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Health Risk Assessment of Pesticides in Drinking Water in South Africa

A case study on Piketberg and Withoogte drinking water treatment plants along Berg River applying QCRA

Master’s Thesis in Infrastructure and Environmental Engineering

Mia Engman and Malin Pettersson

DEPARTMENT OF ARCHITECTURE AND CIVIL ENGINEERING
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Abstract

Pesticides are applied to a broad extent within the South African agricultural sector. The sector lack clear regulations regarding the amount applied or which pesticides are legally permitted to use. Exposure to pesticides has been recognized as one of the main chemical threats to human health globally. Watercourses are often surrounded by agricultural land and the spread of pesticides from these lands poses a risk to the aquatic environment. Berg River is a watercourse located in an agricultural area in the Western Cape, South Africa. The river is used as raw water source for the two drinking water treatment plants, DWTPs, Piketberg and Withoogte. Hence, pesticides may pose a risk to the quality of the drinking water. Consequently, this thesis aims to investigate if long-term exposure to pesticides in drinking water poses a human health risk.

A quantitative chemical risk assessment, QCRA, was conducted to evaluate the health risk. The pesticides atrazine, imidacloprid and simazine were analysed for different population groups; infants, children and adults, and three different scenarios in the DWTPs. These scenarios included normal operation, lack of treatment and normal operation with the addition of a granular activated carbon filter, GAC-filter. Field studies were conducted at both DWTPs where raw water and drinking water samples were collected. The remaining input for the QCRA-model was compiled through a literature study. A sensitivity analysis was performed to evaluate which input affected the result the most.

There were detectable levels of all studied pesticides in the raw water and the drinking water. However, the study concluded that there is no human health risk for long-term consumption of drinking water from Piketberg DWTP and Withoogte DWTP for any of the scenarios. Infants that are formula-fed was the population group that was prone to the highest health risk when exposed to simazine. Adding a GAC-filter resulted in lower concentrations of pesticides in drinking water.

Keywords: QCRA, Pesticides, Atrazine, Imidacloprid, Simazine, Berg River, Piketberg, Withoogte, South Africa, Sensitivity analysis, Health risks, Water treatment

Hälsoriskanalys av bekämpningsmedel i dricksvatten för två dricksvattenverk längs
Berg River i Sydafrika med verktyget QCRA

Masteruppsats inom masterprogrammet Infrastruktur och miljöteknik

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Sammanfattning

Bekämpningsmedel används i stor utsträckning inom den sydafrikanska jordbrukssektorn. Detta görs utan tydliga bestämmelser om tillåten mängd eller vilka bekämpningsmedel som är lagligt tillåtna att använda. Exponering för bekämpningsmedel har erkänts vara ett av de största globala kemiska hoten mot människors hälsa. Vattendrag är ofta omgivna av jordbruksmark och därmed utgör spridning av bekämpningsmedel från dessa marker en risk för vattenmiljön. Berg River är ett vattendrag som omges av jordbruk i Western Cape, Sydafrika. Floden används som råvattenkälla för två vattenverk: Piketberg och Withoogte. Därför kan bekämpningsmedel utgöra en potentiell risk för kvaliteten på dricksvattnet. Följaktligen syftar denna avhandling till att undersöka om långvarig exponering för bekämpningsmedel i dricksvattnet utgör en hälsorisk för människor.

För att utvärdera hälsorisken genomfördes en kvantitativ kemisk riskbedömning. Bekämpningsmedlen; atrazin, simazin och imidakloprid analyserades för olika befolkningsgrupper; spädbarn, barn och vuxna, och inom tre olika scenarier i vattenverken. Dessa scenarier inkluderade normal drift, avsaknad av rening och normal drift med tillägg av granulärt aktivt kol filter, GAC-filter. Fältstudier utfördes vid båda vattenverken där råvatten- och dricksvattenprover samlades in. Återstående indata för modellen sammanställdes genom en litteraturstudie. En känslighetsanalys gjordes för att utvärdera vilken indata som påverkade resultet mest.

Det fanns detekterbara halter av alla bekämpningsmedel i råvattnet och dricksvattnet. Studien kom till slutsatsen att det inte finns någon långsiktig hälsorisk för människor när man konsumerar dricksvatten från vattenverken i Piketberg och Withoogte för något av scenarierna. Spädbarn som förtär mjölkersättning var den befolkningsgrupp som var utsatt för den högsta hälsorisken när de exponerades för simazin. Scenariot där GAC adderades resulterade i lägre koncentrationer av bekämpningsmedel i dricksvattnet.

Nyckelord: Kvantitativ kemisk riskbedömning, Bekämpningsmedel, Berg River, Piketberg, Withoogte, Sydafrika, Känslighetsanalys, Hälsorisker, Vattenrening

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The credibility and the local connection of our thesis would not have been the same without our local supervisors, Chris Swartz and Cordi Lourens, at Chris Swartz Water Utilization Engineers. We are grateful for your continuous support, hospitality and your ability to always solve our problems even if that has led to an extra phone call on your part. Thank you for your guidance and network resulting in field visits and water sampling at the DWTPs. The field visits to the DWTPs have been invaluable and not possible without the help from Wikus Burger at Piketberg DWTP and Garnet Titus at Withoogte DWTP. Thank you for your enthusiasm, cheerfulness and knowledge.

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To Emelie Andersson and Ellen Svärd, who developed the QCRA-model used in this thesis, thank you for leading the way and always answering our questions when needed. Your encouragement has been valuable for us. Furthermore, the quality of our thesis would not have been the same without feedback from our opponent, Frida Byström, thank you. Finally, we would like to express gratitude to our examiner, Professor Sebastien Rauch, at the division of Water Environment Technology. Thank you for taking on our thesis as an examiner and encouraging thesis work abroad.

Mia Engman & Malin Pettersson, Gothenburg, June 2022

List of Acronyms

Below is the list of acronyms that have been used throughout this thesis, listed in alphabetical order:

ADI	Acceptable daily intake
BRIP	Berg River Improvement Plan
BW	Body weight
CEC	Contaminants of emerging concerns
CRA	Chemical risk assessment
DWEL	Drinking water equivalent level
DWTP	Drinking water treatment plant
EU	European Union
GAC	Granular activated carbon
LOAEL	Lowest observed adverse effect level
LOEL	Lowest observed effect level
NOAEL	No-observed adverse effect level
NOEL	No-observed effect level
PoD	Point of departure
QCRA	Quantitative chemical risk assessment
QRA	Quantitative risk assessment
RHP	River Health Program
SADC	Southern Africa Development Community (Angola, Botswana, Comoros, Democratic Republic of Congo, Eswatini, Lesotho, Madagascar, Malawi, Mauritius, Mozambique, Namibia, Seychelles, South Africa, Tanzania, Zambia and Zimbabwe)
SD	Standard deviation
UF	Uncertainty factor
US EPA	United States Environmental Protection Agency
WWTP	Wastewater treatment plant

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1

Introduction

This chapter presents background on pesticide usage in the agricultural sector and its effect on drinking water quality in South Africa. Quantitative Chemical Risk Assessment, QCRA, will be introduced followed by the aim, research questions and limitations of the thesis.

1.1 Background

Contamination of watercourses poses major problems for the society since the consequences could cause long-term effects on human health (Borrull et al., 2021). These pollutants are often referred to as contaminants of emerging concerns, CECs (Borrull et al., 2021; Cantoni et al., 2021). According to Sauvé and Desrosiers (2014) these compounds are persistent, toxic and may have implications for human metabolism. Furthermore, regulatory criteria to safeguard human health is lacking due to the gap in the information associated with the risks of CECs. Different types of chemicals such as pharmaceuticals, industrial chemicals and pesticides may be classified as CECs (Borrull et al., 2021; Cantoni et al., 2021).

Exposure to pesticides has been identified as one of the main chemical threats to human health globally and pesticides are an especially important subject for discussion in countries that rely on agriculture (Degrendele et al., 2022). The use of pesticides within the global agricultural sector has increased from 2.3 million tonnes in 1990 to 4.1 million tonnes in 2018 (FAO, 2021). South Africa relies heavily on agricultural production for export and food security (Quinn et al., 2011). Various types of crops (cultivated plants that are grown commercially) are produced for domestic use and export, such as maize, wheat, sugar cane, citrus and sub-tropical fruits. Over the last five years, South Africa has produced around 15 million tonnes of maize per year which makes them the main maize producer in the Southern Africa Development Community, SADC (International Trade Administration, 2021). As a result, a wide range of pesticides serve as input to this sector and consequently South Africa is the largest consumer of pesticides in sub-Saharan Africa (Dabrowski et al., 2014; Gwenzi & Chaukura, 2018). Despite this, South Africa does not have any publicly available information on the use of pesticides e.g. spray records (Dabrowski et al., 2014).

The benefits of using pesticides are clear, as they enhance output from agricultural production and prevent or mitigate pests which results in higher quality and quantity of crops (Ansara-Ross et al., 2012; Horak et al., 2021). However, the implications that follow have to be investigated further. The case of South Africa is especially interesting as the control of current pesticide compounds is limited (London, Dalvie, et al., 2005). The two most recent pesticide studies based on human health were developed by Dabrowski et al. (2014) and by Dalvie et al. (2009). London, Dalvie, et al. (2005) further explain that the insufficient regulatory standards for pesticides in water are ascribed to the lack of data to serve as support for policy making. Furthermore, regulation of pesticides is not an economic priority nor is there a technical framework for how to analyse pesticides. In addition, enough laboratories with the acquired competence are also missing.

Water pollution by pesticides is an extensively discussed topic as the use of toxicological pesticides can harm aquatic environments and the health of living organisms and humans (Horak et al., 2021; London, Dalvie, et al., 2005; Quinn et al., 2011). The South African water quality guidelines regarding aquatic ecosystems for pesticides are found in DWAF (1996). However, Dabrowski (2011) claims that only the pesticides atrazine and endosulfan are being supervised. As a result, scholars such as Dalvie et al. (2003), Fuhrimann et al. (2021), and London and Bailie (2001) call for policies in South Africa aimed at successful reduction of pesticide contamination. Exposure to pesticides causes chronic health effects and several currently used pesticides are also recognized to be biomagnifying, carcinogenic, neurotoxic or associated with adverse growth effects, disruption of the endocrine system and respiratory problems (Colosio et al., 2003; Degrendele et al., 2022; Quinn et al., 2011). These investigations are not based on long-term exposure through drinking water, which is a field that is not investigated enough. Rather the studies explore exposure from labour within the agricultural sector.

Berg River is a watercourse potentially polluted by pesticides. The river is located in the province Western Cape, close to Cape Town, see Figure 1.1, and its catchment area consists of 53% dryland crops and 7% irrigated crops (DWAF, 2004). Piketberg and Withoogte are the two main drinking water treatment plants, DWTPs, along Berg River. Both the DWTPs employ conventional treatment. Conventional treatment, which includes coagulation, flocculation, sedimentation and rapid gravity sand filtration, with the addition of disinfection is not designed to remove endocrine disrupting compounds such as pesticides (Vieno et al., 2007; Westerhoff et al., 2005). As of today, neither Piketberg DWTP nor Withoogte DWTP measures the concentrations of pesticides in their produced drinking water in their routine measurements. However, measurements of micropollutant levels are conducted once or twice yearly (C. Swartz, personal communication, February 28, 2022).

The DWTPs are using surface water from Berg River as raw water source. To ensure sufficient quality and evaluate potential health risks, a QCRA can be performed. This form of assessment may be conducted on the raw water to evaluate whether pesticides from agriculture may pose a health risk to the consumers of the drinking water from the DWTPs. As the residents around Berg River include infants, children and adults and they respond differently to ingestion of pesticides, it is important to account for different population groups. Earlier studies have been conducted on the health risk posed by pharmaceuticals in Berg River (Andersson & Svärd, 2021). The authors developed a QCRA-model that used raw water data, health data and treatment efficiencies of the DWTPs as input. This thesis will apply that model to evaluate health risks caused by pesticides from agriculture. Moreover, the thesis will be performed in collaboration with Chris Swartz and Cordi Lourens at the consultant company Chris Swartz Water Utilization Engineers, located in Durbanville, South Africa.

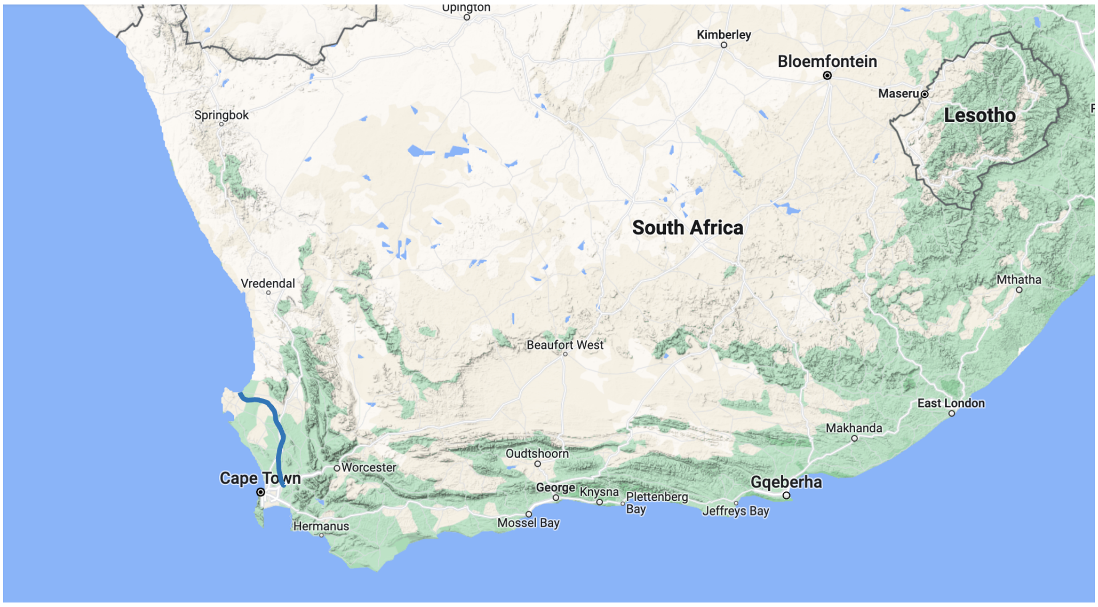

Figure 1.1: Location of Berg River, marked in blue (AfriGIS (Pty) Ltd, 2022).

1.2 Aim

The aim of this project is to evaluate the human health risk caused by long-term exposure to the pesticides atrazine, imidacloprid and simazine through drinking water from two DWTPs, Piketberg and Withoogte, along Berg River, South Africa. The area surrounding Berg River is dominated by agricultural activity, thereby the pesticides are assumed to originate from agriculture. The potential health risks will be evaluated for four population groups; infants formula-fed, infants breastfed, children and adults. By performing a QCRA, a health risk assessment will be conducted. The QCRA will include a sensitivity and uncertainty analysis using Monte Carlo simulations for three potential treatment scenarios for the DWTPs. The thesis will include a field study of the two DWTPs along Berg River where 20 raw water samples and four drinking water samples will be collected and sent for analysis. The four drinking water samples are collected to evaluate the accuracy of the QCRA-model. The thesis will suggest further treatment steps in the DWTPs if the simulation proves that there is a health risk for the consumers.

1.2.1 Research Questions

The following research questions have been identified and will be answered to achieve the aim of the thesis:

- At which concentrations do atrazine, imidacloprid and simazine result in a human health risk for long-term exposure by consuming drinking water?
- Does the drinking water from Piketberg DWTP and Withoogte DWTP pose a health risk to the consumers concerning the analysed pesticides during normal operation (as of today)?
- Is there a risk for human health with regard to pesticide concentration if the DWTPs are lacking treatment due to technical or human error?
- Is the risk for human health with regard to pesticide concentration reduced if the DWTPs have an additional treatment step in the form of granular activated carbon filter, GAC-filter?
- Which input factor has the largest impact on the final drinking water concentration, the drinking water equivalent level and the hazard quotient and thereby contribute to uncertainty for each of the three treatment scenarios?
- How accurate is the QCRA-model and its input data?

1.3 Limitations

The following limitations have been identified:

- The sort and number of laboratory analyses that were available to perform by the University of the Free State in Bloemfontein.
- The thesis does not consider any risks or effects altering the raw quality caused by external impacts. The study only covers the stages of the water cycle from raw water in Berg River to drinking water from the DWTPs.
- The aim of the study is to only consider three identified pesticides from agriculture along Berg River and their potential risk to human health. However, it can not be guaranteed that the three pesticides analysed only originate from agriculture along Berg River.
- The removal efficiencies of Piketberg DWTP and Withoogte DWTP are assumed to be equal and correspond to the results found in the literature.

2

Theory

The following chapter will provide information regarding Berg River followed by theory on agriculture and pesticide use in South Africa. The characteristics and health effects of the pesticides atrazine, imidacloprid and simazine will be provided. Furthermore, the chapter will explain how a general DWTP operates and the technical background regarding GAC-filter. Different standards of health risk assessments will be presented and lastly, a description of how to perform a QCRA will be described.

2.1 Description of Berg River

According to the IWMI (1996), South Africa is one of the countries that will endure physical water scarcity where freshwater availability will be below 1 000 m^3 per capita by 2025. Hence, water resources in South Africa are limited and have to be managed accordingly. Pesticide runoff from agriculture has a negative effect on water quality in surrounding aquatic environments. The state of the raw water quality will have an impact on human health as it is used for drinking water production (Almberg et al., 2018). In addition, even though the drinking water is of good quality, there is a fraction of South Africans who do not have access to drinking water and have to rely on raw water from rivers and boreholes for daily consumption (STATSSA, 2012). The authority further explains that the differences between the provinces are major while Western Cape has one of the best drinking water accesses in South Africa. Hence, good raw water quality is of great importance. One river in Western Cape that serve as raw water source is the Berg River (C. Swartz, personal communication, October 15, 2021).

Berg River, see Figure 2.1 is located in the Western Cape, which is a province in South Africa that sits in the Mediterranean climate zone and acquires winter rainfall (Cullis et al., 2019; Zwane, 2019). The climatic circumstances in the province provide favorable conditions for agriculture. The river begins in the mountains of Franschhoek where the raw water reservoir Berg River Dam is located, see Figure 2.2. The river continues to flow northwest towards Wellington and proceeds towards the western direction of Piketberg and discharges in St Helen Bay on the west coast (DWAF, 2004). The catchment areas of the river serve as a major water supply to the city of Cape Town, provide water for agriculture and serve regional towns with water (Cullis et al., 2019; Görgens & De Clercq, 2006). Berg River, with its length of 300 km, runs through six local municipalities and the catchment area is estimated to 9 000 m^2 (Cullis et al., 2019). The authors further state that rapid urbanisation along Berg River in combination with agriculture has resulted in concerns regarding the raw water quality. This has resulted in the River Health Program, RHP, where Berg River is included. The RHP was initiated in 1994 with the purpose to understand the status and trends of the water resources in Berg River catchment area (DWAF, 2004). One key project identified by the RHP was to construct a dam, Berg River Dam, see Figure 2.2, which serves as a raw water supply for the Western Cape region and ensures the water flow, quantity and quality of the watercourses in the area (Rossouw, 2008). Since 2012, Berg River is also a part of the Berg River Improvement Plan, BRIP, which was initiated by the Department of Environmental Affairs and Developments Planning and The Western Cape Government (Western Cape Government, 2012). The main objectives with the BRIP is to "...Reduce the negative impact from Municipal urban areas..., reduce the negative impact of agriculture on Berg Rivers's water quality to acceptable levels and ensure sustainable resource use efficiency and ecological integrity".

Figure 2.1: Berg River north of Mooreesbug, Swartland.

Figure 2.2: Berg River Dam, located in Stellenbosch municipality.

Piketberg DWTP and Withoogte DWTP are located along Berg River, see Figure 2.3, and uses consequently Berg River as raw water source. There are also four wastewater treatment plants, WWTP, situated upstream the DWTPs along Berg River which release wastewater effluent directly into the raw water source, see Figure 2.3 (DWAF, 2004). Swartz et al. (2020) investigated the quality of wastewater effluent and the results indicated that pesticides are released from wastewater into watercourses despite treatment. However, Berg River is less polluted compared to other rivers in South Africa that are in more critical stages. Berg River is therefore an acceptable option to serve as raw water source (C. Swartz, personal communication, October 15, 2021). Despite that the quality is deemed sufficient, drinking water cannot be produced to satisfy consumption needs if the quantity is deficient (Pegram & Baleta, 2014). As an example, the Western Cape is facing increasing water scarcity. In April 2018 the area of Cape Town suffered from major water scarcity, a scenario referred to as "Day Zero" (Rodina, 2019).

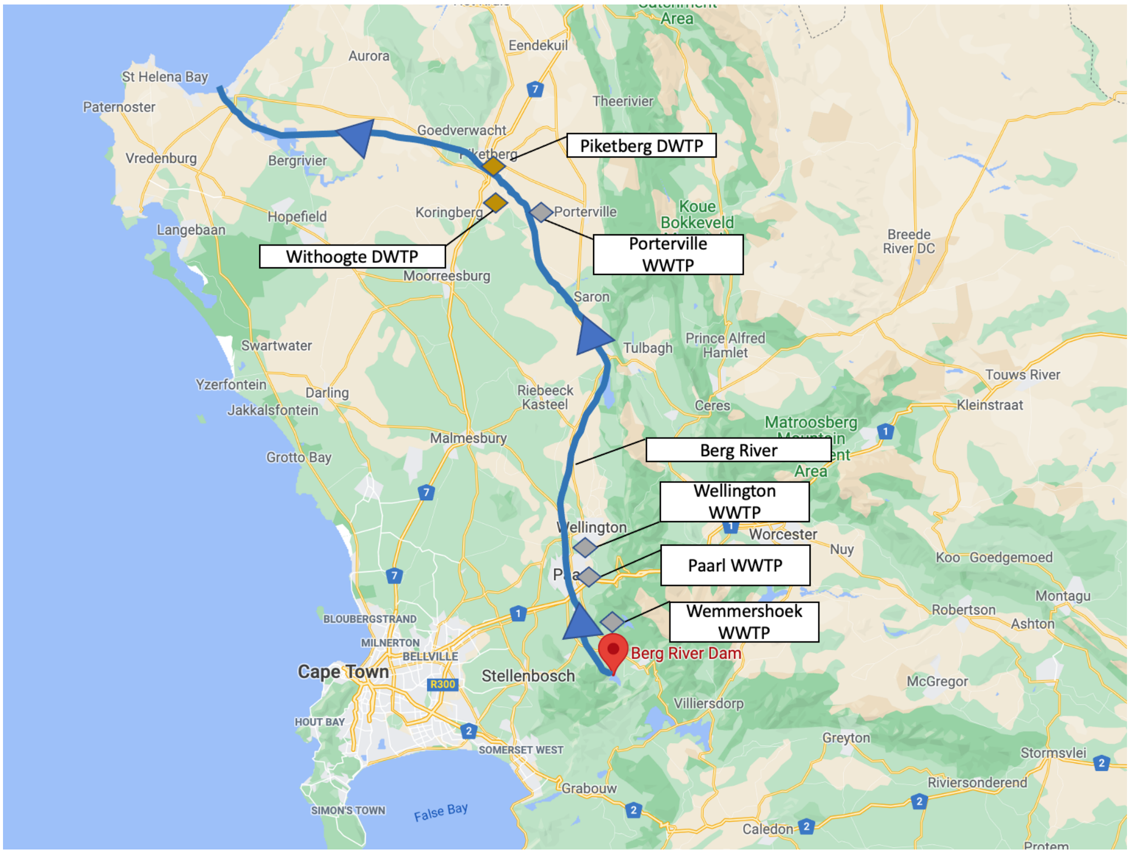

Figure 2.3: Location of Berg River. DWTPs marked in yellow and WWTP marked in grey.

2.2 Agriculture and Pesticides in South Africa

The agricultural sector in South Africa is the sector that consumes the highest quantity of pesticides and over 3 000 different pesticides are currently approved (Dabrowski et al., 2014; Dalvie & London, 2009). Pesticides can be divided into subgroups based on their chemical structure and target organism, e.g. fungicides, herbicides and insecticides (US EPA, n.d.). By killing or incapacitating fungi, fungicides protect plants against fungal diseases and since the 1970s the European Union, EU, has implemented a law that regulates which fungicides are allowed to be produced (Abdollahdokht et al., 2022).

Hand weeding as weed control was substituted by herbicides (LeBaron et al., 2008). As a result, production costs were reduced while agricultural yield increased. In 1930, biological pesticides were introduced to the market whereas the chemical entered in 1947 (Abdollahdokht et al., 2022). The third subgroup, insecticides, is used to prevent insects from engaging in behaviors that may harm the crop (US EPA, n.d.). Insecticides emerged during the second world war and have since been used widely among farmers (Abdollahdokht et al., 2022). In 2009, herbicides accounted for 50% of the sold pesticides in South Africa, fungicides represented 41% and insecticides represented 8% of the total quantity in kilograms (Dabrowski et al., 2014).

The registration of pesticides in South Africa is handled by the Department of Forestry, Fisheries and the Environment, DFFE, while the Department of Health, DOH, is responsible for the approval of the marginal residual limit, MRLs, in agricultural products (Dalvie & London, 2009; Handford et al., 2015). However, the list of approval of MRLs is minimal and has been criticized for not being re-evaluated for many years (Handford et al., 2015). Joemat-Pettersson (2010) states that South Africa has been criticised for being faulty in areas connected to pesticide usage such as surveillance systems, certification to apply pesticides and alternative research on pesticide supplements.

It is important to monitor pesticide usage and application as unintended secondary transport of pesticides may cause damage to ecological and aquatic systems (Ansara-Ross et al., 2012). Pesticides are transported by runoff but also through leachate from soil to watercourses (Dabrowski et al., 2014; Okoya et al., 2020; Syafrudin et al., 2021). Whether pesticides sustain in the environment and pose an increased risk of exposure to human health depends on their characteristics e.g. solubility, persistence and half-life time (Dabrowski et al., 2014). Okoya et al. (2020) discusses that pesticides may enter watercourses through careless disposal of empty pesticide containers or when equipment is washed. Wastewater discharge may also contribute to increased levels of pesticides in the aquatic environment (Münze et al., 2017). There are several examples of pesticide pollution of raw water sources where the levels of pesticides have been sustained through drinking water treatment. Dalvie et al. (2003) exemplifies this in their study on pesticide contamination of raw water and drinking water in the Western Cape. Machete and Shadung (2019) support this and discuss the matter in the context of the province Mpumalanga. Their findings are supported by other studies such as Almberg et al. (2018), Wan et al. (2021), Donald et al. (2007) and Elfikrie et al. (2020) which explore pesticide contamination of drinking water in other parts of the world.

In a study by Mamba et al. (2008) the drinking water guidelines between the Netherlands and South Africa were compared with the notion that the Netherlands is known for its strict standards. The message from this paper was that South African maximum limits were more lenient than the majority of maximum limits within the Netherlands and the EU. Besides, South Africa does not have any limits regulating neither the amount of individual pesticides or the sum of pesticides in drinking water, in contrast to the EU and the Netherlands. The maximum limit for individual pesticide levels and the sum of pesticides are equal for both the EU and the Netherlands. The limits are 0.1 µg/l for individual pesticides and 0.5 µg/l for the sum of pesticides. According to SGU (2020) the threshold limits are also identical to those in Sweden.

2.3 Agriculture and Pesticides along Berg River

Berg River is located in the region Western Cape, which includes 1.9 million ha of agricultural land (Curchod et al., 2020). As illustrated in Figure 2.4 the western part is dominated by grains (dry seeds produced for humans or animals), marked in yellow, while the eastern part is dominated by fruits, marked in red (Waldner et al., 2017; Western Cape Department of Agriculture, 2020). According to the GIS-map produced by Western Cape Department of Agriculture (2020) the area marked as grain produces primarily wheat, followed by canola, lucerne/medics and triticale (a hybrid of wheat and rye) where each field is around 30-90 ha. Appendix A represents an example of how the agricultural land is displayed in GIS. The yellow area with grains also consists of small agricultural patches, 3-15 ha each, such as table grapes, wine grapes, olives, plumes, butternut and guava (Western Cape Department of Agriculture, 2020).

The eastern part is dominated by fruits, primarily wine grapes and table grapes, followed by pears, plums, peaches, nectarines, apples, apricots, persimmons, figs and strawberries (Western Cape Department of Agriculture, 2020). However, there is also some minor agriculture in the form of sweet potatoes, nuts, olives and lemons in the area (Western Cape Department of Agriculture, 2020). The area is represented by fields that are around 2-4 ha, regardless of the fruit. However, the fields with table grapes and wine grapes represent the majority. Berg River and its catchment areas are surrounded by agricultural land where 75 % of the produced crops, mainly wine grapes, fruit and wheat, are exported to EU and the United Kingdom (Western Cape Government, 2012).

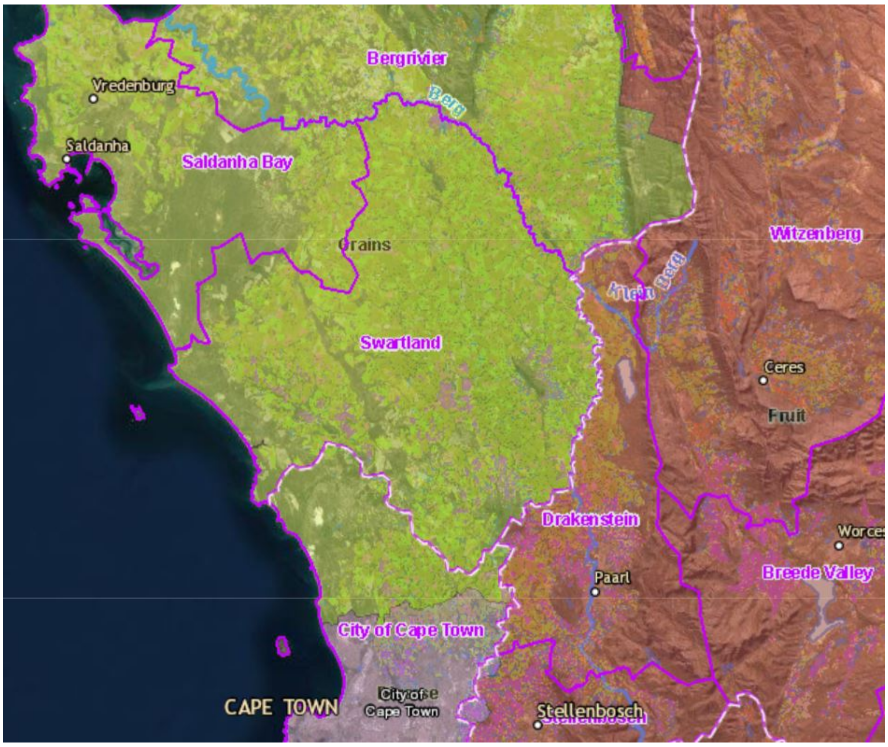

Figure 2.4: Boundaries of the local municipalities and agricultural land distribution along Berg River (marked in light blue) (Western Cape Department of Agriculture, 2020).

The study from Western Cape Department of Agriculture (2020) is supported by Cullis et al. (2019) who has investigated the land use around the Berg River irrigation area in Stellenbosch and Drakenstein municipality, see Figure 2.4. Cullis et al. (2019) state that agriculture in the form of wine grapes represents 102.3 ha of the area, table grapes 45.6 ha of the area, peaches represent 28.3 ha and plums 28 ha. The authors explain that in Swartland, see Figure 2.4, where rain-fed crops are grown, winter grains are represented by 603 ha. This is supported by Curchod et al. (2020) who states that the area around Piketberg (located north of Swartland) and Bergrivier municipality are dominated by grains up to 56% (Curchod et al., 2020).

The study from Curchod et al. (2020) indicates that 82% of the pesticides used in South Africa for wheat, which is highly grown along Berg River, were herbicides. Between 1994 and 1999 the wheat industry used 600 tonnes of pesticides, which is 10% more than the other industries (Dalvie & London, 2009). Previous studies on pesticide contamination of Berg River have been conducted by Curchod et al. (2020), where 35 pesticides were identified that trespassed the limit of quantification, LOQ. LOQ represents the lowest concentration where the pesticide can be quantified at levels with a margin of error. The study found pesticides such as atrazine, imidacloprid and simazine. Hence, pesticide contamination is a troublesome fact considering the fluctuating water availability in the Western Cape (DWAF, 2004). According to Curchod et al. (2020) and their investigation, 23 pesticides were detected that were not reported on the spray records collected by the scholars in the Western Cape.

Dabrowski et al. (2014) investigated which pesticides in South Africa posed the highest risk to human health. This was done by prioritising the pesticides based on the quantity of the pesticide that was used, toxicity potential and the mobility of the pesticide in the environment. These factors were used to calculate the weight hazard potential, which resulted in a list including 69 pesticides that pose a health risk for humans as well as the environment. The list includes several pesticides that were found along Berg River according to Curchod et al. (2020) such as: atrazine (no. 1), imidacloprid (no.9) and simazine (no.14).

Seasonal patterns may affect the concentrations of pesticides in the raw water. The rain period in the Western Cape takes place between April to September when 80% of the annual rain precipitate (Görgens & De Clercq, 2006). Consequently, the concentration of pesticides may be higher in Berg River between October to March, since it has not been diluted by rainfall. However, the spraying season, when pesticides are applied to crops, in South Africa takes place between July to January (Curchod et al., 2020). Hence, the pesticide concentrations that may be found from February to June may be lower than the concentrations that can be found during the rest of the year.

2.4 Selected Pesticides

This section will present general information followed by background information regarding atrazine, imidacloprid and simazine.

2.4.1 General Information Regarding the Chosen Pesticides

Table 2.1 presents a brief explanation of the properties of the pesticides based on the references from the subsections 2.4.2 - 2.4.4. The consequences are based on consumption by humans, however not based on long-term exposure through drinking water.

Table 2.1: Properties of pesticides.

Parameters	Atrazine	Imidacloprid	Simazine
Pesticide type	Herbicide	Insecticide	Herbicide
Chemical formula	$C_8H_{14}ClN_5$	$C_9H_{10}ClN_5O_2$	$C_7H_{12}ClN_5$
Applied for	Wheat, corn, sorghum and sugarcane	Apples, citrus, maize, grapes and wheat	Berries, apples, pears, canola and beans
Consequence when consumed	Adverse births and endocrine disruptive impact	Excessive digestion –> lethal consequences	Endocrine disruption, increased oestrogen levels
Banned in EU?	Yes	Yes	Yes

Table 2.2 is a compilation of the study conducted by Dabrowski et al. (2014). The table illustrates how the total amount of a pesticide has been distributed as a percentage between different crops. The numbers are specific for South Africa and based on investment records for the year 2009, which according to the authors were the latest data they were able to purchase.

Table 2.2: Proportion of pesticide applied to crops according to Dabrowski et al. (2014)

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Pesticide	Apples [%]	Citrus [%]	Maize [%]	Sugar Cane [%]	Table grapes [%]	Wheat [%]	Wine Grapes [%]
Atrazine			87.7	7.5			
Imidacloprid	5.8	68.2	11.5			1.0	
Simazine	0.6	4.2	68.2		12.6		13.8

2.4.2 Atrazine

Atrazine is a herbicide which falls under the category triazine (Hanson et al., 2020; Poulos, 2021). It is sprayed onto the surrounding area of a crop to mitigate the damage caused by broadleaf and grassy weeds (Fegster & Daniels, 2003; Graymore et al., 2001). In 2009, it was the most bought pesticide in South Africa in terms of quantity and there are currently more than 300 pesticide products containing atrazine (Dabrowski, 2015; Hanson et al., 2020). Different products containing atrazine have been created for different purposes and many of these products are created as liquids, sprays and concentrates. These products are used for various types of crops such as wheat, corn, sorghum and sugarcane (Hanson et al., 2020; IUPAC Pesticides Properties DataBase, 2022a).

The herbicide is most effective when it is applied to wet soil, particularly after the winter rain when soils are saturated. The fact that atrazine is applied to saturated soil increases the risk of groundwater leachate and surface runoff (Graymore et al., 2001). Atrazine is a chemical compound that degrades slowly in most conditions by either biological or chemical processes (Miljøministeriet, 2004). The pesticide is a moderately persistent pesticide with a half-life of 75 days (IUPAC Pesticides Properties DataBase, 2022a).

Atrazine is an endocrine disruptive agent and has been banned within the EU (ATSDR, 2003; Bethsass & Colangelo, 2006; IUPAC Pesticides Properties DataBase, 2022a). Atrazine is legal to use in the United States but the regulatory framework concerning atrazine is and has been processed over time, however, it has not generated any prohibition of the pesticide (Bethsass & Colangelo, 2006). Almberg et al. (2018) conducted a study on atrazine contamination of drinking water in Ohio between 2006 to 2008. A correlation was established between atrazine exposure through drinking water and adverse birth outcomes. There was a plausible association between exposure to atrazine and adverse birth outcomes such as toxic effects on fetuses. The scholars suggest that the maximum contamination level of atrazine in drinking water, 3 µg/l, in the United States should be more restrictive to prevent adverse birth outcomes. Other studies also suggest atrazine contamination of drinking water in other parts of the world. For example, Machete and Shadung (2019) explains that detectable levels of atrazine were measured in drinking water collected from the Lomati catchment in South Africa.

2.4.3 Imidacloprid

Imidacloprid is an insecticide often used for apples, citrus, maize, grapes and wheat (Quinn et al., 2011). It is registered for use in South Africa and is used for pest protection of crops to avert losses of agricultural yield (Ahmad Zubairi et al., 2022). The pesticide is not approved for usage within the EU (IUPAC Pesticides Properties DataBase, 2022b). Imidacloprid is a very toxic contaminant that, if spread, can have detrimental impacts on aquatic life and humans (Ahmad Zubairi et al., 2022). It is a systematic insecticide that attaches to the receptors in the brain of the insect and ultimately leads to neurodegeneration even in low concentrations. Hence, the impact of the pesticide is great despite lower doses.

Transportation of imidacloprid is often caused by stormwater runoff which in turn can cause pollution of water bodies. The pollution is exacerbated by the high water solubility of the compound and low soil sorption (Roessink et al., 2013). According to IUPAC Pesticides Properties DataBase (2022b), imidacloprid is persistent in nature and has a half-life of 191 days.

Both Bonmatin et al. (2005) and Whitehorn et al. (2012) explains that studies have found that imidacloprid pollution of sunflowers has had a lethal effect on bees and has ultimately reduced the honey production and the productivity of the bees. For this reason, EU has not renewed the approval of imidacloprid for agricultural activity. Other studies have also found that imidacloprid has had effects on larger animals such as domestic chickens (Franzen-Klein et al., 2020). Furthermore, Proença et al. (2005) investigated cases of human ingestion of imidacloprid which concluded that excessive digestion is deadly for humans. The health implications imidacloprid may have for humans are important seeing as the compound has been detected in raw water and tap water in the province Limpopo, South Africa (Machete & Shadung, 2019).

2.4.4 Simazine

Simazine is an extensively used herbicide that is categorised as a triazine, which is the same group as atrazine belongs to (Gunasekara et al., 2007). There are several differences between simazine and atrazine that contribute to the more far-reaching use of atrazine. Both sorghum and corn are more sensitive to the application of simazine than that of atrazine. In addition, the application of atrazine is less stage-dependent than simazine. Simazine has to be applied before the weeds have developed while atrazine can be sprayed both at the pre-emergence stage as well as the growth stage of the weeds (Cheremisifnoff & Rosenfeld, 2011). The pesticide is mainly used to prevent the growth of broad-leaved weeds and to prevent algae growth in ponds by disrupting the photosynthesis in their target (IUPAC Pesticides Properties DataBase, 2022c; Tahirbegi et al., 2017). It is often applied to fields such as apples, pears and canola (Murray et al., 2010).

The spread of simazine in the environment is a cause of concern as the compound is both water-soluble and moderately persistent with a half-life of 60 days (Comber, 1999; IUPAC Pesticides Properties DataBase, 2022c; Ncube et al., 2012). The pesticide does not tend to sorb to minerals and the likelihood of leaching is high (Gunasekara et al., 2007). Simazine has implications for human health as it may cause endocrine disruptive effects as it has been found to induce increased estrogen production (McKinlay et al., 2008; Sanderson et al., 2000). US EPA (2006) has distinguished simazine as toxic and it is not approved for use in EU (IUPAC Pesticides Properties DataBase, 2022c). Simazine is approved for use in agriculture in South Africa and is used at vineyards (IPW, 2021).

