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TECHNICAL REPORT NO. 37

Flux-based groundwater assessment and management

CRC for Contamination Assessment and Remediation of the Environment

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Flux-based groundwater assessment and management

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Executive summary

In line with international progress, there has been an increasing acceptance in recent years by contaminated sites practitioners in Australia of the usefulness of mass flux concepts for the management of groundwater contamination. However, there is no nationally consistent guidance or methodology on how mass flux or mass discharge estimates may be used to assess and manage groundwater contamination, or the endpoints that should apply. CRC CARE has therefore commissioned this user guide for the better measurement and use of mass flux and mass discharge in the management of groundwater contamination.

The purpose of this guidance is therefore to illustrate how flux concepts, tools and measurements can be used to assess and manage groundwater contamination, including engaging with regulators and other stakeholders.

The assessment and management of groundwater contamination has traditionally been driven by contaminant concentrations, however concentration data alone are sometimes not sufficient to fully understand the behaviour or impact of a plume over time. Mass flux and mass discharge concepts can help fill the gap in understanding, and have been applied successfully both in Australia and internationally to:

- Enhance the conceptual site model (CSM)
- Complement concentration criteria
- Assist with remedy selection
- Optimise remedial design
- Assess remedial performance
- Demonstrate risk reduction, and
- Evaluate compliance/long term monitoring.

In general, current Australian regulations emphasise a pragmatic, risk-based approach to the management of groundwater contamination. Mass flux-based techniques are a valuable tool in supporting this approach, provided the data are robust and well-presented, in consultation with the regulator.

Five key methods have been identified to derive mass flux and mass discharge estimates for dissolved phase contaminants, namely:

- Transect methods
- Passive flux meters
- Well capture/pump test methods
- Transects based on isocontours, and
- Solute transport models.

As with other site investigation approaches, it is necessary to determine the acceptable level of uncertainty for the intended application of the mass flux and/or discharge information and how that level of uncertainty can be achieved, managed and assessed.

Mass flux and mass discharge approaches can be incorporated into site assessment and management through the development of site-specific metrics, i.e. for groundwater extracted for beneficial uses or groundwater discharging into a surface water body. The

guideline emphasises that mass flux and mass discharge estimates will typically be used to complement concentration-based assessments, rather than to replace them.

Mass flux and mass discharge estimates are therefore important tools which may help practitioners and regulators characterise, remediate and manage groundwater contamination. Consideration of these concepts when characterising a site, as well as during remedial design and optimisation, may ultimately result in a more detailed risk-based approach, along with more time- and cost-efficient groundwater remediation programs.

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1. Introduction

The assessment and management of groundwater contamination is traditionally driven by contaminant concentrations; however concentration data alone are sometimes not sufficient to fully understand the behaviour or impact of a plume over time.

Mass flux and mass discharge estimates are important tools to help practitioners and regulators characterise and remediate groundwater contamination. Their inclusion within remedial design and optimisation may ultimately result in more time- and cost-efficient groundwater remediation programmes.

1.1 Purpose and objectives

In line with international progress, there has been an increasing acceptance in recent years by contaminated sites practitioners in Australia of the usefulness of mass flux concepts for the management of groundwater contamination. However, there is no nationally consistent guidance or methodology on how mass flux or mass discharge measures may be used to assess and manage groundwater contamination, or the endpoints that should apply.

The purpose of this guidance is therefore to illustrate how flux concepts, tools and measurements can be used to assess and manage groundwater contamination, including engaging with regulators and other stakeholders.

While this guideline aims to provide the concepts, tools and techniques to measure and use mass flux in groundwater contamination management, it is noted that early and thorough engagement with the site stakeholders to form agreement on the use of mass flux concepts may be just as important to overall success. To that end, this guideline also provides practical steps on communicating results, along with information on mass flux within the Australian regulatory context for the assessment and remediation of contaminated land.

As such, the objectives of this guide are to:

- Define the terms of mass flux and mass discharge and provide a background to these concepts and how they can be measured in the field
- Provide an overview of the potential applications of mass flux in groundwater contamination management in Australia as well as sites and scenarios where mass flux is most likely to be useful
- Provide a complementary means of demonstrating contaminated groundwater management, advancement of the conceptual site model (CSM) or the effectiveness of remediation with a view to site closure
- Encourage practitioners to consider mass flux and mass discharge estimates, where relevant, and apply these concepts appropriately in the management of groundwater contamination, and
- Increase the understanding of the use of mass flux measurements in groundwater contamination management, and hence make regulatory acceptance of remedial objectives specifically related to mass flux and/or discharge more common.

It should be noted that this user guide is specifically focused on mass flux in groundwater. While the technical and mathematical concepts of flux can be applied to other media (such as soil and vapour) this guideline explicitly excludes consideration of these media, except where it aids the understanding of using mass flux in the assessment and management of groundwater contamination.

1.2 Would mass flux concepts be helpful at my site?

Mass flux and mass discharge estimates have numerous applications associated with the investigation and remediation of contaminated groundwater.

Mass flux and mass discharge estimates have a range of potential uses, and are likely to be useful at most sites, depending on site-specific characteristics and the objectives of the project. The following flow chart outlines the decisions and process which should be followed to evaluate if mass flux is an appropriate tool for a particular site (figure 1).

Further detail regarding when and where mass flux concepts are best utilised is provided in section 3.1.

1.3 Background

Contaminated land and groundwater investigation within Australia is guided by the National Environment Protection Council, *National Environment Protection (Assessment of Site Contamination) Measure* (ASC NEPM). This was first published in 1999 and was amended in 2013. As there is no national framework for the remediation of contaminated sites in Australia, CRC CARE is in the process of developing a national remediation framework (NRF), as stipulated in the agreement between the Commonwealth Government and CRC CARE. In developing the framework, CRC CARE is keen to focus on developing harmonised guidance on the practicalities of cleaning up contaminated sites, for use by contaminated land practitioners, regulators and site owners.

In formulating the terms of reference for the NRF, CRC CARE solicited input on appropriate content from stakeholders in contaminated sites investigation and management. As part of this input it was identified that a document outlining the measurement and use of mass flux for groundwater contamination management would be beneficial, particularly considering the successes in utilisation of these techniques within international jurisdictions, and considering the use of mass flux measurements as a critical tool and line of evidence is discussed in several of the existing CRC CARE Technical Reports.
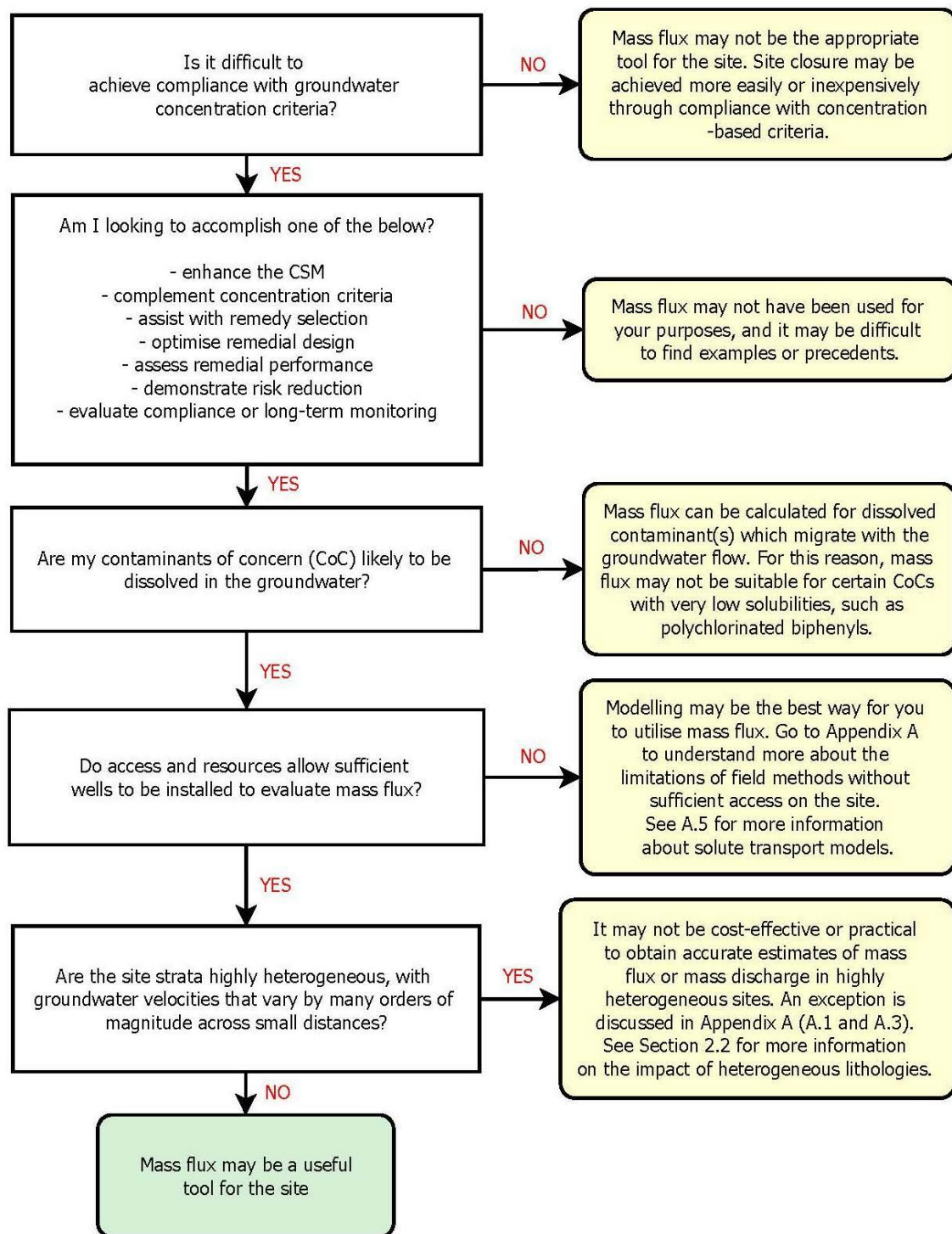
Figure 1 Flow chart to help evaluate if mass flux concepts may be helpful at a site.

In order to inform its internal processes, CRC CARE completed an initial review of available technical information on the subject (*Flux-based Criteria for Management of Groundwater*, CRC CARE 2014). This document reviewed existing international guidance, journal articles, tools and industry practice relating to the application of mass flux for the management of groundwater contamination. It also documented two examples of mass flux being utilised effectively in the management of contaminated sites in Australia and concluded that mass flux in Australia is currently being applied as a measure for both compliance and for site closure. It went on to note that existing Australian contaminated land guidance typically does not reference the concept of mass flux.

Following publication of that report, CRC CARE commissioned this project to provide guidance for the use of flux-based assessment and management of groundwater contamination.

1.4 Australian context

In general, existing Australian national and state groundwater contamination management guidance does not include significant or specific mention of flux-based management techniques. However, as discussed in section4 there is no guidance which specifically precludes the use of mass flux-based techniques. Furthermore, there is a general emphasis on a pragmatic, risk-based approach to management of groundwater contamination.

With this in mind, where mass flux measurements can be robustly demonstrated as being helpful in achieving the overall objectives for a site, regulators may be approached to discuss the inclusion of these measurements and concepts to aid in decision making. It is emphasised that technical veracity is crucial to gaining regulatory approval. Therefore, key aims of this document are to outline the tools which can form part of a robust and defensible approach and to provide guidance on the sites/scenarios where a mass flux-based approach is most feasible.

It is emphasised that acceptance of mass flux-based tools and techniques in the management of site contamination will depend on the technical basis of the proposed techniques (discussed throughout this guideline), and how they are relevant to achieving the overall objectives for a site. These objectives will vary, but are likely to include a demonstration that remediation has been successful in reducing risks to acceptable levels (a risk-based approach).

It should be noted that nothing in this guideline supersedes existing Australian regulatory requirements, and familiarity with relevant state and territory legislation and regulations is necessary before proceeding with environmental investigations or remediation/management. Nevertheless, this guidance has been developed in the context of existing Australian legislation and guidance; as such further discussion of the national legislation and guidance pertinent to the use of flux-based decision-making in Australia is presented in section 4.

Given the limited Australia-specific guidance available on mass flux concepts, during compilation of this document it has been necessary to draw heavily on guidance and journal articles originating in international jurisdictions. In doing this, careful

consideration has been given to the application of the techniques and concepts in the Australian context.

1.5 Users of the guidance

This user guide is primarily aimed at regulators and managers of sites where groundwater contamination is of primary concern, along with the environmental practitioners who assess and manage those sites.

It is anticipated that this guideline will aid in the use of mass flux or mass discharge information, and aid the review or interpretation of the work of others. It is assumed that the reader is familiar with site assessment procedures in accordance with the ASC NEPM (as published), and will consult with guidelines included within the NRF. This guideline and the methods presented are not intended to provide the sole or primary source of information about a site. It is also assumed that sufficient site characterisation data have been obtained to develop a robust CSM prior to the use of mass flux and mass discharge estimates in groundwater management. The user must also be aware of and work in accordance with applicable national and state legislations.

1.6 Structure, content and use of the guideline

This user guide is arranged into nine sections and follows the steps which may be followed when applying mass flux concepts. These steps can be considered when selecting an approach that aligns with the overall objectives for a project/site. Please refer to the flowchart on the following page, which is intended to guide the reader through both the document and the process that may be followed when using mass flux or mass discharge to assess and manage groundwater contamination at a site (figure 2). Each step has been referenced to the section in the guideline where further information can be sought. In addition, worked examples are provided throughout the text in order to highlight important points or show a particular technique, and two Case Studies are presented in Appendix C. Section 8 provides a reference list for those documents used in the compilation of this user guide and section 9 is a glossary of the specific terms, acronyms and formulae used within this guideline.
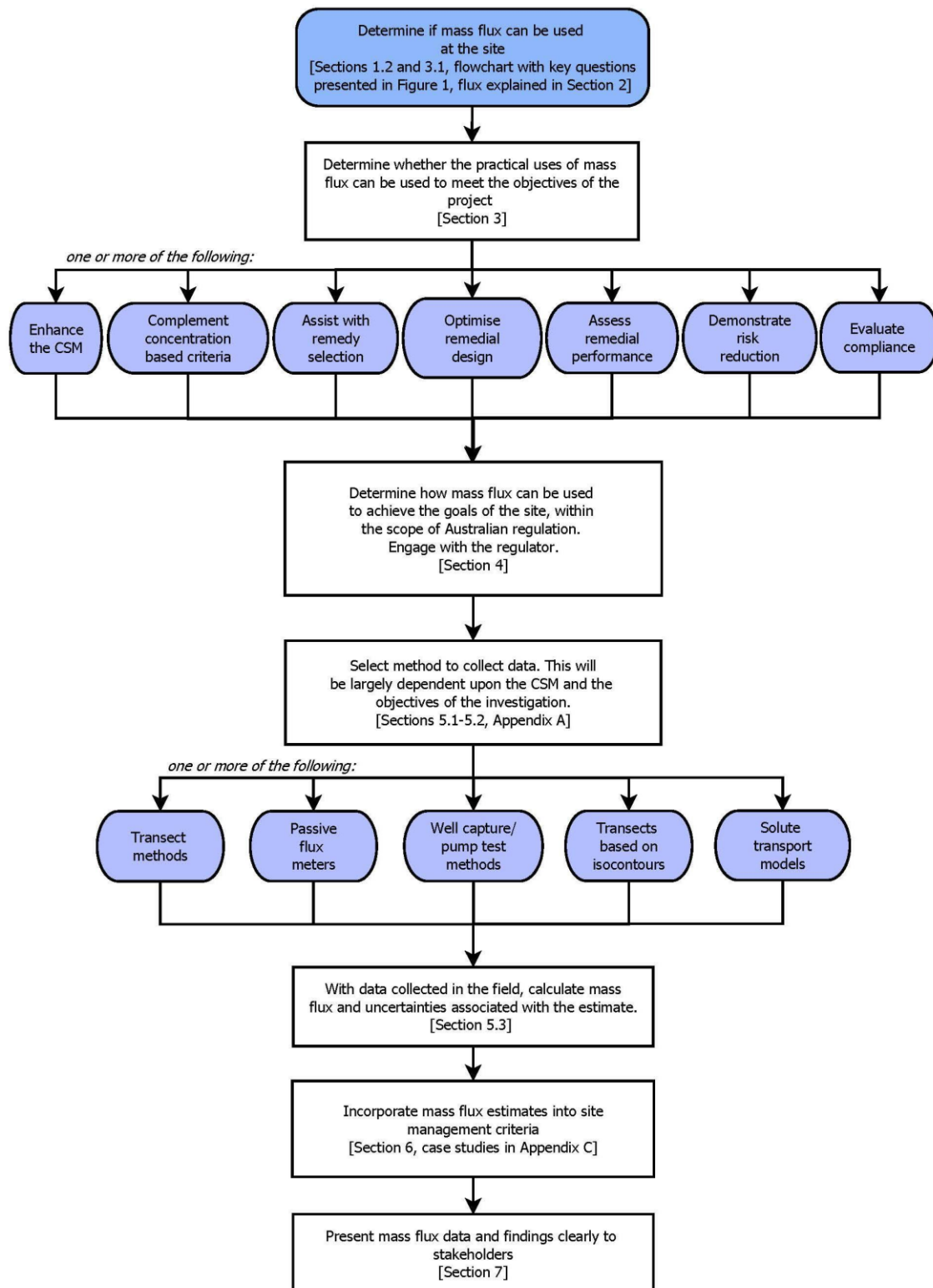
Figure 2. Overview of the process of applying mass flux to assess and manage groundwater contamination, with references to the relevant section within the text. It is noted that these steps are part of an iterative process, and steps may need to be revisited as the CSM evolves.

2. Flux explained

This section provides background information on the mathematics of flux, as well as an introduction to when and how mass flux concepts can be useful in contaminated groundwater assessment and management.

2.1 What is flux?

Flux is broadly defined as flow through a medium. Measurements of flux are made across planes or surfaces that perpendicularly intersect the flow.

This guideline adopts the following definitions from ITRC 2010:

- Groundwater flux is defined as "the velocity (speed and direction) of groundwater through a defined cross-sectional area located perpendicular to the mean direction of groundwater flow"
- Mass flux is defined as "the mass of a chemical that passes through a defined cross-sectional area located perpendicular to the mean direction of groundwater flow over a period of time", and
- Mass discharge is defined as "the total mass of a contaminant moving in the groundwater from a given source."

Further detail on these definitions, and their application to contaminated groundwater assessment and management is provided below.

2.1.1 Groundwater flux

Groundwater flux (q) can be calculated as the product of the saturated hydraulic conductivity (hereafter referred to as *K*) and the hydraulic gradient (*i*):

- q = *K* x *i* where
  - q = groundwater flux, volume/area/time (e.g. cubic metre (m^3)/square metre (m^2)/day (d))
  - *K* = saturated hydraulic conductivity, distance/time (e.g. m/d), and
  - *i* = hydraulic gradient, dimensionless (e.g. m/m).

Groundwater flux is also referred to as Darcy velocity or Darcy flux in some literature, however groundwater flux is used exclusively within this guideline.

2.1.2 Mass flux

The concept of *mass flux* (*J*) follows on from groundwater flux by incorporating the concentration of the contaminant within the groundwater.

Mathematically, mass flux can be calculated as follows:

- *J* = q x C where
  - *J* = mass flux, (e.g. milligrams (mg)/m^2/d)
  - q = groundwater flux, volume/area/time (e.g. m^3/m^2/d or m/d), and
  - C = contaminant concentration, mass/volume (e.g. mg/m^3 or μg/L).

Mass flux is a vector quantity as it includes both the magnitude and direction of the flow, and is expressed as mass/area/time (e.g. mg/m^2/d). Mass flux is specific to a defined area, which is usually small relative to the overall dimensions of the plume. Mass flux will generally exhibit spatial variability, so several individual mass flux measurements may be needed to capture this variability.

As the mass flux incorporates the contaminant, it is sometimes referred to (in other literature) as the contaminant mass flux. This guideline refers to mass flux.

2.1.3 Mass discharge

The concept of *mass discharge* (M_d) follows on from mass flux, as it is the sum (integral) of the individual mass flux estimates across a transect multiplied by the representative area:

- $M_d = J_1 A_1 + J_2 A_2 + J_3 A_3 + \ldots + Jn A_n$

Mass discharge (M_d) is a scalar entity and is expressed as mass/time (e.g. mg/d or g/d).

The relationship between mass flux and mass discharge is depicted in figure 3, where the sum of the mass flux (J_n) across the cross sectional areas (A_n) in a transect comprises the total mass discharge (M_d) across the transect.
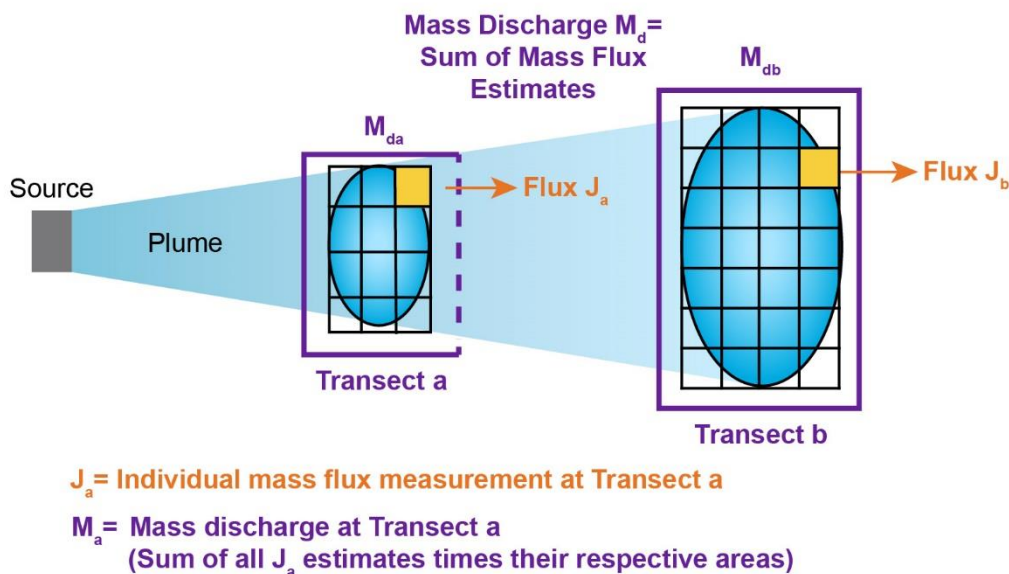
Figure 3 Relationship between the concepts of mass flux (J) and mass discharge (M$_d$) (Adapted from ITRC 2010).

This transect is referred to as the control plane. While it should ideally be perpendicular to the groundwater flow direction the placement in the horizontal plane is typically based on the CSM and measurement objective. Examples of the locations of control planes include a near source, a property boundary, an intersection with a surface water body, or within the plume.

Mass flux may vary both spatially and temporally within the control plane, and this variation may be significant. Spatial and temporal variations in mass flux are caused by variations in both contaminant concentrations and groundwater flow magnitude and

direction. As mass discharge is the product of the groundwater discharge and the contaminant concentration, it can also be obtained directly (instead of through calculations) through methods such as well capture and pumping tests. In these instances, mass discharge can be divided by the cross-sectional area of the plume at the control plane to determine the average mass flux (figure 3):

- $J_{av} = M_d/A$

In other literature, mass discharge may be referred to as contaminant mass discharge, total mass flux or integrated mass flux, however mass discharge is used exclusively in this guideline. Similarly, the term source zone contaminant mass discharge is used specifically when the control plane is immediately down-gradient of the source, before attenuation processes have had an effect.

2.2 Basic concepts of mass flux

The concepts behind mass flux and mass discharge are discussed further in the following sections.

2.2.1 Factors that affect mass flux

At a location along a groundwater contaminant plume, the mass flux represents the integrated effects of transport, storage and degradation along the flow path. By definition, mass flux estimates are impacted by factors that affect groundwater flux, such as the hydraulic conductivity (K) and the hydraulic gradient (i). Therefore estimates of mass flux are affected by such things as:

- changes in groundwater extraction rates
- groundwater elevation changes, and
- seasonal variations in velocity or flow directions (ITRC 2010).

