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REGULAR ARTICLE

Emissions of carbon dioxide, methane and nitrous oxide from soil receiving urban wastewater for maize (Zea mays L.) cultivation

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Abstract We investigated how amending maize with wastewater at 120 kg N ha^{-1} affected crop growth, soil characteristics and emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) compared to plants fertilized with urea. Maize growth response was similar when fertilized with urea or wastewater despite a delayed release of nutrients upon mineralization of the organic material in the wastewater. Applying wastewater to soil significantly increased the mean CO_2 emission rate 2.4 times to 1.74 µg C kg^{-1} soil h^{-1} compared to the unamended soil (0.74 µg C kg^{-1} soil h^{-1}), and cultivating maize further increased it 3.2 times (5.61 µg C kg^{-1} soil h^{-1}). Irrigating soil with wastewater, cultivating it with maize or applying urea had no significant effect on the emission of N_2O compared to the unamended soil (1.49×10^{-3} µg N kg^{-1} soil h^{-1}). Adding urea to soil did no affect the CH_4 oxidation rate (0.1×10^{-3} µg C kg^{-1} soil h^{-1}), nor did cultivating maize in the urea-amended soil, but adding wastewater to soil resulted in a significant production of CH_4 (128.4×10^{-3} µg C kg^{-1} soil h^{-1}). Irrigating soil with wastewater increased the global warming potential (GWP) 2.5 fold compared to the urea amended soil, while in soil cultivated with maize GWP increased 1.4 times. It was found that irrigating crops with wastewater might limit the use of N fertilizer and water from aquifers, but the amount applied should be limited because nitrate (NO_3^-) leaching and emissions of CO_2, N_2O and CH_4 will be substantial and the increased soil salt content will limit crop growth.

Keywords Wastewater irrigation · Global warming potential · Plant development · Soil characteristics · Inorganic N in soil · Valley of the Mezquital

Abbreviations
GWP Global warming potential
GHG Greenhouse gases
PVC Polyvinyl chloride

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Introduction

The use of urban wastewater in agriculture is a centuries-old practice that is receiving renewed attention with the increasing shortage of freshwater around the world (Scott et al. 2004). Irrigation of crops with wastewater is already a common practice in urban and suburban farming communities of the developing world (Rutkowski et al. 2007). Wastewater is often the only water source for agriculture and its use will increase with increased demand for fresh water. Additionally, wastewater contains important nutrients, such as inorganic N and organic matter, which favour crop growth (Di Paolo and Rinaldi 2008; Wang et al. 2008). However, irrigating crops with wastewater might increase human viral and bacterial infections and contamination of the environment with toxic substances (Heidarpour et al. 2007).

In Latin America more than 500,000 ha arable land is irrigated with wastewater (Hamilton et al. 2007), of which 350,000 ha in México (Peasey et al. 2000). In the valley of the Mezquital in the state of Hidalgo (México), 145,000 ha are irrigated with wastewater from Mexico City (Velázquez-Machuca et al. 2002). This has favored the development of the region, but 1,100 ha have already been lost as agricultural land due to increased soil salt contents (Jimenez and Chávez 2004). Additionally, the regular uncontrolled flooding of the cropped area has loaded the soil with large amounts of inorganic N (Ramírez-Fuentes et al. 2002). This might have important environmental consequences, such as ammonia volatilization, NO_3^- leaching, runoff and erosion, which may affect groundwater quality and N_2O emission (Neeteson and Carton 2001). Regular flooding will promote NO_3^- leaching contaminating the groundwater and induce anaerobiosis favouring NO_3^- is reduced to N_2O and N_2. Additionally, water logging will reduce CH_4 oxidation, but stimulate production of CH_4 (Yue et al. 2005).

Nitrous oxide is present in the atmosphere at a low concentration (319 ppb in 2005), but the amount is increasing at rate of 0.25 % y^{-1} (IPCC 2007). Despite its low concentration, N_2O is an important greenhouse gas because of its long lifetime (115 years) and a global warming potential 310 times larger than that of CO_2 (IPCC 2007). Although the N_2O budget remains poorly understood, fertilized agricultural soils where N_2O is produced through microbial nitrification and denitrification, are believed to be a major source of N_2O emission (Mosier et al. 1998). The atmospheric concentration of CH_4 (1.774 ppm in 2005) is much lower than that of CO_2 (379 ppm in 2005), but the amount of CH_4 is increasing by 4.9 ppb y^{-1}, while that of CO_2 1.9 ppm (IPCC 2007). Methane from agricultural origin is emitted by methanogenic microorganisms from anaerobic environments, e.g. rice paddies, manure storage plants and from the rumen of cattle and sheep (Johnson et al. 2007).

The objective of this study was to investigate how wastewater with a N content of 120 kg N ha^{-1} added to maize affected crop growth, soil characteristics and emissions of CO_2, CH_4 and N_2O compared to plants fertilized with urea.

