What is "dust"? Three-decade observations of aerosol chemical composition during dust storms over the continental United States

Daniel Tong[1]

[1]George Mason University

March 10, 2024

Abstract

This work presents 30-year observations of dust chemical composition by the IMPROVE network in the United States. Analysis of 1,253 large dust storms detected at the IMPROVE sites shows that dust PM2.5 (particles less than 2.5 micrometers in fresh dust plumes) crustal materials (64%), organic matter (13%), sulfate (7%), nitrate (2%), Cl, Br, and heavy metals. Dust composition stays relatively stable during near source transport. There are distinct spatial variations in dust composition, including high carbon and sulfate in Oklahoma, high Cl in Washington, and high fractions of heavy metals in Arizona. Compared to the Earth's crust, dust PM2.5 contains less crustal elements but more OC, EC, sulfate, nitrate, and halogen elements due to influence by human activities and biogeochemical processes. This rich pool of dust composition data provides useful information to study the roles played by dust in the Earth system and its effects on human society.

Hosted file

`maintext_dust chemical composition_v2.docx` available at https://authorea.com/users/527222/articles/717361-what-is-dust-three-decade-observations-of-aerosol-chemical-composition-during-dust-storms-over-the-continental-united-states

What is "dust"? Three-decade observations of aerosol chemical composition during dust storms over the continental United States

Daniel Tong[1,2]

1. Department of Atmospheric, Oceanic and Earth Sciences, George Mason University, Fairfax, VA 22030 USA
2. Center for Spatial Information Science and Systems, George Mason University, Fairfax, VA 22030 USA

Corresponding author: Daniel Tong, Email: qtong@gmu.edu

For Submission to: Geophysical Research Letter
January 26, 2024

Abstract

This work presents 30-year observations (1988-2022) of dust chemical composition by the IMPROVE network in the United States. Analysis of 1,253 large dust storms detected at IMPROVE shows that dust $PM_{2.5}$ (particles less than 2.5 micrometers in fresh dust plumes) comprises of crustal materials (64%), organic matter (13%), sulfate (7%), nitrate (2%), Cl, Br, and heavy metals. Dust composition stays relatively stable during near source transport. There are distinct spatial variations in dust composition, including high carbon and sulfate in Oklahoma, high Cl in Washington, and high fractions of heavy metals in Arizona. Compared to the Earth's crust, dust $PM_{2.5}$ contains less crustal elements but more OC, EC, sulfate, nitrate, and halogen elements due to influence by human activities and biogeochemical processes. This rich pool of dust composition data provides useful information to study the roles played by dust in the Earth system and its effects on human society.

Plain Language Abstract:

Dust is often treated as a single aerosol component in climate models, but the chemical composition of dust can have profound effects on the role it plays in the Earth system. We applied a unique dust detection approach to identify more than 1,200 large dust storms from a long-term monitoring network called IMPROVE. Examination of these dust storms reveals that dust is not only made of soil materials, but also a large number of other elements, mostly noticeably organic matter (13%), sulfate (7%), nitrate (2%), Cl, Br, and heavy metals. Large spatial variations of dust composition were detected in different regions. Compared to the Earth's crust, dust $PM_{2.5}$ contains less crustal materials but more OC, EC, sulfate, nitrate, and halogen elements due to influence by human activities and biogeochemical processes.

Keyword: dust, composition, mineral, aerosol, observation, IMPROVE

Key points:

1. Profiles of dust chemical composition are constructed from analysis of 1,253 large dust storms detected at the IMPROVE network
2. There are distinct spatial variations in dust composition in the western United States
3. Compared to the Earth's crust, dust $PM_{2.5}$ contains less crustal elements but more nutrients and halogen elements
4. Dust composition stays relatively stable during near source transport

1. Introduction

Soil-originated mineral dust is the most abundant component of atmospheric aerosols on Earth (Satheesh and Moorthy, 2005; Kinne et al., 2006). Dust affects the Earth's climate, atmospheric chemistry, human health and safety, and land and ocean fertility (Bian and Zender, 2003; Okin et al., 2004; Mahowald et al., 2005; Kok et al., 2023; Tong et al., 2023a,b). The extent to which dust influences climate and the environment, however, is determined by not only the abundance and size distribution of dust particles (Kok et al., 2023), but also their chemical composition and mineralogy (Gaston, 2020; Gonçalves Ageitos et al., 2023). Dust composition affects climate directly through shaping refractive index (Sokolik and Toon, 1999) and indirectly from altering particle hygroscopicity and cloud formation (Rosenfeld et al., 2001; Formenti et al., 2011). The composition of dust also controls soluble fraction and bioavailability of nutrients and trace metals in dust deposition and its biogeochemical impacts on marine and terrestrial ecosystems (Jackells et al., 2005; Yu et al., 2015). Dust elements are a major regulator of global aerosol acidity (Freeman et al., 2018) and some, such as Fe and Mn, acts as catalysts in heterogenous reactions that determine chemical pathways of sulfate formation (Bao et al., 2010). Interactions with dust components (Ca^{2+}, Mg^{2+}, etc) increase

tropospheric burden of aerosol nitrate by 44% (Karydis et al., 2016). Heavy metals in dust are regulated carcinogenic and criteria air pollutants that impacts human health adversely (Tong et al., 2023a).

While dust composition is critical to assess climate and environmental effects of dust aerosols, few studies have investigated the chemical composition of dust particles continuously (e.g., Ganor et al., 1991; Hahnenberger and Perry, 2015; Engelbrecht et al., 2016). This work presents 30-year observations of dust chemical composition by the Interagency Monitoring of Protected Visual Environment (IMPROVE) network in the continental United States (CONUS). Originally designed to monitor regional haze over Class I areas (large national parks and wilderness areas designated by the US Clean Air Act), the IMPROVE pioneered global aerosol monitoring to conduct the world's longest continuous measurements of aerosol chemical composition and size distribution (in term of fine and coarse particles) (Malm et al., 1994; Hand et al., 2020). IMPROVE estimates soil or fine dust based on the abundance of five crustal elements (Al, Ca, Fe, Si and Ti) and their normal oxides (Malm et al., 1994). A method has been developed to identify dust storms from the IMPROVE data records using both aerosol size distribution (ratio of $PM_{2.5}$ to PM_{10}, particulate matter less than 2.5 and 10 micrometers in diameter, respectively) and chemical composition (Tong et al., 2012, 2017). The long-term IMPROVE aerosol measurement dataset, combined with the dust detection method, provides a unique opportunity to investigate aerosol chemical composition during dust storms.

