ARPA LOMBARDIA
Agenzia Regionale per la Protezione dell'Ambiente
Settore Monitoraggi Ambientali
Qualità dell'Aria

Evaluation of 2012 ammonia trend in Lombardy

The ARPA Lombardy Air Quality Network (AQN) ammonia analyzers work with chemiluminescence techniques, that is the light produced by NO-ozone reaction:

$NO_2 \longrightarrow NO$

$NH_3 \longrightarrow NO$

$NO + O_3 \longrightarrow NO_2 + O2 + hv$

The air, sampled through a pump, is conducted in the reaction chamber, where it is blended with ozone by a properozonator. In this way the above reaction occurs, with a NO proportional light emission. This light is read by a photomultiplier that converts the electrical signal in NO concentration.
In particular, NOx concentration measurements ($NO + NO_2$) occur by the process: NO_2 in NO transformation through a molybdenum converter before the reaction chamber; once reached the chamber, the NO reacts with O3 by the characteristics light emission and then is read as NO_x signal.
Similarly, both NO_2 and NH_3 in air sample are transformed in NO by a second converter that works at high temperature (from 750°C to 825°C, depending on the model), helping reaction of NO with O3 and the consequently formation of total nitrogen molecules N_t ($NO + NO_2 + NH_3$). NH_3 concentration is than determined by subtracting $N_t – NO_x = NH_3$.

Ammonia analyzers installed in the Lombardy AQN are working with hourly resolution, and then they allow to evaluate the daily ammonia trend, useful to try to discriminate what emitted locally compared to what transported from the neighborhood of the measurement site.
Ammonia is also an important secondary particulate matter precursor through the reaction:
$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

The ammonium ion then associates mainly with sulphate and nitrate ion, produced from gaseous precursors such as sulfur dioxide and nitrogen oxides with the formation, respectively, of ammonium nitrate and sulfate in the particulate phase.

In Lombardy ammonia measurements began in 2007, at first in 4 sites relevant both from the emissivity and geographical point of view: Bertonico (LO), Corte de Cortesi (CR), Milano-Pascal,andMoggio (LC). During 2011 were added 2 more locations: Cremona-Fatebenefratelli, and Cremona-Gerre Borghi. During 2013 the ammonia AQN was further enhanced with the addition of other 5 measuring points: Piadena (CR), Schivenoglia (MN), Colico (LC), Pavia-Folperti, and Monza-Parco, for a total of 12 sites.

Here it will be discussed the calculations made from the ammonia measurements in 2012, compared with the average of historical data from 2007 to 2011.

By the emissivity point of view, in Lombardy the major NH_3 activities are: agricultural activities in general (including machinery handling), processing and waste disposal activities, traffic and combustion in general (industrial and heating). The percentage contributions in the territory may vary depending on the intensity of sources present, with values generally higher in areas with rural-farming use of soil.

The table 1 shows the processing made for activities involved in ammonia emissions, for the 5 municipalities where ammonia measurements are available in 2012.

INEMAR 2010	Bertonico	Corte de Cortesi	Cremona	Milano	Moggio
NH3 Emissions	(t/y)	(t/y)	(t/y)	(t/y)	(t/y)
Municipal area (km²)	20.22	12.79	70.39	182.07	13.41
Combustions	0.03	0.05	3.56	4.08	0.12
Traffic	0.64	0.26	8.35	53.32	0.17
Other mobile sources and machinery	0.003	0.002	0.01	0.05	0
Waste treatment and disposal	0	0	1.55	14.23	0
Agricolture	247	261	1005	96	0.04
SUM (t/y)	248	262	1019	168	0.33
Percentage vs district (%)	3.6	1.3	5.2	2.9	0.1
Sum respect Region (100060 t/y) (%)	0.25	0.26	1.02	0.17	0.0003
NH3 emission per surface (t/y/km²)	12.25	20.46	14.48	0.92	0.02

Table 1 – NH3 emissions from involved activities (t/y), for the municipalities where ammonia measurements are available (source INEMAR - ARPA Lombardia(2013), Inventario Emissioni in Atmosfera: emissioni in Regione Lombardia nell'anno 2010 – public rewiev).

Since those data were consolidated by administrative municipal boundaries, it was decided to also calculate the emission of NH3 per municipality unit area, to have an index of normalized comparison. From this it appears that, despite of the NH3 emissions from Cremona (1019 t/year, 1% of total into the region) is greater than that of the other municipalities in table (Bertonico 248 t/year, 0.3% of the Region; Corte de Cortesi 262 t/year, 0.3% of the Region; Milano 168 t/year, 0.2% of the Region; Moggio 0.3 t/year, 0.02% of the Region), using the municipal area as normalized ratio, it is evident the strong contributions of agricultural activities in general, and in particular for Corte de Cortesi.

Basing on those criteria, the municipalities of the southern part of Lombardy - in fact characterized by intensive agricultural activities - appear correlated compared to municipalities in central (Milan) and northern (Moggio) area of the region. This is confirmed by a cluster analysis performed on the time series of measured concentrations. The cluster analysis is a technique of clustering of time series based on the similarity of trends (hierarchical analysis on autoscaled series, Pearson coefficient R as similarity index, centroid as the class representative). In figure 1 is shown the processing carried out on daily data of 2012 about 6 sites (Bertonico, Corte de Cortesi, CR-Fatebenefratelli, CR-Gerre, MI-Pascal e Moggio).

