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## Research Article

# Adsorption and Sequestration of Dissolved Carbon and Nitrogen from Carbonated Urine to Mineral Soils

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## Abstract

**Background and Objective:** The CO<sub>2</sub> contributes more than 60% to global warming because of its huge emission amount. The CO<sub>2</sub> could be absorbed into urine or aqueous solutions and could be used as fertilizer. The bicarbonate from these new fertilizers can be deposited as carbonated minerals in the subsoil layers of alkaline soils. The aim of this study was to use agricultural land as a sink for CO<sub>2</sub> after being absorbed in urine. **Materials and Methods:** The application of raw or carbonated urine and urine bubbled with diesel exhaust from a tractor has been studied in relation to the adsorption of C and N in two agricultural soils (loam and silty-clay-loam). Differences between soil-solution treatments were determined using ANOVA with a Bonferroni multiple-comparison test. Soil-chemical properties were examined with linear regression. **Results:** The effect of carbonated urine and urine was similar. The adsorption of salts, ammonium-N and dissolved organic carbon (DOC) to soils increased with the initial urine solution concentration and can be described by a linear approach. The total-N (TN) and organic carbon (OC) contents in soils can be described by a non-linear (square-root initial concentration) model. A parabolic approach showed a good fit to the inorganic carbon (IC) data with a maximum content for soils treated with dilution higher than 1:1 urine-water. **Conclusion:** The comparison of the results of the adsorption experiments with TN and total-carbon (TC) content in soils indicated that the fertilization with urine or carbonated urine after CO<sub>2</sub> absorption, could serve as a method for sequestration of C and N from greenhouse gases in the soils.

**Key words:** Urine, dissolved carbon dioxide, diesel exhaust, soil-adsorption, organic carbon

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**Competing Interest:** The author has declared that no competing interest exists.

**Data Availability:** All relevant data are within the paper and its supporting information files.

## INTRODUCTION

Chemical fertilizers based on nitrogen, phosphorus and potassium (N, P, K) are the main source of crop nutrients for agriculture. However, the fertilizer industry significantly contributes to climate change and global warming. While elevated CO<sub>2</sub> concentrations may benefit crop growth and hence, boost crop yields, it could also aggravate dryness in arid regions<sup>1</sup>. Thus, economically and environmentally, it would be desirable to find technical solutions enabling the use of alternative sources of fertilizers and effective strategies of agricultural water management to face future climatic changes. To improve future crop production, Li *et al.*<sup>2</sup> suggested that the combination of irrigation plus fertilizer NH<sub>4</sub>HCO<sub>3</sub> and elevated CO<sub>2</sub> concentration can have an overall beneficial effect on improving water-use efficiency and grain yield in spring wheat.

Other alternatives, such as nutrients from municipal wastewater and some industrial waste water as olive oil wastewater (OMW) or livestock wastes as poultry litter (W) become key for the future of resource efficiency related to water and nutrient reuse in agriculture and sustainable wastewater management. Thus, urine alone or mixed with OMW could act as NPK-fertilizer Aguilar<sup>3</sup>, being a resource of dissolved carbon and nitrogen (DCN) for the soil and alternative to chemical fertilizer<sup>4</sup>.

Urea as a reducing agent has been investigated in detail for about 10 years to reduce NO<sub>x</sub> emissions from automotive diesel engines<sup>5</sup>. Thus, urine-N alone or mixed with OMW and W has been used to reduce the emissions from a diesel tractor, improving the absorption of greenhouse gases such a CO<sub>2</sub> and NO<sub>x</sub> from diesel exhaust<sup>6</sup>. Moreover, ammonia (NH<sub>3</sub>) released in urine solutions can be used to capture CO<sub>2</sub> gas and produce ammonium bicarbonate, Aguilar<sup>7</sup>, which in alkaline soils can be neutralized by exchange bases, such as Ca<sup>2+</sup> and Mg<sup>2+</sup> and precipitated in carbonate form Lee and Li<sup>8</sup>. In short, the ammonium bicarbonate from hydrolysed urine and carbonated urine from CO<sub>2</sub> absorption or diesel engines could be a resource of C and N for the agricultural soils.

