



30 November 2016

QGC - ADDENDUM TO HYDRAULIC STIMULATION CHEMICAL ASSESSMENT

Chemical Hazard Assessments - Fluid with Scale Inhibitor

Some parts of this report have been redacted to maintain the confidentiality of commercially sensitive information

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ADDENDUM



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Document Number	Issue Date	Revisions
127635006-022-R-Rev0-05300	4 June 2015	-
127635006-022-R-Rev1-05300	30 November 2016	Information redacted to maintain confidentiality.



1.0 INTRODUCTION

QGC has requested that Golder Associates Pty Ltd (Golder) undertake a hazard assessment of [REDACTED] proposed for operational use in QGC's Queensland tenements. The assessment is in regards to its potential toxicity to human health and ecotoxicity in aquatic and terrestrial environments.

This addendum presents the hazard assessment of one (1) chemical, as identified in Table 1.

1.1 Background

Golder has previously assessed a number of hydraulic stimulation chemicals for human health and ecological hazards for QGC. The assessments are documented in the report: *Human Health and Ecological Chemical Assessment – Hydraulic Stimulation Chemical Assessment – QGC Surat and Bowen Basin Operation* (Golder Ref. 127635006-004-R) hereafter called 'HSCA report'. This assessment is provided as an addendum to that Report.

1.2 Chemicals to be assessed

QGC provided Golder with the following documents:

- Fluid Disclosure Report (FDR), 26 February 2015)
- Safety Data Sheet (SDS) (*product confidential*), Version 1, Revision date 23 May 2014

The FDR and SDS have not been included in this report to maintain the confidentiality of commercially sensitive information.

The chemicals listed in the FDR were reviewed by Golder. One chemical identified in the FDR, and shown in Table 1, has not previously been assessed.

Table 1: Additional Stimulation Chemicals

CAS RN	Chemical Name
68715-83-3	2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate

Note: CAS RN - Chemical Abstracts Service Registry Number.

Golder understands that QGC propose to use the product (scale inhibitor) in stimulation activities. A Scale Inhibitor is a chemical agent added to a fluid system to retard or prevent a deposit or coating forming on the surface of metal, rock or other materials during the stimulation process. The service provider states that "scale is caused by a precipitation due to a chemical reaction with the surface, precipitation caused by chemical reactions, a change in pressure or temperature, or a change in the composition of a solution".

1.3 Scope of Work

The approach applied for chemical hazard assessment is documented in the HSCA report (Golder, 2016). This approach was applied to the hazard assessment of the chemical listed in Table 1.

As a part of this assessment, the following scope of work was completed:

- Preparation of a human health toxicological profile (results presented in Appendix A).
- A review of environmental hazards (where possible) using measures of persistence (P), bioaccumulation (B) and toxicity (T) (PBT) and preparation of chemical information sheets and hazard summaries (results presented in Appendix B).
- Mass balance calculations for the stimulation fluid identified in the FDR.
- Preparation of this addendum.



2.0 2-BUTENEDIOIC ACID (2Z)-, POLYMER WITH SODIUM 2-PROPENE-1-SULFONATE

2.1 Overview

2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is a polymer formed from the monomers of maleic acid (cis-butenedioic acid, $C_4H_4O_4$) and sodium 2-methylprop-2-ene-1-sulfonate ($C_3H_5O_3S.Na$). Limited information is available on publically accessible data sources for 2-butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate. Due to the data limitations, the hazard assessment in this report has been based on the functional groups likely to be present in the polymer. This includes the sodium sulfonate group and carboxylic acid groups.

A report by the United States Environmental Protection Agency (US EPA, 2010) Office of Pollution Prevention and Toxics (OPPT)'s titled *TSCA New Chemicals Program (NCP) Chemical Categories* presents groups chemicals with shared chemical and toxicological properties. A group identified in the US EPA (2010) report (that is relevant to 2-butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate) is "anionic surfactants". An anionic surfactant is defined as any molecular structure with a net negative charge and surfactant activity (US EPA, 2010). The document states that this category includes alkyl sulfonates (AS) and alkyl carboxylic acids (ACA) (two functional groups likely to be present in the polymer being assessed). The US EPA (2010) does not list anionic surfactants as a hazard for human health (US EPA, 2010). However, anionic surfactants are toxic to a wide variety of aquatic organisms (US EPA, 2010). Further assessment of the human health and ecotoxicological hazards of anionic surfactants are presented in Section 2.2 and Section 2.3, respectively.

HERA (Human & Environmental Risk Assessment on ingredients of European household cleaning products) released a draft Human Health Risk Assessment on AS in 2002 (HERA, 2002). HERA states the AS molecules have three functional moieties:

- The aliphatic hydrocarbon chain
- The polar, terminal anion
- The countervalent cation or amine.

AS are commonly used in household laundry and cleaning products (including detergents, hand dishwashing liquids, hard surface and bathroom cleaners, spray cleaners, soap bars and surface wipes) (HERA, 2002). The maximum concentrations of AS likely in various household products range from 0.1% to 16.5%.

The assessment of ACA has been based on polycarboxylic acid compounds. HERA also released a review *Polycarboxylates used in detergents (Part II): Polyacrylic/maleic acid copolymers and their sodium salts* (CAS 52255-49-9) in January 2014 (HERA, 2014). The polycarboxylates assessed include a variety of copolymers of acrylic acids (AA) and maleic acids (MA) and their sodium salts. The mean molecular weight (MW) of the copolymers P-AA/MA ranges from approximately 12,000 to 100,000. The residual content of acrylic acid and their sodium salts in polycarboxylates can be as high as 0.5% but is usually lower than 0.1%. The residual percentage of monomers is dependent on the reaction process. Water soluble polycarboxylates are commonly used in various household cleaning products (such as laundry detergents, automatic dishwashing detergents and various hard surface-cleaning formulations) (HERA, 2014). The typical concentration of polycarboxylates in these products is approximately 3%. Polycarboxylates are used in low-phosphate and phosphate-free detergents to avoid incrustation and soil redeposition. They act to disperse calcium carbonate or calcium phosphate and the suspended soils during washing process.

