Lability of Dissolved Organic Carbon in Arctic Rivers on the North Slope of Alaska

by

Breton B. Frazer

Submitted to the Department of Earth, Atmospheric and Planetary Sciences

in Partial Fulfillment of the Requirements for the Degree of

Bachelor of Science in Earth, Atmospheric, and Planetary Sciences

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Author___ Signature redacted________
Department of Earth, Atmospheric and Planetary Sciences
May 17, 2004

Certified by_____ Signature redacted ______
Robert (Max) Holmes
Thesis Supervisor

Certified by______Signature redacted________
Roger Summons
Thesis Supervisor

Accepted by__Signature redacted__________
Samuel Bowring
Chair, Committee on Undergraduate Program

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ABSTRACT

Rivers are an important pathway of organic carbon-mobilization in the arctic, and their influence is projected to grow as precipitation and soil temperatures increase in response to high-latitude warming. This study addresses the bioactivity of arctic riverine dissolved organic carbon (DOC) in three North Slope Alaskan rivers: the Kuparuk, the Colville, and the Sagavanirktok. While lability experiments have previously been conducted during late summer discharge on arctic rivers, none have analyzed the early hydrograph spring-melt peak DOC. During the summer of 2006, water samples were taken from significant periods of the hydrograph (upswing, peak, downswing, and quasi-stable summer) of the three rivers for DOC lability experiments. DOC from spring melt discharge proved to be highly labile and therefore dynamically different from summer DOC. Over a three-month sample incubation period, these samples lost up to 40 and 33 percent of their DOC (with and without added nutrients, respectively) while samples taken later in summer lost merely 9 and 5 percent. As spring melt contributes half of the total annual discharge and DOC flux of winter-freezing rivers, a significant portion of annual arctic DOC is labile and is therefore a large input of bioactive organic DOC to the Arctic Ocean carbon cycle.

Thesis Supervisor: Robert Holmes
Title: Associate Scientist, Woods Hole Research Center

Thesis Supervisor: Roger Summons
Title: Professor, MIT EAPS

Acknowledgments

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Special thanks to the Toolik Field Station 2006 crew that helped make my experiences there some of the best of my life; to my advisor, Leigh Royden, and other supportive faculty including Samuel Bowring, Clark Burchfiel, John Southard, Timothy Grove, Daniel Rothman, and Roger Summons, and, most of all, to my patient, inspirational advisors, Jim McClelland and Robert Holmes.

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INTRODUCTION

Importance

The Arctic's influence on global climate change, as documented by the Intergovernmental Panel on Climate Change (IPCC) in 2001, has led to an increased awareness of the mobilization of organic carbon in arctic ecosystems. Nearly one-fourth of the Northern Hemisphere's land area is underlain by permafrost (Zhang et al. 1999), of which high-latitude permafrost holds 20-60% of the global soil carbon (Finlay et al., 2006; Gorham, 1991; Post et al., 1982). Arctic rivers empty a watershed that is 22.4 x 10^6 km^2, an area 1.5 times that of the Arctic Ocean (Peterson et al., 2002), linking terrestrial and oceanic reserves of organic carbon. Arctic rivers play an especially vital role in the Arctic Ocean carbon cycle, since the Arctic Ocean contains only 1% of the world's ocean volume, yet it receives 10% of river discharge and 11% of the global river dissolved organic carbon (DOC) (Aagaard and Carmack, 1989; Gordeev et al., 1996; Macdonald et al., 1998; Anderson et al., 1998; Köhler et al., 2003).

The climate dependence of factors controlling arctic DOC flux amplifies the role of river transport in the global carbon cycle. As arctic temperatures rise, permafrost thaw periods will lengthen, and active soil horizon temperatures and depth will increase, creating a longer time window for DOC production within soils (Hinzman et al., 2005; Hobbie et al., 2002; Neff and Hooper, 2002; Freeman et al., 2004; Prokushkin et al., 2005). A recent simulation predicted a 30-40 percent increase in active-layer depth in Northern Hemisphere permafrost, with the most extreme increases in the highest-latitude arctic (Stendel and Christensen, 2002). Deepening the thaw depth of permafrost is especially important because higher levels of carbon concentration are found at the top of the permafrost table, due to the process of cryoturbation (Douglas and Tedrow, 1960; Tarnocai and Smith, 1992). Associated predictions in winter precipitation (Symon et al., 2005) will increase spring run off and arctic river discharge as seen in recent years (McClelland et al., 2004, Peterson et al., 2002). With increased spring runoff—a period that is responsible, on average, for 55% of annual terrigenous arctic DOC flux—and longer DOC production periods, it is widely thought that arctic riverine DOC flux will increase with time (Finley et al., 2006; Frey and Smith, 2005), though this view is not entirely accepted (Striegl et al., 2005).

If the Arctic's organic-rich peat and soil are mobilized, and decompose to carbon dioxide or methane, the arctic will switch from being a sink to being yet another source of atmospheric carbon and methane, known greenhouse gases. Therefore, it is necessary to understand the lability of organic carbon in present arctic ecosystems in order to predict the likely effects of increased temperature and precipitation on organic-carbon respiration in the future.

Background: Definition of Terms

While DOC is only one form of riverine carbon, it comprises the greater part of the total organic carbon transported in rivers. In order to distinguish between significant portions, total carbon in rivers is classified on the basis of chemical differences, then on particle size, and then again through biotic reactivity. As shown in Figure 1, the total carbon in rivers (TC) is divided into total organic carbon (TOC) and then total inorganic carbon (TIC). Within TOC, particles exceeding 0.45 μm in size are classified as particulate organic carbon (POC) and particles smaller than that are classified as dissolved

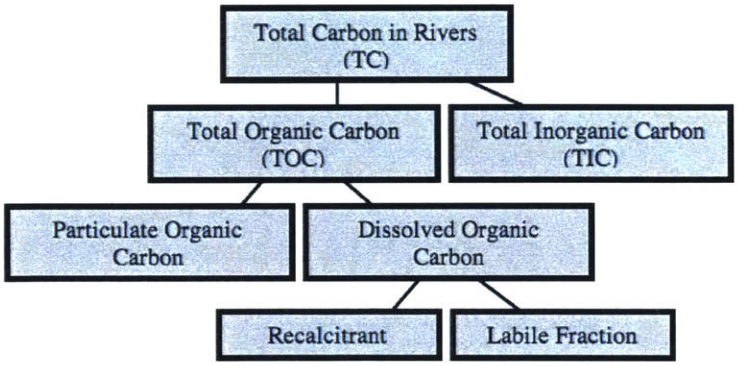

Figure 1: Riverine carbon components.

organic carbon (DOC). The DOC is then split into recalcitrant and labile fractions depending on biotic reactivity, although sometimes DOC is classified as the carbon component of dissolved organic matter (DOM). In either case DOC is the source of bioactive carbon in ecosystems. DOC originates from the degradation of plants, algae, fungi, protozoa, and other complex carbon storages.

