemicals in the source waters at the case study sites. All chemical groups except N-nitrosamines and hormones have screening RQs (median) below one. For the N-nitrosamines, NMOR (N-nitrosomorpholine) was monitored in four sites and in all of them the RQ (calculated with the median value) was much higher than one: 11 at Nardò and Shafdan, 9.6 at Sabadell and 3.5 at Torreele. NDMA (N-Nitrosodimethylamine) RQ value was 1.7 in Sabadell. NDBA and NDEA RQ values in Shafdan were 1.4 and 1.3, respectively. These results indicate that nitrosamines could pose a risk for the human health if the water was used for drinking. For the hormones, estrone E1 had a median RQ value of 2.1 in Sabadell.

Most of the monitored compounds that could be detected had median RQ values close to zero, generally well below one. The compounds whose RQs median values were higher than one pose a risk for the human health, and their possible presence in final waters must be monitored. There were no detections of these compounds at the Parafield site, where the untreated stormwater is used. Due to restrictions of the analytical methods at the time of this study, it was determined the concentrations of the majority of the organic chemicals detected in the source waters (Table 19.2) were too low in the recovered water within the case studies to be accurately determined (Table 19.4).

19.3.2 Recovered waters

Despite the low detection limits, many of the compounds were still detected in the recovered waters of the case study sites. The percentage of compounds detected in every group decreased after the treatment train. Table 19.3 summarizes the number of chemicals analysed for each case study site in the recovered waters and their percentages of detection. Table 19.4 summarizes the number of samples, median and max results for each compound analyzed in recovered waters at each site, as well as the RQ value for each compound (using the median value to calculate it). The compounds that were not detected in any of the case studies do not appear in Table 19.2. These compounds are the following: NDPhA (N-Nitrosodiphenylamine), NDPA (N-Nitrosodipropylamine), NMEA (N-Nitrosomethylethylamine), NPIP (N-Nitrosopiperidine), NPYR (N-Nitrosopyrrolidine), azithromycin, florfenicole, N-acetilsulfamethoxazole, sulfadiazine, sulfadimethoxine, sulfadoxine, sulfamerazine, sulfisoxazole, tiamulin, ioxitalamic acid, estradiol E2, ethinylestradiol EE2, benzoylegconine, codein, diazepam, ibuprofen, mefenamic acid, methadon, morphine, nordiazepam, oxazepam, paracetamol, temazepam and clofibric acid.

At the Atlantis case study site only carbamazepine, with a maximum value of 0.03 μg/L out of 24 could be detected in the recovered water; two orders of magnitude lower than in the source water.

The Gaobeidian case study site also had pharmaceuticals detected in the recovered water. All six antibiotics were detected in the recovered water in some of the campaigns, and at similar concentrations to the source water, thus showing no removal or poor removal. Four contrast media compounds were also detected. Lower concentrations were observed for iohexol and iopromide, with median values in the recovered water of 0.07 and 0.05 μg/L, respectively. However, no removal was measured for diatrizoate. Other pharmaceuticals tested (three) could not be detected in the recovered water, only diclofenac was detected. Complexing agents were removed along the treatment, and much lower values were obtained in the recovered water. Adsorbable organic iodine was also reduced along the treatment train, but still high values up to 13 μg/L.

Nitrosamines and estrone E1 could not be detected in the recovered water for Nardò. Some antibiotics could still be detected, in 21% of the samples, namely clarithromycin, sulfamethoxazole and sulfapyridine, but at lower concentrations than in source water. Contrast media was also removed, and the three compounds detected (diatrizoate, iomeprol and iopamidol) had lower concentrations than in source water. Other pharmaceuticals detected in the recovered water were carbamazepine, diclofenac and primidione, all of them at lower concentrations than in source water. Benzotriazole was detected at a higher concentration than in source water, 2.4 μg/L. Adsorbable organic iodine was present at levels similar to those in source water and bisphenol A maximum concentration was lower (0.05 μg/L).

Table 19.3 Total number of chemicals analysed for each case study site in the recovered waters and the percentage of detections.

Compound detection in source water at each site	Atlantis		Gaobeidian		Nardò		Parafield		Sabadell		Shafdan		Torreele	
	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)	n	Detected (%)
DBPs														
THMS														
HAAs														
N-nitrosamines					9	0			5	20	5	67	6	0
Pharmaceuticals														
Antibiotics	5	0	6	43	11	21			8	11	6	29	13	0
Contrast media	5	0	5	55	6	68			5	40	5	25	5	0
Hormones					1	0			3	0	3	8	3	0
Other	14	4	4	7	7	54			7	56	4	7	6	0
VOC's														
PAH's							1	0						
Dioxin and Furans							1	0						
PCB's							1	0						
Complexing agents			3	73	3	33	1	0	3	100	3	58	3	33
Pesticides and herbicides	1	0	1	0	1	0	1	0	1	0	1	0	1	0
Other chemicals					1	100	1	0	1	100			1	33

For Sabadell, one nitrosamine was still detected in the recovered water, NMOR, at a concentration of 3.3 ng/L. Two out of eight antibiotics could also still be detected, at very low concentrations in only 11% of the samples. Contrast media concentrations were substantially reduced, and the highest value measured was for diatrizoate, 1.1 µg/L. Hormones could not be detected in the recovered water, and other pharmaceuticals detected at low concentrations were bezafibrate, carbamazepine, diclofenac, naproxen and primidone. Complexing agents were still present in the recovered water, and 4-tolyltriazole was detected at a higher concentration (2.0 µg/L) than in the source water. Bisphenol A was not detected in source water but it was detected in the recovered water, at a maximum concentration of 0.05 µg/L.

At Shafdan four nitrosamines were detected in the recovered water: NDBA, NDEA, NDEMA and NMOR. The maximum value measured was for NDEA, 9.9 ng/L, but NMOR was the only one that could pose a risk for the human health, with a median value of 2.8 ng/L. Antibiotics concentrations were reduced after the treatment train, and could be detected in 29% of the samples. Two out of five contrast media were still present in the recovered water, diatrizoate and iopamidol, at much lower concentrations than in source water. Estrone E2 was not detected in source water but it was in the recovered water, at a maximum concentration of 1.2 µg/L. Another pharmaceutical detected was diclofenac. Complexing agents were still present in the recovered water, but at lower concentrations than in source water. Benzotriazole median value was 0.39 µg/L. Adsorbable organic iodine was still high in the recovered water, with a maximum value of 20 µg/L, but lower than in the source water.

In Torreele, the only compounds detected among the 38 compounds monitored in the recovered water were benzotriazole (0.24 µg/L, maximum value), adsorbable organic iodine (2.6 µg/L, maximum value) and bisphenol A (0.23 µg/L, maximum value).

