DIOXIDE MATERIALS™
TECHNOLOGY FOR CO_2 SENSING AND REMEDIATION

Final Report
STTR Phase I: Low-Cost, High-Accuracy, Whole-Building Carbon Dioxide Monitoring for Demand Control Ventilation

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Summary

This STTR Phase I project assessed the feasibility of a new CO_2 sensing system optimized for low-cost, high-accuracy, whole-building monitoring for use in demand control ventilation. The focus was on the development of a wireless networking platform and associated firmware to provide signal conditioning and conversion, fault- and disruption-tolerant networking, and multi-hop routing at building scales to avoid wiring costs. Early exploration of a bridge (or "gateway") to direct digital control services was also explored.

Results of the project contributed to an improved understanding of a new electrochemical sensor for monitoring indoor CO_2 concentrations, as well as the electronics and networking infrastructure required to deploy those sensors at building scales. New knowledge was acquired concerning the sensor's accuracy, environmental response, and failure modes, and the acquisition electronics required to achieve accuracy over a wide range of CO_2 concentrations. The project demonstrated that the new sensor offers repeatable correspondence with commercial optical sensors, with supporting electronics that offer gain accuracy within 0.5%, and acquisition accuracy within 1.5% across three orders of magnitude variation in generated current. Considering production, installation, and maintenance costs, the technology presents a foundation for achieving whole-building CO_2 sensing at a price point below \$0.066 / sq-ft – meeting economic feasibility criteria established by the Department of Energy. The technology developed under this award addresses obstacles on the critical path to enabling whole-building CO_2 sensing and demand control ventilation in commercial retrofits, small commercial buildings, residential complexes, and other high-potential structures that have been slow to adopt these technologies. It presents an opportunity to significantly reduce energy use throughout the United States and beyond.

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Background

The project builds upon important advances in CO_2 sensing achieved by the proposing team, including the landmark discovery of a catalyst mixture that can catalyze the CO_2 reaction at the core of electrochemical CO_2 measurement. The resulting sensing element achieves better signal-to-noise than commercial CO_2 sensors and costs an order of magnitude less to manufacture. The Phase I project was focused on enhancing this sensing element, characterizing its environmental response, and developing the hardware, firmware, and algorithms necessary to integrate the electrochemical sensor as part of a whole-building CO_2 monitoring solution. The Phase I results were excellent, putting the project on a trajectory to achieve whole-building, post-build CO_2 monitoring and direct digital control of building ventilation systems, with transformative impacts on indoor air quality monitoring, ventilation management, and HVAC energy waste.

This project is led through a public-private partnership between Dioxide Materials, Inc. and Florida Atlantic University's Institute for Sensing and Embedded Network Systems Engineering (I-SENSE). The team comprises thought leaders in CO_2 sensing, low-power acquisition, wireless communication, distributed systems, and data management.

Phase I Goals and Milestones

The partnership between Dioxide Materials and Florida Atlantic University is focused on achieving a transformative impact on demand control ventilation through the development of a whole-building CO_2 monitoring solution optimized for post-build installation and integration with commercially available HVAC systems providing direct digital control interfaces. Phase I activities focused on five key goals and associated milestones:

- Phase I sought to increase the sensitivity, stability, and robustness of an existing electrochemical sensor. The approach relied on geometric modifications, as well as the introduction of a new membrane electrode assembly.
- Phase I sought to characterize the environmental response of the new design, emphasizing temperature and humidity impacts. The approach relied on a new sensing platform, a custom acrylic housing, and experimentation in an environmental chamber.
- Phase I sought to develop a low-power data acquisition circuit capable of accommodating highly dynamic CO_2 concentrations. The approach relied on aggressive hardware and software filtering, coupled with dynamic gain adaptation.
- Phase I sought to develop a new sensing platform, optimized for ad hoc, indoor deployment. The approach relied on two new architectures optimized for lab experimentation and in-building deployment, respectively.
- Phase I sought to develop protocols and services for achieving reliable data acquisition, and for integrating sensing endpoints with upper-tier building management systems. The approach relied on a combination of network service

(a) (b)

Figure 1. (a) Top view of base design for electrochemical CO_2 sensor; (b) Top view of modified design, incorporating ad-hoc membrane electrode assembly geometry, increasing sensitivity, stability, and robustness

implementations and new data collection, storage, and access infrastructure.

