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1. INTRODUCTION

Nitrogen losses from agricultural sources have been recognised as one of the most serious threats in industrialised and emerging countries, determining ecosystem eutrophication and groundwater nitrate contamination. This issue has recently become a priority within the European Community Framework Directive for water protection (WFD) which has established a list of measures and limitations to be applied in areas declared "vulnerable to nitrate from agricultural sources". An example is the Ferrara Province (Northern Italy), an intensively cultivated area affected by serious nitrate pollution since decades. The land is fertile and allows the cultivation of some different crops especially winter cereals, maize and energy plants which cover more than 65% of the land.

The Ferrara Province is located in the north-eastern part of Emilia-Romagna Region, Italy (Fig.1) covering an area of 2636 km². The study area is flat with an altitude varying from -11 to 38 m above sea level (a.s.l.) and most of the sediments that outcrop on the surface are recent (Holocene, <10.000 years) and characterized by an elevated spatial heterogeneity due to the presence of paleo-channels interconnected with crevasses splay and marsh lagoon environments. According to the World Reference Base for Soil Resources classification (2006), the dominant soils in the Ferrara Province are: medium and medium-fine textured soils (68% of the territory), medium-fine sands (9% of the territory) and peaty soils (23% of the territory). More than 91% of the agricultural land is fertilized with synthetic fertilizers, mainly urea, only the sandy soil had been amended with chicken manure (70 q/ha). The minimal run-off and an homogeneous inorganic nitrogen load allow to simplify the hydrological and nitrogen balance: excess nitrogen tend to move vertically through the unsaturated zone, becoming one of the most important causes of groundwater contamination.