Simazine has been detected in countries all around the world because of its widespread application within the agricultural sector. It has been detected in both surface and groundwater in the United States according to Tierney et al. (2008), however at lower levels compared to atrazine. Simazine was also detected in a study by Loos et al. (2009) where over 100 European rivers were investigated. Furthermore, Machete and Shadung (2019) detected noteworthy levels of simazine in catchment areas in the Free State, South Africa. Hence, there are records of simazine polluting water bodies. Simazine has been detected in drinking water in Extermadura, Spain and Johannesburg, South Africa (Odendaal et al., 2015; Suárez et al., 2003).

2.5 General Drinking Water Treatment Processes

This section will describe the processes of a conventional DWTP, as Piketberg DWTP and Withoogte DWTP are. The section will also describe the processes of disinfection and GAC-filter.

2.5.1 Conventional Treatment

The processes for a conventional DWTP generally includes coagulation, flocculation, sedimentation and filtration (American Water Works Association, 1995; Snyder et al., 2003). When the water enters the DWTP, the first step is coagulation of the water; to add a coagulant, in most cases iron- or alum salt or a synthetic organic polymer (Snyder et al., 2003). The purpose of this is to create small colloidal particles in the raw water that attach, consequently forming flocs and then precipitating as sediment, which often is referred to as flocculation (American Water Works Association, 1995; Piri et al., 2010). Thereafter, the water passes through the sedimentation tanks. The aim of this step is to let the water pass, with a reduced velocity, through a settling basin where the formed flocs, sand, metal, mud or other sediment can precipitate (Piri et al., 2010). To remove the final particles such as colloidal matter and reduce the turbidity in the settled water, the water passes through filters, e.g sand filters, rapid gravity filters or pressure filters (Zhou et al., 2022). The author further explains that microbes can attach to the sand filter, resulting in a biofilm where various organic pollutants may be removed.

In most cases, there is at least one stabilisation step present within the process. The location of stabilisation within the treatment train depends on the design of the process, the pH of the raw water and what other chemicals are being used (C. Swartz, personal communication, March 09, 2022). It is, therefore, more or less strategically wise to place the stabilisation either early in the treatment, late in the treatment or at several different stages.

2.5.2 Disinfection

After the conventional treatment, the water in a DWTP can be disinfected by chlorination. This is conducted to kill pathogens and make sure that the water is prepared to enter the network without causing any health risk to the consumers (American Water Works Association, 1995; Liu et al., 2022). The amount of chlorine that is added to the water is denominated as the total chlorine (Hais-Guide et al., 1995). The author explains further that as the chlorine reacts with ammonium and organic particles in the water, only a certain percentage, around 85-90 % is used for pure disinfection of the water, which is denominated as the free chlorine. When dosing chlorine in DWTPs in Sweden, the maximum dose allowed is 1 mg/l, denoted as total chlorine (Livsmedelsverket, 2005). Furthermore, the produced water that enters the distribution network, can have a maximum concentration of 0.4 mg/l, denoted as free chlorine (Livsmedelsverket, 2005; Svensson, 2014). In contrast to Sweden, there is no set maximum dose for total chlorine in South Africa (C. Swartz, personal communication, May 12, 2022). However, there is a target value for free chlorine that enters the distribution system that can vary between 0.3-0.6 mg/l (Momba & Thompson, 2009).

Instead of using chlorination as a disinfectant, it is common to use Ultraviolet irradiation, UV, or ozonation (Camel & Bermond, 1998; Liu et al., 2022). Generally, ozonation has been more used in Europe while chlorination is more used in the United States (Snyder et al., 2003). Figure 2.5 explains the treatment processes of a DWTP with conventional treatment and disinfection.

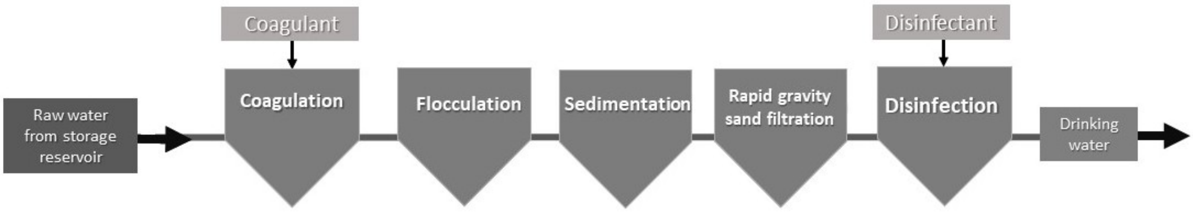

Figure 2.5: Conventional treatment and disinfection of a DWTP.

2.5.3 Granular Activated Carbon

Granular activated carbon filter, GAC-filter, is a treatment step that removes a wide range of organic chemicals from water and is the least costly alternative to better comply with strict quality demands (Acharya et al., 2009; American Water Works Association, 1995; Clark & Adams, 1991). The treatment step is considered to be effective in removing pesticides but also other micropollutants such as natural organic matter and chemicals (Environment Protection and Heritage Council et al., 2008; Moona et al., 2018). The treatment step is designed to filtrate a regulated flow of water through a filter bed of GAC. The GAC adsorbs the pollutants in the water through the microporous surface of the GAC particles, which in combination with the chemical properties enable adsorbent removal (Yuan et al., 2022).

The effectiveness of adsorption largely depends on the surface area and the pore volume of the GAC particles (Jusoh et al., 2011). The surface area usually ranges from 300 to 2 500 m^2/g (Ansari & Sadegh, 2007). Smaller GAC-particles adsorb pollutants quicker as the contact surface for the entire GAC-filter bed is greater (Jusoh et al., 2011). The water within the process must go within the process has gone through pre-treatment steps before filtering through GAC. If none or insufficient pre-treatment is carried through, the filter beds will experience heavy organic load, which eventually will disable the adsorption ability of the GAC particles (Clark & Adams, 1991). For this reason, GAC-filter is often placed after the steps of coagulation and sedimentation. Sufficient pre-treatment will prolong the service life of the filter bed.

The ability of a GAC-filter to adsorb pesticides depend on the chemical interplay between the source of raw water, the pesticide and the sorbate (Hais-Guide et al., 1995). The more humic substances there are in the raw water, the larger the fraction of adsorption surface will be allocated to adsorb these. As a result, other pollutants such as pesticides may not be removed if appropriate pre-treatment is not applied.

2.6 Pesticide Exposure and Associated Health Risk Assessments

It is proven that the extensive use of pesticides leads to pollution of the environment and watercourses around the world (Syafrudin et al., 2021). Pesticides have implications for human health and their nature of exposure may vary (Okoya et al., 2020). Exposure to humans can occur through application exposure, which is an area that has been researched by Dalvie and London (2009) and London, Flisher, et al. (2005). The scholars refer to studies from around the world that conclude that farm workers face serious health consequences because of their work. In addition to physical exposure, ingestion of pesticide residues on agricultural products and contaminated drinking water are other means of exposure that may pose risks to human health (Ansara-Ross et al., 2012; Dalvie & London, 2009). Ansara-Ross et al. (2012) and Machete and Shadung (2019) claim that there is a current information gap connected to pesticide contamination of water and the multifaceted effect of pesticide exposure on human health.

Several different health risk assessments can be conducted to better fill the information gap. A couple of examples of risk assessments are discussed by Rosén et al. (2007). Some of these assessments are directly connected to health risks, such as Quantitative Microbiological Risk Assessment, QMRA, and Human Reliability Assessment, HRA. Other analyses are not intrinsically connected to health as a variable but can be adapted for that purpose, such as Event tree analysis or Failure modes, effects and criticality analysis.

Past studies have used a wide range of methods to determine health risks caused by pesticides in drinking water. In a study by Elfikrie et al. (2020) a health risk assessment was conducted using questionnaires to define the risk of ingestion of pesticides in contaminated water. The questionnaires were subject to statistical analysis and a pre-test to ensure their accuracy. Similarly, W. Dong et al. (2020) conducted a human health risk assessment, associated with both heavy metal and pesticide contamination of drinking water sources. The assessment included both ingestion and dermal exposure and accounted for non-carcinogenic and carcinogenic health effects. As explained by Rosén et al. (2007), health risk assessments are extensively used for quantitative risk assessment and their strength, as well as limitation, are that they commonly focus on a specific substance. To introduce health risk assessments into broader contexts would require a more holistic method.

An example of a more holistic approach is the method of QCRA. The QCRA-model can evaluate the uncertainty of occurrence, fate or hazard of a chemical substance in drinking water and if it may pose a health risk (Cantoni et al., 2021). The scholars further discuss that their study is one of the few pieces of research that applies QCRA in the discipline of drinking water production and consumption.

2.7 Quantitative Chemical Risk Assessment

This section will present a general description of the historical development of a QCRA-model, followed by a short description of the steps included in a QCRA-model.

2.7.1 Historical Development of the QCRA-model

One way to evaluate health risks is to use Quantitative Risk Assessment, QRA. With its systematic and formal method, the QRA can predict the appraisal and consequence of a hazardous event and express the results quantitatively as a risk (Apostolakis, 2004). It is further discussed that a QRA can be applied to most technological solutions such as nuclear power reactors, space systems and water treatment plants. Another method often applied for evaluating health risks connected to chemical substances is Chemical Risk Assessment, CRA (Cantoni et al., 2021).

When combing the QRA with the CRA, a Quantitative Chemical Risk Assessment, QCRA can be applied for evaluating health risks. Compared to a CRA, the QCRA quantifies the probabilistic risk and provides more information since the QCRA uses uncertainty distribution while CRA only uses point values as input (WHO-IPCS, 2018).

The benefit of a QCRA-model is that the whole water supply system (raw water, treatment, distribution) is taken into consideration and that the quality of the drinking water is evaluated (Rosén et al., 2008). Another advantage is that the model includes uncertainties in the calculations and risks in both the exposure and assessment of the chemical (Cantoni et al., 2021). The model can also calculate if the existing treatment processes at the DWTP are sufficient or if an additional treatment step may be implemented. This is favourable to do with a mathematical model such as QCRA since it has a relatively low economical output compared to the alternative of process trials. The drawback with the QCRA-model is the high amount of data that is required and that the person performing the evaluation may require some expert knowledge (Rosén et al., 2007). Environment Protection and Heritage Council et al. (2008) states that a QCRA is based on four steps: hazard identification, dose-response determination, assessment of exposure and risk characterisation.

2.7.2 Hazard Identification

A hazard within a QCRA-model is defined as a chemical agent that has the potential to cause harm (Environment Protection and Heritage Council et al., 2008). Moreover, hazards are usually identified by stakeholders, community members and experts by understanding and systematically reviewing the whole process of a certain event. Hazards may also be identified by brainstorming or check-lists (Rosén et al., 2008).

2.7.3 Assessment of Exposure

Whether or not a chemical substance poses a risk for human health is also dependent on the factor of exposure. Therefore, the main idea with the assessment of exposure is to identify the size and amount of a hazard that the population is exposed to (Environment Protection and Heritage Council et al., 2006). For example, considering drinking water, it is important to establish how high the concentrations of the hazard are in the drinking water. To determine a certain concentration in e.g drinking water, two input parameters are of high importance; concentration in the raw water and how well the DWTP can remove the hazard from the raw water. The assessment includes both intended and unintended exposures of chemical substances that may affect the raw water (Environment Protection and Heritage Council et al., 2006).

2.7.4 Dose-response Determination

To determine the dose-response establishment it is important to account for the relationship between the dose of the hazard and the likelihood of incidence or illness (Environment Protection and Heritage Council et al., 2006; Truhaut, 1991). The authors explain that this can be done by determining the Acceptable Daily Intake, ADI [µg/kg body weight(bw)/day]. ADI represents how much of a substance can be ingested through food and beverages over a lifetime at a daily amount, while still being considered safe. The first step when determining the ADI for a chemical is to decide the point of departure, PoD (Schwab et al., 2005). The PoD is often equal to the highest dose resulting in no-observed effect level, NOEL, or no-observed adverse effect, NOAEL for a specific endpoint. On the contrary, the PoD can also be determined by the lowest dose resulting in an observable effect, LOEL or an observable adverse effect LOAEL. To take uncertainty into consideration and to reduce the PoD to a dose that corresponds to a reasonable certainty that no effect will occur, uncertainty factors may be applied (Environment Protection and Heritage Council et al., 2008; Schwab et al., 2005; Truhaut, 1991). ADI is calculated according to Equation 2.1.

$$ADI = \frac{PoD}{UF1 * UF2 * UF3 * UF4 * UF5} \tag{2.1}$$

where

- PoD = Point of Departure for a substance
- $UF1$ = consider conversion between LOAEL to NOAEL
- $UF2$ = takes the duration of exposure into account
- $UF3$ = handle the interspecies
- $UF4$ = consider intra individual susceptibility
- $UF5$ = consider the general data quality

In cases of chemical exposure through drinking water consumption, the daily consumption of water is decisive and it may also vary depending on the choice of the sample group. When combining ADI, ingestion rate based on population and proportion of the ADI that corresponds to drinking water, the drinking water equivalent level, DWEL, can be calculated. DWEL, represent the 100% exposure of a chemical from drinking water during a lifetime where non-carcinogenic health effect would ever be expected (US EPA, 2012). DWEL can be calculated according to Equation 2.2.

$$DWEL = \frac{ADI * P}{IR} \tag{2.2}$$

where

- ADI = Acceptable daily intake when a substance is considered safe [µg/kg body weight/day]
- P = Proportion of ADI that corresponds to drinking water [%]
- IR = Ingestion rate [l/kg body weight/day]

2.7.5 Risk Characterisation

At the latter stage of the QCRA a risk characterisation is carried through. Hazard identification, exposure assessment and dose-response determination are jointly combined to establish the risk characterisation (Environment Protection and Heritage Council et al., 2006). This step will determine if the consumption of drinking water will pose a health risk for humans concerning long-term chemical substance exposure. This can be done by calculating the hazard quotient, HQ. The hazard quotient compares the exposure concentrations of a pesticide with the DWEL for each population, see Equation 2.3. If the HQ is above one, this indicates that a substance may pose a long-term human health risk for the exposed population (Bokkers et al., 2017; Cantoni et al., 2021; Rezaei Kalantary et al., 2022). Consequently, if the HQ is below one, there is no human health risk associated with long-term exposure to chemical substances in the drinking water for the specific population group. This is the most important result from the QCRA.

$$HQ = \frac{Exposure\ concentration}{DWEL} \tag{2.3}$$

2.7.6 Uncertainty and Sensitivity

When conducting a QCRA it is important to account for variability and uncertainty (US EPA, 2011). The authority explains that since a population is not susceptible in a uniform way to exposure it is important to consider variability. Furthermore, heterogeneity within individuals, time or places results in variability, which is a quantitative description of the spread of values. Uncertainty can be defined as a lack of knowledge of factors that may affect the exposure to risks such as scenario uncertainty, parameter uncertainty or model uncertainty (US EPA, 2011). Sensitivity and uncertainty analysis can be performed on the input data and output mean value, using Monte Carlo Simulations in a spreadsheet software, MS Excel add-in @Risk. This is done to evaluate which input data contributes the most to the main uncertainty and may require more exploration (Bokkers et al., 2017). One way of presenting the uncertainty and sensitivity analysis is to use tornado graphs. The tornado graph illustrates which input parameters that affect the mean output the most and consequently contribute to uncertainty to the output. This is important to know to be able to take necessary measurements regarding the inputs as it will result in output values with big variations. The graph can also demonstrate what the output mean would result in if one of the inputs adopts the highest or lowest input value possible, without that the other input parameters are changed. Appendix B gives an example of how to interpret the tornado graph. To sum up, the sensitivity and uncertainty analysis in the form of tornado graphs is an important result to take into consideration when evaluating risks.

3

Methodology

The methodology for the report will consist of a literature study, a field study of two DWTPs along Berg River moreover the simulation of the QCRA-model to determine the human health risks associated with pesticides in drinking water. The literature study will include reference rivers in South Africa. These values will be compared to the collected field data.

3.1 Field Study: Drinking Water Treatment Plants along Berg River

This section will describe the field study of Piketberg DWTP and Withooghte DWTP along Berg River.

3.1.1 Piketberg DWTP

Piketberg DWTP has been in operation since 1963 and is owned and operated by the Bergrivier municipality (Bergrivier Municipality, 2017). The plant uses Berg River as its raw water source and is designed to produce drinking water for 10 000 citizens in Piketberg (Chris Swartz Water Utilization Engineers, 2017). The design flow of the DWTP is 3 150 m^3/day (W. Burger[1], personal communication, March 15, 2022). Figure 3.1 describes the treatment process of the plant.

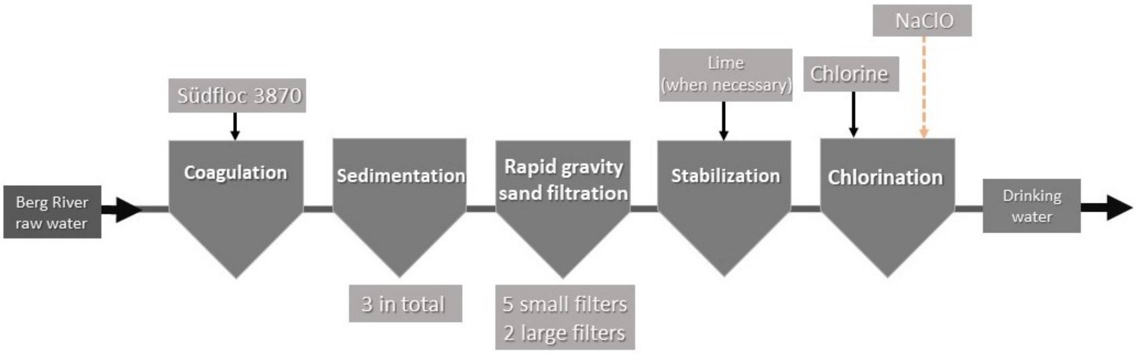

Figure 3.1: Treatment processes in Piketberg DWTP.

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[1] Senior Civil Technician at Piketberg DWTP

The first step within the DWTP is to add a pH-independent polymer coagulant, Südfloc™, see Figure 3.2, for coagulation in the raw water (Chris Swartz Water Utilization Engineers, 2017). The DWTP does not have any flocculation tanks where larger flocs can be formed, due to lack of space. However, the DWTP has a settling tank in which flocs are formed. The retention time in the settling tank is only 40 minutes (Chris Swartz Water Utilization Engineers, 2017). After the settling tank the water enters the vertical and horizontal sedimentation tanks (W. Burger, personal communication, March 15, 2022). Burger further explained that additional flocs continue to be formed in the horizontal sedimentation tank, see Figure 3.3.

The raw water passes through seven parallel rapid gravity sand filters, two larger and five smaller, see Figure 3.4. The sand filters are back washed every second hour (W. Burger, personal communication, March 15, 2022). This rate of backwashing is very frequent compared to other DWTPs and leads to high water losses. However, Piketberg DWTP is improving the settling tanks to reduce the loading on the filters which will ensure longer filter runs and consequently less frequent backwashing (C. Swartz, personal communication, May 04, 2022).

Lime is added to stabilize the final water. Before the water enters the distribution system, it is primarily disinfected with chlorine. However, due to current shortages within the supply, sodium hypochlorite, NaClO, is used instead (W. Burger, personal communication, March 15, 2022). Before the treated water is pumped into the distribution system in the Piketberg area, the water is stored in two low reservoirs (Chris Swartz Water Utilization Engineers, 2017).

Figure 3.2: Addition of coagulant at Piketberg DWTP.

Figure 3.3: Horizontal sedimentation at Piketberg DWTP.

Figure 3.4: Rapid gravity sand filter at Piketberg DWTP.

At least once a day, the operation of the DWTP has to be shut down (W. Burger, personal communication, March 15, 2022). The reason for this is the restricted storage capacity for produced drinking water in combination with design constraints that makes it impossible to regulate the flow through the DWTP. The DWTP is mainly manually operated since the addition of lime and back washing is performed manually while only the addition of coagulant is automated. The DWTP is staffed 24 hours per day. The ordinary measurements of water quality conducted at the DWTP do not include pesticides due to a lack of financial means (C. Swartz, personal communication, March 09, 2022). In South Africa, pesticide analysis is only done at the large plants in the large cities and by the Water Boards (C. Swartz, personal communication, May 04, 2022)

3.1.2 Withoogte DWTP

Withoogte DWTP is located in the north of Berg River and downstream Piketberg DWTP. The plant is designed for a maximum capacity of 45 000 m^3/day while the average capacity is 36 000 m^3/day (G. Titus[2], personal communication, March 09, 2022). Titus further explains that the plant is owned and operated by the West Coast District Municipality and has been in operation for 50 years. The plant provides water for the inhabitants in the municipalities of Swartland, Saldanha Bay and Bergrivier (G. Titus, personal communication, March 09, 2022).

The raw water source for the plant is the constructed Misverstand Dam, situated in Berg River, see Figure 3.5 (G. Titus, personal communication, March 09, 2022). The Misverstand Dam also receives water from a tributary which initiates in Voëlvlei Dam (G. Titus, personal communication, March 09, 2022). The raw water is pumped 16 kilometers from Misverstand Dam to the raw water storage at Withoogte DWTP, see Figure 3.6, during the night due to lower pricing on electricity. An advantage of the raw water storage is the possibility to understand the water quality of the raw water from quality measurements. Thereby can e.g. the chemical dosing and the pH be adjusted according to the raw water quality (G. Titus, personal communication, March 09, 2022). Raw water is also extracted from 15 different boreholes connected to aquifers in the area (G. Titus, personal communication, March 09, 2022). Moreover, these sources of raw water are used when the water levels in the Berg River are low, which especially occurs in the summer. The aquifers are recharged during winter to prepare for future needs.

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[2] Chemical engineer at Withoogte DWTP

Figure 3.5: Misverstand Dam located in Berg River, Swartland.

Before the water enters the coagulation step, lime is added to stabilise the water and adjust the pH, see Figure 3.7 (Chris Swartz Water Utilization Engineers, 2011). The advantage of the coagulant, Südfloc™, is that it is pH-independent and as a result, the addition of lime for pH adjustment is only required at this very first stage. The coagulant is added to remove colour and create flocs, see Figure 3.8 (G. Titus, personal communication, March 09, 2022).

Figure 3.6: Raw water storage at Withoogte DWTP.

Figure 3.7: Lime storage and dosing at Withoogte DWTP.

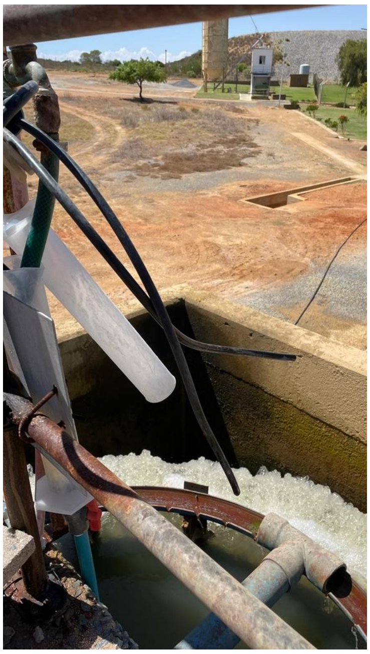

Figure 3.8: Dosing of the coagulant at Withoogte DWTP.

After the addition of the coagulant, the water passes through two different types of sedimentation processes where the flocs may precipitate (G. Titus, personal communication, March 09, 2022). The DWTP has two horizontal sedimentation tanks, see Figure 3.9, and two vertical sedimentation tanks, see Figure 3.10.

Figure 3.9: Horizontal sedimentation at Withoogte DWTP.

Figure 3.10: Vertical sedimentation at Withoogte DWTP.

The next step consists of ten rapid gravity sand filters, which aim to remove turbidity remaining after the settling process (Chris Swartz Water Utilization Engineers, 2011). Before the water enters the distribution network, it is disinfected with chlorine gas. During the winter, the target level for free chlorine residual in the drinking water is 1.6-2.2 mg/l while in summer, the target residual is 0.3-0.5 mg/l (G. Titus, personal communication, March 09, 2022). The plant is considered as semi-automated as e.g. the dosing of lime and control of pH is automated, while the backwash of the sand filters is done manually every 40-50 hours (C. Swartz, personal communication, March 07, 2022). The standard quality measurements performed at the plant do not include pesticide analysis due to economical obstacles (G. Titus, personal communication, March 09, 2022). As mentioned before, pesticide analysis is only done at the large plants in the large cities and the Water Boards (C. Swartz, personal communication, May 04, 2022). Besides, the future plan for the DWTP is to implement chlorine dioxide instead of chlorine as part of the process and deal with the algae problem which is clogging the sand filters. Figure 3.11 explains the processes of the plant.

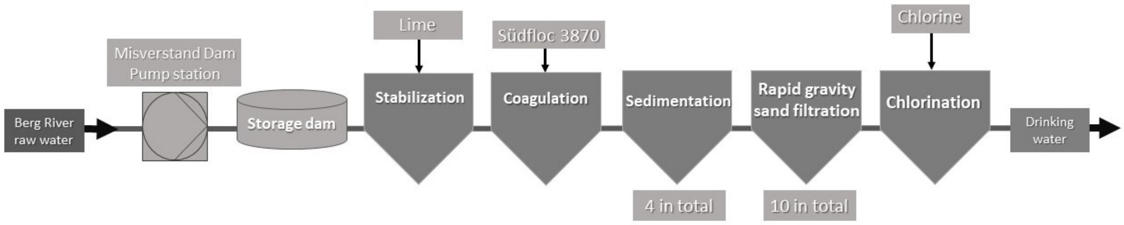

Figure 3.11: Treatment processes in Withoogte DWTP.

3.2 Treatment Scenarios in the DWTP

Three different scenarios were simulated to create a broader understanding of how the variation in risk depended on circumstances. The characterisation of the scenarios is listed in Table 3.1. Raw water concentrations were collected from Piketberg DWTP and Withoogte DWTP, while the raw water concentrations for the reference rivers were found through literature study. The data for each of the sites were simulated for all three scenarios. Hence, the analysis was conducted to understand the health risks for each site based on scenario one, two and three. Furthermore, in this thesis, conventional treatment is referred to as coagulation, flocculation, sedimentation and sand filtration.

For the first scenario, conventional treatment with chlorination was chosen for analysis to cover normal operation at the DWTPs. The second scenario assumed that all treatment in the DWTP was out of order due to technical or human error meaning that the raw water simply passed through the DWTP without any treatment intervention. To implement a constructive measure in case of high pesticide levels in the raw water and if the first scenario proved insufficient, a third scenario was tested. This scenario included conventional treatment and chlorination together with the addition of GAC-filter.

Table 3.1: Scenarios for the DWTP.

Scenario	Treatment process
Scenario 1: Normal operation	Coagulation, flocculation, sedimentation, sand filtration and chlorination
Scenario 2: Lack of treatment	Technical/human error resulting in lack of treatment
Scenario 3: Normal operation with addition of GAC-filer	Coagulation, flocculation, sedimentation, sand filtration, chlorination and GAC-filter

3.3 QCRA-modeling of the DWTPs

The QCRA-model that was used in this thesis was developed by Andersson and Svärd (2021). The model from Andersson and Svärd (2021) was based on the method by Environment Protection and Heritage Council et al. (2008) using the following steps:

- Hazard identification
- Dose-response determination
- Assessment of exposure
- Risk characterisation

The difference between the model from the Environment Protection and Heritage Council et al. (2008) and the model by Andersson and Svärd (2021), is that in the latter model the assessment of exposure is divided into three sub-steps:

- Concentration of pesticides in Berg River
- Removal efficiency in DWTP
- Pesticide concentration in the final drinking water

The Dose-response determination has also been divided into two sub-steps:

- Acceptable Daily Intake, ADI
- Acceptable concentration in drinking water, DWEL

These modifications were applied by Andersson and Svärd (2021) to the QCRA-model used in this thesis to better serve the purpose of evaluating health risks coupled with chemical exposure in drinking water. See Figure 3.12 for the different steps for the QCRA.

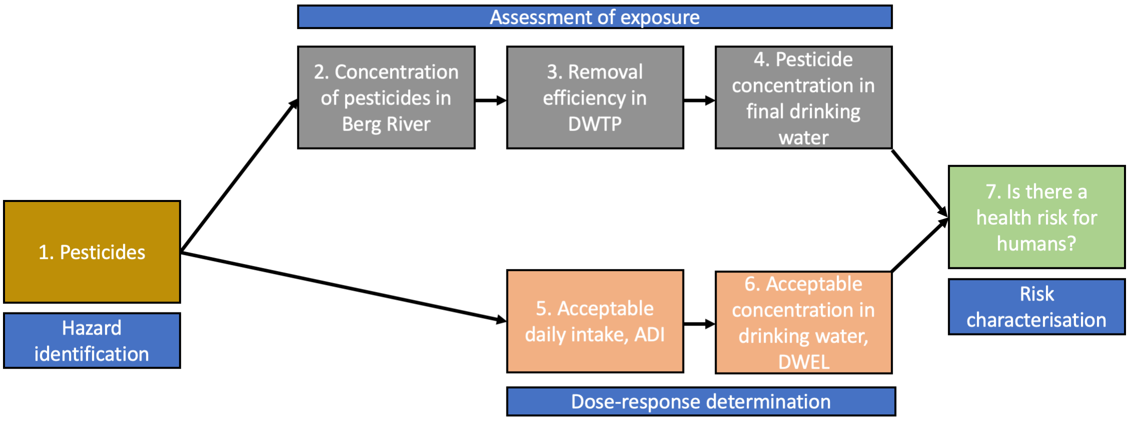

Figure 3.12: Steps of the QCRA-model based on Andersson and Svärd (2021).

The QCRA-model was developed in MS Excel with the unit µg/l as the standard unit for the concentrations. Consequently, all the simulations were performed in MS Excel with results in the unit of µg/l. Based on which distribution represent the input parameter, mean values, standard deviation (SD), minimum, maximum and average values were applied in the model. The advantage of creating a distribution by using two or three input values, instead of using point values, is the possibility to simulate all possible outcomes as the input values are combined in all possible ways. To be able to perform the uncertainty and sensitivity analysis, the program @Risk was used as an add-in to MS Excel.

Since a population is not uniform, the health risk was calculated for four different population groups, see Table 3.2.

Table 3.2: Population groups considered in the model.

Population groups	Age [years]
Infants formula-fed	≤ 1
Infants breastfed	≤ 1
Children	1-10
Adults	20-64

3.3.1 Hazard Identification in DWTPs

From the literature study in Chapter 2 and from consulting Chris Swartz Water Utilization Engineers, who are familiar with the area in the Western Cape, pesticides were identified as a potential hazard for the DWTPs along Berg River and the drinking water quality (C. Swartz and C. Lourens, personal communication, October 15, 2021). This was supported by Bergrivier Municipality (2017), Curchod et al. (2020), and Dabrowski et al. (2014) who discussed the negative effects of pesticides on human health.

To determine which pesticides should be evaluated in the thesis, seven pesticides, see Appendix C were analysed. The selection of the seven pesticides was based on studies conducted in South Africa from Curchod et al. (2020) and Dabrowski et al. (2014). Out of these seven pesticides, atrazine, imidacloprid and simazine were chosen to be evaluated in the thesis. The reason for choosing these pesticides was the fact that they were found at detectable levels in all raw water samples at both DWTPs. The pesticides were also present in five out of six drinking water samples at both DWTPs. The determination of the specific pesticides was also based on the study from Dabrowski et al. (2014) presented in subsection 2.3 and the possibility to find relevant information regarding health data and removal efficiency. Appendix C motivates why the other pesticides were not chosen as a part of the thesis.

3.3.2 Assessment of Exposure

This section describes how the concentration of pesticides in Berg River was determined, how the removal efficiencies in the DWTPs were established by literature study and how the final concentration of pesticides in the drinking water was calculated.

3.3.2.1 Concentration of Pesticides in Berg River and the Final Drinking Water

The concentrations of the pesticides in Berg River and consequently the concentrations at the inlet for the DWTPs were determined by sampling water and conducting analysis at a laboratory. A total of 24 water samples were collected during a five week period between February to March, in which 20 samples were collected from the raw water and four samples were collected from the finalised drinking water, see Table 3.3. Ten samples for raw water and two samples for drinking water were collected for each DWTP.

Table 3.3: Sampling plan.

Sampling week	1	2	3	4	5	9
Sample collectors	Chris, Cordi	Chris, Cordi	Malin, Mia	Malin, Mia	Malin, Mia	
Sampling date	2022-02-22	2022-03-03	2022-03-09	2022-03-15	2022-03-24	
Raw water samples	X	X	X	X	X	
Drinking water samples			X	X		
Sent samples for analysis					2022-04-04	
Received results from analysis						2022-04-21
Other comments			Raw water sampled from Berg River instead of from the raw water inlet			

The flow in Berg River was assumed to be average during all the sampling weeks as there had been no precipitation during the period of sampling (C. Swartz, personal communication, 09 March, 2022). Every week, two raw water samples were collected at the raw water inlet for Piketberg DWTP, see Figure 3.13. At the time of the raw water sampling for week three at Piketberg DWTP, the level in the raw water storage, see Figure 3.13, was too low to collect samples from. This issue was caused by insufficient pumping of the raw water from Berg River to the storage. Therefore, the two raw water samples from Piketberg DWTP were sampled by the process operator directly from Berg River. As a result, the sampling method of these samples differed from the other weeks.

The weekly collection also included two raw water samples from a tap connected to the raw water storage dam at Withoogte DWTP, see Figure 3.14. Before the raw water samples were collected at Withoogte, the water was left to run for 30 seconds in order to not collect stagnated water from the pipe. This resulted in a total of ten raw water samples at each DWTP.

Figure 3.13: Sampling of raw water at Piketberg DWTP.

Figure 3.14: Sampling of raw water at Withoogte DWTP.

One sample for week three and one sample for week four of the drinking water were collected at Piketberg DWTP, see Figure 3.15 and at Withoogte DWTP, see Figure 3.16. This resulted in four water samples of produced drinking water, see Table 3.3. The drinking water samples were collected approximately 30 minutes after the raw water samples were collected. Before the water was sampled at Piketberg DWTP, the water was left to flow for 30 seconds.

Figure 3.15: Sampling of drinking water at Piketberg DWTP.

Figure 3.16: Sampling of drinking water from Withoogte DWTP.

All water samples were collected in 500 ml plastic bottles. The water samples for week one and two were sampled by Chris Swartz and Cordi Lourens, employees at Chris Swartz Water Utilization Engineers. For the remaining weeks the sampling was collected by the authors of this thesis. However, the same procedure was used for all samples. For week one to three, the water samples were stored in a portable electrical cooling box, -4° to -8°C, during transportation until the samples could be placed in the freezer at the office of Chris Swartz Water Utilization Engineers until the date for analysis. For week four to five, the samples were retained in a cooling bag with ice packs, see Figure 3.17, keeping a temperature between 10°-20°C, before they could be frozen with the other samples at -21°C at the office. There were two raw water samples from Withoogte DWTP, sampled during week two, which did not freeze despite being stored at the same temperature as the other samples.

The frozen samples were transported between Durbanville and Bloemfontein, where the analysis was performed, by aircraft overnight by the company The Courier Guy. The water samples were packed together with ice packs and bubble wrap and insulated within a polystyrene container to keep the samples frozen during transport, see Figure 3.18. The samples were sent for analysis on the 4th of April and the results were received on the 21th of April. The pesticide analysis was conducted at the University of the Free State in Bloemfontein in the laboratory department. According to Dr. Gabre Kemp at the University, the water samples arrived in good condition. The analysis was conducted by Dr. Kemp and the method in which he used was developed by himself and based on the publication by Odendaal et al. (2015). For more detail on the method of the lab analysis, see Appendix D.

Figure 3.17: Sampling bottles, cooling bag and ice packs.

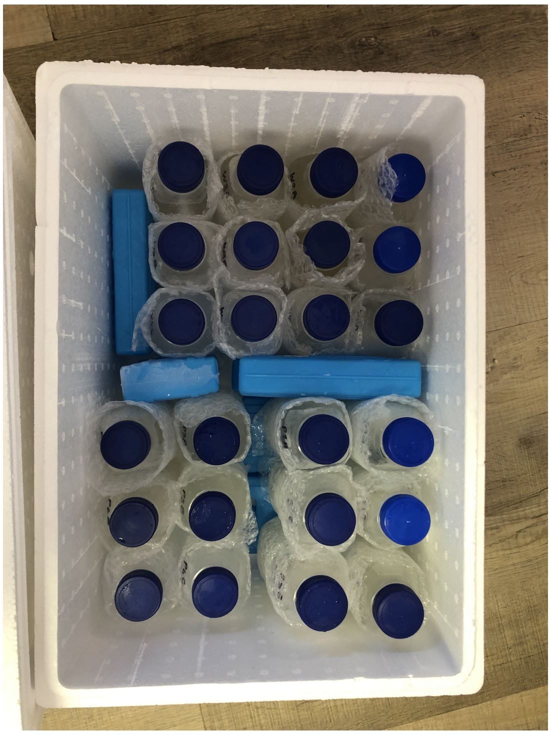

Figure 3.18: Samples and ice packs in a polystyrene container.

Cantoni et al. (2021) performed a QCRA on Bisphenol A where they conducted simulations in Python to adjust the distribution of Bisphenol A in accordance with how it behaved in the environment, which resulted in log-normal behaviour. Bisphenol A is, similarly to pesticides, an industrially produced chemical compound that belongs to the group CECs. The log-normal behaviour of substances in raw water in the environment was also supported by Gurian et al. (2004). Therefore, the distribution of the pesticide concentrations in the raw water was assumed to be log-normal. An illustration of how log-normal distribution behaves can be found in Appendix E, Figure E.1.

To be able to compare the concentrations of pesticides in Berg River, reference rivers for the different pesticides were also used as input in the QCRA-model. The reference river used for atrazine, Upper Vaal River, is located in the provinces Northern Cape, North West and Gauteng (Swartz et al., 2020). The concentrations presented are based on two water samples collected between March 2019 to March 2021. There are four DWTPs as well as three WWTPs along the river.

Concentrations of imidacloprid and simazine were investigated by Machete and Shadung (2019). The samples were collected in September 2012 for imidacloprid and in January and April 2013 for simazine. Detectable levels of imidacloprid were found in the Mzinti River, in the province Mpumalanga. The samples were collected in September 2012. Simazine was sampled in the Vals and Renoster catchments which include the Vals River and the Renoster River. These rivers are located in the Free State province. The raw water concentrations for the reference rivers can be found in Appendix F, Table F.1.

3.3.2.2 Removal Efficiency in DWTPs

Removal efficiency for each pesticides and per treatment step was obtained from a literature study and served as input to calculate the total removal efficiency for the different scenarios. The removal efficiency and treatment processes in Piketberg DWTP as well as in Withoogte DWTP were assumed to be equal. In the model from Andersson and Svärd (2021) the treatment efficiency for coagulation/flocculation, sedimentation and rapid gravity sand filtration, referred to as conventional treatment, was assumed to be combined. The removal efficiency for chlorination and GAC-filter were presented separately. The removal efficiency and the assumed distribution for the different processes for respective pesticides are presented in Table 3.4. Since no specific distribution for conventional treatment nor chlorination was found for the chosen pesticides, a uniform or triangular distribution was used instead (Hesse, 2000). The scholar explained that for the cases where only the minimum and maximum removal efficiencies were to be found, a uniform distribution could be assumed, which will be done in this report. In the case where minimum, maximum and mean value of the removal efficiencies were found, PERT distribution, which is a type of triangular distribution, was used (RiskAMP, n.d.). The removal distribution for pesticides in GAC-filter was assumed to be uniform (Alves Pimenta et al., 2020). The study only investigated atrazine and simazine, however, the assumption regarding uniform distribution was applied to all pesticides. Illustrations of uniform distribution and triangular distribution can be found in Appendix E, Figure E.2 and Figure E.3.

