

Micromitigation: VOC Pollutant Mitigation through Open-Panel Adsorption of Volatile Organic Compounds in Ambient Air using Activated Carbon

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- 1. Brief Summary**

Micromitigation, or Open Panel Adsorption, is an environmental remediation method which uses physisorption by granular activated carbon in open 'adsorption 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, is working to develop this method as a complement to the established regulatory point source-based and facility-based approach to emissions.

2. The Public Health Threat of Volatile Organic Compounds

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 plethora of studies attests to this¹, and to pollutants' inordinate effect on low income and communities of color^{2,3,4}. The problem is global, and underfunded⁵. Such pollutants consist of EPA National Ambient Air Quality Standards pollutants, comprising carbon monoxide, ozone, particulate matter, lead, nitrogen dioxide, and sulfur dioxide, as well as TACs, or toxic air contaminants. Both of these remain a persistent threat in human environments. The current regulatory framework does not ignore pollutants in general, or PM (1.0, 2.5, and 10) in specific⁶. While California measure AB617 is directly addressed to PM 2.5, it includes provisions for increased emissions inventories for VOCs.

However, we are concerned with Volatile Organic Compounds, which present a persistent problem. VOCs are organic and usually carbon-based compounds which readily evaporate at room temperature⁷. 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 unknown⁸. These are not innocuous bad odors, but serious carcinogens with no minimum determination of safety^{9, 10}. 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.

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 California Air Resources Board 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.

2.1. Regulatory Efforts- USA

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." ¹¹

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 national longitudinal 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]¹². 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 TACs¹³.

" 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."¹⁴

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.

2.2. Regulatory Response- Europe

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 Europe¹⁵:

"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.”¹⁶

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.

2.3. Global Regulatory Response

2.4 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 almost one billion people living in slums- according to UN Habitat: “..the world's slum population is expected to reach 889 million by 2020 ”^{17,18}. This is one of the world's key environmental justice issues: to say less does it a disservice.

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 solutions ¹⁹. 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 carried out 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 Chemistry class; 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

4.1 Physiosorption Itself

The separation process of adsorption (not to be confused with mass transfer to another phase, or absorption²⁰) 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 online²¹. *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”²². Alternatively, it is defined as “a process by which material accumulates at the interface between two phases”.²³ 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 individual²⁴.

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.”²⁵

4.2 Mass Transfer and Post-Adsorption Equilibrium

The adhesion of molecules in adsorption is an interfacial or surface phenomenon. The associated bonding is based on weak electrostatic attractive van der Waals forces²⁶ rather than ionic or covalent bonding. The phenomenon's reliance on London dispersion forces rather than dipole

attraction, which explains its reversibility. VOCs will desorb thermally starting at 300 Fahrenheit. The fundamental action of the process of diffusion pressure is understood through Le Chatelier's principle (although as a thermodynamic depiction this does not explain the kinetics), or Henry's Law. This may be enhanced by effusion as implemented in adsorber system design.

The physical process of adsorption, as the molecules move through the adsorbent material, is one of mass transfer, of which more later. The original Langmuir model postulates progress toward a monolayer; other isotherms model a secondary layer. Adsorption heat produced diminishes as the saturation progresses. Saturation is also increased by capillary condensation, within the micropores. Gibbs free energy associated with the the unbound valence electrons at the surface decreases as post-surface adsorption takes place within layers. This enthalpy of the reaction is a matter of the specific heat capacity of different adsorbed species. In practice, empirical isotherms can characterize input and output, at given pressures and temperatures, without close characterization of the thermodynamics that pertain when different species are adsorbed. Post-adsorption, Van der Waals attachment is temperature-independent²⁷. As sorbate molecules attach at all layers, surface free energy decreases- conversely, adsorption works more readily on high SFE substances. When saturation is complete, a dynamic equilibrium between the adsorbate and the adsorbent is reached, and adsorption and desorption rates are equal^{28, 29}.

4.3 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. 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 homogeneous 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"³⁰).

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."³¹. 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 adsorbates^{32, 33}. There is a distinct isotherm for each combination of AC and pollutant and system. However the design system for gas phase adsorption is invariably a tubular or plug flow reactor³⁴. Adsorption systems will be discussed in detail in Chapters Seven and Eight.

4.4 Adsorbent Characteristics and Materials

NEED CHARTS; CHARACTERIZATION OF AC; NEED ILLUSTRATION of

Materials used in adsorption vary significantly by size, shape, and polarity. However, they share the common feature of extensive porous structures and hydrophobic character. By minimizing resistance in the mass transfer process, these molecular features enhance adsorption kinetics, and welcome rather than discourage diffusion. KNAEBEL RE diffusion onto such surfaces;

Zeolite and Molecular Sieves

Zeolite aluminosilicate and SiO₂ are also widely used for adsorption. These are tetrahedral molecules which allow extensive bonding. The uniform-Angstrom external apertures mean that they are relatively discriminating in species adsorbed. Molecular sieves are classified by their aperture size. Metal Oxide Framework adsorbents have higher saturation capacity than AC or zeolites³⁵. Other polymer adsorbents and molecular sieves are made from coal, and include non-woven synthetic fiber filtration media and silica gel (hydrous oxide, SiO₂ in other media).

REFS: PERRY'S, GABELMAN

Carbon as an AC Material

As it often does, carbon wins the popularity contest in terms of overall usage. This is because of its short diffusion path, high mass transfer rate, and heterogeneous adsorbent quality. The large surface area of the carbon atom, which allows the formation of covalent compounds in so many contexts, lends itself to adsorption of gas phase molecules. With four electrons in its valence shell, carbon's structure enhances this possibility.

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 800 to 1000 degrees C³⁶. All VOCs are removed, and extensive internal micro-pores are created in this activation process (EPA Engineering Bulletin 1991, p3). Thus, the surface area can range up from 500-2000 m²/g, and will attract a wide range of organic (and inorganic) molecules. We are primarily interested in Granulated AC, 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."

New Adsorbent Materials

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 great interest in these materials, many of them agricultural byproducts:

"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."³⁷
These are waste by products of agric process, so they could not be cheaper. As we will see in Chapter 5.6, this interest in new materials for adsorption is complemented by increased new R&D into more energy-efficient regeneration processes.

