NCDENR

North Carolina Department of Environment and Natural Resources
Division of Air Quality

Michael F. Easley, Governor | April 20, 2006 | William G. Ross, Jr., Secretary
B. Keith Overcash, P.E., Director

MEMORANDUM

To: Hoke Kimball, Chief, Ambient Monitoring Section HKimball

From: Arun D. Shendrikar, Chemist-II, Projects and Procedures Branch ADS

Through: Joette Steger, Supervisor, Projects and Procedures Branch

Re: Recommendation on the Continuation of Ammonia Monitoring in North Carolina

Since 1999, the Ambient Monitoring Section of the North Carolina Division of Air Quality (NC-DAQ) has been monitoring ambient gaseous ammonia concentrations at three regional sites. This monitoring project was initiated in 1999 with the view of collecting ammonia concentrations data for the next 5 to 7 years in the light of exponential growth of hog farm industries in the State of North Carolina. As required, a Quality Assurance Plan (QAP), specifically for ammonia monitoring was developed, implemented and all its protocols have been followed throughout the entire data collection period.

The three ammonia monitoring sites (see **Figure** 1) are located across a longitudinal transect in Eastern North Carolina where the highest density of animal farms exists relative to the rest of the State. Furthermore, these animal facilities are located upwind of three river basins, one swamp, and coastal areas that are considered to be sensitive to ammonia/ammonium deposition. The selected sites are Clinton Crops Site (Sampson County), Lenoir County Community College (LCC) Site and Martin County Site (Jamesville). The Clinton Crops Site is surrounded by the hog farm industries where the impact of activities of these industries is expected to be monitored (in terms of ammonia emissions) over a time period. The LCC Site is further away, approximately 50 miles North-East of Clinton Crops Site and the Martin County Site (Jamesville) is 50 miles away from the LCC Site but in almost same direction (North-East) where a diluted impact of ammonia emissions from the farm activities can be monitored.

This type of site configuration was intended to provide a valid data set that captures both the spatial and temporal trends of ambient ammonia concentrations across sensitive areas in Eastern North Carolina. The three sites were placed along the predominant wind corridor where 20 percent of the winds come out of the Southwest and South-South-West, with wind speeds ranging from 2 to 20 miles per hour. These monitoring locations

Ambient Monitoring Section
1641 Mail Service Center, Raleigh, North Carolina 27699-1641
2728 Capital Blvd., Raleigh, North Carolina 27604
Phone: 919-715-0665 / FAX 919-733-1812 / Internet: www.ncair.org

One North Carolina *Naturally*

were also considered to provide concentration trends of ammonia from polluted sites (Clinton Crops and LCC) to the so-called further distance away Jamesville Site.

Each site was equipped with:

- Temperature controlled shelter
- Thermo Environmental Instruments (TEI), Model 17C Ammonia analyzer
- TEI, Model 146C Dynamic Gas Calibrator
- Model 111 Zero-Air Supply System
- A site dedicated PC and Modem System, data loggers, sample in-take lines and other related accessories

Statement of Problem(s)

In 2005, within the Ambient Monitoring Section, a study was undertaken to evaluate ammonia data quality from all three sites for years 2001 through 2005. During this study an assessment of the field performance of the 17C ammonia analyzer (in terms of data accuracy and reliability) and other related components was also made.

As a part of the conclusions of the above referenced study, several questions were raised and in this memorandum, an attempt is being made to answer these questions. Specifically, the questions raised were:

A. What does evaluation/assessment of accumulated ammonia data from years 2000 to 2005 indicate?

1. What are the concentrations of monitored ammonia over the years at three sites and do they pose any adverse human health effects, i. e. how these concentrations compare with the ammonia Acceptable Ambient Level (AAL) of 2.3 mg/m^3?
2. Are there any daily, monthly, seasonal or annual trends/patterns associated with the collected ammonia data?
3. Is there a change in ammonia patterns over the monitored years?
4. Are there typical elevated hourly ammonia levels, if so, what time of the day or night do the elevated episode occur, how long the elevated episode (s) last, and how often do such episodes occur?

B. Should NC-DAQ continue monitoring airborne ammonia concentrations?
C. If yes, why (if no, why not)?
D. If yes, how many sites, why and what type of data frequency i. e. hourly, every 12 hours, daily, and data utility?
E. Which monitoring technology (method) should we use/implement and why?

<u>Proposal (Answers to all above Questions)</u>

A. The accumulated data from years 2000 to 2005 indicate that the overall concentrations at all three sites are low and in the ranges of 2 to 15 PPB (1.52 to 11.38 ug/m^3). These monitored concentrations are considered to be very low compare with the established ammonia Acceptable Ambient Level (AAL) of 2.30 mg/m^3 and thus may not pose any adverse human health effects.

Figure 2 includes average ammonia concentrations over the entire project period. As expected, the overall highest concentrations are at the Clinton Crops Site, followed by the Lenoir Community College Site (LCC). The lowest concentrations are recorded at the Jamesville Site that is further away site (about 100 miles in the same direction-North-East from the Clinton Crops Site, see **Figure 1**) from the hog farm industries. Even these high ammonia concentrations recorded at the Clinton Crops Site are considered to <u>not</u> pose any adverse human health effects.

In terms of yearly data patterns, as can be seen in **Figure 3 A, B and C**, there is a rise (peak) in ammonia concentrations some where in third quarter, every year for the last five years, at all three sites. Since Clinton Crops Site is surrounded by the hog farm industries, this third quarter concentration rise is the highest at this site, followed by LCC and Jamesville. This rise in the concentrations in the third quarter (July, August and September) every year, at three sites may be attributed to the regional application of fertilizers that include ammonium salt in their composition. Also these being summer months, the regional high temperatures may be causing increased ammonia emissions from point sources.

An evaluation of ammonia concentrations by the hour at three sites indicates the presence of three peaks in a 24-hour monitoring period. The first peak appears around 4 AM, the second at 9 AM and the third one (relatively small) around 2 PM (see **Figure 4**). This first peak (4 AM) disappears in the fourth quarter of 2003 (see **Figure 5)** and does not show up in the following years of ammonia monitoring. Evaluations of hourly daily ammonia concentrations for the other two sites (LCC and Jamesville) show similar concentration patterns.

Additional evaluation of raw daily hourly ammonia concentration data indicates that the first peak (4 AM) was due to carry over problems of ammonia calibration standards that were used for the auto-calibration. This auto-calibration was performed, at each site, around 4 AM every other day. Thus, there was a carry over (contribution) of part of the ammonia calibration standard while ambient ammonia data were being monitored.

