Scavenging Model and Parameterization

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1 SCAVENGING MODEL

The distribution of ^{231}Pa and ^{230}Th are controlled by absorption, desorption and sinking processes. Assuming no advection by currents, the equations for the trace-element activity in dissolved form X_s and particulate form X_p are descripted by the following equations:

$$\frac{\partial X_d}{\partial t} = Q - kX_d + k_{-1}X_p \tag{1.1}$$

$$\frac{\partial X_p}{\partial t} = kX_d - k_{-1}X_p - s\frac{\partial X_p}{\partial z} \tag{1.2}$$

where $Q(dpmm^{-3}y^{-1})$ is the production rate of ^{231}Pa or ^{230}Th , $k_1(yr^{-1})$ and $k_{-1}(yr^{-1})$ are the exchange rate constants of the elements by adsorption and desorption respectively, S(m/yr) is the sinking rate of particles and z (m) is depth.

The dissolved and particulate pools exchange material through adsorption and desorption. If the scavenging processes are fast enough, it can be assumed that there is a chemical equilibrium between the dissolved and the particulate pool. Assuming the elements are at steady state and introducing the reversible equilibrium between dissolved and particulate phases, equation 1.1 and 1.2 become:

$$0 = Q - kX_d + k_{-1}X_p (1.3)$$

$$0 = kX_d - k_{-1}X_p + s\frac{\partial X_p}{\partial z} \tag{1.4}$$

Assuming Q, k, k₋₁ and s are constants, the analytical solutions of the partial differential equations 1.3 and 1.4 are:

$$X_p = \frac{Q}{s}z + C_1 \tag{1.5}$$

$$X_d = \frac{Q}{k} - \frac{k_{-1}}{k} \left(\frac{Q}{s} z + C_1 \right) \tag{1.6}$$

where C_1 is an intercept from integrating equation 1.4.

2 PARAMETERIZATION

The basic idea to determine the parameters is to fit the analytical solutions with observed data, the locations of which are shown in figure 2.1. There are four important parameters in equation 1.1 and 1.2 that can determine the tracer's distributions. They are production rate Q, sinking rate S, scavenging coefficients k_1 and k_{-1} .

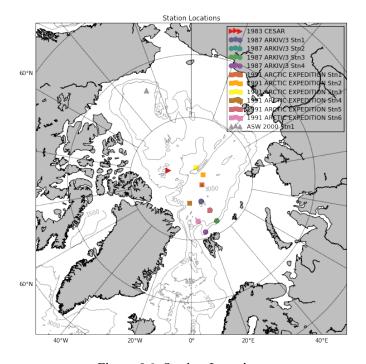


Figure 2.1: Station Locations

Among all the parameters, the production rates of ^{231}Pa and ^{230}Th are best known (0.00246 dpm/m^3y and 0.0267 dpm/m^3y respectively). However, the parameterizations of rest of them are complicated.

2.1 SINKING RATE

2.1.1 ESTIMATE SINKING RATE AT EACH STATION

Sinking rate describes the speed of particulate matter that sinks from the euphotic zone to depth. Note that in equation 1.5, the slope, $\frac{Q}{s}$, contains two parameters, sinking rate, s, and production rate Q. According to the steady analytical solution, ^{231}Pa and ^{230}Th increase with depth linearly. Therefore, least squares method was applied to find the realistic slopes, α , in each station.

To ensure that a high-quality data point influences the fit more than a low-quality data point, the summed square of the residuals, *rss*, is weighted by measurement errors:

$$rss = \sum_{i=1}^{n} w_i (y_i - \hat{y}_i)^2$$
 (2.1)

where n is the number of data points, y_i are the data and $\hat{y_i}$ are the fits. w_i are the weights, which are given by $w_i = \frac{1}{\sigma_i^2}$, where σ_i are the errors reported in the original publication. Assume $\hat{y_i} = \alpha x_i + \beta$,

$$rss = \sum_{i=1}^{n} w_i \left(y_i - \left(\alpha x_i + \beta \right) \right)$$
 (2.2)