2.2 Human Health

The Human Health Toxicity Profile for 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is included in Appendix A, with the results of the review summarised below.

The polymer has been assigned a Hazard Band 3, based on potential acute oral toxicity and corrosive/irritant effects to skin and eyes, primarily associated with the sulfonate group. It is noted that alkyl sulfonate groups



appeared irritating to skin at concentrations above 5% and that concentrations less than 1% are not considered to be an irritant. In addition longer chained alkyl sulfonates tend to be less irritating than shorter chained alkyl sulfonates. Based on this, the functional groups assessed are considered likely to be less toxic once in polymer form and at low concentrations (< 1%).

2.3 Ecotoxicology

No chemical-specific data on 2-butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate was found during the preparation of this addendum. As a result no Chemical Information Sheet is provided for this chemical. However, Chemical Information Sheets are provided in Appendix B for chemicals of functional groups likely to be present in the polymer.

Golder conducted searches of publicly available information sources using the chemical name and the CAS Registry number. The searches undertaken, along with the results of the searches, are summarised below (results are current as of 26 March 2015). Searches included the following (listed in alphabetical order):

- ChemIDplus United States National Library of Medicine. (<http://chem.sis.nlm.nih.gov/chemidplus/rn/>)
 - Limited information found – molecular formula and molecular weight.
- Ecological Structure Activity Relationships ECOSAR™ software version 1.11 dated July 2012 (ECOSAR). (<http://www.epa.gov/oppt/newchemicals/tools/21ecosar.htm>)
 - No CAS match found
- Hazardous Substances Data Bank (HSDB) (<http://toxnet.nlm.nih.gov/>)
 - No records found
- Organisation for Economic Co-operation and Development (OECD) QSAR Toolbox 3.1.0.21. QSAR Toolbox (2013) (www.oecd.org/env/exitingchemicals/qsar)
 - No information found
- Society of Environmental Toxicology and Chemistry (SETAC) Journal Publication (<http://www.setac.org>)
 - No records found
- United States Environmental Protection Agency (USEPA) ECOTOXicology Database Version 4.0. (<http://cfpub.epa.gov/ecotox/>)
 - No records found
- United States Environmental Protection Agency Exposure Tools and Assessment EPISUITE v4.1. (EPISUITE) (<http://www.epa.gov/oppt/exposure/pubs/episuite.htm>)
 - No CAS match found
- World Health Organisation Environmental Health Criteria (WHO EHC) (<http://www.who.int/ipcs/publications/ehc/en/>)
 - No records found

As limited data were available for 2-butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate, the hazard assessment was extended to assess the functional groups likely to be present in the compound. This includes the sodium sulfonate group (alkyl sulfonates (AS)) and two carboxylic acid groups (alkyl carboxylic acids (ACA)).

For the alkyl sulfonates the information used in this assessment is based on a both modelled data (ECOSAR and EPISUITE) and experimental data (HERA 2002). The modelled data used in this assessment are for



alkyl sulfonates with sodium salt and a carbon chain length of 10-18 and the experimental data are for linear alkyl sulfonates (C12-C18) specifically used for cleaning purposes only.

For the carboxylic acid group (2-butenedioic acid – CAS number 6915-18-0) only modelled data (ECOSAR and EPISUITE) were available.

2.3.1 Alkyl Sulfonates – Ecotoxicology assessment

An environmental hazard assessment was undertaken on alkyl sulfonates, based on persistence (P), bioaccumulation (B) and toxic (T) potential (hereafter referred to as PBT). The environmental hazard assessment categorizes a chemical as having potential to pose a high, moderate or low hazard to the environment.

The chemical information sheet or ecotoxicology profile for alkyl sulfonates (provided in Appendix B) presents the available physical and chemical information, in addition to available ecotoxicological data for freshwater organisms.

An overall score (the environmental hazard score) for alkyl sulfonates was calculated based on PBT scores and is presented in Table 2.

Table 2: Toxicity score for alkyl sulfonates

Chemical	Bioaccumulation Score	Persistence Score	Toxicity Score	Overall Hazard Score
Alkyl sulfonates	1	1.6	2	1.5

Based on the PBT assessment, alkyl sulfonates have been given an overall hazard score of 1.5 (1 = lowest, 3 = highest), indicating that is expected to pose a low hazard to the aquatic environment. The low hazard classification was based on chronic toxicological effects (no observed effect concentration (NOEC)) in a freshwater algae. The chronic data sourced from the HERA document (2002) are for alkyl sulfonates with carbon chain length C14. This chain length had the greatest relative toxicity to freshwater organisms and was selected for conservatism. Information provided in this document determined that toxicity increased as carbon chain length increased up to C14 and then decreased due to reduced solubility of the chemicals in solution.

On the basis of the toxicological result, that the chemical is readily biodegradable, and does not bioaccumulate, the moderate hazard classification for ecological effects of alkyl sulfonates is considered to be appropriate.

2.3.2 Alkyl Sulfonates - Terrestrial toxicity assessment

The Chemical Information Sheet presents the physical and chemical information for alkyl sulfonates in addition to available ecotoxicological data for terrestrial organisms. For alkyl sulfonates terrestrial toxicity data were available for mammals and were modelled for invertebrates (earthworms) and plants (lettuce).

Table 3: Terrestrial toxicity data for alkyl sulfonates

	Mammalian LD ₅₀	Ecocar Earthworm LD ₅₀	QSAR earthworm LC ₅₀	QSAR lettuce LC ₅₀
	mg/kg	mg/L	mg/kg	mg/L
Alkyl sulfonates	1,400	3001.1	179	0.962



The terrestrial ecotoxicological data suggest low hazard to terrestrial receptors, with the exception of the QSAR for lettuce which indicates a moderate to high hazard. Based on a K_{oc} of $>1,000$ (log K_{oc} of 3.1), alkyl sulfonates are expected to have moderate mobility if released to soil, and high biodegradation rates (EPISUITE, 2011). Considered together, these data indicate a low to moderate potential hazard to terrestrial receptors.