Properties and Standards of Granulated Activated Carbon

GAC is characterized both qualitatively and quantitatively by a number of properties, and meticulously defined by American Standard Test Method (ASTM) standards³⁸. 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.

INSERT CHART: In order IoN, Molasses number, total ash, AN, CTC, surface area, and 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 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 materials³⁹.

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."⁴⁰ 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).⁴¹ 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 adsorbed⁴². 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 adsorbed⁴³.

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. Current Usage of Activated Carbon Adsorption

5.1 Superfund and Environmental Remediation

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 granulated AC system was employed for leachate treatment at the Love Canal Superfund site in Niagara Falls, NY.”⁴⁴. Interest in AC 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. Moreover, in 2012 the EPA introduced Method 325B, which uses sorbent tubes, deployed for one or two weeks, to carry out fenceline monitoring for BTEX and other VOCs.

5.2 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. Polymeric adsorbents such as acrylic polymers, are more selective in their adsorbent properties and thus unlike activated carbon can be used to reclaim valuable substances in a fluid stream⁴⁵. 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.

5.3 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 pollutants⁴⁶.

5.4 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)⁴⁷. 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 organic 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.

5.5 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 vehicles⁴⁸. 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.⁴⁹

5.6 Ongoing Research

Academic or industrial funding concerning adsorption systems expressly designed for air quality appears to be extremely limited. 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 movement⁵⁰. Alternatively, appropriate technology is kindred in spirit but not in substantive area of application, often addressing agriculture, water purification, and housing⁵¹. All attention is focused elsewhere.

III. Desorption, Regeneration and Reactivation

6. The Regeneration of Spent Activated Carbon

Adsorption is a reversible physical process- and desorption is its reverse complement. Saturated carbon desorption and reactivation is usually carried out in a multiple-hearth kiln at spent carbon reactivation facilities (we will address alternative techniques momentarily). The 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. This process volatilizes the organic compounds which have been adsorbed onto the carbon. The chemical reaction incinerates VOCs and gases by pyrolysis. 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 distinction. Reactivation, as mentioned earlier, is achieved by a subsequent reheating of the carbon at high temperature.

The entirety of MM only works if the reverse logistics are thorough in desorbing and decomposing VOC contaminants- that is, micromitigation is only as good as the entirety of its desorption processes. These processes are, put more generally, its reverse logistics. The centrality of these processes to the larger integrity of MM having been established, both conventional combustion and more chemically sophisticated desorption and regeneration methods are under development.

6.1 Regulation of Regeneration and Reactivation Facilities

The process for regeneration, or desorption, of the mesh, granules, and cartridges once used is well-defined technically and well-regulated governmentally. Spent carbon regeneration facilities fall 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 (NESHAPs) 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.

6.2 Thermal Desorption Equipment and Processes

Most regeneration is carried out by thermal facilities- ovens, essentially. 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 batches. More sophisticated regeneration 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. Economies of scale, given the sheer expense of a hearth or kiln, would be advantageous to MM in practice.

Burning materials, or pyrolysis, is perhaps humanity's oldest technology. But despite its primeval nature it can be carried out at sufficiently high temperatures to comprise a clean burn. Scrutiny of the emissions of kilns is certainly warranted: the history of rich burns and noxious emissions is far more prevalent than the history of complete combustion. However, this is a technical problem which can be addressed technically, if not cheaply, with recognition of its vital importance to human health. The most sophisticated and doubtless the most expensive kilns are used in metallurgical processes in Germany and South Africa. However, wide implementation of MM would bring downward price pressure on the thermal desorption process as well. Given the sophistication of these instruments when desorption for precious metals is involved, it may be that poor functioning in this industry indicates the low priority which has been accorded to clean burns.

The pyrolysis associated with thermal desorption is generally not problematic. At 600 to 800 Centigrade, long chain alkane hydrocarbons decompose to short-lived free radicals and short chain gaseous hydrocarbons as C-H and C-C bonds are ruptured. These can be reused as organic chemical raw materials. While some research indicates that sulfur- and nitrogen-containing compounds can hinder the regeneration process, this is not indicated for hydrocarbons strictly speaking ⁵².

The instance of pyrolysis of aromatic ring HCs and chlorinated HCs could be addressed by using cleaner decomposition and regeneration technologies. Aromatic ring structure HCs- that is, including BTEX- pyrolyze into aryl radicals. These can re form as biphenyl. Moreover, pyrolysis of C4 hydrocarbon 1,3 butadiene and propyne can result in intermediate formation of polycyclic hydrocarbons. However, PAH formation is far less at temperatures below or equal to 800 C (Poddar, Thomas and Wornat 2013⁵³). Even the necessity of this discussion, however, underlines the desirability of alternative technologies for desorption.

6.3 Alternative Regeneration Technologies

Perhaps a dozen alternative treatments for desorption from AC (and from other adsorbent substrates) have been developed during the past decade. The most fully developed of these methods include Microwave treatment^{54 55} , electrochemical decomposition and regeneration, catalytic oxidation, Fenton's reaction, ozonization, UV light, H₂O₂, solvents, ultrasound (produces free radicals through cavitation at critical temperature or pressure), and bioregenerative solubilization with surfactants⁵⁶. These have various advantages and detriments.

Desorption, Decomposition and Regeneration by Microwave

The alternative thermal process of microwave-assisted desorption and regeneration, is encouraging as it offers extremely rapid heating, requires less energy and allows a high level of AC regeneration ^{57, 58, 59}. Another significant improvement is the usage of microwaves combined with UV light at 185 nm to facilitate the decomposition of Chlorine-containing species, especially when aided by O₃ (Y Sun et. al., 2017 p267 ⁶⁰). This significantly ameliorated trouble with intermediate pyrolysis products. The chlorine in question is found in pharmaceutical products, which end up in the water, and is thus less of a concern with aerosols and with the typical HC TACs found near roadways. The photolysis produced by UV light on its own, as per Santos et al., is not particularly impressive as a decomposition or regeneration method.

Moreover, experimental studies of the process, such as Foo and Hameed's 2012 experiments, have used modified home microwave ovens. These can be purchased for less than one hundred dollars in the United States, and seem to have practically speaking no resale value. Thus the capital equipment for such technique may be very economical. Could this method possibly be widely implemented at a small scale, by local environmental regulatory agencies or municipal facilities or community biolabs ?