Likewise by definition, mass flux estimates are affected by variations in contaminant concentrations. Factors that may cause contaminant concentrations to vary include redox changes due to the infiltration of rainwater and variations in dissolved phase concentrations due to sorption and the precipitation/dissolution of contaminants.

Heterogeneity in the lithology can have significant impacts on mass flux and thus should be understood prior to implementing a program to measure and use mass flux Rather than being homogeneous across the full extent of an aquifer, groundwater flow tends to be concentrated in zones of high K that often occupy a relatively small proportion of the aquifer cross section. This heterogeneity results in a range of mass fluxes across the aquifer at one site.

This concept is depicted in Figure 4 Although in this example the concentrations (C) and hydraulic gradients (i) are the same across the three sand layers, the mass flux through each lithology differs considerably due to variable K. As a result, the mass of contaminant that would reach a down-gradient receptor varies significantly in each layer, with the higher K of the gravelly sand resulting in a much greater mass flux. Therefore, whilst the potential risk posed to down-gradient receptors would be considered equal if only concentrations were compared, the use of mass flux illustrates that a greater potential risk may be posed by more transmissive areas. As the various

layers in this example are all sands, such a dissonance in source strength may not have been anticipated if mass flux estimates had not been considered.
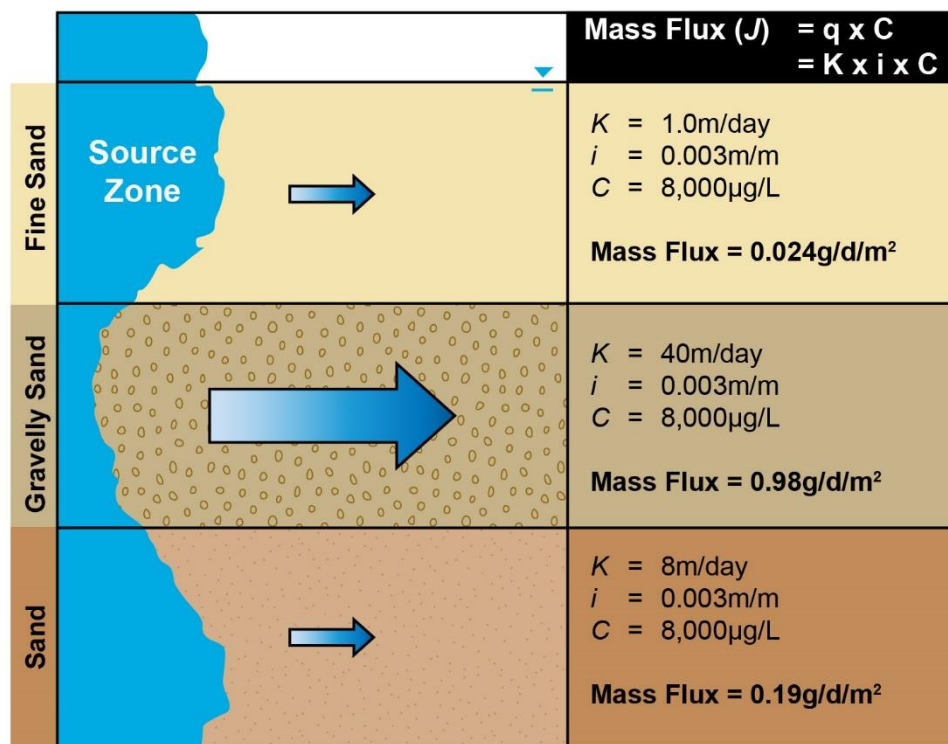
Figure 4 Illustration of the effect of *K* on mass flux, and how considering only concentration data can be ambiguous. Note that 1 microgram (µg)/L = 1 mg/m³ (Adapted from ITRC 2010).

It should be noted that at real sites, the concentration and possibly the hydraulic gradient) can also vary, and therefore the mass flux may span many orders of magnitude.

2.2.2 Plume structure and evolution

In many circumstances mass flux and mass discharge can provide useful information in addition to concentration data to help define the contamination plume structure and its evolution over time. Typical monitoring focuses on delineating plume boundaries and concentration trends. However both concentrations and groundwater flux can vary greatly across a plume, and by focusing only on the plume boundaries, areas of significant contaminant mass flux may be missed (ITRC 2010).

Using a mass balance assessment, mass discharge can be applied to determine whether a groundwater contaminant plume is expanding or contracting. This mass balance is a quantitative comparison of the source zone mass discharge to the plume attenuation rate (ITRC 2008):

- If the source mass discharge is estimated to exceed the attenuation rate, then the plume is considered to be expanding, and
- If the source mass discharge is estimated to be less than the attenuation rate, then the plume is considered to be contracting.

The concept of mass balance, as well as various factors which contribute to source mass discharge into a plume and attenuation of the plume, are illustrated in figure 5.

Groundwater Flow →

Source → Dissolved Plume →

Source Mass Discharge Into Plume	Plume Attenuation Rate
▪ Source flux ▪ Leachate ▪ Desorption ▪ Back Diffusion	Inside Plume: ▪ Biodegradation ▪ Abiotic Degradation ▪ Adsorption At Plume Boundary: ▪ Advection ▪ Dispersion ▪ Volatilisation ▪ Plant Uptake

Expanding Plume: Source Mass Discharge > Attenuation Rate
Contracting Plume: Source Mass Discharge < Attenuation Rate

Figure 5 Using mass balance to assess whether a plume is expanding or contracting (Adapted from ITRC 2010).

Knowledge of mass flux and mass discharge can provide important information regarding source concentration, natural attenuation rates, and areas of the subsurface through which the majority of the mobile contaminant mass is moving (ITRC 2010). This information can be very useful in the management of contaminated groundwater, for example when assessing risks to down-gradient receptors, or estimating the remediation timeframe.

2.2.3 Secondary sources

Mass discharge data can be used to assist in the understanding of plume age and the interaction of the plume with the aquifer lithology. During plume expansion, advective mass discharge occurs across areas of high K. However, mass flux varies substantially from the source zone to the leading edge of the plume, as areas closer to the source have had more time for diffusion from areas of high K to areas of low K. This mass storage of contaminants in low K zones is characteristic of areas that have had prolonged contact with the plume (ITRC 2010).

As the mass of contaminant within the source is depleted through remediation or natural attenuation, residual mass within areas of low K become more important (figure 6). Areas of greater K may therefore become subject to back-diffusion from lower K areas, which act as a second-generation source continuing to supply contaminants to groundwater flowing through areas of higher K (ITRC 2010). Hence, less transmissive areas are sometimes referred to as secondary sources.

a) Transect of an Expanding Plume:

Transverse distance (y-axis)

Depth (z-axis)

Contaminant concentrations in high-conductivity zones exceed those in low conductivity zones.

b) Transect of a Contracting Plume:

Transverse distance (y-axis)

Depth (z-axis)

Contaminant concentrations in high-conductivity zones are lower than those in the low zones. Back-diffusion is acting as a secondary source.

Figure 6 Movement of contaminants in expanding and contracting plumes. A) demonstrates an expanding plume, where contaminant mass is mainly present within areas of high K (dark blue). B) demonstrates that following source mass depletion, contaminant mass may back-diffuse form areas of low K (light blue) to high K (white). (Adapted from ITRC 2010).

The transition from groundwater contamination supplied by the original source zone to contamination supplied by second-generation sources is complex but controlled by mass flux from each zone. Understanding the magnitude of mass flux from each zone can help improve the CSM and prediction of future plume behaviour. Over the lifetime of a plume, the diffusive mass transfer of contaminants for an expanding plume is from areas of high to low K, whilst the diffusive mass transfer for a contracting plume is from areas of low to high K.

Understanding and measurement of this phenomenon can impact the CSM and site management decisions, including the choice of remedial options and the evaluation of remedial performance, as discussed in subsequent sections.

3. Applying mass flux in managing groundwater contamination

The section provides detail on the sites where mass flux concepts are likely to be helpful, along with when they may not be efficient. Additionally, some of the practical uses for mass flux measurements in managing groundwater contamination are presented, in order to provide the reader with context to appreciate how mass flux measurements may be useful in different situations.

The use of mass flux or mass discharge data in managing groundwater contamination requires the early, active, and possibly iterative engagement of the site stakeholders, including the regulators. Agreement on the terms of reference, methodology, assumptions, acceptable uncertainty and end points is crucial to the effective application of mass flux and mass discharge data.

In adopting these techniques on a given site, consideration also needs to be given to the regulatory context to determine whether the technique is useful in achieving the overall site objectives. The regulatory context is discussed further in section 4.

3.1 Site and scenarios

As introduced in section 1.2, mass flux and mass discharge can be helpful for site characterisation and remediation in a wide range of circumstances. Whilst from a technical perspective, mass flux concepts are likely to be suitable for most sites, they may or may not be cost-effective in a particular circumstance. When deciding if mass flux concepts are suitable for a site, there are four main considerations:

- the contaminant of concern
- whether regulatory compliance may be more easily achieved through concentration-based data alone
- the site conditions (access and geology) and budget, and
- the regulatory context.

The first three points are considered in more detail below, while the regulatory context is discussed in section 4.

3.1.1 Contaminants of concern

For mass flux to be calculated, the contaminant of concern must be a dissolved constituent that migrates with the groundwater flow. Examples of these include:

- metals
- chlorinated organics;
- petroleum hydrocarbons;
- pesticides and herbicides
- nutrients, and
- other inorganic ions.

As such, the use of mass flux may not be appropriate for certain contaminants of concern with very low solubilities such as polychlorinated biphenyls.

Similarly, it is important to consider the likely distribution of the contaminant mass between phases: dissolved in groundwater, sorbed onto solids, and/or as an immiscible liquid. Mass flux estimates may be inaccurate if a significant fraction of the contaminant mass is sorbed onto suspended solids (colloids) in the groundwater samples (resulting in an over-estimate of the measurement of the dissolved phase concentration). This can be mitigated by suitable field techniques such as adequate groundwater well development, low-flow sampling techniques, passive sampling, and/or filtering turbid samples.

Specifically regarding the management of sites with non-aqueous phase liquid (NAPL) contamination, it should be noted that the mass flux concepts presented within this guideline are discussed with respect to the dissolved phase. The presence of free product or residual NAPL product should be investigated and managed accordingly. In addition, some Australian jurisdictions mandate the removal of light NAPL free product regardless of the potential risk to receptors. As such, while mass flux and mass discharge estimates can be useful in managing sites with NAPL contamination with regard to the associated dissolved phase risk, these measures may not reflect the risk posed by the presence of NAPL.

3.1.2 Achieving regulatory compliance

Flux information is typically most appropriate for sites where it is difficult to achieve compliance with groundwater concentration criteria alone.

As the estimation of mass flux and mass discharge is more complex than reliance on concentration measurements alone, it may be more costly to obtain these parameters. Therefore at sites where closure can be obtained by meeting groundwater concentration criteria alone, it is unlikely to be necessary to conduct a flux-based site assessment. As such, at simple sites with small plumes, obtaining mass flux data is generally not advantageous.

Similarly, where the remedial end-point is restoration of beneficial uses throughout the aquifer, flux measurements may be of limited value for use as remedial criteria, as such an approach may require concentrations at all locations to remain below the clean-up criteria required from a regulatory perspective. If the measured concentrations are considered to pose unacceptable risks to site receptors, site closure may in some instances require the risks to be managed and/or mitigated, regardless of the estimated mass flux and mass discharge. A discussion on the use of mass flux and mass discharge for a more risk-based approach is provided in section 3.7.

Therefore, it is generally envisioned that mass flux and mass discharge estimates may be used to complement concentration-based assessments, rather than to replace them.

3.1.3 Site access and budget

Obtaining mass flux and mass discharge information can require high resolution data to be collected across transects to account for heterogeneities in the subsurface. Applying these concepts at sites with logistical or technical restrictions, for example sites with limited access to install the required number of monitoring wells, may not be appropriate. Moreover, it may not be cost-effective or practical to obtain accurate estimates of mass flux or mass discharge in highly heterogeneous sites where groundwater velocities vary by many orders of magnitude across small distances.

(Although it is noted that this limitation may also apply to concentration-based data under those field conditions). Exceptions to this are discussed in Appendix A (A.1 and A.3), as certain methodologies such as integral pumping tests remain appropriate for highly heterogeneous sites. It should be noted, however, that the cost-benefit decision in these cases is site and proponent specific, and mass flux techniques may provide additional value for the investment over the long term.

3.2 Using mass flux to enhance the conceptual site model (CSM)

Characterising a site and developing a sound CSM of groundwater contamination is an essential aspect of contamination assessment and management. Whilst mass flux and mass discharge are not explicitly referred to in current Australian (state or territory) regulatory guidance in regards to the development of a CSM, it is recognised that these parameters can provide a more complete measure of the potential impact to a receptor posed by a contaminant plume (CRC CARE 2014).

Understanding the risks that plumes of contamination pose are important aspects of Australian regulatory decision making; whether the plumes are migrating off site, whether they are increasing or decreasing in extent, as well as contaminant concentrations. Assessing mass flux and mass discharge early in a field program, particularly at more complex sites, may have cost benefits as the site can be better characterised at an earlier stage and the data can be used to inform further investigations and remediation at the site.

Mass flux data can be used to track changes in source mass and plume evolution over time. It is noted that groundwater flow direction and contamination concentration are dynamic, and hence the contaminant mass flux fluctuates with changes in groundwater flow (Rein *et al* 2009). Some examples of the numerous applications of mass flux and/or mass discharge to enhance the CSM are discussed in table 1.

Important note about worked examples and case studies used in this guidance:
The purpose of the worked examples and case studies is to demonstrate the practical application of mass flux and mass discharge. It is expected that when a flux approach is applied it will be used as part of a multiple lines of evidence approach, and that there will be a comprehensive understanding of the level of risks in the environment. Worked examples are mostly selected from literature. Case studies are more detailed (in Appendix C). Remediation action plans and site management plans should consider environmental values or beneficial uses based on jurisdictional requirements, and be developed in consultation with regulators.

Table 1 Practical uses of mass flux and mass discharge to enhance the CSM.

Enhance the CSM	Practical application of mass flux and mass discharge in this context
Estimate source mass and source strength (see Case study 1, and worked example 2 and 3)	Mass discharge along the length of a plume can be used to estimate the historical mass discharge from the source and thus the source strength function. This can be important for interpreting other processes such as back-diffusion from areas of lower K. Mass discharge can be applied to establish the baseline source strength at a given point in time. The mass discharge across a transect on the down-gradient edge of the source zone can be measured and used to compare post-remedial mass discharge. Mass flux can be used to identify source zone hot spots and evaluate locations where the source is contributing the highest mass to the plume. Mass discharge is a powerful tool in estimating the source strength function, defined as the change in mass discharge over time with the natural dissolution of the source. It can be quantified as the change over time of the mass discharge at the down-gradient edge of the source zone, known as the source mass discharge (Annable *et al* 2014, Wang *et al* 2014). The source strength function can be estimated using historical and current site data and simplified models, such as exponential decay models or more complex models such as the power law model (Falta *et al* 2005; Annable 2010).
Evaluate trends in the source and plume over time (see worked example 4)	Mass flux and mass discharge estimates can be used to evaluate trends in the source and plume over time. Mass discharge generally decreases from the source zone over time. As mass flux represents the combined effects of contaminant transport, attenuation, and storage processes (including sorption in areas of lower K and diffusion to areas of a higher K) a loss of contaminant mass results in a lower mass flux. Therefore, at the distal end of the plume, mass discharge will naturally decline due to dilution and mass storage in areas of lower K. For a recent source, the drop in mass flux with distance from the source is generally much greater than a more mature source where the plume has advectively spread out over a larger area (ITRC 2010). Therefore, mass flux estimates are also a useful indicator of the age of a plume. Data from older plumes have indicated that as plumes age, groundwater contaminant reduction tends to approach an exponential decay model (Chen & Jawitz 2009). As mass discharge is the sum of the mass flux from each sub area within a transect, the determination of mass discharge at transects at different distances from the source zone can provide estimates of how the mass discharge has changed historically as the plume developed, or through mass loss mechanisms within the plume (CRC CARE 2014).
Evaluate attenuation rates (see worked example 4 and 6)	Mass discharge can be used to evaluate mass attenuation rates within specific areas of the plume. To do this, mass discharge is measured across multiple transects along a common flow path, and the difference is equal to the attenuation rate between the transects (assuming system equilibrium). Mass flux distribution of electron acceptors and donors across transects and comparison to contaminant mass flux distribution may assist in characterising biodegradation reactions responsible for attenuation processes.

Enhance the CSM	Practical application of mass flux and mass discharge in this context
	Mass discharge can be used to carry out mass balance assessments. As discussed in section 2.2.2, mass balance assessments involve the comparison of the source strength into a dissolved phase plume with plume attenuation rates. Plume attenuation rates can be estimated using models and/or historical concentration data, and should take into consideration 'losses' due to sorption, diffusion into areas of higher K and dispersion (ITRC 2010). These types of analyses could provide an additional line of evidence to support application of monitored natural attenuation strategies as noted in CRC CARE Technical Report 15 (Beck & Mann 2010).
Assess whether there is more than one source	Comparison of the source zone mass discharge to the estimated plume attenuation rate can assist in determining whether multiple sources may be contributing to a plume. If the plume attenuation rate exceeds the mass discharge from a known source zone, then there may be additional sources contributing to the plume.
Determine the mobility of the source (see worked example 2)	Mass flux can be used to determine whether the contaminant mass is primarily located within areas of high or low K within the aquifer.
Determine the likelihood of contamination migrating off-site (see case study 1 and worked example 6)	Mass discharge measured close to the source zone is a leading indicator of groundwater concentrations leaving the site, and is therefore useful in the assessment of risk to off-site receptors. Whilst concentrations at the site boundary are not necessarily representative of risks to the receptor due to the processes of attenuation, mass discharge estimates do consider attenuation and may provide a more accurate indicator of risk. The concepts of mass flux and mass discharge can be applied to demonstrate that contamination is unlikely to migrate off-site, if it can be shown that the rate of mass loss through processes such as natural attenuation is such that contaminant mass will reduce and will be contained within the site (CRC CARE 2014).

Worked example 1: Using mass flux to refine the CSM

Worked example 1: Using mass flux to refine the CSM

Mass flux estimates and natural attenuation rate constants were used to characterise a former gasworks site in Germany (Bockelmann *et al* 2001) with the following details:

- The geology was described as shallow Quaternary gravels with locally embedded sand, silt and loamy clay.
- Eight pumping wells were positioned along two transects 140 m and 280 m down-gradient of the source zone.
- BTEX and PAH mass discharges were obtained through the integral pumping test (IPT; see section 5.2, with further details on the methodology presented in Appendix A).
- Well positions, pumping rates and pumping times were optimised to allow the wells to capture the entire groundwater flow downstream of the source zone.
- Overall, PAH mass discharges of 32 g/day (nearest source) and 13 g/day were calculated for the two transects.

The authors made the following observations:

- PAH mass fluxes were found to be over an order of magnitude greater than BTEX mass fluxes.
- Acenaphthene displayed the highest individual contribution to the PAH mass discharge (31 g/day and 13 g/day, the former in the control plane nearest the source), with its mobility attributable to its relatively high water solubility.
- BTEX mass discharge was dominated by benzene, with mass discharges of 1.8 g/day and 0.094 g/day, with the former in the control plane nearest the source.
- First-order attenuation rate constants for the identified BTEX and PAH compounds were calculated based on the quantified changes in contaminant mass fluxes between the two transects.
- Supplementary evidence of microbial degradation was indicated by an increase in dissolved iron mass flux and a reduction of sulfate mass flux between the two transects.

It should be noted that mass flux and mass discharge estimates are only one tool in the development of a CSM, and should be used in conjunction with concentration data and other information gathered regarding a site.

3.3 Complement concentration based criteria with mass flux

Traditionally, decision making in Australian groundwater management is based on criteria that are defined in terms of contaminant concentrations. The ASC NEPM details concentration-based groundwater investigation levels (GILs) which can conservatively be utilised as screening criteria for groundwater (as described in schedule B1 of the ASC NEPM). The GILs have been developed on a risk basis to offer protection to potential receptors on the majority of sites (ANZECC 2000), as further described in section 4. They can be used to screen measured data and identify situations where a potentially unacceptable risk to a beneficial use may exist and therefore may be

followed by further investigation. These GILs are not intended for use as remedial criteria.

If exceedances are identified, further risk assessment can be undertaken (as detailed in Schedule B6 of the ASC NEPM) utilising the GILs as acceptable (concentration-based) criteria at identified or potential points of exposure (considering current and realistic future uses on the site or surrounding areas). These GILs are either compared to concentrations measured at these points of exposure, or through back-calculating (e.g. based on groundwater modelling) to determine groundwater concentrations at a control plane which would result in the GILs at the receptor. It is noted that where a site is intended for a generic, unrestricted use, and/or where a receptor is co-located with the source, it may be difficult to justify the development of site-specific remedial targets which are less stringent than the GILs.

Following this standard framework, concentration-based criteria are commonly used in regulatory decision making for the management of groundwater contamination. While the concentration of a contaminant is a key indicator of the potential for impact of a contaminant on human health and the environment, and is often the trigger for further investigation, it provides a one-dimensional site characterisation and risk profiling tool. In some situations, although a concentration compliance criterion or a clean-up target has not been met, a significant decrease in mass flux and discharge in groundwater may have occurred (CRC CARE 2014), such that the risk may be low and acceptable. Therefore the use of flux-based metrics may provide a complementary means of demonstrating the effectiveness of remediation or management of a site with a view to site closure.

Two of the key ways in which mass flux and mass discharge metrics can be used to complement concentration criteria are discussed further in Table 2.

Table 2: Practical uses of mass flux and mass discharge to complement concentration based criteria

Complement concentration criteria	Practical application of mass flux and mass discharge in this context
Provide estimate of mass of contaminant entering a receiving water body or pumping well (see case study 1, and worked example 6 and 7)	Mass flux concepts can be used to estimate the concentration at the receptor. For example, consideration of the mass discharge rate and mixing rates might show that based on the surface water flow or pumping rate, the resulting contaminant concentration will not exceed acceptable water quality criteria at the receptor. These scenarios are further detailed in sections 6.1 and 6.2. Conversely, if the rate of discharge is large or increasing, then the resulting concentrations may exceed acceptable water quality criteria indicating that remediation is required. This example is illustrative of how augmenting concentration data with mass flux measurements can be useful in further understanding risk to a receptor. It is noted that mixing or dilution on their own are not considered to be acceptable remedial strategies.
Derive remedial criteria (see case study 1, ad worked example 6)	Mass flux and mass discharge metrics can be used to assess performance during remedial works and (where the regulator approves) can be used as additional remedial endpoints. Application of strict concentration-based criteria is a stringent requirement, given that the distribution of contamination is usually variable and non-uniform, with small pockets of higher

Complement concentration criteria	Practical application of mass flux and mass discharge in this context
	concentrations quite often being the norm. Experience and research shows that concentration criteria can rarely be achieved everywhere at a site or in a groundwater plume within an acceptable timeframe or expenditure of resources. It is possible that the application of mass flux and mass discharge considerations could be helpful in such situations, as mass flux and mass discharge can assist in understanding risk and the implications for long term stewardship of sites, and therefore whether remediation is required.

It should be noted that where localised concentrations exist in exceedance of concentration-based remedial criteria, it remains necessary to determine that these impacts do not pose unacceptable risks to receptors, or that these risks can be adequately mitigated/managed.

An example where mass discharge was used to complement concentration criteria at a brominated DNAPL site in Western Australia is detailed in case study 1, presented in Appendix C.

3.4 Using mass flux to assist with remedy selection

Predicting the effectiveness of a remedial method and the time that will be taken to protect and/or restore the beneficial uses of groundwater are essential considerations in selecting one remediation method over another. These factors may assist regulatory decision-making on whether to endorse a proposed remediation approach or not.

