Analysis of the Benefits of Green Remediation Best Management Practices for Local Air Quality

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LIST OF ABBREVIATIONS

BMP	best management practice
CAA	Clean Air Act
CO	carbon monoxide
CO_2	carbon dioxide
CMAQ	Community Multi-Scale Air Quality
DOC	diesel oxidation catalyst
DPF	diesel particulate matter filter
EJ	environmental justice
EPA	Environmental Protection Agency
HC	hydrocarbons
hp	horsepower
HU	Howard University
lb	pound
N_2	nitrogen
NAAQS	National Ambient Air Quality Standards
NO_2	nitrogen dioxide
NOx	nitrogen oxides
O_3	ozone
OSRTI	Office of Superfund Remediation and Technology Innovation
pDPF	partial diesel particulate filter
PM	particulate matter
ppb	parts per billion
ppm	parts per million
RACM2	Regional Atmospheric Chemistry Mechanism, version 2
SCR	selective catalytic reduction
SO_2	sulfur dioxide
SOx	sulfur oxides
VOC	volatile organic compound

1. PURPOSE

Remediation practices employed for cleanup at Superfund sites can consume significant amounts of energy in the form of electricity, gasoline, diesel and other fuels used by mobile and non-mobile sources. The U.S. Environmental Protection Agency (EPA) *Principles for Greener Cleanups* focus on minimizing the environmental "footprint" associated with activities undertaken when cleaning up a contaminated site (EPA, 2009). The Office of Superfund Remediation and Technology Innovation (OSRTI) analyzed the benefits of implementing green remediation best management practices (BMPs) intended to protect local air quality, including reduction of air pollutants and greenhouse gas emissions. The analysis evaluated the impact of integrating advanced diesel technologies for engines and exhaust systems in mobile and non-mobile equipment deployed during remedy construction. Preliminary results of the analysis can also be used to help identify the best mitigation strategies, particularly in non-attainment zones, environmental justice communities, and sensitive subpopulations.

This report highlights the preliminary findings obtained from evaluating changes in local air quality following the application of selective catalytic reduction (SCR) technology using a gas-phase air quality model based on the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2) (Goliff et al., 2012; Stockwell et al., 2012). The report also includes a short description of the RACM2 model, assumptions, data sources, and the overall approach used for the analyses.

2. BACKGROUND

Over the years, EPA has become aware of the environmental footprint associated with cleanup activities. Equipment used during remedy construction includes generators, backhoes, excavators, and dump trucks. Such mobile and stationary sources can emit harmful compounds including oxides of nitrogen (NO_x), sulfur dioxide (SO_2), carbon monoxide (CO), and particulate matter (PM). EPA's 2007 *Cleaner Diesels: Low Cost Ways to Reduce Emissions from Construction Equipment* sector strategies report states that "the construction sector is a significant contributor to emissions, creating 32% of all mobile source NO_x emissions" (EPA, 2007).

The Clean Air Act (CAA) has identified nitrogen dioxide (NO_2), ozone (O_3), lead, CO, SO_2, and PM as the nation's criteria air pollutants (EPA, 2010). Ground-level ozone, which can be inhaled and lead to respiratory problems and other adverse health effects, is produced when photochemical reactions between NO_x and volatile organic compounds (VOCs) occur. State and federal standards for ozone (averaged over one hour) indicate that exposure to concentrations as low as 0.090 to 0.120 parts per million (ppm) can adversely affect lung function. For ozone exposure exceeding 8 hours, average concentrations as low as 0.080 ppm can have an adverse impact (California Air Resources Board, 2008). Efforts to reduce emissions of these compounds and other air pollutants are a key component of green remediation strategies.

EPA's *Green Remediation Best Management Practices: Clean Fuel and Emission Technologies for Site Cleanup* factsheet (EPA, 2010) outlines opportunities for reducing emissions of air pollutants from internal combustion engines in mobile and stationary sources through the implementation of numerous options including advanced diesel technologies. The majority of advanced diesel technologies involve retrofitting vehicle and equipment engines with a form of advanced exhaust after-treatment system to reduce diesel emissions. Relevant green remediation BMPs focus on use of the following diesel retrofit technologies: 1) diesel oxidation catalyst (DOC), 2) diesel particulate matter filter (DPF), 3) partial diesel particulate filter (pDPF), and 4) selective catalytic reduction (SCR). The first three of the four technologies can be integrated to reduce emissions of PM, hydrocarbons (HC), and CO. The fourth technology, SCR, is the only advanced retrofitting technology (of the four) that can be used for NO_x emission reductions. NO_x emissions are particularly important on the local scale, as studies have shown that they play a major role in the production of tropospheric or ground-level ozone.

