The impacts of corrosion additives on ash and combustion efficiency from biomass combustion

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Introduction

A key role of biomass in the transition to low carbon energy is as a replacement for coal within power generation. Biomass is very different to coal, and it is these differences that can be problematic in terms of chlorine-related corrosion, slagging and fouling. To address the risk of corrosion Drax inject a mitigant, and an apparent side-effect of the additive is lowered carbon monoxide concentrations, and hence greater combustion efficiencies. The objective of this project is to understand this relationship and the impacts of the additive on ash and combustion efficiency.

The approach was split into mathematical modelling and laboratory experiments. The experimental side of the problem researched into biomass ash-related corrosion, corrosion prevention additives and their subsequent impacts on combustion. The mathematical modelling investigated the effects of mitigant injection on the combustion environment in two full scale combustion units and its relation to the combustion efficiency.

Background theory

Biomass, its composition and subsequent effects

Potassium is the dominant source of alkali in most biomass fuels and is also the key element that results in the formation of troublesome species at combustion temperatures. Inorganic salts such as potassium chloride, the favoured alkali at highest temperatures, have low melting temperatures and can vaporise during combustion. When the flue gas is then cooled they condense onto the fly ash particles and heat exchanger surfaces causing corrosion, slagging and fouling.

Chlorine content in wood is low, and in agricultural residue is high. Though, even small amounts of Cl will significantly increase the amount found at critical ash deposits and therefore the corrosion rate.

Combustion efficiency and carbon monoxide emissions

The fate of carbon is a critical measurement for all combustion plants. Complete burnout to CO_2 is desirable, and any remaining as CO or as unburned in the ash fractions is wasted heat. Furthermore, excess CO concentrations can become an issue when considering the Large Combustion Plant Directive. The combustion efficiency can be altered by many variables, including race alkali species affecting the oxidation rate of CO .

Additives and their impacts on ash and combustion

Additives (interchangeable with mitigants) refer to minerals or chemicals used to abate ash related operational problems. In this project, the problem of corrosion through:
- Changing the ash chemistry
- Decreasing the concentration of problematic species
- Raising the ash melting temperature

It is beneficial for the additive to be stable at high temperatures, have a large surface area for adsorption, and have a relatively high melting point itself. Additives are categorised according to their reactive compounds. The additives are based predominantly on aluminosilicates, sulphur, calcium, or phosphorous. This study focuses on aluminosilicates that are introduced to capture and convert KCl.

Aluminosilicate additives have been studied in the literature for full-scale pulverised biomass combustion to address the risk of corrosion. The findings are summarised as follows:
- The more Al and Si there is, the better the K-capture
- Impacts are concentrated in the fly ash
- Ash particle morphology and chemical composition changes
- Deposit build-up rates increase, though are easier to remove
- Mechanisms of ash depositions changes
- Flue gas concentrations of SO_2 increases
- Flue gas concentrations of CO decrease to a threshold

Experiments

The analyses undertaken on the biomass fly ash were; Simultaneous Thermal Analysis (STA) with Quadrupole Mass Spectroscopy (QMS), Loss on Ignition (LOI), carbon in ash, Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray analysis (EDX), and moisture. The STA tests were both for ash melting and thermal decomposition of calcium oxalate monohydrate. The furnace bottom ash was then analysed for LOI, carbon in ash and moisture. Both ash samples were provided by Drax, for unit 3, where the fuel was a 95:5 wt.% split between white wood pellets and agricultural residues respectively.