Because the least-squares fitting process minimizes the summed square of the residuals¹, the coefficients are determined by differentiating rss with respect to each parameter, and setting the result equal to zero.

$$\frac{\partial rss}{\partial \alpha} = -2\sum_{i=1}^{n} x_i w_i \left(y_i - \left(\alpha x_i + \beta \right) \right) = 0$$
 (2.3)

$$\frac{\partial rss}{\partial \beta} = -2\sum_{i=1}^{n} w_i \left(y_i - \left(\alpha x_i + \beta \right) \right) = 0 \tag{2.4}$$

The previous equations become:

$$\sum_{i=1}^{n} x_{i} w_{i} (y_{i} - (\alpha x_{i} + \beta)) = 0$$
 (2.5)

$$\sum_{i=1}^{n} w_i (y_i - (\alpha x_i + \beta)) = 0$$
 (2.6)

where the summations run from i = 1 to n. The normal equations are defined as

$$\sum_{i=1}^{n} x_i w_i y_i = \alpha \sum_{i=1}^{n} x_i^2 + \beta \sum_{i=1}^{n} x_i$$
 (2.7)

¹Using weighted least square fit package in python statsmodels.

$$\sum_{i=1}^{n} w_i y_i = \alpha \sum_{i=1}^{n} x_i w_i + \beta \sum_{i=1}^{n} w_i$$
 (2.8)

Sloving for α and β ,

$$\alpha = \frac{n\sum x_i w_i y_i - \sum x_i \sum w_i y_i}{\sum x_i^2 - (\sum x_i)^2} = \frac{Q}{s}$$
(2.9)

$$\beta = \frac{1}{\sum x_i} \left(\sum y_i - \alpha \sum x_i \right) = C_1 \tag{2.10}$$

Based on the weighted least square method, the data was fitted and the results are shown in figure 2.2. With the slope coming from real data set, the sinking rate in each station is given by:

$$s = \frac{\alpha}{Q}. (2.11)$$

Since the amount ^{231}Pa and ^{230}Th produced at z=0 in an infinitely thin layer tends towards 0, marine particulate concentration of this species should be zero, which gives the boundary condition, $C_1 = 0$ in equation 1.5. However, the results from figure 2.2 indicate the amount of particulate ^{230}Th and ^{231}Pa are not zero at the surface, which leads us to another question: whether forcing the intercepts to zero will give a significantly better estimate. This problem can be solved by testing whether the model with 2 degrees of freedom behaves significantly better than the one with 2 degree of freedom. The F-test was therefore employed.

If there are n data points to estimate parameters of both models from, one can calculate the F statistic by:

$$F = \frac{\frac{rss_1 - rss_2}{p_2 - p_1}}{\frac{rss_2}{n - p_2}} \tag{2.12}$$

where rss_i is the residual sum of squares of model i, p and n is the number of predictors and observations.

If we reorganize equation 2.12, we will have:

$$F = \left(\frac{rss_1}{rss_2} - 1\right) \frac{p_2 - p_1}{n - p_2} \tag{2.13}$$

Assuming $\frac{p_2-p_1}{n-p_2}$ in the equation 2.13 stays the same, a high F ratio will be obtained if $\frac{rss_1}{rss_2}$ is large, which means the deviations of predicted from actual observed data in model 2 is much lower than those in model 2. In the F-test, p-value measures the probability of obtaining an F Ratio as large as what is observed. In general, higher the F ratio obtained, smaller probability