This study examines the relationship of DCN urine concentration to retention patterns in soils in order to determine whether the soil irrigation-fertilization with urine or carbonated urine could serve as a method for N and C sequestration in agricultural soils.

## MATERIALS AND METHODS

Two different texture soils (loam and silt-clay-loam) from the farmlands of Granada (Southern Spain) were used for this

study. The characteristics of both soils were described in Aguilar<sup>9</sup>. The OMW collected from St. Anthony oil mill of Viznar (Granada, Spain) in January, 2014, had a pH of 4.1, EC of 12 dS m<sup>-1</sup>, K-8 g L<sup>-1</sup> and total polyphenols- 3.2 g L<sup>-1</sup>. The W had 3.1% of total N content and 26% of total C content.

**Preparation of DCN solutions:** The urine used in the experiments was a mixture of both male and female urine stored 10 days until complete hydrolysis<sup>10</sup>. The collected urine sample was divided among several 2 L bottles. Samples of 1 L of hydrolysed urine with the addition of 0 or 20 mL OMW, 1 g W and (20 mL OMW+1 g W) in volume, respectively, were prepared in brown bottles with 2 replications/treatment. Half of the samples were bubbled with CO<sub>2</sub> from a gas bottle to decrease the pH to around 7.2 and stored in the daylight in the laboratory for 3 months.

Other samples of hydrolysed urine with the addition of 0 or 10 mL OMW in volume, respectively, were prepared. Half bottles were bubbled for 2 h a day for 3 consecutive days with fumes from the exhaust pipe of a tractor to decrease the pH to around 8.2 and stored in the daylight in the laboratory for 6 months.

The chemical composition (pH, electrical conductivity (EC), inorganic carbon (IC), organic carbon (OC) and N-NH<sub>4</sub> contents of these stock DCN solutions were given in Table 1. The solutions treated with CO<sub>2</sub> were significantly of lower pH and higher EC, IC and ammonium-N in relation to non-treated solutions (p<0.05 according to Tukey's test), whereas the exhaust treatment only slightly decreased the pH and ammonium-N.

**Experimental procedure:** The general method used to establish the soil-adsorption characteristics of a certain chemical involves the equilibration of different solute concentrations with the soil under investigation and measuring the amount of adsorbed solute. A flow technique to produce adsorption isotherms was used for this study because the flow systems appear to approximate field conditions most closely<sup>11</sup>.

The initial mass (IM) isotherm establishes a linear relationship between the amount of adsorbed solute (RE) per soil mass (mg g<sup>-1</sup>) and the concentration of the initial solution Xi, also normalized for soil mass (mg g<sup>-1</sup>) according to the equation reported by Novdin *et al.*<sup>12</sup>:

$$RE = m \cdot X_i - b$$

This model was applied to urine-adsorption data recorded in this study.

Table 1: Chemical composition of urine mixtures (1 L) used as stock solutions for the adsorption experiments (n = 2)

Treatments	pH	EC (dS m <sup>-1</sup> )	IC (mg kg <sup>-1</sup> )	OC (mg kg <sup>-1</sup> )	N-NH <sub>4</sub> (mg kg <sup>-1</sup> )
A	8.74	22.8	1839	2529	3596
AC	7.45	30.6	3120	2549	4675
O	8.68	25.5	2035	2954	4018
OC	7.21	30.8	3176	2971	4563
W	8.70	25.6	2035	2954	4005
WC	7.15	31.1	3123	2965	4600
OW	8.60	26.6	2035	2954	4241
OWC	7.10	31.0	3176	2974	4427
TO	8.70	38.7	3770	1596	6808
TOG	8.26	36.4	3921	1615	5282
TA	8.67	28.2	2674	2494	4960
TAG	8.10	29.1	2943	3071	4340

Samples of treated urine and stocked 3 months, A: Urine, O: Urine with 20 mL OMW, W: Urine with 1g W, OW: Urine with 20 mL OMW+1 g W, AC, OC, WC, OWC: The same treatment as above but bubbled with CO<sub>2</sub> (carbonated urine), Samples of treated urine stored for 6 months, TO: Urine with 10 mL OMW, TOG: The same urine bubbled with diesel exhaust, TA: Urine, TAG: The same Urine bubbled with diesel exhaust

Twenty grams of air-dried soils was packed into glass filter units with a 9 cm paper filter in the bottom. The stock DCN solutions were diluted in volume with water to four urine concentrations (control: distilled water, A1-dilution 1:10 urine-water, A2-dilution 1:5 urine-water, A3-urine) in order to cover the range of adsorption reactions from raw urine to urine diluted 10 times as urine dilution from residual wastewaters. Duplicate samples of each soil were prepared for each treatment. Distilled water was used as control.