Key experimental findings
The mitigant was found to partially catalyse CO to CO_2 when decomposing in a blend with calcium oxalate
As the additive injection rate increased, the biomass fly ash was found to have reduced carbon in ash wt.% and reduced LOI, corresponding to an increase in burn out % and leading to potential fuel savings of 75,000 tonnes/year
It was found that the mitigant did not have much of an effect on the bottom ash fraction, due to the small particle size
As the mitigant injection rose; • The mass loss % reduced, which was a possible sign of burn out increasing / carbon in ash decreasing • The ash melting temperatures increased, which was a possible sign of increased % of inert elements / removal of low melting species • KCl and K_2SO_4 concentrations reduced, which is a possible sign of binding with the additive • CO concentrations reduced, which is a possible sign of increased conversion efficiency
Biomass fly ash without the mitigant had K-Cl-S rich particles, then when the mitigant was added; • S was removed, which correspond to increased SO_2 seen in modelling • Cl is removed, possibly to HCl though uncertain
Biomass fly ash with the mitigant changed to K-Al-Si rich particles, where the K was captured onto the surface of the Al-Si rich particle (see figure below). Furthermore, the ash particles became more regularly shaped, more spherical and smaller in size
K-content remained approximately constant, while Al and Si continued to increase and CO decrease. This was interesting as it suggests that although K-capture is taking place, the CO reduction must in part be due to a different cause. A likely theory is due to changes in heat transfer, where more mitigant leads to greater particle surface area in the combustion zone, which increases the radiant heat transfer, which in turn increased oxidation of CO to CO_2. This is consistent with corrosion-reduction, as the increased surface area means more available space for KCl and K_2SO_4 to attach, and hence less goes onto heat exchanger surfaces.
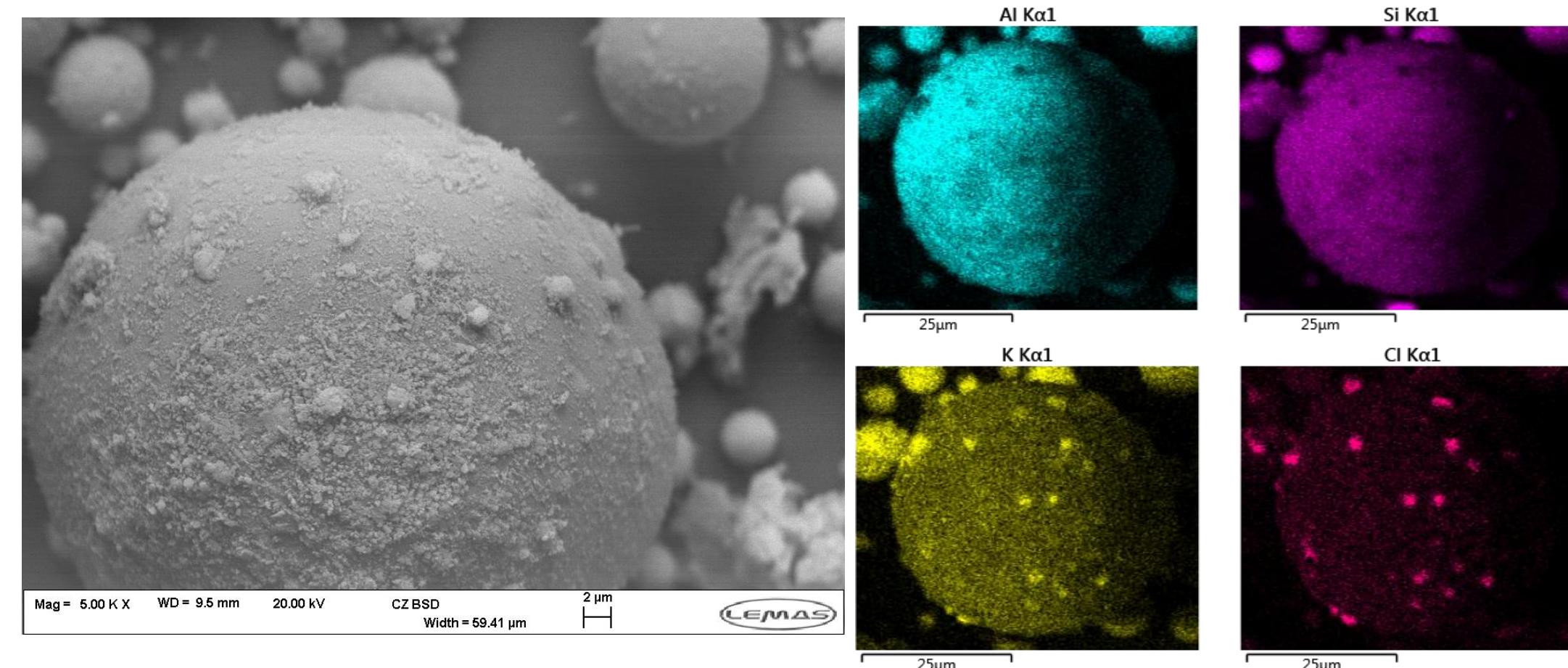
Figures showing SEM/EDX imagery for additive capturing potassium

Conclusion

A corrosion-prevention mitigant was studied to investigate its effects on pulverised biomass combustion ash, conversion and combustion efficiencies. The mitigant was found to reduce the corrosion-risk through capturing and converting KCl and K_2SO_4 to potassium-aluminosilicates, and impacts combustion efficiency through three factors:
1. Mitigant improves conversion efficiency through reducing carbon in ash and increasing burn out
2. Mitigant chemistry changes flue gas composition, which catalyses oxidation of CO to CO2
3. Mitigant injection increase particle surface area in combustion zone, increasing radiant heat transfer, enhancing oxidation of CO to CO_2

The size of the impact that mitigant injection has on CO is mainly dependant on the original concentration of CO in the unit. Mitigant can significantly improve the combustion efficiency, but then differences between different injection rates are hardly noticeable. Data also indicates that the use of additive causes elevation of SO_2 values.

Statistical analysis

For the analysis of unit performance, data focused on two aspects of the mitigant injection: which measures are affected by the mitigant injection into the furnace and how different injection rates affect CO concentrations. Statistical techniques such as principal component analysis (PCA) and analysis of covariance (ANCOVA) were used to find answers to both of these questions.

