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Long-term trajectories of the C footprint of N fertilization in Mediterranean agriculture (Spain, 1860–2018)

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Abstract

Synthetic nitrogen (N) fertilization has helped boost agricultural yields, but it is also responsible for direct and indirect greenhouse gas (GHG) emissions. Fertilizer-related emissions are also promoted by irrigation and manure application, which has increased with livestock industrialization. Spanish agriculture provides a paradigmatic example of high industrialization under two different climates (temperate and Mediterranean) and two contrasting water management regimes (rainfed and irrigated). In this study, we estimated the historical evolution of the C footprint of N fertilization (including all the life cycle GHG emissions related to N fertilization) in Spanish agriculture from 1860 to 2018 at the province level (50 provinces) for 122 crops, using climate-specific N_2O emission factors (EFs) adjusted to the type of water management and the N source (synthetic fertilizer, animal manure, crop residues and soil N mineralization) and considering changes in the industrial efficiency of N fertilizer production. Overall, N-related GHG emissions increased ~12-fold, up to 10–14 Tg CO_2e yr^{-1} in the 2010s, with much higher growth in Mediterranean than in temperate areas. Direct N_2O EFs of N fertilizers doubled due to the expansion of irrigation, synthetic fertilizers and liquid manure, associated with livestock industrialization. Synthetic N production dominated the emissions balance (55%–60% of GHGe in the 21st century). Large energy efficiency gains of industrial fertilizer production were largely offset by the changes in the fertilizer mix. Downstream N_2O emissions associated with NH_3 volatilization and NO_3^- leaching increased tenfold. The yield-scaled carbon footprint of N use in Spanish agriculture increased fourfold, from 4 and 5 Mg CO_2e Mg N^{-1} to 16–18 Mg CO_2e Mg N^{-1}. Therefore, the results reported herein indicate that increased productivity could not offset the growth in manufacture and soil emissions related to N use, suggesting that mitigation efforts should not only aim to increase N use efficiency but also consider water management, fertilizer type and fertilizer manufacture as key drivers of emissions.

1. Introduction

The use of synthetic nitrogen (N) fertilizers, associated with agricultural industrialization, has contributed to large yield increases that have made it possible to feed a growing population (Erisman *et al* 2008) and have helped achieve even larger increases in livestock production, allowing a growing share of animal-based products in the human diet (Lassaletta *et al* 2016). At the same time, there has been a concentration of livestock in some areas, leading to high manure application rates in nearby cropland (van Grinsven *et al* 2012, Le Noë *et al* 2017, Einarsson *et al* 2020). This increase in the availability of N has not only contributed to rising yields, but also N losses and N-derived environmental pollution (Lassaletta *et al* 2016, Sutton *et al* 2021), such as the emission of the greenhouse gas (GHG) nitrous oxide (N_2O) (Thompson *et al* 2019, Wang *et al* 2019). Nitrous oxide emissions are affected by pedoclimatic conditions, fertilizer type and water management, and IPCC Tier-1 approaches could be too coarse to properly estimate emissions (Thorman *et al* 2020). Irrigation allows intensifying N fertilizer application and has been shown to increase N_2O emissions, particularly when combined with N fertilization (Trost *et al* 2013). For example, under semiarid Mediterranean conditions, both the type of irrigation and the type of N fertilizer have a clear influence on soil N_2O emissions (Cayuela *et al* 2017). On the other hand, irrigation and other crop management practices also affect indirect N_2O emissions through their influence on ammonia (NH_3) volatilization and nitrate (NO_3^-) leaching.

Furthermore, fertilizer-related life cycle emissions also include fertilizer manufacture and fossil fuel production, as well as transport of final and intermediate products. Synthetic fertilizer production is an energy- and GHG emission-intensive industrial process. The GHG emission intensity of global synthetic N fertilizer production has been estimated at 5.7 kg CO_2e kg^{-1} N (Kool *et al* 2012), which amounts to 0.6 Pg (10^{18} grams) CO_2e, or 1.2% of 49 Pg CO_2e global anthropogenic GHG emissions in 2010 (IPCC 2013), using 2010 consumption data from FAOSTAT (FAO 2018). Indeed, N fertilizer production usually accounts for a large share of total life cycle emissions in modern agricultural systems (Parton *et al* 2015, Garnier *et al* 2019). The role of fertilizer production in fertilizer-related GHG emissions may be even more important in the GHG emission balance of Mediterranean cropping systems (Sanz-Cobena *et al* 2017), particularly under rainfed conditions, where field N_2O emissions are relatively low (Cayuela *et al* 2017).

From a historical perspective, the changes in yields interact with the changes in N inputs and emission factors (EFs), driven by management changes, potentially resulting in changes in yield-scaled N_2O emissions. On the other hand, the energy efficiency of most industrial processes dramatically increased during the 20th century due to technological advances and scale economies, which is specifically the case of N fertilizers (Smil 2004, Ramírez and Worrell 2006). To our knowledge, the influence of these historical processes on GHG emissions has not been studied in any Mediterranean or semiarid area. Spain presents mostly a Mediterranean but also a temperate climate, contrasting irrigated and rainfed management and important historical changes in the synthetic and organic fertilization mix (Lassaletta *et al* 2014b, Guzmán *et al* 2018).

In this study we aimed to evaluate the effect of these contrasting long-term trends in farming and industry on the agro-environmental implications of N fertilization, particularly on the carbon (C) footprint. To do so, we estimated historical changes in the impact of N fertilization on GHG emissions in Spanish cropland in the long term (1860–2018).

