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Effects of Cr^{3+}, Cr^{6+} and tannery sludge on C and N mineralization and microbial activity in semi-arid soils

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Abstract

The aim of this study was to evaluate the effect of two Cr species (Cr^{3+} and Cr^{6+}) on N and C mineralization and dehydrogenase activity in semi-arid soils. The Cr species (250 mg kg^{-1} soil) were either added alone or mixed with tannery sludge (0.0125 g g^{-1}) to three soils: cultivated soils, and outside and under the canopy of mesquite trees were then incubated for 180 days at 25 °C. Sole Cr^{6+} addition had a higher inhibition of CO_2 production rate in cultivated soil (58–73%) than in soils under the canopy and outside the canopy. Soil outside the canopy amended with Cr^{6+} showed the highest inhibition of dehydrogenase activity (40–100%) followed by cultivated and under the canopy soils. However, Cr^{6+} added alone increased the inhibition of nitrification in soil outside the canopy (68–84%, from 30 to 120 days), followed by under the canopy and cultivated soils. The addition of tannery sludge to Cr^{6+} significantly reduce the CO_2 production rate and dehydrogenase activity in all three soils, and increased the inhibition of nitrification in the following order: outside the canopy, cultivated and under the canopy soils. The addition of Cr^{3+} or Cr^{3+} plus tannery sludge either stimulated or inhibited CO_2 production rate, dehydrogenate activity and ammonification in the three soils in no clearly defined order. Measurement of dehydrogenase activity was the best tool for assessing the harmful effect of Cr^{6+} on soil microbial activity in semi-arid soils exposed for an extended period.
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Keywords: Tannery sludge; Dehydrogenase activity; N mineralization; Chromium; Semi-arid soils

1. Introduction

In arid and semi-arid regions of North of Guanajuato, Mexico, have serious problems with erosion because the decrease of soil organic matter due to deforestation, grazing by cattle and conversion of natural ecosystems into cultivated areas. The vegetation is dominated by mezquite (*Prosopis laeviginata*) and less by huizache (*Acacia tortuoso*) and catclaw (*Mimosa biuncifera*). Application of organic wastes may improve the amount of valuable nutrients to pioneer vegetation, improving the soil organic matter and cation exchange capacity, preventing the degradation of soil structure [1].

Leather processing is an important economic activity in the town of Leon (Guanajuato) that produces up to 64 320 t sludge $year^{-1}$. Awareness of environmental problems has increased considerably during recent years and protecting environment has become a global issue. The use of tannery sludge for reforesting the north of Guanajuato (a natural reserve in Dolores Hidalgo, Guanajuato) is attractive because, it can avoid the soil degradation due to the increasing erosion of this region. In the other hand, it can reduce the contamination by tannery sludge dumping to the open air in León, Guanajuato.

The disposal or reuse of tannery sludge is of major importance due to its accumulation in the environment in forms that could be toxic to living organisms. Both trivalent (Cr^{3+}) and hexavalent (Cr^{6+}) chromium are present in tannery waste. Chromium^{3+} is of low toxicity and therefore represents a minor problem as far as public health is concerned. Chromium^{6+} is much more reactive, toxic and shows a high mobility in the soil. The mobility and toxicity of Cr^{6+} can be reduced by converting it to the reduced state of Cr^{3+} by means of organic matter and inorganic reducing agents in the soil [2].

A few works have been published on the influence of Cr on nitrogen transformation in soils and these have reported somewhat mixed results. James and Bartlett [3] found that nitrification was inhibited by Cr^{6+} at a concentration of 10 μg g^{-1} in soil

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suspensions, but no inhibition was observed in treatments containing Cr^{3+} in sewage sludge or tannery effluent. Chang and Broadbent [4] observed that nitrogen immobilization, mineralization and nitrification were inhibited to a great extent by Cr^{3+} added to a neutral soil, but Cr^{6+} was not measured in the extracting solutions used to characterize soil Cr during the experiment. Barajas-Aceves and Dendooven [5] reported that tannery sludge added to semi-arid soils had no inhibitory effect on N mineralization.

Information on C and N mineralization in relation to available Cr in soils is inconclusive. Therefore, the present study was aimed to assess the effect of high levels of Cr on microbial activity (dehydrogenase activity) and nitrogen and carbon mineralization for an extended period.

2. Materials and methods

2.1. Experimental site

The soils were sampled from the natural reserve "El Cortijo" which the dominant vegetation is mesquite (*Prosopis laeviginata*) located in Dolores Hidalgo, Guanajuato, Mx. The soils were collected from two sites: under the canopy and outside the canopy of mesquite tree. The third soil was sampled from one site cultivated with maize (*Zea mays*) and beans (*Phaesolus vulgaris*) for 20 years, near to the natural reserve (4 km). The average altitude of the sites is between 1750 and 2000 m above sea level and average annual rainfall is between 400 and 600 mm (mainly from June to September).

2.2. Soil sampling

The soil was collected from 0 to 5 cm layer where it shows the highest organic content. The sampling took place under the canopy of four isolated mesquite trees and 1–2 m from the stem in four perpendicular directions selected at random. The second sampling took place in the same perpendicular direction at the distance of 6–8 m from the stem that is outside the canopy cover of the mesquite tree. The cultivated soil was sampled from 0 to 30 cm layer of the agricultural land at Dolores Hidalgo, Gto. The soil was bulked; all the stones, visible roots and fauna removed, sieved to less then 2 mm and stored at 5 °C until used.

2.3. Tannery sludge

Tannery sludge produced during leather manufacturing was sampled from a tannery from Leon (Guanajuato, Mexico). The sludge contained large quantities of hair, soluble proteins and fatty flashings from processing the skin to hide, and sulphide, lime, chromium-sulphate, salts, dyes, acid and leather trimmings from processing the hide to leather. The chemical characterization is shown in Table 1. The tannery sludge was air-dried before used for the experiment at aerobic incubation.

2.4. Aerobic incubation

Before the experiment, the soils were adjusted to 40% of their total water holding capacity (WHC) and conditioned at 25 °C for 7 days in 60 kg sealed drums (4 kg per drum) containing 200 ml distilled water at the bottom to avoid desiccation and containing a beaker with 100 ml of 1 M NaOH solution to trap evolved CO_2.

