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

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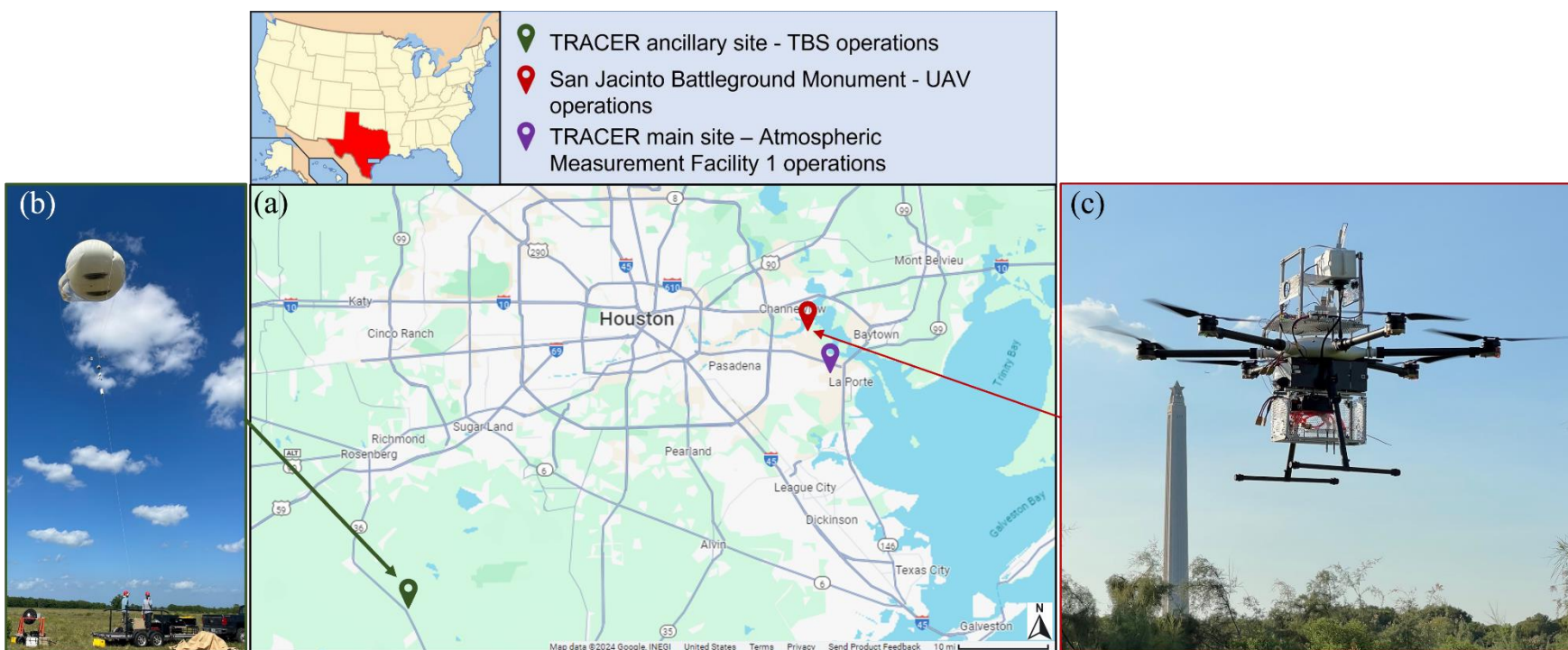*Correspondence to*: Sascha Usenko (sascha_usenko@baylor.edu)