ElectroChemical Decomposition

Another possibility is electrochemical decomposition and regeneration of saturated AC. Saturated AC is placed in an electrolytic cell containing an electrolyte solution, to which potential current is applied (Zanella, Tessaro and Feris 2014). This method has high regeneration capacity, and less modification to the pore structure of the AC than other methods. Because of the design of the process, it may simply be less challenging in terms of heating time and temperature regulation. Unlike thermal kiln or hearths, this machinery also can in some circumstances be deployed in situ.

Catalytic Oxidation

Catalytic oxidation requires the presence of mostly metallic catalytic materials- noble metal, non-metal, and mixed-metal catalysts⁶¹, but can be carried out at a lower temperature than thermal desorption and regeneration⁶².

Fenton's Reaction

Fenton's reaction entails the oxidation of Fe⁺ ions by hydrogen peroxide (H₂O₂) and the resulting production of the hydroxyl radical, in the process decomposing contaminants. It appears to preserve AC for regeneration extremely well ⁶³ (Santos et al. p6). Reducing agents can be added to further facilitate the process.

Currently these methods are too novel to be carried out economically, and this in turn is a prerequisite for scaling. At the first round, MM will have to be implemented using the available thermal desorption facilities. It is encouraging to see a great deal of concern for less polluting methods by which to carry out AC desorption thermally, chemically, and using EMF. The countries in which this research and development work is most vigorously pursued, judging by the technical literature, are Brazil, Spain, China, and Malaysia. Probably not coincidentally, these nations have both strong agricultural and heavy industry sectors, and considerable state influence over economic development. Intensive development of desorption and regeneration methods that do not require combustion would bring the cost down. This would require industrial policies expressly devoted to environmental remediation.

IV. Adsorption Systems and Micromitigation Design

7. The Design of Adsorption Systems

The major distinction in adsorption system design is that between Batch and Plug flow or tubular adsorption⁶⁴. In both cases, the systems are closed but not isolated, and the ingress of fluid flow with contaminants is adiabatic, through a pipe.

7.1 Batch Reactor

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..." is used in fluid streams. However, it is not generally looked upon favorably:

" 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."⁶⁵

The weakness of this design is its passivity so to speak, as it relies on diffusion when the stronger medicine of effusion and pressure swings are available.

Another variant, less often mentioned, is CSTR. The constant stir reactor (steady state; well mixed), improves on batch processing's weaknesses in a similar physical format, albeit with an open rather than closed system⁶⁶. While this is not a nuanced interpretation, we will lump CSTR in with batch reactors for the purposes of this discussion⁶⁷.

7.2 Plug Flow Reactor

The prevailing model is the plug flow reactor (PFR), sometimes called continuous tubular reactor, CTR, or piston flow reactors. Its major design assumptions are relatively low resistance or drag- that is a low Reynold's number- laminar flow with no axial mixing, and a single homogenous reaction taking place in the column. To enhance the partial pressure discrepancy, PFR design relies on effusion as the physical configuration which facilitates partial pressure discrepancy and hence equilibrium. CITE PERRY'S

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 outlet⁶⁸. Adsorption onto the AC adsorbent material continues to equilibrium between the contaminant aerosol (or fluid) stream and the adsorbent material. The moving boundary of the adsorption mass transfer process, as the molecules move through the reactor bed or vessel, is called the mass transfer zone (MTZ). Pressure drop occurs as the contaminant is adsorbed by the adsorbent material. As the MTZ reaches the far end of the reactor bed or column, breakthrough is reached and the system achieves a steady state of dynamic equilibrium. Saturation is gauged when the inlet and outlet have the same pressure and contaminant concentrations. Column testing is used for comparative gauging of the saturation process over time, and to measure heat evolved, as this is an exothermic process.

Such a system often has a temperature swing (TSA) or pressure swing phase (PSA) component, with desorption built in. Packed fixed beds, with a separate effluent stream from the reactor 'bed'- i.e., cylinder- are prevalent for industrial air pollution control^{69, 70}. 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%. Under exposure to extreme high temperature VOCs, there is a possibility of ignition for AC⁷¹. Additional features to cool air are undertaken in this case.

7.3 Canister Adsorbers

Most of the designs in an engineered adsorption system are just that- complete designs which incorporate the feature of desorption. However, in some cases and certainly in the case of MM, adsorption without completing the full desorption and regeneration process is desirable. Half an adsorption system, strictly speaking, is sometimes needed. Disposable or rechargeable canisters, which are filled, then taken away for desorption, are typically employed for intermittent use, or for low-volume exhaust streams or low contaminant concentration waste stream⁷². Since PFR design usually incorporates desorption through pressure or temperature swing, canisters are in essence half of a plug flow reactor system. Rechargeable or disposable canisters have evolved into a relatively simple self-contained product. Off-the-shelf solution 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. The Challenge of Ambient Adsorption Design

Adsorption systems thus use closed reactor beds, 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 in PFR has been reached by maximizing adsorbate concentration on adsorbent surface, achieved by higher partial pressure. Open panel adsorption alters this by using open panels with an only intermittently higher pressure air flow. This would probably forfeit some efficiency, but adequate adsorption would be reached by higher time duration and by using a higher volume of AC ⁷³. 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.

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. There are no mechanisms in OPA to assure that it will be a well-mixed system- that is with uniformity in the adsorbed contents.

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 make use of canonical gas law phenomena, accommodating the fundamental behavior of gases, as in theory, and their manifestations, as in practice. Le Chatelier's Principle dictates that air laden with contaminant aerosols will diffuse across the gas solid boundary and equilibrate. The weaker adsorption associated with Henry's Law will allow equilibration of partial pressure above and at the surface of the adsorbent material. This is the mechanism we would expect to see working at the panels' minimum effectiveness, but we believe that we can achieve better results than this.

We should 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 effusion. As per Graham's law of diffusion, lighter gases effuse faster than heavier gases at a given temperature and pressure. 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. Heavy hydrocarbons such as long-chain species, 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.