2. Method

Aerosol observations at the IMPROVE network

The data of dust chemical composition are extracted from the IMPROVE network. Detailed description of the network can be found in the literature (Malm et al., 1994). Briefly, IMPROVE has been collecting aerosol samples since 1988 at approximately 110

111 locations (the number of sites varies by year), mostly in remote areas, making it
112 preferable for monitoring natural events such as dust storms. All IMPROVE sites used
113 the same instruments, as well as the protocols of sampling and analysis (Malm et al.,
114 1994; Hand et al., 2020, 2023). The network measured total $PM_{2.5}$ and PM_{10} through
115 Gravimetric weighting, 24 elements (Al, As, Br, Ca, Cl, Cr, Cu, Fe, Pb, Mg, Mn, Ni, P, K,
116 Rb, Se, Si, Na, Sr, S, Ti, V, Zn, and Zr) using X-Ray Fluorescence, four ions (Cl^-, NO_3^-,
117 NO_2^- and SO_4^{2-}) using Ion Chromatography, and two Carbon species, organic carbon
118 (OC) and elemental carbon (EC) using Thermal Optical Reflectance and Transmittance.
119 In addition, the IMPROVE dataset also provides nine calculated variables, including
120 fine Organic Matter from Carbon (OMC), fine Sea Salt, fine Soil, Coarse Mass (PM_{10} -
121 $PM_{2.5}$), Reconstructed $PM_{2.5}$ (RCFM), and Reconstructed Total Mass (RCTM). The
122 formulas used to derive these variables can be found in Hand (2023).

123 In order to investigate dust chemical composition, this work includes all explicitly
124 measured elements with a few exceptions. Since chloride (Chl) and Chlorine (Cl) are
125 both measured, only the former is included unless unavailable. For the same reason,
126 Sulfur (S) is excluded since Sulfate (SO_4^{2-}) is included in the analysis. To avoid double
127 counting of the Non-Carbon Organic Matter (NCOM) (NCOM = OMC- OC), OC and
128 NCOM are listed separately, representing the total OMC. Similarly, Non-Chloride
129 SeaSalt (NCSS) is calculated from subtracting Sea Salt by Chloride. Another species,
130 called Others, is added to represent all other chemical components not accounted for.

131 Fine soil, which is often used to represent dust, is calculated in IMPRVOE using a
132 revised formula from Malm et al., (1994) (Hand, 2023):

133 $$\text{Soil} = 2.53 \times [\text{Al}] + 2.86 \times [\text{Si}] + 1.87 \times [\text{Ca}] + 2.78 \times [\text{Fe}] + 2.23 \times [\text{Ti}] \quad (1)$$

134 The soil equation was originally proposed by Malm et al. (1994) to estimate the total
135 mass of soil by summing the major crustal elements, oxygen in their normal oxides, and
136 correction factors for other less abundant compounds. Their correction factors have
137 been increased by 15% based on the findings of Hand et al. (2019) that soil was

underestimated by the Malm (1994) algorithm. This study uses the new Soil formula as in Hand (2023), and lists all five crustal elements (Al, Ca, Fe, Si and Ti) and the Non-Metal OXides (NMOX), which is calculated with the following formula:

$$NMOX = Soil - [Al] - [Si] - [Ca] - [Fe] - [Ti] \quad (2)$$

Identifying dust storms from IMPROVE

Aerosol data during dust storms bear unique chemical and physical fingerprints. Based on the analysis of the aerosol data before, during, and after dust storms observed by satellites, Tong et al (2012) developed five dust indicators, including higher $PM_{2.5}$ and PM_{10} concentrations, lower $PM_{2.5}$ to PM_{10} ratio, higher concentrations and fractions of crustal elements (Si, Ca, Fe and K), lower anthropogenic elements (Zn, Pb and Cu), and low enrichment factors for certain elements. Among these five indicators, the first three are used to identify windblown dust events, while the last two can be helpful to separate natural dust from anthropogenic dust (e.g., road dust, mining/querrying or construction dust).

All IMPROVE data over the continental United States were processed for the period between May 1988 and December 2022 to identify dust events using a revised algorithm from Tong et al. (2012) by imposing the following threshold values: 1) $PM_{10} > 40$ μg/m^3; 2) $PM_{2.5}/PM_{10} < 0.35$; and 3) $Soil/PM_{2.5} > 0.55$. The rationale behind adopting these cutoff values is to ensure these identified events are of large size and/or long duration, close to dust sources, and made predominantly of soil materials. These stringent cutoffs are likely to cause under detection of smaller dust events or events that are large but originated faraway. The identified dust records were further screened based on the abundance and enrichment factors of three anthropogenic elements (Zn, Pb, and Cu) to remove events with anthropogenic influence.

3. Results

Spatial variations of dust composition

From May 1988 to December 2022, a total of 1,253 large dust storms were recorded at the IMPROVE sites, excluding many dust events that either did not meet the criteria or were not measured properly (e.g., missing observations of key elements, carbon species, or ions). This sample size is significantly larger than a previous long-term study in the Middle East (23 dust storms in Isreal) (Ganor et al., 1991) and also at more locations than regional studies or field campaigns (e.g., Fermonti et al., 2003; Hahnenberger and Perry, 2015). Note the term "dust storm" is a meteorological phenomenon, defined as a windblown dust event that causes visibility to drop below 1 km (WHO, 2011; Ardon-Dryer et al., 2023). Although visibility data were not explicitly used in the dust identification method, the requirement of 24-hour average PM_{10} concentrations above 40 $\mu g/m^3$ is assumed to meet such a criterion.

Table 1 lists the abundance of measured elements/ions and selected aggregate components (fine soil, sea salt and organic matter) during these dust storms. The majority of the dust storms were detected in two desert regions, including Arizona (507) in the Sonoran Desert and Texas (135) and New Mexico (108) in the Chihuahuan Desert. A significant number of dust storms were also detected in California (93), mostly in the Mojave Desert and Central Valley, Washington (70) over the Columbia Plateau, and Colorado (59) over the Colorado Plateau and eastern farming areas. There were only 14 dust storms in Nevada, suggesting an under detection of dust activity in the vast Great Basin Desert, due largely to only two active IMPROVE sites deployed near the state borders during this study period (see Figure 1 of Hand, 2023).