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).
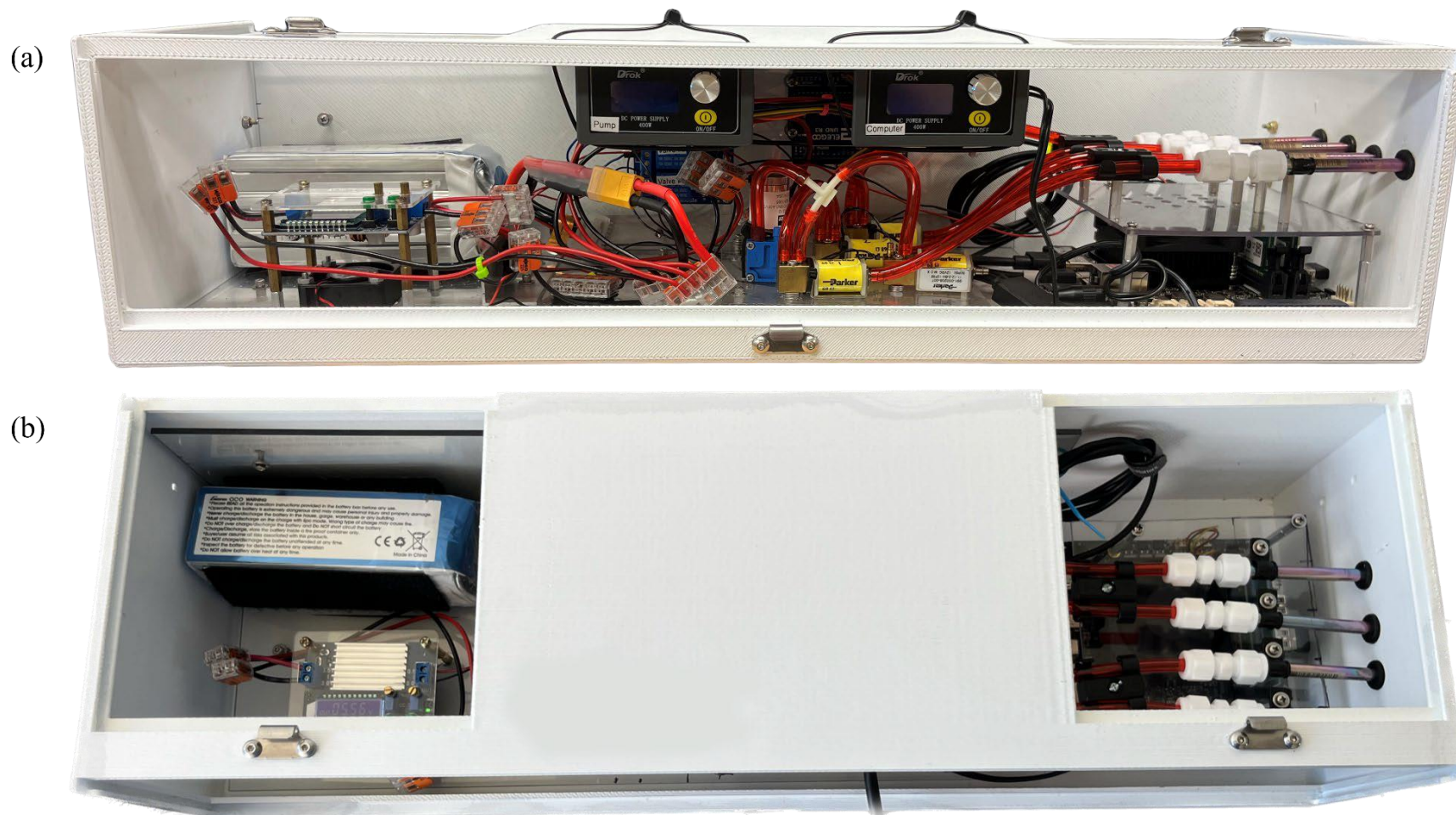
Figure S2. The finalized TBS sampler with side panel access (a) and overhead access (b) to the power source and sorbent tubes for exchange and maintenance. Considering the TBS system's power consumption during sampling (2.4 A) and battery capacity, we estimate the system could conduct continuous sampling 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. Analytical standards list

Compound Class	Target Analyte	Product Number	Calibration range (pg/µL)	
Biogenic*	Isoprene	59240-1ML-F	14	9203
	α-Pinene	CRM40339	13	8108
	β-Pinene	CRM40433	13	8108
	Limonene	CRM40448	13	8108
Transportation	Benzene	CRM47993	97	11,111
	Toluene	CRM47993	97	11,111
	Ethylbenzene	CRM47993	97	11,111
	m&p-Xylene	CRM47993	97	11,111
	o-Xylene	CRM47993	97	11,111
Personal Care & Cleaning Products	D5 siloxane	43217-250MG	156	12946
	Benzyl alcohol	47509-U	13	8108
Industrial Inks & Adhesives	D4 siloxane	235695-25G	152	12662
	PCBTF	C26402-100G	11	7304
	Styrene	45993-250MG	19	12027
	Texanol	538221-1L	154	12838