Open Panel [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 adsorption 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 is the case with batch adsorption. However open panel adsorption is not a closed or isolated system, and does not solely rely on the low cost passivity of batch systems. This model will act alternately as batch and PFR reactor (or rather, canisters since desorption will take place off-site). Most of the time, the system will function as a batch reactor, and time and diffusion (Henry's law) rather than alteration of partial air pressure; will be the agent to facilitate interfacial transfer.

The process will be slow, but will still be economical. Design considerations indicate that if the cycle time is longer, throughput will be lower per unit time; per increment of time ⁷⁴. But this should be taken into consideration along with the fact that open panel's capital equipment requirements are modest, accompanied by low labor and AC costs as it expressly uses commodity AC from coconut shell (and other agricultural by-products). If time is relatively cheaper, slower kinetic process is not so significant. In addition, the restrictions of this design will be far less stringent, since we do not have to worry about keeping fluid flow below critical pressure or temperature, nor about cavitation and related phenomena.

Likewise, we will use aspects of PFR design to best advantage by relying on effusion pressure where or rather when possible. The assumptions of PFR include segregated flow axially [no cross mixture during flow in column], and perfect mixing in the radial dimension. Open panel adsorption has no column depth so this would not apply. 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 bear similarity to the dynamics of PFR isotherms based on pressure and adsorbate adsorbed. PFR creates such pressure by design (closed column) within the system boundary.

In contrast, OPA will utilize air pressure outside the system boundary by carefully considered placement of adsorption panels. The functions carried out by the tubular plug flow reactor are carried out in 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 will substitute the designed features with the surrogate of locations in the environment which have characteristics as close to those in PFR as can be found. Placement in the external environment, in areas of inversions, dust domes, and low buoyancy, will be our kludge. It clearly satisfies rather than optimizes, but we hope that that will be broadly effective in many environments with scant resources. Atmospheric chemistry phenomena of atmospheric dispersion and transport could be used opportunistically to facilitate adsorption, making use of the meteorological phenomena of dust domes, high pressure and inversions both radiational and subsidence⁷⁵, 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.

Like many of life's kludges, the proposed solution of open panel adsorption forfeits obvious aesthetic and technical desiderata in the interest of accomplishing its task. In a laboratory mockup, we could figure out material balances with an air flow meter. In the field it will be difficult or impossible to figure out, as air on all sides of the panels may or may not yield VOC

species and PM particulates to the AC panels. As far as we can tell, this approach may be an EJ activist's dream, and an engineer or chemist's perplexing challenge.

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. 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 and hence the extensive property of surface free energy (designated by force per unit length) and prospective adsorption of the AC even further by designing shallow flat panels open to the air.

The MMWG is experimenting with AC 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 AC materials (cite Army Corps of Engineers document). We wish to see if repeated adsorption instances won't either.

We believe that these strategies are useful adaptations to both the cost constraints and the air transport and pollutant characteristics that communities face. 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 averaged 24-hour data, as per the EPA and CalARB's FRM monitoring. Averaged over the reporting period, data smoothing will greatly understate the severity of such acute incidents.

A single isotherm cannot represent the adsorption process given that it works by two different processes. Will the open adsorption panel system proceed toward EQ in fits and starts, since the air mixing ratio would change? (? punctuated equilibrium?). Pressure in the system will change associated with these episodes as the air itself changes. However, the jar test planned as would allow a material balance calculation by stoichiometry, since the precise mixture of VOC species at both input and output could be measured (without having to calculate molar masses as well, a daunting technical task). We are also overwhelmingly concerned with developing a method that works.

9. 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.

9.1 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 filtration⁷⁶. 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 trepidation, 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.

9.2 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.

9.3 Relative Humidity and Temperature

Another issue of potential concern 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.

9.4 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. This is the case for projects in Oakland as well as many other EJ communities. 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, and long pants are recommended. There is a possibility of eye irritation. The GAC the MMWG has 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.

10. Initial Open Panel Adsorption Design

The design follows in the simplest possible way, as based on the strategy as expressed above and the parameters stated in Part 3. 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 demonstrated that passive adsorption using panels of GAC over a period of several weeks (the time has not been determined), is an effective adsorbent method. The group made use of passive modular, movable adsorption panels with high surface exposure, 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 stores. The first sample of the adsorbed AC was deployed at a six-lane arterial street- more accurately, an intra-urban freeway- near the intersection of Alemany Boulevard and Habitat Terrace in San Francisco.

The sample was tested at an analytical laboratory by GC-MS analysis through thermal desorption (TD GC-MS), using a modified EPA Method TO-17 protocol. The results indicated significant hydrocarbons, mostly long-chain alkanes such as pentane, butane, isohexane, and octadecane, and methylbutane, used in car repair. Also included were aromatic BTEX species and ethanol, a central nervous system depressant.

Chlorinated species, specifically chloroform and methylene chloride, a solvent, were present. This is cause for concern because the pyrolysis of such substances can lead to undesired substances in the intermediate steps of pyrolysis. This is admittedly more of a problem with wastewater treatment, in which dissolved pharmaceuticals and PFOAs is observed. In general the design of MM is such that panels will be placed adjacent to traffic corridors in proximity to human residence and street life. Yet it will have to be addressed, and in fact we have considered this in discussion of alternative desorption and decomposition methods.

The group realized after the fact that we did not specify desorption at a sufficiently high temperature to desorb the VOCs at a higher Celsius. Yet even these preliminary desorption reports indicate that passive ambient adsorption over a period of time does work. The GAC was not blinded by PM 2.5, nor did competition from adsorbed H2O preclude adsorption of VOCs, in an often foggy location.

V. Implementation of Open Panel Adsorption Systems

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

11.1 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.

EDIT - initial reconnaissance;

11.2. Locations Chosen by Emissions

One can assess need for relief from ambient VOCs from any distance, looking at tabular emissions place-based data in a list, or from ground-level and empirical experience of VOCs. Early efforts will not require any more effort than location through local communities.