My focus here is the lability of DOC in arctic rivers. In this context, "lability" is defined as the ability of dissolved organic carbon molecules to be broken down, digested, and respired as CO^2 by microbial agents. Labile DOC thus sustains biota at the base of food webs. The most labile dissolved organic molecules include carbohydrates, sugars, and amino and fatty acids. More complex organic carbon molecules that cannot be broken down on short time scales (defined here as three months) are termed "recalcitrant" or "refractory". The greater part of DOC present in both marine and non-marine systems is refractory (e.g., humic substances and lignin).

Previous Studies

Numerous experiments conducted on Arctic river lability have suggested that arctic riverine DOC is overwhelmingly refractory (Opsahl et al., 1999, Dittmar and Kattner 2003, Rachold et al., 2003, Amon and Meon, 2004). Those studies, however, focused on the stable, late summer fluxes, ignoring the early snowmelt period. New research in the Arctic Ocean's Beaufort Gyre shows that 30-60 percent of terrigenous DOC is labile over 10 years (Hansell et al., 2004, Cooper et al., 2005). These new findings have questioned the accuracy of arctic riverine DOC experiments, because arctic rivers are the main source of the Arctic Ocean's terrigenous dissolved organic content.

METHODS

Sampling Dates

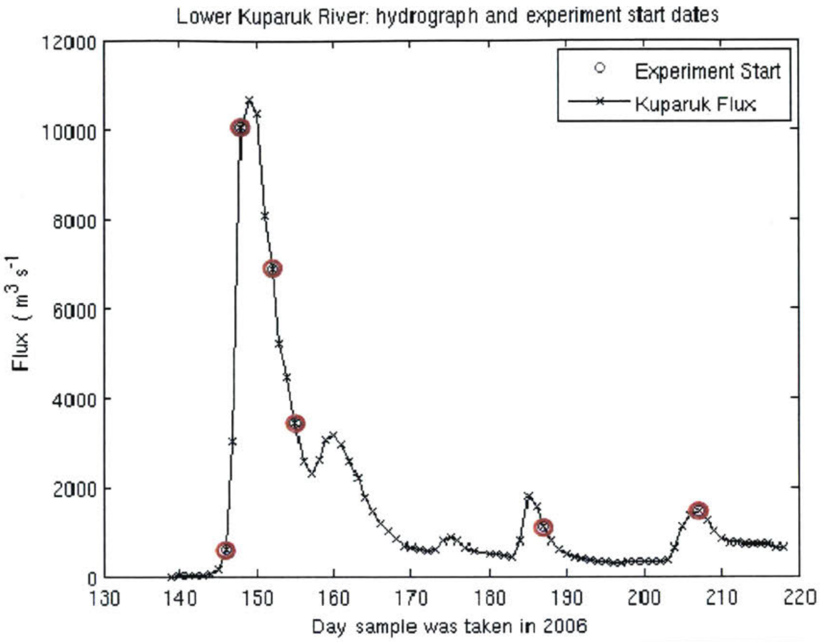

Figure 2: Kuparuk River hydrograph (above) illustrates sampling dates (first incubation time point) with river flow.

To better understand how DOC concentrations and lability respond to large fluctuations in the river flow, this research explored the late May breakup period and the quasi-stable June and July period (See Figure 2) of the Sagavanirktok, Colville, and Kuparuk rivers of the North Slope of Alaska. Although scheduling difficulties inhibited sampling DOC during the spring melt upswing for the Sagavanirktok and Colville Rivers, the entire hydrograph profile was captured for the Kuparuk River.

Sampling

River water was sampled and stored exclusively in polycarbonate bottles (as opposed to carbon leaching containers). Mainstream, fast-moving water approximately thirty-six to 72 cm below surface was targeted to ensure that samples represented the greater part of discharge. Samples were filtered through a 47 mm GF/F (glass fiber filter) upon sampling and then apportioned into thirty separate 50 ml polycarbonate containers. Fifteen (half of total) samples received nutrient amendments of 400 μL of NH^4, 400 μL of 10 mM NO^3, and 800 μL of 625 μM PO^4 per 50 ml (in accordance with the Redfield ratio). The remaining 15 samples were left unamended. Because arctic rivers have notably low nutrient levels, the amended samples show potential labile DOC levels under favorable conditions, while the unamended samples show the lability under conditions at time of sampling.

Incubation Parameters

Controlling incubation temperatures on the North Slope over the course of two seasons was impossible due to extreme temperature fluctuations and limited on-site resources. Consequently, samples were stored at 4°C immediately after sampling to stall biotic activity until initiation of experiment. This delay to incubation totaled, on average, the span of a week where samples were kept in darkness at 4°C. Samples were then put in ice coolers for 1-2 day shipment to Yale University, where they were incubated in the dark at 20°C. DOC loss during this delay, between sampling and the start of incubation at Yale, was quantified with specific time points.

Time points

To characterize rate of DOC disappearance accurately, five distinct time points were taken for each temporal experiment set. At each time point, six samples (three unamended and three amended) were frozen to halt further biochemical degradation: (1) immediately, (2) upon arrival at Yale, (3) after seven days of incubation, (4) after thirty days of incubation, and (5) after ninety days of incubation (Figure 3 below). The difference in concentrations between time points 1 and 2 corresponds to lability in an ~4°C dark environment before incubation at Yale was started.

