Hydrous Pyrolysis of Pole Treating Chemicals:

- A) Initial Measurement of Hydrous Pyrolysis Rates for
Naphthalene and Pentachlorophenol;
B) Solubility of Flourene at Temperatures Up To 150°C**

Prepared for the Southern California Edison Co.

Roald N. Leif
Roger D. Aines
Kevin G. Knauss

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Abstract

The temperature dependencies of the hydrous pyrolysis/oxidation (HPO) aqueous phase oxidation reactions of naphthalene and pentachlorophenol have been determined for phosphate buffered systems using Dickson-type reaction vessels. The HPO experimental temperatures ranged from 114°C to 148°C for naphthalene and 114°C to 137°C for pentachlorophenol. The loss of the organic species was used to determine activation energies of 95.8 kJ/mole for naphthalene oxidation and 84.8 kJ/mole for pentachlorophenol oxidation. Aqueous concentrations of target compounds and reaction intermediates were determined by gas chromatography and compound identification was verified by gas chromatography - mass spectrometry. During the experiments the pollutants were completely mineralized, as indicated by a stoichiometric production of inorganic carbon in the case of naphthalene and inorganic carbon and chloride in the case of pentachlorophenol. HPO of pentachlorophenol produced 2,3,5,6-tetrachlorophenol as an intermediate, whereas no intermediates amenable by GC were observed during the HPO of naphthalene.

Measurements of the aqueous solubility of fluorene in an unbuffered solution have been made covering the temperature range from 20°C to 150°C. There is very good agreement between this data set and data previously published covering the lower temperature range (20°C to 75°C). Extension of the solubility measurements to higher temperatures covers the in situ temperatures achievable during field application of HPO and demonstrated a nearly exponential rise in aqueous solubility as a function of temperature, with a 10 fold increase in aqueous fluorene solubility going from 75°C to 125°C and a 20 fold increase in going from 75°C to 150°C.

Introduction

Southern California Edison's Visalia Pole Yard site is currently contaminated with a DNAPL mixture composed of pole-treating creosote and an oil-based carrier fluid containing pentachlorophenol. Bioremediation of these organic pollutants is extremely slow and therefore thermal treatment of the site, such as used in the recent Dynamic Underground Stripping (DUS) demonstration (Newmark and Aines, 1995), is being used for removal of the free product. As part of the final removal process, Southern California Edison has also implemented HPO, an in situ method of destroying organic contaminants using stoichiometric amounts of supplemental oxygen in the form of injected air. Their primary need for HPO is for the destruction of residual DNAPL components not readily removed by the DUS process.

During Fiscal Year 1996, initial laboratory-based feasibility experiments were conducted to investigate the HPO of actual DNAPL material with excess dissolved O_2 under conditions similar to those achievable during thermal remediation. The experiments demonstrated that dissolved O_2 readily reacted with the compounds present in the DNAPL mixture, also known as BYS, to form partially oxidized products ranging from oxygenated intermediates, such as phenols and carboxylic acids (Fig. 1), to the fully oxidized product CO_2 (Fig. 2). Next, a series of experiments was initiated to study the rates of HPO for the two model compounds naphthalene and pentachlorophenol. Naphthalene is the most abundant component in the PAH class of compounds that makes up BYS and pentachlorophenol is a fungicide/pesticide that was used as a wood treatment preservative and also present in the BYS. The initial emphasis was on determining the rate dependency on dissolved O_2 at temperatures (100° and $125^\circ C$) easily achieved in thermal remediation. We found that at dissolved O_2 concentrations as high or higher than the stoichiometric amount required to oxidize the dissolved naphthalene or pentachlorophenol, the rates were independent of O_2 concentration.

