EXPERIMENTAL ASSESSMENT OF THE ENVIRONMENTAL IMPACT OF ETHANOLAMINE

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Abstract

The environmental impact of ethanolamine, a common amine for carbon dioxide capture, was experimentally investigated in laboratory scale microcosms. By exposing the plant-soil systems to varying amounts of ethanolamine, we assessed the effects a potential leakage or spill to the surroundings of an industrial site including vegetation. The results of this study show that small amounts of ethanolamine have no significant impact of the health of the plants in the scope of three weeks after treatment. Plant health was affected negatively by larger amounts of ethanolamine, but the plants treated with larger ethanolamine concentrations also seemed to be healthier, lusher and greener after three weeks of observation. In the TCCS-11 presentation we will show the results of this experimental study, their statistical interpretation, as well the implications the results have.

Keywords: *biodegradation, amine stability, CO_2 capture, ecotoxicity, plant health*

1 Introduction

One of the most efficient ways of performing capture of carbon dioxide (CO_2) from industrial sources is using amine solvents. This is one of the most mature technologies available for large scale CO_2 capture, as it has been developed and tested over nearly a century. [1-3] Amines bind chemically to the CO_2 molecules in a reaction that can be reversed upon heating up the solvent. Chemical stability of the amine is a necessity in the capture process, where it needs to withstand temperature cycling as well as oxidative conditions. [4] If the amine reaches the environment through emissions or spills from the capture facility, however, stability may no longer be a desirable property. Anything that reaches the environment should have the ability to get incorporated into the environment as non-toxic components that can be consumed by organisms making changes to them or the environment.

Biodegradation is the process of breaking down larger into smaller molecules, performed by microorganisms. Because of the plethora of different microorganisms capable of performing biodegradation, biodegradability can follow manifold pathways. Amines used in CO_2 capture consist of hydrogen (H), carbon (C), oxygen (O) and nitrogen (N) and will ideally be broken down to CO_2, water (H_2O) and ammonia (NH_3), or other small molecules that can be available for plants to use as nutrients.

Assessment of biodegradability of chemicals which are used or considered for use in industrial applications is of immense importance, for mapping potential environmental risks of a spill or leakage of the chemical. A range of biodegradability test guidelines have been developed by the Organisation for Economic Co-operation and Development (OECD), for testing new chemicals, and these are commonly used for assessing new chemicals for industrial use. [5]

Table 1: Summary of the results of previous biodegradation studies of MEA.

Type	Conditions	Results	Ref.
Soil	aerobic and anaerobic	MEA degraded aerobically and anaerobically	8
Soil	aerobic and anaerobic	MEA degraded aerobically and anaerobically	9
Sea water	Aerobic with varying temperatures	Overall high degradability of MEA	10
Sea water	aerobic	MEA readily biodegradable	11
Fresh water	aerobic	MEA is readily biodegradable	12
Bioreactors	aerobic	MEA successfully degraded	13
Bioreactors	aerobic and anaerobic	MEA completely degradable upon PO_4^{3-} addition	14

1.1 Biodegradation of ethanolamine (MEA)

Ethanolamine is naturally occurring [6], a feature that seems to make the amines more likely to be biodegradable than synthetic ones [7]. It has for decades been the benchmark solvent for CO_2 capture and many biodegradation studies have already been performed both aerobically and anaerobically in soils [8, 9], in sea water [10, 11], fresh water [12] and in lab-scale bioreactors under aerobic and anaerobic conditions [13, 14]. Some of these studies have also been performed according to the

previously mentioned OECD guidelines. A quick summary of the findings of these studies is given in Table 1, and it can be observed that all have proven MEA to indeed be biodegradable. Additionally, Eide-Haugmo et al. [11] found that the ecotoxicity of MEA is also acceptably low in the marine species *Skeletonema costatum*.

In this work we try to take the conclusions from all these earlier studies one step further, to assess whether there are any immediate effects of an amine leakages to surrounding plants and soils. The experimental setup is, to our knowledge, novel in the field and provides a further perspective of the biocompatibility and environmental effects of amines and specifically ethanolamine.

2 Materials and methods

2.1 Materials

Ethanolamine (CAS: 141-43-5, purity ≥99.0%) was purchased from Merck Life Science/Sigma Aldrich Norway. Flowering soil ($^1/_3$ cow manure and $^2/_3$ turf, long-term composted over three years) and a mixture of grass seeds for outdoor use, were purchased from a local garden equipment store.

