Australia's National
Science Agency

GISERA | Gas Industry Social and Environmental Research Alliance

Progress report

Fate of hydraulic fracturing fluids/chemicals and geogenic hydrocarbons in surface facilities and in the subsurface

CSIRO | Australia Pacific LNG | QGC | origin | Santos | NSW Government | Australian Government Department of Industry, Science, Energy and Resources | Supported by Government of South Australia | Queensland Government | Northern Territory Government

Progress against project milestones

Progress against milestones/tasks are approved by the GISERA Director, acting with authority in accordance with the GISERA Alliance Agreement.

Progress against project milestones/tasks is indicated by two methods: Traffic light reports and descriptive Project schedule reports.

1. Traffic light reports in the Project Schedule Table below show progress using a simple colour code:

- **Green**:
  - Milestone fully met according to schedule.
  - Project is expected to continue to deliver according to plan.
  - Milestone payment is approved.
- **Amber**:
  - Milestone largely met according to schedule.
  - Project has experienced delays or difficulties that will be overcome by next milestone, enabling project to return to delivery according to plan by next milestone.
  - Milestone payment is withheld.
  - Milestone payment withheld for second of two successive amber lights; project review initiated and undertaken by GISERA Director.
- **Red**:
  - Milestone not met according to schedule.
  - Problems in meeting milestone are likely to impact subsequent project delivery, such that revisions to project timing, scope or budget must be considered.
  - Milestone payment is withheld.
  - Project review initiated by GISERA Director.

2. Progress Schedule Reports outline task objectives and outputs and describe, in the 'progress report' section, the means and extent to which progress towards tasks has been made.

Project schedule table

TASK NUMBER	TASK DESCRIPTION	SCHEDULED START	SCHEDULED FINISH	COMMENT
1	Sampling logistics and field trip planning	Jul-21	Aug-21	Completed
2	Literature Review	Jul-21	Sept-21	Completed
3	Commissioning laboratory equipment and developing experimental program	Jul-21	Oct-21	Completed
4	Sampling campaign	Aug-21	Apr-22	Completed
5	Chemical degradation of hydraulic fracturing fluids under reservoir conditions	Oct-21	Nov-22	
6	Profiling microbial communities from flow-back tanks and treatment ponds	Oct-21	Jun-22	Completed
7	Microbial degradation trials of target chemicals used in hydraulic fracturing associated with shale gas production	Oct-21	Sept-22	This task is underway and will be complete end Dec/early Jan 2023
8	Geogenic hydrocarbons in flow-back water	Oct-21	Oct-22	This task is underway and will be complete Feb 2023
9	Migration behaviour of hydraulic fracturing fluids under reservoir conditions	Nov-21	Aug-22	This task is underway and will be complete Nov 2022
10	Modelling the fate of residual hydraulic fracturing chemicals	May-22	Oct-22	This task is underway, modelling the fate of residual hydraulic fracturing chemicals is dependent on completion of Tasks 5 and 9. This task will be complete Feb 2023.
11	Project Leadership, Task Leadership and Report Writing	Jul-21	Jan-23	This final report is being prepared for completed tasks (1-4 and 6) and is awaiting completion of the remining tasks. This task will be complete May 2023.

TASK NUMBER	TASK DESCRIPTION	SCHEDULED START	SCHEDULED FINISH	COMMENT
12	Communicate findings to stakeholders	Jul-21	Jan-23	This task will be complete May 2023.

Project schedule report

TASK 1: Sampling logistics and field trip planning

BACKGROUND

During Task 1, consult with Santos and Origin representatives in the Northern Territory to prepare for sampling of drill site/sites (up to a maximum of two sites), flow-back water, holding tanks, treatment ponds. Task 1 will establish the potential sampling site/sites from Santos and Origin, and the nature of the samples (i.e. sample type, volume, size, depth and number). This task will also include the safe and environmentally sensitive planning, provisioning, and logistics for the sampling campaign.