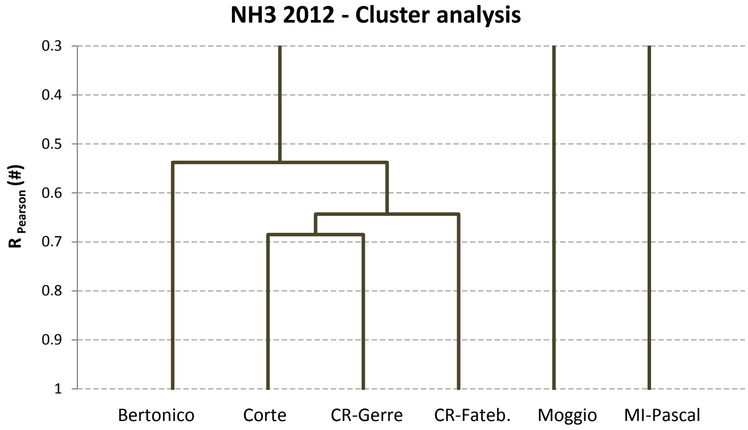
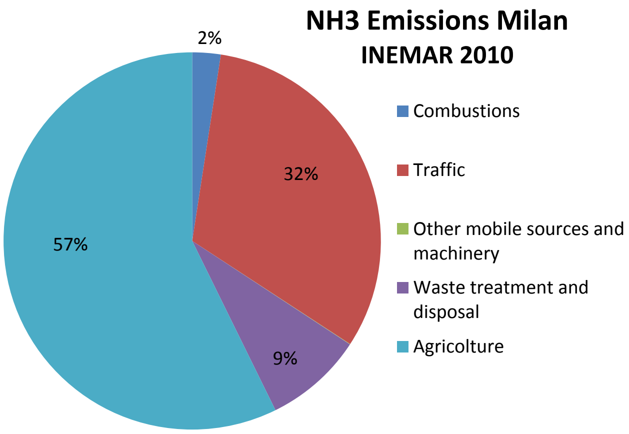


Figure 2 – Cluster analyis on daily data of 2012 in the 6 sites.

Focusing on the two sites less impacted from the point of view of agricultural activities - that are MI-Pascal and Moggio - and analyzing the distribution of graph emission (Figure 2) it is clear that in the case ofMoggio the 51% due to Road transport is not actually a source so significant in the analysis of environmental data, as shown below. In the case of Milan, however, where the transport situation has a significant impact, the traffic is not the primary source, as also the agricultural activities in the neighborhood have a relevant role which will be discussed in the observation of trends times.



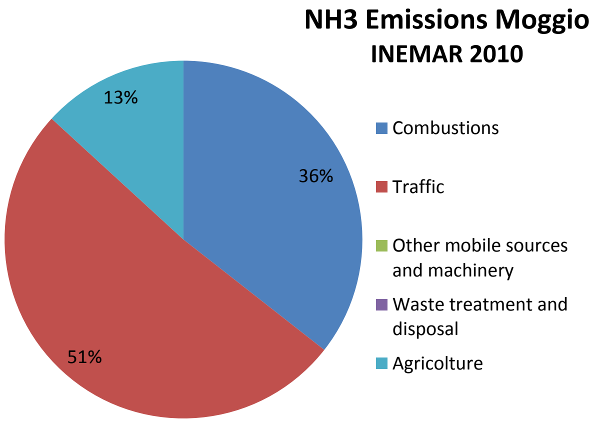


Figure 2 – Ammonia source emission contributions.

The following Figure 3 shows the trend of monthly averages (with relative standard deviation) of ammonia for 2012, compared with the similar processing based on the average of previous years from 2007 to 2011. This processing was obviously made for the stations with adequate time series (Bertonico, Corte de Cortesi, MI-Pascal and Moggio); for the two stations placed at the end of 2011 was carried out the same processing but compared with the averages of Bertonico, with similar placement emissive (Figure 4).
The analysis of the graphs shows the analogy of the southern sites, with similar seasonal fingerprint even in comparison with previous years, albeit with considerably different concentrations. The months most

affected by the formation of ammonia are March and October, probably because of the intensification or the occurrence of typical agricultural activities in the area. This is confirmed in Figure 4 , where the position of Cremona-Fatebenefratelli (more urban) recorded lower values than the other two stations considered in the graph. In general, there was a decrease in the concentrations of ammonia in Bertonico while an increase in Corte de Cortesi. In the first months of 2012 it was required to submit a corrective maintenance for the instrument of MI-Pascal. In general, however, even from data analysis from previous years, there is not a clear seasonality as in previous cases; in 2012 we observe the maximum monthly average in October, as in similar semesters of previous years. Vice versa in Moggio the monthly average of the years 2007-2011 is subjected to an increase of concentrations in the warm season compared to colder months; in 2012 there was a relevant drop in concentration, anyway already low compared to other sites, due to the lack of emission sources and possibly to the high impact of meteorology which has deprived the transport of ammonia from southern areas .