Across all regions, fine soil is the most abundant chemical component of $PM_{2.5}$ during these dust storms, or dust $PM_{2.5}$. On average, fine soil accounts for 64.34% of dust $PM_{2.5}$ over the CONUS (Table 1). Among the five crustal metals used to calculate fine soil (Malm et al., 1994), Si is the most abundant element, contributing an average of 14.49% to dust $PM_{2.5}$, followed by Al (6.02%), Ca (4.04%), Fe (3.40%) and Ti (0.33%). The

192 average Si abundance is also close to the level (18%) measured during 23 dust storms in
193 Israel (Ganor et al., 1991) and the 14% (3%-26%) in resuspended dust $PM_{2.5}$ reported in a
194 global study (Engelbrecht et al., 2016). Non-metal oxides (NMOX), mostly made of
195 oxygen and to a much less extent other metals, contribute 36.06% to dust $PM_{2.5}$,
196 reflecting the fact that oxygen is the richest element in Earth's crust (Taylor, 1964). The
197 contribution of fine soil varies considerably from region to region, ranging from 59.09%
198 in Oklahoma to 75.53% in Colorado. The high percentage of fine soil in Colorado is
199 attributed to above average levels of Si (18.12% vs 14.49% on average) and Al (7.50% vs
200 6.02%), while the concentrations of Ca, Fe and Ti remain close to the average levels.
201 Organic matter (OM) is the second abundant chemical component of dust $PM_{2.5}$ in
202 all regions except Washington. OM includes both organic carbon (OC) and non-carbon
203 OM, which represents the non-carbon portion of the OM, mostly oxygen and hydrogen.
204 OC contributes 7.01% and NCOM 5.60%, with a total of 12.62%, to dust $PM_{2.5}$. The OC
205 fraction is the highest in Oklahoma (8.88%), and the lowest in Washington (1.76%).
206 Although dust OC originates from both parent soils and biomass burning, the low OC
207 content in Washington dust argues against a significant contribution of wildfires in the
208 Northwestern United States (McClure and Jaffe, 2018) to dust chemical composition in
209 the past 30 years. The OM content is much higher than the 3% in eolian dust and
210 surface sediments from northwest Africa (Lepple and Brine, 1976), and OC was not
211 detected in Saharan air layer (Formenti et al., 2003). Besides OM, the fraction of
212 Elemental Carbon (EC) is generally less than 0.01 or 1%, with the highest again in
213 Oklahoma and the lowest in Nevada.
214 Sulfate (SO_4^{2-}) is the third largest component, contributing an average of 7.03% to
215 dust $PM_{2.5}$. The percentage of sulfate is low in Colorado (4.01%) and Nevada (4.27%),
216 and the highest in Oklahoma (9.64%). Nitrate (NO_3^-) and nitrite (NO_2^- or N_2) make 2.47%
217 and 0.11% of dust $PM_{2.5}$, respectively. The other measured ion, Chloride (Chl^-),
218 contributes less than 1% to dust $PM_{2.5}$, but with considerable spatial variations. The

fraction is low in southern Central US, including Colorado (0.26%), Oklahoma (0.39%) and Texas (0.41%), but reaches 2.94% in Nevada and 6.89% in Washington. In contrast, Potassium (K) is relatively evenly distributed across all regions, ranging from 1.31% to 1.92% with a national average of 1.83% of total dust $PM_{2.5}$. This is unexpected given the high solubility of K and uneven contributions from soil wind erosion (Gillett and Passi, 1988) and biomass burning (McClure and Jaffe, 2018).

Dust $PM_{2.5}$ also contains many heavy metals and other elements that are considered hazardous air pollutants (HAPs). These elements, in the highest to lowest order, include Mn, Sr, Zn, Cu, Pb, V, Zr, Rb, As, Cr, Ni and Se. Their abundance falls into in the order of 10s to 100s of parts per million (ppm). Three of these elements (Mn, Zr and Cr) show little spatial variations, while the other elements display large differences in their abundance, often varying by a factor of 3 or more. The fractions of Zn, Cu, Pb, and As are much lower than the national levels in Washington and Nevada. Arizona dust shows the highest levels of these heavy metals. For example, As, a Group-A carcinogen and all forms of which are considered a serious risk to human health, is three-fold more abundant in Arizona dust than that in Colorado, New Mexico, or Washington. The As level in the North America dust is on average 16-fold of that in Israel (Ganor et al., 1991). The fraction of As in the Earth's crust is only 1.5 ppm or 0.00015% (Taylor, 1964). Dust from all regions contains 14- to 40-fold more As than the crust, suggesting substantial anthropogenic enrichment.

