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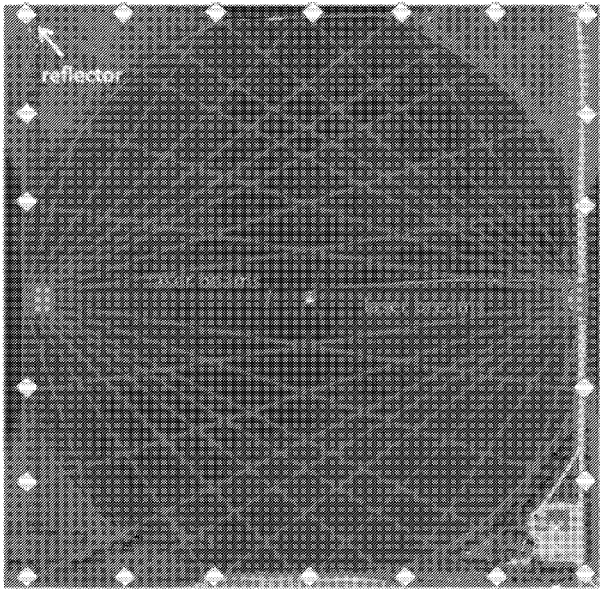


FIG. 1

(57) **Abstract:** Systems and methods are provided for measuring analytes (e.g., greenhouse gases, such as nitrous oxide) in the air over a field or other area. An optical web can be cast over the field, using a laser respectively provided from each of two or more towers disposed around an edge of the field, for the estimation of flux emissions and their spatiotemporal parameters. Each laser can be configured to provide light at a respective predetermined wavelength to one or more reflectors disposed around an edge of the field, providing a path integrated measurement, and then the light returns from the reflector to a detector that is coaligned with each respective laser. By making many such measurements, a set of linear equations can be generated, which can then be used to solve for the emission in any one grid cell of the field.

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DESCRIPTION

SYSTEMS AND METHODS FOR SPATIO-TEMPORAL ANALYTE MEASUREMENTS
OVER A FIELD USING AN OPTICAL WEB

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CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of U.S. Provisional Application Serial No. 63/523,690, filed June 28, 2023, and U.S. Provisional Application Serial No. 63/631,904, filed April 9, 2024, the disclosures of each of which are hereby incorporated by reference in their entirety, including all figures, tables, and drawings.

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GOVERNMENT SUPPORT

This invention was made with government support under Grant No. DE-AR0001385 awarded by the Department of Energy. The government has certain rights in the invention.

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BACKGROUND OF THE INVENTION

In agriculture, many greenhouse gases and air pollutants are generated and can have negative impacts on the environment. Thus, limits are placed by government on the amount of emissions that a particular farm or field may produce before reporting requirements go into effect, implementation of mitigation measures, or before claims can be made on environmental sustainability. If the actual generation of a particular emitted gas is minimized or reduced, the lower environment-impact commodity can be sold in a carbon credit market, generating income for the owner of the farm or field coming in under the limit. Such practices can also be monetized in marketing through environmental sustainability claims for their products. It is therefore important to accurately measure greenhouse gas and air pollutant emissions from agricultural practices.

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BRIEF SUMMARY

Embodiments of the subject invention provide novel and advantageous systems and methods for measuring analytes (e.g., greenhouse gases, such as nitrous oxide (N₂O)) in the air over a field or other area (e.g., a field in an agricultural setting). An optical web can be cast over the field or other area, using a light source (e.g., a laser) disposed or mounted on a tower or platform overseeing the field or other area, along with meteorological data of wind velocity. With two or more towers disposed around an edge of (e.g., just outside) the field or other area, an

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estimation of flux emissions and their spatiotemporal parameters can be obtained. Each light source can be configured to provide light at a respective predetermined wavelength (e.g., a mid-infrared (mid-IR) wavelength) to one or more reflectors (e.g., retroreflectors) disposed around an edge of (e.g., just outside) the field or other area, providing a path integrated measurement, and then the light returns from the reflector to a detector that is coaligned with each respective light source. “Grid cells” are derived from the overlapping light beams (e.g., laser beams) on the field (or other area) based on the density and/or arrangement of the reflectors. By making many such measurements, a set of linear equations can be generated, which can then be used to solve for the emission in any one grid cell of the field (or other area). This information can be coupled with meteorological data in atmospheric inversion models for the final emission (or analyte concentration) estimation.

In an embodiment, a system for measuring at least one analyte in air over a field (e.g., an agricultural field) can comprise: at least two towers disposed at or near a perimeter of the field, wherein each tower of the at least two towers comprises at least one mid-infrared (mid-IR) light source (e.g., laser) disposed thereon and configured to provide light at a predetermined wavelength for a particular analyte, wherein the predetermined wavelength is in a range of from 2 micrometers (μm) to 30 μm ; a plurality of reflectors disposed around the perimeter of the field and configured to reflect light from each mid-IR light source of each tower; and an analyzer unit in operable communication with the at least one mid-IR light source of each tower of the at least two towers. Each tower of the at least two towers can further comprise a detector (e.g., a mercury cadmium telluride (MCT) detector and/or an image sensor) disposed thereon and configured to receive signals of light reflected from the plurality of reflectors. The system can further comprise a meteorology station in operable communication with the analyzer unit, and the meteorological station can be configured to obtain meteorological data of the air over the field, air adjacent to the field, or both. The meteorological data can comprise, for example, wind speed, wind direction, air pressure, air temperature, humidity, or a combination thereof. The meteorology station can be disposed within or adjacent to the field. Each analyte of the at least one analyte can be, for example, a greenhouse gas (e.g., N_2O , ammonia (NH_3), methane (CH_4), carbon dioxide (CO_2), ozone (O_3) or a combination thereof). The system can be configured to measure the at least one analyte with a precision resolving about 1 part in 1000 of the ambient level of each respective gas in the atmosphere away from nearby sources (i.e., background levels). This is on the order of parts per billion (ppb) or less (such as, for example, 100 ppb for CO_2 , 0.1 ppb for N_2O , 0.1 ppb for NH_3 , and 0.1 ppb for O_3). The system can be configured to measure the at least

one analyte with a sensitivity/precision of 100 ppb or less, 10 ppb or less, 1 ppb or less, 0.1 ppb or less, 1 ppb, about 1 ppb, 0.1 ppb, or about 0.1 ppb). The plurality of reflectors can be disposed at regular intervals around the perimeter of the field and/or can be disposed close enough to each other around the perimeter of the field the analyzer unit to generate a map of a concentration of the at least one analyte with a predetermined granularity. The analyzer unit can comprise software stored thereon that is configured to receive the signals of light reflected from the plurality of reflectors and convert them to data indicative of a concentration of the at least one analyte in the air. The analyzer unit can convert the signals via wavelength modulation spectroscopy, direct absorption spectroscopy, or both. The data indicative of the concentration of the at least one analyte in the air can comprise at least one of: spatial information of the concentration of the at least one analyte in the air; vertical profile information of the concentration of the at least one analyte in the air; and a flux of the concentration of the at least one analyte in the air. The system can further comprise a display in operable communication with the analyzer unit, and the analyzer unit can be configured to display the data indicative of the concentration of the at least one analyte in the air on the display. Each reflector of the plurality of reflectors can be, for example, a retroreflector configured to reflect mid-IR light. The retroreflector can comprise a base substrate and a coating layer disposed on the base substrate. The base layer can comprise a thermoplastic material (e.g., a polymer, such as polymethyl methacrylate (PMMA)). The coating layer can comprise a metal (e.g., aluminum (Al), gold (Au), silver (Ag), or a combination thereof). The coating layer can have a thickness of, for example, 10,000 Angstroms or less (e.g., 5,000 Angstroms or less, such as 2,500 Angstroms or about 2,500 Angstroms). The retroreflector can further comprise: an adhesive layer disposed between the base substrate and the coating layer; and/or a protective layer disposed on the coating layer. The adhesive layer can comprise a transition metal (e.g., titanium (Ti), chromium (Cr), or a combination thereof). The adhesive layer can have a thickness of, for example, 10,000 Angstroms or less (e.g., 5,000 Angstroms or less, such as 500 Angstroms or about 500 Angstroms). The protective layer can comprise an insulative material (e.g., silicon oxide). The retroreflector can have a total thickness of 50 millimeters (mm) or less (e.g., 25 mm or less, 10 mm or less, 4 mm or less, about 4 mm, or 4 mm). The at least two towers can comprise two towers disposed symmetrically opposite from each other on opposite sides of the field. The analyzer unit can comprise a field programmable gate array (FPGA), such as a custom FPGA. Each tower of the at least two towers can further comprises a visible light source (e.g., a visible light laser) disposed thereon and configured to provide light at a visible wavelength for ease of

alignment initially during setup. Each tower of the at least two towers can further comprise a gimbal (e.g., a joystick-controlled gimbal) to steer the mid-IR light (e.g., laser beam) to each reflector on the field. The at least mid-IR light source can be, for example, a quantum cascade laser (QCL), an interband cascade laser (ICL), an antimonide laser, a lead-salt laser, a light
5 emitting diode (LED), one or more frequency combs, or light from difference frequency generation. At least two of the towers present can contain a reflector as well (i.e., every tower present may contain a reflector).

In another embodiment, a method for measuring at least one analyte in air over an agricultural field can comprise: i) providing a system as disclosed herein (such as one having any
10 combination of features from the previous paragraph); ii) sending mid-IR light from the at least one mid-IR light source, of a first tower of the at least two towers, to a first reflector of the plurality of reflectors and receiving reflected light from the first reflector; iii) moving the at least one mid-IR light source of the first tower and sending mid-IR light from the at least one mid-IR
15 light source, of the first tower, to another reflector of the plurality of reflectors and receiving reflected light from said another reflector; iv) repeating step iii) for each other reflector of the plurality of reflectors; v) optionally repeating steps ii) – iv) for each other tower of the at least two towers that is present; and vi) using the analyzer unit to convert signals of reflected light to data indicative of a concentration of the at least one analyte in the air. When each of the first
20 tower and a second tower symmetrically opposite from the first tower shines directly to the other, the overlapping pathlengths of the light (e.g., laser beam) allow for an internal calibration of the at least one mid-IR light source of each tower on the exact same optical pathlength. The method can further comprise displaying, on a display in operable communication with the analyzer unit, the data indicative of a concentration of the at least one analyte in the air. Though this paragraph and the previous paragraph disclose at least two towers, a platform can be used instead of any or
25 all towers.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows an image of an overhead view of an agricultural field having towers and reflectors, according to an embodiment of the subject invention. The (red) lines across the field
30 represent paths of laser beams traveling from the towers to the reflectors and back.

