Twenty years of continued application of treated sewage sludge: nitrous oxide emissions induced in agricultural soils.

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Abstract
The application of urban residues to soil, such as sewage sludge that have gone through a thermophilic anaerobic digestion, have the potential to act as mineral fertilizer replacements. The scope of this study was to determine some Nitrogen losses to the atmosphere, specifically nitrous oxide (N_2O) emissions after 20 years of continued application of treated sewage sludge at different dosages. Nitrous oxide emission was measured using the closed chamber technique. Additionally, emission factor was calculated to confirm the extent of N losses in relation to the total N applied. Sewage application induced an increase in daily N_2O emissions, especially in autumn and spring when organic matter mineralization was higher. Sewage can be applied as soil amendments but application rates must be adjusted in order to mitigate N_2O emissions as much as possible.

Introduction
An inevitable by-product of municipal wastewater treatment is sewage sludge (SS). In order to obtain the cleanest water possible, SS is an unavoidably brew of various materials. Its disposal has been in the spotlight for a long time. The main concern is its tendency to concentrate heavy metals, unpleasant odour, diverse pathogens and organic compounds, all coming from waste waters. However, SS is rich in nitrogen, phosphorous and organic matter. This organic matter and all the nutrients are two main elements that make the spreading of this kind of waste on land a good candidate as an alternative fertilizer or a soil amendment. It is important to stress that only the thermophilic anaerobic digestion of SS, which is a widely used process, is capable of removing unpleasant smells, sanitizing and stabilizing this material.

In Europe, the Sewage Sludge Directive 86/278/EEC encourages its use in agriculture, the regulation seeks to control SS usage to prevent damages on the environment. For instance in Spain, approximately $1.2 \cdot Tg\ yr^{-1}$ of dry matter of SS are produced from wastewater treatment, about 4% of this material is destroyed by incineration; 8% is dumped on nearby landfills and almost the remnant 80% is applied to soil as an organic amendment, the rest ends up in soils that are not for agricultural use. Arguably its application to soil would also induce imbalances of N in agricultural lands. When organic matter is applied to the soil, the organic nitrogen has to be mineralized to ammonium (NH_4^+) which later can be oxidized to nitrite (NO_2^-) and then to nitrate (NO_3^-). During this process (nitrification) N_2O is produced. In anoxic conditions, denitrifiers reduce nitrate to N_2O in a first step and up to N_2 in a second step.

It is worth mentioning that in order to fully assess the Global Warming Potential (GWP) of any agricultural activity, such as fertilization management, concurrent consequences of organic matter addition to soil should also be assessed. This is especially true since top soil carbon stock tend to enhance when organic matter is applied to soil; thus, reducing greenhouse gaseous emissions and its deleterious effects because of CO_2 removal from the atmosphere. Moreover, all greenhouse gases have to be evaluated in a holistic approach. But the scope of this work is on N_2O because agricultural soils are a major source of N_2O emission, which is an important greenhouse gas. It has 298 times higher GWP than CO_2. The rates of production largely depend on environmental factors and soil management practices. Among soil management practices, fertilization plays an important rote. For this reason, the objective of this study was to evaluate the impact of long term treated SS application on N_2O emissions and yield.

Material and Methods

Field experiment

A long-term field experiment was established on the year 1992 in Navarre, Spain. The trial is localized in the experimental station of Arazuri, adjacent to the wastewater treatment plant of the Mancomunidad de la Comarca de Pamplona (Federation of Municipalities of Pamplona). The soil is classified as Cambisol calcaric in the FAO world reference base. According to the agro-climate classification system of Papadakis [1] the weather is Humid- template- Mediterranean with a mean annual rainfall of 1000 mm and mean temperature of 12ºC.

Treatments

Five treatments have been applied every year: a control treatment without fertilizer or treated SS, a second one with mineral fertilizer (ammonium sulphate nitrate) and three treatments consisting in different doses of treated SS (40 t ha^{-1} y^{-1}, 80 t ha^{-1} y^{-1} and 40 t ha^{-1} $3y^{-1}$). Treated SS characteristics are found on Table 1. For each treatment a plot of 35 m^2 was identified. The treatment application followed a randomized complete block factorial design with four replicates. On 9th October 2011 oats was sowed and treatments applied. The mineral treatment was split in two applications. The first application was on January (tillering) and consisted of 60 kg N ha^{-1}, while the second was done on March (stem elongation) at a dose of 40 kg N ha^{-1}. The SS was spread to soil surface and incorporated into the soil at 0-30 cm depth every year by means of a chisel plow.

