Stable Isotopes in CO2

Sable Island Preservation Trust
Atlantic Coastal Action Program
Sable Island, 2004

Introduction

CO_2 is an important greenhouse gas, and atmospheric CO_2 concentrations have increased from about 280 ppmv in pre-industrial times to around 365 ppmv presently. This increase is largely due to human activities.

Considerable effort has been expended in developing an understanding of carbon cycles, and as part of that, Sable Island has been collecting CO2 data since the early 1970's. Sable is one of three baseline stations involved in CO_2 measurements by the Meteorological Service of Canada.

This project collected air samples which were analyzed to measure isotopes of carbon and oxygen in the atmospheric CO2.

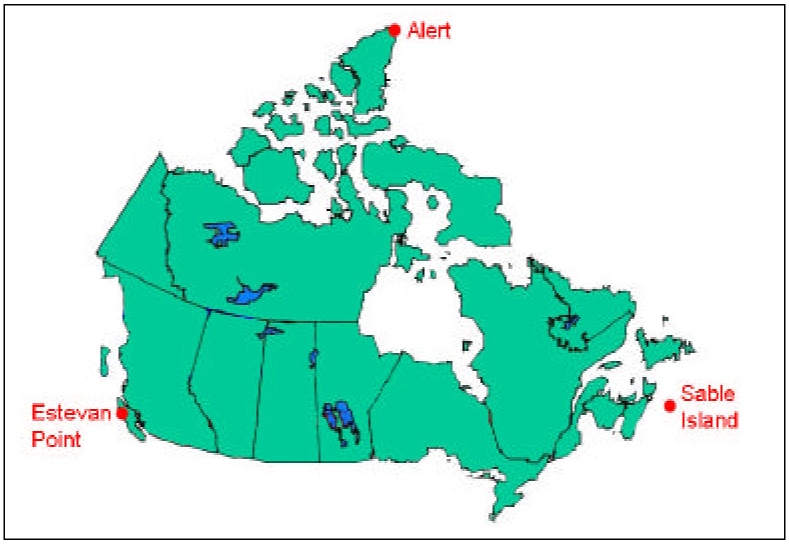

Figure 1: Baseline Stations in Canada

Project Background

Carbon and oxygen are exchanged between atmosphere, oceans, biosphere and even geologic processes, so atmospheric CO2 can provide a link between these components in an ecosystem.

The carbon and oxygen isotopic compositions of these ecosystem components enable determination of the contribution of different components to ecosystem exchange. Together with measurements of concentration or flux, insight can be gained into the sources and sinks of CO2 in the ecosystem.

Carbon:
The largest concern has been with carbon because of its anthropogenic contribution due to combustion of fossil fuels, deforestation, and agriculture.

About half of the carbon produced by burning fossil fuels is observed as an increase of the atmospheric CO2 concentration. The other half is sequestered by other compartments in the ecosystem, and both the oceans and the terrestrial system show a net uptake of carbon.

There are two stable isotopes of carbon, ^{12}C and ^{13}C. Photosynthesis preferentially uses the lighter isotope, so carbon from plants generally has less ^{13}C than was in the CO2 from which it was formed.

The difference is described by the ratio

$$d^{13}C = \frac{[13C/12C]_{sample} - [13C/12C]_{standard}}{[13C/12C]_{standard}} \times 1000$$

Because there's little carbon isotope discrimination associated with exchange of CO2 between the ocean and atmosphere, if the sink is in the land, changes in atmospheric CO2 concentrations will be accompanied by changes in $d^{13}C$, whereas if the sink is due to absorption of CO2 by the ocean, changes in CO2 concentrations will have little effect on $d^{13}C$.

There are two major pathways of photosynthesis called C3 and C4 depending upon the number of carbon atoms comprising the first identifiable product of photosynthesis. The C3 pathway (used by the majority of terrestrial plants) results in $d^{13}C$ of about –16 to –18 ‰ relative to atmospheric values, whereas the C4 pathway (used by less than a quarter of plants) results in $d^{13}C$ of about -4‰. Note that these values change significantly with geography and environment.

An the ecosystem level, discrimination by C3 plants is influenced by environmental factors such as availability of light, water, and nutrients, so this enables $d^{13}C$ changes in atmospheric CO2 to be interpreted in terms of environmental changes such as drought, global warming, etc.