2. Summary of methods

2.1. Scope and system boundaries

GHG emissions associated with N management in Spanish cropland were investigated for the period 1860–2018 from a life cycle assessment perspective. The analysis was performed at the crop (122 crop types) and province (50 provinces) levels, and it includes changes in agricultural N fluxes, industrial efficiency of N fertilizer production and direct and indirect soil N_2O emissions affected by soil, climate, irrigation and fertilizer type. Spanish provinces approximately correspond to the Eurostat NUTS3 classification (table S1 (available online at stacks.iop.org/ERL/16/085010/mmedia)). The provinces were classified as temperate or Mediterranean (figure S1), following the G200 classification (Olson and Dinerstein 2002) (figure S2). The functional units are 1 ha of cultivated land (including fallow) and 1 Mg N produced, thus covering 'from cradle to farm gate'. The analysis includes (a) direct N_2O emissions from the N sources included in the IPCC guidelines (IPCC 2006, 2019), comprising synthetic fertilizers, manure, urban residues, crop residues and roots, weed residues and roots, and net soil organic matter (SOM) mineralization, (b) upstream GHG emissions from the production of industrial fertilizers and (c) indirect (downstream) N_2O emissions from ammonia and nitrate exported from cropland to other ecosystems (figure 1). In the following sections, we describe the main procedures and assumptions. Further details are provided in the supplementary materials.

2.2. Activity data

To calculate N fertilizer-related GHG emissions, activity data regarding all N sources are required. These data include crop residues, which are derived from crop area and production, weed production, fertilizer consumption, manure, which is derived from livestock numbers and intake, and net mineralization of SOM. Crop area and production data at the province level (gathering data for all Spanish provinces), differentiating rainfed and irrigated land, was mainly based on data from the Spanish Yearbook of Agriculture (MAPA 2020) for ca 1890–2018 and from secondary sources and other official records for ca 1860–1890 (table S2). Weed production was estimated in two steps. First, potential weed production was

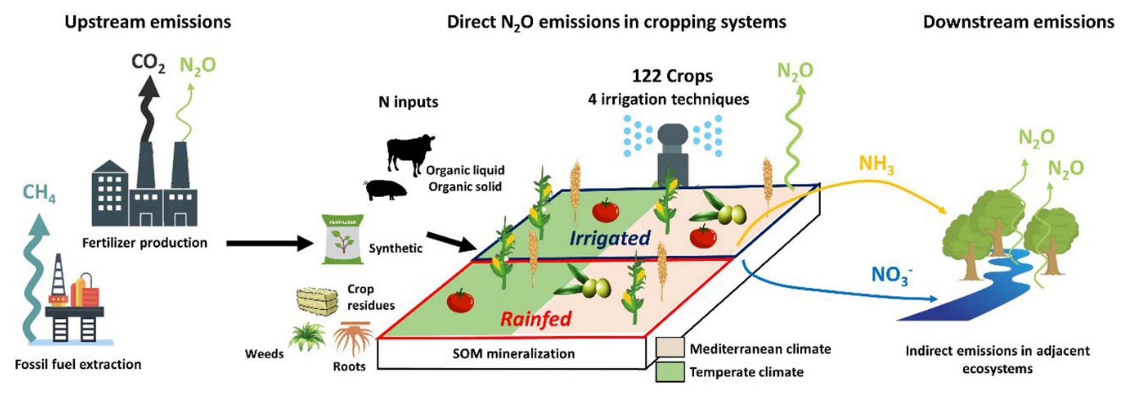

Figure 1. Main GHG fluxes considered in the study. Vectors reproduced with permission from vecteezy.com.

estimated at the province level based on annual water inputs (sum of precipitation and irrigation), using the NCEAS model (Del Grosso *et al* 2008). Second, the estimated potential weed production was modulated to account for the impact of management practices, including tillage and herbicide application, based on historical data in Soto *et al* (2016) and Aguilera *et al* (2018).

We reconstructed the total consumption of industrial N fertilizers in Spain on an annual basis, including synthetic fertilizers, ammonium sulfate from coke-oven gas, saltpeter and guano, mainly based on González de Molina *et al* (2020). Livestock N excretion, N losses during manure management and manure application rates to cropland were estimated by a balance approach including animal N ingestion and retention, as described in Aguilera *et al* (2018). The livestock population for nine species was downscaled to the province level based on their provincial distribution in 13 benchmark years from 1865 to 2016, interpolating the provincial shares and scaling to the total livestock population in the years with no data. Nitrogen from urban sources (municipal solid waste and sewage sludge) were gathered from MAPA (2019) in the 1990–2015 period, and estimated based on population in the remaining years. All N inputs in years outside the 1990–2015 period were allocated to each crop-irrigation-province category based on historical sources (table S3). The N applied to soils in the form of crop and weed residues, as well as the harvested N, was based on a full reconstruction of the net primary productivity and residue destinies (Guzmán *et al* 2014, Soto *et al* 2016, Aguilera *et al* 2018), and expressed in terms of N using N content coefficients for products (Lassaletta *et al* 2014a), roots (IPCC 2019) and residues (table S4). Nitrogen input to the soil from net mineralization of SOM, as well as net N sequestration in SOM, were based on the soil organic carbon (SOC) balance, following IPCC (2019) guidelines, which recommend assuming a C:N ratio in the SOM of 15 for forest and grassland and ten for cropland. The SOC balance was calculated with the HSOC model (Aguilera *et al* 2018), a dynamic SOC model that considers the effect of soil properties, monthly climate parameters, C inputs and soil cover, and is thus sensitive to changes in climate, land use, crop distribution and crop management.

2.3. Estimation of GHG emissions

All estimated GHG emissions were converted to CO_2e using global warming potential (GWP) values with climate feedback reported in the AR5 report of the IPCC (2013), i.e. 34 for CH_4 and 298 for N_2O.