11.2.1 Databases: International Emissions Inventories

Anything that will be improved must be first defined and measured. As this applies to air quality, the existence of such inventories on a national basis has been improved greatly by the existence of the United Nations Economic Commission for Europe (UNECE) Convention on Long-range Transboundary Air Pollution (LRTAP Convention) in 2001 and the subsequent development and regular revision of the MEP/EEA air pollutant emission inventory guidebook. This is improving the quality of national emissions inventories worldwide. These provide numbers, which are aggregative and impressive (by being daunting and discouraging). However, these are so large-scale that not immediately useful for hyperlocal. The old adage, "think globally, act locally" comes to mind.

The same is true of Weather Research and Forecasting, or WRF models, which are also intended for weather reports and predictions. WRF models generally are mesoscale (studying several to hundreds of km), or macroscale (encompassing more than 2000 km), and even when they are microscale are usually insufficiently granular to address the sort of local conditions that we believe our likely constituency will find of concern. More recent computational fluid dynamics (CFD) programs have greater predictive power at even finer spatial resolution, however, and this could suggest particular locations relative to point sources or to transit corridors.

11.2.3 National

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, for NAAQS and even more so for VOCs. 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 from local regulated facilities. Another metric might be proximity to Superfund sites⁷⁷.

11.2.4 State

In the United States, much depends on the specific state as to how useful state data will be. The EPA maintains the AVERT software suite to assist states and other forms of localities to develop emissions inventories. Air Toxic Hot spots can be located through CalARB online tools. HARP, or Hotspots Analysis and Reporting Program⁷⁸, contains a well-articulated database and health risk assessment tools. 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. The other best-known state resource is CalEnviroScreen 4.0, which is an aggregative metadata site and therefore probably not particularly useful for MM.

11.2.5 Air Districts

California's thirty-five local air districts have jurisdiction over regulated stationary sources within their boundaries⁷⁹. They commonly show such regulated facilities on a map on the District website.

11.2.6 Municipal Data

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^{80; 81}. While this rule addresses PM_{2.5}, it would certainly be a good heuristic for VOC pollutants as well. There are comparable programs in other cities, for instance London's Low Emissions Zone LEZ⁸².

What is far more likely is that anyone undertaking micromitigation will be acutely cognizant of need for remediation in a neighborhood location.

11.2.7 Community Knowledge

More informal selection of the sort of microscale air motion in proximity to local vehicular traffic or TAC hotspots is possible and desirable, drawing on the knowledge of community members, drawn on the daily experience of those who experience aerosol contaminants, viscerally and daily. We would suspect that such locations could include, locations 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.

This is emphatically the case given that much VOC measurement, in scientific studies done by air districts and academic institutions, are done by canister sampling over a period of several days⁸³. This is bound to average data, and hence smooth spikes in VOCs.

11.3. Chosen by Topography of the Built Environment

A preliminary statement regarding topography suggests to us notable characteristic topographies, desirable for open panel adsorption. The first is dense, narrow streets in a village on relatively flat and possibly low-lying land. The second is possibly such topography in hilly land, with panels deployed differently. Finally, there are situations with concentrated low turbulent

(laminar) flow, near impermeable walls. We will go over these in order.

The study of air transport appears to commence with a hypothetical space with minimal surface roughness, and then progressively add surface roughness and other impediments to efficient air transport and hence dispersal of pollutants. The urban canyon phenomenon, in which buildings are impermeable and relatively tall, is generally conducive to buoyancy, turbulence, and transport. 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. Street canyons are generally good at allowing transport. This is the design norm in cities in the developed world, and frequently the aspirational design elsewhere.

OPA is better suited to urban topographies in which the opposite is the situation- where turbulence and buoyancy are not working well. 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 rare in the USA ⁸⁴. These locations, including isolated deep canyons, with limited building separation and setbacks, may have poor transport, and considerable inhibition of both turbulence and buoyancy, and hence high personal exposures ^{85, 86}. In addition, such locations often are proximate to valleys or riverbanks, highly correlated to both human habitation and inversions ⁸⁷. 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, at street height ⁸⁸. In addition to VOCs in proximity to street markets and dense residential buildings, such roadside neighborhoods are prone to high PM 2.5 as well ⁸⁹. These are the very underbelly of urban spaces: the ongoing and tiny acute AQ incidents in such locations are environmental micro-aggressions in themselves.

Another characteristic topography is hills with local fuel-burning absent a central electrical grid or even underground gas pipes and central heating sources. 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 OPA could be applied in hilly and dense urban environments, rather than only flat areas with a great deal of vehicle traffic.

11.4 Locations Chosen by 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 sources⁹⁰. 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.

11.5 Emissions Type Desiderata- Mobile Sources

In forensic detective work, one follows the money. In AQ emissions mitigation, one follows the car exhaust. There are copious examples of prospective involving mobile sources. Locations 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 ⁹¹. Simply put, many studies have concluded that all are terrible locations with regard to PM and gas pollutants ^{92, 93}.

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, air transport in which could simulate, in effect, columnar flow. These 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.

Other typical scenarios for TAC emissions 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.

11.6 Location Desiderata in the Immediate Future

In the near future, we are most interested in jar testing ambient air in areas 1) near urban arterial roads; 2) immediately outside residences in streets with high local VMT 3) adjacent or urban parking lots or frequent auto congestion. The Group has discussed finding rural or small-town locations to test, and we are to figure out ideal air pollutant scenarios in such instances.

12. 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.

12.1 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 tremendously⁹⁴. Air Toxic Hot spots can be located through Cal-ARB 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.

12.2 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. Preliminary testing can also be done with passive diffusion tubes PDT⁹⁵, or solid sorbent tubes (SST), readily available and economical.

12.3 Jar Testing and Breakthrough

Empirical isotherms as seen in research reflect careful laboratory conditions with specific gas species and absorbent materials. Ambient air is not as rigorously defined as, methylene blue and activated carbon, or malachite green dye and activated carbon⁹⁶. Characterizing the numerous gas phase species in air by the urban freeway on-ramp would make for an even more complex isotherm. However, we want to put the empirical results before lab testing. Thus will use simple jar testing with activated carbon in order to get at least first empirical results. This is a reasonable first approximation regarding VOCs being taken in. This method does inevitably

omit meteorological conditions that would make adsorption a batch process sometimes and PFR process sometimes.

We cannot conceptualize the movement of the MTZ through the column as typically depicted by column testing in CFR adsorption. 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).