During the 2^{nd} and 3^{rd} quarter of the year 2003, ECB staff and the Site Operators from the Washington Regional Office and Fayetteville Regional Office performed a detail testing of this standard carry over problem for the ultimate resolution of this issue. As a result, this 4 AM peak has not been observed during the monitoring for the following quarters and years (see **Figure 5**).

Monthly day and night time ammonia average concentrations (median) for years 2000 through 2005 for three sites are included in **Figure 6 A, B, and C**. As can be clearly seen, that there is a greater degree of difference between daytime verses nighttime ammonia concentrations particularly at Jamesville than at Clinton Crops and LCC. In summary, ammonia concentrations at Jamesville are relatively higher at night than at day time. Such differences at Clinton Crops and LCC are relatively small (probably negligible) and may be attributed to reactive atmospheres at these sites due to the near by hog farm industries. Additionally the chemical nature and quantities of atmospheric pollutant emissions and abilities of these emissions to react with free airborne ammonia gas may also be contributing factors.

B to E. It is the opinion of this writer that NC-DAQ should continue to monitor airborne ammonia concentration to further determine local trends which may help us, in the future, to develop an effective abatement technology to minimize, if not eliminate, the problem/issues related to hog farm industries and their subsequent ammonia emissions into the regional atmospheres. Additionally, continued ammonia monitoring becomes imperative because:

- Ammonia is the only abundant alkaline gaseous pollutant in our atmosphere
- Ammonia is considered to be responsible for acidic rain and acidic depositions through atmospheric reactions and conversions
- It is also a documented fact (through open literature) that agricultural practices have affects on increased ammonia emissions into the environment
- Ammonia gas is a precursor to $PM_{2.5}$ and thus responsible for $PM_{2.5}$ formation
- Ammonia is also a target pollutant for NCore, Level II Multi-Pollutant Site (US-EPA)

Since the 1980s agricultural ammonia emissions have become one of the major worldwide air pollution problems and have attracted more and more attention from the public and the governmental regulators. Further, it is also widely reported that excessive ammonia emissions from the agriculture and animal (hog farm) industries have caused direct and indirect damages to the eco-system in our region. With the end of growth limitations coming off soon on our regional hog farm industries, the ammonia emissions are likely to rise creating an increased need for them to be monitored/evaluated. The State of North Carolina certainly can play an important role by continuing to monitor regional ammonia ambient concentrations to assess the long-term exposure affects on humans and eco-systems, in general.

It is recommended that ammonia monitoring be continued at a minimum at the three existing sites with two of these (Clinton Crops and LCC) being located around the regional hog farm industries. The third site (Jamesville) may be further away, in almost the same direction, where secondary reaction product(s), if any, can be monitored and or further ammonia dilution (due to distance from point sources) effects may be assessed.

Additional recommendations include that the collection of monitoring data and their frequency remain the same as current. Furthermore, an analyzer should be installed at the Millbrook site to comply with US-EPA's request to monitor ammonia at the NCore, Level II Multi-Pollutant Site.

Next, in terms of this writer's recommendation as to which type of ammonia monitoring method or technology to use/implement, in essence there are two available options. The first option is to continue to use our current TEI Model 17C ammonia analyzers that provide hourly averages. The State, over the years, has become familiar with the way these units operate and thus has the knowledge and experience to keep these units running satisfactorily. The second option would be to conduct research, buy and deploy ammonia analyzers that incorporate latest scientific advances and measure airborne ammonia concentrations directly rather than the current indirect method, the TEI Model 17C utilizes.

TEI Model 17C Ammonia Analyzer

The Ambient Monitoring Section of NC-DAQ currently has a total five TEI Model 17C ammonia analyzers. Three of these are deployed in the field and the other two are designated as spares that can be used in the field, if and when such a need arises (because of mechanical operability problems of the field analyzers). Two analyzers were purchased in 1998, one in 1999, another one in 2000 and the fifth one in 2001.

The attempted ammonia data quality evaluation study of years 2001 through 2005 has indicated the following problems related to data quality and specifically also of TEI Model 17C analyzers:

- The underlying principle of the 17C analyzer operation involves indirect measurements (subtraction of converted ammonia from the total reactive nitrogen oxides) of ambient ammonia concentrations and as a result these monitors may lack the required analytical sensitivity and specificity. A direct ammonia measurement method is the preferred one among the scientific community.
- The accumulated data indicates that the regional ammonia concentrations at all three monitoring sites are in the approximate range of 5 to 15 PPB. The reported detection limit of the TEI analyzer is 1 PPB. Furthermore, the monitor is prone to drift and the analyzer frequently shows sub-zero values because of very low regional airborne ammonia concentrations.
- The TEI Model 17C analyzer has no filter, which can collect and remove the airborne particulate matter. A filter is not used because its presence creates a bias in the ammonia measurements. As a result, the fine particulate matter together with gaseous ammonia enters the monitoring system and clogs up the capillaries, which are ahead of the converter. The clogged-up capillaries are affecting ammonia data quality and as a remedy, capillaries are replaced often (between 3 weeks to a month) at each site. As a part of our current QA protocol, capillary replacement is

always followed by a full three-point calibration and this results in loss of ammonia data for 6 to 8 hours, on a day that this task is performed.

In summary, problems related to TEI, Model 17C analyzers are 1) calibration standards carry over that was observed until 3rd quarter of 2003, 2) capillary clog-up problems and 3) low regional airborne ammonia concentrations. The basic principle of this analyzer (Model 17C) is based on indirect ammonia determination and this may be a contributing factor in determining ambient ammonia concentrations in the ranges of 5-15 PPB. There appears to be no way to overcome this limitation other than by switching to a monitor that utilizes a direct measurement to determine ammonia.

Since as of to-date we already have invested in five of these analyzers and have gone through the learning curve (in terms of field operations) during the last nearly seven years, one solution may be to resolve each of the above issues and if successful, continue using the analyzers to monitor hourly ammonia concentrations at three regional sites.

The calibration standard carry over problem, although currently a relatively minor issue, may be resolved by 1) performing auto-calibration once a week (instead of every other day) with one ammonia calibration (instead of current three) standard e. g. 25 or 50 PPB, and 2) run a zero immediately after the analysis of a calibration standard for one hour or two hours which could eliminate any carry over problem.

The capillary replacement is a serious problem that is affecting data quality. There are four capillaries in the 17C analyzer and this amounts to replacement of about 50 capillaries (based on four capillaries per month) per site. Each capillary cost is about $20 and this requires expenditure of about $3000 per year for all three sites. Some, if not all, capillaries can be cleaned for particulate matter removal using a sonic shaker. However, this will involve labor time of the ECB staff, which may not be available. Importantly capillary replacement involves a full three-point calibration resulting in loss of ammonia ambient data for 6-8 hours on that day, each month per site. This amounts to a total loss of ammonia data for about 290 hours in one year, for three sites.

