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The Use of Titanium Shavings as a Fertilizer Alternative for Maize Production

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INTRODUCTION. – Industrial leather processing involves a series of unit operations that can be classified into three groups: i) pretanning operations, which clean the hides or skins; ii) tanning, which permanently stabilizes the skin or hide matrix; and iii) post-tanning and finishing operations, where aesthetic value is added (THANIKAIVELAN *et al*., 2004). At each stage, various chemicals, such as sodium hydroxide, sodium hypochiorite, enzymes, lime, chlorides, sulphuric acid, formic acid, ammonium salts, kerosene, and other compounds are used and a variety of materials are expelled as liquid effluents and solid wastes (CABEZA *et al*., 1998). One ton of wet salted hides yields 200 kg of leather, along with about 250 kg of tanned solid waste and about 350 kg of nontanned waste (ALEXANDER *et al*., 1991). About 75% of the solid waste is produced when the tanned hide is shaved to a uniform thickness. These shavings are small particles, in a variety of shapes, mainly consisting of collagen cross-linked with metal complexes (SIMENOVA and DALEV, 1996).

The most widespread tanning method is chrome tanning, in which light and inexpensive leathers of high thermal and bacterial resistance are produced using basic chromium sulphate as the tanning agent. Although chromium is a perfect tanning agent in terms of leather performance, three negative attributes pose serious challenges to continued reliance on Cr-tanning: i) it is a limited natural resource, ii) its safety record is cautionary and iii) uncontrolled emission can have a serious environmental impact (Haroun *et al*., 2006).

Recently, titanium has been proposed as a tanning agent, being abundant in nature, easily obtainable, non-toxic even in large doses and it

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does not play any natural role inside the human body. Moreover, it ensures a good quality of leather and a low risk of environmental contamination (PENG *et al.*, 2007). Titanium compounds in general have low solubility, thus once they accumulate in the soil during rock weathering and pedogenesis or following sludge application to soil, they are hardly leached (BRECKLE, 1991).

The leather tanning industry has a major relevance in the Italian economy, covering more than 50% of the leather production in Europe and more than 15% of the one in the world (MERIÇ *et al.*, 2005). The disposal of tanned leather waste is a serious problem, since tannery by-products may contain chromium and toxic organic elements or compounds. Disposal alternatives include soil application, clumping at sea, landfilling and inceneration (SÁNCHEZ-MONEDERO *et al.*, 2004). Among these, incineration and landfilling are the most frequent, but both treatments raise a range of environmental problems, and the potential for reutilization of the material has vanished.

The application of industrial organic wastes to agricultural land has received considerable attention in recent years, as it effectively disposes of waste products while recycling valuable

nutrients into the soil-plant environment (KARLEN *et al.,* 1995; ANTOLIN *et al.,* 2005). Information about crop production in conjunction with leather shavings disposal is not currently available. There is a great concern in regards to the application of shavings to soil, since, following CABEZA *et al.* (1998), they have a high concentration of N, a low C/N ratio (about 3) and their rapid mineralization may result in a ready and high availability of N to crops but also a high risk of N loss by leaching. Thus, composting of shavings could be a valuable alternative to direct application to soil, since the biological aerobic decomposition of the material degrades its labile organic matter to carbon dioxide (GO_2), water vapour, ammonia (NH_3), inorganic nutrients and stable organic material containing humic-like substances, resulting in a more balanced composition of the material, with a higher C/N ratio (DE BERTOLDI *et al.,* 1986).

The purpose of this study was to test the hypothesis that shavings and commercial fertilizer sources produce comparable maize yields. The hypothesis was tested in field trials by comparing the effect on maize yield and N uptake of leather shavings, compost obtained from them, a mixture of shavings and compost, manure and chemical fertilizer. Moreover, in order to evaluate the environmental risks of the application of such amendments, an experiment in semi-controlled field conditions was carried out, for the determination of N leaching, titanium uptake by the crop and its accumulation in the soil. In addition, since titanium shavings may be cross-contaminated by chromium salts utilized in the processing of leather, Cr uptake by the crop and accumulation in the soil were also determined.

MATERIALS AND METHODS. – The experiment was carried out in 2002 at the Department of Agronomy and Agroecosystem Management of the University of Pisa in central Italy (43° 40' N, 10° 19' E and 1 m above sea level). The climate is hot, humid Mediterranean with mean annual maximum and minimum daily air temperatures of 9.5 and 20.2° C respectively, and total annual precipitation of 971 mm, with 431 mm received from May through October (MOONEN *et al.,* 2001).

Four organic amendments and a control were compared in open and controlled field trials. Amendments were i) titanium-shavings at the rates of 15 (S15) and 30 t ha^{-1} dry weight (S30); ii) compost produced from titanium shavings at the rates of 15 (C15) and 30 t ha^{-1} dry weight (C30); iii) a mixture 1.2:1 of titanium-shavings and compost from titanium shavings at the rates of 15 (SC15) and 30 t ha^{-1} dry weight (SC3O); and cattle farmyard manure at a rate of 11 t ha^{-1} dry weight (M). Both experiments also included a control that received no amendments but was chemically fertilized. To avoid crop N shortage owing to manure application, also plots with manure were chemically fertilized, at a rate corresponding to about 2/3 of the estimated needs of a maize crop.

