Chemical Characterization of Isoprene- and Monoterpene-Derived Secondary Organic Aerosol (SOA) Tracers in Marine Aerosols from the Galápagos Islands

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Introduction

Motivation

An important source of $PM_{2.5}$ are the oceans, where aerosols can either be directly emitted from a wind-driven bubble bursting process on the ocean surface,[1] or formed via atmospheric chemistry.[2,3] This chemistry produces secondary organic aerosol (SOA) derived from the oxidative processing of volatile organic compounds (VOCs). Ocean-derived BVOCs participate in SOA formation, however, the amount to which these ocean sources contribute to $PM_{2.5}$ is still unknown. The Galapagos Islands present a pristine environment where anthropogenic emission sources likely have limited influence on aerosols. It is a unique location to investigate the sources and formation chemistry of marine OA.

Goals

On the island of San Cristóbal, the Galápagos Science Center (GSC) provides a fixed location on the coast making it ideal for long-term sampling. Our study aims to understand sources of marine SOA by quantifying amounts of isoprene-derived SOA (iSOA) and monoterpene-derived SOA (mSOA) from remote marine aerosols. This study will serve as a pilot and feasibility study. These results will show the feasibility of the GSC as a long-term measurement site and the capability to identify biogenically derived SOA that could be correlated with marine bioactivity indicators to investigate the influence of marine sources.

Methods

Aerosol Sample Collection/Analysis

- Two sampling sites on San Cristóbal Island, Galápagos Islands:
  - Galápagos Science Center (GSC)
  - Instituto Nacional de Meteorologia e Hidrologia (INAMHI)
- Samples collected on pre-baked quartz filters by High-Volume $PM_{2.5}$ air sampler over 3-week period in July 2017
- Filters analyzed by:
  - HILIC/ESI-HR-QTOFMS for iSOA tracers (2-methyltetrols and IEPOX-OS) and mSOA tracers (terebic and pinonic acids)
  - Ion chromatography for sulfate, chloride, nitrate, MSA, and oxalic acid
  - OC-EC analysis for total organic carbon and elemental carbon

Real Time $PM_{2.5}$ Data

- Real-time $PM_{2.5}$ measurements taken by two TSI DustTrak II Aerosol Monitors 8530 located at sampling site