To resolve the capillary issue, it is recommended to investigate the use of an impactor ahead of the analyzer sample in-take line, to remove airborne particulate matter. Such an impactor is now commercially available from URG, Inc., Chapel Hill, NC at a cost of about $460 each. Again, initial experimental work may be performed at the ECB facility and if this approach resolves the problem, we can implement it at three sites, at a total cost of about $1380.

If our attempts to resolve these problems related to 17C analyzers are successful then we can continue to use all of our five analyzers (and buy one for the NCore, Level II Multi-Pollutant Millbrook site) and may be able to collect quality ammonia ambient data for the next few years. It may also be necessary to contact the analyzer manufacture to resolve some minor related issues such as the analyzer detection limit (since the manufacturer claims the analyzer detection limit to be 1 PPB), generation of 10, 15, 25 PPB ammonia calibration standards, etc.

Other Ammonia Monitoring Options

We have other options for consideration and one would be to replace the 17C ammonia analyzers with a newer and reportedly better monitor, manufactured by "Prananytical", Model Nitrolux^{TM} with a sensitivity of 100 PPT (this range is in line with our regional concentrations) for ammonia. It is estimated that this will cost about $55,000 and for six analyzers, the total cost will be $330,000. Again, for a routine and smooth monitoring site operation, it appears to be imperative that we buy six analyzers of this type, deploy three at three sites, one at the Millbrook, Level II Multi-Pollutant site, and keep two as spares. Importantly, the local US-EPA (contact person Dr. John Walker) has bought one of this "Prananytical" model and we could learn a lot by consulting Dr. Walker about the field operation of this analyzer. Furthermore, it is pointed out that purchase and field deployment of one analyzer of this type at one site may not prove to be beneficial and may create problems related to maintenance for the Site Operator and the ECB staff.

The second option is to purchase (again six) from URG, Inc., ammonia monitors based on denuder technology. These real-time measurement technology monitors costs about $45,000 a piece and can provide continuous and concurrent data on both ambient gaseous ammonia and particulate ammonium in the air.

Conclusions

It is recommended that NC-DAQ continue to monitor regional ammonia concentrations and assess, evaluate and look for continued ambient trends as ammonia levels may rise because of expansion of hog farms, in coming years. The State of North Carolina Hog Farm Moratorium is scheduled to end on September 30, 2007. Additionally, US-EPA's new NCore-Level II Multi-Pollutant requirements will necessitate that the State establish a site at Millbrook with ammonia monitor because this pollutant is considered to be a precursor for PM 2.5 formation.

In summary, this memorandum attempts to evaluate the current ammonia monitoring system in use while pointing out its limitations, ways to overcome these limitations and data quality concerns. Furthermore, available options are pointed out along with their assets and limitations so that management makes the final decision to continue ammonia monitoring.

Acknowledgement: The author of this memorandum (ADS) extends deepest appreciation to Dr. Wayne Cornelius for his time consuming efforts for the statistical treatment of ammonia data from years 2000 to 2005.

Copy To:
. Keith Overcash/Brock Nicholson
. Stephen Vozzo
. Mitchell Revels
. Neil Joyner
. Ernie Fuller
. Frank Stellitano
. Eddie Todd
. Robert Fisher
. Michelle Starkey
. Bob Bishop
. Mark Yirka
. Wayne Cornelius

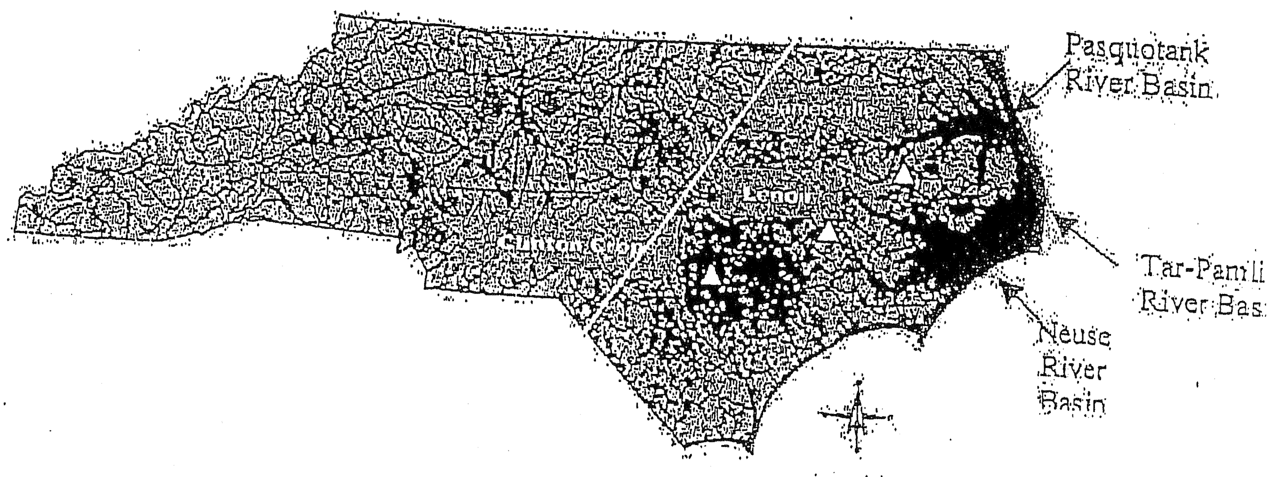


Figure 1. Location of three ammonia monitoring sites (Δ). The solid white line separates Eastern North Carolina