Figure 2 shows an image of a tower disposed at an edge portion of an agricultural field, according to an embodiment of the subject invention. The (red) lines across the field represent

paths of laser beams traveling from the tower to reflectors and back. The inset shows an image of an example reflector that may be used with embodiments of the subject invention.

Figure 3 shows an example of a spatial map of analyte concentration that can be obtained using systems and methods of embodiments of the subject invention. The scale bar at the
5 righthand portion of Figure 3 shows the scale for nitrous oxide (N_2O) flux.

Figure 4 shows an image of an example reflector that may be used with embodiments of the subject invention. The scale bar is 10 millimeters (mm).

Figure 5 shows a schematic view of optics that can be in a tower, according to an embodiment of the subject invention.

10 **Figure 6** shows images of different types of reflectors that can be used with systems of embodiments of the subject invention. Figure 6 also shows a chart of normalized signal strength (in arbitrary units) for different types of reflectors when used with systems of embodiments of the subject invention.

15 **Figure 7** shows images of different types of reflectors that can be used with systems of embodiments of the subject invention.

Figure 8 shows plots of change in N_2O concentration (in parts per billion (ppb)) versus time (in hours for the top plot and in seconds for the bottom two plots).

Figure 9 shows an image of a setup of reflectors and a tower, according to an embodiment of the subject invention.

20 **Figure 10** shows an overhead image (top) of a field that was used to test a system, according to an embodiment of the subject invention, and an image (bottom) of optics that can be in a tower, according to an embodiment of the subject invention.

Figure 11 shows plots of change in N_2O concentration (in ppb) versus time (time of day for the left plot and the top two plots, and in seconds for the bottom two plots on right).

25 **Figure 12** shows a plot of time versus space, showing atmospheric mixing.

Figure 13 shows a calculation of concentration of an analyte in air.

Figure 14 shows an example of spectroscopy.

DETAILED DESCRIPTION

30 Embodiments of the subject invention provide novel and advantageous systems and methods for measuring analytes (e.g., greenhouse gases, such as nitrous oxide (N_2O)) in the air over a field or other area (e.g., a field in an agricultural setting). An optical web can be cast over the field or other area, using a light source (e.g., a laser) mounted or disposed on a tower or

platform overseeing a field or other area with meteorological data of wind velocity. With two or more towers disposed around an edge of (e.g., just outside) the field or other area, an estimation of flux emissions and their spatiotemporal parameters can be obtained. Each light source can be configured to provide light at a respective predetermined wavelength (e.g., a mid-infrared (mid-IR) wavelength) to one or more reflectors (e.g., retroreflectors) disposed around an edge of (e.g., just outside) the field or other area, providing a path integrated measurement, and then the light returns from the reflector to a detector that is coaligned with each respective light source. “Grid cells” are derived from the overlapping light beams (e.g., laser beams) on the field (or other area) based on the density and/or arrangement of the reflectors. By making many such measurements, a set of linear equations can be generated, which can then be used to solve for the emission in any one grid cell of the field (or other area). This information can be coupled with meteorological data in atmospheric inversion models for the final emission (or analyte concentration) estimation, and this can be done as a function of grid cells. Each light source can be, for example, a quantum cascade laser (QCL), an interband cascade laser (ICL), an antimonide laser, a lead-salt laser, a light emitting diode (LED), one or more frequency combs, or light from difference frequency generation. At least two of the towers present can contain a reflector as well (i.e., every tower present may contain a reflector). In many embodiments, each light source is a laser.

Related art sensing technology is limited to either spatial or temporal resolution. For example, drone- or vehicle-based measurements can produce spatially resolved measurements but cannot operate continuously in practice. Eddy covariance and soil flux chambers can be set up to operate for months or longer providing temporal resolution but cannot spatially resolve an entire field or other area. Eddy covariance flux measurements also cannot be done under conditions of light winds or high atmospheric stability, and eddy covariance flux measurements can only measure fluxes over upwind directions. Eddy covariance fluxes cannot resolve spatial heterogeneities within their upwind “footprint”. Flux chambers also disturb the soil that they are embedded into, and analyses require significant labor off-site and consumables to conduct the analyses off-site. Embodiments of the subject invention provide both spatial and temporal resolution and are only spatially limited by the density of the reflectors around the field or other area. The systems and methods of embodiments provide a “gold standard” for measuring emissions of analytes (e.g., gases) of interest, particularly greenhouse gases such as N₂O.

Embodiments of the subject invention can be used for tomographic imaging of analyte (e.g., gas) fluxes over any space. The systems can be built and/or optimized for measurements

over an agricultural field, but any field, body of water, or large indoor/outdoor space (such as an animal feedlot or industrial facility) can also be targeted for measurements. The systems and methods can be used for measuring greenhouse gases, such as N_2O , which is particularly relevant for the carbon credit market and regulatory compliance. In some embodiments, the reflectors can be attached to drones, small radio-controlled (RC) cars or boats, water buoys, towers, or other structures, and the imaging can be done in a diverse set of environments and in a dynamic fashion where the laser tower tracks the moving platform.

In preferred embodiments, a system comprises mid-IR retroreflectors set up along the perimeter of a field and a rotating tower-based optical setup comprising a mid-IR light source (e.g., a laser) and a detector (e.g., a mercury cadmium telluride (MCT) detector and/or an image sensor). The system can also include one or more mirrors and/or custom field programmable gate arrays (FPGA) electronics. The system can also include one or more visible-light lasers to help with the alignment. The gimbal position of each retroreflector can be saved by the analyzer unit (or computer) for repeated probing of each reflector. The gimbal can move the output beam on the respective tower to different retroreflectors. The laser can aim at any one retroreflector for a predetermined amount of time (e.g., in a range of from 1 minute (min) to 10 min, or any subrange contained therein, such as from 2 min to 7 min) before moving on to aim at the next reflector. The path-integrated measurements from every reflector, and in some cases multiple towers, can then be de-convoluted into a map of analyte concentrations across the domain through tomographic methods.

In many embodiments, a meteorology station (e.g., a sonic anemometer or similar meteorological sensor) can be mounted on at least one tower (which can be the same as the tower with a laser or can be separate therefrom) to record wind and/or other meteorological parameters. By combining the wind measurements with the concentration maps through inverse dispersion methods, an emission map can be created as a function of space and time.

Figure 1 shows an image of an overhead view of a field having two towers and a plurality of reflectors, according to an embodiment of the subject invention. Figure 2 shows an image of a tower disposed at an edge portion of a field, according to an embodiment of the subject invention. In Figures 1 and 2, the lines across the field represent paths of laser beams traveling from the tower to reflectors and back. Referring to Figures 1 and 2, the towers can send light (e.g., mid-IR light) to the reflectors, which is then reflected back to the respective tower to be detected by a detector (e.g., an MCT detector and/or an image sensor). The reflectors can be positioned around an outside (e.g., around a perimeter) of the field, such that an optical web or

net of detecting laser beams is generated in use. Figure 5 shows a schematic view of optics that can be used in a tower, in one example. The system can use open-path sensing equipment or sensors (i.e., optics). Open-path sensing equipment or sensor means that air is passively brought through the sample volume either through wind or the motion of the sensing equipment or sensor (e.g., via a moving platform), and the sampling volume is exposed directly to the environmental conditions.

In some embodiments, the system can include an analyzer unit in operable communication with each tower. The analyzer unit can be, for example, a computer with software stored thereon that is configured to receive the signals (or reflected light from the reflectors) and convert them to data indicative of the analyte concentration in the air. The optically absorbed signals can be converted via, for example, wavelength modulation spectroscopy or direct absorption spectroscopy, though embodiments are not limited thereto (see also Figure 14 for an example of spectroscopy). The data indicative of the analyte concentration in the air can include spatial information (e.g., the concentration in space within the field) and/or vertical information (e.g., the concentration spatially and by height from the ground with appropriately spaced reflectors). The data indicative of the analyte concentration can also include a flux of the analyte concentration. The analyzer unit can include custom FPGA electronics. The analyzer unit can be in operable communication with a display on which the data indicative of the analyte concentration in the air can be displayed. The display can be located on a tower having the analyzer unit or can be remote from such tower, in which case the data can be transmitted to the display wirelessly or via a wire (e.g., a buried wire). As the tower(s) send(s) light to reflectors around the field, a full picture of analyte concentration in the entire field can be obtained, as shown in Figure 3.

Each laser can be configured to provide light at a wavelength in the mid IR range (i.e., 2 micrometers (μm) to 30 μm), and at a specific wavelength for a particular analyte. That is, each tower can include at least one laser, which can include a first laser configured to provide light at a first mid-IR wavelength targeted to obtain the concentration of a first analyte, a second laser configured to provide light at a second mid-IR wavelength targeted to obtain the concentration of a second analyte, a third laser configured to provide light at a third mid-IR wavelength targeted to obtain the concentration of a third analyte, and/or a fourth laser configured to provide light at a fourth mid-IR wavelength targeted to obtain the concentration of a fourth analyte, etc. In the case where more than one laser is present, only one laser is operated at a time to obtain the concentration of a single analyte at a time.

The reflectors can be positioned around the field in any reasonable manner. For example, the reflectors can be positioned at regular intervals around the field. The reflectors can also be disposed in a non-regular manner. In a preferred embodiment, the reflectors are disposed at regular intervals around the field and disposed close enough to each other to generate a map of the analyte concentration with a desired granularity. Figures 6 and 7 show images of examples of reflectors that can be used.

Each reflector can be any suitable reflector that reflects mid-IR laser light. In some embodiments, a new type of reflector can be used that is both cheap and effective. Each reflector can be a retroreflector configured for mid-IR light and be of the type that is otherwise only available in the related art for visible light. The retroreflector can comprise a base substrate (e.g., a thermoplastic material, such as a polymer (e.g., polymethyl methacrylate (PMMA))), an optional adhesive layer disposed on the base substrate, a coating layer disposed on the base substrate and any optional adhesive layer, and an optional protective layer disposed on the coating layer. The coating layer can be, for example, a metal such as aluminum (Al), gold (Au), silver (Ag), or a combination thereof. The coating layer can have a thickness of, for example, 10,000 Angstroms or less (e.g., 5,000 Angstroms or less, such as 2,500 Angstroms or about 2,500 Angstroms). The optional adhesive layer can comprise, for example, a transition metal (e.g., titanium (Ti), chromium (Cr), or a combination thereof). The optional adhesive layer can have a thickness of, for example, 10,000 Angstroms or less (e.g., 5,000 Angstroms or less, such as 500 Angstroms or about 500 Angstroms). The optional protective layer can comprise, for example, an insulative material (e.g., silicon oxide). The retroreflector can have a total thickness of, for example, 50 millimeters (mm) or less (e.g., 25 mm or less, 10 mm or less, 4 mm or less, about 4 mm, or 4 mm). Figure 4 shows an image of such a retroreflector. While related art reflectors can cost in the thousands of dollars (USD), retroreflectors of the type discussed in detail herein can be effective while only costing on the order of tens of dollars or less.