Phase I activities were collectively focused on determining and demonstrating the feasibility of the proposed sensing solution for achieving whole-building CO_2 monitoring at low cost, with high fidelity, over long deployment horizons. By all measures, Phase I was successful in demonstrating this feasibility, positioning the team for success in Phase II.

Phase I Results

The following subsections summarize the main activities and results of the Phase I project.

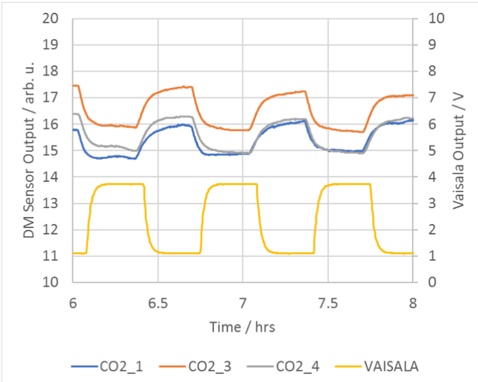
Electrochemical Sensor

Design. The electrochemical sensor at the core of the proposed system was modified from a base design that incorporated metal electrodes deposited onto FR-4, a widely available, electrically-insulating, fiberglass-epoxy composite material. The electrodes were made of a copper layer that adhered directly to the FR-4; these were then plated with gold. The copper adhesion layer was necessary because gold cannot be directly deposited onto FR-4. The base design is shown in Figure 1(a).

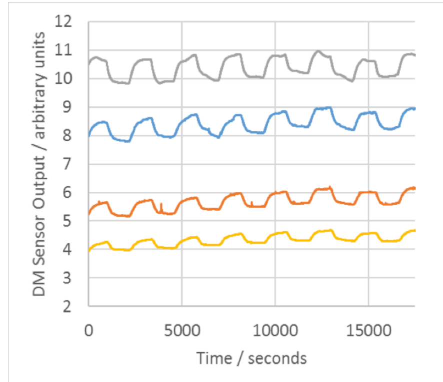
Experimental results conducted as part of Phase I revealed the copper layer as a limiting factor for stability and robustness since it corrodes in open air. To address this limitation, the sensor was modified, depositing Dioxide Materials' Sustainion™ membrane over the electrodes via spin-coating. A silver nanoparticle layer was then spray-painted in a straight line, extending from the central electrode's contact pad to a position on top of the membrane, effectively creating an ad-hoc membrane electrode assembly structure. This silver nanoparticle layer was also infused with Dioxide Materials' Sustainion™ ionomer, ensuring its unique sensitivity to CO_2. The resulting design significantly enhances sensitivity, stability, and robustness. The modified design is shown in Figure 1(b).

Results. All environmental testing was conducted using the sensing platform and associated experimentation interfaces described later in this report. The team developed housing units and testing stations appropriate for determining the electrochemical sensor's sensitivity to CO_2 in the 0-1500 ppm range, their response to variations in humidity and temperature, and their long-term stability.

For testing sensitivity to CO_2, an acrylic housing was developed that fits over the sensing



(a)



(b)

