Biochar can restrict N_2O emissions and the risk of nitrogen leaching from an agricultural soil during the freeze-thaw period

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Freeze-thaw (FT) events in soils can cause a burst of nitrous oxide (N_2O) and enhance N leaching during the spring-thaw event. We studied whether a soil amended with wood-derived (spruce chips) biochar (10 tonnes ha^{-1}), produced at rather low temperatures (400-450°C), could reduce the burst of N_2O and the risk of N leaching from an agricultural soil after a FT event. A short-term laboratory experiment (4 weeks) was conducted with 24 vegetated (*Phleum pratense*) mesocosms (12 controls, 12 biochar-treated) that had spent a dormant season in the dark at 15°C for two months after the growing season. N_2O efflux to the atmosphere and ammonium (NH_4^+-N) and nitrate (NO_3-N) in the percolated soil water were monitored before and after the FT event. N_2O was monitored with the dark chamber method and analyzed using a gas chromatograph. We found that soil amended biochar can significantly diminish the burst of N_2O after the soil FT event (by 61% just after FT event) and substantially reduce the risk of NO_3-N and NH_4^+-N leaching from the agricultural soil. Compared to the control, the decrement in concentrations of NO_3-N and NH_4^+-N in water percolated through the biochar amended soil in the mesocosms was 58% and 22%, respectively.

Key words: ammonium, leachate, N_2O efflux, nitrate

Introduction

The global population and food consumption are predicted to continue to increase in the coming decades (OECD/FAO 2013, United Nations 2013). This sets additional challenges for food production, as agriculture contributes about 14% of global greenhouse gas (GHG) emissions and is the biggest anthropogenic source of nitrous oxide (N_2O) (IPCC 2007). In the boreal zone, soil freeze-thaw (FT) cycles can affect soil nitrogen (N) by increasing the concentration of nitrate (NO_3^-) and ammonium (NH_4^+) in the soil (Yu et al. 2011), by generating an increased efflux of N_2O (Teepe et al. 2001, Koponen and Martikainen 2004, Matzner and Borken 2008) and by posing a risk for N leaching during the snow and soil thawing in spring, which induce melt-water leaching from fields in late April-May. To ameliorate these problems, cultivation techniques must be developed to keep N in the soil and thus increase N utilization by plants. Biochar addition to the agricultural soil could be one possible way to mitigate N leaching and N_2O emissions from agricultural soils (Lehmann et al. 2006, Yanai et al. 2007, Clough et al. 2013). Biochar addition to a soil can change the mobility and availability of NO_3^- (Singh et al 2010, Prendergast-Miller et al. 2011) and NH_4^+ (Ding et al. 2010, Singh et al. 2010) and thus diminish N leaching and the burst of N_2O during the spring thawing.

Our hypotheses were that thawing of the soil generally increases N_2O fluxes but that when biochar has been amended to a soil it would inhibit N_2O fluxes and leaching of NO_3^- and NH_4^+.

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Materials and methods

A short-term (28.1.2011–4.3.2011) laboratory experiment was conducted with 24 vegetated (*Phleum pratense*) mesocosms. Each mesocosm consisted of a 10 cm diameter and 47 cm long PVC-tube closed with a plastic plug at the bottom end. For monitoring the water table, a perforated plastic tube (2 cm diameter, 50 cm long) was inserted into each mesocosm. The soil, a sandy till, was obtained from an abandoned field in Mulo, Joensuu, Finland. The air dried and sieved soil was added to the mesocosms in June 2010. In 12 of the 24 mesocosms, biochar was added to the soil at the rate of 10 tonnes ha^{-1}. The biochar was made from spruce woodchips at rather low temperature (400−450°C) using slow pyrolysis. The final C content was 75%, N content was 0.15% and the specific surface area was 209.7 $m^2 g^{-1}$. The mesocosms were sown with *P. pratense* and the grass yield was harvested three times during the growing season of c. 5.5 months. The mesocosms were fertilized with mineral fertilizer at the beginning of the growing experiment and after the first two harvests. During the growing season, air temperature followed the day/night cycle of 20°C/15°C, respectively and soil temperature was set at 15°C. Surface moisture content of the mesocosms was initially kept at 20−30% of the volume and later increased to 40−50% of the volume (for details of the growing experiment, see Saarnio et al. 2013). After the growing season, the mesocosms spent a dormant season in the dark at 15 °C for two months in a temperature controlled room. Room temperature was further decreased to 5 °C and after an adaptation period of six days, gas flux measurements commenced.