In addition to the HPO study, experiments were begun to measure the aqueous solubility of naphthalene as a function of temperature. Results from the naphthalene solubility experiments are shown in Fig. 3. Sampling difficulties occurred above $50^\circ C$. The large scatter in the data above $50^\circ C$ was most likely caused by an unheated transfer tube from the vessel to the sampling valve causing the naphthalene to come out of solution during sampling. Another potential problem for naphthalene high temperature aqueous solubility runs was neutrally buoyant aqueous and organic phases. At temperatures greater than $80^\circ C$, the density of naphthalene and the density of water approach each other, and at $100^\circ C$ the densities are equivalent at 0.96 g/cm^3 . Because naphthalene becomes neutrally buoyant near $100^\circ C$, it is not possible to obtain meaningful samples for aqueous solubility measurements in this temperature range using the present experimental design.

As a result of the above difficulties, high temperature aqueous solubility measurements for naphthalene were suspended and another set of high temperature aqueous solubility measurements was begun for fluorene. The difficulty of a neutrally buoyant analyte is avoided with fluorene and all subsequent solubility experiments were run with a heated transfer line. The aqueous solubility of fluorene was measured to $100^\circ C$, extending the solubility measurements beyond the maximum temperature of $75^\circ C$ reported by Wauchope and Getzen (1972).

During Fiscal Year 1997 we extended the investigation into the study of the kinetics of HPO destruction for the two model compounds naphthalene and pentachlorophenol. We also extended the measurement of high temperature aqueous fluorene solubility to $150^\circ C$. This report describes the procedures and results from FY97.

Methods

Preparation of stock solutions

The naphthalene and pentachlorophenol HPO experiments were run in aqueous solutions buffered at a pH of 7 using an inorganic phosphate buffer. All stock solutions were made using deionized water and aerated for 15 minutes by bubbling with air to ensure the stock solutions start with initial dissolved oxygen concentrations of approximately 8 ppm. To ensure that the naphthalene and pentachlorophenol HPO experiments had stoichiometric excesses of oxygen, solid naphthalene was added in amounts not exceeding aqueous concentrations of 2.7 ppm, and pentachlorophenol was added in amounts not exceeding aqueous concentrations of 14.8 ppm. The stock solutions were loaded in the reaction vessels after the organic compounds became fully dissolved in the water.

The fluorene solubility experiments were run in deionized water and required no solution preparation. Typically, 2.5 g of solid fluorene was added to a vessel containing about 230g of deionized water.

Vessel sampling protocol

The static autoclave experiments are run in Dickson-type, gold-bag rocking autoclaves. The reaction vessels use a flexible gold bag sealed with a high purity titanium head and are contained within a large super-alloy steel pressure vessel. The vessel is loaded into a furnace capable of being continuously rocked through a 180° arc. Their design allows periodic sampling of the reaction cell under in situ conditions throughout the course of an experiment without disturbing the temperature and pressure of the run. Experimental pressure is held at a constant pressure by adding or removing distilled water from around the sealed gold bag using a precise constant pressure HPLC syringe pump at a total pressure of 500 psi, sufficient to keep the system single phase. Therefore no headspace gas is present and all gases remain dissolved in the liquid phase. This makes sampling, and subsequent mass balance calculations, significantly easier. During the experiment the solution contacts only Au and passivated Ti so that unwanted surface catalytic effects are eliminated. The sampled fluids and dissolved gases were analyzed using a variety of analytical techniques described below.

Analytical

Gas Chromatography. Laboratory analyses of the aqueous organic compounds were conducted on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector. Samples were introduced by direct injection mode on a 30 m (0.53 mm i.d.) fused silica capillary column coated with methylpolysiloxane (DB-5, J & W Scientific; film thickness 0.5 µm).

The GC oven temperature was programmed at isothermal for 2 min. at 60°C, 12°C/min. to 270°C, and isothermal for 2 min. with helium as the carrier gas. Data were acquired and integrated using the Hewlett Packard Chemstation software. Quantitation was done using a multilevel external standard calibration curve.

Gas chromatography-mass spectrometry. Gas chromatography-mass spectrometry (GC-MS) was performed on a Hewlett Packard 6890 gas chromatograph equipped with a 30 m x 0.25 mm i.d. HP-5ms (5% phenylmethylsiloxane) capillary column (0.25 μ m film thickness) coupled to a Hewlett Packard 6890 Series Mass Selective Detector (MSD) operated at 70 eV over the mass range 35-450 dalton and a cycle time of 1.1 s. The GC oven temperature was programmed at isothermal for 2 min. at 50°C, 8°C/min. to 300°C, and isothermal for 6.75 min., with the injector at 250°C, and helium as the carrier gas. The MS data were processed with an on-line Hewlett Packard personal computer. Quantitation was done using relative response factors of internal standards.