The combustion of fossil fuels has changed the $d^{13}C$ of atmospheric CO2, since carbon isotope ratios of older respired CO2 are slightly different from those of modern photosynthesis. This effect makes it more complicated to assess the relative contributions of respiration and photosynthesis to changes in atmospheric CO2, but will be improved in the future through more detailed studies.

In contrast, exchanges with the ocean involve relatively small effects. More than 98% of the CO2 in the air–sea system is dissolved in the oceans, and diffusion of CO2 across the air–sea interface fractionates d^{13}C to about 10% of the amount by terrestrial photosynthesis. At typical long-term ocean production rates, global marine photosynthesis has minimal impact on d^{13}C.

Consequently, atmospheric d^{13}C records can be used to partition the uptake of fossil fuel carbon between oceanic and terrestrial reservoirs. They can also be used to study natural variability in the carbon cycle and in calibrating global carbon models.

Oxygen:
Unlike carbon, the oxygen ratio d^{18}O of atmospheric CO2 is primarily determined by isotope exchange in vegetation, soil water and surface sea water.

Water in plant chloroplasts is usually enriched in ^{18}O relative to soil water due to evaporation where water with the lighter isotope evaporates preferentially. This ^{18}O enrichment is sensitive to humidity and temperature so is highly variable.

Oxygen exchange with soil water occurs mainly through CO2 from soil respiration, which diffuses slowly into the atmosphere.

The oxygen isotopic composition of soil and leaf water can vary considerably (-25‰ to +25‰). Soil water tends to follow the isotope composition of precipitation which is progressively depleted in d^{18}O relative to sea water towards high latitudes and towards the interior of a continent. Oxygen exchange with sea water occurs through the transfer of CO2 molecules across the air–sea interface.

Thus, in combination with concentration measurements, d^{13}C and d^{18}O ratios can be used to distinguish fluxes of CO_2 from the atmosphere to the oceanic and terrestrial biosphere.

These concepts have been successfully applied to providing accurate information on the global atmospheric composition. However, the regional location of carbon flux and identification of processes that influence the global composition remains uncertain, due to limited knowledge of ^{13}C fractionation by land plants, the scarcity of data, the required precision of measurements, and calibration techniques. As well, there’s considerable systematic error when comparing data from different sampling networks. MSC has developed a precision method of calibration, sample treatment, and sampling procedures, and these techniques forms the basis of the measurements from this sampling project.

Flask Sampling Methods

Air samples were collected every Friday morning unless winds were blowing from the sector contaminated by station activities (030° to 100°True). If the winds were from the contaminated sector, sampling was delayed until the earliest opportunity.

The samples were collected by pump suction on a 1/4" Decoron aluminum tube running to the top of an 80-foot tower located southwest of the main station compound. The air was passed through a cryocooler at –50°C to remove moisture, and pumped into evacuated Stainless Steel sample flasks to a pressure of 15 psi.

Results and Summary

For this project, there were significant time constraints in getting the analysis done in time, so the analysis was extended back in time to include samples taken back in 2003.

A total of 98 samples were analyzed, considerably more than the initial target of 26 samples. Analysis results are tabulated in Appendix 1.

The flask analysis data is illustrated in Figure 2. It seems readily apparent that beyond the long-term cycle, there are short-term fluctuations that represent anthropogenic activities from the mainland, and some of the larger fluctuations may reflect local activity such as shipping upwind of the island.

Figure 3 and Figure 4 display the variation in $d^{13}C$ and $d^{18}O$ between the Sable Island samples, and the samples from Alert in Nunavut, and Estevan Point, B.C. It's clear from the variation that overall there's a much larger anthropogenic effect at Sable Island.

The time series is insufficient to make any sweeping conclusions, but the data itself provides a valuable addition to national and international databases.