2.2 Experimental design

6 sets of 6 pots of 8x8x8 cm were filled with approximately 400 mL, which was thoroughly watered before soil and grass seeds were sowed on its surface in the density recommended on the seed package. The grass was watered twice a week, from a dish under the pots for the entire duration of the experiment. After 46 days, when the grass had grown at least 5-8 cm (see Figure 1) and a root system had the time to develop in the soil, treatment was conducted.

Figure 1: Example of grass length before treatment with MEA.

Each set of 6 pots were given one 10 mL addition of water or MEA with Table 2. The liquid was carefully distributed over the soil surface with a disposable syringe, without applying it directly on the plants. The order of treatment was randomized within each set.

Table 2: Treatments overview. Each treatment consisted of 10 mL of the given solution.

Treatment	% MEA
T1	0 (control)
T2	1.0
T3	2.5
T4	5.0
T5	7.5
T6	10

In summary this means that for each of the 6 treatments there were 6 individual samples, randomly located in different sample sets.

2.3 Assessment of plant health

Regular visual scoring of plant health was performed according to Table 3 on day 4, 7, 11, 13, 18 and 21. Every scoring was performed by the same observer, without knowledge of which treatment each given system had been given.

Table 3: Scoring sheet for assessment of plant health.

Score	Percentage of brown leaves
0	0
1	1-10
2	11-30
3	31-40
4	61-90
5	91-100

Figure 2: Browning observed in one set of 6 different treatments after 11 days.

2.4 Statistical tests

A Kruskal-Wallis test was performed to determine the statistical significance in the difference of plant health observed in these experiments. This is a non-parametric statistical test, suitable for the comparison of individual samples and it does not assume a normal distribution of residuals. Variance is quantified as adjusted p-values and an adjusted $p \leq 0.05$ represents a significant difference between two treatments at a given time. The Bonferroni method was used for p-value adjustment.

A Friedman test, which is a non-parametric test for non-replicated data with complete block design, was performed to determine the statistical significance of the

change in plant health over time. Kendall's *W*, as shown in Eq. 1, where *X2* is the Friedman test statistic value, *N* the sample size and *K* the number of measurements. Cohen's interpretation of effect size was used to determine the size of the effect observed within each treatment.

$$W = \frac{X2}{N}(K-1) \qquad \text{Eq. 1}$$

Bonferroni p-value adjustment was used for the identification of statistical difference between the treatments.

3 Results

3.1 Plant health

Browning was typically observed from day three to some degree, and then increasing. An example of the grass health as it was observed some days after treatment can be seen in Figure 2, The results of the plant health testing throughout three weeks after treatment with different amounts of MEA is depicted the means of each treatment in Figure 3 and medians in Figure 4. There is a clear trend seen from T4 to T6, whereas the health of the plants receiving treatments T1 (control) to T3 are more similar and no effect can be immediately distinguished. The statistical relevance of both these and the remaining results were determination by a Kruskal-Wallis test as well as a Friedman test.

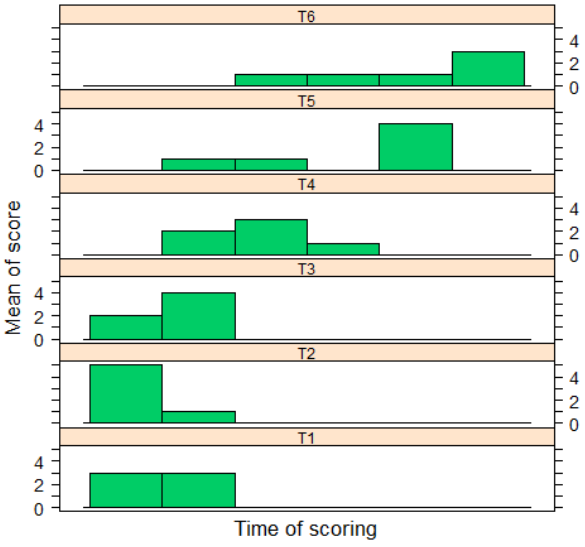

Figure 3: Means of plant health score for all treatments at different times of scoring.

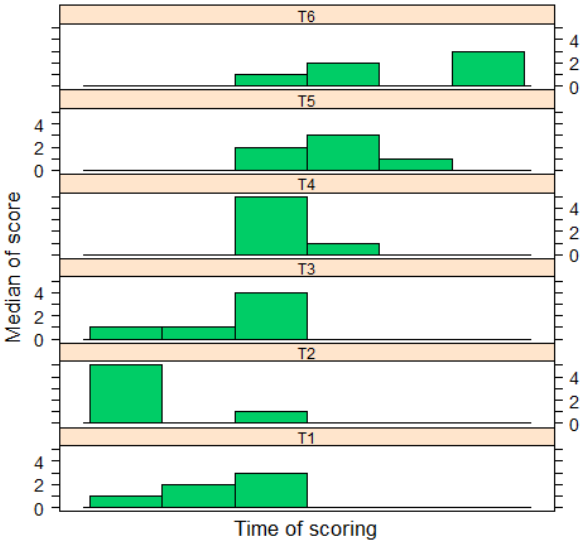

Figure 4: Medians of plant health score for all treatments at different times of scoring.

