



## Research article

## Identifying N fertilizer management strategies to reduce ammonia volatilization: Towards a site-specific approach

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## ABSTRACT

Concerns about ammonia (NH<sub>3</sub>) losses from nitrogen (N) mineral fertilizers have forced policymakers to set emission reduction commitments across Europe. Although best available techniques (BATs) have been recommended, large uncertainties still exist due to poorly targeted site-specific approaches that might compromise their effectiveness. Here we proposed and tested a conceptual framework designed to identify most effective BATs that reduce NH<sub>3</sub> at the site-specific level. The study was conducted in the Veneto region, northeast Italy. After the mapping of NH<sub>3</sub> emission potential areas, BATs and business-as-usual N fertilization scenarios were assessed using a modified version of the DNDC agroecosystem model and compared with urea broadcast distribution under different pedo-climatic conditions. The most promising practices were further tested in a field experiment using a wind tunnel combined with a FTIR gas analyzer. Results showed that closed-slot injection reduced NH<sub>3</sub> emissions with any type of mineral or organic fertilizers. Injected application, with ammonium nitrate or organic fertilizers, reduced NH<sub>3</sub> loss in maize by 75% and 96%, respectively, and in winter wheat by 87% and 98%, compared to surface broadcast. Injection was the most promising technology to support, being already available to farmers. However, some increase in nitrate leaching was observed, mostly in case of winter wheat (+24% for AN injection; +89% for organic fertilizers). By contrast, urea incorporation with hoeing, the most common technique used by farmers in spring crops, did not show satisfactory results, because the partial burial of urea caused strong NH<sub>3</sub> emissions that were even higher compared to surface broadcast. Recommended NH<sub>3</sub> reduction techniques should be tailored to local pedo-climatic and management conditions, and evaluated, in a holistic approach, considering all N fluxes in the environment.

## 1. Introduction

Concerns regarding ammonia (NH<sub>3</sub>) emissions to the atmosphere from anthropogenic sources have escalated in recent years. Ammonia plays an important role in atmospheric aerosol production by reacting with acid gas compounds (SO<sub>2</sub>, NO<sub>x</sub>) (Galloway et al., 2003), and it is an indirect source of the greenhouse gas nitrous oxide (N<sub>2</sub>O) (EPA, 2019). It is estimated that about 80% of the worldwide anthropogenic NH<sub>3</sub> emissions comes from agricultural activities, especially losses from agricultural soils (58%) and manure management (21%) (Van Damme et al., 2014). Mineral nitrogen (N) fertilizer application contributes 33%

of global NH<sub>3</sub> emissions (Beusen et al., 2008) and 20% in Europe (ECETOC, 1994). Emphasis has been placed on urea since it is by far the most prevalent fertilizer type (Sommer et al., 2004), its rate of use is growing (FAO, 2019), and urea-related NH<sub>3</sub> emissions are much greater than those from other N fertilizer types.

The latest National Emission Ceilings Directive (NEC Directive, 2016/2284) has entered into force on December 31st 2016 to reduce, amongst other air pollutants, NH<sub>3</sub> emissions. EU Member States are asked to reduce NH<sub>3</sub> emissions from mineral N fertilizers by using the following approaches: (i) replacing urea-based fertilizers by ammonium nitrate-based fertilizers; (ii) reducing NH<sub>3</sub> emissions by at least 30%

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compared with the surface broadcast reference method (Sutton et al., 2015) where urea-based fertilizer continues to be applied; (iii) replacing inorganic fertilizers with organic ones, or at least spreading them in line with the foreseeable crop or grass requirements. Despite that best available techniques (BATs) exist for preventing and reducing  $\text{NH}_3$  agricultural emissions (UNECE, 2014), large uncertainties still remain regarding their effectiveness at the site-specific level. Greater  $\text{NH}_3$  losses from fertilizers are common in alkali soils (Rao and Batra, 1983; Sommer et al., 2004), while high cation exchange capacity (CEC) lowers emissions due to interactions between  $\text{NH}_4^+$  ( $\text{NH}_3$  precursor) and exchange sites (Duan and Xiao, 2000; Sommer et al., 2004). Climatic influencing factors are wind speed, air temperature and rainfall that affects the soil water content (Sommer et al., 1991). Sommer et al. (2004) reported that cumulative  $\text{NH}_3$  losses can be  $\geq 60\%$  of applied N under specific pedo-climatic conditions.  $\text{NH}_3$  emissions may be strongly reduced with careful fertilizer management, such that emissions can be reduced to  $<10\%$  in well-established crops (Schjoerring and Mattsson, 2001), or to  $<50\%$  with N fertilizer incorporation. However, conflicting results in  $\text{NH}_3$  losses according to N distribution management have been observed. In some cases urea incorporation increased  $\text{NH}_3$  emissions compared to surface spreading due to local variability, e.g., in soil structure and moisture (Pelster et al., 2019). Ammonia volatilization is higher at lower incorporation depths and is impacted by soil-fertilizer mixing methods (Rochette et al., 2013).

Guidelines to prevent and abate  $\text{NH}_3$  emissions should follow a site-specific approach, where BATs are targeted according to a site-vulnerability assessment that combines pedo-climatic and management factors (Burton and Schwarz, 2013). Furthermore, BATs should embrace a broader vision, evaluating their effects on the whole N cycle and loss pathways (e.g., nitrate leaching,  $\text{N}_2\text{O}$  emission) following a holistic approach.

The present study fell within the broad LIFE PrepAIR project that aimed to study reduction methods for  $\text{NH}_3$  emissions from urban to agricultural sources in the Po river basin, northern Italy, one of the most air-polluted areas in Europe. In this context, the main goal of this work was to develop a conceptual framework that should assist policymakers and practitioners to identify most effective BATs at the site-specific level. To this end a number of specific objectives were pursued: i) mapping of the  $\text{NH}_3$  emission potential from soils of the Veneto region (NE Italy); ii) evaluating the business-as-usual N fertilization practices in croplands and their impacts on N losses; iii) identifying the most promising BATs to reduce  $\text{NH}_3$  emissions that can be adopted in the Veneto region, and testing their effectiveness in a field experiment.

## 2. Material and methods

### 2.1. Study area

This research was conducted in Veneto (northeast Italy,  $45^\circ30'$  N  $11^\circ45'$  E), a region that encompasses an area of about  $18,400 \text{ km}^2$ . Its north-south extension, from the Austria border to the Po River, is of ca.

210 km, while the eastern-western territory extends from the Tagliamento River to Lake Garda (ca. 195 km). Most of the region (55%) is occupied by the Venetian plain, where most of the intensive agricultural production takes place. The area is flat and rarely exceeds 100 m above sea level. The continental climate of the Venetian plain is sub-humid, with annual rainfall of about 800–1000 mm (Table 1). Temperatures increase from January to July. The rainfall distribution during the year is characterized by a maximum in May or June (ca. 100 mm) and a minimum in winter (50–60 mm per month from December to February). The major soils of the Venetian plain are Calcisols and Cambisols (WRB, 2014), characterized by a medium natural fertility due to relatively low soil organic carbon content ( $\text{SOC} = 6\text{--}10 \text{ g kg}^{-1}$ ) and a cation exchange capacity from low (in sandy,  $\text{CEC} = 5\text{--}10 \text{ cmol kg}^{-1}$ ) to high (in silty-clay,  $\text{CEC} > 20$ , up to  $55 \text{ cmol kg}^{-1}$ ). Soil reaction mostly ranges from neutral (pH 6.6–7.3) to moderately alkaline (7.9–8.4). Moving northward, soils are composed of calcareous, skeletal (25–47%) loamy and clay loamy soils (Luvisols and Cambisols) (pH  $> 7.9$ ;  $\text{SOC} 10\text{--}12 \text{ g kg}^{-1}$ ). Mountain areas generally comprise sand/clay loamy soils, with poorly differentiated profiles (Leptosols) alternated with deeper ones (Cambisols) (pH moderately acid  $\approx 5.9$ ; high  $\text{CEC} \approx 35\text{--}40 \text{ cmol kg}^{-1}$ ).

### 2.2. Mapping of $\text{NH}_3$ emission potential

Soil information (Regione Veneto, 2005), provided by the Environmental Protection Agency of the Veneto Region (ARPAV), were used to map the susceptibility to  $\text{NH}_3$  emissions from Veneto soils (Fig. 1A), regardless any fertilization practice. They were grouped according to the classification proposed by Duan and Xiao (2000), which identified pH and CEC threshold levels of potential  $\text{NH}_3$  emissions:

- (I) Very low (pH  $< 7$ ;  $\text{CEC} \geq 20 \text{ cmol kg}^{-1}$ );
- (II) Low (pH  $< 7$ ;  $\text{CEC} < 20 \text{ cmol kg}^{-1}$ );
- (III) Medium ( $7 \leq \text{pH} < 8$ ;  $\text{CEC} > 10 \text{ cmol kg}^{-1}$ );
- (IV) High ( $7 \leq \text{pH} < 8$ ;  $\text{CEC} < 10 \text{ cmol kg}^{-1}$ );
- (V) Very high (pH  $\geq 8$ ;  $\text{CEC} < 10 \text{ cmol kg}^{-1}$ ).

### 2.3. Survey on agricultural practices in the Veneto region

Business-as-usual crop management information was collected via an online questionnaire conducted among farmers and farm advisors (Fig. 1B). A number of 30 respondents were selected according to a “snowball” methodology (Dal Ferro et al., 2020), covering the main cropping areas of the Veneto region. Requested information included main crops and practices (varieties, yield, tillage, etc.), and N fertilizer management (type, dosage, timing, etc.).

### 2.4. DNDC agroecosystem model to predict alternative BAT scenarios

The DNDC agroecosystem model (Li, 2012) was used to identify most effective BAT scenarios to mitigate  $\text{NH}_3$  emissions (Fig. 1C). In addition to  $\text{NH}_3$  losses, the trace gas emissions of  $\text{N}_2\text{O}$  along with nitrate leaching

**Table 1**

Soil (0–20 cm) and weather characteristics of the five pedo-climatic areas. Standard errors are reported in brackets.