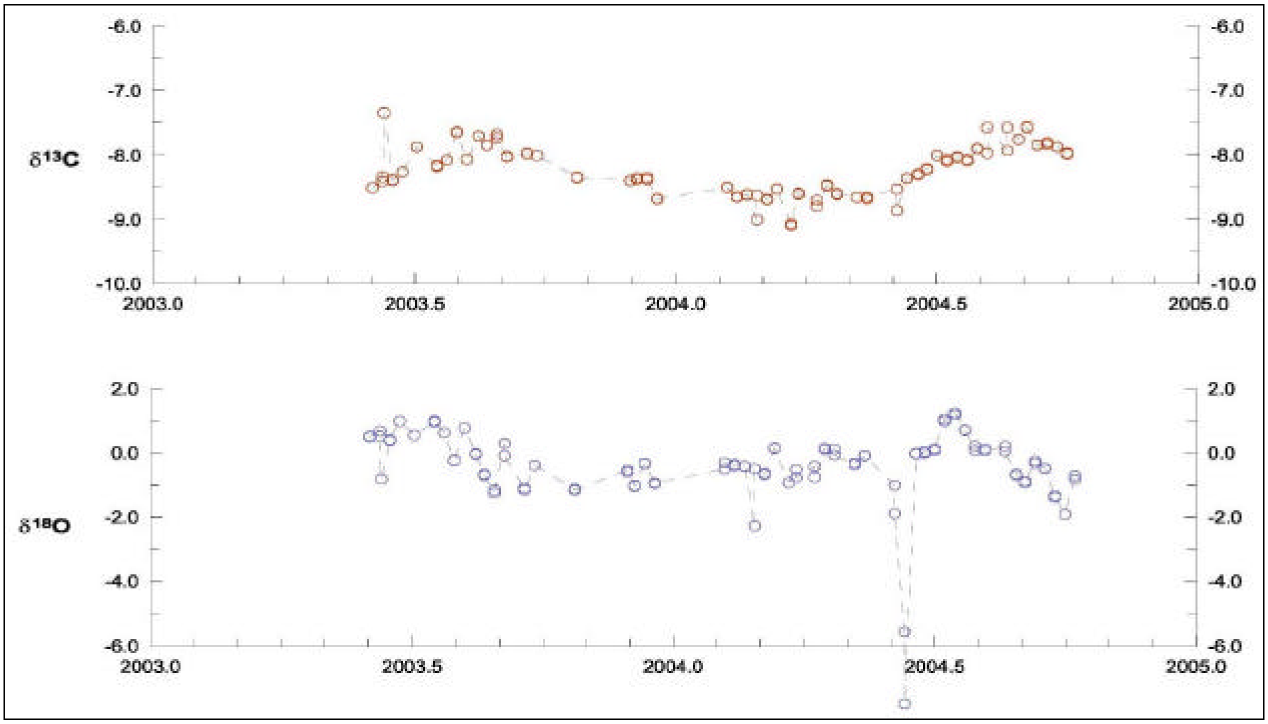

Figure 2: $d^{13}C$ and $d^{18}O$ Isotopic Composition for flask samples from Sable Island