TASK OBJECTIVES

1. Establish contact with representatives in Santos and Origin to guide the sampling campaign.
2. Establish water and sampling site/sites within the Beetaloo sub-basin.
3. Identify suitable core samples from within the Northern Territory Core repositories.
4. Establish sampling requirements, i.e., type, volume, size, sampling depth, number, availability of initial fracturing fluids before injection etc.
5. Identification of any permits, permission or consultation required for sampling.
6. Preparation of sampling equipment/reagents.
7. Preparation for remote sampling fieldwork including accommodation, vehicle hire and OH&S considerations.
8. Logistics of transporting equipment and samples between CSIRO laboratories in Sydney/Melbourne and collection sites in the Northern Territory.
9. Confirm the list of chemicals being investigated in this study with key stakeholders.
10. Detail the analytical requirements from external labs, to inform design of the degradation and migration experiments.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

This task will yield a series of documents describing the contacts, sampling site/sites, relevant permissions, sampling equipment and OH&S considerations.

PROGRESS REPORT

This milestone is complete.

The W26 team has had extensive discussions with Origin and Santos about our requirements for sampling for W26. On completion, the project team will be organising a meeting of the Technical Reference Group to relay our plans for sampling to stakeholders and confirm the chemicals being

examined in the project and their relevance to operations occurring in the Northern Territory. We have prepared microbial preservation solutions, sample bottles for collection of tank, treatment pond and flowback samples for chemical analyses. These have been shipped to Darwin. Origin and Santos will organise collections of these materials in the next two-three weeks, after the Technical Reference Group meeting. At present, due to the lockdown there are some challenges (staff from NSW and Victoria are unable to travel to the Northern Territory) and we have limited access to our Sydney and Melbourne laboratories. We are in the process of developing contingencies to allow for collections to be undertaken in consultation with third-party providers in the Northern Territory.

TASK 2: Literature review

BACKGROUND

Fracturing fluids are primarily composed of freshwater, proppants, and chemical additives such as friction reducers, biocides, surfactants, and scale reducers. Task 2 will focus on the chemicals in the fracturing fluids and review the reasons to use these chemicals in the fracturing fluids, the properties and toxicity of the chemicals and what is known of the degradation, biodegradation and subsurface migration of these chemicals.

TASK OBJECTIVES

1. Information on why these chemicals are used in fracturing fluids.
2. Information on the properties and toxicity of chemicals.
3. Review previous research examining abiotic chemical degradation and migration properties of compounds.
4. Information on the geogenic hydrocarbons produced during the fracturing of shales at other sites.
5. Literature review of the biodegradation of these chemicals.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Task 2 will provide a literature review on chemicals in the fracturing fluids with details about the role of these chemicals in the fracturing fluids, their properties and toxicity along with information on their mobility in the subsurface, abiotic and biotic degradation. This review will constitute the introduction of the final report and will also be submitted in September 2021 as a stand- alone document.

PROGRESS REPORT

This milestone is complete, the literature review has been completed.

TASK 3: Commissioning laboratory equipment for reservoir experimental program

BACKGROUND

Task 3 will involve the detailed preparation for the experimental program for chemical degradation and migration under reservoir conditions. Shale reservoirs for investigation (e.g. Kyalla Fm and/or Velkerri Fm) will be decided in consultation with the Technical Reference Group and based on sample availability determined in Task 1. The composition of the hydraulic fracturing / formation fluid analogue will be decided either following flow-back water collection and analysis, or based on reported hydraulic fracturing fluid composition provided in accordance with the NT Petroleum (Environment) Regulations 2016. The laboratory equipment (batch and core flooding rigs) will be commissioned to meet the project requirements.

TASK OBJECTIVES

The task has the following objectives:

- Modify and commission experimental equipment to meet experimental program requirements (pressure, temperature, sampling).
- Finalise the shale targets, formation water and hydraulic fracturing fluid analogues that will comprise the degradation and migration experimental program.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Experimental program for the degradation and migration experiments under reservoir conditions. Modified and commissioned experimental equipment to meet project requirements.

PROGRESS REPORT

This milestone is complete.

The experimental program has been developed, that will investigate chemical degradation of compounds of interest within Amungee and Velkerri formation shales. The program also investigates migration properties of compounds of interest in Amungee and Velkerri formation shales through core flooding.