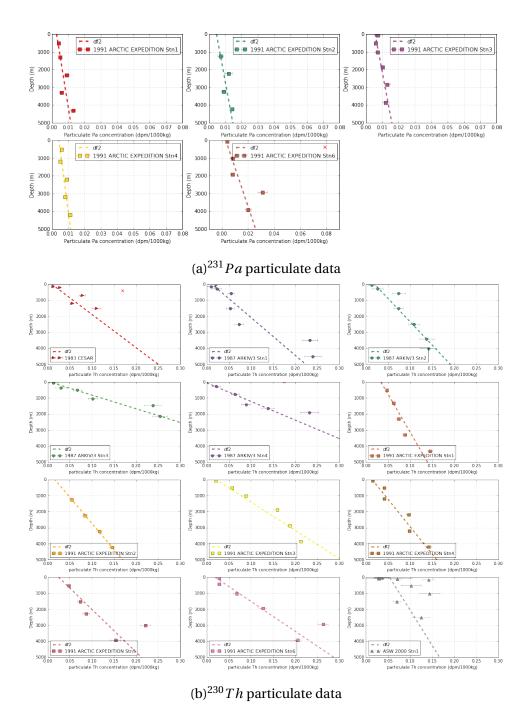


Figure 2.2: The points are the observed particulate data and the lines are given by the weighted least squares regression. The cross stands for the data that is not taken into consideration since it was affected by currents which could tell from the non-linear shape.

to be observed, which leads to a lower p-value. As a result, a lower the p-value can indicate performance of model 1 is better.

Let model 1 to be the fittings without an intercept, $\hat{y_1} = \alpha x$, and set model 2 to be the model with an intercept, $\hat{y_2} = \alpha x_i + \beta$. According to equation 2.13, null hypothesis can be specified as: model 2 does not provide a significantly better fit than model 1. The hypothesis will be rejected if the calculated p value from the data is not less than the critical p-value. In this paper, critical value was set to be 0.05.

Tuble 2111 Results of the F test (Sused of purite date)							
Cruise	Station	F_{230Th}	df ²	$p_{^{230}Th}$	$F_{231}Pa$	df	$p_{^{231}Pa}$
1983 CESAR	stn1	1.45	(1,3)	0.31	-	-	-
1987 ARKIV/3	stn1	0.76	(1,6)	0.42	-	-	-
1987 ARKIV/3	stn2	6.95	(1,5)	0.05	-	-	-
1987 ARKIV/3	stn3	0.19	(1,5)	0.68	-	-	-
1987 ARKIV/3	stn4	0.03	(1,3)	0.86	-	-	-
1991 ARCTIC EXPEDITION	stn1	15.03	(1,3)	0.03	4.20	(1,3)	0.13
1991 ARCTIC EXPEDITION	stn2	166.80	(1,2)	0.01	2.22	(1,2)	0.27
1991 ARCTIC EXPEDITION	stn3	13.06	(1,4)	0.02	55.05	(1,4)	0.00
1991 ARCTIC EXPEDITION	stn4	20.73	(1,4)	0.01	17.64	(1,3)	0.02
1991 ARCTIC EXPEDITION	stn5	1.42	(1,3)	0.32	-	-	-
1991 ARCTIC EXPEDITION	stn6	3.22	(1,4)	0.15	0.88	(1,3)	0.42
AWS 2000	stn1	16.60	(1,8)	0.00	-	_	-

Table 2.1: Results of the F-test (based on particulate data)

Table 2.1 shows that half of the ^{230}Th stations have p-value less than 0.05, which suggests model 2 provides a significantly better fit, while the other half stations have p-values that are not greater than 0.05, which suggest the opposite. As for ^{231}Pa , 3 out of 5 ^{231}Pa stations have p-values larger than 0.05 and the rest 2 stations have lower than 0.05 p-values. That information fails to directly answer the question on whether fitting the data with an intercept is better or not.

However, we can try another way by doing a calculation on all the ^{230}Th and ^{231}Pa profiles. Let $rss_1 = \sum rss_{1i}$, where i stands for the i^{th} station, $p_1 = 1 \times$ number of stations, $p_2 = 2 \times$ number of stations and n= total number of points and then substitude into equation 2.12.

After the calculation, ^{231}Pa turns out to have a F ratio that reaches 11.94, with (5,14) degree of freedom, while ^{230}Th , with (12,51) degree of freedom, has a slightly higher F ratio, 23.06 P-value comes out to be 2.25×10^{-3} for ^{231}Pa and 8.11×10^{-06} for ^{230}Th . Since these numbers are less than 0.05, we can safely draw the conclusion that allowing an intercept to zero enables the weighted least squares to fit the observed ^{231}Pa and ^{230}Th particulate data significantly better

Therefore, the previous regressions are valid in estimating the sinking rates.