Table 1. Physical and chemical properties of the treated sewage sludge.

	pH	E.C.	Dry matter	TOC	Nitrogen Kjeldahl	C/N	P_2O_5	K_2O	CaO	MgO	N-NH_4^+
		µS/m	% w/w	%C/DM	%N/DM		% P/DM	% K/DM	% Ca/DM	% Mg/DM	% N/DM
Treated Sewage Sludge	8.2	1706	14.1	36.75	7.4	4.97	6.12	0.43	5.15	0.89	1.02

Nitrous oxide measurement

Nitrous oxide emissions (N_2O) were measured using the closed chamber technique [2]. In order to minimize diurnal variation, all measurements were done in the morning (between 10:00 am and 12:00 hrs). To obtain the samples, 20mL from the inner air space of the chambers were collected just after closing the chamber and then again after 45 min. The air samples were stored in vacumm tubes for further analysis. Tubes with known concentration standards were also stored and analysed along with the samples. Emission rates were calculated taking into account the concentration increase with time. Samples were analysed by gas chromatography (GC) (Agilent, 7890A) with an electron capture detector (ECD) for N_2O detection. A capillary column (IA KRCIAES 6017: 240ºC, 30 m x 320 mm) was used. The column's temperature ramped from 40ºC to 80ºC and ECD's temperature was 350ºC, and 5% mixture of Ar, with CH_4 was used as carrier and N_2 as make up (15 mL min^{-1}). A headspace autosampler (Teledyne Tekmar HT3) was connected to the gas chromatograph.

N_2O was determined on days: 1, 3, 7, 11, 13, 23, 43 after SS addition to soil in October. Also, after fertilizer addition in February and April, measurements were conducted at the same frequency. To sum up, measurements began on October 2011 after sowing and finished after crop harvest on June 2012. Air and soil temperature (10 cm depth) were measured just before starting N_2O measurements. Moisture content was determined each sampling day on 10 samples of approximately 100g of field-moist soil by drying at 105 ºC for 24 h. Cumulative N_2O emission during the sampling period was estimated by averaging the rate of emission between two successive determinations, multiplying that average rate by the length of the period between the measurements, and adding that amount to the previous cumulative total. At harvest (July), a 16 m^2 (2 m x 8 m) portion at the centre of each plot was sampled. The grain was weighed and it was considered that the humidity percentage was 12%. Dry matter and seed weight were determined by drying the sampled grains at 80ºC to constant weight.

Statistical Analysis

The data presented in this work are the mean values of, at least, four independent replicas per treatment. N_2O emissions followed a logarithmic distribution and log transformations of these emissions were used for statistical analyses. Significance for ANOVAs was assumed at a limit value of $p \leq 0.05$ and Duncan tests for separation of media were conducted at $p < 0.05$. SPSS software, version 19 (IBM), was used for the data analysis.

Results

Nitrous oxide emission

As expected, fertilizer application induced an increase in daily N_2O emissions (Figure 1). According to several authors [3] [4], sewage application induced a significant increase with respect to unfertilized treatment, especially in treatments with annual application. Maximum rates were observed in autumn in treatment with 40 t ha^{-1} y^{-1} and spring in treatment with 80 t ha^{-1} y^{-1}. Maximum rate was of 61 g N_2O-N ha^{-1} d^{-1}. This flux is very low in comparison to those described by Scott et al. [5] after the application of treated SS. These authors measured fluxes up to 1.4 kg N_2O-N ha^{-1} d^{-1}. The emission peaks in our trial were a consequence of more propitious conditions (temperature and soil water content) for the mineralization of the organic matter applied. In fact, the large quantity of organic matter applied in treatment with 80 t ha^{-1} y^{-1} is what induce the peak of N_2O emissions in spring, as result of its mineralization. In winter, the N_2O emissions decrease in all treatments as consequence of the low temperatures and the decrease of microorganism activity. Mineral fertilizer application increased emissions slightly with respect control treatment, although it was not a significant effect. This increase was higher after the first application (tillering) than the second one (stem-elongation), when the application rate was lower.