Table 3 provides detail on the situations where mass flux and/or mass discharge estimates may be useful in remedy selection.

Table 3 Applications of mass flux in remedy selection, including examples.

Use in remedy selection	Practical application of mass flux and mass discharge in this context
Determine the ability of remedial reagents to reach subsurface impacts	In situ chemical oxidation/reduction relies on contamination or reagents being able to migrate rapidly through an aquifer with high mass flux, and may be relatively ineffective where the contamination is stored in areas of low K with low mass flux.
	If this method is deployed in aquifers where contamination is predominantly stored in low K areas, this can result in much of the contamination remaining unrecovered or untreated.
	Therefore a sound understanding of the mass flux across a plume can be helpful in predicting the success of this method in a particular aquifer, and therefore whether the method should be applied or not.

Use in remedy selection	Practical application of mass flux and mass discharge in this context
Evaluate whether secondary sources exist and chose remedial method accordingly	In situ bioremediation may be useful where significant back-diffusion is measured or anticipated. For example, the enhanced reductive dehalogenation of chlorinated solvents may be effective since conditions established to promote biodegradation can be maintained for years, treating chlorinated solvents as they back-diffuse from low to high *K* zones. Therefore, the contaminant mass distribution between high and low conductivity zones should be considered when deciding if *in situ* bioremediation is an appropriate remedial technique.
Establish appropriate contamination reduction targets, allowing the selection of appropriate remedial methods to achieve targets (see case study 2)	Rather than focus entirely on achieving a contaminant concentration as a remedial goal, baseline mass flux and mass discharge estimates can be used to establish appropriate and achievable contamination reduction targets (e.g. 90%, 99%, 99.9%). These reduction targets can then be used to screen for appropriate remedial methods that may achieve this, either alone or in combination with other remedial methods (ITRC 2010). This is particularly useful in situations where entire removal of the contaminant may not be either technically or economically feasible.
Assist in characterising the site, allowing the remedial method to be tailored accordingly (see case study 1, and worked example 2 and 3)	Mass flux measurements can be used to understand the distribution, seasonality and long-term stability of attenuation rates within the plume. This then allows the targeting of areas of the plume that may require additional treatment to achieve the remedial objectives, or those areas that will provide the greatest bang for buck. Understanding the hydrogeology and mass flux distribution (i.e. changes in mass flux across the plume) can allow for a more targeted, effective and efficient remedy.
Prioritise sites for remediation (see worked example 7)	As mass discharge provides a quantitative estimate of source strength and potential impacts to down-gradient receptors, it can be useful metric with which to compare the risks posed by different sites. This could be a useful tool for regulatory agencies and responsible parties to prioritise remediation resources and time frames, and is increasingly applied by industry (ITRC 2010). Large industrial companies have also been noted to voluntarily measure mass discharge down-gradient of their impacted sites in order to monitor their environmental liabilities. These concepts may be used to prioritise sites for remediation within a portfolio of sites. For example, if three sites each have similar concentrations of contamination, yet one site has far greater mass flux due to higher groundwater flux, this site may represent a greater risk to receptors, and therefore be allocated more resources, or resources sooner. Without the aid of mass flux data, this decision may be made for less risk-based reasons.

Use in remedy selection	Practical application of mass flux and mass discharge in this context
Help to determine if remedial actions should focus upon the source or the plume (see case study 1 and worked example 2)	Mass flux and mass discharge can be used to estimate the fraction of the initial contaminant mass that has been removed from the source zone over time, and hence where to focus remedial efforts. Where only a small percentage of source mass has migrated into the contaminant plume or attenuated, the plume is considered young, and therefore the remedial approach should initially focus on the source zone. In contrast, an aged plume is one where the majority of the mass has been removed from the source zone. In this case, remedial efforts should focus on the groundwater plume (and areas of lower K within the plume that may be acting as secondary sources) rather on the depleted primary source zone (Annable 2010).

Worked example 2: Using mass flux to assist with remedy selection

Mass discharge estimates at an expanding dissolved TCE plume at a former manufacturing site in Australia assisted in selecting the most appropriate remedial approach (Basu *et al* 2009), with the following details:

- A source mass discharge of approximately 3 g/day was used to determine that the TCE source mass was small, approximately 10 kg.
- Data from passive flux meters (see Appendix A, A.3) additionally suggested that the TCE source mass was present in low permeability areas, making remediation through active source treatment less effective.
- A TCE mass discharge of 6 g/day at a transect across the plume located 175 m from the source suggested that biodegradation was minimal, which was anticipated given the aerobic geochemical conditions observed within the plume.

Based (in part) on this data, the plume was considered to be large and non-degrading whilst the source strength was small and declining. Therefore remediation of the source was considered unwarranted. Rather, it was recommended that remediation should comprise the containment of the large TCE plume (approximately 1.2 km long, 0.3 km wide and 17 m deep) or institutional controls, along with a long-term mass flux monitoring program.

3.5 Using mass flux to optimise remedial design

As mass flux and mass discharge estimates incorporate the transmissivity of the subsurface and (consequently) the mobility of the contaminant, they can be helpful in optimising remedial designs. Specific examples of the use of mass flux to optimise remedial design are included in Table 4, below.

Table 4 Applications of mass flux concepts in optimising remedial design, including examples.

Optimise remedial design	Practical application of mass flux and mass discharge in this context
Identify where the greatest mass is being discharged (see case study 2 and worked example 3)	Mass discharge estimates can be used to locate zones contributing the most (and the least) contaminant mass to a plume, and hence can provide valuable information for placement of pumping wells, injection points, and monitoring wells (ITRC 2004; 2008 & 2010), as well as where to target treatment for maximum benefit.. Identify where the greatest mass is being discharged, and therefore where treatment should be targeted for maximum benefit. For example, if it is found that mass flux is large in some localised zones, then treatment of these zones may be able to achieve an overall reduction in contamination down-gradient, such that treating all areas of the source zone is not required. This can result in significant cost and resource savings.
Estimate remediation timeframes	Mass flux estimates with approximation of source masses can be used to derive order-of-magnitude estimates of remediation timeframe (API 2003).
Design of permeable reactive barriers	Groundwater flux and mass flux are important design parameters in the design of permeable reactive barriers, which must provide sufficient reactive capacity and retention time to treat the incoming contaminant.
Selection of appropriate reagents	Mass flux can be used to assess the potential for back diffusion from secondary sources. Back diffusion can be addressed by selecting a longer-lasting carbon substrate within a treatment zone, to maintain conditions conducive to bioremediation as the contaminant back-diffuses from areas of low to high K.

In situations where performance monitoring indicates that the current remediation method is not effective, mass flux and mass discharge estimations can be used to evaluate alternative technologies. This is particularly relevant in the case where an active remedial technique is no longer effective because the contaminant mass has been reduced, and corresponding reductions in mass flux can be used to trigger a transition to an alternative remedial technology more suited to the new contaminant profile.

Worked example 3: Using mass flux to optimise remedial design

Mass flux estimates were used to locate and target the source areas that contributed most to a contaminant plume at a site in Washington state, USA, as well as to monitor remedial performance (Brooks *et al* 2008; Annable *et al* 2014), with the following details:

- The site was impacted by a TCE groundwater plume arising from three main source areas.
- The sources were delineated through cores, groundwater samples, historical site activities and drum removal.
- Electrical resistive heating was selected as the most appropriate remedial option.
- Four well transects were installed down-gradient of the treatment zones and data collected using passive flux meters (PFMs) segmented in vertical intervals of approximately 0.3 m to assess local source mass flux.

- The data along each transect were used to produce a flux distribution plot using the computer program Surfer®.
- The plots highlighted the variable nature of the TCE mass flux from the source, likely due to the presence of individual pools of DNAPL up-gradient of the transect.
- The team noted that TCE distributions were less localised in transects further from the source zones, as more time and travel distance allowed for greater mixing and dispersion within the groundwater.

The mass flux and mass discharge data indicated that a reduced remedial treatment zone could be applied by focusing on the areas of higher mass flux.

Additionally, site-wide integrated pumping tests (IPT) were carried out over the surficial aquifer to assess the overall mass discharge from the source into the plume system. This was then used for performance monitoring (section 3.6) and risk assessment (section 3.7) purposes.

The field methodologies used in estimating mass flux and discharge, PFMs and IPT, are introduced in section 5 with greater detail presented in Appendix A.

Mass fluxes at a source control plane have been observed to be relatively stable over time (discussed in section 3.6), and this has implications for remedial design, as the stability of mass fluxes indicate that high-flux zones within the source remain high throughout the dissolution process. Therefore targeted source treatment of the highest mass flux zones will be more effective in reduction of mass discharge than uniform treatment across the entire source control plane.

3.6 Using mass flux to assess remedial performance

In combination with concentration data, mass flux and mass discharge estimates can be used to assess the performance of a remediation method when in operation, and to monitor whether it is performing as designed. If the remedial performance is not meeting the expected milestones, then mass flux measurements can assist in understanding where contaminant reduction is less than expected, and where improvement can be directed (CRC CARE 2014).

The use of mass flux and/or mass discharge estimates to assess remedial performance and examples are detailed in Table 5.

Table 5 The use of mass flux and/or mass discharge estimates to assess remedial performance

Assess remedial performance	Practical application of mass flux and mass discharge in this context
Measure the extent to which contaminant mass is being removed from the system (see case study 1, and worked example 3 and 4)	Baseline mass flux and mass discharge can be compared to current estimates to evaluate the effectiveness of the treatment to date and the rate of contaminant mass removal. A change in mass flux or mass discharge from the source can be used to quantify source remediation performance, whilst changes in the mass flux or mass discharge from the dissolved-phase plume can be used to quantify the response of the plume to either source or plume remediation. This information can assist in determining if the treatment has been appropriately targeted and the hot-spots are being addressed, or whether the treatment needs to be redirected to achieve greater effectiveness (CRC CARE 2014). This is difficult to determine from concentration data alone, as mass discharge is a better indicator of the source mass which remains on the site than concentrations alone.
Assess the potential benefits of applying additional remediation methods	Often remedial techniques are better suited to either low or high K zones, but rarely to both. Therefore post-remediation mass discharge mapping can be useful in identify portions of the plume where contaminants are depleted in areas of higher K, but remain in areas of lower K. In these circumstances an alternative remedial technique may be required if further contaminant reductions are required to achieve site closure. Alternatively, mass flux measurements may indicate that treatment of higher K areas alone is sufficient to allow the remedial targets to be achieved as quickly as treatment of the entire impacted area (ITRC 2010).
Determine the efficiency of treatment reagents	Mass flux and mass discharge estimates may be useful in determining the efficiency of treatment reagents or the distribution of injected reagents within the aquifer. This may assist in the identification of locations not contributing to the overall treatment effort, allowing treatment to be discontinued at those locations and directed to other locations where it will be more effective (CRC CARE 2014).
Identify locations where treatment has affected subsurface hydrodynamics.	Mass flux can be a useful measure in identifying locations where treatments applied during remediation may have affected subsurface hydrodynamics through reducing the K distribution. If treatment causes clogging of the aquifer through precipitation of inorganic by-products, injection of oils, or biomass growth, then this may be able to be identified and quantified through mass flux measurement comparisons before and after remediation (ITRC 2010).
Determine the cause of any changes in contaminant concentrations	Measurement of specific characteristics of the aquifer such as groundwater flux (and hence mass flux) or targeted chemical analysis (e.g. of electron acceptors) can be used to distinguish whether changes in contaminant concentration can be attributed to treatment, natural degradation, partitioning into lower K areas or back-diffusion from areas of lower to higher K. This may assist in determining whether ongoing contaminant mass reduction can occur through natural means and active treatment can cease (CRC CARE 2014).

Assess remedial performance	Practical application of mass flux and mass discharge in this context
Estimate remediation time frame	The estimated remediation time frame can be extrapolated from mass discharge data, however longer-term performance data is required to reduce uncertainty (ITRC 2010). As discussed in section 2.2.3, back-diffusion from areas of low to high K may act as a secondary source of contamination at older sites, and should be taken into consideration when estimating remediation time frames.
Assess performance of monitored natural attenuation (MNA)	Mass flux measurements are commonly used to quantify natural attenuation rates, as discussed in section 3.1. In applying this approach, field measurement and the calculation of mass flux estimates would need to be repeated some time apart (or through spatial separation) to confirm that the differences in mass flux result from attenuation, and not movement of the contaminant plume. This data should also be supported by various chemical measures of MNA.

The relative spatial distribution of the areas of high and low mass flux at a source control plane is thought to be relatively stable over time even as the source strength may decline naturally or due to remedial efforts (Basu *et al* 2006). This is useful for remedial performance monitoring, as it suggests that groundwater flux can be measured once for a particular transect and then assumed to remain constant, allowing the changes in mass flux through time to be estimated simply by measuring concentrations. It should be noted, however, that in regions known to be highly seasonal, groundwater flux measurements may be required throughout the year to account for that seasonality. Moreover, remedial activities that lead to changes in K in areas of a site could lead to changes in the relative spatial distribution of mass flux and thus a post-remedial groundwater flux measurement may be required.

While mass flux estimates can be particularly useful in assessing remediation performance and plume changes over time, there are two key processes that can confound the interpretation of mass flux data:

- Storage processes (partitioning into areas of lower K) must be adequately considered and not be misinterpreted as degradation, and
- The ongoing contribution of secondary source back-diffusion into areas of higher K must be considered, and not be misinterpreted as remedial underperformance.

Worked example 4: Using mass flux to assess remedial performance

Mass flux was incorporated in the Site Management Plan as a metric of remediation performance at a brominated DNAPL impacted site in Perth (Johnston *et al* 2014), with the following details:

- The link between source mass removal and mass fluxes in groundwater were assessed to see how closely the two corresponded.
- The mass flux and mass discharge associated with the brominated DNAPL plume were measured in high resolution immediately down-gradient of the source, both before and after partial source removal.
- The study found that the reduction of source mass at the site corresponded to a reduction in the mass discharge estimated for the plume. The mass discharge of

> brominated DNAPL from the source was additionally used to model attenuation in the aquifer.

Further details on the application of mass flux concepts at this site have been presented in the case study in Appendix C.

Brusseau *et al* (2007) used mass flux estimates to monitor remedial performance at a TCE pump-and-treat system, with the following details:

- Partitioning inter-well tracer testing was used to measure source mass.
- The test indicated that a 50% reduction in source mass had occurred over the 19 years the system had been operational.
- This coincided with a greater than 90% reduction in source mass flux.

Mass flux therefore provided useful information to assess remedial performance beyond that which would have been provided by concentration data alone.

3.7 Using flux to demonstrate risk reduction

Where the consideration of the total contaminant mass reaching a receptor is used as an indicator of the risk posed by groundwater contamination, then the use of mass flux and mass discharge estimates can provide a more comprehensive estimate of the risk than concentrations alone (ITRC 2010). In many cases, point concentrations alone do not provide sufficient information to calculate down-gradient impacts, and mass flux and mass discharge can provide a more complete measure of the potential impact to a receptor posed by a contaminant plume.

For example, as shown in figure 4 in section 2.2.1, whilst two plumes may have the same contaminant concentrations, one may be moving faster and discharging greater contaminant mass over time, and therefore pose a greater risk to potential down-gradient receptors. Moreover, attenuation rates will affect the duration over which the plume is sustained, thereby impacting potential exposure time frames (ITRC 2010).

Additionally, concentration may not account for site characteristics which may significantly impact risks to down-gradient receptors. The mass discharge takes into account the size of the contamination source and/or plume in addition to the concentration, as depicted in figure 7, where the use of concentration only would not differentiate between the two cases. Moreover, the pumping rate of the down-gradient extraction well can be accounted for during mass discharge estimates (as demonstrated in section 6.1 and Appendix A), and would likely be a key factor in the assessment of risks to potential receptors exposed to contaminated groundwater.

Case A: Large Release
High Max. Conc. and High Md
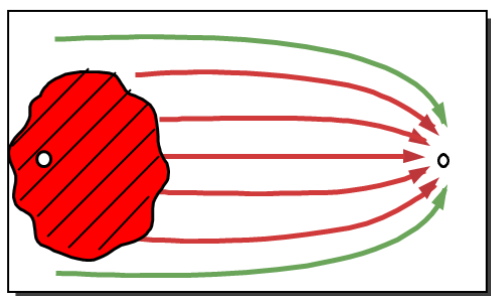
Case B: Small Release
High Max. Conc. and Low Md
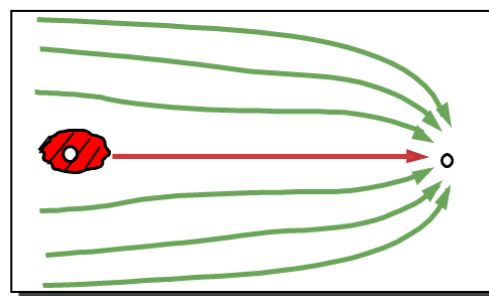
Figure 7 Whilst the concentrations reported at the wells within the source area are the same, the greater source mass in Case A results in a greater mass discharge at the receptor. The relatively small source mass in Case B results in a decreased mass discharge at the receptor. This illustrates the impact of the source mass upon mass discharge, which is not accounted for using concentrations alone.

Mass discharge estimates are particularly useful when contaminant discharge from a plume mixes with non-impacted water at or before the exposure point, such as in the case of supply wells or surface water bodies. Whilst dilution or mixing is not considered to be an appropriate remedial strategy, in these situations estimates of mass discharge to the mixing zone are more useful for risk assessment than the contaminant concentration alone (ITRC 2010).

Worked example 5: Using mass flux estimates to assess risk

Rivett *et al* (2014) used mass flux to assess the architecture and persistence of a 20 to 45 year old DNPL source zone, and hence the risks associated with this source, with the following details:

- The NAPL source zone was in a heterogeneous sand/gravel aquifer. Mass flux was typically found to be dominated by mass transport through more permeable zones.
- In some areas, despite high contaminant concentrations, the associated mass fluxes were low due to the low K in the area.
- The dissolved-phase mass discharge from the source zone across the monitored 4 m by 4 m cross-section of aquifer amounted to 400 kilograms (kg) per annum (about 100 kg of TCE and 300 kg of total ethenes). This was greater than anticipated given the age of the DNAPL source zone and that it was no longer dominated by ganglia.
- This illustrated that the mass discharge from a layer or pool dominated source zone perhaps remained significant, with significant associated risk.

The presence of localised DNAPL additionally led to significant uncertainties in total source zone mass estimates and endorsed the need for high resolution approaches when characterising the site.

3.8 Evaluating compliance or long term monitoring

Mass flux and mass discharge information can be used for regulatory compliance monitoring to supplement concentration-based data. For example, whilst concentration

data may identify an exceedance of the assessment criteria at the compliance point, mass flux data may indicate that there is minimal flow or discharge occurring. On the other hand, low concentration data may be accompanied by elevated mass discharge due to the more rapid flow of groundwater. Compliance metrics in both situations could potentially be based on the maintenance or reduction to a low or negligible mass flux to prevent impacts to down-gradient receptors (ITRC 2010), rather than based solely on concentration data.

Mass flux and mass discharge estimates can be used for regulatory compliance monitoring to augment concentration data. For example, if the remedial goal includes a percentage reduction in contaminant mass, then mass discharge estimates using monitoring wells on the down-gradient boundary of an active treatment zone could be used to identify when the remedial goal has been achieved. When this goal has been achieved the groundwater remedial program can be ceased and (depending on concentrations and regulations) natural attenuation may be relied upon for any residual impacts (ITRC 2010). It is noted that this approach requires engagement of and support from the regulator, and some regulators may not support natural attenuation explicitly as an endpoint of groundwater remediation. Engagement with the regulator is discussed further in section 4.

In some situations, the contaminant concentrations in groundwater may exceed the criteria for the protection of beneficial uses, but the mass discharge and extent of contamination may not be considered to materially affect the use. This situation may form the basis for accepting that remediation may not be required or to help establish appropriate objectives for remediation (CRC CARE 2014). Therefore, an exceedance of a concentration criterion may be considered acceptable if it is localised to a small area that is not material to the land use and does not pose an unacceptable risk to the environment. Situations where this concept may be applied within the Australian context are discussed (along with worked examples) in section 6.

4. Flux within a regulatory context

As illustrated in figure 1, once a practitioner has determined that mass flux *may* be useful in achieving the objectives for the site, attention should be focused on whether those methods *can* be used within the applicable regulatory context.

Basing decision making on whether contamination will or will not materially affect the receptor, rather than focusing on concentration-based criteria, may result in contamination that may be tolerated where the mass flux is small in the context of groundwater use. The acceptability of such an approach is likely to be highly dependent on specific policy requirements for groundwater protection in the local jurisdiction, the demonstration of a robust approach to obtaining and using mass flux and mass discharge data, and agreement from the regulator and other stakeholders regarding the acceptability of such an approach.

Relevant jurisdictional policies and guidelines make very limited (if any) direct reference to the use of flux measurements in managing contaminated groundwater. However, the absence of reference to these techniques does not necessarily indicate that their use would not be acceptable to regulators. Most relevant jurisdictional policies make direct reference to risk-based decision making paradigms, and mass flux methods can support a risk-based approach, but this needs to be demonstrated clearly. For example, the data that are used to demonstrate a risk-based approach should be well-presented and robust, and produced following consultation with the regulator.

As a general rule, regulators should be engaged early in the process to discuss mass flux estimates as a tool for the site, and the proposed approaches. This includes the discussion of any data requirements prior to the implementation of the approach.

It is emphasised that the decision to incorporate flux measurements to support decision making at a site should be undertaken in accordance with jurisdictional guidance and policy. These policies vary, and reference should be made to the relevant policy for the jurisdiction in which the site is located.

This guideline provides a general overview of the key current Australian guidance documents used in the assessment and remediation of groundwater as they relate to the incorporation of mass flux concepts. It is intended to provide the reader with tools to evaluate relevant regulations and guidelines, and to present a logical rationale for the utilisation of flux.

4.1 The National Environment Protection (Assessment of Site Contamination) Measure

The ASC NEPM is expressly focussed on contaminated sites assessment (rather than remediation), but does contain extensive guidance on the risk assessment process, which is linked to the use of mass flux data.

The methods described in the ASC NEPM for assessing risk associated with groundwater impacts primarily focus on defining whether concentrations exceed a limit. There is acknowledgement that it is the overall exposure concentration which determines risk, and the ASC NEPM includes discussion of statistical approaches to

address localised contamination above screening levels. While there is no express discussion of the use of flux measurements to determine remedial end-points, the use of such measurements would be in general accordance with the ASC NEPM approach if it can be demonstrated that the levels correspond to low and acceptable risk as defined within the ASC NEPM. A number of aspects of the guidance presented in Schedules B1, B4 and B6 are pertinent to the use of flux measurements, as summarised below.

Concentration based GILs are presented in Schedule B1 of the ASC NEPM. These GILs are adopted from the National Water Quality Management Strategy (NWQMS) documents for drinking water and the protection of surface water ecosystems described further in section 4.2 (ANZECC 2000; ADWG 2011). Even though they represent the acceptable concentrations at the receptor (e.g. in abstracted water or at a surface water feature), they are intended for use as screening criteria, to be compared with measured groundwater concentrations. As such, screening groundwater concentrations against these criteria may be a conservative assessment (depending on site-specific considerations), and as an extension to that, the ASC NEPM emphasises that these criteria are not intended for use as remediation criteria (clean-up objectives) for groundwater.

A framework for site-specific human health risk assessment (not restricted to groundwater) is presented in schedule B4 of the ASC NEPM. The ASC NEPM framework focuses on the use of exposure point concentrations as an input to assess the risk to a given human health receptor. In this way, there is a focus on the use of groundwater concentrations for the assessment of risk, and the use of mass flux measurements is not specifically referenced in the ASC NEPM. However, as noted in this document, where human health receptors are located away from the source zone, mass flux and mass discharge measurements may provide useful data for predicting exposure concentrations at the receptor (and therefore for estimating the level of risk).