Packed soils received 5 mL of DCN solutions the first and second day and 10 mL on the 3rd day. The pH, EC, N-NH<sub>4</sub> and light absorbance at 250 nm (E<sub>250</sub>) were measured in solution samples collected before and after percolation through the soil column.

The pH was monitored using a pH/ion meter and EC using a conductivity meter (both Crison 2002 models). To estimate DN, the ammonium-N was analysed according to Nelson<sup>13</sup>. The E<sub>250</sub> was used to estimate DOC, following De Haan *et al.*<sup>14</sup>.

After the 3 days, the soils from each treatment were analysed for pH, EC, TN, OC and IC. The EC and pH were measured in a 1:5 soil/water suspensions. The percentage of OC and IC were estimated according to Heiri *et al.*<sup>15</sup>, by loss on ignition (LOI) at 550 and 950°C, respectively, applying the relationship indicated by Craft *et al.*<sup>16</sup>, OC = 0.4 LOI 550 and Dean<sup>17</sup>, IC = 0.273 LOI 950 and TN following Maher *et al.*<sup>18</sup>, using closed vessels in a hot water bath.

**Statistical analysis:** Differences between soil-solution treatments were determined using ANOVA with a Bonferroni multiple-comparison test. Soil-chemical properties were examined with linear regression. For all statistical analyses, statistical significance was established at p>0.05.

## RESULTS AND DISCUSSION

In the stock solutions (Table 1), carbonated samples had lower pH values and higher contents in IC and EC. Ammonium-N was higher for carbonated samples and lower for exhaust samples. This was because a lower pH increased ammonium-N due to NH<sub>4</sub> formation: NH<sub>3</sub>+H<sup>+</sup>→NH<sub>4</sub><sup>+</sup>. Plus carbonic acid itself can put some organic matter in solution increasing ammonium-N. Meanwhile, ammonium-N reduction in exhaust samples can be explained according to Koebel *et al.*<sup>5</sup>, because the NO<sub>x</sub> from diesel vehicles oxidizes the ammonia to nitrogen: 4 NH<sub>3</sub>+4 NO+O<sub>2</sub>→4 N<sub>2</sub>+6 H<sub>2</sub>O.

Sherlock and Goh<sup>19</sup> indicated that volatilization loss was 23% N applied in urine. Lowering the pH could be useful in basic soils to prevent the oxidation and volatilisation of ammonium-N above pH 7.0<sup>20</sup>.

The results of previous studies have shown that the addition of hydrolysed urine to soil resulted in the precipitation of part of the carbonate ion as CaCO<sub>3</sub> when the soil pH rose to 8.8, Kissel *et al.*<sup>21</sup>. Also at this pH between 75 and 90% of the phosphate could precipitate as struvite<sup>22</sup>. The carbonic urine solutions have the advantage over to urine because the pH solution (about 7.2) remained below those percentages, so that the precipitation of calcite, struvite and hydroxyapatite did not take place in these solutions but could take place in the urine solutions and all treated soil due to a rise in pH.

For both soils, the pH, EC, ammonium-N, DOC and TN levels of samples treated with urine, carbonated urine and diesel exhaust were higher than control (p<0.05). Only the raw urine increased the OC and TC loam soil contents. This indicated that the adsorption of ammonium-N, TN and DOC