The air from the polluted site is characterized by Photo-Ionization-Detector. The group is in the process of determining a few target VOC species to test for, as it will make PID testing easier. It would seem that a representative selection would consist of several TACs: HCs both aliphatic and aromatic: benzene, hexane, 1,3-butadiene; chlorinated substances vinyl chloride and CTC. This would seem to cover products of incomplete combustion; solvents and petroleum products associated with ICE engines.

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

12.4 Metrics for Air Intake CFM combined with 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.

12.5 Preliminary Adsorption Testing in Situ

Following the Jar testing, we will start deploying the adsorption panels. For in situ testing, we will need a control site for the Oakland CCL adsorption panels, in a location where VOCs are in relatively short supply in ambient air. The Oakland-Berkeley Hills would be a probable candidate and contrast to North or West Oakland. In situ testing should also include additional sensors for RH T, and PM 2.5. We plan to put together single-board computing modules (RasPi, SparkFun, Particle or the like), with cellular, BLE, or WiFi dataloggers. Another issue that might at some point be considered is a measure to make adsorption panels lighter in color- given that granulated carbon is a blackbody. Finally, we add the caveat that the panels will have to be removed during major wildfire events.

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.

In addition, we are currently planning to use SST solid sorbent tubes- essentially sealed laboratory blanks- in addition to adsorption panels. Method 325B, the EPA's 2012 method for fence-

line monitoring for BTEX, uses such tubes. Eurofins, the environmental testing laboratory company, offers a service to facilitate such testing with SST delivered and deployed in the field for two weeks, then returned in preaddressed envelopes.

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 the imprimatur of EPA TO-17. Since specific VOC species have a signature volatilization point, they should progressively manifest during heating and thermal desorption. This may mean that several VOCs appear 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 ⁹⁷. Foo and Hameed (2009) indicate problems relating to regeneration and reactivation, and present the case for the 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 or other agricultural husks and seeds, and there is much ongoing research on the usage of other fruit and nut shells, with many article citations from China and Malaysia⁹⁸. We have not yet addressed the issue of costs associated with Regeneration.

We wish to see this method work at scale, with many small projects and larger deployments later on. Should it 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 receive far more respect than NAAQS and NE-SHAPs. It seems that no amount is too large for Big Climate- which is overwhelmingly presented as GHG with some concessions to NAAQS pollutants. 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) ⁹⁹. 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. In this context, it is disconcerting that even small amounts are too large for an environmental justice initiative which could be consequential in neglected communities.

While necessary for the longer scenario, removing CO2 and GHG from the troposphere 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 communities which lack effective air pollutant enforcement, or which have only the most limited funds. For such places, this is not the universe of "bigger, better, faster, more". Undue focus on costs essentially dismisses the grave health issues of criteria pollutants and TACs.

VI. Applications and Implications

15. Applications and Implications

Micromitigation could be consequential for public health, architecture, urban planning, and monitoring instrumentation. We will outline changes in several forms.

15.1 Public Health

The immediate applications in ambient air improvement would take considerable time to be quantified through epidemiological studies, necessarily considerably ex post facto. Yet people who breathe better air can usually, if not always, tell by the 'taste' of the air or simply through smell. We eagerly anticipate the development of improvements in OPA, although such process improvements cannot take place without broader participation.

15.2 Prospective Applications in Architecture

MM could introduce a heretofore unrealized possibility for architecture, by integrating building design with improvements to ambient air pollution control. As far as we know, this is not being done at present. LEED and CO2 carbon neutral building materials draw great attention¹⁰⁰. Green building design appears to be generally concerned with building materials and building construction processes, and with indoor air quality and materials for the building occupants. But green buildings are not primarily about the exterior of the building insofar as the ambient air is concerned.

In contrast, it is this opposite side of the building envelope with which we are concerned. The sides of buildings are perhaps the most likely large-scale usage, especially in high-rises and dense residential neighborhoods adjacent to traffic. An interesting possibility is building construction which would facilitate the placement and removal as needed of adsorption panels. For instance brackets could be added to the sides of buildings, at a height of ten to fifteen feet, to facilitate placement of panels.

15.3 The Contributions of Humble Buildings

Micromitigation could give it increased functionality to another sort of built structure, beyond the purpose for which it is constructed. Usually utilitarian structures, frequently associated with transportation, such as bus stops, entrances and safety guards for light rail lines, surfaces of arterial road roadside barriers, utility buildings; onramps and offramps in cities and towns, all have surfaces on which OPA could be implemented. It's no surprise that such structures are typically subject to air pollution: internal combustion engines and to a much lesser extent electric vehicles are major sources of NAAQS and VOC emissions. Other sorts of amenable structures include utility and navigational signage; street signage, utility fencing, safety and traffic diversion structures adjacent to construction work. We wish to improve the functionality of structures which appear to be generally built as an afterthought. This implementation would benefit commuters, residents and shoppers, as well as another cohort which is even more vulnerable than any of these three: the unhoused.

15.4 The Reimagination of AQ as a central concern of public spaces

The increased attention that MM could bring to air quality issues in otherwise ignored public spaces, could be a boon to cohorts typically ignored in urban planning. These include the unhoused as mentioned above, informal economy participants who work at open markets or on

sidewalks or plazas, and basically everyone who lives and works in deep urban canyons. Ostensibly obscure public spaces, often in business or light industrial areas, are actually ones in which people spend a great deal of time. Likewise, far greater attention to urban structures, aspects of the built environment that are also putatively obscure. We want this to take concrete [sic] form by improvement of quotidian, pedestrian public spaces.

Civic Life and Community Space

In addition to air quality mitigation itself, MM could bring about concurrent changes to community life. It could lend even more urgency lent to environmental justice issues in non-attainment neighborhoods. We would also hope for a new and fruitful association between local communities and university and scientific communities;

15.5 Indoor Air Quality

Increased attention to indoor air quality is one of the paltry few positive and constructive advances to have come out of the ongoing horror of the Covid-19 pandemic. This includes new products at all price levels; including economical self-assembled Corsi-Rosenthal boxes ¹⁰¹. Beyond this, MM could draw more attention to the usage of VOCs in household products. This is in itself a public health problem, although one that MM only addresses indirectly.