Pedo-climatic Area	pH	Particle size distribution (%)			CEC <sup>a</sup> (cmol kg <sup>-1</sup> )	SOC <sup>b</sup> (%)	Temperature (°C)			Rainfall (mm yr <sup>-1</sup> )	Risk class
		Sand	Silt	Clay			July (Max) <sup>c</sup>	January (Min) <sup>d</sup>	Mean		
BP	8.09	40	45	15	12	1.02	31.5 (0.8)	0.0 (1.2)	14.3 (0.18)	788.1 (79.1)	III
LE	8.08	51	24	25	17	1.28	30.1 (0.70)	0.48 (1.2)	14.3 (0.19)	888.4 (156.9)	III
BV1	7.66	34	52	14	13	2.30	31.5 (0.9)	0.12 (1.3)	14.4 (0.14)	1012.2 (132.1)	III
BV2	6.84	33	51	16	17	1.53	31.5 (0.9)	0.12 (1.3)	14.4 (0.14)	1012.2 (132.1)	I
FE	7.78	40	32	28	24	3.41	29.4 (0.9)	-4.0 (1.7)	12.1 (0.15)	1574.9 (263.5)	III

<sup>a</sup> Cation exchange capacity.

<sup>b</sup> Soil organic carbon content.

<sup>c</sup> Average maximum of the hottest month.

<sup>d</sup> Average minimum of the coldest month.

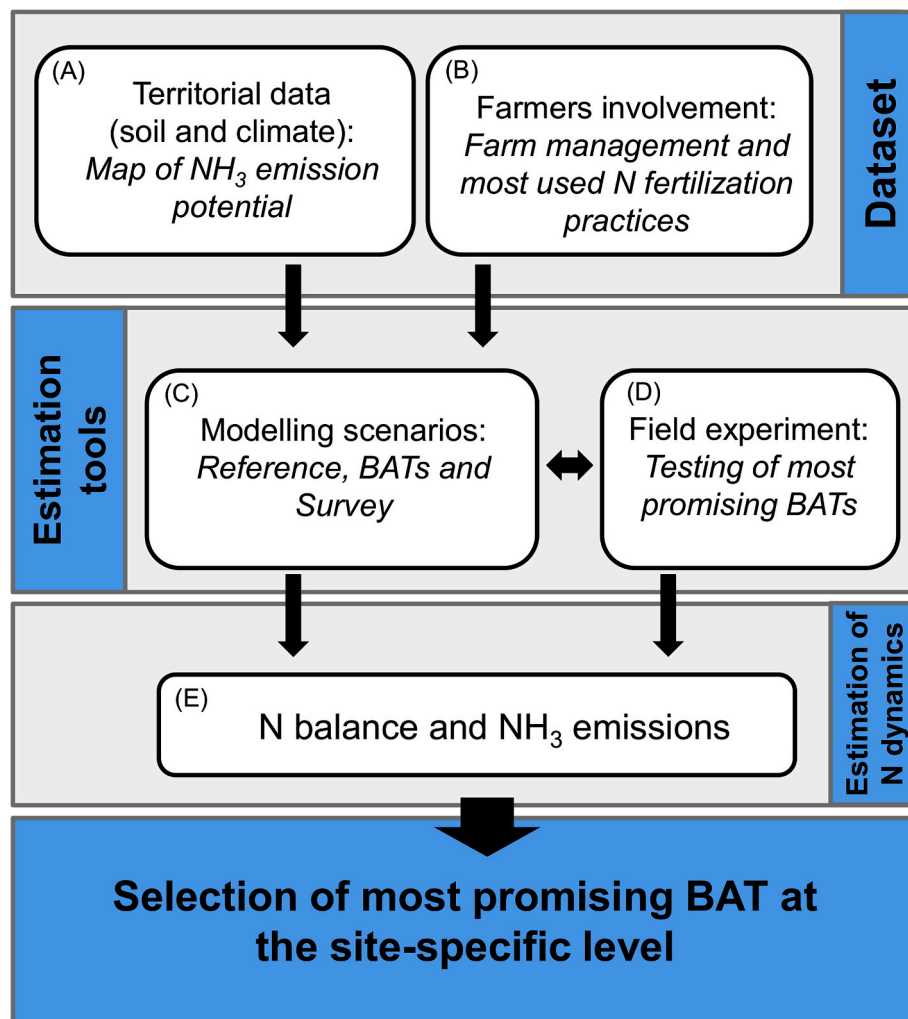


Fig. 1. Outline of steps and processes adopted during the study.

were also considered. DNDC has been successfully used worldwide to predict C and N cycling, including the Venetian plain (Camarotto et al., 2018; Morari, 2010). For this study, a modified DNDC v. CAN version (from DNDC95), suited to predict  $\text{NH}_3$  emission from N fertilizers and animal slurry in temperate agroecosystems, was used. The improved model can simulate soil pH buffering and N fertilizer application at depth, and includes the effect of urea hydrolysis (Congreves et al., 2016; Dutta et al., 2016). The updated version of the DNDC. vCAN model is available directly from the developers (<https://github.com/BrianBGrant/DNDCv.CAN>).

The map of  $\text{NH}_3$  soil emission potential was overlaid with a climatic map to identify five pedo-climatic locations for assessing management impacts using DNDC (Table 1, Fig. 3). The selected locations, namely Bagnolo di Po (BP), Legnaro (LE), Barbarano Vicentino (BV1 and BV2), and Feltre (FE), were chosen because they were equipped with a weather station that provided freely available daily data (ARPAV weather stations), and because they encompassed the climatic macro zones stretching from south to north following a climatic gradient of increasing rainfall and reduction in mean temperature (at FE location). At each location, a total of eight different scenarios was modeled under maize and winter wheat, which represent the main cultivated arable crops in the Veneto region. BATs involving irrigation management were not included in this study.

The reference application technique (hereafter, “SRF<sub>Urea</sub>”) was surface broadcast application of urea-based N fertilizer (Table 2). Besides SRF<sub>Urea</sub>, six alternative scenarios (Table 3) were modeled on the same

Table 2

Main management aspects under reference simulation condition (surface broadcast, SRF<sub>Urea</sub>) simulated using DNDC v.CAN.

	Maize	Winter Wheat
Fertilization (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	248	120
Fertilizer application	Surface broadcast	Surface broadcast
Sowing date	15th April	1st November
Harvest date	15th September	15th June
Base dressing	15th April, NPK 100 kg N ha <sup>-1</sup>	–
Top dressing 1	15th May, urea 74 kg N ha <sup>-1</sup>	15th March, urea 60 kg N ha <sup>-1</sup>
Top dressing 2	15th June, urea 74 kg N ha <sup>-1</sup>	15th April, urea 60 kg N ha <sup>-1</sup>

crops by following the guidelines provided by the UNECE document (UNECE, 2014), i.e. four on mineral fertilization management and two on the substitution with organic fertilizers (injection of slurry and digestate at 15 cm depth). One survey-based scenario per crop, consisting of side-dress urea incorporated at 5 cm depth for maize (INC<sub>5-Urea</sub>) and top-dress ammonia nitrate (SRF<sub>AN</sub>) on winter wheat, was included to represent common practices in the region. Simulations were performed over a 5-year period (years 2013–2017). Apart from fertilization and crop type, all simulations included the same management practices. For each area, a representative site was selected, which



**Table 3**

Modeled fertilization management scenarios including the reference application technique (surface broadcast, SRF<sub>Urea</sub>), BATs (UNECE, 2014) and scenarios to represent survey findings (INC<sub>5-Urea</sub> for maize and SRF<sub>AN</sub> for winter wheat) from farmers and practitioners.

Abbreviation	Description	Maize	Winter Wheat
SRF <sub>Urea</sub>	Surface broadcast distribution of urea	x <sup>a</sup>	x <sup>a</sup>
SRF <sub>AN</sub>	Surface broadcast distribution of ammonium nitrate	x	x <sup>b</sup>
SRF <sub>UAN</sub>	Surface broadcast distribution of urea-ammonium nitrate (UAN, liquid)		x
INJ <sub>6-AN</sub>	Closed-slot injection of ammonium nitrate at 6 cm depth	x	x
INJ <sub>6-Urea</sub>	Closed-slot injection of urea at 6 cm depth	x	x
INH <sub>Urea</sub>	Surface broadcast distribution of urea with urease inhibitor	x	x
INC <sub>15-Slu</sub>	Incorporation of slurry over 15 cm depth	x	x
INC <sub>15-Dig</sub>	Incorporation of slurry over 15 cm depth	x	x
INC <sub>5-Urea</sub>	Incorporation of urea at 5 cm depth	x <sup>b</sup>	

<sup>a</sup> Reference scenario.

<sup>b</sup> Survey-based scenario.

was linked to a pedo-climatic database as input to feed DNDC.

## 2.5. Testing of most promising BATs in a field experiment

Integrating both survey and model results, an experiment was set up to field-test NH<sub>3</sub> emission for the reference application technique and for the most promising BATs (Fig. 1D). The site was at the Experimental Farm “L. Toniolo” of the University of Padova in Legnaro (45° 21' N, 11° 58' E; 6 m above sea level), northeast Italy, where the climate is sub-humid with annual rainfall of about 850 mm distributed fairly uniformly throughout the year and the mean temperature is 14 °C.

