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# A modular approach to volatile organic compound samplers for tethered balloon and drone platforms

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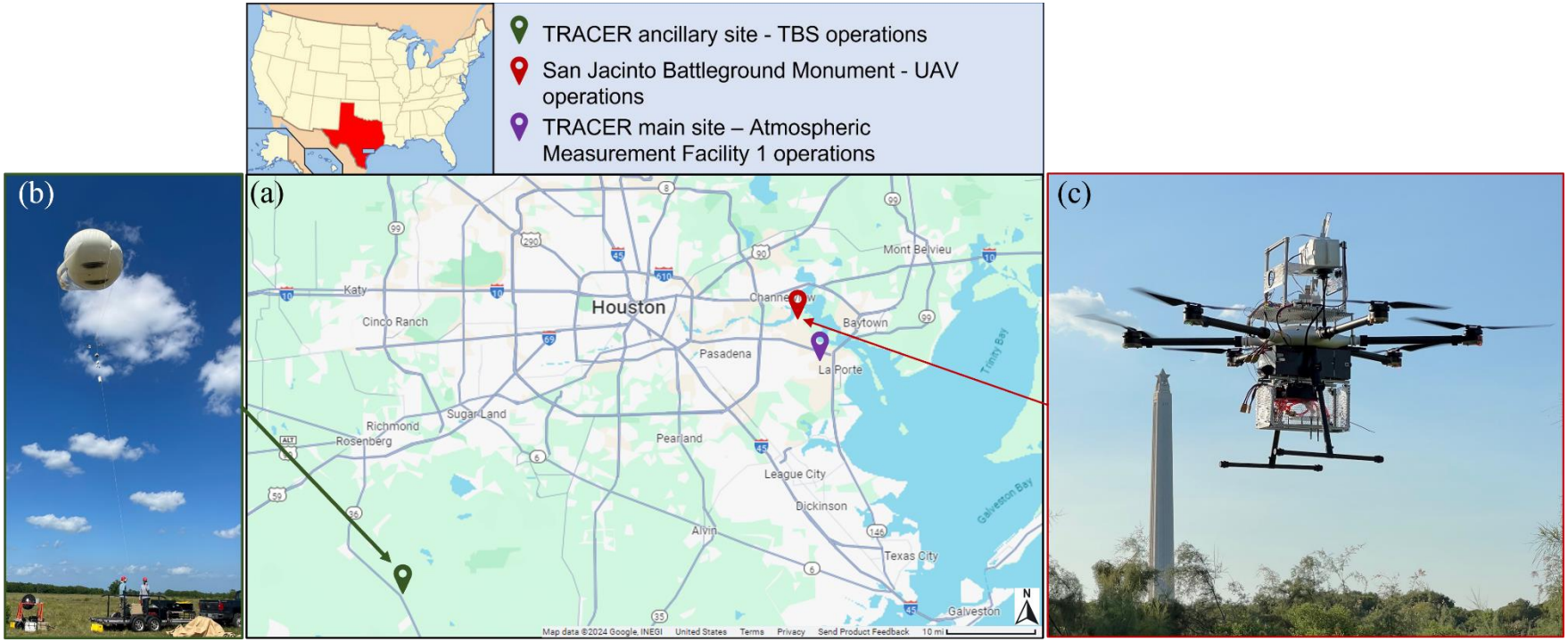


**Figure S1.** Site map of the TBS and UAV operations during the TRACER IOP (a). The ARM TBS flew a baseline payload and guest instrumentation, which combined aerosol, trace gas, and VOC sensors (b). Hexacopter mid-flight at the San Jacinto Battleground Historic Site with ECC ozone sonde above and VOC sampler below the UAV (c).

(a)

(b)


**Figure S2.** The finalized TBS sampler with side panel access (a) and overhead access (b) to the power source and sorbent tubes for exchange and maintenance. Considering the TBS system's power consumption during sampling (2.4 A) and battery capacity, we estimate the system could conduct continuous sampling for 2.2 hours before requiring replacement, equating to 13 consecutive VOC samples (10-minute collection time). When onboard the UAV, the sampling system utilized the internal batteries and consumed 1 A of power during sampling, representing 4% of the capacity.

