

A Study to Link Atmospheric N Deposition with Surface and Ground Water N and Denitrification Capabilities in an Urban New Jersey Wetland

Report to the Water Resources Research Institute

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Numbers of Students Supported:

Zero. Work was primarily completed by a laboratory technician and the investigators. However, one work-study student assisted with the laboratory analyses and report preparation.

Notable Achievements:

This project is one component of the Teaneck Creek Restoration Project. Teaneck Creek Conservancy, a non-profit organization, with assistance from Rutgers University, USGS, and TRC Omni Environmental Corporation is working to restore and enhance 20 acres of urban wetlands within the Bergen County Parks system. The Teaneck Creek Restoration Project has won the following awards:

1. Environmental Excellence Award: States and Healthy Communities, Brownfield to Greenfield, NJ DEP, November, 2005
2. NY-NJ Baykeeper Award, September 2005

Project Summary

Objectives:

Atmospheric deposition is a major source of nitrogen in northeastern U.S. ecosystems. Local sources related to urbanization and regional transport from power plants are both likely to be substantial contributors to atmospheric nitrogen deposition in urban areas. However, atmospheric nitrogen deposition measurements have mostly been made in more remote locations. There have been few measurements of atmospheric nitrogen fluxes to urban ecosystems.

The Teaneck Creek Conservancy, a private non-profit organization, has been granted a long-term license to manage a 46 acre site within the Bergen County Parks system. Scientists at Rutgers University and elsewhere are participating in their effort to characterize, restore and enhance 20 acres of urban wetlands within the public park. A baseline monitoring study is underway to characterize the fluxes of nitrogen species through this system and determine the denitrification capabilities of the system prior to restoration. Inorganic and organic atmospheric wet and dry deposition inputs are being provided through this funding mechanism.

The specific objective of this project is to characterize the amounts and the chemical composition of total N-species, inorganic and organic, present in the atmospheric wet and dry N deposition within the Teaneck Creek site as annual fluxes. This was accomplished through monitoring over all four seasons.

Methodology:

Rainwater was collected using a wet-dry deposition collector (Aerochem Metrics Model 301, Bushnell, FL), fitted with a stainless steel bucket that opened only during storm events. A clean bucket was deployed before each sampling event. The collector was positioned on the roof of the Thomas Jefferson School, adjacent to the Teaneck Creek site. Water was retrieved from the collectors within ~12 hours to minimize microbial degradation of dissolved organic matter and consumption of inorganic nutrients. Sample temperature and pH were measured immediately after collection and samples were filtered through pre-combusted glass fiber filters (Whatman, GFF; baked for four hours at 500 °C; then rinsed with deionized water). Rainwater was frozen in polypropylene screw-capped tubes for storage until analysis. A total of 19 rain events were sampled from spring 2005 through spring 2006 (6 in spring, 6 in fall, 3 in summer, 4 in winter).

The water-soluble component of dry particle deposition was collected using the method of Lindberg and Lovett (1985). Briefly, dry deposition was collected on polycarbonate plates (Fisherbrand, #08-757-12, 100x15mm, sterile polystyrene) exposed to the atmosphere during rain-free periods. Plates were positioned horizontally, 1.6–1.8 m above the ground, on an arm extending laterally from a vertical pole. Measurements were made concurrently about 3 m, 25 m, 47 m, 69 m and 91 m from Degraw Avenue where the Avenue passes through the Teaneck Creek site (Figure 1). Measurements were also made in two locations on the roof of the Thomas Jefferson School, adjacent to the Teaneck Creek site. Duplicate samples were collected at 47 m. Plates were exposed from 1-5 days. Plates were extracted in the laboratory with 20 ml of DI water using an acid washed stir bar, by spinning on a stir plate for 30 min. Each extract was filtered through a 25 mm pre-combusted glass fiber filter (Whatman, GFF; baked for four hours

at 500 °C; then rinsed with deionized water). Extracts were frozen in polypropylene screw-capped tubes for storage until analysis. Early in the experiment plates were acid washed and reused, but we rapidly became aware that these reused plates yielded unacceptably high blank levels. Thus, all reported data were collected with new plates.