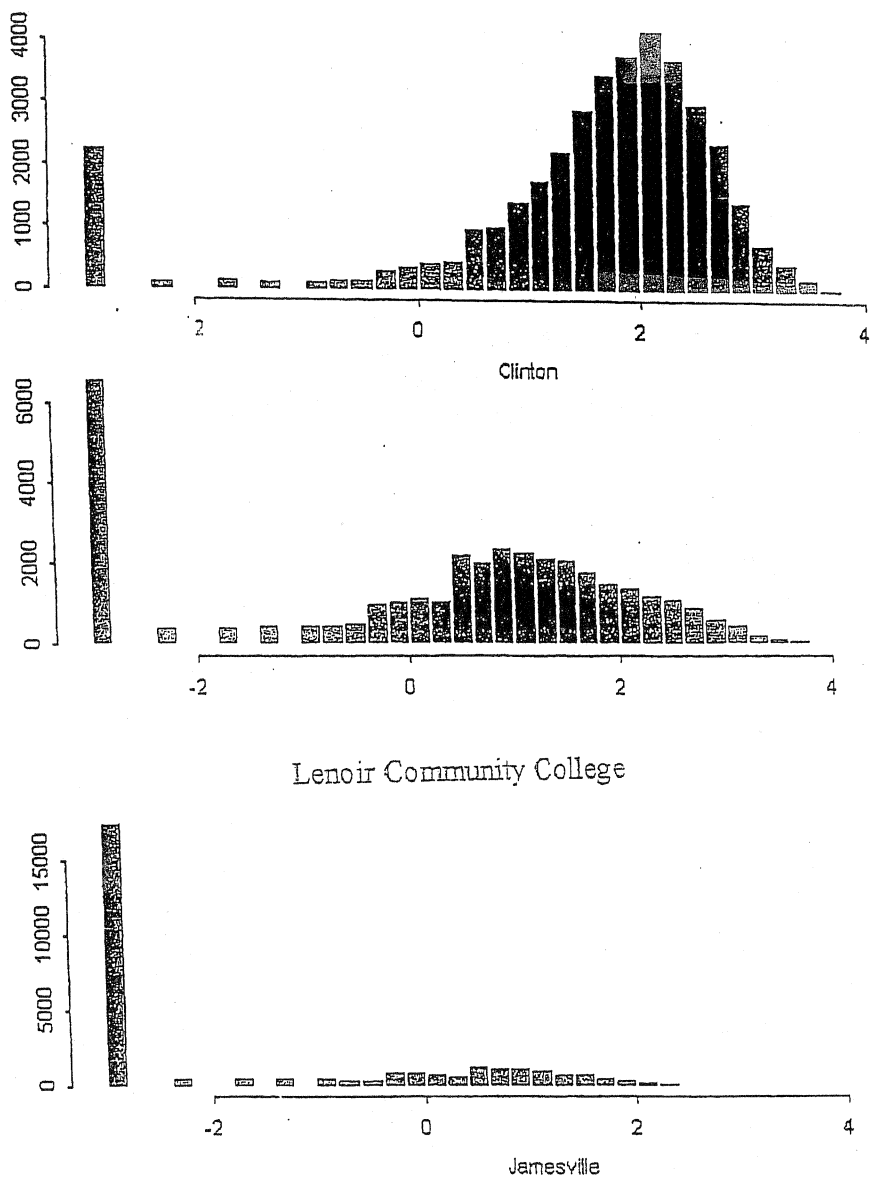
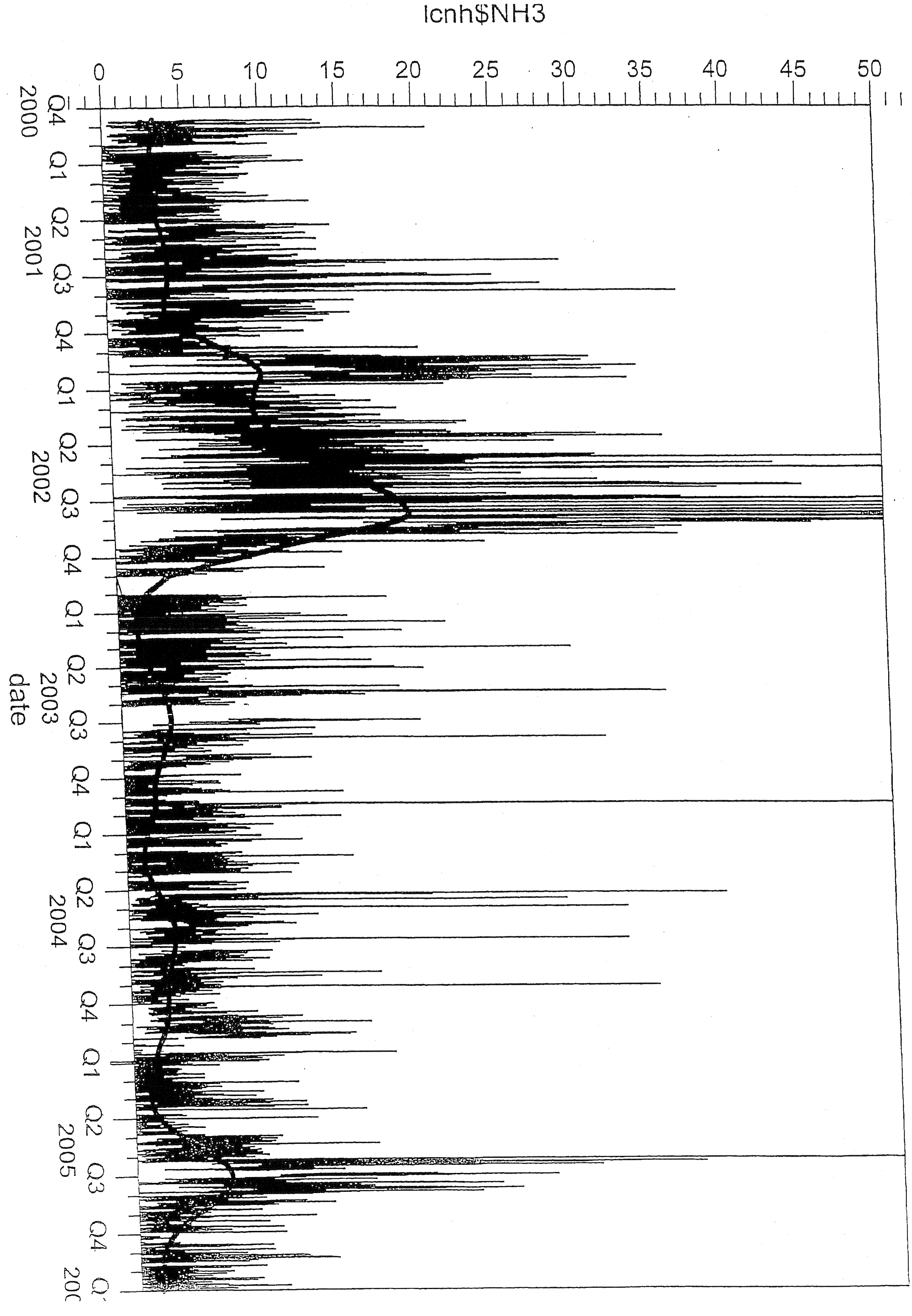
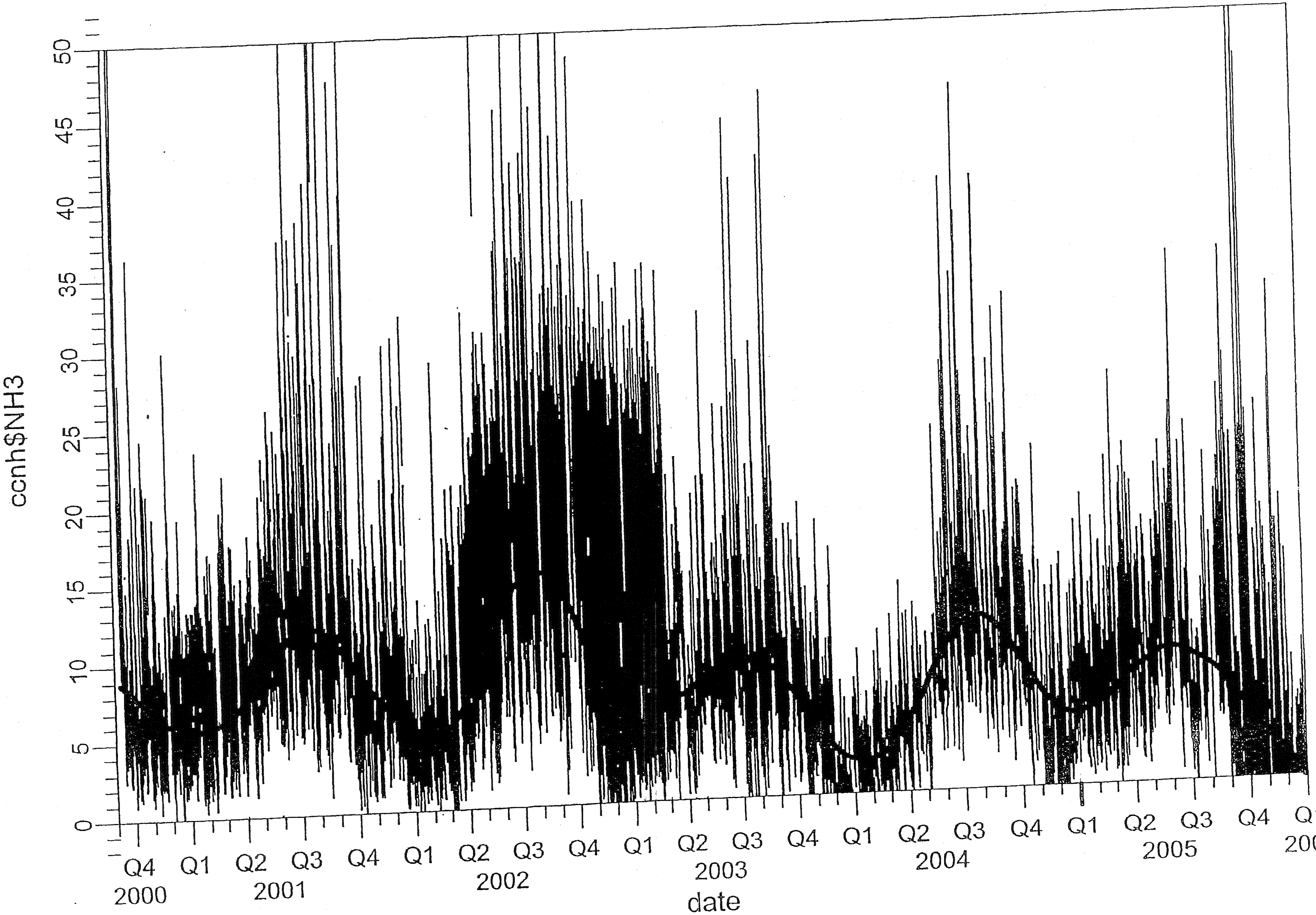