Due to Victoria's COVID restrictions, there has been no lab access from early July to early October. Purchase of required components, and design and construction of equipment by external contractors has continued throughout this period, however, modification and commissioning activities have commenced later than planned.

Following renewed site access, commissioning is complete on equipment for migration studies, and on 8 chemical degradation units (Figure 1). Construction and commissioning on 5 further chemical degradation units is ongoing. This work is expected to be largely complete by the end of October, however, availability of staff access may delay this into November. This would not be expected to delay the completion of the experimental program (Tasks 5 and 9). Current Victorian restrictions do not authorise commencement of new experimental work, while this advice is expected to change in late October, any extended delay to these changes may affect commencement of Task 5 and needs to be monitored.

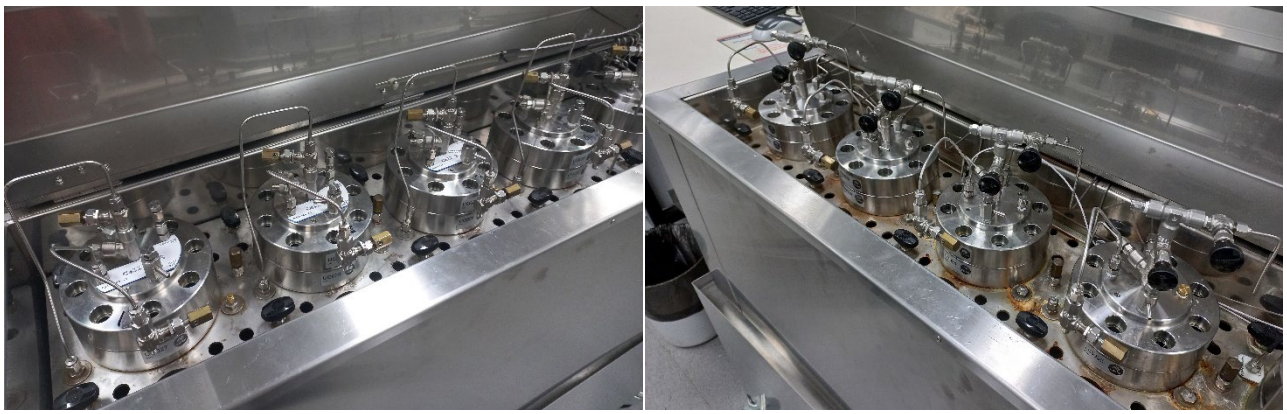

Figure 1 Eight modified and commissioned units for investigating chemical degradation.

TASK 4: Sampling campaign

BACKGROUND

Task 4 will involve two staff travelling to the Beetaloo sub-basin of the Northern Territory with the purpose of collecting water and shale core samples from drilling sites, flow-back water tanks and treatment ponds. While in the field the team will be led by Nai Tran-Dinh who has experience in the Northern Territory at these sites.

TASK OBJECTIVES

1. To collect preserved water samples for microbial community profiling (Task 6) from the site/sites identified by Task 1.
2. To collect microbiological ('live') and matching bulk water samples for microbial degradation trials (Task 7) from the site/sites identified by Task 1.
3. To collect shale core samples for core flooding experiments (Task 5) from the site/sites identified by Task 1.
4. Perform initial water chemistry analyses of collected water samples through a NATA accredited laboratory.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Collection of microbially preserved water samples, microbiological ('live') water samples and bulk water samples. Collection of shale core samples.

PROGRESS REPORT

The initial sampling campaign at Santos' Tanumbirini location has been completed.

A total of 30 microbial community profiling samples, two bulk water samples (for microbial degradation trials and core flood experiments), and ten water chemistry and geogenic hydrocarbon samples were collected. Chemical analyses of the water samples used to make hydraulic fracturing fluids indicated that the bore waters were slightly alkaline (pH range 7.99-8.08) and had a low electrical conductivity (EC of approximately 1280 µS/cm). The flow-back water samples were taken from three different tanks and varied in pH between 7.53 to 8.30. The electrical conductivity in tank 4 water samples were in the range 8150 to 8660 µS/cm. Tank 2 and tank 3 flow-back waters were higher in electrical conductivity at 27,000 and 30,100 µS/cm, respectively.