Embodiments of the subject invention effectively cast an optical web for the estimation of flux emissions and their spatiotemporal parameters. Light can be sent from each tower to the reflectors, providing a path integrated measurement, and then the light returns from the retroreflector to a detector that is coaligned with the laser on the respective tower.

Systems and methods of embodiments of the subject invention can measure spikes in analyte concentration above the background concentration (see also, e.g., Figure 13). In this way, any horizontal flux that may be present from neighboring agricultural fields (e.g., from wind blowing) can already be accounted for in the background, and spikes (and valleys) in analyte

concentration compared to the background can be considered to identify hotspots (or “cold” spots, e.g., deposition) of the analyte in the field being monitored.

The analyte can be a greenhouse gas or air pollutant, such as nitrous oxide (N_2O), ammonia (NH_3), methane (CH_4), or carbon dioxide (CO_2). In some embodiments, the concentration in the air of more than one analyte can be detected, and each analyte may be a greenhouse gas or air pollutants (such as those listed in the previous sentence). Figure 12 shows a plot of atmospheric mixing of many different gases.

The systems and methods of embodiments of the subject invention can detect analyte concentration in the air with a sensitivity of 500 parts per billion (ppb) or less, such as 100 ppb or less, 50 ppb or less, 10 ppb or less, 1 ppb or less, 0.1 ppb or less, about 1 ppb, 1 ppb, about 0.1 ppb, or 0.1 ppb.

In many embodiments, it is important that the distances between each tower and each reflector is known. If the distances are “off” by 1 meter in a 400 meter distance, that can be equivalent to an error of 1 part in 400 or a retrieved concentration of about 1 ppb out of 335 ppb by analogy. Thus, the distance between each reflector and each tower can be determined through direct measurements (e.g., tape measure, laser range finder, etc.) or derived optically (the time delay from a pulse of the light source and the receipt of that pulse, which can be converted to distance based on the speed of light; another option is to look at the phase shift of light going out versus that received in return which can give time (and therefore distance)). The distances between each tower and each reflector should be known to a precision of 1 part in 1000 (i.e., to within an error of no more than 0.1% of the actual distance). The distance can also be determined/known by having robust towers and/or reflector mounts.

In some embodiments, a beam splitter and/or beam expander can be included on at least one tower. If the beam is wider, the alignment gets easier. Though, if the beam is too wide, very little light gets reflected back to the sensor, which leads to more noise and a less accurate measurement of the analyte concentration.

In some embodiments, the system can include a reference cell (e.g., disposed in or on at least one tower) for line-locking and calibration, where a portion (e.g., 5% or about 5%) of the outgoing beam is directed by a beam splitter to a reference cell containing a gas of interest (e.g., N_2O). The light passing through the reference cell can then be focused onto a mid-IR detector. The reference cell can include a reference detector and can be used for an absolute concentration reference and also to line-lock the light source (e.g., laser) to the absorption line of interest. Such line-locking can be important for high-precision, high-stability measurements, as well as in

situations when rain happens and optics get covered with droplets where little or no light may return back from the reflectors.

In some embodiments, some or all of the reflectors and/or at least one of the towers can include a hood (e.g., a short hood) to help minimize precipitation from impacting the measurements. The hood can be, for example, a small umbrella over the outgoing/returning beam and reflectors. This can increase the system robustness.

In some embodiments, the reflectors can be positioned vertically with respect to the towers themselves to get vertical profile information of the analyte (e.g., within the canopy of a crop in the field and perhaps even above the canopy if reflectors are on poles extending above it). This data can be important for accurate flux measurements as the concentration profile helps to determine the flux with the wind speed (which is more predictable with height).

The methods and processes described herein can be embodied as code and/or data. The software code and data described herein can be stored on one or more machine-readable media (e.g., computer-readable media), which may include any device or medium that can store code and/or data for use by a computer system. When a computer system and/or processor reads and executes the code and/or data stored on a computer-readable medium, the computer system and/or processor performs the methods and processes embodied as data structures and code stored within the computer-readable storage medium.

It should be appreciated by those skilled in the art that computer-readable media include removable and non-removable structures/devices that can be used for storage of information, such as computer-readable instructions, data structures, program modules, and other data used by a computing system/environment. A computer-readable medium includes, but is not limited to, volatile memory such as random access memories (RAM, DRAM, SRAM); and non-volatile memory such as flash memory, various read-only-memories (ROM, PROM, EPROM, EEPROM), magnetic and ferromagnetic/ferroelectric memories (MRAM, FeRAM), and magnetic and optical storage devices (hard drives, magnetic tape, CDs, DVDs); network devices; or other media now known or later developed that are capable of storing computer-readable information/data. Computer-readable media should not be construed or interpreted to include any propagating signals. A computer-readable medium of embodiments of the subject invention can be, for example, a compact disc (CD), digital video disc (DVD), flash memory device, volatile memory, or a hard disk drive (HDD), such as an external HDD or the HDD of a computing device, though embodiments are not limited thereto. A computing device can be, for example, a

laptop computer, desktop computer, server, cell phone, or tablet, though embodiments are not limited thereto.

When ranges are used herein, combinations and subcombinations of ranges (e.g., any subrange within the disclosed range) and specific embodiments therein are intended to be explicitly included. When the term “about” is used herein, in conjunction with a numerical value, it is understood that the value can be in a range of 95% of the value to 105% of the value, i.e. the value can be +/- 5% of the stated value. For example, “about 1 kg” means from 0.95 kg to 1.05 kg.

A greater understanding of the embodiments of the subject invention and of their many advantages may be had from the following examples, given by way of illustration. The following examples are illustrative of some of the methods, applications, embodiments, and variants of the present invention. They are, of course, not to be considered as limiting the invention. Numerous changes and modifications can be made with respect to embodiments of the invention.

EXAMPLE 1

A tower system was developed to conduct a laser scan across a field lined with inexpensive reflectors, in essence casting an optical net over a field. An image of the system is shown in Figure 1. Tomographic reconstruction of the laser scans, coupled to meteorological data and atmospheric inversion models, allowed for continual (30 min) and high-resolution (< 1 acre) maps of N₂O emissions. A QCL, coaligned with a visible diode laser and an MCT detector, were aligned with a first retroreflector. The system then rotated to other retroreflectors, spending a few minutes at each reflector, to complete a scan of the entire field. The full system used two towers to make a symmetric and complete scan of the field while maintaining self-calibration when tower is aligned with the other. Custom FPGA electronics controlled the laser, detector, and all signal and data processing and were low power for field deployment. Integrated-path length measurements of N₂O were made across a 400 meter roundtrip, with the results shown in Figure 3.

EXAMPLE 2

The tower system of Example 1 was tested with corner cube array retroreflectors, using the equipment and field shown in Figure 9. The results are shown in Figure 8 and demonstrate that the system worked for long path (400 meters between tower and reflector) measurements.

EXAMPLE 3

A system of was tested using the open-path optical sensor shown in the image at the bottom of Figure 10 (and schematically in Figure 5), over the field shown in Figure 10, using a 4
5 x 4 array of plastic retroreflectors (about 10 meter spacing). The reflectors were positioned closer to the sensor in this example than in Example 2 (e.g., 98 meter roundtrip for the reflector highlighted by the “retroreflector” arrow in Figure 10. The results are shown in Figure 11 and show that the system functioned as intended with high accuracy.

10 It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application.

15 All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

CLAIMS

What is claimed is:

1. A system for measuring at least one analyte in air over a field, the system comprising:

a first tower and a second tower each disposed at or near a perimeter of the field, wherein each of the first tower and the second tower comprises at least one mid-infrared (mid-IR) light source disposed thereon and configured to provide light at a predetermined wavelength for a particular analyte, wherein the predetermined wavelength is in a range of from 2 micrometers (μm) to 30 μm ;

a plurality of reflectors disposed around the perimeter of the field and configured to reflect light from the mid-IR light source of each of the first tower and the second tower; and

an analyzer unit in operable communication with the at least one mid-IR light source of each tower of the at least one tower.

2. The system according to claim 1, wherein each of the first tower and the second tower further comprises a first detector disposed thereon and configured to receive signals of light reflected from the plurality of reflectors.

3. The system according to any of claims 1-2, further comprising a meteorology station in operable communication with the analyzer unit, wherein the meteorological station is configured to obtain meteorological data of the air over the field, air adjacent to the field, or both.

4. The system according to claim 3, wherein the meteorological data comprises wind speed, wind direction, air pressure, air temperature, humidity, or a combination thereof.

5. The system according to any of claims 3-4, wherein the meteorology station is disposed within or adjacent to the field.

6. The system according to any of claims 1-5, wherein each analyte of the at least one analyte is a greenhouse gas or air pollutant.

7. The system according to claim 6, wherein the at least one analyte comprises nitrous oxide (N_2O), ammonia (NH_3), methane (CH_4), carbon dioxide (CO_2), or a combination thereof.

8. The system according to any of claims 1-7, wherein the system is configured to measure the at least one analyte with a sensitivity of 100 parts per billion (ppb) or less.

9. The system according to claim 8, wherein the system is configured to measure the at least one analyte with a sensitivity of 10 ppb or less.

10. The system according to any of claims 8-9, wherein the system is configured to measure the at least one analyte with a sensitivity of 1 ppb or less.

11. The system according to any of claims 1-10, wherein the plurality of reflectors are disposed at regular intervals around the perimeter of the field.

12. The system according to any of claims 1-11, wherein the plurality of reflectors are disposed close enough to each other around the perimeter of the field the analyzer unit to generate a map of a concentration of the at least one analyte with a predetermined granularity.

13. The system according to claim 12, wherein the analyzer unit comprises software stored thereon that is configured to receive the signals of light reflected from the plurality of reflectors and convert them to data indicative of a concentration of the at least one analyte in the air.

14. The system according to claim 13, wherein the analyzer unit converts the signals via wavelength modulation spectroscopy, direct absorption spectroscopy, or both.

