

Micromitigation: Volatile Organic Compound Adsorption in Ambient Air using Activated Carbon: An Introduction
DRAFT

Table of Contents

- a. Photos at start:** an adsorption panel; first deployment at CCL; AC on scale; Alemany Boulevard deployment; mixing chambers, air pumps, flow meter;
- b. List of Illustrations and figures:**
- 0. Brief Summary**

I. Introduction: the World Public Health Crisis of Air Pollution

- 1. Air Pollution as Public Health Crisis**
- 2. The Persistent Problem of Volatile Organic Compound Air Contaminants**
- 3. Hyperlocal VOC Mitigation: A Gedankenexperiment**

II. The Science of Adsorption

- 4. Adsorption Separation Processes**
- 5. Regeneration of Spent Activated Carbon**
- 6. Current Usage of Activated Carbon Adsorption**

III. Adsorption Systems and Micromitigation Design

- 7. The Design of Adsorption Systems**
- 8. Challenges in Ambient Adsorption Design**
- 9. Design Proposal**
- 10. Additional Concerns in Ambient Adsorption**

IV. Implementation

- 11. Meteorological, Topographical, and Emissions-Related Desiderata for Deployment**
- 12. Instrumentation and Testing**
- 13. Desorption and Regeneration**
- 14. Cost**

V. Status Quo

- 15. Pilot Project, Technical Challenges, and Work in Progress**
- 16. Conclusion**

VI. Appendices

- 17. CCL and MMWG Team**
- 18. Bibliography**
- 19. Endnotes**

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Brief Summary

Micromitigation is an environmental remediation method which uses adsorption by granular activated carbon in open panels to mitigate Volatile Organic Compounds at emissions hotspots. This citizen science initiative seeks to establish a universally accessible open-source protocol for the abatement of VOC pollution in environmental justice communities in California and beyond. Adsorption is widely used in industrial emissions systems, and we seek to adopt this technology in an ambient setting. The Micromitigation Working Group, a bi-monthly Meetup hosted since April 2021 by the open science Counter Culture Labs in Oakland, California, seeks to develop this method as a complement to augment the established regulatory point source-based and facility-based approach to emissions.

I. Introduction: the World Public Health Crisis of Air Pollution

1. Air Pollution as Public Health Crisis

The severity of the public health crisis brought about by the climate emergency is not in question. It is beyond all doubt, yet only partially overlapping with the climate crisis, another calamity which is not in question. Air pollutants, specifically “criteria pollutants” designated as harmful to human health by the EPA, have been implicated in adverse respiratory, cardiovascular, and neurodevelopmental outcomes. A surfeit of studies attests to this¹. The problem is global, and relatively underfunded². Greenhouse gases such as CO₂ and CH₄ are indeed an immense threat to global climate, but their mitigation does not obviate the need to ameliorate local criteria pollutant emissions and Toxic Air Contaminants. The EPA National Ambient Air Quality Standards list, comprising carbon monoxide, ozone, particulate matter, lead, nitrogen dioxide, and sulfur dioxide, remain a persistent threat in urban environments. The current regulatory framework does not ignore pollutants in general, or PM (1.0, 2.5, and 10) in specific. There is even new BAAQMD legislation on PM (specifically Regulation 6 in 2018). California measure AB617 is directly addressed to PM 2.5, as well as emissions inventories for VOCs.

2. The Persistent Problem of Volatile Organic Compounds

The dangers of VOCs, a number of which are designated TACs, or Toxic Air Contaminants for which there is no safe threshold level of exposure, are not unknown³. These are not innocuous bad odors, but serious carcinogens with no minimum determination of safety. The Agency for Toxic Substances and Disease Registry at the CDC has specific designations for each TAC, with epidemiological data for each. TACs are tracked by the California EPA's Office of Environmental Health Hazard Assessment (OEHHA), as well as by the European Union and the World Health Organization. They are well-understood in environmental health, and yet much of their regulation is overseen at the state and local level. Even in California, they remain a serious health risk.

Yet for the purposes of enforcement rather than public health study VOCs are, generally, not taken as seriously as they should be. There are instances of air districts in California specifically declining to fund research into local VOC conditions, and Cal ARB projects to do such study have not been funded rapidly. VOCs are an increasing threat in a world with secular trend of higher temperatures, and as an Ozone precursor contribute to its production as a secondary aerosol.

Regulatory Efforts

The ongoing regulatory response over nearly four decades has been multifaceted and effective in improving public health broadly speaking. In 1983, the California Toxic Air Contaminant ID and Control Act [Tanner AB1807] was passed, and OEHHA developed inhalation cancer potency factors for twenty-one TACs. Cal ARB subsequently implemented airborne toxic control measures (ATCMs). The following year, CalARB also implemented TAC

study sites in locations statewide. This was followed in 1987 by the Air Toxics “hot spots” Information and Assessment Act (AB2588), which requires operators of significant-risk facilities to reduce risks from exposure to emitted TACs. These measures generally apply at industrial sites rather than regular ambient air.

In 1990, major amendments to the 1970 Federal Clean Air Act led to an additional 189 specific chemicals added to NESHAPs. In pursuit of this, Maximum achievable control technology (MACTs) were implemented after 1990, and applied widely in industry. The 1970 CAA had set NESHAPs, but only seven were put on the list in the first 20 years:

"The U.S. EPA develops regulations for federally defined major stationary sources and area sources. Major sources are sources that emit over 10 tons per year of any one HAP or 25 tons per year of any combination of HAPs. Area sources are sources that emit lesser amounts of HAPs, like gas stations." ⁴

The administration of NESHAPs emission reductions is delegated to the states. Local agencies may be more stringent if they so decide. For instance, subsequent to the enhanced NESHAPs listing, California's TAC list was amended in 1993 to include all Federal HAPs as well.

Additional longitudinal national studies were launched during the 1980s. These included NATTS and PAMS, the National Air Toxics Trends air toxics study and the PAM monitoring efforts began, measuring metallic and gaseous toxic air pollutants at over 200 locations. This led to systematization as a surfeit of data was gathered:

" Broad access to and use of these data was hampered by a lack of centralized databases and multiple sampling and laboratory protocols, creating data quality and consistency concerns. To address these inconsistencies, the NATTS network was conceived in 2001, consisting of 27 sites. The sampling protocol typically has been every sixth day for 24 hours.

Among the priority ranked 33 air toxics of U.S. concern, observations of benzene and other common aromatics are generally widespread and relatively reliable. However, other potentially important air toxics are less well represented in air monitoring. During the initial start-up of the NATTS, six priority pollutants (formaldehyde, benzene, 1,3- butadiene, hexavalent chromium, acrolein, and arsenic) were targeted for inclusion, based on results of the 1996 National Air Toxics Assessment (NATA; <http://www.epa.gov/ttn/atw/natamain/index.html>).

Another major study was PAMS, the Photochemical Assessment Monitoring Station sites [EPA]⁵. Approximately 75 sites in 22 cities were deployed by state and local agencies in the early 1990s to measure ozone precursors. PAMS and the air toxics network (see below) provide the majority of routinely available non-methane organic carbon (NMOC) measurements. A number of ozone precursor C2-C10 alkanes and alkenes, aromatics, formaldehyde, and acetaldehyde are measured using a combination of continuous methods and sampling techniques over 3- and 24-hour collection periods, often limited to the ozone season (April – October). The 1990 CAA Amendments required areas classified as serious and above with respect to the contemporary (1990-1992) ozone NAAQS to implement PAMS, which has undergone minor modifications since then. Most volatile organic compound (VOC) sampling sites include instrumentation for O₃ and NO_x. Such measures have been consequential. CA's 1996 gas reformulation led to decline in benzene emissions; and ambient concentrations, in consequence of which there have been major reductions in cancer from TACs⁶.

" Statewide cancer risks were determined using the calculated cancer risk factors and ambient statewide levels for each TAC, 1990-2012...[showing] a 76% decline in cumulative increased cancer risk per million people, from 1990 to 2012, due to inhalation of ambient air."7

However, geographically focused studies, such as the South Coast AQMD's MATES, or Multiple air toxics exposure studies, over a number of years, indicated that despite reduced cancer on the basis of gross population, there are still local health illness clusters. Severe intrastate discrepancies remain when considered in a more nuanced fashion by proximity to emissions rather than over the entirety of the state. A staggering amount of study, but less action and certainly continued higher cumulative health effects in certain populations and localities.

