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COMPARISON OF SOURCE APPORTIONMENT OF PARTICLUATE POLLUTANTS AT DIFFERENT PARTS OF TURKEY

Güray Doğan, Ebru (Yörük) Tuna and Gürdal Tuncel

Middle East Technical University, Department of Environmental Engineering, 06531 Ankara, Turkey, gdogan@metu.edu.tr

ABSTRACT

In this study, a receptor oriented method, positive matrix factorization (PMF) is used for the apportionment and quantification of the sources in the Mediterranean, Black Sea and Central Anatolia regions. The results of the PMF analyses showed that aerosol at the Black Sea, Central Anatolia and Mediterranean atmosphere consists of 8, 6 and 7 components, respectively. Two of these components, namely a crustal component and a long range transport component are common in all three stations. Three factors, namely a fertilizer factor, which is highly enriched in NH_4^+ ion, a sea salt component and an arsenic factor are common in the Mediterranean and the Black Sea aerosols. The rest of the factors analyzed in each station are considered as site specific. A second crustal component and a metal factor are distinct sources identified in the Antalya region. The specific sources of Amasra region are three metal factors. The other sources identified at the Çubuk station are identified as motor vehicle source, mixed urban factor, NO_3^- factor and Cd factor.

Key Words: Positive Matrix Factorization, Mediterranean, Black Sea, Central Anatolia, Aerosol

1. INTRODUCTION

Turkey is located in the center of Asia, Africa and Europe and is affected from different emission variations of these three continents. Europe, Eastern Asia (Russia and Ex-Russia) countries and Middle East region are taken into consideration with their high industrial emissions. The emissions from Africa are mainly the transport of Saharan dust to the neighbor countries to the Mediterranean Sea. Therefore, it is essential to determine the source profiles of each sub-region of Turkey to understand the differences and similarities in the source types affecting each region.

In order to determine the source profiles, a receptor oriented method, called Positive Matrix Factorization (PMF) is used. Recently, PMF is most commonly used source apportionment tool instead of Conventional Factor Analysis (CFA) and Principle Component Analysis (PCA). The main advantages of PMF over the other receptor oriented methods are: (1) It utilizes information more efficiently by using error estimates of the measured parameters. (2) It separates sources with better resolution than CFA. (3) Its positive loadings and scores are much more useful for chemical

mass balance models (Huang, 1999). (4) Quantitatively, the factor mass profiles produced by the PMF model can apportion them among the factors in a more reasonable manner. (5) PMF can feed subjective information into factor analysis by using enforced rotation techniques (Qin et al., 2002) and (6) handling of missing and below detection limit values are much better than handling of these values in FA.

PMF uses a weighted least-squares fit with the known error estimates of the elements of the data matrix used to derive the weights. It produces quantitative non-negative solutions which can be written as:

$$X = GF + E \tag{1}$$

or by using the element-wise notation, bilinear factor analytic model is written as:

$$x_{ij} = \sum_{h=1}^{p} g_{ih} f_{hj} + e_{ij} \tag{2}$$

where X is known i x j matrix of the j measured chemical species with species in i samples. G is an i x h matrix of source contributions of the samples (time variations). The F is an h x j matrix of the source compositions (source profiles). E is the residuals matrix, i.e., the difference between the measurement X and the model as a function of the factors G and F.

Based on the standard deviation values of each data point PMF computes individual error estimates for each observed data point. This feature of PMF makes the missing and below detection limit data to be handled by adjusting the corresponding error estimates.

In this article, source profiles of stations located at the Mediterranean coast, Black Sea coast and Central Anatolia are compared.

2. EXPERIMENTAL

The locations of sampling stations are given in Figure 1. The Mediterranean station is located on the Mediterranean coast of Turkey, approximately 20 km to the east of the city of Antalya (31.0ºE, 36.8ºN). The station is located on a rock structure at a height of 20 meters above sea level. In this study, results of 1992 and 1993 aerosol samples will be discussed. During this period, approximately 600 daily aerosol samples were collected.

The Black sea station is located at Bartın, Amasra (32.3^{o}E, 41.5^{o}N), 3 km away from the Black Sea coast of Turkey, between April 1995 and July 1997. Data, which consists of concentrations of approximately 40 elements and ions in 354 daily aerosol samples collected on the Black Sea coast of Turkey, were used.