Table 19.4 summarises the organic chemical risk assessment performed for the detected chemicals at the case study sites. All chemical groups except nitrosamines (NMOR) have screening RQs (median) below 1. The median RQ value for NMOR in Sabadell case study was 3.3, and 2.8 in Shafdan. This RQ values indicate a risk for the human health in case the final water is used for drinking water purposes. However, in the case of Sabadell and Shafdan, the recovered water is not used as drinking water, but as irrigation and streets cleaning water, thus decreasing considerably the risk. The amount of water that can be inhaled when parks irrigation or streets cleaning are performed is between 3 and 4 orders of magnitude inferior to the amount ingested if used as drinking water.

Most of the compounds detected in final waters have median RQ values well below one, close to zero, thus not posing a risk for the human health.

Table 19.4 Organic chemical risk quotients in the case study recovered waters.

	units	LOQ	Atlantis				Gaobeidian				Nardò #500m				Parafield				Sabadell				Shafdan				Torreele				Hth. v.	Reference
			n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med	n	med	max	RQ med		
DBPs																																
N-nitrosamines																																
N-Nitrosodibutylamine (NDBA)	ng/L	3									1	<LOQ	–	–					1	<LOQ	–	–	2	4.4	8.6	0.73	1	<LOQ	–	–	6	USEPA
N-Nitrosodiethylamine (NDEA)	ng/L	0.3									1	<LOQ	–	–					1	<LOQ	–	–	3	1.0	9.9	0.10	1	<LOQ	–	–	10	AGADWS
N-Nitrosodimethylamine (NDMA)	ng/L	0.7									1	<LOQ	–	–					1	<LOQ	–	–	3	2.3	3.0	0.23	1	<LOQ	–	–	10	AGADWS
N-Nitrosomorpholine (NMOR)	ng/L	1.3									1	<LOQ	–	–					1	3.3	–	**3.3**	3	2.8	9.7	**2.8**	1	<LOQ	–	–	1	AGADWS
Pharmaceuticals																																
Antibiotics																																
Clarithromycin	µg/L	0.02	2	<LOQ	<LOQ	–	4	0.03	0.05	0.00	4	0.04	0.05	0.00					2	<LOQ	<LOQ	–	4	0.03	0.05	0.00	3	<LOQ	<LOQ	–	250	AGADWS
Erythromycin	µg/L	0.01	2	<LOQ	<LOQ	–	4	0.03	0.03	0.00	4	<LOQ	<LOQ	–					2	0.01	0.01	0.00	4	0.01	0.04	0.00	3	<LOQ	<LOQ	–	17.5	AGADWS
Roxythromycin	µg/L	0.02	2	<LOQ	<LOQ	–	5	0.04	0.11	0.00	4	<LOQ	<LOQ	–					2	<LOQ	<LOQ	–	4	0.05	0.11	0.00	3	<LOQ	<LOQ	–	150	AGADWS
Sulfamethoxazole	µg/L	0.01	2	<LOQ	<LOQ	–	5	0.07	0.86	0.00	4	0.11	0.22	0.00					2	0.03	0.05	0.00	4	0.04	0.17	0.00	3	<LOQ	<LOQ	–	35	AGADWS
Sulfamethazine	µg/L	0.01					5	0.04	0.11	0.00	4	<LOQ	<LOQ	–					2	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	3	<LOQ	<LOQ	–	35	AGADWS
Sulfapyridine	µg/L	0.01									1	0.03	–	0.00																	35	AGADWS
Trimethoprim	µg/L	0.01	2	<LOQ	<LOQ	–	5	0.01	0.02	0.00	2	<LOQ	<LOQ	–					3	<LOQ	<LOQ	–	4	0.01	0.01	0.00	3	<LOQ	<LOQ	–	70	AGADWS
Contrast media																																
Diatrizoate	µg/L	0.01	2	<LOQ	<LOQ	–	4	1.4	2.1	0.00	4	0.63	0.99	0.00					3	0.28	1.1	0.00	4	0.20	0.29	0.00	3	<LOQ	<LOQ	–	600	LTD
Iohexol	µg/L	0.02	2	<LOQ	<LOQ	–	4	0.07	0.7	0.00	2	<LOQ	<LOQ	–					3	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	3	<LOQ	<LOQ	–	720	AGADWS
Iomeprol	µg/L	0.02	2	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	4	0.08	0.48	0.00					3	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	3	<LOQ	<LOQ	–	375	LTD
Iopamidol	µg/L	0.02	2	<LOQ	<LOQ	–	4	1.7	4.1	0.00	3	0.09	0.56	0.00					3	0.02	0.05	0.00	4	0.02	0.18	0.00	3	<LOQ	<LOQ	–	400	AGADWS

Iopamidol	µg/L	0.02	2	<LOQ	<LOQ	–	4	1.7	4.1	0.00	3	0.09	0.56	0.00					3	0.02	0.05	0.00	4	0.02	0.18	0.00	3	<LOQ	<LOQ	–	400	AGADWS
Iopromide	µg/L	0.02	2	<LOQ	<LOQ	–	4	0.05	0.41	0.00	4	<LOQ	<LOQ	–					3	0.06	0.23	0.00	4	<LOQ	<LOQ	–	3	<LOQ	<LOQ	–	750	AGADWS
Hormones																															
Estrone E1	ng/L	0.5									2	<LOQ	<LOQ	–					1	<LOQ	–	–	4	0.50	1.2	0.02	3	<LOQ	<LOQ	–	30	AGADWS
Other																															
Bezafibrate	µg/L	0.01	2	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–					3	0.01	0.02	0.00	4	<LOQ	<LOQ	–	2	<LOQ	<LOQ	–	300	AGADWS
Carbamazepine	µg/L	0.01	2	0.02	0.03	0.00					4	0.44	0.63	0.00					2	0.08	0.14	0.00					3	<LOQ	<LOQ	–	100	AGADWS
Diclofenac	µg/L	0.01	2	<LOQ	<LOQ	–	3	0.02	0.18	0.01	4	0.01	0.04	0.01					2	0.02	0.03	0.01	4	0.02	0.35	0.01	2	<LOQ	<LOQ	–	1.8	AGADWS
Naproxen	µg/L	0.01	2	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–	4	<LOQ	<LOQ	–					3	0.01	0.03	0.00	4	<LOQ	<LOQ	–	2	<LOQ	<LOQ	–	220	AGADWS
Primidone	µg/L	0.01	2	<LOQ	<LOQ	–					3	0.07	0.08	0.00					2	0.03	0.03	0.00					3	<LOQ	<LOQ	–	125	LTD
Complexing Agents																															
4-Tolyltriazole	µg/L	0.1					5	0.21	0.39	0.03	1	<LOQ	–	–					1	2.0	–	0.28	4	0.05	0.42	0.01	3	<LOQ	<LOQ	–	7	AGADWS
5-Tolyltriazole	µg/L	0.1					5	0.10	0.22	0.01	1	<LOQ	–	–					1	0.20	–	0.03	4	0.05	0.29	0.01	3	<LOQ	<LOQ	–	7	AGADWS
Benzotriazole	µg/L	0.1					5	0.44	0.71	0.06	1	2.4	–	–					1	1.9	–	0.27	4	0.39	1.3	0.06	3	0.21	0.24	0.03	7	AGADWS
Other chemicals																															
Adsorbable organic iodine	µg/L	0.5					4	7.6	13	0.13	1	12	–	0.20									4	12	20	0.21	3	0.80	2.60	0.01	60	ADWG
Bisphenol-A	µg/L	0.01									4	0.35	0.51	0.00					2	0.05	0.05	0.00					3	0.02	0.23	0.00	200	AGADWS