Table 2: Main effect of urine dilution on loam soil parameters

Concentration	Solution		Soil					
	NH <sub>4</sub> (mg g <sup>-1</sup> )	DOC (mg g <sup>-1</sup> )	pH	EC (dS m <sup>-1</sup> )	TN (mg g <sup>-1</sup> )	OC (%)	IC (%)	TC (%)
Control	0.05 <sup>a</sup>	0.003 <sup>a</sup>	8.42 <sup>a</sup>	0.87 <sup>a</sup>	0.204 <sup>a</sup>	1.24 <sup>a</sup>	2.62 <sup>a</sup>	3.86 <sup>a</sup>
A1	0.48 <sup>b</sup>	0.038 <sup>a</sup>	8.49 <sup>b</sup>	0.94 <sup>a</sup>	0.262 <sup>b</sup>	1.28 <sup>a</sup>	2.76 <sup>b</sup>	4.04 <sup>b</sup>
A2	0.99 <sup>c</sup>	0.083 <sup>b</sup>	8.55 <sup>c</sup>	1.21 <sup>b</sup>	0.335 <sup>c</sup>	1.29 <sup>a</sup>	2.78 <sup>b</sup>	4.07 <sup>bc</sup>
A3	3.76 <sup>d</sup>	0.391 <sup>c</sup>	8.59 <sup>d</sup>	4.16 <sup>c</sup>	0.499 <sup>d</sup>	1.43 <sup>b</sup>	2.70 <sup>a</sup>	4.13 <sup>c</sup>
<b>Diesel exhaust</b>								
Control	0.05 <sup>a</sup>	0.003 <sup>a</sup>	8.42 <sup>a</sup>	0.87 <sup>a</sup>	0.204 <sup>a</sup>	1.24 <sup>a</sup>	2.62 <sup>a</sup>	3.86 <sup>a</sup>
A1	0.52 <sup>a</sup>	0.056 <sup>a</sup>	8.52 <sup>b</sup>	1.12 <sup>a</sup>	0.319 <sup>b</sup>	1.29 <sup>a</sup>	2.76 <sup>b</sup>	4.05 <sup>ab</sup>
A2	1.09 <sup>a</sup>	0.114 <sup>a</sup>	8.57 <sup>c</sup>	1.53 <sup>a</sup>	0.354 <sup>b</sup>	1.32 <sup>a</sup>	2.76 <sup>b</sup>	4.08 <sup>ab</sup>
A3	4.57 <sup>b</sup>	0.590 <sup>b</sup>	8.60 <sup>c</sup>	5.54 <sup>b</sup>	0.518 <sup>c</sup>	1.51 <sup>b</sup>	2.64 <sup>a</sup>	4.15 <sup>b</sup>

Different letters within a column indicate different levels of significance ( $p < 0.05$ ) according to Bonferroni's test, Control: Distilled water, A1: Dilution 1:10 Urine-water, A2: Dilution 1:5 Urine water, A3: Urine, adsorbed ammonium-N(NH<sub>4</sub>) and adsorbed organic carbon (DOC) were measured in solution, pH, electrical conductivity (EC), total nitrogen (TN), organic carbon (OC), inorganic carbon (IC) and total carbon (TC) were measured in soil

Table 3: Main effect of urine dilution on silt-clay-loam soil parameters

Concentration	Solution		Soil					
	NH <sub>4</sub> (mg g <sup>-1</sup> )	DOC (mg g <sup>-1</sup> )	pH	EC (dS m <sup>-1</sup> )	TN (mg g <sup>-1</sup> )	OC (%)	IC (%)	TC (%)
Control	0.1 <sup>a</sup>	0.004 <sup>a</sup>	8.42 <sup>a</sup>	1.45 <sup>a</sup>	0.21 <sup>a</sup>	1.94	3.47	5.41
A1	0.40 <sup>a</sup>	0.031 <sup>a</sup>	8.55 <sup>b</sup>	1.50 <sup>a</sup>	0.24 <sup>a</sup>	2.19	3.49	5.70
A2	0.79 <sup>b</sup>	0.126 <sup>b</sup>	8.53 <sup>b</sup>	2.07 <sup>b</sup>	0.36 <sup>b</sup>	2.20	3.51	5.68
A3	3.26 <sup>c</sup>	0.367 <sup>c</sup>	8.59 <sup>c</sup>	4.56 <sup>c</sup>	0.55 <sup>c</sup>	2.28	3.43	5.72
<b>Diesel exhaust</b>								
Control	0.1 <sup>a</sup>	0.003 <sup>a</sup>	8.42 <sup>a</sup>	1.45 <sup>a</sup>	0.21 <sup>a</sup>	1.94	3.47	5.41
A1	0.47 <sup>a</sup>	0.053 <sup>a</sup>	8.49 <sup>b</sup>	1.65 <sup>a</sup>	0.28 <sup>ab</sup>	2.03	3.57	5.60
A2	0.95 <sup>a</sup>	0.126 <sup>a</sup>	8.47 <sup>b</sup>	2.22 <sup>a</sup>	0.30 <sup>b</sup>	2.22	3.46	5.68
A3	4.07 <sup>b</sup>	0.546 <sup>b</sup>	8.58 <sup>c</sup>	5.65 <sup>b</sup>	0.418 <sup>c</sup>	2.24	3.44	5.68