2.3.3 Alkyl Carboxylic Acid – 2-Butenedioic Acid – Ecotoxicology assessment

An environmental hazard assessment was undertaken on 2-Butenedioic acid, based on PBT. The chemical information sheet or ecotoxicology profile for 2-Butenedioic acid is provided in Appendix B.

An overall score (the environmental hazard score) for 2-Butenedioic acid was calculated based on the PBT scores and is presented below in Table 4.

Table 4: Toxicity score for 2-Butenedioic acid

Chemical	Bioaccumulation Score	Persistence Score	Toxicity Score	Overall Hazard Score
2-Butenedioic acid	1	1.3	1	1.1

Based on the PBT assessment, alkyl sulfonate has been given an overall hazard score of 1.1 (1 = lowest, 3 = highest), indicating that is expected to pose a low hazard to the aquatic environment. The low hazard classification was based on acute toxicological effects (lethal effects concentrations to 50% of exposed organisms (LC₅₀)) in a freshwater algae, invertebrate and fish.

On the basis of the toxicological result in freshwater organisms, and that the chemical is readily biodegradable, and does not bioaccumulate, the low hazard classification for ecological effects of 2-Butenedioic acid is considered to be appropriate.

2.3.4 Alkyl Carboxylic Acid – 2-Butenedioic Acid - Terrestrial toxicity assessment

The Chemical Information Sheet presents the physical and chemical information for 2-Butenedioic acid in addition to available ecotoxicological data for terrestrial organisms. For 2-Butenedioic acid terrestrial experimental toxicity data were not available therefore only modelled data for invertebrates (earthworms) and plants (lettuce) are presented in Table 5.

Table 5: Terrestrial toxicity data for 2-Butenedioic acid

	Mammalian LD ₅₀	Ecosar Earthworm LD ₅₀	QSAR earthworm LC ₅₀	QSAR lettuce LC ₅₀
	mg/kg	mg/L	mg/kg	mg/L
2-Butenedioic acid	NA	NA	411	0.355

NA = not available

The modelled terrestrial ecotoxicological data suggests a low hazard to earthworms and a moderate to high hazard for lettuce. Based on a K_{oc} of >7.33 (log K_{oc} of 0.865), alkyl sulfonates are expected to have moderate to high mobility if released to soil, and high biodegradation rates (EPISUITE, 2011). Considered together, these data indicate a low to moderate potential hazard to terrestrial receptors.

3.0 MASS BALANCE

A FDR was provided to Golder for the fluid. The FDR has not been included in this report to maintain the confidentiality of commercially sensitive information. The fluid disclosure provides the total volume of the fluid, a list of individual chemical names/CASR numbers and estimations of mass fractions (%), mass (lb) and volume (gal) of each component.



These fluid components were divided into chemical additives, proppants and water, and the estimated mass of each fluid is summarised in Table 6. Due to the variations in preparation methods and injection protocols, it is assumed that the concentrations reported in Table 6 lie within a range of possible concentrations.

The FDR indicates that the components listed are based on 0.8 megalitres (ML) of fluid. However, QGC indicated that the injected total volumes per well could range from 0.3 to 7 ML of fluid (Kearney 2015, pers. comm). Therefore, the mass of additives, proppants and water added per stimulation have also been calculated using an upper and lower range of injected total volumes (Table 6).

Table 6: Indicative Component Mass per Stimulation Stage

Fluid System		Mass calculated using a range of injected total volumes per well	
Typical fluid Volume ¹	794 936 L (0.8 ML)	0.3 ML of fluid	7 ML of fluid
Additives	3 310 kg (~ 0.3 %)	~ 1 241 kg	~28 960 kg
Proppant	181 471 kg (~19 %)	~ 68 052kg	~1 587 874 kg
Water	791 026 kg (~81 %)	~ 296 635 kg	~ 6 921 478 kg

1. Fluid volume for stimulation, as indicated in the service provider's disclosure statement.

The hydraulic stimulation fluid comprises predominantly water (~ 81%), with a secondary component consisting of proppant (~ 19%) and a minor fraction which consists of additives (~ 0.3%).

Following completion of the hydraulic stimulation process, a percentage fraction of the injected hydraulic stimulation fluids are recovered upon flowback and production of the well. However, it should be noted that most of the additives would have undergone chemical transformations in the sub-surface. In addition, the formation also contributes a certain amount of water and dissolved salts to the flowback and production of the well. If it is conservatively assumed that 20% of the hydraulic stimulation fluid volume remains in the formation (reasonable "worst case") this would correspond to a mass of approximately 662 kg of chemical additives, excluding proppant, remaining in each well, based on 0.8 ML of stimulation fluid. Based on the varying stimulation fluid volumes of 0.3 ML to 7 ML, this mass could range from 248 kg to 5 792 kg of chemical additives.

4.0 RECOMMENDATIONS FOR MONITORING

Golder assessed 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate based on exposure hazards to humans, aquatic and terrestrial ecology and mass balance concentrations. Based on a low to moderate hazard for ecology and human health, 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is considered to present insufficient hazard for inclusion in the analytical suite. Further assessment of the polymer mass fraction in the FDR, indicated the potential concentration level of the polymer in stimulation fluid is less than 0.077 g/L. Thus Golder recommends based on current available data that this analyte is not added to the EA list for laboratory analysis.

5.0 UNCERTAINTY ANALYSIS

The evaluation of the human health and ecological hazards is limited to the quantity and quality of information available in the information sources reviewed and the literature received by Golder from the provider. A measure of the data completeness across the toxicological and hazard parameters used has been estimated expressed as a percentage of the parameters for which data were available. These are presented in each summary in Appendix A and Appendix B.