Sub-samples of 40 g of soil were placed in 110 ml glass bottle, which were subsequently put into 1 l jar containing 10 ml H_2O and a vessel with 20 ml of 1 M NaOH solution.

The following treatments with three replications were applied to the soil: control (without any amendment) Cr^{3+}, Cr^{6+}, tannery sludge, Cr^{3+} + tannery sludge, Cr^{6+} + tannery sludge. Cr^{3+} (Cr_2O_3) and Cr^{6+} ($K_2Cr_2O_7$) were added to the soils at a rate of 250 mg kg^{-1} soil. The concentration of $Cr^{3+}$and Cr^{6+} were selected as a lower doses compared to the upper limits concentration allowed in agricultural soils treated with sewage sludge recommended by EPA [6].

The amount of tannery sludge added was 0.0125 g g^{-1} soils (0.5 g tannery sludge to each sub-samples of 40 g soil) which are

Table 1
Characteristics of semi-arid soils sampled in Dolores Hidalgo, Guanajuato and tannery sludge from Leon, Guanajuato, Mexico

Site	pH	WHC	Moisture (cmol kg^{-1})	CEC (mequiv. 100 g^{-1})	Org C (g kg^{-1})	Total N (g kg^{-1})	Total P (g kg^{-1})	Clay (g kg^{-1})	Silt (g kg^{-1})	Sand (g kg^{-1})
Cultivated	7.06	60.0	100.3	34.1	0.60	0.80	0.88	160	222	614
Outside canopy	6.03	49.6	19.0	22.0	0.27	0.69	0.29	184	112	694
Under canopy	6.18	59.2	13.7	5.3	0.46	1.77	0.33	184	52	764
Tannery sludge	8.09	–	880	–	257.8	18.7	7.5	–	–	–

Site	Zn (mg kg^{-1} soil)	Cu (mg kg^{-1} soil)	Ni (mg kg^{-1} soil)	Cd (mg kg^{-1} soil)	Cr (mg kg^{-1} soil)	Pb (mg kg^{-1} soil)
Cultivated	33.3	9.4	0.61	0.15	9.04	1.95
Outside canopy	34.6	3.8	58.6	0.15	0.00	2.06
Under canopy	57.1	6.1	47.0	2.96	0.30	1.95
EU upper limit[a]	300	140	75	3.0	ND	300
Tannery sludge	89	14	1.3	4	1663	15
EU upper limit[b]	4000	1750	400	40	ND	1200

ND: not given.
[a] EU upper limit value for soils.
[b] Sewage sludge used in agriculture.

the amount which covered three times the requirement region recommended dose of N for maize crop (i.e. 260 kg N ha^{-1}). The jars were sealed with air-tight plastic lids and incubated at 25 °C for 180 days. After 0, 30, 60, 120 and 180 days, the vessel with 20 ml of 1 M NaOH solution was removed, resealed and stored until analysis of CO_2. At the same intervals, the soil was removed for analysis of inorganic N (NH_4^+, NO_2^- and NO_3^-) by shaking for 30 min with 100 ml 0.5 M K_2SO_4 solution and filtering though Whatman no. 42 paper. The extractants were stored at −20 °C until analysis. After 15, 40 and 90 days all the jars were opened, the vessel with 1 M NaOH solution reemplaced with fresh NaOH solution and the jars were resealed and further incubated at 25 °C.

2.5. Dehydrogenase activity

Soil dehydrogenase activity was measured using a modification of the method of Casida [7]. Five grams of fresh soil was incubated at 37 °C for 24 h in test tubes containing 1 ml 3% 2,3,5-triphenyltetrazolium chloride, 67 mg $CaCO_3$ and 2.5 ml distilled water. The accumulation of the end-product triphenyl formazan (TPF) was determined in acetone extracts (50 ml) using a Perkin-Elmer Lamda 3A Spectrophotometer at 520 nm. Dehydrogenase activity was selected from two enzymes activities (urease and phosphatase) tested in previous experiments using two semi-arid soils (under and outside the canopy of mesquite tree) amended with different doses of Cr^{6+}.

2.6. Soil chemical analysis

The CO_2 trapped in 1 M NaOH solution was measured titrimetrically with a standard HCl solution [8]. NH_4^+ in the extracts was determined by distillation with MgO [9], and NO_2^- and NO_3^- by standard colorimetric methods [10]. Total organic C in soil and tannery sludge was measured by dichromate digestion [11], total N by Kjeldahl digestion [12] and total hydrolysable and orthophosphate phosphorus by stannous chloride method after sulphuric acid–nitric acid digestion [10]. Particle-size was analyzed by the hydrometer method [13].

Total metal in sewage sludge were determined after digestion (digiprep TM digestion system) with 4:1 HCl:HNO_3 solution. Total Zn, Cr, Cu and Ni were measured in flame atomic absorption spectrometry, Pb and Cd were determined by absorption atomic spectrometry fitted with a graphite furnace Avanta M System 300, GF 3000 S/N 10288.

All measurements are the mean of triplicate determinations of three separate jars and are given on an oven-dry basis (105 °C, 24 h).

2.7. Statistical analysis

Multivariate analysis of variance (ANOVA) was applied to test significant differences of means between treatments and comparisons of means (Duncan's test at $p \leq 0.05$) were performed using a statistical analysis package SAS [14], Version 9.0. The models were fitted to N and C mineralization data by linear and non-linear regression with the Statgraphics software package (Manusgistics, Inc., Rockville, MD).

3. Results

3.1. The characteristics of soils and tannery sludge

Amounts of organic C, total nitrogen and phosphorus were generally higher under the canopy than outside the canopy (Table 1). Organic C under the canopy of mesquite trees was 1.7 times greater than outside the canopy. Soil cultivated with maize had 1.3 times more organic C than soil from beneath mesquite trees.

Changes in total nitrogen were greatest under the canopy: 2.5 times higher than outside the canopy and 2.2 times higher than in cultivated soils.

The largest amount of total P was found in cultivated soil and was 2.5 times higher than under the canopy of mesquite. The amount of P under the canopy was 1.14 times greater than the amount of P outside the canopy.