Materials and methods

Sampling site, collection and characteristics of soil and wastewater

The Valley of Mezquital (2,000 m above sea level, 100 km north of Mexico City), has been irrigated with wastewater since 1890 (Velázquez-Machuca et al. 2002). The climate is temperate and semi-arid with most of the rainfall occurring between June and September. Mean annual temperature ranges between 16 and 18°C and mean annual rainfall between 400 mm in the northern part and 700 mm in the southern part of the Valley. Irrigation is done by flooding through furrows, and mean annual application rates vary between 1,500 and 2,200 mm depending on crop and soil type. For example alfalfa (*Medicago sativa* L.) would receive more irrigation water than maize and crops grown on Vertisols more than those grown on Leptosols. The sampling site is located near Pachuca in the State of Hidalgo, Mexico, (N.L. 20° 05′ 43″ W.L. 99° 13′ 12″). Its average altitude is 2,060 m above sea level and characterized by a temperate climate with a mean annual temperature of 17°C and average annual precipitation of 850 mm mainly from May through June. The soil is a loamy eutric Vertisol Soil was sampled at random by augering the 0–15 cm top-layer of three approximately 0.5 ha plots. The soil from each plot was pooled and analysed for pH (8.2±0.06) and electrolytic conductivity (EC, 0.8±0.01 dS m^{-1}) organic C content (27.3±1.3 g C kg^{-1} soil) and total N content (1.9±0.07 g N kg^{-1} soil).

During the first half of 1900’s wastewater applied to these fields was of domestic origin, and thus presumably low in heavy metals. During the second half of the century more wastewater from industrial origin has been added to irrigation water. The irrigation water is slightly alkaline pH (8.4), marginally sodic and its salinity hazard is considered medium to high with electric conductivities ranging between 0.75 and 2.3 dS m^{-1}. Its colour is yellow-greenish and the odour is foul. The dominating cation is Na^+ (8.9 mg L^{-1}) followed by Ca^{2+} (5.4 mg L^{-1}), and the dominating soluble anions are HCO_3^- (4.84 mg L^{-1}) and Cl^- (6.4 mg L^{-1}). The concentrations of toxic organic compounds are low, such as chlorinated pesticides (20 picog L^{-1}), polychlorinated biphenyls (64 picog L^{-1}) and, base/neutral/acid semi-volatile organic compounds (9.5 g L^{-1}) (Downs et al. 2000) and heavy metal concentrations, such as Pb (19 mg kg^{-1} dry biosolids), Mn (13 mg kg^{-1} dry biosolids), Ni (63 mg kg^{-1} dry biosolids), Co (63 mg kg^{-1} dry biosolids), Cu (19 mg kg^{-1} dry biosolids), Cr (298 mg kg^{-1} dry biosolids), Zn (162 mg kg^{-1} dry biosolids) and, Cd (8 mg kg^{-1} dry biosolids) are normally lower than the normal levels established by the Mexican Government NOM-001-ECOL-1996 (SEMARNAP 1996) (Jiménez and Landa 1998). Hence it is considered to be of excellent quality. A more detailed characterization of the wastewater has been reported by Jiménez and Landa (1998) and Downs et al. (2000).

The total N content of the wastewater used in this experiment was 33 mg l^{-1} and the concentration of ammonium (NH_4^+) 22 mg N l^{-1}, while $NO_3^-$and NO_2^- were negligible.

Experimental design

The experiment was conducted in a greenhouse. Soil collected from the three sub sites was placed into polyvinyl chloride (PVC) tubes (length 50 cm and diameter (⌀) 16 cm) filled at the bottom with 7 cm of gravel topped up with 3 cm sand (Bellini et al. 1996). The soil was not repacked. As such, a layer of 30 cm soil was obtained. Five treatments combining the use of wastewater or urea and the cultivation of maize were applied to nine soil columns, i.e. the WMAIZE (maize fertilized with wastewater), WASTE (soil only fertilized with wastewater), UMAIZE (maize fertilized with urea), UREA (soil only fertilized with urea) and CONTROL (soil only watered with tap water). The soil in the WMAIZE and WASTE treatments was irrigated with 1 l wastewater every 7 days from the first day onwards, i.e. 13 times overall, so that a total amount of inorganic N equivalent to 120 kg N ha^{-1} was added to each maize plant, i.e. the recommended amount of N fertilizer for maize. The UMAIZE and MAIZE treatment were irrigated with tap water and fertilized with 0.62 g urea per soil column. At sowing time, 0.31 g urea was added per soil column and 0.31 g urea $tube^{-1}$ 12 days after seedling emergence. As such, 120 kg N ha^{-1} was added. The CONTROL treatment was irrigated with tap water every seven days and no fertilizer was added. The tap water used in this experiment contained 0.45 mg NO_2^- -N and 1.92 mg NO_3^- -N l^{-1}. As such, 12 kg mineral-N ha^{-1} was additionally added to the maize plants over the growing season. At the onset of the experiment, a 20 g sub-sample of soil was taken from each treatment and characterized for inorganic N, pH and electrolytic conductivity.

Three seeds were planted into soil columns for the UMAIZE and WMAIZE treatments. The PVC tubes were placed on a plastic recipient to collect water leached out from the columns in a greenhouse for 90 days. After eight days, two plantlets were discarded. During the first experiment (18th of July to 18th of October of 2007), 1,000 ml water was added to each column every 7 days. At the onset of the experiment and every two days, the columns were closed with a PVC column. At time 0 and after 3, 15 and 30 min, the atmosphere was sampled and analyzed for CO_2, N_2O and CH_4. The water leached from the columns was analyzed for NH_4^+, NO_3^- and NO_2^-. The volume of water leached was low and never >50 ml and nearly no water was leached towards the end of the experiments.

Thirty, 60 and 90 days after planting, three PVC tubes were selected at random from each treatment. The entire soil column was removed from the PVC tube and the 0–15 cm and a 15–30 cm layer sampled taken care not to damage the root structure. The roots were separated from the shoots and the root and shoot length measured. Roots and shoots were air-dried, weighted and analyzed for total N. The whole experiment was repeated twice from the 19th of November to 19th of February 2008 and from the 3rd of March to 3rd of June 2008.