Ion Chromatography. Chloride was determined using a Hewlett Packard 1090M HPLC coupled to a Waters 431 conductivity detector. Data were processed using an on-line Hewlett Packard personal computer using Chemstation software.

Total Inorganic Carbon. Samples submitted total inorganic analysis were analyzed using an OI Model 524 analyzer. A weighed sample was injected in a purge vessel containing a 25% phosphoric acid solution which is continuously purged with nitrogen gas. The dissolved inorganic carbon is converted to CO₂ and swept into a non-dispersive infrared detector where the total inorganic carbon, in the form of carbon dioxide, is measured.

Dissolved Oxygen. Dissolved oxygen in the naphthalene and pentachlorophenol HPO experiments was measured using Microelectrodes Inc. Model OM-4 oxygen membrane sensor. The sampled were allowed to come to room temperature in a gas-tight syringe before measuring dissolved oxygen to avoid drift due to temperature differences.

Results and Discussion

Oxidation of Naphthalene

The experiments used to generate the Arrhenius plot for naphthalene oxidation are listed in Table 1. This set of experiments consists of five experiments at four different temperatures spanning a temperature range from 114°C to 148°C. Replicate experiments were performed at 114°C. Table 1 reports all the data as a function of time for the five experiments. The data in Table 1 is presented in graphical form for each of the five experiments in Fig. 4 to Fig. 8. Fig. 9 is a plot of naphthalene concentration as a function of time for the five experiments. The slope of the plot

of [naphthalene] vs. time at $t=0$ is by definition the initial rate of the reaction. Because the data points for each individual experiment were fairly linear, the initial rates were determined using data points of naphthalene concentrations as low as 5×10^{-6} mol/kg. Fig. 10 is the Arrhenius plot generated from the rates calculated from the plots in Fig. 9. The activation energy under these conditions was determined to be 95.8 kJ/mol.

Oxidation of Pentachlorophenol

The experiments used to generate the Arrhenius plot for pentachlorophenol oxidation are listed in Table 2. This set of experiments consists of three experiments at three different temperatures spanning a temperature range from 114°C to 137°C. Table 2 reports all the data as a function of time for the three experiments. The data in Table 2 is presented in graphical form for each of the three experiments in Fig. 11 to Fig. 13. Fig. 14 is a plot of pentachlorophenol concentration as a function of time for the three experiments. The slope of the plot of aqueous pentachlorophenol concentration vs. time at $t=0$ (initial rate of the reaction) was determined using the method of Chandler et al. (1987) by fitting the concentration-time data to a polynomial expression and calculating the slope of the tangent at $t=0$. Fig. 15 is the Arrhenius plot generated from the rates calculated from the plots in Fig. 14. The activation energy under these conditions was determined to be 84.8 kJ/mol. The data set for the HPO of pentachlorophenol is presently being supplemented and refined by additional experiments.

High Temperature Aqueous Solubility of Fluorene

The experimental results used to generate the fluorene aqueous solubility plot are listed in Table 3. The data listed in Table 3 is plotted in Fig. 16 and the symbols indicate from which direction the equilibrium concentration was approached, either from under-saturation or over-saturation. There was good agreement between the two data sets at each temperature and therefore indicates that the reported values represent the equilibrium solubility of fluorene at the selected temperatures. Fig. 17 is a plot of aqueous fluorene solubility vs. temperature at the lower temperature range for literature data and measurements from this study.

Summary

Data have been reported for the HPO destruction rates for naphthalene and pentachlorophenol, components that are representative of two compound classes present in the soils and groundwater of the Southern California Edison pleyard complex in Visalia, Ca. High temperature aqueous solubility values for fluorene have also been measured up to 150°C. The

reported data contribute to a better fundamental understanding of the aqueous geochemistry of these organic compounds and are valuable for assessing the behavior of these compounds when subjected to field HPO conditions.