The concentration of Cr added with the tannery sludge (Table 1) was 5.5 times higher than the critical level for Cr (300 mg kg^{-1}) for acceptable utilization of waste and bioproducts in agriculture as established by the US Environmental Protection Agency, Part 503 [see 13]. The total nitrogen content in tannery sludge (1.87%, Table 1) fits the description for low-nitrogen biosolids (1–3%).

3.2. C mineralization

The CO_2 production was significantly ($p \leq 0.001$) greater in all the treatments compared with control soils except the treatments amended with Cr^{6+} in the three soils (cultivated, under and outside the canopy of mesquite) (Fig. 1). Thus, CO_2 production in the control for cultivated soils was 3.4 times higher than treatment with Cr^{6+} at 60 days incubation, followed by under the canopy (1.4 times) and outside the canopy (0.87 times) soil.

CO_2 production showed a similar pattern in both amended and unamended tannery sludge. However, the difference in CO_2 production in treatments amended with tannery sludge was higher than that for non-amended soils: 13.4 times higher in soils outside the canopy, 3.2 times higher in cultivated soils, and 1.5 times higher in soils under the canopy.

The highest inhibition of CO_2 production rate was in Cr^{6+} added alone to cultivated soils (58–73%) followed by under the canopy soil (16–58%). Outside-canopy soils amended with Cr^{6+} alone showed a no clear trend of CO_2 production rate (Table 2), although there was 46% inhibition of CO_2 production rate after 120 days incubation. The inhibition of CO_2 production rate in cultivated soils was reduced significantly when tannery sludge was added plus Cr^{6+} (2.8–9.8%) and in under the canopy soils (7.6–38%). In soils outside the canopy with tannery sludge added plus Cr^{6+} there was a lower inhibition of CO_2 production (12–22%) (data not shown).

The addition of Cr^{3+} alone had no effect on CO_2 production rate in soils under and outside the canopy (Table 2) but it had an effect on cultivated soils from 14 to 17% inhibition at 30 and 60 days incubation. C mineralization in cultivated soils amended with Cr^{3+} plus tannery sludge decreased from 0 to 7.8% at 30 and 60 days incubation. Soils outside the canopy treated with

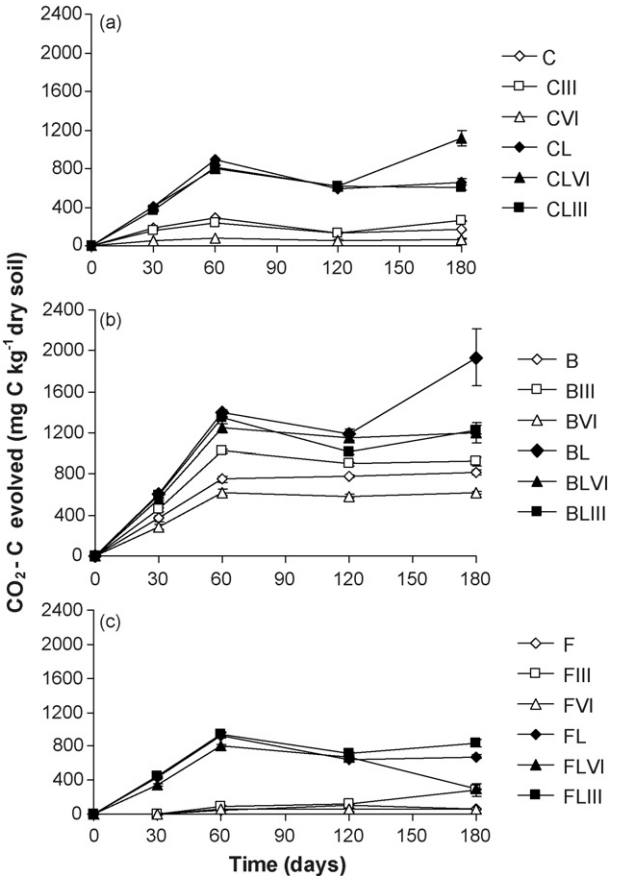

Fig. 1. CO_2-C evolved (mg C kg^{-1} dry soil) in: (a) cultivated, (b) under the canopy and (c) outside the canopy soils from Dolores Hidalgo, Gto., incubated at 25 °C for 180 days. Treatments were: control (◊), soil amended with Cr^{3+} (□), Cr^{6+} (△), tannery sludge (♦), tannery sludge and Cr^{3+} (■) and tannery sludge plus Cr^{6+} (▲). Bars indicate standard deviation.

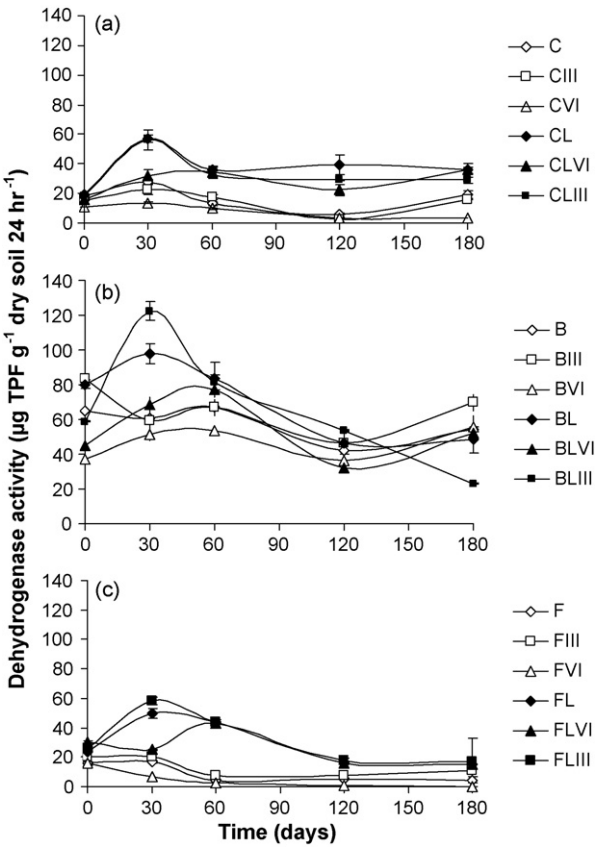

Fig. 2. Dehydrogenase activity (mg TPF kg^{-1} dry soil) in: (a) cultivated, (b) under the canopy and (c) outside the canopy soils from Dolores Hidalgo, Gto., incubated at 25 °C for 180 days. Treatments were: control (◊), soil amended with Cr^{3+} (□), Cr^{6+} (△), tannery sludge (♦), tannery sludge and Cr^{3+} (■) and tannery sludge plus Cr^{6+} (▲). Bars indicate standard deviation.