The Central Anatolia station is located at Çubuk, which is approximately 50 km away from the city of Ankara (33.10^{o}E, 40.10^{o}N). Çubuk station is the only operational EMEP station in Turkey. The station is operated by the Ministry of Health and collected data is delivered to the EMEP secretariat, where it is entered to the EMEP data base. The station became operational in 1992 and air and

precipitation samples are being collected since 1993. In this study, aerosol samples collected between February 1993 and December 2000 were used.

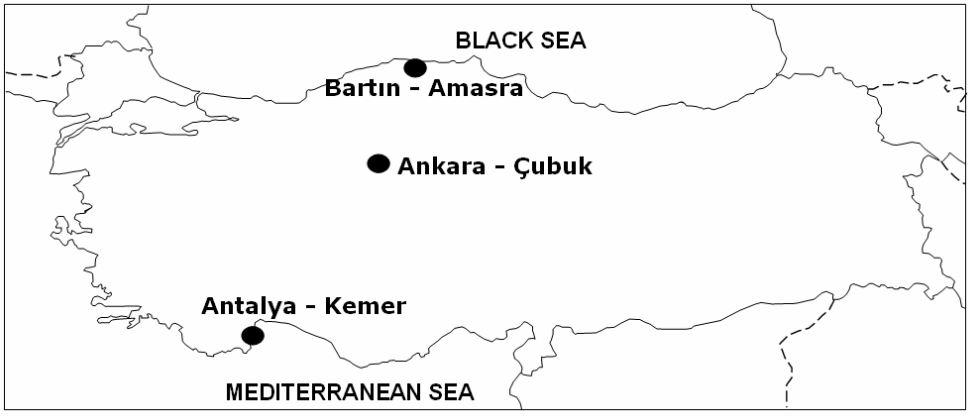


Figure 1. Locations of the sampling stations

During this time period 1806 daily aerosol samples were collected. Aerosol samples were analyzed in the laboratories of Ministry of Health, Refik Saydam Hygiene Center.

A detailed discussion of sampling and analytical methodology is discussed elsewhere (Güllü et al., 1998). Sampling at Antalya and Amasra stations were done using a Sierra Anderson Model SAUV-10H PM-10 High Volume Air Sampler, where atmospheric particles are collected on Whatman-41 cellulose filters. In these two stations, the analysis of the samples were done using atomic absorption spectrophotometer (AAS), ion chromatography (IC), VIS-spectrophotometer and instrumental neutron activation (INAA) methods. Except INAA analysis, the other analyses of these two stations are carried in our laboratories. The INAA analyses were performed in Massachusetts Institute of Technology. For Amasra and Antalya stations, since the elemental concentrations of aerosols are low, a quality control program is applied. This program includes preparation of samples, analyses of blank samples, SRM analyses, parallel analyses and re-analyses of certain samples.

In the Central Anatolia station, the samples were collected with Hi-Vol samplers on cellulose filters. The gas phase pollutants, SO_2, HNO_3 and NH_3, sampling are done using specific chemical impingements. All of the samples collected in this station are analyzed by the Ministry of Health, Refik Saydam Hygiene Center Laboratory. The analysis of the samples was done using AAS, IC and VIS-spectrophotometer. For Çubuk station, an EMEP Quality Assurance manager at the Chemical Coordinating Center and a National Quality Assurance manger of Turkey are responsible for implementing harmonized quality assurance system, including documentation of standards and reference materials.

The global minimum of the PMF solutions were tested by using different seeds for the pseudo-random initial values (Kim et al., 2004). In this study robust mode was

used to reduce the influence of possible outliers on the PMF solution. That is, a data point is processed as an outlier if the residual exceeds α times the standard deviation (Song et al., 2001). The α value of 2.0 was used for Antalya and Amasra data sets where as of 4.0 was used for the Çubuk station. To control the rotations a parameter called FPEAK is used in the PMF algorithm. PMF is run several times with different FPEAK values to find out a range within which the objective function Q value does not change much. The final acceptable rotations were determined by trial and error and based on the evaluation of the resulting source profiles (Song et al., 2001).