**Table S1.** VOC sampler components

| | Item | Vendor | Manufacturer | Country of origin | Part number | Specification |
|---|---|---|---|---|---|---|
| Electronics | Computer | UDOO | UDOO | Italy | Bolt V3 | |
| | Microcontroller | Amazon | ELEGOO | China | EL-KIT-004 | |
| | USB B to USB C cable | Amazon | Cable Matters | United States | 201002-BLK-1m | |
| | Relay board | Lystin | Songle | China | SRD-05VDC-SL-C | 4 channel, 5V DC |
| | Wire connectors | Amazon | WAGO | Germany | 221 series | |
| | Battery | Gens Ace | Gens Ace | China | B-45C-5500-6S1P | 5500mAh, 22.2V, 45C |
| Flow control | Valves | Parker-Hannifin | Parker | United States | 991-000208-007 | 1/8" barb ports |
| | Pumps | Parker-Hannifin | Parker | United States | E242-12 | 1/8" barb ports |
| | Sorbent tubes | Markes International | Markes International | United Kingdom | C3-CAXX-5304 | |
| Software | Arduino Software | Arduino | Arduino | Italy | | |
| UAV framing | Miniature T-Slotted framing | McMaster Carr | McMaster Carr | United States | 1959N1 | |
| | High-flow aluminum perforated sheets | McMaster Carr | McMaster Carr | United States | 92725T51 | |

**Table S2.** List of analytical standards used in this study (purchased from Sigma Aldrich)

| Compound Class | Target Analyte | Product Number | Calibration range (pg/µL) | |
|---|---|---|---|---|
| Biogenic* | Isoprene | 59240-1ML-F | 14 | 9,200 |
| | α-Pinene | CRM40339 | 13 | 8,100 |
| | β-Pinene | CRM40433 | 13 | 8,100 |
| | Limonene | CRM40448 | 13 | 8,100 |
| Transportation | Benzene | CRM47993 | 97 | 11,000 |
| | Toluene | CRM47993 | 97 | 11,000 |
| | Ethylbenzene | CRM47993 | 97 | 11,000 |
| | *m&p*-Xylene | CRM47993 | 97 | 11,000 |
| | *o*-Xylene | CRM47993 | 97 | 11,000 |
| Personal Care & Cleaning Products | D5 siloxane | 43217-250MG | 150 | 13,000 |
| | Benzyl alcohol | 47509-U | 13 | 8,100 |
| Industrial Inks & Adhesives | D4 siloxane | 235695-25G | 150 | 12,000 |
| | PCBTF | C26402-100G | 11 | 7,300 |
| | Styrene | 45993-250MG | 19 | 12,000 |
| | Texanol | 538221-1L | 150 | 13,000 |

* The compounds listed here have historically been classified as biogenic; however, they can also be emitted from anthropogenic sources, including the production and usage of volatile chemical products.

**Table S3.** Electron impact (70 eV) MS/MS ion transitions of VOCs

| Analyte | Retention Time (min) | Ion transition Q1 (m/z) | Q3 (m/z) | Collision Energy (eV) |
|---|---|---|---|---|
| Isoprene | 5.12 | 68 | 67* | 5 |
| | | 67 | 41 | 10 |
| | | 67 | 65 | 5 |
| Benzene | 9.44 | 78 | 50* | 25 |
| | | 78 | 52 | 15 |
| | | 78 | 77 | 10 |
| Toluene | 13.18 | 91 | 39* | 25 |
| | | 91 | 65 | 15 |
| | | 92 | 91 | 10 |
| PCBTF | 15.79 | 180 | 130* | 15 |
| | | 180 | 145 | 15 |
| | | 180 | 161 | 20 |
| Ethylbenzene | 15.95 | 91 | 39* | 25 |
| | | 91 | 65 | 15 |
| | | 106 | 91 | 10 |
| *m*- & *p*-Xylene | 16.16 | 106 | 91* | 10 |
| | | 91 | 65 | 15 |
| | | 105 | 77 | 15 |
| *o*-Xylene | 16.86 | 91 | 39* | 25 |
| | | 91 | 65 | 15 |
| | | 106 | 91 | 15 |
| Styrene | 16.91 | 103 | 77* | 10 |
| | | 104 | 78 | 10 |
| | | 104 | 103 | 15 |
| α-Pinene | 17.45 | 93 | 51* | 25 |
| | | 93 | 77 | 10 |
| | | 93 | 91 | 10 |
| D4 siloxane | 18.05 | 281 | 73* | 25 |

| | | | | |
|---|---|---|---|---|
| | | 281 | 205 | 30 |
| | | 281 | 249 | 20 |
| β-Pinene | 18.63 | 93 | 51* | 25 |
| | | 93 | 77 | 10 |
| | | 93 | 91 | 10 |
| Limonene | 19.48 | 68 | 67* | 5 |
| | | 93 | 77 | 15 |
| | | 93 | 91 | 10 |
| Benzyl Alcohol | 20.38 | 79 | 77* | 10 |
| | | 108 | 79 | 15 |
| | | 108 | 107 | 10 |
| D5 siloxane | 20.5 | 267 | 179* | 35 |
| | | 267 | 250 | 15 |
| | | 355 | 267 | 10 |
| Texanol | 23.45 | 56 | 41* | 10 |
| | | 71 | 41 | 10 |
| | | 71 | 43 | 5 |