The gas samples were taken from a dark, static chamber (ca. 3.5 dm^3) equipped with a small fan to mix the air. The chamber was placed with an air tight rubber seal on the top of the mesocosm for a sampling period of 15 min. The 20-ml gas samples were drawn into 60-ml air-tight syringes from the top of the chamber via a thin plastic tube. The same amount of substitution air went into the chamber via a thin plastic tube from an air bag (c. 50 dm^3) containing room air. The samples were taken at 2, 6, 10 and 15 min intervals after the closure of the chamber and put into vacuumed glass tubes closed by butyl rubber septa (12 ml, Labco Ltd, High Wycombe, UK). The gas samples were analyzed in MTT Agrifood Research Finland, Jokioinen using a gas chromatograph (HP 6890 Series, GC System, Hewlett Packard, USA). The coefficient of variation for the analysis of atmospheric concentrations of N_2O was 0.3 % (for more details, see Saarnio et al. 2013). N_2O flux rates ($\mu g\ m^{-2}\ h^{-1}$) were calculated using the ideal gas law and required unit conversions from the linear ($r^2>0.9$) change in the gas concentration (ppb) in the chamber. Measurements with a non-linear change were also accepted if the change in N_2O concentration was less than 6 ppb min^{-1} (so called "zero" fluxes).

Topsoil moisture content ($m^3\ m^{-3}$, volumetric soil moisture) and groundwater level (cm below the top of the soil) were monitored after N_2O measurements (for more details about monitoring methods see Saarnio et al. 2013). Soil moisture in all mesocosms was kept as similar as possible by watering them individually with deionised water after N_2O measurements. The irrigation water was added to the top of the soil. During the experiment, mesocosms received on average 513 ± 8 ml and 373 ± 21 ml deionised water in the control and biochar treatments, respectively.

Water samples were taken before freezing and following the thawing of mesocosms. First, all standing water was sucked away from the bottom of the mesocosms via a water table monitoring tube using a thin, 50 cm long silicone hose connected to a 60-ml plastic syringe. Then 500 ml of deionised water was added to the top of the mesocosms and, after the water had percolated through the soil to the bottom of mesocosms, water samples of 250 ml (on average) were taken with a 60 ml plastic syringe from a perforated tube via a 50 cm long silicone hose. The concentration of NO_3^- and NH_4^+ in the water samples were determined by a flow injection analyzer (standard SFS-EN ISO 13395:1997) and spectrophotometrically (standard SFS 3032:1976), respectively.

Two days after taking water samples, the mesocosms were transferred to a freezer at -20 °C for 12 days. Before transfer to the freezer, the free water at the bottom of mesocosms (c. 10 cm i.e. water level between -32 to -34 cm) was sucked away in order to prevent rupture of the mesocosms during freezing. After that, the mesocosms were thawed at 5 °C. It lasted three days before the frozen soil started to soften, free water appeared to the bottom of mesocosms and gas flux measurements were started. All mesocosms were measured twice a week during the three week measurement period; twice before freezing and four times after thawing. All measurements were done at a temperature of 5°C.