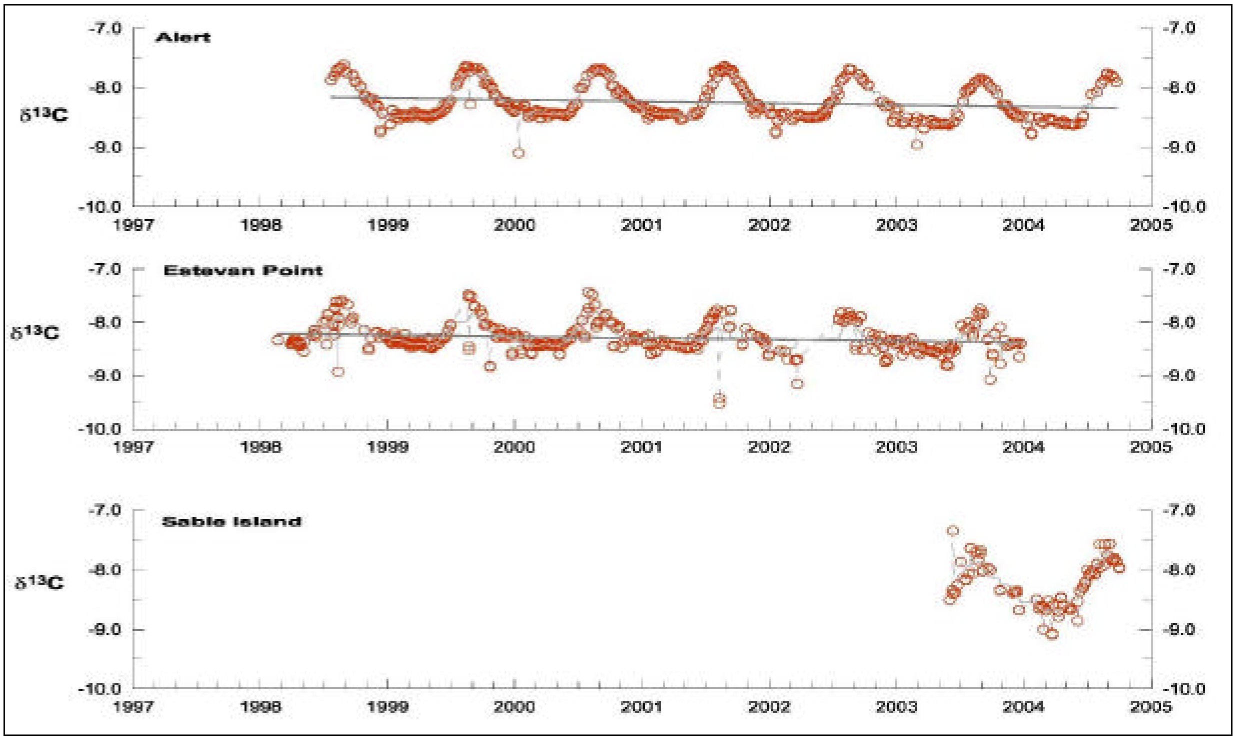

Figure 3: Comparison of d^{13}C samples from Alert, Nunavut, and Sable Island

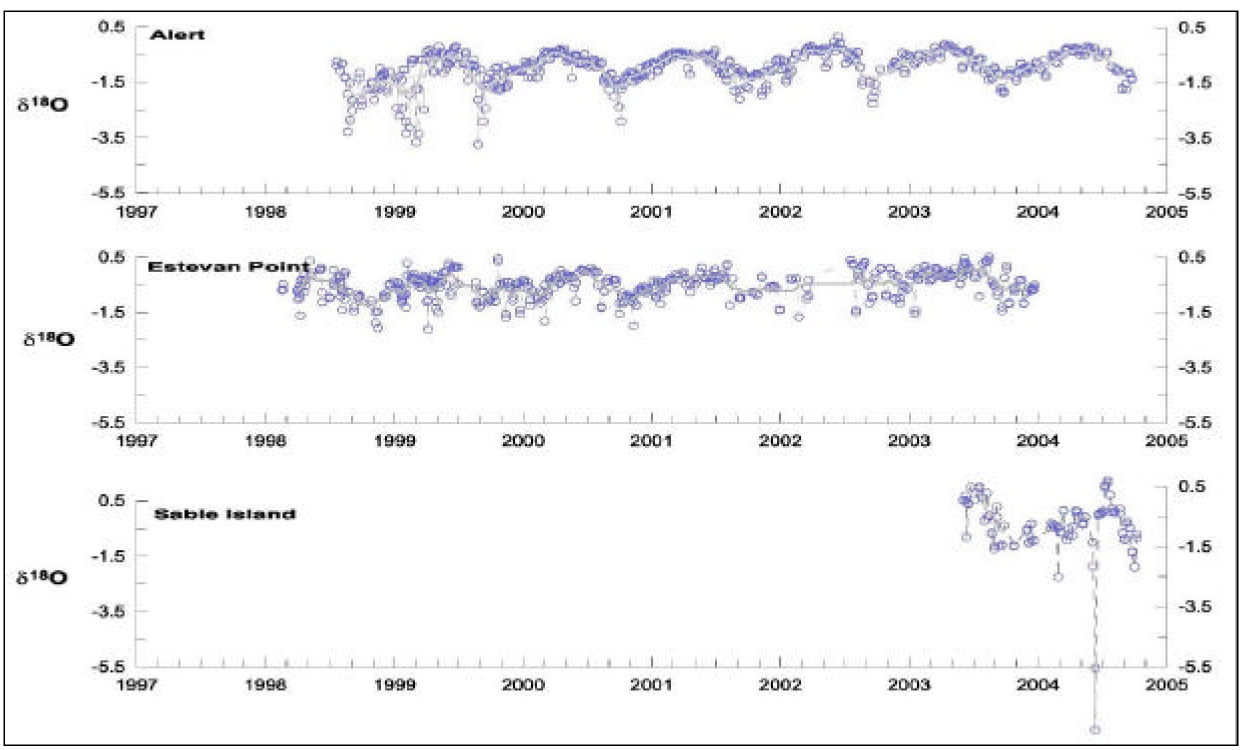

Figure 4: Comparison of d^{18}O samples from Alert, Estevan Point, and Sable Island

Acknowledgements:

This project would not have happened without the assistance of Lin Huang and Doug Worthy of the Meteorological Service of Canada, and particular thanks are due to the staff of the Sable Island station who spent considerable time ensuring the samples were done right.