The average characteristics of organic amendments are reported in Tables 1 and 2.

The rate of 15 t ha^{-1} dry weight corresponds to the maximum level permitted by the current Italian legislation when soil pH ranges from 6 to 7.5. When pH is over 7.5, this level is increased to 22.5 t ha^{-1} (DL 27.1.1992 n. 99). Treatments at double level (30 t ha^{-1}) of shavings, compost and shavings plus compost were included in order to evaluate detrimental effects on plant growth and environment.

TABLE 1. – *Chemical composition of shaving, compost and manure. Values are expressed on a dry weight basis.*

		Shaving	Compost	Manure
Total nitrogen	%	14.4	2.7	2.7
Umidity	%	38.0	31.0	25.3
C/N	3.6	11.6	15.5	
Calcium	%	0.3	4.6	3.9
Soluble Chlorides	%	3.7	1.0	1.6
Chromium	mg kg^{-1}	15.4	4.2	12.1
Total phosphorus	g kg^{-1}	0.2	0.2	12.3
Potassium	%	0.2	0.5	3.5
Sodium	%	2.3	0.6	0.6
Organic matter	%	89.2	62.6	83.8
Titanium	g kg^{-1}	10.0	2.7	-

TABLE 2. – *Chemical characteristics of shaving. Values are expressed on a dry weight basis.*

Character	Unit	
Crude proteins	%	82.8
Lipids	%	1.5
Ash	%	8.4

The compost used derived from tannery shavings produced by a local company that were mixed with wheat straw and sawdust. The mixture was composted in the plant using a two-step process involving: first, turning of the feedstock every 7 days to promote aeration, and, second, mechanical mixing of the feedstock and collection after three months of stabilization. The final compost met the Italian legal standards for pathogenic microorganisms, organic trace elements, and heavy metals.

Daily weather data were obtained from a meteorological station within 100 m of the plot location. Air temperatures during maize cycle were close to the long-term average, while rainfall was over 40% higher (185 mm).

Experiment 1. – Eight treatments were arranged in the field in a randomized block design with three replications. The plot surface was 50 m^2 (10 x 5 m).

The research was carried out in a loam soil, whose main soil physical and chemical properties were 61.1% sand (0.05 mm < Ø < 2.00 mm), 28.5% silt (0.002 mm < 0 Ø 0.05 mm), 10.4% clay (Ø < 0.002 mm), pH 8.0, 19.0 g kg^{-1} organic matter (Lotti method), 8.9 g kg^{-1} total $CaCO_3$ (Scheibler method), 0.9 g kg^{-1} total nitrogen (Kjeldhal method), 36.6 mg kg^{-1} available P (Olsen method), 164 mg kg^{-1} available K ($BaCl_2$ + TEA method), 53.0 mg kg^{-1} Cr (Aqua Regia extraction and atomic absorption spectrometry) and 153.0 mg kg^{-1} Ti (Aqua Regia extraction and atomic absorption spectrometry). The preceding crop was durum wheat.

Amendments were surface applied in spring (2 May 2002) and incorporated with a mediumdepth ploughing (30 cm). Seedbed preparation was carried out prior to sowing by harrowing twice, once with a disc harrow, and the second with a rotating harrow.

Maize hybrid PR35P12 (Pioneer, FAO class 400) was seeded on 20 May 2002 at a rate of 8 plants per m^2 in rows spaced 50 cm apart. Weed control was performed by herbicides distributed at the stage 1 (collar of 4^{th} leaf visible) of the scale of HANWAY (1963). Manure and control plots were chemically fertilized at a rate of 180 kg N ha-1, as urea, (on 19 May 2002) immediately before seeding, and 100 kg ha^{-1} of P_2O_5 (as triple mineral phosphate) and 100 kg ha^{-1} of K_2O (as potassium sulphate) with the application of amendments. Maize crop was not irrigated.

At grain physiological maturity (24 October 2002) plants in 5 rn^2 area were cut at ground level and separated into leaves, stalks, cobs and grain. All plant parts were oven dried at 65°C to constant weight for dry weight determination. Plant samples were analyzed for nitrogen (microKjeldahl), titanium (Aqua Regia extraction and atomic absorption spectrometry) and chromium (Aqua Regia extraction and atomic absorption spectrometry) concentration and N, Ti and Cr contents were calculated by multiplying the N, Ti and Cr concentration by dry weight.