The United States response has been uneven in the formation of rules, and weaker in their implementation. However, Volatile organic compounds are taken seriously in Europe8:

"The World Health Organization (WHO) Air Quality Guideline for Europe [in 2000] establishes guideline values for toluene, 260 ug/m3 over 1 week, for formaldehyde, 100ug/m3 over 30 min and for tetrachloroethylene, 250 ug/m3 over 1 year. Additionally, it sets the guideline values for benzene corresponding to the concentration levels associated with an excess lifetime risk of 1/10,000, 1/100,000 and 1/1,000,000 equal to 17, 1.7, and 0.17 ug/m3, respectively. In 2010, the WHO Guidelines for Air Quality in Indoor Air confirmed the guideline values given in 2000 for benzene... the European Air Quality Directive AQD defines as mandatory the monitoring of benzene in ambient air. The AQD states that the reference method for the measurement of BTEX consists of active or online sampling followed by desorption and gas chromatography."9

However, there are as mentioned inordinate health effects on environmental justice neighborhoods. There are also and innumerable environments outside California- both in the USA and beyond- in which criteria pollutants are ignored, and the idea of regulating TAC emissions sounds like an idealistic fantasy. As the human cost is increasingly taken seriously, we anticipate that the cost of VOC emissions mitigation will increasingly seem less and less expensive. Notwithstanding this prognostication, it has not happened yet, and we recognize that EJ communities are on their own.

The Intractable Challenge of Enforcement

There are many settings in which TACs are prevalent, which are neither major stationary polluters (the Air District's bailiwick), or major mobile source polluters, diesel trucks in particular being Cal-ARB's nemesis. These include minor stationary facilities including dry cleaners, auto body shops, junkyards, aboveground parking structures, gas stations, barbeque restaurants, in the vicinity of old cars, and other locations with ongoing, and widely tolerated fugitive emissions. Such locations are, practically speaking, miniature pollution hotspots with emissions from "grand polluter" vehicles that have escaped being smog-checked, diesel trucks idling, construction dust, roofing work, etc.

Local ambient air quality is an intractable problem and will continue to be so in the foreseeable future. Enforcement- in dozens of countries and hundreds of cities- is almost always carried out locally, and subject to local indifference and corruption. This, not national or state standards, or even conscientious AQ monitoring, is the weak link. National and state standards especially for stationary permitted facilities are invariably enforced locally, and typically very unevenly. Air Districts, the Department of Toxic Substances Control and Cal-ARB, pursue enforcement, and citizens' groups such as the IVAN reporting network report on these and other contaminants. But these stakeholders essentially play whack-a-mole with local hotspot violations. How may the immediate effects of pollutants be lessened- without assistance from increased enforcement? Moreover, even these enforcement woes are the complaint of the privileged, and are not representative of the world as a whole. Californians are fortunate in that we have a venerable

and aggressive state EPA and local Air Districts. But the world has a billion poor people living in one million slums, in one hundred thousand cities¹⁰.

3. Hyperlocal VOC Mitigation: A Gedankenexperiment

The world does not need expensive, photogenic environmental solutions. In fact, outdoor air purifiers have done nothing to gain respect for AQ solutions¹¹. Instead, the world could benefit from a solution that looks very different in terms of cost, divisible capital inputs, labor inputs required, and even the way in which it is developed. The constraints within which such a solution must be implemented are quite stringent. We need to envision a dirt cheap (dust cheap?) ambient VOC mitigation technology. The method should be amenable to implementation in a highly distributed form- since VOC pollutants are present beyond the ambit of emissions at regulated facilities (and since many polluting facilities that should be regulated, are not). Geographically dispersed microscale implementation is complemented by a design that can be implemented in highly incremental form. Ideally, this means a rudimentary design that leverages polluted air transport patterns to the furthest extent possible. We should avoid proprietary patented processes, and have no moving parts, and no engineered inlet or outlet, and no power source; because this would make the engineering too expensive and usage more difficult. Thus capital inputs will be modest, or more accurately put, skeletal. Labor inputs shall be as well. They must be at the level of an AP class in chemistry; applied to environmental science. The technology should be amenable to implementation by high school students, and chemistry teachers at the college and high school level.

Air mixing ratios typically change both diurnally and across geographic locations. Precise mixing ratios change, but in the locations which we intend to target will always include fugitive emissions usually from VMT and other products of incomplete combustion. We will round up the usual suspects, and lock them up time and time again.

We turn to mitigation rather than fight the same, often losing, battle hundreds of times. Open Panel adsorption, or Micromitigation, can be carried out with simple materials, without proprietary technology, using long-established technologies. It deploys granulated activated charcoal (GAC) to adsorb pollutants in shallow screened adsorption panels on outdoor walls, patios, on fences, at road medians, and on other surfaces immediately adjacent to ambient pollutants. These panels are then periodically removed and the VOCs desorbed through commercial carbon regeneration services.

II. The Science of Adsorption

We start by discussing adsorption itself, and then its implementation using Activated Carbon.

4. Adsorption Separation Processes

The separation process of adsorption (not to be confused with absorption¹²) is canonical in chemical engineering, with prior art in technical guides ranging from the U.S. Army Corps of Engineers and the EPA to college courses, all readily available online¹³. *Adsorption*, or *physiosorption* is a basic “process by means of which gases are taken in but do not chemically combine with the substrate which they interact with”¹⁴. Alternatively, it is defined as “a process by which material accumulates at the interface between two phases”¹⁵. These phases may be liquid-liquid, liquid-solid, gas-liquid, or gas-solid. We are mostly concerned with the latter. In physical adsorption, electrons are not shared or transferred; the species remain individual¹⁶.

This adhesion is a surface phenomenon, rather than ionic or covalent bonding, but is instead based on weak electrostatic attractive van der Waals forces¹⁷. The phenomenon's reliance on London dispersion forces rather than dipole attraction explains its reversibility: VOCs will desorb

through thermal desorption starting at 300 Fahrenheit. However, O₂ will chemisorb, and will be removed at more elevated temperatures.

Adsorption is extremely common, seen but unnoticed in everyday life, as in mundane silica gel packets in shoeboxes, and activated carbon in charcoal in fish tanks and indoor air purifiers. It is also ubiquitous in molecular separation in the chemical, natural gas, mining, petroleum, and food industries. Industrial processes for stationary source control typically use adsorptive materials in fluidized reactor beds for emissions controls. More specifically:

"the application of adsorption technology or pollution control usually deals with the control of organic compounds. VOCs, pesticides, PCBs, phenolics, and complex synthetic organics are typical adsorbates."¹⁸

Mass Transfer and Post-Adsorption Equilibrium

The physical process of adsorption, as the molecules move through the reactor bed or vessel, is mass transfer. The moving boundary of this adsorption is called the mass transfer zone (MTZ). Pressure drops occur as the contaminant is adsorbed by the adsorbent material. The point at which the MTZ reaches the far end of the reactor bed or column is called breakthrough. When saturation is complete, a dynamic equilibrium between the adsorbate and the adsorbent is reached, and adsorption and desorption rates are equal^{19, 20}.

Column testing is used for comparative gauging of the saturation process over time, and to measure heat, as this is an exothermic process. Adsorption heat produced diminishes as the saturation progresses. Saturation is also increased by capillary condensation, within the micropores. Chemical potential theory indicates that Gibbs free energy decreases as post-surface adsorption takes place within layers. Post-adsorption, Van der Waals attachment is temperature-independent²¹ As sorbate molecules attach at all layers, free energy decreases.

Isotherms

The characteristics of this equilibration process are dependent on the physical properties of both adsorbate (partial pressure of different gas species and surface kinetics relative to those different species) and adsorbent, specifically CTC, AN, surface area of GAC, and polarity. Isotherms are developed to express empirical relationships, characterizing the percentage concentration of adsorbate in the inlet stream, the partial pressure of the fluid or gas phase pollutants (molecules), and the percentage adsorbate which the adsorbent will ultimately take in.