<LOQ: value below the limit of quantification; AGADWS: Australian Guidelines for Water Recycling: Augmentation of Drinking Water Supplies; LTD: Lowest Terapeutic Dose; USEPA: United States Environmental Protection Agency (IRIS website).

Note: for those compounds were data included measured values and values <LOQ, the values <LOQ were substituted for the actual LOQ for the compound in order to calculate the median value.

A chemical characterisation of case study sites source waters was also conducted including metals and other inorganic compounds, nutrients and organic chemicals. Trace organic chemical contaminants tested for were found in low concentrations (Table 19.2), which indicate that the reclaimed effluent source waters are similar. The presence of toxic contaminants is often a function of the industrial effluent component of the source water and therefore stormwater and wastewater quality is primarily determined by the presence and nature of industries discharging waste and the treatment processes applied. For example, the Parafield stormwater catchment area is mainly residential and commercial although there is also some light manufacturing and automotive industries which may contribute hydrocarbons to the stormwater quality.

Of the organic chemicals analysed most were detected in at least one of seven study sites taken from the source waters (Table 19.2). Pharmaceuticals were commonly detected in low concentrations (ng/L to low μg/L) in the wastewater sources and pesticides and herbicides were more commonly detected in the stormwater sources consistent with the reviewed international studies (Ayuso-Gabella *et al.* 2009). Despite the detection of pharmaceuticals in the wastewater derived source waters, the human health risk assessment indicates a low health significance.

A reduction of screening RQ (mean) values was observed for most sites. These results are consistent with other studies reporting natural filtering and attenuation of pharmaceuticals and other pollutants within aquifers. However, the removal efficiencies differ for each case study site. When biodegradation occurs, redox (e.g. the presence or absence of oxygen) can have a significant impact (Ying *et al.* 2008). Some organic chemicals are most effectively removed under aerobic conditions while others are only removed under anoxic conditions (Dillon *et al.* 2009). Given the strong influence of redox conditions on removal rates of many organic chemicals, it is optimal to have different redox zones in the MAR system such that water is exposed to differing conditions to maximise opportunity for organic chemical degradation (Dillon *et al.* 2009).

The dominant human health risk of water recycling via aquifers is related to pathogens and not to chemicals. A quantitative assessment of human health risks from pathogens is given in the following section.

19.4 QUANTITATIVE MICROBIAL RISK ASSESSMENT METHODOLOGY

The quantitative microbial risk assessment (QMRA) methodology adopted in RECLAIM WATER follows the approach outlined in WHO (2004) and NRMMC-EPHC-AHMC (2006). The traditional approach to identifying tolerable risk has been to define maximum levels of infection or disease. However, this approach fails to consider the varying severity of outcomes associated with different hazards. This shortcoming can be overcome by measuring severity in terms of disability adjusted life years (DALYs). DALYs have been used extensively by agencies such as the World Health Organization (WHO) to assess disease burdens (WHO, 2004). For microbial risk assessment three representative pathogens; rotavirus, *Cryptosporidium* and *Campylobacter*, were used to assess the risk of viruses, protozoa and bacteria as described in WHO (2004) and NRMMC-EPHC-AHMC (2006). As the risk estimates are probability distribution functions (PDFs), the mean, median and 95th percentile were routinely calculated for each pathogen risk. The tolerable mean risk adopted is 10^{-6} DALYs per person per year (WHO 2004).

For the risk assessment case study sites discussed in this Chapter, a qualitative residual risk assessments were initially performed as part of the RECLAIM WATER project (Ayuso-Gabella *et al.* 2007, 2009). In furthering the qualitative understanding of the pathogenic hazards at each case study site, a QMRA was performed to determine the residual risk for each case study site and the value of the aquifer treatment. The residual risks are risk probability estimates assuming normal operating conditions i.e. where source waters are not exposed to unusual hazard inputs and treatment processes are operating according to specifications. The QMRA reported below is derived from the work of Page *et al.* (2010b; 2010d and Ayuso-Gabella *et al.* (in press).

19.5 QMRA OF THE CASE STUDIES

This section considers QMRA case studies that form part of the larger RECLAIM WATER project. Each risk case study site utilises a non-traditional water source and an engineered water treatment train coupled to an aquifer recharge system for augmenting urban drinking water supplies or irrigation. The three case studies using the recovered water for augmenting drinking water supplies are: Atlantis (South Africa), Parafield (Australia) and Torreele/St. André (Belgium). The three case studies using the recoverd water for crops irrigation, green space irrigation or street cleaning are: Nardò (Italy), Sabadell (Spain) and Shafdan (Israel). Each case study was assessed using a QMRA approach and the aquifer treatment contribution compared across the four case study sites. Special attention has been given to the contribution of the aquifer barrier within the broader treatment train and its importance in managing human health risks.

The treatment trains and important attributes of the case studies have been previously summarised in Part A of this book. They range from almost total reliance on the subsurface passage and residence time for water quality improvement (e.g. Shafdan, Israel) to advanced tertiary treatment (e.g. Torreele/St-André, Belgium) where there is almost no reliance on the aquifer for water quality improvements. At Atlantis, South Africa, Parafield, Australia and Shafdan, Israel the aquifer plays an important complementary role to the engineered treatment systems.

The risk models for simulating hazard reduction, consumption, infection and disease burden were constructed using MS Excel program [2003] enhanced with @ Risk Industrial v. 4.5 and v. 5.5 (Palisade Corp, USA). The minimum value calculated was 1.0×10^{-10} DALYs per person per year.

A triangular probability distribution function (PDF) describing each engineered treatment barrier was adopted from literature for each pathogen (Smeets *et al.* 2006; NRMMC-EPHC-NHMRC, 2006; Cleary, 2005). The triangular distribution was defined by a minimum, most likely and maximum $\log_{10}$ removal value (Smeets *et al.* 2006; NRMMC-EPHC-NHMRC, 2006) and is shown in Table 19.5 and Table 19.6.