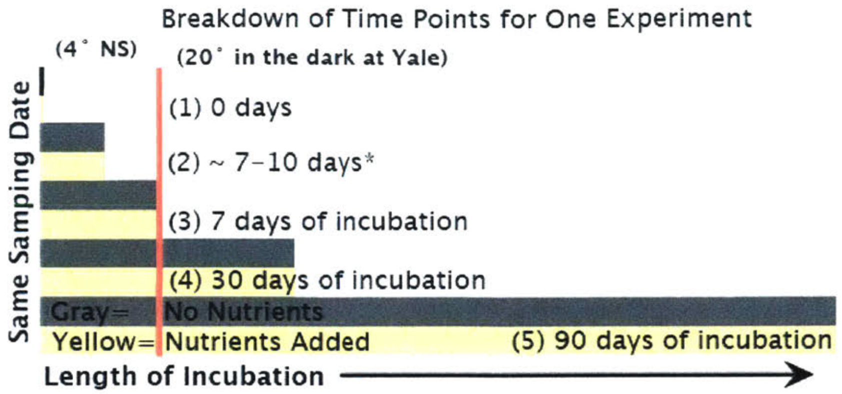

Figure 3: Illustration of time points per one experiment. All subsamples for one experiment are from the same sample but were incubated for different periods of time with two different treatments (Nutrients Added/No Nutrients). Each band of gray/yellow represents 3 repetitions. Left of the red line, time points were kept in 4°C in the dark while those to the right were treated initially the same as the others but then incubated at Yale at 20°C.

Analysis

DOC concentrations were measured with three repetitions per sample at Yale University using a Shimadzu TOC-5000A analyzer. This process requires melting frozen samples and then oxidizing the water to produce carbon dioxide (CO^2) through combustion in an oxidizing gas; organic carbon is then detected using a nondispersive infrared (NDIR) detector. During this analysis, organic-carbon standards were run approximately every 18-21 samples, yielding nearly five complete standard curves per run (because 93 positions were on their wheel). Because the Shimadzu gives a drift in readings that is not always in the same direction, Kari Mull and Peter Raymond at Yale corrected the data individually, accounting for difference in run curves. In addition to using triplicate samples, the Shimadzu TOC-5000A analyzer ran 3–5 injections per sample, injecting each sample until the coefficient of variation was less than 2%, or five injections, whichever came first.

RESULTS

DOC and Lability Analysis

The analyses revealed several relationships between seasonal fluctuations in DOC concentrations, lability, and nutrient availability. The dependence of DOC concentration levels on time of sample will be explored first, followed by an investigation into changes in lability of DOC, with respect to time of sample as well as changes in lability over the incubation period. Analysis of all relationships will include both unamended and nutrient-amended results, in that order. Only Kuparuk River experiment profiles are shown here, though results on the Colville and Sagavanirktok were very similar to the Kuparuk dataset trends. Analogous figures for the other two rivers are given in the Appendix.

Temporal DOC Concentrations

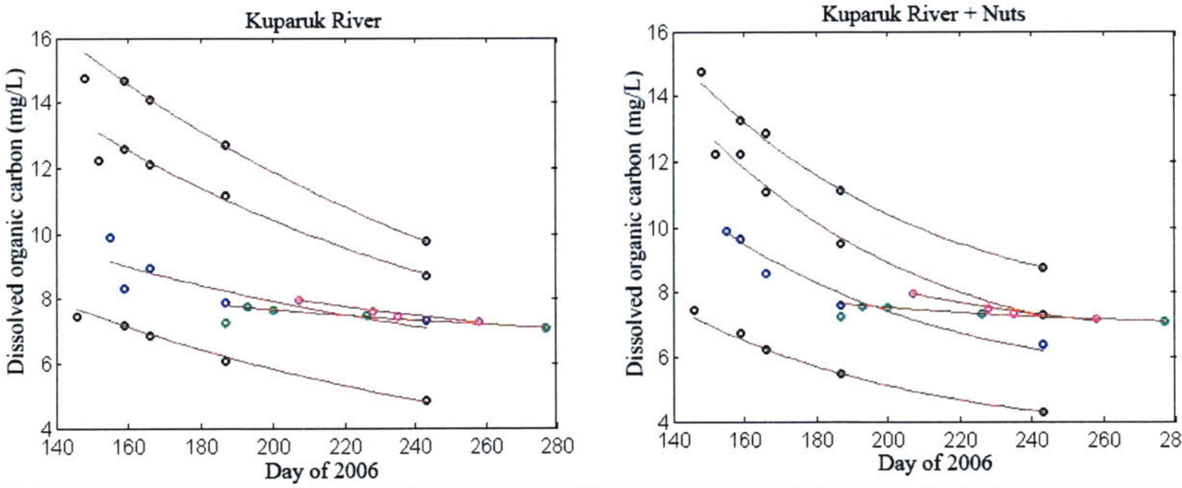

Figure 4: DOC concentrations during each experiment (open circles). Each data plot begins on the day that the sample was taken. Lines in red show the best fit to the data using a fixed half-life for all experiments. Left panel: unamended samples. Right panel: nutrients added to samples

Figure 4 illustrates the fluctuations in DOC concentration during the active summer months (initial data points in set) as well as the decline in DOC over time during incubation. Early snowmelt (i.e., peak-hydrograph) samples not only have higher initial values of DOC concentration, but they also show more rapid declines with time (indicating lability). Comparing unamended samples (left column) with those with nutrients added (right column) shows a heightened lability in amended samples. Nutrients also appear to have a greater influence on earlier samples than samples taken later in summer, indicating a higher percentage of recalcitrant DOC in later samples. This relationship is not surprising, since nutrients can only amplify the potential of labile DOC to be consumed; i.e., they cannot affect the proportion of labile to recalcitrant DOC within samples.