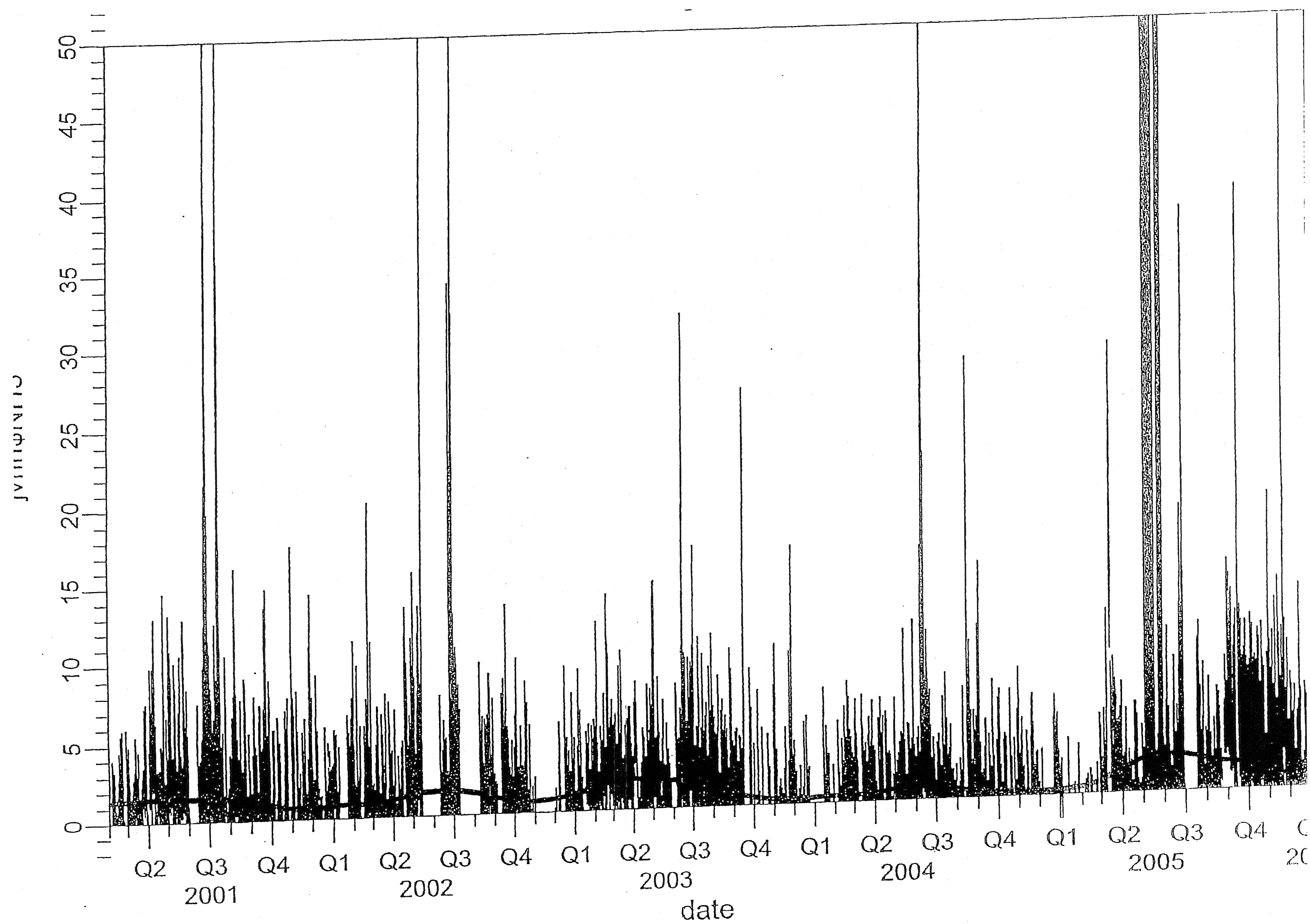
Figure 2. Over the project period average ammonia concentrations at three sites



lcnh$NH3
0
5
10
15
20
25
30
35
40
45
50
date
2000
2001
2002
2003
2004
2005
Q1
Q2
Q3
Q4