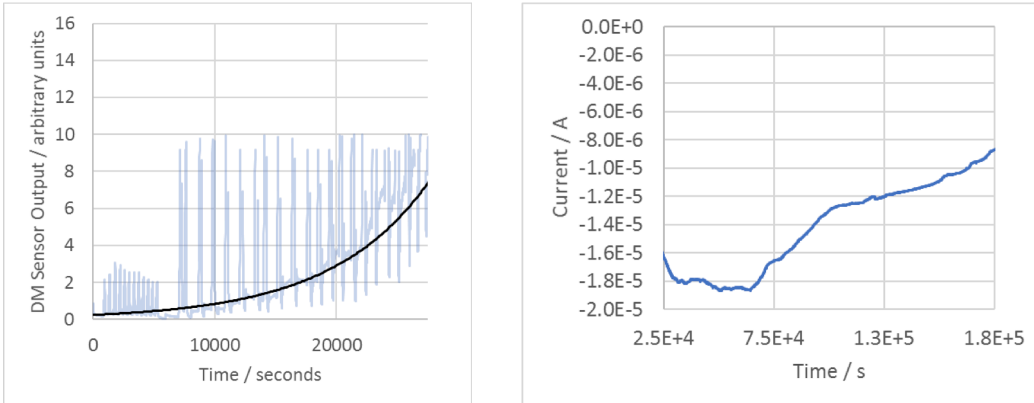
Figure 2. (a) Comparison of three sensor outputs to commercially available, $3K optical sensor; (b) Comparison of four sensor outputs, switching between 400 and 950ppm of CO_2

platform developed in Phase I, allowing gases of a known concentration of CO_2 to be flowed over up to six sensors simultaneously. The output of these sensors was recorded and observed to check for clear and consistent response to the change in CO_2 concentration. The electronics were designed to situate individual sensors in a 2x3 array, simplifying the design and implementation of the housing.

Testing the impact of variation in temperature and humidity was conducted using a Thermotron environmental control chamber. For these tests, the circuitry of the sensing platform was coated with a polyurethane layer that protected it from corrosive effects at higher humidities and temperatures. Six sensors were simultaneously tested at decade intervals of percent relative humidity, ranging from 20% to 90%. Temperatures ranging from 25C to 45C were also tested. In each case, the CO_2 concentration did not vary, so as to determine the effect of each variable on the sensor's output baseline. This testing apparatus also allowed us to determine the failure mode of these sensors, which informed the modified design shown in Figure 1(b).

Testing for sensitivity, alternating between 400ppm and 1500ppm of CO_2, shows a consistent, repeatable signal as the gas flows across all six sensors. Sample data is shown in Figure 2(a). Note that a higher output signal corresponds to a lower CO_2 concentration. Hence, the graphical signal readout should correspond to the inverse of an optical sensor, which is what is observed.

Sensitivity across narrower concentration ranges has also been established, and the sensing platform and associated analog front-end shows no apparent greater difficulty in acquiring these smaller signals. Figure 2(b) shows results from multiple sensors simultaneously responding to switches between 400ppm and 950ppm of CO_2. Figures 3(a) and (b) summarize results of an experiment focused on evaluating the humidity and temperature sensitivity of the sensor design, respectively. In general, precise data on the scaling of output baseline with temperature or humidity is difficult to acquire at this point due to the limitations of the environmental chamber and the correlation between temperature and relative humidity. Periodic air pump cycles caused by the environmental chamber's attempts to maintain a specified humidity level result in the large brief current spikes seen in Figure 3(a); nevertheless, a regression curve can be applied to model the average baseline response to increases in relative humidity from 20% to 90%. Similarly, Figure 3(b) shows preliminary evidence of a baseline current increase as the temperature is increased from 20C to 45C, but this is confounded by an inexorable rise in relative humidity as temperature increases.



(a) (b)

Figure 3. (a) Cycled humidity response, from 20% to 90% relative humidity; (b) Temperature response, from 20C to 45C