In a study from Thuy et al. (2008), surface water from Dijle River in Belgium and distilled water was treated for atrazine (10 µg/l) by the coagulant alum in different concentrations in a jar test using conventional treatment. The result indicated that with no coagulant, 43% of the atrazine was removed with conventional treatment. With 100 mg, 200 mg and 300 mg of added coagulant, the removal efficiency resulted in 30%, 14% and 7% respectively. The fact that the effect of a coagulant is reversed for atrazine, is expected due to known charge reversal behaviour of coagulation (Thuy et al., 2008). A study performed at a DWTP in Spain using the Ebro River as a raw water source evaluated each step of the conventional water treatment plant, which has an addition of GAC-filter (Borrull et al., 2021). The plant uses iron, Fe, and diallyldimethyl ammonium chloride homopolymer, polyDADMAC, as a coagulant (Borrull et al., 2021). The study concluded that conventional treatment resulted in an addition of atrazine of 2.2%. The addition of atrazine may be caused by the coagulant, as discussed above (Thuy et al., 2008). The study sampled water between every process in the DWTP, and the highest value the study found where used when calculating the removal efficiencies used in this thesis. With these values as a base, the removal efficiency for conventional treatment of atrazine was assumed to be triangular. The values from the study by Borrull et al. (2021)

which assumed an increase of atrazine were disregarded since Piketberg DWTP nor Withoogte DWTP uses the combination of Fe-coagulants and polyDADMAC. Consequently, the minimum removal efficiency was set to 0%, the maximum removal was set to 30% and the mean removal efficiency was set to 10.5% ((7+14)/2), see Table 3.4.

The study from Borrull et al. (2021) concluded that only using chlorination and sodium hypochlorite, resulted in a 7% removal of atrazine. The removal efficiency for chlorination is assumed to correspond well to the removal efficiency at Piketberg DWTP and Withoogte DWTP since sodium hypochlorite is also used there. A study where 2 mg/l of free chlorine was added to drinking water, resulted in no significant removal of atrazine (Jiang & Adams, 2006). A third study conducted on a river in Spain, Llobregat River, evaluated the removal efficiency between February to August in a DWTP by adding 100 mg/l of the compound to the plant and measuring between every removal step (Rodriguez-Mozaz et al., 2004). The study concluded that the average removal by chlorination resulted in 25%. These values were set to represent the minimum, average and maximal removal of atrazine for chlorination, and consequently, the distribution was set to triangular, see Table 3.4.

The removal efficiency for atrazine in a GAC-filter in a study where analytical standard and commercial product of atrazine were mixed with synthetic water, resulted in a 99.12% removal (Alves Pimenta et al., 2020). The study from Borrull et al. (2021) concluded that the efficiency when only using the GAC-filter resulted in a removal efficiency of 34%. A study from Ormad et al. (2008) conducted on the Ebro River basin in Spain evaluated the removal efficiency for different pesticides with activated carbon adsorption, referred to as GAC-filter in this thesis. The study concluded that the removal efficiency was 55%. The values from Borrull et al. (2021) and Alves Pimenta et al. (2020) were used as the minimum and maximum removal efficiencies in the uniform distribution for removal with GAC-filter, see Table 3.4.

Concerning imidacloprid, it was also evaluated by Borrull et al. (2021). According to their study, the removal efficiency for conventional treatment resulted in 5.9%. Another study from H. Dong et al. (2021) concluded that 19.3% of imidacloprid was removed with conventional treatment. These values were used as the minimum and maximum values for the uniform distribution, see Table 3.4.

The removal efficiency when only using chlorination resulted in a 100% removal of imidacloprid (Borrull et al., 2021). A study from (Klarich et al., 2017) concluded that chlorination with hypochlorous acid at the DWTP at the University of Iowa removed 18.28%. Despite that Piketberg DWTP and Withoogte DWTP applies another substance for chlorination, sodium hypochlorite, it was assumed that the same removal efficiency may be applied. The minimum value for the removal efficiency was therefore set to 18.28% and the maximum removal was set to 100% for the uniform distribution, see Table 3.4.

Only using GAC-filter resulted in 92.75% removal of imidacloprid, which was used as the maximum removal efficiency for the uniform distribution (Borrull et al., 2021). The removal efficiency in a DWTP in Iowa City resulted in a removal efficiency of 80% using GAC-filter (Klarich et al., 2017). These values were used as indata for the uniform distribution in the model, see Table 3.4.

Regarding simazine, the removal efficiency for conventional treatment resulted in an addition of 21.96% according to the study from Borrull et al. (2021). As mentioned earlier, values that indicated an increase of a pesticide were disregarded due to that Piketberg DWTP and Withoogte DWTP does not use the same coagulants as the DWTP in the study from Borrull et al. (2021). Therefore, the minimal removal efficiency was set to zero. Since no other value for removal efficiency when only using conventional treatment for simazine was found, the maximum value for removal of atrazine was used. Atrazine and simazine are very similar and belong to the same triazine group. Therefore, the maximum removal efficiency was equal to 30% (Borrull et al., 2021), see Table 3.4.

If only chlorination was to be used, 100% of the simazine would be removed (Borrull et al., 2021). Another study discussed above, (Rodriguez-Mozaz et al., 2004) concluded that chlorination removed 29.31% of simazine. These values were used as minimum and maximum for the uniform distribution, see Table 3.4.

The study of Borrull et al. (2021) also included simazine. When only using GAC-filter, 65% of the simazine was removed. Alves Pimenta et al. (2020) indicated a removal efficiency of 98.3% when using GAC-filter. The study from Ormad et al. (2008) concluded that the removal efficiency for GAC-filter were 55%. As a result, the minimum value for the removal efficiency was determined to 55% while the maximum was determined to 98.3%, see Table 3.4.

Table 3.4: Removal efficiency for atrazine, imidacloprid and simazine based on treatment processes.

Pesticide	Statistics	Conventional treatment [%]	Chlorination [%]	GAC-filter [%]
Atrazine	Min; average; max	0; 10.50; 30	0; 7; 25	34; -; 99.12
	Distribution	Triangular	Triangular	Uniform
Imidacloprid	Min; average; max	5.90; -; 19.30	18.28; -; 100	80; -; 92.75
	Distribution	Uniform	Uniform	Uniform
Simazine	Min; average; max	0; -; 30	29.31; -; 100	55; -; 98.30
	Distribution	Uniform	Uniform	Uniform

3.3.2.3 Pesticide Concentration in Final Drinking Water

To calculate the final exposure concentration for the consumers of atrazine, imidacloprid and simazine, Equation 3.1 was used. Since scenario two did not include any treatment, the concentration of the final drinking water was equal to the concentration in the raw water for all pesticides.

$$Exposure\ concentration = C_{raw\ water} * (1 - \frac{TE_1}{100}) * (1 - \frac{TE_2}{100}) * (1 - \frac{TE_3}{100}) \quad (3.1)$$

where

- $Exposure\ concentration$ = Concentration in drinking water [µg/l]
- $C_{raw\ water}$ = Concentration of atrazine, imidacloprid and simazine in the raw water [µg/l]
- $TE1$ = Removal efficiency by conventional treatment [%]
- $TE2$ = Removal efficiency by chlorination [%]
- $TE3$ = Removal efficiency by GAC-filter [%]

3.3.3 Dose-response Determination of the Chosen Pesticides

This section will describe the procedure for determining the ADI and the DWEL.

3.3.3.1 Acceptable Daily Intake of the Pesticides

Three different ADIs were compiled:

- ADI based on PoD from literature and calculated with Equation 2.1, denoted as ADI from toxicological data.

- ADI taken directly from the literature study denoted as ADI from literature.

- ADI based on a combination of the calculated ADI and the theoretical ADI, see Figure 3.19. These ADIs were used to perform a distribution of the ADI that was used in the QCRA-model, denoted as simulated ADI.

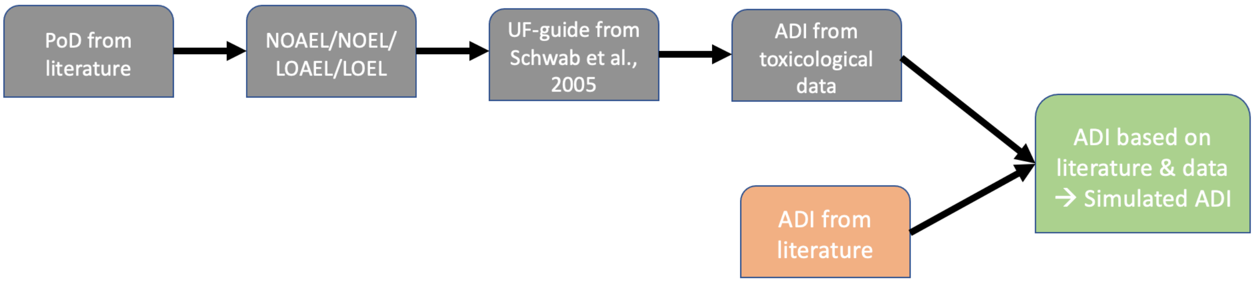

Figure 3.19: Process for the determination of the simulated ADI.

To determine the ADI based on toxicological data for each pesticide, the PoD had to be determined. This was carried through by researching journal articles to compile relevant health data in the form of NOAEL, LOAEL, NOEL or LOEL for each pesticide, see Table 3.5. The found health data was never based on humans but rather on different animals. If NOAEL or LOAEL values were found, these values were chosen as they are considered more reliable and consider the "adverse" effect.

Regarding atrazine, a study investigated 30 female rats and 30 male rats from the company Charles River, that were fed orally with technical atrazine (97%) (Miljøministeriet, 2004). The study concluded that a reasonable NOAEL value was 3 700 µg/kg bw/day. The male rats were fed with different dosage per day; 0, 800, 3 800, 39 000 µg/kg bw/day while the female rats were fed with 0, 900, 3 700, 43 000 µg/kg bw/day. The endpoint resulted in decreased body weight and food consumption. The length of the study was not presented. This value is denoted as NOAEL in Table 3.5. A study from ATSDR (2003) concluded that a LOAEL for a pig was 1000 µg/kg bw/day. The study was conducted on cross-bred Swedish and German Landrace pigs which received 2 mg of atrazine per body mass for 19 days. The endpoint for the pig was hormone disruption. This value is denoted as LOAEL 1 in Table 3.5. The last point of departure, a LOAEL value, for atrazine was found in the report from Miljøministeriet (2004). The report investigated rats where the endpoint resulted in decreased body weight and food consumption in parental animals. The LOAEL resulted in 39 000 µg/kg bw/day, denoted as LOAEL 2 in Table 3.5.

The health data for imidacloprid was extracted from three different papers. In the study by Franzen-Klein et al. (2020) domestic chickens were probe fed with increasing quantities of imidacloprid continuously over one week. The study group included both males and females of different ages; six and nine weeks of age. Neurobehavioural abnormalities were observed such as depression, muscle twitches and disorganised coordination. Furthermore, the scholars determined the NOAEL value to 3 420 µg/kg bw/d, denoted as NOAEL 1 in Table 3.5 and LOAEL to 10 250 µg/kg bw/d, denoted as LOAEL in Table 3.5. This was done by applying mean clinical severity scores. Studies on how the exposure of imidacloprid affected rats was conducted according to European Chemicals Agency (2015). Detail on the duration of the study was not provided. Rats were fed imidacloprid and reproductive disturbances were observed as a result of the pesticide exposure. The level at which these issues occurred was at a NOAEL measuring 50 000 µg/kg bw/d. In a neurotoxicity study, the effect of imidacloprid on rats was assessed (ESFA, 2008). The duration of the study was 90 days. A NOAEL of 9 300 µg/kg bw/d, denoted as NOAEL 3 in Table 3.5, was determined based on decreased body weight and reduction in the function of the observation battery, which is a method for determining gross sensory and motor deficits.

The NOAEL for rats who were exposed to simazine was 10 000 µg/kg bw/d according to Miljøministeriet (2004), denoted as NOAEL 1 in Table 3.5. The test species was fed increasing doses of simazine during 13 weeks. In addition, the second NOAEL, denoted as NOAEL 2 in Table 3.5, is extracted from the same paper, however, the experiment investigates dogs instead. The value of NOAEL was established at 700 µg/kg bw/d.

Table 3.5: Health data for the chosen pesticides.

PoD	Value [ug/kg bw/day]	Animal	End point effect	Duration	Source
Atrazine					
NOAEL	3 700	Rat	Decreased body weight and food consumption	n.d	Miljøministeriet (2004)
LOAEL 1	1 000	Pig	Hormone disruption	19 days	ATSDR (2003)
LOAEL 2	39 000	Rat	Decreased body weight and food consumption	n.d	Miljøministeriet (2004)
Imidacloprid					
NOAEL 1	3 420	Chicken	Dose dependent neurobehavioural abnormalities	1 week	Franzen-Klein et al. (2020)
NOAEL 2	50 000	Rat	Complication with reproduction	21 days	IUPAC Pesticides Properties DataBase (2022b)
NOAEL 3	9 300	Rat	Decreased body weight & effects in the functional observational battery	90 days	Kontiokari and Mattsoff (2011)
LOAEL	10 250	Chicken	Dose dependent neurobehavioural abnormalities	1 week	Franzen-Klein et al. (2020)
Simazine					
NOAEL 1	10 000	Rat	Decreased body weight and food consumption	13 weeks	Miljøministeriet (2004)
NOAEL 2	700	Dog	Reduced weight gain and red cell blood cell parameters	n.d	Miljøministeriet (2004)

After the determination of the PoD, uncertainty factors were applied to each PoD-value for each pesticide according to Appendix G, Figure G.1 based on Schwab et al. (2005). The applied uncertainty factors for the chosen health data with a justification are presented in Appendix G, Table G.1 to Table G.3. The ADI based on toxicological data was calculated according to Equation 2.1.

ADI from literature was compiled by conducting a literature study. A comparison between the toxicological ADI and ADI based on literature was performed. A minimum and maximum value for the ADIs were selected and the mean value for ADI was calculated for each pesticide. The minimum, maximum and mean values of the ADI were used as a triangular input in the QCRA-model to create a distribution of the simulated ADI. A triangular distribution was used due to the uncertainty associated with the behaviour of the ADI distribution (Hesse, 2000), see Appendix E, Figure E.3 for an illustration of the distribution. Converting the point values (minimum, maximum and average) of the ADI into a distribution results in the possibility to get a wider understanding of how the values for ADI may differ. The $5^{th} - 95^{th}$ percentile was determined to get an understanding of the uncertainty. By converting the point values into a distribution, a mean value and standard deviation of the simulated ADIs can be determined. The mean values of the simulated ADIs were then used to calculate the corresponding DWEL for each pesticide.

3.3.3.2 DWEL of the Pesticides

The second step within the Dose-response determination was to determine the DWEL value for each pesticide. Three different DWEL values were compiled:

- Theoretical DWEL taken directly from the literature study denoted as theoretical DWEL
- DWEL calculated with Equation 2.2 in the QCRA-model based on the mean values for the simulated ADI, denoted as simulated DWEL
- DWEL based on points values from literature and a mean value of the ADI based on literature, denoted as DWEL point values literature. Calculated with Equation 2.2

Regarding the ingestion rate, US EPA (2012) inform that the daily drinking water consumption for an adult of 70 kg is 2 l/day while a child of 10 kg is assumed to consume 1 l/day. This represents an ingestion rate for children of 0.1 l/kg bw/day (1 l/day and 10 kg body weight) while IR for adults corresponds to 0.029 l/kg bw/day (2 l/day and 70 kg body weight), see Table 3.6. US EPA (2019) and US EPA (2012) reports about another ingestion rate, based on tap water (both sexes combined) for different population groups, see Table 3.6. The normal and log-normal distributions were determined by US EPA (2019) and US EPA (2012) and can be found in Appendix E, Figure E.1. South Africa on the other hand, does not have any records regarding the ingestion rate of tap water. The ingestion rate varies depending on which community you live within (C. Swartz and C. Lourens, personal communication, April 04, 2022).

Table 3.6: Ingestion rate of tap water based on population.

Population exposed	Distribution	Statistics	Ingestion rate [l/kg bw/day]	Source
Infants formula fed	Normal	Mean	0.146	US EPA (2019)
		SD	0.24	
Infants breast fed	Log-normal	Mean	0.0435	US EPA (2019)
		SD	0.0425	
Children (ages 1-10 yr)	Log-normal	Mean	0.0355	US EPA (2019)
		SD	0.0229	
Adults (ages 20-64 yr)	Log-normal	Mean	0.0199	US EPA (2019)
		SD	0.0108	
Children	Point value	-	0.100	US EPA (2012)
Adult	Point value	-	0.029	US EPA (2012)

The percentage of the ADI for a pesticide that enters the human through drinking water can vary between 1-80% (World Health Organization, 2011). However, the authority states that an allocation to ADI of 10% represents a conservative assessment of the risk and therefore the allocation to ADI of 20% is often used. The allocation of ADI connected to pesticides in drinking water was expected to be 20%, while the rest is expected to enter through other origins, e.g. ingestion of food that contains pesticide residues (Hamilton et al., 2003). To consider a variety of the population, 10-20% of the allocated percentage of ADI for drinking water was selected for children and adults. Infants, on the other hand, were assumed to have a higher percentage of ADI for drinking water, between 40-50% since they consume a lot of drinking water in their daily diet. The percentage of pesticides connected to ADI when consuming drinking water and the corresponding distribution for each population is presented in Table 3.7. The choice of a uniform distribution for the values from Hais-Guide et al. (1995) and World Health Organization (2011) was done according to Hesse (2000).

Table 3.7: Percentage of drinking water related ADI for different pesticides.

Population exposed	Distribution	Percentage (min, max) [%]	Source
Infants formula fed	Uniform	40,50	-
Infants breast fed	Uniform	40,50	-
Children (ages 1-10 yr)	Uniform	10,20	Hamilton et al. (2003) and World Health Organization (2011)
Adults (ages 20-64 yr)	Uniform	10,20	Hamilton et al. (2003) and World Health Organization (2011)
Children	Point value	20	Hamilton et al. (2003)
Adult	Point value	20	Hamilton et al. (2003)

The theoretical DWEL was compiled by a literature study. The simulated DWEL was determined by Equation 2.2. The ADI was based on the mean values of the distribution for the simulated ADI. Regarding the ingestion rate for South Africa, the lower ingestion rates, with normal and log-normal distributions, according to US EPA (2019) were used (C. Swartz and C. Lourens, personal communication, April 04, 2022). For the proportion allocated to ADI, the values of the uniform distribution were used.

For the DWEL based on point values from the literature, the ADI was based on the average ADI based on literature. The ingestion rate was based on the point values from US EPA (2012) in Table 3.6 and the percentage of drinking water related to ADI based on the point values from Hamilton et al. (2003), see Table 3.7.

Both the theoretical DWEL and DWEL based on literature were determined to be able to compare with the simulated DWEL. Neither the theoretical DWEL nor the DWEL based on literature was performed as a distribution.

3.3.4 Risk Characterisation of the Pesticides

To determine if there was a human health risk for the consumers, the Hazard quotient, HQ, for each pesticide was calculated according to Equation 2.3. Two different HQ were calculated:

- HQ based on the calculated DWEL, with a sensitivity and uncertainty analysis, denoted as HQ simulation.

- HQ based on DWEL point values from literature, without sensitivity and uncertainty analysis, denoted as HQ based on point values.

This calculation that results in the determination of whether or not the pesticides pose a health risk is the most important result.

3.3.5 Uncertainty and Sensitivity Analysis

A total of 10 000 Monte Carlo simulations with the add-in program @RISK in MS Excel were performed for each calculation where all the inputs were randomly combined with their estimated statistical distribution (Cantoni et al., 2021). With help from the 10 000 simulations for each calculation, an uncertainty and sensitivity analysis that was presented in the form of tornado graphs could be done. The uncertainty and sensitivity analysis were performed on the inputs for the simulated DWEL, exposure concentrations and the simulated HQ.

3.3.6 Accuracy of the QCRA-model

To determine the accuracy of the model, the concentrations in the final drinking water based on the lab analysis were compared with the concentrations in the drinking water based on the QCRA-model. Despite that only two samplings occasions for the drinking water took place, the average concentration was compared to the concentration based on the QCRA-model. This since for a long period of time, the concentration that the population groups will be exposed to will most likely be a combination of low and high concentrations, consequently an average value. If the exposure concentrations from the lab analysis and those calculated by the QCRA-model are of the same order of magnitude, the model is assumed to be accurate and reliable.

The accuracy of the model was also controlled by comparing the applied removal efficiencies based on the literature study with the actual removal efficiencies at Piketberg DWTP and Withoogte DWTP. The removal efficiencies for Piketberg DWTP and Withoogte DWTP was calculated by comparing the average raw water concentration for week three and four with the final drinking water concentrations for week three and four. The removal efficiencies for the applied values based on literature study were calculated for scenario one since that is the only scenario that may be compared to the result from the lab analysis. The average removal efficiency based on the literature values for conventional treatment and chlorination was calculated.

A hypothetical raw water concentration was assumed and the concentrations after each removal step were calculated. Then the combined removal efficiency for conventional and chlorination was calculated by comparing the hypothetical raw water concentration with the hypothetical drinking water concentration after the chlorination. If the removal efficiencies applied to the QCRA-model differ more than the margin of error, ±10%, compared to the actual removal efficiency, the model and its input values was assumed not to be accurate.

4

Results

This chapter will present the results for ADI, DWEL, exposure concentration of the drinking water and the HQ. The result for the exposure concentrations and the HQ will be based on the three scenarios, with raw water concentrations from Piketberg DWTP, Withoogte DWTP and the reference rivers. The result will consider atrazine, imidacloprid and simazine and apply to each population group. For DWEL, final drinking water concentration and HQ, a sensitivity analysis will be presented.

4.1 Acceptable Daily Intake

The ADIs based on the toxicological data, the average ADI taken directly from literature and the mean value and 5^{th}- 95^{th} percentile for the simulated ADI are presented in Table 4.1. The ADIs based on literature with corresponding sources and the ADI based on the toxicological data for each PoD can be found in Appendix H, Table H.1 and Table H.2. The average literature values are higher than the ADI based on toxicological data in all cases except for simazine. The simulated ADI based on the triangular distribution which is based on the minimum, average and maximum ADI values found in Appendix H, Table H.3, are between the toxicological and average literature value. This is reasonable since the simulated ADI is based on the ADI from the toxicological data and literature values.

Table 4.1: Toxicological ADI, average ADI based on literature followed by mean values and 5th-95th percentile of the simulated ADI.

ADI based on [µg/kg bw/day]				
Pesticide	Toxicological data for resp. PoD	Average literature	Simulation	
			Mean	5th-95th
Atrazine	1.23	13	7.17	1.88-13.63
	0.11			
	1.30			
Imidacloprid	11.40	30.3	21.48	5.75-40.76
	16.67			
	10.33			
	3.42			
Simazine	11.11	5	5.45	2.12-8.87
	0.23			

The widest observable range for the pesticides in Table 4.1 is found for imidacloprid while the percentiles for simazine differ the least. An ADI with a large span between the 5th and 95th percentile indicates that the ADI may vary and deviate from the mean value. Consequently, it is a more uncertain value that will affect the following calculations for e.g imidacloprid. Simazine results in the lowest ADI, indicating that it is the most harmful pesticide that can be ingested through food and beverage.

4.2 Drinking Water Equivalent Level

This section will present the results for DWEL for each population group and pesticide. Three different DWEL-values will be presented; DWEL taken directly from the literature, DWEL simulated with the QCRA-model and DWEL calculated with point values from literature but not done as a distribution. This section will also include a sensitivity analysis regarding the DWEL values based on the QCRA-model.

4.2.1 Result DWEL

Table 4.2 to 4.4 presents the simulated DWEL for each pesticide. The 5th percentile represents the part of the population that can ingest less pesticides through drinking water compared to the other 95% of the population before it is considered a human health risk. Therefore, the 5th percentile takes into account the most sensitive part of the population. The most sensitive population group is formula-fed infants and this applies to all pesticides since the population has both the lowest 95th percentile and mean value. On the other hand, breastfed infants are the least sensitive population group. For each population group, simazine is the most harmful pesticide to ingest, followed by atrazine and imidacloprid. Regarding the SD, imidacloprid is the pesticide which has the widest range indicating that the result is less reliable compared to atrazine and simazine which have much lower SD.

Table 4.2: Calculated DWEL for atrazine based on the QCRA-model.

DWEL Atrazine	Mean [µg/l]	SD [µg/l]	5^{th} percentile [µg/l]
Infants breastfed	143.14	168.16	15.76
Infants formula-fed	31.23	128.24	5.42
Children 1-10 years	42.68	38.38	6.71
Adults 20-64 years	70.01	57.82	12.42

Table 4.3: Calculated DWEL for imidacloprid based on the QCRA-model.

DWEL Imidacloprid	Mean [µg/l]	SD [µg/l]	5^{th} percentile [µg/l]
Infants breastfed	433.33	507.07	45.88
Infants formula-fed	97.13	580.84	16.04
Children 1-10 years	127.51	114.86	20.18
Adults 20-64 years	209.62	174.47	37.61

Table 4.4: Calculated DWEL for simazine based on the QCRA-model.

DWEL Simazine	Mean [µg/l]	SD [µg/l]	5^{th} percentile [µg/l]
Infants breastfed	110.13	122.86	15.12
Infants formula-fed	25.19	158.63	5.77
Children 1-10 years	32.64	26.74	6.57
Adults 20-64 years	53.27	39.81	12.48

Table 4.5 presents the DWEL-values based on theory, the point values from literature and the simulated DWELs. Comparing the simulated DWELs and the DWELs based on point values with the theoretical DWELs found in literature it is evident that the theoretical data is remarkably higher. The theoretical values are not adjusted for a specific population group. It is noticeable that the DWEL-value for simazine increases from 2000 to 2012.

Comparing the DWEL that is based on point values from literature with the simulated DWELs it is evident that the literature value for children, regardless of pesticide, is smaller than the simulated value. The biggest difference occurs for children that is exposed to imidacloprid, where the QCRA-model indicates a value that is 66.91 µg/l larger than the literature value. For atrazine the literature value is greater than the simulated value while for simazine, the simulated value is greater than the literature value.

Table 4.5: Comparison of theoretical DWELs, DWELs based on point values in literature and DWELs based on simulation in the QCRA-model.

DWEL based on	Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]	Source
Theoretical	All	700	-	700	US EPA (2012)
		1000	-	200	US EPA (2000)
Point values literature	Children	26.0	60.6	10.0	-
	Adults	91.0	212.1	35.0	-
Simulation in QCRA-model	Children	42.68	127.51	32.64	-
	Adults	70.01	209.62	53.27	-

4.2.2 Uncertainty and Sensitivity Analysis DWEL

The following parameters may affect the simulated DWEL-values based on the QCRA-model for the different populations and pesticides and were thereby a part of the sensitivity analysis:

- The value of ADI
- The proportion of the ADI that is allocated to drinking water, P
- The ingestion rate denoted as "Population group / Step 5: Drinkin..."

The input parameter that has the largest impact on the mean of the DWELs is the ingestion rate, for all pesticides and population groups, see Figure 4.1, Figure 4.2 and Appendix I, Figure I.1 to I.10. This implies that changing the ingestion rate will affect the DWEL remarkably.

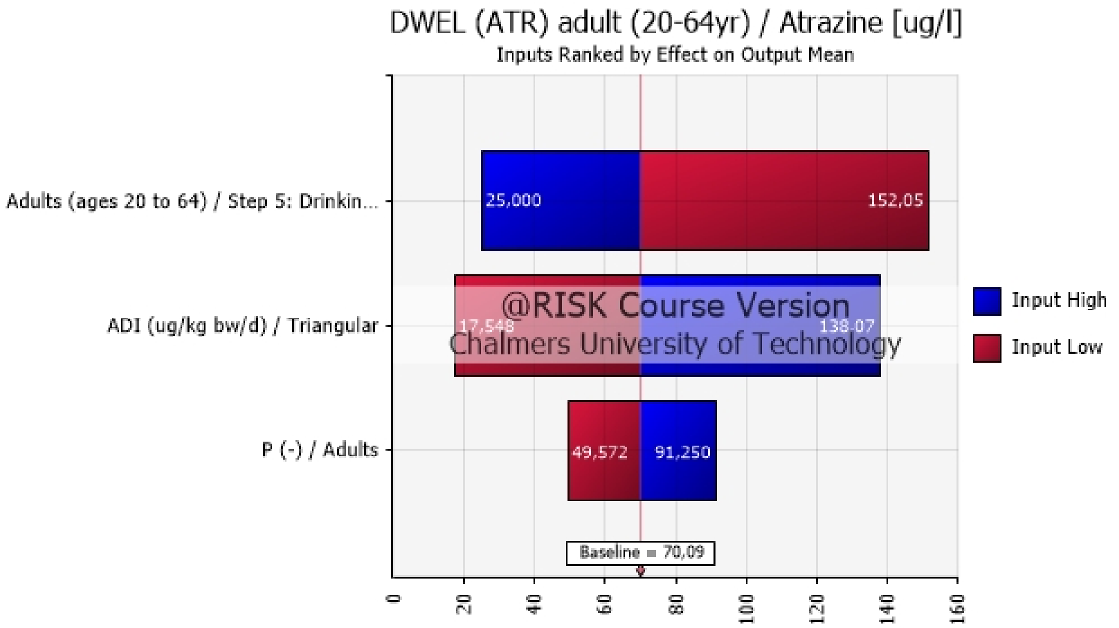

Figure 4.1: Tornado graph illustrating the inputs affecting the mean of DWEL for atrazine for adults.

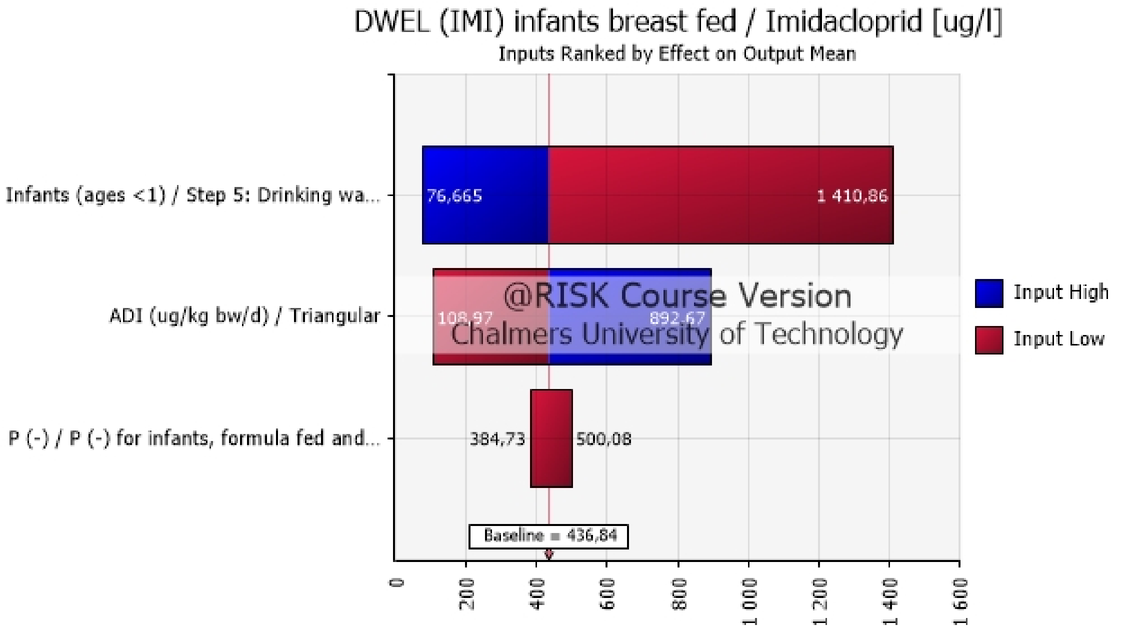

Figure 4.2: Tornado graph illustrating the inputs affecting the mean of DWEL for imidacloprid for breastfed infants.

The second most sensitive parameter for all pesticides and population groups is ADI while the least sensitive parameter is the percentage of ADI allocated to drinking water. It is evident that a higher ingestion rate, (Input High), would result in a lower value of the DWEL, see Figure 4.1 and Figure 4.2. The reason for this is that the population group will be exposed to a higher concentration of a pesticide and thereby can cope with a lower DWEL without being exposed to risk. In contrast, a higher ADI (Input High) would result in a higher value of DWEL. For adults, regardless of pesticide, see Figure 4.1, Appendix I, Figure I.6 and Figure I.10 the ADI has almost as big influence and contribution to sensitivity as the ingestion rate, which is not the case for the other population groups.

4.3 Exposure Concentrations in Drinking Water

This section will present the exposure concentrations of pesticides in the drinking water based on the lab analysis and the QCRA-model. The following results are based on the raw water concentrations received from the lab analysis for Piketberg DWTP and Withoogte DWTP, presented in Appendix F, Table F.2 and Table F.3. The raw water concentrations for the reference rivers are presented in Appendix F, Table F.1. An evaluation of the QCRA-model and its input data was also performed. A sensitivity analysis regarding the exposure concentrations based on the QCRA-model will also be presented.

4.3.1 Exposure Concentration According to Lab Analysis

The lab analysis resulted in detectable levels of atrazine, imidacloprid and simazine in the drinking water from Piketberg DWTP and Withoogte DWTP as can be seen in Table 4.6. The only exception was imidacloprid on the 15th of March which was below the level of quantification, 0.001 µg/l. The level of quantification of 0.001 µg/l was applied to all pesticides. Since only two sample events occurred, the results are very uncertain and not representative for a long period of time. Simazine resulted in the highest concentrations for both Piketberg DWTP and Withoogte DWTP while imidacloprid resulted in the lowest concentrations. In four out of six cases, Withoogte DWTP produced water with higher pesticide concentrations compared to Piketberg DWTP. Simazine is observed at a level of 0.0748 µg/l which was the highest observed concentration overall.

Table 4.6: Exposure concentrations of pesticides in drinking water at Piketberg DWTP and Withoogte DWTP from lab analysis.

Pesticide	Sampling date	Piketberg DWTP concentration [µg/l]	Withoogte DWTP concentration [µg/l]
Atrazine	2022-03-09	0.0086	0.0071
	2022-03-15	0.0020	0.0097
Imidacloprid	2022-03-09	0.0012	0.0019
	2022-03-15	<LOQ	0.0013
Simazine	2022-03-09	0.0630	0.0423
	2022-03-15	0.0216	0.0748

4.3.2 Exposure Concentrations According to the QCRA-model

The exposure concentration and SD for each pesticide in the respective reference river are presented in Table 4.7. In general, atrazine has the highest exposure concentration. Scenario two resulted in the highest exposure concentrations for all pesticides, while scenario three resulted in the lowest concentrations. The SDs are very small in scenario three, while simazine has the highest SDs, especially for scenario two.

Table 4.7: Exposure concentrations of pesticides in drinking water based on reference rivers according to the QCRA-model.

Pesticide	Reference river	Statistics	Scenario 1 [µg/l]	Scenario 2 [µg/l]	Scenario 3 [µg/l]
Atrazine	Upper Vaal River	Mean	0.2999	0.3725	0.1006
		SD	0.1043	0.1254	0.0699
Imidacloprid	Mzinti River	Mean	0.0143	0.0400	0.0036
		SD	0.0173	0.0356	0.0039
Simazine	Vals and Renoster River	Mean	0.1055	0.3520	0.0283
		SD	0.1278	0.3217	0.0426

Table 4.8 presents the exposure concentrations of drinking water produced by Piketberg DWTP. Simazine produced the highest concentrations in all scenarios while imidacloprid resulted in the lowest concentrations. The SD for simazine is higher compared to the other pesticides, which indicates that the data dissemination is widespread. Scenario two results in the highest concentrations while scenario three results in the lowest concentrations for all pesticides.

Table 4.8: Exposure concentrations of pesticides in drinking water at Piketberg DWTP according to the QCRA-model.

Pesticide	Statistics	Scenario 1 [µg/l]	Scenario 2 [µg/l]	Scenario 3 [µg/l]
Atrazine	Mean	0.0078	0.0098	0.0026
	SD	0.0011	0.0011	0.0015
Imidacloprid	Mean	0.0005	0.0015	0.0001
	SD	0.0004	0.0005	0.0001
Simazine	Mean	0.0226	0.0751	0.0053
	SD	0.0141	0.0134	0.0047

The exposure concentrations in the drinking water produced by Withoogte DWTP are presented in Table 4.9. Simazine resulted in the highest exposure concentrations for all scenarios, while imidacloprid resulted in the lowest concentrations. When comparing the scenarios, scenario two resulted in the highest concentrations while scenario three resulted in the lowest concentrations for all pesticides.

Table 4.9: Exposure concentrations of pesticides in drinking water at Withoogte DWTP according to the QCRA-model.

Pesticide	Statistics	Scenario 1 [µg/l]	Scenario 2 [µg/l]	Scenario 3 [µg/l]
Atrazine	Mean	0.0081	0.0101	0.0027
	SD	0.0010	0.0010	0.0016
Imidacloprid	Mean	0.0007	0.0020	0.0001
	SD	0.0005	0.0006	0.00007
Simazine	Mean	0.0237	0.0788	0.0055
	SD	0.0145	0.0118	0.0049

The comparison between the reference rivers with the raw water entering from Berg River to Piketberg DWTP and Withoogte DWTP demonstrates that the reference rivers result in higher exposure concentrations and will thereby represent a worst-case scenario. Comparing the exposure concentrations, the lowest difference occurs between Vals and Renoster River and Piketberg DWTP for scenario three, since the reference river only resulted in a twice as high exposure concentration. The largest difference is found in scenario three for atrazine, where using Upper Vaal River as raw water results in 39 times higher exposure concentration compared to the raw water for Piketberg DWTP. The SD for exposure concentrations at Piketberg DWTP and Withoogte DWTP based on Berg River is much lower compared to the reference rivers.

The results based on the QCRA-model for both DWTPs indicate that scenario two reveals higher concentrations while scenario three demonstrates the lowest concentrations. Another consistent result from both DWTPs is that simazine has the highest SD compared to the other pesticides. Comparing the two DWTPs for scenarios one, two and three, Piketberg DWTP resulted in the lower concentrations in seven out of nine cases. The exceptions for imidacloprid are present in scenario three where the exposure concentration is the same for both DWTPs and for simazine in scenario three where the exposure concentration is lower at Withoogte DWTP.

4.3.2.1 Uncertainty and Sensitivity Analysis Exposure Concentration

The following parameters may affect the exposure concentrations for the different pesticides and are thereby a part of the sensitivity analysis:

- Scenario one: Raw water concentration, removal efficiency of conventional treatment and chlorination.

- Scenario two: Raw water concentration (assumed no treatment)
  This scenario will not be evaluated considering sensitivity and uncertainty as it is only dependent on one input parameter, raw water concentration.

- Scenario three: Raw water concentration, removal efficiency of conventional treatment, chlorination and GAC-filter.

Evaluating the parameters that affect the reference rivers, see Appendix J, Figure J.1 to J.6, the raw water concentration has the biggest impact on all pesticides for scenario one. Regarding scenario three, raw water also affected the mean output for the exposure concentration for imidacloprid and simazine while the GAC-filter has the biggest impact on atrazine.

Regarding both Piketberg DWTP, see Appendix J, Figure J.9 to J.11 and Figure 4.3 and Withoogte DWTP, see Appendix J, Figure J.14 to J.16 and Figure 4.4, conventional treatment has the minimum effect on the exposure concentration for imidacloprid and simazine. Regarding atrazine for scenario one and three, chlorination has the least impact for both Piketberg DWTP and Withoogte DWTP, see Appendix J, Figure J.7, Figure J.8, Figure J.12 and Figure J.13. The GAC-filter has the biggest impact regarding atrazine for scenario three for both DWTPs, see Appendix J, Figure J.8 and Figure J.14.

The reduction of simazine was mainly affected by chlorination for both scenario one and scenario three at Piketberg DWTP and Withoogte DWTP, e.g. see Figure 4.3. However, the difference in influence of chlorination versus GAC-filter is minor, see Figure 4.3 and Appendix J, Figure J.16. This indicates that both chlorination and GAC-filter contribute with great uncertainty to the mean exposure concentration. If the chlorination or GAC-filter are reduced in capacity (Input Low) this will result in an exposure concentration of 0.0099 µg/l or 0.0096 µg/l respectively compared to 0.0053 µg/l as it is today. On the other hand, if the chlorination or GAC-filter performs at its best, the exposure concentration will decrease to 0.00051 µg/l or 0.00089 µg/l.