An assessment of the quality of the available data is beyond the scope of this work. In the absence of such a review Golder has relied on primary literature sources from established, robust and reputable sources such as the WHO, Organisation for Economic Cooperation and Development (OECD) and US EPA where available. As new toxicological data are generated and become available in the published literature, the information presented in this hazard evaluation and the associated conclusions may be subject to change.



On this basis the hazard profiles are dated to enable future review as may be appropriate. This is particularly pertinent across human health parameters within the highest Hazard Band category (4) which includes such areas as endocrine disruption potential and carcinogenicity. It is noted that no chemical in this addendum was assigned a Hazard Band category of 4.

6.0 EXCLUSIONS

This document provides a hazard assessment which reflects the potential concerns associated with the intrinsic toxicity of the substances reviewed. This does not include exposure assessment considerations that may realise the expression of this toxicity, however, comment is made to place exposures into perspective associated with fate and transport properties and specific physico-chemical properties.

7.0 CONCLUSIONS

Table 7 and Table 8 summarise the outcomes of the human health and ecological toxicity reviews, respectively.

Table 7: Summary of Human Health Toxicity Hazard Band Ranking

Compound	Human Health Hazard Band ¹	Comment
2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate	3	Ranking based on potential acute oral toxicity and corrosive/irritant effects to skin and eyes, primarily associated with the sulfonate group. However, toxicity appears to be depended on concentration and chain length, with the functional groups assessed considered likely to be less toxic once in polymer form and at low concentrations (< 1%) (See Human Health Toxicity Profile for further detail, Appendix A).

Note: 1. A ranking of 0 represents the lowest toxicity and 4 represents the highest toxicity.

Table 8: Summary of Ecotoxicology Ranking

Compound	Aquatic Hazard	Aquatic Hazard Comment	Terrestrial Hazard	Terrestrial Hazard Comment
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Compound	Aquatic Hazard	Aquatic Hazard Comment	Terrestrial Hazard	Terrestrial Hazard Comment
2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate	Low	Data Lacking. Hazard assessment was based on available information for chemicals of functional groups likely to be present in the polymer (modelled and experimental data for alkyl sulfonates and modelled for 2-butenedioic acid (an alkyl carboxylic acid)). The data gathered indicate 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is expected to pose a low hazard to aquatic receptors.	Low-Moderate	Although data was lacking for the polymer, the hazard assessment was based on available information for chemicals of functional groups likely to be present in the polymer (modelled and experimental data for alkyl sulfonates and modelled for 2-butenedioic acid (an alkyl carboxylic acid)). The data gathered indicate 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is expected to pose a low to moderate hazard to terrestrial receptors.

The overall conclusions of the *Human Health and Ecological Chemical Assessment – Hydraulic Stimulation Chemical Assessment – QGC Surat and Bowen Basin Operation* report (Golder, 2016) are not changed by the outcomes of this assessment.

8.0 LIMITATIONS

Your attention is drawn to the document - "Limitations", which is included in Appendix C. The statements presented in this document are intended to advise you of what your realistic expectations of this report should be. The document is not intended to reduce the level of responsibility accepted by Golder, but rather to ensure that all parties who may rely on this report are aware of the responsibilities each assumes in so doing.

9.0 REFERENCES

HERA (Human & Environmental Risk Assessment), 2002. *Draft Human Health Risk Assessment - Alcohol Sulphates*. Human & Environmental Risk Assessment on ingredients of European household cleaning products, December 2002. Available at <http://www.heraproject.com/RiskAssessment.cfm?SUBID=3>, accessed 16/03/2015

HERA (Human & Environmental Risk Assessment), 2014. *Polycarboxylates used in detergents (Part II): Polyacrylic/maleic acid copolymers and their sodium salts (CAS 52255-49-9)*, January 2014. Available at: <http://www.heraproject.com/RiskAssessment.cfm?SUBID=51>, accessed March 2015.

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US EPA (United States Environmental Protection Agency), 2010. *TSCA New Chemical Program (NCP), Chemical Categories*. Office of Pollution Prevention and Toxics, US EPA. Available at <http://www.epa.gov/oppt/newchemicals/pubs/npcchemicalcategories.pdf>, accessed 16/03/2015



Report Signature Page

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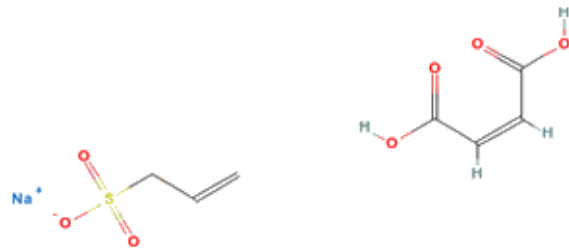
APPENDIX A

Human Health Chemical Profile

Project number: 127635006

Project name: Chemical Hazard Assessment, Southwest Queensland

Client name: QGC

Name	2-Butenedioic acid, (2Z)-, polymer with sodium 2-propene-1-sulfonate (Surrogate Group: Alkyl sulfates)
Synonyms	-
CAS number	68715-83-3
Molecular formula	(C ₄ H ₄ O ₄ .C ₃ H ₅ O ₃ S.Na) _x
Molecular Structure (of monomers)	