Cr^{3+} plus tannery sludge showed an inhibition of 98% at 30 days incubation and soils under the canopy showed an inhibition from 1 to 36.5% from 30 to 180 days incubation (data not shown).

3.3. Dehydrogenase activity

Maximum dehydrogenase activity, in terms of μg of TPF per gram of dry soil per 24 h, was observed in all the soils (cultivated, under and outside the canopy) amended with tannery sludge alone or plus Cr^{3+} or Cr^{6+} incubated up to 30 days followed by a slow and progressive decrease in activity over the next 180 days (Fig. 2).

Outside the canopy soils amended with Cr^{6+} alone showed an inhibition of dehydrogenase activity from 40 to 100%, cultivated soil from 27 to 84% and under the canopy soils from 15 to 20% (data not shown). The addition of tannery sludge plus Cr^{6+} to the three soils reduced significantly ($p \leq 0.05$) the inhibition of dehydrogenase activity: 50% at 30 days in soils outside the canopy, 43% in cultivated soils at 30 and 120 days and from 8 to 31% at 30 to 120 days in soils under the canopy.

The addition of Cr^{3+} alone to cultivated and soils outside the canopy showed a significant ($p \leq 0.05$) inhibition and stimulation on dehydrogenase activity in different days in no clearly defined order. Cultivated soils plus Cr^{3+} showed only stimulation of dehydrogenase activity at 120 and 180 days incubation (9–29%). The addition of tannery sludge plus Cr^{3+} to outside and under the canopy and cultivated soils showed a significant ($p \leq 0.05$) inhibition and/or stimulation of dehydrogenase activity in no clearly defined order.

3.4. Nitrogen mineralization

The NH_4^+ concentrations were greater in soils treated with tannery sludge than in the unamended with tannery sludge (Fig. 3b and c). Soils outside the canopy amended with tannery sludge plus Cr^{6+} showed a gradual increase in NH_4^+ concentration, suggesting either retarded mineralization or inhibition of nitrification (Fig. 3). Addition of Cr^{6+} alone or tannery sludge plus Cr^{6+} to the three soils had an eventual and significant ($p \leq 0.05$) inhibition or stimulation of NH_4^+ concentration.

Concentration of NO_3^- exhibited a different pattern (Fig. 4). The NO_3^- concentration in cultivated and outside the canopy soils increased after 30 days incubation in all the treatments. Thus, in both soils no more than 10 mg N kg^{-1} soil of NO_3^- was accounted for in the first 30 days of incubation. This indicates that the soils were depleted in N. A similar high inhibition

Table 2
CO_2 production rate (mg C kg^{-1} dry soil day^{-1}) in cultivated, under the canopy and outside the canopy soils from Dolores Hidalgo, Mexico, incubated at 25 °C for 180 days

Treatment sludge	Cr	CO_2 production rate (mg C kg^{-1} soil day^{-1})			
		30 (days)	60 (days)	120 (days)	180 (days)
Cultivated					
0	0	6.10 (0.00) h	4.71 (0.13) j	1.12 (0.03) i	0.94 (0.05) ef
	Cr^{3+}	5.22 (0.00) i	3.92 (0.00) k	1.12 (0.08) i	1.45 (0.04) e
	Cr^{6+}	1.74 (0.00) j	1.27 (0.06) l	0.47 (0.08) j	0.39 (0.04) f
12.5 mg g^{-1}	0	13.35 (0.50) d	14.80 (0.00) f	4.97 (0.11) h	3.68 (0.15) d
	Cr^{3+}	13.35 (0.00) d	13.64 (0.25) g	5.17 (0.14) gh	6.20 (0.18) b
	Cr^{6+}	12.19 (0.50) e	13.35 (0.50) g	5.11 (0.05) gh	3.35 (0.45) d
Under the canopy					
0	0	12.19 (0.87) e	12.48 (0.50) h	6.49 (0.08) d	4.53 (0.11) c
	Cr^{3+}	15.09 (0.50) c	17.08 (0.29) d	7.49 (0.14) c	5.13 (0.22) c
	Cr^{6+}	9.57 (0.87) g	10.41 (0.49) i	4.86 (0.17) h	3.43 (0.08) d
12.5 mg g^{-1}	0	20.09 (0.13) a	23.39 (0.29) a	9.86 (0.49) a	10.74 (1.54) a
	Cr^{3+}	19.88 (0.25) a	22.56 (0.17) b	9.61 (0.17) a	6.82 (0.24) b
	Cr^{6+}	18.57 (0.50) b	20.75 (0.21) c	8.41 (0.21) b	6.66 (0.53) b
Outside the canopy					
0	0	0.23 (0.03) k	0.81 (0.16) l	0.82 (0.16) i	0.59 (0.06) f
	Cr^{3+}	0.22 (0.04) k	1.41 (0.44) l	0.94 (0.03) i	1.32 (0.43) e
	Cr^{6+}	0.23 (0.03) k	0.99 (0.03) l	0.44 (0.15) j	1.50 (0.02) e
12.5 mg g^{-1}	0	14.43 (0.50) c	15.49 (0.50) e	5.35 (0.22) gf	3.02 (0.15) d
	Cr^{3+}	0.22 (0.50) k	15.70 (0.55) e	5.97 (0.17) e	4.66 (0.04) c
	Cr^{6+}	11.24 (0.50) f	13.46 (0.26) g	5.57 (0.13) f	1.66 (0.25) e
ANOVA		***	***	***	***

*** Significant at $p \leq 0.001$. Values in parenthesis are standard deviations of three measurements. Values in the same column followed by the same letter are not statistically significant at $p \leq 0.05$, according to Duncan's test.

of NO_3^- concentration by Cr^{6+} added alone and tannery sludge plus Cr^{6+} was observed in outside the canopy (69–84% from 30 to 120 days and 62–95% from 30 to 180 days respectively). Under the canopy soils with the same treatments showed lower values of inhibition of NO_3^- concentration (53% at 30 days and 6.5–52% at 60 and 120 days incubation respectively). However, cultivated soils showed a grater inhibition of NO_3^- concentration by tannery sludge plus Cr^{6+} than with Cr^{6+} added alone (51–69% from 30 to 120 days and 12–18% from 30 to 120 days, respectively) (data not shown).