Direct soil N_2O emissions were estimated by multiplying fertilizer inputs *F* by climate-specific EFs considering the type of water management and the types of fertilizer applied (equation (1)). The combination of both types of categorization (fertilizers, *f*, and irrigation, *i*) in each climate type (*c*) was made by transforming the fertilizer-specific EFs into modifying factors (MFs) (table 1, equation (2))

$$N_2O_{\mathrm{Direct}} - N_{c,i,f} = F_{c,i,f} \cdot \mathrm{EF}_{c,i,f}. \tag{1}$$

$$\mathrm{EF}_{c,i,f} = \mathrm{EF}_{c,i} \cdot \mathrm{MF}_f. \tag{2}$$

The EF_{ci} in temperate areas were taken from the 2019 revision of the 2006 IPCC guidelines (IPCC 2019), and in Mediterranean areas they were taken from a global meta-analysis of empirical studies under Mediterranean climate conditions (Cayuela *et al* 2017). The MFs in temperate areas were derived from IPCC (2019), and in Mediterranean areas from Cayuela *et al* (2017) and IPCC (2019) (table 1). The calculation of MFs from the data in Cayuela *et al* (2017) was made by deriving the fertilizer-specific EFs reported in this source by the average EF in all Mediterranean areas (0.5%). The use of fertilizer-specific MFs resulted in lower EFs for organic solid fertilizers and crop residues and higher EFs for organic liquid fertilizers than for synthetic fertilizers, which is in accordance

Table 1. MFs for direct N_2O EFs.

Climate type	Water management	Fertilizer type	EF_{ci} (%)	MF_f	EF_{cif} (%)	MF source
Mediterranean	Rainfed	Synthetic	0.27	1.00	0.27	Cayuela *et al* (2017)
Mediterranean	Rainfed	Organic solid, recycling and SOM	0.27	0.38	0.10	Cayuela *et al* (2017)
Mediterranean	Rainfed	Organic liquid	0.27	1.70	0.46	Cayuela *et al* (2017)
Mediterranean	Rainfed	Excreta, cattle and monogastric	0.27	0.20	0.05	IPCC (2019), dry areas
Mediterranean	Rainfed	Excreta, other	0.27	0.30	0.08	IPCC (2019), dry areas
Mediterranean	Drip	Synthetic	0.51	1.00	0.51	Cayuela *et al* (2017)
Mediterranean	Drip	Organic solid, recycling and SOM	0.51	0.38	0.19	Cayuela *et al* (2017)
Mediterranean	Drip	Organic liquid	0.51	1.70	0.87	Cayuela *et al* (2017)
Mediterranean	Drip	Excreta, cattle and monogastric	0.51	0.20	0.10	IPCC (2019), dry areas
Mediterranean	Drip	Excreta, other	0.51	0.30	0.15	IPCC (2019), dry areas
Mediterranean	Sprinkler	Synthetic	0.91	1.00	0.91	Cayuela *et al* (2017)
Mediterranean	Sprinkler	Organic solid, recycling and SOM	0.91	0.38	0.35	Cayuela *et al* (2017)
Mediterranean	Sprinkler	Organic liquid	0.91	1.70	1.55	Cayuela *et al* (2017)
Mediterranean	Sprinkler	Excreta, cattle and monogastric	0.91	0.20	0.18	IPCC (2019), dry areas
Mediterranean	Sprinkler	Excreta, other	0.91	0.30	0.27	IPCC (2019), dry areas
Mediterranean	Furrow	Synthetic	0.47	1.00	0.47	Cayuela *et al* (2017)
Mediterranean	Furrow	Organic solid, recycling and SOM	0.47	0.38	0.18	Cayuela *et al* (2017)
Mediterranean	Furrow	Organic liquid	0.47	1.70	0.80	Cayuela *et al* (2017)
Mediterranean	Furrow	Excreta, cattle and monogastric	0.47	0.20	0.09	IPCC (2019), dry areas
Mediterranean	Furrow	Excreta, other	0.47	0.30	0.14	IPCC (2019), dry areas
Mediterranean	Flood	All	0.19	—	0.19	Not used
Temperate	All non-flood	Synthetic	1.00	1.60	1.60	IPCC (2019) wet areas
Temperate	All non-flood	All organic, recycling and SOM	1.00	0.60	0.60	IPCC (2019) wet areas
Temperate	All non-flood	Excreta, cattle and monogastric	1.00	0.60	0.60	IPCC (2019) wet areas
Temperate	All non-flood	Excreta, other	1.00	0.30	0.30	IPCC (2019) wet areas
Temperate	Flood	All	0.40	—	0.40	Not used

with the results of a global meta-analysis of organic fertilizers (Charles *et al* 2017).

Emissions associated with the production of industrial fertilizers were estimated accounting for the impacts along the full production chain of the inputs. The emission coefficients were based mainly on the embodied energy data compiled by Aguilera *et al* (2015c) converted into GHG emissions using typical values of GHG emissions from fuel combustion and primary energy in Aguilera *et al* (2019a), which include CH_4 emissions in fossil fuel production and transport. We have also included N_2O emissions from nitric acid (HNO_3) production, based on IFA (2009) and Zhang *et al* (2013). This way, the total GHG emissions of each type of industrial fertilizer s in a given year t is given by multiplying the amount of fertilizer applied F by the CO_2, N_2O and CH_4 EFs (expressed as CO_2e) involved in its production and transport (equation (3)). The disaggregated EFs are shown in tables S5–S8

$$CO_2e_{s,t}^{\mathrm{Upstream}} = F_{s,t} \cdot \left(EF_{s,t}^{CO_2} + EF_{s,t}^{N_2O} \cdot GWP_{N_2O} + EF_{s,t}^{CH_4} \cdot GWP_{CH_4}\right). \quad (3)$$

Ammonia volatilization was estimated using the MANNER model (Misselbrook *et al* 2004, Sanz-Cobena *et al* 2014), which considers the type of fertilizer, both manures and synthetic, the application method and timing, as well as the soil pH and weather variables highly affecting N volatilization such as rainfall, temperature and wind conditions. NO_3^- leaching was estimated considering the soil water balance and the N surplus, which was calculated by subtracting N outputs (crop product and residue harvest, and net N sequestration in SOM) from external (synthetic and organic fertilizers and biological N fixation) and intra-cycle N inputs (net N mineralization). The shares of this N surplus that were denitrified or leached were calculated based on soil properties and specific drainage rates, following Meisinger and Randall (1991). The estimated NH_3–N and NO_3^-–N quantities were multiplied by specific EFs to obtain indirect N_2O emissions (equation (4))

$$N_2O_{\mathrm{Indirect}} - N_{c,i,f} = \left(NO_3^- - N_{c,i,f} \cdot EF_{NO_3^-}\right) + \left(NH_3 - N_{c,i,f} \cdot EF_{c,i}\right). \quad (4)$$