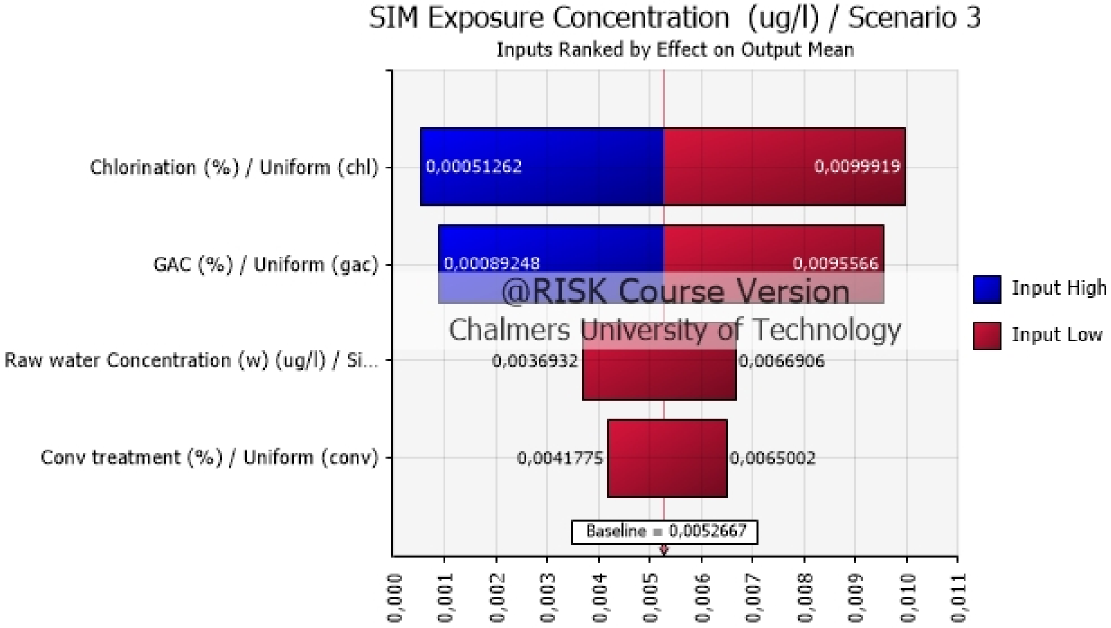

Figure 4.3: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for simazine, Piketberg DWTP, in scenario three.

As Figure 4.4 displays, chlorination contributes with considerable uncertainty followed by the raw water concentration for imidacloprid in scenario one at Withoogte DWTP. The same reasoning applies for imidacloprid in scenario one at Piketberg DWTP, see Appendix J, Figure J.9. For Figure 4.4 the highest raw water concentration results in an exposure concentration of 0.0011 µg/l compared to 0.0007 µg/l.

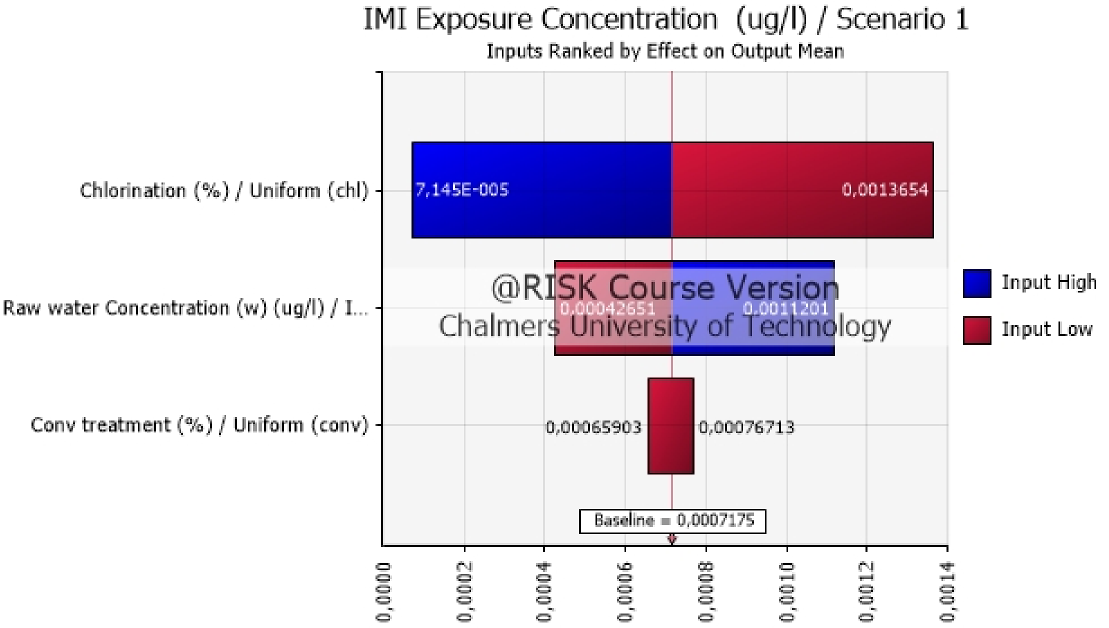

Figure 4.4: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for imidacloprid, Withoogte DWTP, in scenario one.

4.3.3 Accuracy of the QCRA-model

Table 4.10 presents the concentrations of drinking water based on the lab analysis for week three and four and the results based on the QCRA-model for scenario one. Important to mention is that the values from the lab analysis are only based on two values, week three and four, and are thereby subject to uncertainty and variation. The results from the lab analysis can only be compared to scenario one for the QCRA-model since scenario two is based on lack of treatment and scenario three includes an addition of treatment.

For atrazine detected at Piketberg DWTP and Withoogte DWTP, the simulated concentrations are lower compared to the measured values from the lab analysis. However, the result for Withoogte DWTP is very similar, it only differs 0.0003 µg/l. Regarding imidacloprid detected at Piketberg DWTP, the result from the lab analysis demonstrated a higher concentration compared to the results based on the QCRA-model. In contrast, the concentration simulated for imidacloprid at Withoogte DWTP, indicates a higher value compared to the concentration based on the lab analysis. For simazine, the result from the lab analysis is higher compared to the result from the QCRA-model. However, even if the measured concentrations are generally higher compared to the simulated values, the difference is insignificant. Hence, with regard to concentrations in drinking water, the QCRA-model produces accurate values.

Table 4.10: Comparison between concentrations in drinking water from lab analysis and the QCRA-model.

Concentration drinking water [µg/l]				
Pesticide	Average lab analysis Piketberg DWTP	QCRA-model Scenario 1 Piketberg DWTP	Average lab analysis Withoogte DWTP	QCRA-model Scenario 1 Withoogte DWTP
Atrazine	0.0053	0.0078	0.0084	0.0081
Imidacloprid	0.0012	0.0005	0.0016	0.007
Simazine	0.0423	0.0226	0.0586	0.0237

A comparison between the actual removal efficiency based on the results from the lab analysis and the estimated applied removal efficiency based on the literature study can be found in Table 4.11. Since the removal efficiency applied in the QCRA-model is added separately for conventional treatment and chlorination, an estimated combined removal efficiency had to be calculated for comparison. Hence, the removal efficiency in Table 4.11 is an estimated calculation. Piketberg DWTP has a higher removal efficiency compared to Withoogte DWTP for all pesticides. For imidacloprid and simazine, the applied removal efficiencies are higher than the actual removal efficiencies. Since the removal efficiencies when comparing the applied one and the actual one differ more than the margin of error, ±10%, the input values for the model are not accurate with regard to this evaluation criteria.

Table 4.11: Comparison between actual removal efficiency and applied removal efficiency

Pesticide	Removal efficiency Piketberg DWTP [%]	Removal efficiency Withoogte DWTP [%]	Estimated removal efficiency applied in the model [%]
Atrazine	43.32	15.15	22.73
Imidacloprid	41.46	21.95	64.29
Simazine	46.35	25.75	69.96

4.4 Hazard Quotient and Potential Health Risks

This chapter will present the simulated HQ, at what raw water concentrations and drinking water concentrations would result in an HQ>1, followed by a sensitivity analysis for the simulated HQ.

4.4.1 Simulated HQ

Table 4.12 displays the HQ for the reference rivers. An HQ above one indicates a human health risk. Regarding scenario one, the most sensitive population group is formula-fed infants. Atrazine resulted in the highest HQ of 0.0206 for formula-fed infants. Infants that are breastfed are exposed to the lowest HQ and thereby the lowest risk posed by pesticides. Considering the SD it is evident that imidacloprid has the lowest variation while atrazine has the widest. Among the SDs for atrazine, children has the largest. Infants that are formula-fed and exposed to atrazine adapt the highest 95^{th} percentile, 0.0568.

Regarding scenario two, formula-fed infants are still exposed to the highest risk for all pesticides. The HQ for formula-fed infants exposed to simazine results in a value of 0.0262, which is the highest mean value for all population groups and pesticides, however, despite this value there is no health risk. The highest 95^{th} percentile occurs for children exposed to simazine, which results in a value of 0.0656. Considering the mean values, children are subjected to the second largest risk regardless of which pesticide is evaluated, however, simazine poses the highest risk with a value of 0.0198. Similar to scenario one, scenario two shows that infants breastfed are exposed to the least health risk from pesticides in drinking water.

For scenario three, infants formula-fed result in the highest HQ, however, the values are lower compared to the previous scenarios. Atrazine poses the highest risk when compared to the other pesticides and has the biggest SD which occurs for formula-fed infants, 0.0107. Imidacloprid poses the lowest risk for all population groups and has a relatively low SD. To sum up, if Berg River was more polluted, similarly to Upper Vaal River, Mzinti River or Vals and Renoster River, it would still not be a risk for the consumers of Piketberg DWTP and Withoogte DWTP even if the DWTPs lack treatment.

Table 4.12: HQ Reference Rivers based on the QCRA-model.

HQ [-] Reference Rivers Scenario 1					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0061	0.0206	0.0154	0.0086
	SD	0.0154	0.0134	0.0244	0.0142
	95th percentile	0.0197	0.0568	0.0467	0.0260
Imidacloprid	Mean	0.0001	0.0003	0.0002	0.0001
	SD	0.0004	0.0001	0.0005	0.0003
	95th percentile	0.0004	0.0011	0.0009	0.0005
Simazine	Mean	0.0023	0.0078	0.0059	0.0033
	SD	0.0009	0.0131	0.0126	0.0067
	95th percentile	0.0087	0.0276	0.0213	0.0118

HQ [-] Reference Rivers Scenario 2					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0074	0.0253	0.0191	0.0107
	SD	0.0122	0.0328	0.0338	0.0146
	95th percentile	0.0251	0.0709	0.0573	0.0318
Imidacloprid	Mean	0.0003	0.0009	0.0007	0.0004
	SD	0.0007	0.0017	0.0014	0.0010
	95th percentile	0.0010	0.0029	0.0024	0.0013
Simazine	Mean	0.0079	0.0262	0.0198	0.0112
	SD	0.0153	0.0373	0.0338	0.0177
	95th percentile	0.0287	0.0118	0.0656	0.0377

HQ [-] Reference Rivers Scenario 3					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0021	0.0068	0.0051	0.0028
	SD	0.0045	0.0107	0.0093	0.0046
	95th percentile	0.0075	0.0218	0.0170	0.0094
Imidacloprid	Mean	0.00001	0.00004	0.00003	0.00002
	SD	0.00003	0.00008	0.00007	0.00004
	95th percentile	0.00005	0.0002	0.0001	0.00007
Simazine	Mean	0.0005	0.0018	0.0014	0.0008
	SD	0.0015	0.0036	0.0029	0.0015
	95th percentile	0.0021	0.0072	0.0052	0.0031

Regarding the health risk when consuming water from Piketberg DWTP, the result for the simulated HQ are expressed in Table 4.13 while the HQ based on point values are presented in Appendix K, Table K.1 to K.3. Comparing the result from the simulated HQ and the HQ based on point values for children, the magnitudes are the same. For adults, the simulated HQ was higher in five out of nine cases while in the rest of the cases, the magnitude was the same.

For scenario one, regarding the simulated HQ, formula-fed infants are exposed to the greatest health risk followed by children, regardless of which pesticide. Infants breastfed pose the least health risk regardless of pesticide. The highest HQ and SD was obtained for infants formula-fed for simazine, which resulted in 0.0017 and 0.0020 respectively. In general, imidacloprid has the lowest SDs. Considering the 95^{th} percentile, the highest value that may be obtained occurs for infants formula-fed exposed to simazine. However, it is still not a risk since the HQ results in 0.0049.

For scenario two, with lack of treatment, generally marginally higher values were obtained. Infants that are formula-fed still pose the highest health risk followed by children regardless of pesticide. Simazine poses the greatest health risk when comparing pesticides, and results in a mean value of 0.0017 for infants formula-fed. Imidacloprid poses the least risk for all populations. Infants that are breastfed are the least exposed population group. Evaluating the 95^{th} percentile, it is evident that infants that are formula-fed and exposed to simazine result in the highest value, 0.0049. Generally, simazine has the largest SD while imidacloprid has the lowest values.

Regarding scenario three, when GAC-filter is added, the results are similar to scenario one and two but lower. Formula-fed infants followed by children are exposed to the largest risk among the population groups, while breastfed infants are far from being exposed to risk. Simazine still poses the highest risk when comparing the pesticides while imidacloprid poses the least possible risk for harming human health. The SDs for atrazine and imidacloprid are very similar. The highest 95^{th} percentile has a value of 0.0013 for infants formula-fed exposed to simazine.

Table 4.13: HQ Piketberg DWTP based on the QCRA-model.

HQ [-] Piketberg DWTP Scenario 1					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0002	0.0005	0.0004	0.0002
	SD	0.0003	0.0006	0.0006	0.0003
	95th percentile	0.0005	0.0015	0.0012	0.0007
Imidacloprid	Mean	0.000003	0.00001	0.000009	0.000005
	SD	0.000007	0.00002	0.00002	0.00001
	95th percentile	0.00001	0.00004	0.00003	0.00002
Simazine	Mean	0.0005	0.0017	0.0013	0.0007
	SD	0.0009	0.0020	0.0018	0.0009
	95th percentile	0.0017	0.0049	0.0040	0.0022
HQ [-] Piketberg DWTP Scenario 2					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0002	0.0007	0.0005	0.0003
	SD	0.0003	0.0008	0.0007	0.0005
	95th percentile	0.0006	0.0019	0.0015	0.0008
Imidacloprid	Mean	0.00001	0.00003	0.00003	0.00001
	SD	0.00002	0.00004	0.00004	0.00001
	95th percentile	0.00003	0.0001	0.00008	0.00002
Simazine	Mean	0.0005	0.0017	0.0013	0.0007
	SD	0.0008	0.0018	0.0017	0.0009
	95th percentile	0.0017	0.0049	0.0041	0.0022
HQ [-] Piketberg DWTP Scenario 3					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0001	0.0002	0.0001	0.0001
	SD	0.0001	0.0003	0.0003	0.0001
	95th percentile	0.0002	0.0005	0.0004	0.0003
Imidacloprid	Mean	0.000001	0.000002	0.000002	0.000001
	SD	0.000002	0.000004	0.000003	0.000002
	95th percentile	0.000003	0.00001	0.00001	0.000004
Simazine	Mean	0.0001	0.0004	0.0003	0.0002
	SD	0.0003	0.0005	0.0005	0.0002
	95th percentile	0.0005	0.0013	0.0011	0.0006

The HQ for each pesticide and population group simulated for Withoogte DWTP is illustrated in Table 4.14. The HQ based on point values are presented in Appendix K, Table K.4 to K.6. Comparing the result from the simulated HQ and the HQ based on point values for children regardless of pesticide, the HQs are of the same magnitude in the majority of the cases. In five out of nine cases when comparing adults, the simulated HQ is higher. In the rest of the cases, the HQ has the same magnitude.

Regarding the simulated HQ for scenario one, the HQ is lowest for infants that are breastfed for imidacloprid and simazine. Infants that are formula-fed and exposed to simazine are the population group that is most prone to risk as the value of HQ is 0.0018 and the 95^{th} percentile is 0.0051. The SD is largest for formula-fed infants that are exposed to simazine. Children are the second most vulnerable population group considering that the HQ is the second largest.

The simulation of scenario two shows similar results to scenario one, but mostly higher mean values. Formula-fed infants are the population that is at most risk regardless of pesticides. The highest value that may occur is 0.0058 which applies for simazine. Similar to scenario one regarding atrazine, imidacloprid and simazine, infants that are breastfed are exposed to the least risk. Infants that are formula-fed and children that are exposed to simazine have the highest SD. The highest 95^{th} percentile appears for infants that are formula-fed with a value of 0.0140 which is still below one.

The values from scenario three are lower compared to scenario one and scenario two. This is reasonable due to the addition of the GAC-filter. Infants that are formula-fed and exposed to simazine measure the highest HQ, 0.0004, meaning that they are prone to the highest risk compared to the other population groups. The largest overall SD applies to simazine regardless of the population group. Infants that are formula-fed and exposed to simazine represent the highest 95^{th} percentile of 0.0014, which is still far from an HQ value of one. In all the above cases, infants that are breastfed are directly coupled with the lowest level of risk. An exception applies for imidacloprid where both adults and infants breastfed are subjected to the same level of risk as both groups have an HQ value of 0.000001.

Table 4.14: HQ Withoogte DWTP based on the QCRA-model.

HQ [-] Withoogte DWTP Scenario 1					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0002	0.0006	0.0004	0.0002
	SD	0.0003	0.0007	0.0006	0.0003
	95th percentile	0.0005	0.0015	0.0013	0.0007
Imidacloprid	Mean	0.000005	0.00002	0.00001	0.00001
	SD	0.00001	0.00002	0.00002	0.00001
	95th percentile	0.00002	0.0001	0.00004	0.00002
Simazine	Mean	0.0005	0.0018	0.0013	0.0007
	SD	0.0008	0.0020	0.0018	0.0009
	95th percentile	0.0018	0.0051	0.0041	0.0022

HQ [-] Withoogte DWTP Scenario 2					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0002	0.0007	0.0005	0.0003
	SD	0.0004	0.0009	0.0007	0.0004
	95th percentile	0.0007	0.0019	0.0015	0.0008
Imidacloprid	Mean	0.00001	0.0001	0.00003	0.00002
	SD	0.00002	0.0001	0.0001	0.00002
	95th percentile	0.00004	0.0001	0.0001	0.0001
Simazine	Mean	0.0017	0.0058	0.0044	0.0025
	SD	0.0023	0.0047	0.0047	0.0023
	95th percentile	0.0054	0.0140	0.0121	0.0063

HQ [-] Withoogte DWTP Scenario 3					
Pesticide	Statistics	Infants, breastfed	Infants, formula-fed	Children	Adults
Atrazine	Mean	0.0001	0.0002	0.0002	0.0001
	SD	0.0001	0.0003	0.0006	0.0002
	95th percentile	0.0002	0.0006	0.0005	0.0003
Imidacloprid	Mean	0.000001	0.000002	0.000002	0.000001
	SD	0.000002	0.000004	0.000003	0.000002
	95th percentile	0.000003	0.00001	0.00001	0.000003
Simazine	Mean	0.0001	0.0004	0.0003	0.0002
	SD	0.0003	0.0006	0.0005	0.0003
	95th percentile	0.0005	0.0014	0.0011	0.0006

Overall the values for Piketberg DWTP and Withoogte DWTP are relatively similar. Infants formula-fed is exposed to the greatest risk while infants breastfed are subject to the lowest risk. Scenario two always results in the highest HQ while scenario three results in the lowest HQ. There is no 95^{th} percentile exceeding the HQ value of one.

Table 4.15 and Table 4.16 indicate at what exposure concentrations in the drinking water and what concentrations in the raw water would result in an HQ ≥ 1. The population group formula-fed infants are at the greatest risk for all pesticides, for all scenarios and both Piketberg DWTP and Withoogte DWTP. The tables also indicate that scenario one may result in higher raw water concentrations of the pesticides without posing any human health risks compared to scenario two. The same reasoning goes for scenario three in relation to scenario one.

Infants breastfed is the population group that may be exposed to the highest exposure concentration in the drinking water without being harmed, especially for imidacloprid with a concentration of 176.58 µg/l for both DWTPs. Infants formula-fed, on the other hand, is the group that may be exposed to the least concentrations in drinking water. In a scenario without treatment, scenario two, for both Piketberg DWTP and Withoogte DWTP this population group can be exposed to 21.00 µg/l atrazine, 52.30 µg/l imidacloprid and 16.35 µg/l simazine in the raw water. On the other hand, if the DWTPs have normal operation with an addition of GAC-filter, scenario three, infants formula-fed can be exposed to concentrations of 78.26 µg/l, 1074.81 µg/l and 233.05 µg/l of atrazine, imidacloprid and simazine respectively in the raw water. These values are far from the exposure concentrations that are used as input for the DWTPs as they vary between 0.0015-0.0751 µg/l for Piketberg DWTP and 0.0020-0.0788 µg/l for Withoogte DWTP.

Table 4.15: Exposure and raw water concentration associated with risk, Piketberg DWTP.

Piketberg DWTP								
Population	Exposure conc. when HQ ≥ 1	Exposure conc. S1	Exposure conc. S2	Exposure conc. S3	Raw water conc. with risk S1	Raw water conc. with risk S2	Raw water conc. with risks S3	Raw water conc. Piketberg DWTP
Atrazine [µg/l]								
Infants, breastfed	70.89	0.0078	0.0098	0.0026	88.36	70.89	264.24	0.0098
Infants, formula-fed	21.00	0.0078	0.0098	0.0026	26.17	21.00	78.26	0.0098
Children	28.96	0.0078	0.0098	0.0026	36.09	28.96	107.93	0.0098
Adults	51.65	0.0078	0.0098	0.0026	64.39	51.56	192.54	0.0098
Imidacloprid [µg/l]								
Infants, breastfed	176.58	0.0005	0.0015	0.0001	494.46	176.58	3629.08	0.0015
Infants, formula-fed	52.30	0.0005	0.0015	0.0001	146.44	52.30	1074.81	0.0015
Children	72.12	0.0005	0.0015	0.0001	201.96	72.12	1482.30	0.0015
Adults	128.66	0.0005	0.0015	0.0001	360.29	128.66	2644.30	0.0015
Simazine [µg/l]								
Infants, breastfed	55.20	0.0226	0.0751	0.0116	183.74	55.20	786.89	0.0751
Infants, formula-fed	16.35	0.0226	0.0751	0.0116	54.42	16.35	233.05	0.0751
Children	22.55	0.0226	0.0751	0.0116	75.05	22.55	321.41	0.0751
Adults	40.22	0.0226	0.0751	0.0116	133.88	40.22	573.36	0.0751

Table 4.16: Exposure and raw water concentration associated with risk, Withoogte DWTP.

Withoogte DWTP								
Population	Exposure conc. when HQ ≥ 1	Exposure conc. S1	Exposure conc. S2	Exposure conc. S3	Raw water conc. with risk S1	Raw water conc. with risk S2	Raw water conc. with risk S3	Raw water conc. Withoogte DWTP
Atrazine [µg/l]								
Infants, breastfed	70.89	0.0081	0.0098	0.0027	88.36	70.89	264.24	0.0101
Infants, formula-fed	21.00	0.0081	0.0098	0.0027	26.17	21.00	78.26	0.0101
Children	28.96	0.0081	0.0098	0.0027	36.09	28.96	107.93	0.0101
Adults	51.65	0.0081	0.0098	0.0027	64.39	51.56	192.54	0.0101
Imidacloprid [µg/l]								
Infants, breastfed	176.58	0.0007	0.0015	0.0001	494.46	176.58	3629.08	0.0020
Infants, formula-fed	52.30	0.0007	0.0015	0.0001	146.44	52.30	1074.81	0.0020
Children	72.12	0.0007	0.0015	0.0001	201.96	72.12	1482.30	0.0020
Adults	128.66	0.0007	0.0015	0.0001	360.29	128.66	2644.30	0.0020
Simazine [µg/l]								
Infants, breastfed	55.20	0.0237	0.0751	0.0055	183.74	55.20	786.89	0.0788
Infants, formula-fed	16.35	0.0237	0.0751	0.0055	54.42	16.35	233.05	0.0788
Children	22.55	0.0237	0.0751	0.0055	75.05	22.55	321.41	0.0788
Adults	40.22	0.0237	0.0751	0.0055	133.88	40.22	573.36	0.0788

4.4.2 Uncertainty and Sensitivity Analysis of HQ

The following parameters may affect the simulated HQ and are therefore a part of the uncertainty and sensitivity analysis:

- Scenario one: ADI, ingestion rate, proportion allocated to ADI, raw water concentration, removal efficiencies of both conventional treatment and chlorination.
- Scenario two: ADI, ingestion rate, proportion allocated to ADI, raw water concentration (assumed lack of treatment).
- Scenario three: ADI, ingestion rate, proportion allocated to ADI, raw water concentration, removal efficiencies of conventional treatment, chlorination and GAC-filter.

The common denominator for all pesticides in all scenarios for the reference rivers and the DWTPs is that formula-fed infants are in all cases the most sensitive group. Therefore, tornado graphs are only presented for infants formula-fed while the sensitivity analysis for the other population groups are compiled in tables, found in Appendix L, Figure L.9, Figure L.18 and Figure L.27.

The results of the tornado graphs for infants that are formula-fed from @Risk for the reference rivers are found in Appendix L, Figure L.1 to L.8 and in Figure 4.5. A compilation of the data for all population groups is found in Appendix L, Figure L.9. ADI has the largest impact on the HQ values for atrazine for all population groups. The only exception to this is breastfed infants in scenarios one and three where the ingestion rate is the most sensitive parameter. Simazine and imidacloprid have similar results for scenarios one and three for the reference rivers. In these cases, infants that are breastfed are most affected by the ingestion rate while all the other population groups are most affected by the raw water concentration. Regarding scenario two for imidacloprid, breastfed infants are affected the most by the ingestion rate. The other population groups are mainly affected by ADI. Scenario two for simazine proves that the most sensitive parameter for breastfed infants is the ingestion rate, as in the case of imidacloprid. For all other population groups exposed to simazine, raw water concentration is the most uncertain parameter.

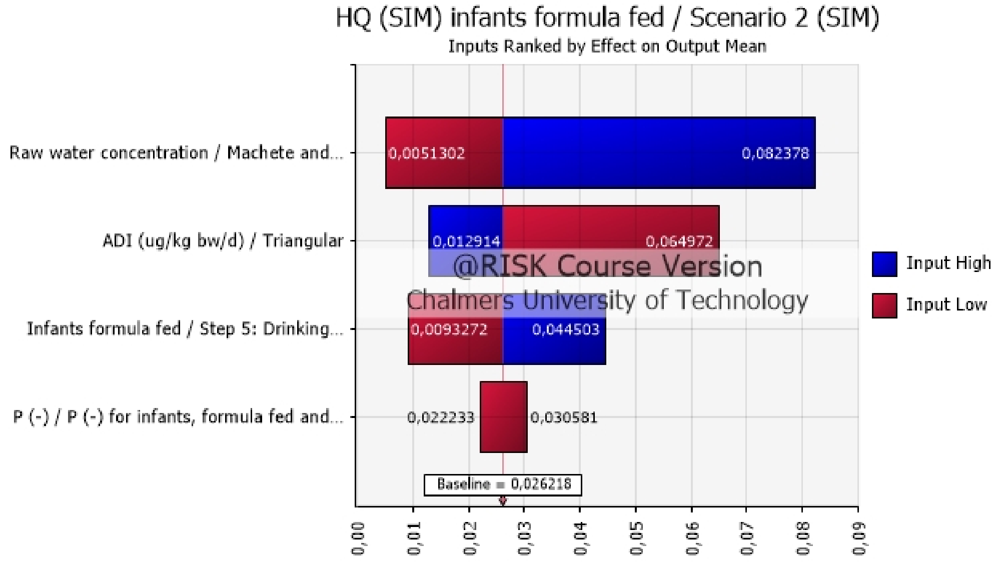

Figure 4.5: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, reference river, scenario two.

For the reference rivers, a low raw water concentration result in a lower HQ, see Figure 4.5 compared to what it is today and a low ADI result in a higher HQ compared to what it is today. The case in Figure 4.5 represent that the highest HQ, 0.08, for the reference rivers occur when using the highest raw water concentration available, however the HQ is still below one.

Simulations for Piketberg DWTP are included in Appendix L, Figure L.10 to L.18 and Figure 4.6. The results for Withoogte DWTP are found in Appendix L, Figure L.19 to L.27 and Figure 4.7. The worst-case that may occur at Piketberg DWTP would be scenario two, exposure by simazine and with the lowest ADI possible, see Appendix L, Figure L.16. Moreover, the case associated with the most risk for Withoogte DWTP would be exposure by atrazine for scenario one assuming an input of the lowest possible ADI, see Appendix L, Figure L.19. However, the HQ in both cases does not result in a value above one. In all cases simulated for Piketberg DWTP and Withoogte DWTP, ADI is the most sensitive parameter for infants that are formula-fed. The only time GAC-filter is the second largest contributor to uncertainty at the two DWTPs is in scenario three for infants formula-fed exposed to atrazine, see Figure 4.6 and Appendix L, Figure L.21. For breastfed infants, the largest uncertainty factor is the ingestion rate and this matter applies to both DWTPs. The only occasions chlorination has a significant influence on the HQ, being the second largest contributor to uncertainty, is for scenarios one and three at both DWTPs for imidacloprid and simazine. An example of this is illustrated in Figure 4.7.

The most sensitive factor for children exposed to atrazine or imidacloprid in all scenarios at both DWTPs is ADI. Moreover, the most sensitive input for children exposed to simazine is the ingestion rate which applies to all scenarios at both DWTPs. The most sensitive parameter for adults for both DWTPs, all scenarios and pesticides are ADI. Finally, the most sensitive parameters for both DWTPs are either the ingestion rate or the ADI. This applies to all population groups and pesticides.

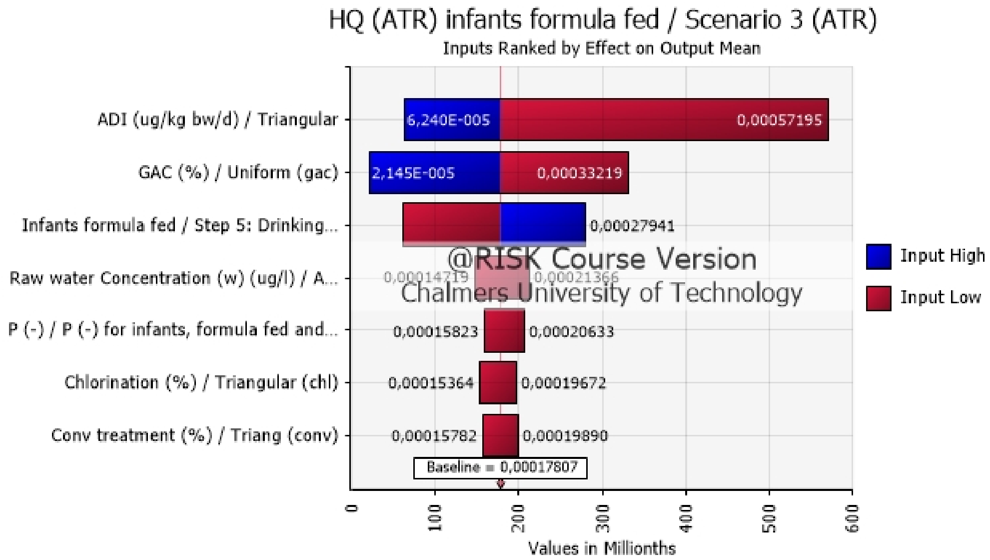

Figure 4.6: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, Piketberg DWTP, scenario three.

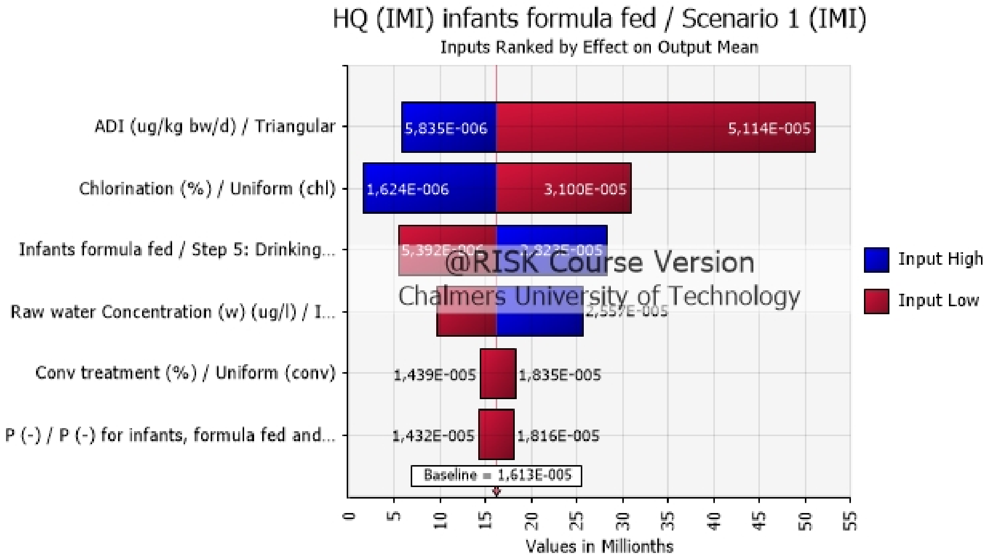

Figure 4.7: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, Withoogte DWTP, scenario one.

5

Discussion

This chapter will discuss the input parameters to the QCRA-model, the exposure concentrations, the hazard quotient followed by a discussion regarding the accuracy of the model and its input data.

5.1 Input Parameters to the QCRA-model

Uncertainty factors are required to account for the uncertainty of the ADI, however, an over-use of these factors ultimately creates unrealistic values similar to the outcome if the UFs are not applied. One uncertainty within the determination of the ADI is the lack of studies for the PoD (NOAEL, LOAEL, NOEL and LOEL). Often are the studies for the PoD based on animals, e.g rats, mice or chickens and the number of studies is very limited. The results from animal studies together with uncertainty factors are used to calculate the PoD for humans, as there are no corresponding results involving human testing. The conversion contributes to uncertainty even if that is the current way of working. To better determine which concentrations induce human health consequences more studies of the PoD must be conducted in ways that are transferable to humans. However, there is an ethical question regarding how these studies should be performed. Uncertain ADIs contribute to less reliable DWELs which ultimately affect the accuracy of the HQ. The calculations regarding PoD, ADI, DWEL and HQ included in the model are as good as possible, considering the limited data that is available today. To sum up, if there are more reliable health data available, the PoD, ADI, DWEL and HQ would be more trustworthy and this would strengthen the credibility even more of the QCRA-model as a whole.

Legislation on pesticide commerce and application is highly regulated within the EU and it is a topical subject. However, more studies on the health effects of pesticides must be conducted and these studies must also be transmittable from potential test species to humans. To broaden the information basis for individual pesticides it is recommended that potential cocktail effects of pesticides are analysed. Not much is known about the health effects coupled with the ingestion of low doses of many different pesticides at the same time.

It is proven that the simulated DWELs are much more similar to the literature values, see Table 4.5, compared to the theoretical DWELs. The reason to why these values differ is due to the fact that the theoretical values from US EPA (2000) and

US EPA (2012) are not specific to any population group but only general DWELs. Hence, it is more appropriate to use the simulated DWELs as the values are more conservative in the majority of cases and connected to specific population groups.

The least sensitive population group according to the simulated DWELs are breastfed infants. The reason for this may be the low ingestion rate which is confirmed to be the main sensitivity factor as illustrated in Figure 4.2. Infants that are breastfed only consume very little quantities of water as their diet mainly relies on breast milk. Hence, whatever pesticides may be present in the drinking water, infants that are breastfed are less likely to ingest significant amounts of these.

The most sensitive parameter for DWEL for all population groups is the ingestion rate. This fact applies regardless of which pesticide these groups are being exposed to. Furthermore, the ingestion rate is not likely to be altered in the future seeing as the ingestion rate is static and the reason for its variation is mainly dependent on the stage in life. However, more research regarding the ingestion rate in South Africa would be favourable. This would be necessary to get more accurate results since the ingestion rate applied in the QCRA-model are based on values from the United States. Nevertheless, the parameter that is deemed more likely to increase and prone to change is the ADI as the ADI exclusively depends on what type of research has been conducted.

The raw water samples for week three from Piketberg DWTP that deviated from the sampling procedure did not result in any outlier. Nor did the water samples for week two at Withoogte DWTP that did not freeze result in any outlier. This is beneficial due to the low frequency of samples where an outlier would affect the result remarkably. Furthermore, as the samples were collected during February and March, which are not the months where most pesticides are applied, it can be discussed if the raw water concentrations are higher during the other months of the year. This may result in exposure concentrations that are more similar to the reference rivers. However, as displayed in Table 4.16 a raw water concentration of 0.04-0.3725 µg/l as in the reference rivers would not result in a health risk for long-term exposure even if the DWTPs are out of order. It would be interesting to simulate a QCRA-model based on raw water concentrations sampled during the spraying season (July to January) to better investigate health risks coupled with concentrations throughout the year.

Since the raw water concentrations only are based on ten samples for each DWTP during a two months period, their relevance may be questioned. It is important to acknowledge that these results are not representative of pesticide concentrations throughout the year. To acquire data that is more precise and reliable, more frequent sampling over the year would be necessary. Due to the few samples, it was hard to determine what kind of distribution the raw water is most likely to follow. Based on Cantoni et al. (2021) and Gurian et al. (2004) a log-normal distribution was chosen. If more samples were available, investigations regarding what distribution that represents the data and how that affects the results would be favourable.

The same reasoning applies to the removal efficiency. More literature studies would result in that more trustworthy distributions can be applied for conventional treatment and chlorination, as for the GAC-filter.

Finding proper removal efficiency for each treatment step and pesticide is a challenge. Especially for simazine, where the highest removal efficiency for conventional treatment had to be adopted from the findings for atrazine. This since no relevant studies were found. For future work, it is important to find literature studies where the same coagulant is used, the same number of sand filters, the correct disinfectant and the same magnitude of raw water concentrations as in the DWTP investigated. This would result in a more representable removal efficiency. However, this is a difficult task, due to the lack of studies regarding pesticide removal within DWTPs. More research on this subject is crucial. The lack of studies resulted in the decision to apply a removal efficiency of zero for conventional treatment for atrazine and simazine since the only studies found resulted in an addition of the pesticides. This decision affects the result remarkably.

For the input data for the model to be more representative in regards to which pesticides that are used for the case along Berg River, spray records would have been an asset. As of today, South Africa does not have any public accessible spray records, which makes it difficult to determine which pesticides that are of relevance and should be evaluated in the model. Public spray records would not just benefit this thesis, it would benefit the agricultural sector in South Africa. This as South Africa would get an understanding of which pesticides are used, to what extent and when they are applied. By implementing spray records, it would be easier for the authorities to regulate the use of pesticides, as this is something that South Africa has been criticised for. Another benefit of spray records would be the possibility to evaluate which pesticides that should still be allowed to use in South Africa for agricultural purposes. Worth mentioning is that all three pesticides that are investigated in this thesis are banned in the EU. It is understandable that if it is not clear which pesticides are used within the country, South Africa in this case, it is hard to be able to regulate which should be allowed. Consequently, this thesis highlights the connection between the agricultural sector and its pesticide use with the demand for spray records which may result in the regulation of pesticides which will affect the raw water quality and thereby the drinking water quality. The agricultural sector and drinking water sector often have conflicting interests, however, it is important to understand that what the agricultural sector does affects the drinking water quality which might have an impact on the health of future generations. Important to consider is that according to Dabrowski et al. (2014), atrazine, imidacloprid and simazine are all in the top 15 pesticides that pose a major health risk for humans and the environment. The fact that they are present in Berg River despite BRIP and RHP, which aim to keep Berg River in good health, is an indication that regulations of pesticides are required.