Labile and Recalcitrant Components

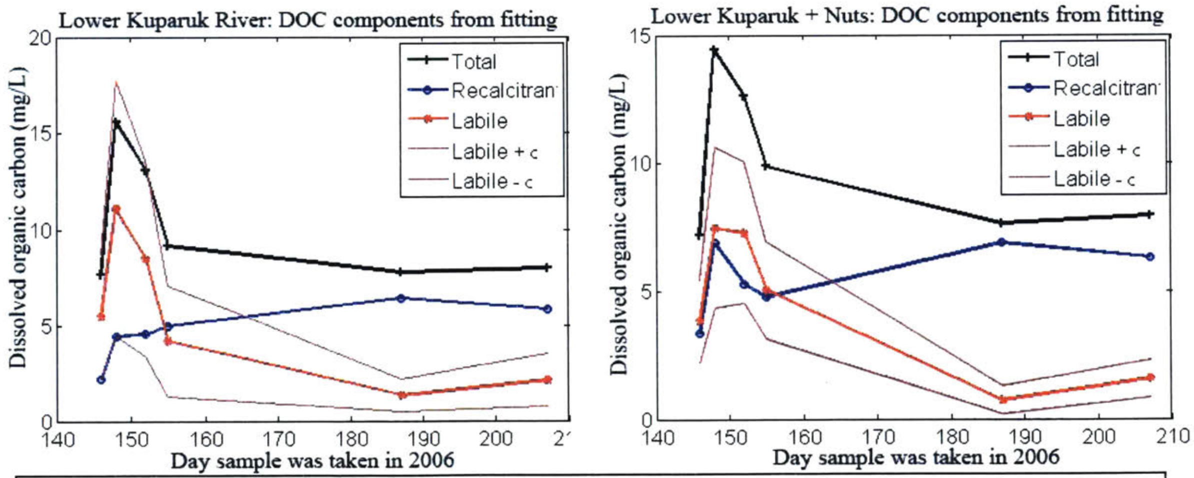

Figure 5: Total, labile and recalitrant DOC during summer. Left panel: unamended samples. Right panel: nutrients added.

Figure 5 shows the DOC concentrations for each experiment versus time, broken down into labile and recalcitrant components estimated using a constant DOC half-life, with error estimates for the labile component. (The error for recalcitrant is the error for labile divided by $\sqrt{2}$.)

Immediately after spring break up both components of DOC have peaks, but it is important that the labile DOC peak exceeds the recalcitrant peak—a relationship that switches in later months.

Temporal Fluctuations in Labile DOC Concentrations

Kuparuk DOC concentrations are shown with the Kuparuk hydrograph. Flux estimates are not available at this time for the Colville and the Sagavanirktok, though model estimates will be forthcoming from another arctic study. The samples for these two rivers show samples taken only during: the declining hydrograph data (see appendix), stable summer values, and then a final sample value during a summer storm fluctuation (Look for corresponding spike on Kuparuk hydrograph). Refer to Figure 2 for exact sample dates with respect to the hydrograph. The Sagavanirktok and Colville sampling was initiated on the date of the second sampling of the Kuparuk River.

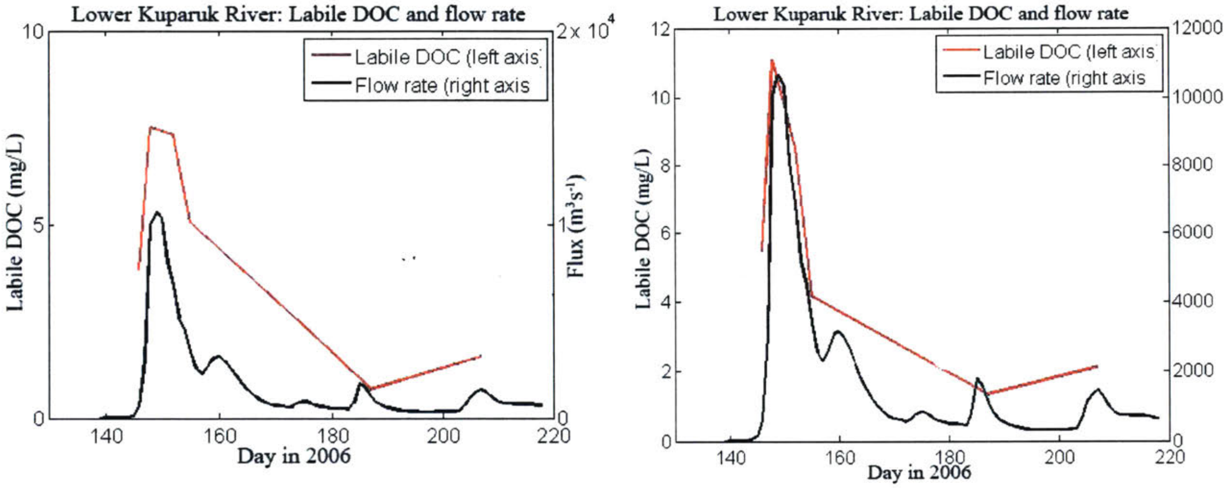

Figure 6: Kuparuk hydrograph with labile DOC: unamended samples (left panel); nutrient amended (right panel).

Although flux was not recorded for the Sagavanirktok and Colville rivers, the hydrograph profiles of those rivers should be similar to that of the Kuparuk during spring peak and summer.

However, the Sagavanirktok is glacier fed and thus not dependent on changes in precipitation in later summer months.

CONCLUSION

Concentration Fluctuations

Considerable differences can be seen in DOC concentrations over the fluctuations in the hydrograph. Even small perturbations caused by rainstorms correlate with elevated levels of DOC. These results corroborate the paradigm that time-specific data cannot be extrapolated over the whole hydrograph because concentration fluctuates greatly throughout the summer months.

Considerable Lability

While refractory DOC remains the main component throughout the summer months, a significant peak in the fraction of labile DOC occurs during spring breakup. The effects of this peak on carbon inflow to the Arctic Ocean are amplified by simultaneous peaks in total DOC concentration and hydrographic flux. This new data suggest that further investigation, involving larger, more influential arctic rivers is well warranted in view of the implications for global climate.

Initial-Temperature Effect

An unexpected effect, the initial disappearance of DOC between time points 1 and 2, which corresponds to the delay from sampling and initiation of incubation experiment at Yale, when samples were kept in darkness at 4° C during shipping, shows that DOC was still being lost, even at near-freezing temperatures. Therefore it is likely that the elevated levels of DOC are actively being consumed during peak river flow in late May.

Nutrient Effect

While a considerable fraction of DOC proved to be labile, the addition of nutrients amplified the effects of lability during early months, while little effect was seen in later months when the majority of DOC remained recalcitrant. Because arctic rivers are notorious for low levels of nutrients, significant lability achieved with naturally low levels of nutrients heightens the importance of these results. While water stagnant within polycarbonate bottles kept in the dark does not fully represent conditions within rivers and the ocean, lability obtained in cold conditions with no artificial stimulants shows that DOC in arctic rivers has a much larger role than is currently thought.