3. Results and discussion

3.1. Soil N inputs and direct nitrous oxide emissions

Nitrogen inputs in Spanish cropland were dominated by internal N recycling from crop and weed residues and roots (also including biological N fixation) until the mid-20th century, when synthetic N fertilizers became dominant (figures 2(a) and b)). Direct excreta by grazing animals and manure application accounted for nearly one-quarter of N inputs during most of the period studied, with lower shares during the 2nd half of the 20th century due to the dominance of synthetic fertilizers and net SOM mineralization (figure S3) in that period. Direct soil N_2O emissions increased five- to six-fold from the 19th century to the 21st century, with synthetic fertilizers accounting for more than one-half of total emissions since ca 1960 (figure 2(c)). By contrast, as shown in figure S4, growth was much lower when estimated with the reference Tier 1 EF (IPCC 2006), particularly in Mediterranean areas, due to the higher estimated N_2O emissions in the 19th century with the reference Tier 1 EF. This underlines the importance of using climate and management-specific EFs for the estimation of soil N_2O emissions.

This growth in N_2O emissions associated with industrialization is comparable to the values estimated for France by Garnier *et al* (2019), but larger than the estimations for the Great Plains of the United States of America by Parton *et al* (2015), probably due to a lower contribution of SOM mineralization during preindustrial periods in Spain, where the relative cropland expansion over grassland or natural areas was lower than in the Great Plains. The growth in crop productivity expressed in terms of N extraction, approximately three- to four-fold (figure 2(d)), was lower than the growth in soil N_2O emissions (figure 2(e)), leading to a 10%–118% increase in yield-scaled emissions between preindustrial periods and the 21st century (figure 2(f)). This increase in yield-scaled emissions was not observed in temperate areas. The analysis of the shares accounted for by each climate-irrigation type shows a minor contribution of temperate and irrigated Mediterranean categories to cropland area (figure 2(g)), but these categories reached more than half of total N inputs (figure 2(h)) as a result of higher N rates, and up to 75% of total N_2O emissions (figure 2(i)) due to the additional contribution of higher EFs (figure 3). The continued growth in yield-scaled N_2O emissions in Mediterranean irrigated systems could be partially explained by the specialization on low-N crops, such as fruit orchards and horticultural crops, which resulted in a decrease in N yield in the 21st century (figure 2(d)).

The estimated average direct N_2O EF in Spain doubled during the period studied, from 0.18% to 0.36% N_2O–N N applied^{-1} (figure 3), which is still lower than the reference IPCC Tier-1 value (1%) (IPCC 2006) and than the revised EF for dry areas (0.5%) (IPCC 2019). By input category, the only input in which significant growth of EF was observed was manure, due to the transition from solid to liquid manure management (data not shown), which resulted in a higher EF for manure as compared to synthetic fertilizers since ca 1990 (figure 3(a)). The changes in the EF were particularly pronounced in irrigated Mediterranean systems (figure 3(b)), in which they increased threefold, because the changes in N inputs were combined with changes in irrigation technologies, which have a large effect on N_2O emissions (Cayuela *et al* 2017).

The analysis of the spatial distribution of N_2O emissions (figures 4 and S5–S9) shows major differences in area-scaled emissions between temperate areas (on the northwestern coast) and Mediterranean areas (in the rest of the country) and between preindustrial (1900) and modern (2018) agriculture. In 2018, N_2O emissions per unit area in Mediterranean areas were similar to those in temperate systems in 1900. In 1900, manure was a major component of N_2O emissions in temperate areas, but rarely surpassed one-third of emissions (figure 4(a)). In 2018, the uneven distribution of livestock specialization resulted in some provinces showing more than one-half emissions derived from manure (figure 4(b)).