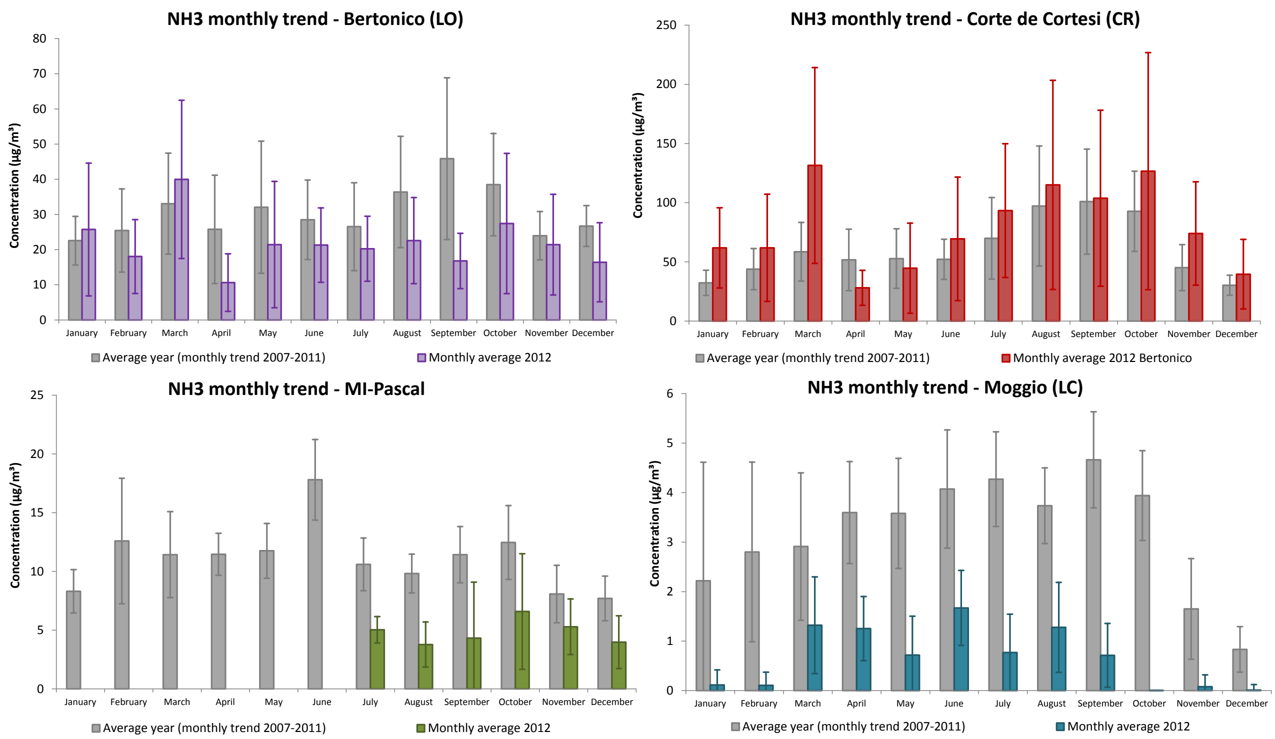


Figure3 – Monthly trend: 2007-2011 and 2012 comparisons.

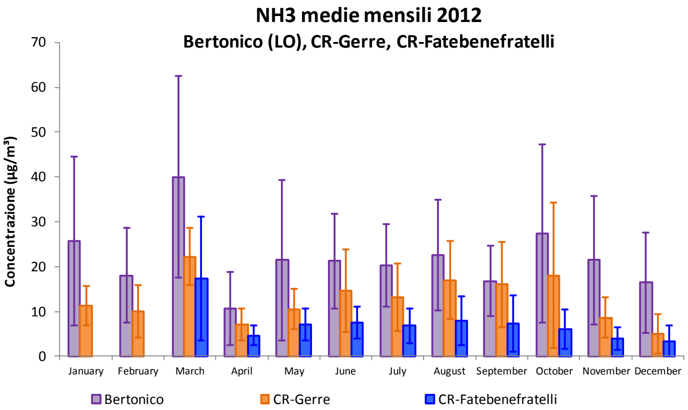


Figure 4 – 2012 monthly trend for CR-Gerreand CR-Fatebenefratelli, compared with Bertonico.

From the hourly data was drawn a typical week for the year 2012 for each site (Figure 5). As for the stations in the graph on the left, the weekly trend has the same pattern, with higher average concentrations at the sites in a rural area. The highest concentrations are measured from Thursday to Saturday - consistent with the hypothesis of the influence of farming and breeding - andless intense on the weekends. In the graph on the right it cannot be detected a weekly cyclical pattern, also due to a lower variability of the concentration values.