Soil and wastewater characterization

The pH was measured in 1:2.5 soil/H_2O (*w*/*w*) suspension Titrino pH meter (Metrohm Ltd. CH.-901, Herisau, Switzerland) fitted with a glass electrode (Thomas 1996). The electrolytic conductivity was determined in a 1:5 soil/H_2O suspension as described by Rhoades et al. (1989). Total N in soil and plant was measured by the Kjeldhal method using concentrated sulfuric acid (H_2SO_4), potassium sulfate (K_2SO_4) and mercury oxide (HgO) to digest the soil and plant samples (Bremner 1996). Soil particle size distribution was determined by the hydrometer method as described by Gee and Bauder (1986). NH_4^+, NO_3^- and NO_2^- in 1:10 soil/ K_2SO_4 0.5 M (*w*/*v*) suspension whereas the extracts and the leachates were determined colourimetrically on a San Plus System—SKALAR automatic analyzer (Mulvaney 1996).

Emissions of CO_2, N_2O and CH_4

A cylindrical PVC chamber (length 50 cm and ⌀ 16 cm) was placed on the PVC tube and was made air tight by sealing with professional grade brown duct tape. Zero, 3, 15 and 30 min after the upper cylindrical chamber was sealed, 20 cm^3 air was injected into the PVC chamber headspace, while the gas was mixed by flushing at least 2–3 times with the air inside the chamber followed by gas collection for analysis and an equal amount was sampled and injected into 17-ml evacuated vials. The amount of CO_2 and N_2O was determined with an Agilent 4890D gas chromatograph fitted with an electron capture detector. A J&W Scientific GS-Q column was used to separate CO_2 and N_2O from the other gases; the carrier gas, N_2, flowing at a rate of 5 ml min^{-1}. Injection, detection and column-oven temperatures were set at 100°C, 225°C, and 35°C, respectively. The amount of CH_4 was determined with an Agilent 4890D gas chromatograph fitted with a flame ionization detector. A Porapak Q column was used to separate CH_4 from the other gases with the carrier gas He flowing at a rate of 25 ml min^{-1}. Injection, detection and column-oven temperatures were set at 100°C, 310°C, and 32°C, respectively. For each analysis, an aliquot of 1 cm^3 was injected into the chromatograph using a Teflon sealed glass syringe (Hamilton®, USA).

Concentrations of CO_2, N_2O and CH_4 were calculated by comparing peak areas against a standard curve prepared from known concentrations, i.e. 10 and 2,500 ppm N_2O in N_2, 5 ppm CH_4 in N_2 and 2,500, 20,000 and 40,000 ppm CO_2 in N_2, every time samples were analysed.

Emission of CO_2, CH_4 and N_2O was regressed on elapsed time using a linear model forced to pass through the origin, but allowing different slopes (production rates) for each treatment. This approach is supported by the theoretical considerations that no CO_2, CH_4 and N_2O was produced at time zero and the amount of CH_4, N_2O and CO_2 in the atmosphere at time zero was subtracted from the values obtained after 3, 15 and 30 min.

Statistical analyses

Significant difference between plant and soil characteristics as a result of the different treatments were determined by analysis of variance (ANOVA) and based on the least significant difference using the General Linear Model procedure (PROC GLM, SAS Institute 1989). This procedure can be used for an analysis of variance (ANOVA) for unbalanced data, i.e. when data are missing. Significant differences between treatments for production of CO_2 and N_2O were determined using PROC MIXED considering repeated measurements (SAS Institute 1989). The global warming potential (GWP) of the gasses emitted was calculated considering the CO_2-equivalent emission of 310 for N_2O, 21 for CH_4 and 1 for CO_2 (IPCC 2007) minus the C stored in the roots, i.e. it was assumed 40% of the total root dry weight was C.

All data presented were the mean of three plants cultivated in soil or samples taken from that soil, from three different plots and that from three consecutive experiments done in a greenhouse, i.e. $n=27$.

Results

Soil and plant characteristics

The electrolytic conductivity was generally larger in the WMAIZE and WASTE treatments than in the other treatments in the 0–15 cm and 15–30 cm layers (Fig. 1a, b). In the 15–30 cm layer, the electrolytic conductivity decreased in all treatments after 30 days. Treatment, layer and time of sampling had no significant effect on soil pH ($P>0.05$) (Fig. 1c, d).

Concentrations of NO_3^- in the 0–15 cm layer decreased when maize was cultivated compared to the