SCR technology has been used previously for industrial boilers, but is emerging as an excellent NO_x emission reduction tool for on-road and off-road vehicles. According to information available from the North American SCR Stakeholders Group, "selective catalytic reduction has the ability to reduce NO_x and PM emissions while delivering a 3-5% diesel fuel savings, making it one of the most cost-effective and fuel-efficient diesel engine emissions control technologies available." SCR technology can also be combined with filters and catalytic technologies to help reduce emissions of other criteria air pollutants. An SCR system involves three components: 1) a catalytic converter, 2) hot exhaust, and 3) diesel exhaust fluid consisting of a solution of urea and purified water. It is called "selective" because it reduces levels of NO_x by using ammonia as a reductant within a catalyst system. The diesel exhaust fluid is vaporized and injected into the exhaust stream of a diesel engine. When the hot exhaust combines with diesel exhaust fluid vapor within the SCR catalyst, it is broken down into nitrogen (N_2) and water (North American SCR Stakeholders Group, 2008). Application studies performed by EPA's Clean Diesel Emerging Technologies Program suggest that SCR technology could reduce NO_x emissions by 65%.

3. METHODS AND MODE

This analysis involved atmospheric chemistry modeling to predict air quality changes for a hypothetical remediation scenario in which SCR technology was applied. Sections 3.1 through 3.3 of this report provide details about the scenario and describe the simulation methods, analytical assumptions, and overall approach to analysis.

3.1 Scenario

NO_x emissions were taken from a hypothetical site scenario illustrating onsite air emissions from onsite activities involved with soil remediation. The scenario estimated NO_x emissions resulting from an ex situ solidification/stabilization process to treat 50,000 cubic yards of soil, using two 100-horsepower (hp) backhoe/loaders for 1,400 hours, one 200-hp excavator for 1,400 hours, and two 330-hp dump trucks onsite. Assumptions and calculations were based on conversion factors that were used in the development of EPA's August 2010 *Green Remediation Best Management Practices: Clean Fuel and Emission Technologies for Site Cleanup* fact sheet. Table 1 below provides a breakdown of the NO_x emission calculations for each individual source.

Table 1. Assumptions and Calculations Supporting Hypothetical Scenario of Onsite Emissions

Ex Situ Solidification/Stabilization Equipment (to treat 50,00 cubic years of soil)	**Rate of Fuel Use** (gallons/hour)	**Duration** (hours)	**Diesel Consumed** (gallons)	**NO_x Emitted** (pounds)
Backhoe/front end loader (Caterpillar 446D 110 HP)	4	1,400	5,600	883.68
Backhoe/front end loader (Caterpillar 446D 110 HP)	4	1,400	5,600	883.68
Excavator (CAT 330 Diesel)	8	1,400	11,200	1,767.36
Dump truck (300 HP)	8	1,400	11,200	1,767.36
Dump truck (300 HP)	8	1,400	11,200	1,767.36
Total			**44,800**	**7,069.44**

1) Associated emissions based on conversion factors used in developing August 2010 "Green Remediation Best Management Practices: Clean Fuel and Emission Technologies for Site Cleanup," (page 3 table); per 1 gallon of diesel consumed: NO_x=0.15780 pounds; http://www.cluin.org/greenremediation/docs/Clean_FuelEmis_GR_fact_sheet_8-31-10.pdf
2) Activities extrapolated from June 2009 draft workbook on energy and air emissions associated with solidification/stabilization, as developed for OSRTI by EMS, Inc.

3.2 Simulation Methods

A chemical box model (Seefeld, 1997; Seefeld and Stockwell, 1990) based on a version of the Regional Atmospheric Chemistry Mechanism, version 2 (RACM2) (Goliff et al., 2012) was used to estimate numerical values for the production and loss of tropospheric ozone. RACM2 is a gas-phase chemical mechanism widely used for atmospheric chemistry modeling that includes a total of 118 chemical species and 356 chemical reactions. It has been tested against numerous environmental reaction chamber experiments and recently implemented in EPA's Community Multi-Scale Air Quality (CMAQ) model (Byun and Ching, 1999).