Overview	References
2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is a polymer formed from the monomers of maleic acid (cis-butenedioic acid, C₄H₄O₄) and sodium 2-methylprop-2-ene-1-sulfonate (C₃H₅O₃S.Na). Limited information is available on publically accessible data sources for 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate. As limited data is available for the polymer, the hazard assessment has been based on the functional groups likely to be present in the polymer. This includes the sodium sulfonate group and two carboxylic acid groups. The United States Environmental Protection Agency (US EPA) Office of Pollution Prevention and Toxics (OPPT)'s <i>TSCA New Chemicals Program (NCP) Chemical Categories</i> groups chemicals with shared chemical and toxicological properties. A group identified in the report is "anionic surfactants". An anionic surfactant is defined as any molecular structure with a net negative charge and surfactant activity (US EPA, 2010). The document states that this category includes alkyl sulfonates (AS) and alkyl carboxylic acids (ACA) (two functional groups likely to be present in polymer being assessed). The US EPA OPPT does not list anionic surfactants as a hazard concern for human health (US EPA, 2010). However, anionic surfactants are toxic to a wide variety of aquatic organisms (US EPA, 2010) (it is noted that ecotoxicology is not the purpose of this review). HERA (Human & Environmental Risk Assessment on ingredients of European household cleaning products) released a draft Human Health Risk Assessment on AS in 2002. AS were evaluated as a single chemical category for the HERA hazard evaluation, based on: ■ Structural similarity ■ Shared mechanisms of toxic action derived from their physico/chemical properties ■ Similar toxicokinetics in mammals ■ Common pathways of metabolism in mammals ■ Comparable toxicological profiles in mammals. HERA states the AS molecules have three functional moieties: ■ The aliphatic hydrocarbon chain	US EPA 2010, HERA 2002

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Project name: Chemical Hazard Assessment, Southwest Queensland

Client name: QGC

■ The polar, terminal anion ■ The countervalent cation or amine. The HERA review reports that acute toxicity studies demonstrate that AS compounds are of a low order of acute toxicity by the oral and dermal route. AS display toxic effects related to their surfactant properties. AS are irritant to skin and eyes when applied undiluted or as a concentrated solution (>5%). However, AS concentrations below 1% were essentially non-irritating to the human skin (HERA, 2002). HERA also released a review <i>Polycarboxylates used in detergents (Part II): Polyacrylic/maleic acid copolymers and their sodium salts (CAS 52255-49-9)</i> in January 2014 (HERA, 2014). The polycarboxylates assessed include a variety of copolymers of acrylic and maleic acids and their sodium salts. The residual content of acrylic acid and their sodium salts in polycarboxylates can be as high as 0.5% but is usually lower than 0.1%. The residual percentage of monomers is depending on the reaction process. This review concluded that polycarboxylates are of low toxicity by all exposure routes examined. Low acute toxicity were reported for polycarboxylates, with LD50 > 5 000 mg/kg bw/d. The copolymers showed no irritating potential on either target tissue (skin/eyes) based on the available data and were not considered to be sensitising. Based on the low toxicity observed, polycarboxylates have not been assessed further in this review. It is also assumed that the residual monomers (maleic acid and sodium 2-methylprop-2-ene-1-sulfonate) are either not present or present at trace concentrations. As a consequence the focus of this profile is on assessment of alkyl sulfonates.	HERA, 2014
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Human Health Toxicity Summary	Reference
Carcinogenicity 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate has not been evaluated by the International Agency for Research on Cancer (IARC) as to its carcinogenicity. The HERA review concluded that AS are not carcinogenic. This conclusion was based on the results of a chronic feeding study (life-time exposure and test material dosed at 0, 0.015, 0.15 and 1.5 % in the diet) and a 2 year skin painting study. Both studies are summarised further in the HERA review. In addition, the absence of mutagenic responses in <i>in vitro</i> and reliable <i>in vivo</i> tests further supports this conclusion (discussed below).	IARC 2015 HERA 2002
Mutagenicity/Genotoxicity The HERA review concluded that AS are not mutagenic. The review found that AS show a consistent absence of mutagenic activity when tested in <i>in vitro</i> tests. AS compounds consistently showed negative results in studies performed to evaluate chromosomal effects (tests included mammalian bone marrow chromosome aberration tests and mammalian erythrocyte micronucleus tests). Neither AS or its metabolites contain electrophilic functional groups or functional groups associated with mutagenic activity, further supporting the conclusion that AS are not mutagenic.	HERA 2002
Reproductive Toxicity No reproductive studies of AS were available for review by HERA. In the absence of AS studies, a reproductive toxicity study on alpha olefin sulfonate (AOS) was reviewed, as this compound was considered to be a structurally similar surfactant material by HERA. The 2-generation reproductive study on the AOS mixture showed a complete absence of treatment-related effects on reproductive capacity or systemic organ pathology at systemic dose ranges from	HERA 2002

Project number: 127635006

Project name: Chemical Hazard Assessment, Southwest Queensland

Client name: QGC

approximately 1000 – 250 mg/kg/day based on food intake. In addition, the lack of reproductive organ toxicity in dietary, repeated does studies on varies AS surfactants, even at doses in excess of the No Observed Effect Level (NOEL) (see chronic study review below) further supports the absence of effects on the reproductive organs from surfactant molecules.	
Developmental Toxicity/Teratogenicity The HERA review found that developmental toxicity studies have consistently shown that exposure to AS compounds do not affect skeletal or visceral development in the foetus. The Lowest Observed Effect Level (LOEL) for maternal effects in the rat was approximately 300 mg/kg/day and was based on depression of body weight and/or local irritation. For developmental effects the NOEL was also approximately 300 mg/kg/day. The review does note that in some studies there was evidence of slightly delayed foetal development but this effect was only observed at dose levels inducing toxicity in the maternal animals.	HERA 2002
Endocrine Disruption 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is not identified in the European Commission (EC)'s report, <i>"Towards the establishment of a priority list of substances for further evaluation of their role in endocrine disruption"</i> as a substance of interest.	EC 2000
Acute Toxicity (oral, dermal, inhalation) The SDS for the product containing 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate identifies the following GHS classifications for this compound: Acute Tox. 4 (H302) – Harmful is swallowed. HERA reports that acute toxicity of AS is primarily a function of their surfactant properties. Based on this similar acute effects are observed for various AS. Oral Oral Lethal Dose (LD₅₀)s range from 1 400 to 7 800 mg/kg in rats and 2 600 to greater than 8 000 mg/kg in mice, depending on carbon chain length. Generally, shorter chain lengths are more acutely toxic (based on assessment of a homologous series of sodium salts of AS, ranging from chain length C₈ to C₁₈). The clinical symptoms of acute oral exposure to rodents included reduced activity, tremors and diarrhoea and are considered indicative of gastrointestinal distress (it is noted that the AS were administered by gavage). Acute exposure to high doses of the surfactants lead to pathological changes including fluid distention and irritation of the forestomach, irritation of the small intestine and pale livers and kidneys in decedents. Animals that survived displayed thickening of the stomach wall. Dermal The HERA summary reports that the skin irritation potential of the materials was demonstrated in acute dermal toxicity studies. Application of 500 mg/kg to rabbit skin induced local skin irritation, eschar formation and necrosis, with sloughing at days 6-21, and residual hyperpigmentation. When AS were applied to intact or abraded skin, there was no evidence of systemic toxicity. This is considered to be consistent with the fact that dermal penetration of the surfactants is low. The oral absorption of anionic surfactants is consistently greater than dermal absorption and thus the dermal acute toxicity for 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is expected to be greater than 2000. This expectation is consistent with the supplier Safety Data Sheet classification for acute dermal toxicity. Inhalation An acute median lethality study is not available however the supplier SDS does not classify the polymer based on acute toxicity following inhalation. Anionic surfactants are generally considered respiratory irritants. Irritation of the respiratory tract was observed in mice, following inhalation of aerosolised solution of AS, as reported by HERA. After 2 minutes of exposure, a	2014 HERA 2002