Experiment 2. – The research was carried out using 24 open-air containers of 100-L volume (0.25 m^2 area and 0.4 m height) where the eight treatments were arranged in a randomized block design with three replications. Containers were arranged in two rows of 12, spaced 10 cm, and were embedded in expanded clay to smooth daily fluctuations in soil temperature. Containers were filled with the same soil of the field experiment, tamped to about original soil bulk density, and were attached to a 5 cm rigid PVC drain that ended in a central collection facility.

Amendments were distributed on soil surface on 24 April 2002 and incorporated though a moderate hoeing. Maize seeding was carried out in seedling trays on 3 May 2002 and plants were transplanted in containers on 25 May 2002, at the crop stage 1 (collar of 4^{th} leaf visible) of the scale of HANWAY (1963). In each container two plants were planted, corresponding to a plant density of 8 plants m^2. Maize hybrid PR35P12 (Pioneer, FAO class 400) was utilized. Manure and control were chemically fertilized at a rate of 180 kg N ha^{-1}, as urea, 100 kg ha^{-1} of P_2O_5 (as triple mineral phosphate) and 100 kg ha^{-1} of K_2O (as potassium sulphate) on 23 May 2002.

During all maize cycle, irrigation was performed to satisfy the water demand of the crop. Containers were irrigated to field capacity, based on estimated water holding capacity of the soii, using a drip/trickle microirrigation system consisting in 2 compensating emitters per container at a rate of discharge of 2 L h^{-1} per emitter. Water regime consisted of daily irrigation replacing about 100% estimated crop evapotranspiration (ET). Crop ET was estimated as PET x kc, using the kc values calculated by DOORENBOS and PRUITT (1977). At 80 days from amendments distribution plots were irrigated to obtain percolation in order to evaluate the mineralization rate and to evidence the leaching risk of N.

Leachates from each container were collected during all maize cycle in a 20-L PVC tank. Five leachates occurred following five rainfall events (30 August, 18 and 24 September, 11 and 24 October 2002). Leachate volumes were measured and their N-NO_3, Ti and Cr concentrations were determined with an Orion ion analyzer model 502A (Orion Research Inc., Boston, MA, USA). The flow-weighted N-NO_3 concentration for the whole leaching period was calculated by summing up the N-NO_3 mass collected in the period divided by the total leachate volume collected in the period.

At grain physiological maturity the plants in each container were harvested. Plants were cut at ground level and separated into leaves, stalks, cobs and grain. Roots were separated from the soil by washing with water until they were totally clean. All plant parts were oven dried at 65°C to constant weight for dry weight determination. Plant samples were analyzed for nitrogen (microKjeldahl), titanium (Aqua Regia extraction and atomic absorption spectrometry) and chromium (Aqua Regia extraction and atomic absorption spectrometry) concentration and N, Ti and Cr contents were calculated by multiplying the N and Ti concentration by dry weight.

The balance of Ti and Cr in soil was determined by the difference between the metals applied and the metals taken up by the crop, estimated with the sum of the content in leaves, stalks, cobs and grain. Changes in soil metals storage were not determined by measuring changes in metals soil content, as differences would be difficult to assess after one year.

Data were statistically treated by ANOVA. Duncan's multiple range test was used to separate the means when the ANOVA F-test indicated a significant effect of the treatment (STEEL *et al.,* 1997).

RESŪLTS AND DISCUSSION. – *Experiment 1*. – Plant growth. - The effect of manure on plant growth was similar to fertilized control. All other amendments as well, except shavings, did not modify grain yield of field-grown maize plants compared to fertilized control, that ranged from 9 to 9.8 t ha^{-1} (Table 3). Shavings at 15 t ha^{-1} increased grain yield by 29% and at 30 t ha^{-1} by 42%. Similar increases were recorded for the other plant parts, so that the aerial plant part was 21% higher than the control with S15 and 30% higher with S30.

Mineral uptake. - Compared to fertilized control, shavings increased N concentration of leaves and grain only at the higher rate (by 24% and by 35%), while S15 and all the other amendments did not produce any significant change (Table 4). Conversely, N concentration of stalks and cobs was not affected by amendments.

Following the patterns of both dry weight and N concentration, N uptake of grain and cobs was significantly increased, compared to the control, by S15, S30 and SC30 and N uptake of the aerial plant part increased from about 130 kg ha^{-1} in control to 170 kg ha^{-1} in SC3O, to 190 kg ha^{-1} in S15 and to 230 kg ha^{-1} in S30 (Table 4).

