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DECOMPOSITION OF CHROMIUM-CONTAINING LEATHER RESIDUES IN A SANDY SOIL

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RESUMEN

DESCOMPOSICION DE RESIDUOS DE CUERO CURTIDOS CON CROMO EN UN SUELO ARENOSO

Se llevaron a cabo experimentos a largo término (0-16 semanas) de incubación aeróbica de residuos de cuero curtidos con Cr (TLR) en un suelo arenoso serie Roma y se confrontan la mineralización del carbono orgánico (como CO_2) y nitrógeno (NO_3^-, NH_4^+), actividades enzimáticas y solubilidad del Cr, con objeto de ensayar los efectos tóxico-nutricionales del TLR. El suelo y el suelo con Cr_2O_3 (100 μg Cr g^{-1} suelo seco: la misma cantidad adicionada como TLR), se incubaron separadamente. De acuerdo con el índice de mineralización de Stanford-Smith, un 100% del nitrógen del cuero se mineralizó después de 8 semanas de incubación y en la misma proporción que el fertilizante comercial de rápida descomposición "Ureaform 56", deducido en base a la evolución del CO_2 y NO_3^- los cuales presentan una buena correlación ($r > 0.95, p < 0,05$). A pesar de descomponerse rápidamente, el TLR libera en las soluciones del suelo cantidades traza (< 0.5 μg g^{-1} de Cr (III) y Cr (VI) que parecen no afectar a las propiedades bioquímicas del suelo. Después de 16 semanas de incubación, las actividades enzimáticas tienden a incrementarse (BAA-proteasa y ureasa), a permanecer inalteradas (fosfatasa, la que tiene un papel marginal en el ciclo C-N del cuero) y a decrecer (caseina-proteasa).

Palabras clave: Cuero, cromo, enzimas, mineralización.

SUMMARY

Long-term laboratory experiments (0-16 weeks) of aerobic incubation of chrome-tanned leather residues (TLR) in a sandy soil, Roma series, were carried out and the mineralization of organic/carbon (as CO_2) and nitrogen (as NO_3^-, NH_4^+), enzyme activities and chromium solubility were checked to test toxic-nutritional effects of TLR. The soil and soil plus Cr_2O_3 (100 μg Cr g^{-1} dry soil: the same amount added as TLR), were incubated separately. According to the Stanford-Smith index of mineralization, a 100% of leather-N was mineralized after 8 weeks of incubation and at the same rate of fast-decomposing "Ureaform 56" commercial fertilizer, as deduced on the basis of CO_2 and NO_3^- evolution, which showed a good correlation ($r > 0.95$, $p < 0.05$).

Although rapidly decomposable, TLR released into soil solutions trace amounts (< 0.5 μg g^{-1}) of Cr (III) and Cr (VI) which did not seem to affect the biochemical properties of the soil. After 16 weeks of incubation, enzyme activities were found to increase (BAA-hydrolysing protease and urease), to remain unchanged (phosphatase, which had a marginal role in the leather –C –N cycling), and to decrease (casein-hydrolysing protease).

Key Words: Leather, chromium, enzymes, CO_2 -respiration N-mineralization.

INTRODUCTION

This paper concerns the descomposition of chrome-tanned leather residues (TLR) in a sandy soil. Tanned leather residues have been accepted in the list of the nitrogenous organic fertilizers by Italian regulation. Despite their high contents of mineralizable nitrogen and organic matter, doubts arise as to whether the large amount of Cr trapped in chrome-tanned leather is released during the decomposition of the organic matrix. Although Cr (III) is normally insolubilized in soil (Silva and Beghi, 1986; Bartlett and Kimble, 1976), oxidation and/or organication may cause metal leaching and translocation to groundwater and plants (James and Bartlett, 1984); however the behavior and eventual fate of Cr in soil is still under investigation. A recent paper (Ciavatta and Sequi, 1989) has shown that the release of Cr from leather when used as fertilizer is of little agronomic or enviromental significance, but Ceccanti *et al.* (1989) have reported that the solubility of Cr in TLR-treated soils are impredictable and strongly dependent on soil properties and redox conditions.

MATERIALS AND METHODS

Soil

A sandy soil (Roma series) sampled at the Experimental Station of the Istituto Sperimentale per la Nutrizione delle Piante, was used in the experiments. TLR, originating from the industry of leather manufacture and finishing, was toasted at 250 °C and ground to pass a 1 mm sieve. The soil and TLR analysis are reported in Table 1: TLR was characterized by a high amount of organic matter, nitrogen and a high amount of potentially toxic Cr.