The success of PMF strongly depends on the estimated uncertainties for each data values. The uncertainty estimation provides a useful tool to decrease the weight of missing and below detection limit data in the solution as well as to account for the variability in the source profiles. The concentrations values were used for the measured data and the error estimate, S_{ij} for the measured concentration, X_{ij}, of chemical component j in sample i was calculated using the formula (Qin et al., 2002):

$$S_{ij} = T_j + U_j \sqrt{\max\left(\left|X_{ij}\right|, \left|Y_{ij}\right|\right)} + V_j \max\left(\left|X_{ij}\right|, \left|Y_{ij}\right|\right) \qquad (3)$$

where Y_{ij} is the fitted value for X_{ij} using a PMF and T, U and V are matrices of same size as the observed matrix X. Different approaches are available to estimate uncertainties in measured values. In some researches sum of analytical uncertainty with the one third of the detection limit were also used for the measured value error estimate. Values below detection limit were replaced by half of the detection limit values and their overall uncertainties were set at 5/6 of the detection limit values. Missing values were replaced by the geometric mean of the measured values and their accompanying uncertainties were set at four times this geometric mean values.

To be able to figure out the most reasonable solution, 3 to 10 factor run solutions are interpreted and for Antalya and Amasra stations, crustal enrichment factors are calculated for each of the solution by using F-Loading values of each factor. For the crustal enrichment factor calculations, in most of the cases, Al is used for the reference element. Explained variance of each element in each factor was also used to identify sources represented by factors. The software also produce so called "G-factor matrix", which consist of factor score values for each factor.

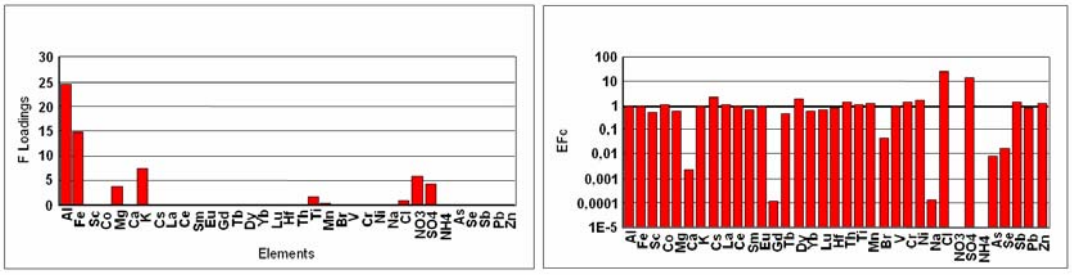
3. RESULTS AND DISCUSSION

For the Antalya station, seven sources were resolved and explained variations of factors are represented in Table 1. To check the correct solution, crustal enrichment factor of the crustal factor is calculated using F-Loading value of Factor 3 and is represented in Figure 2. The EFc calculation is performed by using Mason's reference soil composition (Mason, 1966). Aluminum is used as the reference element for EFc determination. For the soil factor, it is expected to observe EFc values between 1 and 10. As depicted from the figure, the EFc values of elements are generally around unity indicating that this factor is a real crustal factor.

Table 1. Explained Variations of Antalya Factor Results

	PMF 1	PMF 2	PMF 3	PMF 4	PMF 5	PMF 6	PMF 7
NO_3^-				0.52			
SO_4^{2-}				0.75			
NH_4^+	0.97						
Na		0.63					
Mg		0.32					
Al			0.74				
Cl		0.83					
K			0.35				0.26
Ca						0.64	
Sc			0.55			0.28	
Ti			0.65				
V			0.23	0.46			
Cr			0.21		0.52		
Mn			0.51				
Fe			0.6				
Co			0.51				
Ni			0.24		0.28		
Zn				0.49			
As							0.96
Se				0.45			
Br		0.28			0.35		
Sb					0.68		0.16
Cs			0.31		0.2		
La			0.44			0.31	
Ce			0.41			0.36	
Sm			0.41			0.36	
Eu			0.51			0.29	
Gd						0.83	
Tb			0.33			0.34	
Dy			0.59				
Yb			0.46			0.31	
Lu			0.49			0.33	
Hf			0.44			0.37	
Pb					0.23		
Th			0.48			0.30	
%Variance	5.07	7.30	28.00	11.40	9.90	16.40	5.20
Probable Source	Fertilizer	Marine	1st Crustal	1st Anthr.	2nd Anthr.	2nd Crustal	Local Anthr.