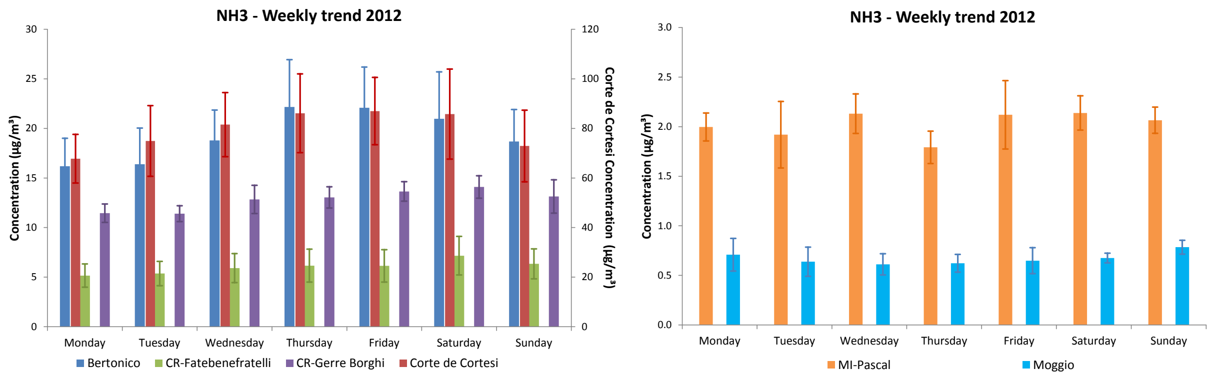


Figure 5 – Ammonia weekly trend for Bertonico, CR-Fatebenefratelli, CR-Borghi, and Corte de Cortesion the left side; MI-Pascal andMoggio on the right side.

In order to observe the behavior of ammonia during the day, taking into account the influence of the season both on emission levels and on the chemical and physical transformations of the compound, they were drawn standard days divided into 4 seasons of 2012 and compared with the same processing performed on the average of previous years (Figure 6-10).

It is observed, in general, that the standard day in Corte de Cortesi (Figure 6) maintains the same fingerprint during the years, highlighting a conservative behavior in the variability emissive ammonia. In particular it is observed a relative peak at 9 am with subsequent deposition in the course of the day, with the exception of the autumn season characterized by an emissive almost uniform in the course of the day, with higher concentration values.

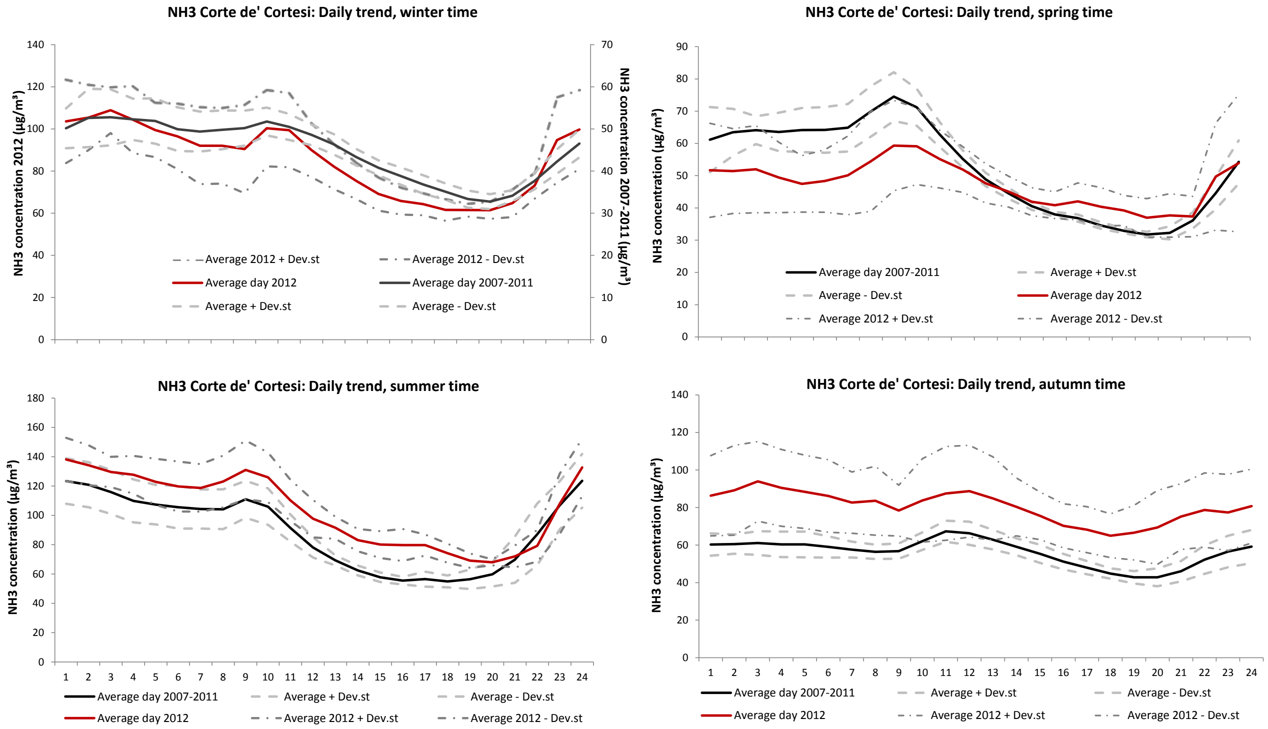


Figure 6 – Ammonia day typefor Corte de Cortesi per season with standard deviation; 2012 in red and the average 2007-2011 in black.