Table 1: Sample Data

Flask_ID	Sample	d13C	d18O	d13C Pair diff	d18O Pair diff	CO2 (ppm)	N2O(ppb)
P2-142	03-Jun-03	-8.51	0.52	0.00	0.02	380.27	318.63
P2-144	03-Jun-03	-8.51	0.50			380.30	318.13
P2-141	10-Jun-03	-8.34	0.69	0.07	0.16	378.84	319.43
P2-143	10-Jun-03	-8.40	0.53			378.94	319.29
P2-124	11-Jun-03	-7.35	-0.81			385.40	316.64
P2-149	17-Jun-03	-8.38	0.38	0.01	-0.03	377.86	317.95
P2-150	17-Jun-03	-8.39	0.41			377.90	318.11
P2-151	24-Jun-03	-8.26	0.99			377.09	318.75
P2-121	04-Jul-03	-7.87	0.55			369.01	318.08
P2-153	18-Jul-03	-8.16	0.96	0.02	-0.05	376.04	317.86
P2-156	18-Jul-03	-8.17	1.01			376.12	318.12
P2-155	25-Jul-03	-8.07	0.63			374.46	318.20
P2-129	01-Aug-03	-7.64	-0.23	0.01	-0.01	364.70	317.93
P2-131	01-Aug-03	-7.65	-0.22			364.62	317.92
P2-132	08-Aug-03	-8.06	0.78			375.14	318.30
P2-112	16-Aug-03	-7.70	-0.04	0.00	-0.02	365.34	317.83
P2-110	16-Aug-03	-7.70	-0.02			364.84	317.56
P2-133	22-Aug-03	-7.84	-0.66	0.00	0.03	369.51	317.45
P2-135	22-Aug-03	-7.84	-0.70			369.61	317.86
P2-134	29-Aug-03	-7.67	-1.24	0.05	-0.09	365.18	317.53
P2-136	29-Aug-03	-7.73	-1.15			366.12	317.50
P2-119	05-Sep-03	-8.01	0.29	0.01	0.37	373.47	318.39
P2-120	05-Sep-03	-8.03	-0.08			373.46	318.60
P2-139	19-Sep-03	-7.97	-1.08	-0.01	0.06	371.04	317.97
P2-140	19-Sep-03	-7.96	-1.15			371.06	317.84
P2-137	26-Sep-03	-8.00	-0.39			371.55	318.55
P2-113	24-Oct-03	-8.34	-1.12	0.01	0.04	377.32	317.91
P2-114	24-Oct-03	-8.35	-1.15			377.39	318.19
P2-121	30-Nov-03	-8.39	-0.53	0.00	0.06	379.74	318.62
P2-122	30-Nov-03	-8.40	-0.59			379.86	318.38
P2-123	05-Dec-03	-8.37	-1.01	-0.01	0.03	379.07	318.53
P2-124	05-Dec-03	-8.36	-1.03			378.91	318.00
P2-154	12-Dec-03	-8.35	-0.34	0.03	-0.02	378.02	318.71
P2-156	12-Dec-03	-8.38	-0.32			378.04	318.66
P2-153	19-Dec-03	-8.67	-0.96	0.01	-0.03	384.43	318.70
P2-155	19-Dec-03	-8.68	-0.93			384.45	318.83
P2-134	06-Feb-04	-8.49	-0.51	0.01	-0.20	381.79	318.52
P2-135	06-Feb-04	-8.50	-0.30			382.04	318.70
P2-133	13-Feb-04	-8.65	-0.36	-0.01	0.04	384.33	319.22
P2-136	13-Feb-04	-8.64	-0.40			384.36	318.82
P2-146	20-Feb-04	-8.61	-0.41	0.01	0.00	382.75	318.28
P2-147	20-Feb-04	-8.61	-0.42			382.99	318.57
P2-145	27-Feb-04	-9.00	-2.26	-0.38	-1.77	385.35	318.06
P2-148	27-Feb-04	-8.62	-0.49			383.31	318.80
P2-110	05-Mar-04	-8.69	-0.67	-0.01	-0.04	385.17	318.73
P2-112	05-Mar-04	-8.68	-0.63			385.13	318.56
P2-109	12-Mar-04	-8.52	0.16	0.00	0.01	381.11	318.47
P2-111	12-Mar-04	-8.52	0.14			381.16	318.28
P2-117	22-Mar-04	-9.07	-0.92	0.03	0.00	391.94	319.60
P2-118	22-Mar-04	-9.09	-0.92			392.03	319.57
P2-119	27-Mar-04	-8.60	-0.51	-0.01	0.25	383.65	318.47
P2-120	27-Mar-04	-8.59	-0.76			383.74	318.32
P2-129	09-Apr-04	-8.70	-0.42	0.09	0.34	384.24	319.28
P2-130	09-Apr-04	-8.79	-0.76			385.08	319.25
P2-131	16-Apr-04	-8.47	0.15	-0.01	0.03	380.27	318.78
P2-132	16-Apr-04	-8.46	0.11			380.36	318.90
P2-125	23-Apr-04	-8.61	0.12	-0.01	0.19	382.31	318.83