The geogenic hydrocarbon samples have been stored and are awaiting analysis. The microbial community profiling of preserved water samples has been completed and analysis of the 16S rDNA data and OTU tables is currently underway. Initial analysis indicates a number of novel taxa identified from both bore water samples and from the flow-back water tanks. The microbial communities differ markedly between the bore water samples and the flow-back tanks, and also between tanks 2, 3 and 4.

In late April through early May 2022, two CSIRO staff conducted field work to collect samples from Santos, Origin and the core shed in Darwin. At Origin's Kyalla site, our staff were able to collect samples of the bore water (RN041132) along with samples from the evaporation pond on site. At Santos's site at Tanumbirini water was collected RN040930 along with several flow back water storage tanks and a site where the flowback water was newly arrived from the subsurface. It should be noted that sampling from the newly arrived flowback water was difficult and that these flowback waters were heterogenous in nature and had an oily phase on top of an aqueous phase.

Water collected from the bores was neutral to alkaline in pH with values of 7.61 and 7.84 for RN041132 and RN04930, respectively. Both bores had similar electrical conductivity (~1200 µS/cm). The evaporation pond at Origin had low pH (5.5) and very high salinity (~192,000 µS/cm) consistency with the process undertaken (evaporation) in this pond. The flowback storage tank waters had moderate salinity with all samples from Tanumbirini having electrical conductivity of ~15,000 µS/cm and more alkaline pHs (~8.8). Detailed water chemistry is available now for use in further analyses by the project. Consistent with their use in fracturing processes, flowback water (regardless of the site) had elevated inorganic and organic carbon concentrations. The former is likely dissolved carbonates from interactions with subsurface carbonates, while the latter is geogenically derived compounds obtained from fossilised organic matter in the shales. Total recoverable hydrocarbons (TRH C10-C36) were most elevated in the freshly returning flowback water which had ~30,000mg L^{-1} TRH (C10-C36). This value, however, is due to the heterogenous nature of the sample and the ratio of the oily phase collected. TRH (C10-C36) measurements in the storage tanks were numerous orders of magnitude lower and were ~280 µg L^{-1}. Benzene, toluene, ethylbenzene and xylene (BTEX) concentrations were also measured, however, no BTEX compounds were observed in any water samples. Numerous weak acids were also detected at low concentrations in all the samples except the two bore waters, these consisted of formic, acetic, propionic acids, which, except for the sample from the evaporation pond at Kyalla, were probably in their conjugate base forms (e.g. formate, acetate and propionate) as the pH of these water samples are well above 7. In the Kyalla pond sample, these may represent weak acids in the water as the pH in the Kyalla evaporation pond was ~5.5.

Four half-sawn core samples were retrieved from the Northern Territory Geological Survey core shed in Darwin. Two samples each representing the Velkerri Formation from the Tanumbirini-1 and the Amungee NW-1 wells. These core samples will be utilised in core flooding experiments in Task 9 of the project.

TASK 5: Chemical degradation of hydraulic fracturing fluids under reservoir conditions

This task is due for completion November 2022.

TASK 6: Profiling microbial communities from flow-back tanks and treatment ponds

BACKGROUND

The microbially preserved water samples will be subject to DNA extraction along with 16S rDNA sequencing.

TASK OBJECTIVES

The task will include the following objectives:

1. Filter preserved water samples from flow-back tanks and treatment ponds onto 0.1µM PVDF filters.
2. Complete DNA extractions from all samples.
3. Process DNA for 16S NGS sequencing.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Raw sequencing data from microbial community profiling available.

PROGRESS REPORT

This milestone is complete.

Profiling of microbial communities from flow-back tanks and treatment ponds collected from both Santos and Origin have been completed. The raw sequencing data have been analysed and are available on request.

TASK 7: Microbial degradation trials of target chemicals used in hydraulic fracturing associated with shale gas production

BACKGROUND

Replicated water microcosms using flow-back tank water and treatment pond water will be established and used to determine the ability of microbial communities present in these waters to degrade chemicals potentially used in hydraulic fracturing associated with shale gas production. Chemical degradation will be determined through direct measurement of the chemicals at NATA accredited laboratories or through this project.