The fundamental action of the pressure is understood through Le Chatelier's principle. Isotherm equations for adsorption were first described by Irving Langmuir in 1916, in work for which he subsequently won the 1932 Nobel Prize. The Langmuir isotherm's assumptions assume a monolayer adsorbent material. In its derivation Langmuir isotherm refers to homogenous adsorption which each molecule possess constant enthalpies and sorption activation energy (all sites possess equal affinity for the adsorbate, with no transmigration of the adsorbate in the plane of the surface."²² Alternatively, the Freundlich isotherm does not assume a monolayer, and "is widely applied in heterogenous systems especially for organic compounds or highly interactive species on activated carbon and molecular sieves."²³

The linear isotherm, expressing partial pressure and Henry's Law, is simpler and embodies relative humidity, temperature, and partial pressure inputs. More recently, new variables have been added, including chemical potential additions to isotherm to address adsorption post-surface adsorption. Various isotherm equations are reached for different combinations of adsorbents and adsorbates²⁴. There is a distinct isotherm for each combination of AC and

pollutant and system. However in most cases the design system involving adsorption for air pollution is a tubular or plug flow reactor ²⁵.

Materials Used for Adsorption

Materials used in gas phase adsorption include coal, peat, bamboo, nut shells, fruit stones such as olive pits, durian seed, coconut shell and petroleum residue, in the form of activated carbon granules, powder and mesh. The past decade or so has seen much more interest in various materials:

"Realizing the complication [posed by expensive activated carbon], a growing exploitation to evaluate the feasibility and suitability of natural, renewable, and low-cost materials (bamboo dust, peat, chitosan, lignite, fungi, moss, bark husk, chitin, coir pith, maize cob, pinewood sawdust, rice husk, sugar cane bagasse, tea leaves, and sago waste) as alternative adsorbents in water pollution control, remediation and decontamination processes has been exerted."²⁶

Non-woven synthetic fiber filtration media are also used for adsorption with the molecular sieve zeolite (aluminosilicate), silica gel (hydrous oxide), polymer adsorbents and molecular sieves made from coal, which have different activation process and specific rather than non-discriminating adsorption. Adsorption characteristics vary significantly between these materials, which may be characterized by size, shape, and polarity. However, all share the common feature of extensive porous structures. We are primarily interested in GAC, made from wood, coal, or coconut shell, as it is favored for organic aerosols. Powdered activated carbon cannot be regenerated and is out of our concern. According to the EPA's Engineering Bulletin:

"Adsorption by activated carbon has a long history of use as a treatment for municipal, industrial and hazardous waste streams... GAC is a relatively non-specific adsorbent and is effective for removing many organic and some inorganic contaminants from liquid and gaseous streams."

The large surface area of the carbon atom, which allows the formation of covalent compounds, also allows van der Waals forces and lends itself to adsorption of gas phase molecules. The surface area can range up from 500-2000 m²/g, and will attract a wide range of organic (and inorganic) molecules. Engineered adsorptive materials are processed to enhance this natural advantage, making the surface area as extensive as possible. The surface for adsorptive activity is increased by the burning off (pyrolysis) of tar and ash from carbonaceous material at 400 to 500 hundred. All VOCs are removed, and extensive internal micro-pores are created in this activation process (EPA Engineering Bulletin 1991, p3).

GAC Properties and Standards

GAC is characterized both qualitatively and quantitatively by a number of properties, and meticulously defined by American Standard Test Method (ASTM) standards²⁷. Standards promulgated by the EN or European Norm, CEFIC, and DIN also apply internationally. In addition, NSF certification is used in the USA. Attributes used to characterize GAC include iodine number (IoN); molasses number; total ash; abrasion or hardness number; CTC number, surface area (N₂ BET); and U.S. Standard sieve size.

Relative surface area, or the available surface area in m² /gram of virgin carbon, is measured by the Iodine Number or IoN, (ASTM D4607). This tells us the micro-pore and transport pore structure. (Micropores, as defined in IUPAC classification system are .2 to one nanometer in radius). The caramel or "Molasses number" indicates the number of mesopores and macropores in an AC. (Mesopores are one to 25 nanometers in radius, and macropores are greater than 25 nanometers in radius). Total ash (max ash ASTM D 2866 94) indicates relative saturation ability, based on level of impurities. Typically, coconut shell substrate has the lowest ash number. A high level of porosity means that at saturation can load to .1 lb. or 45 ml on

volumetric basis per pound of GAC. The abrasion number (AN, or ASTM D 3802 89) is based on a mechanical test of abrasion and measures structural strength, or the media's ability to withstand abrasion or size reduction when tumbled. This is significant for backwash, during which Particulate Matter or large-gauge matter is repelled. Shell carbons have a 90 AN resistance; coal is average 70 AN; below 70 won't hold up to backwash. The CTC, or carbon tetrachloride number (CCl₄ number ASTM D 3467 04), relates to the degree of activation and the adsorption potential of a given GAC product. More precisely, CTC activity number is the percentage by weight of CTC adsorbed at 25 degrees Celsius (77 degrees f) from dry air saturated at 0c (32 f). Surface area, calculated using the N₂ BET method based on nitrogen, is sometimes given as well. U.S. Standard sieve size (ASTM D 2862 10) designates the granularity range of a given carbon product. The 4 x 10 mesh designation means that 90% of the granules are no larger than 4.75mm or .187 inch (No. 4), and no smaller than 2.0 mm or .0787 (No. 10) inches. Mesh of 4 X 6, 4 x 8, 8 X 12, 12 X 20, 6 X 12 are all common. Further metrics include apparent density (ASTM D 2854 09) and moisture as packed (ASTM D 2867 99).

Different material substrates have different pore characteristics, and hence different appropriate adsorbates. Coconut shells have a higher percentage of micro-pores, and are better for small organics and disinfection byproducts. Wood carbons have more macro-pores, and are suited to larger organics. Coal bases have intermediate pore structure, and are more frequently used for general purpose organic reduction. For gas (vapor) phase adsorption, adsorbents with larger number of smaller pores are favored. Smaller particle size typically results in less adsorbent required. Polar sorbents take in H₂O vapor as they are soluble in water. Thus, non-polar sorbents are used for air pollution applications. Another distinction is the choice of virgin or reactivated carbon, the latter being much cheaper. Bituminous and lignite coal is typically favored for gas phase VOCs and PM, and generally for organic adsorbate materials.

Chemisorption and Impregnated GAC

Physical adsorption (physiosorption) as discussed so far relies on van der Waals interaction, with strength no more than 50 kJ/mole. In contrast, Chemisorption relies on stronger ionic, covalent or metallic interaction and thus produces an adsorbate which does not permit a reversible desorption process. Catalytic impregnants to GAC facilitate gas phase adsorption for precise species. Mentioned here for completeness although our proposal does not propose to use it, chemisorption uses specialized products subjected to treatments which facilitate the oxidation of various different chemicals such as silver, ethylene, and mercury, among others.

Parameters Adsorbed by GAC

A wide variety of contaminants in ambient AQ can be adsorbed- it is broad spectrum, so to speak: " In general, any organic compound having molecular weight greater than 45 is likely to be a good adsorbate on activated carbon."²⁸ The EPA Engineering Bulletin indicates that GAC is capable of high levels of adsorption of Total Organic Carbon (a measure of the total amount of carbon in organic compounds).²⁹ This lack of discrimination is good for adsorbing VOCs, and useless at adsorbing criteria pollutants. GAC cannot adsorb low molecular weight CO, and is a poor adsorbent for SO₂ (which transforms to SO₃) and NO₂ (which transforms to HNO₃). It can adsorb ozone (O₃) and PM, but the latter may blind and clog adsorbents.

Among the greenhouse gases (apart from ozone), GAC cannot adsorb CO₂, or methane. However, it can adsorb a host of other heavy hydrocarbons, including smog, many petroleum-derived hydrocarbons, such as asphalt fumes, octane and heptane and kerosene from the methane series; and turpentine. Other gases adsorbed well include fertilizer; pyridine from tobacco; nicotine; fuels (gasoline, kerosene, and oil); tar acids (an aliphatic acid); dioxins; oxidizers, automotive and diesel fumes; and some metals, both volatile and non-volatile.