Samples were collected April 8-13, 2005, August 17-19 and 23-27, 2005, October 17-21 and 26-31, 2005, January 25-29, 2006, and February 6-10, 2006. During August and October, 2005 an experiment was conducted to examine the assumption that samples obtained really provide a measure of particle deposition fluxes and do not reflect gaseous dry deposition fluxes. Initially this method was used by the deposition community to provide estimates of total dry deposition. However, recently researchers have become increasingly convinced that this method provides, instead, an estimate of particle dry deposition. Gases are expected to deposit until adsorbed phase – gas phase equilibrium is achieved. After that point, no further net deposition is expected. Particles, on the other hand, will continue to deposit at a rate dependent on their size, concentration in the atmosphere, wind speed and surface roughness. Thus, if the fluxes measured were dominated by gaseous deposition, composites of short duration measurements would yield larger fluxes than longer duration measurements collected concurrently. If measured fluxes really provide a measure of particle deposition, as the deposition community is now concluding, calculated fluxes would be independent of sample duration.



Figure 1. Location of dry deposition sampling locations at Teaneck.

Dry Deposition Plate #	Site ID	Post Height
1	Degraw1	5'10"
2	Degraw2	5'3"
3	Degraw3	5'6"
4	Degraw4	5'6"
5	Degraw5	5'6"
6	Degraw6	5'9"

Bulk nutrients ($\text{NO}_3^- + \text{NO}_2^-$, NH_4^+ , PO_4^{3-}) in each rain sample and dry deposition extract were measured with an automated nutrient analyzer and standard colorimetric methods (Lachat, Inc; QuickChem methods, NH_4^+ : 31-107-06-1-A; $\text{NO}_3^- + \text{NO}_2^-$: 31-107-04-1-A; PO_4^{3-} : 31-107-04-1-A). Dissolved organic nitrogen (DON) was determined as the difference between total dissolved N measured with an Antek 7000 TN Analyzer (Seitzinger and Sanders, 1999) and the dissolved inorganic nitrogen ($\text{NO}_3^- + \text{NO}_2^-$, and NH_4^+). DOC was measured with a Shimadzu 5000A TOC analyzer (Sharp et al. 1993).

The depositional flux of nutrients in each rainwater event sampled was calculated by multiplying the nutrient concentration by the volume of rainwater and normalizing to a m^2 area ($\mu\text{moles}/\text{m}^2\text{-event}$), taking into account the surface area of the rainwater collector (0.0642 m^2). Dry particle deposition for each sample ($\mu\text{moles}/\text{m}^2\text{-day}$) was calculated by multiplying the measured concentration (μM) by the volume of DI water used for extraction (20 mL) and dividing by the area of the deposition plate ($5.67 \times 10^{-3} \text{ m}^2$) and the time (days) the plate was deployed.

Principal Findings and Significance:

Concentrations of nitrate plus nitrite (2-72 μM), ammonium (2-51 μM), DON (0-27 μM), DOC (16-311 μM) and phosphate (0.1-1.0 μM) in wet deposition showed considerable variation among rain events during the study period (Table A1; Figure 2). In general, higher concentrations were measured during relatively small rain events and lower concentrations during high volume rain events for all constituents (Figure 2). The range of nutrient concentrations in rainwater collected at Teaneck Creek was similar to the range in concentrations measured in rainwater collected at other locations in New Jersey, including New Brunswick, Camden and the Pinelands during the past 5 years (Seitzinger et al. 2005).

The total amount of rainwater sampled at Teaneck Creek during the study period (March 2005-February 2006) was 323 mm. Rainwater volume at a nearby location, Pascack, NJ, is measured by the USGS (unpublished data). The most recent data, however, for that site are only available through 2005. During 2005 a total of 1324 mm of rain fell at Pascack. Therefore, until more recent data is available, we assumed that the total rainfall during our annual study period was similar to that during the 2005 calendar year. Based on that assumption, we measured the nutrient concentrations in approximately 25% of the total annual rainfall. We estimated the total annual amount of inorganic and organic nitrogen deposited in wet deposition at Teaneck Creek by multiplying the total measured nutrient flux in all events sampled during the March 2005-February 2006 period (Table 1) by a factor of 4, to account for deposition during events that we did not sample. The annual wet deposition was estimated to be: $\text{NO}_3^- + \text{NO}_2^-$: 15,560 $\mu\text{mol}/\text{m}^2\text{-year}$ (2.18 kg N/ha-year); NH_4^+ 11,600 $\mu\text{mol}/\text{m}^2\text{-year}$ (1.62 kg N/ha-year); DON 6,850 $\mu\text{mol}/\text{m}^2\text{-year}$ (0.96 kg N/ha-year). These rates are slightly lower than reported by NADP for the Hudson/Raritan watershed (3.9 and 1.9 kg N/ha-year for $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ , respectively; Meyers et al. 2001). However, given the relatively small number of sampling dates in the current study relative to that from the multi-year NADP measurements, no firm conclusions should be drawn about differences at this time. Overall, the rates we measured at Teaneck are within the range of rates reported for inorganic N deposition to thirty watersheds along the East and Gulf coasts of the US from