The framework for site-specific groundwater assessment is presented in schedule B6, advocating a tiered approach:

- Tier 1: groundwater concentrations are compared directly to the GILs (as described above for schedule B1).
- Tier 2: groundwater concentrations at the receptor (e.g. in abstracted water or at a surface water feature) should not exceed the GILs. Based on this principle, the level of risk can be estimated by predicting the concentrations at the receptor (e.g. by using a fate and transport model), and comparing these estimated concentrations to the GILs. Remedial groundwater targets can be similarly back-calculated as the concentrations in groundwater which will result in the GILs at the receptor. The use of flux measurements is not specifically referenced in this Schedule, but an understanding of mass flux is highly relevant to predicting the level of impact at an off-site receptor, and therefore the level of risk.
- Tier 3: more detailed site-specific assessment is undertaken, focusing on the receptors specific to the site. For example, ecological assessments could include a receptor survey and direct toxicity assessment. As discussed in section 4.2.1, ANZECC (2000) provides examples of where flux-based criteria could be utilised as remedial targets for specific contaminants and receptors.

4.2 National Water Quality Management Strategy

The NWQMS is the primary national framework for water quality management in Australia. Included in the NWQMS is a framework for groundwater quality protection and several documents detailing general water quality guideline values which may be utilised to help achieve this aim. These documents include (but are not limited to):

- *Guidelines for Groundwater Protection in Australia* 2013 (GGPA 2013)
- *Australian Drinking Water Guidelines* (ADWG 2011) which details acceptable concentrations of a range of potential contaminants in drinking water, and
- *Australian and New Zealand Guidelines for Fresh and Marine Water* Quality (ANZECC 2000), which includes guideline values for the protection of human health.

Each of these documents, as they relate to the use of mass flux and mass discharge information, are discussed further below.

4.2.1 Australian and New Zealand Guidelines for Fresh and Marine Water Quality 2000

The NWQMS document most pertinent to the discussion of the use of flux measurements is ANZECC (2000). The water quality guidelines and water quality objectives for the protection of freshwater and marine ecosystems presented in ANZECC 2000 are generally numerical concentration limits. These criteria apply at the receptor (e.g. within freshwater and marine surface waters), and flux measurements may be relevant to estimating concentrations at the receptor, through the use of fate and transport modelling, or by considering the effects of mixing (for example as described in sections 6.1 and 6.2 of this guideline).

Furthermore, while ANZECC 2000 focuses on numerical concentration limits, it expressly states that numerical concentrations are not the only, or necessarily the best, approach to determine whether environmental values are protected:

> "The philosophical approach for using (ANZECC 2000) is this: protect environmental values by meeting management goals that focus on concerns or potential problems, e.g. toxicity. This is in contrast to previous approaches which more often focused on simple management of individual water quality parameters, e.g. toxicant concentration, to meet respective water quality guidelines or objectives. First, identify the water quality concern…and establish and understand the environmental processes that most influence or affect the particular concern. Then select the most appropriate water quality indicators to be measured, and identify the relevant guidelines."

In this context, ANZECC 2000 includes discussion of the use of load-based criteria (rather than concentration-based criteria) for nutrients and sediments as preferred criteria for these parameters:

> "Traditionally, water quality guidelines have been expressed in terms of the concentration of the stressor that should not be exceeded if problems are to be avoided (ANZECC 1992). Such concentration-based guidelines are based primarily on the prevention of toxic effects. In other situations, guidelines are better expressed in terms of the flux or loading (i.e. mass per

unit time), rather than concentration. While algal growth rate (or productivity) is related to the concentration of key nutrients in the water column, the biomass is more controlled by the total mass of these nutrients available to the growing algae…Load-based guidelines are applicable also for assessing the effects of sedimentation of suspended particulate matter in smothering benthic organisms. Both the rate of sedimentation and the critical depth of the deposited material are load-based."

The use of load-based criteria is also described in volume 1, section 3.3.2.8 of ANZECC 2000, and volume 2 details several case studies describing the development and use of load based criteria in Australia, including:

- **Case study 4** (presented in volume 2, section 8.3.2.1): describes the establishment of sustainable nutrient loads for standing waterbodies across the Murray-Darling basin. Phosphorus loading was identified as the key stressor for increasing the probability of algal blooms. Trigger values (expressed as sustainable phosphorus loads, or mass discharge) were developed for each of the critical water bodies throughout the basin based on a management target for algal bloom frequency, and site-specific observed relationships between phosphorus, chlorophyll a concentrations, and algal bloom frequency.

- **Case study 5** (presented in volume 2, section 8.3.2.1): describes the establishment of a process for defining sustainable particulate loads for rivers across the Australian Capital Territory, in which the target is to avoid adverse effects on benthic macro-invertebrates due to sedimentation. A sedimentation rate of <2 millimetres/year was identified as a management target. Based on this target and site specific data for a specific river reach, modelling can be undertaken to estimate a sustainable sediment load, or mass discharge, for the specific river reach.

The discussion of non-concentration based criteria within ANZECC 2000 supports the utilisation of flux-based criteria for groundwater management, where it can be demonstrated that such criteria are appropriate and relevant to protect environmental values.

4.2.2 Guidelines for Groundwater Protection in Australia, 2013

Guidelines for groundwater protection in Australia (ARMCANZ & ANZECC 1995) were initially published in 1995 to provide a framework for jurisdictions to develop groundwater protection policies (discussed in more detail in section 4.3 below). This document was superseded in 2013 by GGPA 2013. These updated guidelines specify that they:

"should primarily be used by government agencies developing legislation and policies regarding groundwater management and developing groundwater quality protection plans"

Although it is noted that few jurisdictions have modified their policies since the release of this updated guideline.

To this end, GGPA 2013 discusses potential beneficial uses of groundwater which should be protected. These include uses for which groundwater may be extracted or otherwise utilised, and a requirement to protect and maintain ecosystems (including subterranean ecosystems within aquifers themselves, such as stygofauna).

GGPA 2013 references other documents within the NWQMS in which numerical, concentration-based criteria protective of these beneficial uses have been developed (e.g. ADWG 2011 and ANZECC 2000). There is no specific mention of the use of flux concepts or measurements within GGPA 2013.

It should be noted that the protection of all potential beneficial uses (e.g. maintaining groundwater quality such that an abstraction bore of unknown specifications could be placed at any location) will often require concentrations to remain below criteria throughout the aquifer, and in this context flux measurements may be of limited value in demonstrating that beneficial uses are maintained at all locations.

However, GGPA 2013 emphasises that a risk-based approach should be adopted:

> "the key objective of adopting a risk-based approach is to guide investment in groundwater quality protection that is commensurate with the level of risk to the assigned Environmental Value for the groundwater system."

On this basis, an approach which takes into consideration the practical limits to groundwater remediation, and the likelihood that certain beneficial uses could be realised is in accordance with this principle. The use of flux measurements, as detailed in this guideline, may support such an approach.

4.2.3 Australian Drinking Water Guidelines, 2011

The *Australian Drinking Water Guidelines, 2011* (ADWG 2011) define acceptable concentrations of a range of potential contaminants (and other water quality parameters) in drinking water. The use of flux measurements is not directly referenced in ADWG 2011, however the criteria are defined to be applicable at the consumer's tap, after water treatment. Therefore flux measurements may be relevant to estimating concentrations in abstracted groundwater (for example, by predicting concentrations at a defined abstraction point and/or accounting for the extraction rate together with the mass flux, as described in section 6.1).

4.3 State and territory groundwater policies and guidance

Environment protection is generally managed by state and territory based environmental protection agencies or environment departments. The states and territories have developed groundwater protection policies to enforce groundwater protection in general accordance with the NWQMS (although as detailed above, the NWQMS framework for groundwater protection has been recently updated and these updates are yet to be carried through to state and territory policies). The state and territory policies vary, and reference should be made to the relevant policy for the relevant jurisdiction.

5. How to measure mass flux and mass discharge

This section provides an overview of the methods, tools and calculations which can be used to measure groundwater flux, mass flux and mass discharge. Further detail has been provided in Appendix A.

5.1 Data required

As outlined in section 2.1.2, mass flux can be calculated as follows:

- $J = q \times C = K \times i \times C$ where
  - J = mass flux (e.g. $mg/m^2/d$)
  - q = groundwater flux, volume/area/time (e.g. $m^3/m^2/d$ or m/d)
  - K = saturated hydraulic conductivity, distance/time (e.g. m/d)
  - i = hydraulic gradient, dimensionless (e.g. m/m), and
  - C = contaminant concentration, mass/volume (e.g. mg/m^3 or µg/L)

Therefore, to calculate the mass flux, the following parameters should be measured in the field or estimated through modelling:

- saturated hydraulic conductivity (K)
- hydraulic gradient of the groundwater (i)
- contaminant concentration in groundwater (C), and
- area over which the measurements or estimates are made (transect).

Whilst contaminant concentrations are typically obtained from groundwater sampling and laboratory analysis, obtaining K and the hydraulic gradient of the groundwater can be both more complicated technically and associated with increased uncertainty. In addition, the area over which the mass flux is measured or calculated is an important parameter. Potential uncertainties associated with estimating the area need to be recognised and accounted for. As there are a variety of methods that can be used to obtain these values, and a wide spectrum in the level of effort required to undertake these methods, the selection of a methodology should be goal specific.

Gathering data at sufficient density to be helpful has a financial and temporal cost. The use of resources in gathering such data should be weighed against other site constraints. In order to do this, in accordance with the ASC NEPM, the data quality objectives (DQO) process relating to the use of mass flux or a mass discharge estimate should be adopted such that an appropriate method with sufficient data density is used. For brevity the DQO process is not covered in this guideline, but can be found in the ASC NEPM schedule B2 Section 18 as well as in the US EPA DQO guidance (2000).

To guide the reader in the likely level of data density required in a variety of scenarios the ITRC working group has compiled the indicative relative data density needed for the use of mass flux data across a variety of applications, reproduced for convenience in Table 6. ITRC noted that data densities are only intended to provide a relative frame of reference and to make it clear that different objectives require different data, rather than to specifically recommend the quantity of data to be gathered (which will be site specific).

Table 6 Relative data density required for particular applications of mass flux data (Adapted from ITRC 2010).

Remedial applications	Mass flux data use	Relative data density needed
To determine whether active remediation is required	Estimate source strength	Low
	Estimate plume stability	High [a]
	Estimate balance between mobile contaminant mass and natural attenuation capacity of a plume	Medium to High [a]
Evaluate risk to groundwater receptor(s)	Estimate risks and exposures at various points of potential exposure	Low to Medium
Select appropriate remedial technology	Determine remedial action objectives	Low to High [b]
	Determine appropriate remedial technology(ies) for source and/or plume treatment	Low to High [b]
Develop or optimise remedial design	Evaluate heterogeneities in source architecture	High
	Estimate source strength reductions necessary to change to alternate methods (e.g. MNA)	Low
	Estimate distribution of contaminants relative to transmissive zones	High
Evaluate remedial performance	Compare actual mass removal to design	Low to High [b]
Evaluate compliance or long term monitoring	Determine mass discharge or flux limits to achieve remedial goals	Low to Medium

[a] If using multiple plume transects
[b] Depending on system design and treatment volume(s)

5.2 Data collection methods

At a conceptual level, there are two fundamentally different ways to collect mass flux data in the field. Point scale techniques include the use of conventional sampling methods or passive flux meters, and are characterised by taking measurements at discrete points in space and time. In contrast, integral methods include collecting data from wells that are screened to be representative of the groundwater in a particular region of the aquifer, and therefore delineate plumes based on average concentrations.

There are four general methods for estimating mass flux and mass discharge in the field, namely:

- Conventional sampling methods, which allow vertical delineation through the use of nested or clustered wells where individually installed monitoring wells within individual or adjacent boreholes are sampled using low-flow methods (point-scale).
- Transect methods, an established method to sample the width and depth of the plume at a control plane across the contaminant plume (point scale).

- Passive flux meters (PFMs), a more novel technology comprising permeable sock-like structures that are placed in well screens forming a transect to obtain simultaneous chemical mass and groundwater flux data (point scale).
- Well capture/pump test methods, including well capture, integral pump test (IPT), modified integral pump test (MIPT) and tandem circulating wells (TCW) (integral).

In addition to collecting new data, the historical data from existing monitoring well networks can be used to estimate mass flux and mass discharge through the use of transects based on isocontours. Potentiometric contour maps can be used to obtain hydraulic gradient and groundwater flux data, allowing the calculation of mass information from existing data.

Similarly, solute transport models, e.g. BIOSCREEN and REMChlor, can be used in isolation or in conjunction with the above methods to calculate mass flux and mass discharge associated with groundwater contamination.

If site constraints do not allow the transect to be perpendicular to the groundwater flow direction, trigonometry can be used to calculate the perpendicular component of the mass flux or mass discharge. However this technique should only be used when other options have been exhausted, as it can introduce further uncertainty.

In order to assist the reader in choosing the appropriate data collection method for their site, the principles behind these methods, their application to estimate mass flux, as well as their advantages, limitations, and inherent assumptions are discussed in further detail in Appendix A.

Additional field methods have recently been developed to assess sites with complex hydrogeologic settings, such as fractured and karst bedrock. These settings pose substantial technical challenges both for characterisation and remediation. Background information and appropriate methods to measure mass flux and mass discharge in these scenarios are presented in Appendix B. Combining mass flux measurements with existing data can greatly improve the CSM at these complex sites and improve the ability to manage risks associated with contaminated groundwater. One such advancement is the fractured rock passive fluxmeter (FRPFM).

5.3 Uncertainty

As with any field measurement (including concentration-based data), mass flux and mass discharge estimates carry elements of uncertainty associated with the methods used to derive them and the complexity of the site. As part of the data collection design, it is necessary to determine the acceptable level of uncertainty for the intended application of the mass flux and/or discharge information, and how this can be managed. It should be noted that expressing and adequately managing the level of uncertainty in the mass flux data can be a key factor in attaining regulatory approval.

The magnitude of uncertainty will be driven by:

- site-specific elements, such as contaminant properties and risks to potential receptors, and
- project-specific elements, such as the budget, phase of the project, and the experience assessors have with mass flux estimates.

Key factors that may contribute to the level of uncertainty associated with a mass flux and/or mass discharge estimate include:

- mass discharge estimates may span many orders of magnitude
- sampling density
- subsurface heterogeneity, and
- assumptions regarding groundwater flow direction.

More detailed discussion on the sources of uncertainty for each measurement technique, methods for estimating uncertainty, and suggested mitigation measures are presented in Appendix A.

6. Deriving mass flux and mass discharge metrics to manage groundwater contamination

In addition to the practical uses for mass flux in managing groundwater contamination presented in section 3, mass flux data can be utilised to develop site specific management (or clean-up) criteria. Regulatory input is essential to identifying whether mass flux and discharge approaches are likely to be acceptable.

Often management (or clean-up) criteria are based on agreed concentration criteria that are then used to calculate the mass discharge for a particular site under a particular scenario. Along with being helpful in achieving remediation and site closure objectives, mass discharge metrics can also aid in conducting hypothetical exposure scenario modelling, and in demonstrating the likely remedial works that would be required to achieve remediation or site closure.

This section provides information on the practical aspects of utilising mass flux data to develop site-specific management criteria, and includes the three specific scenarios of groundwater extracted for beneficial use, groundwater discharging into a surface water body, and special consideration for sensitive receptors. Each of these scenarios is illustrated with worked examples, and also within case study 1.

In order to assist the reader in successfully communicating their mass flux and mass discharge data to their stakeholders, this section also features information on the effective presentation of flux data.

6.1 Developing mass flux and mass discharge metrics for groundwater extracted for beneficial uses

If the use of groundwater involves pumping at a certain minimum extraction rate (e.g. potable, irrigation, stock, swimming pool make up, or industrial use), localised contamination that exceeds the use concentration-based criterion may be acceptable if the source mass discharge is such that the use criteria will not be exceeded when the extraction rate is taken into account. In this case the formula for the maximum acceptable discharge could be based on (CRC CARE 2014):

- Mass discharge < (concentration criterion for use) x (extraction rate)

The above formula is based on the framework developed by Einarson and Mackay (2001) for using mass discharge to assess risk and prioritise sites by considering the interaction of a contaminant plume with a down-gradient water supply well. Mass discharge can be used to estimate the resulting exposure concentration in water produced from the well, according to the following formula:

- $C_{sw} = M_d/Q_{sw}$ where
    - C_{sw} = contaminant concentration in water from the supply well, mass/volume (e.g. mg/L)
    - M_d = mass discharge of contaminant form the supply well, mass/time (e.g. mg/d), and
    - Q_{sw} = pumping rate of supply well, volume/time (e.g. L/d).

It is noted that the protection of all potential beneficial uses (e.g. maintaining groundwater quality such that an abstraction bore of unknown specifications could be placed at any location) will often strictly require numerical concentrations to remain below criteria throughout the aquifer, and in this context flux measurements may be of limited value when used in isolation. In addition, in some instances this rationale may be considered dilution. Whilst the remediation of a site should not rely on dilution through a water supply well, the above calculations can help to estimate potential risks to receptors. Therefore, as discussed in section 4 it is recommended that the regulator is consulted before adopting an approach which incorporates assumed extraction rates into a determination of the maximum acceptable flux.

Worked example 6: Applying mass discharge to assess risks on the use of groundwater

The mass flux and mass discharge of tetrabromoethane (TBA) and its daughter products were quantified down-gradient of the source zone using PFMs before and after remediation through source removal (Johnston *et al* 2014*)*, with the following details:

- State regulatory authorities and the auditor were actively engaged in the works, including early and continual communication and agreement on the preferred approach and mass flux criteria developed for the site.
- Mass discharge was used to model attenuation in the aquifer and to provide estimates of pumped concentrations from a hypothetical well on the site boundary.
- A source zone mass discharge target of 5 g/day was back-calculated from the irrigation water quality concentration criteria which were agreed to by the regulator.

The derivation of the source zone mass discharge target provided an additional way in which to assess the risk to down-gradient receptors, as this parameter is a key indicator of the concentrations of contaminants which may leave the site. The source zone mass discharge target became a supplementary means in which to monitor remediation process with the goal of ultimately demonstrating that the anticipated pumped concentrations would be below the mass discharge target and provide another line of evidence that remedial works may cease.

The applications of mass flux concepts at this site are further detailed in the case study (Appendix C).

6.2 Developing mass flux and mass discharge metrics when groundwater is discharging into a receiving surface water body

If groundwater is discharged to a receiving water body, contamination that exceeds the concentration-based criterion for protection of the receiving water body may be acceptable if the mass discharge is low (e.g. perhaps indistinguishable from that occurring naturally) and the water quality criterion will not be exceeded in the receiving water body or over a short reach or mixing zone within the receiving water body. Jurisdictions may define mixing zones differently and therefore it is useful early in the project to ensure that mixing zone is clearly understood and consistent with relevant jurisdictional requirements.

In this case the formula for maximum allowable mass discharge might be based on (CRC CARE 2014):

- Mass discharge < (concentration criterion for receiving water) x (flowrate of receiving water)

This concept may be able to be extended to determine the mass discharge given the flowrate through a mixing zone, as is often applied when licensing discharges to receiving water. The formulae for maximum allowable mass discharge could be adapted in terms of the receiving water flow through the area where mixing with the receiving water will take place (CRC CARE 2014):

- Mass discharge < (concentration criterion at boundary of mixing zone) x (flowrate through mixing zone)

Note that in assessing such situations, if the contaminants are such that they may bioaccumulate then consideration should also be given to possible effects of bioaccumulation in the ecosystem, as provided for in ANZECC 2000.

The effects of volatilisation in the stream reach may also be important to consider for the mass discharge from groundwater. This involves consideration of vapour flux, not included within this guideline. In a number of Australian jurisdictions there is a policy requirement that the compliance point for the protection of receiving water bodies be placed immediately up-gradient of the receiving water body. Where this is the case, it may not be possible to adopt an approach which incorporates consideration of mixing with the receiving water body without agreement from the regulator. However, mass flux may still be a useful concept for modelling the likely concentrations at the compliance point.

Worked example 7: Mass discharge of chlorinated solvents into a Danish river

Mass discharge of contaminants to surface water through groundwater has been addressed in the *European Water Framework Directive*
(European Commission 2010), which requires the evaluation of all types of contamination sources (e.g. point and diffuse) within a specific watershed in order to assess their impact on water quality and ecosystem health. Mass discharge has been used to prioritise sites under this framework.

Mass discharge was applied to assess the impact of a contaminant plume on a stream in Denmark. At the site, a groundwater plume consisting of chlorinated solvents was migrating east to ultimately intercept a stream boundary where the plume discharged to surface water. The CSM, depicted in the figure below, illustrates the mixing zone that is established between the zone of mass discharge along the stream bank and stream base to the point at which the stream is mixed and the concentration uniform. This basic model can serve as a template for many plume discharges to streams.
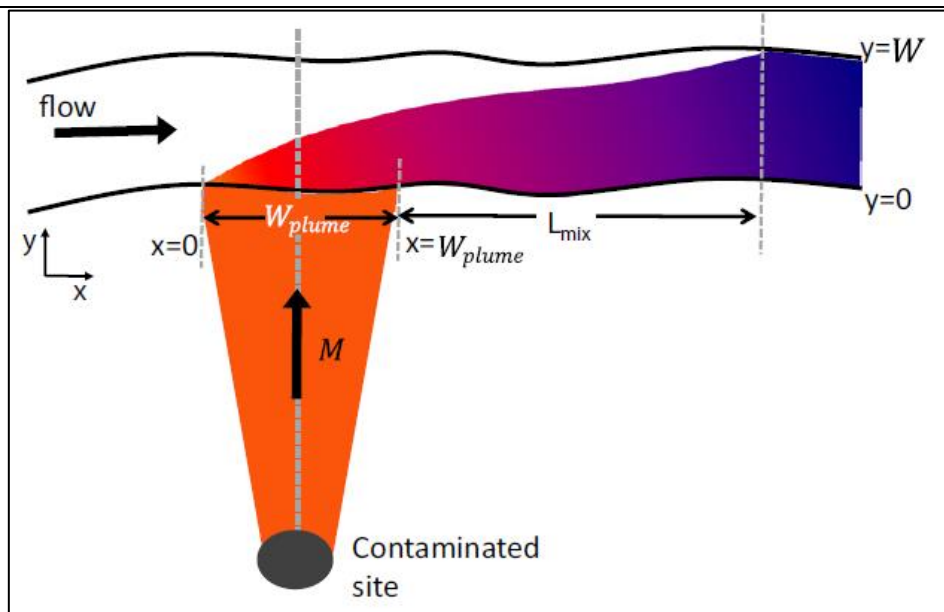
From Aisopou *et al* 2015

The mass discharge of TCE into the stream was measured by water samples collected along its length. Seepage meter samplers were placed in the hyporheic zone (the region beneath and alongside a stream bed, in which mixing of shallow groundwater and surface water occurs) to measure TCE concentrations in groundwater entering the stream. By measuring the stream flow during sampling events, the mass discharge along the stream was calculated according to the following formula:

- $M_D = Q\ C_{avg}$

In this calculation, 'M_D' is the mass discharge, 'Q' is the water flow in the stream, and 'C_{avg}' is the average concentration in the stream. The stream is assumed to be completely mixed, and therefore average concentrations were used. If the stream is not completely mixed, then multiple samples collected across the stream may be required or sampling further downstream where fully mixed conditions may be achieved.

Aisopou *et al* (2015) modelled different discharge configurations at the same stream in Denmark and other sites using COMSOL Multiphysics 4.3 (a 2D finite elements tool) to predict contaminant concentrations in the stream. The mixing process of pollutants, as well as transport, volatilisation and dilution processes, were modelled to look at mass discharge into the stream.

Discharge may be along the stream bed or along the stream's bank. Modelling using different scenarios indicated that this was found to be largely determined by the aquifer depth, hydrogeology, recharge rate, and source location. It was concluded that a source located within 0.5 km of the stream will typically discharge through its bank.