The soil was a silty-loam Calcaric Cambisol (sand 35%, silt 48%, clay 17%), with a pH of 8.1, CEC of 12.5 cmol kg<sup>-1</sup>, SOC content of 12 g kg<sup>-1</sup>, and C/N ratio of 7.4. According to ARPAV (Regione Veneto, 2005), the Calcaric Cambisols cover almost 50% of the Venetian plain. The soil was classified as *medium* susceptibility to NH<sub>3</sub> emissions (class III). The field test was conducted on bare soil in 12 plots, 0.75 m wide and 3.5 m long,

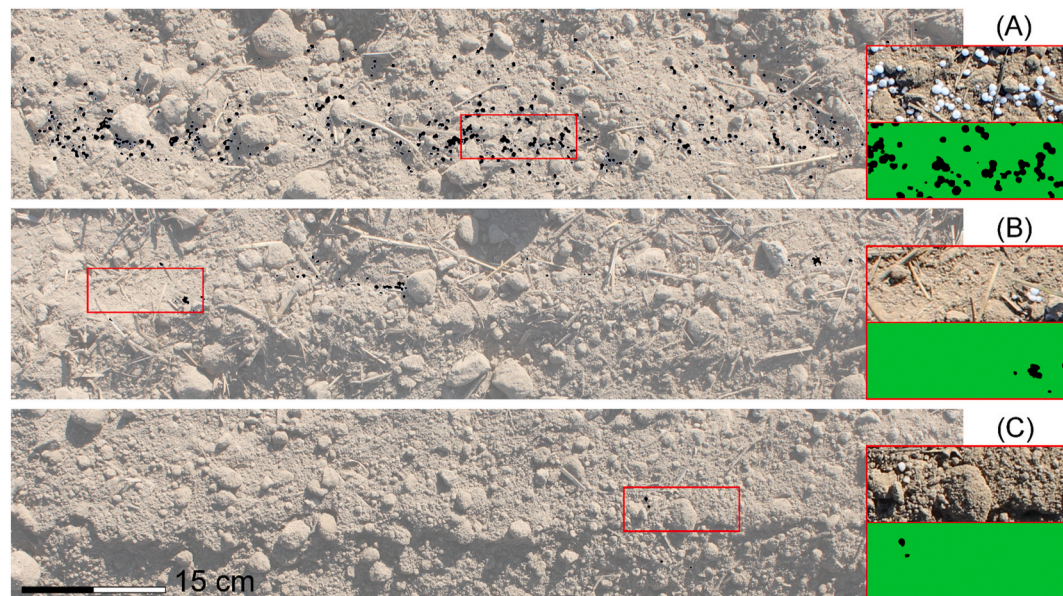
spaced 0.75 m apart. The experimental layout was a randomized block design with three replicates. The tested treatments were: i) control surface broadcast distribution of urea (SRF<sub>Urea</sub>); ii) side dressing by incorporation of urea in the top 3 cm by hoeing (INC<sub>3-Urea</sub>); iii) side dressing by incorporation of urea in the top 6 cm by hoeing (INC<sub>6-Urea</sub>); iv) side dressing by closed-slot injection of urea at 6 cm depth (INJ<sub>6-Urea</sub>). The experiment started on September 23rd 2019, when each plot received granular urea (N = 46%) at a rate of 200 kg N ha<sup>-1</sup> followed by different incorporation methods. After urea application, each plot received a daily amount of simulated rainfall to keep the soil wet, from 0.5 to 3.0 mm, leading to cumulated rainfall of 30.6 mm.

## 2.6. Quantification of broadcast incorporation of urea through image analysis

The rate of urea incorporation during side dressing and hoeing with an inter-row cultivator at different depths (INC<sub>3-Urea</sub> and INC<sub>6-Urea</sub>) was quantified through image analysis techniques. To identify urea granule incorporation or surface maintenance, a known quantity of urea granules was spread and incorporated with hoeing. At least five pictures of the soil surface in different positions along the row were perpendicularly taken at 150 cm height with an 18-megapixel RGB camera (EOS 1200D, Canon, Tokyo, Japan). A digital image analysis procedure based on machine learning algorithm (Arganda-Carreras et al., 2017) was used to identify surface urea, and separate it from the incorporated urea. Hoeing at 3 cm depth resulted in 15% surface urea granules, while at 6 cm hoeing depth only 1% was not incorporated (Fig. 2). These results were used to simulate the mechanical effect of hoeing during the field test.

## 2.7. Ammonia emission monitoring system

Ammonia emissions were measured starting from September 23rd to October 17th 2019 using a wind tunnel apparatus (Lockyer, 1984; Sommer and Misselbrook, 2016) combined with a FTIR multi-gas analyzer Gasmet DX4015 (Gasmet Technologies, Vantaa, Finland). The wind tunnel was 0.4 m wide and 2.5 m long, where the open area was 1.6 m long (measurement area 0.64 m<sup>2</sup>). The section area was 0.11 m<sup>2</sup>. At the end of the tunnel, a fan drew air at a constant speed of 0.7 m s<sup>-1</sup>. A



**Fig. 2.** Images identifying urea after surface broadcast (A), incorporation with hoeing at 3 (B) and 6 cm (C) depth. Black dots in the main pictures are urea granules on the soil surface. Magnifications of selected areas are reported on the right-side images: true color imagery is reported on the top, and binarized imagery with urea (black) on the soil surface (green) is reported on the bottom. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article).

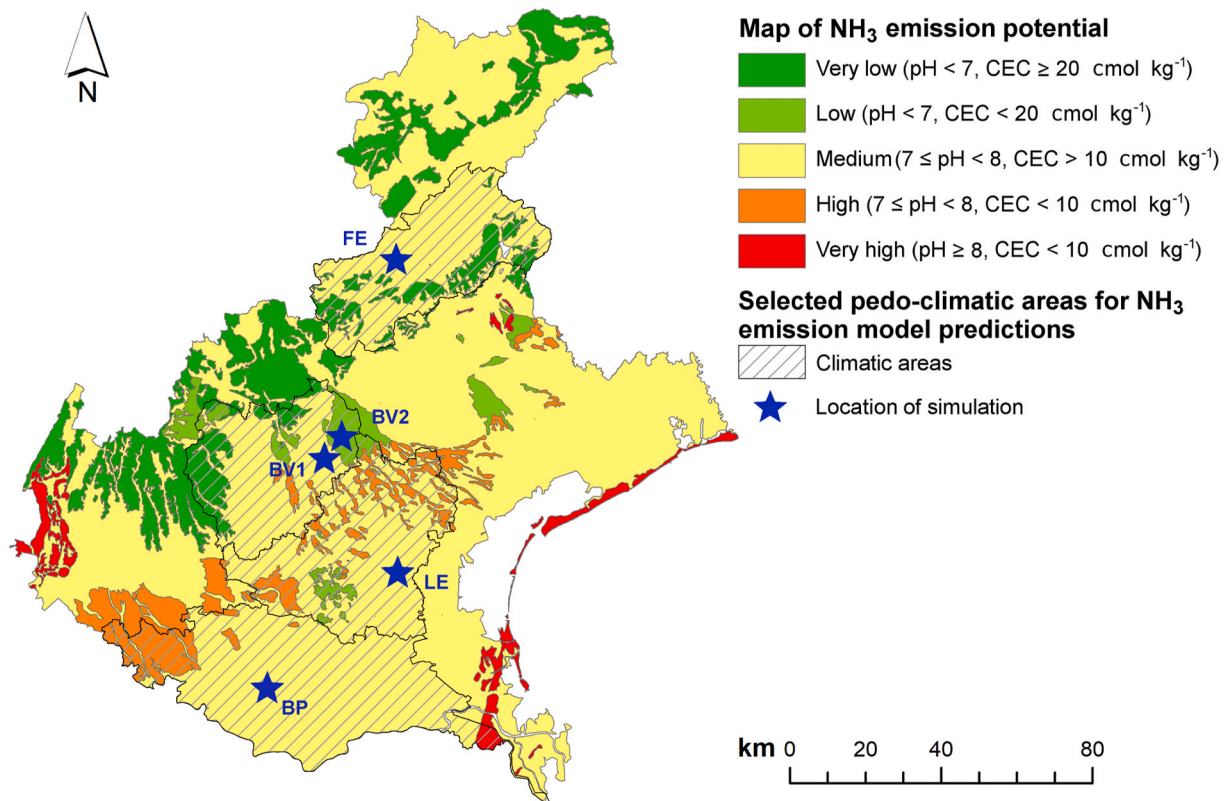


Fig. 3. Map of NH<sub>3</sub> emission potential across the Veneto region.

small hole positioned at the top of the tunnel, provided a means to measure wind speed inside the duct using an anemometer, and to measure ammonia using the gas analyzer probe. The probe was a cable made of polytetrafluoroethylene (PTFE) that prevented NH<sub>3</sub> adsorption during gas sampling. The detection limit of the gas analyzer for NH<sub>3</sub> was 0.065 ppm.

The experimental site was equipped with a meteorological station consisting of an anemometer (HD54.3, DeltaOhm Srl, Selvazzano Dentro, Italy) and an air temperature (T, °C)-relative humidity (UR, %) probe (HP3517TC2.2, DeltaOhm Srl). Each plot had a soil temperature (T, °C)-water content (VWC, %) probe (HP3910.2, DeltaOhm Srl) at 1 cm depth; all probes were connected to a datalogger (HD35EDLMTC.E and HD35EDLWS/3 T, DeltaOhm Srl). Probes were calibrated in laboratory providing an accuracy of ±3%.

## 2.8. NH<sub>3</sub> emission dynamics

Ammonia concentration was measured twice a day in the first two weeks and, subsequently, at incremental intervals for a total of 14 monitoring days. Ammonia concentrations were converted into fluxes (kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>) using the following equation (Eq. (1)), as in Rochette et al. (2009):

$$J_{N-NH_3} = \frac{Q}{A} \times (C_0 - C_i) \quad (1)$$

where  $Q$  (m<sup>3</sup> h<sup>-1</sup>) is the air flow rate through the tunnel calculated as the product of the wind speed and the sectional area of the tunnel;  $A$  (m<sup>2</sup>) is the enclosed surface area;  $C_0$  and  $C_i$  (mg m<sup>-3</sup>) were the background (out of the tunnel) and internal N-NH<sub>3</sub> concentrations, respectively.