A multiplicity of designated TACs can be adsorbed³⁰. This includes the BTEX aromatic hydrocarbons (benzene C₆H₆, toluene, and xylene), and also formaldehyde (HCHO), carbon tetrachloride (CTC, CCl₄), and tobacco smoke. Vinyl chloride (C₂H₃Cl), monitored by the State of California, and hexavalent chromium can be adsorbed, as can inorganic HAPs such as hydrogen sulfide (H₂S). Chlorinated solvents such as Perc, used in dry cleaning, can be adsorbed³¹.

Other gases that can be adsorbed are irritating and less acutely dangerous than the aforementioned. Mercaptans (methanethiols, with carbon, sulfur and hydrogen), are not considered hazardous at low levels, and can be adsorbed, as can cooking odors. Such additional adsorbents speak to prospective improvements in aesthetics and the livability of urban areas. These are present in abundance in the aerosol soup of a regulated but terribly under-enforced ambient urban environment.

5. The Regeneration of Spent Activated Carbon

Adsorption is a reversible physical process- and desorption is its reverse complement. Saturated carbon desorption and reactivation is carried out at spent carbon reactivation facilities, by processes including drying; thermal desorption, which subjects the materials to temperatures elevated to at least eight hundred degrees (often as high as 1100 f.), then steam. The process is carefully managed to avoid oxidation of the GAC under a closed environment (steam creates positive pressure, helping to ensure against oxidation). The chemical reaction incinerates VOCs and gases by pyrolysis. This process volatilizes the organic compounds which have been adsorbed onto the carbon. Thermal decomposition essentially completes the combustion process which was not completed when the hydrocarbon was first burned. Alternatively, some contaminants can be recaptured and reused. Regeneration and reactivation are technically distinct processes but are often referred to without this nicety. Reactivation, as mentioned earlier, is achieved by a subsequent reheating of the carbon at high temperature.

Regulation of Regeneration and Reactivation Facilities

The industrial process for regeneration, or desorption, of the mesh, granules, and cartridges once used is well-defined by industry. What is allowed to be processed in this manner is regulated governmentally. Spent carbon regeneration facilities are under the purview of the Environmental Protection Agency throughout the USA, and by the Department of Toxic Substances Control in California. The 1976 Resource Conservation and Recovery Act provides authority for the EPA and state agencies to regulate carbon disposal and to regulate the regeneration of such carbon materials. Both entities require certification that the spent carbon is not hazardous waste. EPA standards and DTSC procedures define this term according to 40 CFR Part 261.3 and Title 22 of the California Code of Regulations, respectively. Characteristics of hazardous waste according to the EPA's Hazard Codes are: ignitable (with flash point less than 140 degrees Fahrenheit); corrosive (acidic or basic); reactive (unstable under normal conditions), toxic (containing mercury, lead, DDT, PCBs), and acute hazardous waste or toxic waste.

In addition to following the EPA standards, the DTSC requires the specification of the non-hazardous- or hazardous nature of such wastes. This includes a number of specified wastes: F list (various manufacturing and industrial processes); K list (specific industries, petroleum and pesticides); P list (industrial chemicals), U list (discarded commercial chemical products), and M-list (mercury). Activated carbon granules and cartridges from ambient AQ collection would appear to fall into none of these forbidden categories, according to the detailed spec sheets for CC. To comply, those submitting material to a carbon regeneration facility must fill out a Spent Carbon Profile, as well as submitting analytical lab reports of an EPA 8260D mass spectrometry process which tests for quantities of Hazardous air pollutants NESHAP and VOCs in spent carbon. Custom or pool regeneration processes are available; the latter groups spent carbon

into batches, making the process cheaper per unit. CalCarbon and California Carbon, the two such facilities in California, are both in Los Angeles. Both sell supplies as well as regen services, including carbon adsorption materials designed for ambient conditions similar to those we specify (California Carbon's Coconut Shell Activated Carbon and Pelletized or Granular Coal Carbon). Other U.S. providers include General Carbon (NJ), Calgon, and TreeCo, and dozens of others worldwide.

Capital Equipment for Carbon Regeneration

The major distinction in capital equipment is between multi-hearth furnaces and rotary kilns. The former lasts longer and has greater capacity. Alternatively, a rotary kiln requires less skill to operate, requires more fuel, and can manage smaller applications. More sophisticated regen facilities include kilns or furnaces equipped with SCADA-controlled sensors to ensure avoiding LEL and UEL oxygen levels in the enclosed space of the facility, as well as exhaust handling system to control emissions.

6. Current Usage of Activated Carbon Adsorption

The comprehensive process of GAC adsorption and regeneration in the United States appears to be devoted overwhelmingly to environmental remediation and to industrial usage. The 1990 Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) mandated that the EPA design remedial action protocols for hazardous substances and pollutants at Superfund sites. This includes soil, air and water remediation. Adsorption was one of the treatments of choice at Superfund sites, and was increasingly widely adopted throughout the course of the 1990s. For instance, "a GAC system was employed for leachate treatment at the Love Canal Superfund site in Niagara Falls, NY."³² Interest in GAC for air pollution control seems to have peaked with the implementation of CERCLA, between 1990 and 2000, and thereafter stabilized in industrial effluent and regulatory issues. In the late 1990s through the early 2000s, various patents were issued, all consisting of existing design with modifications, i.e., a secondary filtration or adsorption process, expressly for air quality.

Usage in Industry

The activated carbon industry in the USA is apparently largely devoted to the oil and gas sector, to the food sector, and to remediation for other processes (see IQS guide). In South Africa and Europe, adsorption and regeneration are heavily used in the gold mining industry. There are both GAC and rotary and multi-hearth kilns manufacturers and providers in the USA, China, Denmark, Germany, India, Mexico, South Africa, Bulgaria, Sri Lanka, and Thailand. Distributors can be found in dozens more countries.

Adsorption in Commercial IAQ

The field of filtration materials for Indoor Air Quality saw urgent, renewed interest in 2020 as people were confined indoors due to the Covid-19 pandemic. These devices are being used for private home indoor air quality control, not for ambient AQ pollution.

More recently, the venture-backed startup Airlabs in London has developed proprietary patented technology for technology for local air filtration in outdoor settings (for urban smart city projects) as well as in passenger vehicles. The company's patented products are complex devices using onboard filtration with impregnated AC and nanotechnology to adsorb specific, targeted pollutants.

The State of the Art in Greenhouse Gas and Novel Materials Adsorption

There has been considerable development of novel new adsorption substances, especially for CO₂. It is interesting that adsorption materials for air pollutants, both nanotechnology and plant-derived, appears to be more heavily studied in China than in the United States. Alternatively, much consideration of adsorption in the USA is in the context of advanced materials such as

Carbon Nanotubes (CNTs)³³. At U.C. Berkeley, advanced chemical separation processes have been honored with a DOE Center of Excellence. The Center has carried out pioneering work in especially metal oxide framework designs for the selective adsorption of CO₂ and other greenhouse gases, although none of the more than a dozen featured projects is aimed at other criteria pollutants. Generally similar adsorbent processes for CO₂ adsorption by metal oxide frameworks has also been done at Stanford.

Cleantech and the Green Economy

Ambient urban pollutant capture is not a priority in the burgeoning green tech and cleantech fields. Generally speaking, these focus on the decarbonization of the energy system through large capital projects which incorporate renewal energy sources, direct air capture (DAC), and electric vehicles³⁴. Associated areas of concern include IAQ; battery storage; Green building standards; solar energy; and wind power. Despite the enormous boom in climate-related government and commercial initiatives, there is no obvious move to alter current adsorption remediation practices. Deep Carbonization, a favorite topic in national policy study, is heavily concerned with low-carbon fuel and the decarbonization of the electrical supply using wind, nuclear, and solar energy.³⁵

Ongoing Research

Since there is no academic or industrial funding concerning adsorption systems expressly designed for air quality, there is very little academic research as well. An online search yields only a handful of Ph.D. dissertations and a limited number of academic articles on the usage of coconut coir as a low-cost adsorbent material. There appears to be no movement toward development of a low-cost, universal VOC remediation process. Amidst the immense popularity of Direct Air Capture, Carbon Capture and Sequestration, biochar, grid electrification, our topic has- to use Silicon Valley's most overused term- no traction whatsoever. It is overwhelmed by the star qualities of the carbon removal movement. Alternatively, appropriate technology is kindred in spirit but not in substantive area of application, often addressing agriculture, water purification, and housing. All attention is focused elsewhere.