Normality of the distributions of the N_2O fluxes, NH_4^+ and NO_3^- ($\mu g\ l^{-1}$) concentrations in the leachate, were tested using the Kolmogorov-Smirnov test. The homogeneity of the variances was tested using Levene statistics. If parameters were not satisfied, a non-parametric test was used, otherwise a t-test was employed. All the statistical analyses were performed using SPSS Statistics 19 (IBM, New York, USA).

Results and discussion

Before FT, the flux of N_2O was near zero (Fig. 1), which is most likely due to N limitation as the previous fertilization was conducted almost four months earlier (see Saarnio et al. 2013). After thawing, a clear burst of N_2O was observed, which is in line with previous studies (Koponen and Martikainen 2004, Matzner and Borken 2008), and after two weeks the rate of N_2O flux was back to near zero (Fig. 1). However, during the first measurement after FT, the burst of N_2O was significantly lower ($p < 0.05$, Mann-Whitney U Test) from the biochar-amended soil compared to the soil without biochar. Presumably, biochar in the soil can retain N which is released from microbes (Müller et al. 2002, Groffman et al. 2006) and/or roots (Fitzhugh et al. 2001) dying due to the frost and, thus, inhibit the formation of N_2O. Taghizadeh-Toosi et al. (2011) stated that N adsorbed by biochar is bioavailable, but the results of this study do not fully support the statement. Our results indicate that biochar retains, at least temporarily, both NH_4^+ and NO_3^- in the soil (Fig. 2) restraining simultaneously microbial consumption (Fig. 1).

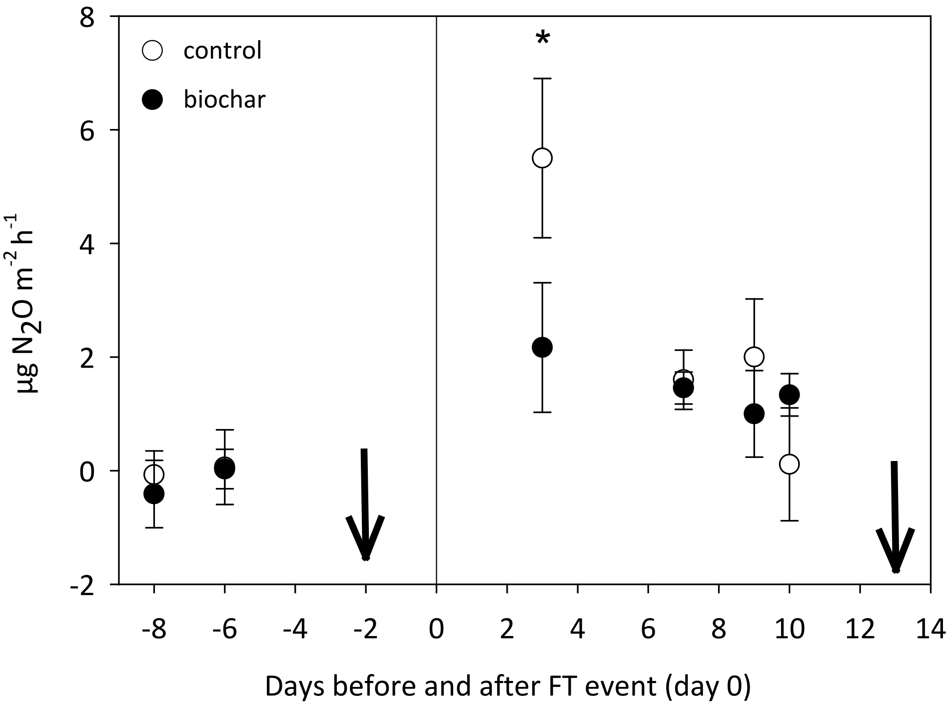

Fig. 1 .The average (± SEM) rate of N_2O efflux during the experiment. Star indicates statistically significant differences between biochar treatments over a certain measurement time. Arrows indicate the occasion of water sampling. *n* = 12.