Incubation experiment

Two soil portions of TLR and Cr_2O_3 were added separately, (each at a rate of 100 mg Cr Kg^{-1}) and incubated at 30 °C at field water capacity for 16 weeks and in conditions of persistent aerobiosis; a portion of untreated soil was incubated as a control. During incubation, samples were taken for the analysis of nitrates, ammonia, available Cr (III) and Cr (VI) and enzyme activities; CO_2 evolutions was measured as already reported (Nigro *et al.*, 1979).

TABLE 1

Soil and TLR analysis.

		SOIL	TLR
pH		7.5	3.8
Carbon	(%)	2.44	43.22
Organic Matter	(%)	4.21	87.75
Nitrogen	(%)	0.18	13.29
C/N		13.94	3.25
Available N-NO_3^-	(%)	–	0.21
Available N-NH_4^+	(%)	–	0.71
Total Cr	(mg kg^{-1})	15	27000
Soluble Cr (III)	"	0.0	395.0
Soluble Cr (VI)	"	0.0	0.25
Total Mn	"	8.30	–
C.E.C.	($cmol_c$ kg^{-1})	37.9	–
Sand	(%)	88.6	–
Silt	"	2.1	–
Clay	"	9.3	–
Ash	"	–	12.25
Humidity	"	–	11.8

Analysis

Water extracts of soil (1/4 w/v ratio) were carried out; nitrates were determined in the water extracts by Ion Chromatrograph Dionex 2000i system (Dionex Corp., Sannyvale, CA, USA); Cr (VI) was determined after reaction with s-diphenylcarbazide (Bartlett and Kimble, 1976); total available Cr was determined by Atomic Absorption (Perkin Elmer) and Cr (III) was calculated by subtracting the amount of Cr (VI) from the total Cr. The rate of TLR mineralization and the capability of soil to mineralize organic-N to NO_3-N were determined according to Stanford and Smith (1972): mineral or organic nitrogen were added to the soil at the ratio of 250 mg Kg^{-1} and incubated for four weeks at 30 °C ± 0.5 and at field capacity; the index of mineralization was expressed as percent of NO_3^--N produced from added nitrogen and corrected by soil native nitrogen mineralized in the same conditions. Enzyme activities, urease, phosphatase, casein-hydrolysing and BAA-hydrolysing proteases were measured during incubation, using urea, p-nitrophenylphosphate (PNPP), casein and benzoyl-L-arginamide as substrates, respectively (Nannipieri *et al.*, 1980). Three replicates were made for the incubation experiments and analysis.

RESULTS AND DISCUSSION

Mineralization

73% of TLR mineralized within two weeks rising to 100% after 8 weeks as deduced from nitrate production (Table 2). Also carbon dioxide evolution was taken as an index of organic matter decomposition since good correlations (Figure 1 a, b, c) were found between CO_2 and NO_3^- ($r = 0.964$ for the control; $r = 0.953$ for TLR; $r = 0.981$ for Cr_2O_3) Table 3 shows the capability of the soil to mineralize several