The fingerprint in Bertonico (Figure 7) appears rather different in thedifferent seasons, except autumn. In particular, we observe a different behavior between 2012 and previous years, showing the daily relative peak during the afternoon. In autumn the behavior returns to be consistent both within the day that compared to previous years.

For CR-Fatebenefratelli (fuchsia) and CR-GerreBorghi (purple) they are shown in Figure 8 the standard days for the period available, namely 2012. With the exception of little punctual variations, the imprint daily appears comparable between the two sites, confirming the good correlation detected.

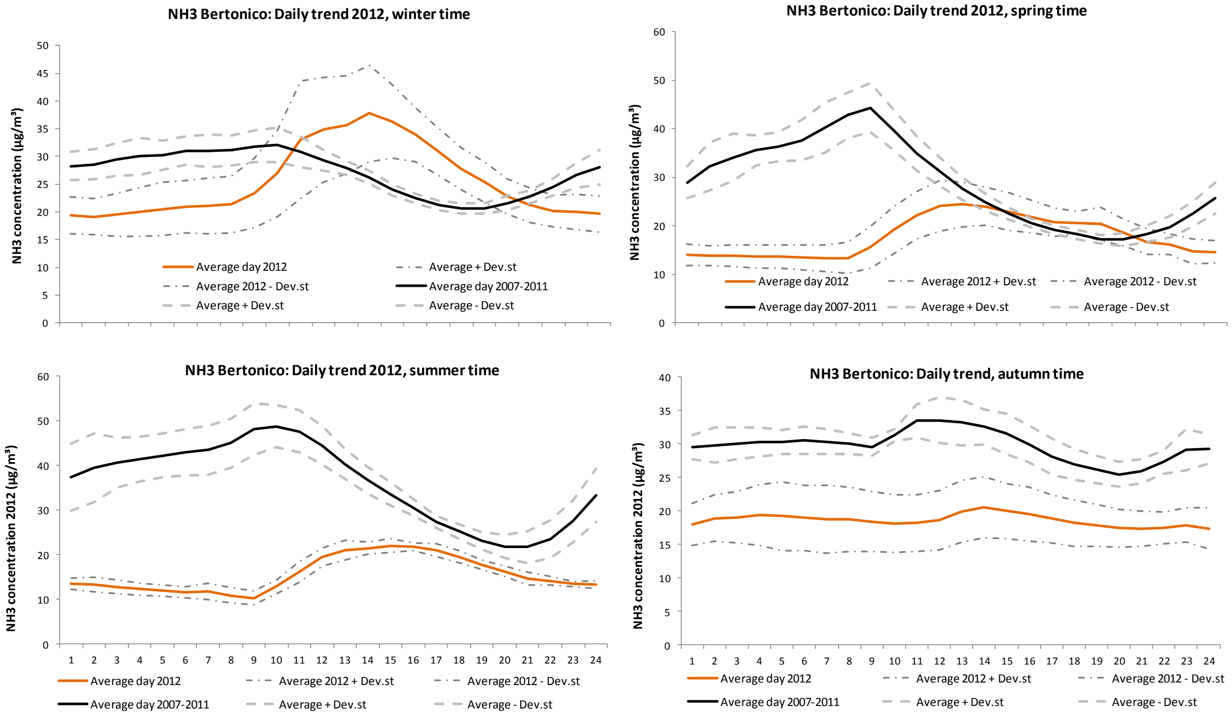


Figure 7 – Ammonia standard day for Bertonico per season with standard deviation; 2012 in orange and the average 2007-2011 in black.