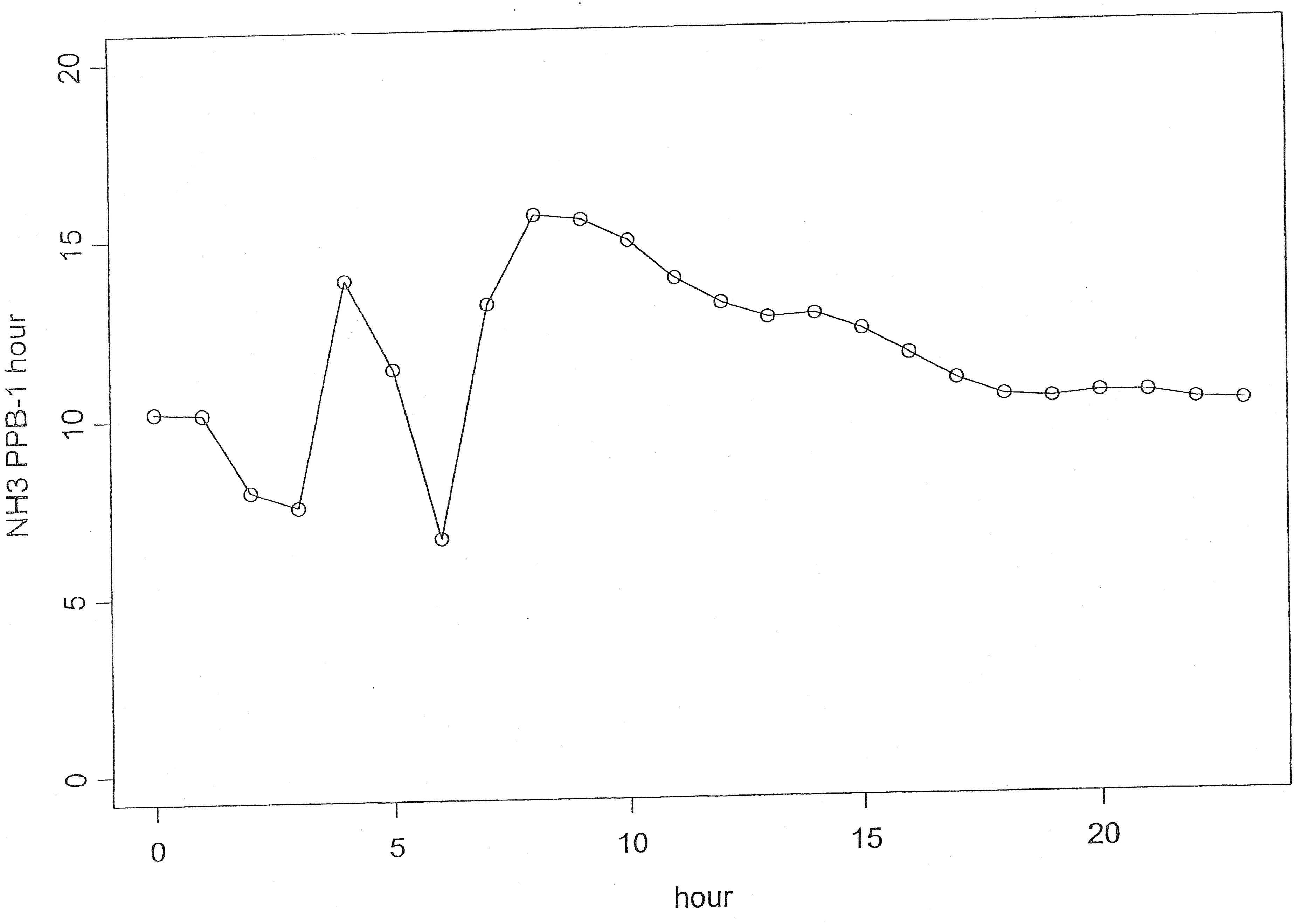
Figure 3 B. LCC Site yearly ammonia data patterns for years 2000 to 20005