Maine to Texas (1.2-4.4 and 1.1-2.8 kg N/ha-year for $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ , respectively; Meyers et al. 2001).

Annual dry deposition fluxes were estimated from Degraw Avenue sample fluxes by multiplying the average of seasonal measurements by the number of days in calendar year 2005 with no rain (242 days; USGS Pascack). The annual particle dry deposition of $\text{NO}_3^- + \text{NO}_2^-$ and NH_4^+ were more than one order of magnitude lower than the wet deposition. Particle dry deposition of dissolved organic nitrogen (DON) is only a factor of two smaller. DON fluxes were highly variable from sample to sample, and thus the uncertainties in the annual flux of DON are reasonably large.

Lovett et al. (2000) measured particulate NO_3^- deposition within and north of New York City in June – September, 1997 and found deposition fluxes of 16, 7, and 3 $\mu\text{mol NO}_3^-/\text{m}^2\text{-day}$ a distance 11, 45, and 128 km from Central Park. The particulate NO_3^- deposition fluxes from this study are within this range, and more similar to the suburban measurements of Lovett than the NYC measurements (1 - 11 $\mu\text{mol NO}_3^-/\text{m}^2\text{-day}$).

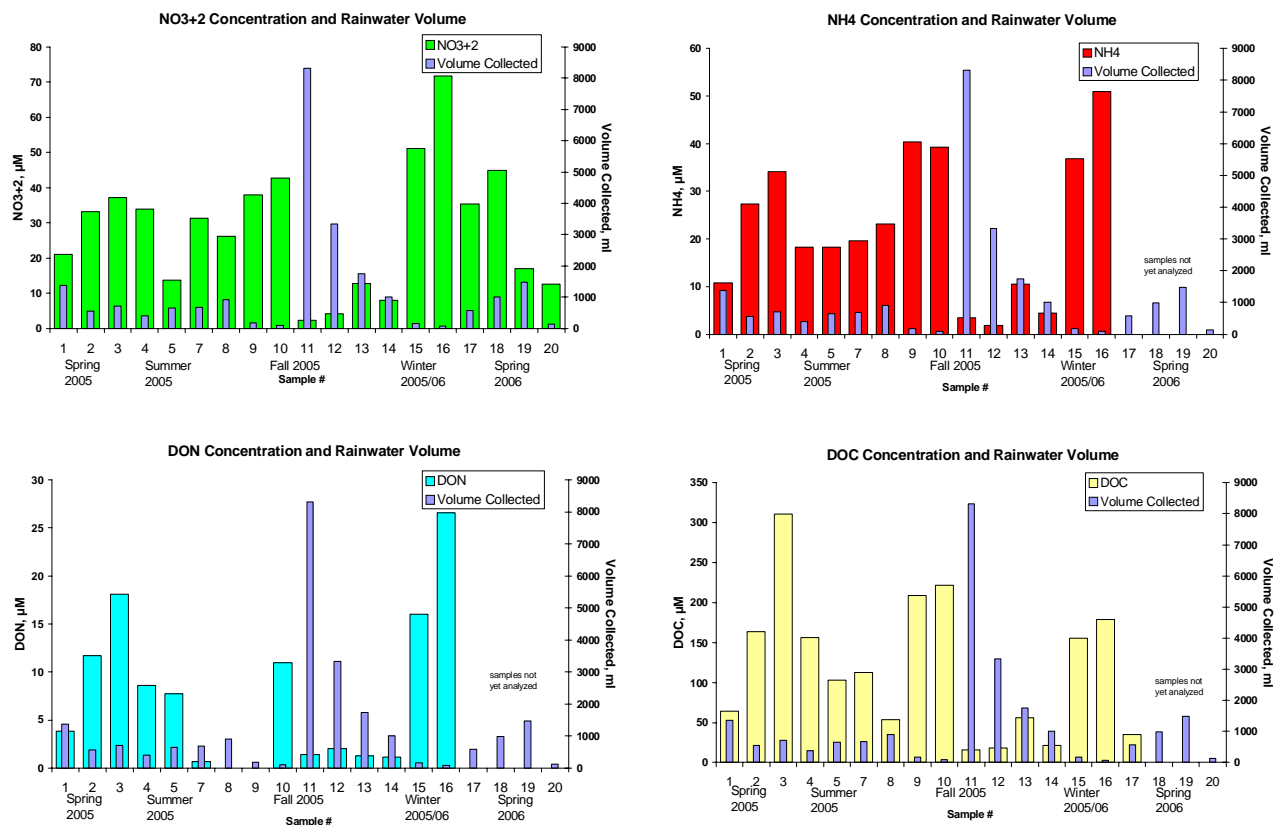


Figure 2. Nutrient concentrations and rainwater volume collected during rainwater events sampled during 2005-2006 at Teaneck Creek, NJ.

Table 1. Dry deposition fluxes calculated from deposition plate measurements.

Seasonal fluxes have units of ($\mu\text{mol}/\text{m}^2\text{-day}$) and annual average fluxes are in units of ($\mu\text{mol}/\text{m}^2\text{-year}$). Shown are mean \pm 1 standard deviation of seasonal measurements made at all 5 Degraw Ave locations (Figure 1). **indicates samples not yet analyzed; NO_3 represents $\text{NO}_3^- + \text{NO}_2^-$. DOC is dissolved organic carbon. TDN is total dissolved nitrogen. DON is dissolved organic nitrogen. $\text{DON} = \text{TDN} - \text{NO}_3 - \text{NH}_4$.