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Appendix A. The Colville River and the Sagavanirktok River

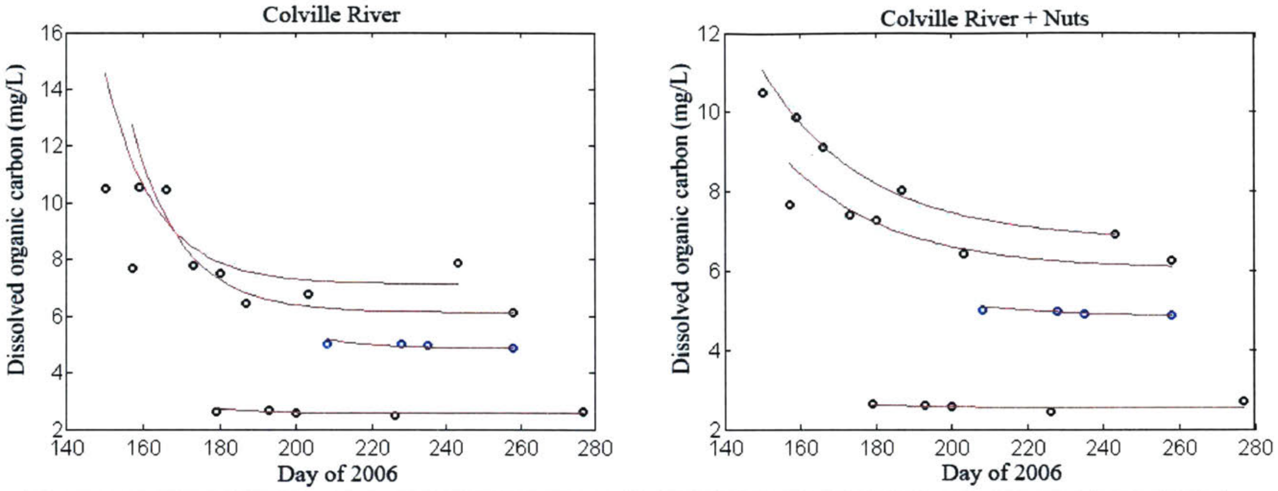
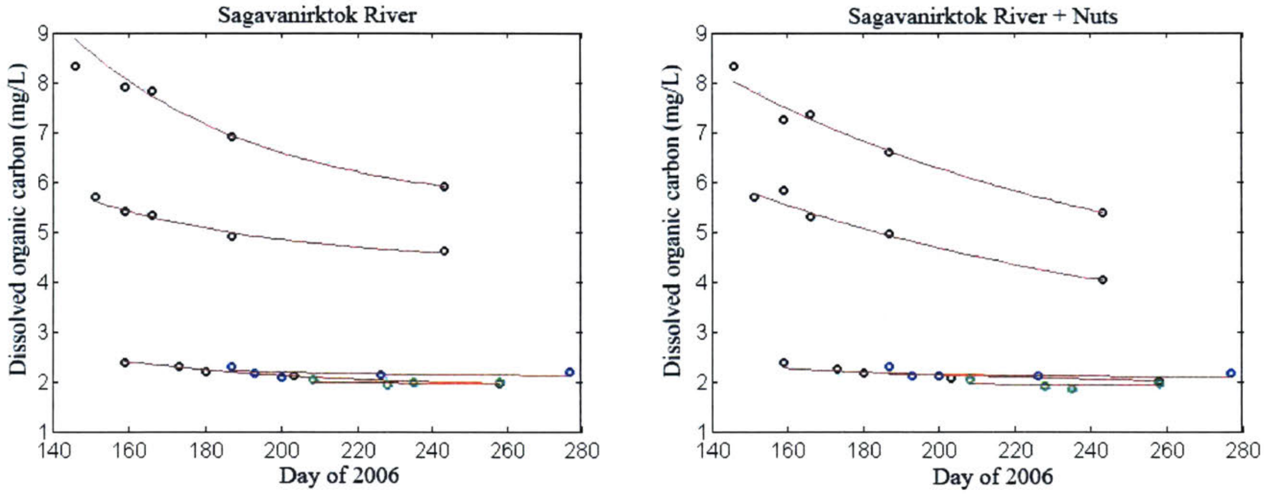


Figure 4B: Colville River (Above) and Sagavanirktok River (Below) experimental data as corresponds to Figure 4 in Results section.



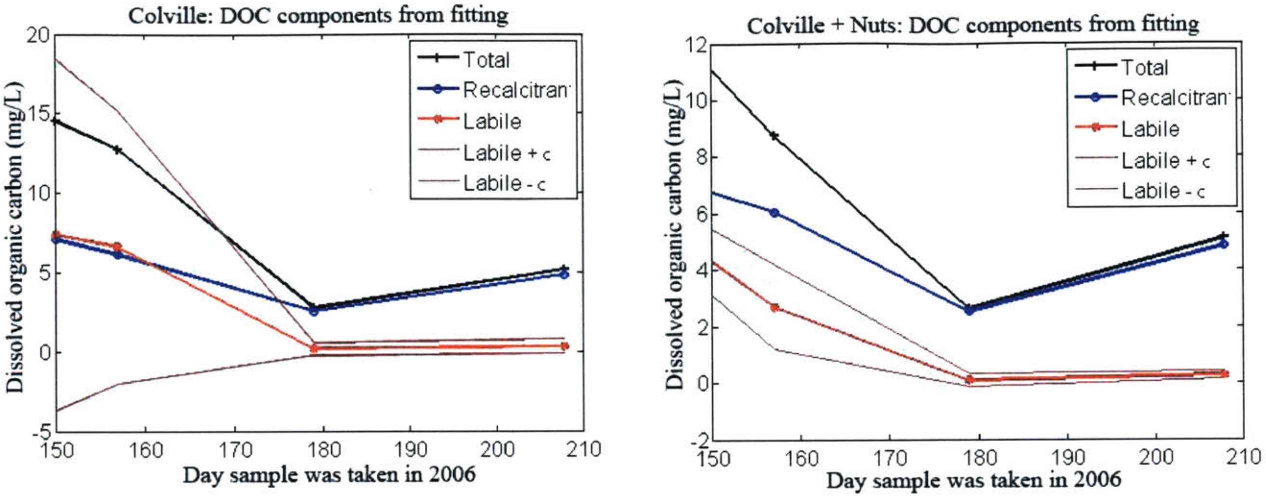
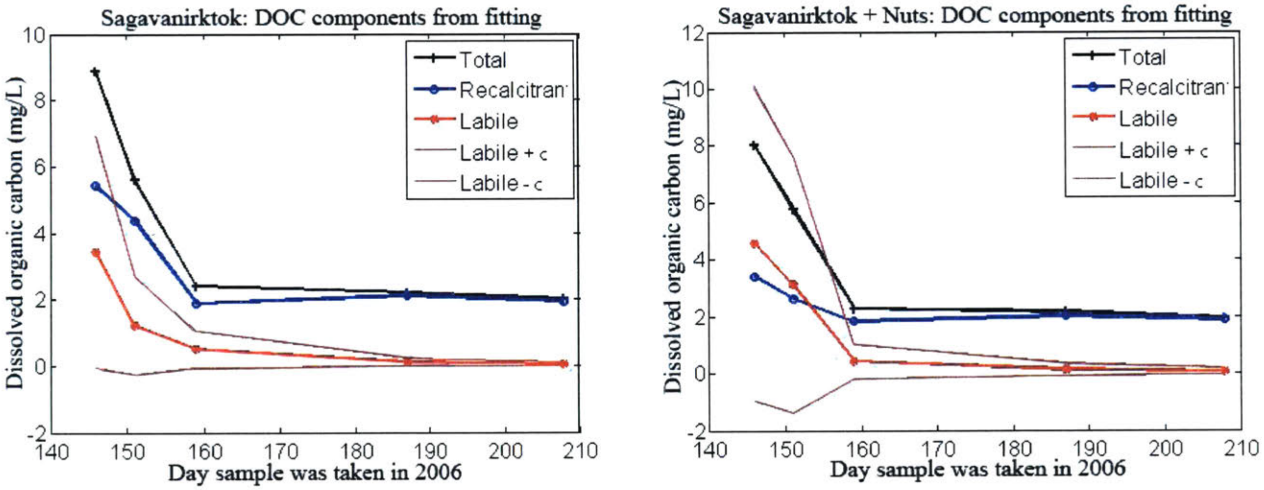