Box-model simulations were made based on a polluted urban atmosphere. An initial background ozone mixing ratio of 30 parts per billion (ppb) was used for each simulation. The photolysis rate coefficient calculations were based on latitude of 40° at summer solstice (Stockwell et al., 2012). Simulations were made for 5 days with 10 and 14 hour increments to reflect a 7 am-5 pm working day with NO_x emissions and a 5 pm-7 am non-working period without NO_x emissions. The delta-Eddington radiative transfer model was used to calculate the photolysis rate coefficients for each photochemical reaction (Madronich, 1987). Table 2 below shows the initial ambient conditions used for the simulations. Background VOC mixing ratios were based on summertime measurements made at Howard University's (HU) Beltsville Research Center in Beltsville, Maryland. The HU research center is in close proximity to highways and trees. This is representative of typical urban/suburban airshed conditions for one-third of the American population. Table 3 shows background ambient conditions used for each simulation. Figure 1 shows a breakdown of each VOC class of species derived from the Beltsville field study.

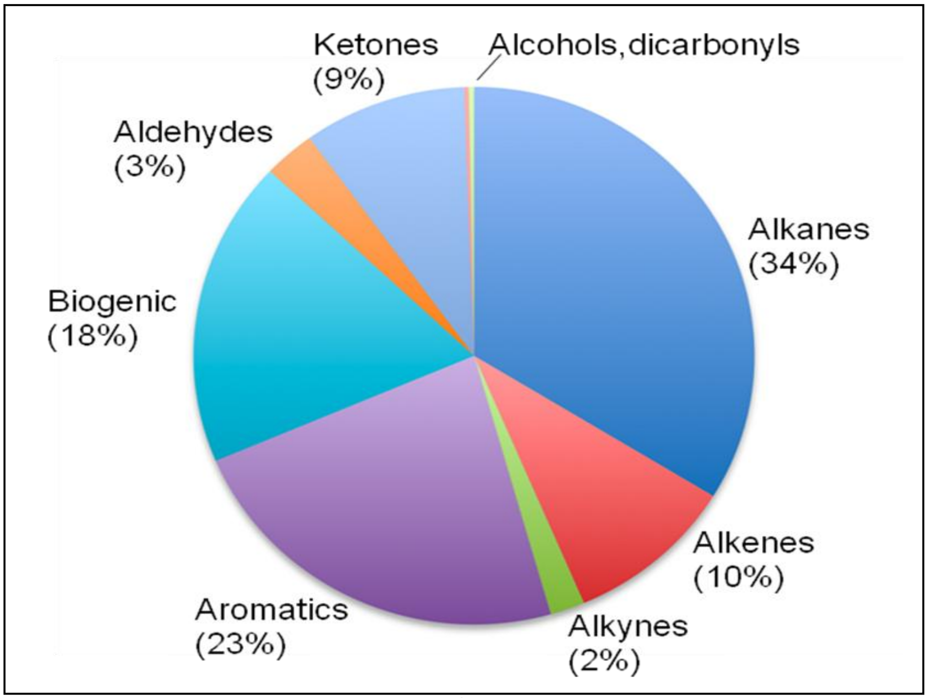
Table 2. Initial Ambient Conditions Used for Each Simulation
(before any machinery is turned on)

Initial condition	Value
Start time	6:00 am
Duration	7 days
Temperature	298 K
Pressure	1013.25 millibar
H_2O mixing ratio	15,500 ppm
H_2 mixing ratio	550 ppb
Relative humidity	50%
Date for photolysis calculations	June 21

Table 3. Background Ambient Conditions Used for Each Simulation
(before any machinery is turned on)

Species	**Initial Concentration** (ppb)
O_3	30
NO	0.5
NO_2	2.0
SO_2	5.0
CO	100
VOCs	200
VOC/NO_x ratio	80 ppbC/ppbN

Figure 1. VOC Mixture Used for Initial Simulations
(200 ppb carbon)



NO_x emissions from the site scenario were the only source of NO_x emissions considered for each simulation. VOC emissions were included for each simulation to account for natural emissions of various compounds.

The box model domain was set to have a ground surface area of 5 miles^2 (the size of an arbitrary local city). The size of the soil remediation site was chosen to be a square approximately 0.3 miles on a side. This was based on a soil remediation project with 50,000 cubic yards of evacuated soil and a digging depth of 6 inches. The mixing height was set to 100 meters for both the remediation site and the local city. NO_x emission rates from the mobile sources (equipment in Table 1) deployed directly on the site were determined to be approximately 49.0 ppb per hour with all the NO_x emitted as NO. The NO emissions were assumed to rapidly mix into the air above over the city due to atmospheric convection. Therefore, the NO emission rate directly over the site was corrected to account for the city area resulting in an urban NO emission rate of 0.18 ppb per hour.