In general, FT increased NH_4^+ and NO_3^- (g l^{-1}) concentrations in the leachate in both treatments (Fig. 2). NH_4^+ concentration increased by 81% and 109% in the control and biochar treatments, respectively. Although FT increased the concentration of NH_4^+ in the leachate (Fig. 2a), the amount of NH_4^+ was significantly lower in the biochar treatment compared to the control both before ($p < 0.01$, t-test) and after the FT ($p < 0.01$, t-test). It would seem that biochar can retain more NH_4^+ in the soil and thus diminish NH_4^+ leaching during soil melt. This finding is supported by Ding et al. (2010), Singh et al. (2010) and Güereña et al. (2013) who found that biochar can significantly reduce NH_4^+ leaching from the soil. However, on the basis of our results it would seem that the retained NH_4^+ was not available for nitrifiers. Furthermore, while the concentration of NO_3^- increased after FT in the leachate in the control by 236% , NO_3^- concentration in the biochar treatment decreased significantly ($p < 0.01$, Mann-Whitney U Test) 36% (Fig. 2b). Although biochar amended mesocosms received less irrigation water, they were more moist than the control mesocosms (Fig. 3). The significant difference in water table level did not, however, enhance N_2O flux, probably due to the capability of biochar to retain NO_3^- (Mizuta et al. 2004, Knowles el al. 2011, Clough et al. 2013) and hence inhibit denitrification. All biochar types do not adsorb NO_3^- (Clough et al. 2013, Hale et al. 2013) but our biochar has been observed to decrease NO_3^- leaching in several experiments. On the other hand, it is possible that N_2O was further reduced to N_2 under wet conditions and thus N_2O flux was not enhanced.