242 Table 1. Chemical compoisition of airborne soil particles (dust) at IMPROVE ground
243 monitoring sites

Species/ST	AZ	CA	CO	NM	NV	OK	TX	UT	WA	All[1]
DataNum	507	93	59	108	14	42	135	28	70	1253
Soil[2]	64.047	61.521	75.528	59.3793	64.805	59.092	66.573	64.982	60.838	64.342
SeaSalt[3]	1.5681	1.777	0.4506	1.27643	5.2941	0.7107	0.7393	1.4368	12.244	1.4689
OM[4]	12.842	13.856	9.4675	12.0525	8.4402	15.983	11.669	10.457	3.1676	12.618
Al	6.0091	5.8432	7.4987	4.9993	4.6335	5.7253	6.3058	5.4923	6.9722	6.0160
As	0.0066	0.0033	0.0024	0.0023	0.0030	0.0025	0.0049	0.0038	0.0021	0.0049
Br	0.0186	0.0195	0.0140	0.0160	0.0114	0.0150	0.0166	0.0181	0.0071	0.0167
Ca	3.9902	3.1020	3.7499	5.7173	7.9023	3.1232	4.6924	5.8502	1.7971	4.0419
EC	0.9962	0.6450	0.3536	0.5775	0.0888	0.9576	0.5155	0.4498	0.3064	0.7764
OC	7.1343	7.6978	5.2598	6.6958	4.6890	8.8797	6.4826	5.8093	1.7598	7.0099
Chl	0.8764	1.0220	0.2555	0.7091	2.9411	0.3948	0.4096	0.7982	6.8857	0.8234
Cr	0.0039	0.0048	0.0053	0.0031	0.0026	0.0042	0.0064	0.0046	0.0055	0.0043
Cu	0.0285	0.0111	0.0036	0.0066	0.0031	0.0058	0.0081	0.0054	0.0065	0.0171
Fe	3.5996	3.2906	3.0765	2.6346	2.5322	3.0499	2.9100	2.9489	3.8079	3.4007
Pb	0.0153	0.0083	0.0067	0.0084	0.0050	0.0080	0.0111	0.0103	0.0057	0.0124
Mg	1.2607	1.7530	1.9135	1.4070	3.2687	0.6707	1.3500	2.3802	0.9986	1.3629
Mn	0.0901	0.0755	0.0695	0.0688	0.0583	0.0631	0.0623	0.0739	0.0636	0.0819
Ni	0.0033	0.0024	0.0026	0.0021	0.0010	0.0022	0.0027	0.0027	0.0034	0.0030
NO3	2.4913	3.6686	1.6115	2.3471	0.7033	3.6017	1.7957	2.4373	2.5410	2.4677
N2	0.1022	0.1180	0.1542	0.0708	0.0445	0.1313	0.1036	0.0515	0.1671	0.1097
P	0.0347	0.0432	0.1275	0.0426	0.3990	0.0218	0.0218	0.0160	0.0063	0.0413
K	1.9015	1.9221	1.9117	1.6950	1.8871	1.5522	1.9539	1.8994	1.3099	1.8337
Rb	0.0094	0.0092	0.0089	0.0085	0.0100	0.0074	0.0106	0.0097	0.0064	0.0091
Se	0.0016	0.0016	0.0008	0.0014	0.0004	0.0035	0.0012	0.0015	0.0016	0.0016
Si	14.2721	14.0904	18.1150	13.0111	14.1296	13.4246	15.2477	14.3235	13.1761	14.4880
Na	1.8119	2.8652	1.5200	2.5488	6.4207	1.1499	2.1531	2.1950	5.6891	2.1376
Sr	0.0333	0.0503	0.0335	0.1233	0.1194	0.0228	0.0501	0.0666	0.0279	0.0452
SO4	6.8475	7.3333	4.0111	9.5238	4.2695	9.6426	6.4558	5.9732	7.8697	7.0255
Ti	0.3445	0.2893	0.3329	0.2526	0.2162	0.3080	0.2842	0.2893	0.4173	0.3310
V	0.0125	0.0122	0.0145	0.0071	0.0069	0.0118	0.0141	0.0088	0.0133	0.0121
Zn	0.0419	0.0338	0.0178	0.0244	0.0141	0.0263	0.0252	0.0213	0.0139	0.0333
Zr	0.0123	0.0092	0.0084	0.0127	0.0101	0.0105	0.0098	0.0105	0.0095	0.0115
NCOM	5.7075	6.1582	4.2078	5.3567	3.7512	7.1038	5.1861	4.6474	1.4078	5.6079
NCSS	0.6916	0.7550	0.1950	0.5673	2.3529	0.3159	0.3297	0.6386	5.3581	0.6455
NCOX	35.8312	34.9053	42.7553	32.7644	35.3907	33.4611	37.1331	36.0777	34.6674	36.0641
Other	5.8201	4.2567	2.7624	8.7945	4.1343	6.3028	6.4466	7.4848	4.6958	4.0676

244

245 1 – All dust events detected in the Continental United States are included.
246 2 – Fine Soil is calculated using Soil = 2.53 × [Al] + 2.86 × [Si] + 1.87 × [Ca] + 2.78 × [Fe] + 2.23 × [Ti]
247 following Hand (2023);
248 3 – Sea salt is calculated using Sea Salt = 1.8 × [Chl];
249 4 – NCOM: Non-carbon organic matter. NCOM = [OMC] – [OC]
250 5 – NCSS: Non-Chloride Sea Salt. NCSS = 0.8 × [Chl]
251 6 – NMOX: Non-Metal OXides. NMOX = Soil - [Al] - [Si] - [Ca] - [Fe] - [Ti]
252

Dust composition and plume aging

Does the chemical composition of dust $PM_{2.5}$ change with the aging of dust plumes? While it is well established that long-range transport can alter aerosol composition through heterogenous chemical reactions (Gaston, 2020), it is unclear if this process occurs within a short distance, such as during a locally detected dust storm. Although the dust detection algorithm used in this study was designed to identify local windblown dust events, the IMPROVE monitors are not always located in the immediate proximity of dust sources. These observations may still represent regionally transported dust events. Here, the ratio of $PM_{2.5}$ to PM_{10} can serve as a proxy of dust plume aging. A smaller ratio indicates a younger plume, since larger particles are heavier and settle faster than smaller ones during transport. For this purpose, all IMPROVE dust records were regrouped based on the $PM_{2.5}$ to PM_{10} ratio into five bins (< 0.05, 0.05-0.10, 0.15-0.20, 0.20-0.25, and 0.25-0.35) to examine the difference in aerosol chemical composition among these ratio bins.