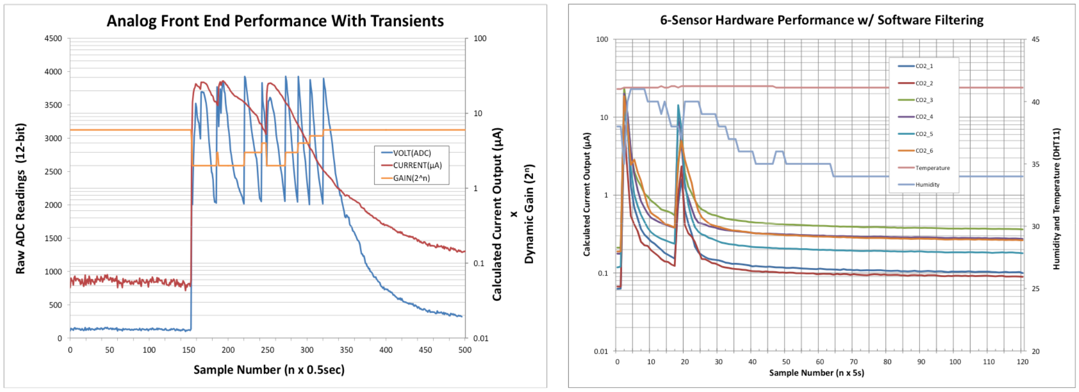
As noted previously, this analysis provided insight into the primary failure mode of the base sensor design, which is corrosion of the copper adhesion layer on the FR-4 substrate. Corrosion of the copper layer results in an expanding volume of copper oxide that leeches out from beneath the gold electrodes. These corrosive effects become visible within the first 24 hours of continuous operation. In less than one week of continuous operation, copper oxide layers both destabilize the gold layer and cause shorting across the electrodes. Future designs will use a silicon chip design that employs inert titanium adhesion layers, rather than copper layers, obviating any further concerns about corrosion. These silicon and titanium-based designs have already been tested for their stability, and versions with gold top layers for the electrodes are already being fabricated and will soon be ready for testing.

Proposed Milestones Addressed. *(1) We will build a flow cell to test the device in a known CO_2 concentration range, from 0-1500ppm. (2) We will test the sensor in a Thermotron^{TM} environmental chamber to determine how humidity and temperature affect performance. (3) Failure modes will be used to improve the sensor's packaging design.* Milestone achievements were as anticipated.

Analog Acquisition Stage

Design. Design of a robust analog acquisition stage for the CO_2 sensor presented unanticipated challenges. The sensor is, in general, high impedance, but the impedance varies as a function of temperature and humidity. Laboratory tests demonstrated impedance variation of several orders of magnitude, resulting in currents ranging from nanoamps to milliamps. The associated challenge is to design an analog acquisition stage capable of adapting to this dynamism, achieving high fidelity (i.e., gain) measurements without saturating the analog-to-digital converter. The resulting design consists of three principal sections: voltage rail conditioning, current sensing, and signal amplification for dynamic scaling.

The voltage rail conditioning section comprises a Pi filter, followed by a precision 3V reference. The filter dampens high frequency oscillations (e.g. switching power supply noise), with low DC resistance. The voltage reference has an initial accuracy of 0.2%, a 25mA drive capability, and quiescent current of 42µA. It serves as the primary analog-to-digital reference, powers the CO_2 sensor, and establishes a virtual ground through a high impedance divider and active voltage follower. The virtual ground is used to bias the analog



(a) (b)

Figure 4. (a) Analog acquisition stage, dynamic gain transient response; (b) Analog acquisition stage, six-sensor comparative performance

ground for the current sensor and the second stage amplifier.

The current sensing section uses a precision current sensing IC, which measures voltage across a precision resistor in series with the CO_2 sensor. The IC has a rail-to-rail output structure, a high common mode rejection ratio, and ±0.5% gain accuracy. A low pass filter is used on the output to reduce any noise generated by the IC. The IC can generate a signal as low as 1mV; the virtual ground noted above shifts this output voltage to a stable region acceptable to the final stage of the circuit. This is required when the CO_2 sensor is operating at nanoamp levels.

The signal amplification section achieves dynamic scaling using a programmable gain amplifier. The amplifier is controlled by the microcontroller core, scaling the input in gain orders of 2^n. The IC includes a 10-channel input multiplexer, internal linearity calibration, and a software shutdown feature. The amplifier output is fed through a low-pass filter in the path to the analog-to-digital converter.