The persistence of pesticides in nature depends on the half-life time of the compounds. The raw water concentrations of imidacloprid were low compared to those of atrazine and simazine. As mentioned in Chapter 2.4, all three pesticides are prone to leach, however, imidacloprid has the highest half-life time. The reason for not finding higher concentrations of imidacloprid despite its high persistence must indicate that it is not used to a broad extent in the area. This is supported by Dabrowski et al. (2014) who states that imidacloprid is mostly used for citrus, which is not cultivated to a higher extent in the area. On the contrary, it is reasonable to find higher concentrations of simazine (which according to Dabrowski et al. (2014) is applied to grapes) as the cultivation of wine grapes and tables grapes expand over the eastern part as illustrated in Figure 2.4. Furthermore, the concentrations found of atrazine were unexpected considering that it is mostly applied to maize which is not the main crop cultivated in the area. This indicates that atrazine is used for other crops than what Dabrowski et al. (2014) found. However, this is reasonable seeing as the study dates back to investment records from 2009. Curchod et al. (2020) discussed that the spray records obtained in their study did not correspond to the actual concentrations in the raw water. This could possibly be one reason why the proportion of pesticides applied to specific crops, according to Dabrowski et al. (2014), does not correspond to the findings of this thesis.

5.2 Exposure Concentration from the DWTPs and Reference Rivers

In four out of six cases the simulated QCRA-values of the exposure concentration are lower compared to the lab analysis. To receive a more conservative result, it would be preferable if the simulated concentration are higher than the lab analysis. One reason that the QCRA-model produces lower concentrations may be that higher removal efficiencies are applied for imidacloprid and simazine in the model than what is actually taking place.

5.2.1 Scenario One

For scenario one, the concentrations in the reference rivers were high with the exception of imidacloprid. The level of atrazine nor simazine complies with Dutch, Swedish or EU standards of 0.1 µg/l of individual pesticides in drinking water. However, if all these pesticides were to be measured in the same river the concentrations would be within the limit of 0.5 µg/l for the sum of all pesticides in drinking water. Since South Africa does not have any target values in place concerning neither individual nor the sum of pesticides, the concentrations in the reference rivers are not a legal issue. On the other hand, Piketberg DWTP and Withoogte DWTP are able to comply with the Dutch, Swedish and EU standards. The highest mean exposure concentration in scenario one is simulated to 0.0237 µg/l for simazine at Withoogte DWTP. However, this concentration is approximately four times lower than the individual pesticide standard according to the Netherlands, Sweden and the EU.

As it turns out, conventional treatment has a limited significance in altering the mean of the exposure concentration. This is expected since conventional treatment is known to have a limited removal efficiency regarding pesticide removal.

5.2.2 Scenario Two

The scenario which resulted in the highest exposure concentrations was scenario two. This was expected considering that the scenario assumed no treatment was applied. The exposure concentrations of the reference rivers exceeded those of Piketberg DWTP and Withoogte DWPT, which was anticipated as the raw water concentrations showed higher levels of pollution. The simulations of the reference rivers in scenario two show that the standards are exceeded for the sum of pesticides in drinking water, 0.7645 µg/l > 0.5 µg/l, and also for atrazine and simazine regarding the levels of individual pesticides. None of the simulated values for neither Piketberg DWTP nor Withoogte DWTP go beyond the standard limits.

Investigating scenario two is important in the context of South Africa as not all South Africans access treated drinking water. It is therefore important to make sure that both drinking water and raw water quality are sufficient. However, as explained by STATSSA (2012), there are major differences between provinces within South Africa. Hence, it is more important to provide access to drinking water and improve the quality of the raw water in other provinces where a proportion of the population lack access to piped water. For example, in Mpumalanga and North West where the reference rivers are located, 12.57% respectively 8.39% lack access to drinking water. In contrast the proportion of inhabitants that have no access to piped water in the Western Cape only amount to 0.87%.

5.2.3 Scenario Three

This scenario produced lower exposure concentrations compared to scenario one which was anticipated as the removal efficiencies of the GAC-filter, for all pesticides, are the most efficient form of treatment. The only case in which the Dutch, Swedish and EU standards were not being met was for the concentration of individual pesticides concerning atrazine in the reference rivers.

Worth noting is that the service life and efficiency of the GAC-filter are dependent on the efficiency of the prior conventional treatment. The conventional treatment needs to remove organic load to avoid exhausting the GAC-filter. Hence, in a real-world scenario, the ability of the GAC-filter to remove pesticides would be dynamic and depend on other quality parameters of the raw water and the efficiency of the conventional treatment. Monitoring how the removal efficiency of pesticides by GAC-filter varies in relation to organic load would result in more accurate removal efficiencies.

5.3 Hazard Quotient and Potential Health Risks

The results from the case study indicate that there is no health risk (HQ>1) when consuming the drinking water from Piketberg DWTP and Withoogte DWTP that is produced from raw water in Berg River in February and March 2022. In the case of lack of treatment, the water is still safe to drink. Since Monte Carlo simulations were included in the QCRA-model, there was a possibility to simulate a range of possible outcomes and scenarios based on different raw water concentrations, different ADIs, different ingestion rates in combination with deficient and excellent removal efficiency. The certainty of the results from the QCRA-model is therefore trustworthy and indicates that there is no risk of exposure to atrazine, imidacloprid and simazine for any of the population groups from the two DWTPs as it is today.

The HQs for the reference rivers may be more representative since the sampling for the DWTPs is not done during spraying season. The highest HQ that may occur is 0.08 which applies for scenario two for atrazine and simazine for infants that are formula-fed, see Appendix L, Figure L.2 and Figure 4.5. Worth mentioning is that infants that are formula-fed will not be infants for their whole life, therefore a short period with a higher HQ will not represent their long-term exposure. Scenario two is in the best case only temporary, consequently, the exposure by scenario two will not be permanent, despite that, it is not a risk if it would have been long-term.

The highest risk occurs in scenario two. This is reasonable since this scenario indicates a lack of treatment. The highest HQ and thereby greatest risk occurs for infants that are formula-fed in scenario two for simazine at Withoogte DWTP as it results in an HQ of 0.0144. This is also reasonable, based on the earlier discussion regarding formula-fed and ingestion rate. Moreover, it is logical that infants that are breastfed and adults are exposed to the least risk for human health. One reason for this is that infants do not ingest tap water directly from the tap as frequently and consequently have the lowest ingestion rate. The reason behind why adults are exposed to low levels of risk may be that adults have the lowest ingestion rate of all population groups. This may be since adults consume a lot of other drinks e.g. coffee, tea, juice or soda. Moreover, adults weigh more and are fully developed and may therefore cope with higher concentrations of pesticides before it is considered a hazard.

Comparing the current concentrations in Berg River with the concentrations that it can be without posing any health risks (HQ>1), see Table 4.16, it is clear that the concentrations can be extremely higher. This is interesting since the agricultural sector along Berg River most likely will continue. Another factor that may continue to increase the concentration of pesticides in Berg River is the WWTPs. To minimize the risk of pesticide exposure from the WWTPs in the raw water intake, it would be favourable if South Africa regulated the location of the WWTPs with respect to the DWTPs. However, it is important not to misuse this information and stop caring and working towards less pesticide use. The future environment, water courses, animals and humans would benefit from as low concentrations of pesticides as possible.

To sum up, it is important to mention that an HQ below one doubtlessly indicates no human health risk for long-term exposure to a pesticide. On the contrary, if the HQ is greater than one, it is no longer safe to say that there will not be a risk, at the same time it is not certain that an exposure would result in an increased risk either.

5.4 Accuracy of the QCRA-model

The determination of the accuracy of the model and its input data may be questioned. Partly since the determination is only based on two criteria regarding the input data; How well the exposure concentrations and removal efficiencies based on the lab analysis and the QCRA-model is consistent. To be able to do a proper evaluation of the model and its input data, ingestion rate, health data and annual raw water concentrations have to be evaluated. However, the two parameters that are evaluated give a brief understanding of whether or not the model produced accurate results based on the input data. Since the model produced results that are partly accurate for scenario one, the only scenario that can be compared, one can draw the conclusion that the model produces results that are accurate for both scenario two and three as well. On the other hand, as mentioned before, the exposure concentration based on the lab analysis is only based on two samples. These measured final concentrations do not have to be representative for the other 50 weeks of the year.

Evaluating the removal efficiencies, the input data for the model does not fulfil the requirements regarding the margin of error ±10% from the actual removal efficiency. The reason for this may be that the applied removal efficiencies are higher in all cases except for the removal of atrazine for Piketberg DWTP. It is remarkable that despite applying higher removal efficiency for both DWTPs, the actual exposure concentrations and the simulated concentrations are identical. This indicates that the other steps in the QCRA-model e.g. ADI, DWEL or IR also contributes to the results.

Performing and evaluating a QCRA-model and its input values are a complex process since not many QCRA-models have been performed, nor is there an admitted method regarding QCRA-modelling, especially for pesticides. The lack of QCRA-models applied within the drinking water sector and pesticides are discussed within the branch of industry, e.g by Cantoni et al. (2021) as mentioned before. To conclude, a more accurate and precise QCRA-model for evaluating the health risks coupled with long-term exposure to pesticides through drinking water can only be achieved with more accurate input data. Research on health data (PoD), ingestion rate for a specific country and removal efficiencies for each pesticide and treatment step are required. This in combination with a broader application to adapt and adjust the QCRA-model and create an everyday use of the tool.

6

Conclusion and Future Studies

This chapter will present the final results of the study followed by suggestions for future studies.

6.1 Conclusion

- The concentrations of atrazine, imidacloprid and simazine that result in a human health risk during long-term exposure are high compared to the concentrations based on the lab analysis and the QCRA-model. Current exposure concentrations in scenario one are 0.0081 µg/l for atrazine, 0.0007 µg/l for imidacloprid and 0.0237 µg/l for simazine. For the levels to pose a health risk for the population groups, the concentrations would have to amount to 21.00-70.89 µg/l of atrazine, 52.30-176.58 µg/l of imidacloprid or 16-55.20 µg/l simazine. It is evident that infants that are breastfed can be exposed to the highest concentrations while infants formula-fed may be exposed to the least concentrations without any health risk.

- The result from the QCRA-model indicates that there is no risk for human health for the studied population groups when consuming drinking water during long-term exposure from Piketberg DWTP and Withoogte DWTP. This applies when considering atrazine, imidacloprid and simazine. There is no health risk during normal operation nor is there a health risk for any of the population groups if technical or human error results in lack of treatment.

- An addition of GAC-filter in the DWTPs results in lower concentrations compared to the normal operation and the scenario with lack of treatment, for all pesticides. Hence, there is no human health risk for any of the population groups. If the concentrations of atrazine, imidacloprid and simazine would increase in Berg River in the future, it is recommended to implement an additional treatment step, for example, GAC-filter.

- Simazine results in the highest HQ of all pesticides and thereby poses the highest risk for human health. If the future in South Africa and along Berg River results in higher raw water concentrations due to pollution in combination with lack of treatment at the DWTPs, the result from the QCRA-model signifies that formula-fed infants would be exposed to the greatest human health risk of all the population groups.

- The input factor that contributes the most to the DWEL is the ingestion rate for all population groups. Regarding the exposure concentration from drinking water, it differs depending on scenario. For scenario one and three, chlorination contributes to the most uncertainty in eight out of twelve cases. As scenario two only depends on raw water concentrations, it is the most uncertain input. The most sensitive parameter affecting the output mean for the HQ was the ADI in the majority of cases.

- The accuracy of the QCRA-model and its input data is determined to be partly sufficient. This since the exposure concentration simulated from the QCRA-model are of the same magnitude as the exposure concentrations determined by the lab analysis. However, the applied removal efficiencies differ more than the margin of error ±10% compared to the actual removal efficiencies.

- There is a limited number of studies regarding health data (PoD) and removal efficiency connected to pesticides which affect the credibility of the input data to the QCRA-model.

6.2 Future Studies

- Future studies can include mapping of the spray records of pesticide use along Berg River. This to better apply pesticides in the QCRA-model that may be used in the area and thereby pose a health risk for the consumers.

- Studies in the future may investigate other chemical compounds such as other pesticides, pharmaceuticals, hormones or PFAS. The same QCRA-model as used in this thesis may be applied and just modified according to the chosen chemical compounds. An advantage of evaluating other chemical substances would be the possibility to rank the substances with regard to human health risks. The ranking may be used as decision support when deciding treatment steps in a DWTP and deciding which chemical substances that should be regularly monitored.

- Rivers that are polluted, such as the reference rivers, may be evaluated since Berg River is a fairly decent raw water source. As mentioned earlier, the inhabitants in certain provinces suffer from low access to treated drinking water. Therefore it is important to investigate and monitor raw water sources that informally serve as drinking water.

- Studies on health data (PoD) for long-term exposure to pesticides and removal efficiencies in DWTPs for pesticides are other suggestions. This since the literature study in this thesis highlights the gap of information for these subjects.

- Another interesting study would be to investigate the cocktail effect when humans are exposed to multiple pesticides at the same time. How can the cocktail effect be considered and accounted for in the model? What are the consequences for future generations exposed to cocktail effects?

- Developing the QCRA-model from an Excel sheet into a software e.g. Python or Java would strengthen the model and result in a more user-friendly and accurate model.

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A

Appendix: Example of Agricultural Land Use

This appendix illustrates an example of the land use distribution along Berg River.

Figure A.1: Agricultural land distribution Misverstand Dam (Western Cape Department of Agriculture, 2020).

B

Appendix: Example of Tornado Graph

This appendix present an example of a tornado graph and with an explanation of how to interpret the result.

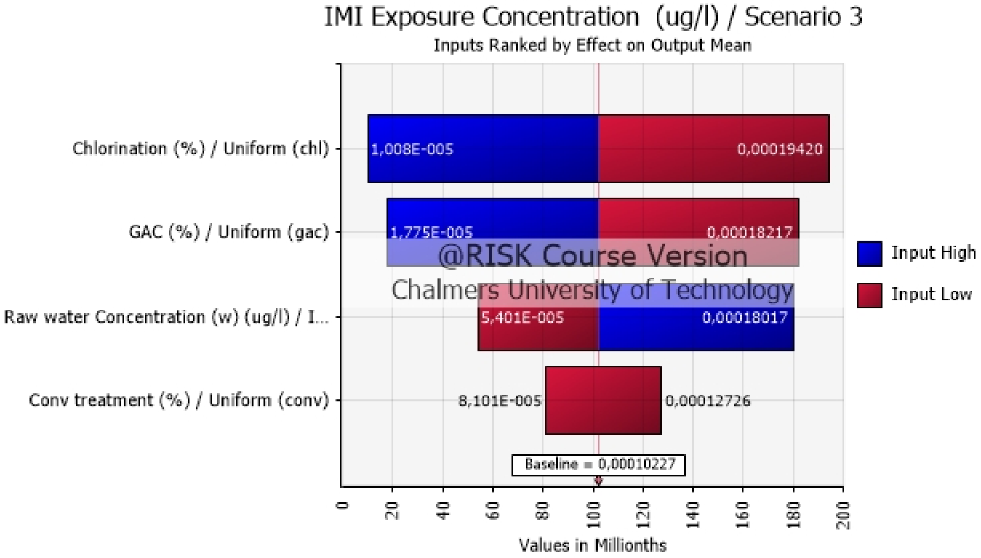


Figure B.1: Tornado graph illustrating the inputs affecting the mean exposure concentration for imidacloprid, Piketberg DWTP, scenario three.

To evaluate whether the input parameters affect the mean value of the output positively or negatively, one have to consider if a decrease of an input (marked as red, "Input Low") will result in a higher (to the right of the baseline) or lower out put (to the right of the baseline). The same goes for if an increase of an input parameter (marked as blue, "Input High") results in an increase of the output or a decrease. This reasoning is only applicable when altering one input while keeping the rest constant. The numbers on each side of the horizontal bars indicates that value the output would take if the input are changed to the highest/lowest possible value. In this case would an increase of chlorination (Input High) result in a decrease of the exposure concentration of imidacloprid (left side of base line). If the highest possible chlorination is applied, the exposure concentration would be 0.00001 µg/l.

C

Appendix: Selection Chart for Pesticides

This appendix presents the seven pesticides that were analysed for in Berg River with a motivation to why they were evaluated in the thesis or not.

Table C.1: Analysed pesticides and explanation of the selection of pesticides.

Pesticides	Detectable raw water [no. of samples]	Detectable drinking water [no. of samples]	Available data about removal efficiency & health data?	Evaluated in the thesis	Motivation
Atrazine	20/20	4/4	Yes	Yes	Found in raw and drinking water. Information available.
Bromoxynil	1/20	0/4	Hardly	No	Not found in raw and drinking water. Information not available.
Carbendazim	20/20	1/4	Yes	No	Only found in raw water. Information not available.
Chlorpyrifos	6/20	0/4	Yes	No	Barely found in raw and drinking water.
Diuron	20/20	0/4	Hardly	No	Not found in drinking water. Information not available.
Imidacloprid	20/20	3/4	Yes	Yes	Found in raw and drinking water. Information available.
Simazine	20/20	4/4	Yes	Yes	Found in raw and drinking water. Information available.

D

Appendix: Method for Lab Analysis

Methods used for water analysis.

The method is compiled by Gabre Kemp.

Extraction of water samples:

Water samples were first filtered through glass fibre filters and concentrated onto methanol conditioned C18 6mL solid phase extraction cartridges (Strata, Phenomenex) at a flow rate of 5mL/min. Bound analytes were slowly eluted off the dried cartridges using 2mL methanol followed by 2mL ethyl acetate. The eluant was vacuum dried (Thermo Scientific Savant Speedvac) until almost dry, and reconstituted in a 1/1000 of the original samples' volume consisting of H2O with 0.1 % formic acid.

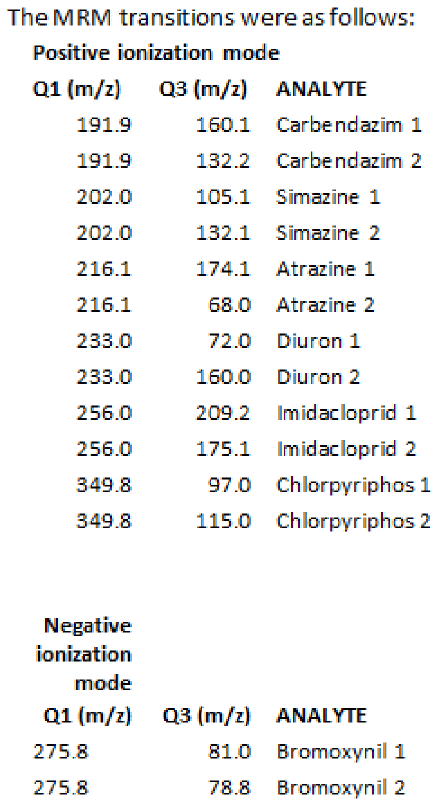
To create a calibration curve, six 500mL purified water samples were spiked with all the analytes and extracted by SPE as described above. From this a 6 level calibration curve was constructed with concentrations ranging from 0.0001 ppm, 0.001 ppm, 0.01ppm, 0.1 ppm, 1 ppm and 10 ppm.

Analysis:

Water samples were analysed using an ABSCIEX 4000 QTRAP hybrid triple quadrupole ion trap mass spectrometer with a Shimadzu HPLC stack as a front end. All data acquisition and processing was performed using Analyst 1.5 (AB SCIEX) software.

Samples were analysed in both positive and negative ionization mode. In positive mode, 20µL of each extracted sample was separated on a C18 (150mm x 2.0mm, Luna Phenyl-Hexyl, Phenomenex) column at a flow rate of 400 uL/min using a 15 min gradient from 5 % solvent A (H2O/0.1 % formic acid) to 95 % solvent B (MeOH/0.1 % formic acid) with a total run time of 23 min to allow for column re-equilibration. In negative ionisation mode, 20 µL of each sample was separated on a C18 (150mm x 2.0mm, Luna Phenyl-Hexyl, Phenomenex) column at a flow rate of 300µL /min using a 1 min gradient from 5 % solvent A (H2O/0.1 % formic acid) to 95 % solvent B (ACN/0.1 % formic acid) with a total run time of 10 min to allow for column re-equilibration. Eluting analytes were ionised by electrospray in the TurboV ion source with 400oC heater temperature to evaporate excess solvent, 30 psi nebuliser gas, 30 psi heater gas and 20 psi curtain gas. In positive ionisation mode the ion spray voltage was set at 5500 V and -4500 V in negative ionisation mode.

The targeted analyses were performed using 2 MRM (multiple reaction monitoring) transitions (see below) per analyte. The peak area on the chromatogram generated from the first and most sensitive transition was used as the quantifier while the second transition is used as a qualifier. The qualifier serves as an additional level of confirmation for the presence of the analyte, the retention time for these two transitions needs to be the same. The peak areas of the unknown samples were related back to a quantified value using the calibration curve for each analyte.



The MRM transitions were as follows:

Positive ionization mode

Q1 (m/z)	**Q3 (m/z)**	**ANALYTE**
191.9	160.1	Carbendazim 1
191.9	132.2	Carbendazim 2
202.0	105.1	Simazine 1
202.0	132.1	Simazine 2
216.1	174.1	Atrazine 1
216.1	68.0	Atrazine 2
233.0	72.0	Diuron 1
233.0	160.0	Diuron 2
256.0	209.2	Imidacloprid 1
256.0	175.1	Imidacloprid 2
349.8	97.0	Chlorpyriphos 1
349.8	115.0	Chlorpyriphos 2

Negative ionization mode

Q1 (m/z)	**Q3 (m/z)**	**ANALYTE**
275.8	81.0	Bromoxynil 1
275.8	78.8	Bromoxynil 2

Figure D.1: Table of the multiple reaction monitoring transitions.

E

Appendix: Examples of Distributions

This appendix illustrates the different distributions that are used in the thesis.

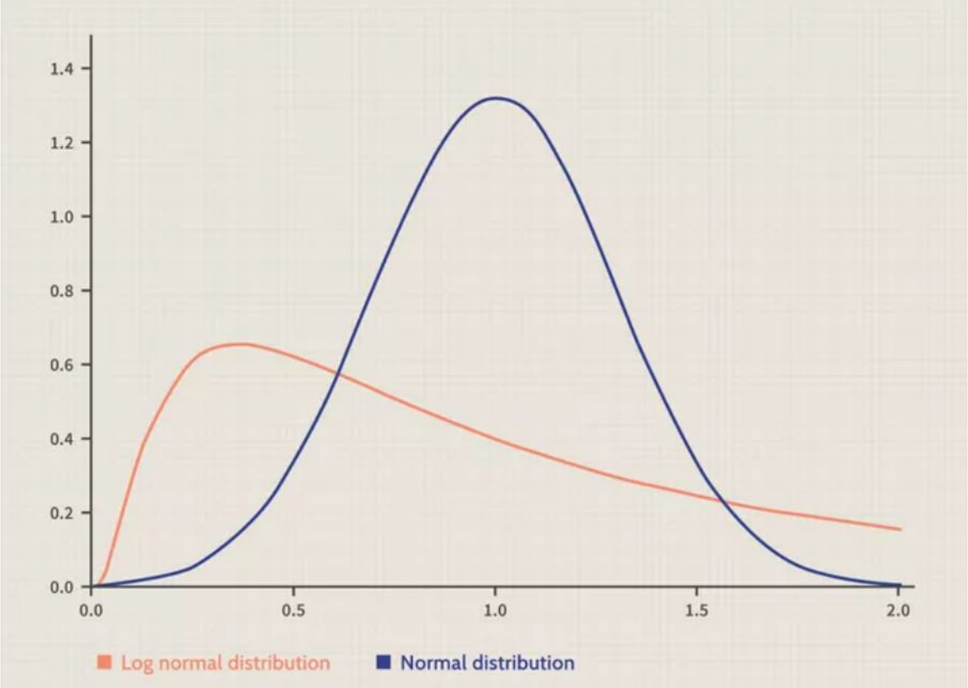


Figure E.1: Normal and log normal distribution (Sabrina Jiang, 2020).

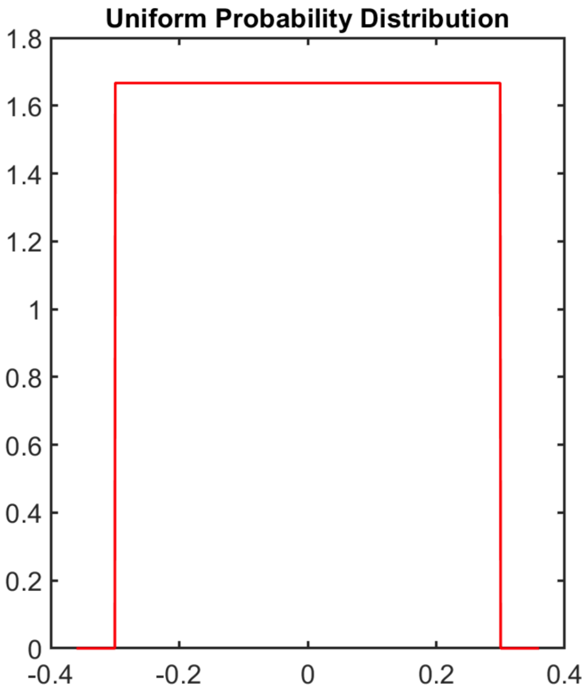


Figure E.2: Uniform distribution (Wikimedia Foundation, 2019).

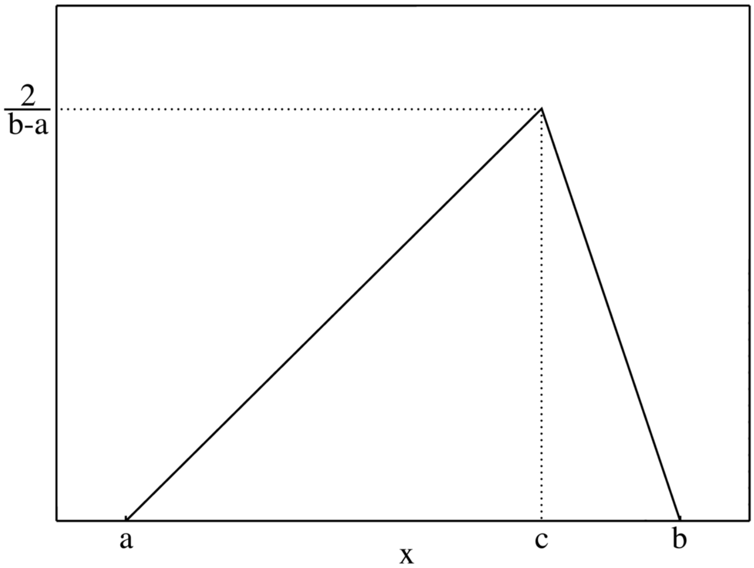


Figure E.3: Triangular distribution (Wikimedia Foundation, 2005).

F

Appendix: Pesticide Concentrations in Reference Rivers and Berg River

The tables present the pesticide concentrations in the raw water for the reference rivers and the analysed pesticide concentrations in the raw water at the inlet of Piketberg DWTP and Withoogte DWTP. The concentrations for the DWTPs were measured at the laboratory at the University of the Free State, Bloemfontein.

Table F.1: Reference rivers for each pesticide with corresponding concentrations.

Pesticide	Reference rivers river	Statistics	Concentration [µg/l]	Source
Atrazine	Upper Vaal	Mean	0.3725	Swartz et al. (2020)
		SD	0.1255	
Imidacloprid	Mzinti River	Mean	0.0400	Machete and Shadung (2019)
		SD	0.0356	
Simazine	Vals River and Renoster River	Mean	0.3520	Machete and Shadung (2019) }
		SD	0.3245	

Table F.2: Concentrations of pesticides at the inlet of Piketberg DWTP.

Sampling date	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
2022-02-22	0.0109	0.0015	0.1070
2022-02-22	0.0076	0.0027	0.0623
2022-03-03	0.0115	0.0019	0.0812
2022-03-03	0.0098	0.0016	0.0746
2022-03-09	0.0095	0.0015	0.0763
2022-03-09	0.0089	0.0012	0.0580
2022-03-15	0.0092	0.0010	0.0800
2022-03-15	0.0098	0.0009	0.0689
2022-03-24	0.0101	0.0013	0.0696
2022-03-24	0.0102	0.0010	0.0732

Table F.3: Concentrations of pesticides at the inlet of Withoogte DWTP.

Sampling date	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
2022-02-22	0.0099	0.0027	0.0759
2022-02-22	0.0112	0.0027	0.0971
2022-03-03	0.0110	0.0018	0.0650
2022-03-03	0.0105	0.0012	0.0960
2022-03-09	0.0098	0.0022	0.0743
2022-03-09	0.0090	0.0018	0.0739
2022-03-15	0.0103	0.0026	0.0753
2022-03-15	0.0105	0.0016	0.0919
2022-03-24	0.0079	0.0013	0.0673
2022-03-24	0.0107	0.0022	0.0709

G

Appendix: Criterion for UFs and Applied UFs

This appendix will present the criteria for applying the uncertainty factors, followed by the applied uncertainty factors for atrazine, imidacloprid and simazine. The factors were applied to be able to calulcate the ADI based on the health data.

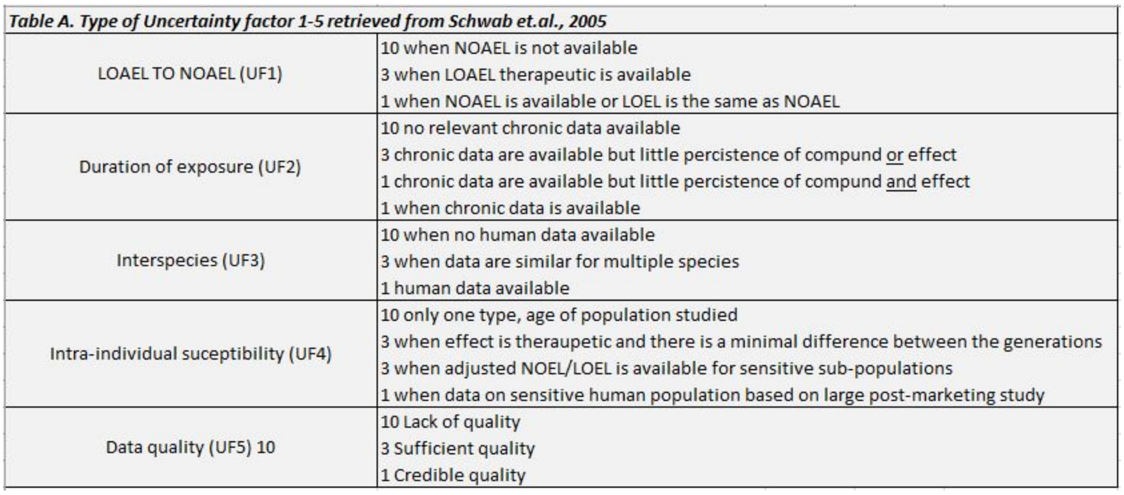


Table A. Type of Uncertainty factor 1-5 retrieved from Schwab et.al., 2005	
LOAEL TO NOAEL (UF1)	10 when NOAEL is not available 3 when LOAEL therapeutic is available 1 when NOAEL is available or LOEL is the same as NOAEL
Duration of exposure (UF2)	10 no relevant chronic data available 3 chronic data are available but little percistence of compund or effect 1 chronic data are available but little percistence of compund and effect 1 when chronic data is available
Interspecies (UF3)	10 when no human data available 3 when data are similar for multiple species 1 human data available
Intra-individual suceptibility (UF4)	10 only one type, age of population studied 3 when effect is theraupetic and there is a minimal difference between the generations 3 when adjusted NOEL/LOEL is available for sensitive sub-populations 1 when data on sensitive human population based on large post-marketing study
Data quality (UF5) 10	10 Lack of quality 3 Sufficient quality 1 Credible quality

Figure G.1: Criteria for uncertainty factors.

When determining the values for UF2, the duration of exposure ATSDR (2003) was used as reference. If the study was conducted for 14 days or less, the end point was considered acute toxicity which resulted in a factor of ten. In the case when the study was conducted for 15-364 days, the end point was assumed to intermediate and a UF factor of three was applied. Chronic effects were assumed to occur if the duration of a study was more than 365 days, which resulted in a UF value of one. Figure G.1 presents the guidelines used for determining all UF factors, based on Schwab et al. (2005).

Table G.1: Applied uncertainty factors, UF, for atrazine.

Atrazine			
Health Data	Uncertainty type	Applied value	Justification
NOAEL	UF1	1	NOAEL is given
NOAEL	UF2	10	No chronic data available
NOAEL	UF3	10	No human data
NOAEL	UF4	10	Only one type/age population studied
NOAEL	UF5	3	Sufficient quality
LOAEL 1	UF1	10	NOAEL is not given
LOAEL 1	UF2	3	Chronic data available but little persistence
LOAEL 1	UF3	10	No human data
LOAEL 1	UF4	10	Only one type/age population studied
LOAEL 1	UF5	3	Sufficient quality
LOAEL 2	UF1	10	NOAEL is not given
LOAEL 2	UF2	10	No chronic data available
LOAEL 2	UF3	10	No human data
LOAEL 2	UF4	10	Only one type/age population studied
LOAEL 2	UF5	3	Sufficient quality

Table G.2: Applied uncertainty factors, UF, for imidacloprid.

Imidacloprid			
Health Data	Uncertainty type	Applied value	Justification
NOAEL 1	UF1	1	NOAEL is given
NOAEL 1	UF2	10	No chronic data available
NOAEL 1	UF3	10	No human data
NOAEL 1	UF4	3	NOAEL available for different subpopulations
NOAEL 1	UF5	1	Credible quality
NOAEL 2	UF1	1	NOAEL is given
NOAEL 2	UF2	3	Chronic data available but little persistence
NOAEL 2	UF3	10	No human data
NOAEL 2	UF4	10	Only one type/age population studied
NOAEL 2	UF5	10	Lack of quality
NOAEL 3	UF1	1	NOAEL is given
NOAEL 3	UF2	3	Chronic data available but little persistence
NOAEL 3	UF3	10	No human data
NOAEL 3	UF4	10	Only one type/age population studied
NOAEL 3	UF5	3	Sufficient quality
LOAEL	UF1	10	NOAEL is not given
LOAEL	UF2	10	No relevant chronic data
LOAEL	UF3	10	No human data
LOAEL	UF4	3	NOAEL available for different subpopulations
LOAEL	UF5	1	Credible quality

Table G.3: Applied uncertainty factors, UF, for simazine.

Simazine			
Health Data	Uncertainty type	Applied value	Justification
NOAEL 1	UF1	1	NOAEL is given
NOAEL 1	UF2	3	Chronic data available but little persistence
NOAEL 1	UF3	10	No human data available
NOAEL 1	UF4	10	Only one type/age population studied
NOAEL 1	UF5	3	Sufficient quality
NOAEL 2	UF1	1	NOAEL is given
NOAEL 2	UF2	10	No chronic data available
NOAEL 2	UF3	10	No human data available
NOAEL 2	UF4	10	Only one type/age population studied
NOAEL 2	UF5	3	Sufficient quality

H

Appendix: Compilation of ADI

This appendix presents the ADI based on the literature study, the ADI based on toxicological data and what minimum, mean, and maximum values of the ADI that was used as input to determine the simulated ADI.

Table H.1: ADI based on literature for the chosen pesticides.

Pesticide	ADI [µg/l]	Mean value	Species	Source
Atrazine	6	13	Human, 70 kg	Olatoye et al. (2021)
	20		Human, 55-60 kg	FAO and WHO (2007)
Imidacloprid	60	30.3	Human	Wang et al. (2022)
	0.6		Human, 55-60 kg	Lovaković et al. (2021)
Simazine	5	5	Human	Bányiová et al. (2016)
	5		Human	Murray et al. (2010)

Table H.2: ADI based on toxicological data for the pesticides.

Pesticide	Point of Departure	Value [µg/kg bw/day]	Calculated ADI with UF [µg/kg bw/day]
Atrazine	NOAEL	3 700	1.23
	LOAEL 1	1 000	0.11
	LOAEL 2	39 000	1.30
Imidacloprid	NOAEL 1	3 420	11.40
	NOAEL 2	50 000	16.67
	NOAEL 3	9 300	10.33
	LOAEL	10 250	3.42
Simazine	NOAEL 1	10 000	11.11
	NOAEL 2	700	0.23

Table H.3: Minimum, maximum and mean ADI based on toxicological ADI and ADI from literature.

Pesticide	Min ADI [µg/kg bw/-day]	Max ADI [µg/kg bw/-day]	Mean ADI [µg/kg bw/day]
Atrazine	0.11	20.0	5.73
Imidacloprid	0.6	60.0	17.07
Simazine	0.23	11.11	5.34

I

Appendix: Tornado Graphs for DWEL

This appendix will include tornado graphs illustrating which input parameters have the largest effect on the mean of DWEL. The graphs will be produced for atrazine, imidacloprid and simazine for each population group: infants breastfed, infants formula-fed, children and adults.

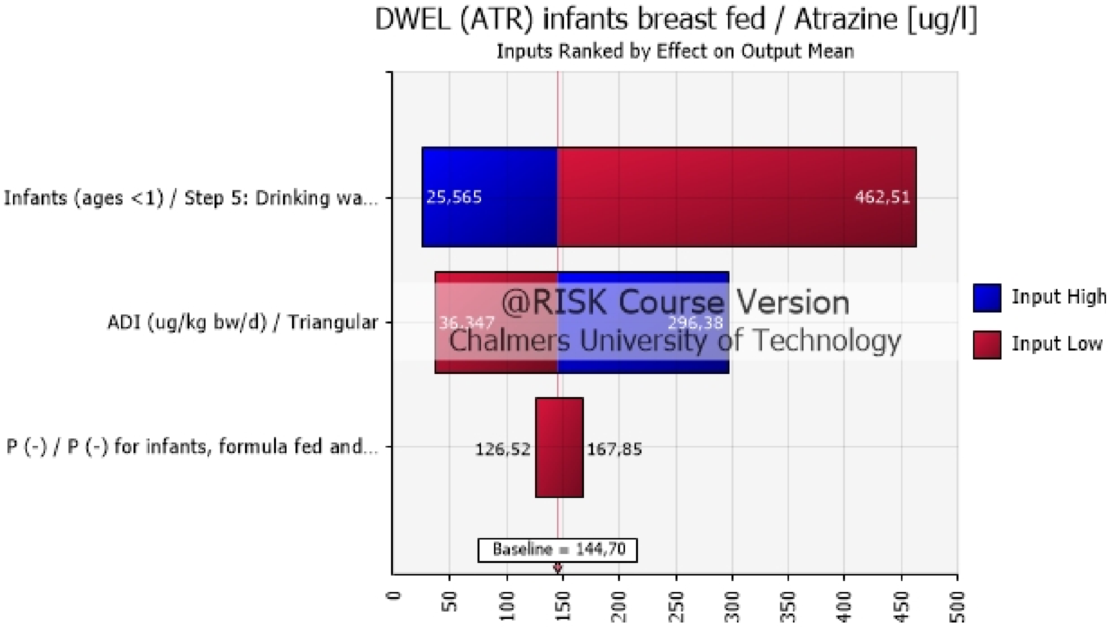


Figure I.1: Tornado graph illustrating the inputs affecting the mean of DWEL for atrazine for infants breastfed.