References

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List of Tables

Table 1. Data from the hydrous pyrolysis / oxidation (HPO) experiments of naphthalene.

Table 2. Data from the hydrous pyrolysis / oxidation (HPO) experiments of pentachlorophenol.

Table 3. Data from the aqueous solubility measurements of fluorene.

List of Figures

- Figure 1. Organic compounds in pole tar experiments, measured by EPA method 8270A.
- Figure 2. Oxygen consumption and carbon dioxide production during pole tar experiment BYS02.
- Figure 3. Aqueous solubility measurements of naphthalene vs. temperature from experiments NPS01 and NPS02.
- Figure 4. Naphthalene destruction and carbon dioxide production during HPO experiment NAP10 (114°C).
- Figure 5. Naphthalene destruction and carbon dioxide production during HPO experiment NAP14 (114°C).
- Figure 6. Naphthalene destruction and carbon dioxide production during HPO experiment NAP08 (128°C).
- Figure 7. Naphthalene destruction and carbon dioxide production during HPO experiment NAP07 (137°C).
- Figure 8. Naphthalene destruction and carbon dioxide production during HPO experiment NAP09 (148°C).
- Figure 9. Summary plot of naphthalene destruction during HPO experiments (114°C to 148°C).
- Figure 10. Arrhenius plot of naphthalene destruction during HPO experiments (114°C to 148°C).
- Figure 11. Concentrations of pentachlorophenol, 2,3,5,6-tetrachlorophenol, carbon dioxide and chloride ion during HPO experiment PCP08 (114°C).
- Figure 12. Concentrations of pentachlorophenol, 2,3,5,6-tetrachlorophenol, carbon dioxide and chloride ion during HPO experiment PCP07 (124°C).
- Figure 13. Concentrations of pentachlorophenol, 2,3,5,6-tetrachlorophenol, carbon dioxide and chloride ion during HPO experiment PCP09 (137°C).
- Figure 14. Summary plot of pentachlorophenol destruction during HPO experiments (114°C to 137°C).
- Figure 15. Arrhenius plot of pentachlorophenol destruction during HPO experiments (114°C to 137°C).
- Figure 16. Aqueous solubility measurements of fluorene vs. temperature from experiments FLU02, FLU03, FLU04 and FLU06.
- Figure 17. Aqueous solubility measurements of fluorene vs. temperature (20°C to 75°C).

Oxidative Destruction of Aqueous Creosote Components

Figure 1. Organic compounds in pole tar experiments, measured by EPA method 8270A.

Figure 2. Oxygen consumption and carbon dioxide production during pole tar experiment BYS02.

Figure 3. Aqueous solubility measurements of naphthalene vs. temperature from experiments NPS01 and NPS02.

Figure 4. Naphthalene destruction and carbon dioxide production during HPO experiment NAP10 (114°C).

Figure 5. Naphthalene destruction and carbon dioxide production during HPO experiment NAP14 (114°C).

Figure 6. Naphthalene destruction and carbon dioxide production during HPO experiment NAP08 (128°C).

Figure 7. Naphthalene destruction and carbon dioxide production during HPO experiment NAP07 (137°C).

Figure 8. Naphthalene destruction and carbon dioxide production during HPO experiment NAP09 (148°C).

Figure 9. Summary plot of naphthalene destruction during HPO experiments (114°C to 148°C).

Figure 10. Arrhenius plot of naphthalene destruction during HPO experiments (114°C to 148°C).

Figure 11. Concentrations of pentachlorophenol, 2,3,5,6-tetrachlorophenol, carbon dioxide and chloride ion during HPO experiment PCP08 (114°C).

Figure 12. Concentrations of pentachlorophenol, 2,3,5,6-tetrachlorophenol, carbon dioxide and chloride ion during HPO experiment PCP07 (124°C).

Figure 13. Concentrations of pentachlorophenol, 2,3,5,6-tetrachlorophenol, carbon dioxide and chloride ion during HPO experiment PCP09 (137°C).