Table 2.2 and 2.3 show the estimate sinking rates, which values vary from station to station and the ^{231}Pa ones are always faster than the ^{230}Th 's. This result is consistant with our knowl-

²df stands for degree of freedom. For each F distribution, df is $(p_2 - p_1, n - p_2)$.

Table 2.2: Station Locations, Calculated Sinking Rates and Error(particulate ²³⁰ Th)

Cruise	Station	^{230}Th Sinking rate	$^{230}Th\sigma_{Sinking}$
1983 CESSAR	stn1	555.0m/yr	256.9m/yr
1987 ARKIV/3	stn1	629.3m/yr	171.0m/yr
1987 ARKIV/3	stn2	778.8m/yr	113.4m/yr
1987 ARKIV/3	stn3	228.5m/yr	313.9m/yr
1987 ARKIV/3	stn4	310.0m/yr	113.4m/yr
1991 ARCTIC EXPEDITION	stn1	1267.9m/yr	308.0m/yr
1991 ARCTIC EXPEDITION	stn2	871.8m/yr	150.6m/yr
1991 ARCTIC EXPEDITION	stn3	470.9m/yr	50.2m/yr
1991 ARCTIC EXPEDITION	stn4	914.1m/yr	104.4m/yr
1991 ARCTIC EXPEDITION	stn5	711.5m/yr	359.6m/yr
1991 ARCTIC EXPEDITION	stn6	497.0m/yr	93.1m/yr
AWS 2000	stn1	1178.6m/yr	2946.5m/yr

Table 2.3: Station Locations, Calculated Sinking Rates and Error(particulate ²³¹Pa)

Cruise	Station	^{231}Pa Sinking rate	$^{231}Pa\sigma_{Sinking}$
1991 ARCTIC EXPEDITION	stn1	1424.7m/yr	915.7m/yr
1991 ARCTIC EXPEDITION	stn2	1240.0m/yr	1267.2m/yr
1991 ARCTIC EXPEDITION	stn3	1205.9m/yr	325.2m/yr
1991 ARCTIC EXPEDITION	stn4	1731.4m/yr	810.2m/yr
1991 ARCTIC EXPEDITION	stn6	559.4m/yr	361.0m/yr

edge that preferential scavenging of ^{230}Th and ^{231}Pa are relative to different marine particles (lithogenic materials and biogenic particles, respectively).

Given the fact that the marine particles accounts for the effect of sinking, one would expect a higher sinking rate of particulate matter at the area where the concentration of biological particles is high. Since the number of oceanic particles are related to the ocean primary production, which is affected by sea ice concentration that controls the light availability in the water, further effort was made to explore the correlations between sinking rates with sea ice concentrations.

2.1.3 CORRELATION WITH SEA ICE CONCENTRATIONS

Historical sea ice concentrations were taken from the sea ice dataset of polar research groups in University of Illinois Urbana-Champaign (http://arctic.atmos.uiuc.edu/SEAICE/).

Since the suspended particles in the deep water must experience a long time for the gains and losses of the radionuclides before it comes to balance, monthly historical ice cover data of each sampling locations was averaged over 2 years before correlated with the corresponding sinking rates.

However, to complete all our knowledge of how the sinking rate changes with the sea ice concentration, we need more data in the areas without the cover of sea ice. For that purpose,

we included sinking rate (500m/yr) of zero ice concentration regions from previous research.

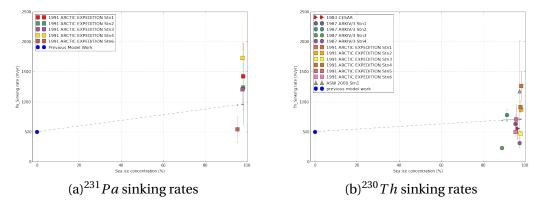


Figure 2.3: The sinking rates were estimated from the particulate data and the steady state analytical solution. Sea ice concentrations came from the historical sea ice dataset of polar research groups, the University of Illinois Urbana-Champaign.