15.6 TAC Monitoring, per se and its longitudinal practices

MM requires monitoring at every step. The preliminary realization of VOCs' abundance, prior to any changes brought about by MM itself, could be consequential. Even the institution of more measurement of VOCs- prior to OPA adsorption technology- may alter perception of the AQ map. The realization would have to be carried along by the political and regulatory processes, neither of which we are directly concerned with.

Yet a perceived need for increased AQ monitoring begs the question: how ? This immediately leads to the problem of VOC measurement itself. Typically, VOCs are assessed by canister measurement. For instance, data on odor complaints is gathered over time by BAAQMD. Scholarly studies in Edmonton (Alberta) and Naples, addressed elsewhere in this document, used canisters deployed over several days. In some cases, H₂S and other VOCs are only measured following complaints, possibly days later depending on scheduling and staffing issues. Canisters which collect data over several days smooth that data in a way that may outrage local residents who are well aware of such acute episodes. VOC measurement at a finer temporal resolution would be a welcome advance which the adoption of MM could help to encourage. There are commercial advances in this area, notably Entanglement Technologies, Project Canary, 2B tech sensors, and a new EPA grant program (beginning in 2022) that will address increased monitoring for HAPs in non-attainment neighborhoods.

OPA as Applied Atmospheric Chemistry and Reactor Design

The wide implementation of OPA could offer compelling, challenging, Interdisciplinary projects. OPA MM does not represent any new science and uses existing engineering practice. However the fields of instrumentation that OPA it relies on are novel and growing, and this is indicative of the perceived imperative of better VOC data at higher spatial resolution. There is plenty of scholarly study, along with studies made possible by more powerful and accessible computing power. Computational Fluid Dynamics has revolutionized the spatial resolution with which aerosols can be predicted. There is at present enormous cache of monitoring studies, and increasingly advanced instrumentation, including CFD modeling and land use regression models (LUR) ¹⁰². However, such study is positive and predict AQ pollutants rather than actually including implementation. But as with the epidemiological work, much study documenting dangerous atmospheric conditions. Regulations have not caught up- and enforcement almost never can catch up. An AQ solution than can be implemented on the cheap, episodically, in small-scale

locations is an excellent complement to a field of study that can predict such locations computationally.

Thus, OPA projects offer action as well as analysis, by joining the chemical engineering side with observational atmospheric chemistry and VOC monitoring instrumentation. OPA implementation could thus populate the intersection of urban planning, with atmospheric chemistry. This crossroads appears to be deserted at the moment. By bringing in a prescriptive rather than only analytical component aspect to the highly technical field of applied atmospheric chemistry, it could make this data make prescriptively powerful. Because of the pragmatic nature of the projects, it could add to academic knowledge while carrying out projects that fulfill its goal of mitigating VOC pollutants.

VII. Status Quo of Project

16. Pilot, Work in Progress, and Technical Challenges

16.1 Instrumentation and the Pilot

God is in the details- but so is the devil. The inevitable issues and concerns threaten initial idealism. In some ways, this endeavor is as modest in cost as it looks at first. The inputs of AC and OPA panels with inert mesh, are indeed economical. (Impregnated GAC is expensive, but commodity GAC remains cheap). As in many scientific endeavors, instrumentation is central- initially a stumbling block but subsequently a source of strength.

Analysis of results is easy to figure out in terms of scientific method- gas chromatography with mass spectrometry, with the desorption carried out thermally at an analytical lab. But this is definitely not cheap, especially for the earliest stages- as we have no funding yet. Over the long term, it will be prohibitive to many prospective participants. We have a practical, logistical, and ideological imperatives to keep it modestly priced. The central question, the means by which to save the day, will be better usage of instrumentation, such as perhaps using proxy or highly correlated gas species measured with a four-gas monitor to discern prospective deployment locations.

The central question, the means by which to save the day, will be cheaper instrumentation; Apparently, the day can be saved by working on this to figure out how to do it cheaply;

16.2 First Deployment

Our initial experiment used adsorption panels, screened containers of 4x8 mesh coconut-shell AC, purchased from an online mass retailer.

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. We tested the dust produced by handling the GAC. Very little dust was produced in a test with a paper towel, and Counter Culture Labs determined that it was safe to proceed. One container of 350 grams (3/4 lb.) of AC, wrapped in fine cloth gauze was placed on the 48th Street side of Counter Culture Lab's location at the Omni Commons in Oakland's Temescal neighborhood. This is a high-VOC and vehicle emissions location. Another 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.

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. We also 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. 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, and immediately north of a Bart train overpass on Alemany Boulevard near the northern border of Daly City ¹⁰³.

The testing time also needs to be determined. EPA method 325B used for BTEX analysis in fenceline locations, recommends two weeks. We started, however, with a much longer time period.

16.3 Analytical Laboratory Testing

The first sample of the adsorbed AC, from a six-lane arterial street near the intersection of Alemany Boulevard and Habitat Terrace in San Francisco, was tested at an analytical laboratory by GC-MS analysis through thermal desorption (TD GC-MS), using a modified EPA Method TO-17 protocol. The results indicated significant hydrocarbons, although we realize that we did not specify desorption at a sufficiently high temperature to desorb the VOCs at a higher Celsius. The results should have been higher. Yet even these preliminary desorption reports indicate that passive ambient adsorption over a period of time does work. Despite our worries, the AC was not blinded by PM 2.5 nor did competition from adsorbed H₂O preclude adsorption of VOCs.

16.4 Timed Tests, Photoionization Detector and Thermal Desorption

There are many potential avenues of improvement by which the process may be bettered, and we are trying to figure out how to obtain such results economically. To determine how rapidly breakthrough occurs, we are carrying out timed tests of AC sorbent material in glass jar, with VOC-saturated air, with a Photo-Ionization Detector. We can also heat the saturated AC with a thermal desorber, or alternatively, a heating block could be used at a much lower price, to heat samples from tubes.

16.5 Walkthroughs with four-gas monitor

Another way to assess prospective locations for deployment could be to use a four-gas monitor, available for far less than a PID. We will be using the TAC Tetra 3 (about \$275) to conduct walkthroughs of promising locations. The gas CO correlates highly with vehicle emissions; CO, NO_x, VOCs, PM. CH₄ and H₂S highly correlate with urban biological decay and unhealthy environments. (O₂ is a safety measure, of course).