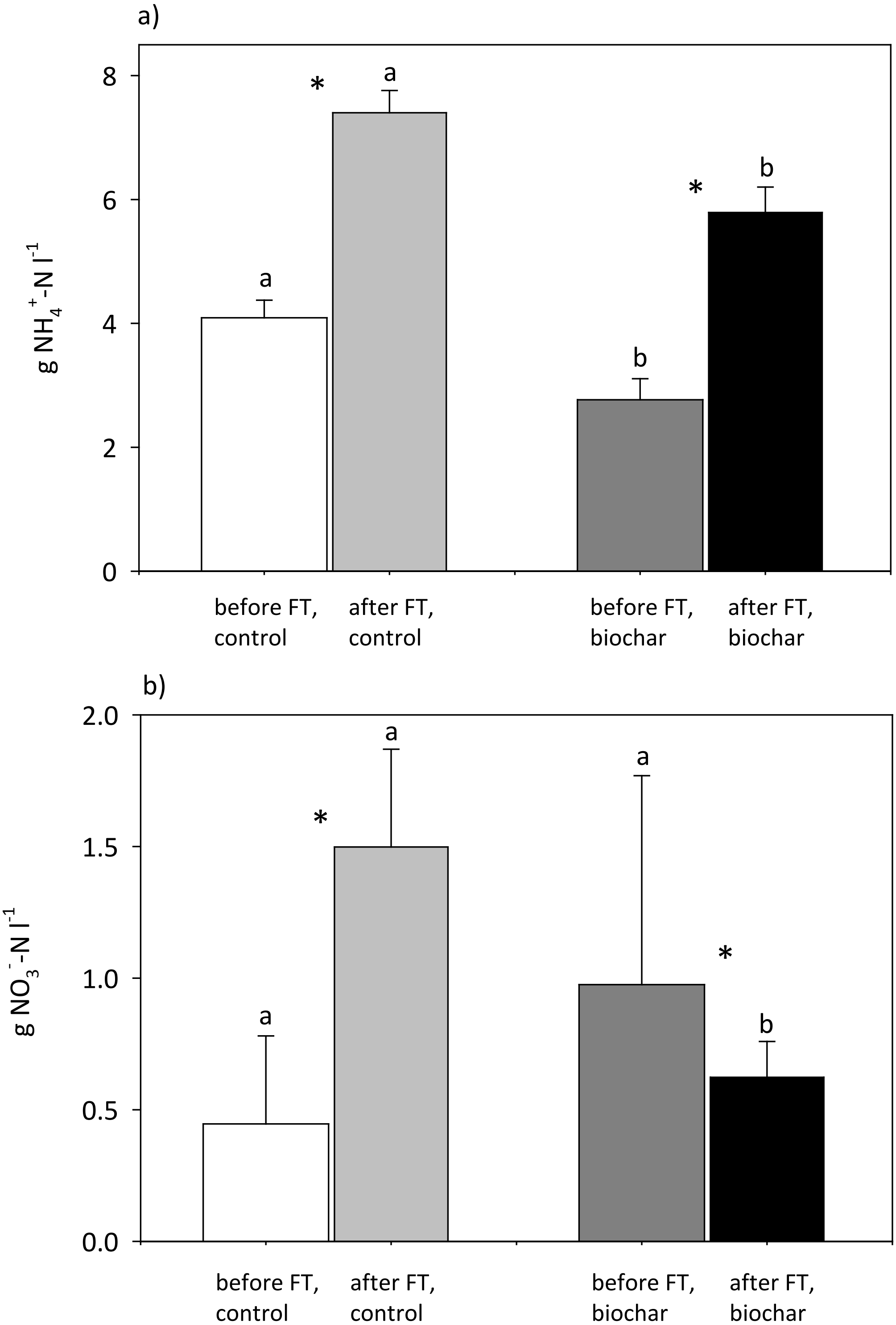

Fig. 2. The average (+ SEM) amount of NH_4^+ (a) and NO_3^- (b) in leachate before and after the freeze-thaw event with or without biochar soil amendment. Stars indicate statistically significant differences before and after the freeze-thaw event. Small case letters indicate statistically significant differences between biochar treatments. *n* = 12.