Analysis. Evaluation of the analog acquisition stage focused on current sensing accuracy and adaptability to variation in CO_2 concentration. Through bench-top experimentation using a high-precision current source, the accuracy of the acquisition system was determined to be within 1.5% of ground truth with currents at or above the microamp range. In the nanoamp range, the signal is viable, but the signal-to-noise ratio is reduced due to the use of higher gain stages. This is currently mitigated through oversampling and filtering in software. Acquisition improvements at the nanoamp range are ongoing.

Dynamic scaling is achieved by altering the gain stage of the amplifier based on measured changes to the output. If the raw analog-to-digital reading falls below half of the allowable range (i.e., 4095 for 12-bit resolution), the gain is increased until the reading is above half of the allowable range, or the gain limit has been reached. In the descending gain direction, when the analog-to-digital reading is above a specified threshold (e.g., 4000 for 12-bit resolution), the gain is reduced. As illustrated through the sample data shown in Figure 4(a), this approach works well. As the analog-to-digital reading increases (blue line), the gain stage varies (orange line) to maintain readings below the saturation point. As the readings fall, the gain increases to keep the results in the optimal range. The calculated current is appropriately scaled based on the selected gain stage (red line).

Similar tests were performed with the six-sensor version of the platform, and the results were analogous. Sample data is shown in Figure 4(b). Note that given the precision of the 12-

bit analog-to-digital converter, a minor offset is observed between sensing channels. This is due to variability in the traces connecting the individual sensors to the data acquisition stage. While this can be addressed in software, controlling for trace variability in hardware is optimal. Note that the results highlight the impact of software filtering. In Figure 4(a), the signal begins to reach the noise floor as the sensor's impedance increases. This is caused by the second stage of the acquisition circuit amplifying the small amount of noise present in the output of the current sensor. This is mitigated in Figure 4(b) through oversampling.

Proposed Milestones Addressed. *(1) The new sensing platform will demonstrate* CO_2 *signal acquisition and conditioning.* Note that the high dynamic range of the CO_2 sensing element was not anticipated, introducing a significant adaptation challenge that was overcome through a combination of hardware and software design.