III. Adsorption Systems and Micromitigation Design

7. The Design of Adsorption Systems

Adsorption systems are presented in university instruction and in industry journal articles in a straightforward manner³⁶. The major distinction is between Batch and Plug flow or tubular adsorption. The batch reactor, "in which the adsorbent [usually Powdered activated carbon] is mixed with the polluted stream and the system is allowed to approach equilibrium... the use of a single batch reactor results in low removal efficiency and requires the use of pure carbon... because the desired high effluent quality equilibrates with a low solids concentration."³⁷ Its weakness is its passivity so to speak, relying on diffusion when the stronger medicine of effusion and pressure swings are available. The CSTR, or constant stir (steady state; well mixed), improves on batch processing's weaknesses in a similar physical format. While this is not a nuanced interpretation, we will lump CSTR in with batch reactors for the purposes of this discussion³⁸.

The prevailing model by far is the plug flow reactor (PFR, sometimes called continuous tubular reactor, CTR, or piston flow reactors). Le Chatelier's Principle and Henry's Law dictates that air laden with contaminant aerosols will diffuse across the gas solid boundary and equilibrate faster at higher pressure. To enhance the partial pressure discrepancy, PFR design relies on effusion as the physical configuration which facilitates partial pressure discrepancy and hence EQ. Its major design assumptions are relatively low resistance or drag, that is laminar flow with no axial mixing, and a single homogenous reaction taking place in the column.

The columnar continuous plug flow configuration consists of a canister or tank or other 'column'- an enclosed cylinder with a bed of carbon at various thicknesses- and an inlet and outlet³⁹. Adsorption onto the AC adsorbent material is effectuated by pressure drop, which allows equilibrium between the contaminant aerosol (or fluid) stream and the adsorbent material. Saturation is gauged when the inlet and outlet have the same pressure and contaminant concentrations. Packed fixed beds, with a separate effluent stream from the reactor 'bed'- i.e., cylinder- are prevalent for industrial air pollution control ^{40, 41}.

Usually a system comprises two reactor column beds that are regularly exchanged, so that one is always in use. Two small beds, rather than one large one, can be used to allay the dangers associated with exothermic processes. However, these are usually cautioned when GAC is used in a closed space or with peroxides or ketones. Another common feature is a heat exchanger to alleviate the degradation of adsorption capacity associated with relative humidity above 50%.

Disposable or rechargeable canisters are typically employed for intermittent use, or for low-volume exhaust streams or low contaminant concentration waste stream⁴². Rechargeable or disposable canisters have evolved into a relatively simple self-contained product. Off-the-shelf solutions include the Air General Pollution Control barrel (from General Carbon) for H₂S and other gas phase pollutants, and the Wolverine Pollution Control Barrel (from Simple Solutions), selling for less than a thousand dollars. Such products allow relatively low CFM or intermittent inlet flow, and deployment as needed.

8. Challenges in Ambient Adsorption Design

Adsorption systems typically use closed reactor beds, temperature and pressure swings, and above all, a closely controlled, unchanging temperature, and specified cubic feet per minute inlet, maximizing adsorbed colloidal molecules at chemical equilibrium and making measurement of breakthrough convenient.

Adsorption system design does not appear to consider open-column, at all; because under most constraints it is not the optimal way to optimize adsorbed pollutant percentage as fast as possible. Optimization seems to have been addressed as maximizing adsorbate concentration on adsorbent surface, achieved by higher partial pressure (or by temperature swing). MM's interest in altering this, as proposed in Part 3, is by having open air panels with an only intermittently higher pressure air flow. This would probably forfeit a good deal of efficiency, but would be compensated by higher time duration and higher quantity of AC used. Our constraints differ because our constituency has more time than money; cannot use effusion, and must adapt the design opportunistically to adsorption in the ambient environment in numerous emissions hotspot locations. Designing for lower ambient pressure, but more time, will require further questions;

This design challenge has apparently not been explored in any context other than closed column reactors. It appears that chemical process engineering for adsorption has not brought to bear atmospheric chemistry phenomena of atmospheric dispersion and transport, which could be used to facilitate adsorption. These opportunistic methods could include using the meteorological phenomena of dust domes, high pressure and inversions both radiational and subsidence (Godish, p83), and turbidity with low pollution dispersion adjacent to pollutant sources. This approach to a design problem that attacks a serious public health issue is not evident in the literature as far as we know.

Ambient-air adsorption will have to rely on adsorption under less expressly designed conditions. Neither the composition nor the inflow gradient of ambient air can be characterized with the assurance of a closed system. On the contrary, its composition and its speed in

reaching the adsorbent is erratic and idiosyncratic. Whatever its patterns, there will be frequent disruptions. Ambient air is affected by vehicle traffic and nearby stationary sources, and undergoes diurnal differences and differences according to days of the week. Moreover, relative humidity and temperature vary- and outside of a highly temperate range less than 50% RH, this will affect adsorption.

AC can adsorb a great variety of air pollutants, but conditions which will facilitate this process in ambient air have not been established. The central problem in designing a simple, cheap adsorption system for ambient air is the low adsorption of pollutants due to the low partial pressure of pollutants in ambient air. The partial pressure, even superficial pressure, of each gas phase component is certainly far less than in an industrial process with effusion designed into the reactor's narrow aperture.

How will results be achieved with the characteristic lower concentrations and pressure of ambient air- even heavily polluted ambient air? We can't escape the nature of ambient air, but we can use partial pressure and Graham's Law to the best possible advantage, exploiting slow diffusion rather than effusion because we don't have the physical opportunity afforded by effusion⁴³. As per Graham's law of diffusion, lighter gases effuse faster than heavier gases at a given temp and pressure (Masterson p191). Graham's law of Diffusion states that the rate of diffusion of a gas is inversely proportionate to the square root of its molar mass. This suggests that VOCs and HCs should be sought opportunistically, and with calculation, as close to the source as the adsorption panels can be placed. Density in the air is high, and diffusion is relatively slower, with heavier gases. So hydrocarbons diffuse more slowly, as the molecules are typically heavy. In addition to being more prone to a slower mean free path, such heavy hydrocarbons are very often TACs, often the products of incomplete combustion of gasoline. This is also the case with Dalton's Law of Partial Pressure. The additive nature of the latter law- stating that total pressure is additive relative to the combined partial pressures of other components in the air's mixing ratio- would suggest that some such locations are regularly relatively high-pressure, even when the air is ambient rather than fed through an inlet. If so the culprits, so to speak, can be caught more easily: near vehicular emissions and point sources both occasional and predictable- are regularly relatively high-pressure, on an intermittent basis.

Micromitigation Adsorption Strategy: Repeated Flows, Longer GAC Adsorption Time, High Surface Area

Ambient localized VOC adsorption needs a design that will facilitate adsorption in circumstances of lower air pressure than is optimal for this separation process. To this end, Micromitigation, or open panel design, will absorb, so to speak, aspects of both batch and tubular (PFR), and strive to use both to their best advantage. It will use direct contact between adsorbent and adsorbate, as per batch adsorption. However open panel adsorption is not a closed system, and does not solely rely on the low cost passivity of batch systems. Likewise we will use CFR to its best advantage by using effusion pressure where or rather when possible.

Some of the time, partial pressure even with open panels will be relatively higher because of proximity to emissions from higher wind or tailpipe or other combustion source emissions. At such times the system will have similarity to the dynamics of CFR isotherms based on pressure and adsorbate adsorbed. But CFR creates such pressure by design (closed column) within the system boundary. In contrast, Micromitigation will utilize air pressure outside the system boundary by the most carefully considered possible placement of adsorption panels. The functions carried out by the tubular plug flow reactor are carried out in MM open panel adsorption by ambient air flow. Said air flow will vary widely between different adsorption panel locations, depending on local and diurnal conditions. We are substituting the designed features with surrogate location in the environment which have the same physical characteristics, or

characteristics as close to those in CFR as we can find. Placement in the external environment, in areas of inversions, dust domes, and low buoyancy, will be our kludge.