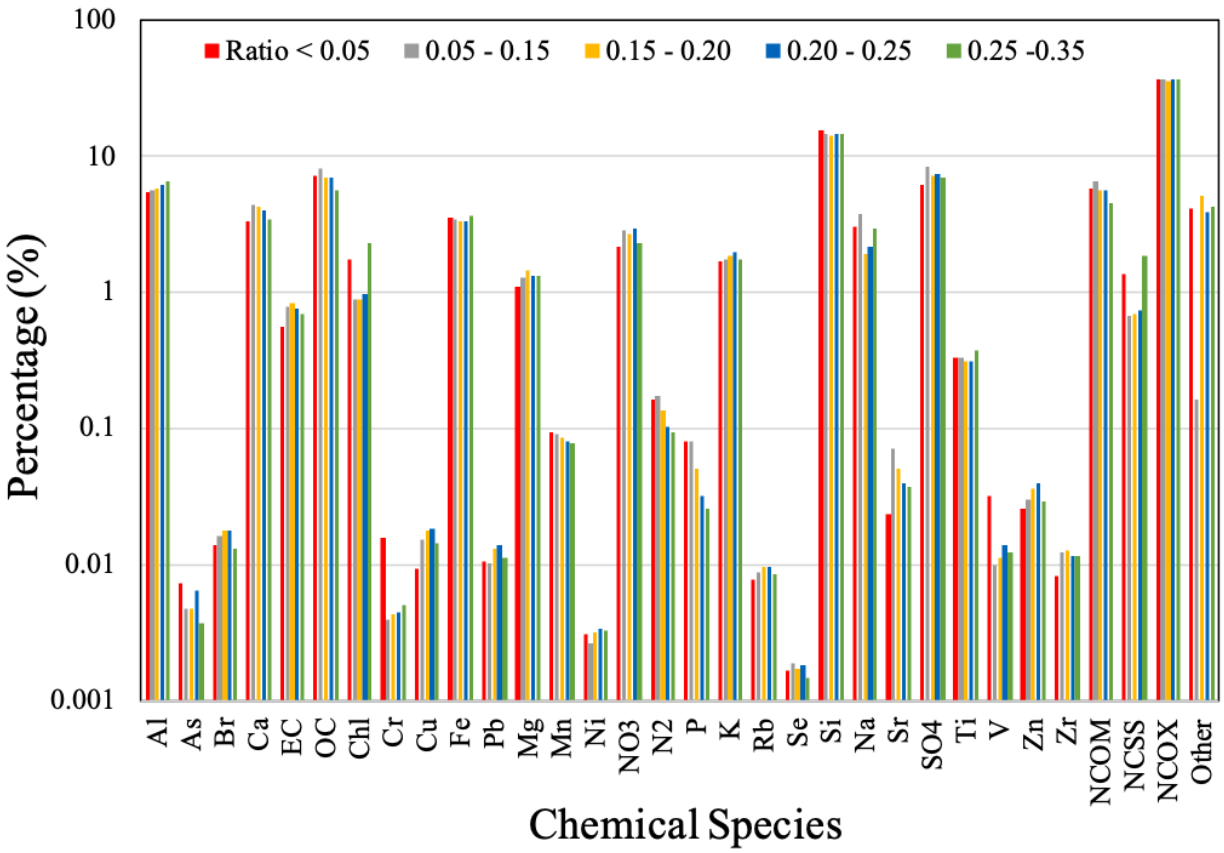

Figure 1. Abundance of dust $PM_{2.5}$ chemical components related to $PM_{2.5}$ to PM_{10} ratio during dust storms observed by the IMPROVE network during 1988 and 2022 in the continental United States. The ratio serves as an indicator of dust plume aging, with a small ratio indicates a young plume.

Most of the dust components do not change with the $PM_{2.5}$ to PM_{10} ratio. The abundance of these components stays constant or with small changes. Al is the only element that shows a consistently increasing trend, although the magnitude of these changes is small. There are two elements (P and Mn) and the NO_2^- ion show a slightly decreasing trend with increasing aging. It is interesting that two elements (Cr and V) are much more abundant in the youngest dust plumes. There were only a small number of dust samples (21) in the smallest ratio bin (ratio < 0.05) compared to these in other ratio bins (154 - 456). This suggests that the chemical composition may have been influenced by a few local events. Further investigation of these events indeed revealed

that there was a dust storm on April 23, 1994 detected at the Great Sand Dune National Park (GRSA1) site during which the Cr and V concentrations reached 1,138 ppm and 3,228 ppm, significantly higher than the average levels of 45 ppm and 120 ppm, respectively.

Overall, the chemical composition of dust particles does not change considerably with the $PM_{2.5}$ to PM_{10} ratio, suggesting the chemical composition of dust $PM_{2.5}$ does not change with plume aging in the short distances between dust sources and IMPROVE monitors, confirming that the method used in this study can extract reliable information of dust chemical composition.

Element enrichment during dust storm

Table 2 lists the concentrations, ratios to Al, and enrichment factors of select elements in the observed dust $PM_{2.5}$. The concentrations of major crustal elements (Si, Al, Ca, Fe, K and Ti) in dust $PM_{2.5}$ are only 50%-75% of that in the continental crust (Taylor, 1964). The concentrations of C (OC + EC), S, N (N content in nitrate and nitrite), and halogen elements (Cl and Br), however, are considerably higher in the dust $PM_{2.5}$ than in the crust.

Mass ratios of elements, an indicator frequently used to identify source regions, are calculated to compare the North America dust to that elsewhere. For major crustal elements, the mass ratios of Si/Al, Ca/Al, Fe/Al, K/Al, Ti/Al, referred as mineral-to-aluminum (MAL), measured at IMPROVE are 2.3, 0.61, 0.56, 0.29 and 0.06, respectively. These values are close to the observed MAL mass ratios (2.03, 0.45, 0.54, 0.21, 0.052, respectively) in a Sahara dust layer during the Saharan Dust Experiment (SHADE) airborne campaign (Formenti et al., 2003). SHADE measured only a few elements in the fine fraction, so the ratios in the coarse fraction are used when the elements are not measured for fine dust, assuming similar ratios between the two fractions (Formenti et al., 2003; Hahnenberger and Perry, 2015). These ratios are also comparable to these at

upper continental crust (Taylor 1964) and a large number of dust samples in major dust source regions compiled by Liu et al., (2019) (Table 2 therein). The differences in ratios are generally larger for minor elements. For examples, the ratios to Al for Sr and Zn are 0.0003 and 0.0054 in the IMPROVE dust, while these ratios for Saharan dust are 0.0070 and 0.0017. The larger variations for these minor elements are likely caused by both natural abundance and anthropogenic influence of parent soils (Formenti et al., 2011).

To illustrate to the levels of differences, enrichment factors are calculated for select elements. An enrichment factor is defined as the ratio of Element X to a reference element (X_{ref}, usually Si, Al, Fe or Ca) in dust $PM_{2.5}$ divided by that in the average upper continental crust, following Taylor and McLennan (1985):

$$EF_X = (X/X_{ref})_{dust} / (X/X_{ref})_{crust} \quad (3)$$

The enrichment factor technique is an accepted way to characterize aerosol provenance, but with its limitations, such as the factors may vary drastically for minor soil elements (Hahnenberger and Perry, 2015). Nevertheless, it provides a useful measure to assess if samples are enriched for some elements and their differences between source regions. Enrichment factors are calculated using both Si and Al as the reference elements, yielding similar values for most of the elements (Table 2).