Different letters within a column indicate different levels of significance ( $p < 0.05$ ) according to Bonferroni's test, Control: Distilled water, A1: Dilution 1:10 Urine-water, A2: Dilution 1:5 urine water, A3: Urine

Table 4: Effect of CO<sub>2</sub> gas and diesel exhaust on loam soil parameters

Concentration	Solution		Soil					
	NH <sub>4</sub> (mg g <sup>-1</sup> )	DOC (mg g <sup>-1</sup> )	pH	EC(dS m <sup>-1</sup> )	TN(mg g <sup>-1</sup> )	OC(%)	IC (%)	TC(%)
Control	0.05	0.003	8.42 <sup>a</sup>	0.87	0.20	1.24	2.62 <sup>a</sup>	3.86 <sup>a</sup>
G1	1.66	0.189	8.55 <sup>b</sup>	2.10	0.36	1.33	2.75 <sup>b</sup>	4.07 <sup>b</sup>
G2	1.83	0.152	8.54 <sup>b</sup>	2.10	0.37	1.34	2.75 <sup>b</sup>	4.09 <sup>b</sup>
<b>Diesel exhaust</b>								
Control	0.05	0.003	8.42 <sup>a</sup>	0.87	0.20 <sup>a</sup>	1.24	2.62	3.86 <sup>a</sup>
T1	2.32	0.311	8.59 <sup>c</sup>	3.15	0.41 <sup>b</sup>	1.43	2.71	4.13 <sup>b</sup>
T2	1.80	0.195	8.54 <sup>b</sup>	2.32	0.38 <sup>ab</sup>	1.32	2.74	4.06 <sup>ab</sup>

Different letters within a column indicate different levels of significance ( $p < 0.05$ ) according to Bonferroni's test, Control: Distilled water, G1: Urine, G2: Urine bubbled with CO<sub>2</sub>, T1: Urine, T2: Urine bubbled with diesel exhaust

increased with the initial urine-solution concentration for both soils, whereas OC increased only in loam soil with a lower content than in silt-clay-loam soil (Table 2, 3).

In treated soils, the pH rose over time, perhaps due to the production of NH<sub>3</sub> as a result of degradation and mineralization of nitrogenous organic compounds. The CO<sub>2</sub> acidity was neutralized by carbonates present in the soil, thus generating soluble calcium bicarbonate, which moved towards the lower horizons, where it again precipitated as calcium carbonate. The carbonate dissolution caused by carbonic acid could be neutralized by the carbonate precipitation due to the pH increase by the mineralization of

urea from urine and nitrogenous organic compounds. This study results agree with those of Overrein and Moe<sup>23</sup> and Aguilar<sup>3</sup>, who indicated that the pH of soil in the zone of urea or urine application attained a maximum pH of 8.8 as well as with those of Clark *et al.*<sup>24</sup>, who reported that a farming system with animal-manure applications had higher soil OC, soluble P and exchangeable K and pH.

The comparative effect of carbonated urine and urine was similar in the soils. There were no significant differences between untreated samples and those treated with CO<sub>2</sub> or diesel exhaust (Table 4, 5). However, the soil contents for all parameters studied pH, EC, NH<sub>4</sub>, DOC, TN, OC, IC and TC were

Table 5: Effect of CO<sub>2</sub> gas and diesel exhaust on silt-clay-loam soil parameters