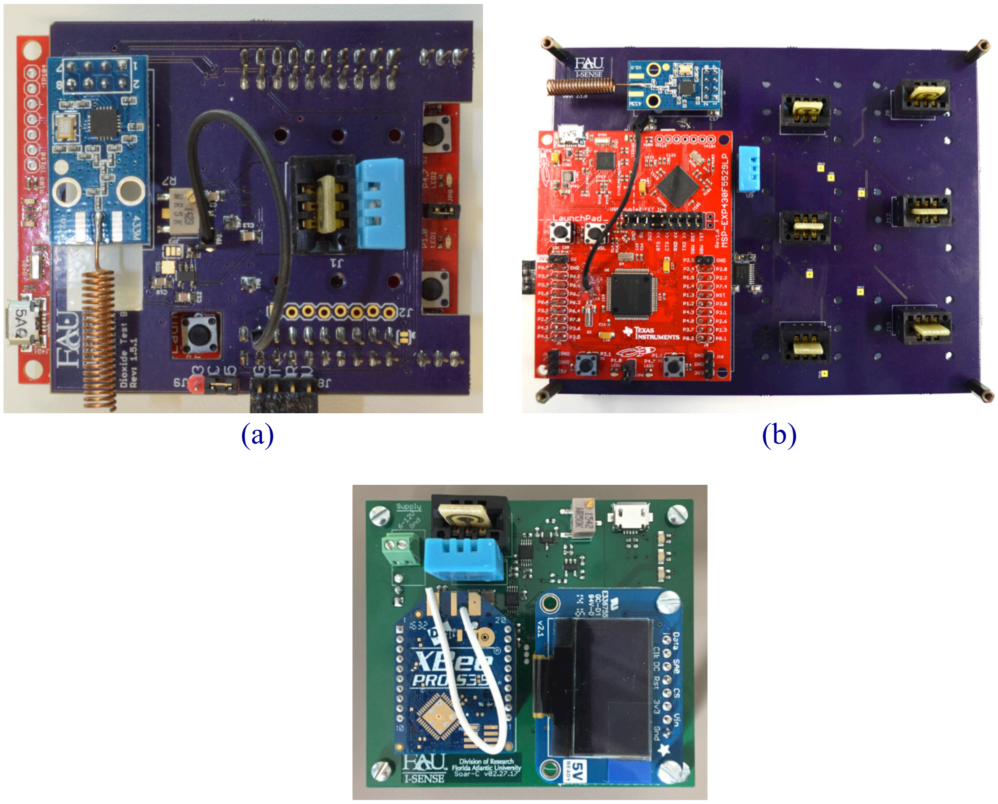
Wireless Sensing Platforms

Design. The Phase I project resulted in three sensing platform designs supporting both wired and wireless communication. The first two designs were optimized for laboratory experimentation, and the third was optimized for in-building deployment. The top-view of each design is shown in Figure 5.

The first platform, shown in (a), is based on the popular LaunchPad core (in red) from Texas Instruments. The core is built on the MSP430F5529, a 16-bit, ultra-low-power microcontroller, with an integrated 12-bit analog-to-digital converter. The extension board (in purple) includes the analog acquisition stage and CO_2 sensor, coupled with an integrated temperature and humidity sensor (in blue). The extension board also includes USB support for wired communication, and Texas Instruments' CC1101 wireless transceiver. The transceiver is a low-power, high-sensitivity radio, operating at 433MHz. The frequency was chosen to enable signal penetration in typical indoor environments. Supporting firmware, including a custom driver for the CC1101 was also developed to enable laboratory experimentation. The driver includes support for packet acknowledgments and retries to improve reliability.

The second platform, shown in (b), is based on the same LaunchPad core (in red). The design includes six CO_2 sensors, multiplexed to the same analog acquisition stage used in (a). The platform was designed to enable simultaneous experimentation across all six sensors to assess response consistency. The mounting holes surrounding the sensor elements are used to ensure a tight seal between the circuit board and the acrylic housing used to control CO_2 concentration during laboratory tests, as discussed previously.

The final platform, shown in (c), is a standalone design optimized for in-building deployment, rather than laboratory experimentation. The design relies on an Atmel AT90USB1286, a low-power, 8-bit microcontroller, with an integrated 10-bit analog-to-digital converter. While 10 bits of precision is sufficient, oversampling was implemented in firmware to increase resolution and/or reduce noise. The analog acquisition stage, aside from layout, remains unchanged from the previous two designs. The platform does, however, include a number of important enhancements. First, the device integrates 256K of battery-backed NVSRAM to support disruption-tolerant networking. The associated firmware implementation leverages the team's prior work in resource-constrained, crash-tolerant file system design, ensuring file system consistency in the presence of unanticipated faults. Second, the device incorporates a power-gated, low-power OLED display, with a resolution of 128x64. Combined with the tactile switch on the underside of the board, the display can be used for in-field diagnostic reporting (e.g., days active, battery voltage, CO_2 concentration). Finally, the device incorporates Digi's 900MHz XBee Pro wireless transceiver. The



(a) (b)

(c)

Figure 5. (a) Single-sensor laboratory platform, 433MHz, MSP430; (b) Six-sensor laboratory platform, 433MHz, MSP430; (c) Single-sensor deployment platform, 900MHz, AT90USB128

transceiver may be used for point-to-point communication, leveraging a radio driver previously developed by the team. Alternatively, the transceiver may be used in DigiMesh mode, leveraging a full multi-hop routing stack developed by Digi. Finally, the design includes power regulation circuitry that allows the 900MHz module to be replaced with Digi's XBee Cellular module, enabling LTE Cat 1 connectivity. While not the focus of the current effort, cellular-based CO_2 sensing expands the potential applications of the technology, creating new market opportunities to be explored (e.g., carbon sequestration monitoring).