Most of these elements are considered not enriched (enrichment factor < 2.5), consistent with that reported in earlier studies. This group includes all major crustal elements (Si, Al, Ca, Fe, K and Ti), and Cr, Mg, Mn, Ni, P, Rb, Na, Sr, V and Zr. There are three elements Cr, Ni and P, of which the enrichment factors are smaller than unity. The lowest value is for P (0.7 of EF-Si or 0.48 of EF-Al), which is much lower than that reported in the Great Salt Lake, Middle East, Sahara or elsewhere (Ganor et al., 1991; Rahn et al., 1979; Hahnenberger and Perry, 2015). Elements with anthropogenic origins, such as As, Cu and Pb, have higher enrichment factors (51.25, 5.63 and 19.36, respectively). S, Cl and Br show very large enrichment factors, ranging between 180.03 and 238.14. The factors for both halogen elements are 5-10 times of that reported in

Israel (Ganor et al., 1991), but lower than that in both fine and coarse dust observed over the Great Salt Lake, Utah, USA (Hahnenberger and Perry, 2015). The highest enrichment factors are found for C, N and Se, all higher than 700. Note these are the average values calculated from more than 1,200 dust storms. The values of enrichment factors can be significantly higher for individual events, such as the 1994 Great Sand Dune National Park dust storm. In addition, the enrichment factors of minor elements in fine dust are usually higher than in coarse dust, although this is not the case for many major elements (Hahnenberger and Perry, 2015).

Table 2. Chemical composition (%), mass ratios (X/Al), and enrichment factors (EFs) of select elements in the dust $PM_{2.5}$ over the continental Untied States using Si and Al, and Fe as the reference element, and comparisons to crustal elements from Taylor (1964), EFs in Israel from Ganor et al. (1991), and EFs in the World from Rahn et al. (1979).

Element	Dust $PM_{2.5}$ (%)	X/Al	Crust (%)	EF (Si)	EF (Al)	EF (Al) Isreal	EF (Al) World
Al	6.2299	1.0000	8.23	1.46	1.00	1.00	1.00
As	0.0048	0.0008	0.00018	51.25	35.03	3.05	310.00
Br	0.0157	0.0025	0.00025	121.71	83.19	9.06	-
Ca	3.7950	0.6092	4.15	1.77	1.21	6.83	2.80
C	7.2516	1.1640	0.02	700.75	478.99	-	-
Cl	1.6017	0.2571	0.013	238.12	162.77	30.60	-
Cr	0.0048	0.0008	0.01	0.92	0.63	1.66	8.10
Cu	0.0160	0.0026	0.0055	5.63	3.85	1.05	102.00
Fe	3.5131	0.5639	5.63	1.21	0.82	1.18	2.10
Pb	0.0125	0.0020	0.00125	19.36	13.23	10.20	-
Mg	1.3434	0.2156	2.33	1.11	0.76	2.17	2.40
Mn	0.0818	0.0131	0.095	1.66	1.14	1.15	3.90
Ni	0.0032	0.0005	0.0075	0.83	0.57	1.11	-
N	0.6364	0.1022	0.002	566.73	387.38	-	-
P	0.0379	0.0061	0.105	0.70	0.48	4.42	-
K	1.8091	0.2904	2.09	1.67	1.14	0.74	2.00
Rb	0.0090	0.0014	0.009	1.94	1.33	0.98	3.40
Se	0.0017	0.0003	0.000005	647.86	442.83	-	-
Si	14.5653	2.3380	28.15	1.00	0.68	1.23	-
Na	2.6970	0.4329	2.36	2.21	1.51	0.40	4.40
Sr	0.0433	0.0070	0.0375	2.23	1.53	1.63	-
S	2.4220	0.3888	0.026	180.03	123.06	-	-

Ti	0.3471	0.0557	0.57	1.18	0.80	1.62	1.39
V	0.0125	0.0020	0.0135	1.79	1.22	1.34	14.00
Zn	0.0333	0.0054	0.007	9.21	6.29	3.66	2.60
Zr	0.0118	0.0019	0.0165	1.38	0.94	-	-

Conclusion

Chemical composition of dust particles has important implications for their effects on climate, human health, and ecosystems. Three decades of continuous aerosol monitoring at the IMPROVE network resulted in a large pool of dust storm data over the continental United States. Analysis of this rich dataset reveals several interesting features of dust composition. First, what is dust? It is often assumed that dust is a single chemical species, made predominantly of mineral dust or crustal materials. The results show that, at locations near dust sources, dust $PM_{2.5}$ (particles smaller than 2.5 micrometers in a fresh dust plume) is comprised primarily of crustal materials, including crustal elements such as Si, Ca, Al and Fe, and their oxides, together called fine soil. Fine soil, however, accounts for less than two thirds (64%) of total dust $PM_{2.5}$. The rest of dust $PM_{2.5}$ is comprised of organic matter (13%), sulfate (7%), nitrate (2%), Na (2%), halogen and other species. Clearly, soils in North America have been altered so much that there is a distinction between mineral dust and the actual aerosols during a typical dust storm. Fine soil in IMPROVE cannot be used to accurately represent dust particles, since it misses more than one third of other dust components, which may have important public health and climate implications. It is recommended that a factor of 1.5 be applied to the IMPROVE fine soil in order to represent total dust $PM_{2.5}$ to study, for example, dust exposure and health effects.

Does dust composition change with the aging of dust plumes? It is well-known that long-range transport alters chemical composition of dust particles. Our results show that this process does not occur during short-range transport. There are, however, distinct spatial variations in dust composition. The fractions of fine soil, sulfate, OC, halogens and heavy metals in dust $PM_{2.5}$ vary considerably from region to region.

The word "dust" is commonly used to refer to mineral dust originated from the Earth's Crust. Do modern dust particles mimic the chemical composition of crust materials? Compared to the Earth's upper continental crust, dust $PM_{2.5}$ contains lower concentrations of major crustal elements (Si, Al, Ca, Fe, K and Ti), but higher levels of OC, EC, sulfate, nitrate halogen elements (Cl and Br). Most elements are not enriched (enrichment factors < 2.5). The elements of human influence, such as As, Cu, Pb, S, Cl, and Br have higher enrichment factors (between 5 and 238). The highest enrichment factors are found for C, N and Se, all larger than 700. This rich pool of dust composition data provides useful information to study the roles played by dust in the Earth system and its effects on human society.

