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# Dissolved organic nitrogen as an indicator of livestock impacts on soil biochemical quality

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ABSTRACT

Soil degradation in the Mediterranean and other arid and semi-arid regions of the world is caused mainly by cultivation and grazing. A consequence of de-vegetation due to overgrazing has been a decrease in organic matter (litter) input to soil and a decrease of aggregate size and stability making soils more susceptible to erosion and to organic matter losses. This study provided evidence linking the Dissolved Organic Nitrogen (DON) export from river basins to livestock grazing intensity and the resulting decrease in vegetation. Koiliaris River Basin in Crete was selected to study the effects of livestock grazing on water quality because it offers a unique morphologic situation due to its karstic hydrogeology draining the upland grazing areas through karstic springs. Mass balance calculations of N loads indicated that organic N is behaving as a conservative substance. It is postulated that the two potential mechanisms of Mineralization–Immobilization-Turnover and Direct Uptake did not operate in the degraded soils of the karst and arguments are presented justifying the hypothesis. De-vegetated soils of the area had lower C and N content, the same bacterial count, but lower microbial activity, lower fungi counts and species richness and lower mineralizable N compared to naturally vegetated soils. DON was the predominant N species in both extracted soluble N pools. De-vegetated soils had lower decomposition potential compared to vegetated soils. Mineralization and plant uptake appeared to be restricted and leaching of soluble low aromaticity organic matter was favored. A linear relationship between DON export and livestock N load was obtained for five Greek basins suggesting a mechanism that operates on regional scales. The de-vegetation of grazing lands in Koiliaris River highland calcaric leptosols was shown to be a primary factor causing the decline of soil biochemical quality and DON can be used as a reliable indicator for livestock grazing impacts to soil biochemical quality.



## 1. Introduction

Soil degradation in the Mediterranean and other arid and semi-arid regions of the world is caused mainly by cultivation and grazing (Li et al., 2007). Livestock grazing alone is responsible for 23% of soil degradation in Europe (RCEP, 1996) and is particularly intense in the Mediterranean region. Free grazing of uncontrolled length and frequency and high stocking densities are responsible for the de-vegetation of many areas within this region. The Greek island of Crete represents a characteristic case of land degradation resulting from intensive grazing (Hill et al., 1998). Since Greece joined the European Communities in 1981, grazing in mountainous regions has expanded due to subsidies that became available through the Common Agricultural Policy (Hill et al., 1998). A consequence of de-vegetation due to overgrazing has been a decrease in organic matter (litter) input to soil and a decrease of aggregate size and stability making soils more susceptible to erosion and to organic matter losses (Bastida et al., 2006). Dissolved Organic Nitrogen (DON) has been found to be decoupled from the production of DOC in such soils and has proportionally more labile soluble organic matter (Ghani et al., 2007). However, detailed information on the nature, bioavailability, and fate of the mobilized dissolved OM following a change in land use such as de-vegetation is still lacking (Akagi and Zsolnay, 2008).

Mediterranean watersheds appear to export a larger fraction of N in organic form compared to watersheds of continental Europe and North America. However, no systematic analysis of existing data has been made to date. The objective of this work was to test the hypothesis that livestock grazing (and the resulting de-vegetation) degrades soil quality and enriches surface and ground waters with DON by examining data on three different scales.

## 2. Results

### 2.1. N balance of karstic system

The Koiliaris River Basin in Crete was selected to study the effects of livestock grazing on water quality because it offers a