Amendments affected neither the Ti and Cr concentration nor the uptake in any plant part (Table 5). Averaged over treatments, the Ti concentration was lowest in grain, intermediate in stalks and cobs, and highest in leaves. The Ti uptake was over two times higher in vegetative plant parts than in grain and, consequently, leaves and stalks accounted for about 70% of the Ti uptake of the aerial plant part, while grain accounted

TABLE 3. – *Experiment 1. Dry weight of leaves, stalks, grain and cobs of maize plant as affected by organic amendments.*

Treatment	Leaves	Stalks	Grain	Cobs
			t ha^{-1}	
Ctrl	3.1 a	6.4 ab	8.5 a	2.4 a
M	2.8 a	5.7 a	9.0 ab	2.5 ab
S15	3.2 a	7.5 cd	11.0 bc	3.0 ab
S30	3.4 a	7.8 d	12.1 c	3.2 b
C15	2.7 a	6.1 ab	8.9 ab	2.6 ab
C30	2.8 a	6.2 ab	9.2 ab	2.9 ab
SC15	2.8 a	6.8 bcd	9.6 ab	2.7 ab
SC30	3.0 a	6.7 abc	9.8 ab	2.6 ab

Values followed by the same letter are not significantly different at $P \leq 0.05$.

TABLE 4. – *Experiment 1. Nitrogen concentration and uptake of leaves, stalks, grain, cobs, and aerial plant part of maize as affected by organic amendments.*

Treatment	Leaves	Stalks	Grain	Cobs
		Nitrogen concentration (g kg^{-1})		
Ctrl	4.9 a	3.2 a	10.4 a 3.2 a	
M	5.2 ab	3.2 a	10.8 ab	3.2 a
S15	5.4 ab	3.9 a	11.9 ab 3.9 a	
S30	6.1 b	3.6 a	14.0 b 3.6 a	
C15	4.9 a	3.6 a	10.8 ab	3.6 a
C30	5.2 ab	3.5 a	11.1 ab	3.5 a
SC15	5.0 a	3.6 a	10.4 a	3.6 a
SC30	5.2 ab	3.9 a	12.0 ab	4.1 a
		Nitrogen uptake (kg ha^{-1})		
Ctrl	15.3 a	20.5 ab	88.4 a	7.8 a
M	14.2 a	18.4 a	97.2 ab	8.1 ab
S15	17.3 ab	29.3 c	130.9 c 11.8 c	
S30	20.7 b	28.1 c	169.4 d 11.5 c	
C15	13.2 a	22.0 ab	96.1 ab	9.4 abc
C30	14.6 a	21.7 ab	102.1 abc	10.1 abc
SC15	14.0 a	24.5 bc	99.8 ab	9.7 abc
SC30	15.6 ab	26.1 bc	117.6 bc	10.7 bc

Values followed by the same letter are not significantly different at $P \leq 0.05$.

for 14%. Averaged over treatments, the chromium concentration of all plant parts was very low and below the threshold limit of toxicity, reported to be in the range from 5 to 30 mg kg^{-1} (BORIES, 1997). Furthermore, the Cr uptake of all the organs and of the total aerial plant part was very low, not exceeding 10 g ha^{-1} (Table 5). Leaves and stalks accounted for about 77% of the total Cr uptake, while grain accounted for 10%.

Experiment 2. – Plant growth. - The biomass production of all the plants grown in containers was higher compared to those from the plants grown in open field conditions. This was expected, since in this experiment the plants were irrigated and border effect further increased values. Thus, averaged over all the treatments, grain yield was 15% higher in this experiment compared to the one recorded in the field.

Application of amendments to maize plants significantly affected plant growth and grain yield (Table 6). Compared to fertilized control,

TABLE 5. – *Experiment 1. Titanium and chromium concentration and uptake* of *leaves, stalks, grain, cobs, and aerial plant part of maize.*

	Titanium concentration mg kg^{-1}	Titanium uptake g ha^{-1}	Chromium concentration mg kg^{-1}	Chromium uptake g ha^{-1}
Leaves	5.3	15.8	0.3	4.4
Stalks	3.2	21.3	0.2	3.5
Grain	0.7	7.3	0.1	1.0
Cobs	3.3	9.0	0.2	1.4
Aerial plant part	2.4	53.4	0.2	10.3

whole plant and grain dry weight increased by 28% and 39% with shavings at 15 t ha^{-1}, while the higher rate of shaving did not further increase values. All other amendments did not produce any significant increase from control.

Mineral uptake. - The application of amendments had little effect on the N concentration of separate plant organs. The differences from control were lower than 2 g kg^{-1} for vegetative organs and about 3.5 g kg^{-1} for grain, with the highest N concentration recorded with the application of shavings (Table 7). All amendments except shavings did not modify N uptake compared to control. With S15, N uptake was higher by 82 kg ha^{-1} than control in grain and by 29 kg ha^{-1} in residu-

TABLE 6. – *Experiment 2. Dry weight of leaves, stalks, grain, cobs, and roots of maize plant as affected by organic amendments.*

Treatment	Leaves	Stalks	Grain t ha^{-1}	Cobs	Roots
Ctrl	3.5 ab	7.3 a	9.7 a	2.8 a	2.5 a
M	3.2 a	6.6 a	10.4 a	2.9 ab	2.8 a
S15	4.5 c	7.7 a	14.1 b	4.1 c	2.5 a
S30	4.8 c	7.8 a	14.3 b	3.8 c	2.1 a
C15	3.9 abc	7.3 a	10.5 a	3.7 bc	2.7 a
C30	4.2 bc	7.4 a	10.6 b	3.4 abc	2.8 a
SC15	4.1 abc	7.9 a	9.7 a	3.9 c	2.5 a
SC30	4.4 bc	7.4 a	10.7 a	4.0 c	2.8 a

Values followed by the same letter are not significantly different at $P \leq 0.05$.