Result is shown in Figure 2.3. Starting at 500m/yr at zero sea ice concentration, the slope of ^{231}Pa in figure 2.3(a) was 6.01 ± 1.92 (m/y%). The overall F-statistic ratio³ is 5.14 and the corresponding p value is 0.09. This p value is slightly higher than 0.05, which suggests that a non-zero slope model might be not suitable. Therefore, a f-test between a zero slope model and a non-zero slope model has to be conducted before making model selection. Let model 1 to be $\hat{s}_1 = \bar{s}$, where the \bar{s} stands for the averaged sinking rate from table 2.3, and model 2 to be $\hat{s}_2 = \alpha'C + \bar{s}$. The p-value turns out to be 3.76×10^{-14} , which is certainly statistically significant and therefore support the idea that the approximation with non-zero slope model is significantly better in describing the realtionship between sea ice concentration and the ^{231}Pa sinking rate.

So for ^{231}Pa , its sinking rate is described as:

$$s = 6.01C + 500m/yr. (2.14)$$

where C is the ice concentration.

The slope for ^{230}Th was 2.26 ± 0.80 (m/y%). The ^{230}Th F-statistic ratio was 7.13 with a low p value, 0.02. The result strongly indicates the confident level linear relationship between sea ice concentration and the k value is ^{230}Th significant.

So the sinking rate of ^{230}Th is parameterized as a function of sea ice concentration:

$$s = 2.26C + 500m/yr. (2.15)$$

where C is the ice concentration.

³The overall F-statistic is used as a preliminary test of the significance of the model prior to performing model selection. For the overall F-statistic, null hypothesis H_0 is all non-constant coefficients in the regression equation are zero while the alternate hypothesis is at least one of the non-constant coefficients in the regression equation is non-zero. The F ratio is obatain by the same equation we used before (equation 2.12). In our case, the overall F-statistic value is generated by the weighted least square module in python statsmodels.

2.2 SCAVENGING COEFFICIENTS

Scavenging coefficients, k and k_{-1} , are applied to describe the how rapidly the element adsorbs onto falling particles and desorbs back to water column. To parameter k and k_{-1} , we should take a look back on equation 1.6. Reorganzing it gives:

$$x_d = \frac{k_{-1}}{k} \frac{Q}{s} z + \frac{Q + k_{-1} C_1}{k},$$
(2.16)

Assuming the regression function is given in the form of $\hat{y} = ax + b$, the slope will be equal to:

$$a = \frac{k_{-1}}{k} \frac{Q}{s},\tag{2.17}$$

while the intercept, b, can be described as:

$$b = \frac{Q + k_{-1}C_1}{k}. (2.18)$$

Solving the equation above gives the values of k and k_{-1} :

$$k_{-1} = \frac{aks}{Q},\tag{2.19}$$

$$k = \frac{Q^2}{Qb - asC_1},\tag{2.20}$$

where C_1 is equal to the intercepts obtained from the previous regressions (figure 2.2). The uncertainty of k and k_{-1} follows the equations below:

$$\sigma_{k} = \left| \frac{\partial k}{\partial b} \right| \sigma_{b} + \left| \frac{\partial k}{\partial C_{1}} \right| \sigma_{C_{1}} + \left| \frac{\partial k}{\partial a} \right| \sigma_{a} + \left| \frac{\partial k}{\partial s} \right| \sigma_{s}, \tag{2.21}$$

$$\sigma_{k_{-1}} = \left| \frac{\partial k_{-1}}{\partial k} \right| \sigma_k + \left| \frac{\partial k_{-1}}{\partial a} \right| \sigma_a + \left| \frac{\partial k_{-1}}{\partial s} \right| \sigma_s, \tag{2.22}$$

The regressions $\hat{y} \approx f(z)$ were shown in figure 2.4. The corresponding k and k_{-1} rates were shown in table 2.4.

2.2.1 PARAMETERIZE ABSORPTION RATE (k)

To further parameterize k and k_{-1} with the numbers in table 2.4 and 2.5, we should realize the absorption and desorption are two different processes that should be parameterized separately. In the this section, we will parameterize absorption rate first and then move to desorption rate in the next section.

