DEFINING THE CRUSTAL FRACTION (PM10-2.5) OF PM EMITTED BY AGRICULTURAL OPERATIONS

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Abstract

In 2006, EPA set the National Ambient Air Quality Standard (NAAQS) for the coarse fraction of particulate matter (PM) in ambient air. The coarse fraction particles are those particles between 2.5 and 10 micrometers aerodynamic equivalent diameter (AED). The initial proposal was to set the $PM_{10-2.5}$ NAAQS at 70 μg m^{-3}. It was perceived that this would be equivalent to the PM_{10} NAAQS of 150 μg m^{-3}. The method used to measure the coarse fraction concentration was the "subtraction" method. This consisted of measuring the PM_{10} and $PM_{2.5}$ concentrations with federal reference method (EPA approved) samplers and subtracting the $PM_{2.5}$ concentration from the PM_{10} concentration. This proposal was a problem for agriculture because very little PM emitted by this industry is $PM_{2.5}$. In effect, it would have lowered the regulatory level of ambient PM to less than 50% of the previous level. EPA chose to set the $PM_{10-2.5}$ NAAQS at 150 μg m^{-3}. Much of the PM emitted by agriculture and mining was deemed as crustal (derived from soil). The initial $PM_{10-2.5}$ NAAQS proposal was to provide credit for these two industries in the form of a crustal exclusion. The larger soil particles were not perceived to be a health problem for the public. However, there was no objective, scientific procedure to quantify the mass fraction of crustal captured by the sampling methods. This paper outlines the progress made to quantify the mass fraction of crustal PM coarse concentration measurements using chemical and physical speciation procedures.

Introduction

The EPA considered adding a crustal credit for agriculture and mining PM emissions in the course size range of 2.5 to 10 micrometers aerodynamic equivalent diameter (AED) to the recent update to Title 40 of the Code of Federal Regulations Part 50 (40CFR50) (USEPA, 2006a). However, when the final version was promulgated in September, 2006, the crustal credit was not included. EPA chose to promulgate a PMc National Ambient Air Quality Standard (NAAQS) of 150 μg/m^3 and to use the Federal Reference Method PM_{10} sampler as an indicator for PMc. It is likely that within the next 5 years EPA will promulgate a PMc NAAQS lower than the current 150 μg/m^3 and would consider a crustal credit for agricultural sources for future versions of 40 CFR Part 50. If this concept were to be adopted, agricultural sources would only be regulated on the mass fraction of PMc emitted that was not considered to be crustal. This could aid in the permitting and regulation of all agricultural sources emitting PMc.

The NAAQS is used as a "bench mark" for determining whether an area is classified as in attainment or not in attainment. If there are sufficient numbers of measured concentrations exceeding the NAAQS, the area is classified "non-attainment" and the State Air Pollution Regulatory Agency (SAPRA) must address how the area will be brought back into attainment in their state implementation plan (SIP). Watson et al. (1997) published EPA guidance for the siting of samplers used for determining attainment status. The community oriented sampler sites should be in locations where (1) the public "live, work, and play", (2) locations that are not dominated by a single source, and (3) should have neighborhood- to urban-scale zones of representation.

SAPRA permit engineers and enforcement personnel have utilized a special use of the NAAQS in a number of states. This special use consists of limiting concentrations from a single source to concentrations less than the NAAQS. In effect, it is a concentration limit at the property line (and beyond) not to be exceeded. In order to utilize this special use of the NAAQS, measured or modeled concentrations at the property line and beyond are determined. Based upon EPA guidance (Watson et al., 1997), these "fence line" concentrations should not be used for determining whether areas are in attainment but some states have continued to do so. There is some disagreement as to whether SAPRAs may use fence line concentrations not to exceed the NAAQS in their respective regulatory processes. Some agricultural sources of PMc will have difficulty meeting the PMc NAAQS at the property line. However, by obtaining credit for the mass fraction of crustal PM emissions, these facilities may be able to comply with the NAAQS. It is essential that a precise definition for crustal PMc be established and an objective scientific method for determining the crustal mass fraction of PMc be developed. It is hypothesized that the crustal mass fraction of PMc will be a function of the physical and chemical properties of the various PM sources and this relationship can be quantified for various agricultural sources, including cattle feedlots.