Concentration	Solution		Soil					
	NH <sub>4</sub> (mg g <sup>-1</sup> )	DOC (mg g <sup>-1</sup> )	pH	EC(dS m <sup>-1</sup> )	TN(mg g <sup>-1</sup> )	OC(%)	IC (%)	TC(%)
Control	0.1	0.004	8.42 <sup>a</sup>	1.45	0.21	1.94	3.47	5.41
G1	1.37	0.187	8.56 <sup>b</sup>	2.64	0.38	2.20	3.48	5.68
G2	1.59	0.162	8.55 <sup>b</sup>	2.78	0.39	2.24	3.47	5.71
<b>Diesel exhaust</b>								
Control	0.1	0.004	8.42 <sup>a</sup>	1.45	0.21 <sup>a</sup>	1.94	3.47	5.41
T1	2.03	0.284	8.52 <sup>b</sup>	3.58	0.35 <sup>b</sup>	2.20	3.46	5.66
T2	1.63	0.199	8.50 <sup>b</sup>	2.77	0.31 <sup>ab</sup>	2.13	3.52	5.65

Different letters within a column indicate different levels of significance ( $p < 0.05$ ) according to Bonferroni's test, Control: Distilled water, G1: Urine, G2: Urine bubbled with CO<sub>2</sub>, T1: Urine, T2: Urine bubbled with diesel exhaust

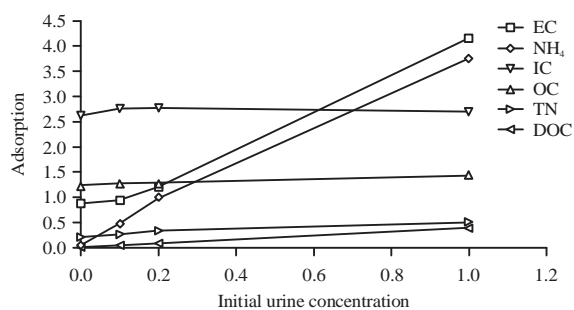


Fig. 1: Sorption to loam soil

slightly higher than in the control treatment. In agreement with Aguilar<sup>9</sup>, irrigation with water bubbled with CO<sub>2</sub> increased in OC (1.9% in loam and 2.5% in silt-clay-loam) in the soils, whereas, irrigation with urine resulted in sharper increases of OC in the soils (7% in loam and 13% in silt-clay-loam), TN (a mean of 80% in both soils) and IC (5% only in loam soil).

Carbonated urine increased OC (1-2%) and TN (2-5%) more than urine samples, but did not affect IC in either soil, whereas, the diesel-exhaust treatment increased soil IC (1-1.4%, respectively) but moreover produced a reduction of OC-(9-4%) and TN (14-19%). Exhaust fumes oxidize ammonia to nitrogen and destroy a small fraction of the organic matter of urine. That leads to versus control, urine increase more soil organic matter than diesel exhaust.

There was a significant discrepancy between the amount of added IC from stock solution and the amount of IC measured on the soil surfaces. In this case, 36-58 % of initial IC was measured as IC in loam soil. These results agreed with McCracken *et al.*<sup>11</sup>, who comparing soil solutions and measuring OC retention, indicated that only 32-46% of the DOC lost from a solution was measured as soil OC at the end of the experiment. This missing C may have been released as CO<sub>2</sub> or may have been leached as carbonic acid. The fact that there was no carbon assimilation in clay soil may be due to their higher content carbonates (saturation state).

Only 6.5-13.3% of adsorbed ammonium-N was measured as TN into the soils. This results for inorganic-N were lower than Chadwick *et al.*<sup>25</sup>, which indicated a soil N assimilation between 37-56 % of the organic N added.

In view of the TN and TC values measured into the soils for different treatments concluded that urine triggered higher assimilation of organic matter in the soils than did water. Compared with urine, the carbonated urine increase this assimilation and diesel exhaust reduced it. In any case, the effect could be significantly appreciated only with repeated treatments over the long term.

Figure 1 illustrated the initial mass isotherms in which adsorbed DOC, adsorbed NH<sub>4</sub> and soil EC, (normalized to soil mass) was regressed against the initial urine concentration in solution. The perfect linearity between adsorption of ammonium-N, EC and DOC on the one hand and on the other, the amount of urine initially added means that the adsorption capacity of both soils was not exhausted within the range of urine added. The slope of the IM isotherm, represents a partition coefficient, which is the ionic fraction retained by the soil. These coefficients indicated that the loam soil had more adsorption capacity of DOC and NH<sub>4</sub> than did silt-clay loam (Table 6).