Factors 3 and 6 of PMF are two crustal factors with high loadings of crustal elements. However, there are some significant differences in compositions of these two soil factors. Factor 3 has high loadings of elements Al, Sc, Ti, Mn, Fe, Co, and



(a) (b)

Figure 2. The F-Loading and EFc profiles of Antalya crustal factor

rare earths. Factor 6 is another crustal factor. However, this factor has high Ca loading and moderate loadings of Sc and rare earth elements. Loadings of major crustal elements such as Al and Fe are less than 0.2 in this PMF factor, indicating that this is a soil factor enriched with Ca, Sc and rare earth elements. Transport of dust form Saharan to Mediterranean region is well documented (Moulin et al., 1997). Calcium is known to be a good marker element for Saharan Dust (Chiapello et al., 1997).Güllü et al. (2004) have shown that rare earth elements are enriched in transported Saharan Dust particles compared to local dust in the Eastern Mediterranean atmosphere. Based on these previous observations, Factor 6 probably represent atmospheric aerosol transported from North Africa. Factor 3 and Factor 6 explains 28 % and 16.4% of the system variances, respectively. Factor 2 is loaded with Na, Mg, Cl and Br and is a marine factor, representing sea salt component in Eastern Mediterranean aerosol. This factor explains 7.30% of the system variance.

Factor 1 is consisted only of NH_4^+ ion. Previous studies in the same location have clearly demonstrated that NH_4^+ in this region is strongly associated with fertilizer use (Güllü et al., 1998). Consequently Factor 1 in PMF is identified as fertilizer factor. Factor 4 has high loadings of NO_3^-, SO_4^{2-}, V, Zn and Se. This factor is identified as mixed anthropogenic factor, owing coexistence of coal combustion related species, such as SO_4^{2-}, Se, oil combustion related element V and Zn which is an element generally associated with industrial activities. Factor 5 has high loadings of Cr, Ni, Sb, Br and Pb. This factor is a second mixed anthropogenic factor as it includes well known marker of particles emitted from motor vehicles, such as Pb, Br and elements associated with particles emitted from smelters, such as Cr, Ni, and Sb. The Cr smelter in the city of Antalya, is the most likely candidate for this factor, because, the smelter is located within the city and ant mechanism that brings its emissions to our station is also expected to bring urban emissions. Lead and Br which are indicators of urban plume is also observed in this particular factor. Factor 7 with high loadings of As and Sb is the second anthropogenic factor. This factor is attributed to local anthropogenic emissions. This factor explains 5.20 % of the system variance.

The explained variation profiles of PMF results of Amasra station is depicted in Table 2. The PMF results showed that Black Sea aerosols have eight components. The first factor of Amasra station explains the most of the variance of litophilic elements indicating that this factor is due to re-suspension of soil. The crustal factor explains 24.12% of the system variance. The third factor is highly loaded with Na

and Cl and is identified as marine factor. As well as smaller fraction of variances of NO_3^- ion and crustal elements variances are also explained in this factor.

There are three metal factors identified for Amasra region with different seasonal trends and different elemental composition. The monthly contributions to the metal factors are represented in Figure 3. Elements with mixed sources such as Mn, V, Cr, and Ni are slightly enriched in Factor 3. As observed from the Figure 3a, there is no net seasonal variation for this factor. Factor 5 is the second metal factor with high explained variation of Co. As seen from Figure 4a, Co, Br, Cl, As, Se, Sb and Zn are highly enriched in this factor. Figure 3b indicates that the factor scores are higher during summer period. Factor loading values of Factor 5 is given in Figure 5. In this factor NH_4^+ has the highest concentration; besides NO_3^- and some crustal elements are also in high concentrations. The third metal factor is Factor 8, explaining almost all variance in Zn. As in the case of Factor 2, factor scores of Factor 8 do not show any seasonal variation. All three metal factors explain 19.20% of the system variance.