Objectives

The goal of this research is to develop a scientific basis for determining the mass fraction of crustal for ambient concentrations of PMc associated with agricultural operations. This paper will outline the approach used to address the following objectives:

1. To define the physical and chemical characteristics of crustal particulate matter.
2. Develop a procedure to determine the mass fraction of crustal in measured concentrations of PMc associated with PM emissions from cotton gins or other agricultural sources.

Methodology

Defining Crustal

Currently researchers and regulatory groups do not agree on a definition of the crustal fraction of PMc concentrations. Without a standard definition there can be no clear method for determining the mass fraction of crustal PM in measured or modeled PMc concentrations for regulatory purposes. When defining crustal, both the physical and chemical characteristics must be considered. This is because many particulate matter sources may have similar chemical characteristics (i.e. elemental makeup) but the physical characteristics (i.e. particle size distribution) may be very different. Including both the chemical and physical characteristics will allow researchers to better determine which sources are contributing the crustal fraction downwind from an agricultural facility. The chemical characteristics we will study will be the chemical makeup of the sources contributing to the downwind PMc and TSP concentrations as well as the samples collected downwind from the sources. The physical characteristics will include the particle size distributions (mass vs. AED) of the sources and downwind samples, the particle density of the particulate matter, the meteorological conditions during the time of sample collection, and the time and location of sample collection.

Field Sampling

High volume total suspended particulate (TSP) samplers should be placed on each side of the source with multiple samplers located on the downwind side. The downwind side of the source is the side which is opposite to the predominant wind direction for the time of year sampling occurs. Meteorological data should be collected at the time the samplers are running using a weather station setup on the downwind side of the source. An example of sampler siting is shown in figure 1 for a feed lot in the Texas high plains area.

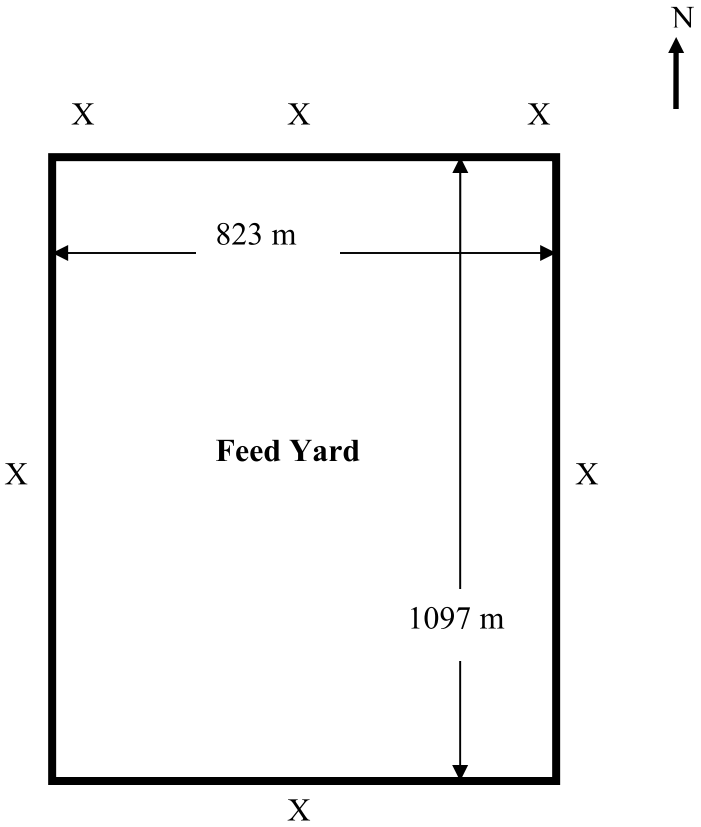

Figure 1. Typical Feedyard C sampler siting with hi-vol TSP samplers located on each side of the yard. North side has multiple samplers since wind direction is predominantly from the south.

The samplers should be operated on a continuous basis for a period of at least one week. The samplers should run for a sufficient period of time in order to get at least 200 µg of PM mass on the filters. The filters used in our sampling equipment are 20.3 by 25.4 cm borosilicate glass microfiber filters (Pall Corp., Pallflex Emfab filter material, East Hills, NY). The filters should be weighed before and after the sampling event to determine the mass collected on the filter. The filters should be handled according to the methodology described by Faulkner and Shaw (2006).

One to two pound source samples should be taken from the major sources contributing to the downwind concentrations. For a feedyard, we would recommend taking source samples from the pens, feed, roads, and surrounding fields. These samples along with the filters will be taken to the laboratory for physical and chemical analysis.