15. The system according to any of claims 13-14, wherein the data indicative of the concentration of the at least one analyte in the air comprises at least one of: spatial information of the concentration of the at least one analyte in the air; vertical profile information of the concentration of the at least one analyte in the air; and a flux of the concentration of the at least one analyte in the air.

16. The system according to any of claims 13-15, further comprising a display in operable communication with the analyzer unit, wherein the analyzer unit is configured to display the data indicative of the concentration of the at least one analyte in the air on the display.

17. The system according to any of claims 1-16, wherein each reflector of the plurality of reflectors is a retroreflector configured to reflect mid-IR light.

18. The system according to claim 17, wherein the retroreflector comprises a base substrate and a coating layer disposed on the base substrate.

19. The system according to claim 18, wherein the retroreflector further comprises at least one of: an adhesive layer disposed between the base substrate and the coating layer; a protective layer disposed on the coating layer.

20. The system according to claim 19, wherein the adhesive layer comprises a transition metal.

21. The system according to any of claims 19-20, wherein the adhesive layer has a thickness of 10,000 Angstroms or less.

22. The system according to any of claims 19-21, wherein the protective layer comprises an insulative material.

23. The system according to any of claims 18-22, wherein the base layer comprises a thermoplastic material.

24. The system according to any of claims 18-23, wherein the coating layer comprises a metal.

25. The system according to claim 24, wherein the coating layer comprises aluminum (Al), gold (Au), silver (Ag), or a combination thereof.

26. The system according to any of claims 18-25, wherein the coating layer has a thickness of 10,000 Angstroms or less.

27. The system according to any of claims 17-26, wherein the retroreflector has a total thickness of 50 millimeters (mm) or less.

28. The system according to claim 27, wherein the retroreflector has a total thickness of 10 mm or less.

29. The system according to any of claims 1-28, wherein the first tower and the second tower are disposed symmetrically opposite from each other on opposite sides of the field.

30. The system according to any of claims 1-29, wherein the analyzer unit comprises a field programmable gate array (FPGA).

31. The systems according to any of claims 1-30, wherein each of the first tower and the second tower further comprises a visible light source disposed thereon and configured to provide light at a visible wavelength.

32. The systems according to any of claims 1-31, wherein each of the first tower and the second tower further comprises a gimbal.

33. The system according to claim 32, wherein the gimbal is a joystick-controlled gimbal.

34. The system according to any of claims 1-33, wherein the at least one mid-IR light source is a laser.

35. The system according to any of claims 1-34, wherein at least one of the first tower and the second tower further comprises a reference detector disposed thereon and configured for line-locking and calibration.

36. A method for measuring at least one analyte in air over a field, the method comprising:

- i) providing the system according to any of claims 1-35;
- ii) sending mid-IR light from the at least one mid-IR light source, of the first tower, to a first reflector of the plurality of reflectors and receiving reflected light from the first reflector;
- iii) moving the at least one mid-IR light source of the first tower and sending mid-IR light from the at least one mid-IR light source, of the first tower, to another reflector of the plurality of reflectors and receiving reflected light from said another reflector;
- iv) repeating step iii) for each other reflector of the plurality of reflectors;
- v) repeating steps ii) – iv) for the second tower; and
- vi) using the analyzer unit to convert signals of reflected light to data indicative of a concentration of the at least one analyte in the air.

37. The method according to claim 36, wherein, when overlapping beams occur between the first tower and the second tower, a first detector of the first tower and a second detector of the second tower are calibrated internally to one another.

38. The method according to any of claims 36-37, further comprising displaying, on a display in operable communication with the analyzer unit, the data indicative of a concentration of the at least one analyte in the air.

39. A retroreflector, comprising:
a base substrate; a coating layer disposed on the base substrate;
an adhesive layer disposed between the base substrate and the coating layer; and a protective layer disposed on the coating layer,
wherein the retroreflector has a total thickness of 50 millimeters (mm) or less.

40. The retroreflector according to claim 39, wherein the adhesive layer comprises a transition metal.

41. The retroreflector according to any of claims 39-40, wherein the adhesive layer has a thickness of 10,000 Angstroms or less.

42. The retroreflector according to any of claims 39-41, wherein the protective layer comprises an insulative material.

43. The retroreflector according to any of claims 39-42, wherein the base layer comprises a thermoplastic material.

44. The retroreflector according to any of claims 39-43, wherein the coating layer comprises a metal.

45. The retroreflector according to claim 44, wherein the coating layer comprises aluminum (Al), gold (Au), silver (Ag), or a combination thereof.

46. The retroreflector according to any of claims 39-45, wherein the coating layer has a thickness of 10,000 Angstroms or less.

47. The retroreflector according to any of claims 39-46, wherein the retroreflector has a total thickness of 10 mm or less.