Flask_ID	Sample	d13C	d18O	d13C Pair diff	d18O Pair diff	CO2 (ppm)	N2O (ppb)
P2-126	23-Apr-04	-8.60	-0.07			382.41	318.86
P2-114	07-May-04	-8.65	-0.36	0.00	-0.05	384.02	318.65
P2-113	07-May-04	-8.65	-0.32			384.00	318.41
P2-115	14-May-04	-8.67	-0.07	-0.02	0.01	384.32	318.64
P2-116	14-May-04	-8.65	-0.09			384.34	318.74
P2-155	04-Jun-04	-8.53	-1.00	0.33	0.88	382.86	319.04
P2-156	04-Jun-04	-8.86	-1.89			384.62	318.41
P2-137	11-Jun-04	-8.35	-5.54	0.01	2.24	378.00	318.61
P2-138	11-Jun-04	-8.36	-7.79			376.13	318.61
P2-139	19-Jun-04	-8.30	-0.02	-0.01	-0.02	378.60	318.15
P2-140	19-Jun-04	-8.29	-0.01			378.54	318.49
P2-149	25-Jun-04	-8.21	0.00	0.02	-0.04	376.06	318.78
P2-151	25-Jun-04	-8.22	0.04			376.20	318.64
P2-150	02-Jul-04	-8.00	0.07	0.00	-0.05	373.47	318.62
P2-152	02-Jul-04	-8.00	0.13			373.41	318.67
P2-141	09-Jul-04	-8.07	1.05	0.03	0.06	377.17	319.76
P2-144	09-Jul-04	-8.09	0.99			377.05	319.91
P2-142	16-Jul-04	-8.03	1.18	-0.01	-0.06	374.97	320.16
P2-143	16-Jul-04	-8.02	1.25			374.91	320.22
P2-135	23-Jul-04	-8.07	0.71	0.02	-0.01	376.62	319.29
P2-136	23-Jul-04	-8.08	0.72			376.64	319.34
P2-133	30-Jul-04	-7.90	0.08	-0.01	-0.13	373.29	319.39
P2-134	30-Jul-04	-7.89	0.21			373.09	319.62
P2-109	06-Aug-04	-7.96	0.13	-0.39	0.06	372.72	319.74
P2-111	06-Aug-04	-7.57	0.06			372.43	319.84
P2-110	20-Aug-04	-7.92	0.21	-0.35	0.16	365.44	319.02
P2-112	20-Aug-04	-7.57	0.05			365.46	318.91
P2-114	28-Aug-04	-7.75	-0.66	0.00	0.03	367.48	319.14
P2-115	28-Aug-04	-7.75	-0.69			367.48	319.12
P2-153	03-Sep-04	-7.56	-0.92	0.01	-0.05	364.11	318.44
P2-154	03-Sep-04	-7.57	-0.88			364.20	318.57
P2-155	10-Sep-04	-7.83	-0.25	0.01	0.07	369.60	318.90
P2-156	10-Sep-04	-7.84	-0.32			369.71	319.13
P2-117	17-Sep-04	-7.83	-0.47	-0.02	0.02	370.27	318.69
P2-118	17-Sep-04	-7.80	-0.49			370.31	318.83
P2-119	24-Sep-04	-7.86	-1.33	0.00	0.05	371.04	318.95
P2-120	24-Sep-04	-7.87	-1.38			371.05	318.87
P2-129	01-Oct-04	-7.97	-1.91	-0.01	0.00	373.37	319.18
P2-130	01-Oct-04	-7.96	-1.91			373.35	319.30
P2-131	08-Oct-04	-8.03	-0.71	0.04	0.12	374.02	319.51
P2-132	08-Oct-04	-8.07	-0.83			374.29	319.56