Acknowledgement

The authors are grateful of the visionary designers of the IMPROVE network that made this work possible. IMPROVE is a collaborative association of state, tribal, and federal agencies, and international partners. US Environmental Protection Agency is the primary funding source, with contracting and research support from the National Park Service. The Air Quality Group at the University of California, Davis is the central analytical laboratory, with ion analysis provided by Research Triangle Institute, and carbon analysis provided by Desert Research Institute. The authors thank Dr. Jenny Hand for insightful discussion in data use.

Open Research

The IMPROVE data is publicly available through the Federal Land Manager Environmental Database (https://views.cira.colostate.edu/fed/Pub/DatasetDetail.aspx?dssl=1&dsidse=10001), which requires login. A copy of the dataset is also available at Zenodo: https://doi.org/10.5281/zenodo.10611046.

Reference

Bian, Huisheng, and Charles S. Zender. "Mineral dust and global tropospheric chemistry: Relative roles of photolysis and heterogeneous uptake." *Journal of Geophysical Research: Atmospheres* 108.D21 (2003).

Chung, Yong-Seung. "On the observations of yellow sand (dust storms) in Korea." Atmospheric Environment. Part A. General Topics 26.15 (1992): 2743-2749.

Engelbrecht, J. P., Moosmüller, H., Pincock, S., Jayanty, R. K. M., Lersch, T., & Casuccio, G. (2016). Mineralogical, chemical, morphological, and optical interrelationships of mineral dust re-suspensions. *Atmospheric Chemistry and Physics*, *16*(17), 10809-10830.

Freedman, Miriam Arak, Emily-Jean E. Ott, and Katherine E. Marak. "Role of pH in aerosol processes and measurement challenges." *The Journal of Physical Chemistry A* 123.7 (2018): 1275-1284.

Formenti, P., Elbert, W., Maenhaut, W., Haywood, J., & Andreae, M. O. (2003). Chemical composition of mineral dust aerosol during the Saharan Dust Experiment (SHADE) airborne campaign in the Cape Verde region, September 2000. *Journal of geophysical research: Atmospheres*, *108*(D18).

Hahnenberger, M., & Perry, K. D. (2015). Chemical comparison of dust and soil from the Sevier Dry Lake, UT, USA. *Atmospheric Environment*, *113*, 90-97.

Ganor, E., Foner, H. A., Brenner, S., Neeman, E., & Lavi, N. (1991). The chemical composition of aerosols settling in Israel following dust storms. *Atmospheric Environment. Part A. General Topics*, *25*(12), 2665-2670.

Gaston, Cassandra J. "Re-examining dust chemical aging and its impacts on Earth's climate." Accounts of chemical research 53.5 (2020): 1005-1013.

Gillette, Dale A., and Ranjit Passi. "Modeling dust emission caused by wind erosion." *Journal of Geophysical Research: Atmospheres* 93.D11 (1988): 14233-14242.

Gonçalves Ageitos, M., Obiso, V., Miller, R. L., Jorba, O., Klose, M., Dawson, M., ... & Pérez García-Pando, C. (2023). Modeling dust mineralogical composition: sensitivity to soil mineralogy atlases and their expected climate impacts. *Atmospheric Chemistry and Physics*, *23*(15), 8623-8657.

Hahnenberger, M., & Perry, K. D. (2015). Chemical comparison of dust and soil from the Sevier Dry Lake, UT, USA. *Atmospheric Environment*, *113*, 90-97.

Hand, J. L., Prenni, A. J., Schichtel, B. A., Malm, W. C., & Chow, J. C. (2019). Trends in remote PM2. 5 residual mass across the United States: Implications for aerosol mass reconstruction in the IMPROVE network. *Atmospheric Environment*, *203*, 141-152.

Hand, J. L., Prenni, A. J., Copeland, S., Schichtel, B. A., & Malm, W. C. (2020). Thirty years of the Clean Air Act Amendments: Impacts on haze in remote regions of the United States (1990–2018). *Atmospheric Environment*, *243*, 117865.

Hand, J., 2023. IMPROVE DATA USER GUIDE 2023 (VERSION 2). Available online at: http://vista.cira.colostate.edu/Improve/wp-

content/uploads/2023/10/IMPROVE_Data_User_Guide_24October2023.pdf (accessed on January 3, 2024).

Jickells, T.D., An, Z.S., Andersen, K.K., Baker, A.R., Bergametti, G., Brooks, N., Cao, J.J., Boyd, P.W., Duce, R.A., Hunter, K.A. and Kawahata, H., 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *science*, *308*(5718), pp.67-71.

Karydis, V. A., Tsimpidi, A. P., Pozzer, A., Astitha, M., & Lelieveld, J. (2016). Effects of mineral dust on global atmospheric nitrate concentrations. *Atmospheric Chemistry and Physics*, *16*(3), 1491-1509.

Kinne, S., Schulz, M., Textor, C., Guibert, S., Balkanski, Y., Bauer, S. E., Berntsen, T., Berglen, T. F., Boucher, O., Chin, M., Collins, W., Dentener, F., Diehl, T., Easter, R., Feichter, J., Fillmore, D., Ghan, S., Ginoux, P., Gong, S., Grini, A., Hendricks, J., Herzog, M., Horowitz, L., Isaksen, I., Iversen, T., Kirkevåg, A., Kloster, S., Koch, D., Kristjansson, J. E., Krol, M., Lauer, A., Lamarque, J. F., Lesins, G., Liu, X., Lohmann, U., Montanaro, V., Myhre, G., Penner, J., Pitari, G., Reddy, S., Seland, O., Stier, P., Takemura, T., and Tie, X.: An AeroCom initial assessment – optical properties in aerosol component modules of global models, Atmos. Chem. Phys., 6, 1815–1834, https://doi.org/10.5194/acp-6- 1815-2006, 2006.

Kok, Jasper F., Trude Storelvmo, Vlassis A. Karydis, Adeyemi A. Adebiyi, Natalie M. Mahowald, Amato T. Evan, Cenlin He, and Danny M. Leung. "Mineral dust aerosol impacts on global climate and climate change." Nature Reviews Earth & Environment 4, no. 2 (2023): 71-86.

Lepple, F. K., and C. J. Brine, Organic constituents in eolian dust and surface sediments from northwest Africa, J. Geophys. Res., 81, 1141– 1147, 1976.