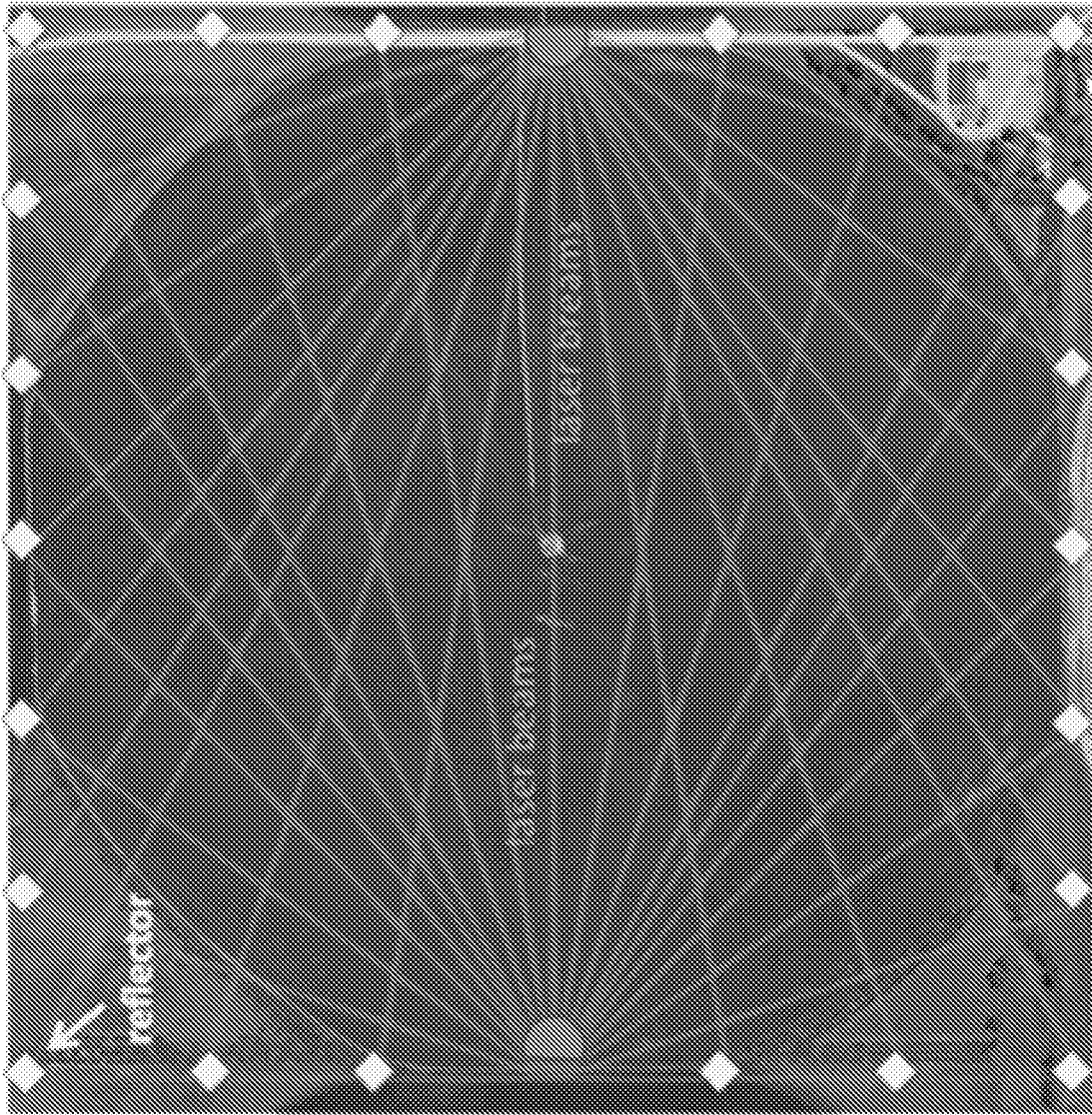


FIG. 1



FIG. 2

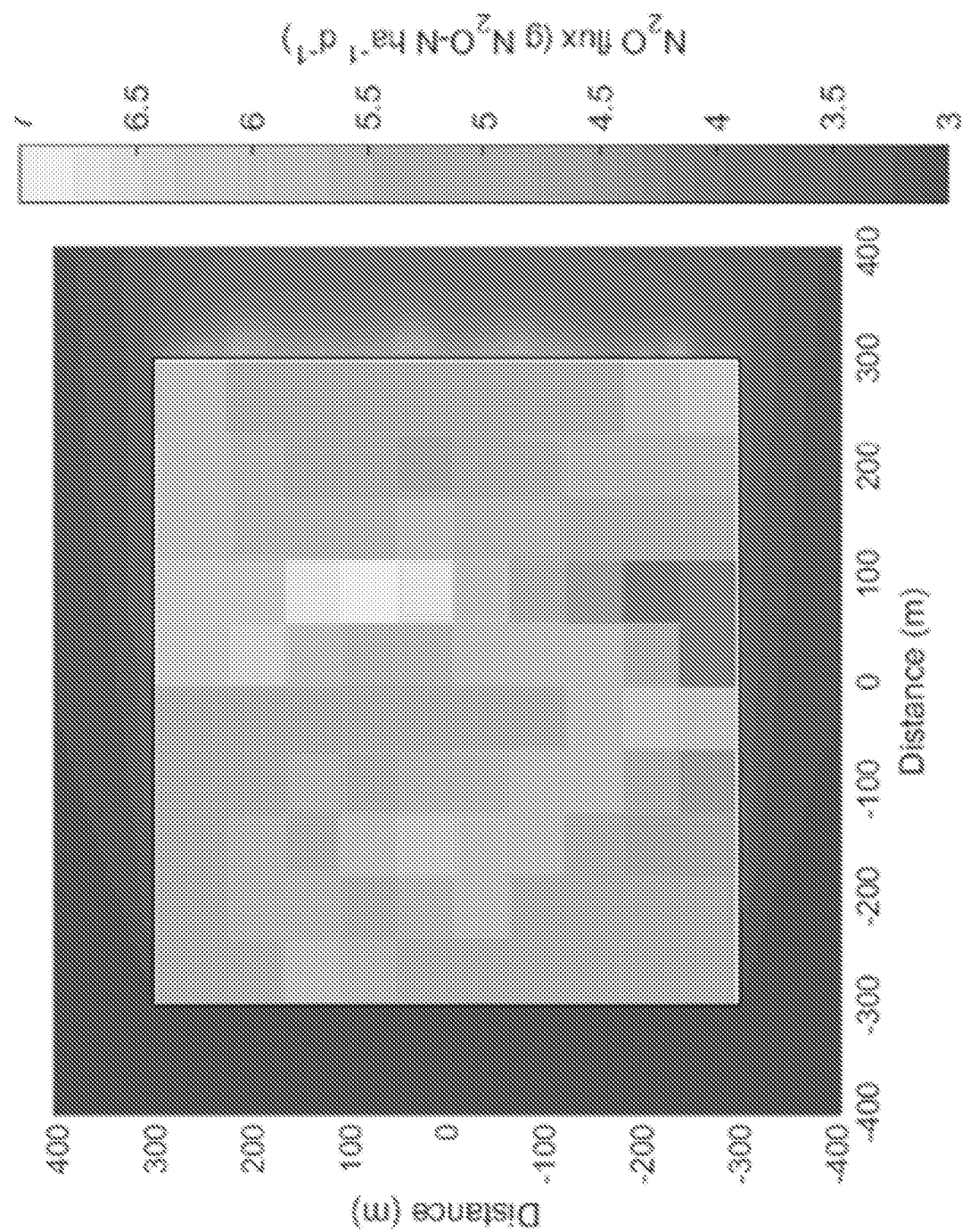


FIG. 3

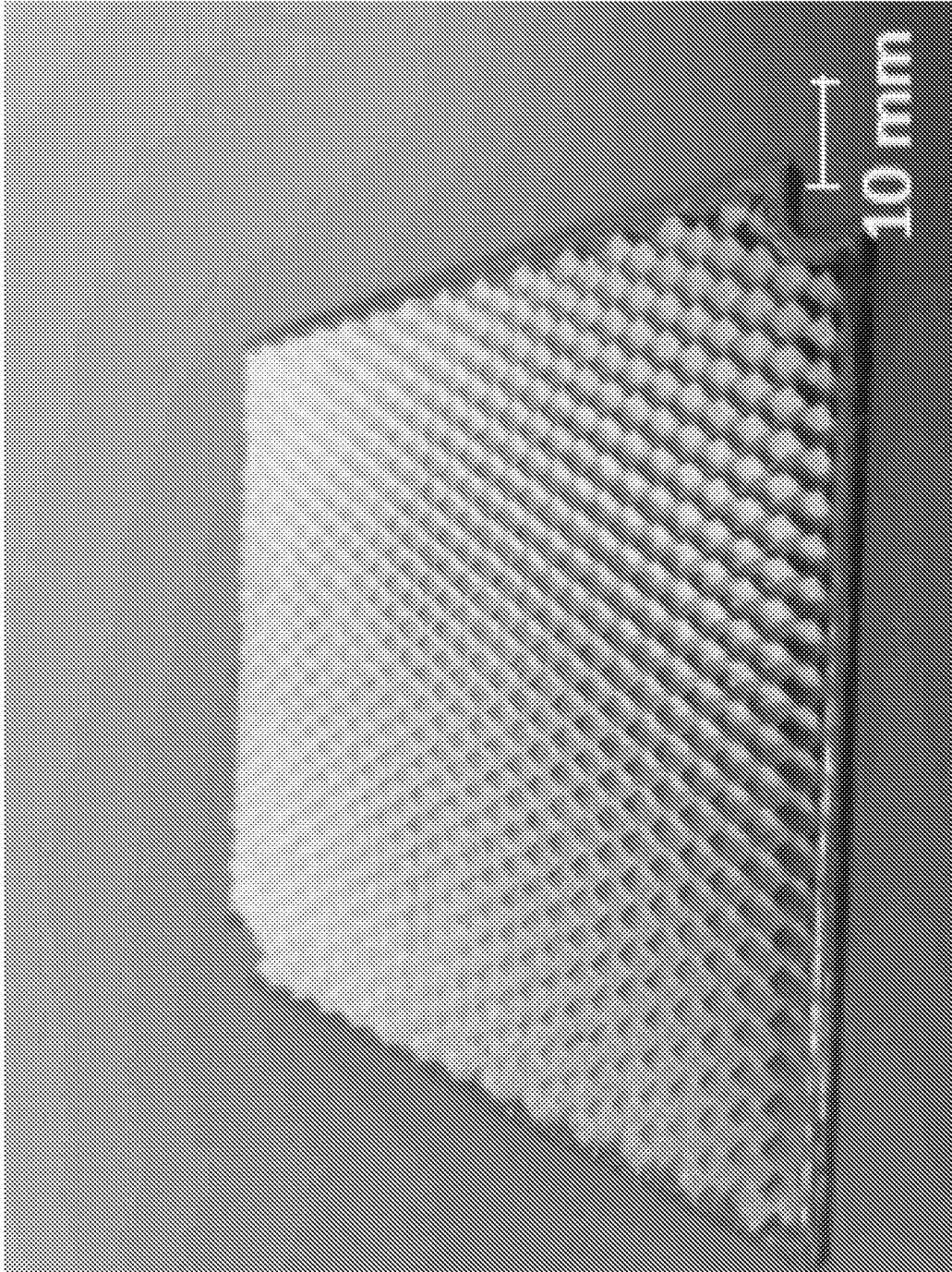


FIG. 4