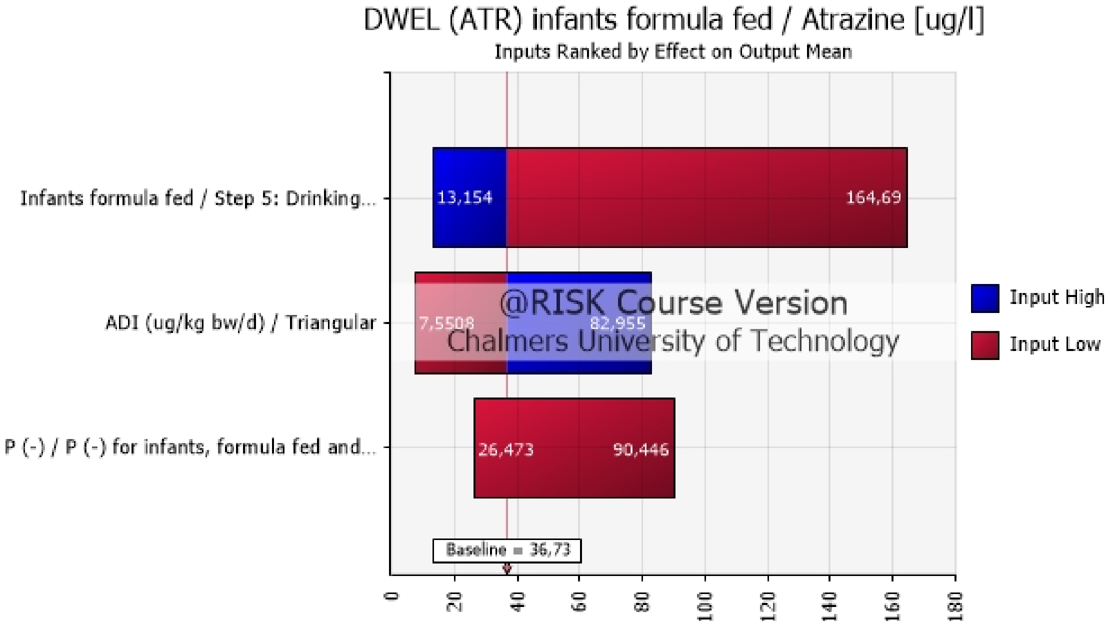


Figure I.2: Tornado graph illustrating the inputs affecting the mean of DWEL for atrazine for infants formula-fed.

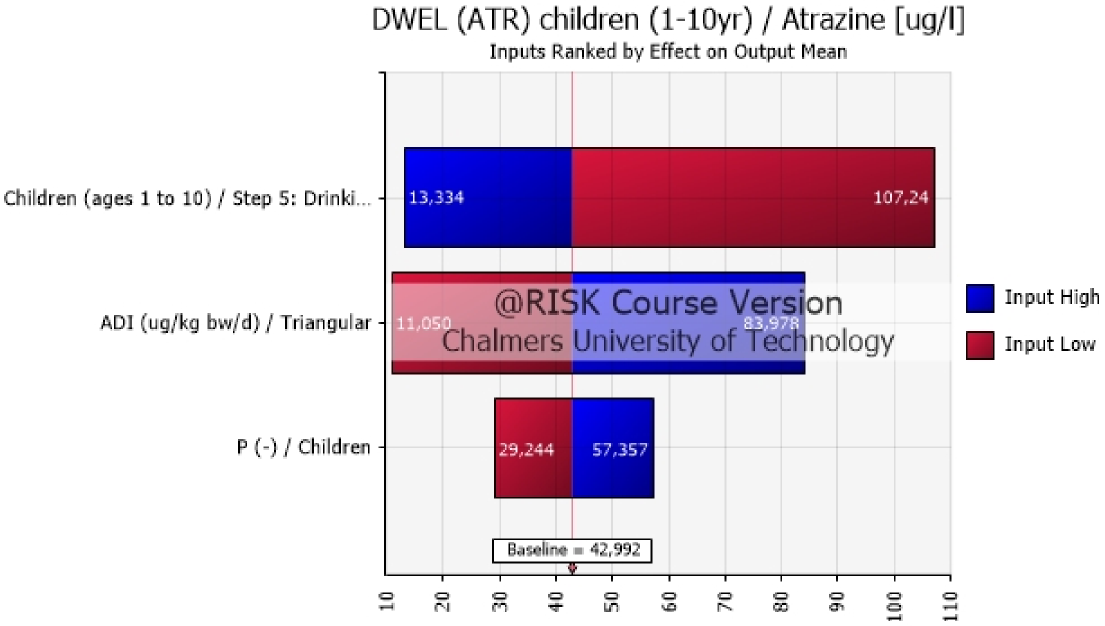


Figure I.3: Tornado graph illustrating the inputs affecting the mean of DWEL for atrazine for children.

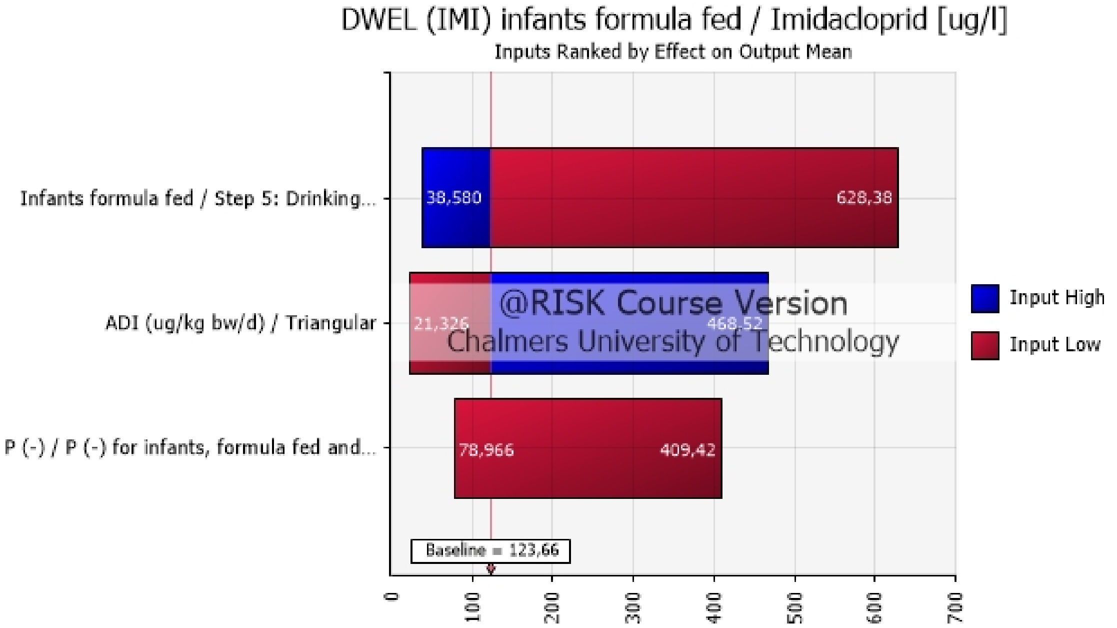


Figure I.4: Tornado graph illustrating the inputs affecting the mean of DWEL for imidacloprid for infants formula-fed.

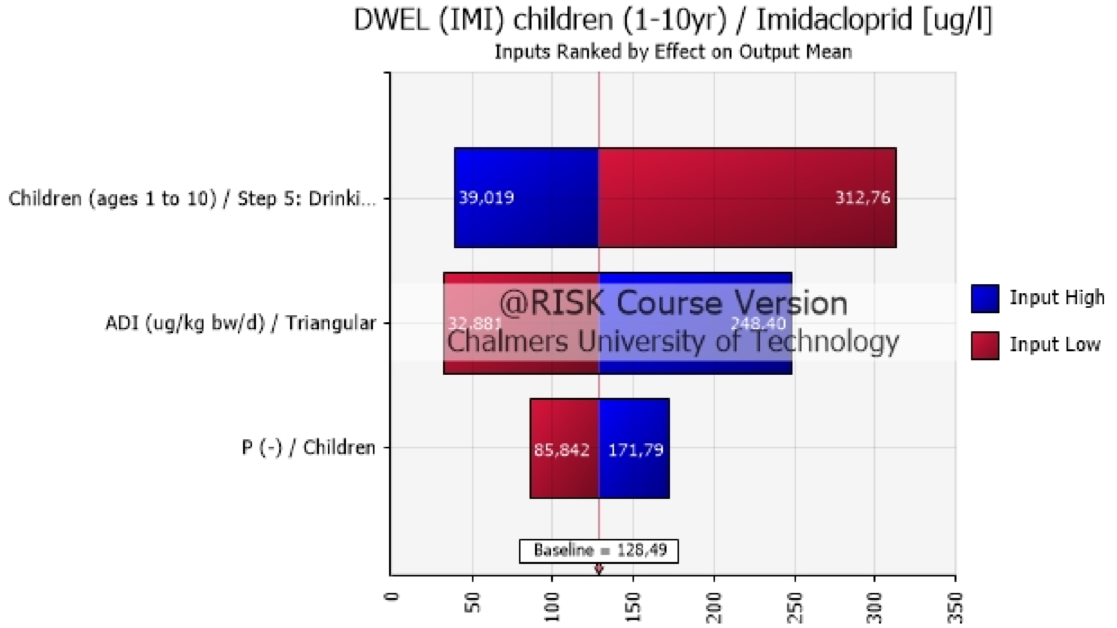


Figure I.5: Tornado graph illustrating the inputs affecting the mean of DWEL for imidacloprid for children.

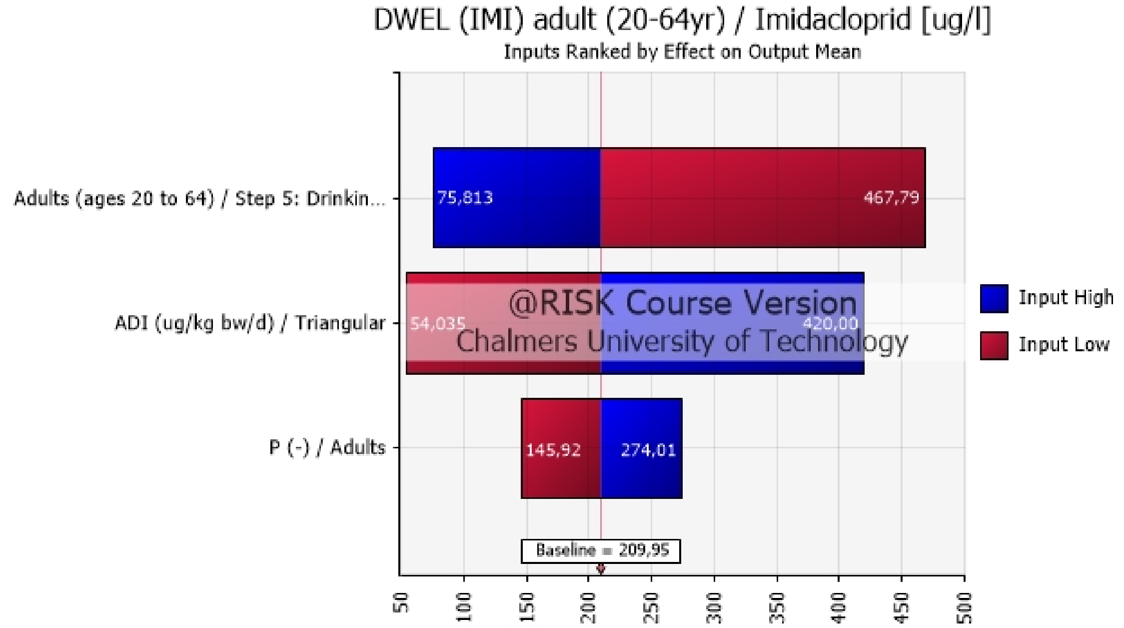


Figure I.6: Tornado graph illustrating the inputs affecting the mean of DWEL for imidacloprid for adults.

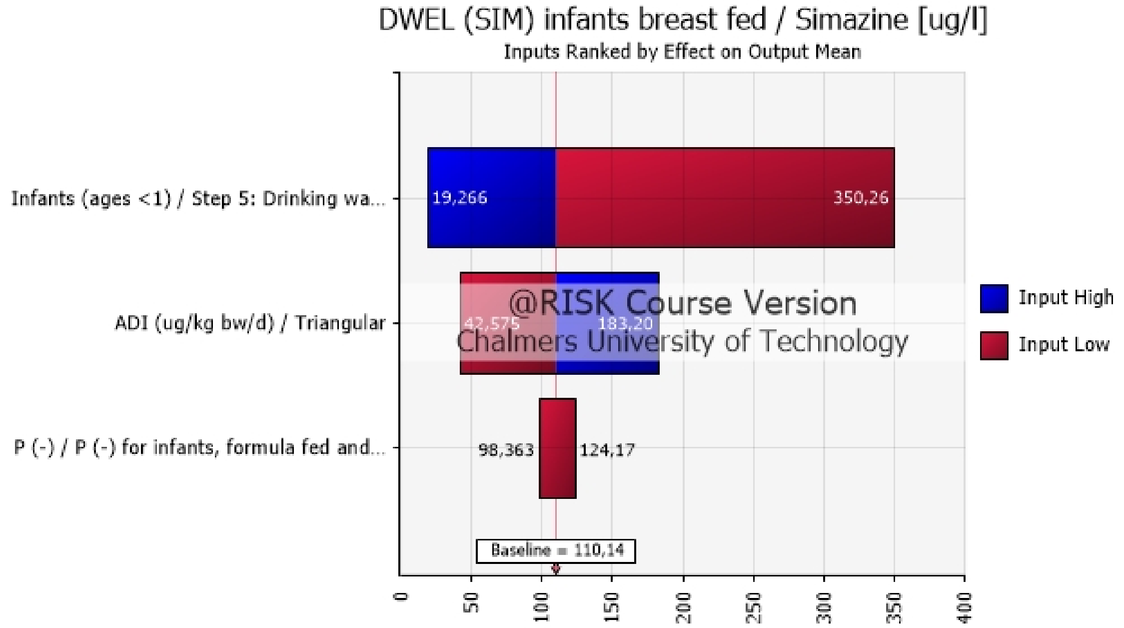


Figure I.7: Tornado graph illustrating the inputs affecting the mean of DWEL for simazine for infants breastfed.

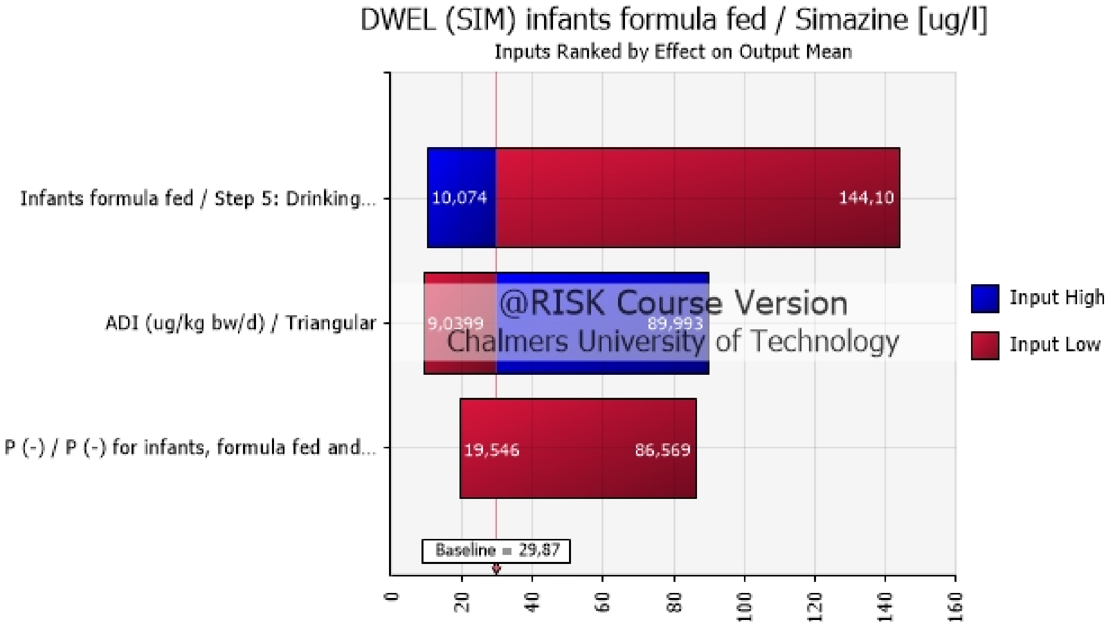


Figure I.8: Tornado graph illustrating the inputs affecting the mean of DWEL for simazine for infants formula-fed.

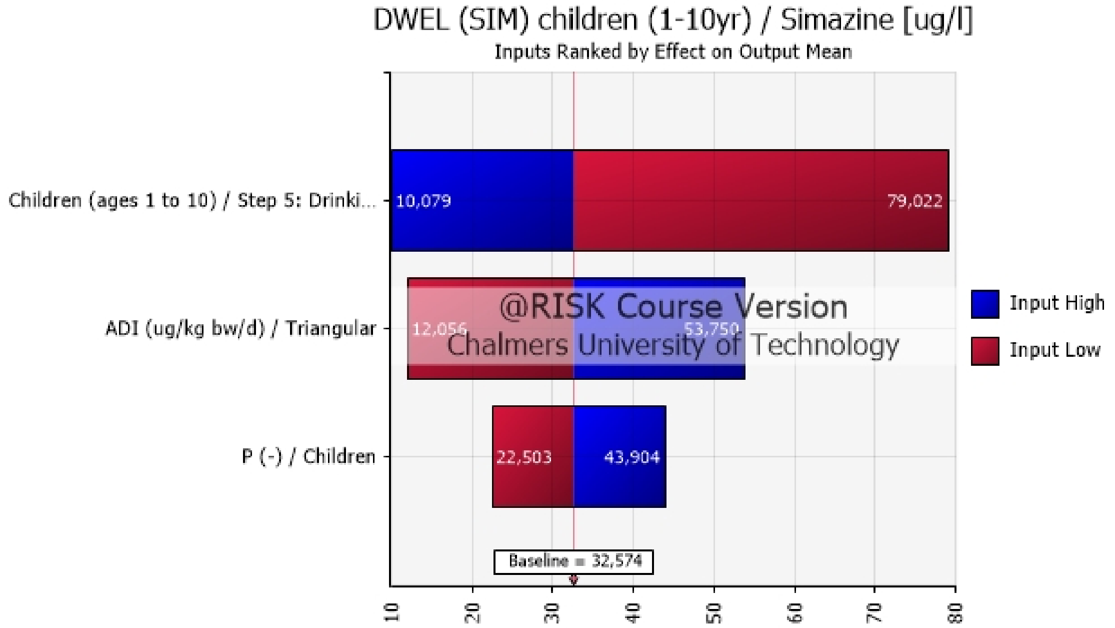


Figure I.9: Tornado graph illustrating the inputs affecting the mean of DWEL for simazine for children.

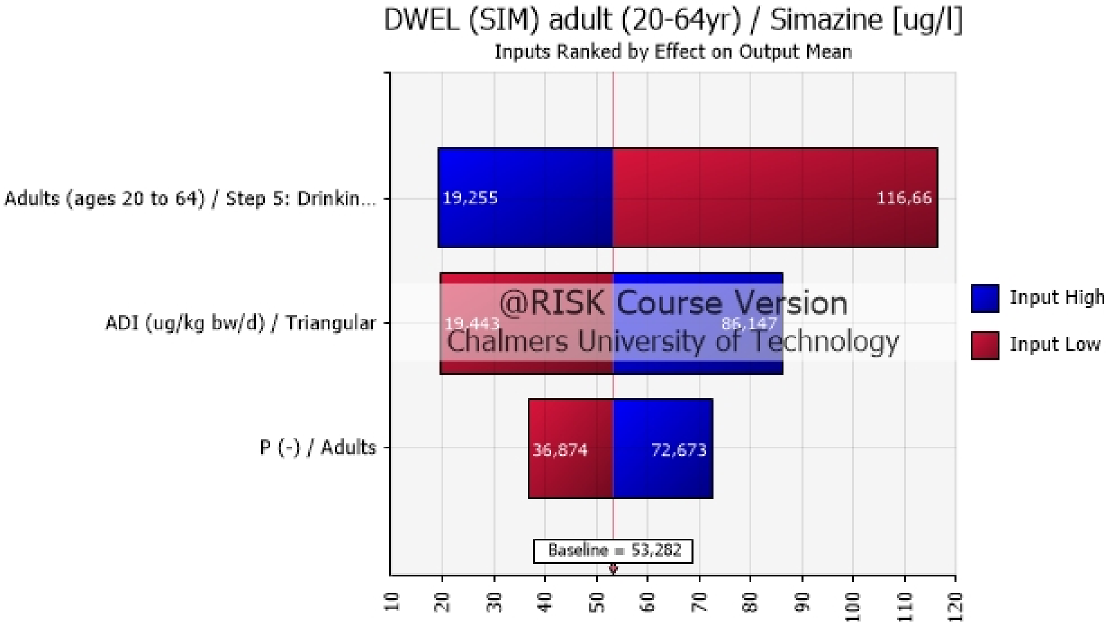


Figure I.10: Tornado graph illustrating the inputs affecting the mean of DWEL for simazine for adults.

J

Appendix: Tornado Graphs for Exposure Concentrations

This appendix will include tornado graphs illustrating which input parameters have the largest effect on the mean of the exposure concentrations. The graphs will be produced for atrazine, imidacloprid and simazine from reference rivers, Piketberg DWTP and Withoogte DWTP for scenario one and scenario three. Scenario two will not be included as it is only dependent on one input parameter, raw water concentration.

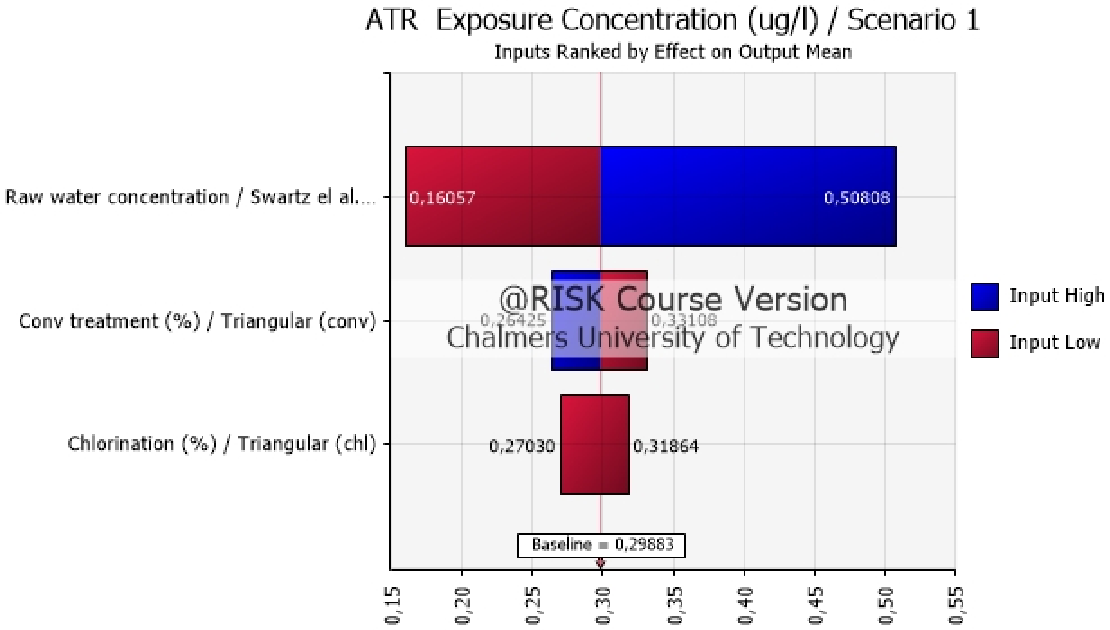


Figure J.1: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for atrazine, reference river, in scenario one.

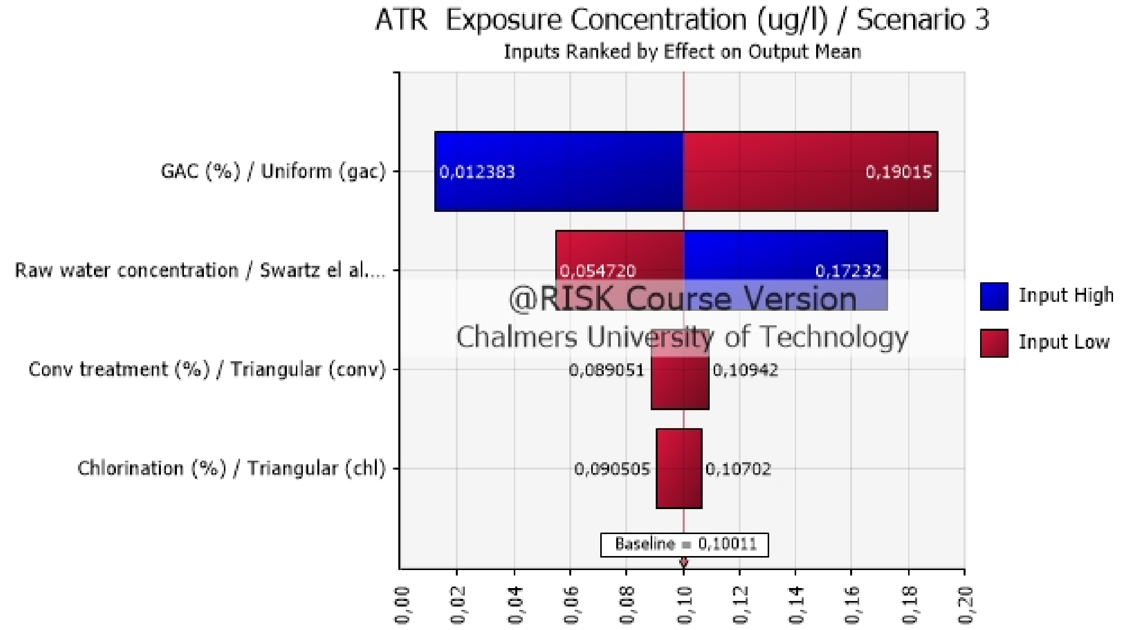


Figure J.2: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for atrazine, reference river, in scenario three.

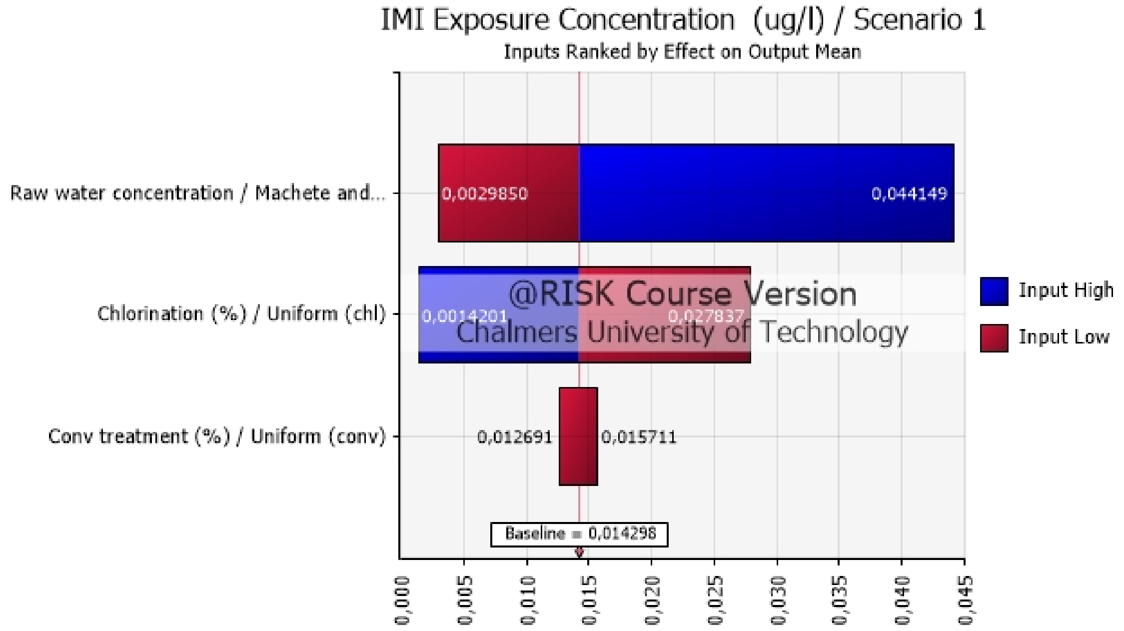


Figure J.3: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for imidacloprid, reference river, in scenario one.

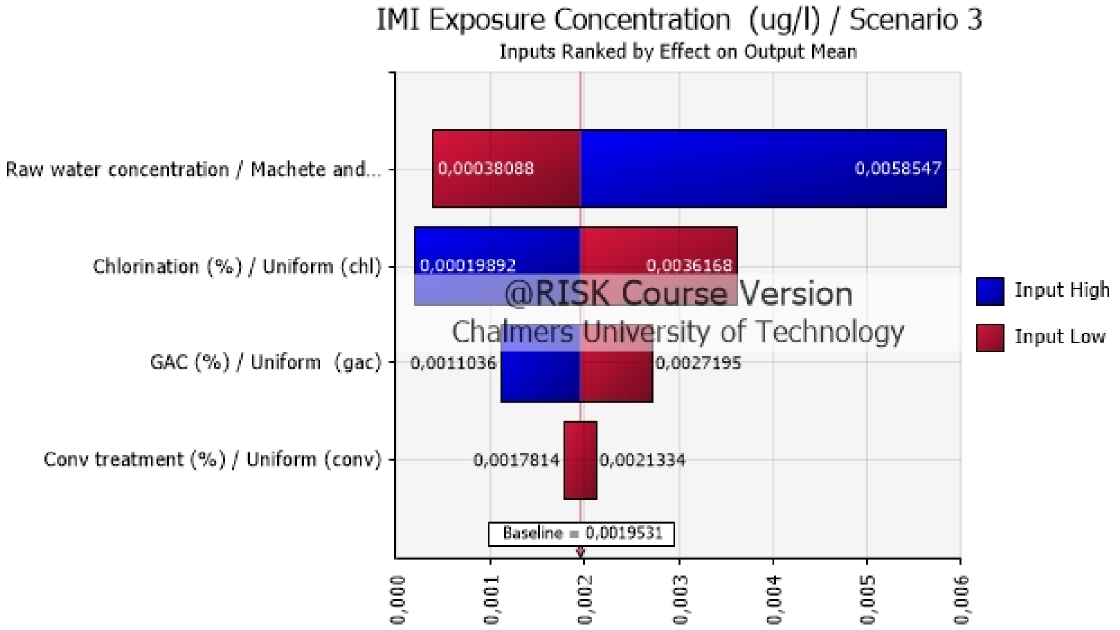


Figure J.4: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for imidacloprid, reference river, in scenario three.

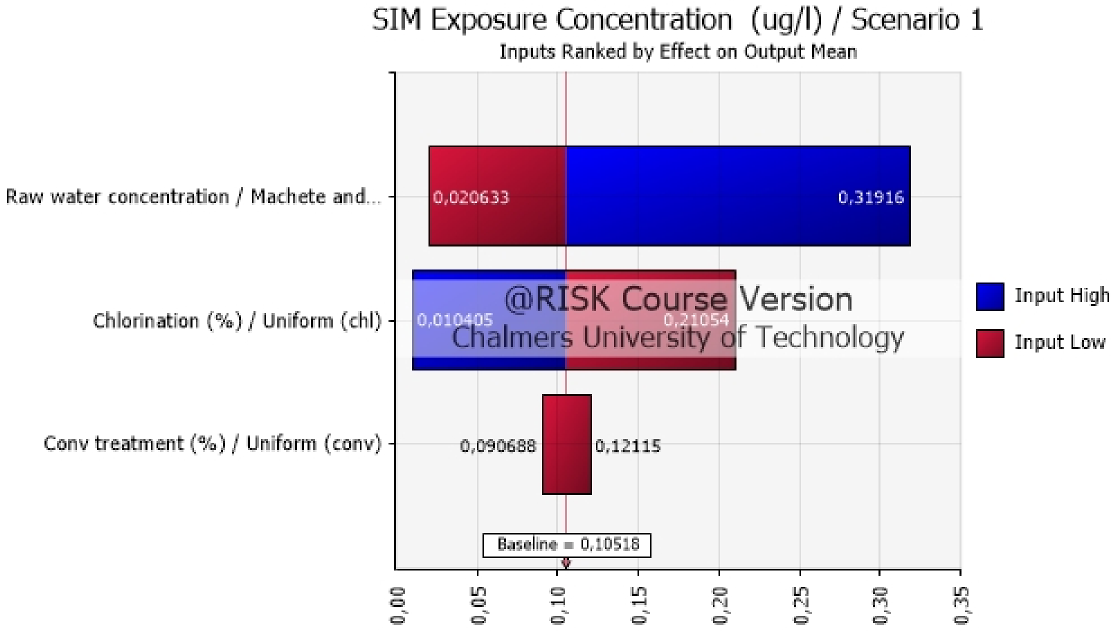


Figure J.5: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for simazine, reference river, in scenario one.

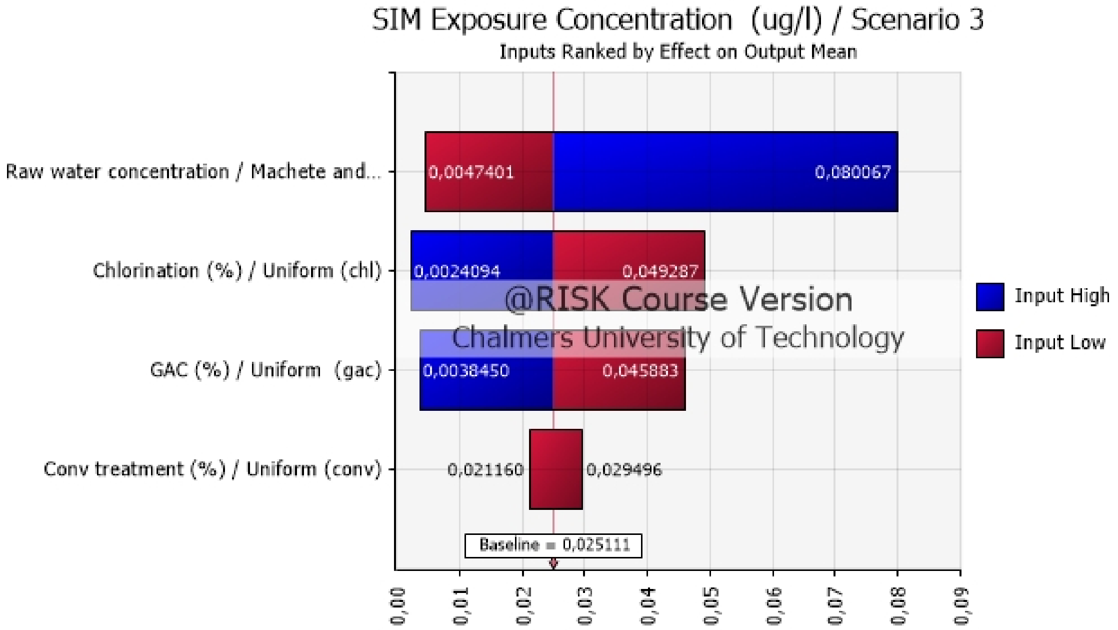


Figure J.6: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for simazine, reference river, in scenario three.

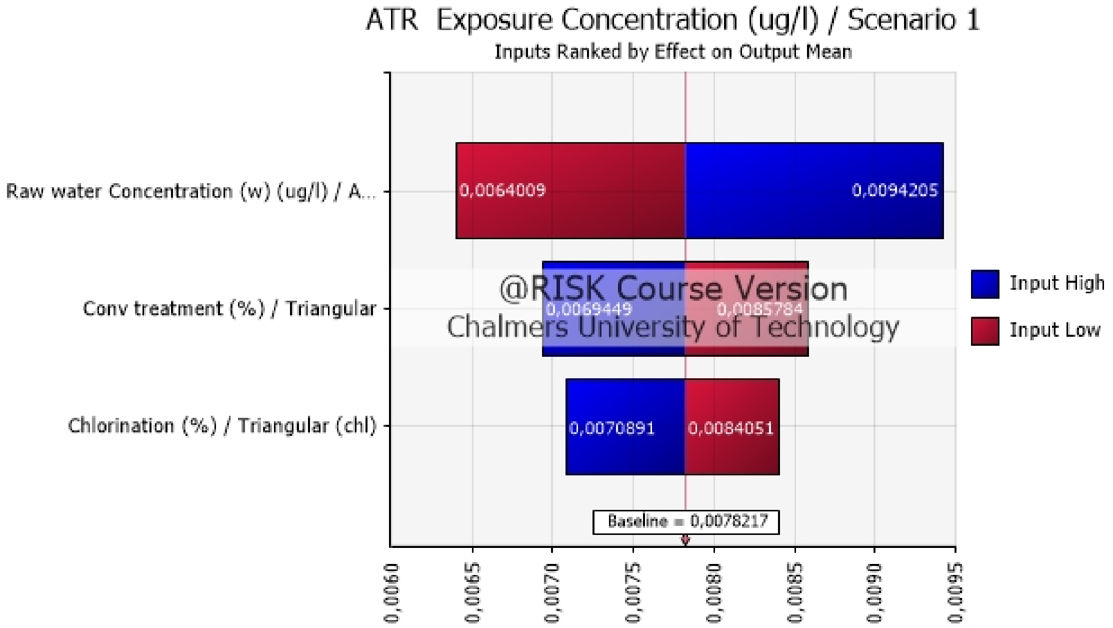


Figure J.7: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for atrazine, Piketberg DWTP, in scenario one.

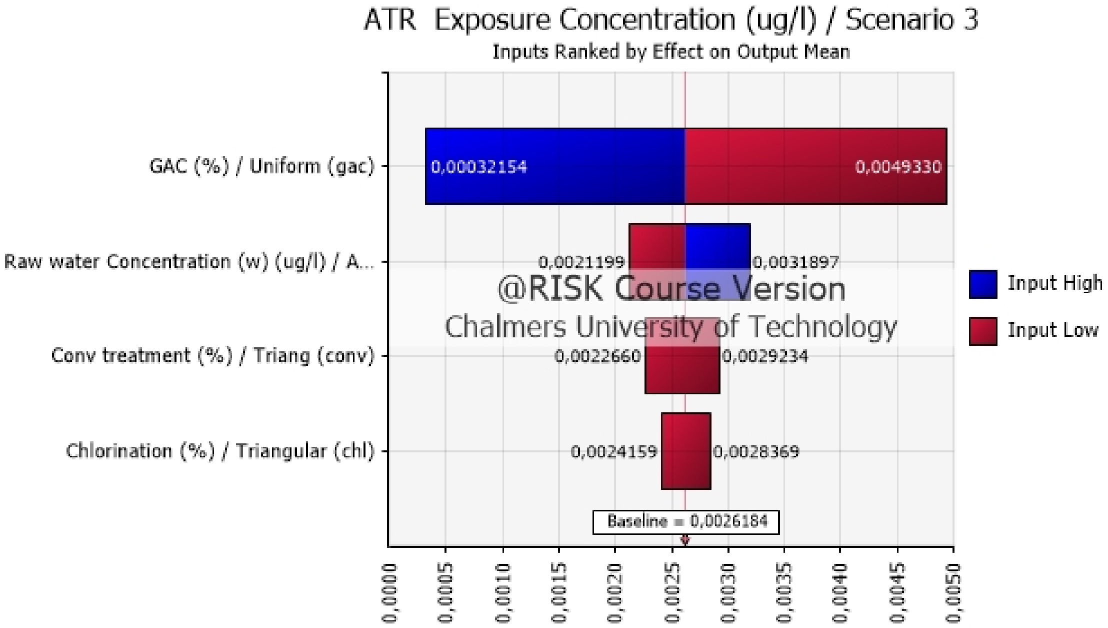


Figure J.8: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for atrazine, Piketberg DWTP, in scenario three.