Key statistical findings
During mitigant injection, measured concentrations of carbon in dust, CO and oxygen decreased. This indicates more carbon is fully oxidized to CO_2, hence improvement in combustion efficiency is taking place.
The CO concentration drops to a third when mitigant injection is taking place in comparison to when no additive is added. The corresponding increase in generated heat, due to the improvement in the combustion efficiency, is estimated to be equivalent to fuel feed rate increase by 2%.
The additive seems to influence the combustion efficiency only when high CO concentrations are observed. When CO levels are already low (when no mitigant is injected), the decrease in CO is hardly noticeable.
Injecting mitigant at different levels does not seem to influence the CO concentration greatly.
The SO_2 concentration in the flue gas is elevated during the mitigant injection.
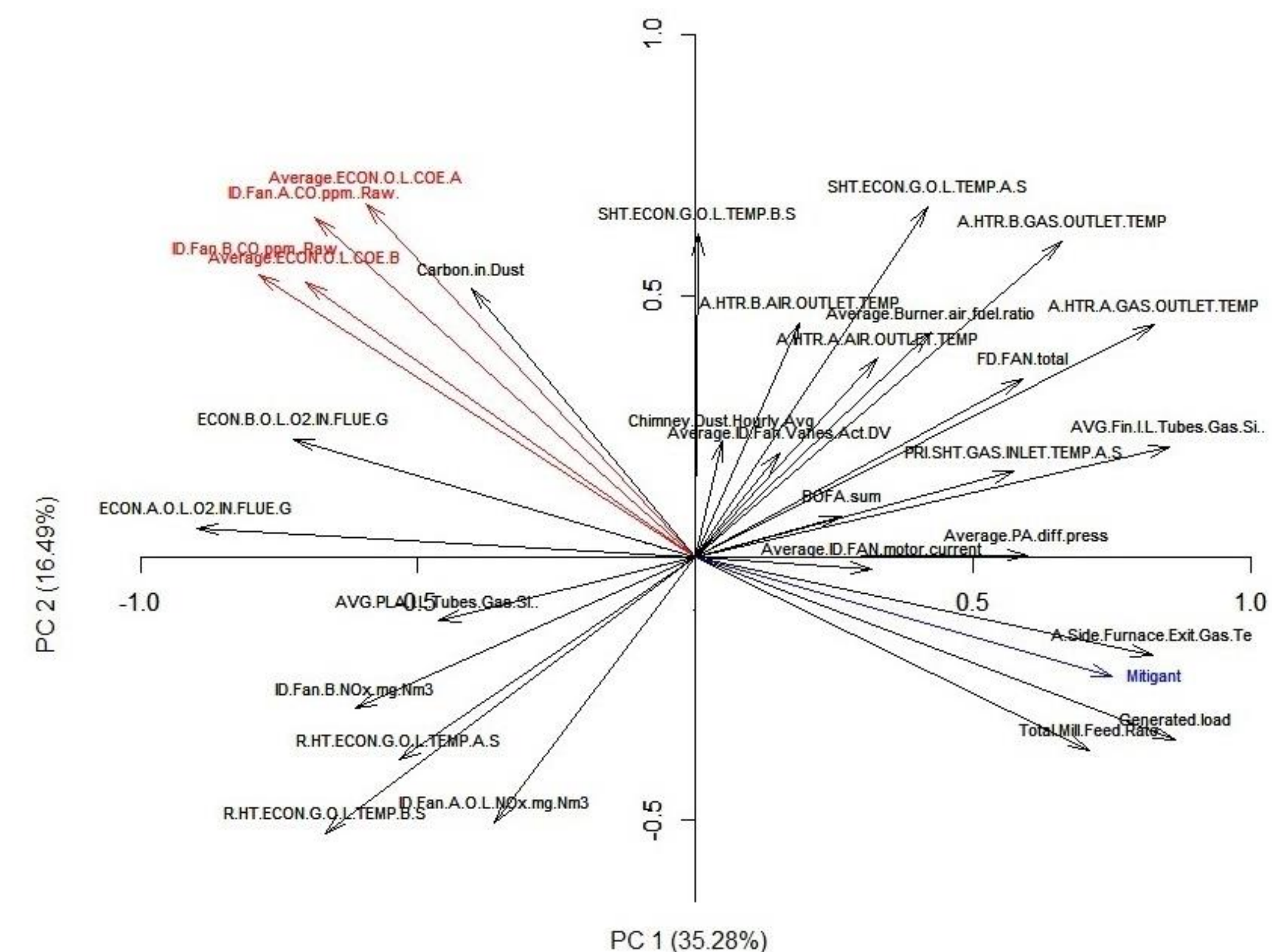
PCA – Bi-plot representing loading values of each variable on PCs 1 and 2

Future Work

The key areas for further work from the experimental side of the project would look into the changes in heat transfer experienced by the ash particles with and without the additive at varying levels. This would require computational fluid dynamic modelling. Also to study ash samples from unit 2 where a strong correlation with CO was found in the modelling, to investigate different injection rates to see if the trends continue or change and to look into the optimum additive chemical composition.

Statistical analysis can be performed further to define the optimum mitigant rate for different situations. For example, by studying interactions between variables used for building ANCOVA model, the optimum mitigant injection rate at different fuel feed loads can be determined. Also, for further statistical analysis, variables measuring HCl concentration in the flue gas should be included to fully understand the effect of the mitigant on Cl behaviour.