Fluxes obtained from each plot were interpolated to calculate the cumulative NH<sub>3</sub> loss by implementing the model proposed by Demeyer et al. (1995), as follows:

$$\frac{dY}{dt} = \vartheta acie \left( -c \frac{1}{T} \right) \left[ 1 - e \left( -c \frac{1}{T} \right) \right]^{(i-1)} \quad (2)$$

where  $dY/dt$  is the NH<sub>3</sub> emission flux rate (kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>), which is a function of soil temperature ( $T$ , °C), soil moisture ( $\vartheta$ , %), time ( $t$ , h), while  $a$  (value of the asymptote),  $c$  (rate constant, >0) and  $i$  (describing the shape of the sigmoidal curve,  $i > 1$ ) are fitting parameters. Monitored wind speed, soil temperature and soil water content were used to estimate hourly cumulative NH<sub>3</sub> fluxes for the duration of the experiment.

## 2.9. Statistical analysis

The non-parametric Kruskal-Wallis method was used to compare NH<sub>3</sub> emission concentrations during the field experiment; data were reported in box-plots including the median, 25% and 75% percentiles (box values), non-outlier range (whiskers values = 1.5 × the height of the box) and outlier values. Post hoc comparison of mean ranks for all groups was performed according to Siegel and Castellan (1988).

## 3. Results

### 3.1. Map of NH<sub>3</sub> emission potential

A map of the Veneto region showed five distinct areas of cropland which were at differing levels of susceptibility to NH<sub>3</sub> emissions due to mineral N fertilizer use (Fig. 3). To note that the map represented only the NH<sub>3</sub> emission potential that was independent of the impacts of any fertilization practice. The most vulnerable areas, which were characterized by pH > 7 and CEC < 10 cmol kg<sup>-1</sup>, covered approximately 8.6% of the total regional area. Intermediate potential emissions accounted for 69.9% of total surface, where pH-driven NH<sub>3</sub> emissions were offset

by  $\text{NH}_4^+$  adsorption due to greater cation exchange capacity ( $\geq 10 \text{ cmol kg}^{-1}$ ). By contrast, soils with low emission potential were those with  $\text{pH} < 7$ . They differed in CEC by a threshold level that identified low ( $\text{CEC} < 20 \text{ cmol kg}^{-1}$ ), and very low ( $\text{CEC} \geq 20 \text{ cmol kg}^{-1}$ )  $\text{NH}_3$  emission potential. These soils comprised approximately 13.7% and 1.7% of the regional arable cropland areas, respectively.

### 3.2. Results from the survey conducted with farmers and farm advisors

The main cultivated crops by 20 respondents were maize and winter wheat, which represented 32% and 21% respectively of the total investigated crops. Several minor crops were grown discontinuously, or on small agricultural areas (Table 4). Despite being low the number of surveys (20), farmers and farm advisors accounted for about 10,000 ha of cropland area in the Veneto region.

In maize, base dressing consisted of localized placement at 5 cm depth of NPK (80% of cases) or urea (20% of cases), just before sowing. Average doses were  $100 \pm 15 \text{ kg N ha}^{-1}$ . Top dressing, mostly with urea, was generally split in two events between May and June (total average =  $148 \pm 16 \text{ kg N ha}^{-1}$ ). Fertilizers were applied with top or side dressing (27% of cases), or as localized placement in the row with closed-slot injection (36% of cases) and incorporation (37% of cases). In 60% of the cases, N top dressing was the only fertilization in winter wheat, amounting totally to a total of  $122 \pm 14 \text{ kg N ha}^{-1}$ . Localized placement with ammonium nitrate (AN) or urea-based fertilizers was never used. Few farmers (27%) used a direct localized application of liquid urea-ammonium nitrate (UAN).

### 3.3. Modeling BAT scenarios

#### 3.3.1. N fluxes

Estimated N losses using the DNDC model (summarized in Table S1 shown as average values across pedo-climatic locations) mainly stemmed from N removed by crop harvest, N losses through gaseous emissions and N leaching. The DNDC model predicted average maize and winter wheat N uptake of  $231 \pm 8.4$  and  $65.7 \pm 2.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ , respectively. Broadcast application of urea-based N fertilizer (reference scenario,  $\text{SRF}_{\text{Urea}}$ ) resulted in the lowest N uptake (maize =  $185.9 \pm 26.1$  and winter wheat =  $58.00 \pm 5.3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) (Table S1). The surface application of only organic fertilizers followed by immediate incorporation (the simulated N input rate was the same as the N mineral one, Table S1) showed the highest values, both for maize with slurry ( $254.4 \pm 5.6 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) and in winter wheat with digestate ( $74.2 \pm 2.3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ). Such systems had also the higher simulated N leaching than when mineral fertilizers were applied. The FE location was the most prone to N leaching, being characterized by the highest yearly cumulative rainfall ( $1574.9 \pm 263.5 \text{ mm yr}^{-1}$ ) compared to the other

locations ( $893.1 \pm 64.5 \text{ mm yr}^{-1}$ , on average). An increase of N leaching was also observed when AN-based fertilizers were used, both with surface broadcast and closed-slot injection. Simulated cropping systems and fertilization management had an average annual soil N loss of  $31.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in maize, and surplus of  $0.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  in winter wheat.

#### 3.3.2. $\text{NH}_3$ emissions

Across the Veneto region, predicted  $\text{NH}_3$  emissions from urea-based surface broadcast application ( $\text{SRF}_{\text{Urea}}$ ) in maize were on average  $136.5 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ , ranging between 62.0 and  $187.0 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$  (Fig. 4A). Ammonia losses  $> 50\%$  of N fertilizer input ( $248 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) were observed at the southern BP location as well as in the central locations (LE and BV1), all classified as areas with *medium* susceptibility to  $\text{NH}_3$  emissions (Fig. 3). In contrast,  $\text{NH}_3$  losses were 25% of N fertilizer input in the central BV2 location, being characterized by soils with *low* susceptibility to emissions ( $\text{pH} = 6.84$ ,  $\text{CEC} = 17 \text{ cmol kg}^{-1}$ ).

Simulated emissions when the BATs were applied averaged  $47.5 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ , from zero to  $137 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ , which were considerably lower than for surface applied urea ( $130.8 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$  on average). Strong variability stemmed from differences in fertilizer placement and formulation as well as local pedo-climatic conditions. For instance, closed-slot injection of urea ( $\text{INJ}_{6\text{-Urea}}$ ) and use of urease inhibitor ( $\text{INH}_{\text{Urea}}$ ) reduced average emissions by  $76.8 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$  (i.e., 44%) and  $67.7 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$  (i.e., 51%), respectively. In this context,  $\text{NH}_3$  losses were  $< 3\%$  for the *low* emission potential location BV2, while they showed values  $> 50\%$  of applied N at the *medium* emission potential locations, following the same trend of reference scenario. Closed-slot injection of ammonium nitrate ( $\text{INJ}_{6\text{-AN}}$ ) showed the lowest  $\text{NH}_3$  losses. Emissions were flattened to values  $< 20 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$  when organic fertilizers were used.

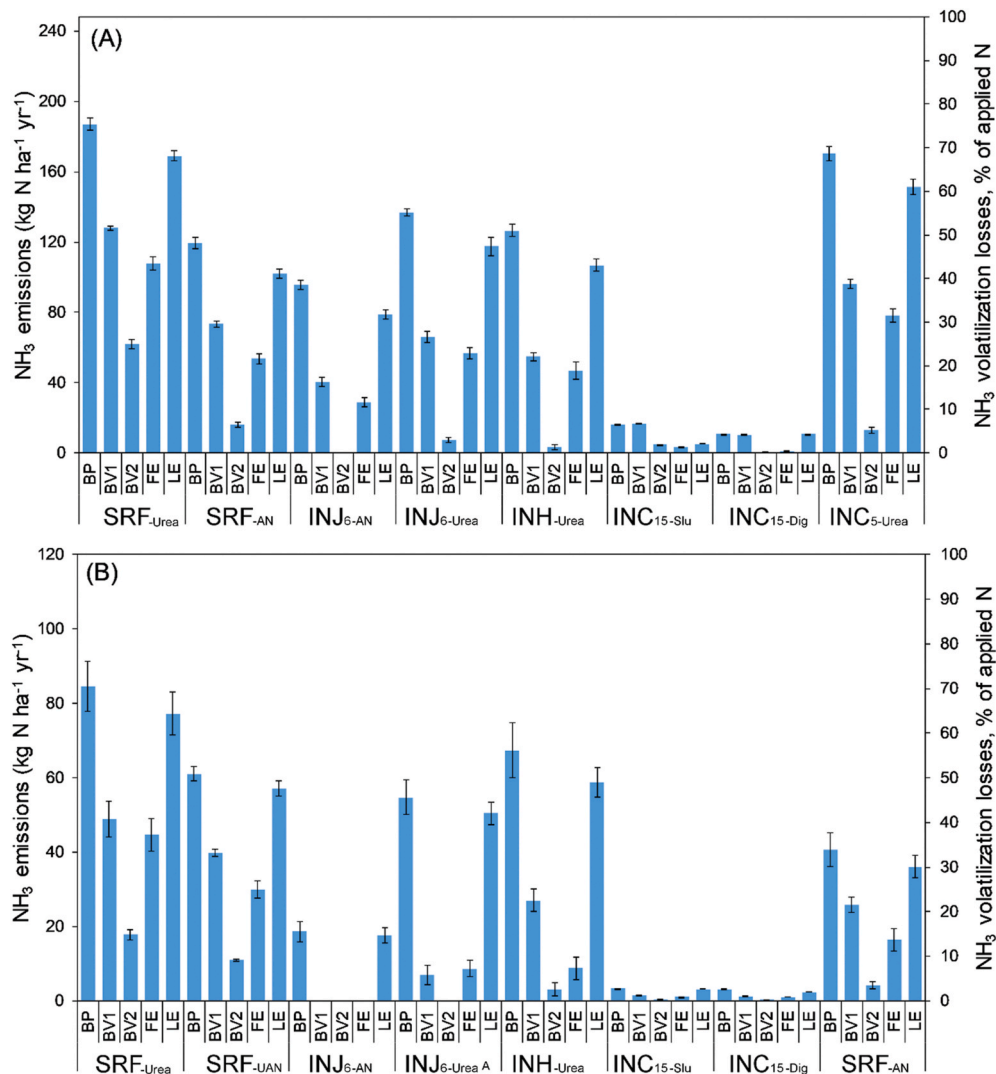
Similar to maize, DNDC simulated the highest  $\text{NH}_3$  emissions for winter wheat from the  $\text{SRF}_{\text{Urea}}$  scenario (on average  $54.6 \pm 12.0 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ ), ranging between a minimum of 14.8% in BV2 and a maximum of 70.4% in BP of N applied ( $120 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) (Fig. 4B). In contrast to maize, average  $\text{NH}_3$  emissions from  $\text{SRF}_{\text{AN}}$  ( $24.7 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ ) were similar to those from mineral-fertilized BATs ( $26.1 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ ). The only exception was  $\text{INJ}_{6\text{-AN}}$ , which frequently showed zero emissions as a result of closed-slot AN injection under peculiar pedo-climatic conditions (high rainfall and low pH in BV1, BV2, FE areas, Table 1). Organic N input, applied with the same N rate as the mineral one (Table S1), strongly reduced  $\text{NH}_3$ , being always lower than  $3 \text{ kg N-NH}_3 \text{ ha}^{-1} \text{ yr}^{-1}$  as a result of 15 cm-depth incorporation before sowing.