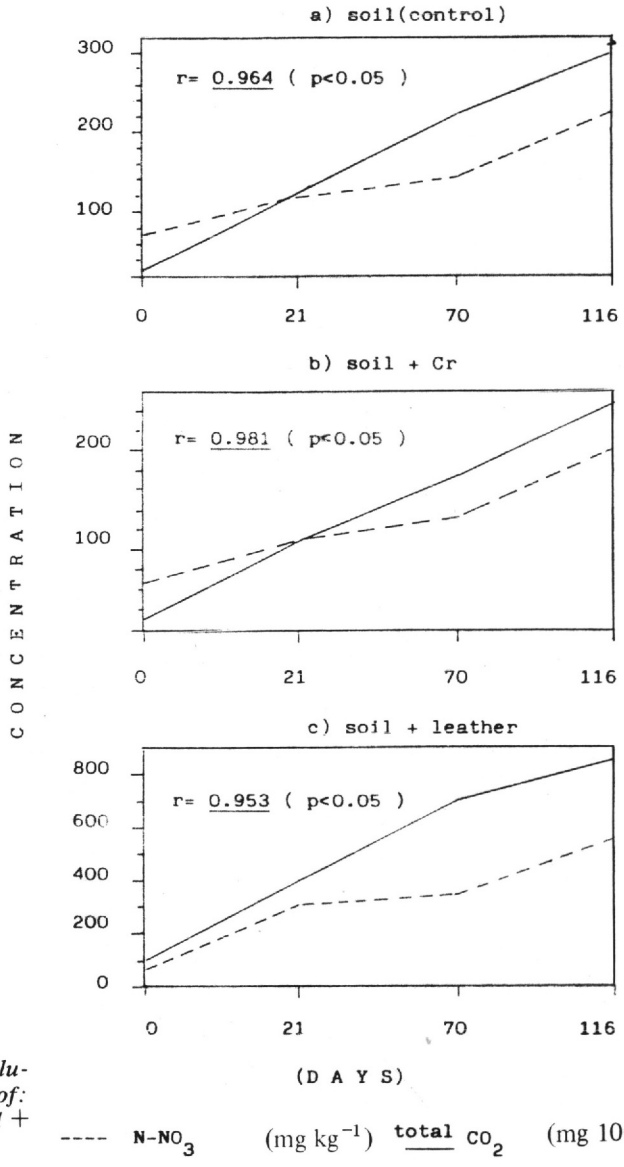

FIG. 1.—*CO_2 and NO_3^- evolution during the incubation of: a) soil; b) soil + Cr; c) soil + + TLR.*

TABLE 2

Mineralization capability of TLR in Soil.

	Weeks			
	2	4	8	12
Soil + TLR . . . . . (A)	224	276	326	350
Soil. . . . . (B)	41	59	75	95
% of mineralization	3	4.3	5.5	7
TLR . . . . . (*)	183	217	251	255
% of mineralization	73	87	100	100

(The values are expressed in mg NO_3^- Kg^{-1}).

(*): Net TLR-nitrogen mineralization given by (A) - (B) experimental values.

nitrogenous substrates. Within the first two weeks, 80 % of ammonium-N tranformed to nitrate, reaching 100% after 4 weeks thus confirming the exceptionally high nitrifying activity of the soil. The indices of mineralization of TLR and Ureaform 56 were very similar and varied from about 70% (two weeks) to 100% (eight weeks). Apparently, there were not toxic effects of Cr on nitrification.

Enzyme Activities

A decrease of all the activities were observed in the 0-21 period,

TABLE 3

Mineralization capability of several nitrogenous substrates in soil.

Substrates	Weeks			
	2	4	8	12
Casein	65	74	78	80
Ureaform 29.	42	58	67	80
Ureaform 45.	50	69	79	100
Ureaform 56.	72	88	100	100
$(NH_4)_2SO_4$	80	100	100	100
TLR	73	87	100	100

(The values are expressed as % of $N\text{-}NO_3^-$ produced).

with the exception of urease in TLR treatment (Figs. 2 and 3); the decrease was probably due to the death of microorganisms caused by soil rewetting and forced aerobic conditions or by Cr (VI) inhibition which formed at this period (Fig. 4 b); a stabilization of phosphatase, a slight increase of BAA-hydrolysing protease, a slight decrease of casein-hydrolysing protease and urease were observed thereafter. Phosphatasè showed little variation throughout the incubation. Nannipieri *et al.* (1979) reported that the protease was inducible in soils and that newly sinthesized protease was rapidly lost due to the short-living microbial populations involved. It has also been reported (Hattori, 1988) that the protease activity was, among eight tested enzynes, the best index to follow the degradation of nitrogen-rich organic sludges, and that sludge decomposition depended on protein content. According to the