17. 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 on-line 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 and many more colleagues. Yet we have been immensely fortunate in our initial team and organizational home. The work continues to inspire. It is early days.

VIII. Appendices

18. 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 extensive discussions and material contributions from Drs. Bill Horn (UC Davis), Pete Palmer (SFSU), Patrik D'Haseleer (CCL and Lawrence Livermore National Laboratory), Deep Sengupta (UC Berkeley).

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²¹ Dobbs, Jimenez, Wankat, Denn's Chemical Engineering: An Introduction.

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³⁸ 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).

³⁹ Gabelman, Alan. P.E." Adsorption Basics: Part 2". American Institute of Chemical Engineers. aiche.org/cep. August 2017. p 38.

⁴⁰ Noll p 1

⁴¹ Continental Carbon Group's discussion of "What Parameters can Granular Activated Carbon (GAC) remove?" (2021) contains further details.

⁴² Engineering Bulletin, Table 2, p2.

⁴³ Perchloroethylene (PERC) has been banned in CA in 2011, with planned targeted 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.

⁴⁴ EPA Engineering Bulletin GAC 1991, p5

⁴⁵ Babelman Adsorption Basics: Part 2. p41-42.

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⁴⁷ 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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⁴⁸ 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.

⁴⁹ 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.

⁵⁰ Concern with carbon removal and specifically GHG over air pollution mitigation is salient in both the pro-market and green contingents of climate crisis discussion. Barnes, Climate solutions: a Citizen's Guide. White River Junction, VT: Chelsea Green Publishing. 2008.

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⁵⁴ Foo and Hameed 2009.

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⁵⁶ With micelles, which form in colloidal suspension, which form according to polar charge.

⁵⁷ Foo and Hameed 2009.

⁵⁸ K.Y. Foo, B.H. Hameed." Microwave-assisted regeneration of activated carbon." Bioresour Technology 119 (2012) 234-240.

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- ⁶³ Santos et al., " Saturated activated carbon regeneration by UV Light, H₂O₂ and Fenton reaction".
- ⁶⁴ Kevin Dunn, McMaster U Adsorption Lesson.
- ⁶⁵ Noll p8
- ⁶⁶ Jimenez, J.L." Introduction to Flow Reactors". Advanced Atmospheric Chemistry (CHEM 5152) Spring 2015. http://ocw.mit.edu/courses/chemical-engineering/10-37-chemical-and-biological-reaction-engineering-spring-2007/lecture-notes/lec05_02212007_g.pdf.
- ⁶⁷ See Denn 2012 regarding CSTR and other reactor formats.
- ⁶⁸ ibid., p9.
- ⁶⁹ "GAC treatment of contaminated gas streams is done almost exclusively in fixed-bed reactors. EPA Engineering Bulletin
- ⁷⁰ Fluidized reactor beds (FRB), with onboard desorption utilizing pressure or temperature swing, are more expensive and will not be considered further here.
- ⁷¹ Twumasi, E., M. Forslund, P. Norberg, C. Sjostrom." Carbon-silica composites prepared by the precipitation method", J. Porous Matter. 19 (2012): 333-343. requested from library.
- ⁷² Godish p374.
- ⁷³ Knaebel, Kent S." A "How To" Guide for Adsorber Design". Adsorption Research, Inc. Dublin, Ohio 43016. n.d. Accessed December 5 2021. p4.
- ⁷⁴ Knebel article p4.
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- ⁷⁷ <https://www.epa.gov/superfund/search-superfund-sites-where-you-live>.
- ⁷⁸ Found on the California Air Resources Board website, <https://ww2.arb.ca.gov/homepage>, this replaced the pre-existing CEIDARS program. HARP includes an air dispersion modeling program, a risk assessment tool, and emission inventory module.
- ⁷⁹ David Carle. Introduction to Air in California. U.C. Press. 2006: 183-188..

⁸⁰ 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.

⁸¹ https://www.sfdph.org/dph/files/EHSdocs/AirQuality/AirPollutantExposureZoneMap_2020.pdf.

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⁸³ M.A. Bari, W.B. Kindzierski. " Ambient Volatile Organic Compounds (VOCs) in Calgary, Alberta: sources and screening health risk assessment", Science of the Total Environment 631-632 (2018) 627-640.

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⁸⁷ María A. Rubio & Eduardo Lissi & Hector Jorquera & Elizabeth Salinas & Julio Castro & Marcela Cádiz. " Carbon Monoxide Concentrations in Santiago city at street level and their vertical gradient". Environ Monitoring Assess (2008) 140:161–173. DOI 10.1007/s10661-007-9857-1.

⁸⁸ Lin, Chi-Chi; Chitsan Lin, Lien-Te Hsieh; Chin-Ying Chen, and Jr-Ping Wang. " Vertical and diurnal characterization of Volatile Organic Compounds in Ambient Air in Urban Areas". Journal of the Air and Waste Management Association. July 2011 v 61: 714-720.

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⁹³ Flavia de Nicola; Fabio Murena; M Antonietta Costagliola; Anna Alfani; Daniela Baldantoni, M Vittoria Prati; Ludovica Sessa; Valeria Spagnuolo; and Simonetta Giordano. " A multi-approach monitoring of particulate matter, metals and PAHs in an urban street canyon". Envir Sci Pollut Res. (2013) 20: 4969-4979.

⁹⁴ UN/ECE Taskforce on Emission Inventories and Projections;
Aether; UK Company that works on Emissions inventories for many countries

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⁹⁶ K.V Kumar, S Sivanesan." Pseudo second order kinetics and pseudo isotherms for malachite green onto activated carbon: comparison of linear and non linear regression methods". J Hazard Mater. B136(2006) 721-726.

⁹⁷ p16-63 to 16-66.

⁹⁸ China and Malaysia: refs to articles on nut and fruit seed substrate.

⁹⁹ 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.

¹⁰⁰ Brent Constantz, founder of Blue Planet, which makes CO₂-rich and thus carbon-negative concrete, has found himself a celebrity in Green circles in recent years. At one talk he gave in 2018, he paused and surveyed the packed audience, and said" "People didn't used to be this interested in concrete !"

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