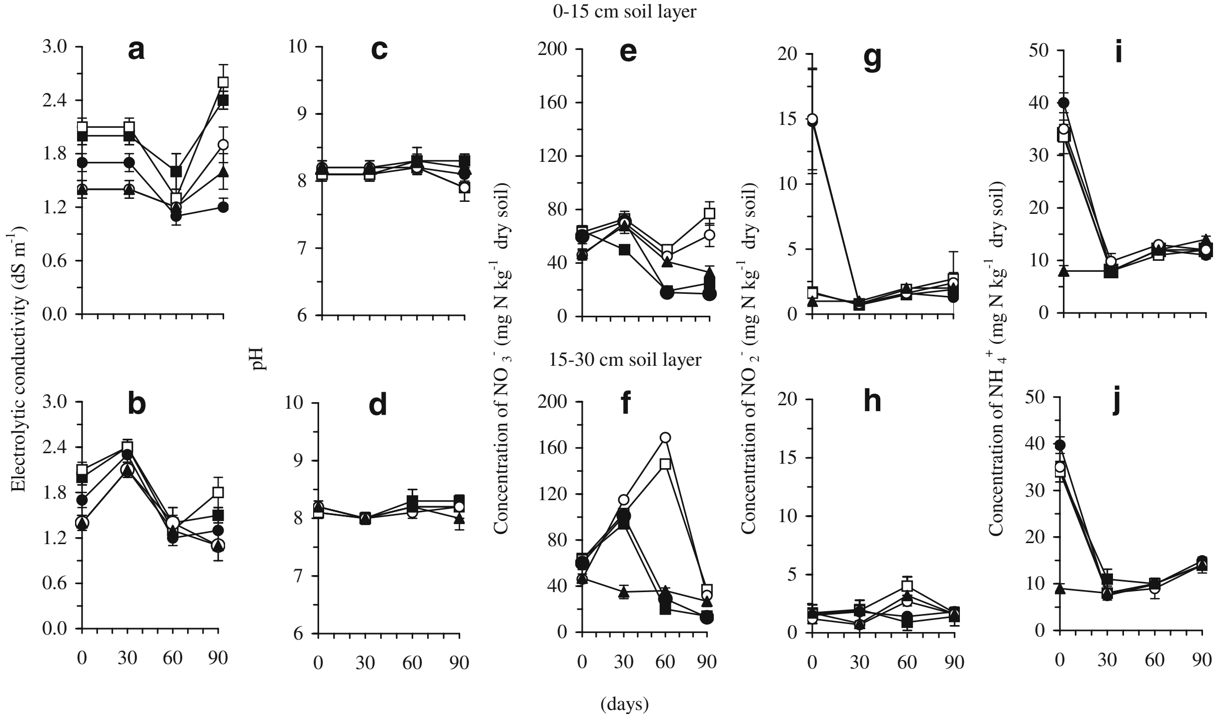

Fig. 1 Electrolytic conductivity (**a**, **b**), pH (**c**, **d**) and inorganic N concentrations (**e**–**j**) of the soil cores (0–15 cm and 15–30 cm layers) cultivated with maize plants (*Zea mays* L.) and irrigated with wastewater (WMAIZE treatment, ■), or with tap water and amended with urea (UMAIZE treatment, ●), or uncultivated soil irrigated with wastewater (WASTE treatment, □) or with tap water (UREA treatment, ○), CONTROL treatment (▲) was irrigated with tap water and no fertilizer was added. Wastewater and urea were added at a rate equivalent to 120 kg N ha^{-1}. Data were pooled for the three experimental replications

uncultivated soil (Fig. 1e). The mean concentration of NO_3^- was significantly lower in the CONTROL treatment compared to the WASTE and UREA treatments ($P<0.05$). While in WMAIZE and UMAIZE treatments the concentrations of NO_3^- were significantly lower compared with the other treatment and decreased at day 30 and thereafter. In the 15–30 cm layer, the concentration of NO_3^- increased in all treatments at day 30 compared to the amount found at day 0, except for the CONTROL treatment where it decreased (Fig. 1f). The concentration of NO_3^- decreased in the WMAIZE and UMAIZE treatments after 30 days and in the UREA and WASTE treatments after 60 days.

Concentrations of NO_2^- remained ≤4 mg N kg^{-1} in all treatments and both soil layers at all times except in the urea-amended soil when 15 mg N kg^{-1} was found in the 0–15 cm layer at day 0 (Fig. 1g, h).

Concentrations of NH_4^+ were >30 mg N kg^{-1} in both layers at the onset of the incubation except in the CONTROL treatment (Fig. 1i, j). After 30 days, however, concentrations were similar in all treatments and remained <15 mg N kg^{-1} soil.

The amount of NH_4^+ leached remained <0.25 mg N kg^{-1} at each sampling day and was not significantly different between the treatments (Fig. 2a). The amount of NO_2^- leached remained <0.6 mg N kg^{-1} at each sampling day and was generally larger in the WMAIZE than in the other treatments (Fig. 2b). The concentrations of NO_3^- in the leachate decreased over time but increased towards the end of the experiment in the WASTE and UREA treatments (Fig. 2c). The amounts of NO_3^- in the leachate were significantly lower in the WMAIZE (1.4 mg N kg^{-1} soil), UMAIZE (1.7 mg N kg^{-1} soil) and CONTROL treatments (1.9 mg N kg^{-1} soil) than in the WASTE (2.6 mg N kg^{-1} soil) and UREA (2.5 mg N kg^{-1} soil) treatments (minimum significant difference 0.5 mg N kg^{-1} soil) ($P<0.0001$).

Plant characteristics were not affected by fertilizer type, i.e. urea or wastewater (Table 1).