Addition of Cr^{3+} alone to cultivated soils had no significant effect on NO_3^- concentration and a significant stimulation in under and outside the canopy soils. Similarly Cr^{3+} plus tannery sludge had a significant ($p \leq 0.05$) stimulation or inhibition effect in the three soils.

The results suggest that soils were not depleted in N in Cr^{6+} alone and Cr^{6+} plus tannery sludge at 30 days for all the soils and at 120–180 days for outside the canopy soils. After 180 days incubation, the N was immobilized in under the canopy and cultivated soils amended with tannery sludge plus Cr^{3+} or Cr^{6+} and under the canopy plus Cr^{3+} alone.

The amounts of NO_2^- measured in all the treatments and all the soils were less than 0.85 mg N kg^{-1} soil except the values under the canopy amended with Cr^{6+} and tannery sludge. Substantial amounts of NO_2^- were measured at 0, 60 and 180 days incubation in soils under the canopy amended with tannery sludge, Cr^{6+} plus tannery sludge and Cr^{3+} plus tannery sludge (from 1.32 to 2.56 mg N kg^{-1} soil) and outside the canopy at 180 days (1.42 mg N kg^{-1} soil) (data not shown).

3.5. Models used to described N and C mineralization kinetics

An initial estimate to fit the mathematical model was done using SAS in order to identify the appropriate parameters (NH_4^+, NO_3^-, NO_2^-, net mineralization and cumulative CO_2-C evolved).

To time-course of N mineralization in the three soils for each treatment were analysed by fitting the experimental values to tree kinetic models commonly used (Table 3). To identify the

Table 3
Models used to describe soil N and C mineralization kinetics

Model	Equation	Reference
Zero-order	$N_t = k_t + \text{intercept}$	[38]
	$C_t = k_t + \text{intercept}$	
Linearized power function	$N_t = k_t^m$	[39]
	$C_t = k_t^m$	[40]
First-order	$N_t = N_0(1 - \exp^{-kt})$	[39]
	$C_t = C_0(1 - \exp^{-kt})$	[41]

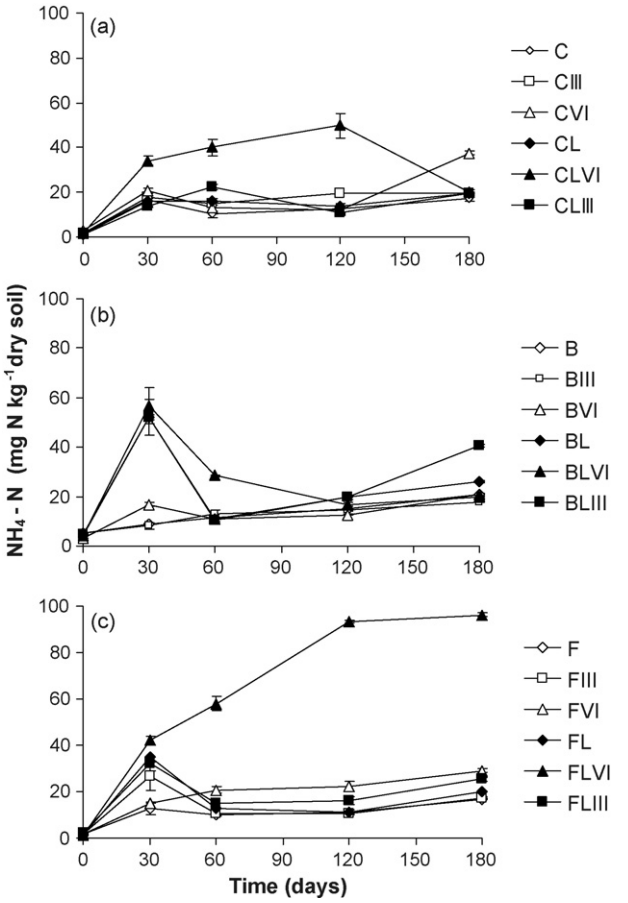

Fig. 3. NH_4^+ concentration (mg N kg^{-1} dry soil) in: (a) cultivated, (b) under the canopy and (c) outside the canopy soils from Dolores Hidalgo, Gto., incubated at 25 °C for 180 days. Treatments were: control (◊), soil amended with Cr^{3+} (□), Cr^{6+} (△), tannery sludge (♦), tannery sludge and Cr^{3+} (■) and tannery sludge plus Cr^{6+} (▲). Bars indicate standard deviation.

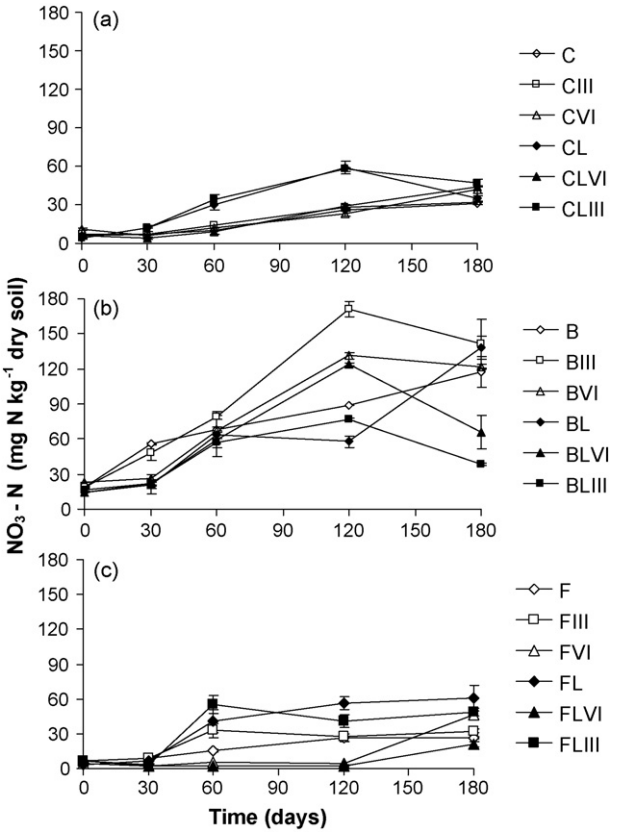

Fig. 4. NO_3^- concentration (mg N kg^{-1} dry soil) in: (a) cultivated, (b) under the canopy and (c) outside the canopy soils from Dolores Hidalgo, Gto. incubated at 25 °C for 180 days. Treatments were: control (◊), soil amended with Cr^{3+} (□), Cr^{6+} (△), tannery sludge (♦), tannery sludge and Cr^{3+} (■) and tannery sludge plus Cr^{6+} (▲). Bars indicate standard deviation.