*Quantitation ion

**Table S4.** Summary of flight conditions during TBS VOC sampling on 4 August 2022

| | Minimum | Maximum |
|---|---|---|
| Altitude (m AGL) | 0 | 442 |
| Temperature (°C) | 27.5 | 39.7 |
| Relative Humidity (%) | 4.1 | 91.7 |
| Wind Speed (m/s) | 0 | 10.6 |
| Vertical Wind Speed (m/s) | -1.3 | 2.1 |
| Pressure (mb) | 964 | 1013 |
| Ascent Rate (m/s) | -1.3 | 0.94 |
| $O_3$ Mixing Ratio (ppmv) | 0.013 | 0.033 |

**Table S5.** Summary of VOCs and concentrations (ppbv) collected on the TBS on 4 August 2022

| TBS Sample | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Time (GMT) | 14:38 - 14:58 | 17:49 - 18:09 | 18:14 - 18:34 | 20:21 - 20:41 | 20:46 - 21:06 | 21:11 - 21:31 |
| Altitude (m) | 180 | 400 | 300 | 400 | 300 | 200 |
| Isoprene | 1.1 | 2.4 | 3.3 | 8.7 | 8.4 | 8.5 |
| Benzene | 0.22 | < MDL | < MDL | < MDL | < MDL | < MDL |
| Toluene | 0.58 | < MDL | 0.07 | 0.39 | 0.66 | 0.63 |
| Ethylbenzene | 0.01 | < MDL | < MDL | 0.03 | 0.05 | 0.07 |
| *m*&*p*-Xylene | 0.02 | < MDL | < MDL | 0.04 | 0.08 | 0.16 |
| *o*-Xylene | 0.02 | < MDL | < MDL | 0.04 | 0.07 | 0.15 |
| α-Pinene | 0.04 | 0.04 | 0.05 | 0.07 | 0.07 | 0.08 |
| β-Pinene | 0.20 | 0.26 | 0.30 | 0.62 | 0.63 | 0.66 |
| Limonene | 0.03 | 0.01 | 0.01 | < MDL | 0.01 | 0.01 |
| Styrene | < MDL | < MDL | < MDL | 0.28 | 0.30 | 0.60 |
| Benzyl alcohol | 0.15 | 0.01 | 0.01 | 0.10 | 0.17 | 0.15 |
| D4 siloxane | < MDL | < MDL | < MDL | N.D. | < MDL | < MDL |
| D5 siloxane | 0.01 | < MDL | < MDL | < MDL | < MDL | < MDL |
| PCBTF | 0.002 | < MDL | < MDL | N.D. | N.D. | N.D. |
| Texanol | 0.021 | N.D. | N.D. | 0.007 | 0.034 | 0.019 |
| Total (ppbv) | 2.4 | 2.8 | 3.7 | 10.3 | 10.5 | 11.1 |

**Table S6.** Summary of VOCs and concentrations (ppbv) collected on the UAV on 13 September 2022

| UAV Sample | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Time (GMT) | 21:39 - 21:49 | 21:50 - 22:00 | 22:27 - 22:37 | 22:38 - 22:48 |
| Altitude (m) | 120 | 60 | 120 | 60 |
| Isoprene | 0.63 | 0.09 | 0.06 | < MDL |
| Benzene | 3.38 | 2.08 | < MDL | 0.49 |
| Toluene | < MDL | < MDL | < MDL | < MDL |
| Ethylbenzene | 0.07 | 0.19 | 0.20 | 0.00 |
| *m*&*p*-Xylene | 0.14 | 0.25 | 0.38 | 0.16 |
| *o*-Xylene | 0.11 | 0.18 | 0.30 | 0.13 |
| α-Pinene | 0.08 | 0.03 | < MDL | < MDL |
| β-Pinene | 0.03 | 0.01 | < MDL | < MDL |
| Limonene | 0.10 | 0.03 | < MDL | < MDL |
| Styrene | 0.11 | < MDL | < MDL | < MDL |
| Benzyl alcohol | 0.21 | 0.02 | < MDL | < MDL |
| D4 siloxane | < MDL | < MDL | N.D. | N.D. |
| D5 siloxane | 0.06 | 0.01 | < MDL | N.D. |
| PCBTF | < MDL | < MDL | < MDL | < MDL |
| Texanol | 0.11 | < MDL | < MDL | < MDL |
| Total (ppbv) | 5.0 | 2.9 | 0.9 | 0.8 |


**Figure S3.** During TRACER-AQ2, a single tube sampler (a) with identical internal power and flow components as the aerial samplers described in this study was deployed in the field (b).