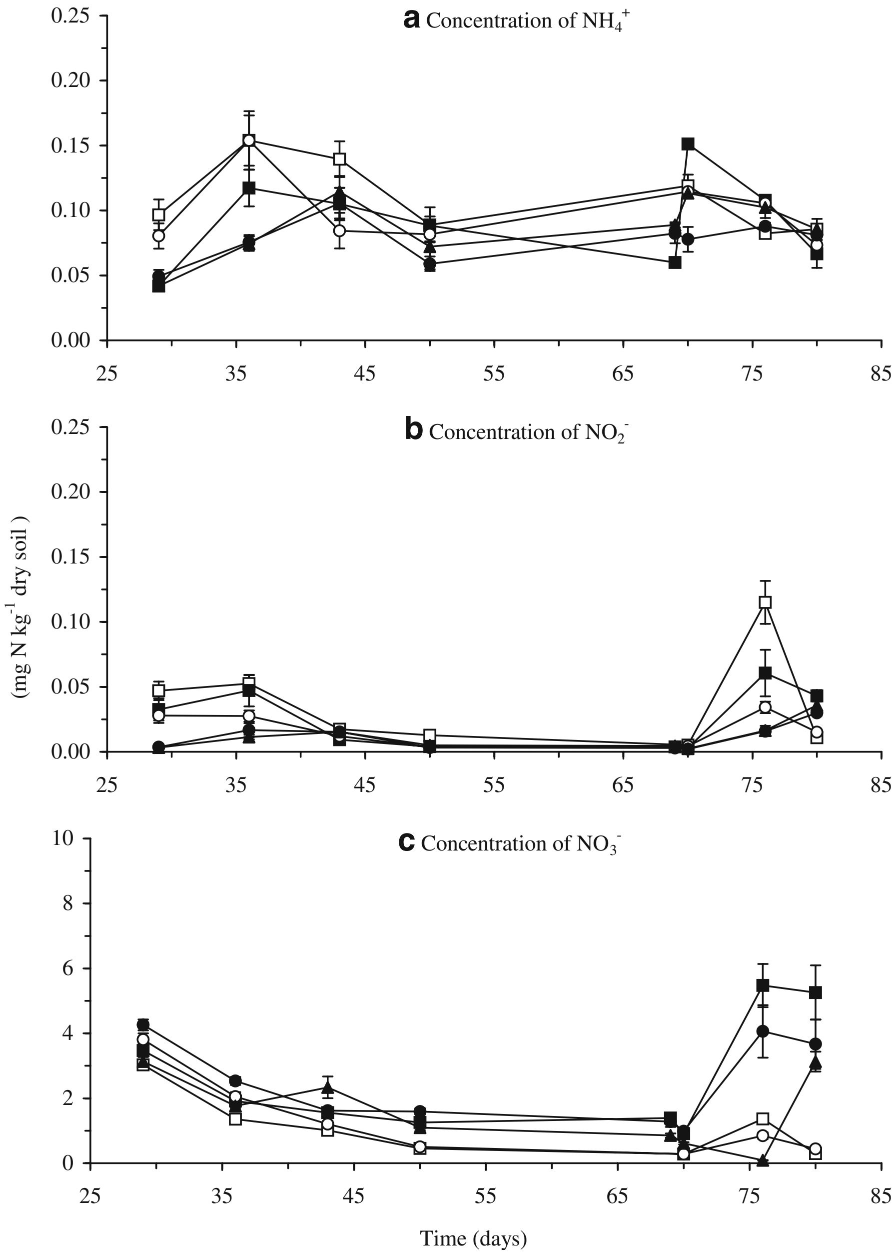

Fig. 2 Concentrations of NH_4^+ (**a**), NO_2^- (**b**) and NO_3^- (**c**) in the leachate from soil cultivated with maize plants (*Zea mays* L.) and irrigated with wastewater (WMAIZE treatment, ■), or with tap water and amended with urea (UMAIZE treatment, ●), or uncultivated soil irrigated with wastewater (WASTE treatment, □) or with tap water (UREA treatment, ○), CONTROL treatment (▲) was irrigated with tap water and no fertilizer was added. Wastewater and urea were added at a rate equivalent to 120 kg N ha^{-1}. Data were pooled for the three experimental replications

Greenhouse gas emissions

The daily CO_2 emission rate ranged from very low (0.04 µg C kg^{-1} soil h^{-1}) to a maximum of 30.99 µg C kg^{-1} soil h^{-1} (Fig. 3a). Adding urea to soil had no significant effect on the mean CO_2 emission rate compared to the unamended soil, but cultivating maize in the urea-amended soil increased it 6.7 times ($P<$ 0.05) (Table 2). Applying wastewater to soil significantly increased the mean CO_2 emission rate 2.4 times compared to the unamended soil, and cultivating maize further increased it 3.2 times ($P<0.05$).

The daily N_2O emission rate ranged from undetectable amounts to a maximum of 0.040 µg N kg^{-1} soil h^{-1} (Fig. 3b). Adding urea to soil increased the mean N_2O emission rate 2.2 times compared to the unamended soil, and cultivating maize further increased it 1.4 times (Table 2). Applying wastewater to

Table 1 Characteristics of maize plants (*Zea mays* L.) cultivated in an agricultural soil irrigated with wastewater (WMAIZE treatment) or with tap water and amended with urea (UMAIZE treatment). Wastewater and urea were added to get a fertilizer doses such as 120 kg N ha^{-1}. Data were pooled among the three experiments repetitions

Plant characteristics	WMAIZE	UMAIZE	LSD[a]
Root length (cm)[b]	45 A	49 A	4
Plant height (cm)[b]	72 A	74 A	9
Root dry weight (g)[b]	6 A	7 A	2
Shoot dry weight (g)[b]	13 A	14 A	4
Root total N (g N kg^{-1} dry plant)[b]	8 A	7 A	1
Shoot total N (g N kg^{-1} dry plant)[b]	15 A	16 A	2

[a] *LSD* least significant difference ($P<0.05$)

[b] Values within the row values with the same letter are not significantly different ($P<0.05$)

soil increased the mean N_2O emission rate 1.7 times and cultivating maize in the wastewater–amended soil 1.8 times.