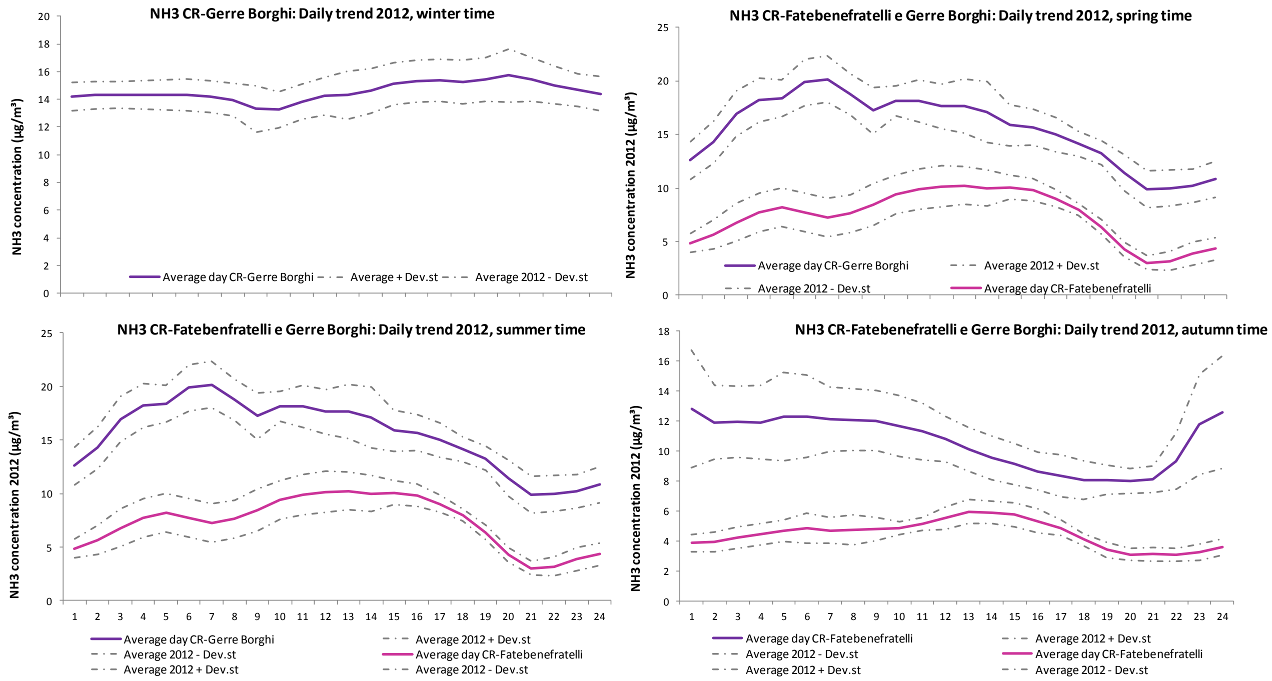


Figure 8 - Ammonia day type for CR-GerreBorghi (purple)e CR-Fatebenefratelli (fuchsia) per season, with standard deviation.

For MI-Pascal (Figure 9) they were calculated the standard days for seasons available, namely summer and fall. With the exception of the concentration values tips, trends remain unchanged in the transition from 2007-2011 average to 2012.

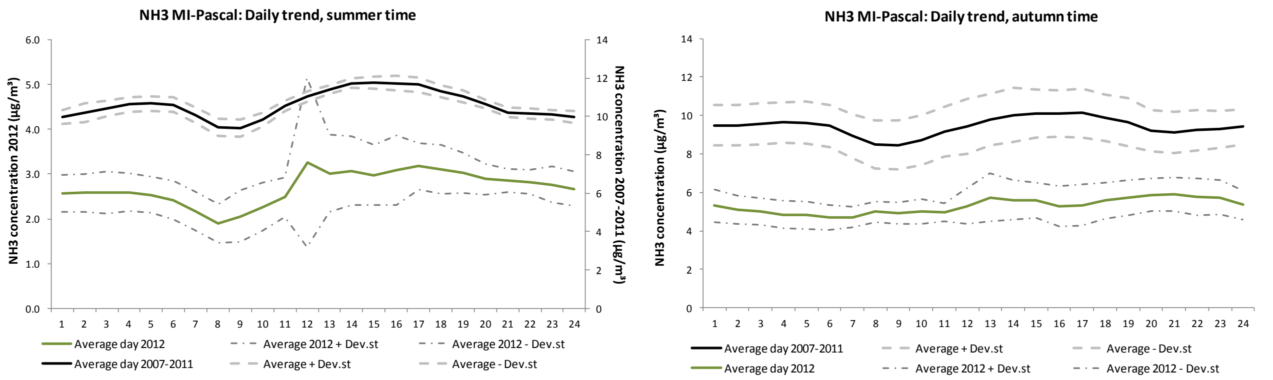


Figure 9 – Ammonia standard day for MI-Pascal per season with standard deviation; 2012 in green and the average 2007-2011 in black.

Similarly to Bertonico ,the Moggio footprint (Figure 10) of the standard day looks different in 2012 compared to previous years. However, the concentration is close to the instrumental detection limits so being quantitatively insignificant