The risks associated with recontamination at each treatment barrier were not specifically assessed. For the aquifer treatment barrier, the product of two PDFs; the aquifer residence time and a daily pathogen decay rate (expressed in $\log_{10}$/day) were used to calculate the $\log_{10}$ removal value. Initial pathogen numbers in the stormwater and wastewater were derived from literature (Kocwa-Haluch & Zalewska, 2002; NRMMC-EPHC-NHMRC, 2006; NRMMC-EPHC-NHMRC, 2009a; Robertson *et al.* 2006; Sedmark *et al.* 2005; Montemayor *et al.* 2005; Westrell, 2004). For the Atlantis case study, the two source waters were mixed to derive a final PDF of pathogen concentration for the injectant. Each of the PDFs (including pathogen numbers and aquifer and non-aquifer treatments) was subsequently used in the Monte Carlo simulations to calculate the residual risk.

Once the residual risks were calculated for each MAR scheme a sensitivity analysis was performed which standardises the factors which affect risk and is termed the factor sensitivity (FS) (Zwietering and van Gerwen, 2000). For each MAR scheme the residual risk was then recalculated in the absence of each barrier in turn (such as the aquifer treatment barrier). The FS is a ratio calculated by dividing the revised residual risk estimate (in DALYs) when a factor (e.g. a treatment step) is removed from the treatment train [denoted *N(Barrier)*], by the baseline mean risk, *N(Mean)* also in DALYs from the residual risk assessment and then $\log_{10}$ transforming the ratio (Equation 1):

$$\mathrm{FS} = \log_{10}[N(Barrier)/N(Mean)] \tag{19.1}$$

Higher FS values means the factor has a larger effect on risk. Following assessment of FS a risk-based approach for determining suitable aquifer residence times for MAR schemes is proposed. Aquifer treatment uses the surrogate parameter, aquifer residence time to estimate the value of the aquifer treatment as part of the multiple barrier system. Simulations of changes in the aquifer residence time allow the aquifer barrier to be quantified and compared to the acceptable risk, 1.0×10^{-6} DALYs (WHO 2004). This allows the determination of a required average residence time and associated monitoring can be utilised to manage this barrier within the treatment system.

19.5.1 Aquifer barrier treatment characterisation

Aquifer treatment characteristics were derived from the probability distribution functions (PDFs) of the residence time in the aquifer and the reported $\log_{10}$ decay rates for pathogens (see Tables 19.5 and 19.6). The aquifer and engineered (non-aquifer) treatment barrier characteristics are reported as $\log_{10}$-removals (Table 19.7) which conveys the order of magnitude of the removal for each of the reference pathogens.

Removal $\log_{10}$ values for each treatment barrier were considered additive and thus the Torreele/St-André scheme with multiple engineered barriers resulted in the highest $\log_{10}$ removal for the 'non-aquifer' treatment component. All $\log_{10}$ removal values accredited to aquifers were capped at a maximum of 6.0 $\log_{10}$ consistent with the reported values for engineered treatments in NRMMC-EPHC-NHMRC (2008). Each of the MAR sites placed a different value on the aquifer removal characteristics compared to the engineered treatments. Some relied heavily on the aquifer, like Shafdan and Atlantis, whereas others like Torreele/St-André had extensive redundancy in their system due to a long treatment train of engineered barriers and as such relied little on the aquifer. Torreele/St-André and Sabadell had a low calculated $\log_{10}$ removal capability for the aquifer whereas Parafield, Shafdan and Atlantis had greater calculated treatment capacities due to the longer residence times of water in the subsurface at these sites. Pathogen decay rates applied impacted considerably the effectiveness of the aquifer in removing pathogens.

In order to provide safe drinking water with MAR an integrated approach to managing risks needs to be adopted which includes characterisation of the aquifer treatment barrier. To date there have been no reported case studies where the aquifer treatment barrier of a MAR scheme is accredited with $\log_{10}$ removals for pathogens much like in conventional drinking water treatment. In valuing the treatment capacity, integrity and independence of aquifers, MAR can be utilised in the same way as conventional engineered water treatment in an integrated water supply system.

The value of the aquifer barrier was determined by the relative $\log_{10}$ removal characteristics with respect to the reference pathogens (Table 19.7). The $\log_{10}$ removals for *Campylobacter* are potentially >6.0 $\log_{10}$, if the decay rate measured at Parafield is used for the sites, as is in Atlantis and Torreele/St André. For instance, in Sabadell and Shafdan the decay rates used come from a review of different studies published on pathogens in groundwater (John and Rose, 2005), and in Nardò a much lower decay rate measured in the site (La Mantia *et al.* 2008) is used. A similar value of >6.0 $\log_{10}$ units removal is attributed to other water treatment technologies such as reverse osmosis (NRMMC-EPHC-AHMC, 2006). For *Cryptosporidium* the value of the aquifer treatment is dependant on the residence time. *Cryptosporidium*

Table 19.5 Probability distribution functions used for the quantitative risk assessment in case studies using the recovered water for crops irrigation, green space irrigation or streets cleaning purposes.

Site	Nardò			Sabadell			Shafdan		
Pathogen	**Campylobacter**	**Cryptosporidium**	**Rotavirus**	**Campylobacter**	**Cryptosporidium**	**Rotavirus**	**Campylobacter**	**Cryptosporidium**	**Rotavirus**
Pathogen source water number (n/L)	U(10^3, 10^5)[a]	LN(225.7, 83.7)[b]	LN(1342.6; 6329.9)[c]	U(10^3, 10^5)[a]	LN(225.7, 83.7)[b]	LN(1342.6; 6329.9)[c]	U(10^3, 10^5)[a]	LN(225.7, 83.7)[b]	LN(1342.6; 6329.9)[c]
WWTP (log_{10})	T(1, 2, 3.5)[d]	T(0.5, 1, 1.5)[d]	T(0.5, 1, 2.1)[d]	T(1, 2, 3.5)[d]	T(0.5, 1, 1.5)[d]	T(0.5, 1, 2.1)[d]	T(1, 2, 3.5)[d]	T(0.5, 1, 1.5)[d]	T(0.5, 1, 2.1)[d]
Channel/river mixture (log_{10})	T(0, 0.7, 1.6)[e]	T(0.1, 1, 2)[e]	T(0, 0.5, 1.4)[e]	LL(−1.6, 1.9, 4.4)[h]	E(0.63)[h]	T(−1, 0, 2)[h]			
Subsurface storage (days)	T(13, 23, 65)	T(13, 23, 65)	T(13, 23, 65)				T(180, 270, 365)	T(180, 270, 365)	T(180, 270, 365)
Subsurface pathogen decay rate (log_{10}/day)	0.038[g]	0.057[g]	0.12[g]	T(0.02, 0.08, 1.5)[i]	N(0.012, 0.0030)[f]	T(0.012, 0.16, 0.83)[j]	T(0.007, 0.2, 1.4)[i]	N(0.012, 0.0030)[f]	T(0.03, 0.33, 1.3)[j]
UV (log_{10})				T(2.0, 3.0, 4.0)[a]	T(2.0, 3.0, 3.5)[a]	T(1.0, 2.0, 3.5)[a]			
Chlorination (log_{10})				T(2.0, 3.0, 4.0) [d]	T(0.0, 0.0, 0.5)[d]	T(1.0, 1.5, 3.0)[d]	T(2.0, 3.0, 4.0) [d]	T(0.0, 0.0, 0.5)[d]	T(1.0, 1.5, 3.0)[d]
Rapid sand filtration (log_{10})				T(0.0, 0.0, 0.5) [d]	T(0.0, 0.0, 0.5) [d]	T(0.0, 0.0, 0.5)[d]			
Volume ingested (L)[d,k]	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})	U(10^{-3}, 10^{-4})
Exposures per year[k]	U(183, 365)	U(183, 365)	U(183, 365)	U(183, 365)	U(183, 365)	U(183, 365)	U(183, 365)	U(183, 365)	U(183, 365)