**Table 4**

Main results from the survey conducted with farmers and farm advisors on mineral N-fertilizer management. Average values are followed by standard errors (in brackets).

Main investigated crops	Irrigation	Base dressing			Top dressing			
		Fertilizer	Rate (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	Management	Number and period of applications	Fertilizer	Rate (kg N ha <sup>-1</sup> yr <sup>-1</sup> )	Management
Maize	Sprinkler	NPK	100 (15)	Injection (5 cm)	2; May–June	Urea	148 (16)	Incorporation by hoeing (5 cm)
Winter wheat	–	–	–	–	2; January–May	AN	122 (14)	Surface broadcast
Soybean	Sprinkler	NPK	33 (2)	Injection (5 cm)	–	–	–	–
Other winter cereals (barley, einkorn, oat, etc.)	–	–	–	–	2; February–April	UAN	113 (13)	Surface broadcast
Sugarbeet	Sprinkler	Urea; NPK	75 (0)	Incorporation (7 cm)	1; April	AN	100 (25)	Surface broadcast
Permanent meadow	–	–	–	–	1; March	NPK; Calcium Nitrate	63 (12)	Surface broadcast
Rapeseed	–	NPK	50 (0)	Incorporation (5 cm)	–	–	–	–





**Fig. 4.** Predicted ammonia emissions under different fertilization managements and pedo-climatic conditions for maize (A) and winter wheat (B). Details about fertilization management are reported in Table 2.

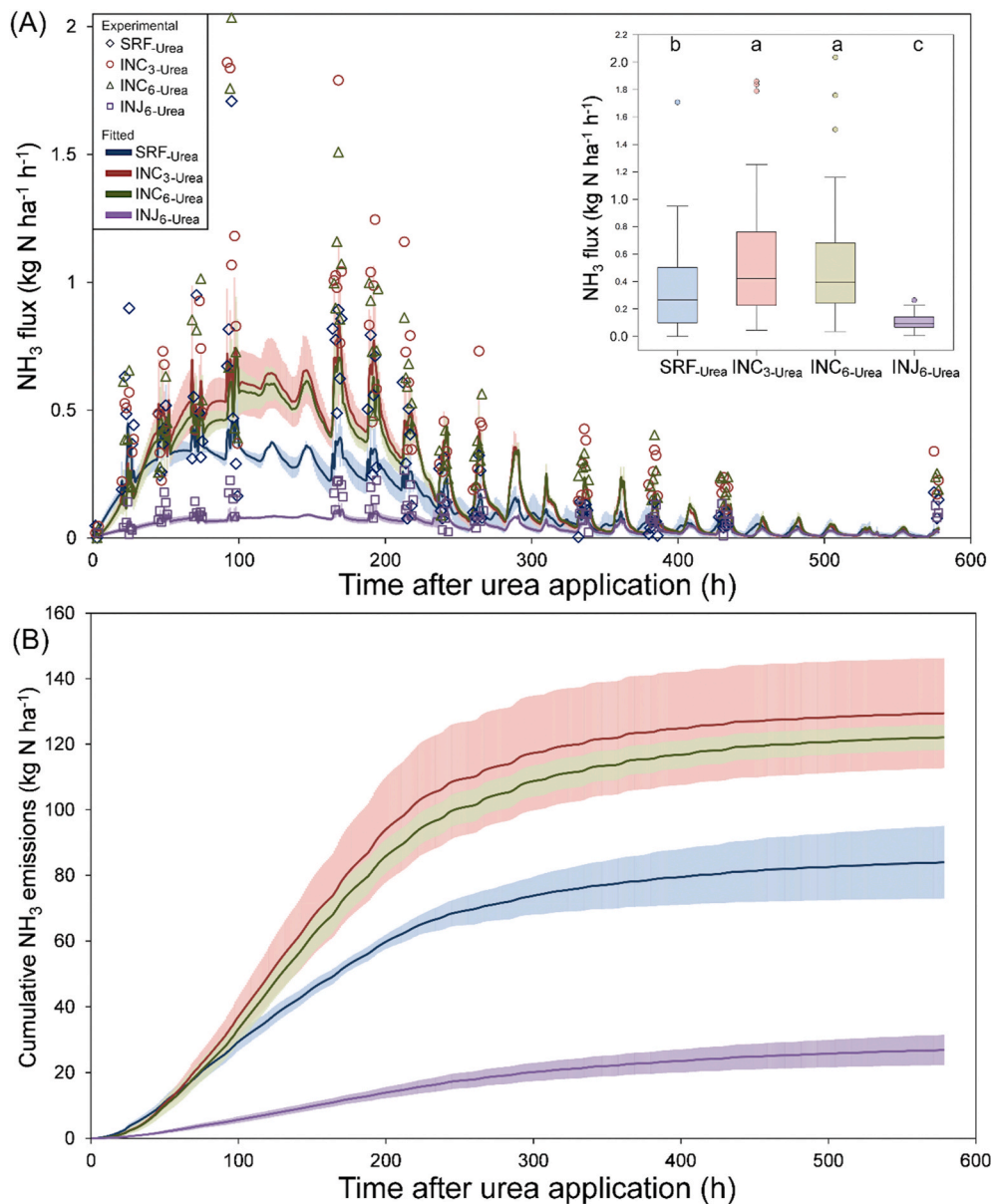
### 3.4. Evaluation of ammonia emissions based on field studies

The field experiment lasted 24 days after urea application, in which air temperature averaged 17.8 °C (max = 30.1 during the day, min = 8.7 °C during the night) and wind speed was 0.42 m s<sup>-1</sup>, ranging between a minimum of 0.4 and a maximum of 1.0 m s<sup>-1</sup>. Soil conditions close to the surface (1 cm depth) showed a higher temperature (19.8 ± 0.11 °C among treatments) and a lower variability (max = 29.8 ± 0.67 °C; min = 13.3 ± 0.25 °C among treatments) compared to air temperature. Soil moisture averaged 0.098 ± 0.008 m<sup>3</sup> m<sup>-3</sup> among treatments, ranging from a minimum of 0.077 ± 0.005 m<sup>3</sup> m<sup>-3</sup> that was initially found upon urea treatment, to a maximum of 0.131 ± 0.011 m<sup>3</sup> m<sup>-3</sup> due to rainfall.

Ammonia emission dynamics showed increasing losses from the first day after urea application until the 3rd day under SRF-Urea (1.71 kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>), the 5th day under INC<sub>3</sub>-Urea (1.86 kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>) and INC<sub>6</sub>-Urea (2.03 kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>). Then, a gradual decrease of NH<sub>3</sub> emissions until less than 0.5 kg N ha<sup>-1</sup> h<sup>-1</sup> was observed (Fig. 5A). In contrast, closed-slot injection of urea (INJ<sub>6</sub>-Urea) had values always < 0.27 kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>, with a maximum reached at 192 h (8 days) after N application. A second peak of NH<sub>3</sub> emissions was found in INC<sub>3</sub>-Urea and INC<sub>6</sub>-Urea after 7 days, which was associated with the maximum recorded air temperature (27.7 °C, on average). The interpolated NH<sub>3</sub>

emission dynamics highlighted the combined effect of time and soil conditions (temperature and moisture) to control NH<sub>3</sub> emissions. Notably, experimental NH<sub>3</sub> fluxes were significantly ( $p < 0.05$ ) higher under INC<sub>3</sub>-Urea and INC<sub>6</sub>-Urea (0.42 and 0.49 kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>, respectively) than SRF-Urea and INJ<sub>6</sub>-Urea (0.26 and 0.09 kg N-NH<sub>3</sub> ha<sup>-1</sup> h<sup>-1</sup>, respectively) (Fig. 5A).

The estimated parameters used to interpolate fluxes (Table S2) emphasized different emission dynamics between treatments: in particular, the  $a$  parameter ranged between 0.28 with INJ<sub>6</sub>-Urea and 1.26 in INC<sub>3</sub>-Urea, which indicated higher cumulative fluxes when urea was incorporated and mixed with hoeing (INC<sub>3</sub>-Urea and INC<sub>6</sub>-Urea) than when injected or maintained at the surface, as also shown in Fig. 5B. Moreover, urea reactivity leading to NH<sub>3</sub> emissions changed between treatments. A noticeable increase of the  $i$  parameter was observed when the fertilizer interacted with the soil after mixing (INC<sub>3</sub>-Urea and INC<sub>6</sub>-Urea) or injection (INJ<sub>6</sub>-Urea), than when superficially applied (SRF-Urea), emphasizing a stronger sigmoidal curve trend in cumulative flux (Fig. 5B), as also suggested by Demeyer et al. (1995).