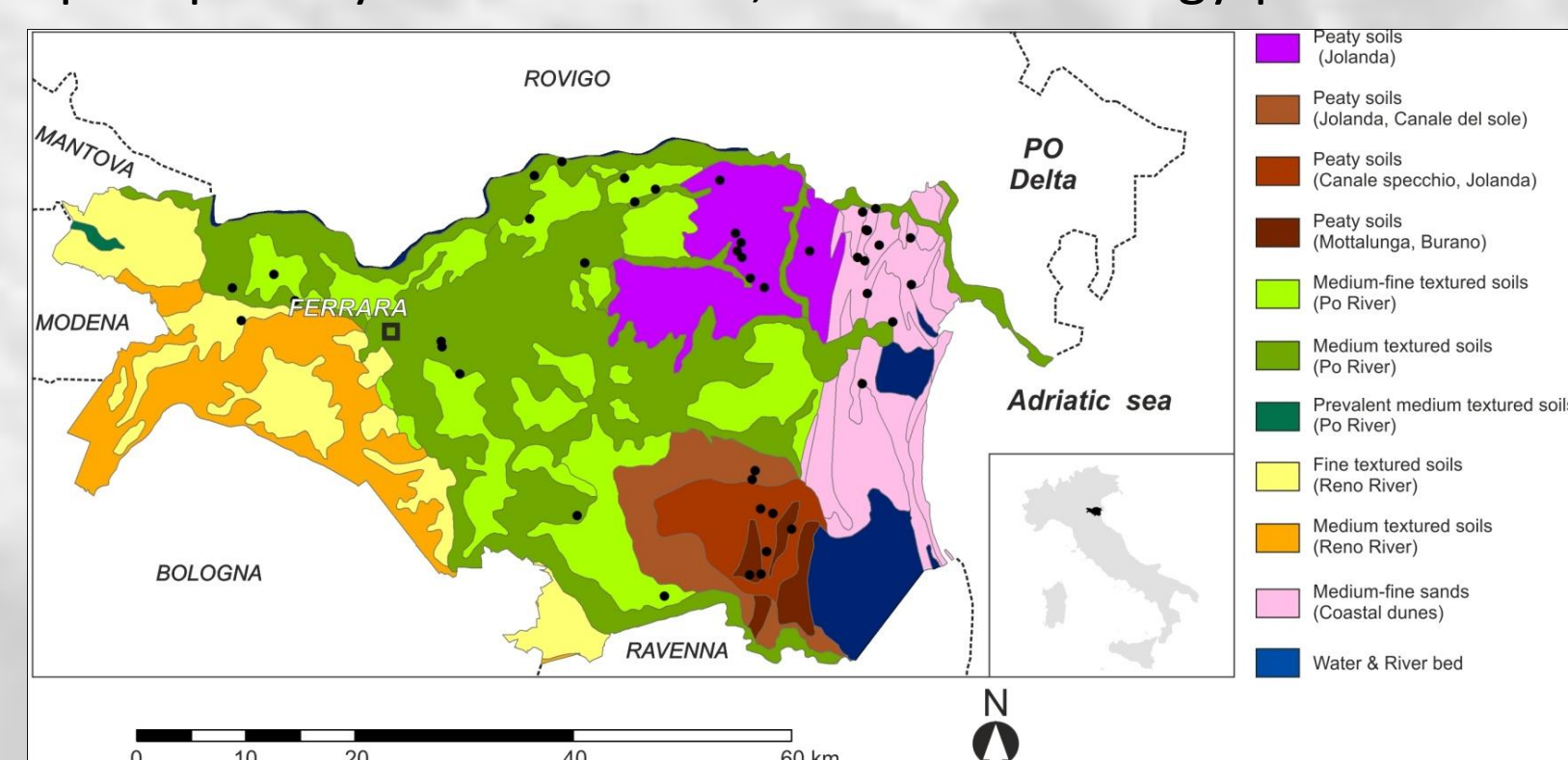


Fig. 1 – Location and soil map of Ferrara province. Black dots represent soil sampling points.

2 MATERIALS AND METHODS

To define the readily available nitrogen present in the whole Ferrara province, between the 2009 harvest and the 2010 sowing, 742 core samples were manually taken with an Eijelkamp Agrisearch auger equipment (Fig 2), in 67 different agricultural plots, fertilized in 2009 with Urea, respectively with 240 kg/ha for plots cultivated with wheat and 160 kg/ha for plots cultivated with maize. The soil samples were divided in two distinct layers: the upper one stressed by tillage, roots growth and weathering (0 to 50 cm of depth) and the lower undisturbed one (50 to 100 cm of depth). Samples were kept in special refrigerated containers until arrival at the laboratory. Sampling points were georeferenced via GPS. The different species of nitrogen, ammonia (NH₄⁺) nitrous (NO₂⁻) and nitrate (NO₃⁻) present in soil samples were extracted using a solution of KCl 1N (Galvis-Spinola et al., 1998). The obtained concentrations have been integrated and converted to kg N ha⁻¹. From each sample, previously thoroughly mixed, were taken 10 g of fresh sediment, which was suspended in 100 ml of 1N KCl and kept on a rotating shaker plate at a speed of 60 revolutions per minute (rpm) for 45 minutes and centrifuged at 3000 rpm per 15 minutes (Fig.3). The supernatant was taken for carrying out the analysis of dosage of nitrogen compounds. Ammonia was determined colorimetrically, following the protocol of Bower and Holm-Hansen (1980), while nitrous and nitric nitrogen was determined colorimetrically via Tecnicon Industrial Systems Autoanalyser II (Armstrong et al., 1967; APHA, 1992). The total inorganic nitrogen, was simply obtained by the sum of the three species. CO(NH₂)₂ (Urea) was determined according to Price and Harrison (1987) and Bower and Holm Hansen (1982) using a double beam Jasco V-550 UV/VIS spectrophotometer.

3D Analyst and Spatial Analyst tools of ESRI ArcMap 9.3 were used to obtain surface models for each variables, via geostatistical interpolation methods. Grid maps of NH₄⁺, NO₃⁻, NO₂⁻ and N-inorganic distribution were the results of the interpolations, both for the upper layer (0-50 cm of depth) and the lower layer (50-100 cm of depth). The results of geoprocessing operation for each variables, expressed in kg N ha⁻¹, has been represented in maps grouped into 5 classes (0-10, 10-20, 20-50, 50-100 and more than 100).



Fig. 2 - Eijelkamp Agrisearch auger equipment.



Fig. 3 soil cores

3 RESULTS AND DISCUSSION

The results indicate that residual nitrogen species are present, at different concentration, in the whole province. Inorganic nitrogen species are present in both upper and lower layer. The concentrations are higher in the lower layer (50-100 cm of depth) for each species, as shown in table 1.