TABLE 7. – *Experiment 2. Nitrogen concentration of leaves, stalks, grain, cobs, and roots of maize plant as affected by organic amendments.*

Treatment	Leaves	Stalks	Grain	Cobs	Roots
		Nitrogen concentration (g kg^{-1})			
Ctrl	5.0 a	3.4 a	11.1 a	3.4 a	4.8 a
M	5.5 ab	3.8 ab	11.8 ab	3.8 ab	4.7 a
S15	6.3 be	4.4 be	13.4 be	4.4 be	6.1 be
S30	7.1 c	4.8 c	14.6 c	4.8 c	6.3 c
C15	5.5 ab	3.8 ab	12.O ab	3.8 ab	4.7 a
C30	6.1 abc	4.1 abc	12.2 ab	4.1 abc	5.0 ab
SC15	5.9 abc	4.1 abc	12.0 ab	4.1 abc	4.9 ab
SC30	6.4 be	4.6 be	13.1 abc	4.6 be	5.7 abc

Values followed by the same letter are not significantly different at $P \leq 0.05$.

als, while with S30 it was higher by 102 kg ha^{-1} in grain and by 38 kg ha^{-1} in residuals (Fig. 1).

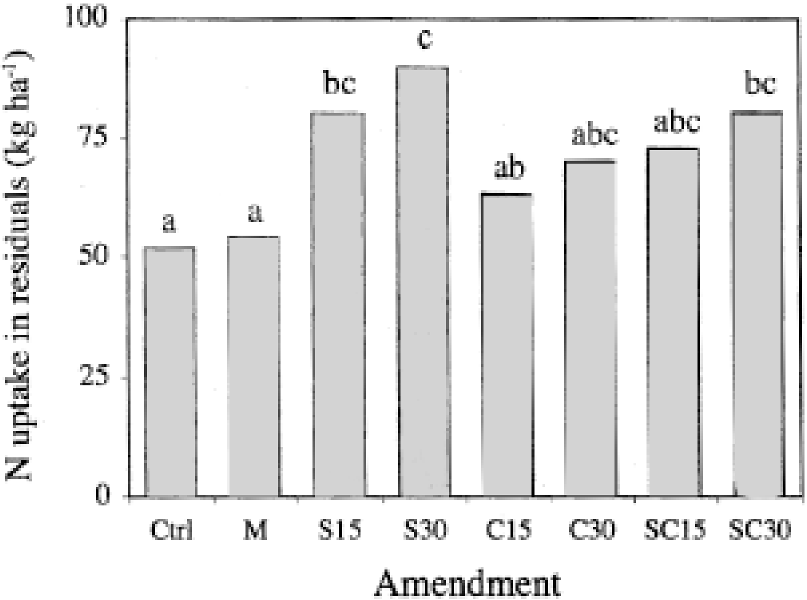

FIG. 1. - Experiment 2. Nitrogen uptake in grain (up) and in residuals (down) of maize plants as affected by organic amendments

TABLE 8. – *Experiment 2. Titanium and chromium concentration and uptake of leaves, stalks, grain, cobs, roots and whole maize plant.*

	Titanium concentration mg kg^{-1}	Titanium uptake g ha^{-1}	Chromium concentration mg kg^{-1}	Chromium uptake g ha^{-1}
Leaves	5.3	21.7	1.5	6.0
Stalks	3.2	23.6	0.5	3.8
Grain	0.7	8.0	0.1	1.1
Cobs	3.2	11.3	0.5	1.8
Roots	51.9	133.9	6.2	15.9
Whole plant	6.9	198.5	1.0	28.7

The amendments did not affect either the concentration or the uptake of Ti in any plant part (Table 8). Averaged over treatments, the Ti concentration was lowest in grain, intermediate in stalks, cobs and leaves, and highest in roots. As a consequence of both Ti concentration and dry matter yield, Ti uptake was low in grain and cobs (8-11 g ha^{-1}), intermediate in leaves and stalks (22-24 g ha^{-1}), and high in roots (134 g ha^{-1}). Thus, roots retained the highest proportion of the total Ti taken up by the plant (67%) and grain the lowest (4%).

Similarly to Ti, Cr concentration of all plant parts was not affected by the amendments (Table 8). Averaged over treatments, values were very low and below the threshold limit of toxicity (5-30 mg kg^{-1}), but in roots values were higher than in the other plant organs. As well as concentration, also Cr uptake was unaffected by the treatments and values were very low. Roots retained the higher proportion of the total Cr taken up by the plant (56%), while grain accounted for only 4%.