most convenient model, the values of correlation coefficient (r), R-squared (R^2); the residual mean of square and standard deviation were considered. The values of NH_4^+, NO_3^-, and NO_2^-, showed a high sum of residual square with a week significant correlation coefficient (r) in all the soils for zero-order and first-order models. Nitrogen mineralization and cumulative CO_2-C evolved were tested in the three kinetic models. Results from Tables 4–6 showed that a single model did not fit to all the soils mineralization. Thus, N mineralization in cultivated and outside the canopy soils treated with Cr^{3+}, Cr^{6+} or control fitted well with zero order models. But the treatments with tannery sludge and tannery sludge plus Cr^{3+} or Cr^{6+} fitted to linearized power function for cultivated soils and to first-order for outside the canopy soils (Table 4). Under the canopy soils treated with Cr^{3+}, Cr^{6+} fitted to linearized power function and treatments with tannery sludge and tannery sludge plus Cr^{3+} fitted to zero-order model.

The zero-order models using data from cumulative CO_2-C evolved showed a high sum of residual square with a not significant correlation coefficient (r) in all the soils. The best fitted model for cumulative CO_2-C evolved from under the canopy soils with all the treatments was the linearized power function (Table 5). Cultivated and outside the canopy soil treated with Cr^{3+}, Cr^{6+}, tannery sludge or tannery sludge plus Cr^{6+} fitted well to first-order model (Table 6).

4. Discussion

4.1. Tannery sludge

Total heavy metals content in tannery sludge and soils (Table 1) were lower than the European Union (EU) upper limits for use in agriculture [15].

Low-N biosolids has been reported to be less reactive and less readily decomposed than high-N biosolids, being for this reason more stable [16]. Low-N biosolids are excellent fertilizers, although higher application rates are usually required to meet N needs of a crop. However, in this particular case, the higher application requirement could be detrimental because it would also involve a higher concentration of Cr applied to soils.

4.2. C mineralization

Soils under the canopy amended with tannery sludge and both amended and unamended with Cr^{3+} and Cr^{6+} had the greatest

Table 4
Fit of different models to N mineralization data for three semi-arid soils from Dolores Hidalgo, Guanajuato, amended with Cr^{3+}, Cr^{6+}, tannery sludge and mixtures

Treatment	Zero-order		Linearized power		First-order	
	r	R^2 (%)	r	R^2 (%)	r	R^2 (%)
Cultivated (C)						
C	0.874**	76.34	0.820**	67.19	0.835**	69.8
C + Cr^{3+}	0.950**	90.28	0.933**	87.04	0.916**	83.9
C + Cr^{6+}	0.894**	79.95	0.815**	66.42	0.874**	75.43
C + T S	0.655*	42.91	0.811**	65.75	0.525 ns	27.53
C + TS + Cr^{3+}	0.804**	64.60	0.882**	77.75	0.815**	66.47
C + TS + Cr^{6+}	0.728**	53.06	0.868**	75.46	0.600*	35.98
Under the canopy tree (B)						
B	0.917**	84.08	0.903**	81.53	0.900**	81.07
B + Cr^{3+}	0.812**	65.98	0.928**	86.08	0.785**	57.51
B + Cr^{6+}	0.352 ns	12.71	0.943**	28.92	0.928**	86.10
B + TS	0.838**	70.33	0.729**	53.14	0.369 ns	13.70
B + TS + Cr^{3+}	0.813**	65.98	0.671*	45.06	0.439 ns	19.28
B + TS + Cr^{6+}	0.356 ns	12.71	0.453 ns	20.50	0.371 ns	13.82
Outside the canopy tree (F)						
F	0.960**	92.22	0.946**	90.15	0.949**	90.06
F + Cr^{3+}	0.584*	34.46	0.549 ns	30.16	0.599*	35.92
F + Cr^{6+}	0.884**	78.13	0.852**	72.60	0.769**	59.24
F + TS	0.865**	74.82	0.808**	65.30	0.887**	76.52
F + TS + Cr^{3+}	0.704**	49.61	0.631*	39.86	0.723**	52.30
F + TS + Cr^{6+}	0.974**	94.78	0.986**	97.18	0.977**	95.01

*$P<0.05$, **$P<0.01$. ns: not significant, correlation coefficient (r), R-squared (R^2).

respiration activity compared with the cultivated and outside soils. This was probably due to higher organic C levels in the soil which had been built up by previous addition of organic C from natural vegetation grown in this area. Microbial activity measured by CO_2 evolved was stimulated by tannery sludge. These results are in agreement with those reported by Ferreira et al. [17] and Kanazawa et al. [18].

Using the mineralization of native organic C in metal-contaminated soils has conflicting effects because of the stimulation and inhibiting effect on respiration [19,20]. Thus, in the case of under the canopy and cultivated soils, Cr^{6+} may have effects on complex soil organic matter and render it less available by reducing Cr^{6+} to Cr^{3+} [21,22]. Thereafter, under the canopy soil (which had more organic C) had less inhibition of CO_2 production rate than cultivated soils.

In the case of soil with low organic matter (outside-canopy soil), Cr^{6+} may have an effect on substrate availability which increase with the death of cells. Therefore, the CO_2 produced by the death of microorganisms, and the small amount of CO_2 production by the surviving microorganisms, will reflect a small or not inhibition of CO_2 production by Cr^{6+}. The addition of tannery sludge to Cr^{6+}-amended soils might have the effect of Cr^{6+} complexing with organic matter from tannery sludge and reducing as a result, the inhibition of CO_2 production rate [22].