The daily CH_4 production rate ranged from −0.02 µg C kg^{-1} soil h^{-1} to a maximum of 0.66 µg C kg^{-1} soil h^{-1} (Fig. 3c). Adding urea to soil did no affect the mean CH_4 oxidation rate, nor did cultivating maize in the urea-amended soil (Table 2). Adding wastewater to soil resulted in a significant production of CH_4, but cultivating maize reduced it again ($P<0.05$). The peaks observed in the emission of CH_4 from soil amended with wastewater occurred when the wastewater was applied. Wastewater added organic material and induced anaerobic conditions thereby stimulating production of CH_4.

Applying urea increased the GWP from 0.26 g C kg^{-1} soil to 0.36 C kg^{-1} and wastewater sludge to 0.90 g C kg^{-1} after 90 days (Table 2). Cultivating the soil further increased GWP with the largest increase found when wastewater sludge was added to soil.

Discussion

Soil and plant characteristics

The wastewater applied to soil had a high salt content so when applied to soil it increased electrolytic conductivity. Consequently, the electrolytic conductivity was larger in the WMAIZE and WASTE treatments in the 0–15 cm layer compared to the other treatments. Plants take up only small amounts of salts so their influence on the soils' electrolytic conductivity is minimal. In the 15–30 cm layer, the electrolytic conductivity decreased in all treatments as salts were leached. This did not happen in the upper 15 cm as evaporation and a constant supply of salts maintained the electrolytic conductivity. Similar results were reported by Heidarpour et al. (2007) and Assadian et al. (2005). A high soil salt content is known to inhibit plant growth, although a possible negative effect depends on soil and plant characteristics (Brady and Weil 1999). However, although the salt content increased in soil amended with wastewater, maize growth was not inhibited.

Wastewater and urea had no effect on soil pH in the experiment reported here because the soil is a eutric Vertisol with clay 2:1 type, which have a large capacity to absorb or provide protons, and therefore a high buffering capacity. Heidarpour et al. (2007) found similar results when an agricultural soil from Iran was irrigated with wastewater. However, it has been shown that the soil pH increases when amended with urea (Du et al. 2005) as the hydrolysis of urea produces one molecule of CO_2 and two molecules of NH_3 (Estiu and Merz 2007). Because CO_2 is emitted from soil, this reaction rapidly increases soil pH through the production of ammonium hydroxide (Du et al. 2005). In the long term, however, the NH_4^+ formed decreases soil pH as it oxidized to NO_3^- generating a proton (Enwall et al. 2007).

In the research reported here, the concentration of NH_4^+ was larger in the urea and wastewater-amended soil than in the unamended soil as urea was hydrolyzed and the wastewater contained high