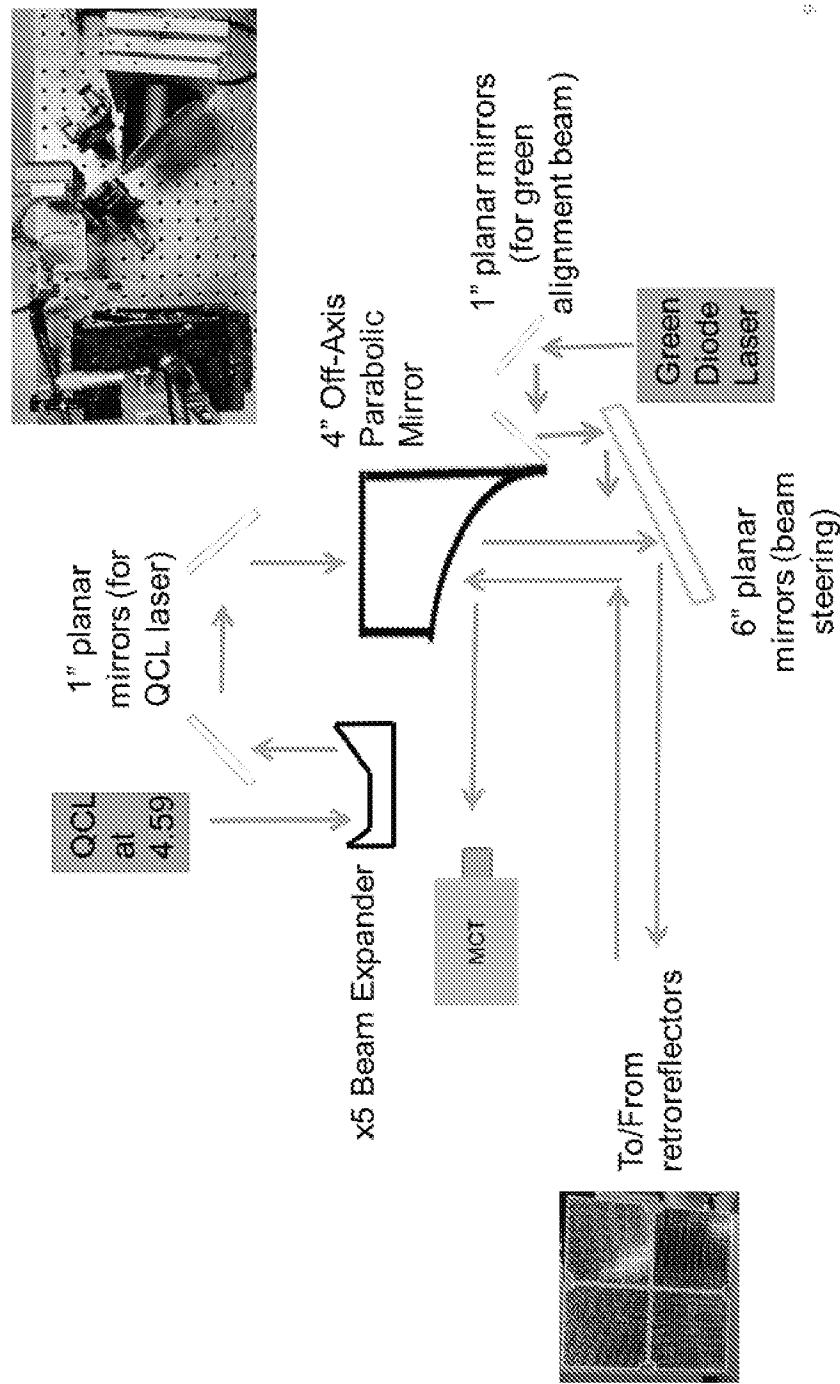


FIG. 5

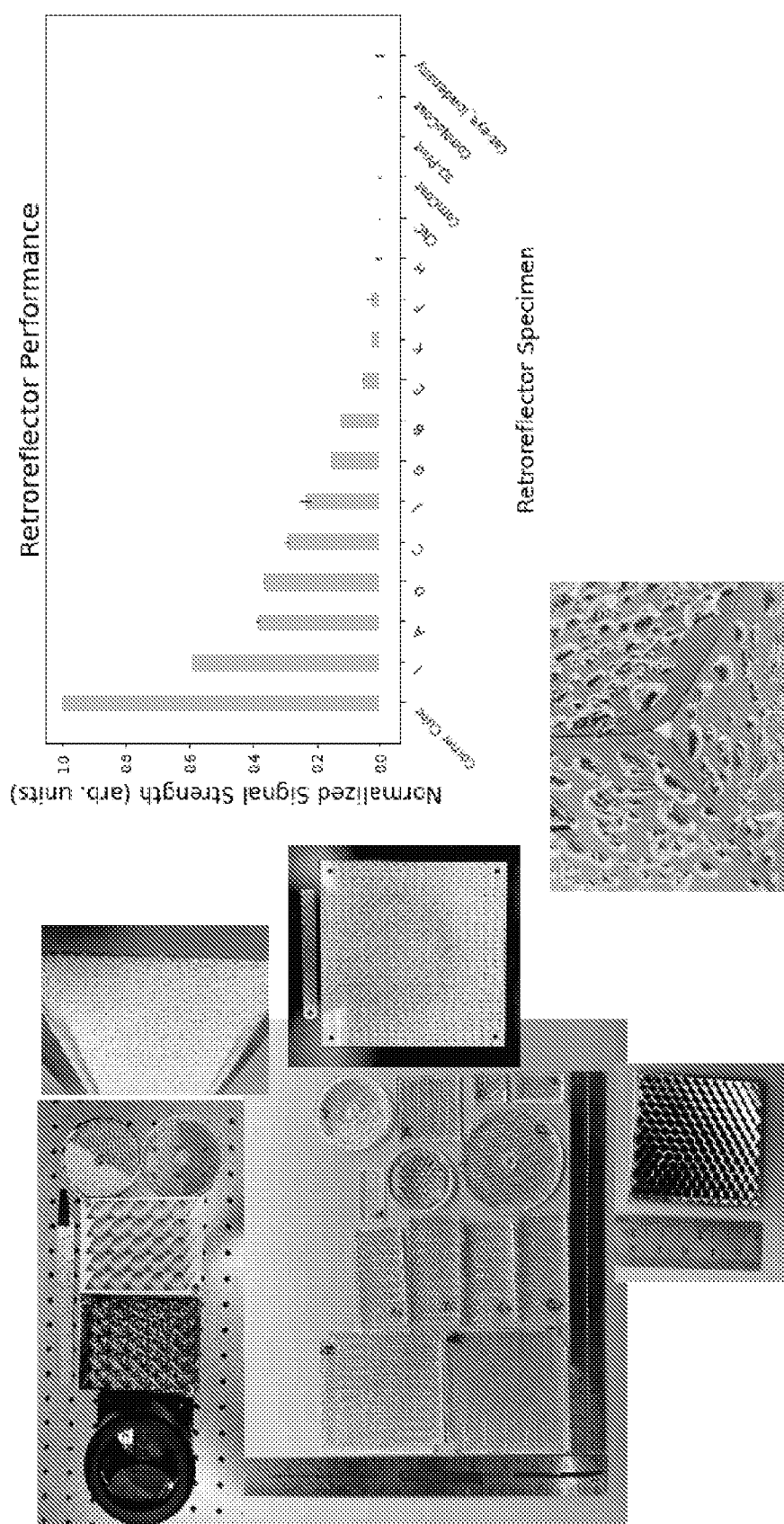


Fig. 6

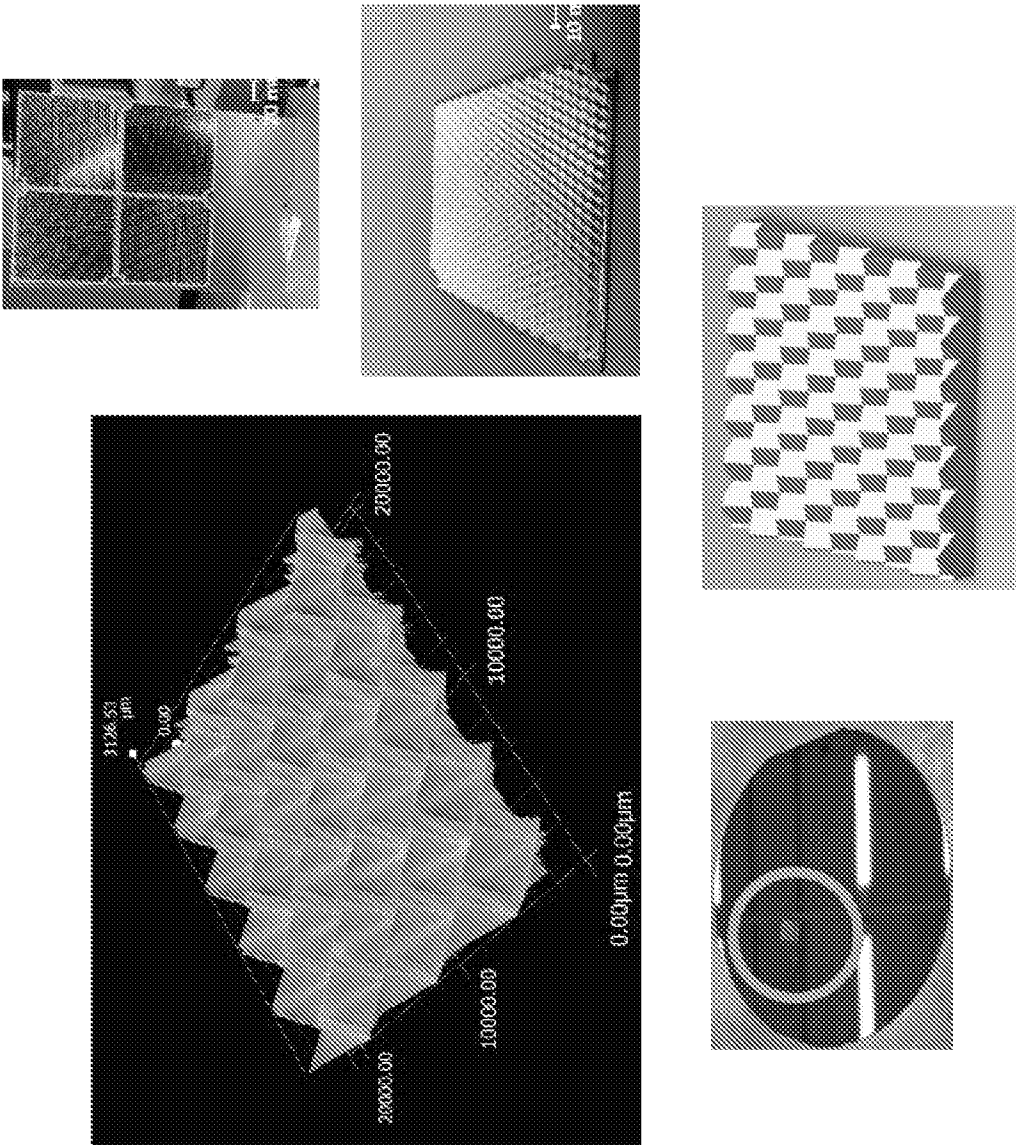


FIG. 7