Figure 5B: Colville River (Above) and Sagavanirktok River (Below) experimental data as corresponds to Figure 5 in Results section.



Appendix B. Matlab code used to analyze the data

```
% filename = RiversNew.m
% Plots dissolved organic carbon (DOC) input data. Here is the format of the data structure for LKU. Other rivers
% are similar.
% LKU.name = 'Lower Kuparuk'
% COL.doc = [array of values]
% LKU.shift= 'shift
% LKU.day = [array of days]
% LKU.err = [array of errors in measurement of doc]
clear all
Sagavanirktok;
[nrows, ncols] = size(SAG.doc);
nexp = nrows; % number of experiments
% create arrays for later use.
labile = zeros(1,nexp); % This will hold the labile DOC for all experiments
recalcitrant = zeros(1,nexp); % This will hold the recalcitrant DOC ...
total = zeros(1,nexp); % The total DOC for each experiment
halflife = zeros(1,nexp); % The halflife for the labile DOC
Numdays = zeros(1,nexp); % Number of days in each experiment
firstval = zeros(1,nexp); % DOC on day 1 of experiment
lastval = zeros(1,nexp); % DOC on last day of experiment.

fig1 = figure(1);
% This figure shows the data for each experiment (open circles).
% Each data plot begins on the day that the sample was taken.
% The lines (in red) show the best fit to the data using the model
% D = K + L*exp(-log(2)*t/thalf) .
% To set the weights for fitting note that...
% in experiments 1,2,3,5 &6 the first point seems clearly to be an outlier;
% in experiment 4 the second point seems clearly to be an outlier.
% Note that the model has three free parameters:
% K (recalcitrant DOC),
% L (labile DOC), and
% thalf (the halflife of the labile component, in days).
% Three free parameters is a lot, considering that some experiments have
% only 4 data points.
% The parameter least constrained by the data is halflife.
for i=1:nexp % loop over number of experiments
plotmark = 'ok';
switch i
case 4
plotmark = 'ob';
case 5
plotmark = 'og';
case 6
plotmark = 'om';
end
shift = SAG.shift(i);
day = SAG.day(i,:);
day = day(day ~= 999);
Numdays(i) = sum(day ~=999);
```

```
t = day - day(1);
doc = SAG.doc(i,:);
doc = doc( doc ~= 999);
firstval(i) = doc(1);
dayone(i) = day(1);
lastval(i) = doc(length(doc));
err = SAG.err(i,:);
err = err(err ~= 999);
plot(day, doc, plotmark, 'LineWidth',2); % REMOVED SHIFT
hold on
xlabel('Day of 2006');
ylabel('Dissolved organic carbon (mg/L)');
title( 'DOC data (black) and fits (red). (Fits use K, L, & halflife.)');
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed Fontsize
N = length(doc);
weights = 1./err;
switch i
case 1
weights(1) = 0.001*weights(1); % first point is an outlier.
case 2
weights(1) = 0.001*weights(1); % first point is an outlier.
case 3
weights(1) = 0.001*weights(1); % first point is an outlier.
case 5
weights(1) = 0.001*weights(1); % first point is an outlier.
end
opts = fitoptions('Method','Nonlinear', ...
   'Lower', [0 ,doc(1)-doc(N), 0], ... % Lower bounds for K,L,
   'Upper', [doc(N), 10000, 100], ... % Upper bounds for K,L,c
   'StartPoint', [doc(N),doc(1)-doc(N),1/(day(N)-day(1))], ... % Start search at these values of K,L,thalf
   'Weights',weights, ... % Weights for the data
   'Normalize', 'Off', ... % Don't normalize the data before fitting
   'MaxFunEvals',1000); % Maximum number of steps in search for best fit
ftype = fittype('K + L*exp(-log(2)*c*x)','options', opts); % Specify model for fitting
fresult = fit(t',doc',ftype); % Now do the fit
K = fresult.K; L = fresult.L; thalf = 1/fresult.c; % Best-fit coefficients K,L,thalf
tt = linspace(0,day(N)-day(1),50); % New array of times to display fitted function
bfdoc = K + L*exp(-log(2)*tt/thalf); % Best-fit DOC
plot(tt+day(1),bfdoc,'-r');
labile(i) = L;
recalcitrant(i) = K;
total(i) = labile(i) + recalcitrant(i);
halflife(i) = thalf;
end % for i==i:nexp

fig2 = figure(2);
% Shows K & L gotten from the fits in Figure 1.
startday = SAG.day(:,1);
plot(startday, total, '+-k', ...
startday, recalcitrant, 'o-b', ...
startday, labile, '*-r');
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed Fontsize
legend('Total','Recalcitrant','Labile');
xlabel('Day sample was taken in 2006');
ylabel('Dissolved organic carbon (mg/L)');
```

```
title( 'Lower Kuparuk River. DOC from fits with variable Labile half life.');

fig3 = figure(3);
% Shows halflife found by the fits in Figure 1.
plot(startday, halflife, '*-k');
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed Fontsize and fontsize
xlabel('Day sample was taken in 2006');
ylabel('Half life of labile DOC in days');
title( 'Half life of labile DOC from fits');
% The results from fitting aren't impressive.
% So let's try using the raw data

fig4 = figure(4);
% Shows a lower bound for labile & an upper bound for recalcitrant.
% gotten by taking recalcitrant to be the last DOC value in each experiment
% and labile to be the first DOC value minus the last doc value.

plot(dayone, firstval, '+-k', ...
dayone, lastval, 'o-b', ...
dayone, firstval-lastval, '*-r');
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed Fontsize and fontsize
legend('Total DOC', 'Upper bound for Recalcitrant DOC','Lower bound for Labile DOC');