The models were compared with field data, and were found to provide useful information on the risk posed by different groundwater plumes to the stream, such as

peak concentrations, the mixing length and recommendations for location of the point of compliance.

The approach gained regulatory approval in Denmark. Aisopou *et al* (2015) noted that the approach is suitable for regulatory use and has recently been implemented in the risk assessment tool developed by the Danish EPA in response to the EU Water Framework Directive.

Worked example 8: Using mass discharge to estimate dilution factors in a tidal river and derive mass discharge metrics.

Note: Contaminated sites affecting surface water bodies and coasts are usually complex and it is critical to consider a range of environmental values applicable to the site, including all water quality objectives such as those which may apply to benthic organisms (See ANZECC 2000). Wilful discharge of contaminants into river systems and groundwater is prohibited by law. Dilution factors in this example are to show that flux concepts are useful for understanding mass discharges entering the river system. Where feasible, this can be complementary to current methods which roughly estimate resultant instream calculations using river and contaminated groundwater discharge parameters. Typically, protection of groundwater quality and benthic biota is required.

This worked example is a hypothetical scenario that has been adapted from a project in the United States. In the Australian regulatory context, it is generally envisioned that flux-based metrics may be used to complement concentration-based assessments and management, not to replace them. It is expected that when a flux approach is applied it will be used as part of a multiple lines of evidence approach, and that there will be a comprehensive understanding of the risk levels of any discharges to the environment. In addition, other factors relevant to regulatory decision-making may also be present (e.g. aesthetics of foreshores, waste management principles, prescribed levels of ecosystem protection).

In this example, two approaches are shown to understand the usefulness of the flux concept in close proximity to the tidal river i.e. average mass discharge versus fixed volume discharge. In Australia, water quality objectives are related to environmental values, including the level of ecosystem protection prescribed in jurisdictions rather than town planning context. This worked example is about dichloroethylene (DCE) contaminated groundwater within a brownfield precinct.

Dichloroethylene (DCE) and its daughter products were identified in both the shallow and deep aquifer at a site. Only the calculations for the shallow aquifer site is shown here. The plumes were moving north-easterly towards a tidal river, with data indicating the mass discharge of contaminants into the surface water.

Mass discharge into the river was evaluated using two methods:

- A groundwater flow model was used to estimate groundwater flux at the river edge and groundwater concentrations were then used to derive the mass flux, and
- Mass flux was based on concentrations in porewater and measured gradients.

For simplicity, we will assume that there was no existing background DCE levels in the river, nor DCE discharges from diffuse and point. In reality, it would be important to take account of the combined effect of all discharges (and any background levels) in order to understand the impact on the environment. We will also assume that the contaminants are diluted in the whole section of the adjacent river i.e. length x width x breadth. In reality, having a mixing zone across a whole stream would not be permitted and could be unlawful. Discharges typically fan out from shorelines in the direction of current movement (see worked example 7). The example has other simplifications that would need to be addressed in an informed submission to regulators. The example assumes the tide only goes out, there is no entrainment in incoming tides, the volume of tidal exchange is the whole river depth and rather than just the tidal prism (i.e. volume of water above the low tide level), the estuary never experiences stratification and that full mixing rapidly occurs.

As part of the risk assessment, the dilution of the contaminants of concern (COC) mixing with the receiving surface water (a tidal river) was calculated using two different approaches for the shallow aquifer to understand which method would have lower mass discharges.

1. **Average mass discharge method:** used to quantify dilution as DCE discharges from shallow groundwater into the river. Mass discharge for the COCs were identified using plume plots to quantify plume dimensions and data derived from a site specific MODFLOW model to quantify groundwater discharge according to plume dimensions.

   Dilution factor = river flux ÷ groundwater flux

   (MODFLOW: quantify discharge according to plume dimensions)

   $= 426,000 \ m^3/d \div 22 \ m^3/d$

   (considering variations in the flux at cross-sections of the plume)

   $= 19,363$

   In developing and presenting flux data and models, consider the hydrogeological and biological regime of the river, contaminant fate, transport and behaviour, and also outline any assumptions and uncertainties. For example, tidal cycles.

2. **Fixed volume method:** A fixed volume of groundwater was assumed to discharge into a fixed volume of receiving surface water. This method was used to evaluate the 'worst case' scenario based on discharges of groundwater into the river during a slack stage in the tidal cycle. Discharge rates for each COC were derived using a combination of plume plots and outputs from the MODFLOW model. The discharge rate was converted to a volume by assuming a fixed time period of discharge of one hour.

Dilution factor = volume of mixing zone* ÷ volume of groundwater entering river in 1 hr *mixing zones can vary, and for any particular case should be discussed with the regulator.*

Volume of mixing zone = length of river section x river width x river depth
$$= 120 \text{ m} \times 80 \text{ m} \times 0.5 \text{ m}$$
$$= 4,800 \text{ m}^3$$

Dilution factor = $4,800 \text{ m}^3 \div 0.92 \text{ m}^3$
$$= 5,240$$

A comparison of the empirical dilution calculations (groundwater concentrations ÷ surface water concentrations (accounting for annual trends, etc.)), it was found that the average discharge method was a better fit for the shallow groundwater in this case. This means that the mass discharge calculations was able to demonstrate that there was less mass discharge into the river system using the average mass discharge method (*c.f. the Fixed Volume Method was a better fit for the deep aquifer – not detailed in this worked example*).

NB: as the average discharge method is based on a daily average mass discharge rather than an hourly average mass discharge, it could be inferred that the average discharge model had limitations in predicting environmental concentrations over shorter times frames.

It is noted that whilst reliance on contaminant dilution in surface water is not considered acceptable, similar calculations may be useful inputs into risk assessments and in understanding the contaminant behaviour within the river. Mass

discharge values were used to understand the maximum thresholds from the dilution for each COC on an empirical basis to understand risks. For example, for DCE:

- DCE water quality standard for the river: 10 µg/L
- Dilution factor: 19,400
- Thus, empirically, the maximum threshold for DCE in the water discharging into the mixing zone of the river would be 194,000 µg/L (NB benthos may need to be considered).

The measured mean concentration based on 2013 data was 210,000 µg/L to 1,400,000 µg/L, both of which exceeded the empirically derived maximum threshold of 194,000 µg/L. Similar calculations for other COCs resulted in means less than the empirical maximum threshold derived using mass discharge. NB: Applying *annual* mean concentrations for assessing toxicants is not acceptable for substances with acute or chronic toxicity as these criteria are typically determined over much shorter time frames.

Tidal data indicated that peak concentrations are recorded during the flood tide. Consideration should be given to pre-entrained contaminants that could be flushed back upstream. At low tide, mass discharge remained high, however at this point it started to fall. Slack conditions, where net river discharge equals zero, occurred twice during the tidal cycle: once after high tide at the early stages of the ebb tide and once after low tide at the early-mid stages of the flood tide. In this case, slack conditions that occur after low tide were considered to represent the potential worst case scenario as groundwater will discharge into a lower volume of receiving water (a simplistic interpretation is given for demonstration purposes).
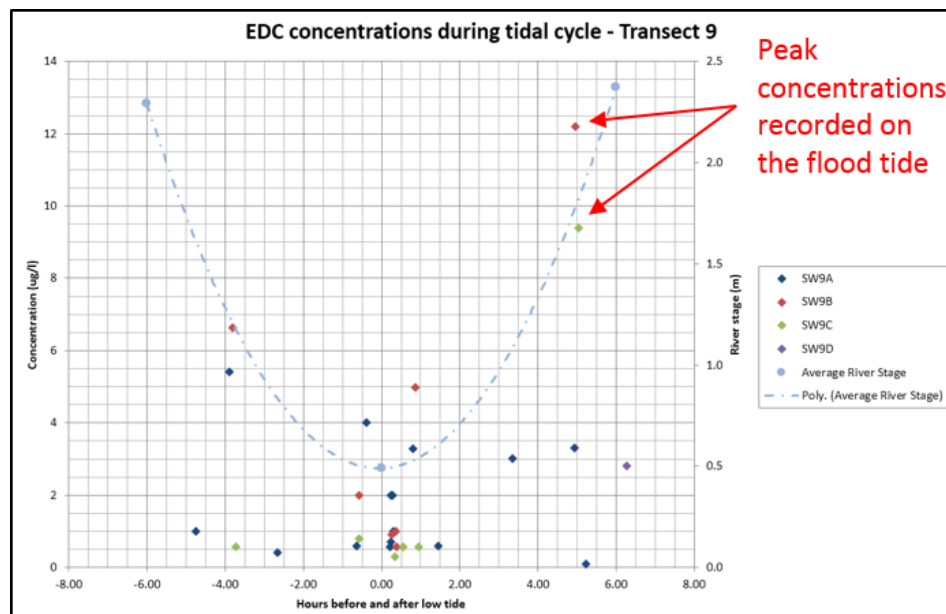
Conservative assumptions assist in addressing uncertainty. Calculations and assumptions informed by good quality site data and a good understanding of the hydrogeological regime is needed. This simplified example noted:

- well delineated contaminant plumes
- good understanding of groundwater discharges using MODFLOW Model;
- river water data, which allowed the comparison of measured dilution with theoretical calculations; and

> - tidal or other data allowing the exploration of worst case impact (this would normally need to be very detailed; for example, flushing of contaminants from a tidal river would need to be evaluated to ensure that they will not accumulate in the environment)
>
> As indicated earlier, contaminated sites affecting surface water bodies and coasts are usually complex in that a range of environmental values may need to be considered. This requires a robust understanding of the contamination in relation to the environmental trends and the issues affecting use of the site.

6.3 Impact on sensitive receptors

6.3.1 Risk to human health

If groundwater discharges through an area at risk of impact (such as a shoreline), contamination may be accepted if the areal extent of exceedance does not result in an unacceptable effect on human health. Whether the effect is acceptable or not may be determined, for example, by the application of the process of human health risk assessment as outlined in the ASC NEPM (schedule B4).

In such an assessment the areal extent of exceedance relevant for determining exposure can vary. For example, in the case of health risk assessment it can be appropriate to average the contaminant concentration over the exposure area of interest (this might be 50 m x 50 m in the case of passive recreation, or perhaps 7 m x 7 m in the case where there is a relatively intense and continuing use) and the discharge may be accepted if the concentration averaged over this area will not give rise to unacceptable exposure. Assuming we are dealing with a dissolved contaminant that does not accumulate in sediments, exposure will depend on concentration passing through the surface and can be quantified in terms of flux through the area of interest.

In this case, the metric for the maximum allowable mass flux across the area over which exposure occurs could be based on:

- Mass flux < (average concentration over exposure area) x (flow rate through the exposure area)

If the contaminant accumulates in sediments, additional risk assessment must be undertaken for risks associated with sediment concentrations e.g. pica behaviour and dermal contact rather than sole reliance on mass flux rates.

6.3.2 Risk to ecosystems

Risks to ecosystems are inherent in trigger levels for water and sediment quality in the ANZECC *Water Quality Guidelines for Fresh and Marine Waters* and sediment. For example, trigger levels for toxicants vary with the level of ecosystem protection prescribed for the water and generally relate to the proportion of species adversely affected. For physico-chemical stressors, the degree of departure from a reference condition is used to indicate acceptable risk. A similar approach is adopted in terrestrial environments for ecological risk assessment in the ASC NEPM (schedule B5a).

It is possible that this concept can be extended to determining when additional impact on a shoreline ecosystem is acceptable, although this will depend on whether and how the effect varies with concentration, which may not be readily quantifiable. For

example, an additional effect will commence occurring when the concentration exceeds the effect criterion as indicated for example in the ANZECC *Water Quality Guidelines for Fresh and Marine Waters* (sections 3.1, 3.2, 3.3, 3.4 and 3.5) or local criteria developed by States where available . If the concentration exceedance is small, then it may be that only some additional species will be affected, whereas if the exceedance is large many more species will be affected. The proportion of species adversely affected is likely to rise in line with the character of the species sensitivity distribution for the contaminant. As such, as the flux increases over an area that is significant, the additional impact may become more significant in terms of the overall ecosystem. If the risk relates to an indicator based on a reference approach e.g. physicochemical stressor or biological indicator, as noted in section 3.1.4.3 of the ANZECC Guidelines which deals with establishing reference condition, the area of interest may vary in size from a few square metres, as in the case of a stretch of an upland stream, to a few square kilometres, as in the case of a large seagrass bed.

In this case, the metric for the groundwater discharge giving rise to a significant effect on an ecosystem may be able to be characterised in terms of an equation such as:

- Mass flux < (concentration criterion for ecosystem effect) x (flow through the area of significance)

As noted in section 6.2, consideration should also be given to possible effects of bioaccumulation in the ecosystem where relevant.

It is recommended that liaison with the regulator and other stakeholders occurs to determine the acceptability of such an approach on any given site.

6.3.3 Risk to other values

Impacts on shorelines may relate to other values such as recreation, aesthetics and public amenity. In these cases, the affected environment may not pose a problematic risk to human or ecological health but may be aesthetically unacceptable. Section 3.6 of schedule B1 of the ASC NEPM provides advice on some circumstances whereby aesthetic considerations may be relevant. Jurisdictional requirements should also be ascertained.

7. Effective presentation of mass flux data

The presentation of mass flux and mass discharge data should be carefully considered in order to communicate the concept and ideas effectively. Sound communication can help engage stakeholders such as site owners, auditors or regulators so that the mass flux data aids the decision-making process.

It is important to visualise the data in some way, and relate the mass flux and mass discharge to 3D space, rather than presenting tables of numerical results that must be internally visualised by the reader. Examples of visualisation techniques include:

- the use of hydrogeological cross sections to plot data to show the link between the data and the hydrogeology
- examples of mass flux distribution along a transect and changes along the plume
- graphical presentation of plume behaviour over time
- graphics with heat-maps indicating areas of high mass flux, and
- flow chart to summarise the process.

7.1 Visualising mass discharge distribution along a transect

Data collected at sites using point measurements of mass flux can be used to visualise the contaminant flux distribution within a control plane or to consider changes that occur in mass flux distribution either in space or time (see case study 2).

Spatial variation of mass flux can take place along the plume axis as decay rates influence concentration or as heterogeneous flow fields influence plume behaviour. Thus control planes along the plume centre line can be used to visualise this information.

7.2 Heat maps

Models can be used to illustrate the heterogeneity of the subsurface and the resulting distribution of areas of high mass flux. Heat maps such as the one in figure 8 by Basu *et al* (2008) provide a useful representation of the heterogeneity at a site, and together with concentration data, can be used to develop a similar mass flux heat map.

7.3 Visualising before-and-after data

Changes in mass flux and mass flux distribution are quite informative for both the design and the evaluation of remedial activities (Brooks *et al* 2008). Contour surfaces collected before and after remediation allowing for adequate time for plume recovery at the control plane, can articulate processes that were effective for remediation.

In the example below, the effects of remediation through surfactant flushing was measured using PFMs in a monitoring well transect at one site with a TCE plume. The presentation of before-and-after mass flux data across the transect in figure 9 illustrates the order of magnitude reduction in TCE mass flux as a result of remediation.
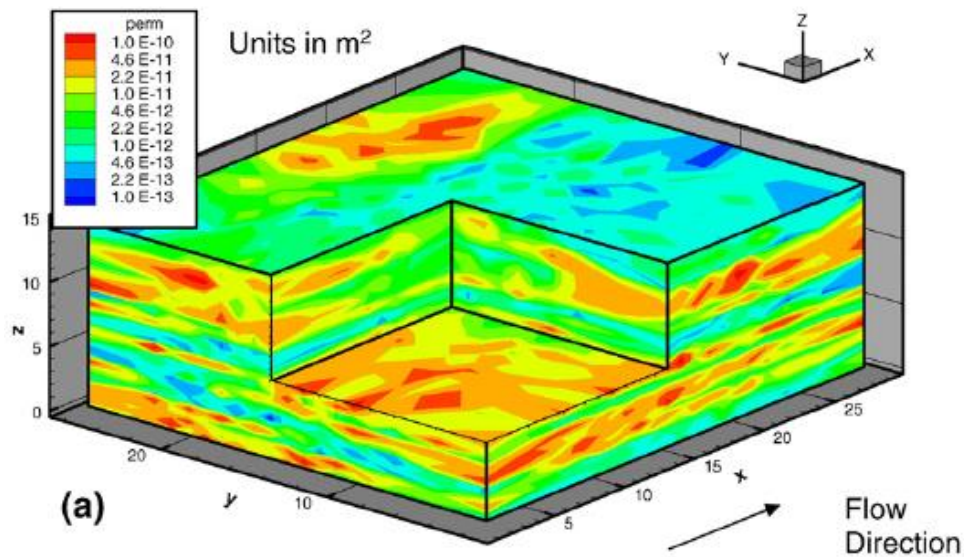
Figure 8 Mapping of the permeability field which impacts the source and mass flux distributions (Basu *et al* 2008).
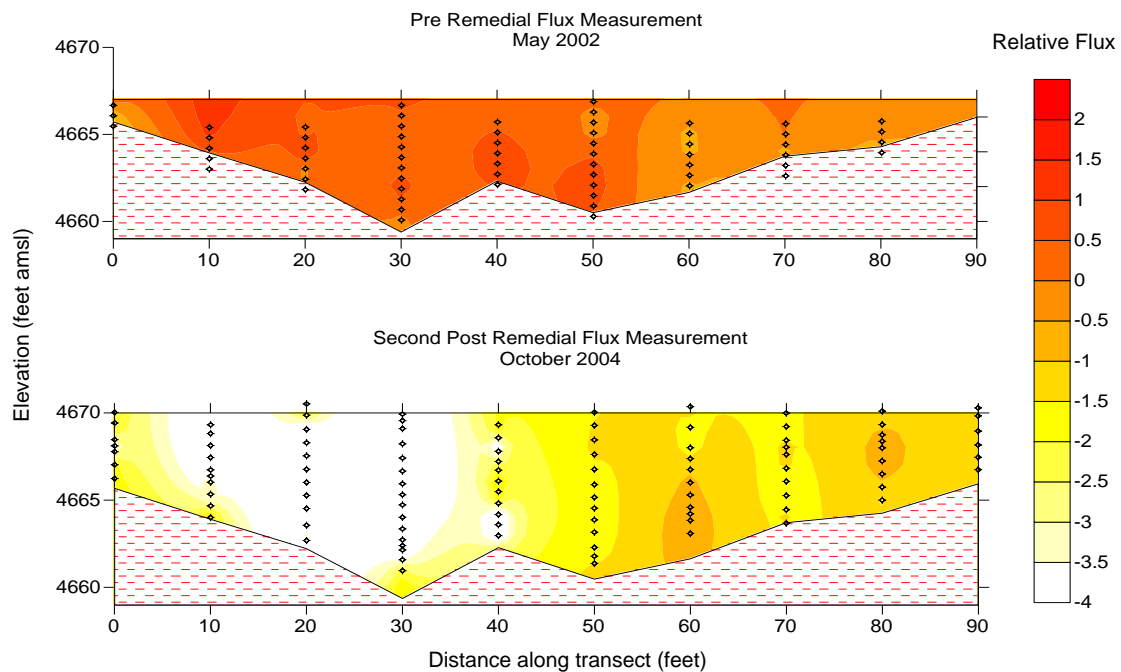
Figure 9 Presentation of the mass flux data pre- and post- remediation, demonstrating the reduction in TCE mass flux across the transect following remediation and hence, the effectiveness of remediation. Wells and data points from the PFMs are depicted to show the spatial resolution of the data. Colour scale is depicted relative to the pre remedial flux measurement. (Source: CH2M).

7.4 3D models

3D graphical representations of groundwater plumes can be used as a more sophisticated data visualisation technique. In the example below, a 3D graphical representation was developed to illustrate the change in a TCE plume as a result of remedial actions (installation of a biobarrier), shown in figure 10. In this case mass flux, determined through multilevel transects and a hydraulic model, was used to monitor remedial performance.
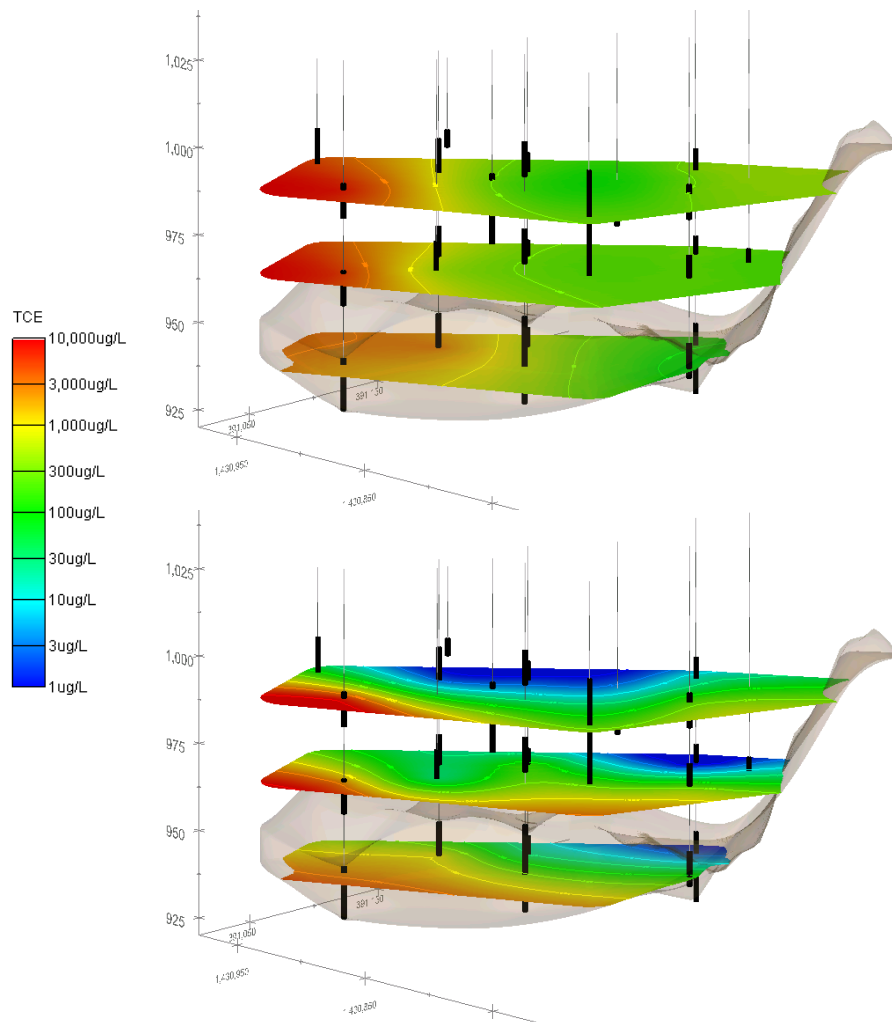
Figure 10 Presentation of a reduction in TCE following remediation (Source: CH2M).

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9. Glossary

9.1 Terms

Term	Definition
Advection	Mass transport caused by the bulk movement of flowing groundwater.
Attenuation	The reduction in mass, toxicity, mobility, volume or concentration of contaminants by physical, chemical and biological processes
Attenuation rate	The changes in contaminants due to attenuation per unit of time. As this is a ratio, it is unit-less
Aquifer	In Australia, the definition of an aquifer varies according to jurisdiction. ANZECC 2000, a national document, defines an aquifer as 'an underground layer of permeable rock, sand or gravel that absorbs water and allows it free passage through pore spaces.'
Beneficial use	Uses which should be protected, including the maintenance of ecosystems, human health, buildings and structures, aesthetics and production of food, flora and fibre.
Bio-degradation	The chemical dissolution of contaminants by bacteria, fungi, or other biological means.
Contaminant	Any chemical existing in the environment above background levels and representing, or potentially representing, an adverse health or environment risk.
Diffusion	Migration of substances by natural movement of their particles. Migration of chemicals along a concentration gradient in accordance with Fick's Law.
Dispersion	Irregular spreading of solutes due to aquifer heterogeneities at pore-grain scale (mechanical dispersion) or at field scale (macroscopic dispersion).
Flux	The rate of flow of fluid, particles, or energy through a given surface.
Ganglia	Isolated disconnected globules of LNAPL trapped within pore spaces.
Groundwater flux	The velocity (speed and direction) of groundwater through a defined cross-sectional area located perpendicular to the mean direction of groundwater flow
Hydraulic conductivity	A coefficient of proportionality describing the rate at which water can move through a permeable medium.
Hydraulic gradient	The change in total head with a change in distance in a given direction.
Hydraulic head	The height to which water rises in a bore. It is the resting groundwater level.
Hyporheic zone	The region beneath and alongside a stream bed, in which mixing of shallow groundwater and surface water occurs.
In situ	A Latin phrase that translates literally to "on site" or "in position". It refers to remediation that occurs on the site, without excavating the soils and removing them.