* 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)	Q1 (m/z)	Q3 (m/z)	Collision Energy (eV)
			Ion transition	
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
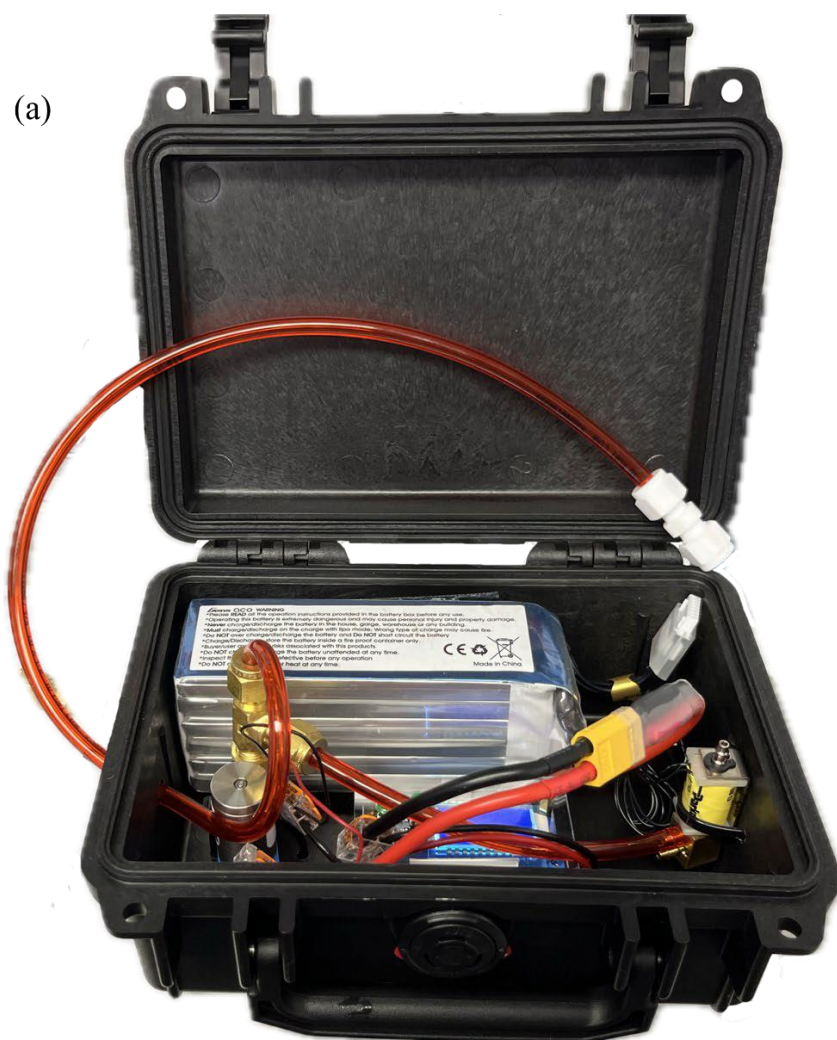
Figure S3. During TRACER-AQ2, a single tube sampler (a) with identical internal power and flow components as the aerial samplers described in this study was deployed in the field (b).

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

```
1 String command;
2
3 #define pump 11
4 #define valve01 10
5 #define valve02 9
6 #define valve03 8
7
8 void setup()
9 { Serial.begin(9600);
10  pinMode (11,OUTPUT); // connected to terminal 11 - pump
11  pinMode (10,OUTPUT); // connected to terminal 10 - valve 01
12  pinMode (9,OUTPUT); // connected to terminal 9 - valve 02
13  pinMode (8,OUTPUT); // connected to terminal 8 - valve 03
14
15 delay(2000);
16
17 Serial.println("Type Command (one, two, three, four, cycle, off)");
18 }
19
20 void loop()
21
22 { if (Serial.available()){
23    command = Serial.readStringUntil('\n');
24    command.trim();
25
26    if (command.equals("one")){ //sampling tube #1 only
27 //delay(4000); // delay for 4 seconds before sampling
28  digitalWrite(11,HIGH); // pump - ON        turn relay ON, red light is on, normally closed contact is closed
29  digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
30  digitalWrite(9,LOW); // valve 02 - flow from bottome port
31  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
```

```
65 delay(600000); // delay 8 min before sampling
66  digitalWrite(11,HIGH); // pump - ON        turn relay OFF, red light is off, normally open contact is closed
67  digitalWrite(10,LOW); // valve 01 - flow from bottom port (flow through valve 02 - not powered, therefore
through bottom port)
68  digitalWrite(9,HIGH); // valve 03 - flow from top port (tube #2)
69 delay(1200000);// delay 20 min for sampling
70  digitalWrite(11,LOW); // pump - OFF        turn relay ON, red light is on, normally closed contact is closed
71  //sampling tube 4 only
72 delay(600000); // delay 8 min before sampling
73 digitalWrite(11,HIGH); // pump - ON
74 digitalWrite(10,HIGH); // valve 01 - flow from top port (valve 03)
75  delay(1200000);// delay 20 min for sampling
76  digitalWrite(11,LOW); // pump - OFF        turn relay ON, red light is on, normally closed contact is closed
77 }
78 else if  (command.equals("off")){ //pump off
79 digitalWrite(11,LOW); // pump - OFF
80 }
81 else{
82  Serial.println("bad command");
83 }
84 Serial.print("Command: ");
85 Serial.println(command);
86 }
87
88
89
90 }
```