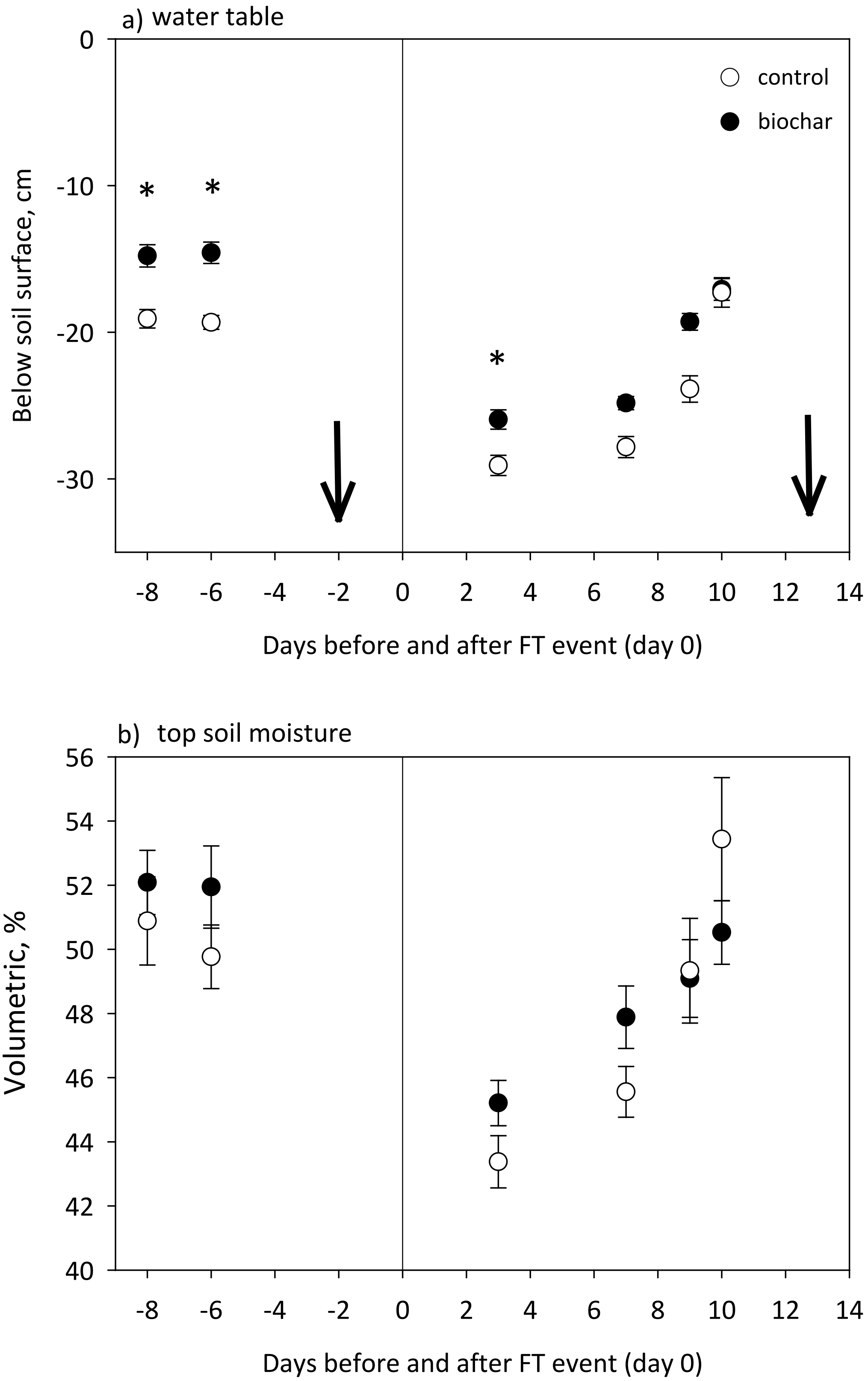

Fig. 3. Water table (cm) and topsoil moisture content (%) during the experiment. Vertical lines indicates freeze-thaw event. Arrows indicate the occasion of water sampling. Stars indicate statistically significant differences between biochar treatments on certain measurement days. *n* = 12.

In this study, the used biochar was made from spruce chips under rather low temperatures (400-450°C). Some earlier studies have found that wood-originated biochar can absorb N (Taghizadeh-Toosi et al. 2011, 2012, Dempster et al. 2012) and increase the amounts of inorganic and organic N in the soil (Clough et al. 2010, Biederman and Harpole 2013, Güereña et al. 2013) but N is available for plants (Taghizadeh-Toosi et al. 2011) and microbes (Dempster et al. 2012). Our results, however, show that the wood-originated aged biochar characterized by a moderate specific surface area (209.7 m^2 g^{-1}) can retain N and thus diminish N_2O flux and leaching of NH_4^+ and NO_3^- during FT. Our results are supported by Singh et al. (2010), who stated that according to their experiment, which lasted over 5 months, the effectiveness of biochar in reducing N_2O emissions and NH_4^+ leaching increased with the ageing of biochar in the soil. Our FT experiment was conducted over more than seven months after the application of biochar to the soil.

Conclusions

In conclusion, we can state that during the FT event, biochar can reduce leaching of N from agricultural mineral soils and, thus, diminish N pollution on the water system. Although more N is retained in the soil due to the biochar, it does not enhance the burst of N_2O during the thawing of soil. This indicates that more N may potentially be available to plants during the early growth in spring. However, we urgently need more research to determine the effects of biochar on N cycling during the FT cycle as the findings presented here concern only one type of biochar and one soil type. It is well recognized that biochar originating from different types of feedstock or pyrolyzed at different temperatures can have diverse effects on soil functions (Rajkovich et al. 2011, Clough et al. 2013).

Acknowledgements

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