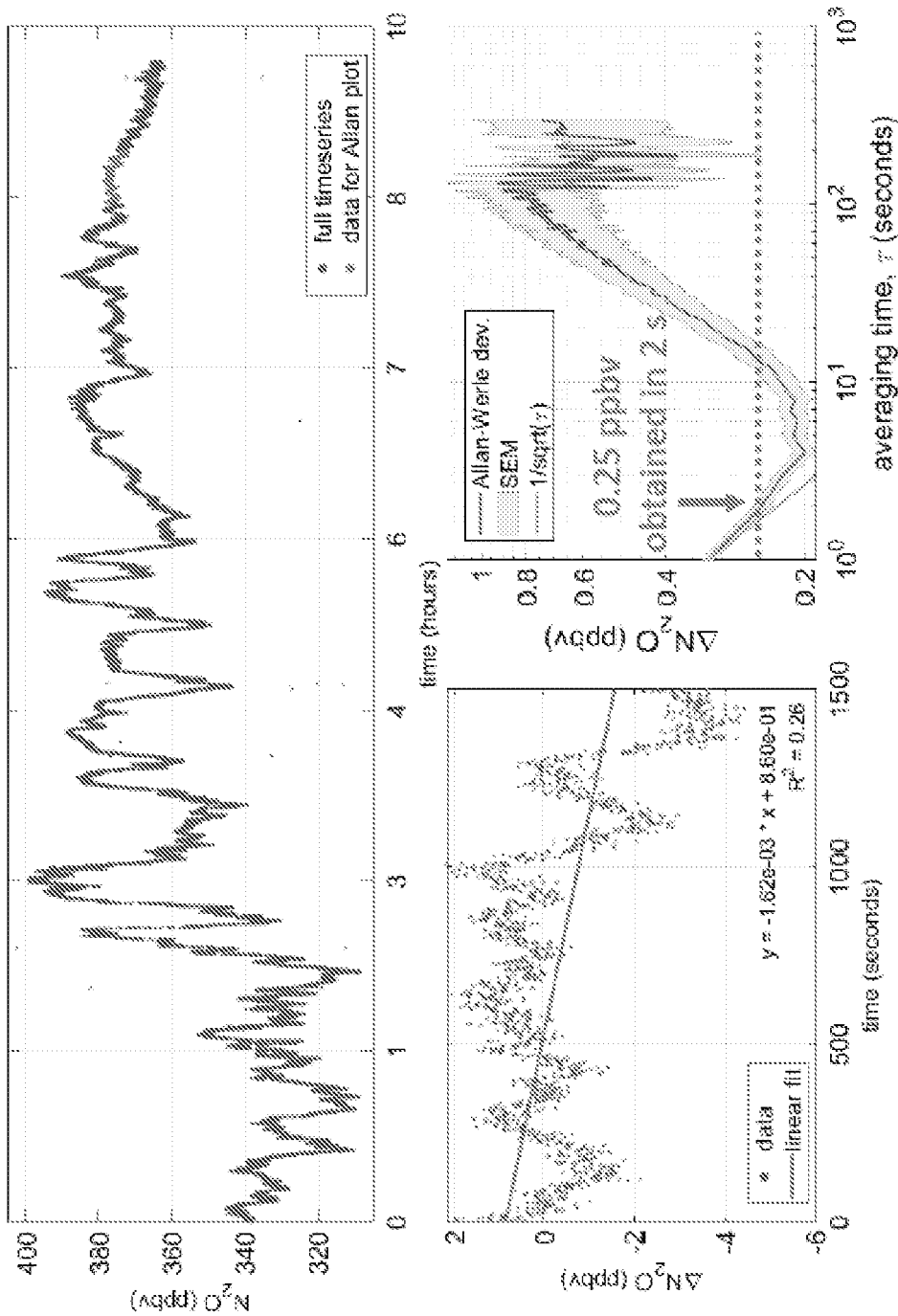


FIG. 8

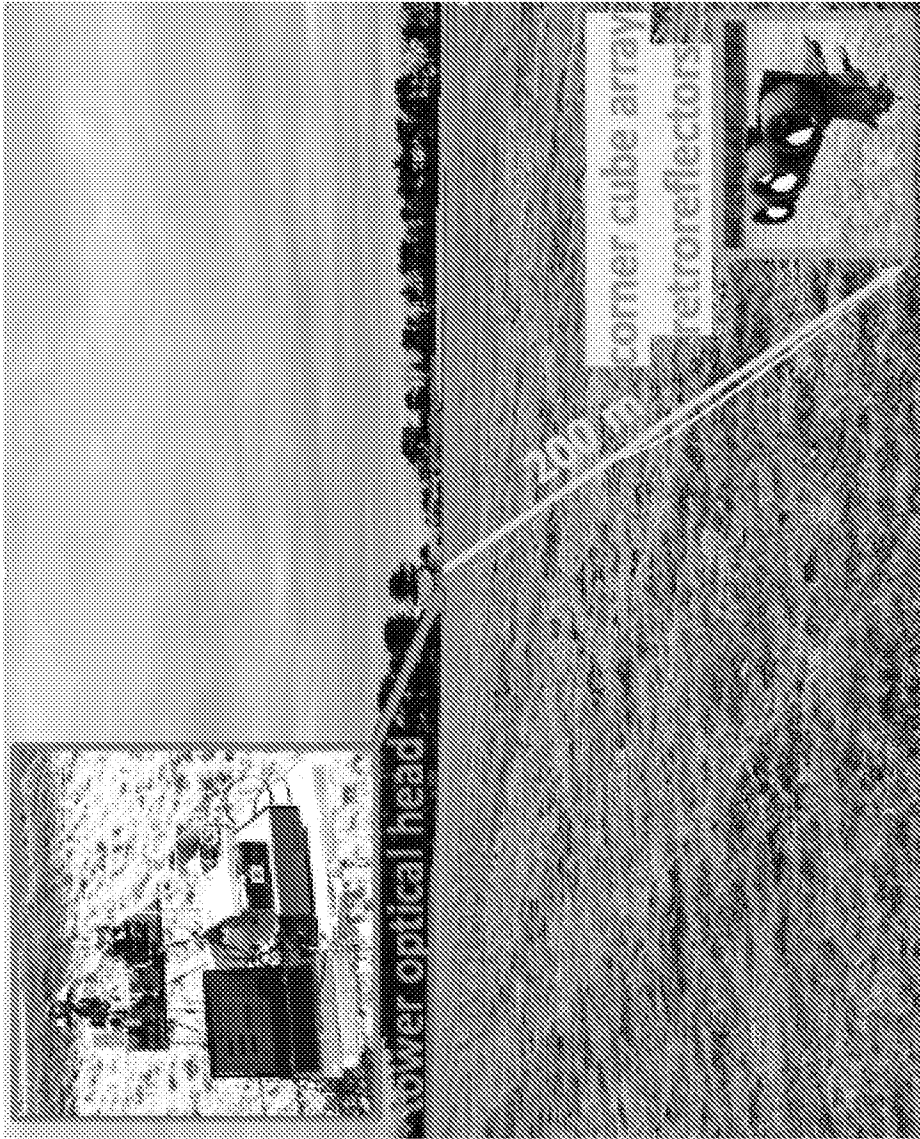


FIG. 9

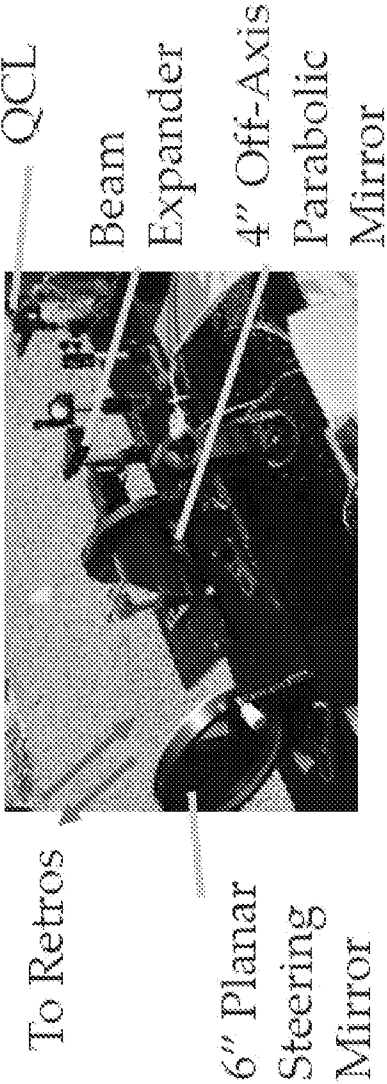
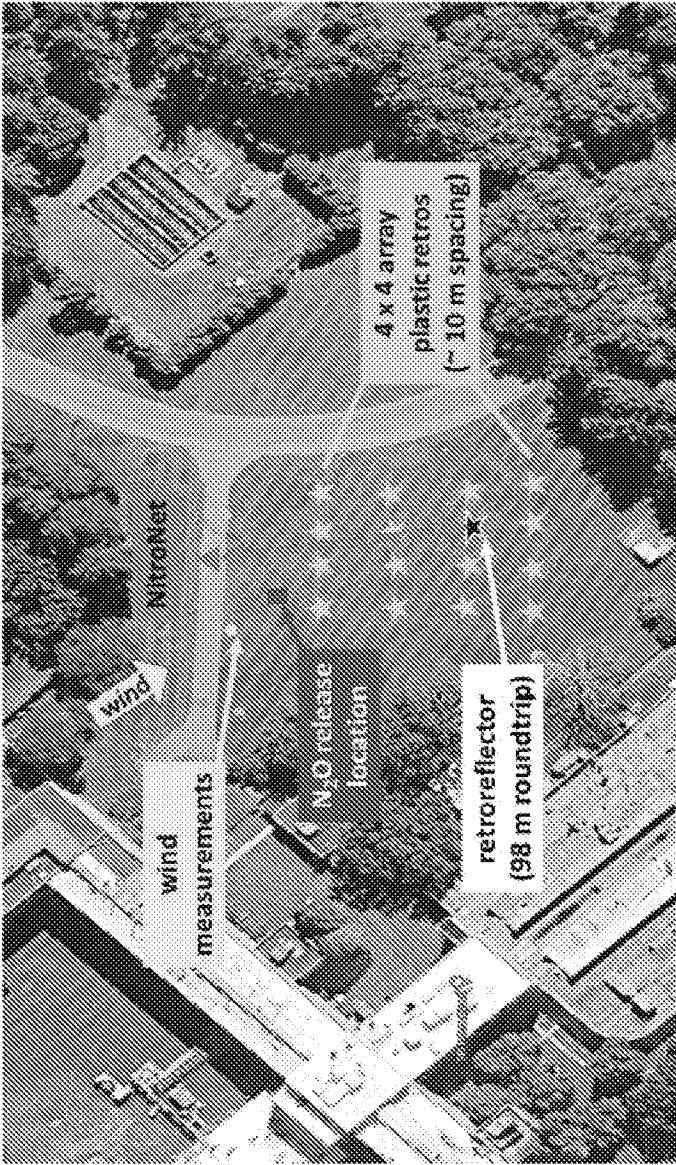