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unique morphologic situation due to its karstic hydrogeology draining the upland grazing areas through karstic springs. The main contributor to the Koiliaris River flow (136 million $m^3$/a) is the Stilos karstic spring (109 million $m^3$/a) (Fig. S1, SI). The spring recharges a karst area (85 $km^2$) with thin skeletal soils largely de-vegetated due to grazing (Kourgialas et al., 2010). DIN concentrations of the karstic flow were similar to rain water (0.91 ± 0.33 mg/L). On the other hand, rain water had an average DON concentration of 1.2 mg/L, while the spring DON concentration was 3.40 mg/L. A mass balance analysis on N species was conducted for the Koiliaris karstic system (Fig. 1). The spring DON flux (374 t/a) was the main contributor to river DON export (438 t/a). Approximately 25000 sheep/goats were grazing in the karstic highlands of Koiliaris River. The annual dry manure production was estimated to be 5550 t/a, assuming 0.222 t/head a. The annual N production from manure has been estimated to be 175 t/a (Sorensen and Jensen, 1995). The input of DON from precipitation was 161 t/a bringing the total estimated DON load to 336 t/a. The input load was of the same order of magnitude as the spring DON fluxes suggesting that DON was acting as a conservative substance. Mass balance analyses on $NH_3$–N and $NO_3$–N suggested different behaviours of these species compared to DON. The net $NH_3$–N load (assuming 0.433 urine production t/head a and 0.79% urine N content) was estimated at 61 t/a while the spring flux at 2.8 t/a suggested a 95% reduction, most likely due to nitrification (Hoogendoorn et al., 2010; Emerick et al., 1959). Similarly, the $NO_3$–N load was estimated at 114 t/a and the spring flux at 69.8 t/a. The mass balance of the inorganic N loads was expected, however the question is why the organic N is behaving as a conservative substance. In analyzing this question, one can identify two possible mechanisms for DON (Nikolaidis and Bidoglio, 2011): the Mineralization–Immobilization-Turnover and Direct routes. It is postulated that these two mechanisms did not operate in the degraded soils of the karst for the following reasons. A hypothesis could be developed if the semi-arid, cold climatic conditions occurring at the site where the no-rain period extends up to 6–7 months and the rain-snow conditions the remaining 5–6 months is considered. During the no-rain period, the sheep and goat excreta are being dehydrated and physically aged. The mineralization is a function of the micro-organisms present for degradation, whose taxa depend on the organic input to the soil. It can be assumed then that livestock degraded soils have typical organisms (mostly bacteria) that degrade aerobically organic mater similar to that found in wastewater treatment plants. These organisms effectively degrade the carbonaceous organic matter by converting a fraction of organic C to $CO_2$ and the remaining to cell biomass. This biomass also contains the organic N which can be mineralized to $NH_3$ by anaerobic bacteria following the acid fermentation pathway. It is concluded in this hypothetical analysis that the thin soils, the hot–dry and cold–wet conditions and the flashy nature of the system are not conducive for the appropriate bacterial population to develop for anaerobic fermentation of organic N. Along the same lines, direct plant uptake of organic N has been found to be an important mechanism in cool and wet climates which is consistent with the high altitude micro-climate of the area. However, the limited aerial extent of plants minimizes the significance of this mechanism.

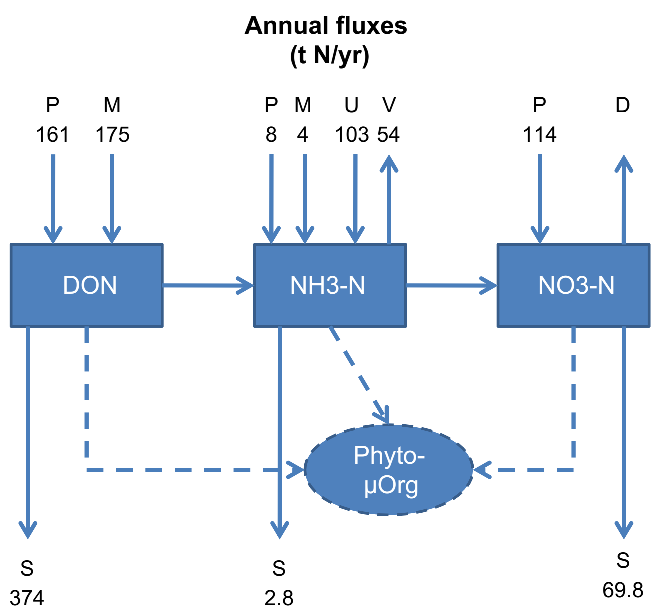


**Fig. 1.** Annual fluxes of Nitrogen in the karstic system discharging from Stilos spring, where P = Precipitation flux, M = Manure flux, U = Urine flux, V = Volatilization flux D = Denitrification flux, and S = Spring flux.