The addition of Cr^{3+} had a significant stimulation effect on CO_2 production rate in under the canopy soils and cultivates soils, but not significant effect on outside the canopy soils. These results might suggest that Cr^{3+} from tannery sludge

Table 5
Linearized power function model to describe the cumulative CO_2-C evolved during 180 days of incubation in under the canopy soils (B) amended with Cr^{3+}, Cr^{6+}, tannery sludge and mixtures

Treatment	r	R^2 (%)
B	0.826**	68.32
B + Cr^{3+}	0.735**	54.10
B + Cr^{6+}	0.816**	66.50
B + TS	0.864**	74.62
B + TS + Cr^{3+}	0.789**	62.30
B + TS + Cr^{6+}	0.797**	63.53

**$P<0.01$, correlation coefficient (r), R-squared (R^2).

Table 6
First-order model to describe the cumulative CO_2-C evolved during 180 days incubation in cultivated and outside the canopy soils amended with Cr^{3+}, Cr^{6+}, tannery sludge and mixtures

Treatment	Co	k	r	R^2 (%)
Cultivated (C)				
C	–	–	–	–
C + Cr^{3+}	204.21	0.0095	0.915**	83.65
C + Cr^{6+}	69.54	0.00918	0.762**	58.04
C + T S	852.76	0.0134	0.977**	95.42
C + TS + Cr^{3+}	854.11	0.00500	0.122 ns	1.49
C + TS + Cr^{6+}	1243.21	0.2721	0.760**	57.80
Outside the canopy tree (F)				
F	–	–	–	–
F + Cr^{3+}	112.88	0.0773	−0.660*	43.6
F + Cr^{6+}	39.57	0.1127	−0.999**	98.97
F + TS	873.32	0.0128	−0.9479**	90.18
F + TS + Cr^{3+}	–	–	–	–
F + TS + Cr^{6+}	481.86	0.0039	0.876**	80.31

*$P<0.05$, **$P<0.01$. ns: no significant, –: cannot performed the analysis, correlation coefficient (r), R-squared (R^2).

could be oxidized to Cr^{6+} if the presence of Mn IV and III is high [23–25]. The content of total Mn measured in cultivated soils was higher (274 mg kg^{-1} soil) compared to outside the canopy (185 mg kg^{-1} soil) and under the canopy soils (144 mg kg^{-1} soil), however we did not measured the active Mn in the soils. Reports from the literature have shown that the oxidation of Cr_2O_3 to CrO_3 under aerobic conditions should be thermodynamically feasible at high temperature (200–300 °C) in the presence of oxygen [26].

The inhibition of CO_2 production rate in cultivated soils amended with Cr^{3+} alone deserves further studies.

4.3. Dehydrogenase activity

The highest inhibition of dehydrogenase activity by Cr^{6+} added alone followed by addition of tannery sludge plus Cr^{6+} was in soil outside the canopy. This finding can be attributed to the toxic effect exerted by Cr^{6+} on microorganisms in low-organic C soil [27]. There was an increase in enzymes activity with the addition of C substrates from tannery sludge up to 30 days, but this activity subsequently declined (after 60 days) as the available C was exhausted [28,29]). Thus, values for dehydrogenase activity in all the soils treated with tannery sludge and Cr^{3+} or Cr^{6+} reached similar values as the controls in 60 days except for cultivated soils and soils outside the canopy treated with Cr^{6+}. In both these soils, the dehydrogenase activity still remained 57 and 75% (respectively) less than the controls after 180 days. These results suggest that adding Cr^{6+} alone to low-organic-C soils will affect the soil microbial activity for long time (more than 180 days). The addition of sludge will protect the microorganisms after 60 days incubation.

The increases in microbial activity may be ascribed to the easily biodegradable organic matter included in the tannery sludge, which stimulates the growth of soil microorganisms, increasing the activity of dehydrogenase enzyme up to 30 days incubation in all the soils. The decrease may be attributed either to a possible decrease in the level of microorganisms [30], in particular of the fraction introduced with the tannery sludge which could be less competitive than the endogenous microorganisms, or to exhaustion of easily biodegradable organic matter introduced into the soil with tannery sludge.

The inhibition effect of Cr^{3+} plus tannery sludge on dehydrogenase activity in cultivated soils and under the canopy soils, respectively, suggests that soluble organic ligands in cultivated soils or the addition of organic matter from tannery sludge may facilities the oxidation of Cr^{3+} to Cr^{6+} [31]. Furthermore, Milacic and Stupar [32] reported that in tannery-waste-amended soils, 0.45% of total chromium added was oxidized in sandy soils and 1.1% in clay soils. The initial increase of Cr^{6+} was measured during the first 5 months after the tannery sludge application. Care should be taken with soils low in organic matter and high in manganese (IV), where oxides are able to oxidize chromium.

4.4. Nitrogen mineralization

Soils outside the canopy showed a similar high inhibition of nitrification with Cr^{6+} added alone or Cr^{6+} plus tannery sludge. The higher inhibition of nitrification in cultivated soils treated with Cr^{6+} plus tannery sludge compared to Cr^{6+} added alone suggest that the pH of the soils and tannery sludge produce a high concentration of ammonia (NH_3) and since Nitrobacter is more sensitive to NH_3 toxicity than is Nitrosomonas. This can lead to an accumulation of NO_2^- and might be lost of N through chemical reactions involving NO_2^- [33,34]. Inorganic N mineralization in the three soils was not affected by Cr^{6+} or Cr^{6+} plus tannery sludge. These findings are in agreement with those reported in the literature that nitrification is a more sensitive parameter than N-mineralization, because a small number of bacteria, the nitrifiers, are involved in the process [35].

The results from this study showed that nitrification is sensitive to Cr^{6+} added alone in soils outside the canopy and cultivated soils from 30 to 120 days incubation and to Cr^{6+} plus tannery sludge from 30 to 180 days in soils outside the canopy and from 30 to 120 days in cultivated soils. The highest values of inhibition were found in soils outside the canopy treated with Cr^{6+} plus tannery sludge, followed by Cr^{6+} added alone. Thus, after 180 days incubation, in soils outside the canopy treated with Cr^{6+} plus tannery sludge the values of NO_3^- reached 40% of the values of NO_3^- for the control (with tannery sludge).