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50% reduction in respiratory rate occurred at concentration of 88, 114 and 135 µg/L for the sodium (Na), ammonium (NH₄) and triethanolamine (TEA) salts, respectively. The HERA report also stated that systemic toxicity was not reported.	
Chronic/repeat dose toxicity (oral, dermal, inhalation) Oral Similar oral toxicity was noted in repeated dose studies reviewed by HERA for AS with different carbon chain lengths (different from that observed for acute toxicity). The values reported for NOEL (61 - 252 mg/kg/day) and LOEL (123-503 mg/kg/day), in various rat studies, were comparable regardless of the mode of administration (dietary or gavage) or exposure duration. The lowest oral NOAEL was observed following repeated administration in rats, receiving C₁₆-C₁₈ AS in the diet at concentrations of 0.07% (which is equivalent to 61 mg/kg/day) for 90 days. This NOAEL was based on liver toxicity. A change in primary target organs was observed to correspond with a change in the mode of administration. This finding is consistent with surfactants being primary irritants and that local irritation predominated where the test material was delivered. The common target organ of toxicity following oral exposure was the forestomach in gavage studies and the liver and kidneys in dietary studies. HERA report that minor differences in potency amongst the AS surfactants tested were consisted with what would be expected based on toxicity mechanisms (in particular relative irritancy of the salts). For instance, in a 28-day gavage study on C₁₂ AS Na and C₁₂-C₁₄ AS TEA compounds, changes were partially reversible for C₁₂ AS Na and fully reversible for C₁₂-C₁₄ AS TEA. Dose-dependent irritation, inflammation, edema and ulceration of the forestomach were the primary observed toxic effects. Dermal The HERA review indicates that the effects at the site of application of AS in dermal studies were consistent with the irritant properties of the test material. This was based on four studies with C₁₂-C₁₅ AS Na assessing repeated dose toxicity in mice.	HERA 2002 HERA 2002
Sensitisation of the skin or respiratory system The HERA review considers AS to be non-sensitising to the skin.	HERA 2002
Corrosion (irreversible)/irritation (reversible) effects on the skin or eye The SDS for the product containing 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate identifies the following GHS classification for this compound: Skin Corr. 1 B (H314) – Causes severe skin burns and eye damage. Skin The HERA review concluded that AS at concentration above 5% was a moderate to strong irritant and lower concentrations produced slight to moderate irritation. The HERA review indicated that AS with longer carbon chains (C₁₆-C₁₈) tend to be less irritating than shorter chained AS (C₁₂-C₁₅). Based on test results, concentrations of 10% or greater for shorter carbon chained AS consistently produced moderate to severe irritation reactions. For exposure to lower concentrations (1 – 7%), responses ranged from non to severe. The longer carbon chain length material AS (C₁₂-C₁₈) produced strong reactions at concentrations above 25%. However, at lower concentration, no or slight reactions were observed. The HERA review also comments that reports from controlled human exposure to AS confirm that low concentrations are non-irritating. Eye Eye irritation studies on AS indicated that the compounds would be classified as substantial eye	2014 HERA 2002 HERA 2002



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irritants based on test results (application of 5% of AS in rabbit eye irritation test). However, as with skin irritation, the longer chain length material (C ₁₆ -C ₁₈) tend to produce less irritation. Eye irritation effects were also reported to be reduced at lower concentrations (i.e. <2%).	
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Physical Hazards	Reference
Flammable Potential Not classified as an explosive substance.	[REDACTED] 2014
Explosive Potential Not classified as an explosive substance.	[REDACTED] 2014

Toxicity Values	Value	Reference
Animal Toxicity Data		
Acute Toxicity		
LD₅₀		
Rat, oral	1 400 to 7 800 mg/kg	HERA 2002
Mouse, oral	2 600 to > 8 000 mg/kg	HERA 2002
LC₅₀		
Rat	NDF	
High Chronic/Repeat Dose Toxicity		
LOAEL, oral, rat	123-503 mg/kg/day	HERA 2002
NOAEL, oral, rat, 90 d, feeding, C ₁₆ -C ₁₈ AS	61 mg/kg/day (0.07% in diet)	HERA 2002

Footnotes:

LD₅₀ – lethal dose for 50% of experimental population

LC₅₀ – lethal air concentration for 50% of experimental population

LOAEL – Lowest Observed Adverse Effect Level

LOAEC – Lowest Observed Adverse Effect Concentration

NDF – No data found within the limits of the search strategy

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Human Health Toxicity Ranking*		
	Hazard data	Comment
Hazard Band 4		
Carcinogenicity (IARC Group 1 or 2A)	No	Based on conclusion of HERA 2002
Mutagenicity/Genotoxicity (GHS Category 1A and 1B)	No	Based on conclusion of HERA 2002
Reproductive Toxicity/Developmental toxicity (GHS Category 1, 1A and 1B)	No	Based on conclusion of HERA 2002
Endocrine Disruption ¹	No	Based on not being listed by EC
Hazard Band 3		
Carcinogenicity (IARC Group 2B)	No	Based on conclusion of HERA 2002
Mutagenicity/Genotoxicity (GHS Category 2)	No	Based on conclusion of HERA 2002
Reproductive Toxicity/Developmental toxicity (GHS Category 2)	No	Based on conclusion of HERA 2002
Acute Toxicity (oral, dermal or inhalation) Very Toxic/Toxic - oral LD₅₀ ≤ 300 mg/kg² - dermal LD₅₀ ≤ 1000 mg/kg - inhalation LC₅₀ ≤ 10 mg/L³ (or mg/m³) (vapour)	No	LD ₅₀ , oral, rat: 1 400 to 7 800 mg/kg, HERA 2002
High Chronic/repeat dose toxicity - oral LOAEL ≤ 10 mg/kg/d²; - dermal LOAEL ≤ 2 0 mg/kg/d; - inhalation LOAEC (6 h/d) ≤ 50 ppm/d for gases, ≤ 0.2 mg/L/d for vapours or ≤ 0.02 mg/L/d for dust/mists/fumes³	No	LOAEL, oral, rat: 123– 503 mg/kg/day, HERA 2002
Corrosive (irreversible effect)	Yes	HERA 2002
Respiratory sensitiser	NDF	
Hazard Band 2		
Harmful chronic/repeat dose toxicity - oral LOAEL > 10 mg/kg and ≤ 100 mg/kg/d - dermal LOAEL > 20 mg/kg/d and ≤ 200 mg/kg/d - inhalation (6-h/d) LOAEC > 50 mg/L ≤ 250 mg/L/d for gases, > 0.2 mg/L ≤ 1 .0 mg/L/d for vapours or > 0.02 mg/L ≤ 0.2 mg/L/d for dust/mists/fumes³	No	LOAEL, oral, rat: 123– 503 mg/kg/day, HERA 2002
Skin Sensitiser	No	Based on conclusion of HERA 2002
Hazard Band 1		
Acute Toxicity-Harmful - oral LD₅₀ > 300 mg/kg ≤ 2000 mg/kg - dermal LD₅₀ >1 000 mg/kg ≤ 2000 mg/kg; - inhalation LC₅₀ (6 h/d) > 10 mg/L ≤ 20 mg/L for vapours)³	Yes	LD ₅₀ , oral, rat: 1 400 to 7 800 mg/kg, HERA 2002
Irritant (reversible effect)	Yes	AS at concentration above 5% was a moderate to strong irritant, HERA 2002
Hazard Band 0	-	

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All indicators outside criteria listed in Hazards 1-4		
Physical Hazards		
Flammable potential	NDF	
Explosive potential	NDF	
Hazard Evaluation (highest band) not including physical hazards	3	
Uncertainty analysis /data confidence (out of 12 parameters)	11/12	92 %

* Based on IMAP Framework [NICNAS (2013) Inventory Multi-tiered Assessment and Prioritisation (IMAP) Framework. National Industrial Chemicals Notification and Assessment Scheme. Department of Health and Aging, Canberra].

¹ Based on list of endocrine disrupting chemicals from the European Commission's Endocrine Disruptors website.

² milligrams per kilogram body mass (mg/kg) or milligrams per kilogram body mass per day (mg/kg/d)

³ Based on GHS cut-offs for hazard classification. For chronic/repeat dose toxicity, GHS cut-offs are provided as guidance values (i.e. the dose/concentration at or below which significant health effects are observed)". (p 18, NICNAS 2013).

Human Health Guidelines		
Media	Concentration (mg/m ³ ; mg/L; mg/kg)	Reference
Occupational Exposure Limits		
Air (OEL)		
8-h TWA	NDF	
STEL	NDF	
Peak Limitation	NDF	
Environmental Exposure		
Air, ambient	NDF	
Air, indoor	NDF	
Water, potable	NDF	
Water, recreational		
Soil, residential	NDF	
Soil, commercial/industrial	NDF	

Footnotes:

OEL = Occupational Exposure Limit

TWA = 8 h Time-Weighted Average

STEL = (15 min) Short-term Exposure Limit

Qualifying Summary Comments

2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate is a polymer formed from the monomers of maleic acid (cis-butenedioic acid, C₄H₄O₄) and sodium 2-methylprop-2-ene-1-sulfonate (C₃H₅O₃S.Na). Limited information is available on publicly accessible data sources for 2-Butenedioic acid (2Z)-, polymer with sodium 2-propene-1-sulfonate. As limited data is available for the polymer, the hazard assessment has been supplemented with data based on the functional groups likely to be present in the polymer. This includes the sodium sulfonate group and two carboxylic acid groups.



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The polymer has been assigned a Hazard Band 3, based on potential acute oral toxicity and corrosive/irritant effects to skin and eyes, primarily associated with the sulfonate group. It is noted that the alkyl sulfonate groups appeared irritating to skin at concentrations above 5% and that concentrations less than 1% are not considered to be an irritant. In addition longer chained alkyl sulfonates tend to be less irritating than shorter chained alkyl sulfonates. Based on this, the functional groups assessed are considered likely to be less toxic once in polymer form and at low concentrations (< 1%).