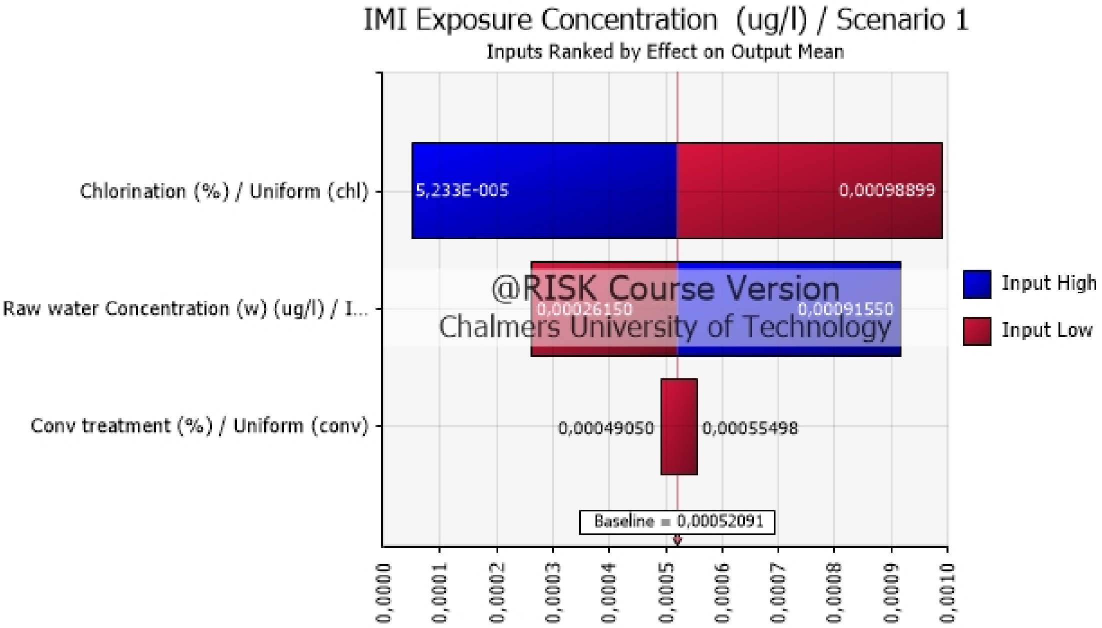


Figure J.9: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for imidacloprid, Piketberg DWTP, in scenario one.

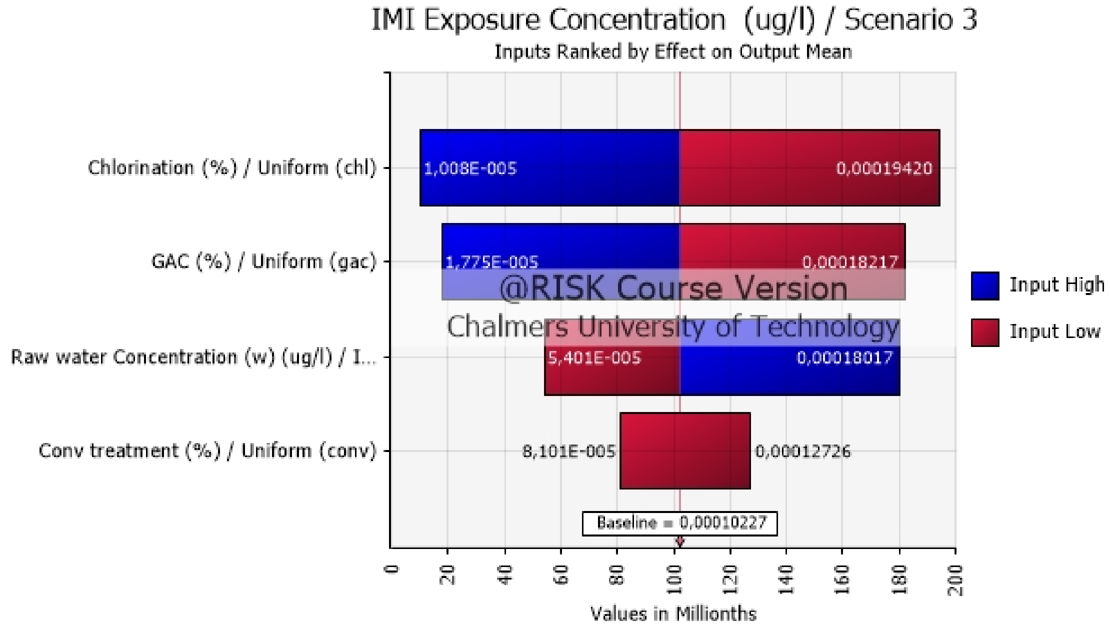


Figure J.10: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for imidacloprid, Piketberg DWTP, in scenario three.

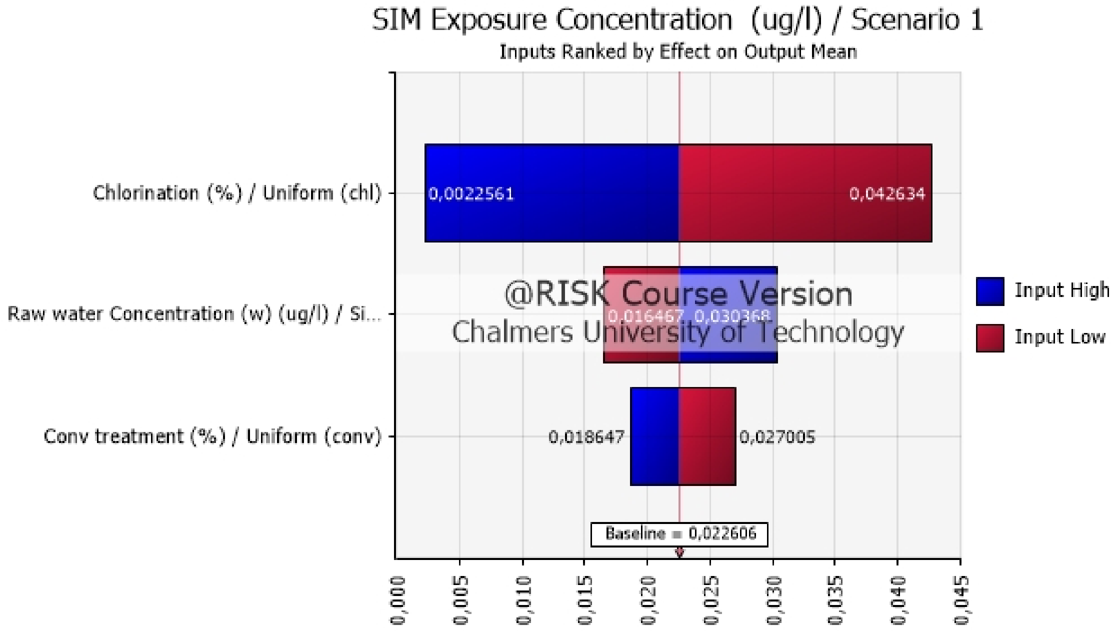


Figure J.11: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for simazine, Piketberg DWTP, in scenario one.

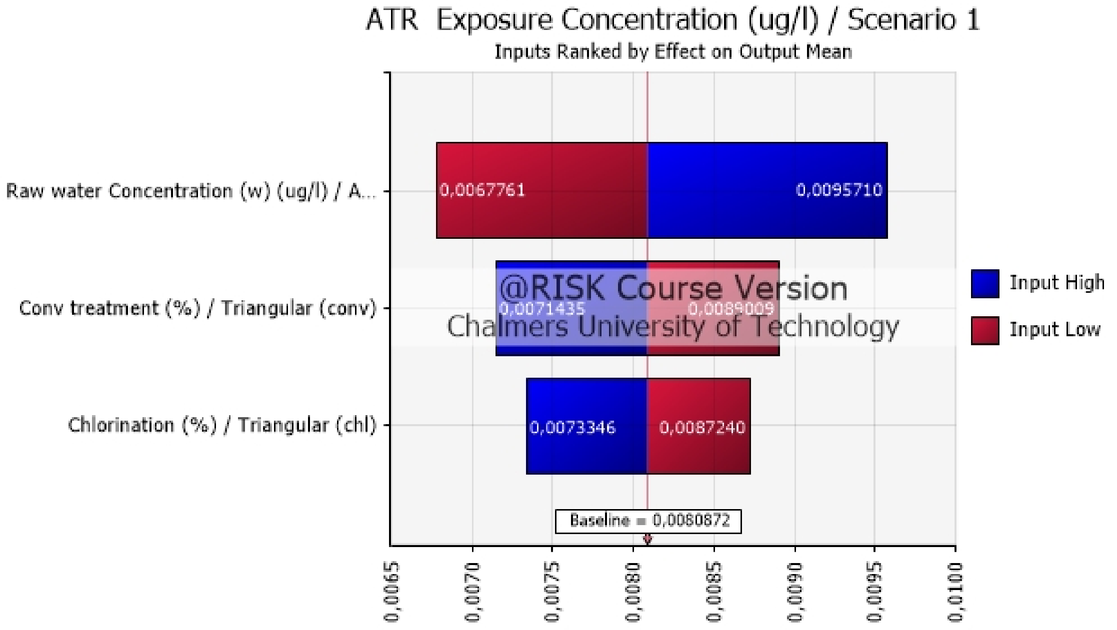


Figure J.12: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for atrazine, Withoogte DWTP, in scenario one.

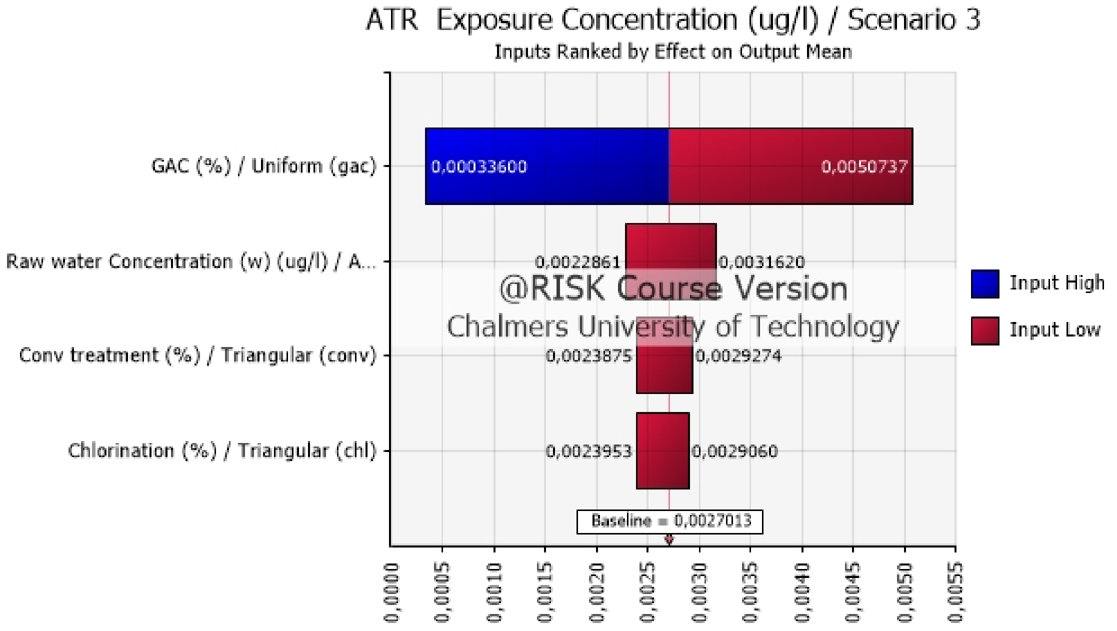


Figure J.13: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for atrazine, Withoogte DWTP, in scenario three.

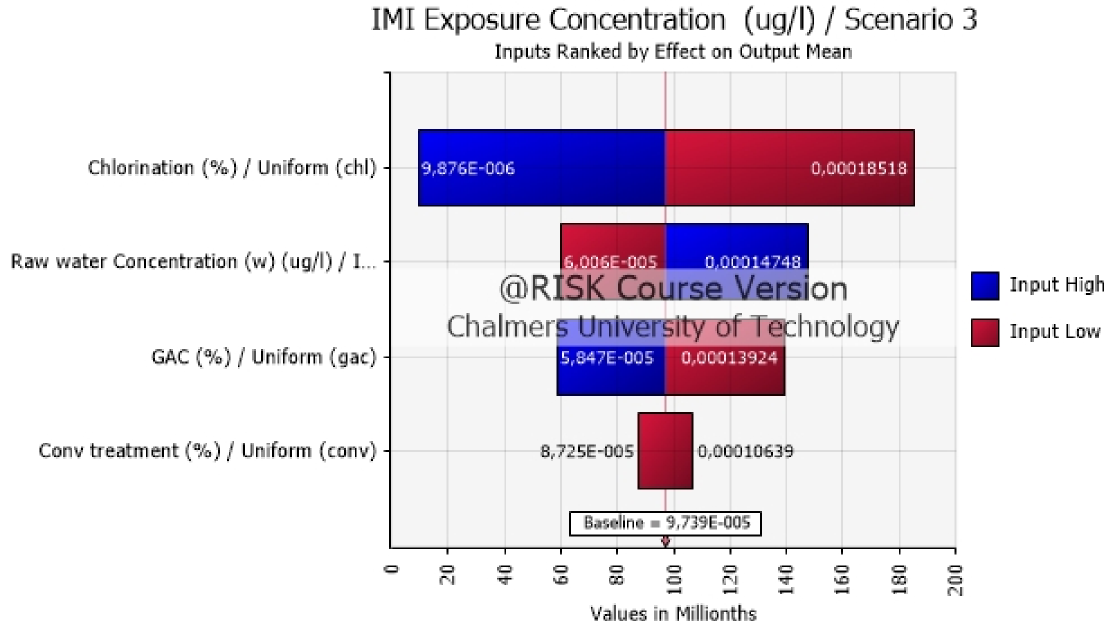


Figure J.14: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for imidacloprid, Withoogte DWTP, in scenario three.

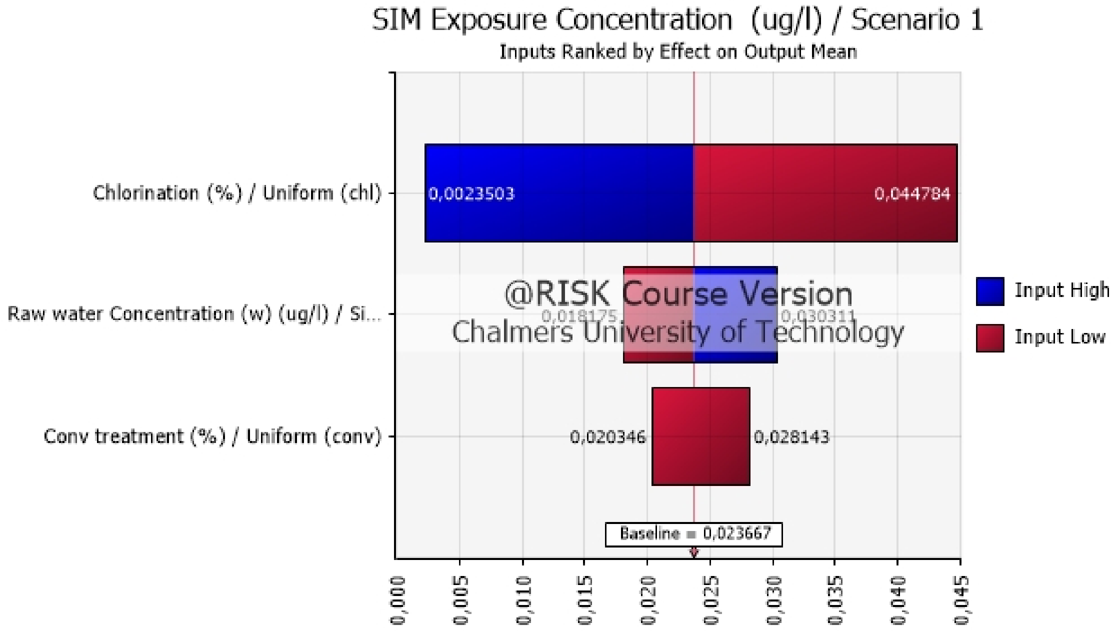


Figure J.15: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for simazine, Withoogte DWTP, in scenario one.

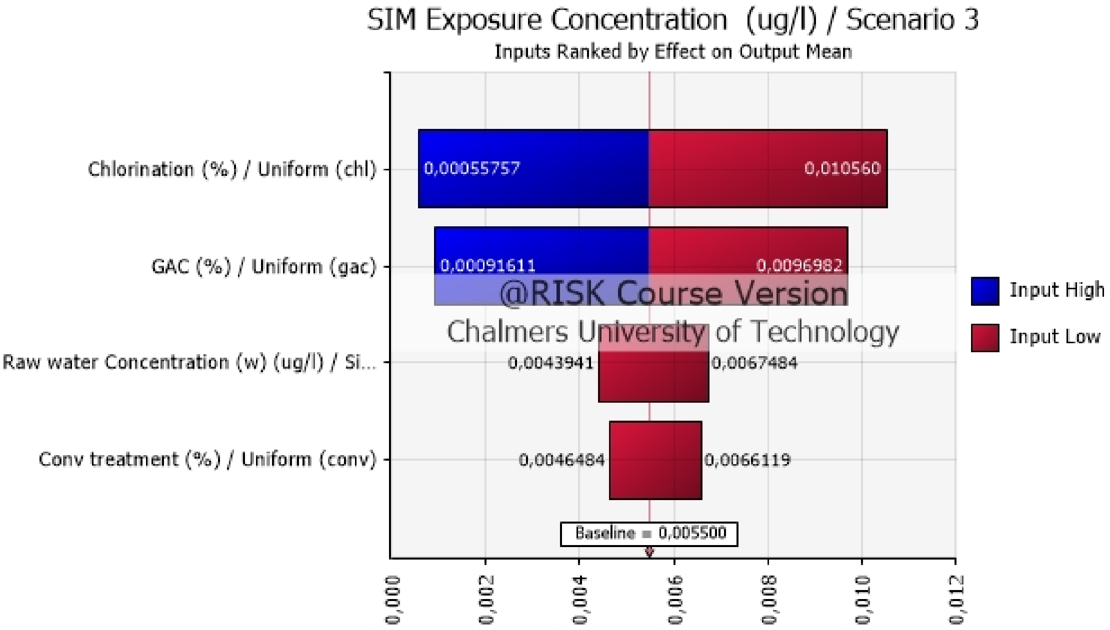


Figure J.16: Tornado graph illustrating the inputs affecting the mean of the exposure concentration for simazine, Withoogte DWTP, in scenario three.

K

Appendix: HQ Based on DWEL Point Values from Literature

This appendix presents the calculated HQ based on DWEL point values from literature for all scenarios for both Piketberg DWTP and Withoogte DWTP.

Table K.1: HQ based on DWEL point values from literature, scenario one Piketberg DWTP.

HQ Scenario 1 Piketberg DWTP			
Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
Children	0.0003	0.000009	0.0023
Adults	0.000086	0.000002	0.00065

Table K.2: HQ based on DWEL point values from literature, scenario two Piketberg DWTP.

HQ Scenario 2 Piketberg DWTP			
Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
Children	0.00038	0.000024	0.0075
Adults	0.00011	0.000007	0.002

Table K.3: HQ based on DWEL point values from literature, scenario three Piketberg DWTP.

HQ Scenario 3 Piketberg DWTP			
Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
Children	0.0001	0.000002	0.00053
Adults	0.000029	0.0000005	0.00015

Table K.4: HQ based on DWEL point values from literature, scenario one Withoogte DWTP.

HQ Scenario 1 Withoogte DWTP			
Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
Children	0.0003	0.000012	0.0024
Adults	0.000089	0.000005	0.00068

Table K.5: HQ based on DWEL point values from literature, scenario two Withogte DWTP.

HQ Scenario 2 Withoogte DWTP			
Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
Children	0.00039	0.00003	0.0079
Adults	0.00011	0.000009	0.0023

Table K.6: HQ based on DWEL point values from literature, scenario three Withoogte DWTP.

HQ Scenario 3 Withoogte DWTP			
Population group	Atrazine [µg/l]	Imidacloprid [µg/l]	Simazine [µg/l]
Children	0.0001	0.000002	0.0055
Adults	0.00003	0.0000005	0.00016

L

Appendix: Tornado Graphs HQ

This appendix will include tornado graphs illustrating which input parameters have the largest effect on the mean of the HQ. The graphs will be produced for infants formula-fed exposed to atrazine, imidacloprid and simazine from reference rivers, Piketberg DWTP and Withoogte DWTP for all scenarios. The population group infants formula-fed was chosen as it is the most sensitive group.

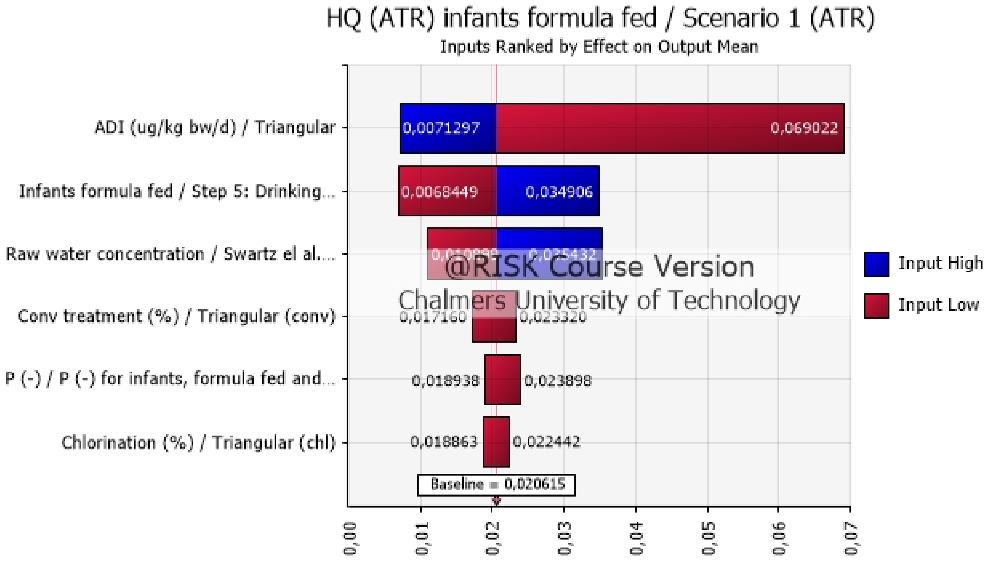


Figure L.1: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, reference river, scenario one.

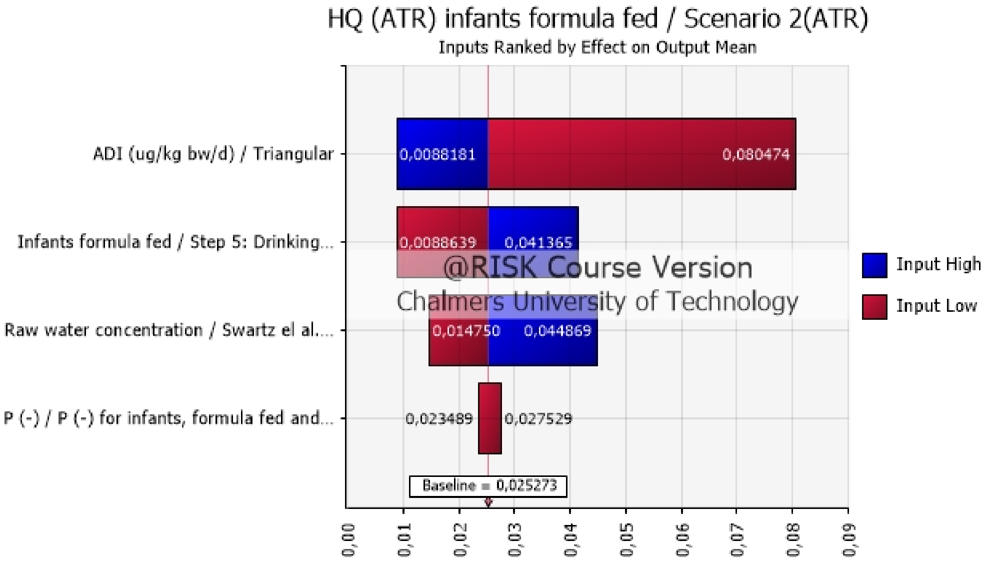


Figure L.2: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, reference river, scenario two.

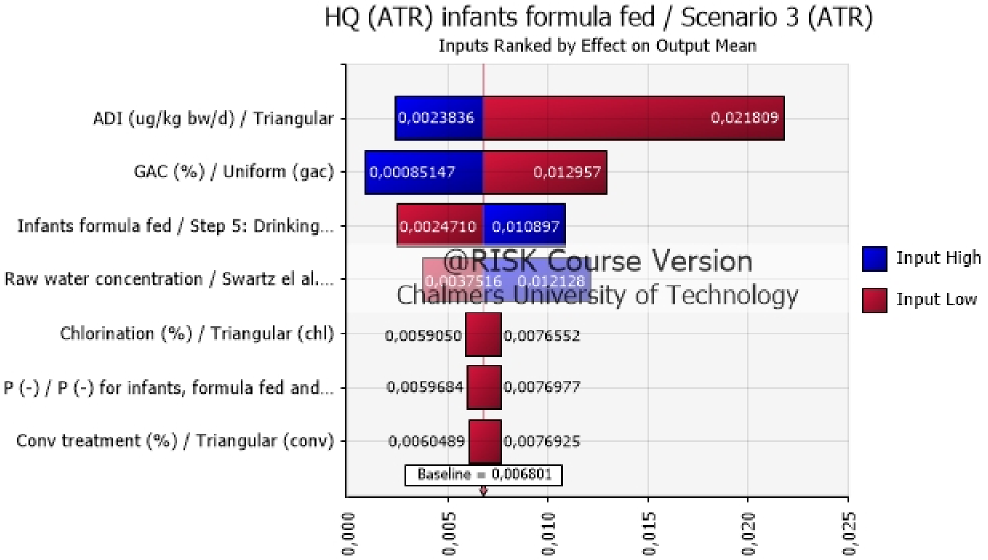


Figure L.3: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, reference river, scenario three.

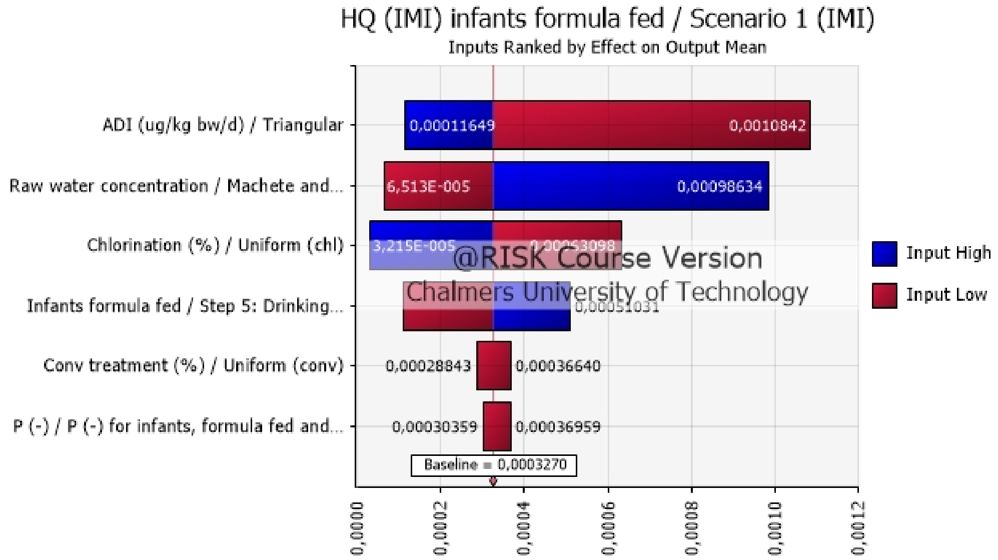


Figure L.4: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, reference river, scenario one.

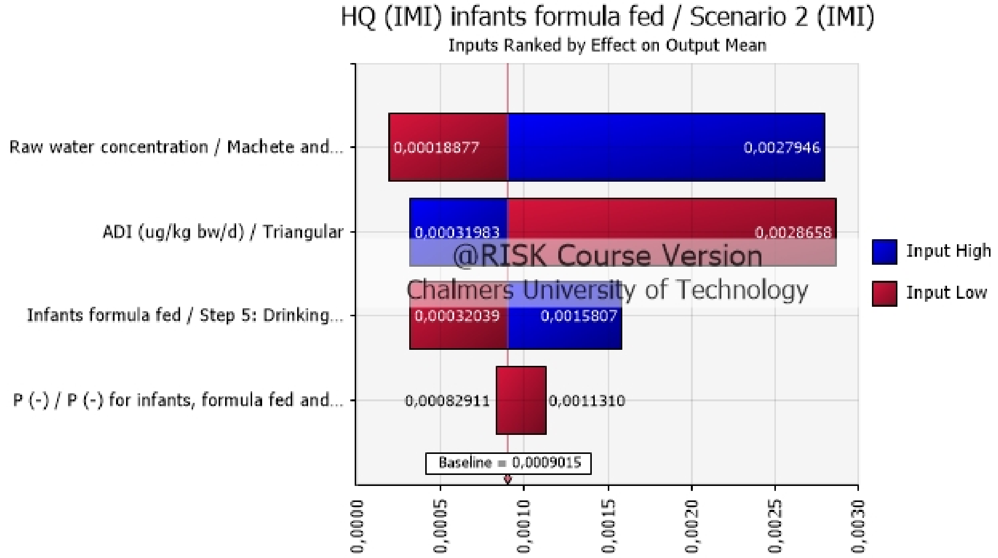


Figure L.5: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, reference river, scenario two.

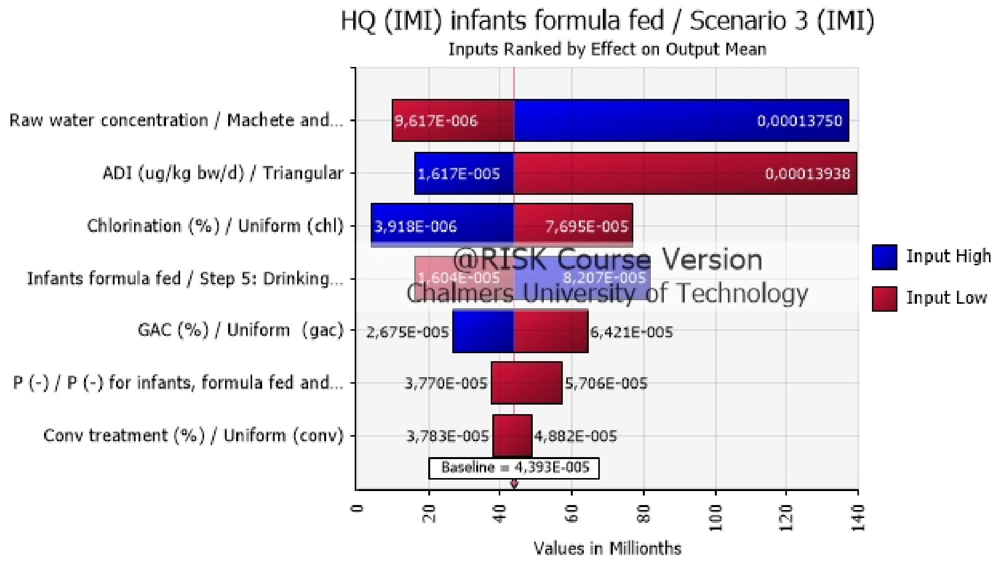


Figure L.6: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, reference river, scenario three.

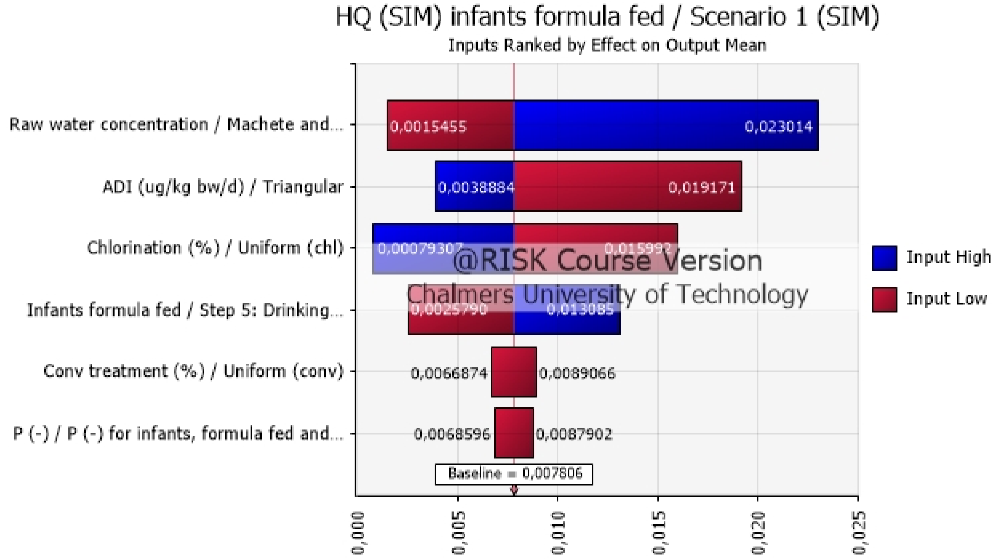


Figure L.7: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, reference river, scenario one.

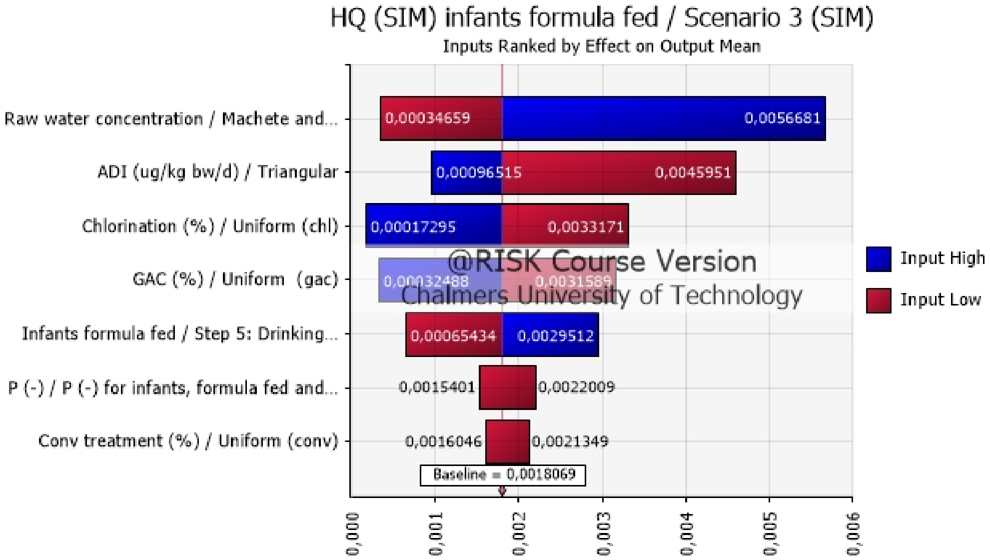
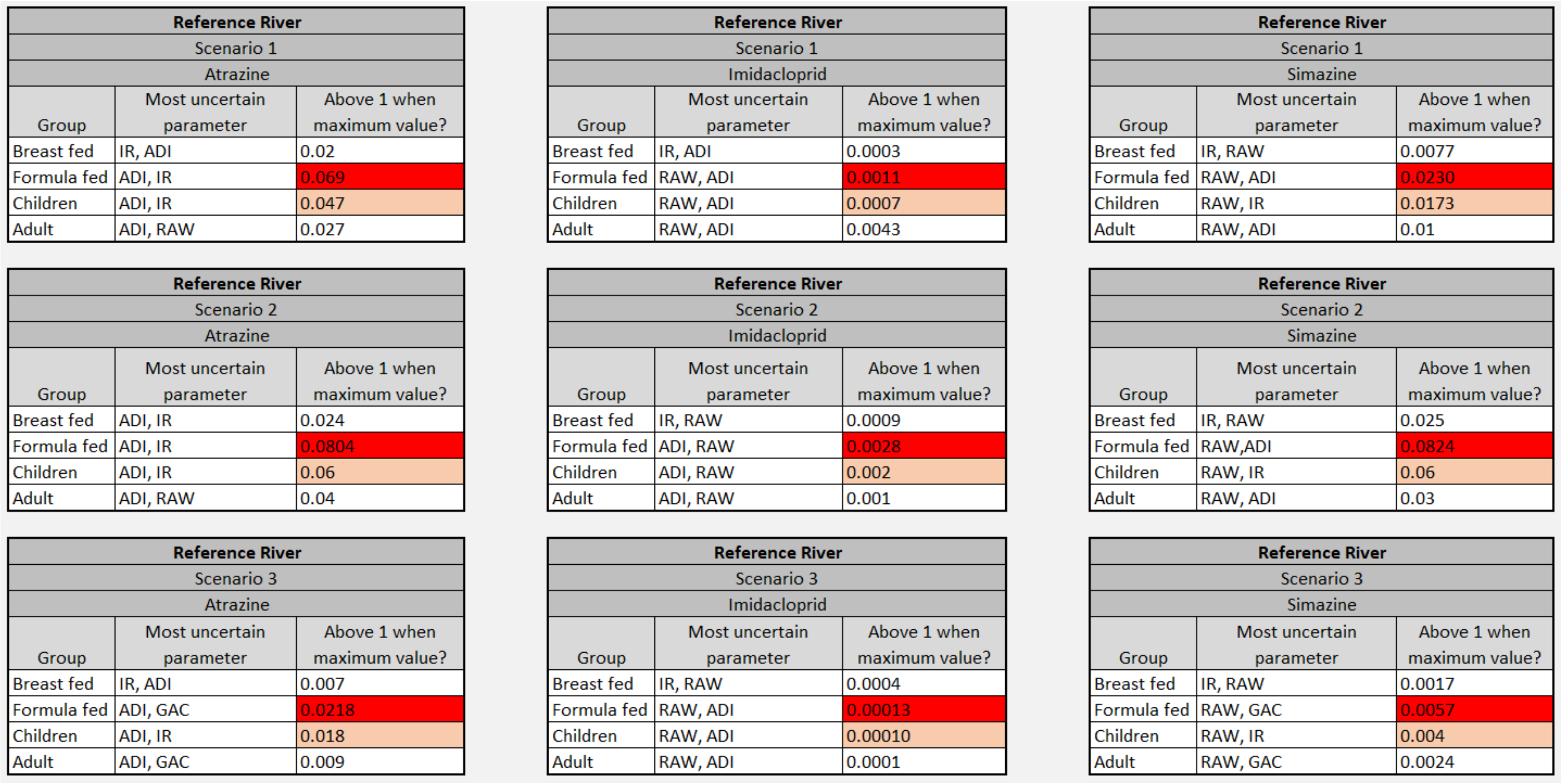


Figure L.8: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, reference river, scenario three.



Reference River		
Scenario 1		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.02
Formula fed	ADI, IR	0.069
Children	ADI, IR	0.047
Adult	ADI, RAW	0.027

Reference River		
Scenario 1		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0003
Formula fed	RAW, ADI	0.0011
Children	RAW, ADI	0.0007
Adult	RAW, ADI	0.0043

Reference River		
Scenario 1		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, RAW	0.0077
Formula fed	RAW, ADI	0.0230
Children	RAW, IR	0.0173
Adult	RAW, ADI	0.01

Reference River		
Scenario 2		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	ADI, IR	0.024
Formula fed	ADI, IR	0.0804
Children	ADI, IR	0.06
Adult	ADI, RAW	0.04

Reference River		
Scenario 2		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, RAW	0.0009
Formula fed	ADI, RAW	0.0028
Children	ADI, RAW	0.002
Adult	ADI, RAW	0.001

Reference River		
Scenario 2		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, RAW	0.025
Formula fed	RAW,ADI	0.0824
Children	RAW, IR	0.06
Adult	RAW, ADI	0.03

Reference River		
Scenario 3		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.007
Formula fed	ADI, GAC	0.0218
Children	ADI, IR	0.018
Adult	ADI, GAC	0.009

Reference River		
Scenario 3		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, RAW	0.0004
Formula fed	RAW, ADI	0.00013
Children	RAW, ADI	0.00010
Adult	RAW, ADI	0.0001

Reference River		
Scenario 3		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, RAW	0.0017
Formula fed	RAW, GAC	0.0057
Children	RAW, IR	0.004
Adult	RAW, GAC	0.0024

Figure L.9: Compilation of the tornado graphs for all population groups for the reference rivers. Red mark indicates when HQ is closest to one, while pink indicates the second closest value.