The MMWG is testing three strategies. The first is repeated flows to the adsorbent material, achieving saturation over a long duration. Time is not of the essence here. Capillary condensation, a secondary process that takes place once initial diffusion to surface of adsorptive material AC has occurred, should not be dismissed. The MMWG wonders if repeated iterations of this second process could enhance adsorption onto GAC. The second is deployment locations carefully chosen in order to maximize persistent and episodic acute air pollutant concentrations. To use the famed real estate adage: location, location, location. Finally, we will increase the surface area of the adsorptive AC even further by designing panels open to the air.

The MMWG is experimenting with GAC with a high surface area exposed to ambient air, and rely on repeated instances of adsorption of temporarily high readings of a wide variety of gas pollutants. Adsorption does not saturate most GAC materials (cite Army Corps of Engineers document). Thus, we wish to see if repeated adsorption instances won't either.

The empirical reality of AQ incidents is in most cases intermittent episodes of high pollution, often acute, but of short duration. These instances are often unpredictable: for instance, a barbeque, a car or diesel truck that idles for fifteen minutes, an unannounced one-hour sideshow, a two-day roofing job. Such instances take place near both sensitive receptors and other people, and often repeatedly and in close proximity, as in car exhaust streetside, or construction in residential areas or high-pedestrian usage streets. Such instances may well not trigger AQ episodes based on Federal monitoring standards of either 1 hour or 24-hours, as per the EPA and CalARB's FRM monitoring. Averaged over the reporting period, data smoothing will greatly understate their severity. That does a disservice to those who breathe in polluted air at the time, on the spot.

9. Design Proposal

The design follows in the simplest possible way, as based on the strategy as expressed above. The MMWG's first effort at a micromitigation starts from the aforementioned desiderata of: a) repeated exposure, typically at low ambient air pressure, subject to intermittent acute exposure to pollutants from urban and vehicle emissions; b) extremely selective location, as discussed regarding Meteorological and Topography and regarding Emissions concerning specific urban conditions, and c) high surface area.

The initial experiment is intended to demonstrate that passive adsorption using panels of GAC over a period of several weeks or months, is an effective adsorbent method. The group made use of passive modular, movable adsorption panels with high surface exposure- filling the role of canisters, with desorption elsewhere at EPA-approved facilities. These initially took the form of screened open pouches of window screening material, of inert non-oxidizing mesh. The materials were readily purchased from hardware store or household products store.

10. Additional Concerns in Ambient Adsorption

There are other issues, variously concerning the adsorbent material and the outside environment. These namely: higher-micron diameter matter which can blind or clog GAC; the air composition (mixing ratio); the relative humidity and temperature of the air; and the low and unpredictable CFM of ambient air; and Safety Concerns.

Blinding and Clogging

Particulate matter can clog the pores of the AC. In a high-cfm system, a precipitous pressure drop will take place when suspended solids in the column are too high. Stopping the column's mass transfer process and removing suspended colloids ('Backwash') is then required. This

might be alleviated by changing the adsorbent material more frequently, or by complementing the activated carbon with baghouse filtration⁴⁴. Such filtration materials for PM are, like GAC itself, cheap both absolutely and relative to the health impacts of cumulative inhalation of PM and other criteria pollutants. Despite our fears, however, our initial test showed that GAC did adsorb VOCs notwithstanding both H2O and PM 2.5. We should also be reminded that the EPA uses solid sorbent tubes (SST) for its new method 325B, required as a fence-line monitoring test for BTEX. If the method is considered reputable by the EPA, it is certainly good enough for us.

Air Composition and Pollutants Adsorbed

A second issue is that of air composition and what pollutants can be adsorbed. The typical mixing ratio, or “zero air” proportions are N₂ (78%), O₂ (21%), and 1% carbon, helium, methane, argon and hydrogen. Vehicle emissions are predominantly made up of NO_x, VOCs, O₃, Co, HAPs, PM (10 and 2.5), and CO₂. As discussed, GAC is a broad spectrum adsorbent for all organics and some inorganic gases, and we are favorably disposed to any organic aerosols that could be desorbed. However, after we have initially established that this process is feasible, there is the issue of specific sort of GAC best suited to these particular emissions. We will discuss the specific air issues proximate to the Omni location at 4799 Shattuck Avenue in Oakland later on.

Relative Humidity and Temperature

Another issue is that of relative humidity and temperature of the air. Heating the air to dry it is often implemented because RH above 50% lowers the efficacy of the adsorption process. Yet the heat exchanger in question cannot carry this too far because this is an exothermic process. Hence adsorption processes are often kept at room temperature. What will be done when ambient air is far hotter, and with far higher relative humidity? Isotherms, which are developed after initial pilots with sample amounts of adsorbent material, typically assume that the temperature is fixed. This is not at all the case with ambient air, of course.

GAC Dust and Safety Issues

As an environmental justice community, Oakland in general and West Oakland in particular are sensitive areas where coal is concerned. The Micromitigation project uses coconut shell rather than coal-based GAC, but the safety issues relating to carbon must in themselves be considered. The Safety Data sheet for Coconut Shell Activated Carbon from California Carbon indicates that only minimal precautions are necessary. The product's Hazardous Materials ID System (HMIS) rating of 0 indicates no health concerns. Safety glasses with a side shield or goggles, gloves, long sleeves or a lab coat, long pants are recommended. There is a possibility of eye irritation. The GAC we have started working with is made of coconut coir, but coal-based GAC is typically preferred for the adsorption of heavy molecules such as hydrocarbons. However, GAC preparation includes treatment to burn out tars and any VOCs. This is not the same as an open boxcar of coal, something to which Oakland residents have strenuously objected to in the recent past.

IV. Implementation

11. Meteorological, Topographical, and Emissions-Related Desiderata for Deployment

Location Desiderata in Brief

Opportunity made our original choice for us. The first location was in downtown Oakland, a few hundred feet east of the confluence of several freeways. However, the new choices will be determined by meteorological science and atmospheric chemistry.

Suggested Locations

A. Chosen by Emissions Data:

In trying to pick location by air quality monitoring data, one would be hard-pressed to find adequately precise data, whether looking for NAAQS or for NESHAPs. Detailed hyperlocal AQ data is the exception rather than the rule, even in the United States and the EU. It is however, easy to determine where to carry out micromitigation if one chooses by emissions rather than the nearest EPA Federal Reference Method station which may be several miles, or dozens of miles away. Thus, choose by emissions sources, which are usually painfully self-evident;

Some of the choice could be based on formal search of existing regulatory agency databases. California bill AB2588 established the Toxic Air hotspot emissions database, which is accessed with a simple interface and a zip code. Alternatively, more informal selection of the sort of microscale air motion in proximity to local vehicular traffic or TAC hotspots is possible. A preliminary means by which to pick this would be from a foot to a meter above the ground, near vehicle emissions: at roadside medians; on the traffic-facing side of parklets; school bus stops; bus stops; affixed to grillwork on metal gates at entrance to residential buildings. Various public health measures, such as San Francisco's Health Code Article 38, require additional ventilation systems for PM_{2.5} in areas that fall into the 2014 Air Pollutant exposure zone ⁴⁵. While this rule addresses PM 2.5, it would certainly be a good heuristic for VOC pollutants as well.

B. Chosen by built environment topography

The urban canyon phenomenon, in which buildings are impermeable and relatively tall, is generally conducive to buoyancy, turbulence, and transport. But this is the design norm in cities in the developed world. Street canyons are generally good at allowing transport (CITE). We are also concerned with urban topographies in which the opposite is the situation- where turbulence and buoyancy are not working well. Gases move within the troposphere due to transport and to chemical reactions. Small molecules such as NAAQS pollutants characteristically do not persist because of photolysis. However, we seek to place adsorptive AC in proximity to human exposure, as the latter pollutants, as well as others such as VOCs and heavier-molecule HCs may be in relatively high concentration near their source, and may not dissipate so readily. These other sorts of urban topographies, are common worldwide although quite rare in the USA: alleyways, narrow streets; alleyways near the entrance to restaurants or food stalls. These locations may have poor transport, and considerable inhibition of both turbulence and buoyancy. San Francisco's original Chinatown, the most densely populated place in North America after Manhattan, would be an excellent site. These are the very underbelly of urban spaces: the ongoing and tiny acute AQ incidents in such locations are environmental micro-aggressions in themselves.