Term	Definition
Integral pumping test	A field method used to obtain the necessary data to estimate mass flux and mass discharge. Multiple pumping wells perpendicular to groundwater flow are used to measure contaminant concentrations, and time series data used to back-calculate the mass discharge.
Investigation Levels	The concentration of a contaminant above which further appropriate investigation and evaluation will be required.
Isocontour	Figures that are drawn by joining areas of equal water level measurements based on available sampling points.
Mass balance assessment	A quantitative comparison of the source zone mass discharge and the plume attenuation rate. This can be used to determine whether a plume is expanding or contracting.
Mass flux	The mass of a contaminant that passes through a defined cross-sectional area located perpendicular to the mean direction of groundwater flow over a period of time.
Mass discharge	The total mass of a contaminant moving in the groundwater from a given source. Also referred to in literature as contaminant mass discharge, total mass flux and integrated mass flux.
Monitored natural attenuation	Monitoring of groundwater to confirm whether natural attenuation processes are acting at a sufficient rate to ensure that the wider environment is unaffected, and that the remedial objectives will be achieved within a reasonable time scale.
Natural attenuation	The effect of naturally occurring physical, chemical and biological processes to reduce the mass, toxicity, mobility, volume or concentration of contaminants in groundwater.
Passive flux meter	A device used in the field to obtain the necessary data to estimate mass flux and mass discharge. They comprise a permeable sorbent infused with soluble tracers packed in a nylon mesh tube.
Permeable reactive barriers	An in situ remedial method which entails the emplacement of reactive materials through which a dissolved contaminant plume must move as it flows.
Plume	A zone of dissolved contaminants in groundwater. A plume usually originates from the source and extends in the direction of groundwater flow.
Redox potential	An expression of the oxidising or reducing power of a solution relative to a reference potential. This potential is dependent on the nature of the substances dissolved in the water, as well as on the proportion of their oxidised and reduced components.
Remediation	The actions to assess or break a source-pathway-receptor linkage and thereby manage risks associated with the presence of contaminants in the environment.
Risk	A statistical concept defined as the expected likelihood or probability of undesirable effects resulting from a specified exposure to known or potential environmental concentrations

Term	Definition
	of a material. A material is considered safe if the risks associated with its exposure are judged to be acceptable.
Secondary Source	A concept used to describe the back-diffusion of contaminants stored within areas of lower hydraulic conductivity back into groundwater flowing through areas of higher hydraulic conductivity.
Solute	The minor component in a solution, dissolved in the solvent.
Solute transport model	Models used to process input data relating to groundwater flow and contaminant transport processes, and output time-series contaminant concentration data, which can be post-processed into contaminant mass flux data.
Sorption	Process whereby contaminants in soils adhere to the inorganic and organic soil particles.
Sorbent	A material used to adsorb or absorb liquids or gases.
Source strength	Mass discharge at the source zone.
Stratigraphy	A branch of geology which studies rock layers (strata) and layering (stratification).
Steady-state	The non-equilibrium state of a system in which matter flows in and out at equal rates so that all of the components remain at constant concentrations (dynamic equilibrium).
Stygofauna	Any fauna that live in groundwater systems or aquifers.
Tandem circulating wells	A field method used to obtain the necessary data to estimate mass flux and mass discharge. Two dual-screened wells are used to one extracting water and pump it in a circular fashion.
Tracer	A substance introduced into system so that its subsequent distribution and movement may be readily followed.
Transect	A path along which one collects data. Transects are usually parallel, such as in the case of rows of groundwater bores perpendicular to groundwater flow.
Transect methods	A group of field methods used to obtain the necessary data to estimate mass flux and mass discharge. They involve the use of groundwater wells or multilevel samplers arranged in transects perpendicular to the flow direction of the plume, in order to measure contaminant concentrations and water levels for groundwater table gradients.

9.2 Acronyms

Acronym/symbol	Definition
A	Area
ADWG	Australian Drinking Water Guidelines
ANZECC	Australian and New Zealand Guidelines for Fresh and Marine Water Quality
ASC NEPM	National Environment Protection (Assessment of Site Contamination) Measure 1999 (2013 amendment)
C	Concentration
CH2M	CH2M HILL Australia Limited
COC	Contaminant of concern
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
CSM	Conceptual site model
CUTEP	Clean Up to the Extent Practicable
d	Day
DCE	Dichloroethene
DER	Department of Environment Regulation [Western Australia]
DNAPL	Dense non-aqueous phase liquid
DQO	Data quality objective
EPA	Environment Protection Authority
FRPFM	Fractured Rock Passive Fluxmeter
g	Gram
GIL	Groundwater investigation level
GGPA	Guidelines for groundwater protection in Australia
GQRUZ	Groundwater Quality Restricted Use Zones
i	Hydraulic gradient
IPT	Integral pump test
ITRC	The Interstate Technology & Regulatory Council (USA)
J	Mass flux
LNAPL	Light non-aqueous phase liquid
m	metre
M_d	Mass discharge
mg	Milligram
MIPT	Modified integral pump test
MNA	Monitored natural attenuation
K	Saturated hydraulic conductivity
NAPL	Non-aqueous phase liquid
NRF	National Remediation Framework
NWQMS	National water quality management strategy
q	Groundwater flux

SA	South Australia
PFM	Passive flux meter
TCE	Trichloroethylene
TCW	Tandem circulating wells
µg	microgram
US	United States

9.3 Formulae

This section provides a consolidated list of the formulae provided in the guideline. It does not encompass all the possible formulae that may be applicable when applying mass flux concepts. It is noted that a formula may be adapted to suit specific site scenarios, and this section and guideline therefore aim to provide generic formulae that can guide the reader forward.

Formula List

Groundwater flux (q) (section 2.1.1)
 	
 The product of the saturated hydraulic conductivity and the hydraulic gradient:
 	
 • q = K x i – where
    – q = groundwater flux, volume/area/time (e.g. cubic metre (m^3)/square metre (m^2)/day (d))
    – K = saturated hydraulic conductivity, distance/time (e.g. m/d)
    – i = hydraulic gradient, dimensionless (e.g. m/m)

Mass flux (J) (Section 2.1.2)
 	
 The product of the groundwater flux and contaminant concentration in a given area:
 	
 • J = q × C – where
    – J = mass flux, (e.g. milligrams (mg)/m^2/d)
    – q = groundwater flux, volume/area/time (e.g. m^3/m^2/d or m/d)
    – C = contaminant concentration, mass/volume (e.g. mg/m^3 or µg/L)

Mass Discharge (M_d) (section 2.1.3)
 	
 The integral of the spatially variable mass flux estimates across a transect multiplied by the representative area:
 	
 • $M_d = \int_A J \, dA$ where
    – M_d = mass discharge, mass/time (e.g. g/d)
    – J = spatially variable mass flux
    – A = area of the control plane
 	
 Simplified, mass discharge can be calculated as the sum of the individual mass flux estimates multiplied by the representative areas:
 	
 • $M_d = J_1 A_1 + J_2 A_2 + J_3 A_3 + … + Jn A_n$
 	
 As mass discharge is the product of the groundwater discharge and the contaminant concentration, it can also be obtained directly (instead of through calculations) through methods such as well capture and pumping tests. In these instances, mass discharge can be divided by the cross-sectional area of the plume at the control plane to determine the average mass flux:
 	
 • $M_d/A = \bar{J}$

Deriving mass discharge metrics – use of groundwater (section 6.1)

If the use of groundwater involves pumping at a certain minimum extraction rate, localised contamination that exceeds the use criterion may be acceptable if the source mass discharge is such that the use criteria will not be exceeded when the extraction rate is taken into account. In this case the formula for the maximum acceptable flux could be based on (CRC CARE 2014):

- Mass discharge < (concentration criterion for use) x (extraction rate)

Deriving mass discharge metrics – impact on receiving water body (section 6.2)

If groundwater is discharged to a receiving water body, contamination that exceeds the criterion for protection of the receiving water body may be acceptable if the mass discharge is low (e.g. perhaps indistinguishable from that occurring naturally) and the water quality criterion will not be exceeded in the receiving water body or over a short reach or mixing zone within the receiving water body. In this case the formula for maximum allowable mass discharge might be based on (CRC CARE 2014):

- Mass discharge < (concentration criterion for receiving water) x (flowrate of receiving water)

This concept may be able to be extended to determine the mass discharge given the flowrate through a mixing zone, as is often applied when licensing discharges to receiving water, the formula for maximum allowable mass discharge could be adapted in terms of the receiving water flow through the area where mixing with the receiving water will take place:

- Mass discharge < (concentration criterion at boundary of mixing zone) x (flowrate through mixing zone)

Deriving mass discharge metrics – impact on a shoreline (section 6.3)

Human health risk
Assuming we are dealing with a dissolved contaminant that does not accumulate in sediments, exposure will depend on concentration passing through the surface and can be quantified in terms of flux through the area of interest.

In this case, the metric for the maximum allowable mass flux across the area over which exposure occurs could be based on:

- Mass flux < (average concentration over exposure area) x (flow rate through the exposure area)

Ecological risk
If the concentration exceedance is small, then it may be that only some additional species will be affected, whereas if the exceedance is large many more species will be affected. The proportion of species adversely affected is likely to rise in line with the character of the species sensitivity distribution for the contaminant. As such, as the flux increases over an area that is significant, the additional impact may become more significant in terms of the overall ecosystem. If the risk relates to an indicator based on a reference approach e.g. physicochemical stressor or biological indicator, as noted in section 3.1.4.3 of the ANZECC Guidelines which deals with establishing reference condition, the area of interest may vary in size from a few square metres,

as in the case of a stretch of an upland stream, to a few square kilometres, as in the case of a large seagrass bed.

The formula for groundwater discharge that may give rise to an unacceptable risk to an ecosystem could be based on:

- Mass discharge < (concentration criterion for ecosystem effect) x (flow rate through the area of significance)

APPENDIX A.

Methodologies to measure mass flux and/or discharge

The key methods for estimating mass flux and mass discharge for dissolved phase contaminants introduced in **Section 5** are further detailed in this appendix. These methods include:

- Transect methods
- Passive flux meters (PFMs)
- Well capture and pump tests, including integral pump test (IPT), modified integral pump test (MIPT) and tandem circulating wells (TCW)
- Isocontours, and
- Solute transport models.

The application of these methods is discussed in further detail below, as well as their advantages, disadvantages and assumptions associated with the methodology. Additionally, tools and software which may be used to estimate mass flux and mass discharge have been discussed, as have the relative uncertainties associated with both point scale and integral methods, and how to estimate and mitigate that uncertainty.

A.1 Transect methods

Transect methods are the most established and well recognised manner in which to derive mass flux information. They involve the use of groundwater wells or multilevel samplers arranged in transects perpendicular to the flow direction of the plume, in order to measure contaminant concentrations and water levels for groundwater table gradients.

Each transect is then divided into a series of sub areas, both horizontally and vertically, with each area representing a discrete area of mass flux, assumed to be uniform in groundwater flux and concentration.

Data collected from these wells, both concentration and K, allow the estimation of groundwater and contaminant mass flux (figure 11). The wells (and hence the measurements) should preferably extend over the full width and depth of the plume and characterise the distribution of contaminant concentrations within the plume (API 2003).
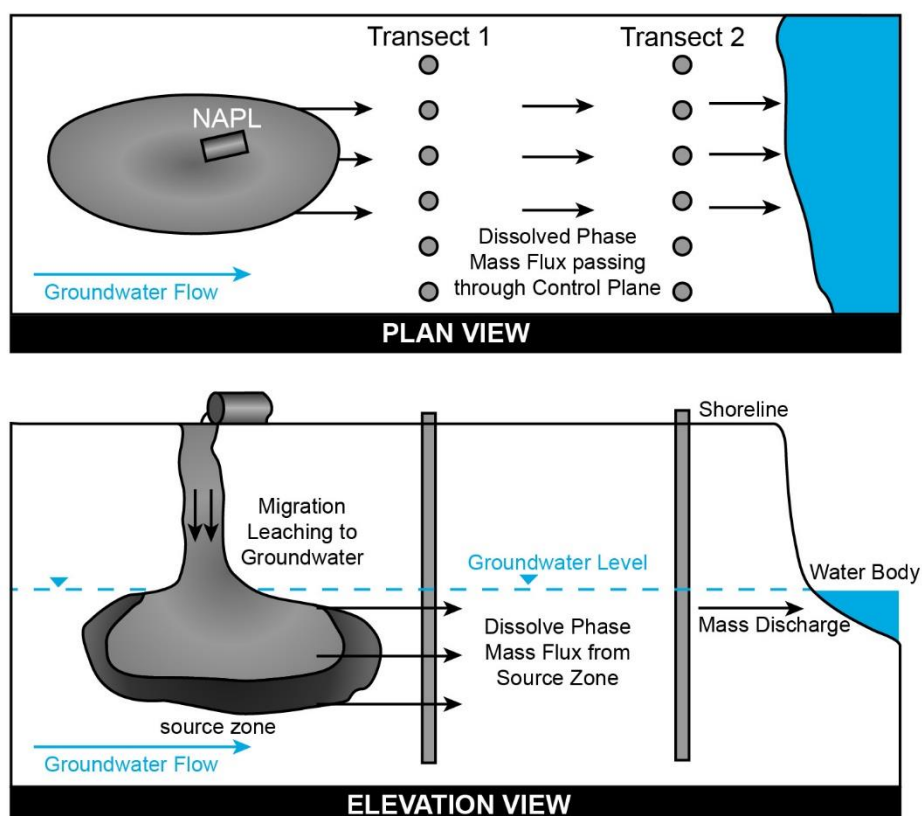
Figure 11 Transects can be used to estimate mass flux and mass discharge and changes with distance from the source and towards potential receptors such as a groundwater bore or a water body. (Adapted from CRC CARE 2014).

Contaminant concentrations are determined from measurements made at each screened well, or multilevel point, along the transects.

In order to estimate the groundwater flux, K can be estimated by conducting pumping tests or slug tests. A potentiometric contour map based on static water level measurements can be used to estimate groundwater flow direction and hydraulic gradient (API 2003). Tools such as high resolution piezocones (a type of membrane interface probe) and hydraulic profiling tools can be utilised to provide high resolution hydraulic head, soil type data and K (ITRC 2010). Additionally, some of these direct push approaches can also determine contaminant concentrations and thus produce high resolution flux profiles.

Whilst the groundwater flow is usually horizontal, estimates should consider whether there is a significant vertical component, and if so, consider altering the transect angle so that it remains perpendicular to groundwater flow (ITRC 2010). Fractured rock aquifers and karst environments are lithologies that may have a significant vertical component that requires special consideration, and this is discussed further in Appendix B.

The key steps involved in applying a transect method to estimate the mass flux and/or mass discharge at a site are as follows (Einarson & Mackay 2001):

3. Characterise plume concentrations. Groundwater sampling is required to delineate the lateral extent of the plume as well as its thickness and contaminant distributions within the plume.

4. Characterise groundwater flow. Measurements of *K* and hydraulic gradient are required for each plume transect to calculate the groundwater flux (as discussed in section 2.1.1) and flow direction.

5. Use information in Steps 1 and 2 to select the location and spacing of plume transects. The transects should extend across the full width and depth of the plume, perpendicular to groundwater flow.

6. Apply interpolation method. Depending on the quantity of data points, interpolation may be required to fill concentration and groundwater flux data points to support mass flux calculations.

7. Calculate mass discharge through the transect by adding the contributions from each polygon or rectangle (i.e. concentration of contaminant at polygon x groundwater flux at polygon x area through the polygon).

Aquifers are often heterogenous, with considerable variation in groundwater flow rates. Therefore, concentration measurements and groundwater flux estimates need to be made at sufficiently close intervals, both vertically and horizontally, which may necessitate a large number of closely spaced monitoring points. As discussed in section 5.1, there are no specific rules on what constitutes an appropriate sample density, and professional judgement along with the DQO process should be used to determine the sample density appropriate for each field program.

Estimates of the concentration and groundwater flux at each point will need to be made either based on direct measurement and simple interpolation, or more advanced methods such as kriging, nearest neighbour, Thiessen polygons, or specialised software such as the Mass Flux Toolkit (ITRC 2010). The most commonly used method, Thiessen polygons, comprises dividing each transect into subareas (rectangles or polygons), with lines drawn halfway between sampling points. Where monitoring points are evenly spaced, rectangles can be used to simplify calculations. Mass flux and mass discharge estimates are then commonly calculated using specialised software (refer to section 5.4).

Sampling programs that sample more of the area of the transect (either through the use of a larger number of points or through long screens that average concentrations) will be more likely to capture the high mass flux zones (ITRC 2010). Single-level screened wells may be useful if the plume has a limited vertical extent or the media is relatively homogeneous. In fact, wells screened across the full depth of the plume and pumped to provide a flow-weighted average concentration for the location can be used to estimate the average mass discharge. Whilst this method is approximate and does not provide detailed vertical characterisation, it may result in useful estimates and for that reason is commonly used. For example, where the goal is to understand the mass discharge of a contaminant across a compliance boundary or into a surface water boundary, then an integrated measure is appropriate. However, current literature does not always agree if this approach is appropriate. Careful consideration of the aquifer lithology is needed prior to installing a long-screen well, to avoid potentially bridging and connecting areas of higher *K* (ITRC 2010).

Moreover, the use of methodologies such as passive diffusion bags (PDB) or snap samplers allow the collection of vertical distribution data within long screened wells.

PDB are purpose-built low-density polyethylene bags filled with deionized water which acts as semi-permeable membranes and are suspended in a well to passively collect groundwater samples (ITRC 2002). PDB sampling is considered a cost-effective means to provide vertical contaminant concentration profiles and have been used at purposely long-screened wells to vertically profile dissolved chlorinated solvent contamination.

A summary of the advantages and limitations of the transect method, relative to the others discussed in section 3.2, is presented in Table 8.

Table 7: Evaluation of transect methods to calculate mass flux and mass discharge (Adapted from ITRC 2010).

Transect methods	
Advantages	- Method is well established and widely documented in literature. - Easier to implement as it requires no special expertise beyond hydrogeology - Spatial information including variations across the plume obtained, unlike with pumping test methods (Section 03) - Involves direct measurement, and is an extension of accepted technology - Fewer regulatory concerns than other methods as it does not require the injection of tracers into the aquifer (such as with TCW and PFM), reinjection of contaminated groundwater (as with TCW) or contaminated groundwater extraction (as with IPT and MIPT) (Section 0)
Limitations	- Large number of sampling points required for high resolution characterisation in a variable aquifer - The interpolation methods may not be robust between transects and carry some inherent uncertainties - Uncertainties may be associated with the measured concentrations, K and hydraulic gradients - Samples a relatively small volume of the groundwater, therefore localised areas with high mass flux may not be included. - Considered more expensive than integral methods
Assumptions	Groundwater samples are not highly turbid (i.e. collected through low-flow sampling methods, passive sampling or filtering samples). If a large fraction of the contaminant is sorbed to suspended solids in the groundwater samples, the mass flux calculations may be incorrect.

A.2 Passive flux meters

The PFM is a technology that comprises a permeable sorbent infused with soluble tracers packed in a nylon mesh tube (Hatfield *et al* 2004). The device is placed in a borehole or monitoring well for a known exposure period (from few days to a month), where it intercepts the groundwater flow and causes dissolved contaminants to sorb to the sorbent and the soluble tracers to leach out. The measurements of the contaminants and the remaining resident tracer can then be used to estimate time-averaged groundwater and contaminant mass fluxes. By using several passive flux meters across a transect, the average mass flux and total mass discharge through a control plane can be estimated (ITRC 2010).

PFMs are generally placed in wells along a transect and screened across the vertical extent of the contaminant plume. The PFM spacing should be based on the geology and groundwater flow characteristics of the aquifer (Annable *et al* 2005), and may be separated into different vertical zones isolated by impermeable barriers such as rubber/neoprene washers to prevent vertical flow within the PFM and allow the PFM to be used to assess different zones in the aquifer (ITRC 2010). The PFM should have approximately the same diameter as the borehole or monitoring well in which it is installed, so that the groundwater flows through the meter rather than bypassing it.

The sorbent can be varied based on the contaminant. As every sorbent has a limited capacity to trap contaminants, estimates of contaminant concentration and groundwater flux should be used to select the appropriate duration to avoid loading the sorbent to capacity. It should be noted that the tracers used in the PFM are typically alcohols, and therefore should be carefully considered in regards to the CSM (as some tracers in certain environments could act as contaminants) and stakeholders prior to deployment.

The extent to which traces are removed from the PFM and the contaminants are sorbed onto the PFM is determined by:

- The groundwater velocity
- The affinities of tracers and contaminants to the sorbent, and
- The concentration of the contaminants in the groundwater flowing through the PFM.

When the PFM is removed, the sorbent is extracted to quantify the mass of contaminants sorbed to it and the mass of tracer remaining. Permeability differences between the aquifer and the PFM may cause the flow to converge or diverge near the PFM, and this must be taken into account when determining the undisturbed aquifer flow. It is noted that this also applies for streamlines around the monitoring well and filter pack (Basu *et al* 2006). Further details regarding this method and calculations required are detailed in ITRC (2010).

This approach is referred to as passive in contrast to methods that require the pumping of water. This is a benefit in remote areas, where access to power may be limited, or at sites where disposing of extracted groundwater may be problematic or expensive.

PFMs are appropriate for use in characterising plumes at depth, and have been applied at a depth of 67 m at a landfill near Perth (Annable *et al* 2014).

A summary of the advantages and limitations of using PFMs to determine mass flux and/or mass discharge, relative to the others discussed in section 3.2, is presented in Table 8.

Table 8 Evaluation of the use of PFMs to calculate mass flux and mass discharge (Adapted from ITRC, 2010).

Passive flux meters	
Advantages	- Easy to install in the field - Provides a simultaneous measure of both cumulative groundwater and contaminant mass fluxes (Hatfield *et al* 2004) - Gives a direct measurement of subsurface contaminant mass flux at specific monitoring locations (which the transect method does not)

Passive flux meters		
	• Can show variations in groundwater and mass flux over the depth of an aquifer, contributing to better spatial interpretation and characterisation of the plume • Concentration measurements may be more representative in variable field conditions, as measurements are collected over a longer term (Verreydt *et al* 2013) • Reduced change to hydraulic flow field than pumping methods (Martin *et al* 2003) • Reduced volatilisation during sampling (Martin *et al* 2003)	
Limitations	• Relatively difficult to implement as specialised expertise is required to design customised PFMs for a given site, quantify the remaining tracer and contaminant sorbed onto the PFM, and to estimate the aquifer area associated with each PFM. However, this can be subcontracted to a specialist supplier; • Considered more expensive than integral methods (Goltz *et al* 2007) • May not be applicable to wells that contain light non-aqueous phase liquids (LNAPL) or free product as mass flux will be over-estimated. • Does not quantify contaminants not intercepted and sorbed by the PFM • Currently better suited to quantify mass discharge in a permeable unconsolidated aquifer. • Uncertainty regarding area of aquifer associated with each PFM • Potential for tracer loss during PFM deployment (Verreydt *et al* 2013)	
Assumptions	• As with the other methods, it relies on horizontal groundwater flow without a significant vertical component • Monitoring well is in "good status," with proper surrounding filter pack and open filter slits (<0.3 mm), with well diameter 41-80 mm. Characteristics of well and filter pack should be known to calculate the flow convergence or divergence through the well filter and PFM (Verreydt *et al* 2013).	

