Elevated CO_2 and nitrogen effects on dissolved organic carbon of two calcareous and non calcareous soils

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Abstract
Dissolved organic carbon (DOC) pools can be considered as suitable indicators of soil quality that are very sensitive to CO_2 levels, nitrogen fertilizer and plant residues. In this research controlled chambers were used to investigate the effects of elevated atmospheric CO_2 concentrations (350 vs. 760 ppm) under two level of nitrogen fertilizer (0 vs. 200 kg N ha^{-1}) and two different plant residues (alfalfa residue and wheat straw) on DOC of two calcareous and non calcareous soils. The results showed that elevated CO_2 significantly increased DOC in calcareous and non calcareous soils. In the soils that received high rates of nitrogen fertilizer, release of DOC at elevated and ambient CO_2 increased by approximately 30% compared to soils without nitrogen fertilizer. The amount of DOC tended to be affected by organic matter in both elevated and ambient CO_2. In calcareous soil exposed to elevated and ambient CO_2, concentrations of DOC in samples receiving high or no N fertilizer were always higher than for non-calcareous soil. We conclude that release of DOC in elevated CO_2 is controlled by multifactors such as soil organic matter, N and $CaCO_3$ levels of soils.

Key Words
Enhanced Carbon Dioxide, DOC, nitrogen fertilization, calcareous soils, C/N Ratio

Introduction
Increasing CO_2 levels are expected to have numerous direct and indirect effects on terrestrial ecosystems (Bazzaz 1990). Among those effects, changes of above ground plant processes such as photosynthesis, transpiration, biomass accumulation and microbial respiration (lekkerkerk *et al*. 1990; Norby 1994) have been identified. Few studies have documented the effects of an elevated atmospheric CO_2 on the dynamics of soil soluble organic carbon (Hill *et al*. 2005; Cheng *et al*. 1998) and most of these data were obtained from non calcareous soils. In addition, the application of nitrogen fertilizer during normal agricultural practices which leads to enrichment of ecosystems with nitrogen intensifies the importance of the fate of the applied nitrogen and its effect on DOC. It is generally believed that the amount of available nitrogen in the plough layer of agricultural soils usually meets the demands during the decomposition of straw and change the concentration of soil carbon (Christensen 1985)

The impacts of elevated CO_2 and nitrogen availability on soil DOC have shown contradictory and inconsistent results. In some cases, elevated CO_2 has been predicted to increase soil carbon storage. For example, Ross *et al*. 2002 suggested that increase in organic carbon in soil exposed to high CO_2 might have been caused by preferential metabolism by the decomposer populations of easily decomposable soil carbon. Indeed, Hu *et al*. 2001 reported an increase in available carbon for microbes under annual grasslands after 5 years of elevated CO_2. In other case elevated CO_2 has been observed to decreased soil carbon storage. Sowerby *et al*. (2000) concluded that in soil exposed to CO_2, soil carbon storage decreased more rapidly than in soils under ambient CO_2.

The objective of the present study was to quantify (i) the short-term effects of elevated CO_2 and nitrogen fertilizer on DOC, and (ii) different effect of elevated CO_2 in two calcareous soils. We hypothesize that dissolved organic carbon quickly decreases in elevated CO_2. We further hypothesize that nitrogen availability affects the response of soil DOC to elevated CO_2. The uses of calcareous and non calcareous soils enable us to distinguish the contributions of lime, CO_2 and nitrogen on DOC.

Materials and methods
Soil sampling
We used two mineral soils representing calcareous and non calcareous soils. These soils were obtained from 0-30 cm of Kardeh dam (Soil 1) and Saghravan zone (Soil 2) in Mashhad, Khorasan Razavi province, Iran.

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Soil samples were air dried, sieved (2mm) and stored at 4°C until treatments were performed. Table 1 provides a summary of soils properties.

Table1. Physical and chemical properties of soil samples.