Desiderata regarding urban topography for mitigation would include topography that encourages stationary pollutants, such as cul de sacs hemmed in by impermeable walls; areas marked by extreme density in streetside human activity; street markets with cooking or fuel-burning; enclosed alleys. It would also be interesting to try adsorption panel placement in the eaves of buildings, on the first or second story, and see if this would allow some benefit from adiabatic lapse in air temperature as air rises. This would suggest that micromitigation could be applied in hilly and dense urban environments, rather than only flat areas with a great deal of vehicle traffic.

C. Emissions- Stationary Sources

Watched over with various levels of zeal and enforcement, by the BAAQMD and the DTSC, some emissions sources are obvious. Regulated stationary sources include permitted facilities such as near cement plants, rendering plants, and sewage treatment plants. Emissions plumes create pollution dispersion from point sources⁴⁶. These regulated locations are persistent. Other point sources are intermittent but still can be lengthy in duration, and non-compliant with emissions standards. These would include long-term construction sites, construction dust, street work, portable generators, short-duration roofing, and proximity to fugitive emissions.

D. Emissions Type Desiderata- Mobile Sources

There are also copious examples involving mobile sources. Source characterization would be, basically, anywhere near an internal combustion engine, adjacent to tailpipes. This includes inner city freeway off ramps, near roadway areas, and habitual locations of traffic jams on arterial roads. Other pertinent circumstances include locations in which traffic jams occur, turning streets into de facto parking garages. Entrances to parking garages, often backed up onto the adjacent street, and parking lots as well, are often episodic and on a predictable schedule. In addition, these locations often feature impermeable walls which could either be covered with adsorption panels or examined for aerosol effects that increase movement of aerosol contaminants toward a particular spot- which again could be covered with adsorption panels. The same is true of school bus stops and school drop-off locations. Others are less predictable, and are best spoken of as opportunistic, but occur before they can be permitted or shut down. Acute episodic conditions include motorcycle or car rallies or sideshows, as spontaneous and difficult to manage as a flash mob. Much of this won't be evident in case of a place with favorable overall AQI, as per the FRM station, but will result in poor AQI with regard to hyperlocal conditions.

11. Instrumentation and Testing

Air quality monitoring and testing are integral to Micromitigation at every stage. These steps include finding the best locations at which to place panels; testing prospective locations once located; Jar Testing and Breakthrough in the lab, using air from the sites once determined; and finally testing the adsorption panels after a field deployment.

A. Preliminary Choice of Adsorption Locations

The protocol calls for testing the ambient air quality in immediate proximity to adsorption sites. First, to start out in searching for MM sites, one may not need to test at all. An initial search of national, state or local FRM sites will yield reference instrumentation levels for VOCs, although even in CA, coverage varies tremendously⁴⁷. Air Toxic Hot spots can be located through CalARB online tools. Such databases offer preliminary consideration of a location for MM. More likely is that anyone undertaking micromitigation will be acutely cognizant of need for remediation in a neighborhood location.

B. Preliminary Air Quality Monitoring

Trust but verify, as the proverb goes. Once located through extant data sources, specific locations can be tested using a Photo Ionization Detector. The MMWG is going to use the existing model as carried out in industrial hygiene, as this sort of walk-through is commonly carried out at industrial facilities. Such walkthroughs would serve as an essential part of the implementation process, but would serve an additional purpose of engagement for community and educational environmental groups.

C. Jar Testing and Breakthrough;

The air from the polluted site is characterized by PID. But how to establish a breakthrough volume in the absence of any pre-existing isotherms or other experiments? The most economical way to start is to employ a timed test with a glass flask and GAC, with air from the chosen location. This is done as follows. Glass flasks are cleaned with distilled water, and air is collected over a chosen time interval. The MMWG decided on 24-hour averaging, which is the CalARB standard; for vinyl chloride (and other NAAQS pollutants).

How to properly fill the flasks so that sure it is entirely air from the designated spot? A simple DIY flask hack uses appropriate technology, specifically a plastic liter water bottle, then hot glue two plastic straws inside. The flask is left aside for at least a day in order to off-gas the VOCs from the hot glue. Following this, air is collected and piped to the glass flask (ADD CITATION-BILL HORN'S FLASK PHOTO ⁴⁸).

Following this, the measured unused AC is placed in the flask. In order to ascertain breakthrough, the sealed air is tested at timed intervals using a photo-ionization detector. The air is characterized by PID at two week intervals. At some point the air's composition in the sealed flask will no longer change, indicating that no further adsorption is taking place.

Metrics for Air Intake CFM combined w AC adsorption panel

The timed tests offer a way to determine breakthrough by duration, but do not characterize material balances even in an imprecise sense. We need a more precise metric for figuring out the volume of air adsorbed, and total adsorption of VOCs over period of time, so that we can start to generally characterize a few profiles for different AC and breakthrough timing circumstances. A first version of this can be determined, with great economy, using a constant flow fixed air pump. This can be modified to get a metric of how much air is going in. One of the MMWG members is currently working on such a pump, which takes in .47 liters per minute.

Following the Jar test, deploy the adsorption panel, and then test the actual results.

D. Preliminary Adsorption Testing in Situ

EPA Protocol Tests of Saturated AC, and Possible Alternatives

It is necessary to start by running an initial test with an adsorption panel placed in ambient air in proximity to vehicle emissions and other VOC sources, then testing what has been desorbed. The test that has been advised by chemists and laboratory technicians is EPA TOC-17 (ISO 16006-1), which vets the entire Technical Bulletin 530 (Rev 17) Quantitative and Semi-Quantitative list. Although TO 17 is an EPA approved and respected method, Thermal Desorption with Gas Chromatography and Mass Spectrometry is indeed costly.

The cost of lab services and implementation is the most problematic aspect of MM so far. The MMWG is also considering the potential of a less costly test, also based on ionization energy levels. Thermal Desorption with Photo-Ionization Detector would be more economical, even if lacking TO-17 imprimatur. Since specific VOC species have a signature volatilization point, they should progressively manifest during heating and thermal desorption. This may mean several VOCs appearing at once, but would give a general idea of the makeup of adsorbed chemicals in AC.

13. Desorption and Regeneration

Desorption requires essential elements of heat, leading to pyrolysis and volatilization, carried out in either a rotary kiln or a multi hearth kiln. References in industry sources vary as to the temperature and timing of the regeneration and reactivation processes; Perry's Chemical Engineer's Handbook 8th Edition 2008 covers this topic in detail ⁴⁹. Foo and Hameed (2009) indicate problems relating to regeneration and reactivation, and present usage of microwave energy for both desorption and reactivation.

14. Cost

Micromitigation is intended for communities in which time is all too abundant but money is all too scarce. Both the material inputs and the implementation itself are extremely modest in price, and the technique is meant to be deployed incrementally. Activated Carbon is extremely cheap: the five-pound bag of AC for our first experiment cost twenty dollars for AC and ten dollars for shipping. Unit prices drop dramatically when one orders large quantities. It is doubtful that the world will ever face a shortage of coconut shell, and there is much ongoing research on the usage of other fruit and nut shells, with many article citations from China and Malaysia⁵⁰. We have not yet addressed the issue of costs associated with Regeneration.

We wish to see MM work at scale, with many small projects and hopefully a number of far larger deployments once MM is an established practice. Should MM prove to be expensive, there are ways to deploy in a more discrete and calculated manner, such as intra-city arterial

roads, and the densest streets of inner cities. Deployment can be relegated to the most strategic locations, in more conservative and calibrated quantities and locations;

We bring this issue up because it is repeatedly brought up, and the fact that it is mentioned as a prospective impediment suggests that GHG continues to receive far more respect than NAAQS and NESHAPs. It seems that no amount is too large for Big Climate- which is overwhelmingly presented as GHG with some concessions to NAAQS pollutants- and it is disconcerting that even small amounts are too large for an EJ initiative which could benefit so many people. Staggering sums are being spent by the DOE and all major oil and gas companies, for DAC and CCS projects. For instance, the cost of the machinery of the Orca Project being created by Climeworks, announced in September 2021, is given as between ten and fifteen million dollars (Bloomberg) ⁵¹. This is meant to mitigate 4,000 tonnes of CO2 per year, produced by 870 cars. The high prices of new capital equipment are fixed upfront sunk costs, and it is understood that new technologies are not the most cost-effective incarnation of any technology or process.