Flux ($\mu\text{mol}/\text{m}^2\text{-day}$)	NO_3	NH_4	PO_4	DOC	TDN	DON
Spring (Apr 8-13, 2005)	4.8 ± 0.7	2.8 ± 0.7	3.1 ± 1.5	378 ± 194	43 ± 20	36 ± 20
Summer (Aug 17-19; 23-27)	4.9 ± 3.5	2.1 ± 1.0	0.5 ± 0.2	139 ± 52	12.3 ± 4.8	4.8 ± 3.2
Fall (Oct 17-21; 26-30)	4.2 ± 3.6	2.0 ± 2.1	0.4 ± 0.2	55 ± 26	10.4 ± 6.7	5.1 ± 2.6
Winter (Jan 25-29; Feb 6-10)	4.9 ± 1.6	**	0.3 ± 0.6	**	**	**
Annual Avg Flux ($\mu\text{mol}/\text{m}^2\text{-year}$)	1,140	557	260	129,600	14,200	3,700
Annual Avg Flux (kg N, P or C/ha-year)	0.16	0.08	0.08	15.6	2.0	0.52

Detection limits for dry deposition samples, expressed as three times the standard deviation of the plate blank, were $\text{NO}_3^- + \text{NO}_2^-$: $1.8 \mu\text{M}$ ($1.3 \mu\text{mol}/\text{m}^2\text{-day}$); NH_4^+ $0.3 \mu\text{M}$ ($0.2 \mu\text{mol}/\text{m}^2\text{-day}$); PO_4 : $0.1 \mu\text{M}$ ($0.08 \mu\text{mol}/\text{m}^2\text{-day}$); and DOC $2.6 \mu\text{M}$ ($1.9 \mu\text{mol}/\text{m}^2\text{-day}$). (Detection limits in parentheses are fluxes and assume a 5-day sample). Detection limit calculations for TDN and DON are awaiting analysis of a final set of samples. A total of 80% of $\text{NO}_3^- + \text{NO}_2^-$, 100% of NH_4^+ , 56% of PO_4 and 100% of DOC samples were above detection limits. Samples were not blank corrected.

Dry deposition fluxes calculated from composites of short duration samples (1-2 days) were not significantly different from those calculated from concurrently-collected long duration samples (2-4 days) according to a paired t-test with 95% confidence values. (Calculations were performed for NO_3 and NH_4 only, with $N=6$ and $N=4$, respectively.) The fact that these differences are not significant agrees with the growing body of evidence from the broader dry deposition research community (G. Lovett, personal communication) that dry deposition plates predominantly collect particle dry deposition and do not reflect gaseous dry deposition.