Soil property	Calcareous Soil (Soil 1)	Non calcareous Soil (Soil 2)
Clay (%)	20	25
Silt (%)	34	35
Sand (%)	46	40
pH	8.02	6.8
N (%)	0.111	0.13
$CaCO_3$ (%)	32.66	3.4
OC (%)	1.663	1.530
EC (dS/m)	3.53	2.9

Experimental design and Analytical procedures

A factorial, completely randomized design including two soil types (soil 1with 32% and soil2 with 3.4% lime), two CO_2 levels (350 and 760 ppm), two levels of nitrogen fertilizer as Urea (0, 200 Kg ha^{-1}), two organic matter residue treatments (wheat straw and alfalfa residues) and a control (without organic matter) with two replications were employed in this experiment. Three subsamples were made from each soil sample, one set of subsamples were mixed with wheat straw (2 mm in size, 2.5 %), another set were mixed with alfalfa residue (2 mm in size, 2.5 %) and a control treatment. Organic matter was applied uniformly to soil subsamples. Nitrogen fertilizer was applied to half of the subsamples. The experimental design consisted of 2 chambers (aluminum frame and clear plastic walls 120 ×240×70 cm high). The halves of samples were transferred to the chamber with 760 ppm and the other half were placed in the chamber with 350 ppm of CO_2. CO_2 measurements were performed several times a day for the first month and then daily afterwards. The use of closed chambers, as opposed to open-top chambers, ensure that concentrations rarely deviate more than 50 µmol ppm from their set point and that that CO_2 concentration homogeneous within the chamber (Barnard *et al*. 2005). Distilled water was applied to all samples to increase moisture content to 70 % of field capacity. The soils were checked every 2 to 3 days to keep soil moisture constant. To minimize the effect of environment both elevated and ambient chambers kept equal conditions during the experiment. Soil samples were analyzed after 0, 10, 20, 40, 60 and 90 days. A subsample of 10 g of soil was oven-dried at 105° C for 24 h for determining soil moisture. For DOC measurements, water samples were collected, filtered by 0.45-µm filters and were analyzed using TOC-Shimadzu V CPH analyzer (Shymadzu Coro., Kyoto, Japan).

Results and Discussion

The result of this study showed that DOC concentrations significantly increased in both soils exposed to elevated CO_2 compared with ambient CO_2 (Figure 1). The response of DOC concentrations was presumably caused by increased decomposer activity and quantity in elevated CO_2. Recent studies suggest that the activity and biomass of microorganisms appeared to be enhanced under elevated CO_2 (Wall 2001). Our findings are also in line with Kang *et al*. (2005) who found that elevated CO_2 increased DOC concentrations in wetlands, as soil microbes appeared to be affected. However, other studies detected that elevated atmospheric CO_2 did not affect the concentration of DOC in soil (Ross *et al*. 1995). For calcareous soil (Soil 1) the DOC concentration was almost 1.45 times greater than for non calcareous soil (Soil 2) for both elevated and ambient CO_2 (Figure 1). It seems that high amounts of $CaCO_3$, organic matter and higher pH in soil1 intensified microbial activity and resulted in increasing DOC (Filep *et al*. 2003).

Nitrogen fertilizer significantly affects the concentration of DOC in both calcareous and non calcareous soils (Figure 2). Nitrogen fertilizer application increased DOC significantly. The observed N-fertilization effect on DOC confirms our conclusion that microbial growth and activity may have increased, which may have allowed a partial release of DOC. Similarly, Sitaula *et al.* (2004) found that the application of N fertilizers had positive effects on organic matter decomposition and DOC release in forest soils. They indicated that high N addition might also have a direct effect on microbial activity and increase DOC mobility in soil. Curtis *et al.* (1995) also reported that soil nitrogen indirectly affects the release of organic nutrients such as DOC. The results also showed that DOC concentration in non calcareous soil is lower than for calcareous soil. It seems that the lower pH in non calcareous soil can be considered as a factor to amplify DOC adsorption by soil mineral particles and consequently DOC concentration decline in soil solution.

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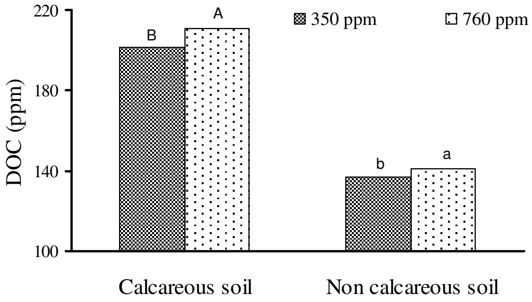

Figure 1. Influence of elevated and ambient CO_2 on DOC concentration (Means were separately compared in each soil).