T: Triangular distribution; LL: Loglogistic; LN: Lognormal distribution; N: Normal distribution; U: Uniform distribution; E: Exponential distribution

[a] Adapted from NRMMC–EPHC–AHMC, 2006; Westrell, 2004.

[b] Adapted from Montemayor *et al.* (2005).

[c] Adapted from Sedmark *et al.* (2005).

[d] Adapted from NRMMC–EPHC–AHMC (2006).

[e] Data from Nardò site on indicators was used to construct the PDFs (Böckelmann *et al.* 2009; Levantesi *et al.* 2010; Aharoni *et al.* 2008).

[f] From Sidhu *et al.* (2010).

[g] Single value only, using indicators data, from La Mantia *et al.* (2008).

[h] Data from Sabadell site on indicators was used to construct the PDFs (Böckelmann *et al.* 2009; Levantesi *et al.* 2010; Aharoni *et al.* 2008).

[i] Adapted from John and Rose (2005).

[j] Adapted from Pedley *et al.* (2006).

[k] The scenario considered is an accidental aerosols inhalation during irrigation by growers/irrigators. This scenario was the worst case as per Ayuso-Gabella *et al.* submitted).

Table 19.6 Probability distribution functions used for the quantitative risk assessment in case studies using the recovered water for augmenting urban drinking water supplies.

Site	Atlantis			Parafield			Torreele/St-André		
Pathogen	**Campylobacter**	**Cryptosporidium**	**Rotavirus**	**Campylobacter**	**Cryptosporidium**	**Rotavirus**	**Campylobacter**	**Cryptosporidium**	**Rotavirus**
Pathogen source water number (n/L)	LN(3.9, 9.8)[a]/ U(10^1–10^4)[d]	LN(0.5, 1.2)[a]/ LN(200, 100)[c]	LN(0.3, 0.6)[a]/ LN(443, 220)[b]	LN(3.9, 9.8)[a]	LN(0.5, 1.2)[a]	LN(0.3, 0.6)[a]	U(10^1–10^4) [d]	LN(200, 100)[a]	LN(443, 220)[c]
Artificial wetland (log_{10})	T(1.5, 2, 2.5)[e]	T(0.5, 0.5, 1.0)[e]	T(0.0, 0.0, 0.0)[e]	T(1.5, 2.0, 2.5)[e]	T(0.5, 0.5, 1.0)[e]	T(0.0, 0.0, 0.0)[e]			
WWTP (log_{10})	T(0.6, 1.4, 3.7)[e]	T(0.4, 1.8, 3.8)[e]	T(0.2, 1.7, 2.3)[e]				T(0.6, 1.4, 3.7)[f]	T(0.4, 1.8, 3.8)[f]	T(0.2, 1.7, 2.3)[f]
UF (log_{10})							T(4.0, 4.0, 7.0)[f]	T(3.0, 3.0, 7.0)[f]	T(4.0, 4.0, 6.5)[f]
RO (log_{10})							T(4.0, 4.0, 7.0)[f]	T(3.0, 3.0, 7.0)[f]	T(2.7, 3.0, 6.5)[f]
UV (log_{10})							T(2.0, 3.0, 4.0)[f]	T(2.0, 3.0, 4.0)[f]	T(2.0, 2.0, 3.0)[f]
Subsurface storage (days)		T(182, 365, 730)			LN(241, 58)			T(30, 35, 40)	
Subsurface pathogen decay rate (log_{10}/day)[g]	5.6	N(0.012, 0.0030)	N(0.0055, 0.0036)	5.6	N(0.012, 0.0030)	N(0.0055, 0.0036)	5.6	N(0.012, 0.0030)	N(0.0055, 0.0036)
Rapid sand filtration (log_{10})							T(0.8, 1.5, 3.3)[f]	T(0.8, 2.9, 5.4)[f]	T(0.1, 0.5, 3.9)[f]
UV (log_{10})				T(2.0, 3.0, 4.0)[e]	T(2.0, 3.0, 4.0)[e]	T(2.0, 2.0, 3.0)[e]	T(2.0, 3.0, 4.0)[f]	T(2.0, 3.0, 4.0)[f]	T(2.0, 2.0, 3.0)[f]
Chlorination (log_{10})	T(2.0, 4.0, 6.0)[e]	T(0.0, 0.0, 0.5)[e]	T(1.0, 2.0, 3.0)[e]	T(2.0, 4.0, 6.0)[e]	T(0.0, 0.0, 0.5)[e]	T(1.0, 2.0, 3.0)[e]			
Volume ingested (L)[h]	2	2	2	2	2	2	2	2	2
Exposures per year[h]	365	365	365	365	365	365	365	365	365

T: Triangular distribution; LN: Lognormal distribution; N: Normal distribution; U: Uniform distribution

Engineered treatment efficacy log_{10} removal efficiencies come from; except Torreele/St-André from Ayuso-Gabella *et al.* (2007)

[a] 95th Percentile as per TableA3.1 of the Guidelines for Stormwater Harvesting and Reuse: *Campylobacter* 15 n/L; *Cryptosporidium* 1.8 n/L; rotavirus 1 n/L (NRMMC-EPHC-NHMRC 2009a).

[b] Robertson *et al* (2006).

[c] Cited in Kocwa-Haluch and Zalewska (2002).

[d] Adapted from NRMMC–EPHC–AHMC (2006).

[e] Adapted from Smeets *et al.* (2006); NRMMC–EPHC–NHMRC (2006).

[f] From Ayuso-Gabella *et al.* (2007).