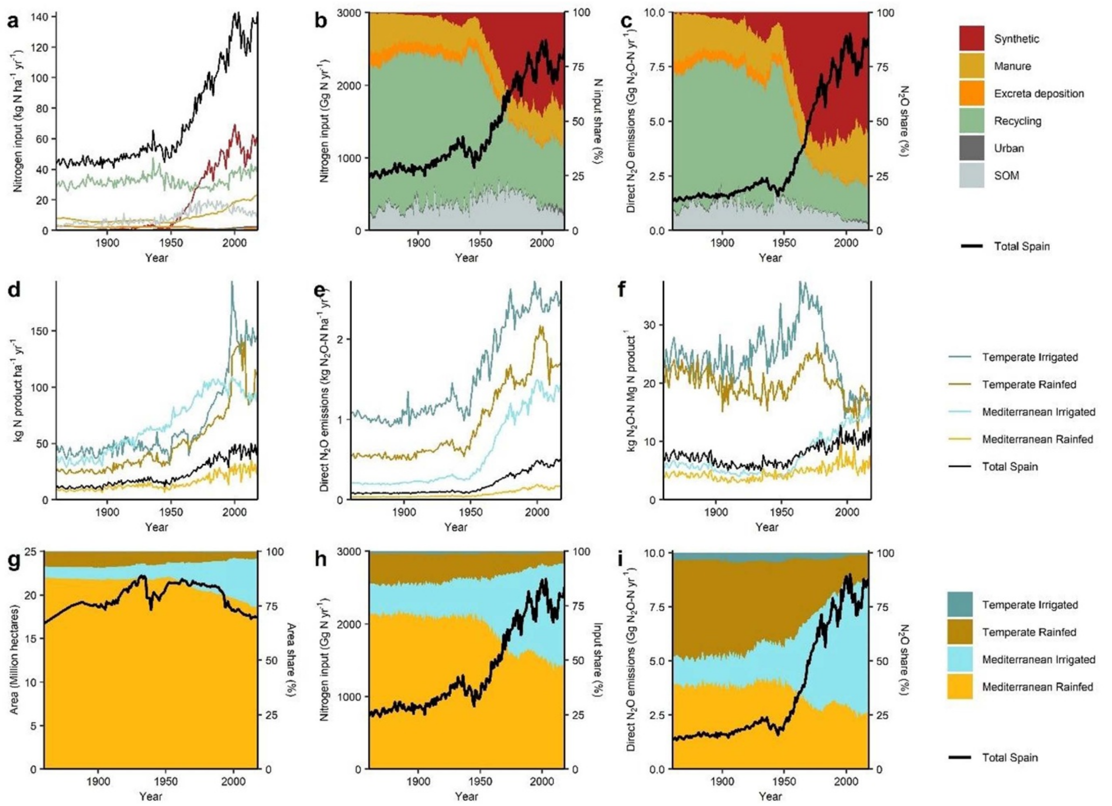

Figure 2. Nitrogen inputs and outputs and direct soil N_2O emissions in Spanish cropland (1860–2018). Nitrogen inputs considered for N_2O estimation per unit area (a); shares of inputs by input category and total N application (b); shares of direct N_2O emissions by input category and total N_2O emissions (c); crop production (including products and harvested residues) per unit area in each climate-irrigation category (d); direct N_2O emissions in each climate-irrigation category (e); yield-scaled N_2O emissions in each climate-irrigation category (f); and shares, by climate-irrigation category, of cropland areas (g), N inputs (h) and soil N_2O emissions (i).

The contribution of irrigated cropping systems was usually minor in 1900 (figure 4(c)), but in some provinces it surpassed one-half of emissions, particularly in the Mediterranean coastal provinces of the east of the country. In 2018, irrigated land was the main source of emissions in most Mediterranean provinces, surpassing 90% of total emissions in 4 out of 41 Mediterranean provinces (figure 4(d)). The Mediterranean provinces showing the largest area-scaled emissions in 2018 were those with a large share of irrigation in combination with a large share of manure (figures 4(b) and (d)).

3.2. Fertilizer consumption and upstream GHG emissions

Industrial N fertilizer consumption (including synthetic N and N from mining sources) increased from 1–10 Gg N yr^{-1} in the 19th century to 1279 Gg N yr^{-1} in 2000, falling to 740 Gg N yr^{-1} in 2008 but recovering to ca 1000 Gg N yr^{-1} in the 2010s (figure 5(a)). Industrial N sources were first dominated by imported mined materials (guano and saltpeter) and ammonium sulfate from coke oven gas. Consumption levels started growing strongly in the 1950s, when the Spanish economy opened to the world in a context of expansion of Haber–Bosch-derived N sources. Fertilizer production GHG emissions plateaued at 9–13 Tg CO_2e yr^{-1} during the 1969–2004 period, falling to 6–8 Tg CO_2e from 2005 onwards (figure 5(b)). The lack of recovery of GHG emissions in the 21st century was partially due to the decreasing trend in upstream emission intensity (figure 5(c)), with annual rates averaging 0.6%–1.6% for individual fertilizers, which was largely driven by increases in manufacturing energy efficiencies (Smil 2004, Ramírez and Worrell 2006, Aguilera *et al* 2015c). However, the average emission intensity of industrial fertilizers was similar in the 21st century and in the early 20th century, as 'energy-cheap' fertilizers were replaced by more energy-demanding synthetic fertilizers, which were not limited by mining deposits or coke production. Another process affecting fertilizer production GHG emissions was the contribution of CH_4 and N_2O (figure 5(d)). Fossil fuel production became a globally important source of global CH_4 emissions during the 20th century (Ghosh *et al* 2015), and these emissions are particularly high for natural gas (Schwietzke *et al* 2016). Consequently, the role of CH_4 in the C footprint of N fertilizer production grew when the use of natural gas in ammonia synthesis became generalized in the mid-20th century (peaking at 52% in 1932), and decreased afterwards due

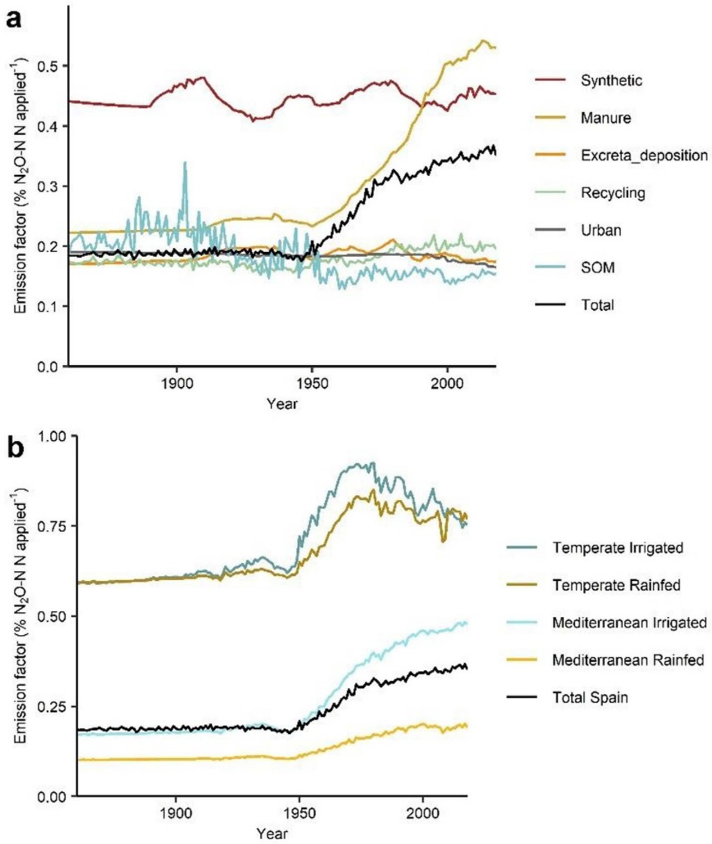

Figure 3. Weighted average direct N_2O EFs in Spanish cropland (1860–2018) according to the type of N input (a) and the climate-irrigation category (b).

to the decrease in CH_4 losses from fossil fuel production (Aguilera *et al* 2019a). Nitrous oxide is emitted in nitric acid production, an intermediate process of the nitrate fertilizer production process (IFA 2009), so the contribution of this gas peaked in 1960–1980 (above 30% of the total GWP), when the use of nitrate-based fertilizers was most generalized.