**Fig. 5.** Experimental and interpolated  $\text{NH}_3$  emissions (A), and estimated cumulative fluxes (B) for different urea application methods during the field experiment. SRF-Urea, surface broadcast application; INC<sub>3</sub>-Urea, broadcast incorporation in the top 3 cm by hoeing; INC<sub>6</sub>-Urea, broadcast incorporation in the top 6 cm by hoeing; INJ<sub>6</sub>-Urea, closed-slot injection at 6 cm depth. Average values (solid lines)  $\pm$  standard error (colored areas) are reported. Box-plots in the inner pane summarize  $\text{NH}_3$  emissions rates throughout the experiment. Treatments were significantly different when labelled with different letters ( $p < 0.05$ ).

## 4. Discussion

### 4.1. Outcomes from the proposed methodological approach

Mapping of the Veneto region according to soil properties was a first step towards identifying potential  $\text{NH}_3$  emissions scenarios and mitigation strategies at the site-specific level. Several studies emphasized the benefits of adopting site-specific approaches to quantify impacts of agricultural practices and identify best strategies that improve environmental outcomes (Primdahl et al., 2010). This aspect is rapidly emerging for policies addressing environmental management (Zasada et al., 2017). Based on the outcomes from Duan and Xiao (2000), our approach revealed that about 70% of the Veneto region was characterized by *medium*  $\text{NH}_3$  emission potential (Fig. 3). According to previous studies (Dal Ferro et al., 2018), it was estimated that about 80.5% of farming activities was under *medium* susceptibility to  $\text{NH}_3$  emissions, while only 0.75% and 3.4% had high and very high susceptibility, respectively. Different approaches were used to map  $\text{NH}_3$  emissions. For instance, Kelleghan et al. (2019) collected N management data across Ireland, and identified  $\text{NH}_3$  risk categories by integrating  $\text{NH}_3$  sources

with indicators of ecological impacts. Collection of data from farm surveys was also used to identify subtle N management changes, that otherwise are difficult to capture. Sometimes these inventories have been criticized because they can suffer from poor spatial resolution, and are not specific for each environmental condition (Insausti et al., 2020). In this study, survey findings helped to identify the most common N management practices among farmers, and to understand the extent to which actions are required to achieve  $\text{NH}_3$  emissions reduction targets. Moreover, involvement of farmers and farm advisors was essential to target best management solutions that combine effectiveness, acceptance and, finally, their application (Dal Ferro et al., 2020; Enengle et al., 2014).

According to UNECE guidelines (UNECE, 2014), management solutions such as closed slot-injection and incorporation of urea-based fertilizers can reduce  $\text{NH}_3$  emissions in the range of 50–90%. In both cases, pedo-climatic conditions (e.g., soil pH, texture) and management factors (e.g., a delay of incorporation after application, depth) can greatly affect  $\text{NH}_3$  emissions. A major role was provided by soil pH, that sharply reduced  $\text{NH}_3$  emissions, e.g., in BV2 ( $\text{pH} = 6.8$ ) compared with BV1 ( $\text{pH} = 7.7$ ), under similar climatic conditions of the central Veneto region.



Anyway, even the climate modified the volatilization rate, being lower the emissions when higher was the cumulative rainfall, with similar soil properties at different latitudes (e.g., the northernmost simulated location FE Vs. the central area BV1) (Table 1). About management, most of the respondents declared that mineral fertilizers in maize were injected or incorporated, suggesting that BATs for  $\text{NH}_3$  emissions reduction were already adopted. In Veneto, fertilizer incorporation in maize was always performed immediately after fertilizer application (hoeing), varying the depth at 3 cm (33%), 5 cm (58%), and 6 cm (9%). Incorporation was never done in winter wheat because fertilizer equipment is not yet available on the market. Survey findings highlighted that in most of the cases AN and UAN were used, which should reduce  $\text{NH}_3$  losses up to 90% (Pan et al., 2016; UNECE, 2014) relative to urea application. However, in some cases there are risks in tradeoffs with other forms of N pollution, such as higher N leaching by using AN or organic fertilizers (Table S1), especially in areas of the low-lying Venetian plain that has shallow water table and loose soils (Morari et al., 2012).

To note that in this study each simulated BAT was applied across each entire area, despite its applicability is always limited by the farmers' management strategy and the characteristics of each agro-ecosystem, as highlighted by Sanz-Cobena et al. (2014). For example, using AN in maize at top dressing is infrequent due to lower N content and higher price than urea. Furthermore, it was assumed that slurry and digestate were always incorporated at equal N rates as the mineral fertilizers and within 12 h, which was in some cases very optimistic and a quicker practice than that required by national legislation (24 h). This suggests that stakeholder perspectives and appraisal tools for their quantification is pivotal to address site-specific measures (Okpara et al., 2020), which in turn should be better integrated into the decision making and evaluation of BAT strategies.

#### 4.2. Suggested $\text{NH}_3$ reduction strategies across the Veneto region

Modeling and experimental results were strongly affected by pedo-climatic and management conditions. These factors modified the magnitude of  $\text{NH}_3$  emissions under  $\text{SRF}_{\text{Urea}}$  and BATs scenarios, and have non-linearly influenced the BATs ability to reduce  $\text{NH}_3$  emissions compared to surface broadcast. Regardless of the application of BATs, soil pH was the main driver that affected  $\text{NH}_3$  emissions. Simulations on BV2 soil, that showed low vulnerability to  $\text{NH}_3$  emission potential, provided the greatest  $\text{NH}_3$  reductions when BATs were applied (Table 5). Ammonia emissions reduction was always > 74%, apart for  $\text{SRF}_{\text{UAN}}$  which reduced emissions by 38.7%. In contrast, simulations of the effectiveness of BATs under medium vulnerability was on average 59%. Notably, each BAT varied greatly in its effectiveness within the same soil class (coefficient of variation up to 60.7%) due to weather variability, particularly rainfall. The effect of temperature cannot be excluded, although the slight differences in temperature between selected locations likely limited the variability in  $\text{NH}_3$  emissions. These results emphasize that mapping pedo-climatic conditions is pivotal because they can affect  $\text{NH}_3$  emission at different scales, and across scales (Corstanje et al., 2008). Especially for coarse scale mapping ( $\geq 2000$  m), the authors suggested CEC and bulk density as main factors explaining the variability of  $\text{NH}_3$  emission, which in turn reflected differences between parent materials. Moreover, they found that small-scale emission measurements are prone to substantial variation –thus their relevance is closely linked to well-known pedo-climatic conditions– and their transferability to a broader scale difficult.

Similarly, our study showed differences in  $\text{NH}_3$  emissions reduction by comparing coarse-scale modeling with field-scale experiment (Table 5). We tested different incorporation techniques of urea because they were readily applicable by farmers to reduce  $\text{NH}_3$  emissions, and because urea was the most common fertilizer used. Therefore, solutions limiting  $\text{NH}_3$  emissions from urea can cover most of the used arable area

**Table 5**

Percentage  $\text{NH}_3$  emissions reduction compared to the reference scenario (surface broadcast urea) in maize and winter wheat. BATs marked with an asterisk (\*) reduced emissions by at least 30% compared with the reference method. The coefficient of variation (CV) is reported for every scenario. Details about fertilization management are reported in Table 2.

BAT	Fertilizer	Method	$\text{NH}_3$ emission potential	Crop	Validation	$\text{NH}_3$ emissions reduction (%)	CV (%)
INJ <sub>6-Urea</sub> *	Urea	Closed-slot injection, 6 cm	Medium	Maize	Modelling	38.3	29.5
INJ <sub>6-Urea</sub> *	Urea	Closed-slot injection, 6 cm	Medium	Wheat	Modelling	60.1	44.8
INJ <sub>6-Urea</sub> *	Urea	Closed-slot injection, 6 cm	Medium	Bare Soil	Experimental	67.9	—
INJ <sub>6-Urea</sub> *	Urea	Closed-slot injection, 6 cm	Low	Maize	Modelling	88.5	6.2
INJ <sub>6-Urea</sub> *	Urea	Closed-slot injection, 6 cm	Low	Wheat	Modelling	100	0.0
INC <sub>5-Urea</sub>	Urea	Incorporation by hoeing, 5 cm	Medium	Maize	Modelling	17.9	53.3
INC <sub>5-Urea</sub> *	Urea	Incorporation by hoeing, 5 cm	Low	Maize	Modelling	79.3	7.5
INC <sub>5-Urea</sub>	Urea	Incorporation by hoeing, 3 cm	Medium	Bare Soil	Experimental	−54.2	—
INC <sub>5-Urea</sub>	Urea	Incorporation by hoeing, 6 cm	Medium	Bare Soil	Experimental	−51.0	—
INH <sub>Urea</sub> *	Urea	Urease inhibitor	Medium	Maize	Modelling	45.7	28.3
INH <sub>Urea</sub> *	Urea	Urease inhibitor	Medium	Wheat	Modelling	43.4	60.7
INH <sub>Urea</sub> *	Urea	Urease inhibitor	Low	Maize	Modelling	94.8	5.4
INH <sub>Urea</sub> *	Urea	Urease inhibitor	Low	Wheat	Modelling	80.3	29.2
SRF <sub>AN</sub> *	AN	Surface broadcast	Medium	Maize	Modelling	42.2	14.3
SRF <sub>AN</sub> *	AN	Surface broadcast	Medium	Wheat	Modelling	54.2	12.5
SRF <sub>AN</sub> *	AN	Surface broadcast	Low	Maize	Modelling	74.4	3.9
SRF <sub>AN</sub> *	AN	Surface broadcast	Low	Wheat	Modelling	75.8	7.4
INJ <sub>6-AN</sub> *	AN	Closed-slot injection, 6 cm	Medium	Maize	Modelling	61	19.3
INJ <sub>6-AN</sub> *	AN	Closed-slot injection, 6 cm	Medium	Wheat	Modelling	89.1	14.1
INJ <sub>6-AN</sub> *	AN	Closed-slot injection, 6 cm	Low	Maize	Modelling	100	0.0
INJ <sub>6-AN</sub> *	AN	Closed-slot injection, 6 cm	Low	Wheat	Modelling	100	0.0
SRF <sub>UAN</sub>	UAN	Surface broadcast	Medium	Wheat	Modelling	27.2	25.5
SRF <sub>UAN</sub> *	UAN	Surface broadcast	Low	Wheat	Modelling	38.7	12.8
INC <sub>15-Slu</sub> *	Slurry	Incorporation, 15 cm	Medium	Maize	Modelling	93.0	5.2
INC <sub>15-Slu</sub> *	Slurry	Incorporation, 15 cm	Medium	Wheat	Modelling	96.7	0.7
INC <sub>15-Slu</sub> *	Slurry	Incorporation, 15 cm	Low	Maize	Modelling	91.8	0.8
INC <sub>15-Slu</sub> *	Slurry	Incorporation, 15 cm	Low	Wheat	Modelling	97.9	0.3
INC <sub>15-Dig</sub> *	Digestate	Incorporation, 15 cm	Medium	Maize	Modelling	92.5	5.9
INC <sub>15-Dig</sub> *	Digestate	Incorporation, 15 cm	Medium	Wheat	Modelling	93.7	1.3
INC <sub>15-Dig</sub> *	Digestate	Incorporation, 15 cm	Low	Maize	Modelling	94.5	0.5
INC <sub>15-Dig</sub> *	Digestate	Incorporation, 15 cm	Low	Wheat	Modelling	98.3	0.3