[g] From Sidhu *et al.* (2010). Single value only for *Campylobacter*.

decay rate has only been measured at Parafield (Sidhu *et al.* 2010) and to date, there are no other published studies that measure this decay rate in aquifers. Then, the highest $\log_{10}$ unit removals by aquifer treatment for *Cryptosporidium* are obtained at Atlantis, Shafdan and Parafield, that have longer residence times. In Sabadell, a very low residence time is considered, and the triangular function created for the residence time could be adjusted according to hydrogeological modelling and tracer tests studies, that are still required at the site. Rotavirus had different $\log_{10}$ removals in the aquifer (Table 19.7) depending on the decay rates used (Tables 19.5 and 19.6). For Atlantis, Parafield and Torreele/St. André the decay rate used was the one measured at Parafield aquifer, which was low, thus rendering low removals. For Nardò, the decay rate for viruses was measured in the site, and it was higher than for bacteria (La Mantia *et al.* 2008). For Shafdan and Sabadell, decay rates from the literature were used (Pedley *et al.* 2006), and removal for Shafdan was very high.

Table 19.7 Calculated aquifer barrier and engineered treatment (non-aquifer) removal efficiency in $\log_{10}$ units.

Case study		Atlantis		Nardò		Parafield		Sabadell		Shafdan		Torreele/St-André	
Treatment removal	$\log_{10}$	Aquifer	Non-aquifer	Aquifer	Non-aquifer	Aquifer	Non-aquifer	Aquifer	Non-aquifer	Aquifer	Non-aquifer	Aquifer	Non-aquifer
Campylobacter	Min	≥6.0	4.1	0.5	1	≥6.0	5.5	≤0.1	3.6	2.7	3	≥6.0	13.4
	Most likely	≥6.0	7.4	1.2	2.7	≥6.0	9.0	0.5	8.2	≥6.0	5	≥6.0	16.9
	Max	≥6.0	12.2	2.5	5.1	≥6.0	12.5	1.5	15	≥6.0	7.5	≥6.0	29.0
Cryptosporidium	Min	0.3	0.9	0.8	0.6	0.1	2.5	≤0.1	2.7	0.2	0.5	≤0.1	11.2
	Most likely	5.0	2.3	1.8	2	2.8	3.5	≤0.1	4.6	3.1	1	0.4	16.7
	Max	≥6.0	5.3	3.7	3.5	≥6.0	5.5	0.3	8	≥6.0	2	0.9	31.2
Rotavirus	Min	≤0.1	1.2	1.6	0.5	≤0.1	3.0	≤0.1	1.5	≥6.0	1.5	≤0.1	8.3
	Most likely	2.5	3.7	3.8	1.5	1.4	4.0	2.1	4.5	≥6.0	2.5	0.2	17.2
	Max	≥6.0	5.3	≥6.0	3.5	≥6.0	≥6.0	≥6.0	11.1	≥6.0	5.1	0.7	25.2

Note: In those case studies where the recovered water is used for irrigation purposes (Nardò, Sabadell and Shafdan) the non-aquifer treatment does not include the postharvest decay and washing treatments.

Knowledge of both the aquifer residence time and the rate of decay are essential for enabling the treatment value of the aquifer to be determined (Table 19.7). The decay of pathogens in groundwater during MAR is influenced by a range of factors such as the activity of indigenous groundwater microorganisms, temperature, redox status, oxygen concentrations and organic carbon concentrations (Gordon & Toze, 2003; Toze *et al.* 2004). Research has shown that bacteria tend to survive for much shorter times in aquifers than enteric viruses and protozoa (Toze *et al.* 2004) but the relative times can be aquifer-dependent. Virus decay rate is not always linear. The decay of some pathogens, in particular the more resistant viruses have been observed to have a decline in decay rate with time. Thus, in these cases a broken stick model of decay with different rates of decay may be more appropriate than a single rate of decay. The most appropriate decay rates to use will need to be verified in future risk assessments.

19.5.2 Case study sites human health risk assessment

The results in DALYs of the risk assessment are reported in Table 19.8. In the case studies where the recovered water is used for crops irrigation, green space irrigation or streets cleaning, the scenario considered is the accidental aerosols inhalation by growers and/or irrigators, as it is the worst case among the scenarios tested in Ayuso-Gabella *et al.* (submitted). The other scenarios tested were accidental aerosols inhalation by local communities and crops consumption. All these scenarios are recommended to be evaluated in the WHO Guidelines for Wastewater Reuse in irrigation (WHO, 2006).

Table 19.8. Mean, Median and 95th percentile residual risk assessment in DALYs.

Pathogen		Atlantis	Nardò	Parafield	Sabadell	Shafdan	Torreele/St-André
Campylobacter	Mean	$<1.0 \times 10^{-10}$	$\mathbf{4.2 \times 10^{-5}}$	$<1.0 \times 10^{-10}$	2.9×10^{-10}	$<1.0 \times 10^{-10}$	$<1.0 \times 10^{-10}$
	Median	$<1.0 \times 10^{-10}$	$\mathbf{9.7 \times 10^{-6}}$	$<1.0 \times 10^{-10}$	$<1.0 \times 10^{-10}$	$<1.0 \times 10^{-10}$	$<1.0 \times 10^{-10}$
	95th	$<1.0 \times 10^{-10}$	$\mathbf{1.9 \times 10^{-4}}$	$<1.0 \times 10^{-10}$	5.1×10^{-10}	$<1.0 \times 10^{-10}$	$<1.0 \times 10^{-10}$
Cryptosporidium	Mean	$\mathbf{7.0 \times 10^{-6}}$	8.9×10^{-7}	7.7×10^{-9}	5.3×10^{-8}	7.6×10^{-7}	$<1.0 \times 10^{-10}$
	Median	5.3×10^{-9}	2.1×10^{-7}	2.0×10^{-10}	2.0×10^{-8}	8.6×10^{-8}	$<1.0 \times 10^{-10}$
	95th	$\mathbf{1.2 \times 10^{-5}}$	$\mathbf{3.8 \times 10^{-6}}$	1.8×10^{-8}	2.1×10^{-7}	$\mathbf{3.0 \times 10^{-6}}$	$<1.0 \times 10^{-10}$
Rotavirus	Mean	$\mathbf{2.3 \times 10^{-4}}$	$\mathbf{1.7 \times 10^{-6}}$	8.5×10^{-7}	9.1×10^{-8}	1.4×10^{-10}	$<1.0 \times 10^{-10}$
	Median	$\mathbf{4.9 \times 10^{-5}}$	2.5×10^{-8}	5.0×10^{-8}	1.6×10^{-10}	$<1.0 \times 10^{-10}$	$<1.0 \times 10^{-10}$
	95th	$\mathbf{8.3 \times 10^{-4}}$	$\mathbf{5.7 \times 10^{-6}}$	$\mathbf{3.1 \times 10^{-6}}$	1.1×10^{-7}	5.2×10^{-10}	$<1.0 \times 10^{-10}$

Bold value indicates value exceeds guideline of 1×10^{-6} DALYs; limit of calculation is 1×10^{-10} DALYs.