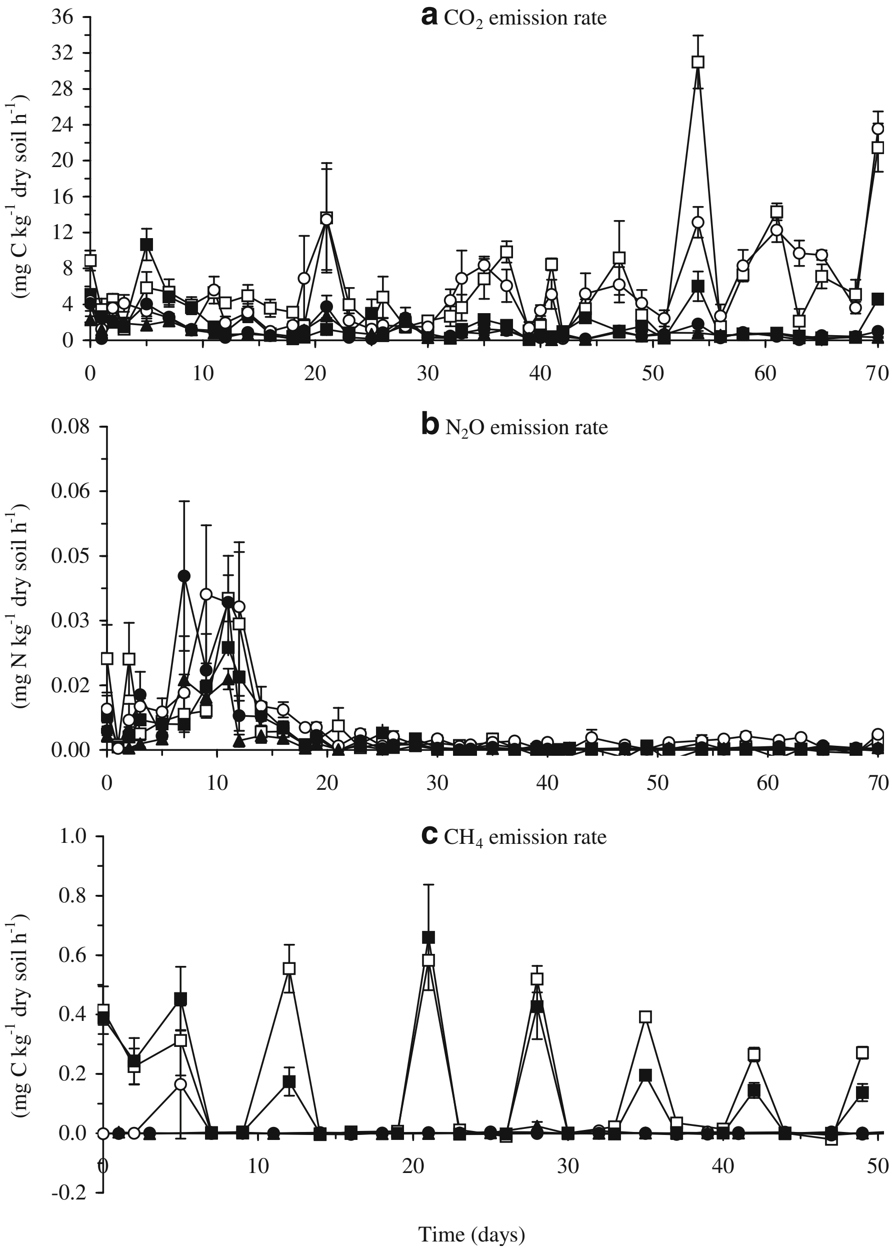

Fig. 3 CO_2, N_2O and CH_4 emissions from soil cores cultivated with maize plants (*Zea mays* L.) and irrigated with wastewater (WMAIZE treatment, ■) or with tap water and amended with urea (UMAIZE treatment, ●) or uncultivated soil irrigated with wastewater (WASTE treatment, □) or with tap water (UREA treatment, ○), CONTROL treatment (▲) was irrigated with tap water and no fertilizer was added. Wastewater and urea were added at a rate equivalent to120 kg N ha^{-1}. Data were pooled for the three experimental replications

concentrations of NH_4^+. After 30 days, however, the concentrations of NH_4^+ were similar in all treatments as the NH_4^+ was oxidized to NO_3^-, taken up by the maize plants or volatilized as NH_3 as the soil pH was 8.3. An alkaline soil is known to favor NH_3 volatilization (Cordovil et al. 2007).

The concentration of NO_3^- in the soil is highly variable as it is the end product of N mineralization,

Table 2 Emission of CO_2, CH_4 (μg C kg^{-1} soil h^{-1}) and N_2O (μg N kg^{-1} soil h^{-1}) from uncultivated and unamended soil (CONTROL) or amended with urea and cultivated with maize (*Zea mays* L.) (UMAIZE) or not cultivated (UREA) or amended with wastewater and cultivated with maize (WMAIZE) or left uncultivated (WASTE). Wastewater and urea were added at 120 kg N ha^{-1}

Treatment	CO_2 (μg C kg^{-1} h^{-1})	N_2O (μg N kg^{-1} h^{-1})	CH_4 (μg C kg^{-1} h^{-1})	Root C[a] (g C kg^{-1} soil)	GWP[b] (g C kg^{-1} soil)
WMAIZE	5.61 A[c]	2.75×10^{-3} A	163.6×10^{-3} A	0.037	1.97
WASTE	1.74 B	2.48×10^{-3} A	128.4×10^{-3} B	0	0.90
UMAIZE	4.95 A	4.49×10^{-3} A	8.4×10^{-3} C	0.043	1.44
UREA	0.89 C	3.31×10^{-3} A	0.1×10^{-3} C	0	0.36
CONTROL	0.74 C	1.49×10^{-3} A	1.5×10^{-3} C	0	0.26
SEE[d]	0.37	1.61	12.4		

[a] The root C was considered 40% of total root dry weight and expressed kg^{-1} soil (total soil in a column was 6.5 kg)

[b] The global warming potential (GWP) of the gasses emitted was calculated considering the CO_2-equivalent emission of 310 for N_2O, 21 for CH_4 and 1 for CO_2 (IPCC 2007) emitted over a 90-day period minus the C that was stored in the roots per kg soil

[c] Values with the same letter are not significantly different between the treatments, i.e. the columns ($P<0.05$)

[d] SEE standard error of the estimate ($P<0.05$)

can be taken up by plants, immobilized by microorganisms when NH_4^+ is lacking, reduced under anaerobic conditions to N_2O and N_2 or leached. NO_3^- is highly mobile and easily leached, especially when the soil is not cultivated (Giles 2005). The NO_3^- concentration was lower in the 0–15 cm and 15–30 cm layers in the WMAIZE and UMAIZE treatments compared to the other treatments. It has been reported that maize has the ability to take up and utilize both NH_4^+ and NO_3^-, but the latter is preferable taken up thereby decreasing the concentration of NO_3^- in soil (Subbarao et al. 2006). The concentration of NO_3^- also decreased in the 15–30 cm of the uncultivated soil amended with urea or wastewater towards the end of the experiment.

Greenhouse gas emissions

Addition of wastewater to soil doubled the production of CO_2 in our experiment and approximately 0.2 g C was emitted from soil due to the decomposition of the wastewater after 70 days i.e. 34% wastewater C was mineralized. Wastewater contains organic material, which upon decomposition will increase the emission of CO_2 from soil (Rosso and Stenstrom 2008). Adding urea to soil has normally no effect on emission of CO_2 from soil (Khalil and Inubushi 2007). However, urea might occasionally stimulate CO_2 emission when a soil is N depleted (Castro-Silva et al. 2008).

Plants take CO_2 up from the atmosphere, but mineralization of root exudates increases emission of CO_2 (Drury et al. 1998). As such, the emission of CO_2 was larger from the soil cultivated with maize than from the uncultivated soil and approximately 2.2 g C was emitted from soil due to decomposition of the root exudates. The production of CO_2 increased towards the end of maize growth. This indicated that the phenological stage of the plant affected the CO_2 emission. Yevdokimov et al. (2006) showed that maximum CO_2 emissions in soil cultivated with oat plant coincided with the completion of intensive root growth (tillering/booting stages) when root growth began to slow down (earing/flowering stages). Later on the production of CO_2 will decrease when the plant reaches the senescent stage.