As seen in Figure 5, the Kruskal Wallis test shows that a higher degree of browning was seen on day 21 with T5 and T6 compared to T1-T3. On day 4, no significant differences were observed between any treatments, but at day 7, T6 showed more browning than T3 ($p < 0.01$). The difference between these two treatments remained significant throughout the whole experiment. After 11 days T6 had more browning than T1-T3 ($p < 0.3$ in all cases) and this is when T5 also started being browner than T2 ($p = 0.02$).

	T1	T2	T3	T4	T5
T2	1				
T3	1	1			
T4	0.9	0.4	0.9		
T5	0.03	0.01	0.03	1	
T6	0.04	0.01	0.04	1	1

Figure 5: Adjusted p-values for the average plant scores on day 21. Statistical significance given at $p \leq 0.05$.

At no time of scoring was there a significant difference in browning between T1-T4, meaning that the addition of 1.0-5.0% MEA into the plant-soil systems makes no difference from not adding any MEA, the plant health is deemed the same.

The overall change in plant health over time was quantified by the Friedman test to be *large*. Within treatments, the effect was *small* in T1 and T2, *moderate* in T3 and T4 and *large* in T5 and T6 using Kendall's W and the Cohen interpretation of effect size. The effects of the treatments were studied using multiple pairwise comparisons and the Bonferroni adjusted p-values are given in Figure 6. According to these results treatments T3 to T6 have differences in plant health over time compared to T1 (control) to T3.

	T1	T2	T3	T4	T5
T2	0.7				
T3	1	1			
T4	$4 \cdot 10^{-3}$	$9 \cdot 10^{-6}$	$1 \cdot 10^{-4}$		
T5	$4 \cdot 10^{-6}$	$7 \cdot 10^{-8}$	$2 \cdot 10^{-7}$	0.04	
T6	$2 \cdot 10^{-8}$	$7 \cdot 10^{-10}$	$1 \cdot 10^{-9}$	$7 \cdot 10^{-5}$	1

Figure 6: Adjusted p-values for the mean of the plant scores through the entire experiment time of 21 days. Statistical significance given at $p \leq 0.05$.

Interestingly, a few weeks after the experiment was concluded, the pots containing plants treated with T5 and T6 seemed lusher and healthier than the plants where less MEA had been added. Since the observer from the duration of the experiment was not available, this data could not be logged. Attempts were made to extract remaining MEA and potential degradation compounds from the soil using a KOH extraction method followed by centrifuging and filtering. No MEA could be observed in the soil extracts in the subsequent cation IC analysis. This phenomenon could either be due to an insufficiently low detection limit, having the strong signal of K^+ in the chromatogram, or it could be simply because the MEA was already biodegraded. Further research is needed to conclude on this matter.

4 Discussion and conclusions

Just like previous biodegradability ecotoxicity testing, these experiments show that MEA is not harmful for a plant-soil system, at least in small doses. For the three weeks after treatment with MEA there was no observable difference between plant-soil systems given up to 0.5 mL of MEA per 400 mL soil. This must mean that the buffer capacity of the soil is good enough to account for the potential pH increase when adding MEA, as well as that there's no observable toxic effect on the plants. The higher concentrations of MEA had a significant impact on the plants, making them browner in the experimental observation time of three weeks. In these cases, it can be hypothesized that the MEA has a negative impact in the soil, either by killing off some of the microbes or damaging the root systems of the plants. This is likely to be caused by the high pH of the MEA causing a chemical burn. The less likely explanation is that MEA has a toxic effect causing the plants to go brown. This is less likely because of previous testing, but also because of the subsequent healing of the plants after the end of the experiment.

The fact that the plants which had received a higher concentration of MEA actually seemed healthier after the experiment had ended, than those with less or no MEA added, indicates that the MEA that initially may have made the plants health decline, now was biodegraded into components that acted as nutrients for the plants. Nitrogen is a valuable nutrient in the plant kingdom, that the plants need to absorb from soil and water, as they are not able to convert nitrogen from air. Hence, the addition of nitrogen in the form of MEA may initially be harmful, but then have been biologically (biodegraded) converted to bioavailable small molecules by the soil microbes. This would most definitely be an interesting starting point for any further studies of the environmental impact of amines.

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