Titanium, chromium and nitrogen leaching. - The leachate volume obtained in the whole cultural period in consequence of both irrigation and rainfall was not significantly affected by the amendment applied, averaging 205 L m^2. Six drainages occurred in the period 19 July - 24 October, but most of the drainage (over 50%) occurred following two major rainfall event, on 24 September and 11 October (results not shown).

No Ti and Cr leaching loss were recorded in this experiment, as leachate samples had Cr and Ti concentration below the analytical detection limit of the instrument.

The concentration of N-NO_3 in leachates tended to decrease with time from about 70 mg L^{-1} on 19 July, averaged over all treatments, to 3 mg L^{-1} on 24 October (Fig. 2). No statistically significant difference among the treatments was recorded within each leaching event, except for the ones on 18 and 24 September. In the former, the $N\text{-}NO_3$ concen-

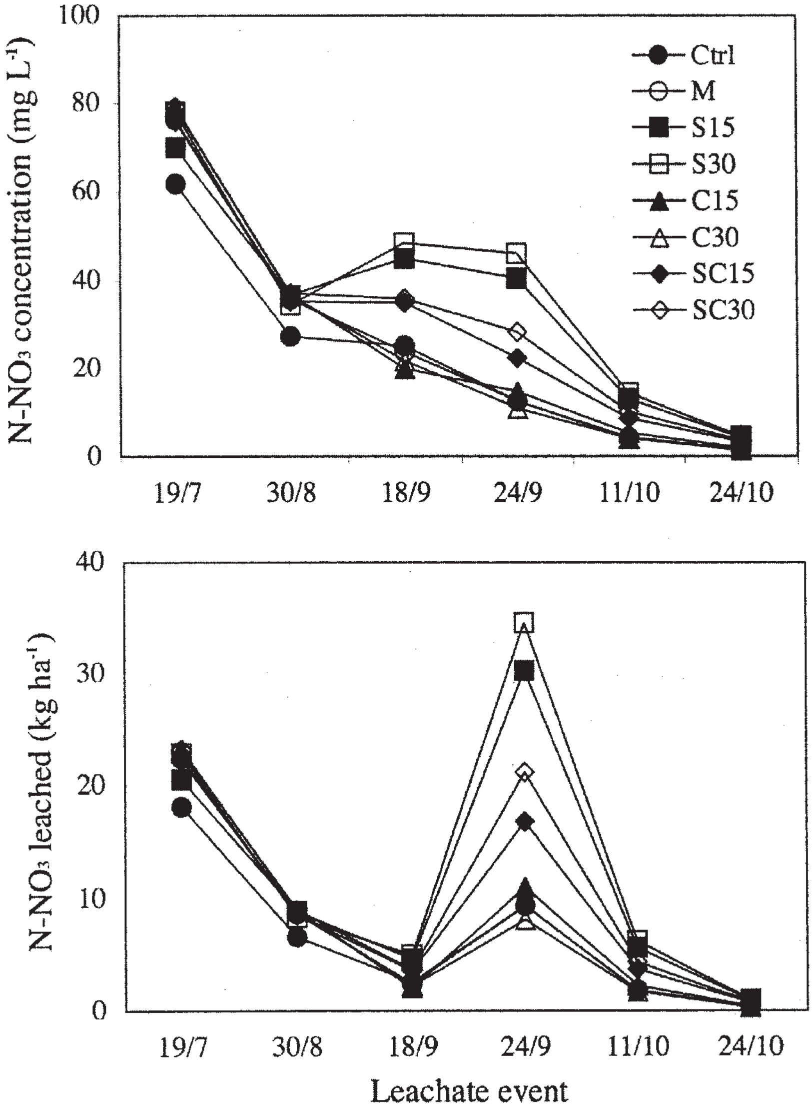

FIG. 2. - Experiment 2. Nitrogen concentration (up) and N mass (down) in leachates during maize cycle as affected by organic amendments.

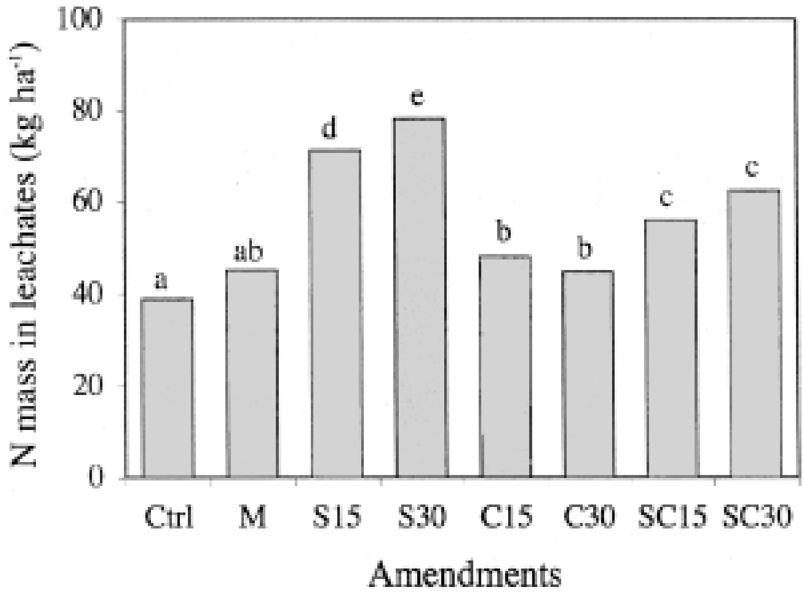

FIG. 3. - Experiment 2. Nitrogen mass in leachates from maize crop during the whole leaching period as affected by organic amendments.