Irrigation with wastewater did not increase the emission of N_2O compared with the CONTROL treatment. In the field, addition of organic wastes, such as wastewater, pig slurry and compost, often increases emission of N_2O, but not always. Meijide et al. (2007) found that emission of N_2O increased in the field when untreated pig slurry or composted pig slurry plus urea were added to soil, but not when digested thin pig slurry fraction or municipal solid waste plus urea were added. They stated that denitrification was the most important process responsible for N_2O emissions when organic fertilizers were applied to soil. Mackenzie (1998) stated that wastewater increased the amount of N_2O emitted due to microbial transformation of the nitrogen contained in the wastewater, i.e. oxidation of NH_4^+ under aerobic conditions or reduction of NO_3^- under anaerobic conditions.

Addition of urea significantly increased the N_2O emission compared to the unamended soil, i.e. 0.20 and 0.07 µg N_2O-N kg^{-1} h^{-1}, respectively. Aulakh et al. (1984) showed that the N_2O emission significantly increased in soil cultivated with wheat and added with urea. Nitrification was presumably the process that most contributed to the N_2O production (Beck-Friis et al. 2000; Harrison and Webb 2001; Meijide et al. 2007). Different processes and factors control N_2O emission from soil, but nitrification and denitrification are normally the most important processes (Menendez et al. 2008). They are controlled by environmental factors, cropping systems, soil management practices (Ellert and Jansen 2008), inorganic or organic fertilization and by water regime (Zou et al. 2007). Denitrification is usually the main source of N_2O especially under condition of high soil water content (Azam et al. 2002).

In the first week of the experiment, large amounts of N_2O were emitted from the soil, but emissions decreased after 10 days. Eicher (1990) analyzed direct measurements of fertilizer-derived N_2O emissions from 104 field experiments published before 1990 and found that at the onset of an experiment N_2O emission increases, but decreases thereafter. As mentioned before, the concentration of NO_3^- decreased at the end of the experiment, which could indicate that NO_3^- was reduced to N_2O (Figs. 1 and 2).

Soils can be a net sink or source of CH_4, depending on moisture, N level and ecosystem (Gregorich et al. 2005; Liebig et al. 2005). Methane is consumed by soil methanotrophes, which are ubiquitous in many soils (McLain and Martens 2006), and is produced by methanogenic microorganisms in the anaerobic locations of a soil (Chan and Parkin 2001). Agricultural systems usually are normally not a large source or sink of CH_4 (Chan and Parkin 2001). They are only sources of CH_4 after application of manure or other organic materials (Johnson et al. 2007). Our results also showed that soil irrigated with wastewater with or without maize increased the CH_4 emission significantly, most likely due to the sudden addition of nutrients contained in the wastewater. It is known that application of N fertilizer inhibits the CH_4 oxidation in soils (Kravchenko et al. 2002), which often results in a net increase in CH_4 emitted from soils (Bronson and Mosier 1994). However, the CH_4 emission in soil cropped with maize and fertilized with urea was not affected by addition of inorganic N. The emission of CH_4 in soil irrigated with wastewater occurred when the wastewater was added, i.e. the emission of CH_4 was controlled by soil moisture content and addition of organic material. Approximately 70 mg CH_4-C evolved from the soil column as a result of the wastewater application and that increased a further 36 mg CH_4-C in the maize cultivated soil. The addition of wastewater inhibited O_2 diffusion and the decomposition of the organic material in the wastewater further increased anaerobiosis thereby stimulating CH_4 production. Decomposition of root exudates in maize cultivated soil amended with wastewater further increased CH_4 emission. Boeckx and Van Cleemput (1996) who studied the CH_4 emissions in soils with different moisture indicated that water content might modify the production and oxidation of CH_4. They found that methane is produced by microorganisms in a flooded soil and oxidized by methanotrophesc in an aerobic soil where both O_2 and CH_4 were available.

Application of urea increased the global warming potential (GWP) 1.4-times and wastewater sludge 3.5 times (Table 2). Similar results were reported by Chu et al. (2007) for a barley field on an Andisol in Japan fertilized with 90 kg N-urea ha^{-1} where urea increased the GWP 1.3 times compared to an unamended soil. Irrigating soil with wastewater increased the GWP 4 times compared to urea-amended soil. Although urea-application increased emissions of N_2O, the increase in emission of CO_2 and CH_4 due to the addition of wastewater had a larger overall effect on the GWP. Cultivating maize in wastewater-amended soil more than doubled the GWP.

Conclusions

It was found that fertilizing maize with urea or wastewater had a similar effect on plant development, so wastewater can be used as crop fertilizer. Wastewater did not affect soil pH, but it increased the electrolytic conductivity in the top 0–15 cm layer, which could limit its long time use. Some soils of the valley of the Mezquital are already to saline due to excessive uncontrolled irrigation with wastewater. Addition of wastewater increased the emissions of CO_2 and production of CH_4 upon application compared to the urea-amended soil, but not emissions of N_2O. Irrigating soil or maize cultivated soil with wastewater increased GWP >2-fold compared to the urea amended soil. It has to be remembered, however, that the emissions of GHG during production of urea and transport was not included. Additionally, irrigating crops with wastewater might on the long term be far more environmental friendly than using water from aquifers that take long to be replenished, as long as the amount of wastewater applied is restricted to the amount required by the cultivated crop because losses of inorganic N through NO_3^- leaching, NH_3 volatilization and emissions of CO_2. CH4 and N_2O might be substantial and soil salinization will set in quickly.

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