Analysis. The resulting platforms served as the principal means of laboratory experimentation for the CO_2 sensors, as described previously. The platforms and associated firmware were also subject to validation through unit testing, and experimental characterization, emphasizing connectivity performance.

During laboratory trials with the 433MHz platform, unacceptable packet losses and delays were experienced. Root cause analysis revealed that the losses and delays resulted from congestion introduced when multiple sensing platforms were sampling at a high rate. The congestion was confounded by the underlying acknowledgment and retry mechanism introduced in the radio driver. A TDMA-based MAC implementation will resolve this congestion, as demonstrated in prior work. For laboratory experimentation, the USB implementation was satisfactory, achieving 100% packet delivery and low latency (i.e., < 5ms) when acquiring data from up to four sensing platforms, each sampling at 60Hz. Additional sensing platforms and higher sampling rates are achievable, but were not tested as part of the Phase I effort.

In contrast to Digi's XBee 900, the CC1101 (used in the laboratory platforms) is a basic transceiver that does not include a full network stack. The acknowledgement and retry implementation was insufficient by itself to achieve high reliability. As a potential enhancement, Texas Instruments' low-power SimpliciTI protocol stack was explored. SimpliciTI was developed by Texas Instruments to provide reliable communication support for small wireless networks operating over resource-constrained devices. The stack was integrated as part of the platform firmware and achieved low packet loss rates without clear channel assessment enabled. Improved integration of the SimpliciTI stack is part of ongoing work.

The team's existing point-to-point radio driver for the XBee 900 is known to achieve physical packet reception rates above 95% in indoor environments. At a sampling rate of 60Hz, simple store-and-forward strategies will ensure 100% data delivery. Further, for ventilation control, the sampling rate can be reduced significantly – 1Hz is more than sufficient.

Proposed Milestones Addressed. *(1) Hardware will be produced for a 900MHz, single-sensor platform. (2) Associated firmware will be implemented. (3) All driver test suites will be demonstrated to illustrate hardware and software correctness. (4) Single-hop network connectivity will be demonstrated. (5) Hardware support for multi-hop, disruption-tolerant networking will be completed.* Note that the team significantly over-performed in this category, delivering three distinct sensing platforms, operating at 900MHz and 433MHz, and supporting single-sensor and six-sensor deployments, all with analog stages supporting adaptive gain control over a wide dynamic sensing range. The 900MHz platform includes native hardware support for multi-hop, disruption-tolerant networking. Associated software support and evaluation are ongoing.

Upper-Tier Integration

Design. The team's trajectory is focused on enabling whole-building CO_2 sensing for purposes of demand control ventilation. Achieving the connection between the sensing system and the ventilation control system requires a combination of network services that enable configuration of sensing endpoints, reception and storage of CO_2 measurements, and access to the endpoints and their data from upper-tier control services. The Phase I project resulted in prototype implementations of these services, optimized for managing the experiments conducted throughout Phase I. The services provide an excellent foundation for Phase II. The implementation comprises network aggregation points (i.e., base stations, sinks), an upper-tier data management server, and a web portal for data access.

Each base station, shown in Figure 6, serves as a bidirectional communication bridge between its sensing endpoints and the upper-tier data management server. It forms the center of a star sensing topology. Base station services are implemented for the Third Generation Raspberry Pi, a widely used, single-board Linux computer, but are readily adapted to other devices. The Raspberry Pi includes native USB support and was configured to include a 433MHz CC1101 radio for use in communicating with the sensing endpoints. Through a periodic messaging mechanism (i.e., heartbeat) implemented on the sensing platforms, each base station monitors its local neighborhood, communicating an account of active and inactive platforms to the upper-tier data management server. SSH Reverse Tunneling was configured on each base station, enabling remote connections, even in NAT networks, simplifying software enhancements and profiling between the two primary test facilities.