TASK OBJECTIVES

The task will include the following objectives:

1. Establish replicated anoxic microcosms for flow-back tank water samples.
2. Establish replicated oxic microcosms for treatment pond water samples.
3. Spike microcosms with a mixture of target compounds used in hydraulic fracturing associated with shale gas production at realistic concentrations.
4. Analysis of target chemicals before microbial degradation experiments

5. Harvest all water treatments after 8 weeks and perform microbial community profiling and analysis of target chemicals.
6. Statistical analyses of the resultant data.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Replicated experimental data on the degradation of target compounds. Data prepared for analysis and final reporting.

PROGRESS REPORT

Replicated water microcosms using collected flow-back tank water and treatment pond water samples have been established. The microcosm experiments will be harvested in November/December on completion of the 8 week incubation period. All microcosm experiments were established under oxic conditions as the microbial community profiles (Task 6) indicated no discernible difference between water samples collected from the top and bottom of flow-back tanks. The concentration of target compounds used to spike microcosms was determined based on the maximum concentrations observed in the flow-back ponds (Task 4). This task will be complete late Dec/early Jan.

TASK 8: Geogenic hydrocarbons in flow-back water

BACKGROUND

Natural rock formations contain compounds that could be mobilised into flowback and produced water during hydraulic fracturing. Organic chemicals such as phenol, polycyclic aromatic hydrocarbons (PAHs) and total recoverable hydrocarbons (TRHs) were detected in extracts of powdered rock samples based on the GBA report in 2020. However, these compounds only represented a small fraction of the total organic geogenic compounds present in the sample extracts. Most organic compounds in the sample extracts were unidentified and are required further 'forensic' analysis for their identification and quantification. Their risk to aquatic environments is unknown. This task will focus on characterizing the geogenic hydrocarbons in details in the flow-back, tank, treatment pond water associated with shale gas development, as well as water after microbial degradation experiment in task 7 using the in-house gas chromatograph-mass spectrometry (GC-MS) method.

TASK OBJECTIVES

The task will include the following objectives:

1. Detailed geogenic hydrocarbons of a sub-set of samples will be analysed by the in-house gas chromatography-mass spectrometry method.

2. Semi-quantitative or quantitative data of hydrocarbons such as TRH (C6-C40), BTEX, VOCs, PAHs, volatile organic acids, phenols and halogenated hydrocarbons will be screened through a NATA accredited laboratory for all the samples.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Composition of the geogenic hydrocarbons in a sub-set of the water samples (up to 20) and the microbial degradation experiment water samples (up to 12) will be characterised in greater details based on the results of semi-quantitative data of TRH (C6-C40) or quantitative data of BTEX, VOCs, PAHs, volatile organic acids, phenols and halogenated hydrocarbons in the collected water samples (up to 44) and microbial degradation experiment water samples (up to 12) analysed through the NATA accredited laboratory.

PROGRESS REPORT

All collected water samples from Task 4 have been extracted, and the geogenic hydrocarbons have been analysed for 12 samples. No geogenic hydrocarbons were found in any of the bore water samples. Low abundance of n-alkanes were detected from two samples from a flow-back water holding pond. Initial microcosm samples from Task 7 have been extracted, and the remaining Task 7 microbial degradation experimental samples will be analysed on completion of incubation. It is expected that analyses for geogenic hydrocarbons from Task 7 microbial degradation experimental samples will be completed at the end of February 2023.

Quantitative analyses of hydrocarbons such as TRH (C6-C40), BTEX, VOCs, PAHs, volatile organic acids, phenols and halogenated hydrocarbons have been completed for all collected samples.