Sieving

Before the physical and chemical analysis can be conducted, the source samples must be sieved in order to have a more uniform sample. The shaker machine uses 10 sieves in two stacks ranging in size from 2200 to 75 µm. Start by placing 500-700 g of material into the largest sieve on the first stack. Close the lid and run the machine for 20 minutes. When the shaker has run for the allotted time, empty the material collected in the pan from the first stack into the top of the second stack. Close the lid and run the machine for 20 minutes. Once the shaker has stopped, weigh each of the 10 sieves and the two pans to the nearest 0.01 g being careful not to lose any material. The material collected in the second pan should be placed into a container to be used for the physical and chemical analyses to follow. There should be at least 15 g of material less than 75 µm in the second pan in order to perform all the necessary analyses.

Density Analysis

The first physical property to consider is the particle density of the PMc collected after sieving and on the filters. An AccuPyc 1330 (Micromeritics, AccuPyc 1330 Pycnometer, Norcross, GA) pycnometer is used to measure the particle density of the samples. The pycnometer measures density using gas displacement. The pycnometer releases helium of known volume into a container with a known volume. The two volumes are then subtracted to determine the volume of the PM inside the container. The mass of the PM should be measured before inserting the sample into the pycnometer. The density is then calculated using equation 1. The densities for Feedlots C and E are shown in table 1.

$$\rho = \frac{m}{V} \tag{1}$$

where:

ρ = particle density of sample (g/cm^3),
m = mass of sample (g), and
V = volume of material sample less open void space (cm^3).

Table 1: Particle densities for each of the contributing sources on or near Feedyards C and E.

Sample ID	Particle Density (g/cm3)
FYC Feed	1.4
FYC Soil	2.3
FYC Road	2.4
FYC Pen	1.7
FYE Soil	2.5
FYE Road	2.6
FYE Pen	1.7
FYE Auxiliary Pen	2.2
Soil Average	2.4
Road Average	2.5
Pen Average	1.7

Particle Size Distributions

The second physical characteristic to analyze is the particle size distribution (PSD). Approximately 3 grams of the sieved material as well as the filters that have a change in mass greater than 200 µg can be analyzed using either the Coulter Counter Multisizer^{TM} 3 (Beckman Coulter Inc, Mutisizer 3, Hialeah, FL) or Malvern Instruments Mastersizer 2000 (Malvern Instruments Ltd., Mastersizer 2000, Worcestershire, UK). These instruments provide particle size distribution data in terms of percent volume versus equivalent spherical diameter (ESD). The particle diameter data should be corrected from ESD to AED as follows.

$$AED = ESD\sqrt{\frac{\rho_p}{\rho_w}} \tag{2}$$

where:

AED = aerodynamic equivalent diameter (µm),
ESD = equivalent spherical diameter (µm),
ρ_p = particle density of the sample (g/cm^3), and
ρ_w = particle density of water (1 g/cm^3).

The Coulter Counter Multisizer^{TM} 3 can determine particle size distributions for PM in the range of 0.4 to 1200µm. For this study, we will be concentrating on particles with a diameter less than 100 µm in order to fully compare the samples collected on the filters with the samples collected from the sources. The collected PM samples are dispersed into a 5% Lithium Chloride Methanol electrolyte solution. Using the Coulter method, the PM and electrolyte are drawn through an aperture while a constant current is passed between two electrodes. As a particle passes through the aperture, the current flow between the two electrodes is impeded. Onboard circuitry converts the temporary current fluctuation to a voltage pulse proportional to the volume of the particle (Beckman Coulter, 2000). A normal Coulter Counter PSD will include the results of measuring at least 300,000 particles. It is assumed that the particle density is constant for the different size particles. Hence, percent volume is equivalent to percent mass. Prior to any PSD analysis, the Coulter Counter is calibrated with particles traceable to NIST standards.

The Malvern Mastersizer 2000 can determine PSDs for PM in the range of 0.02 to 2000µm. One advantage of the Mastersizer 2000 is the ability to analyze both wet and dry samples. The Mastersizer 2000 measurement principal is based on light scattering (Mie) where a red light is use to produce forward, side, and back scattering and a blue light is used to produce wide angle forward and back scattering of light once it hits the particles. Thousands of light scatter patterns (collected by the instrument) are used to develop the percent volume versus ESD PSD for the sample (Malvern Instruments, 1999). The PSDs for Feedlots C and E are shown in table 2.