Factor 4 explains most of the variance in As concentrations. The factor also explains variances of some crustal and anthropogenic elements. Factor scores of this factor are presented in Figure 2d and are higher during winter month, suggesting a local contribution. Factor 6 is a clear SO_4^{2-} factor. The significant part of the variances of SO_4^{2-} and NH_4^+ are explained by this factor. This factor also explains the variances of Sb, Pb and some crustal elements. The EFc values are calculated for this factor and represented in Figure 4b. Chloride, SO_4^{2-}, As, Se, Sb and Zn are enriched in this factor. An important point to note in this factor is that species SO_4^{2-}, As and Se are well documented thermal power plant marker species. Since all power plant marker species are enriched in Factor 6, this factor represents a component derived from power plant emissions. Factor 7 explains variance of Se concentrations. Besides, smaller fractions of variances of other anthropogenic and crustal elements are also explained. This factor is considered as combustion factor.

In Central Anatolia region aerosols are composed of 6 components. The explained variances of factor results are represented in Table 3. Since the number of tracers measured at Çubuk station is less, it is very difficult to interpret the results. Factor 4 is identified as the crustal factor since this factor explains variances of some major litophilic elements like Ca, Mg and K. However, this factor also explains almost all variances of NH_3. Observing NH_3 in a factor can be due to fertilizer volatilization over the region. Consequently, Factor 4 is probably a soil-fertilizer application within Turkey.

Factor 1 explains high variance of NO_2 and low variances of Mg, Ca and HNO_3. This factor can be related to motor vehicle emissions. The main source of Mg and Ca in the atmosphere is the resuspension of soil dust. These parameters are frequently observed to be associated with motor vehicle factors in source apportionment studies, because transport of traffic related pollutants to the receptor also brings road dust to the sampler (Liu et al., 2003). Factor 2 has high concentration of SO_2. The source of

Table 2. Explained Variations of Amasra Factor Results

	PMF 1	PMF 2	PMF 3	PMF 4	PMF 5	PMF 6	PMF 7	PMF 8
NO_3^-	0.08	0.08	0.28	0.16		0.16		
SO_4^{2-}		0.09		0.11		0.51	0.23	
NH_4^+		0.14	0.06		0.08	0.56		0.06
Na			0.64	0.11				
Mg	0.38	0.06	0.23			0.06		
Al	0.67	0.09				0.07	0.05	
Cl			0.75					
K	0.18		0.08	0.31	0.13			
Ca	0.36		0.07			0.11		0.07
Sc	0.68	0.11						
Ti	0.43		0.08	0.07			0.08	
V	0.12	0.12		0.17		0.20		0.10
Cr	0.15	0.16	0.10	0.10				0.13
Mn	0.25	0.31				0.10	0.10	0.08
Fe	0.45	0.25	0.06	0.12				
Co					0.73	0.08		
Ni	0.15	0.13		0.27		0.05		0.08
Zn							0.07	0.90
As				0.83	0.06		0.05	
Se							0.95	
Br	0.09		0.29	0.16		0.13		
Sb		0.06		0.35		0.20		0.07
Cs		0.71			0.14			
La	0.66	0.10						
Ce	0.66							
Sm	0.69	0.12						
Eu	0.19		0.18	0.24				
Tb			0.38				0.29	
Dy	0.26	0.07	0.26					
Yb	0.52						0.10	
Lu	0.63							
Hf						0.44		
Pb		0.12	0.07	0.07		0.26		0.15
Th	0.50				0.25			
%Variance	24.12	8.24	10.96	9.32	5.27	9.09	6.68	5.50
Probable Source	Crustal	1st Metal	Marine	Local Anthr.	2nd Metal	Anthr.	Combust.	3rd Metal

this component is local. Factor 3 includes high variances of SO_4^{2-}, NH_4^+ and Ca. This factor is due to long range transport of pollutants.

Factor 5 and Factor 6 are not very clear. Factor 5 includes primarily NO_3^- and Factor 6 is composed of NH_4^+, HNO_3 and Cd. The variance in the factor is explained mostly by Cd.