Sensing platforms periodically transmits CO_2, temperature, and humidity data to their

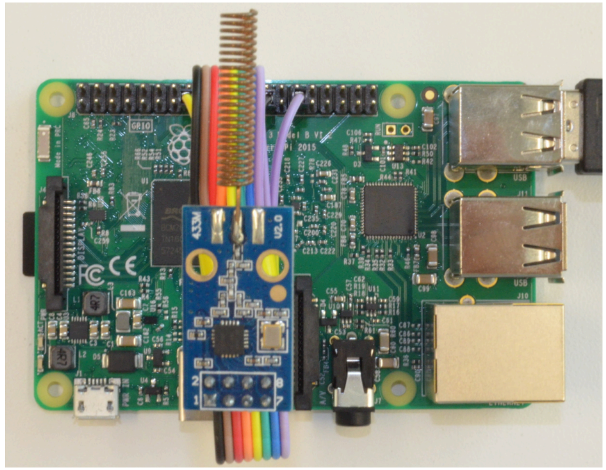


Figure 6. Base station (sink), single-board Linux computer, integrated 433MHz CC1101

local base stations. When a base station receives a message, it decodes the message and invokes a corresponding service on the data management server (e.g., `store-CO2-reading`)[1]. Similarly, when the web portal is used to configure or activate a particular sensing endpoint, the data management server invokes a corresponding service on the appropriate base station (e.g., `begin-timed-trial`), which in turn relays a message to the target sensing platform.

The data management server exposes a web interface for users to interact with a deployed network, including real-time charting of measurements. Sample screenshots from the web interface are shown in Figure 7. The interface allows users to control and manage individual sensing platforms, and both active and past experiments conducted over those platforms. Users can view available platforms, start and stop (timed) experiments, monitor experiments in real-time, and download experimental results, as shown in Figure 7. The server relies on MongoDB, a widely used NoSQL store that can be scaled to accommodate very large datasets through distribution. The store records a variety of data about the sensing system and its current state, including user authentication information, deployed devices, active experiments, and most importantly, experimental results.

Analysis. The infrastructure implementation was a central enabler for experimentation in Phase I and provides an excellent foundation for Phase II. The system has already supported over 600 experiments, collecting over 1.5 million samples. Availability has been exceptional.

Proposed Milestones Addressed. *(1) Available control protocols for demand control ventilation will be explored, focusing on strengths and limitations.* The exploration revealed wide availability of TCP/IP-based (or "Internet Ready") control systems, simplifying the analysis, leaving opportunity for unanticipated development and experimentation. The team significantly over-performed in this category.

Conclusions

Phase I project results provide strong evidence for the technical feasibility of the proposed

[1] In Phase I, the data management server was hosted within a private cloud environment, but could be readily relocated to a commercial environment (e.g., Amazon's EC2).

Figure 7. Web portal screenshots

approach to enabling low-cost, high-accuracy, whole-building carbon dioxide monitoring for use in demand control ventilation. Indeed, project milestones demonstrate progress beyond feasibility; *performance* has been demonstrated in each of the five goal categories: (1) Sensitivity, stability, and robustness of the electrochemical CO_2 sensor have been improved. (2) The environmental response of the CO_2 sensor to variation in temperature and humidity has been characterized. (3) A low-power data acquisition circuit capable of dynamically adapting to CO_2 concentrations over several orders of magnitude has been designed. (4) Distinct wireless CO_2 sensing platforms have been demonstrated, optimized for laboratory experimentation and in-building deployment, respectively. (5) Base station, data storage, and data access infrastructure have been demonstrated, providing a foundation for integration with upper-tier building management systems. **The project is poised for success in Phase II.**

Acknowledgment

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Disclaimer

Products

As detailed in the original proposal, foundational work completed prior to the start of the Phase I project resulted in numerous publications and patents. While additional products are anticipated, there is nothing yet to report.

Personnel

- **Dr. Jason O. Hallstrom** is the Director of I-SENSE and a Professor in the Department of Computer and Electrical Engineering and Computer Science.
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Literature Cited

Not applicable