⁴The unusually huge error is mainly given by the particulate non-linear vertical profile.

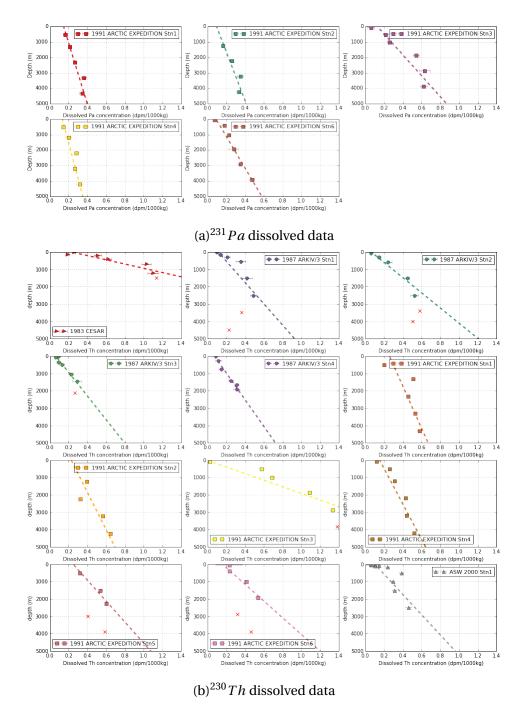


Figure 2.4: The points are the observed dissolved data and the lines are given by the weighted least squares regression. The cross stands for the data that is not taken into consideration since it was affected by currents which could tell from the non-linear shape.

Table 2.4: Station Locations, Calculated Scavenging Coefficients (^{230}Th)

Cruise	Station	^{230}Th k rate	$^{230}Th\sigma_k$	$^{230}Th \ k_{-1}$ rate	$^{230}Th\sigma_{k_{-1}}$
1983 CESAR	stn1	0.06/yr	0.04/yr	1.11/yr	1.51/yr
1987 ARKIV/3	stn1	0.16/yr	0.09/yr	0.63/yr	0.62/yr
1987 ARKIV/3	stn2	0.14/yr	0.07/yr	0.90/yr	0.68/yr
1987 ARKIV/3	stn3	0.38/yr	0.14/yr	0.47/yr	0.31/yr
1987 ARKIV/3	stn4	0.39/yr	0.33/yr	0.59/yr	0.77/yr
1991 ARCTIC EXPEDITION	stn1	0.07/yr	0.03/yr	0.27/yr	0.28/yr
1991 ARCTIC EXPEDITION	stn2	0.09/yr	0.04/yr	0.29/yr	0.25/yr
1991 ARCTIC EXPEDITION	stn3	0.14/yr	0.07/yr	1.30/yr	0.88/yr
1991 ARCTIC EXPEDITION	stn4	0.13/yr	0.03/yr	0.44/yr	0.22/yr
1991 ARCTIC EXPEDITION	stn5	0.07/yr	0.04/yr	0.33/yr	0.42/yr
1991 ARCTIC EXPEDITION	stn6	0.11/yr	0.04/yr	0.44/yr	0.32/yr
AWS 2000	stn1	0.05/yr	$0.12/{\rm yr}^4$	0.40/yr	$1.98/{ m yr}^4$

Table 2.5: Station Locations, Calculated Scavenging Coefficients (²³¹Pa)

Cruise	Station	^{231}Pa k rate	$^{231}Pa\sigma_k$	$^{231}Pa\ k_{-1}$ rate	$^{231}Pa\sigma_{k_{-1}}$
1991 ARCTIC EXPEDITION	stn1	0.010/yr	0.005/yr	0.305/yr	0.403/yr
1991 ARCTIC EXPEDITION	stn2	0.010/yr	0.012/yr	0.316/yr	0.783/yr
1991 ARCTIC EXPEDITION	stn3	0.005/yr	0.001/yr	0.328/yr	0.287/yr
1991 ARCTIC EXPEDITION	stn4	0.009/yr	0.004/yr	0.281/yr	0.314/yr
1991 ARCTIC EXPEDITION	stn6	0.015/yr	0.013/yr	0.336/yr	0.548/yr

For the absorption rate, because the spatial variation in productivity and particle flux affects the absorption intensity, correlation between sea ice concentration and k values was investigated.