Table 2: Particle size distributions for each of the contributing sources from Feedyards C and E performed on the Coulter Counter.

	Coulter Counter		**Malvern**	
Sample ID	**MMD (µm)**	**GSD**	**MMD (µm)**	**GSD**
FYC Feed	20	1.43	19	1.80
FYC Soil	44	2.05	45	1.87
FYC Road	33	2.31	24	2.20
FYC Pen	34	1.99	38	2.40
FYE Soil	20	2.64	14	2.52
FYE Road	13	2.55	9	4.04
FYE Pen	34	1.86	34	2.38
FYE Auxiliary Pen	43	2.14	39	2.64
Soil Average	32	2.34	29	2.20
Road Average	23	2.43	16	3.12
Pen Average	34	1.92	36	2.39

Ash Analysis

The first chemical characteristic to be studied is the ash content of the samples. Ash analysis provides the amount of organic and inorganic matter in each source. The organic matter is consumed during the ashing process while the inorganic remains. Ash analysis should be conducted according to ASTM standard E 1755-01, Standard Test Method for Ash in Biomass (ASTM, 2001a). The samples should be prepared according to ASTM standard E-1757-01 (ASTM, 2001b). Approximately 5 g of material from each source is needed to perform the ash analysis. The material should be weighed before it is put into the furnace and after it is removed. The mass of PM remaining after the material is removed from the furnace is made up of inorganic material. The percentage of organic and inorganic material in the samples will contribute to the determination of the crustal mass fraction in the PMc concentrations. Table 3 gives the percentage of ash on a dry basis for samples taken on or near Feedyards C and E.

Table 3: Ash percentage by dry basis for Feedyards C and E including samples taken from the pens in the feedlot, the roads around and through the feedlot, feed from the feed mill, and the soil surrounding the feedlot.

Sample ID	% Ash Dry Basis
FYC Feed	8.9
FYC Soil	86.3
FYC Road	87.6
FYC Pen	39.3
FYE Soil	94.6
FYE Road	91.0
FYE Pen	37.7
FY Auxiliary Pen	76.0
Soil Average	90.5
Road Average	89.3
Pen Average	38.5

Elemental Chemical Analyses

There are several chemical analysis methods available for use. One method is Neutron Activation Analysis (NAA). NAA relies on either irradiation or radioactive decay. Using NAA, it is possible to measure more than 30 elements without chemical processing. The advantages NAA has over other chemical analysis methods is that it can provide both qualitative and quantitative results, can analyze trace elements in samples, and it is more sensitive than other methods. NAA is also considered to be the "referee method" for new methods (Glascock, 2006). However, samples must sit in radiation for a period of 30 days for a full analysis to be completed, making this method the most time consuming. Table 4 shows the results of the NAA performed on samples collected at Feedyard E from the pens, roads, and soil.

Table 4: Neutron Activation Analysis results for the pens, road, and soil found on or near Feedyard E. The micrograms of each element contained in one gram of the sample material is provided.

		Sample Material (µg element/g sample)		
Symbol	Element	Soil	Road	Pen
AL	Aluminum	52640	14792	14867
CU	Copper	0	188	458
DY	Dysprosium	6	2	1
MG	Magnesium	2320	1782	2068
MN	Manganese	566	143	205
TI	Titanium	4272	1215	933
V	Vanadium	67	27	18
AS	Arsenic	6	5	2
K	Potassium	24820	7665	29056
LA	Lanthanum	37	11	8
LU	Lutetium	1	0	0
NA	Sodium	7345	2347	9645
SM	Samarium	6	2	1
U	Uranium	3	2	1
YB	Ytterbium	4	1	1
BA	Barium	485	640	168
CE	Cerium	72	22	17
CO	Cobalt	8	5	3
CR	Chromium	53	19	14
CS	Caesium	4	1	1
EU	Europium	1	0	0
FE	Iron	21621	7331	5951
HF	Hafnium	24	10	4
ND	Neodymium	27	7	6
NI	Nickel	5	9	14
RB	Rubidium	78	24	35
SB	Antimony	1	0	0
SC	Scandium	7	2	2
SR	Strontium	120	602	170
TA	Tantalum	1	0	0
TB	Terbium	1	0	0
TH	Thorium	11	4	3
ZN	Zinc	72	94	296
ZR	Zirconium	661	260	92