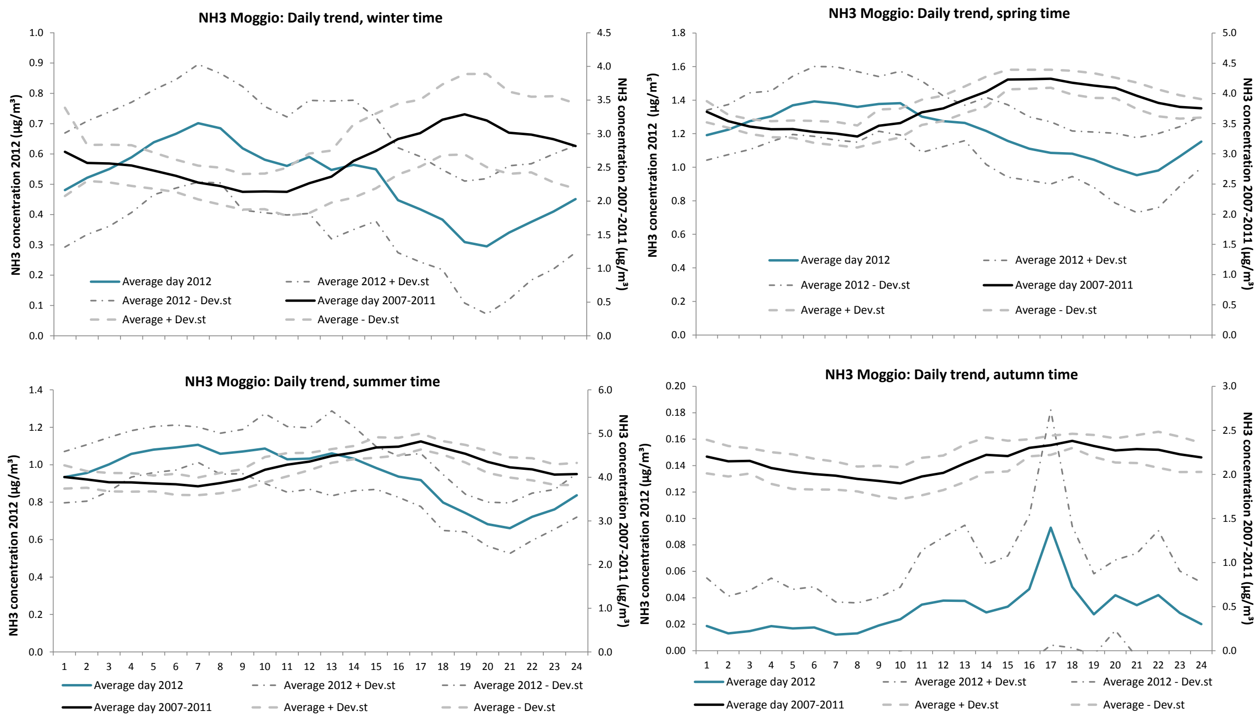


Figure 10 – Ammonia day type for Moggio per season with standard deviation; 2012 in blue and the average 2007-2011 in black.

The analysis of the different fingerprint here observed has suggested the possibility to investigate the phenomenon in order to discriminate between what locally emitted and what is transported from the surroundings and/or transformed. For this purpose they were drawn ammonia roses, basing on hourly concentrations measured with local data of wind speed and direction in the 4 seasons of 2012 for each site (Figure 11), normalized to the maximum value for representation purposes.

The rose for MI-Pascal in particular, shows that concentrations in summer and autumn are mainly coming from southern areas suggesting the overlap of the local broadcast with the component transported from agricultural areas.

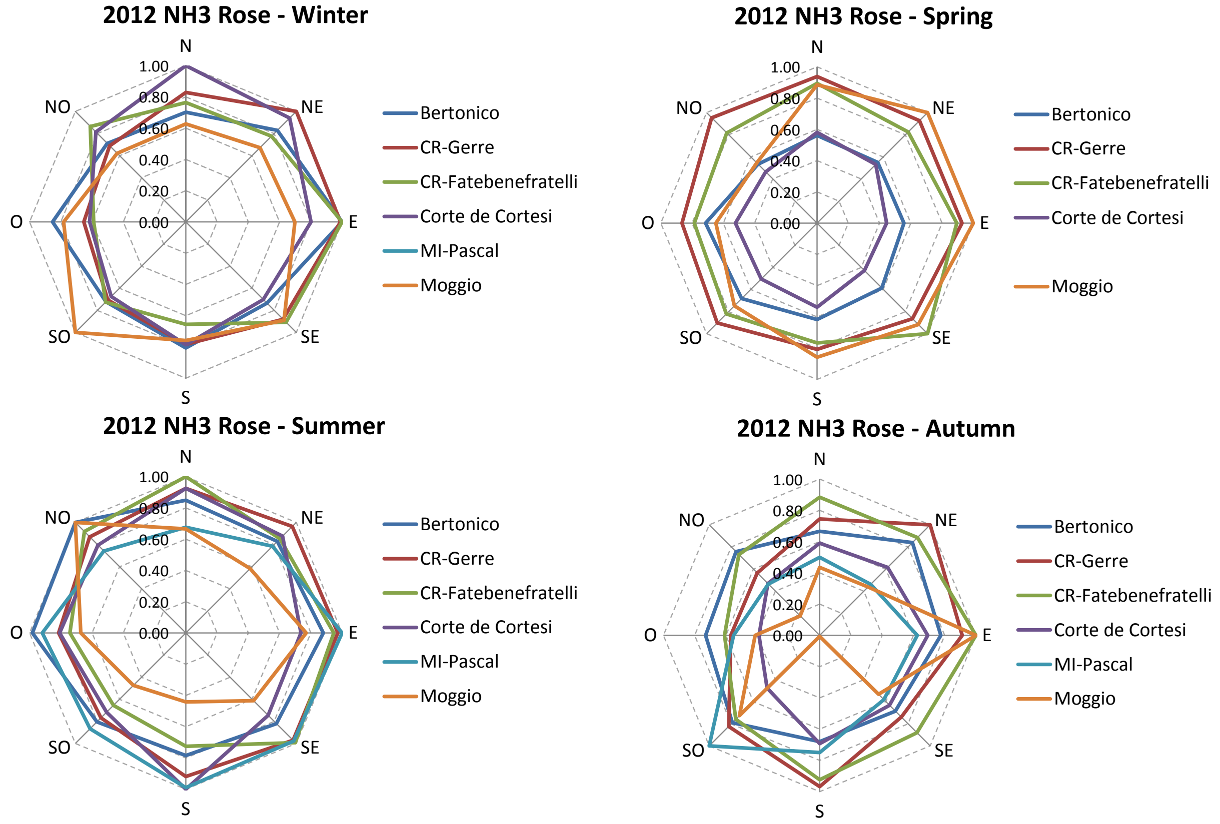


Figure 11 – Ammonia roses per site and per season.