3.3. Sources of downstream indirect N_2O emissions

Average area-based NH_3 volatilization in Spanish cropland increased four- to six-fold, from 1.8–2.4 kg NH_3–N ha^{-1} yr^{-1} in the 19th century to 7.5–11.1 kg NH_3–N ha^{-1} yr^{-1} in the 2010s (figure 6(a)). This increase was mostly a direct consequence of the intensive surface application of ammonium-based fertilizers (figure 5(a)) and livestock slurries, with a high concentration of NH_4^+ (Recio *et al* 2018, Sanz-Cobena *et al* 2019), and the increasing share of urea within the synthetic fertilizer mix. Ammonia volatilization in irrigated Mediterranean areas was about one order of magnitude higher than in rainfed areas, while temperate systems showed intermediate values. These results highlight the importance of implementing effective fertilizer application strategies to abate N volatilization such as fertilizer incorporation onto the upper soil. In addition, the estimated greater emission from irrigated Mediterranean cropping systems shows the enormous potential for NH_3 abatement if irrigation and N fertilization are managed in an integrated manner (Sanz-Cobena *et al* 2011).

Regarding area-based NO_3^- leaching, there was very high variability (mostly related to rainfall variability), particularly in rainfed systems, in which it ranged between zero (absence of drainage water) and 20 kg NO_3^-–N ha^{-1} yr^{-1} in the 21st century (figure 6(b)). In spite of this variability, a strong growth trend was also identified, as leaching increased one order of magnitude from 1–3 to 10–30 kg NO_3^-–N ha^{-1} yr^{-1}. This increase was much higher in Mediterranean areas than in temperate areas, suggesting a more pronounced impact of industrialization on water pollution under the Mediterranean climate. These trends are currently contributing to severe NO_3^- pollution problems in underground and surface waterbodies in many areas of Spain (Tortosa *et al* 2011, Arauzo and Valladolid 2013), particularly in those with a high livestock concentration (Penuelas *et al* 2009), underlining the need to reduce NO_3^- leaching and promote NO_3^- abatement by reducing N inputs, improving water management and supporting beneficial practices (Quemada *et al* 2013) such as agroforestry (Blanc *et al* 2019).

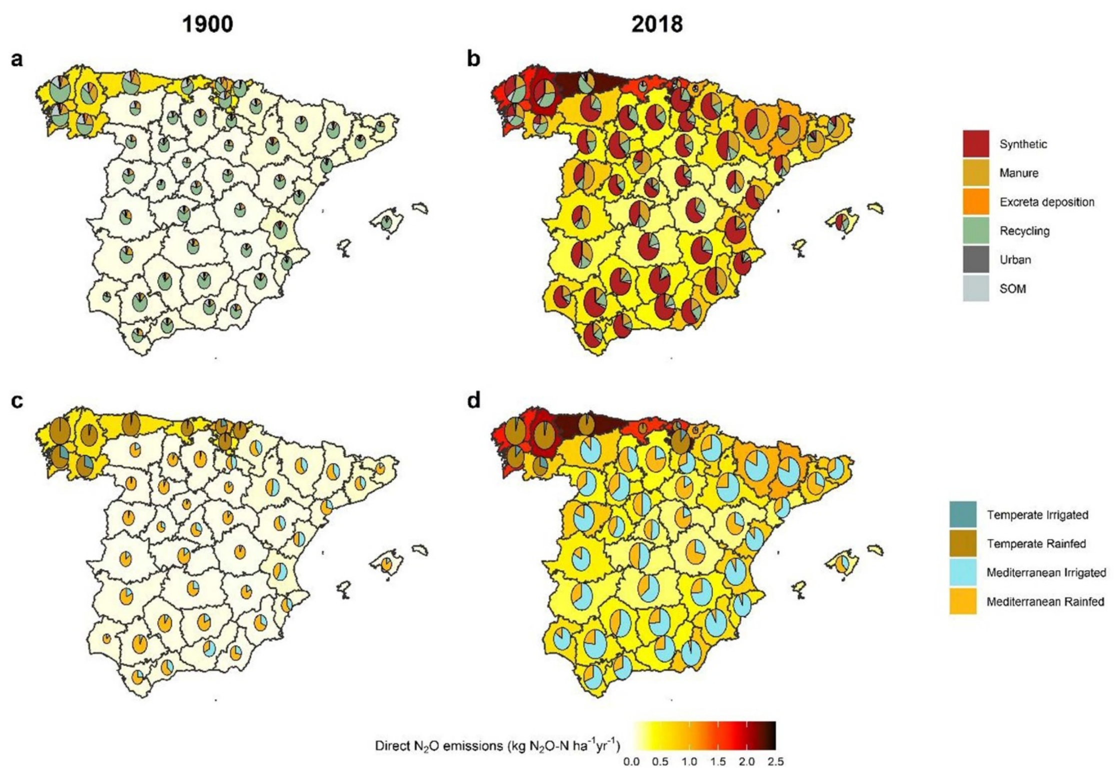

Figure 4. Spatial distribution of N_2O emissions, colored by area-based emissions (a)–(d), and showing the distribution by type of fertilizer (a), (b) and by climate-irrigation category (c), (d) in 1900 (a), (c) and 2018 (b), (d). The size of the pie charts is proportional (in a logarithmic scale) to absolute N_2O emissions in each province. The Canary Islands are not shown. See a full disclosure of province-level N_2O trends in the supplementary materials.