Other possible methods that can be used in place of NAA are inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence (XRF). The benefit of ICP-MS is that it can detect up to thirty-six elements. This is a good method to use if you are measuring concentrations at a location that is affected by many sources (Aeschlinman et al., 2003). XRF is the most common chemical analysis method but it is the least accurate. XRF must be paired with an elemental and organic carbon (EC/OC) analysis to increase the accuracy of the results. One EC/OC analysis that can be used is the thermal optical transmittance (TOT). In general, most elements can be measured using XRF or ICP techniques in place of NAA (Flocchini et al., 1972. Marcazzab, 2004. and Schmeling, 2004). If the chemical composition on the filter is unknown then it would be best to start with NAA then include either ICP or XRF for further confirmation of the chemical analysis results.

Chemical Mass Balance Modeling

Once the chemical analysis is completed, the results can be placed into a model to determine location and percent contributions of the major sources. There are many models available to use. The models allow the users to input the results from the chemical analysis as either element mass or element percentages. The models use the masses or percentages to determine which source the element was derived from. The US EPA developed the Chemical Mass Balance Analysis (CMB or MBA) model as well as the UNMIX model to trace elements back to their sources. (Almeida et al., 2006. Coulter, 2004. Pekney et al., 2006. and Watson, 2004). Other available models are the Multilinear Regression Analysis (MLRA), Principal Component Analysis (PCA), and Positive Matrix Factorization (PMF). Almeida et al. compared MBA and MLRA which showed very similar results. Hopke et al. (2006) compared PCA, UNMIX, and PMF and found that regardless of the model, source determination was consistent. This gives rise to the belief that all models will provide similar source determinations for each sample. Typical model inputs for CMB are given in Table 5, although all models have similar inputs which are based on the results of the chemical analyses.

Table 5: Typical model inputs for EPA's CMB 8.2 as determined by chemical analysis.

	Inputs
General	Site ID Date Duration Start Hour
	Total Mass Concentration (µg/m^3)
Elements, (µg/m^3)	Aluminum Ammonium Bromine Calcium Chloride Chromium Copper Elemental Carbon Iron Lead Manganese Nickel Nitrate Organic Carbon Potassium Silicon Sodium Soluble Potassium Sulfate Sulfur Titanium Vanadium Zinc

The model will predict the contribution of each source to the downwind concentration. Combining the results of the chemical and physical analyses with the results from the model we will be able to determine the crustal mass fraction in the PMc emissions from an agricultural source.

Importance

To apply this methodology to cotton gins, the contributing sources to the downwind concentrations need to be identified. Possible sources include the roads around the gin and the particulate matter coming from the cyclones or covered condenser drums. Grab samples from both sources would need to be analyzed for ash content, particle density, and particle size distribution. Concentration measurements taken at the property line would need to be evaluated along with the source samples for chemical content before modeling the analysis to determine the crustal fraction of the downwind concentrations. If 50% of the PM emission for a cotton gin were crustal then the permitting limit at the property line would be 300 µg m^{-3} measured or modeled instead of the PM_{10} NAAQS of 150 µg m^{-3}.

An alternate use of this method is to determine the ash content of the particulate matter coming from the cyclones or covered condenser drums. If it is assumed that the crustal fraction is equivalent to the fraction of inorganic (derived from soil) material, then the ash content can be applied to the emission factor for permitting. For example, if the gin is regulated based on 1.2 lb PM_{10} per bale and the ash content of the material coming from the cyclones was 15%, then the gin would be regulated based on the non-crustal fraction or 1.02 lb PM_{10} per bale.

Conclusions

There are a number of methods that may be incorporated into a scientific basis for determining the mass fraction of the crustal component of PMc emissions from agricultural sources. Previous research on speciation has focused on urban areas or national parks. There has not been a study to date that has studied crustal matter from agricultural sources. Previous studies have investigated chemical analysis methods or source determination models. No studies have combined these two in order to determine the mass fraction of crustal in measured or modeled concentrations of PMc emitted from agricultural sources. EPA considered adding a crustal credit for agricultural and mining PMc emissions to the recent update to 40 CFR Part 50 and did not do so. It is likely that within the next 5 years, EPA will lower the PMc NAAQS and provide a crustal credit for agricultural emissions in future versions of 40CFR Part 50. In order for a crustal credit to be considered by EPA, a scientific method for determining the mass fraction of crustal in PMc concentrations downwind from agricultural sources is needed.

Disclaimer

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