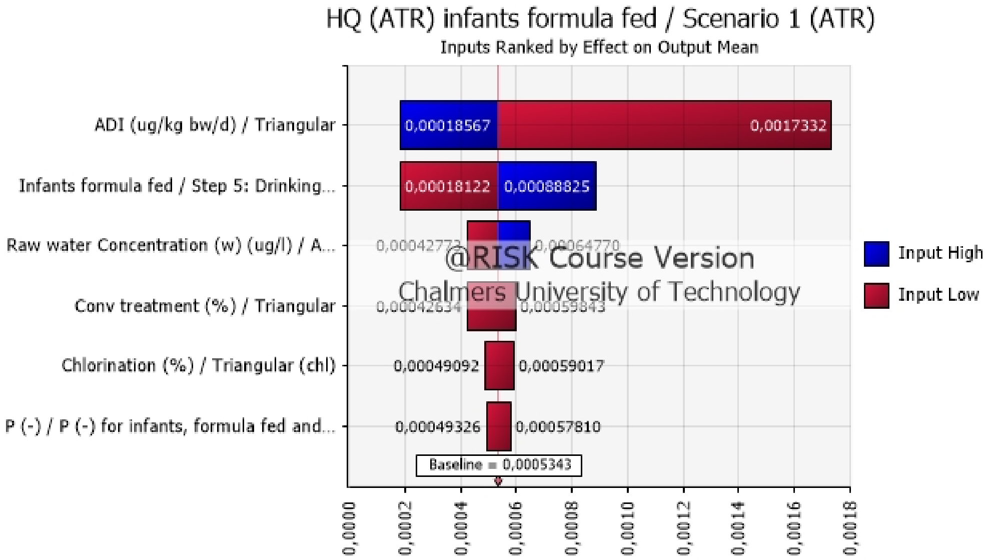


Figure L.10: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, Piketberg DWTP, scenario one.

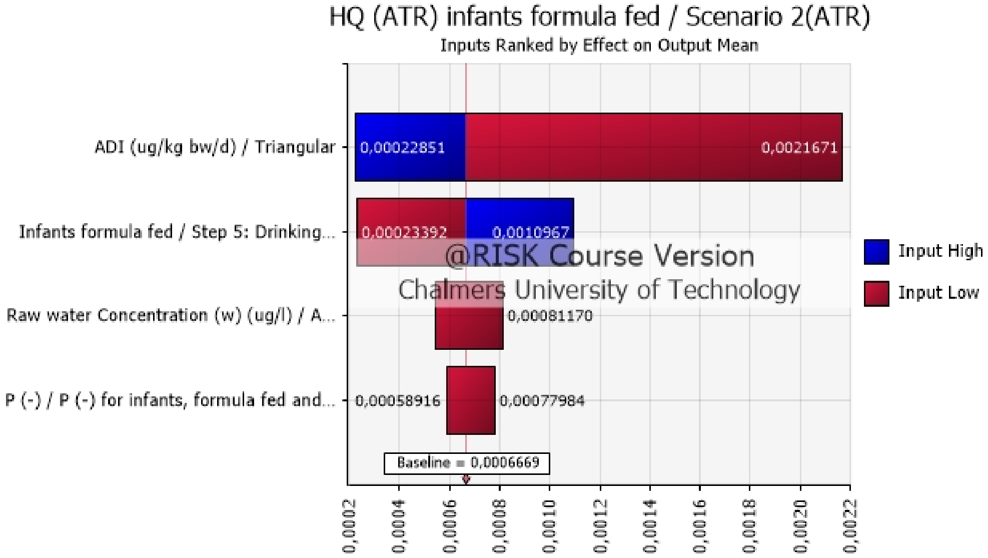


Figure L.11: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, Piketberg DWTP, scenario two.

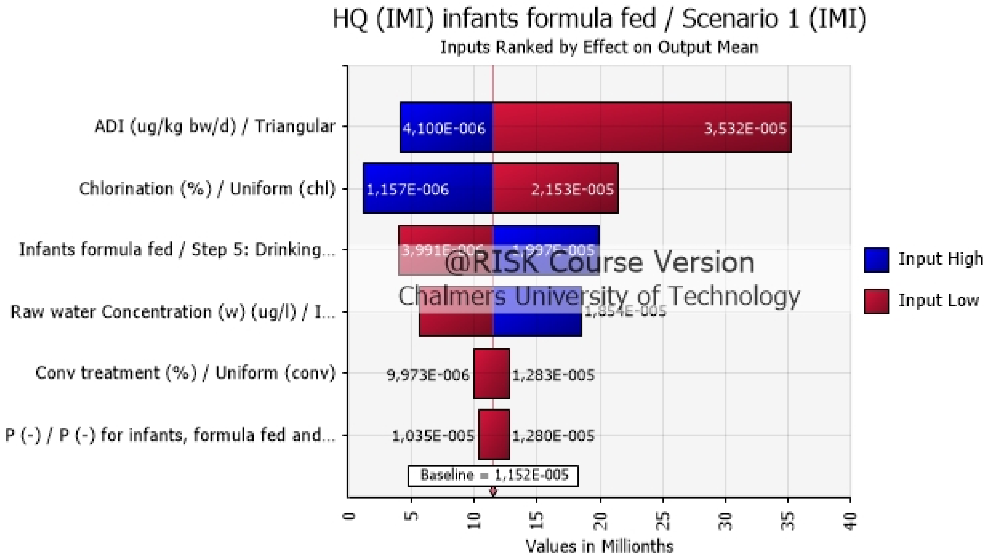


Figure L.12: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, Piketberg DWTP, scenario one.

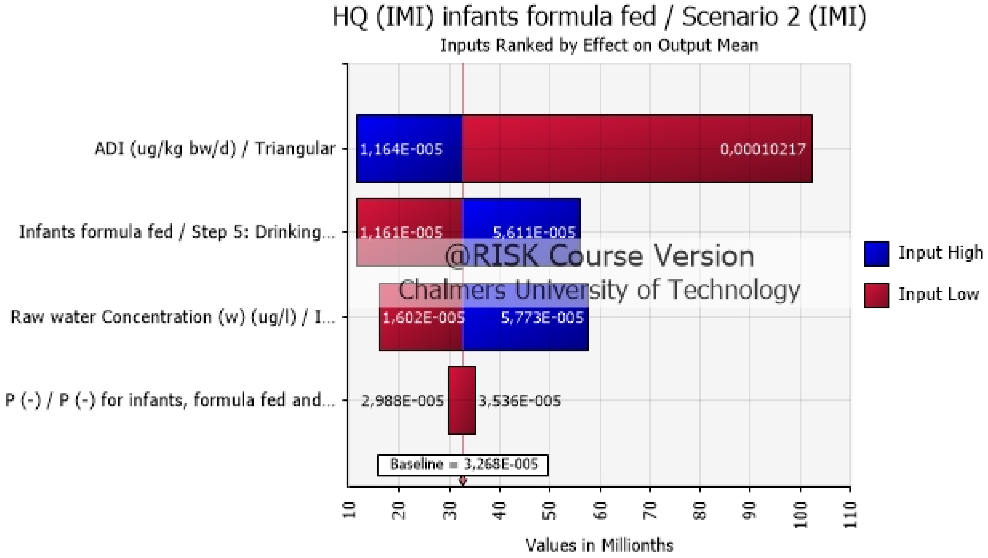


Figure L.13: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, Piketberg DWTP, scenario two.

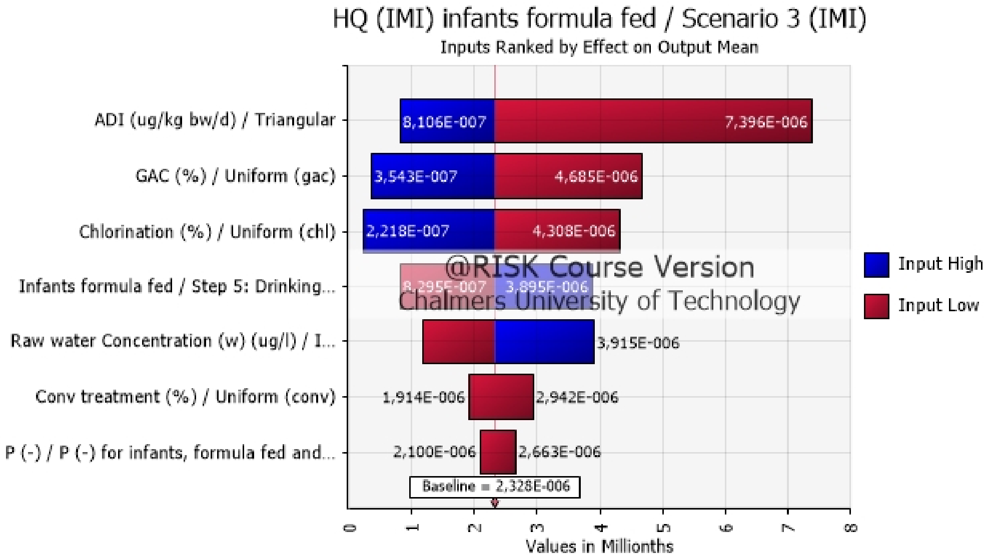


Figure L.14: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, Piketberg DWTP, scenario three.

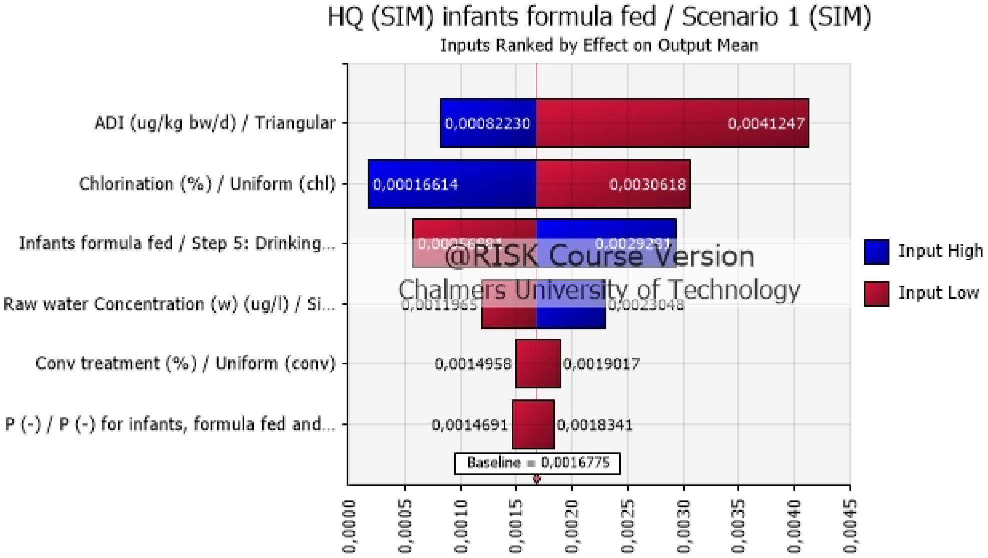


Figure L.15: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, Piketberg DWTP, scenario one.

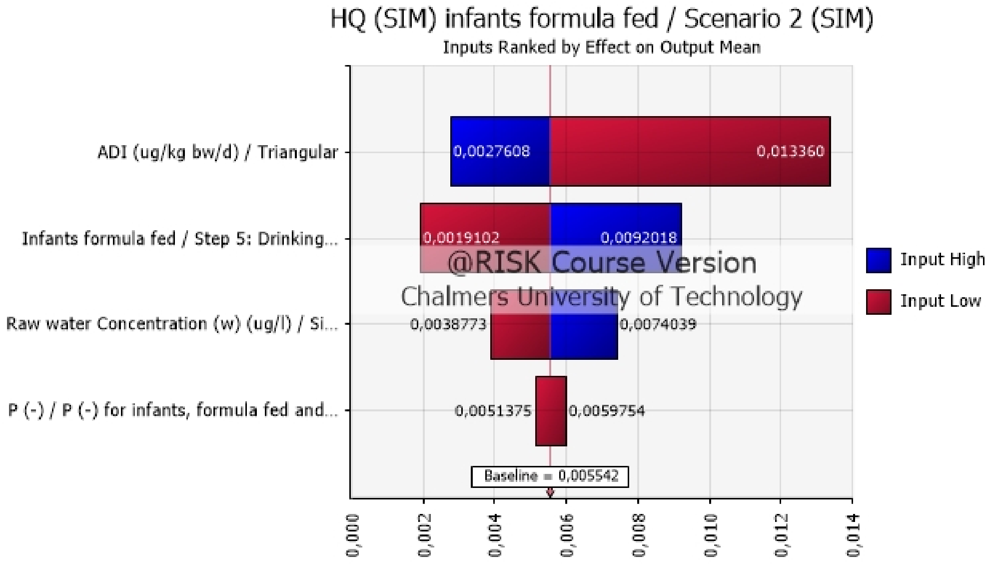


Figure L.16: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, Piketberg DWTP, scenario two.

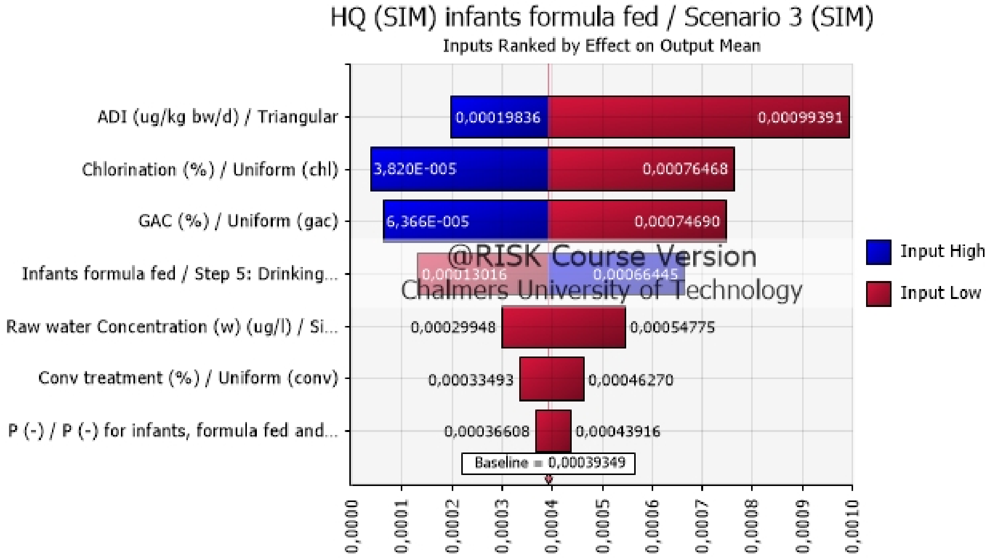
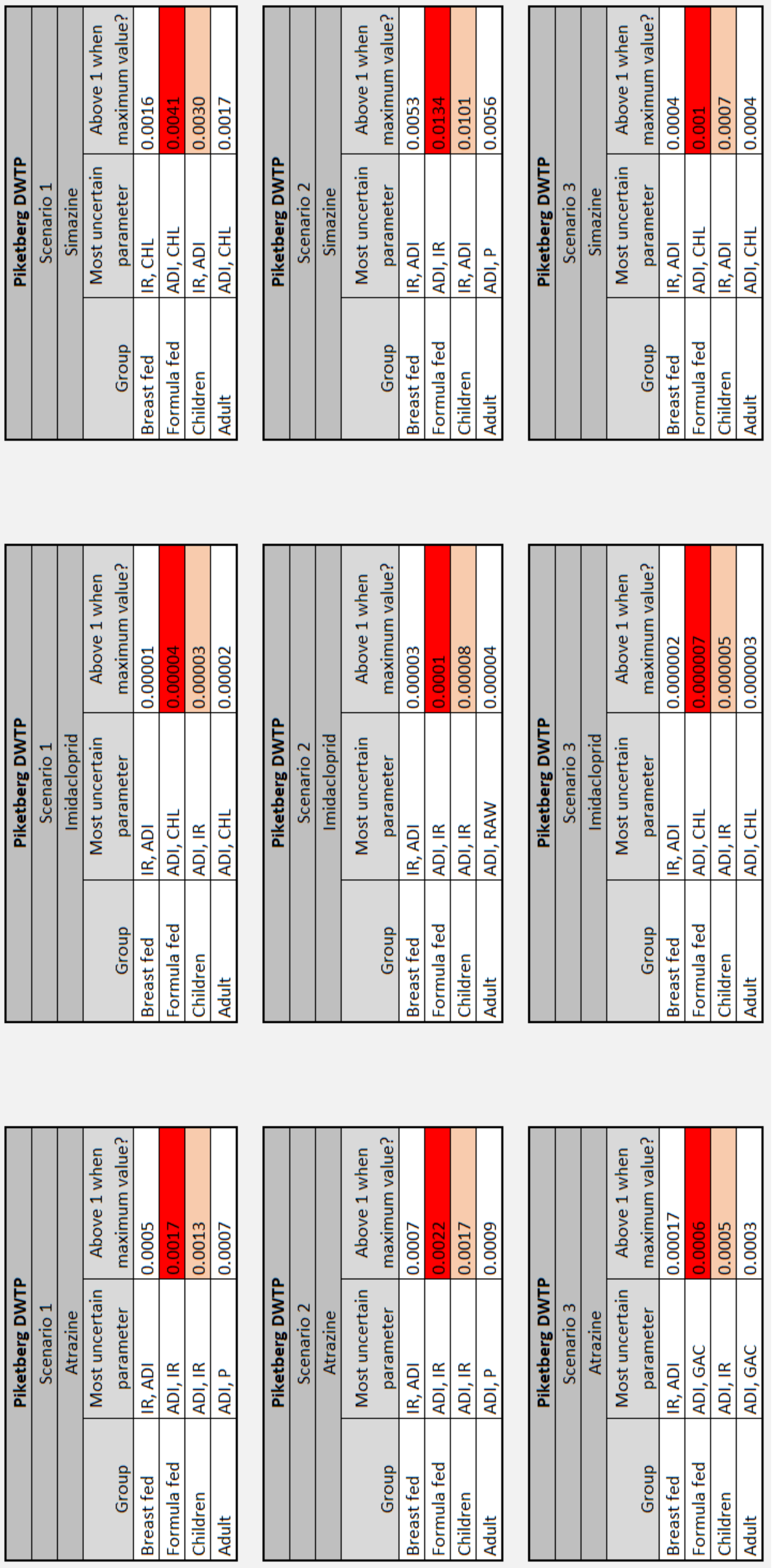


Figure L.17: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, Piketberg DWTP, scenario three.



Piketberg DWTP		
Scenario 1		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0005
Formula fed	ADI, IR	0.0017
Children	ADI, IR	0.0013
Adult	ADI, P	0.0007

Piketberg DWTP		
Scenario 1		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.00001
Formula fed	ADI, CHL	0.00004
Children	ADI, IR	0.00003
Adult	ADI, CHL	0.00002

Piketberg DWTP		
Scenario 1		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, CHL	0.0016
Formula fed	ADI, CHL	0.0041
Children	IR, ADI	0.0030
Adult	ADI, CHL	0.0017

Piketberg DWTP		
Scenario 2		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0007
Formula fed	ADI, IR	0.0022
Children	ADI, IR	0.0017
Adult	ADI, P	0.0009

Piketberg DWTP		
Scenario 2		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.00003
Formula fed	ADI, IR	0.0001
Children	ADI, IR	0.00008
Adult	ADI, RAW	0.00004

Piketberg DWTP		
Scenario 2		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0053
Formula fed	ADI, IR	0.0134
Children	IR, ADI	0.0101
Adult	ADI, P	0.0056

Piketberg DWTP		
Scenario 3		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.00017
Formula fed	ADI, GAC	0.0006
Children	ADI, IR	0.0005
Adult	ADI, GAC	0.0003

Piketberg DWTP		
Scenario 3		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.000002
Formula fed	ADI, CHL	0.000007
Children	ADI, IR	0.000005
Adult	ADI, CHL	0.000003

Piketberg DWTP		
Scenario 3		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0004
Formula fed	ADI, CHL	0.001
Children	IR, ADI	0.0007
Adult	ADI, CHL	0.0004

Figure L.18: Compilation of the tornado graphs for all population groups for Piketberg DWTP. Red mark indicated when HQ is closest to one, while pink indicates the second closest value.

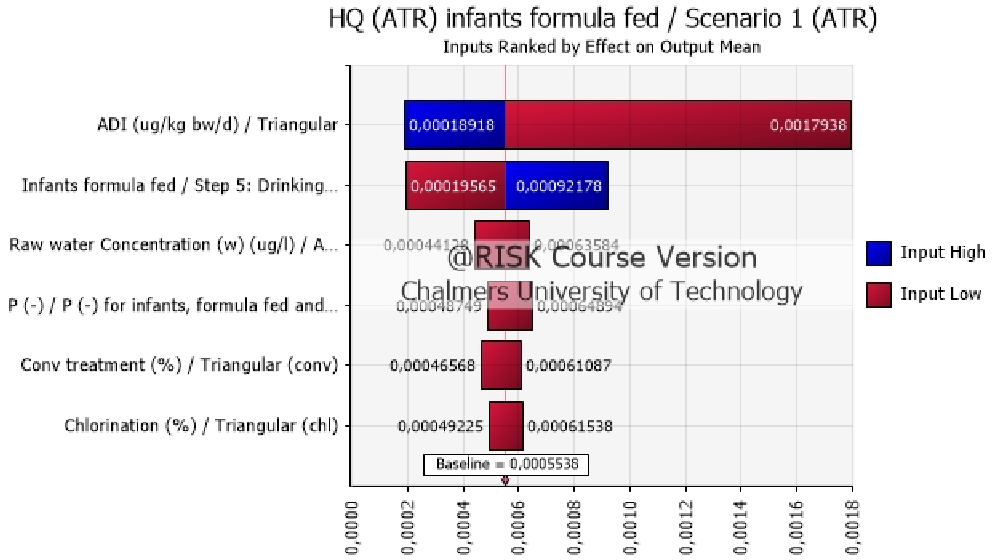


Figure L.19: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, Withoogte DWTP, scenario one.

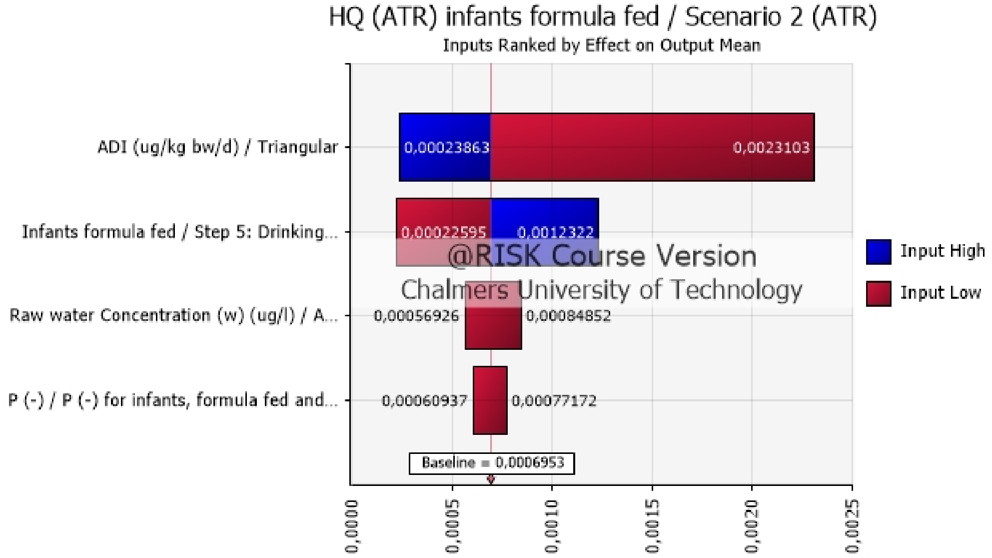


Figure L.20: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, Withoogte DWTP, scenario two.

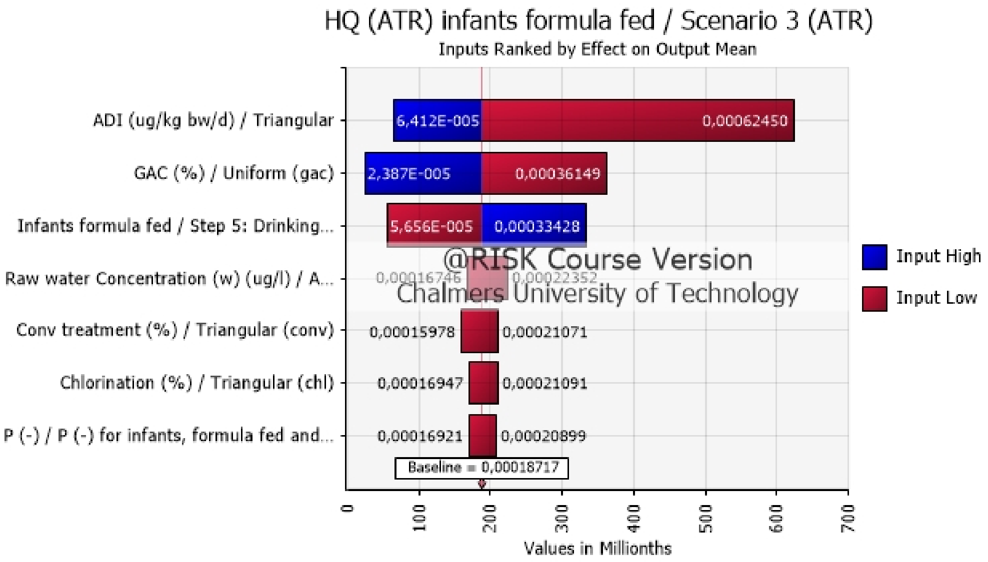


Figure L.21: Tornado graph illustrating the inputs affecting the mean of HQ for atrazine for infants formula-fed, Withoogte DWTP, scenario three.

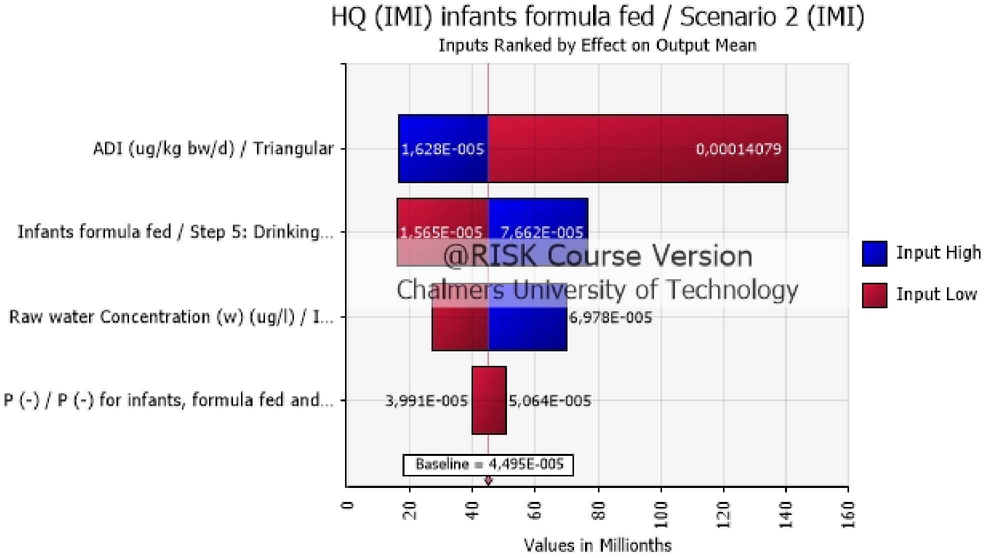


Figure L.22: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, Withoogte DWTP, scenario two.

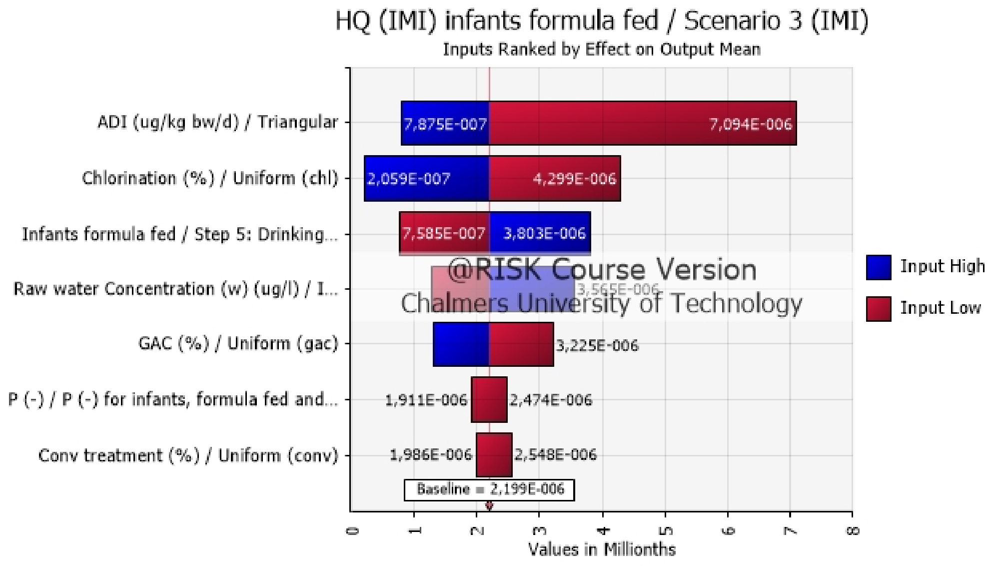


Figure L.23: Tornado graph illustrating the inputs affecting the mean of HQ for imidacloprid for infants formula-fed, Withoogte DWTP, scenario three.

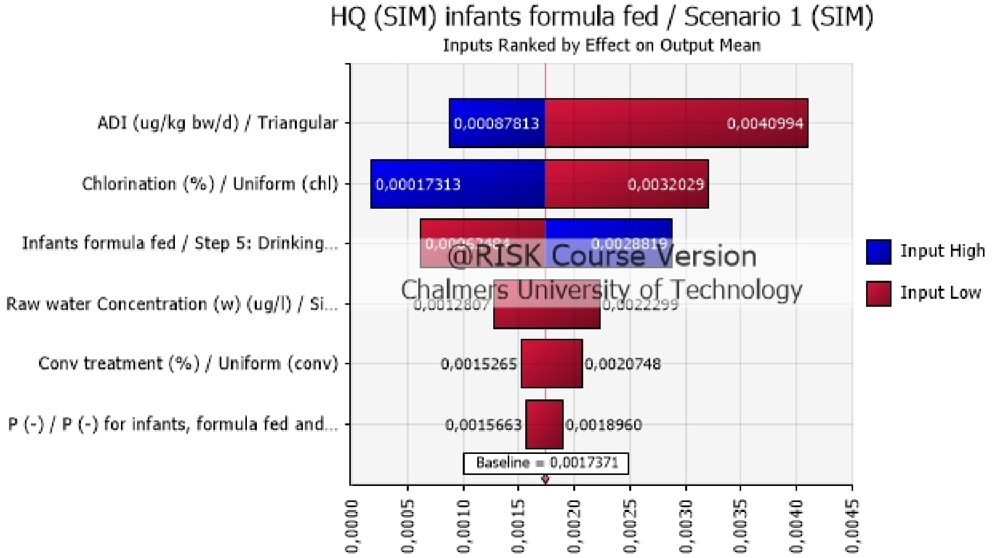


Figure L.24: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, Withoogte DWTP, scenario one.

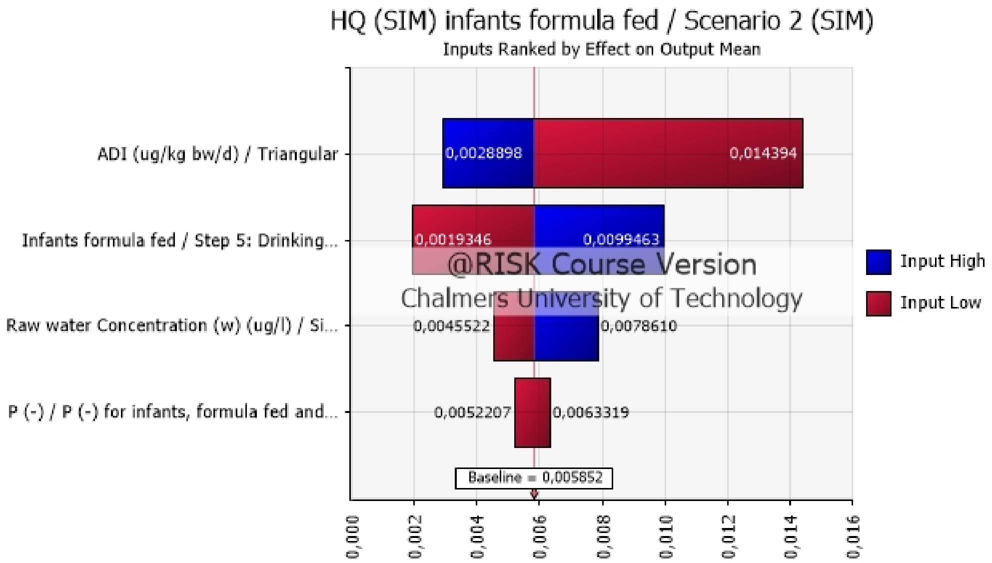


Figure L.25: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, Withoogte DWTP, scenario two.

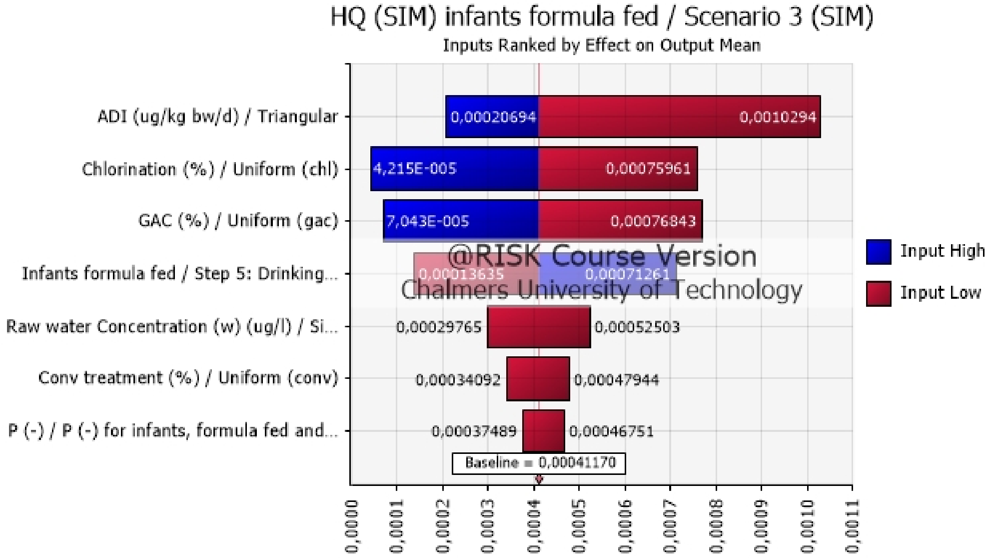
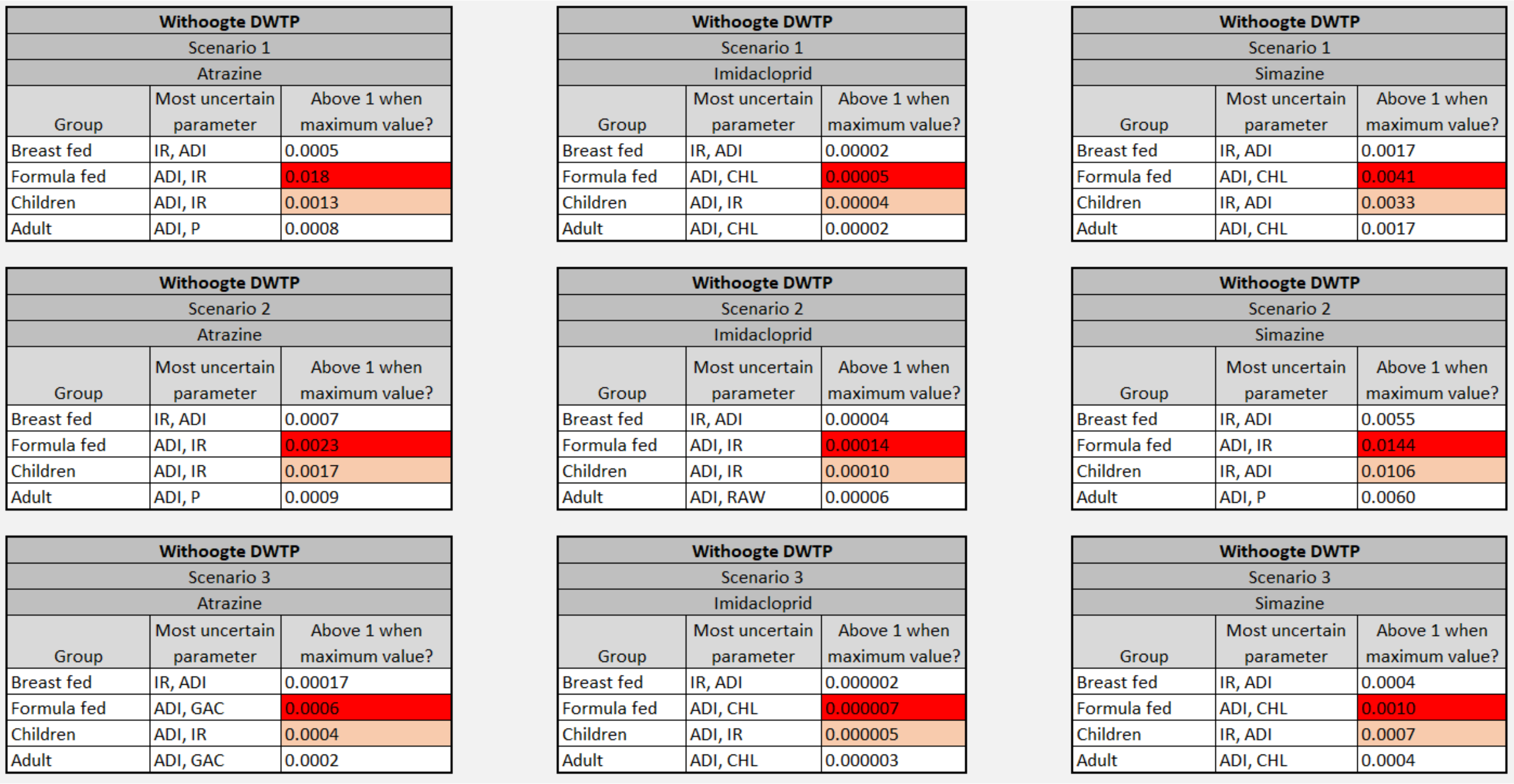


Figure L.26: Tornado graph illustrating the inputs affecting the mean of HQ for simazine for infants formula-fed, Withoogte DWTP, scenario three.



Withoogte DWTP		
Scenario 1		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0005
Formula fed	ADI, IR	0.018
Children	ADI, IR	0.0013
Adult	ADI, P	0.0008

Withoogte DWTP		
Scenario 1		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.00002
Formula fed	ADI, CHL	0.00005
Children	ADI, IR	0.00004
Adult	ADI, CHL	0.00002

Withoogte DWTP		
Scenario 1		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0017
Formula fed	ADI, CHL	0.0041
Children	IR, ADI	0.0033
Adult	ADI, CHL	0.0017

Withoogte DWTP		
Scenario 2		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0007
Formula fed	ADI, IR	0.0023
Children	ADI, IR	0.0017
Adult	ADI, P	0.0009

Withoogte DWTP		
Scenario 2		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.00004
Formula fed	ADI, IR	0.00014
Children	ADI, IR	0.00010
Adult	ADI, RAW	0.00006

Withoogte DWTP		
Scenario 2		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0055
Formula fed	ADI, IR	0.0144
Children	IR, ADI	0.0106
Adult	ADI, P	0.0060

Withoogte DWTP		
Scenario 3		
Atrazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.00017
Formula fed	ADI, GAC	0.0006
Children	ADI, IR	0.0004
Adult	ADI, GAC	0.0002

Withoogte DWTP		
Scenario 3		
Imidacloprid		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.000002
Formula fed	ADI, CHL	0.000007
Children	ADI, IR	0.000005
Adult	ADI, CHL	0.000003

Withoogte DWTP		
Scenario 3		
Simazine		
Group	Most uncertain parameter	Above 1 when maximum value?
Breast fed	IR, ADI	0.0004
Formula fed	ADI, CHL	0.0010
Children	IR, ADI	0.0007
Adult	ADI, CHL	0.0004

Figure L.27: Compilation of the tornado graphs for all population groups for Withoogte DWTP. Red mark indicated when HQ is closest to one, while pink indicates the second closest value.

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