The inhibition and stimulation of nitrification throughout the incubation in soils under the canopy treated with Cr^{6+} alone or Cr^{6+} plus tannery sludge might suggest that Cr^{6+} may affect the soil microbial biomass and subsequently stimulation or inhibition of inorganic mineralization. Thus, fungal mycelia have been shown to be more sensitive than bacteria to chromium pollution [36].

There are scarce data to conclude whether the nitrification is sensitive to Cr stress (either Cr^{6+} or Cr^{3+}) because its power as a soil bioassay is low, duo to of the high variability of the end point between uncontaminated soils.

4.5. Mineralization models

The zero-order and linearized power function provide a good fit to most of the data for N mineralization. These results might suggest that tannery sludge and type of soil (i.e. under de canopy soils) might provide a similar pool of mineralizable N or tannery sludge contained a great amount of recalcitrant organic matter fraction and the incubation time were not enough to assess a decrease of these pools [37,38,40]. Similarly, zero-order kinetics can hold for extend of period at high temperature (180 days, 25 °C) [42] up to 25 °C, 20 weeks, [43] up to 20–35 °C, 26 weeks).

The values of potentially mineralizable N (N_0) of first order model in outside the canopy soils treated with tannery sludge and mixed with Cr^{3+} and Cr^{6+} (116.90–157.92 mg kg^{-1} N) were in the range reported in the literature (97–194 mg kg^{-1}) [44,45]. However, the values of N_0 in this work were obtained at lower moisture (40% WHC) and lower temperature incubation (25 °C) than those suggested by Wang et al. [46] (55–65%WHC and 35 °C). Further studies are necessary to evaluate N_0 and the mineralization rate constant (k) under conditions suggested by Wang et al. and Benbi and Richter [46,47].

The observed good fit of linearized power function to the data of cumulative CO_2-C evolved from under canopy soils might suggest that a considerable amount of soluble mineral C or a labile fraction could be important as mineralizable C source, i.e. free carbohydrates derived from decaying plant material [48]. Voroney et al. [49] reported that soil organic matter comprises three fractions which decompose at different rates: a readily available fraction, fraction degraded at much slower rate and a fraction highly resistant to degradation. A minimum of two organic C fractions are considered to significantly contribute towards C mineralization first-order model. Riffaldi et al. [50] reported that among 14 different agricultural soils, the potentially mineralizable C was related negatively to organic C. A possible explanation for the fitting of linearized power function in under the canopy soil is that the highest organic C in the soil had a relatively low recalcitrant organic matter with highest labile organic C.

The potential mineralizable C (C_0) for the decomposition of organic C in all the treatments in cultivated and outside the canopy soils (except controls and tannery sludge plus Cr^{3+}) ranged from 69.5 to 1243.2 mg C kg^{-1} soil and from 39.6 to 481.8 mg C kg^{-1}, respectively. The C_0 values are low compared to agricultural soils and sewage sludge treated soils (142–1861 mg kg^{-1} soil) [51,52].

The low values of C_0 in soils treated with Cr^{6+} or Cr^{3+} alone and the high values on treatments with tannery sludge reflects the mineralizable C that is correlated with total C and microbial biomass contained in the soil and/or supplied by tannery sludge [53].

The presence of Cr^{6+} alone in both soils (cultivated and outside the canopy) shows a lower potential mineralization compared to treatments with tannery sludge plus Cr^{6+} or Cr^{3+} alone. The low values of C_0 in soils amended with Cr^{6+} alone reflect that microbial activity was deteriorated as was shown by CO_2-C evolved and dehydrogenase activity (Figs. 1 and 2). However, C_0 did not reflect the actual available C substrate in treatments with tannery sludge plus Cr^{6+}.

It was not possible to identify various phases involved in decomposition of organic matter of tannery sludge added to cultivated and outside the canopy soils, because few determination of CO_2-C evolved were included in the experiments of this study.

Measurement of dehydrogenase activity seems to be a useful tool in assessing the harmful effects of Cr on the overall activity of microbial population in the three semi-soils exposed for an extended period.

Finally, using the tannery sludge application to fertilized semi-arid soils increased C and N mineralization and did not affect biological functioning. However, the accumulation of Cr^{3+} in the topsoil and phytoavailability to pioneer plants should be considered in order to avoid harmful effects on the natural reserves, especially in the long term [54].

5. Conclusions

The results of this study suggest that: Application of Cr^{6+} alone to all the soils inhibited the CO_2 production rate and dehydrogenase activity in the following order: cultivated, under and outside the canopy for CO_2 production rate; and outside-canopy, cultivated and under-canopy soils for dehydrogenase activity.

Addition of tannery sludge to Cr^{6+}-amended soils significantly reduce the inhibition of CO_2 production and dehydrogenase activity in the order: cultivated, under and outside the canopy soils.

Addition of Cr^{6+} alone inhibited the nitrification in soils outside the canopy and cultivated soils from 30 to 120 days.

The inhibition of nitrification in soils outside the canopy and cultivated soils increased with the addition of tannery sludge plus Cr^{6+} from 30 to 180 days and from 30 to 120 days, respectively. Soils under the canopy, amended with the same treatment, did not show a constant effect on nitrification throughout the incubation time.

Cr^{3+} added alone or Cr^{3+} plus tannery sludge added to the three soils had no specific effect on the microbial activities (CO_2 production or dehydrogenase activity) or N-mineralization.

In the present study, measurements of dehydrogenase activity was shown to be the best tool in assessing the harmful effect of Cr^{6+} and Cr^{6+} plus tannery sludge in the three semi-arid soils exposed to Cr for a extended period of time.

Most of the data for N mineralization was best fitted to zero-order and linearized power function. First-order model described the nitrogen mineralization in outside the canopy soils treated with tannery sludge plus Cr^{6+} or plus Cr^{3+}.

Cumulative CO_2-C from under the canopy soils with all the treatments was described by linearized power function and cultivated and outside the canopy soils by first-order model. The potential mineralizable C (C_0) showed low values in both soils treated with Cr^{6+} added alone.

Further studies are necessary to evaluate the role of Cr in soil microbial health in natural environment experiments where more parameters are involved in Cr cycling, including long periods of drought and short rainy seasons in the natural ecosystem.

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