The following Arduino code was used to operate the valves and pumps via the microcontroller in the TBS VOC sampler:

```
String command;

#define pump 11
#define valve01 10
#define valve02 9
#define valve03 8

void setup()
{ Serial.begin(9600);
  pinMode (11,OUTPUT); // connected to terminal 11 - pump
  pinMode (10,OUTPUT); // connected to terminal 10 - valve 01
  pinMode (9,OUTPUT); // connected to terminal 9 - valve 02
  pinMode (8,OUTPUT); // connected to terminal 8 - valve 03

delay(2000);

Serial.println("Type Command (one, two, three, four, cycle, off)");
}

void loop()

{ if (Serial.available()){
    command = Serial.readStringUntil('\n');
    command.trim();

    if (command.equals("one")){ //sampling tube #1 only
  //delay(4000); // delay for 4 seconds before sampling
  digitalWrite(11,HIGH); // pump - ON      turn relay ON, red light is on, normally closed contact is closed
  digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
  digitalWrite(9,LOW); // valve 02 - flow from bottome port
  digitalWrite(8,LOW); // valve 03 - flow from bottom port (tube #1)
```

```
32    }
33  else if (command.equals("two")){ //sampling tube #2 only
34  digitalWrite(11,HIGH); // pump - ON       turn relay OFF, red light is off, normally open contact is closed
35  digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
36 digitalWrite(8,HIGH); // valve 03 - flow from top port (tube #2)
37  }
38 else if (command.equals("three")){ //sampling tube #3 only
39 digitalWrite(11,HIGH); // pump - ON       turn relay OFF, red light is off, normally open contact is closed
40 digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
41 digitalWrite(9,HIGH); // valve 02 - flow from top port (tube #3)
42 }
43 else if  (command.equals("four")){ //sampling tube #4 only
44 digitalWrite(11,HIGH); // pump - ON
45 digitalWrite(10,HIGH); // valve 01 - flow from top port (tube #4)
46
47 }
48 else if  (command.equals("cycle")){ //cycle through all four tubes for designated amount of time
49  //sampling tube #1 only
50 delay(900000); // delay 15 min before sampling
51 digitalWrite(11,HIGH); // pump - ON      turn relay ON, red light is on, normally closed contact is closed
52  digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
53  digitalWrite(9,LOW); // valve 02 - flow from bottome port
54  digitalWrite(8,LOW); // valve 03 - flow from bottom port (tube #1)
55 delay(1200000); // delay 20 min for sampling
56 digitalWrite(11,LOW); // pump - OFF      turn relay ON, red light is on, normally closed contact is closed
57  //sampling tube #2 only
58 delay(6000); // delay 8 min before sampling
59  digitalWrite(11,HIGH); // pump - ON       turn relay OFF, red light is off, normally open contact is closed
60  digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
61  digitalWrite(8,HIGH); // valve 02 - flow from top port (tube #2)
62 delay(6000);// delay 20 min for sampling
63  digitalWrite(11,LOW); // pump - OFF      turn relay ON, red light is on, normally closed contact is closed
64  //sampling tube #3 only
```

```
delay(600000); // delay 8 min before sampling
 digitalWrite(11,HIGH); // pump - ON       turn relay OFF, red light is off, normally open contact is closed
 digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore through bottom port)
 digitalWrite(9,HIGH); // valve 03 - flow from top port (tube #2)
delay(1200000);// delay 20 min for sampling
 digitalWrite(11,LOW); // pump - OFF      turn relay ON, red light is on, normally closed contact is closed
 //sampling tube 4 only
delay(600000); // delay 8 min before sampling
digitalWrite(11,HIGH); // pump - ON
digitalWrite(10,HIGH); // valve 01 - flow from top port (valve 03)
 delay(1200000);// delay 20 min for sampling
 digitalWrite(11,LOW); // pump - OFF      turn relay ON, red light is on, normally closed contact is closed
}
else if  (command.equals("off")){ //pump off
digitalWrite(11,LOW); // pump - OFF
}
else{
 Serial.println("bad command");
}
Serial.print("Command: ");
Serial.println(command);
}


}
```