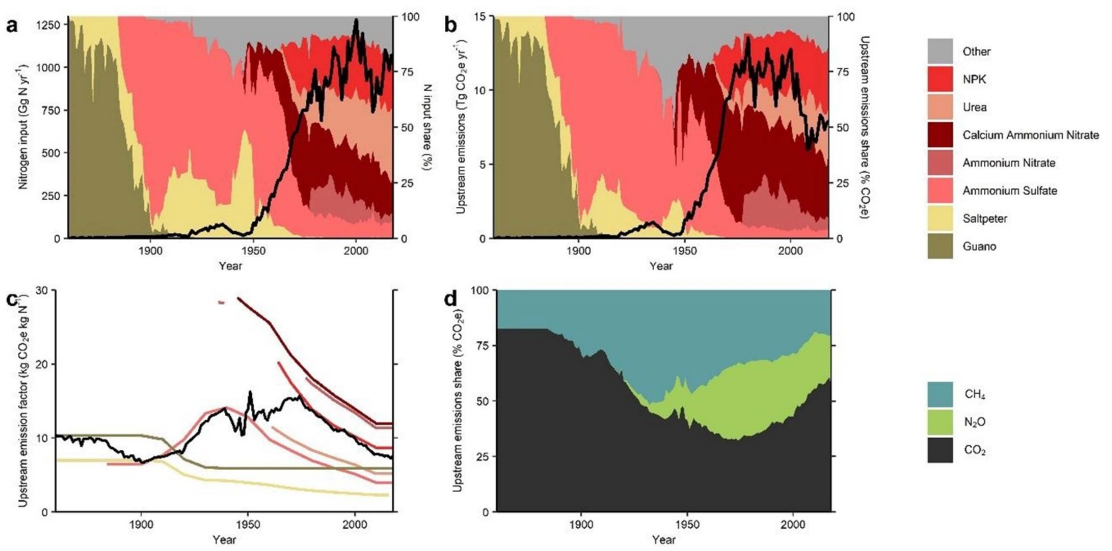

Figure 5. External N fertilizer input (a), GHG emissions from N fertilizer production, categorized by fertilizer type (b), and GHG (d), and upstream emission intensity of N fertilizers (c), 1860–2018.

3.4. Total GHG emissions and C footprint

Total fertilization-related GHG emissions in Spain increased about 16-fold with industrialization, from 0.8–1.2 Tg CO_2e yr^{-1} in the 19th century to 13.1–19.5 Tg CO_2e yr^{-1} in the 1970–2004 period, decreasing afterwards to 10.5–14.2 Tg CO_2 yr^{-1} (figure 7(a)). Much lower reductions in area-scaled emissions than in total emissions were observed in the 21st century (figure 7(c)) due to the decrease in rainfed Mediterranean cropland area during this period. The growth in the GWP of temperate systems was much lower than the growth in Mediterranean systems, and large differences among provinces were also observed (figures S10–S15). For example, area-based

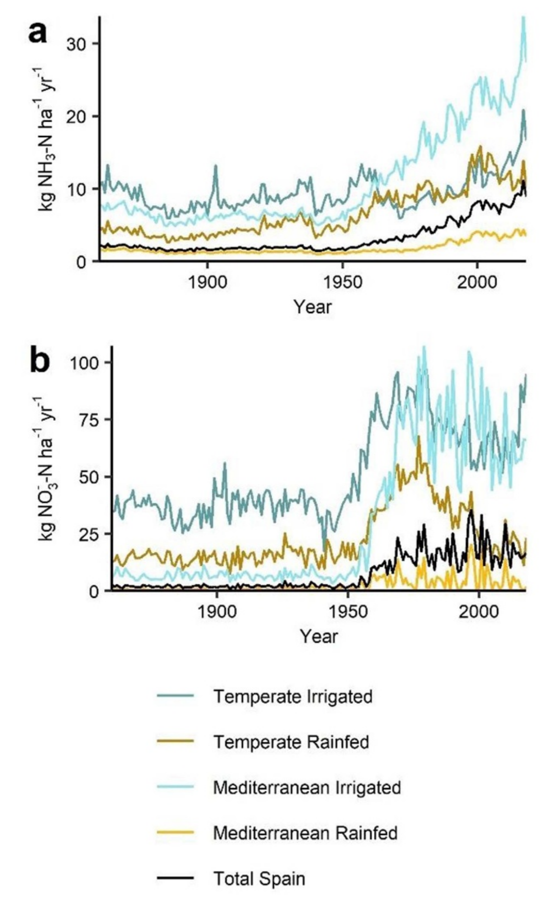

Figure 6. Area-based sources of indirect N_2O emissions, including NH_3 volatilization (a) and NO_3^- leaching (b).

emissions increased ca 20-fold in Mediterranean areas and ca fourfold in temperate areas. Yield-scaled emissions across Spanish cropland increased ca fourfold, from 4 and 5 Mg CO_2e Mg N^{-1} to 16–18 Mg CO_2e Mg N^{-1} (figure 7(d)), which indicates that the increase in yields (figure 2(d)) only partially offset the growth in emissions. Huang *et al* (2017) found that yield-scaled GHG emissions associated with fertilizer inputs in grain crop cultivation in Chinese agriculture increased from 1978 to 2012, despite the increase in yields. By contrast, yield-scaled emissions in Spain actually decreased by about one-third between 1970 and the 2010s, but this was after huge growth in the mid-20th century (ca sixfold between 1940 and 1970).

There were large differences in the contribution of the different emission types to the total GWP between temperate (figure 7(e)) and Mediterranean (figures 7(f) and (g)) systems, with highly pronounced historical changes in the latter. The contribution of upstream emissions was greater in Mediterranean systems due to the low N_2O EFs. In fact, upstream emissions accounted for more than half of all fertilizer-related emissions as early as 1920 in Mediterranean rainfed systems, surpassing 80% in most years after 1970. Specific studies of herbaceous and woody crops in Spain have shown that fertilizer production is associated with generally higher GWP than soil N_2O emissions (Aguilera *et al* 2015a, 2015b, Guardia *et al* 2016, Montoya *et al* 2021); this pattern has also been found in Mediterranean systems in Australia (Biswas *et al* 2011). This comparative study shows that the role of upstream emissions is much higher in Mediterranean than in temperate systems (figure 7). Today direct and downstream emissions only amount to 42% of fertilization emissions, although this share is increasing.