FIG. 10

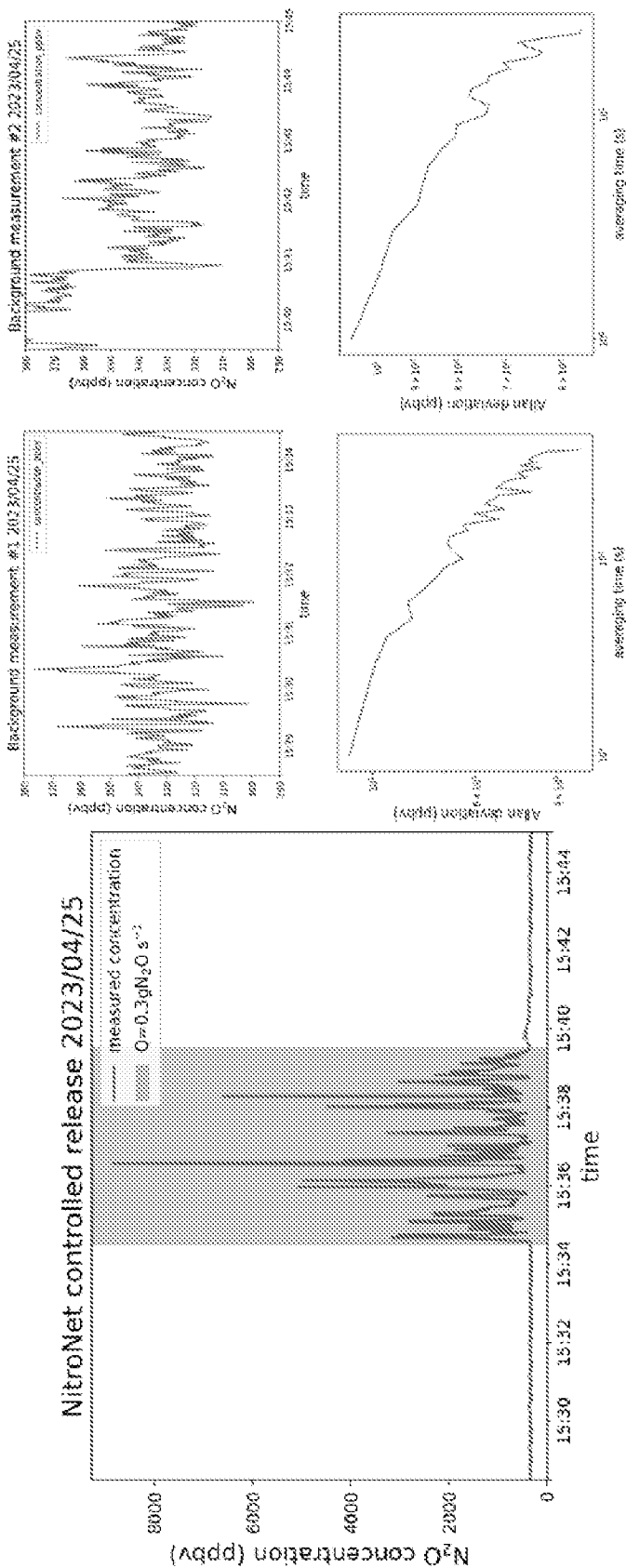


FIG. 11

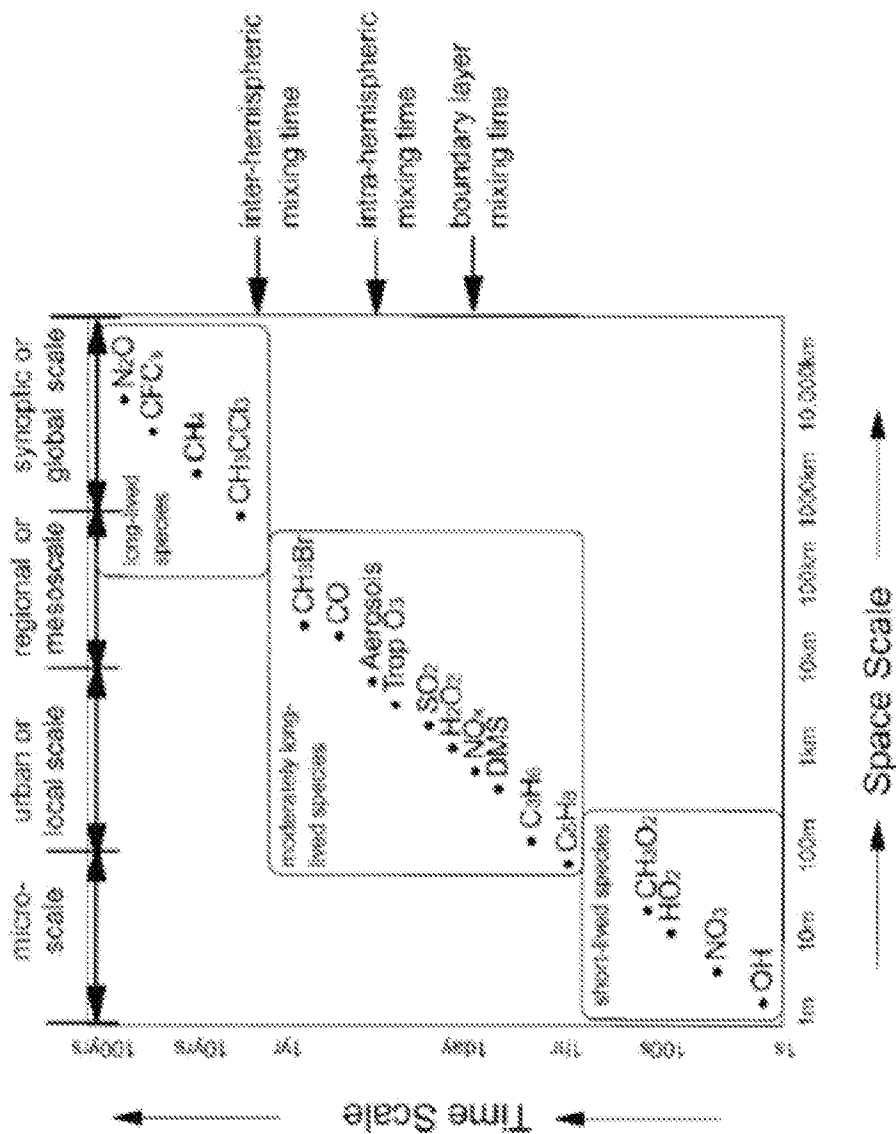


FIG. 12

$$C(x, y, z) = \frac{Q}{2\pi\sigma_y\sigma_z u} \cdot e^{\frac{-y^2}{2\sigma_y^2}} \cdot \left[e^{\frac{-(z-h)^2}{2\sigma_z^2}} + e^{\frac{-(z+h)^2}{2\sigma_z^2}} \right]$$

- C = concentration
- h = source height
- Q = reference emission rate
- u = mean wind speed
- σ_z = vertical dispersion
- σ_y = horizontal dispersion

$$Q = \frac{\sum C_{\text{Observation}} - C_{\text{Background}}}{\sum C_{\text{Model}}} \times Q_{\text{ref}}$$

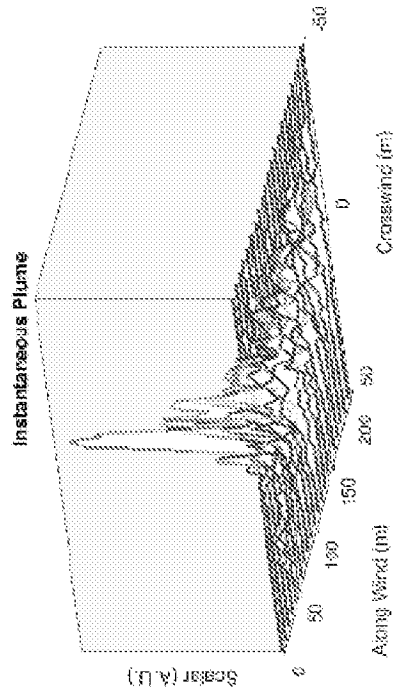


FIG. 13

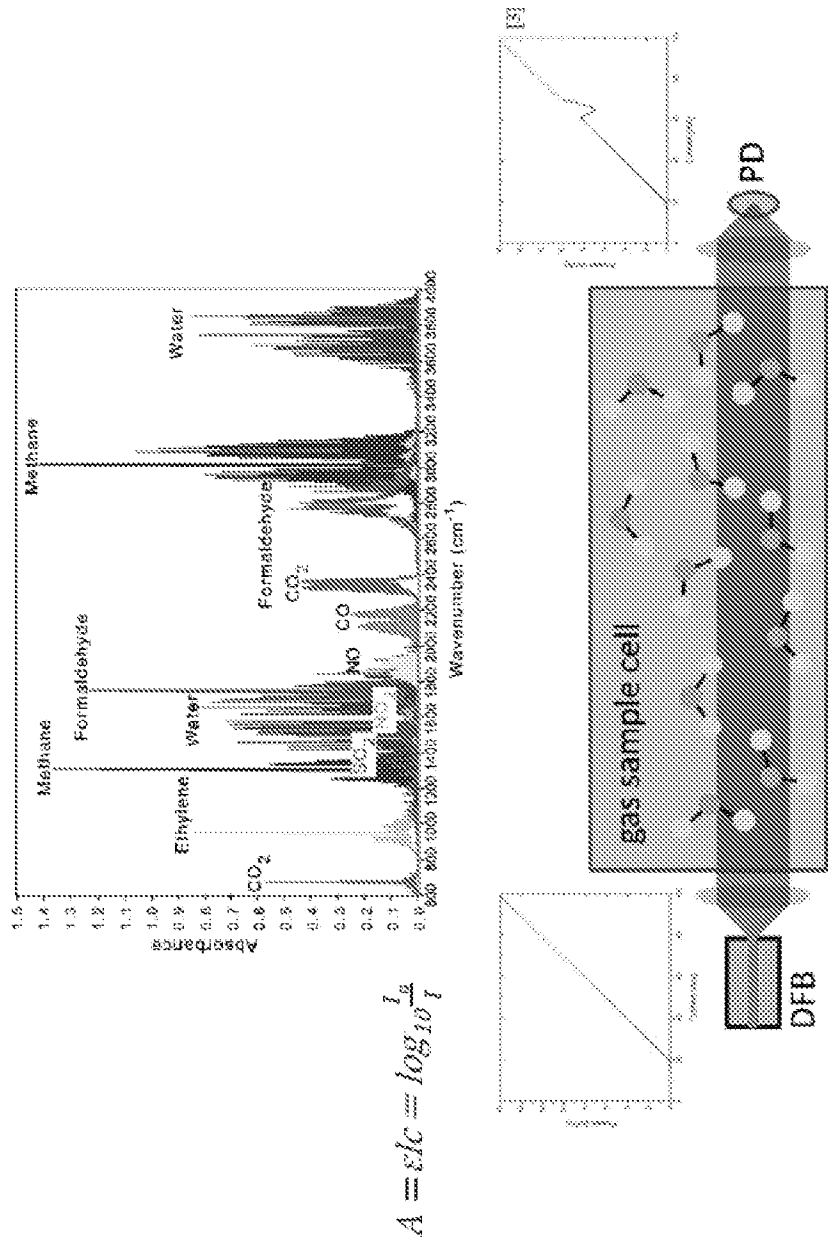


FIG. 14

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/035801

A. CLASSIFICATION OF SUBJECT MATTER G01N 21/3504(2014.01)i; G01N 33/00(2006.01)i; G01W 1/02(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) G01N 21/3504(2014.01); G01M 3/16(2006.01); G01N 21/35(2006.01); G01W 1/02(2006.01); G02B 1/10(2006.01); G02B 5/08(2006.01); G02B 5/124(2006.01) Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models Japanese utility models and applications for utility models Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS(KIPO internal) & Keywords: gas sensing device, tower, reflector, analyzer, detector, mid-infrared light, meteorology station, greenhouse gas, base substrate, coating layer, adhesive layer, protective layer		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2018-0045596 A1 (GOVERNMENT OF THE UNITED STATES OF AMERICA, AS REPRESENTED BY THE SECRETARY OF COMMERCE) 15 February 2018 (2018-02-15) paragraphs [0029]-[0107], claim 1, and figures 1-10	1-38
Y	US 2019-0113445 A1 (ZHANG et al.) 18 April 2019 (2019-04-18) paragraphs [0040]-[0062], claim 1, and figures 1-4	1-38
X	US 2022-0291428 A1 (AVERY DENNISON CORPORATION) 15 September 2022 (2022-09-15) paragraphs [0036]-[0068] and figures 1A, 1B	39-47
Y		18-28
A	JP 2008-096228 A (YANMAR CO., LTD.) 24 April 2008 (2008-04-24) paragraphs [0019]-[0030] and figures 1-3	1-47
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents: “A” document defining the general state of the art which is not considered to be of particular relevance “D” document cited by the applicant in the international application “E” earlier application or patent but published on or after the international filing date “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “O” document referring to an oral disclosure, use, exhibition or other means “P” document published prior to the international filing date but later than the priority date claimed “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art “&” document member of the same patent family		
Date of the actual completion of the international search 23 October 2024		Date of mailing of the international search report 23 October 2024
Name and mailing address of the ISA/KR Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon 35208, Republic of Korea Facsimile No. +82-42-481-8578		Authorized officer PARK, Tae Wook Telephone No. +82-42-481-3405

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2024/035801

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014-0352685 A1 (GEE et al.) 04 December 2014 (2014-12-04) claim 1 and figure 9	1-47

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/US2024/035801

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				US	10690562	B2	23 June 2020
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				CN	107764765	B	12 February 2021
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				CN	114502990	B	29 March 2024
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				KR	10-2022-0038793	A	29 March 2022
				WO	2021-025838	A1	11 February 2021
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				CN	108490512	A	04 September 2018
				CN	108490512	B	29 May 2020
				US	10042094	B2	07 August 2018
				WO	2013-036220	A1	14 March 2013