Although the differences were not significant, it must be noted that composites of short duration samples yielded fluxes that were 20% and 16% higher (for NO_3 and NH_4 , respectively), on average, than long duration samples. A composite of two short duration particle deposition samples would have twice the gas adsorption artifact of a single concurrently-collected long duration sample. Thus, there is some evidence of a gas adsorption artifact, suggesting that particle dry deposition fluxes reported here are upper limit estimates.

Figure 3 shows NO_3 particulate dry deposition flux ($\mu\text{mol}/\text{m}^2\text{-day}$) with distance from Degraw Avenue. A decreased flux with distance is clearly evident within 100 m of the roadway. Inorganic NO_3 in ambient atmospheric particles is found primarily in the form of NH_4NO_3 in continental areas, and is predominantly formed in the atmosphere (secondary) from nitric acid and ammonia. Because nitric acid is also predominantly

formed in the atmosphere (i.e., from oxides of nitrogen), its concentrations are fairly homogeneous over large areas. A decreased flux with distance from the roadway suggests that, in close proximity to this busy roadway (within 50-100 m), roadway emissions are contributing to particle dry deposition. The enhancement is on the order of 20-50% greater than the values at 100 m. This could be a result of either primary nitric acid emissions and/or primary ammonia emissions converting ambient nitric acid (gaseous) to particulate ammonium nitrate.

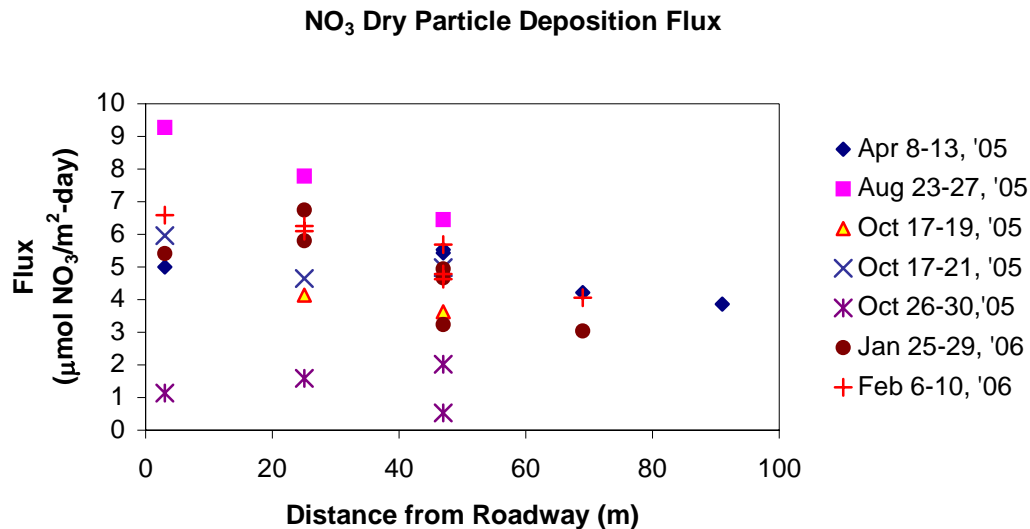


Figure 3. NO₃ Particle Dry Deposition Flux (μmol/m²-day) and distance from Degraw Avenue.

Ongoing Activity:

Analyses of wet and dry (particle) deposition are being completed for a few samples collected after the end date of the award. In addition, a sampler to measure dry gaseous deposition of N is being tested and samples will be collected at Teaneck for selected dates in the upcoming months.

References:

- Lindberg, S. and G. M. Lovett. 1985. Field measurements of dry deposition to foliage and inert surfaces in a forest canopy. *Environ. Sci. Technol.* 19:238-244.
- Lovett, G.M., M.M. Traynor, R.V. Pouyat, M.M. Carreiro, W.X. Zhu, and J.W. Baxter 2000. Atmospheric Deposition to Oak Forests Along an Urban-Rural Gradient. *Environ. Sci. Technol.* 34:4294-4300.

Meyers, T., J. Sickles, R.Dennis, K. Russell, J. Galloway, and T. Church 2001. Atmospheric nitrogen deposition to coastal estuaries and their watersheds. Chapter 3 pages 53-76 in *Nitrogen Loading in Coastal Water Bodies, An Atmospheric Perspective*. Coastal and Estuarine Studies No. 57; American Geophysical Union, Washington, DC.