in northern Italy. Only the closed-slot injection reached the 30% reduction threshold in soils with *medium* potential emission, ranging from modeled average of 49.2% to field-test of 67.9% (Table 5). Notably, differences in  $\text{NH}_3$  emissions between tested locations did not change compared to  $\text{SRF}_{\text{Urea}}$ , suggesting that similar dynamics occurred under different pedo-climatic conditions (Fig. 4). When injection was applied to ammonium nitrate, sometimes  $\text{NH}_3$  emissions were completely cut, thus flattening the differences in effectiveness between areas with *low* and *medium* susceptibility to emissions. Urea incorporation with hoeing was below the threshold according to DNDC simulations, and even increases in emissions were found with field-testing. It was hypothesized that a combination of factors may have led to these results, which can be summarized as follows: (i) with surface broadcast, a lower rate of urea hydrolysis (catalyzed by urease) than incorporation likely occurred because of dry soil conditions (Rochette et al., 2009); as our soil was close to wilting point at the soil surface ( $< 0.10 \text{ m}^3 \text{ m}^{-3}$ ), the limited soil water content would have reduced both urea and carbamate hydrolysis rate during the two-stage urea degradation process (Ferguson and Kissel, 1986; Sommer et al., 2004); (ii) the partial coverage of urea during soil mixing with hoeing likely enhanced the interaction with urease compared to surface broadcast (Fig. 2); (iii) an increase in macroporosity with hoeing would have lowered resistance to  $\text{NH}_3$  diffusion (Rochette et al., 2013) compared to urea injection.

In this context, differences from field-tested treatments may have been even greater, being the fitting model (Eqn 2) able to describe the daily fluctuation of  $\text{NH}_3$  volatilization, although it underestimated some peaks  $> 1.5 \text{ kg NH}_3\text{-N ha}^{-1} \text{ h}^{-1}$  (Fig. 5). In contrast, results of  $\text{NH}_3$  dynamic from DNDC model did not include the effect of partial coverage of urea with hoeing, as well as the changes in soil porosity that likely affected  $\text{NH}_3$  losses. Despite these differences, results were consistent to exclude hoeing as a viable practice to reduce significantly  $\text{NH}_3$  emissions across the Veneto region.

Promising findings were obtained by replacing mineral fertilizers with the organic ones that often achieved  $\text{NH}_3$  reductions  $> 90\%$ . Organic fertilizers include a mixture of organic and ammonium N, which means a reduced propensity to volatilize  $\text{NH}_3$  in comparison to urea regardless the soil type; moreover, the simulated BATs included 15 cm incorporation within few hours of distribution which strongly reduced  $\text{NH}_3$  losses (Sommer and Hutchings, 2001; Sutton et al., 2015). However, organic fertilizers usually have lower N use efficiency compared to mineral fertilizers in the intensive cropping systems of Veneto region, and there can be high N losses to surface and ground water, particularly due to continued mineralization in off season when no crop is grown. Attention should be paid also to impacts on the atmosphere, because slurry or digestate injection may enhance  $\text{N}_2\text{O}$  production due to favored microbial activity and anaerobic conditions in N-abundant soils (Duncan et al., 2017; Smith et al., 2019).

## 5. Conclusions

The present study proposes a methodological approach, where BATs to limit  $\text{NH}_3$  emissions from agricultural soils must be tailored to site-specific management and pedo-climatic conditions, assisting practitioners and policymakers to identify most effective practices not only at specific locations, but across scales. Moreover, the N balance is considered such that mitigation of  $\text{NH}_3$  emissions does not worsen, e.g., N leaching or  $\text{N}_2\text{O}$  emissions. The initial mapping of the Veneto region revealed substantial homogeneity in  $\text{NH}_3$  emission potential from croplands. However, an in-depth territorial modeling highlighted greater differences, where each specific soil and its interaction with the climate may determine changes in  $\text{NH}_3$  emission. This suggests that the same scale of susceptibility to  $\text{NH}_3$  emissions cannot be adopted to the entire region. The closed-slot injection is suggested to reduce  $\text{NH}_3$  emissions with any type of mineral or organic fertilizers. This is likely the most promising practice being already adopted by farmers. However, research of new technologies should be pursued to allow for deep

placement and cover of the fertilizer during top-dressing, especially in winter wheat. By contrast, the most common technique of urea incorporation with hoeing did not show satisfactory results. Indeed, only partial burial of urea can increase  $\text{NH}_3$  emissions, to a level that is sometimes greater than under surface broadcast. Use of urea inhibitor, or different types of fertilizers (ammonium-nitrate, organic fertilizers) is also suggested to reduce  $\text{NH}_3$  emission. Nevertheless, there may be side-effects due to increased N leaching to surface and ground water, and  $\text{N}_2\text{O}$  gas emission. All fluxes should be carefully evaluated according to a holistic approach that include the whole N cycle, and that quantifies all the impacts generated on agroecosystems.

## Credit author statement

Mencaroni M., Methodology, Investigation, Writing - original draft. Dal Ferro N., Conceptualization, Methodology, Investigation, Writing - original draft. Furlanetto J., Investigation, Writing - review & editing. Longo M., Investigation, Writing - review & editing. Lazzaro B., Funding acquisition, Writing - review & editing. Sartori L., Resources, Writing - review & editing. Grant B.B., Resources, Writing - review & editing. Smith W.N., Resources, Writing - review & editing. Morari F., Conceptualization, Methodology, Investigation, Resources, Writing - review & editing, Supervision, Funding acquisition.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jenvman.2020.111445>.

## References

- Arganda-Carreras, I., Kaynig, V., Rueden, C., Eliceiri, K.W., Schindelin, J., Cardona, A., Sebastian Seung, H., 2017. Trainable Weka Segmentation: a machine learning tool for microscopy pixel classification. *Bioinformatics* 33, 2424–2426. <https://doi.org/10.1093/bioinformatics/btx180>.
- Beusen, A.H.W., Bouwman, A.F., Heuberger, P.S.C., Van Dreht, G., Van Der Hoek, K.W., 2008. Bottom-up uncertainty estimates of global ammonia emissions from global agricultural production systems. *Atmos. Environ.* 42, 6067–6077. <https://doi.org/10.1016/j.atmosenv.2008.03.044>.
- Burton, R.J.F., Schwarz, G., 2013. Result-oriented agri-environmental schemes in Europe and their potential for promoting behavioural change. *Land Use Pol.* 30, 628–641.
- Camarotto, C., Dal Ferro, N., Piccoli, I., Polese, R., Furlan, L., Chiarini, F., Morari, F., 2018. Conservation agriculture and cover crop practices to regulate water, carbon and nitrogen cycles in the low-lying Venetian plain. *Catena* 167. <https://doi.org/10.1016/j.catena.2018.05.006>.
- Congreves, K.A., Grant, B.B., Dutta, B., Smith, W.N., Chantigny, M.H., Rochette, P., Desjardins, R.L., 2016. Predicting ammonia volatilization after field application of swine slurry: DNDC model development. *Agric. Ecosyst. Environ.* 219, 179–189. <https://doi.org/10.1016/j.agee.2015.10.028>.
- Corstjanje, R., Kirk, G.J.D., Pawlett, M., Read, R., Lark, R.M., 2008. Spatial variation of ammonia volatilization from soil and its scale-dependent correlation with soil properties. *Eur. J. Soil Sci.* 59, 1260–1270. <https://doi.org/10.1111/j.1365-2389.2008.01087.x>.
- Dal Ferro, N., Camarotto, C., Piccoli, I., Berti, A., Mills, J., Morari, F., 2020. Stakeholder perspectives to prevent soil organic matter decline in northeastern Italy. *Sustainability* 12, 378. <https://doi.org/10.3390/su12010378>.
- Dal Ferro, N., Cocco, E., Berti, A., Lazzaro, B., Morari, F., 2018. How to enhance crop production and nitrogen fluxes? A result-oriented scheme to evaluate best agri-