xlabel('Day sample was taken in 2006');
ylabel('Dissolved organic carbon (mg/L)');
title( 'Lower Kuparuk River: Bounds for labile and recalcitrant DOC');

% A little math shows that if K and L are known, the error in the estimate
% of reciprocal half life is inversely proportional to L. Thus the best
% estimate of thalf is likely to be obtained from the experiment with the
% largest labile component. For the Lower Kuparuk River, that is the second experiment.
% Accordingly, we use the half life estimated from the second experiment to fit
% the data from all the experiments. With half life assumed known, the fit to K and L
% is linear, giving easy estimates for the errors in K and L.

fig5 = figure(5); % Like fig1, except the fitting procedure is different.
% Experimental data (black circles). Lines in red show the best fit to the data
% using a fixed half life for all experiments.
% It is important to look at this figure to check that the assumed half life
% gives a good fit. If it doesn't, adjust the half life and try again.
% Note that there is no need to use a nonlinear fitting function, since
% when half life is fixed the problem is linear. Rivers3.m does it with
% the usual generalized inverse and gets the same answer as this code
% gives.
c = 1/halflife(1); % Lock the half life.
for i=1:nexp % loop over experiments
plotmark = 'ok';
switch i
case 4
plotmark = 'ob';
case 5
plotmark = 'og';
case 6
plotmark = 'om';
end
shift = SAG.shift(i);
```

```
day = SAG.day(i,:);
day = day(day ~= 999);
Numdays(i) = sum(day ~=999);
t = day - day(1);
doc = SAG.doc(i,:);
doc = doc( doc ~= 999);
firstval(i) = doc(1);
dayone(i) = day(1);
lastval(i) = doc(length(doc));
err = SAG.err(i,:);
err = err(err ~= 999);
plot(day, doc, plotmark,'LineWidth',2);
hold on
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed Fontsize
xlabel('Day of 2006');
ylabel('Dissolved organic carbon (mg/L)');
title( 'Fits to data using same Labile half life for all experiments');
N = length(doc);
weights = 1./err;
switch i
case 1
weights(1) = 0.001*weights(1); % first point is an outlier.
case 2
weights(1) = 0.001*weights(1); % first point is an outlier.
case 3
weights(1) = 0.001*weights(1); % first point is an outlier.
case 5
weights(1) = 0.001*weights(1); % first point is an outlier.
end

opts = fitoptions('Method','Nonlinear', ...
   'Lower', [0 ,doc(1)-doc(N)], ... % Lower bounds for K,L
   'Upper', [doc(N), 10000], ... % Upper bounds for K,L
   'StartPoint', [doc(N),doc(1)-doc(N)], ... % Start search at these values of K,L,t half
   'Weights',weights, ... % Weights for the data
   'Normalize', 'Off', ... % Don't normalize the data before fitting
   'MaxFunEvals',1000); % Maximum number of steps in search for best fit
ftype = fittype('K + L*exp(-log(2)*c*x)','options', opts,'problem','c'); % Specify model
fresult = fit(t',doc',ftype,'problem',c); % Now do the fit
K = fresult.K; L = fresult.L; % Best-fit coefficients K,L
tt = linspace(0,day(N)-day(1),50); % New array of times to display fitted function
bfdoc = K + L*exp(-log(2)*c*tt); % Best-fit DOC
plot(tt+day(1),bfdoc,'-r');
labile(i) = L;
recalcitrant(i) = K;
total(i) = labile(i) + recalcitrant(i);
% Now do error estimates for K,L.
% Assume data error is the same for all data points.
% Take data error to be the largest data residual.
bf1doc = K + L*exp(-log(2)*t/thalf); % Best-fit DOC at data point times
data_error = max(abs(doc-bf1doc)); % Get largest data residual.

% To get a method for estimating errors in K and L, difference the relation
% D=K+L*exp(-ct). This gives...
% dD(t=0) = dK + dL, and dD(t=\inf) = dK.
```

```
% Therefore...
% (dK)^2 = (dD(t=\inf))^2 and
% (dL)^2 = (dD(t=0))^2 + (dK)^2 = (dD(t=0))^2 + (dD(t=0)))^2
% Set dD(t=0) and dD(t=0) equal to the largest residual dD. Then...
% (dK)^2 = (dD)^2, and (dL)^2 = 2*(dD)^2.
K_err(i) = data_error; % error in estimate of K
L_err(i) = sqrt(2)*data_error; % error in estimate of L
end % for i=i:nexp

fig6 = figure(6); % This is an important figure because it gives error
% estimates for the labile component. (The error for recalcitrant is
% the error for labile divided by sqrt(2).)
% Plot fixed-thalf DOC estimates, with estimated error.
startday = SAG.day(:,1);
plot(startday, total, '+-k', 'LineWidth',2); hold on
plot(startday, recalcitrant, 'o-b', 'LineWidth',2);
plot(startday, labile, '*-r', 'LineWidth',2);
plot(startday, labile+L_err, '-r', 'LineWidth',1);
plot(startday, labile-L_err, '-r', 'LineWidth',1);
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed Fontsize and fontsize
legend('Total','Recalcitrant','Labile', 'Labile + \sigma', 'Labile - \sigma');
xlabel('Day sample was taken in 2006');
ylabel('Dissolved organic carbon (mg/L)');
title( 'Sagavanirktok: DOC components from fitting');

fig8 = figure(8);
% Trying to convert from kuparuk labile doc graph with hydro data, to one
% with just doc values
plot(startday,labile','LineWidth',2,'Color', 'r');
set(gca, 'FontName', 'Helvetica', 'FontSize', 16); % Changed fontsize
xlabel('Day sample was taken in 2006');
ylabel('Labile DOC  ( mg/L )');
title('Sagavanirktok: Labile DOC
```