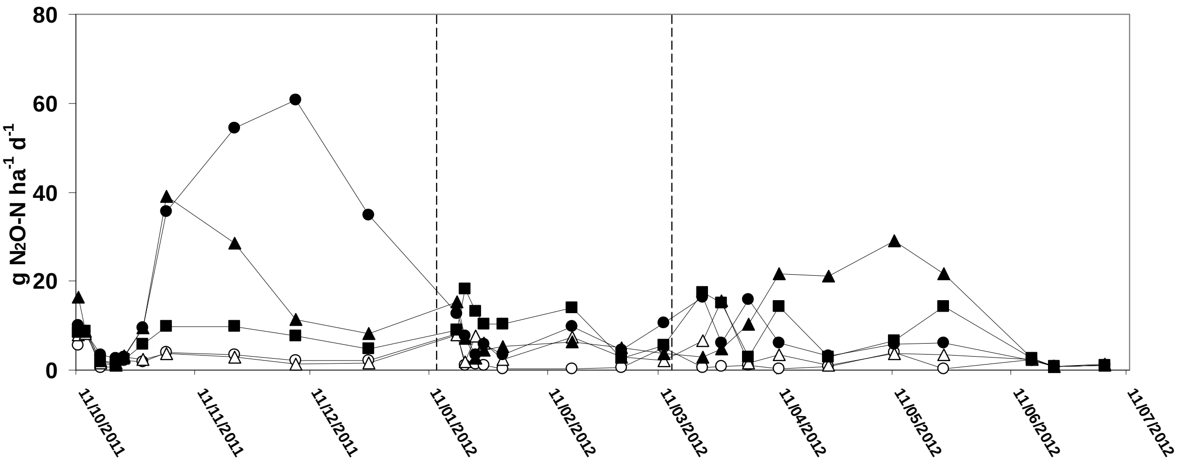

Figure 1. Nitrous oxide emission rates. (○)Control, (Δ) Ammonium sulfate nitrate, (●) 40 t ha^{-1} y^{-1}, (▲) 80 t ha^{-1} y^{-1} and (■) 40 t ha^{-1} $3y^{-1}$. Discontinued lines show ASN application moments.

Table 2. Cumulative N_2O emissions and yield production.

	kg N_2O-N ha^{-1}	Emission Factor (%)	Yield (t ha^{-1})
Control	0.58 b	-	3288 c
Ammonium sulfate nitrate	0.91 b	0.33	6057 a
40 t ha^{-1} y^{-1}	4.39 a	0.91	4856 b
80 t ha^{-1} y^{-1}	3.49 a	0.35	3701 c
40 t ha^{-1} $3y^{-1}$	1.92 a	0.32	4604 b

Different letters within a column indicate significantly different rates (P < 0.05; n = 4).

As consequence of daily emissions, cumulative losses in treatments with sewages were 4-7 times higher compared to the unfertilized treatment (Table 2). The annual application of sewage increased losses respect to the treatment that received sewage every 3 years. In the case of ammonium sulphate nitrate losses increased 2 times with respect to unfertilized treatment. The emission factor was determined on the total-N applied to soil (Table 2) and as it can be seen, ASN, 80 t ha^{-1} y^{-1} and 40 t ha^{-1} y^{-3} showed the same emission factor. The most significant differences were found on the 40 t ha^{-1} y^{-1}, in spite of the increase, none of them surpassed IPCC top estimate of 1%.

Mineral fertilizer caused significant increase in yield (Table 2). In the case of SS, application rates played an important role, increasing yields when were applied at a rate of 40 t ha^{-1}. The frequency of the application of this rate (every year or every 3 years) did not affect to the yield. To the contrary, the highest rate (80 t ha^{-1} y^{-1}) induced the lodging of the oats as consequence of an excess of nitrogen and reduced significantly the yield in this treatment. These results agree with Ball et al. [6] who described an increase of yield after sewage application with respect to unfertilized treatment but lower than the mineral fertilization. It should be stress that evidence on N excess is shown by the decrease in oats yields, which is a commonly encountered problem in oats, intimately related to lodging problems.

Conclusion and perspectives

The addition of treated SS every 3 years showed lower N_2O losses and the same yield than the annual application. So, it can become an advisable soil amendment but further research must be carried out to optimize its application rates. If application rates are adjusted more precisely, N_2O emissions could be reduced and yield would not be affected by an excessive fertilization.

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