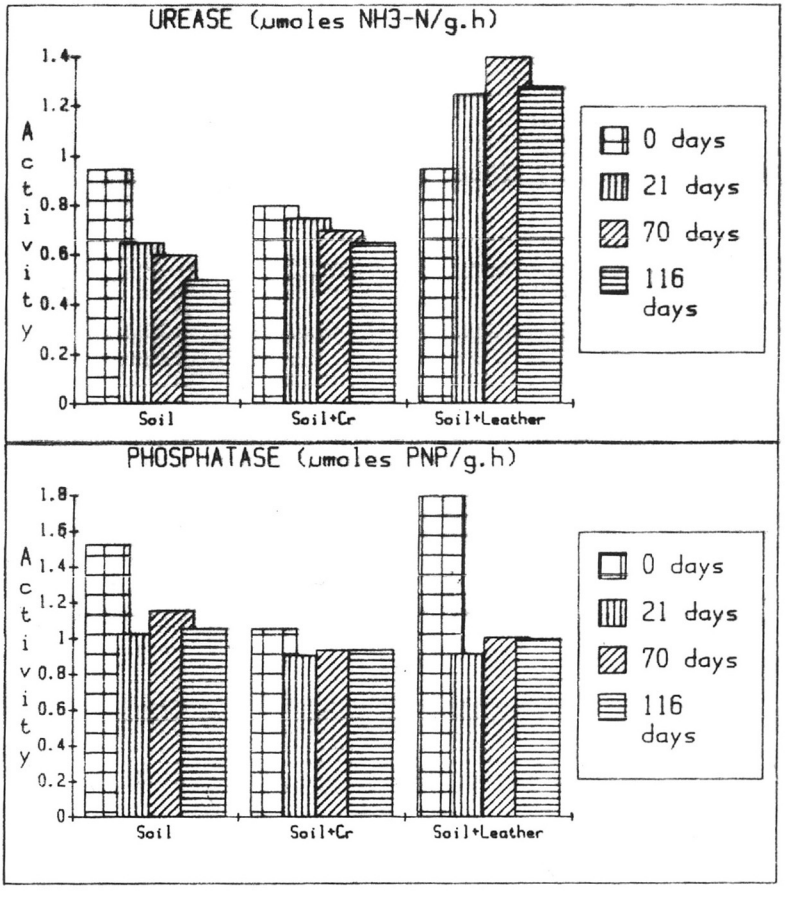

FIG. 2.—*Changes of urease and phosphatase with time.*

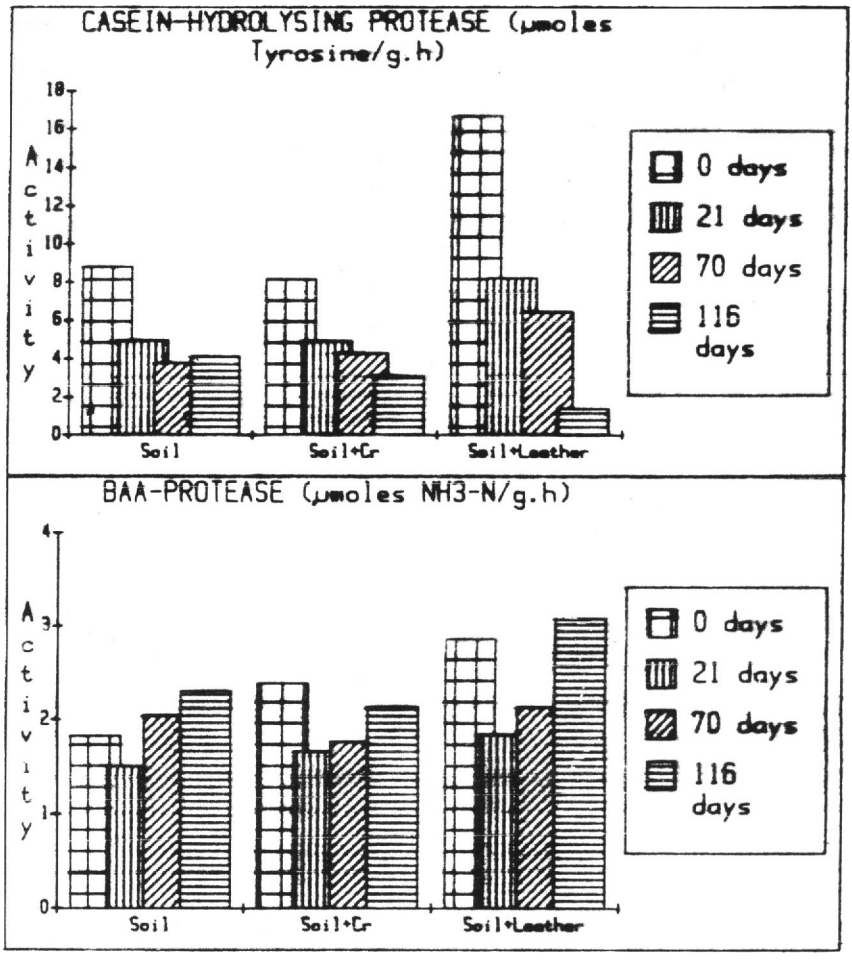

FIG. 3.—*Changes of BAA– and casein–hydrolysing proteases with time.*

literature, our results showed that casein-N (Table 3) and "Casease" (Fig. 3) decreased markedly with time, supporting the hypothesis that the synthesis of casein-hydrolysing protease at the early days of incubation was replaced by a synthesis of BAA-hydrolysing protease acting on low molecular weight nitrogenous compounds (intermediate metabolites); urease activity instead decreased in the control and in soil-Cr treatment, but increased in the soil-TLR treatment, probably due to both microbial growth or enzyme synthesis following TLR addition. The increase of these activities with time also indicated that adaptation of microbial populations to Cr in our experiments might have occurred. Ueda *et al.* (1988) have found Cr-tolerant bacteria in Cr-treated soils.

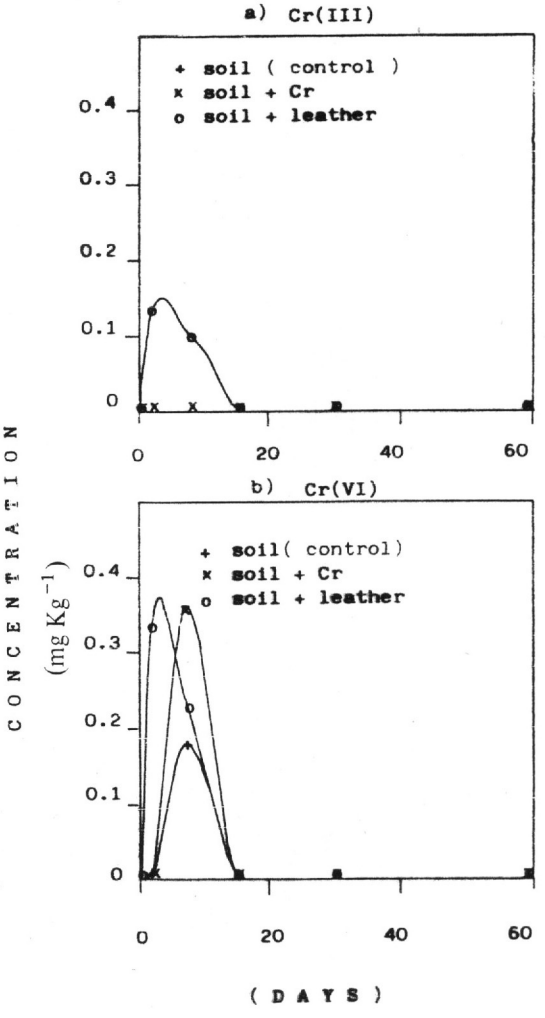

FIG. 4.–*Dynamics of Cr (III)/ Cr (VI) evolution with time.*

Cr oxidation