tration in leachates was 41% higher in SC15 and SC30, compared to control, and 86% higher in S15 and S30; in the latter it was 102% higher in SC15 and SC30 and 245% higher in S15 and S30.

Following the pattern of both leachate volume and N-NO_3 concentration, the mass of leached N-NO_3 in the whole cultural period differed from control only in the S and SC treatments (Fig. 3). Compared to control, leached N increased by 17 kg ha^{-1} with SC15 and by 30 kg ha^{-1} with S15. Doubling the level of shavings and of the mixture of shavings and compost increased the amount of leached N by over 7 kg had. The differences among the treatments resulted mainly from the leachate event on 24 September, when N-NO_3 mass from SC15 and SC30 were over 70% higher than control, manure, C15 and C30, and the ones from S15 and S30 were over 200% higher (Fig. 2).

The time trend of the leaching data indicates that the timing of the release of available N from amendments was not synchronized with maize N demand. Amendments released mineral N during the entire maize cycle. But, while by the first four months until anthesis the uptake of N by the crop was consistent, after anthesis the uptake of N declined, probably because the crop had already attained its maximum size. From

TABLE 9. – *Experiment 2. Balance of titanium in soil as affected by organic amendments.*

Treatment	Amendment	Plant uptake* kg ha^{-1}	Balance**
Ctrl	-	0.06	-0.06
M	0.022	0.05	-0.03
S15	150.0	0.07	149.9
S30	300.0	0.08	299.9
C15	40.5	0.06	40.4
C30	81.0	0.07	80.9
SC15	100.2	0.07	100.1
SC30	200.4	0.07	200.4

* Aerial plant part only. ** Soil storage, error.

anthesis to maturity over 40% of the total N leaching of amendments occurred.

Balance of titanium, chromium and nitrogen in soil. - The balance of Ti in soil was carried out by determining the differences between the input of the metal through the amendments and the output by the uptake of the aerial plant part of the crop and by leaching (Table 9). Titanium content of roots was not included in the uptake, since roots remain in the soil. The load of Ti in the soil following amendment application increased from manure (22 g Ti ha^{-1}) to C15, C30, SC15, SC30, S15, and S30 (300 kg Ti ha^{-1}). The amount of the Ti taken up by the plants was negligible and was not affected by the treatments, averaging 65 g ha^{-1} and leached Ti was null. Thus, the balance practically reflects the quantity of Ti distributed with the amendments. As a consequence, with the distribution of shavings at 30 t ha^{-1}, the Ti concentration in the top layer of soil (0-50 cm) would increase from 153 mg kg^{-1} at the beginning of the experiment to 213 at the end.

Therefore, a large application of shavings will increase total soil Ti, but not necessarily the plant available portion of it, since Ti in shavings is bound to functional groups of collagen proteins, whose solubility are at least in part controlled by organic matter decomposition and the resultant soluble organic carriers of metals (SINGH and AGRAWAL, 2008). Following MCBRIDE (1995) trace metals bioavailability in soil is also dependent on the form of organic matter, i.e. soluble (fulvic acid) or insoluble (humic acid). With stabilization of organic matter decomposition rates, as in the case of composting, the level of soluble organic matter reduces, leading to a reduction in the bioavailability of metals (Korboulewsky *et al.,* 2002).

The amount of Cr distributed to the soil varied with the amendment applied (Table 10). It is noticeable that in the plots amended with manure the soil was loaded with 133 g Cr ha^{-1}. The lowest value of Cr upload corresponds to C15 (63 g ha^{-1}) and the highest to S30 (462 g ha^{-1}). The plant Cr uptake was very low for all the amendments tested, never exceeding 16 g ha^{-1}. The balance of Cr in the soil consequently varied according to the amendment, ranging from -10 g ha^{-1} for fertilized control to 446 g ha^{-1} for S30. The Cr loading rate in the soil, however, is not high enough to produce a significant variation in the concentration of Cr in soil. The load of 450 g Cr ha^{-1} would increase the Cr concentration in the soil recorded at the beginning of the experiment from 53 to 53.1 mg kg^{-1}.