Seitzinger, S.P., H. Hartnett, G. Spyres, R. Lauck 2005. Chemical Composition and Bioavailability of Dissolved Organic Nitrogen in Atmospheric Wet Deposition from Urban and Rural New Jersey Sites. Final Report, December 2005, NJDEP.

Seitzinger, S.P. and R.W. Sanders. 1999. Atmospheric inputs of dissolved organic nitrogen stimulate estuarine bacteria and phytoplankton. *Limnol. Oceanogr.* 44:721-730.

Sharp, J.H., R. Benner, L. Bennett, C.A. Carlson, R. Dow, and S.E. Fitzwater. 1993. Re-evaluation of high temperature combustion and chemical oxidation measurements of dissolved organic carbon in seawater. *Limnol.Oceanogr.* 38:1774-1782.

Publications or Presentations

1. Mak, Michael, 2006, "Development of an Urban Hydrological Model Linking Denitrification Potential to Urban Wetland Restoration," Poster presentation including wet deposition data, presented at the National Water Quality Conference, San Jose, CA, May 7-11, 2006.

2. www.rerc.rutgers.edu, 2006, Data from all aspects of the Teaneck Creek Restoration Project are posted at this web site for use by all Project Investigators.

3. Ravit, Beth, 2006, Presentations to 200 Middle School Students on Wetlands Ecology using Teaneck Creek research results to provide a site-specific example; 1200 Student-hours (200 students/day x 5 days), Curriculum Enrichment, Teaneck Middle School, Teaneck, NJ.

4. Ravit, Beth, Mary Arnold, 2006, "What in the World Science," Teacher handbook (5 modules) on Wetlands Ecology using Teaneck Creek as a Site-Specific Example, Designed for the Teaneck Middle School, Teaneck, NJ.

APPENDIX

Table A1. Nutrient concentrations and rainfall amount for wet deposition at Teaneck Creek, NJ. Blank cells indicate samples not yet analyzed.

Collection Date	Sample #	Volume collected (ml)	Deposition Amount (mm)	pH	NO ₃ (μM)	NH ₄ (μM)	DON (μM)	DOC (μM)	PO ₄ (μM)	NO _{3,2}	NH ₄	DON
μmol N/m ² /event												
4/8/2005	1	1365	21.3	4.1	21.0	10.8	3.8	64	0.9	446	230	59
4/28/2005	2	555	8.6	4.2	33.1	27.4	11.7	164	0.3	286	237	182
5/23/2005	3	710	11.1		37.2	34.1	18.1	311	0.8	411	377	282
6/7/2005	4	395	6.2	4.4	33.9	18.2	8.6	156	0.2	209	112	134
6/28/2005	5	645	10.0	4.2	13.8	18.3	7.7	103	0.2	138	184	120
7/5/2005	7	675	10.5	4.0	31.3	19.6	0.7	112	0.1	329	206	11
9/16/2005	8	910	14.2	4.7	26.2	23.1	0.0	54	0.1	371	327	0
9/27/2005	9	170	2.6	4.7	37.9	40.4	0.0	209	0.1	100	107	0
9/30/2005	10	99	1.5	4.1	42.7	39.3	11.0	222	0.3	66	61	171
10/10/2005	11	8320	129.6	3.9	2.4	3.5	1.4	16	0.1	311	454	22
10/26/2005	12	3330	51.9	5.0	4.1	1.8	2.0	18	0.1	213	93	31
11/18/2005	13	1745	27.2	n/a	12.8	10.5	1.3	56	0.1	348	285	20
12/12/2005	14	1000	15.6	5.0	7.9	4.4	1.1	22	0.1	123	69	17
1/31/2006	15	165	2.6	4.2	51.1	36.8	16.0	156	0.1	131	95	249
2/7/2006	16	82	1.3	4.0	71.8	51.0	26.6	179	0.5	91	65	414
2/14/2006	17	573	8.9	4.7	35.3			35	1.0	315		
4/6/2006	18	994	15.5	4.3	44.9				0.1	695		
4/10/2006	19	1476	23.0	4.7	17.1				0.2	392		
5/4/2006	20	127	2.0	4.7	12.5				0.2	25		