Removing CO2 and GHG does not keep anyone from getting cancer or respiratory diseases. The assertive regulations imposed by CalARB on TACs saved lives. How many other states- and how many other places in the world could benefit from this? This is emphatically so in places which don't have CalARB, or which have only the most limited funds. For such places, this is not the universe of "bigger, better, faster, more". Harping on costs essentially dismisses the grave health issues that affect most of the people of the world. Criteria pollutants, comprising the EPA "NAAQS" list enumerated above, hold serious immediate consequences for human health, receives far less attention.

V. Status Quo Report

15. Pilot Project, Technical Challenges, and Work in Progress

Initial Pilot

God is in the details- but so is the devil. We are looking at the inevitable issues and concerns. We commenced by hanging a container of 350 grams (3/4 lb.) of 4x8 mesh coconut-shell AC out the window of the Counter Culture Lab's location at the Omni in Oakland, on June 5. Very little dust was produced in a test with a paper towel, and CCL determined that it was safe to proceed. The 4 x 8 mesh designation means that 90% of the granules are no larger than 4.75mm or .187 inch (No. 4), and no smaller than 2.360 mm or .0929 (No. 8) inches. The second test, with containers made up of fine cloth bags, started on June 12. One such container was placed next to the first on the 48th Street side of the Omni; the other was hung on the ledge of the windows facing Shattuck Avenue on the east side of the building. These containers are each about ten to twelve feet above sidewalk level.

It is vitally important that this project deploy AC in the appropriate locations. We are concerned with gaining proximity to pollutants which have not yet been dispersed by vertical transport from buoyancy and turbulence and horizontal transport from winds. The transport of pollutants far above street level is of concern. We wish to adsorb at closer proximity, as well as at 12 or 15 feet above ground. Thus, RES has placed several cloth bags of 100 grams of AC in inconspicuous locations in parklets and near the curb adjacent to the street a few feet from vehicular traffic and not more than a meter above the ground, in her neighborhood in the Outer Sunset (June 12 and 13). In addition, she left one such cloth bag in a location on Mariposa Street near Utah Street, next to parked cars, about fifty feet above traffic on the adjacent Highway 101 through San Francisco (June 15); and immediately north of a Bart train overpass on Alemany Boulevard near the northern border of Daly City (June 16). The testing time also needs to be determined, although it should encompass several stages, perhaps 2 weeks, four weeks, and six weeks.

Work in Progress

Planned Work 2022

Technical Challenges

Implementation Challenges

Laboratory work;
TD GC MS expense;
Vs PID TD;
timed tests for ersatz empirical equilibrium, such that $t_1 \neq t_2$;

16. Conclusion: prospects for wider deployment

Micromitigation could be consequential for environmental justice communities, and should be explored fully. Implementation should demonstrate the merits of this approach, and be generic and inexpensive. Our goal is the development vernacular micromitigation technology, described and developed by open online protocol. The technology will be developed by a distributed online working group which meets by Zoom call. The possibilities of such 'vernacular mitigation' go beyond coastal California, a place blessed with ample environmental-regulation monies and good will. In America's countless neglected communities, and in countries with weak AQ standards and enforcement (Latin America and East Asia come to mind)- towns or neighborhoods could initiate these projects autonomously if governmental regulatory agencies have weak enforcement powers. This process is intended to be adopted, adapted, and carried out by any person or group, of any means and with limited technical expertise. We are starting on a shoestring, which will provide ample self-discipline in creating a technology that can be implemented on a shoestring.

The technology and implementation call for considerable development, but the work continues to inspire. It is early days.

VI. Appendices

17. MMWG Team Biographies

Counter Culture Labs:

Micromitigation could not have been developed without the unique environment of the Counter Culture Labs. The CCL is the first home of the Open Insulin Project, as well as ongoing work on Mycology, Vegan Cheese, Kombucha genomics; Open Bioprinter, among other projects.

This document has also benefitted from discussions and material contributions from Bill Horn (UC Davis), Pete Palmer (SFSU), Patrik D'Haseleer of CCL and Lawrence Livermore.

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19. Endnotes

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¹⁰ H. Ritchie, "Urbanization: our world in data 2018; see web our world in data; Timon McPhearson New School, urban ecology.

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¹³ Dobbs, Jimenez, Wankat, Denn's Chemical Engineering: An Introduction.

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²⁴ Elsevier article re isotherms; Foo and Hameed 2009.

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²⁷ Broom, Darren." Characterizing Adsorbents for Gas Separation". Reprinted with permission from *Chemical Engineering Progress (CEP)*, March 2018. Copyright © 2018 American Institute of Chemical Engineers (AIChE).

²⁸ Noll p 1

²⁹ Continental Carbon Group's discussion of "What Parameters can Granular Activated Carbon (GAC) remove?" (2021) contains further details.

³⁰ Engineering Bulletin, Table 2, p2.

³¹ Perchloroethylene (PERC) has was banned in CA in 2011, with planned targetted phaseout from dry cleaning operations by 2023. The EPA approved adoption of CA's regulations, so that CA's more restrictive approach to this TAC can be enforced by Federal EPA and by the citizens of CA. Targeted News Service (USA), March 7, 2011.

³² EPA Engineering Bulletin GAC 1991, p5

³³ Stein, Itai Y.; Lachman, Wardle, and Devoe." Exohedral Physisorption of Ambient Moisture Scales Non-monotonically with Fiber Proximity in Aligned Carbon Nanotube Arrays"

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³⁴ This includes agency plans, as evidenced in a 10 29 2021 CalARB workshop on the 2022 Scoping Plan, which was almost entirely about carbon neutrality through emissions reduction. These measures included energy generators and reduction in VMT (e.g., EVs). It generally did not focus on air quality amelioration- perhaps because it generally amortizes the emissions numbers across the entire CA population.

³⁵ The projects associated with the CleanTech movement are myriad: Impossible Labs and the XPrize for DAC, the Global CO2 Initiative at U Michigan; ClimateWorks, the Pisces Foundation; Project Drawdown; the Green buildings movement and LEED standards;

³⁶ Kevin Dunn, McMaster U Adsorption Lesson.

³⁷ Noll p8

³⁸ See Denn 2012 regarding CSTR and other reactor formats.

³⁹ *ibid.*, p9.

⁴⁰ "GAC treatment of contaminated gas streams is done almost exclusively in fixed-bed reactors. EPA Engineering Bulletin

⁴¹ Fluidized reactor beds (FRB), with onboard desorption utilizing pressure or temperature swing, are more expensive and will not be considered further here.

⁴² Godish p374.

⁴³ "process by which a gas under pressure escapes from one compartment of a container to another by passing through a small opening" Masterson p191

⁴⁴ Godish, Air Quality Fifth Edition, p375.

⁴⁵ Health Code article 38 established the following air pollutant exposure zone criteria: particulate matter is greater than 10 ug/m³ or where the risk of cancer from air pollutants is greater than 100 in a million; in health vulnerable locations where PM 2.5 is greater than 9 ug/m³ or where the risk of cancer from air pollutants is greater than 90 in a million; as well as locations within 500 feet of any freeway. SF Planning APEZ CityWide health risk assessment February 19, 2020.

⁴⁶ Godish, p90.

⁴⁷ UN/ECE Taskforce on Emission Inventories and Projections;
Aether; UK Company that works on Emissions inventories for many countries

⁴⁸ ADD CITATION- BILL HORN'S FLASK PHOTO.

⁴⁹ p16-63 to 16-66.

⁵⁰ China and Malaysia: refs to articles on nut and fruit seed substrate.

⁵¹ Numerous and well-publicized DAC and CCS (Climeworks, Global Thermostat, Blue Planet, Carbon Engineering, Mosaic Materials) are a different species of effort, not NAAQS-oriented.