Different adaptations of the PFM have been developed to make them suitable for a variety of site conditions and to overcome some of the limitations listed above. For example, a new type of PFM has been developed for fractured-rock applications (refer to Appendix B for further information), and Martin *et al* (2003) found that using ceramic dosimeters for the passive sampler in place of polymer membranes has the advantage of being an inert material which does not swell in contact with organic compounds.

Similarly, the Fluxsampler obtains simultaneous measurements of groundwater flux and contaminant concentration (De Jonge and Rothenberg 2005). It combines a single salt tracer which is released over time and a sorptive resin (a versatile polymer) to measure organics or an ion-exchange resin to measure nutrients and metals (Verreydt *et al* 2010). It is likely less difficult to gain approval for the use of a salt tracer, however it may be limited in the range of groundwater velocities that it can detect.

A.3 Well capture/pump test methods

There are various methods of estimating mass discharge based on pumping from groundwater wells, including the following:

- Well capture
- Integral pump test (IPT)
- Modified integral pump test (MIPT), and
- Tandem circulating wells (TCW).

These methods all involve pumping water from a well to collect information that is representative of the groundwater in a particular region of the aquifer. Using the flux averaged concentration of contaminants in the pumped water and relating this to groundwater flow provides a measure of the mass discharge within the capture zone of each pumping well. These methods assume that the zone of influence of the pumping wells capture the entire plume in order to determine the plume mass discharge. The methods generally require fairly simple calculations, as mass discharge is the product of the groundwater flow and contaminant concentration.

These methods are aimed at quantifying the average mass flux or mass discharge without obtaining the level of high resolution information that other techniques do (such as transect and PFMs), and may therefore be suitable at highly heterogeneous sites where it would be difficult to carry out other techniques.

A summary of the advantages and limitations of using well capture/pump test methods to determine mass flux and/or mass discharge, relative to other methods discussed in this guideline, is presented in Table 9.

Table 9 General advantages, limitations and assumptions associated with well capture/pump test methods to calculate mass flux and mass discharge (Adapted from ITRC 2010).

Well capture/pump test methods	
Advantages	- Samples large quantities of plume water, improving the accuracy and integration of flow and concentration data - Less likely to miss hot-spots of contaminant mass flux in the plume - Fewer wells required
Limitations	- Pumping may induce changes in the natural flow regime through the source zone, and may draw water from areas of lower K that would not otherwise contribute to the contaminant mass flux - Pumping can induce geochemical changes as it will affect the aquifer matrix as well as the groundwater quality - Uncertainties exist in extrapolating from induced-flow measurements to flux under natural flow conditions - Less spatial information compared with via point scale techniques - Difficult to determine whether all of the plume has been captured
Assumptions	- As with the other methods, it relies on horizontal groundwater flow without a significant vertical component - Monitoring well is in "good status," with appropriate size filter pack and well screen (slits <0.3 mm). Characteristics of well and filter pack should be known to perform calculations and assure adequate flow

The four well capture/pump test methods are detailed in ITRC (2010). A brief summary of how the methods are performed and their relative advantages, limitations and assumptions is provided in Table 10.

Table 10 The four main well capture/pump test methods, their advantages, limitations and assumptions (Adapted from ITRC 2010).

Method	Premise	Advantages	Limitations	Assumptions
Well capture	Extraction well fully captures a contaminant plume. Mass discharge estimated by measuring the concentration and flow rate of the well (Nichols and Roth 2004) *Mass discharge = (concentration from the extraction well) x (flow rate of the extraction well)* A single value estimate of mass discharge is provided	• The method integrates flow and concentration, likely capturing small concentration hot-spots and high transmissivity zones • Data from an existing pump and treat system that captures the entire plume can be used, making the method inexpensive and easily performed	• Spatial distribution of mass flux across the plume and locations of high discharge are not determined unless multiple recovery wells are involved • Over pumping may result in dilution and reduced concentrations that are difficult to measure accurately	• Well or well system fully captures the horizontal and vertical extent of the plume • The extraction point is far enough down-gradient of the source to not induce an increased discharge of contaminants from the source. • Relatively steady state conditions have been achieved
Integral pump test (IPT)	Multiple pumping wells perpendicular to groundwater flow used to measure contaminant concentrations, and time series data used to back-calculate the mass discharge IPT provides a way of obtaining an estimate of contaminant mass flux averaged over a large subsurface volume (Goltz *et al* 2007)	• Does not require interpolation of contaminant concentrations between sub-areas • Requires fewer wells • Can utilise existing wells to avoid the costs of installing new wells • Can be applied to deep aquifers (Annable *et al* 2014) • Considered less expensive than point-based methods (Goltz *et al* 2007)	• Generates large volumes of contaminated water, which must be managed • If pumping in the source zone, dissolution rate may change compared to conditions prior to pumping • No information on the spatial distribution of contamination parallel to groundwater flow • Requires relatively complex interpretation of concentration vs time data (Bockelmann, Ptak & Teutsch 2001; Zeru & Schäfer 2005)	• Steady-state conditions • Homogeneous or moderately heterogeneous conditions • Negligible or linear contaminant concentration gradient within each capture well zone flow path

Method	Premise	Advantages	Limitations	Assumptions
Modified IPT (MIPT)	A variation of the IPT, used to estimate contaminant mass flux averaged over a large subsurface volume The groundwater flux is measured directly by measuring the head difference between pumping wells and monitoring wells when the pumping wells are pumped at different flow rates Mass flux is calculated as the product of the groundwater flux and the average contaminant concentration at the pumping well	• Simple and easily implemented, relative to TWC and IPT (Goltz *et al* 2007) • Avoids need for complex data analysis • Considered less expensive than point-based methods (Goltz *et al* 2007)	• May underestimate the mass flux (Goltz *et al* 2009) • Generates large volumes of contaminated water, which must be managed • If pumping in the source zone, dissolution rate may change compared to conditions prior to pumping • No information on the spatial distribution of contamination parallel to groundwater flow obtained	• Aquifer is confined, isotropic and homogeneous • Aquifer has a uniform thickness • Steady-state and uniform flow conditions
Tandem circulating wells (TCW)	Utilises two dual-screened wells, one extracting water from a lower depth and pumping it upward to inject at a shallow depth, with the second well operating in the opposite direction. This results in the water circulating between the two wells. The hydraulic gradient is determined by the piezometric surface with the pumps turned off and a third well nearby, and the *K* is measured by pumping the wells and measuring head changes. Groundwater samples are collected from the wells to determine the contaminant concentration, and the mass discharge is obtained by combining the gradient, conductivity and concentration data.	• Measures mass flux integrated over a large sub-surface volume • No wastewater is produced • May be more economical than IPT and MIPT for larger areas (Wheeldon 2008) • May be modified with the addition of a tracer (see below for further details).	• Considered difficult to implement due to the construction of special dual-screened wells. • Data interpretation requires complex inverse modelling techniques. • Involves the reinjection of contaminated groundwater into an aquifer, so it may be difficult to gain regulatory approval (even if the aquifer is already contaminated and the groundwater is not pumped above the surface).	• Acceptance of method by regulator.

Methods such as TCW may be modified with the addition of a tracer to determine the fractional flow between the two wells. Ideally, a tracer is conservative in that it flows with groundwater and does not interact with contaminants nor aquifer materials.

There are many factors that should be considered in selecting a tracer including:

- The hydrogeologic setting
- Contaminant of interest
- Chemical characteristics of tracer
- Analytical detection limit
- Amount of tracer needed
- Cost of tracer
- Toxicity of tracer
- Background concentration of tracer
- Availability
- Cost of analytical methods, and
- Ease of handling and injection.

Commonly used tracers include bromide, chloride and nitrate. Bromide is often regarded as an ideal conservative tracer since it is usually present naturally at only trace concentrations, it is relatively inexpensive and readily available, it is easy to handle and mix and analytical methods are straightforward and inexpensive. In contrast, chloride and nitrate are typically present in much higher concentrations naturally and can have multiple possible sources, so they may not be ideal tracers in many cases. If chloride concentrations are at similar concentrations to chlorinated VOCs which may be degrading (i.e. shedding chloride ions), then a chloride tracer should not be used.

A.4 Transects based on isocontours

Another method for determining mass flux and mass discharge first involves estimating the hydraulic gradient and groundwater flow direction from a potentiometric contour map, based on water level measurements at available sampling points.

This method also involves using data obtained from an existing monitoring well network to construct a contour map of contaminant concentrations in groundwater across the plume, and from this to estimate concentrations across particular transects perpendicular to flow (Nichols & Roth 2004). The contour maps can be drawn by hand or using computer contouring tools; both methods require hydrogeological experience to give a reliable output. The method is similar to the transect method, however concentration information is derived from an interpretation of existing data from wells across the plume.

Use of isocontours based on existing data requires a sufficient number of monitoring points. As such, the results are more reliable when the well network is dense, when the network intercepts all or a large fraction of the contamination plume thickness, and when data represents a flow-weighted average concentration.

A summary of the advantages and limitations of using transects based on isocontours to determine mass flux and/or mass discharge, relative to the other methods discussed in section 3.2, is presented in Table 11.

Table 11 Evaluation of the use of transects based on isocontours to calculate mass flux and mass discharge (Adapted from ITRC 2010**).**

	Transects based on isocontours
Advantages	• Inexpensive method as it utilises an existing monitoring well network and data • Contour maps of contaminant plume concentrations may already have been developed and be available for immediate use • Can be used as an initial screening tool to plan additional mass flux assessments
Limitations	• Low resolution, so may have more uncertainty than other methods • Information from the monitoring well network may not consider the site-specific geology and any preferential pathways that exist • Isocontour accuracy relies on the hydrogeologist's best estimate of the distribution of contaminants in a plume • May not provide maximum concentrations of contaminants if long single-screen wells are used to estimate changes in mass discharge over time, due to vertical averaging • Greater uncertainty at sites with low hydraulic gradients than with other methods due to errors in measurement (Devlin *et al* 2006)
Assumptions	• Monitoring well network intercepts majority of contaminant plume • Sufficient number of monitoring wells present to accurately draw isocontours, based on site-specific conditions

A.5 Solute transport models

Solute transport models process input data relating to groundwater flow and contaminant transport processes, and output time-series contaminant concentration data, which can be post-processed into contaminant mass flux data through the use of an external spread sheet or dedicated routines. Models discussed in ITRC (2010) and their key focus and sources include:

- BIOSCREEN (www2.epa.gov/water-research/bioscreen-natural-attenuation-decision-support-system) an analytical model applied to fuel hydrocarbon MNA
- BIOCHLOR (www2.epa.gov/water-research/biochlor-natural-attenuation-decision-support-system), an analytical model applied to chlorinated solvent MNA
- BIOBALANCE Tool Kit (www.gsi-net.com/en/software/free-software/biobalance-toolkit.html, an analytical model applied to chlorinated solvent MNA
- MODFLOW/RT3DMS (water.usgs.gov/ogw/modflow/MODFLOW.html), a numerical model used in sequential degradation scenarios, and
- REMChlor (www2.epa.gov/water-research/remediation-evaluation-model-chlorinated-solvents-remchlor), an analytical groundwater transport model that combines source behaviour with solute transport in the plume. It has been applied to hydrocarbon or chlorinated solvent scenarios.

Other numerical modelling codes, such as *Hydrus-1D, MODFLOW-SURFACT, PHT3D* and *FEFLOW* could also be used to determine groundwater flux and/or mass flux.

Like any model, the accuracy of the mass flux estimates will depend on the accuracy of the inputs such as the conceptual site model and associated boundary conditions, the physical and chemical input data, and on the type of model (e.g. screening-level model versus a more comprehensive model).

Analytical models make use of simplifying assumptions and can be more appropriate for screening or planning purposes. However, if the simplifying assumptions are too restrictive, then numerical model codes can be used for a wide range of problems from screening-level evaluations to other evaluations for which greater defensibility is warranted (e.g. remedial design).

A summary of the advantages and limitations of using solute transport models to determine mass flux and/or mass discharge, relative to the other methods discussed in section 3.2, is presented in Table 12. Specific information regarding individual solute transport models should be sought to determine which one(s) is most appropriate for a given set of modelling objectives.

Table 12 Evaluation of the use of solute transport models to calculate mass flux and mass discharge (Adapted from ITRC 2010).

Solute Transport Models	
Advantages	- Using historical data, models can be used to assess trends and forecast the transport and fate of a plume, particularly following a remediation event. - Does not require a special field study. Can use existing monitoring system or historical data. - More than one model can be used to compare results
Limitations	- Accuracy of mass flux data from numerical models is dependent upon the accuracy of the input data for flow and contaminant concentration, the CSM, and the selected transport formulation - Requires specialised training to develop, execute, and interpret reasonable and appropriate models that achieve the modelling objectives
Assumptions	Different models are constrained by different assumptions and calculation techniques

A.6 Tools (software) to use

In addition to the solute transport model REMChlor, discussed in **Appendix A**, ITRC (2010) references two key tools developed by GSI Environmental to use when calculating and using mass flux and/or mass discharge to manage groundwater contamination:

- Mass Flux Toolkit (2011) to evaluate groundwater impacts, attenuation, and remediation alternatives. Simple excel-based spreadsheets to calculate mass flux and mass discharge from transect data. The user choses the interpolation method. The software can also be used to do uncertainty/sensitivity analysis, assess potential impacts upon wells and surface waters, and as a resource for how to use mass flux data (from gsi-net.com/en/software/free-software/mass-flux-toolkit.html), and
- Matrix Diffusion Toolkit (2012). Uses indirect contribution of contamination sources within low-K zones to estimate mass discharge and the mass of contaminants and concentrations in the less transmissive zones (from www.gsi-net.com/en/software/free-software/matrix-diffusion-toolkit-version-1-2.html).

Along with tools for estimating mass flux, ITRC (2010) provides one tool for trend analysis:

- Mann-Kendall Toolkit (2012) for constituent trend analysis. Simple spreadsheet for analysing time-series groundwater monitoring data to quantitatively determine if the measured concentrations are increasing, decreasing, or stable over time (from www.gsi-net.com/en/software/free-software/gsi-mann-kendall-toolkit.html).

A.7 Uncertainty in mass flux measurements

As discussed briefly in section 5.3, mass flux and mass discharge estimates carry elements of uncertainty associated with the methods used to derive them and the complexity of the site.

Key factors that may contribute to the level of uncertainty associated with a mass flux and/or mass discharge estimate include:

- *Mass discharge estimates may span many orders of magnitude*: both *K* values and contaminant concentrations can range over six or seven orders of magnitude. In this context, it is considered that the accuracy of mass flux or mass discharge estimations may be acceptable for site management even with an order of magnitude of uncertainty (ITRC 2010).
- *Sampling density*: method uncertainty was assessed by Kubert and Finkel (2006) by comparing both point and integral methods (e.g. PFM and IPT) using an extensive Monte Carlo analysis on a hypothetical site. In general, uncertainty was reduced by increasing the sampling density. As an example, the uncertainty in mass discharge was less than 10% for all heterogeneities simulated, when a high point density of 5 pts/m^2 was employed. If this was reduced to 0.1 pts/m^2 (a more real-world sampling density), the uncertainty increased to approximately 30 to 60%. This study clearly demonstrated how uncertainty could be managed and how multiple methods for measuring mass discharge performed based on measurement uncertainty.
- *Subsurface heterogeneity*: published literature to date has indicated that relatively large uncertainties (>50%) may result from subsurface heterogeneity. At sites with highly heterogeneous aquifers, it may not be feasible to collect enough samples to reduce the uncertainty to an acceptable level using conventional statistical methods. New statistical approaches are therefore needed to allow for cost-effective determination of integrated mass flux in natural aquifers (ITRC 2010). Moreover, it has been noted that conventional investigation methods often use simplified conceptualisations of geology (Quinnan *et al* 2012), with average *K* estimates for an entire cross-section or hydrostratigraphic unit. Because aquifers often exhibit orders of magnitude variation in permeability both laterally and vertically, this can lead to significant errors in estimation. The authors therefore encouraged the use of high resolution characterisation methods, such as direct push injection logging tools like the Geoprobe® Hydraulic Profiling Tool or the Waterloo Advanced Profiling System™ (Waterloo APS).
- *Assumptions regarding groundwater flow direction*: the majority of the methods used to estimate mass discharge across control planes rely on wells perpendicular to groundwater flow, however it is recognised that groundwater flow direction and magnitude varies seasonally and with rainfall and anthropogenic factors.

Therefore, there are additional uncertainties involved with the use of prevailing groundwater flow direction to design studies at a given site.

The level of uncertainty in the methods presented within this guideline can roughly be characterised by either the point-scale method or the integral method. As such the further discussion presented below on understanding uncertainty has been arranged according to these categories.

Following this discussion information is presented regarding estimating and then managing uncertainty.

Understanding Uncertainty

Uncertainty in point scale methods

When applying the transect method to measure mass flux, it is noted that considerable uncertainty is associated with mass flux calculations as they are often based on average values of *K*, site wide hydraulic gradient, and flux-averaged concentrations from wells. Each of these values can by highly variable within the aquifer and across a control plane. If wells are used in the calculation of mass discharge based on the transect methods, then integral values of each component are used to calculate mass discharge (Annable *et al* 2014). Reducing uncertainty requires additional samples to be taken, thereby increasing sampling and analytical costs. One study estimated that the error involved in field sampling with multilevel transects was significantly greater than the error in an integral pump test at the same site, and indicated that a relatively large number of samples would be required in order to reduce the uncertainty to a comparable level (Béland-Pelletier *et al* 2011).

The use of PFMs allows for greater vertical resolution and reduced uncertainty given that the PFM is sampled continuously over the vertical profile in a well (Kubert & Finkel 2006). The transect method using PFMs still generates uncertainty in the spatial integration of point data from the wells caused by the well spacing and unsampled information between wells. Additional uncertainties can arise due to biostimulation and tracer loss during deployment, and should be considered when applying this method. Klammler *et al* (2012) presents novel methods for quantifying uncertainty using PFM data collected using wells forming a control plane for mass discharge characterisation.

Li *et al* (2007) found that the magnitude of mass discharge affects the uncertainty of a given sampling density. In the case of a higher mass discharge (319 g/d), a lower sampling density (0.1 pt/m^2) lead to an error of about 20%. When measuring a much lower mass discharge (15 g/d), the lower sampling density produced 180% error and the sampling density had to be increased to 3 pt/m^2 to bring the error back to 20%. Whilst this demonstrated that uncertainty can be managed with higher sampling density, it is noted that the cost of such high density measurements may be prohibitive.

A recent study by Brooks *et al* (2015) investigated point method uncertainty using groundwater flow and transport simulations within a Monte Carlo framework. Uncertainty in mass discharge estimates was related to the local mass flux, local mass discharge and the sample density.

Uncertainty in integral methods

Goltz *et al* (2007) noted that when using pumping tests to assess mass discharge information, one can reduce uncertainty by increasing the pumping rate over time. They recommended that the pump tests start at less than the estimated natural groundwater flow rate and monitoring continues whilst stepping up the rate until reaching a pumping rate that completely captures the contaminated plume without risking overcapture.

Studies focusing on integral methods have generally found that uncertainties can be reduced with proper design of the IPT. Jarsjo *et al* (2005) typically found errors ranging from 10 to 40%. Through a sensitivity analysis conducted by Dietze and Dietrich (2011), it was determined that the mass discharge was relatively insensitive to *K* and porosity. In another study, Béland-Pelletier (2011) found a maximum uncertainty of 28% for mass discharge measured by IPT.

A recent study by Chen *et al* (2014) evaluated uncertainty in various pumping methods (sequential, concurrent and TCW) using Monte Carlo modelling as a function of the contaminant plume position and width, and as a function of the pumping conditions used in the different pumping tests. Sequential pumping was found to be 5 to 12 times less uncertain than the other pumping approaches. For all methods, uncertainty decreased as the plume width increased. When the plume width to well spacing ratio was >2, it was concluded that uncertainty is similar for all the pumping methods tested.

Comparison of uncertainty in point scale and integral methods

Studies comparing the use of point scale and integral investigation methods to estimate mass discharge have found that where the monitoring network is sparse, point scale methods are subject to high levels of uncertainty (Li *et al* 2007, Li and Abriola 2009, Mackay *et al* 2012). Kavanaugh *et al* (2011) reported field study results using a bromide tracer injection with a known mass discharge. They report three applications of multiple methods with error from −8% to 31%. Where there are a sufficient number of monitoring points, given the complexity of the site, the methods have been found to be comparable. The authors concluded that the IPT provides more reliable results where the monitoring network is sparse, and point scale methods are more appropriate when the contaminant plume is of homogeneous shape (a normal distribution shape) and an adequate sampling grid is used.

A field study investigating the differences between benzene mass discharge and groundwater flow rate estimates resulting from point scale samples and IPT were 6.44% and 6.97%, respectively, demonstrating the applicability of both methods at the site (Dietze & Dietrich 2011).

Estimating uncertainty

Estimating the uncertainty inherent to a particular method, and integrating this estimate into the calculations, is an important part of interpreting the mass flux data collected and the implications for the CSM.

There are various methods for estimating uncertainty associated with mass flux estimates, and many different supportive data analysis functions available, including:

- Monte Carlo
- Mann-Kendall
- GSI mass flux toolkit uncertainty tests

- Wilcoxon-Mann-Whitney test
- Sen's test
- Testing for distributional relationships that affect interpolation
- Evaluating seasonality of the data, and
- Testing for outliers.

For example, conditional simulation using geostatistical analysis techniques can be used to analyse uncertainty in the concentration, K, and hydraulic gradient measurements (Li *et al* 2007). The data mean and variance can be used to determine what the 95% confidence level is that the mass discharge target will not be exceeded. Joint conditional simulation of K and contaminant concentration allows the generation of multiple, equally probable realisations of local mass flux, which can then be upscaled to provide the probability distribution of mass discharge. An important benefit of this approach is the quantified uncertainty of the mass discharge estimate, providing not only the best estimate of mass discharge but also confidence intervals around that estimate (Zuansi Cai *et al* 2010).

Software such as the GSI Mass Flux Toolkit (discussed in Appendix A) typically incorporate tools with uncertainty tests to estimate uncertainties associated with the mass flux estimates. It is noted that which methodology was used will influence whether the inbuilt uncertainty test is appropriate for the data.

Managing uncertainty

As discussed previously, what is considered an acceptable level of uncertainty varies depending on site and project-specific factors. General constraints in managing or reducing uncertainty associated with mass flux and mass discharge estimates include the following (ITRC 2010):

- *Cost*: increased data collection and infrastructure to reduce uncertainty will increase capital and labour costs
- *Application of mass flux estimates*: i.e. the demonstration of MNA processes may tolerate more uncertainty than demonstrating compliance
- *Phase of project*: more accurate data may be required during certain phases or tasks, justifying more sampling and infrastructure installation, and
- *Experience with mass flux*: the experience of the project team and stakeholders with using mass flux or mass discharge in groundwater management, and hence the confidence they may have in the estimates.

One method to reduce uncertainty comprises the collection of additional samples to reduce the amount of interpolation required between data points and areas lacking data. This must be balanced with increased sampling and analytical costs.

Another method to reduce uncertainty involves sampling in stages. Li and Abriola (2009) demonstrated that a staged sampling strategy was able to produce results with comparable uncertainty to reducing the sampling density to 50% or less, indicating optimised sampling strategies can be employed to reduce cost. Other strategies to manage uncertainty include pre-characterising the site.

It should be noted that the intended use of the mass flux information will influence the acceptable level of uncertainty. For instance, mass flux measurements intended for use in communicating compliance to the regulator may require less uncertainty than mass flux measurements used to support remedial design. As described in section 5.1, the

DQO process should be used throughout the life of a groundwater contamination project, and will assist in specifying the level of uncertainty that is acceptable to achieve site objectives.

As has been demonstrated, uncertainty can be quantified after measurements are completed and uncertainty can be managed through the above measures. Whilst every method of estimating mass flux and mass discharge carries elements of uncertainty that should be recognised and quantified, it is noted that concentration-only data may have similar or greater levels of uncertainty.