Similar with the parameterization to the sinking rate, the value of k from previous model work was included and used as the value of zero ice concentration regions $(0.06 \pm 0.02 \ yr^{-1})$ for ^{231}Pa ; $0.75 \pm 0.25 \ yr^{-1}$ for ^{230}Th).

Figure 2.5 shows the removals of the isotopes would be less intensive in the area of higher sea ice concentration. The slope of $\hat{k} \approx f(C)$, where C is the sea ice concentration, turned out to be $-0.0005~(yr\%)^{-1}$ for ^{231}Pa and $-0.0067~(yr\%)^{-1}$ for ^{230}Th . Both of them has a close-to-zero error. Their p-values of the overall F-statistic are 2.15×10^{-6} and 7.40×10^{-15} respectively. Since these p-values are less than the significance level, which indicates a significant relationship between sea ice concentrations and absorption rate, we can parameter the k value as a function of sea ice concentration: For ^{231}Pa ,

$$k = -0.0005C + 0.06\gamma r^{-1} \tag{2.23}$$

For ^{230}Th ,

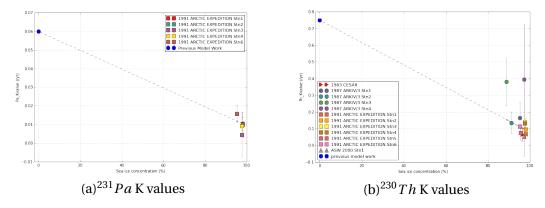


Figure 2.5: The k values were estimated from equation 2.20.

$$k = -0.0067C + 0.75yr^{-1}. (2.24)$$

where C is the sea ice concentration.

2.2.2 PARAMETERIZE DESORPTION RATE (k_{-1})

Different from the absorption rate, desorption rates are independent of the particle concentrations [*Clegg, S. L., Bacon, M. P.* (1991)]. Therefore, it is inappropriate to correlate the desorption rates with sea ice concentrations.

Note that there are wide variations in the ^{230}Th desorption rate in the Arctic. The method to parameterize k_{-1} of ^{230}Th is to find the basin scale difference by interpolating⁵ the desorption rates in the Arctic based on the k_{-1} value in table 2.4.

The interpolation was shown in figure 2.6. This result suggests high k_{-1} in the Alpha Ridge and Lomonosov Ridge, slightly high k_{-1} in the Nansen-Gakkel Ridge and low k_{-1} in Canada biasin, Nansen Basin and Amundsen Basin.

Different from ^{230}Th , the five ^{231}Pa stations exhibit a small variation in desorption rates (table 2.5). In addition, we do not have data in the western Arctic to support a basin scale difference idea, we thus assume the release of ^{231}Pa by the particulate matter is approximately uniform in the Arctic. Therefore, its desorption rate is set to be a constant, $k_{-1} = 0.31$. The value is given by the averge ^{231}Pa k_{-1} value in table 2.5.

REFERENCES

[Clegg, S. L., Bacon, M. P. (1991)] Application of a generalized scavenging model to thorium isotope and particle data at equatorial and high latitude sites in the Pacific Ocean. Journal of Geophysical Research: Oceans (1978-2012), 96(C11), 20655-20670.

⁵The interpolation used PyKrige 0.1.2 Python package.

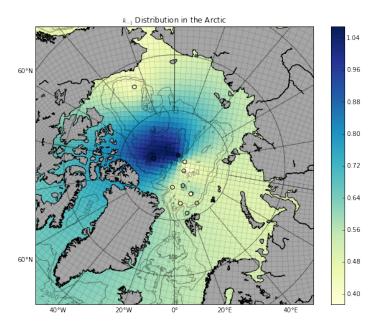


Figure 2.6: The $^{230}Th\ k_{-1}$ values (/yr) in the Arctic. The colour of points shows the calculated value of k_{-1} , which could be referred from table 2.4.