### 2.1. Soil biochemical quality

A comparison of the soil quality parameters of de-vegetated (DVs) and naturally vegetated (NVs) soils is presented in Fig. 2, Table 1 and Table S2 in the SI. The OC and TKN density (t/ha) in DVs was found to be 36.3% and 25.5% lower as compared with the adjacent NVs. Similar patterns were found by Albaladejo et al. (1998) in Spain. The acid-hydrolysable carbohydrates were statistically the same between the DVs and NVs. Dehydrogenase activity as a general measurement of microbial activity suggested that de-vegetated lands exhibited more than two times lower activity (33.2 ± 21.8 mg/kg) compared to vegetated soils (72.0 ± 17.5 mg/kg). In addition, bacteria counted at 22–37 °C were statistically the same among DVs and NVs. NVs exhibited double fungi counts

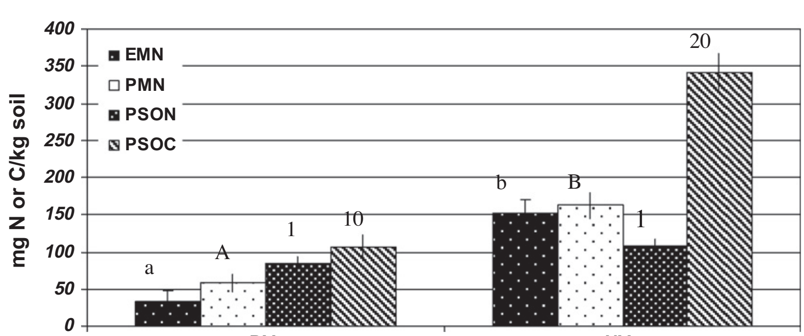


**Fig. 2.** Exchangeable mineral nitrogen (EMN), Potential mineralizable nitrogen (PMN), Potential soluble organic nitrogen (PSON), and Potential soluble organic carbon (PSOC) of soil samples. Values followed by the same letter or number under the same series label are not significantly different ($p < 0.05$).

**Table 1**
Physicochemical characteristics of soil samples (standard deviation in parenthesis).

| ID | Altitude (m) | Bulk density ($kg/m^3$) | Texture[a] | pH | Conductivity (μS/cm) | Organic carbon (%) | Total Kjeldahl Nitrogen (%) | C/N | Carbon-Carbohydrates (mg/kg) | Dehydro-genase activity (mg TPF/kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| DV | 1483 (29) | 914 (24) | SL/L | 7.08 (0.44) | 114 (36) | 3.9 (1.1) | 0.42 (0.11) | 9.4 (0.3) | 432 (92) | 33.2 (21.8) |
| NV | 1513 (40) | 857 (30) | CL | 7.64 (0.07) | 205 (18) | 6.5 (0.5) | 0.60 (0.18) | 11.2 (2.0) | 440 (195) | 79.1 (17.5) |

[a] CL(Clay Loam), SL(Sandy Loam), L (Loam).

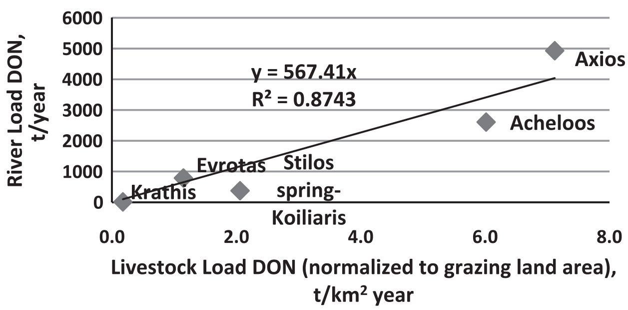


**Fig. 3.** A comparison of the annual dissolved organic nitrogen (DON) river export versus livestock DON input (normalized to the grazing land area) for 5 rivers of Greece.

and greater fungi species richness compared to DVs, but the differences were not statistically significant.

EMN and PMN were 4.6 and 2.8 times higher in NVs (Fig. 2). These results were in line with Thompson et al. (2005) who found the mineralized N of bare soils to be two times lower than that of vegetated soils. The PSOC was also 3.2 times higher in NVs (341 ± 27 mg C/kg soil) compared to DVs (106 ± 17 mg C/kg soil). Xie and Steinberger (2001) also found a 2–2.5 times decrease in this pool of de-vegetated grazing lands. On the other hand, the PSON was statistically the same.