Tab. 1 – Min, max and mean values of inorganic nitrogen species in Ferrara province.

N-inorganic species (depth cm)	min (kg N ha ⁻¹)	max (kg N ha ⁻¹)	mean (kg N ha ⁻¹)
NH ₄ ⁺ (0-50)	0.53	166	9
NH ₄ ⁺ (50-100)	0.37	227	24
NO ₃ ⁻ (0-50)	1.26	142	26
NO ₃ ⁻ (50-100)	1.16	200	53
NO ₂ ⁻ (0-50)	0.09	4	1
NO ₂ ⁻ (50-100)	0.17	8	2
N tot (0-50)	1.88	312.02	36.59
N tot (50-100)	1.71	435.29	78.34

Total inorganic nitrogen is represented for more than 97% by NH₄⁺ and NO₃⁻ for both upper and lower layer, with a relevant prevalence of the NO₃⁻. NO₂⁻ concentration represent respectively the 2 and 3 % of total inorganic nitrogen of the upper and lower layer. NO₂⁻ is an unstable intermediate species of most of the nitrogen transformation reactions (Appelo and Postma 2005) and the low concentration suggest that microbial processes are very fast. CO(NH₂)₂ concentration are very low too, with values that range between 0.35 and 10.95 kg N ha⁻¹ and mean value of 4.6 kg N ha⁻¹. This suggest that, in the both soil horizons investigated, was readily transformed into one of the inorganic nitrogen species. In both NH₄⁺ maps (Fig. 4A and 4B) higher concentrations are located in correspondence with peaty soils, that are moderately acid (5.4-6.2) and characterized by high values of organic matter content (Tab. 2).

Tab. 2 - Soil classification based on World Reference Base for Soil Resources (2006)..

Soil (Origin)	Soil group	Sub-unit	O.M. (%)	pH
Medium-fine textured soils (Po River)	1B	/	2	8.2
Medium textured soils (Po River)	1C	/	1.3	8.3
Prevalent medium textured soils (Po River)	3B	/	1.2	8.2
Fine textured soils (Reno River)	2A	/	1.6	8.3
Medium textured soils (Reno River)	3A	/	1.2	8.1
Medium-fine sands (Coastal dunes)	1D	/	1.4	7.9
Peaty soil	1A	Jolanda	28.3	5.4
		Jolanda Canale del sole,	25	8.2
		Canale specchio, Jolanda	25.5	6.1
		Mottalunga, Burano	6.8	6.2

These factors, linked with the very low hydraulic conductivity of these soils, inhibit nitrification processes, so determining an accumulation of ammonia. The NH₄⁺ lower layer map show moderately high values also in the south-eastern zone of the province, where peaty soils, characterized by a neutral or slightly alkaline pH, are present. Presence of NH₄⁺ accumulation can be explained by the strong salinization of the soil (4-5 ppt). NO₃⁻ maps (Fig. 4C and 4D) show that higher concentration, as for NH₄⁺, are present in the lower horizon. The upper one show concentrations ranging between very low to medium, increasing from West to East. The lower horizon show the higher values in the soils where the alkaline pH don't inhibit the nitrification processes. The lower values are in correspondence with peaty soils, where the stable form is the NH₄⁺. Differences between upper and lower horizon can be explained in consequence of the high winter precipitations that selectively washed the upper layer of the soils, determining an higher accumulation in peaty soils, where water retention is higher than the rest of the province.

4 CONCLUSIONS

On the basis of the results of this study is possible to express the following considerations:

- A considerable amount of residual nitrogen of the 2009 fertilization is present in the soils of the province in the first months of 2010 before the new sowing.
- Nitrogen is present as NH₄⁺ and NO₃⁻ with a considerable prevalence of the NO₃⁻
- Highest concentrations for both NH₄⁺ and NO₃⁻ are present in the lower layer of soils (from 50 to 100 cm of depth)
- pH and organic matter have an important role in the nitrification processes, determining the nitrogen species accumulation
- NO₂⁻ and CO(NH₂)₂ concentrations are negligible and this means that NO₂⁻ is very unstable because of the high velocity of the microbial processes and CO(NH₂)₂ in the whole territory is readily transformed into inorganic nitrogen

All of these observations may lead to an informatics system that, from year to year, and depending on the crop cycle, can allow to accurately establish the quantities of nitrogen-based fertilizer to use, in order to obtain high yields and minimize risks of pollution of the water surface.