Table 6 illustrated the correlation between adsorbed ammonium-N (NH<sub>4</sub>), dissolved organic carbon (DOC) and soil initial contents and urine initial dilution. The perfect linearity between adsorption de NH<sub>4</sub> and DOC and the amount of urine initially added means that the adsorption capacity of both soils was not exhausted within the range of urine added. The slope of the IM isotherm represents a partition coefficient, which is the ionic fraction retained by the soil. These coefficients indicated that the loam soil had more adsorption capacity of DOC and NH<sub>4</sub> than did silt-clay loam.

The results for adsorbed DOC (37-59%) agreed with Riffaldi *et al.*<sup>26</sup>, who indicated that the DOC fraction retained by the soil ranged from 9-60% for the different soils and proved to be closely related to their clay content ( $p = 0.001$ ). Adsorbed DOC and NH<sub>4</sub> in samples bubbled with diesel

Table 6: Significant linear correlations ( $p < 0.001$ ) between adsorbed ammonium-N ( $\text{NH}_4$ ), dissolved organic carbon (DOC), soil contents and urine dilution

Loam soil	Correl	Max ( $\text{mg g}^{-1}$ )	Silt-clay-loam	Correl	Max ( $\text{mg g}^{-1}$ )
$\text{DOC} = 0.811 \text{ DOC}_i$	0.998	0.81	$\text{DOC} = 0.767 \text{ DOC}_i$	0.998	0.77
$\text{DOC} = 0.389 \text{ U}_i$	0.977	0.39	$\text{DOC} = -0.89 + 0.455 (\text{U}_i)^{1/2}$	0.959	0.37
$\text{NH}_4 = 0.11 + 0.86 \text{ NH}_{4i}$	0.997	0.86	$\text{NH}_4 = 0.04 + 0.75 \text{ NH}_{4i}$	0.999	0.75
$\text{NH}_4 = 0.18 + 3.59 \text{ U}_i$	0.990	3.77	$\text{NH}_4 = 0.12 + 3.14 \text{ U}_i$	0.989	3.26
<b>Diesel exhaust</b>					
$\text{DOC} = 0.828 \text{ DOC}_i$	0.997	0.83	$\text{DOC} = 0.752 \text{ DOC}_i$	0.999	0.75
$\text{DOC} = 0.593 \text{ U}_i$	0.937	0.59	$\text{DOC} = 0.540 \text{ U}_i$	0.952	0.54
$\text{NH}_4 = 0.85 \text{ NH}_{4i}$	0.999	0.85	$\text{NH}_4 = 0.76 \text{ NH}_{4i}$	0.998	0.76
$\text{NH}_4 = 4.46 \text{ U}_i$	0.968	4.46	$\text{NH}_4 = 3.97 \text{ U}_i$	0.962	3.97

Subscript i indicates the initial soil content of the parameter

Table 7: Significant non linear correlations ( $p < 0.001$ ) between total N (TN), organic carbon (OC), inorganic carbon (IC), total carbon (TC) and urine dilution

Loam soil	Correl	Max $\text{mg g}^{-1}$	Silt-Clay-loam	Correl	Max $\text{mg g}^{-1}$
$\text{TN} = 0.174 + 0.326 (\text{U}_i)^{1/2}$	0.965	0.50	$\text{TN} = 0.142 + 0.414 (\text{U}_i)^{1/2}$	0.964	0.56
$\text{OC} = 12.02 + 2.28 (\text{U}_i)^{1/2}$	0.657	14.30	No correlation		
$\text{IC} = 26.87 + 6.22 \text{ U}_i - 6.12 \text{ U}_i^2$	45.06%	28.45	No correlation		
$\text{TC} = 41.40 + 0.467 \ln \text{ U}_i$	0.597	41.40	No correlation		
<b>Diesel exhaust</b>					
$\text{TN} = 0.216 + 0.304 (\text{U}_i)^{1/2}$	0.943	0.52	$\text{TN} = 0.207 + 0.210 (\text{U}_i)^{1/2}$	0.905	0.42
$\text{OC} = 11.91 + 3.15 (\text{U}_i)^{1/2}$	0.672	15.06	No correlation		
$\text{IC} = 26.71 + 6.85 \text{ U}_i - 7.15 \text{ U}_i^2$	67.5%	28.65	No correlation		
$\text{TC} = 41.65 + 0.555 \ln \text{ U}_i$	0.576	41.65	No correlation		

Subscript i indicates the initial soil content of the parameter

exhaust were slightly higher than in carbonated samples. This result could be due to the fact that diesel exhaust fumes introduced, besides  $\text{CO}_2$  gas, more additional DCN from C,  $\text{NO}_x$  and motor-combustion particles whereas carbonated samples added only  $\text{CO}_2$ .