3.5. Limitations of the assessment

Nitrate leaching to waterbodies contributes to the increase in their degree of eutrophication, which is a major driver of waterbody CH_4 emissions (Deemer *et al* 2016, IPCC 2019). Methane emissions from irrigation-related waterbodies in Spain has been estimated to be 2.7 Tg CO_2e yr^{-1} in 2008 (Aguilera *et al* 2019b), which is similar to the 2.6 Tg CO_2e yr^{-1} direct soil N_2O emissions estimated in this study. Therefore, considering these indirect effects of NO_3^- leaching on waterbody CH_4 emissions could potentially lead to much higher fertilizer-related GHG emissions. Another limitation of the methodology relates to the assumption that no reactive N from the surplus is retained in the soil from year to year, given that all surplus N (excluding NH_3 volatilization and N incorporation to SOM) was assumed to be either denitrified or leached. However, despite there is evidence that some of the NO_3^- can be adsorbed to soil particles or retained in the microbial biomass, this retention is generally low and short-term (Abdelwaheb *et al* 2019). Also, the relationship between N fertilization and soil C sequestration was not analyzed in the study. Nitrogen fertilizers have been related to enhanced soil C sequestration (Xu *et al* 2021), although there is a controversy on this issue (Khan *et al* 2007). This trend has also been observed in Mediterranean cropping systems, in which soil C was lower in nonfertilized plots than in fertilized plots (Aguilera *et al* 2013). In the case of indirect N_2O from volatilized NH_3, it should be noted that historical information regarding fertilizer incorporation was not included, although the share of fertilizers being incorporated could be assumed to be low. These processes should be studied in future research.

3.6. Policy implications

The current reform of the European Union (EU) Common Agricultural Policy offers the opportunity to adapt actions to regional conditions. The results of this study clearly support the notion that only specific assessments tailored to the regional scale can effectively respond to the current challenges, as recently suggested by Lassaletta *et al* (2021). Thus, a transition from Tier-1 to Tier-3 approaches to estimate N_2O emissions is strongly recommended in all countries (Thompson *et al* 2019). The present Tier-2 estimation

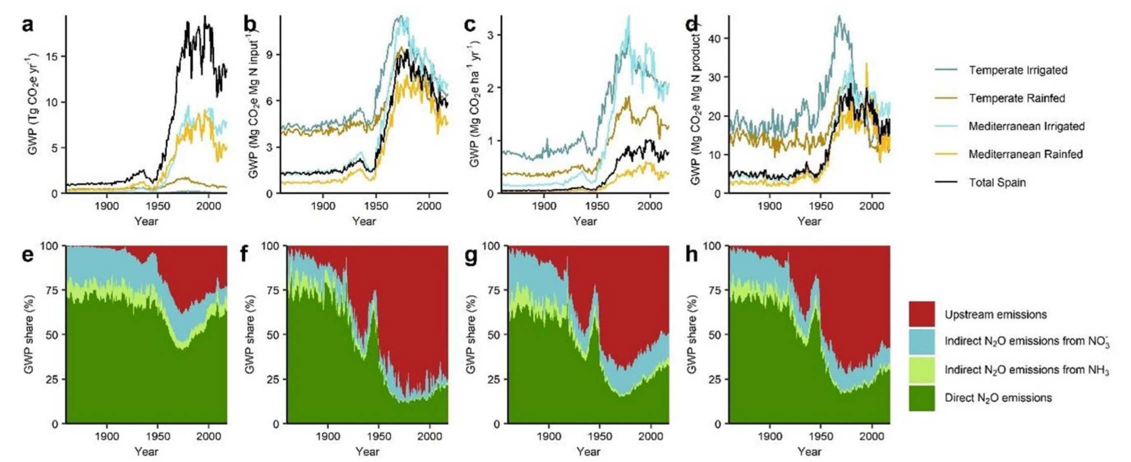

Figure 7. Total GHG emissions from N management in Spanish cropland, expressed as absolute values (a), emissions related to N inputs (b), area-based emissions (c), product-based emissions (d), and as shares of emission types over total emissions in temperate rainfed (e), Mediterranean rainfed (f), Mediterranean irrigated (g) and in total Spain (h) areas.

of N_2O emissions is an important step in this direction. Successful implementation of the recent EU Farm to Fork Strategy (European Commission 2020) aiming to reduce fertilization 20% and N losses 50% by 2030, should also be sustained on crop-specific and regionally adapted assessments. The present study provides a detailed assessment of fertilizer-related emissions in Spain that distinguishes emission hotspots in each province, thus helping design effective mitigation policies.

4. Conclusions

The long-term approach starting at 1860, thus covering a century more than most global statistical data sets, e.g. FAOSTAT (FAO 2021), in combination with detailed subnational analysis differentiating climate and irrigation types, made it possible to identify significant growth and structural changes before 1960, which cannot be done easily using global approaches. For example, synthetic fertilizers production already played an important role in total fertilizer-related GHG emissions in the early 20th century and has completely dominated the emission balance since the mid-20th century. This analysis also shows that historical changes in N_2O emissions in Mediterranean systems were much more pronounced than in temperate systems, mainly due to the expansion of irrigation and industrial livestock production, which were associated with larger increases in N inputs and EFs. The major role of upstream emissions from fertilizer production, particularly in rainfed Mediterranean systems and in the late 20th century, was driven by low soil N_2O EFs in these systems as well as the contribution of N_2O and CH_4 in the fertilizer life cycle. We conclude that the development of efficient mitigation strategies to reduce GHG emissions associated with fertilization has to focus on emission hotspots such as the ones identified in our study, and be based on assessments considering: (a) specific EFs adapted to regional agro-environmental conditions, (b) a full C footprint evaluation including upstream and downstream emissions.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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