The current environmental regulation in Italy poses no limit to Cr and Ti concentration in the sludge and in the soil. In the USEPA regulations, it is suggested that particular attention should be given to the application loading of chromium on the land and not the concentration of Cr in the sludge (Chaney *et al.,* 1997). The cumulative limit for Cr is 3000 kg ha^{-1}, which is far higher than the higher Cr loading rate applied in this research.

The amount of leached N plus N taken up by the crop exceeded the amount of applied N only in the fertilized control by about 30 kg N ha^{-1}. Native soil N present in the soil is the likely source for this unaccounted N. Conversely, for all the other amendments, recovered N was

Table 10. – *Experiment 2. Balance of chromium in soil as affected by organic amendments.*

Treatment	Amendment	Plant uptake* g ha^{-1}	Balance**
Ctrl	-	10.1	-10.1
M	133.1	10.1	123.0
S15	231.0	14.0	217.0
S30	462.0	16.1	445.9
C15	63.0	13.5	49.5
C30	126.0	11.7	114.3
SC15	154.6	13.8	140.8
SC30	309.2	12.9	296.3

* Aerial plant part only. ** Soil storage, error.

TABLE 11. - *Experiment 2. Balance of nitrogen in soil as affected by organic amendments.*

Treatment	Amendment and/or fertilizer	Leaching	Whole plant uptake	Balance*
		kg ha-1		
Ctrl	180	39.0	170.8	-29.7
M	477	45.2	189.4	242.4
S15	2160	71.1	284.2	1804.7
S30	4320	78.2	312.7	3929.1
C15	405	48.0	201.4	155.6
C30	810	44.8	213.8	551.5
SC15	1362	55.9	200.7	1105.5
SC30	2724	62.4	236.2	2425.5

* Soil storage, gaseous losses, error.

lower than applied N. The amount of unaccounted N, likely to be either denitrified, volatilized or stored in the soil, increases from 150 kg ha^{-1} of Cl5 to 3900 kg ha^{-1} of S30 (Table 11). We have not measured denitrified and volatilized N, thus we can't precisely assess the amount of N stored in the soil.

CONCLUSIONS. – The results of this study demonstrated that Ti shavings, compost from shavings and the mixture of both could substitute mineral fertilization of maize, since all amendments provided the same yields and eventually higher (shavings) as inorganic fertilizer and fertilized manure. Moreover, soil application of Ti shavings is an effective alternative method of disposal of an organic material that has a considerably lower environmental impact than that of chromium shavings.

Among shavings amendments, the higher maize grain yield was recorded with shavings at 15 and 30 t ha^{-1}. The positive effect of S15 and S30 in increasing plant growth is due to the high release of available N. The high rate vs. the low rate of shavings had no effect on dry matter yield, but increased the N uptake in the whole plant and grain, suggesting a luxury consumption of N and an improvement of grain quality. Manure, although chemically fertilized, was not able to increase grain yield of maize, compared to control.

The amendments released mineral N during the whole crop cycle, so the N leaching risk become consistent about five months from application, when the crop had attained its maximum size and the uptake of N declined. In addition, the N leaching risk was more severe with shavings and shavings and compost at the higher amendment rate than at the lower one. Thus compost at the low level is the best choice to reduce the N leaching risk. However, rainfall recorded in the present research during maize cycle was particularly high, compared to the normal amount, leading to high leaching losses of N in all treatments. Consequently, the results of the present work do not allow for a conclusive consideration to be drawn.

With respect to heavy metal composition, our study showed that the uptake of Ti and Cr by maize was very low and was not modified by the amendment applied. Moreover, the highest concentration of both metals was in the roots, whereas it was very low in grain, which indicates a restricted translocation from the vegetative to the reproductive organs. Consequently, there is no clear evidence of health hazard for either Ti or Cr in food stuff.

Conversely, the application of shavings and compost greatly increased total Ti concentration in the soil, while total Cr concentration was little affected. As the bioavailability of Ti in the soil may increase owing to long-term use, it would be useful to develop and test a soil extractant which would accurately predict plant metal uptake from soil in order to ascertain whether additional sludge could be applied to land.

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SUMMARY. – Application of leather shavings to agricultural crops may represent an effective disposal alternative, providing a good source of plant nutrients. The effect of shavings, compost obtained from them, a mixture of shavings and compost, manure and chemical fertilizer on maize was studied in field and in controlled environment trials. Shavings, compost and the mixture of shavings and compost were applied at 15 and 30 t ha^{-1} dry weight. Shavings at both rates increased grain dry weight and N uptake by over 45% compared to fertilized control, owing to the high release of available N. Conversely, all other amendments did not produce any significant increase. The uptake of Ti and Cr by maize plants was very low, never exceeding 80 g Ti ha^{-1} and 14 g Cr ha^{-1}, and was not modified by all amendments. Leached N increased by 17 kg ha^{-1} with SC15 and by 30 kg ha^{-1} with S15, compared to control. Doubling the level of shavings and of the mixture of shavings and compost increased leached N by over? kg ha-1.