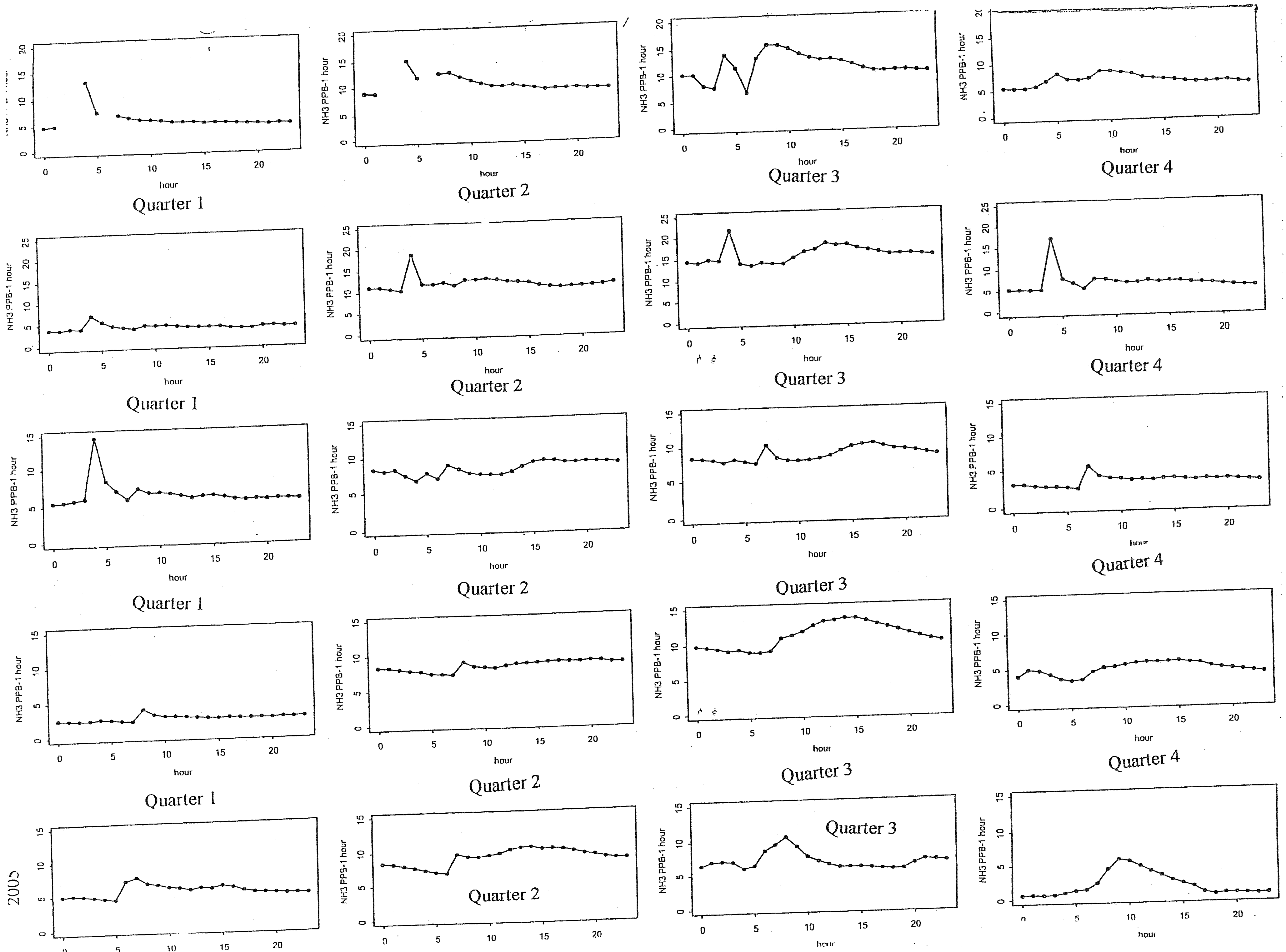




0
5
10
15
20
25
30
35
40
45
50
Q2
Q3
Q4
Q1
Q2
Q3
Q4
Q1
Q2
Q3
Q4
Q1
Q2
Q3
Q4
Q1
Q2
Q3
Q4
2001
2002
2003
2004
2005
date

Figure 4. Ammonia diurnal daily hourly averages for Clinton Crops Site, 3rd quarter 2001





... Clinton Crops Site. Note that the first peak at Quarter 4

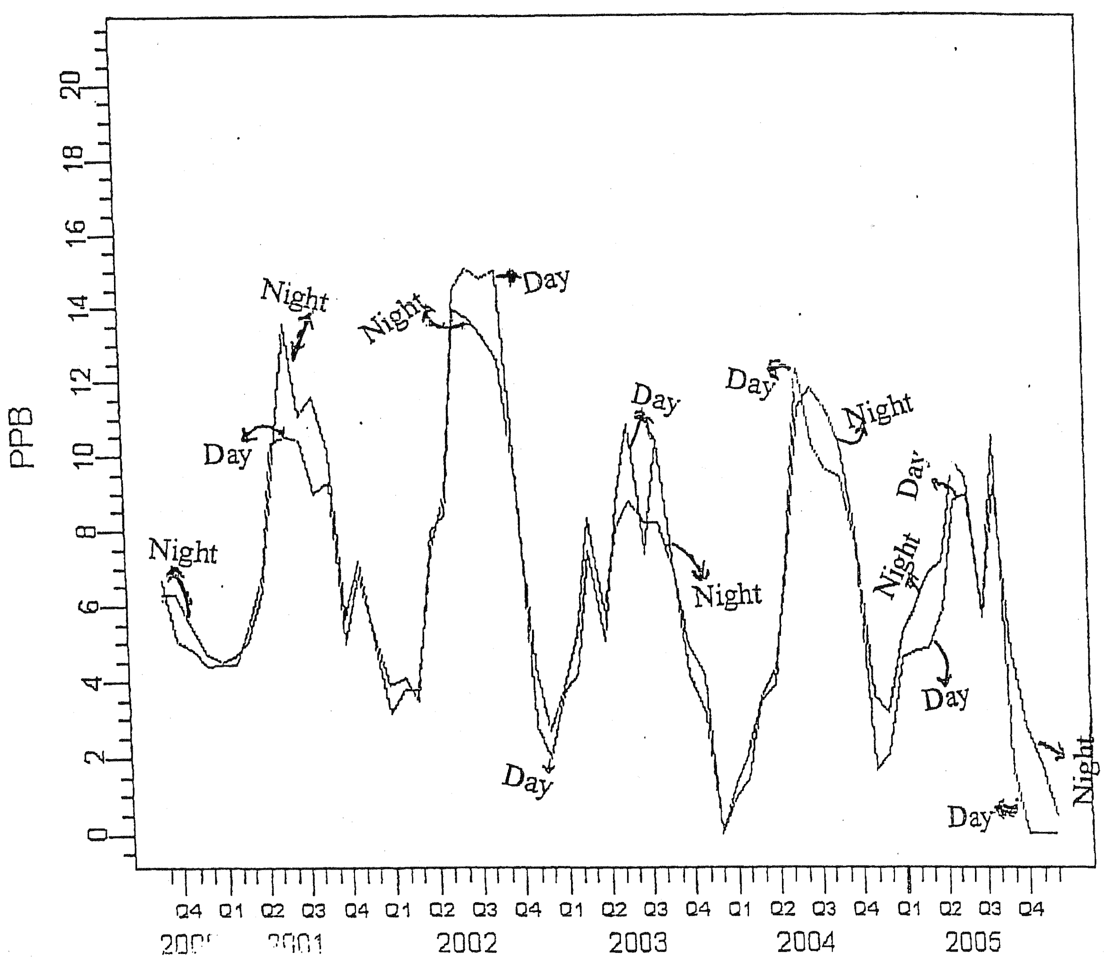


Figure 6 A. Clinton Crops Site ammonia day and night time monthly median averages