References

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Created by:	MGT	Date: 16/03/2015
Reviewed by:	JF	Date 19/03/2015



APPENDIX B

Ecotoxicology Profiles



Project number: 127635006

ORGANIC

Name	2-Butenedioic acid
Synonyms	
CAS Number	6915-18-0
Molecular Formula	C4H4O4

Physical Properties	Value	Reference
PhaseState:		
Molecular Weight (g/mol):	110.984	EPISUITE 2011 v4.1
Melting Point (°C):	84.12	EPISUITE 2011 v4.1
Boiling Point (°C):	285.25	EPISUITE 2011 v4.1
Density / Specific Gravity (Enter Unit):		
Vapour Pressure (mm Hg at 25°C):	0.00000000000943	EPISUITE 2011 v4.1
Solubility (mg/L):	441,000.00	EPISUITE 2011 v4.1
Henry's Law Constant (atm m ³ /mole):	8.48E-14	EPISUITE 2011 v4.1
Organic carbon partition coefficient (Koc):	7.33	EPISUITE 2011 v4.1
Log organic carbon partition coefficient (log Koc):	0.87	EPISUITE 2011 v4.1
Log octanol - water partition coefficient (log Kow):	4.60E-01	EPISUITE 2011 v4.1

Persistence / Bioaccumulation	Value	Reference
Biowin 3 (Ultimate Survey Biodegradation):	3.6719	EPISUITE 2011 v4.1
Biowin 4 (Primary Biodegradation):	4.4514	EPISUITE 2011 v4.1
EPISUITE Ready Biodegradability:	Biodegrades fast	EPISUITE 2011 v4.1
Biowin 7 (Anaerobic Model Prediction):	1.0626	EPISUITE 2011 v4.1
Fugacity_Air: (%)	0.0673	EPISUITE 2011 v4.1
Fugacity_Water: (%)	29	EPISUITE 2011 v4.1
Fugacity_Soil: (%)	70	EPISUITE 2011 v4.1
Fugacity_Sediment: (%)	0.059	EPISUITE 2011 v4.1
Bioconcentration factor (BCF):	3.162	EPISUITE 2011 v4.1
Biotransformation half - life (Days):	0.1841	EPISUITE 2011 v4.1

Aquatic Ecotoxicological Data

Acute toxicity data							
SpeciesName	Common Name	Endpoint	Effect	Effect Measure	Test Time (Days)	Conc mg/L	Reference
	Fish	Fish LC50	MOR	Mortality	4	53316	ECOSAR 2012
	Daphnid	Invertebrate LC50	MOR	Mortality	2	25295	ECOSAR 2012
	Algae	Plant EC50	GRO	Growth	4	8964	ECOSAR 2012

Terrestrial Ecotoxicological Data

Common Name	Endpoint	Effect	Effect Measure	Test Time (Days)	Conc	Reference	Units
Worms	QSAR worms	MOR	Mortality		411	Calculated	mg/kg
Lettuce	QSAR lettuce	GRO	Growth		0.355	Calculated	mg/L

Created By: Naomi Cooper

Date: 27/03/2015

Checked By: Kirsten Broadgate

Date: 27/03/2015



Project number: 127635006

ORGANIC

Name	Alkyl Sulfonates
Synonyms	
CAS Number	68037-49-0
Molecular Formula	(C3H6O3SNa)x

Physical Properties	Value	Reference
PhaseState:		
Molecular Weight (g/mol):	316.4	HERA 2002
Melting Point (°C):	264.80	HERA 2002
Boiling Point (°C):	611.7	HERA 2002
Density / Specific Gravity (Enter Unit):		
Vapour Pressure (mm Hg at 25°C):	0.0000000000141	HERA 2002
Solubility (mg/L):	5.13	HERA 2002
Henry's Law Constant (atm m ³ /mole):	0.000000503	EPISUITE 2011 v4.1
Organic carbon partition coefficient (Koc):	1,155.00	EPISUITE 2011 v4.1
Log organic carbon partition coefficient (log Koc):	3.06	EPISUITE 2011 v4.1
Log octanol - water partition coefficient (log Kow):	4.60E-01	HERA 2002

Persistence / Bioaccumulation	Value	Reference
Biowin 3 (Ultimate Survey Biodegradation):	3.0748	EPISUITE 2011 v4.1
Biowin 4 (Primary Biodegradation):	3.8922	EPISUITE 2011 v4.1
EPISUITE Ready Biodegradability:	Biodegrades fast	EPISUITE 2011 v4.1
Biowin 7 (Anaerobic Model Prediction):	0.7767	EPISUITE 2011 v4.1
Fugacity_Air: (%)	0.657	EPISUITE 2011 v4.1
Fugacity_Water: (%)	21	EPISUITE 2011 v4.1
Fugacity_Soil: (%)	78	EPISUITE 2011 v4.1
Fugacity_Sediment: (%)	0.828	EPISUITE 2011 v4.1
Bioconcentration factor (BCF):	70.79	EPISUITE 2011 v4.1
Biotransformation half - life (Days):	0.3739	EPISUITE 2011 v4.1

Aquatic Ecotoxicological Data

Acute toxicity data							
SpeciesName	Common Name	Endpoint	Effect	Effect Measure	Test Time (Days)	Conc mg/L	Reference
	Fish	Fish LC50	MOR	Mortality	4	36.376	ECOSAR 2012
	Daphnid	Invertebrate LC50	MOR	Mortality	2	24.85	ECOSAR 2012
	Algae	Plant EC50	GRO	Growth	4	39.761	ECOSAR 2012

Chronic toxicity data							
SpeciesName	Common Name	Endpoint	Effect	Effect Measure	Test Time (Days)	Conc mg/L	Reference
Selenastrum	Algae	Plant NOEC	GRO	Growth	4	12	HERA 2002

Terrestrial Ecotoxicological Data

Common Name	Endpoint	Effect	Effect Measure	Test Time (Days)	Conc	Reference	Units
Rat	Mammalian LD50	MOR	Mortality		1400	HERA 2002	mg/kg
Worms	QSAR worms	MOR	Mortality		179	Calculated	mg/kg
Lettuce	QSAR lettuce	GRO	Growth		0.962	Calculated	mg/L

Common Name	Endpoint	Effect	Effect Measure	Test Time (Days)	Conc	Reference	Units
Earthworm	1	MOR	Mortality		3001	ECOSAR 2012	mg/L

Created By: Naomi Cooper

Date: 27/03/2015

Checked By: Kirsten Broadgate

Date: 27/03/2015



APPENDIX C

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