Simulations were performed with modeling conditions representing pre-SCR and post-SCR technology implementation. Both pre-SCR and post-SCR simulation cases incorporated the initial conditions (as shown in Tables 2 and 3) and included emissions of VOCs (Figure 1). Pre-SCR simulations used the established NO_x emission rate of 0.18 ppb/hour. Post-SCR simulations reflected a 65% reduction in NO_x emissions, resulting in a revised NO_x emission rate of 0.063 ppb/hour. Table 4 shows the NO_x emission rates based on the NO_x emissions calculated for cleanup equipment involved in the onsite scenario (Table 1).

Table 4. Calculated NO_x Emission Rates
(based on NO_x emissions for hypothetical scenario discussed in Table 1.*)

NO_x Emission Rate	ppb/hour	Area (square miles)
Directly over soil remediation site	49.0	0.3
For the local city before SCR implementation	0.18	5.0
For local city after 65% reduction following SCR implementation	0.063	5.0
*Total NO_x emission in pounds (lbs) for Table 1 onsite scenario: 7,069.44 lbs		

Sensitivity studies were also performed, including adjusting the initial background VOC mixing ratio by ± 20% and performing simulations using a range of temperatures from 280 to 310 K (6.85°-36.85°C).

3.3 General Assumptions

The following basic assumptions were applied in this analysis of pre-SCR and post-SCR technology simulation cases.

1. Assume no wind and clear sky
2. Assume convective mixing due to surface heating
3. Assume constant meteorological conditions; physical loss processes such as the deposition of ozone and other compounds to the ground were not included
4. Assume an even distribution of NO_x within the box domain (5 miles^2 x 100 meters) upon emission

5. Assume that each solidification/stabilization process is occurring simultaneously for 1,400 hours not including nights and weekends
6. Associated emissions are based on conversion factors; per one gallon of diesel consumed: NO_x=0.15780 pounds
7. Model cannot account for PM emissions
8. Assume that emissions do not diffuse outside of the box-model domain
9. NO_x emissions from the site were the only source of NO_x emissions considered; traffic and other NO_x emission sources were not included in the simulation

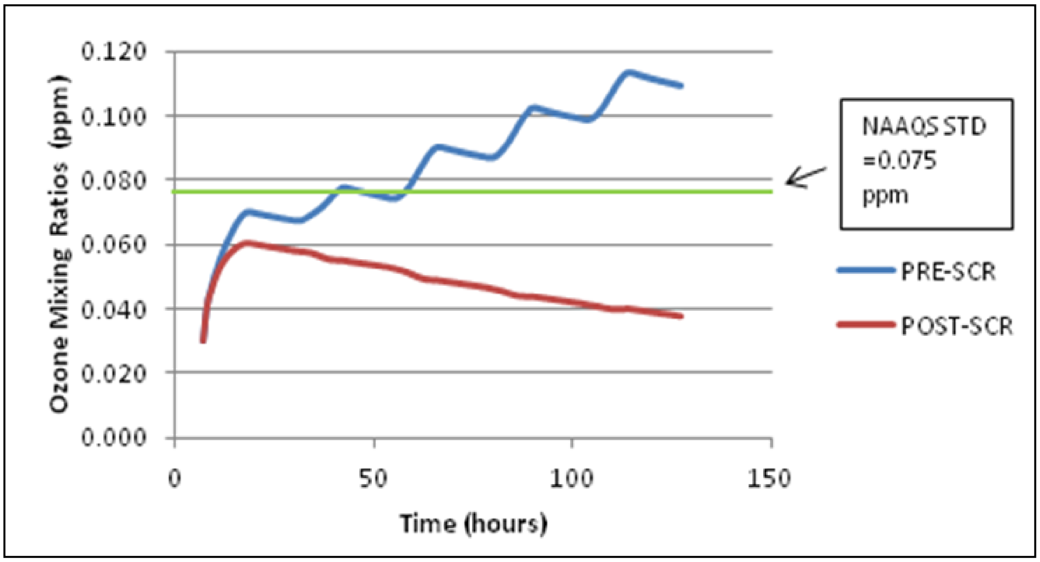
4. RESULTS AND DISCUSSION

Box-model simulations were made using RACM2 in order to evaluate changes in local air quality before and after integration of SCR technology for diesel engines used onsite during the remediation. In addition, sensitivity studies were performed for the pre-SCR case to examine the response of the model's ozone estimates to changes in key input variables such as temperature and initial VOC background concentrations. Sections 4.1 and 4.2 of this report present preliminary findings of the analysis and discuss how the findings can be useful in helping to establish the potential benefits of BMP implementation at cleanup sites for local air quality.