Soils have a great possibility of transforming Cr (III) to soluble and toxic Cr (VI), as repeatedly demonstrated (Bartlett and James, 1979; Ceccanti and Silva, 1980). Figures 4 a, b show the equilibrium between Cr (III)/Cr (VI) in each treatment during incubation. In the TLR treated soil, Cr (III) and Cr (VI) peaked to 0.15 and 0.30 mg kg^{-1} respectively; in the Cr_2O_3 treatment and in the control Cr was present only in the Cr (VI) form; the presence of Cr (VI) in the control demonstrated that even native soil Cr participated in redox transformations, provided the conditions were strictly aerobic and the microbial biomass active.

CONCLUSIONS

Chrome-tanned leather residues (TLR) decomposed rapidly in a Roma sandy soil and released small amounts of Cr (III) which was insolubilized at the pH near neutrality: Cr (VI) was produced in comparable amounts to Cr (III) (less than 0.5 mg kg^{-1} dry soil) but it was rapidly reduced and insolubilized. The results proved that nitrogenous compounds decomposed rapidly in this soil regardless of molecular weights, forms and sources, and that considerable amount of nitrate may be lost causing environmental pollution. Only soil enzymes involved in the organic-N transformations seemed to be affected by TLR decomposition. More soils and experiments need to confirm the release of Cr (VI) and $N\text{-}NO_3^-$ at toxic levels.

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