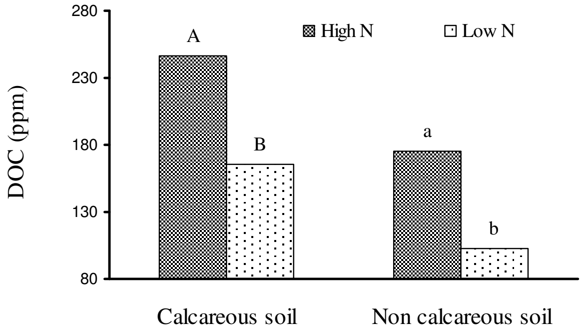

Figure 2. Influence of N availability on DOC concentration. (Means were separately compared in each soil).

In both soils N availability strongly influenced the effect of elevated CO_2 on DOC concentration (Figure 3). Although in both soils elevated CO_2 increased DOC concentration for high N availability treatments, for low N availability in the non calcareous soil elevated CO_2 caused DOC to decrease and it did not have a significant effect for the calcareous soil. The high availability of nitrogen increased microbial activity and DOC concentration in soil. Limited nitrogen availability for unfertilized treatments limited microbial growth which may have decreased accumulation of DOC (Hoosbeek *et al.* 2007). As it is obvious in Figure 3, elevated CO_2 had the greatest effect on DOC concentration for N treatments in calcareous soil (soil 1).

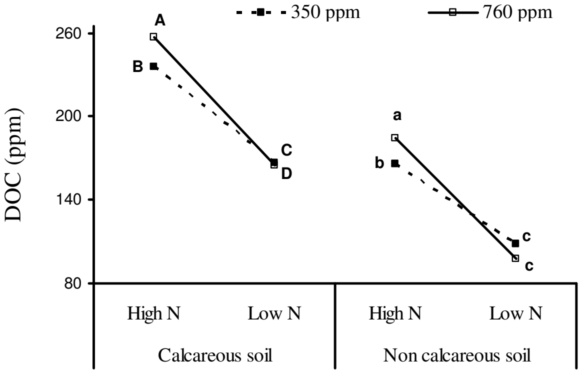

Figure 3. Interaction effects of CO_2 and N availability on DOC concentration. (Means were separately compared).

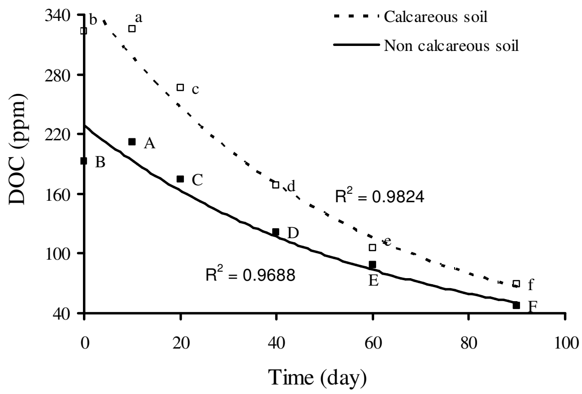

Figure 4. Exponential trends of DOC concentration with time.

The concentrations of DOC declined almost exponentially with time for elevated and ambient CO_2 in both soils (Figure 4). It seems that residue decomposition and emission of CO_2 from soils resulted in decreasing DOC concentration for both soils. The negative effect of time on DOC agrees with several similar studies (Karlik 1995; Anderson *et al.* 1999). Paustian *et al.* (1997) have shown that through time organic matters respired by soil microorganisms.

Conclusion

The results showed that CO_2 concentration had a same effect on DOC concentration for both calcareous and non calcareous soils and DOC concentrations increased in both soils for the elevated CO_2 treatment. Nitrogen fertilizer had a positive effect on DOC concentration of soil samples. Application of N fertilizer increased DOC in all treatments. However in non-calcareous soil the concentration of DOC was lower than calcareous soil for all elevated and ambient treatments, possibly because of the higher pH in calcareous soil and consequent higher microbial activity. Additional research will be required to determine whether the composition and size of the soil microbial community will change under elevated CO_2 and for different N treatments in calcareous and non-calcareous soils.

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