HPO - Pentachlorophenol

Figure 14. Summary plot of pentachlorophenol destruction during HPO experiments (114°C to 137°C).

Figure 15. Arrhenius plot of pentachlorophenol destruction during HPO experiments (114°C to 137°C).

Figure 16. Aqueous solubility measurements of fluorene vs. temperature from experiments FLU02, FLU03, FLU04 and FLU06.

Figure 17. Aqueous solubility measurements of fluorene vs. temperature (20°C to 75°C).

Table 1. Data from the hydrous pyrolysis / oxidation (HPO) experiments of naphthalene.

Experiment Sample ID	Time (days)	Time' (days)	Temperature (°C)	[Naphthalene] ($\mu\text{mol/g}$)	[Carbon Dioxide] ($\mu\text{mol/g}$)
NAP10-0	-0.25		24	1.92E-02	6.25E-02
NAP10-1	0.95	0.00	113	1.80E-02	5.90E-02
NAP10-4	3.62	2.67	114	1.57E-02	7.70E-02
NAP10-6	5.60	4.66	114	1.39E-02	8.11E-02
NAP10-8	7.60	6.66	114	1.14E-02	1.03E-01
NAP10-11	10.61	9.66	114	7.82E-03	1.24E-01
NAP10-13	12.63	11.68	114	5.86E-03	1.23E-01
NAP10-15	14.61	13.67	114	n.d.	1.28E-01
NAP10-25	24.25	23.30	114	n.d.	2.35E-01
NAP14-0	-0.01		22	1.78E-02	1.14E-01
NAP14-0.2	0.13	0.00	109	1.68E-02	1.10E-01
NAP14-1	1.01	0.88	114	1.62E-02	1.14E-01
NAP14-2	2.07	1.94	114	1.54E-02	1.32E-01
NAP14-3	2.93	2.81	114	1.41E-02	1.61E-01
NAP14-4	3.95	3.83	114	1.27E-02	1.73E-01
NAP14-7	6.94	6.81	115	8.84E-03	2.08E-01
NAP14-8	7.93	7.81	114	7.29E-03	2.34E-01
NAP14-9	8.92	8.79	114	6.25E-03	2.47E-01
NAP14-10	10.03	9.90	114	n.d.	2.63E-01
NAP14-11	10.92	10.80	114	n.d.	2.72E-01
NAP14-14	13.94	13.81	114	n.d.	3.07E-01
NAP14-15	14.95	14.82	114	n.d.	3.60E-01
NAP14-18	17.94	17.82	114	n.d.	3.66E-01
NAP8-0	-2.71		25	1.86E-02	n.a.
NAP8-1	0.36	0.00	123	1.81E-02	n.a.
NAP8-2	0.97	0.60	128	1.63E-02	9.72E-02
NAP8-3	1.95	1.59	128	1.30E-02	1.17E-01
NAP8-4	2.96	2.59	128	9.70E-03	1.34E-01
NAP8-5	3.95	3.59	128	6.11E-03	1.51E-01
NAP8-8	6.98	6.61	128	n.d.	2.31E-01
NAP8-9	7.97	7.61	128	n.d.	2.61E-01
NAP8-10	8.96	8.60	128	n.d.	2.93E-01
NAP8-11	9.95	9.59	128	n.d.	3.10E-01
NAP7-0	-0.03		25	2.20E-02	n.d.
NAP7-1	0.29	0.00	135	2.08E-02	n.d.
NAP7-2	0.98	0.69	137	1.49E-02	n.d.
NAP7-3	2.08	1.79	137	6.61E-03	1.35E-01
NAP7-4	2.98	2.69	137	n.d.	1.80E-01
NAP7-7	5.95	5.66	137	n.d.	3.20E-01
NAP7-8	6.95	6.66	137	n.d.	3.23E-01
NAP7-9	7.94	7.65	137	n.d.	3.17E-01
NAP9-0	-2.69		24	1.84E-02	n.a.
NAP9-1	0.38	0.00	144	1.66E-02	n.a.
NAP9-2	0.99	0.61	148	9.44E-03	1.02E-01
NAP9-2.3	1.36	0.98	148	5.48E-03	1.38E-01
NAP9-3	1.97	1.59	148	n.d.	2.03E-01
NAP9-3.3	2.33	1.95	148	n.d.	2.41E-01
NAP9-4	2.97	2.59	148	n.d.	2.82E-01
NAP9-4.3	3.30	2.92	148	n.d.	3.00E-01
NAP9-5	3.97	3.59	148	n.d.	3.37E-01
NAP9-5.3	4.31	3.93	148	n.d.	3.09E-01
NAP9-8	6.99	6.60	148	n.d.	3.32E-01