APPENDIX B.

Measuring water and contaminant mass flux in fractured and karst formations

Complex hydrogeologic settings, such as fractured and karst bedrock, pose substantial technical challenges both for characterisation and remediation. These technical challenges lead to the need for cost-effective monitoring tools that can be used in concert with existing borehole characterisation technologies to quantify groundwater and contaminant flux. When such flux measurements are combined with data gathered from other available borehole technologies, the CSM can be greatly improved and the ability to manage risk can be enhanced.

One recent advancement in this areas in the development of the Fractured Rock Passive Fluxmeter (FRPFM). When implemented within a fractured media formation, the FRPFM provides measurement of the following elements (ESTCP Final Report ER-200831; Acar *et al* 2013):

- Presence or absence of flowing fractures
- Specific location of active fractures
- Flowing fracture orientation, i.e. dip and dip direction
- Direction of groundwater flow in each fracture
- Cumulative magnitude of groundwater flux in each fracture, and
- Cumulative magnitude of contaminant flux in each fracture.

Other technologies are capable of measuring the first three elements listed, however the FRPFM is the only technology that also measures latter three elements.

The FRPFM is designed with an inflatable core separated from upper and lower end packers (a flexible inflatable liner) for isolation. The core consists of a packer covered with an internal nonreactive layer of permeable mesh which is then wrapped in a permeable layer of sorbent material such as activated carbon, ion exchange resin, or similar material impregnated with tracers. The core is then encased in a thin external permeable layer of dyed cloth for visualization. The core is inflated separately following inflation of the two end packers to provide isolation. The inflated core holds the fabric layers against the face of the borehole and any fractures intersecting that borehole. As currently designed, the FRPFM provides high resolution characterisation over a short characterisation zone (typically one meter).

During the deployment of the FRPFM in a borehole, visible dyes and tracers are leached from the internal and external sorbent layers which yields complex patterns of dye and tracer distributions. Visual inspection of the external layer leads to estimates of flowing fractures, their location along the borehole, the number of fractures, individual fracture orientations (dip and dip direction), cumulative groundwater flux and groundwater flow direction. Fracture characteristics can generally be obtained through existing borehole imaging technologies for fractures ≥1 mm; however, the technologies do not distinguish active from inactive fractures or measure the magnitude or direction of fracture flow. Analysis of the FRPFM internal sorbent layers at flow locations indicated by dyes yields additional estimates of cumulative groundwater flux in fractures and cumulative contaminant flux.

Given the high resolution of the FRPFM data, optimum application is likely for targeted borehole depth intervals, and not for characterising conditions over an entire borehole. FRPFM prototypes have been tested in 100 mm and 150 mm fractured rock wells.

At the time of writing, the advancement of the PFM technologies for karst settings had been recently initiated. The design developed for emplacement in karst cavities in rock boreholes is based on modification of a design used previously for surface water flow and contaminant flux measurements (Padowski *et al* 2009). The device is a circular hard shell construction with ports for intake and exhaust of water similar to the surface water applications. The interior of the device has a granular sorbent, typically activated carbon, with impregnated tracers. This device is suspended in a karst cavity intersected by the borehole for a duration appropriate for the estimate groundwater velocities. These velocities can be much higher than traditional groundwater, thus deployment durations may be shorter. The media used in the karst device can be manipulated to optimise deployment duration. This device is currently under testing in a limestone karst aquifer in Florida in the United States.

Appendix C

Case study 1 – Remediation of a brominated DNAPL plume

Background

A former mineral processing facility in Belmont, Perth, which had used the dense non-aqueous phase liquid (DNAPL) tetrabromoethane (TBA) for mineral separation, was acquired by Argyle Diamonds in 2000. When the drainage system beneath the laboratory was found to be corroded and leaking, investigation revealed that the groundwater was contaminated with TBA and its daughter products, principally tribromoethene (TBE) and dibromoethene (DBE), with lower concentrations of vinyl bromide (VB).

Investigations indicated that the majority of the impact lay within the intermediate aquifer comprising sands and silts (9–10 m thick), which contained two high conductivity zones (4–6 m/d). The water table was ~3 m below ground level (mbgl) and the gradient was approximately 0.009m/m in a north-westerly direction. The CSM[1], presented on the following page, illustrates the DNAPL and dissolved groundwater plume as well as the pathways and receptors at the site. The primary beneficial use of the groundwater is for irrigation of gardens and landscaping in this light industrial area, and the key receptors were identified as people who may be exposed to contaminated groundwater during irrigation or vapour migration to indoor or outdoor air, and ecological receptors in the down-gradient Belmont South Drain, which drains into the Swan River.

Argyle focused on open and regular engagement from the outset with state government agencies (Western Australia Department of Environmental Regulation (DER), Water Corporation and Swan River Trust (now Department of Parks and Wildlife)) and local stakeholders. This was particularly important given the unusual nature of the contaminants and the potential impact on neighbouring landholders. Through a public statement in 2002, Argyle committed to prevent health effects on neighbours and to protect the river environment. It also expressed the company's intent to actively remediate the site to the extent practicable.

Remediation comprised control of vapours and odours by soil vapour extraction, the hydraulic containment and recovery of the plume and then source zone DNAPL mass removal (mass flux reduction, as discussed in section 3.5). This case study focuses on how mass flux and mass discharge concepts were applied to understand plume behaviour, assess risk to irrigation workers and monitor remedial performance.

Applications of Mass Flux Concepts:

This site is an excellent example of the application of mass flux concepts in Australia, resulting in improved characterisation of the plume as well as enabling more effective remedial targets to be set. Examples for each of the applications discussed in section 3, are summarised as follows:

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[1] The CSM was prepared by Golder Associates Pty Ltd (Golder) in 2014 as part of a risk assessment carried out at the site.

1. **Enhance the CSM (section 3.2).** Quarterly TBE concentration data were used to track the dissolved TBE mass (estimated at 200–300 kg in 2003, and 110–190 kg in 2004). Installation of additional wells in the source area in 2004 enabled initial estimates of mass discharge, which appeared to be in the range of 10 kg/year. Coupled with observations of decreasing concentrations (and hence mass flux) in source area wells these mass and flux estimates informed the initial CSM development. Mass flux estimates were also used to estimate natural attenuation rates in situ (compared with lab determined degradation rates). Later, more detailed measurements of mass flux using passive flux meters (PFMs) were instrumental in identifying the correlations between permeability, the location of the source mass and the flux of contaminants. This showed that concentration data alone were not able to identify the main transmission routes of the contaminants in the aquifer (and were in fact misleading). The spatial distribution of mass flux also provided insights into depletion of the DNAPL source over time, both naturally and under the influence of pumping.

2. **Complement concentration criteria (section 3.3).** PFMs, a partitioning inter-well tracer test (PITT) in the source zone, and an integral pump test (IPT) at the site boundary were completed in 2006–2007, immediately prior to the commencement of remediation to complement conventional investigation methods to estimate source mass (220 kg TBA and TBE) and quantify source mass discharge (~40 kg/year TBE) prior to commencement of remediation. Once the success of the source zone pump and treat system and PFMs were demonstrated, the auditor and DER were consulted in regards to the potential use of mass flux-based performance criteria.

3. **Assist with remedy selection (section 3.4).** Risk assessments and early thinking on remedial design were both informed by the mass and flux estimates and the results of PFM, IPT and PITT. The spatial distribution of mass flux estimates in sub-units of the intermediate aquifer particularly enabled assessment of how flushing technologies may have been deployed if pumping alone was not able to reach remediation targets.

4. **Optimise remedial design (section 3.5).** Design initially focused on the hydraulic containment of the plume, targeting the intermediate aquifer (with ~80% of the mass) with pumping only at the down-gradient site boundary. Once the water treatment process was proved in operation, including with water from the source zone, focus shifted from plume containment to mass extraction (to drive down the mass discharge feeding the plume). Subsequent monitoring aimed to measure changes in mass flux across two control planes (i.e. fluxes leaving the source zone and also across the site boundary). Results were used to inform a decision to cease pumping at the site boundary and continue mass extraction by pumping from the source zone.

5. **Assess remedial performance (section 3.6).** Once the auditor and DER provided in-principle support for the concept, mass flux-based remediation criteria were derived. PFMs were again used in 2011 to directly measure mass flux reductions achieved by pumping. Source zone mass discharge was reduced by 70%, but was greater than the target so groundwater extraction continued. The IPT was also repeated in 2014, and showed that flux across the site boundary had been reduced by 95%. Decreasing mass discharge from the key pumping wells was also monitored over time. Correlations between mass discharge from the wells and the mass flux/discharge across the control planes were also used to assess remedial performance.

6. **Demonstrate risk reduction (section 3.7).** Lower mass fluxes across the down-gradient boundary and from the source indicated a reduced risk in down-gradient exposure scenarios. Concentration and mass discharge targets have been developed for a hypothetical well used to extract groundwater for irrigation, as part of the proposed approach to validate the remediation.

7. **Evaluate compliance or long term monitoring (section 3.8).** Mass flux-based criteria for the source are considered to be protective of down-gradient receptors and take account of travel time and attenuation between source and receptor.

Derivation of mass flux/mass discharge criteria:

The derivation of mass discharge criteria was used to assess risk associated with the use of the groundwater for irrigation. The derivation example below guides the reader through the work that was carried out and the calculations that were made, so that these steps may be adapted to other sites using site-specific data.

Determine receptors/beneficial uses to be protected

Irrigation was identified as the primary use of groundwater, with a risk assessment identifying persons watering local gardens and landscaped areas as the main receptors. Whilst no irrigation bores are located in or near the plume and a restriction has been placed on groundwater use, this is a potential use of the groundwater.

Select concentration criteria

No regulatory risk based groundwater criteria were available for TBA or its daughter products. Risk based screening levels were developed by Golder and updated over the course of the project to reflect new information. This culminated in site specific remediation criteria to protect people who may be exposed to: contaminated groundwater during irrigation (through direct contact, ingestion or vapour inhalation); or contaminants in indoor air in the commercial premises at the site; or contaminants in outdoor air. Criteria were conservative and did not include attenuation factors. The remediation criteria derived were for TBA (260 µg/L), TBE (480 µg/L), DBE (52 000 ug/L) and VB (120 ug/L). For the irrigation scenario, concentration criteria were based on an assumed groundwater extraction rate of 0.16 L/sec, and an exposure duration of 15 min/d, 3 d/wk.

Source zone mass discharge

Pump tests were undertaken to assess hydraulic conductivities and this information, together with concentration data, were used in early estimates of the mass discharge of contaminants from the source zone. Direct measurement of mass fluxes and discharge were also made using PFMs in 2006 and 2011. Modelling which incorporated pump test data, hydraulic conductivity, flow rates and contaminant concentrations was then used to estimate mass discharge at the down-gradient site boundary, for given source zone mass discharge.

Mass discharge target

Mass discharge targets for the down gradient boundary, and for the source zone, were calculated based on the concentration criteria for a hypothetical irrigation well discharge on down gradient properties (focusing on TBE as the risk driver for this exposure scenario). A linear correlation between the source zone mass discharge and the down-gradient site boundary concentrations was noted from the modelling. This was used to identify the required mass discharge target at both the source zone (5 g/day TBA plus TBE) and the down-gradient site boundary (1.4 g/day TBE) to achieve compliance with the derived concentration criterion for irrigation water.

Mass discharge calculations

A TBE source zone mass discharge target of 5 g/day was derived from irrigation water quality criteria. Direct PFM measurements have only been obtained twice in the project to date. For most quarterly monitoring events, mass discharge is calculated for each well interval in the source zone control plane (5 nests of 3 wells) using the following equation:

- MFW = [k] × [c] × [q] × [A] – where
    - MFW = Mass discharge for well interval (g/day)
    - k = conversion factor to adjust for differing units
    - c = Concentration of TBE (µg/L)
    - q = flow rate (cm/day), and
    - A = Cross sectional area (m^2).

Mass discharge across the flux plane is the sum of the mass discharges calculated for each well interval in the flux plane (when there is no pumping from the source zone extraction well, and after a suitable period for re-establishment of flux across the control plane). Note that the two PFM measurements were used to assess the uncertainty associated with these estimates.

Data for cross sectional area (A) is calculated using an assumed width and interpreted depth for each well. The width is the assumed effective width of the well which is from the mid-point to mid-point between adjacent flux plane wells. The depths have been interpreted from borelogs and cross sections for the flux plane wells.

Flow rate (q) was established through PFM testing. Alternatively the flow rate can be calculated using the interpreted hydraulic gradients and hydraulic conductivities.

- q = [K] × [i] – where
    - K = hydraulic conductivity (m/day)
    - i = hydraulic gradient (dimensionless)

Data for K estimated from slug tests for each well and from analysis of pump test data.

Data for i estimated from water level data.

Compare mass discharge measurements with derived targets

The mass discharge of dissolved brominated organics across the source zone control plane decreased from 104 g/day to 30 g/day following one year of groundwater

extraction from the source zone (2008–9) and two years natural flux to 2011. Therefore, the source zone mass discharge exceeded the target mass discharge, indicating that downgradient groundwater would not be suitable for irrigation use, and remediation should continue.

After a further three years groundwater extraction, a second IPT was performed in late 2014 to measure the flux across the downgradient site boundary. This showed a TBE flux of 0.5–0.7 g/day (total BrVOC flux of 1 g/day), significantly less than the established target of 1.4 g/day, and 95% lower than that measured in 2007. As a result, a decision was made to terminate pumping on the boundary, but continue pumping the source zone well.

Advantages of mass discharge/flux

The contaminant plume at this site is quite narrow, with steep concentration gradients at the periphery. The plume is also dynamic, with its location relative to monitoring wells varying over time in response to recharge and pumping, including the groundwater extraction for remediation. This results in highly variable point concentration measurements from some monitoring wells. Mass discharge measurements allow for more reliable assessment and management of risk, since it gives a whole of plume view, and smooths the often extreme variability of point contaminant concentrations. Understanding the mass discharge allows for greater understanding of the site within the CSM and acts as a better predictive tool for remediation performance.

Acknowledgement

DRAIN

(H) Adult/Child in Park (in,dc,ih)

Aquatic Ecosystem

(E) Domestic Pets

Vapour

(H) Worker irrigating Plants

Irrigation (in,dc,ih)

OFF-SITE BOUNDARY

(E) Irrigated Plants

(H) Workers in or outdoors (ih)

Worker in Basement (ih)

(H) Construction Worker (in,dc,ih)

Vapours   **Vapours**

Source Zone

Groundwater Flow

Remediation Extraction Well

Groundwater Flow

LEGEND

▽ ──── INFERRED WATER TABLE LOCATION - INTERMEDIATE AQUIFER

▦ HISTORICAL TBE PLUME EXTENT

(E) ECOLOGICAL RECEPTOR

(H) HUMAN HEALTH RECEPTOR

← GROUNDWATER FLOW DIRECTION

in - INGESTION

dc - DIRECT CONTACT

ih - INHALATION

UPPER AQUIFER		
	BASSENDEAN SAND	
	GUILDFORD FORMATION	
SUPERFICIAL SEDIMENTS		
INTERMEDIATE AQUIFER	GNANGARA SANDS	
	ASCOT FORMATION	
LOWER AQUIFER	KINGS PARK FORMATION	MULLALOO SANDSTONE

SANDY FILL

CLAYEY SILT / PEAT

MODERATELY TO WELL SORTED MEDIUM SANDS

CLAYEY SANDS

POORLY SORTED SAND WITH SOME SILT AND/OR CLAY

SILTY SANDS

FINE TO VERY FINE SANDS WITH SOME CLAY

FINE TO COARSE SAND LAYERS AND LESSER SILTY SAND LAYERS

CALCAREOUS SHELLY SILTY SAND / SUBORDINATE SILT AND CALCARENITE LAYERS

CALCAREOUS SHELLY SILTY SAND / SUBORDINATE SILT AND CALCARENITE LAYERS AND CLAY

POORLY SORTED FINE TO VERY COARSE SANDS WITH SOME CLAY AND SILT

0 10 20 30 40 50 m

1:750

TITLE

CONCEPTUAL SITE MODEL

Appendix D

Case study 2 – Mine tailings ponds leakage

Background

A mine tailing pond leaked heavy-metal contaminated water into groundwater.

The pond is located immediately upgradient of a listed sensitive receptor, being an intertidal zone including sand dunes, ephemeral freshwater wetlands and mangroves. The landscape geology is coarse-grained marine sands overlying marine muds, which overly weathered fractured granite bedrock, becoming more competent with depth.

The zinc contaminated water had percolated from the tailings dams into the groundwater, and the groundwater was then transporting the contamination into the intertidal and mangrove areas. Thus, the contaminated groundwater required delineation and management.

After a series of investigations the project team identified that the majority of contaminant mass was being transported by groundwater within a particularly coarse sandy lense, corresponding to a former creekline (filled in during pond construction) and dense vegetation.

Traditional monitoring wells were installed into the sands, the marine muds and the underlying bedrock. Concentration data from these wells showed that the marine muds were acting as an effective aquitard and the zinc contamination was isolated to the overlying sands only. Thus, remediation was to focus on this lithology.

During the course of the investigation, both the state regulator and an auditor became involved in the management of the groundwater contamination. Eventually, it was decided that remediation should focus on a particular portion of the site located immediately downgradient of the ponds.

Optimising remedial design

During investigation, two monitoring wells reported elevated concentrations of dissolved zinc and cadmium. These were located immediately downgradient of the leaking pond and close to the site boundary.

Based on concentration data alone, the remedial area would need to encompass both of these monitoring wells. However, using flux techniques, the project team were able to demonstrate that the reported concentration in only one of the wells was contributing significant mass discharge, whereas the mass discharge related to the concentration in the other well was negligible.

Method:

- The field program was designed to investigate the mass flux across a transect corresponding to the anticipated extent of the remediation (the control plane);
- Existing monitoring wells were utilised for measuring K
- New sampling points were established along the transect and concentrations were measured by the use of a hand held groundwater spear, and

- The data was used to calculate groundwater flux and then mass discharge at each point along the transect.

The data is displayed in figure 12, with mass discharge of zinc (g/day) against chainage plotted. This clearly shows that the mass discharge at MW01 was negligible, and the mass discharge at MW02 was high.

Using this data, the project team effectively communicated to the auditor that remediation at MW01 was not warranted. The auditor agreed and remedial works were restricted to the area around MW02.
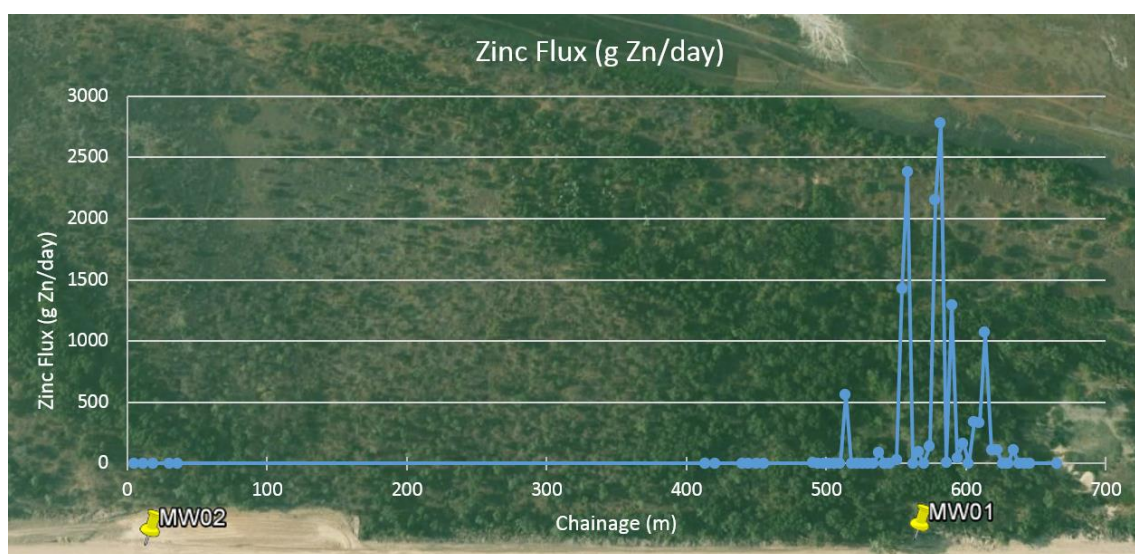
Figure 12: Zinc mass discharge vs chainage, overlaid on an aerial photograph of the site to aid visualisation

Calculating site-specific remedial criteria

Due to the sensitive and unique nature of the potential receptor, the project team was required to calculate site-specific remedial criteria. Concentration-based criteria were imposed by the regulator at the point of potential exposure (i.e. within the mangroves), however the challenge lay in converting this receptor-based criteria into something that could be measured at the source.

To solve this challenge, the project team chose to use the flux data to back-calculate the mass discharge at the source that would correspond to the concentration at the receptor. This technique was preferred as:

- It afforded actual protection (was based on measured data at the sensitive receptor) for the most sensitive receptor
- Referential data for the ecosystem or groundwater bearing zone was not available, and
- It worked across a range of discharge scenarios, given the high seasonal variability of the receptor and groundwater system.

Method

- Metal concentrations were measured in the receiving environment over a number of years and seasons and the health of the ecosystem was also measured at these times
- Various site specific parameters were measured or calculated using estimates (presented in figure 13)
- The surface water hydrology was assessed to help calculate the surface water volume and chemical composition that would discharge into the receptor
- The extent to which the sensitive receptor relied on groundwater was determined, as a proportion of surface flows
- The maximum allowable mass flux was then calculated (based on dilution only) for a worst case scenario at the proposed location of the remedial system foot print, and
- No allowance was made for retardation as the hydraulic conductivity was high and the lithology had minimal adsorption potential.

The auditor agreed that this technique was useful, and endorsed it as clean up criteria for the remedial program, as well as for monitoring compliance criteria following completion of the remedial works.

Parameter	Value	Derivation
Concentration (mg/L)	500	
K (m/d)	0.01	Literature-derived estimate for clay
Hydraulic gradient	0.003	Measured in adjacent groundwater
Porosity	0.3	Literature-derived estimate for clay
Velocity (m/d)	0.0001	v= i*k / n*e
Thickness in contact with wetland (m)	0.3	Based on highest recorded groundwater levels and shallowest hydraulic gradient
Width in contact with wetland (m)	70	Measured from aerial imagery
Cross sectional area (m2)	21	Length x depth
Groundwater contribution (m3/d)	0.0021	Q = v*a
Flux (mg zinc/d)	1050	F = Q*C
Wetland catchment area (m2)	40500	Measured from aerial imagery
Wetland area (m2)	7800	Measured from aerial imagery
Runoff coefficient	0.1	From local council regulations
Average rainfall (m)	0.896	On site weather station data
Surface water contribution (m3/d)	82.656	Runoff x rainfall x catchment area minus wetland area, plus wetland area x rainfall
Surface water zinc (mg/L)	0.05	Assumed based on historical monitoring in
Surface water flux (mg zinc/d)	4132.8	F = Q*C
Groundwater volume contribution	0.0025%	
Wetland concentration measured (mg/L)	0.07	Measured highest concentration with no
Calculated concentration (mg/L)	0.062702	Zinc and surface water flux divided by annual surface water and groundwater discharge

Figure 13: parameters and calculations for site specific criteria based on mass discharge

Compliance monitoring

As mentioned above, the mass-discharge based clean up criteria were able to be used as compliance monitoring during and following remediation.

This technique was useful, as it allowed a metric to be measured at the source rather than the receptor. Thus, if the compliance criteria was exceeded there was still time to act and prevent actual exposure at the receptor.

Lessons learned in using flux measurements:

- Early and open communication with the regulator and the auditor was essential
- Visualisation of the data was important. Cross-sections, CSMs and graphs were utilised strategically to portray the nature of the contamination, and the concepts behind the remedial design, and
- Adequate field planning and contingency provisions were essential. It was important for field staff to know which data were critical, so if things went wrong they could prioritise and still achieve the objectives.

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