Appendix C. Data sets used with Matlab code

1. Lower Kuparuk (No Nutrients)

```
LKU.name  = ['Lower Kuparuk'];

LKU.day   = [146, 159,  166,  187,  243;
             148, 159,  166,  187,  243;
             152, 159,  166,  187,  243;
             155, 159,  166,  187,  243;
             187, 193,  200,  226,  277;
             207, 228,  235,  258,  999];

LKU.doc   = [ 7.449,  7.18,  6.85,   6.09,  4.83;
             14.76, 14.68, 14.10, 12.69,  9.78;
             12.23, 12.59, 12.13, 11.15,  8.73;
              9.91,   8.31,   8.94,   7.90,  7.32;
              7.27,   7.78,   7.65,   7.48,  7.10;
              7.98,   7.61,   7.47,   7.31,  999];
```

```
LKU.err  = [ .070,  .012, .100,  .281, .094;
             .028,  .094, .026,  .173, .019;
             .032,  .045, .127,  .115, .070;
             .100,  .090, .040,  .070, .107;
             .250,  .910, .066,  .137, .170;
             .060,  .550, .430,  .190,  999];
```

1. Lower Kuparuk (Nutrients Added)

```
LKUN.name  = ['Lower Kuparuk + Nutrients'];

LKUN.day   = [ 146,  159,  166,  187,  243;
               148,  159,  166,  187,  243;
               152,  159,  166,  187,  243;
               155,  159,  166,  187,  243;
               187,  193,  200,  226,  277;
               207,  228,  235,  258,  999];

LKUN.doc   = [7.449,  6.76,  6.22,  5.48,  4.31;
              14.76, 13.24, 12.85, 11.12,  8.77;
              12.23, 12.23, 11.07,  9.49,  7.31;
               9.91,  9.66,  8.61,  7.62,  6.39;
               7.27,  7.59,  7.53,  7.33,  7.11;
               7.98,  7.49,  7.35,  7.16,  999];

LKUN.err   =     [.032,  .212,  .023,  .039,  .048;
                  .757,  .133,  .306,  .073,  .055;
                  .073,  .081,  .049,  .214,  .074;
                  .834,  .019,  .207,  .081,  .088;
                  .088,  .040,  .008,  .066,  .042;
                  .019,  .063,  .051,  .031,   999];
```

2. Colville (No Nutrients)

```
COL.name  = ['Colville'];

COL.day   = [  150,  159,  166,  187,  243;
               157,  173,  180,  203,  258;
               179,  193,  200,  226,  277;
               208,  228,  235,  258,  999];

COL.doc   = [10.49, 10.56, 10.47,  6.45, 7.86;
             7.672,  7.78,  7.51,  6.77, 6.13;
             2.640,  2.65,  2.58,  2.50, 2.64;
             5.002,  5.01,  4.99,  4.86, 999];

COL.err   = [ .086,  .047,  .074,  .057, .066;
              .176,  .107,  .055,  .073, .096;
              .009,  .012,  .009,  .014, .014;
              .078,  .014,  .010,  .012, 999];
```

3. Colville (Nutrients Added)

```
COLN.name  = ['Colville + Nutrients'];

COLN.day   =     [  150,  159,  166,  187,  243;
                    157,  173,  180,  203,  258;
```

```
                    179,  193,  200,  226,  277;
                    208,  228,  235,  258,  999];

COLN.doc   = [10.49,  9.88,  9.12,  8.02,  6.91;
               7.672,  7.40,  7.27,  6.44,  6.25;
               2.640,  2.62,  2.59,  2.45,  2.70;
               5.002,  4.97,  4.92,  4.88,   999];

COLN.err   = [ .102,  .064,  .045,  .300,  .018;
               .132,  .120,  .022,  .033,  .089;
               .030,  .018,  .015,  .007,  .019;
               .054,  .001,  .001,  .011,   999];
```

4. Sagavanirktok (No Nutrients)

```
SAG.name  = ['Sagavanirktok No Nutrients'];

SAG.day  =     [ 146,  159,  166,  187,  243;
                 151,  159,  166,  187,  243;
                 159,  173,  180,  203,  258;
                 187,  193,  200,  226,  277;
                 208,  228,  235,  258,  999];

SAG.doc  =     [8.328,  7.91,  7.83,  6.90,  5.92;
                5.690,  5.42,  5.33,  4.90,  4.63;
                2.389,  2.29,  2.20,  2.13,  1.96;
                2.312,  2.18,  2.09,  2.14,  2.20;
                2.030,  1.94,  1.98,  1.98,  999];

SAG.err  =     [ .382,  .467,  .183,  .113,  .122;
                 .072,  .087,  .040,  .062,  .095;
                 .044,  .032,  .062,  .029,  .024;
                 .022,  .037,  .020,  .018,  .028;
                 .053,  .014,  .006,  .019,   999];
```

5. Sagavanirktok (Nutrients Added)

```
SAGN.name  = ['Sagavanirktok + Nutrients'];

SAGN.day   = [ 146,  159,  166,  187,  243;
               151,  159,  166,  187,  243;
               159,  173,  180,  203,  258;
               187,  193,  200,  226,  277;
               208,  228,  235,  258,  999];

SAGN.doc  =    [8.328,  7.25,  7.36,  6.59,  5.38;
                5.690,  5.83,  5.29,  4.95,  4.04;
                2.389,  2.26,  2.18,  2.07,  2.02;
                2.312,  2.12,  2.13,  2.13,  2.18;
                2.030,  1.92,  1.86,  1.97,  999];

SAGN.err  =    [.385,  .596,  .143,  .115,  .008;
                .127,  .275,  .080,  .413,  .079;
                .075,  .042,  .045,  .039,  .006;
                .035,  .020,  .003,  .053,  .064;
                .072,  .007,  .011,  .004,   999];
```