n.d. = not detected

n.a. = not analyzed

Table 2. Data from the hydrous pyrolysis / oxidation (HPO) experiments of pentachlorophenol.

Experiment Sample ID	Time (days)	Time' (days)	Temperature (°C)	[Pentachlorophenol] (umol/g)	[Tetrachlorophenol] (umol/g)	[Carbon Dioxide] (umol/g)	[Chloride] (umol/g)
PCP8-0	-0.02		21	0.0462	n.d.	n.d.	n.d.
PCP8-0.2	0.21	0.00	112	0.0448	n.d.	n.d.	n.d.
PCP8-1	0.97	0.76	114	0.0340	0.0225	0.0540	0.0309
PCP8-2	2.11	1.90	114	0.0210	0.0403	0.0785	0.0940
PCP8-3	3.22	3.01	114	0.0149	0.0493	0.0926	0.0950
PCP8-4	3.97	3.76	114	0.0104	0.0375	0.1016	-
PCP8-4.1	4.11	3.90	114	n.a.	n.a.	n.a.	0.1145
PCP8-7	6.96	6.74	114	0.0079	0.0320	0.1353	0.1457
PCP8-8	8.00	7.78	114	n.d.	0.0319	0.1417	0.1598
PCP8-9	8.97	8.75	114	n.d.	0.0289	0.1637	0.1681
PCP8-10	10.13	9.92	114	n.d.	0.0248	0.1776	0.1811
PCP8-11	10.95	10.74	114	n.d.	0.0233	0.1859	0.1822
PCP8-14	13.96	13.75	114	n.d.	0.0136	0.2317	0.2244
PCP8-15	14.96	14.75	114	n.d.	0.0117	0.2382	0.2293
PCP8-16	15.95	15.74	114	n.d.	0.0065	0.2728	0.2280
PCP7-0	-2.93		23	0.0408	n.d.	n.d.	n.d.
PCP7-1	0.29	0.00	122	0.0366	0.0084	n.d.	0.0064
PCP7-1.7	1.04	0.75	123	0.0211	0.0360	0.0522	0.0609
PCP7-2	2.01	1.72	124	0.0127	0.0462	0.0925	0.1089
PCP7-3	3.06	2.77	124	0.0090	0.0403	0.1158	0.1390
PCP7-4	4.04	3.75	124	n.d.	0.0335	0.1388	0.1567
PCP7-7	7.01	6.72	124	n.d.	0.0191	0.2288	0.2049
PCP7-8	7.99	7.70	124	n.d.	0.0144	0.2479	0.2322
PCP7-9	8.99	8.69	124	n.d.	0.0058	0.2802	0.2404
PCP7-14	14.01	13.72	124	n.d.	n.d.	0.3646	0.2843
PCP9-0	-3.00		22	0.0517	n.d.	0.0530	0.0054
PCP9-0.4	0.37	0.00	132	0.0376	0.0189	0.0734	0.0280
PCP9-1	1.01	0.64	137	0.0097	0.0376	0.1292	0.1085
PCP9-1.4	1.32	0.95	137	0.0063	0.0364	0.1547	0.1358
PCP9-2	2.03	1.66	137	0.0080	0.0235	0.2170	0.1876
PCP9-2.4	2.32	1.95	137	n.d.	0.0193	0.2482	0.2024
PCP9-3	3.19	2.82	137	n.d.	0.0078	0.3124	0.2499
PCP9-4	4.01	3.64	137	n.d.	0.0026	0.3780	0.2651
PCP9-7	7.02	6.65	137	n.d.	n.d.	0.3838	0.2857
PCP9-8	8.02	7.65	137	n.d.	n.d.	0.3729	0.2854

n.d. = not detected

n.a. = not analyzed

Table 3. Data from the aqueous solubility measurements of fluorene.