- environmental measures in Veneto Region. Italy. Arch. Agron. Soil Sci. <https://doi.org/10.1080/03650340.2018.1442573>.
- Demeyer, P., Hofman, G., Van Cleemput, O., 1995. Fitting ammonia volatilization dynamics with a logistic equation. Soil Sci. Soc. Am. J. 59, 261–265. <https://doi.org/10.2136/sssaj1995.03615995005900010041x>.
- Duan, Z., Xiao, H., 2000. Effects of soil properties on ammonia volatilization. Soil Sci. Plant Nutr. 46, 845–852. <https://doi.org/10.1080/00380768.2000.10409150>.
- Duncan, E.W., Dell, C.J., Kleinman, P.J.A., Beegle, D.B., 2017. Nitrous oxide and ammonia emissions from injected and broadcast-applied dairy slurry. J. Environ. Qual. 46, 36–44. <https://doi.org/10.2134/jeq2016.05.0171>.
- Dutta, B., Congreves, K.A., Smith, W.N., Grant, B.B., Rochette, P., Chantigny, M.H., Desjardins, R.L., 2016. Improving DNDC model to estimate ammonia loss from urea fertilizer application in temperate agroecosystems. Nutrient Cycl. Agroecosyst. 106, 275–292. <https://doi.org/10.1007/s10705-016-9804-z>.
- ECETOC, 1994. Ammonia emissions to air in western Europe. ECETOC Tech. Rep. No. 62.
- Engel, B., Penker, M., Muhar, A., 2014. Landscape co-management in Austria: the stakeholder's perspective on efforts, benefits and risks. J. Rural Stud. 34, 223–234.
- EPA, 2019. Inventory of U.S. Greenhouse Gas Emissions and Sinks 1990–2017.
- FAO, 2019. World Fertilizer Trends and Outlook to 2022 (Rome, Italy).
- Ferguson, R.B., Kissel, D.E., 1986. Effects of soil drying on ammonia volatilization from surface-applied urea. Soil Sci. Soc. Am. J. 50 (2), 485–490.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., 2003. The nitrogen cascade. Bioscience 53, 341. [https://doi.org/10.1641/0006-3568\(2003\)053\[0341:tnc\]2.0.co2](https://doi.org/10.1641/0006-3568(2003)053[0341:tnc]2.0.co2).
- Insausti, M., Timmis, R., Kinnersley, R., Ruffino, M.C., 2020. Advances in sensing ammonia from agricultural sources. Sci. Total Environ. <https://doi.org/10.1016/j.scitotenv.2019.135124>.
- Kellegan, D.B., Hayes, E.T., Everard, M., Curran, T.P., 2019. Mapping ammonia risk on sensitive habitats in Ireland. Sci. Total Environ. 649, 1580–1589. <https://doi.org/10.1016/j.scitotenv.2018.08.424>.
- Li, C., 2012. User's guide for the DNDC model. In: Institute for the Study of Earth, Oceans and Space, University of New Hampshire. Institute for the Study of Earth, Oceans and Space. University of New Hampshire, Durham, NC, USA.
- Lockyer, D.R., 1984. A system for the measurement in the field of losses of ammonia through volatilisation. J. Sci. Food Agric. 35, 837–848. <https://doi.org/10.1002/jsfa.2740350805>.
- Morari, F., Lugato, E., Polese, R., Berti, A., Giardini, L., 2012. Nitrate concentrations in groundwater under contrasting agricultural management practices in the low plains of Italy. Agric. Ecosyst. Environ. 147, 47–56.
- Okpara, U.T., Fleskens, L., Stringer, L.C., Hessel, R., Bachmann, F., Daliakopoulos, I., Berglund, K., Blanco Velazquez, F.J., Dal Ferro, N., Keizer, J., Kohnova, S., Lemann, T., Quinn, C., Schwilch, G., Siebielec, G., Skaalsveen, K., Tibbett, M., Zoumides, C., 2020. Helping stakeholders select and apply appraisal tools to mitigate soil threats: researchers' experiences from across Europe. J. Environ. Manag. 257, 110005. <https://doi.org/10.1016/j.jenvman.2019.110005>.
- Pan, B., Lam, S.K., Mosier, A., Luo, Y., Chen, D., 2016. Ammonia volatilization from synthetic fertilizers and its mitigation strategies: a global synthesis. Agric. Ecosyst. Environ. 232, 283–289. <https://doi.org/10.1016/j.agee.2016.08.019>.
- Pelster, D.E., Watt, D., Strachan, I.B., Rochette, P., Bertrand, N., Chantigny, M.H., 2019. Effects of initial soil moisture, clod size, and clay content on ammonia volatilization after subsurface band application of urea. J. Environ. Qual. 48, 549–558. <https://doi.org/10.2134/jeq2018.09.0344>.
- Primdahl, J., Vesterager, J.P., Finn, J.A., Vlahos, G., Kristensen, L., Vejre, H., 2010. Current use of impact models for agri-environment schemes and potential for improvements of policy design and assessment. J. Environ. Manag. 91, 1245–1254.
- Rao, D.L.N., Batra, L., 1983. Ammonia volatilization from applied nitrogen in alkali soils. Plant Soil 70, 219–228. <https://doi.org/10.1007/BF02374782>.
- Regione Veneto, 2005. Carta dei Suoli del Veneto alla scala 1: 250.000, 3 vols. ARPAV - Osservatorio Regionale Suolo, Castelfranco Veneto.
- Rochette, P., Angers, D.A., Chantigny, M.H., Gasser, M.O., MacDonald, J.D., Pelster, D.E., Bertrand, N., 2013. Ammonia volatilization and nitrogen retention: how deep to incorporate urea? J. Environ. Qual. 42, 1635–1642. <https://doi.org/10.2134/jeq2013.05.0192>.
- Rochette, P., MacDonald, J.D., Angers, D.A., Chantigny, M.H., Gasser, M.O., Bertrand, N., 2009. Banding of urea increased ammonia volatilization in a dry acidic soil. J. Environ. Qual. 38, 1383–1390. <https://doi.org/10.2134/jeq2008.0295>.
- Sanz-Cobena, A., Lassaletta, L., Estellés, F., Del Prado, A., Guardia, G., Abalos, D., Aguilera, E., Pardo, G., Vallejo, A., Sutton, M.A., Garnier, J., Billen, G., 2014. Yield-scaled mitigation of ammonia emission from N fertilization: the Spanish case. Environ. Res. Lett. 9, 125005. <https://doi.org/10.1088/1748-9326/9/12/125005>.
- Schojerring, J.K., Mattsson, M., 2001. Quantification of ammonia exchange between agricultural cropland and the atmosphere: measurements over two complete growth cycles of oilseed rape, wheat, barley and pea. Plant Soil 228, 105–115. <https://doi.org/10.1023/A:1004851001342>.
- Smith, W., Grant, B., Qi, Z., He, W., VanderZaag, A., Drury, C.F., Vergé, X., Balde, H., Gordon, R., Helmers, M.J., 2019. Assessing the impacts of climate variability on fertilizer management decisions for reducing nitrogen losses from corn silage production. J. Environ. Qual. 48, 1006–1015. <https://doi.org/10.2134/jeq2018.12.0433>.
- Sommer, S.G., Christensen, B.T., Olesen, J.E., 1991. Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry. J. Agric. Sci. 117, 91–100. <https://doi.org/10.1017/S0021859600079016>.
- Sommer, S.G., Hutchings, N.J., 2001. Ammonia emission from field applied manure and its reduction - invited paper. Eur. J. Agron. [https://doi.org/10.1016/S1161-0301\(01\)00112-5](https://doi.org/10.1016/S1161-0301(01)00112-5).
- Sommer, S.G., Misselbrook, T.H., 2016. A review of ammonia emission measured using wind tunnels compared with micrometeorological techniques. Soil Use Manag. 32, 101–108. <https://doi.org/10.1111/sum.12209>.
- Sommer, S.G., Schojerring, J.K., Denmead, O.T., 2004. Ammonia Emission from Mineral Fertilizers and Fertilized Crops 82, 557–622. [https://doi.org/10.1016/s0065-2113\(03\)82008-4](https://doi.org/10.1016/s0065-2113(03)82008-4).
- Sutton, M.A., Dalgaard, T., Cordovil, C., Howard, C., 2015. United Nations Economic Commission for Europe Framework Code for Good Agricultural Practice for Reducing Ammonia Emissions.
- UNECE, 2014. Guidance Document on Preventing and Abating Ammonia Emissions from Agricultural Sources 1–100. EB.AIR/WG.5/2001/7.
- Van Damme, M., Clarisse, L., Heald, C.L., Hurtmans, D., Ngadi, Y., Clerbaux, C., Dolman, A.J., Erisman, J.W., Coheur, P.F., 2014. Global distributions, time series and error characterization of atmospheric ammonia (NH<sub>3</sub>) from IASI satellite observations. Atmos. Chem. Phys. 14, 2905–2922. <https://doi.org/10.5194/acp-14-2905-2014>.
- WRB, I.W.G., 2014. World reference base for soil Resources 2014. In: International Soil Classification System for Naming Soils and Creating Legends for Soil Maps, World Soil Resources Reports No. 106. FAO, Rome. FAO Rome, Italy.
- Zasada, I., Häfner, K., Schaller, L., van Zanten, B.T., Lefebvre, M., Malak-Rawlikowska, A., Nikolov, D., Rodríguez-Entrena, M., Manrique, R., Ungaro, F., Zavalloni, M., Delattre, L., Piorr, A., Kantelhardt, J., Verburg, P.H., Viaggi, D., 2017. A conceptual model to integrate the regional context in landscape policy, management and contribution to rural development: literature review and European case study evidence. Geoforum 82, 1–12. <https://doi.org/10.1016/j.geoforum.2017.03.012>.
- Morari, F., 2010. Sud-project 2. Crop rotation and fertilisation. Action 2: Evaluation at the farm scale. In: Identification of innovative cropping systems in Venice lagoon watershed. Summary results. Eds. Veneto Agricoltura, Legnaro, Padova, Italy, pp. 37–48 (In Italian).