Meteorological Data Collection

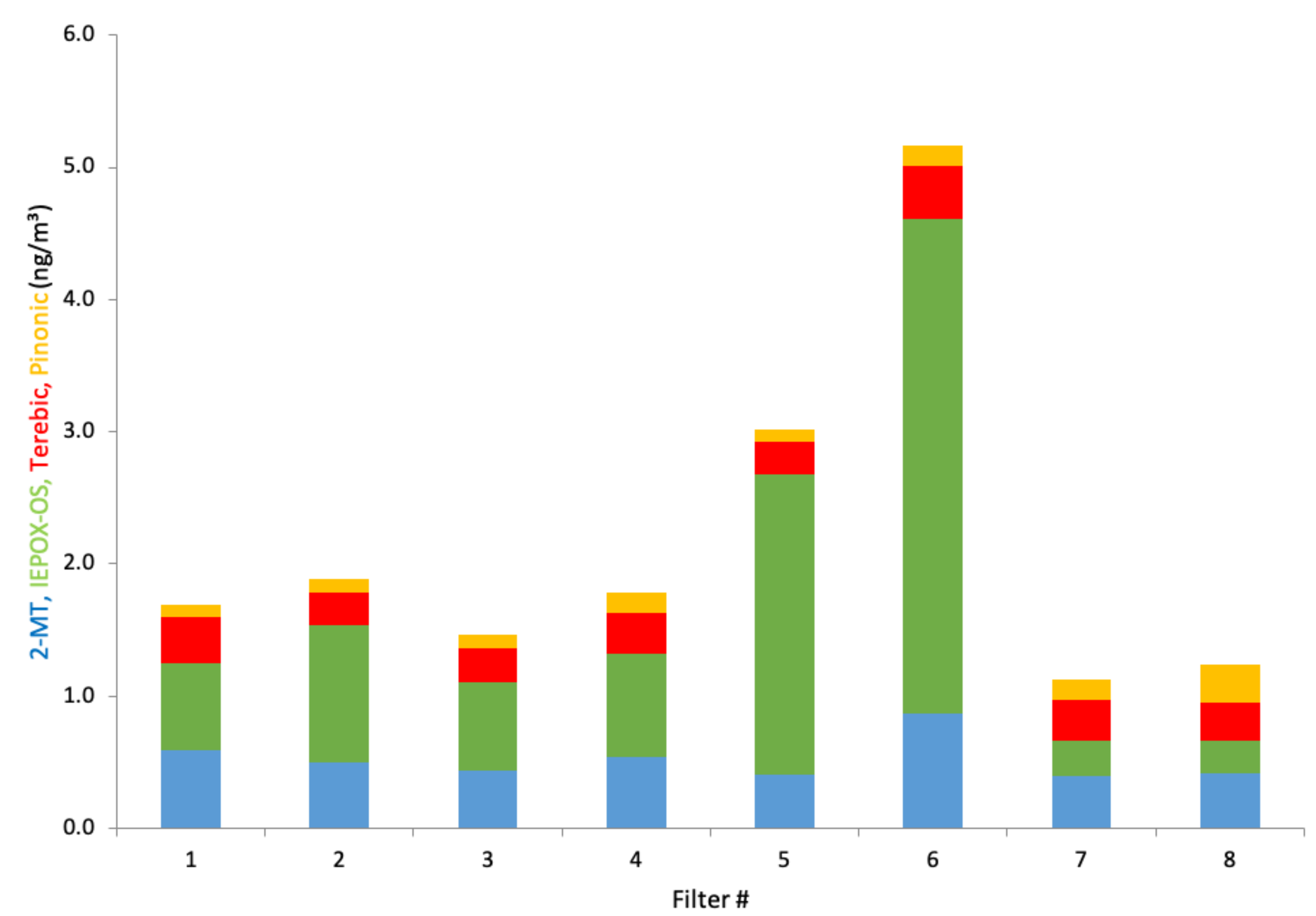
- Five-minute meteorological data (wind speed, relative humidity, and temperature) taken at GSC for first two weeks of study
- Meteorological data (precipitation, wind direction/speed, temperature, pressure, humidity) collected three times a day at INAMHI station

Results

Table 1 Summary of filter sampling location, duration, and recorded $PM_{2.5}$ mass. The average flow rate for the sampling period was 1.176 ± 0.03 m^3/minute.

Filter	Site	Start Time 1	End Time 1	Start Time 2	End Time 2	Hours	Air Sampled (m^3)	$PM_{2.5}$ (mg)	$PM_{2.5}$ (µg/m^3)
1	GSC	7/2/17- 9:15am	7/5/17- 8:45am	-	-	71.5	5091	50.47	10.51
2	GSC	7/5/17- 8:55am	7/8/17- 8:55am	-	-	72.0	5126	40.84	8.45
3	GSC	7/8/17- 9:05am	7/11/17- 8:35am	-	-	71.5	5090	34.01	7.08
4	GSC	7/11/17- 9:15am	7/13/17- 8:20 am	-	-	47.1	3352	32.83	10.39
5	INAMHI	7/13/17- 12:05pm	7/14/17- 3:57pm	7/15/17- 7:03am	7/15/17- 6:00pm	38.8	2763	29.13	11.20
6	INAMHI	7/16/17- 6:00am	7/16/17- 6:00pm	7/17/17- 7:00am	7/17/17- 6:10pm	23.2	1649	14.37	9.24
7	INAMHI	7/18/17- 7:00am	7/18/17- 6:50pm	7/19/17- 7:00am	7/19/17- 6:50pm	23.7	1684	15.23	9.58
8	INAMHI	7/20/17- 7:00am	7/20/17- 6:50pm	7/21/17- 6:50am	7/21/17- 4:00pm	21.0	1494	-	-

Figure 1 Bar chart of measured concentrations of iSOA and mSOA tracers.