Experiment FLU2			Experiment FLU3			Experiment FLU4			Experiment FLU6		
Sample ID	T (°C)	[Fluorene] (mg/kg)	Sample ID	T (°C)	[Fluorene] (mg/kg)	Sample ID	T (°C)	[Fluorene] (mg/kg)	Sample ID	T (°C)	[Fluorene] (mg/kg)
FLU2-11a	25	1.3	FLU3-21a	100	67.5	FLU4-10a	21	1.2	FLU6-20a	151	463.2
FLU2-11b	25	1.5	FLU3-21b	100	70.9	FLU4-10b	21	1.2	FLU6-20b	151	459.5
FLU2-14a	25	1.3	FLU3-22a	101	70.5	FLU4-11a	21	1.2	FLU6-21a	151	616.1
FLU2-14b	25	1.5	FLU3-22b	101	73.5	FLU4-11b	21	1.1	FLU6-21b	151	452.5
FLU2-17a	25	1.3	FLU3-23a	101	70.9	FLU4-12a	21	1.1	FLU6-22a	151	451.5
FLU2-17b	25	1.5	FLU3-23b	101	74.1	FLU4-12b	21	1.5	FLU6-22b	151	463.6
FLU2-22a	52	6.3	FLU3-28a	75	21.6	FLU4-31a	100	70.2	FLU6-23a	151	444.9
FLU2-22b	52	6.2	FLU3-28b	75	21.7	FLU4-31b	100	73.7	FLU6-23b	151	450.8
FLU2-23a	52	6.1	FLU3-29a	75	21.4	FLU4-32a	100	73.0	FLU6-28a	126	226.2
FLU2-23Bb	52	6.5	FLU3-29b	75	21.8	FLU4-32b	100	73.2	FLU6-28b	126	236.4
FLU2-24a	52	6.2	FLU3-30a	75	22.8	FLU4-33a	100	68.0	FLU6-29a	126	220.4
FLU2-24b	52	6.3	FLU3-30b	75	22.0	FLU4-33b	100	74.4	FLU6-29b	126	212.6
FLU2-28a	77	22.9	FLU3-35a	52	7.3	FLU4-66a	126	217.3	FLU6-30a	126	211.7
FLU2-28b	77	21.4	FLU3-35b	52	7.2	FLU4-66b	126	213.2	FLU6-30b	126	223.4
FLU2-29a	77	22.6	FLU3-36a	51	6.2	FLU4-67a	126	209.0	FLU6-34a	126	201.0
FLU2-29b	77	22.1	FLU3-36b	51	6.3	FLU4-67b	126	218.6	FLU6-34b	126	233.0
FLU2-30a	77	21.0	FLU3-37a	51	5.6	FLU4-70a	126	231.7	FLU6-40a	126	215.6
FLU2-30b	77	20.3	FLU3-37b	51	6.3	FLU4-70b	126	213.3	FLU6-40b	126	208.1
FLU2-35a	101	63.6	FLU3-38a	51	5.7	FLU4-80a	151	466.4	FLU6-49a	100	60.4
FLU2-35b	101	62.1	FLU3-38b	51	5.8	FLU4-80b	151	459.0	FLU6-49b	100	64.6
FLU2-36a	101	64.2	FLU3-49a	20	0.8	FLU4-81a	151	471.8	FLU6-50a	100	62.1
FLU2-36b	101	62.0	FLU3-49b	20	0.8	FLU4-81b	151	454.8	FLU6-50b	100	67.2
FLU2-37a	101	70.6	FLU3-50a	20	0.8	FLU4-82a	151	472.3	FLU6-51a	100	67.3
FLU2-37b	101	69.9	FLU3-50b	20	0.8	FLU4-82b	151	513.3	FLU6-51b	100	64.2
			FLU3-51a	20	0.8						
			FLU3-51b	20	0.8						