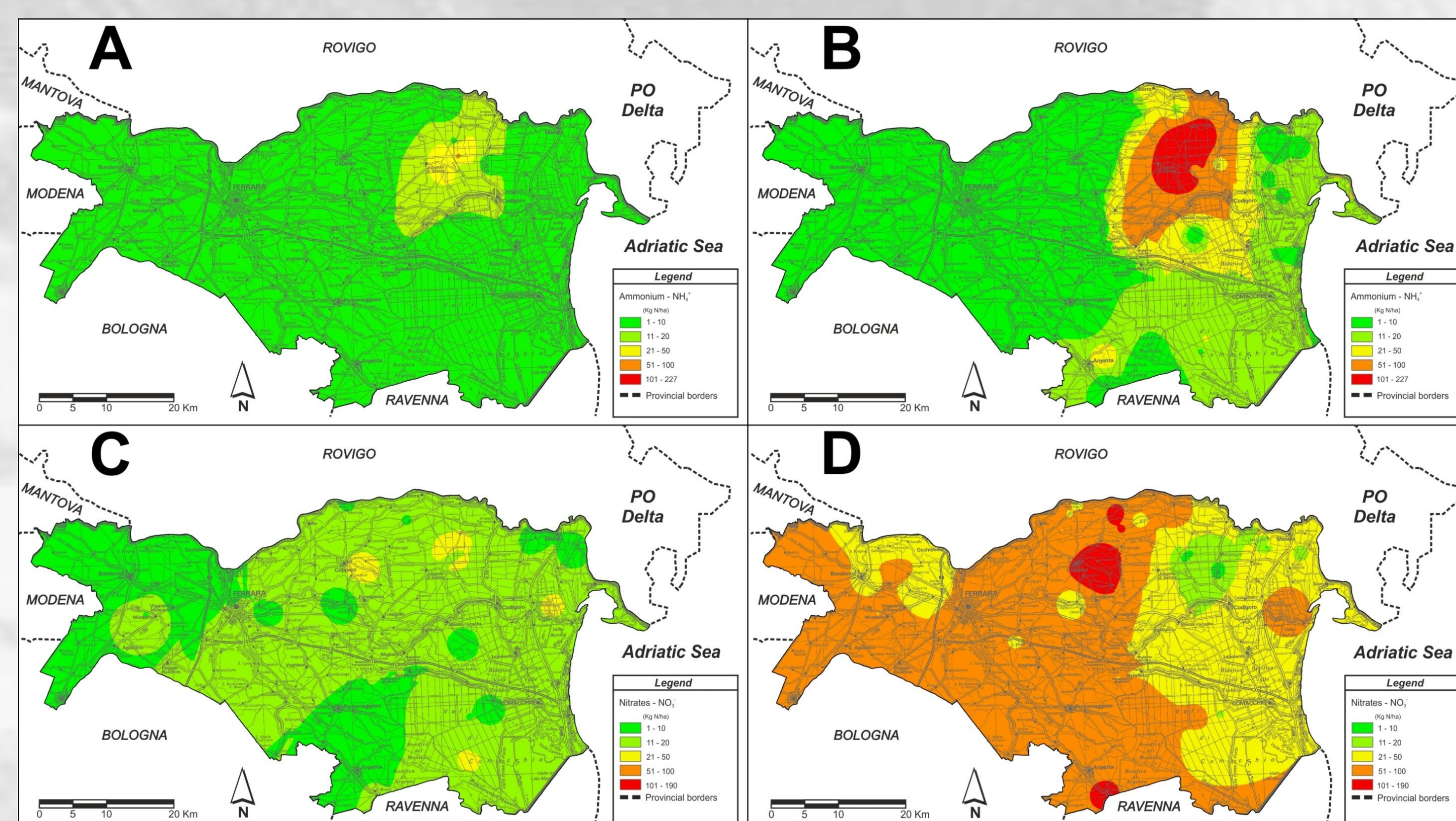


Fig. 4 – Residual NH₄⁺ and NO₃⁻ maps for both upper (A and C) and lower horizons (B and D).