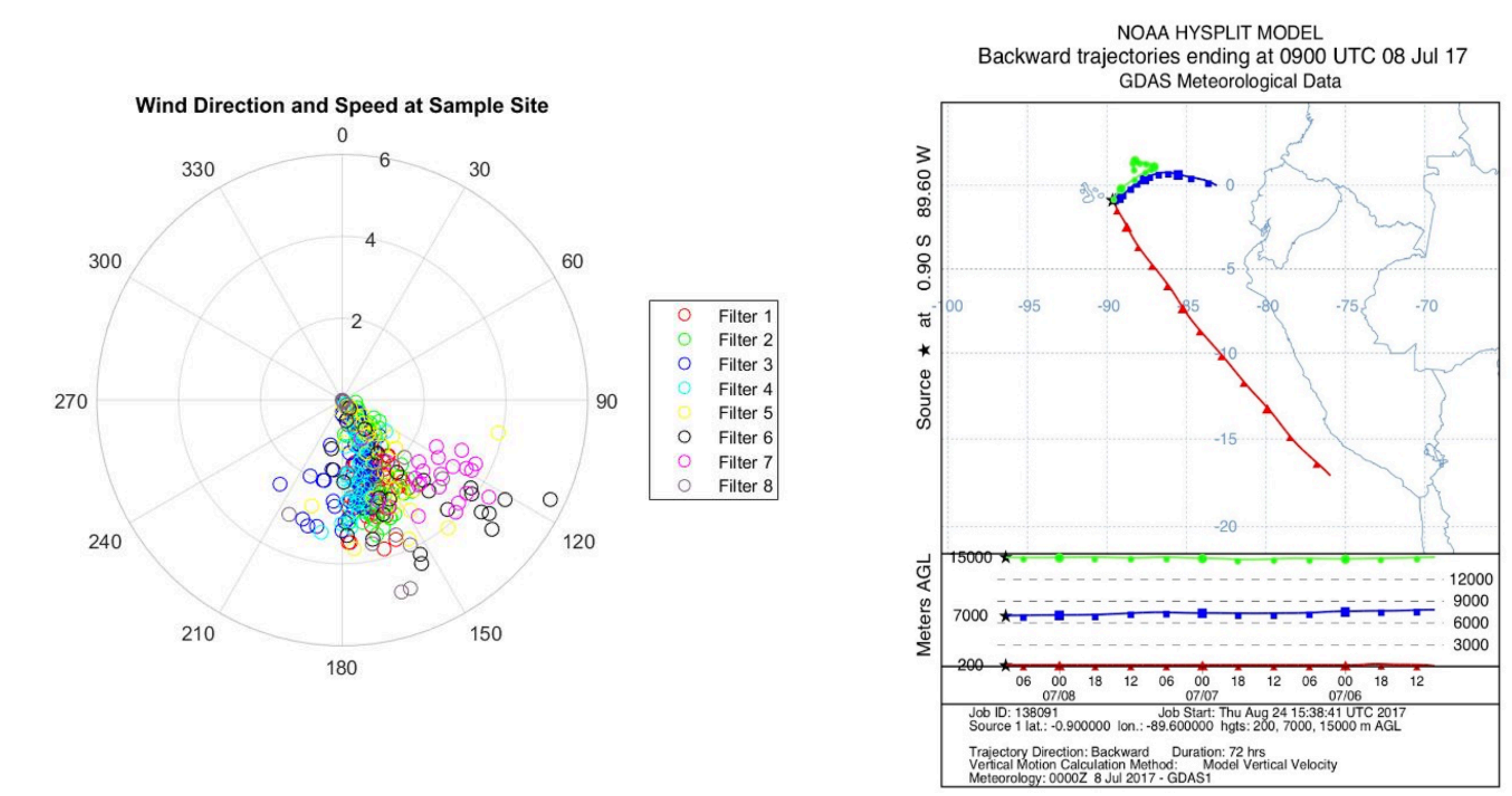
- Similar concentrations of iSOA and mSOA seen in Cape Grim, a similar pristine marine environment[4]
- Concentrations of iSOA much lower than previous data collected on iSOA tracers off the lower Central American coast.[5]
- IEPOX-OS production is the dominant iSOA pathway
- Detected ~ 75% less mass of mSOA than that of iSOA
- Dominant mSOA constituent was the formation of terebic acid, nearly double that of pinonic acid