4.1 Preliminary Findings

Figure 2 below shows time-dependent mixing ratios of ozone over the 5-day simulation before and after the application of SCR technology. Pre-SCR technology ozone mixing ratios (blue) follow the diurnal cycle with steadily increasing ozone levels that exceed National Ambient Air Quality Standards (NAAQS) of 0.075 ppm for ground-level ozone. Eight-hour averages for pre-SCR implementation were found to be as high as 0.22 ppm for the conditions examined. Post-SCR technology ozone mixing ratios (red) also follow the diurnal cycle but are significantly decreased after applying a 65% reduction in NO_x emissions. These results show that a 65% NO_x reduction leads to a 46% ozone reduction over a 5-day period. More specifically, for the conditions examined, for every 1% reduction in NO_x, a 0.9% reduction for peak ozone mixing ratios was achieved.

Figure 2. Simulated Ozone Mixing Ratios.



Ozone over a 5-day period for pre- and post-SCR implementation denoted by blue and red lines, respectively. The horizontal green line represents the NAAQS for ozone (0.075 ppm).

4.2 Sensitivity Studies

Temperatures ranging from 280-310K (6.85°-36.85°C) were incorporated into the model for individual pre-SCR simulations in order to examine how ozone mixing ratios depend upon changes in temperature. Results showed a linear correlation between the ozone mixing ratios and temperature. The simulations also showed that the maximum ozone mixing ratio is less sensitive to changes in temperature as it increases. At higher temperatures, the ozone precursors react to produce all the ozone that is possible during the simulated period given their initial concentrations and emission rates.

Changes to the VOC background concentrations and the VOC emissions from natural sources were also performed. Background VOC concentrations and VOC emissions were varied by ± 20%. As previously stated, ground-level ozone formation is strongly dependent upon reactions between VOC and NO_x. In other words, the formation of ground-level ozone is controlled by the VOC to NO_x ratio. A 20% decrease in background VOC concentrations and VOC natural emissions resulted in an increase in ozone mixing ratios for the pre-SCR implementation simulation. Contrarily, an increase of 20% led to decreased ozone levels. VOC to NO_x ratios can provide a useful perspective for developing local and regional ozone precursor control strategies (Center for Air Pollution Impact and Trend Analysis, 1994).

5. CONCLUSIONS

This analysis evaluated the benefits of integrating SCR technology for a local air quality parameter. Simulations of gas-phase ozone formation before and after SCR implementation were made with a photochemical model based on the Regional Atmospheric Chemistry Mechanism, version 2. The box-model simulations were representative of a fairly polluted urban atmosphere, with an initial ozone mixing ratio of 30 ppb. Changes to the temperature and VOC initial mixing ratios were also made to examine model sensitivity. The simulations showed that implementation of SCR technology can significantly benefit local air quality. Ground-level ozone formation was greatly reduced following the application of SCR. Pre-SCR simulations showed ozone mixing ratios steadily ascending and exceeding the NAAQS for ozone by day 2. Post-SCR simulations, reflecting a 65% NO_x reduction, drastically decreased ozone formation, staying below the NAAQS for all 5 days. Results also showed that ozone levels are proportional to temperature variation and highly sensitive to VOC to NO_x ratios.

The conditions and assumptions examined were most favorable for ozone formation. The assumption that NO_x emissions do not diffuse outside of the box domain may have contributed to higher ozone formation; however, this assumption does support conditions for little to no wind. Additionally, it was assumed that NO_x emissions from the site were the only source of NO_x emissions in the simulated urban area. In reality the site emissions would be added to NO_x from traffic and other emission sources.

The information obtained from this analysis is particularly relevant to EJ communities near cleanup sites. EJ communities consist of racial minority and low income populations disproportionately exposed to air pollution, hazardous waste facilities and other environmental risks (Environmental Equity, 1992). Studies show that African Americans and Hispanics were more likely to be exposed to ground-level ozone and several other air pollutants known to cause health problems. The findings can be helpful in determining the proper mitigation strategies to implement in these communities and in non-attainment zones, where ozone levels exceed NAAQS. Information gained can also be used to further assess short-term impacts for communities in close proximity to remediation sites.

More thorough analyses are necessary to validate the preliminary findings discussed in this report. Additional sensitivity studies for other input parameters should also be considered. Furthermore, future studies are also needed to assess additional green remediation BMPs, individually, and in combination with other green remediation strategies.

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