Liu, X., Turner, J. R., Hand, J. L., Schichtel, B. A., & Martin, R. V. (2022). A global-scale mineral dust equation. *Journal of Geophysical Research: Atmospheres*, *127*, e2022JD036937. https://doi.org/10.1029/2022JD036937

Mahowald, Natalie M., Alex R. Baker, Gilles Bergametti, Nick Brooks, Robert A. Duce, Timothy D. Jickells, Nilgün Kubilay, Joseph M. Prospero, and Ina Tegen. "Atmospheric global dust cycle and iron inputs to the ocean." *Global biogeochemical cycles* 19, no. 4 (2005).

Malm, W. C., Sisler, J. F., Huffman, D., Eldred, R. A., & Cahill, T. A. (1994). Spatial and seasonal trends in particle concentration and optical extinction in the United States. *Journal of Geophysical Research: Atmospheres*, *99*(D1), 1347-1370.

McClure, Crystal D., and Daniel A. Jaffe. "US particulate matter air quality improves except in wildfire-prone areas." *Proceedings of the National Academy of Sciences* 115.31 (2018): 7901-7906.

476 Meinander, Outi, et al. "Newly identified climatically and environmentally significant
477 high-latitude dust sources." Atmospheric Chemistry and Physics 22.17 (2022): 11889-
478 11930.
479 Okin, G.S., Mahowald, N., Chadwick, O.A., Artaxo, P., 2004. Impact of desert dust on
480 the biogeochemistry of phosphorus in terrestrial ecosystems. Glob. Bio- geochem.
481 Cycles 18, GB2005. http://dx.doi.org/10.1029/2003GB002145.
482 Pye, H. O. T., Nenes, A., Alexander, B., Ault, A. P., Barth, M. C., Clegg, S. L., Collett Jr., J.
483 L., Fahey, K. M., Hennigan, C. J., Herrmann, H., Kanakidou, M., Kelly, J. T., Ku, I.-T.,
484 McNeill, V. F., Riemer, N., Schaefer, T., Shi, G., Tilgner, A., Walker, J. T., Wang, T.,
485 Weber, R., Xing, J., Zaveri, R. A., and Zuend, A.: The acidity of atmospheric particles
486 and clouds, Atmos. Chem. Phys., 20, 4809–4888, https://doi.org/10.5194/acp-20-4809-
487 2020, 2020.
488 Rahn K. A., Borys R. D., Shaw G. E. and Schutz L. (1979) Long-range impact of desert
489 aerosol on atmospheric chemistry: two examples. In Scope 14: Saharan Dust
490 (Mobilization, Transport, Deposition) (edited by Morales C.), pp. 243-266. John
491 Wiley, Chichester.

492 Rosenfeld, D., Rudich, Y., Lahav, R., 2001. Desert dust suppressing precipitation: a
493 possible desertification feedback loop. Proc. Natl. Acad. Sci. 98, 5975e5980.
494 http://dx.doi.org/10.1073/pnas.101122798.

495 Satheesh, S. K. and Moorthy, K. K.: Radiative effects of natural aerosols: A review,
496 Atmos. Environ., 39, 2089–2110, 2005.

497 Sokolik, Irina N., and Owen B. Toon. "Incorporation of mineralogical composition into
498 models of the radiative properties of mineral aerosol from UV to IR
499 wavelengths." *Journal of Geophysical Research: Atmospheres* 104.D8 (1999): 9423-9444.

500 Taylor, S. R. (1964). Abundance of chemical elements in the continental crust: a new
501 table. *Geochimica et cosmochimica acta*, *28*(8), 1273-1285.
502 Tong, D. Q., Dan, M., Wang, T., and Lee, P., 2012. Long-term dust climatology in the
503 western United States reconstructed from routine aerosol ground monitoring,
504 Atmos. Chem. Phys., 12, 5189-5205, doi:10.5194/acp-12-5189-2012.
505 Tong, D. Q., Wang, J. X., Gill, T. E., Lei, H., & Wang, B. (2017). Intensified dust storm
506 activity and Valley fever infection in the southwestern United States. Geophysical
507 Research Letters, 44(9), 4304-4312.
508 Tong, Daniel Q., William A. Sprigg, Thomas E. Gill, Robert Scott Van Pelt, Alexander
509 Baklanov, Bridget Marie Barker, Jesse Bell, Juan Castillo, Santiago Gassó, Cassandra
510 Gaston, Dale W Griffin, Nicolas Huneeus, Ralph A. Kahn, Arunas P. Kuciauskas,
511 Luis A. Ladino, Junran Li, Olga L. Mayol-Bracero, Orion Z. McCotter, Pablo A.

Méndez-Lázaro, Pierpaolo Mudu, Slobodan Nickovic, Damian Oyarzun, Joseph Prospero, Graciela B. Raga, Amit U. Raysoni, Ling Ren, Nikias Sarafoglou, Andrea Sealy, Ziheng Sun, Ana Vukovic Vimic (2023a). Health and safety effects of airborne soil dust in the Americas and beyond. Reviews of Geophysics, 61(2), e2021RG000763. https://doi.org/10.1029/2021RG000763

Tong, D., I. Feng, T. E. Gill, K. Schepanski, and J. Wang, 2023b: How Many People Were Killed by Windblown Dust Events in the United States? Bull. Amer. Meteor. Soc., https://doi.org/10.1175/BAMS-D-22-0186.1, 104 (5), E1067-E1084

Van Pelt, R. Scott, and Ted M. Zobeck. "Chemical constituents of fugitive dust." *Environmental Monitoring and Assessment* 130 (2007): 3-16.

Yu, H., Chin, M., Yuan, T., Bian, H., Remer, L. A., Prospero, J. M., ... & Zhao, C. (2015). The fertilizing role of African dust in the Amazon rainforest: A first multiyear assessment based on data from Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observations. *Geophysical Research Letters*, *42*(6), 1984-1991.

Zhao, A., Ryder, C. L., and Wilcox, L. J.: How well do the CMIP6 models simulate dust aerosols? Atmos. Chem. Phys., 22, 2095–2119, https://doi.org/10.5194/acp-22-2095-2022, 2022

World Meteorological Organisation (WMO) (2011). Manual on Codes, Volume II – Regional Codes and National Coding Practices. **WMO-No. 306, ISBN:** 978-92-63-10306-2. Available online: https://library.wmo.int/idurl/4/35717 (accessed on January 3, 2024)