Table 2 Pearson correlation coefficients for select tracers

	2-MT[a]	IEPOX-OS[b]	Terebic	Pinonic	Levo.[c]	MSA[d]	Oxalate	Sulfate	Chloride	Nitrate	EC[e]	OC[f]	OC1[g]	OC2[h]	OC3[i]	OC4[j]	OCp[k]
2-MT	1.00	0.73	0.82	-0.05	-0.23	0.35	0.19	0.35	0.56	0.40	-0.50	-0.24	-0.19	-0.14	-0.25	-0.19	-0.40
IEPOX-OS		1.00	0.41	-0.21	0.09	0.22	0.61	0.25	0.33	0.21	-0.33	0.39	0.35	0.46	0.27	0.40	0.27
Terebic			1.00	0.23	0.06	-0.02	-0.05	0.03	0.45	0.33	-0.80	-0.37	-0.11	-0.43	-0.41	-0.39	-0.43
Pinonic				1.00	-0.11	-0.52	-0.55	-0.42	-0.25	-0.04	-0.89	-0.48	-0.20	-0.61	-0.67	-0.54	-0.22
Levo.					1.00	-0.61	0.14	-0.57	-0.39	-0.50	-0.52	0.53	0.70	0.35	0.45	0.46	0.54
MSA						1.00	0.50	0.96	0.72	0.73	0.42	0.10	-0.17	0.30	0.28	0.19	-0.14
Oxalic							1.00	0.55	0.51	0.50	0.09	0.83	0.71	0.84	0.81	0.82	0.71
Sulfate								1.00	0.85	0.83	0.27	0.15	-0.11	0.31	0.32	0.27	-0.07
Chloride									1.00	0.91	-0.18	0.04	-0.05	0.08	0.16	0.12	-0.13
Nitrate										1.00	-0.05	0.04	0.02	0.06	0.09	0.06	-0.04
EC											1.00	0.10	-0.20	0.29	0.23	0.12	0.10
OC												1.00	0.89	0.95	0.95	0.97	0.93
OC1													1.00	0.74	0.75	0.78	0.91
OC2														1.00	0.95	0.97	0.82
OC3															1.00	0.97	0.80
OC4																1.00	0.86
OCp																	1.00

- Positive correlation observed between oxalic acid and iSOA tracers, possibly points to similar atmospheric production mechanisms as both species are photochemically produced.
- Weaker correlations between OC1 to OC4 and IEPOX-OS vs. oxalic acid show that IEPOX-OS may be long-lived but may be not as photochemically stable as oxalic acid.

Figure 2 Polar cluster plot (Left) of the hourly averaged wind direction (degrees from North) and speed (m/s) during sample collection. A 72-hour HYSPLIT back trajectory (Right) for July 8, 2017 at three elevations.



- Filter 5, which had the greatest average $PM_{2.5}$ concentration, was observed to have some of the highest wind speeds with maximum wind speed of 4.1 m/s mainly from the southeast, suggesting that wave-breaking was more pre-dominant at this time.

Conclusions

- **The work presented here demonstrates the feasibility for the Galapagos Islands as a location to collect and chemically characterize marine aerosols.**
- **The results show, for the first time, evidence of isoprene-derived SOA on the Galápagos Islands.**
- **The chemical data from these aerosols, and the meteorological conditions suggest a sampling location heavily influenced by the marine environment with little impact from anthropogenic sources.**

Future Works

- **Analysis of Chl-a data (and corresponding phytoplankton concentrations) taken from Puerto Bacquerizo Moreno (closely located to GSC) for potential isoprene emission**
- **Analysis of iSOA and mSOA tracers from data collected from GSC in Summer 2018 and Summer 2019 for multi-year trends**
- **Analysis of iSOA and mSOA tracers from data collected from ship traversing Galápagos Islands in October 2018 for spatial trends across islands**

References

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