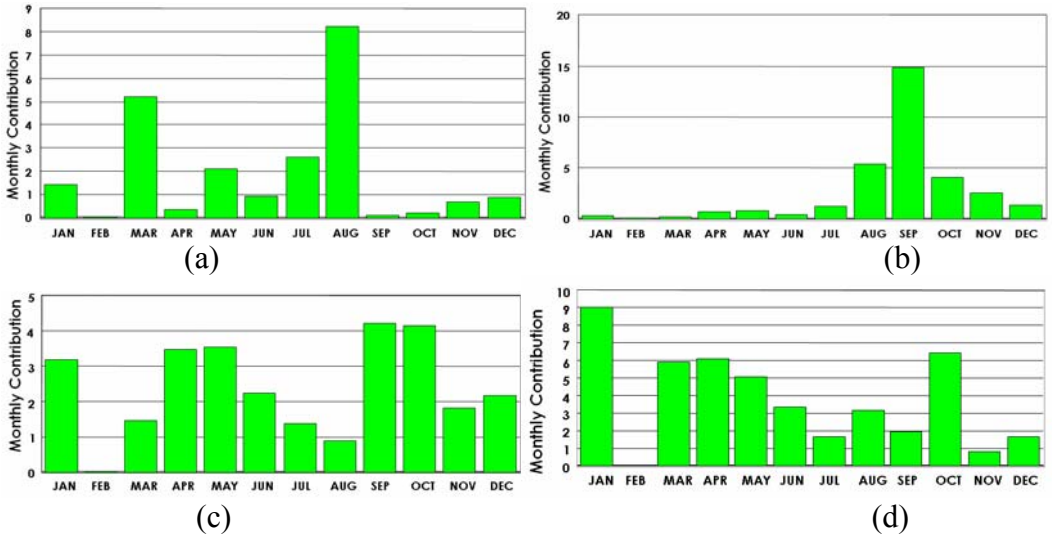


Figure 3. Monthly contributions of (a) Factor 2, (b) Factor 5, (c) Factor 8 and (d) Factor 4 of Amasra Station

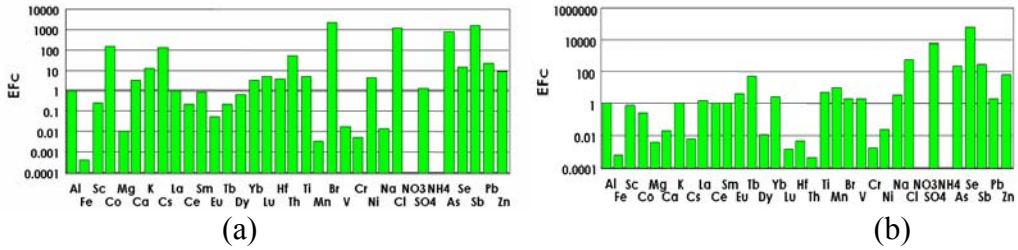


Figure 4. Crustal enrichment factor results of (a) Factor 5 and (b) Factor 6 of Amasra Station

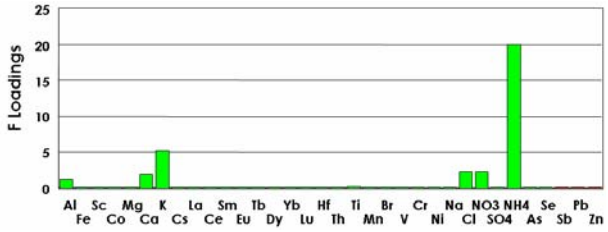


Figure 5. Factor Loading value of Factor 5 of Amasra Station

4. CONCLUSION

The evaluations up to now showed that the measurements that were held in three stations have two similar factors. First one is crustal component which is composed of litophilic elements and the second one is the anthropogenic component, which is mainly composed of SO_4^{2-} and transported to each station site by means of long range transport. The PMF analyses in the Mediterranean and Black Sea regions showed that aside from these three factors, sea salt, arsenic and particles due to use of fertilizer are other common components. However, since the marker elements for the characterization of factors did not measured in Çubuk station, it is impossible to judge on the existence of similar aerosol components in the Central Anatolia region.

The other factors identified in each of the regions are realized to be distinct to each station site.

Table 3. Explained Variations of Çubuk Factor Results

	PMF 1	PMF 2	PMF 3	PMF 4	PMF 5	PMF 6
NO_3^-					1	
SO_4^{2-}			0.93			
NH_4^+			0.50		0.05	0.18
Mg	0.08			0.57		
K				0.42	0.20	
Ca	0.10		0.33	0.29		
Cd						0.95
NH_3				0.89		
SO_2		0.98				
NO_2	0.93					
HNO_3	0.18		0.05	0.15		0.41
% Variance	11.73	8.91	16.45	21.09	11.36	14.00
Probable Source	Motor Vehicle	Mixed Urban Factor	Long range factor	Crustal	NO_3^- Factor	Cd Factor

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