Atlantis had acceptable risk for *Campylobacter*, but higher risk for *Cryptosporidium* and very high risk for rotavirus. Parafield and Shafdan had low risks for each of the pathogens. Torreele/St-André had a very low risk for each pathogen due to the large pre- and post-recovery treatment trains. Sabadell had also a very low risk for each pathogen, due to the large post-recovery treatment trains. Nardò had medium risks for *Campylobacter* and rotavirus, even though the dose considered is low as the water is used for irrigation purposes. At Atlantis, Parafield and Torrele/St. André case studies the recovered water will be used for drinking water and potable purposes, assuming a daily ingestion of 2 L. In Sabadell, the recovered water is not intended for drinking water purposes, but for urban parks irrigation and streets cleaning. In Shafdan and Nardò the recovered water is used for crops irrigation, but at Nardò the water is recovered from a different well than the one considered for the calculations. The dose considered is according to an accidental aerosol ingestion by a grower or irrigator, and it ranges from 0.0001 to 0.001 mL, which is a dose between 3–4 orders of magnitude lower than the drinking water dose.

While the mean gives an assessment of the average risk, and the median its central tendency, the 95th percentile gives an estimate of the variability and reasonable maximum of the risk. Where the 95th percentile was below the acceptable risk threshold, the risk assessment was considered to be robust. As such the risk assessment from rotavirus for Parafield is not as robust and further work is required to reduce the uncertainty of this risk estimate or further treatment is required to reduce the risk. Something similar is observed for *Cryptosporidium* in Shafdan and Nardò. For the other case study sites, the median and 95th percentile are similar indicating that the assessments are generally robust.

To evaluate the risk from enteric pathogens during MAR the potential presence of these pathogens and their numbers need to be determined. The major source of all enteric pathogens is faecal contamination, particularly from human faecal material. The largest number of enteric pathogens can be expected to be detected in untreated wastewater (Tables 19.5 and 19.6) with numbers reducing through the non-aquifer and aquifer treatment processes (Table 19.7). The potential presence of enteric pathogens in the recharge water is directly linked to the potential of human faecal matter contaminating the water. Thus, in this study, the pathogen risk for Torreele/St-André was assessed to be very low due to the high level of treatment prior to MAR. On the other hand, the level of treatment of the wastewater prior to MAR is much lower in Sabadell, Shafdan and Nardò, thus highly increasing the risk of pathogen presence in the recharged water. The Atlantis scheme has less opportunity for the presence of microbial pathogens due to the blending of treated wastewater and stormwater, while the risk in the Parafield system is limited to the potential for sewer pump-station overflows and contamination from animal faeces.

A number of limitations to the QMRA approach with MAR systems have been previously identified by Toze *et al.* (2010), including factors such as variability in pathogen decay rates. An accurate risk assessment also requires the input of accurate pathogen numbers. The initial pathogen numbers in the recharge water are influenced by a range of factors such as disease burden of the local population and the level of treatment for the recharge water. The numbers of some pathogens are also less accurate due to the difficulties in detection. For example, the detection of *Cryptosporidium* oocysts and rotavirus is difficult due to the lack of suitable culture methods and the low numbers ($\leq$100 units) usually present in large volumes of water ($>$1 L). Numbers in river, canal and recreation water for *Cryptosporidium* oocysts have been quoted as between 5 and 240 oocysts per 10 litres (Schets *et al.* 2008; Plutzer *et al.* 2008; Mons *et al.* 2009). In comparison rotavirus numbers in similar water types have been reported to be between 2 and 200 detectable units per litre (Mehnert *et al.* 1993; Lodder *et al.* 2005).

In general, the risks evaluated for each of the MAR sites (Table 19.8) were in the order Atlantis > Nardò > Parafield and Shafdan > Sabadell > Torreele/St-André for *Cryptosporidium* and rotavirus, and all of the sites but Nardò had low risks for the bacterial pathogen, *Campylobacter*. Only Atlantis and Nardò did not meet the tolerable risk value for all the reference pathogens (Table 19.8).

19.5.3 Valuing the aquifer barrier in MAR schemes

A sensitivity analysis was performed for each barrier in the treatment train for each case study site and the factor sensitivity (FS) calculated. The FS calculation standardises the comparison between each of the water treatment barriers and the aquifer and thereby aids in valuing the aquifer as part of the larger treatment train. A value of 1.0 indicates a ten-fold increase in risk. Table 19.9 gives a comparison of the FS values for each of the treatment barriers across the MAR systems.

For Atlantis and Shafdan the FS analysis indicated that the aquifer was the single most important barrier in determining risk from all pathogens. For Atlantis, >6 orders of magnitude increase in risk would result if the aquifer was removed from the treatment train for *Campylobacter*. For Shafdan, 6 orders of magnitude increase in risk would result if the aquifer was removed from the treatment train for *Campylobacter* and rotavirus. If the aquifer barrier is in place at Atlantis the other barriers have little influence in determining the residual risk from *Campylobacter*. For *Cryptosporidium*, the secondary wastewater treatment plant had a slightly lower capacity to reduce the residual risk than the aquifer. In the case of Shafdan, if the aquifer barrier is in place the other barriers have little to no influence in determining the residual risk for all of the pathogens.

Table 19.9. Factor Sensitivity ratio – relative importance of barriers.

	Atlantis	Nardò	Parafield	Sabadell	Shafdan	Torreele/St-André
Campylobacter						
Constructed wetland	0.00*	–	0.00*	–	–	–
Secondary treatment	0.00*	1.3	–	1.8	2.1	0.00*
Ultra filtration	–	–	–	–	–	0.00*
Reverse osmosis	–	–	–	–	–	0.00*
UV disinfection	–	–	–	–	–	0.00*
Channel/River mixture	–	0.6	–	0.1	–	–
Aquifer	7.57	0.9	1.29	1.3	6.0	0.00*
Rapid sand filtration	–	–	–	–	–	0.00*
UV disinfection	–	–	0.00*	2.7	–	0.00*
Chlorination	0.00*	–	0.00*	2.9	2.9	–
Rapid sand filtration	–	–	–	0.2	–	–
Cryptosporidium						
Constructed wetland	0.78	–	0.61	–	–	–
Secondary treatment	1.65	0.9	–	0.9	0.9	1.24
Ultra Filtration	–	–	–	–	–	3.48
Reverse Osmosis	–	–	–	–	–	3.48
UV disinfection	–	–	–	–	–	2.57
Channel/River mixture	–	0.8	–	0.6	–	–
Aquifer	1.93	1.5	2.03	0.1	2.3	0.00*
Rapid sand filtration	–	–	–	–	–	1.92
UV disinfection	–	–	2.78	2.7	–	2.57
Chlorination	0.05	–	0.14	0.1	0.2	–
Rapid sand filtration	–	–	–	0.2	–	–
Rotavirus						
Constructed wetland	0.00	–	0.00	–	–	–
Secondary treatment	0.35	1.0	–	1.0	1.1	1.14
Ultrafiltration	–	–	–	–	–	4.51
Reverse osmosis	–	–	–	–	–	3.49
UV disinfection	–	–	–	–	–	2.23
Channel/River mixture	–	0.5	–	0.1	–	–
Aquifer	0.55	2.2	0.94	1.2	5.7	2.23
Rapid sand filtration	–	–	–	–	–	0.92
UV disinfection	–	–	1.94	1.6	–	2.23
Chlorination	0.43	–	1.66	1.5	1.7	–
Rapid sand filtration	–	–	–	0.1	–	–