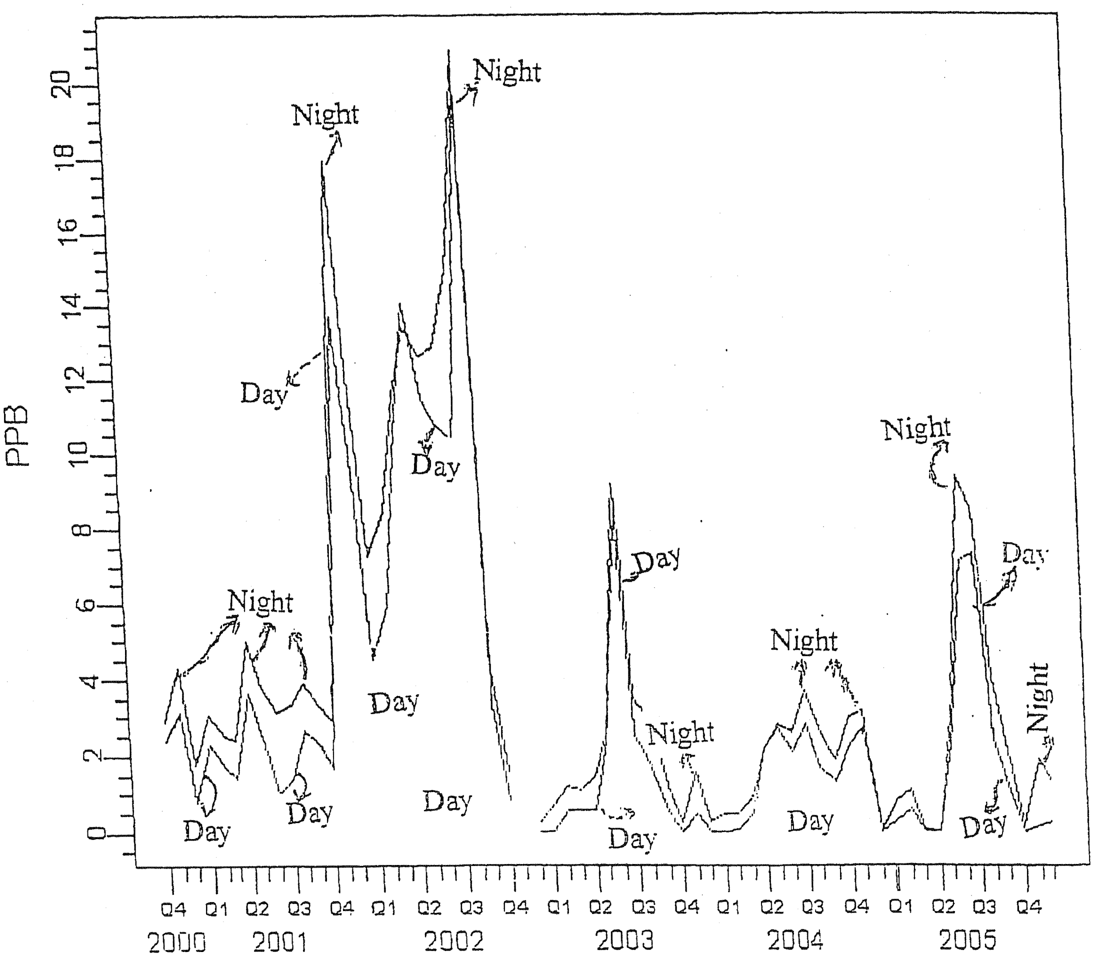


Figure 6 B. LCC Site ammonia day and night time monthly median averages

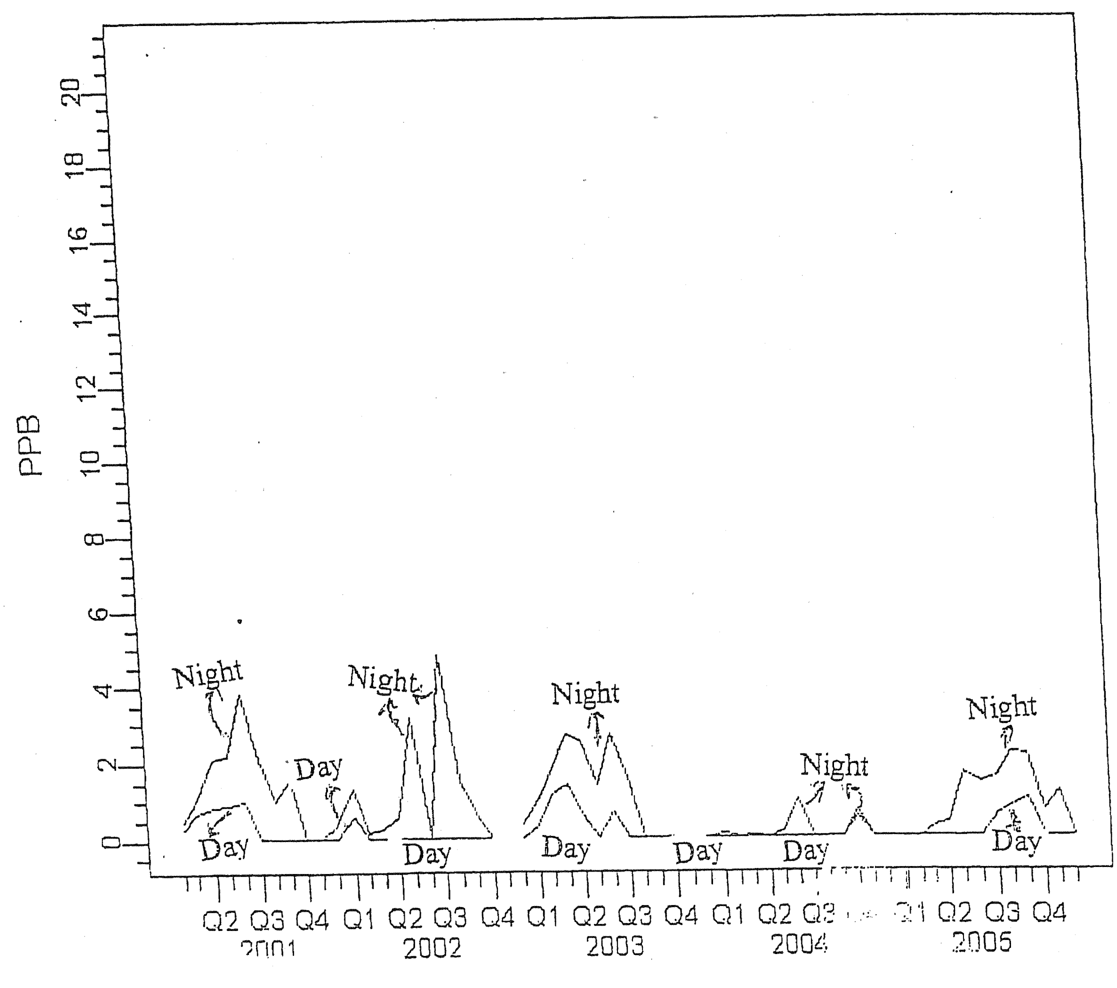


Figure 6 C. Jamesville Site ammonia day and night time monthly median averages