TASK 9: Migration behaviour of hydraulic fracturing fluids under reservoir conditions

BACKGROUND

This task involves the experimental determination of key properties that affect the subsurface migration behaviour of compounds of interest present as additives in hydraulic fracturing fluid. Characterisation of these properties under reservoir conditions is key to accurately representing the migration behaviour, as many properties are strongly influenced by the specific in-situ conditions associated with the sub-surface environment. Adsorption will be measured through experiments where the compounds of interest are flowed through a core sample under reservoir conditions. A non-adsorbing tracer will be used to calculate the effective flow velocity, allowing for adsorption for the compounds of interest to be determined. Core flooding experiments would characterise the properties affecting migration according to the experimental program developed in Task 1. Shale is an extremely low permeability rock, and liquid flow rates within the core floods are expected to be low, therefore the number and duration of core floods will depend on the liquid analysis requirements and on the availability of cores from target reservoirs established in Task 1.

TASK OBJECTIVES

The task has the following objectives:

1. Undertake core flooding experiments which will measure the adsorption behaviour of compounds of interest under reservoir conditions, for different shale gas target reservoirs decided in consultation with the Technical Reference Group.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Experimental data detailing the adsorption behaviour of the compounds of interest in shale under reservoir conditions. Data prepared for analysis and final reporting.

PROGRESS REPORT

This task is due for completion November 2022

TASK 10: Modelling the fate of residual hydraulic fracturing chemicals

BACKGROUND

The migration behaviour of residual hydraulic fracturing chemicals is influenced by the properties investigated in Tasks 5 and 9, and these properties will be used in representative migration modelling case studies to investigate the fate of chemicals under conditions representing the Beetaloo sub-basin. Case studies based on Mallants et al (2017) and planned with Technical Reference Group will investigate the fate of hydraulic fracturing chemicals under the established scenarios. The number of scenarios investigated will depend on the extent of the experimental program completed in Tasks 5 and 9, which are dependent on sample availability. The task will require acquisition of software with the capability for adequately modelling the advective transport behaviour.

TASK OBJECTIVES

The task has the following objectives:

1. Complete modelling case studies that characterise the fate of hydraulic fracturing chemicals under scenarios represented in the Beetaloo sub-basin.

TASK OUTPUTS AND SPECIFIC DELIVERABLES:

Chapter in the final report detailing the results of the modelling case studies.

PROGRESS REPORT

This task is underway, modelling the fate of residual hydraulic fracturing chemicals is dependent on completion of Tasks 5 and 9. This task will be complete Feb 2023.

Variations to Project Order

Changes to research Project Orders are approved by the GISERA Director, acting with authority, in accordance with the GISERA Alliance Agreement. Any variations above the GISERA Director's delegation require the approval of the relevant GISERA Research Advisory Committee.

The table below details variations to research Project Order.

Register of changes to Research Project Order

DATE	ISSUE	ACTION	AUTHORISATION

17/03/22	Due to covid border restrictions and company provision of samples, delays to sampling occurred.	Milestone 4 delivery date extended from October 2021 to April 2022	
17/03/22	Due to covid border restrictions and company provision of samples, delays to sampling occurred.	Milestone 5 delivery date extended from September 2022 to November 2022	
17/03/22	Due to covid border restrictions and company provision of samples, delays to sampling occurred.	Milestone 6 delivery date extended from February 2022 to June 2022.	
17/03/22	Due to covid border restrictions and company provision of samples, delays to sampling occurred.	Milestone 7 delivery date extended from May 2022 to September 2022.	
17/03/22	Due to covid border restrictions and company provision of samples, delays to sampling occurred.	Milestone 8 delivery date extended from August 2022 to October 2022.	

As Australia's national science agency and innovation catalyst, CSIRO is solving the greatest challenges through innovative science and technology.

CSIRO. Unlocking a better future for everyone.

Contact us

1300 363 400
+61 3 9545 2176
csiro.au/contact
csiro.au

For further information

1300 363 400
gisera.csiro.au

GISERA is a collaboration between CSIRO, Commonwealth and state governments and industry established to undertake publicly-reported independent research. The purpose of GISERA is to provide quality assured scientific research and information to communities living in gas development regions focusing on social and environmental topics including: groundwater and surface water, greenhouse gas emissions, biodiversity, land management, the marine environment, and socio-economic impacts. The governance structure for GISERA is designed to provide for and protect research independence and transparency of research.