*FS score could not be calculated as the resultant risk was equal to the residual risk.

For Parafield the aquifer barrier again dominated the risk from *Campylobacter*, resulting in over ten fold increase in risk if it were not present. The aquifer was the third most important barrier with respect to rotavirus and second for *Cryptosporidium* risk (UV slightly higher), but post-recovery UV and chlorine disinfection was each superior to the aquifer in reducing risk for rotavirus.

For Torreele/St-André the aquifer only played a measurable role in reducing residual risk for rotavirus. The most important barriers were ultrafiltration and reverse osmosis for each of the reference pathogens. The FS value of the aquifer could not be calculated for *Cryptosporidium* and *Campylobacter* as the revised risk in removing the barrier was equal to the initially calculated residual risk, $<1.0 \times 10^{-10}$ DALYs.

For Sabadell the aquifer was not the most important barrier to reduce the risk, achieving a similar effect to the secondary treatment for *Campylobacter* and rotavirus. The key barriers to reduce the risk for all the pathogens were the UV disinfection and chlorination.

At Nardò the results were rather different, being the aquifer the most important barrier to reduce *Cryptosporidium* and rotavirus, and the second most important barrier to reduce the risk for *Campylobacter*.

From the FS analysis of Table 19.8, the subsurface treatment steps were identified as being highly variable in the treatment train in reducing the calculated residual risk. The initial pathogen numbers in the water to be recharged for each MAR site is a function of the pre-treatment barriers. Torreele/St-André with its large pre-treatment train (average $\log_{10}$ removals of 14.7, 10.8, 12.4 for rotavirus, *Cryptosporidium* and *Campylobacter* respectively) begin with very low numbers of pathogens in the recharge water. Atlantis and Parafield have lower numbers than Torreele/St-André but Parafield has much lower numbers of pathogens than Atlantis as its recharge water was solely urban stormwater as opposed to reclaimed effluent with a minor component of stormwater. The pathogen numbers for each site steadily decreased as a function of the decay rate and the residence time in the aquifer reported in Table 19.5 and Table 19.6.

19.5.4 Integrating aquifer treatment with engineered treatments

To date aquifer treatment is being slowly integrated into an engineered water treatment train due to the difficulty in measuring a quantifiable reduction in risk. This is in part due to the adoption of risk-based management systems, such as the Hazard Analysis and Critical Control Point (HACCP) approach. HACCP concepts have been adopted by the water industry and promoted as a more proactive approach to managing drinking water supplies (WHO, 2004; NRMMC-EPHC-NHMRC, 2008), as well as recycled water systems (NRMMC-EPHC-AHMC, 2006) and even MAR systems (NRMMC-EPHC-NHMRC, 2009b). Yet, aquifer treatment remains difficult to integrate as there are no easily identifiable critical limits and control points such as for the more common water treatment technologies, like chlorination which uses contact time, UV disinfection which uses UV-transmittance and membrane treatments which use pressure and electrical conductivity.

It is proposed that an extension of the FS sensitivity analysis could also be used to provide a means of generating evidence-based critical limits to manage critical control points. While there are no health-based targets for pathogen numbers QMRA can be used to address the issue of setting critical limits. This is done by treating the DALYs estimates as representing acceptable estimates of "absolute" risk and comparing them to the agreed international human health risk benchmarks, 1.0×10^{-6} DALYs (WHO 2004). In this instance, the comparison of the Parafield risk estimate indicated that the residual risk was acceptable for *Campylobacter* when compared to this benchmark and this conclusion was robust as indicated by the 95th percentile being less than the benchmark value. However, for rotavirus the assessment was less robust and the required aquifer residence time was just great enough for the scheme to support so additional post-recovery treatment could be required. An illustrative example for setting of critical limits for mean aquifer residence time comes from the *Cryptosporidium* for the Atlantis site, where the mean residence time needs to exceed ~550 days to achieve tolerable levels of risk. Again, this assumes that the pathogen decay rates of Sidhu *et al.* (2010) are linear and are representative of the processes occurring in the subsurface of this site. Use of the residence time critical limit could also be used to design infiltration and extraction pumping regimes to ensure the mean residence time in the aquifer is achieved. Where aquifer residence time is not accurately known, such as in the Sabadell case study site, it can be determined by use of suitable groundwater tracers. This can include both applied tracers, substances injected into the groundwater intentionally and thereby in controlled doses, time intervals and locations (such as SF_6) or natural tracers (such as the recharge water electrical conductivity if this has marked variation from the ambient groundwater). Knowledge of the residence time in the aquifer coupled with pathogen decay rates could then be used to fully appreciate the water treatment function of the subsurface and integrate the aquifer barrier with the engineered treatments in the provision of safe drinking water.

19.6 CONCLUSIONS

MAR case studies were evaluated for chemical (organic compounds) and microbiological risks.

For the organic compounds, the RQ methodology was used, and the results showed no risk for the human health in the case studies evaluated.

To assess the microbiological risks, the QMRA methodology was used. QMRA provides a means of quantifying the combined effects of aquifers and engineered treatments for reference pathogens in terms of $\log_{10}$ removal characteristics. The use of QMRA was found to be a useful tool in establishing the value of the aquifer within the treatment train and allowed the assessment of human health risk from pathogens in terms of DALYs. In general, the risks were below the benchmark value of 1.0×10^{-6} DALYs for all the reference pathogens, except for some exceptions. A sensitivity analysis was used to assess which of the treatment barriers was most important in each of the MAR systems. In this case, some sites relied completely in the aquifer to reduce the risks, whereas in others the aquifer had nearly no effect in reducing the human health risks. Nevertheless, the QMRA approach allows the integration of the aquifer treatment characteristics into the larger engineered treatment train and could be used in the future to quantitatively assess the reduction of human health risk for MAR systems more generally.

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