DON was the predominant N species in both extracted soluble N pools (7-day and 1-day extraction) in DVs compared to NVs. PSON as a percentage of total soluble N in the 7-day extracted pool, followed the pattern NV(21 ± 5%) < DV(49 ± 7%). The DOC-to-DON ratio of the extracted pools of the DVs was lower (1.24 ± 0.08) compared to NVs (3.14 ± 0.08) indicating a different composition of the OM pools. Finally, the DOC aromaticity was found to be significantly lower in de-vegetated lands (0.957 ± 0.366 L/mg C m) compared to vegetated (2.155 ± 0.136 L/mg C m), confirming the hypothesis. DOC aromaticity observed in DVs was in the lower range of values observed in the literature (Akagi and Zsolnay, 2008; Corvasce et al., 2006).

*2.2. Livestock grazing intensity and DON export*

Based on previous published studies, the N load from five different size, mixed land use watersheds in Greece was apportioned and related to the export of N species from the watersheds. A comparison of the annual dissolved organic N (DON) river export versus livestock DON input (normalized to the grazing land area) is presented in Fig. 3 and the load calculations are presented in the supporting information. River DON export was found to be linearly correlated with livestock DON load that is input to the watershed for five basins in Greece.

Finally, the patterns of dissolved N export from Mediterranean watersheds were compared to forested and mixed land use watersheds from other climatic regions reported in the literature in order to elucidate the differences in response at a larger scale. River water in mixed agricultural watersheds exhibited different patterns of dissolved inorganic N (DIN) versus DON-to-TDN ratio compared to forested watersheds and mixed watersheds of other climates (Fig. 4 and Table S3 SI). Forested watersheds had low DIN concentrations and a high DON-to-TDN ratio while mixed land use watersheds of the Mediterranean with a significant livestock grazing contribution exhibited higher DIN and DON-to TDN ratios compared to other watersheds, providing additional evidence that DON could be a reliable indicator of livestock grazing impacts.

## 3. Conclusions

This study provided evidence linking the DON export from river basins to livestock grazing intensity and the resulting decrease in vegetation. A linear relationship between DON export

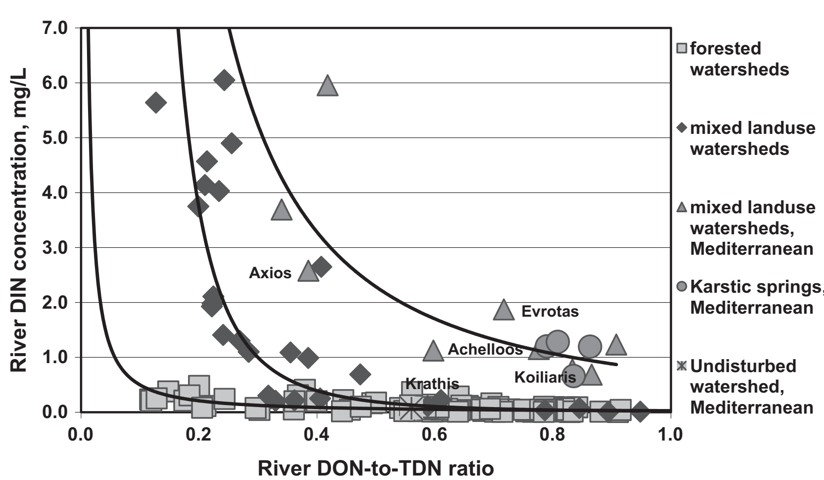


**Fig. 4.** River cconcentration of dissolved inorganic nitrogen (DIN) relative to the DON/TDN ratio in different watershed types (see detailed data in Table S1, SI).

and livestock N load was obtained for five Greek basins suggesting a mechanism that operates on regional scales. The de-vegetation of grazing lands in the Koiliaris River highland calcaric leptosols was shown to be a primary factor causing the decline of soil biochemical quality. De-vegetated soils had lower decomposition potential as compared to vegetated soils. Mineralization and plant uptake appeared to be restricted and leaching of soluble low aromaticity organic matter was favored. The evidence provided by this study suggested that DON can be used as a reliable indicator for livestock grazing impacts to soil biochemical quality.

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## Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apgeochem.2011.03.070.

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