As a final processing (Figure 12) it is proposed for each site the daily ammonia rose, elaborated for 4 representative hours, such as 6:00, 12:00, 16:00, and 21:00.

The stations located in the south of the region show hourly ammonia roses almost homogeneous within the day, albeit with differences related to the location of the site. Instead in MI-Pascal, the rose of the concentrations is not immediately recognizable, but it is noted that higher concentrations of ammonia during the day (12:00 and 16:00) are not measured when the site is downwind in relation with the most densely urbanized area of the city. Such behavior suggests that the contribution of the primary traffic is not so significant compared to other phenomena such as the transport of air masses from the southern areas or other chemical and physical phenomena to be further investigated.

In general it was observed that in many of the rural sites the concentration profiles during the day are essentially modulated by the height of the mixed layer, as it happens with many of the pollutants emitted continuously in the lower layers . This behavior is different for Bertonico, the site where activities related to the breeding of pigs are particularly high. These differences will be object of further study taking into account not only the ammonia in the gas phase but also the species that are generated from it in the particulate phase .

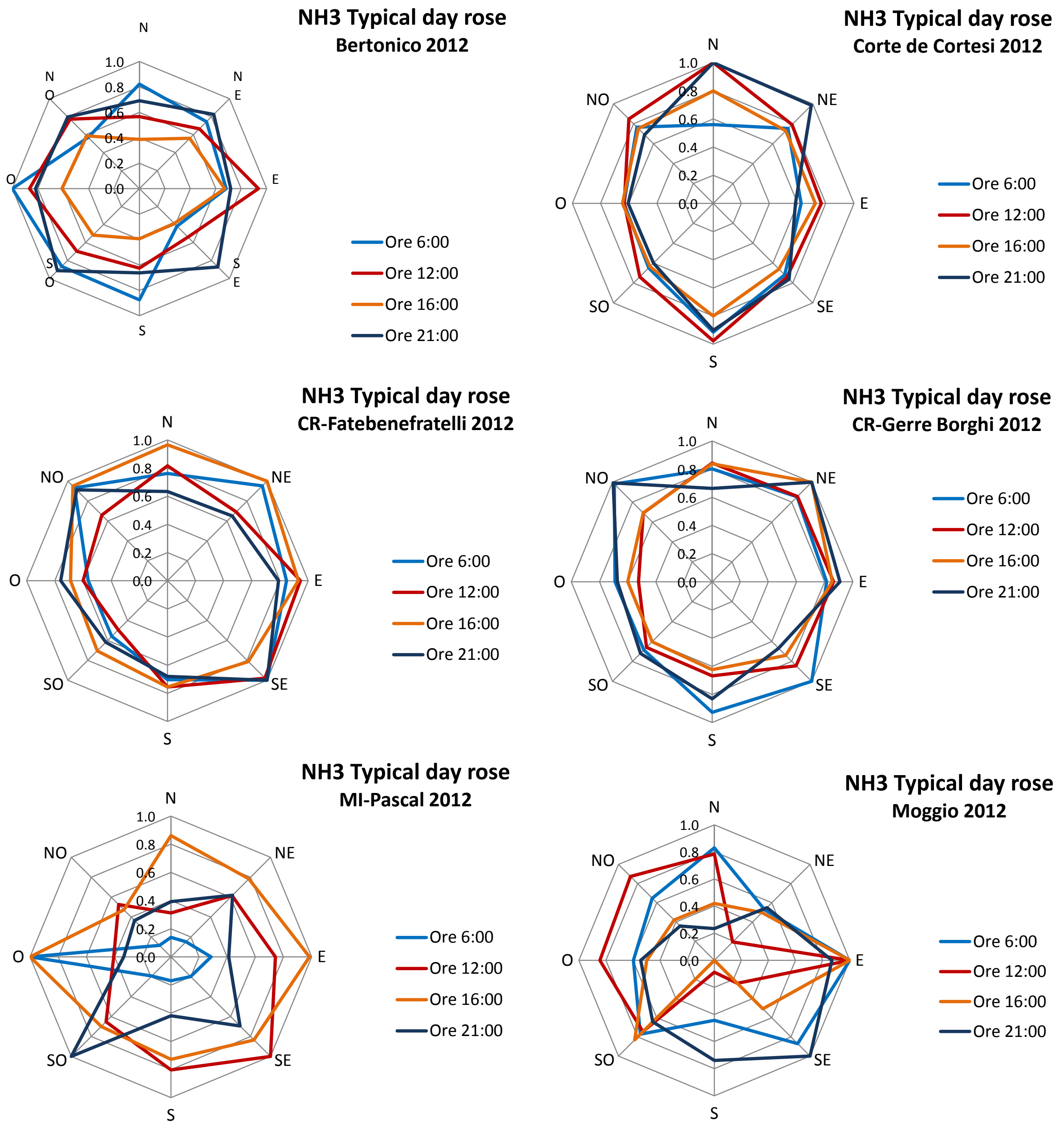


Figure 12 – Hourly ammonia roses per site.

Centro Regionale Monitoraggio della Qualità dell'Aria
Ufficio Progetti Speciali

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