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ORIGINAL ARTICLE

Impact of hydroquinone used as a redox effector model on potential denitrification, microbial activity and redox condition of a cultivable soil

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Abstract In this microcosm study, we analyzed the effect produced by hydroquinone on the expression of soil biological denitrification, in relation to the redox state of the soil, both in terms of intensity factor (Eh′) and capacity factor (amount of oxidized or reduced compounds).

The supplementation of an Argiudoll soil with hydroquinone decreased the soil apparent reduction potential (Eh′) and soil dehydrogenase activity (formazan production from tetrazolium chloride reduction; redox capacity factor), the relationship between both factors being highly significative, $r = 0.99$ ($p < 0.001$). The bacterial population (measured by colony forming units) increased, and the production of N_2O was greater ($p < 0.001$) at 200 and 400 μg/g dry soil doses. Furthermore, there was an inverse relationship between soil dehydrogenase activity and the number of bacteria ($r = -0.82$; $p < 0.05$), increased denitrification activity and changes in the CO_2/N_2O ratio value. These results suggest that hydroquinone at supplemented doses modified the soil redox state and the functional structure of the microbial population. Acetate supplementation on soil with hydroquinone, to ensure the availability of an energy source for microbial development, confirmed the tendency of the results obtained with the supplementation of hydroquinone alone. The differences observed at increased doses of hydroquinone might be explained by differences on the hydroquinone redox species between treatments.

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PALABRAS CLAVE
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Dosis de hidroquinona

El impacto de la hidroquinona usada como un modelo de efector redox sobre la desnitrificación potencial, la actividad microbiana y las condiciones redox de un suelo cultivable

Resumen En este trabajo estudiamos, en condiciones de microcosmos, el efecto que produce la hidroquinona sobre la expresión de la desnitrificación en relación con el estado de óxido-reducción del suelo, en términos de factor de intensidad (Eh′) y de factor de capacidad (cantidad de compuestos oxidados o reducidos).

La suplementación de un suelo argiudol con hidroquinona disminuyó el potencial de reducción aparente (Eh′) y la actividad deshidrogenasa (producción de formazán a partir de la reducción de cloruro de tetrazolio; factor de capacidad redox), la relación entre ambos factores fue altamente significativa, $r = 0{,}99$ ($p < 0{,}001$). La población bacteriana heterotrófica (medida como unidades formadoras de colonias) aumentó y la producción de N_2O fue mayor ($p < 0{,}001$) con las dosis de 200 y 400 μg/g de suelo seco. Además se observó una relación inversa entre la producción de formazán y el número de bacterias ($r = -0{,}82$; $p < 0{,}05$), la actividad desnitrificadora aumentó y se produjeron cambios en el valor del cociente CO_2/N_2O. Estos resultados sugieren que la hidroquinona, en las dosis empleadas, modificó el estado redox del suelo y la estructura funcional de la población microbiana. La suplementación con acetato en el suelo con hidroquinona, a fin de asegurar la disponibilidad de una fuente de energía para el desarrollo bacteriano, confirmó la tendencia de los resultados obtenidos con la suplementación con hidroquinona solamente. Las diferencias observadas con el incremento en la dosis de hidroquinona podrían explicarse por las diferencias sobre las especies redox de la hidroquinona entre los tratamientos.

Introduction

Soil phenolic compounds and their derivatives are originated in the soil by the degradation of microorganisms, plants and other soil humic substances. In agro-ecosystems they may be added through agrochemicals or their degradation products. Hydroquinone (HQ) is one of the most important phenolic compounds in soil. It is a quinone type found mainly as a lignin constituent[25] and together with semiquinones, they are the main redox reactive groups of humic substances in soil.[8] Their oxidation, even within the humic substance group, produces semiquinone and quinone, creating a redox cycle, with electron and proton transfer among different electroactive species ($QH_2 \Leftrightarrow QH \Leftrightarrow Q$), minerals and microbial components in soil.[16,29] This speciation behavior is conducted by several physicochemical conditions of the system, among them acid-base state and redox state,[20] and affect the amount of redox effectors (redox capacity factor) and the apparent redox potential value (Eh′, redox intensity factor). These redox species may act differently upon biological and non-biological processes that involve e-transfers, i.e., denitrification or Fe^{2+} oxidation.[22,28]

In certain environments such as water, HQ has a direct toxic effect on microorganisms.[4,6] In complex microbial environments, such as in the humic-mineral matrix of soil, HQ interacts with minerals and there is not such a direct effect on microorganisms. HQ is known to be degraded through microbial activity,[12,31] to undergo oxidation by light[37] or minerals when it is in contact with soil clay-humic structures, and to get involved in humic substance polymerization.[13]

Denitrification is a process mediated by a great variety of microorganisms which respire nitrate (use NO_3^- as electron final acceptor), produce NO_2^- and N oxides among them N_2O.[11] The relevance of N_2O deserves great attention due to the fact that N_2O shows high reactivity over the ozone layer. According to estimations made by Revell and his collaborators,[26] in the coming years, N_2O may be one of the gases having the greatest negative influence on the greenhouse effect. Moreover, the denitrification process is relevant for its negative effect on soil fertility due to the extraction of nitrogen from the soil.[11]

In soil, microbial respiration generates many redox reactions that transfer e^- to NO_3-R,[35] free radicals and H_2O_2,[10] or to acceptors introduced as triphenyl tetrazolium chloride (TTC), which is reduced to triphenyl formazan (TPF).[9] The TPF production was also used to determine the number of heterotrophic microorganisms[2] from the microbial dehydrogenase activity since TTC may act as substrate for these enzymes.[32,36] In other words, in our study, the same reaction (TTC reduction) may inform on two related process (i) changes in the redox capacity of the system, and (ii) quantify the evolution of the heterotrophic microbial population.

In this research, we studied the pathways through which HQ affects denitrification expression, in relation to soil oxidation–reduction processes in terms of both redox intensity (Eh′) and redox capacity (amount of TPF produced, number of oxidized or reduced compounds). The study was carried out under controlled laboratory conditions, and the parameters assessed were the number of heterotrophic bacteria, dehydrogenase activity, apparent reduction