The slope of ammonium-N and that of soil EC isotherms proved similar. This could indicate that the increased soil EC could be due to prevailing adsorption of ammonium-N.

Non linear isotherms (square root-X) could be fit to the data of TN and OC to soils (Table 7), indicated a maximum adsorption capacity of the soils. TN and OC increases could be explained by the same cause, i.e., a net assimilation of organic matter into the soils.

These results are consistent with Riffaldi *et al.*<sup>26</sup>, in that adsorption of DOC and OC contents bore no relation. This could be because the mean variation of DOC absorbed ( $0.22 \text{ mg g}^{-1}$ ) was small compared to the mean OC content in the soil ( $13.1\text{--}21.5 \text{ mg g}^{-1}$ ). This would explain the fact that in loam soils with lower organic matter content, the urine treatments caused significant differences in soil OC and IC whereas, in silt-clay loam the differences were not significant with respect to a water control.

The transition from conventional to organic farming was accompanied by changes that affected soil chemical properties and fertility. Long-term poultry-litter application can sequester C and N in the soil compared with inorganic N fertilization<sup>27</sup>.

Moreover, environmental aspects need to be considered. Thus, in relation to the introduction and transmission of

pathogens in the soil, Hoglund *et al.*<sup>28</sup> have indicated that urine stored at  $20^\circ\text{C}$  for at least 6 months may be considered safe to use as a fertilizer for any crop. On the other hand, OMW specific fractions augmented with natural phenolic ingredients at low pH values could reduce the number of pathogens and may be utilized as a source of bioactive compounds to control pathogenic bacteria for their antimicrobial activity against Gram-positive bacteria *Streptococcus pyogenes* and *Staphylococcus aureus* and Gram-negative *Escherichia coli* and *Klebsiella pneumoniae*<sup>29</sup>.

Organic wastes can increase the immobilization of inorganic or mineralized N in soils. Thus, urine or carbonated urine mixed with an organic waste such as OMW or W should produce a new fertilizer with a higher agricultural-efficiency index for N, according to Buondonno *et al.*<sup>30</sup>. These fertilizers, after being incorporated into soil organic matter, could sustain fertilization over a long period<sup>31</sup>.

Considering urine as an absorbent of  $\text{CO}_2$ , fertilization with urine-carbonated urine-urine bubbled with diesel exhaust to cause mean increases of 5-5.7-4.7% TC and 81-85-69% TN, respectively, in the soils, could serve as a method for long-term adsorption and sequestration of C and N in the soils.

## CONCLUSION

The effect of carbonated urine and urine proved similar in the soils. The adsorption of ammonium-N, DOC, OC and TN to soils increased with the initial urine solution concentration

and can be described by a linear or curvilinear approach. The highest IC adsorption was for the dilution higher than 1:1 urine-water in the loam soil whereas for silty-clay-loam soil was independent of urine dilution. Comparing the results of the adsorption experiments with TN and TC content in soils indicated that the fertilization with urine or carbonated urine and similar urban wastewaters could served as a method for adsorption and sequestration of C and N in the soils.

### SIGNIFICANCE STATEMENTS

This study gives a real-life example of how to use urine and some wastes on the absorption of CO<sub>2</sub> and NO<sub>x</sub> from diesel exhaust and chimneys and convert CO<sub>2</sub> emissions into valuable fertilizers that can be beneficial for increase C and N into the agricultural soils. This study will help the researcher to uncover the critical areas of use urine and CO<sub>2</sub> as ecological resource to produce fertilizers that many researchers were not able to explore. Thus a new theory on increase C and N on soil with wastewaters and CO<sub>2</sub> emissions may be arrived at.

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