First observations of the fourth generation synthetic halocarbons HFO-1234yf, HFO-1234ze(E), and HCFO-1233zd(E) in the atmosphere

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1) HFO data at Jungfraujoch and Dubendorf are produced under the auspices of CLIMGAS, a joint project of the Swiss Federal Office for the Environment (FOEN) and Empa.

2) While these compounds were named 'HFCs' in the original 2015 publication, we came to the decision to call them HFOs (hydrofluoroolefines) to better distinguish them as a seprate compound class compared to the saturated hydrofluorocarbons (HFCs).

3) In the 2015 publication, a distinction was made in Figure 1 between measurements of the HFOs below or above detection limits. However, the update here is now not including this distinction in the respective figure, all measurements (regardless of detection limits) are drawn in the same color for each of the two stations. Accordingly, the caption is adapted.

4) Starting with the update in 2018, all HFO-1234yf results are converted to the new METAS-2017 primary calibration scales (this results in a lowering of the mole fractions by 10% compared to a reporting on the old Empa-2013 calibration scale). HFO-1234zeE and HCFO-1233zdE remain on the Empa-2013 calibration scale (no other calibration scales prepared so far).

5) Cautionary note on the Dubendorf results for 2019 and 2020: The Dubendorf measurements are conducted with an instrument titled 'empa-medusa'. Empa-medusa was temporarily relocated from Dubendorf to the Beromunster (Swiss midlands) tall tower site from August 2019 to September 2020 as part of a measurement campaign. The Beromunster measurements of the HFOs (and most other compounds) yield significantly lower concentrations compared to Dubendorf due to its more remote character. This is reflected in the statistic for some of the compounds and years.

6) Interpretation, Results: Since the Jungfraujoch and Dubendorf measurements were

published in 2015, the 3 HFOs/HCFOs have continued to grow in the atmosphere, both in frequency of detectable mole fraction as well as on their intensities/magnitudes. Examples:

While HFO-1234yf at Jungfraujoch was detected in none of the 4150 samples in 2011, when measurements began, it was detected in 10% of all samples in 2015, in 30% in 2016, in 45% in 2017, in 71% in 2018, in 75% in 2019, and in 87% in 2020. Also, while the mean and median mole fractions in the first years remained at 0.002 ppt (dominated by measurements below detection limits), they increased to 0.15 ppt and 0.10 ppt by 2020, respectively.

HFO-1234zeE was detectable in 30% of all measured samples at Jungfraujoch in 2011, when measurements began, and has now grown to 95% by 2020. Its mole fraction has grown to 0.21 ppt (mean) and 0.14 ppt (median) by 2020.

HCFO-1233zdE, the longest-lived (ca 30 days) of all three HFOs reported on, can be detected in all samples since 2015 at both stations. It mole fraction is still considerably lower compared to that of the two HFOs (2020 yearly averages are 0.19 ppt (mean) and 0.16 ppt (median) at Jungfraujoch. Inspection of the magnitude and frequency of pollution events recorded at the two sites, suggests that this compound was not widely used in Switzerland before 2017.

Table 1: Measured dry-air mole fractions in ppt (parts-per-trillion, 10^{-12}, pmol mol^{-1}) of the hydrofluoroolefines HFO-1234yf and HFO-1234ze(E), and the hydrochlorofluoroolefines HCFO-1233zd(E) at the Jungfraujoch and Dubendorf stations.

	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	combined years
HFC-1234yf											
Jungfraujoch											
mean [ppt]	0.002	0.002	0.002	0.002	0.004	0.012	0.026	0.074	0.104	0.150	0.037
median [ppt]	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.050	0.065	0.101	0.000
numb of obs	4150	3223	3253	3695	3440	3679	3993	4218	4311	3181	37143
% detectable	0.00	0.37	0.80	4.28	9.65	29.27	45.38	70.72	74.76	86.95	33.35
Dubendorf											
mean [ppt]	—	—	0.033	0.126	0.358	1.035	2.275	2.970	2.188	1.560	1.416
median [ppt]	—	—	0.014	0.062	0.141	0.550	1.302	1.787	0.977	0.567	0.488
numb of obs	—	—	2501	2554	2345	2156	2817	3279	2685	3232	21569
% detectable	—	—	62.38	93.03	100.00	100.00	100.00	100.00	100.00	100.00	94.81
HFC-1234ze(E)											
Jungfraujoch											
mean [ppt]	0.011	0.013	0.039	0.034	0.031	0.023	0.032	0.085	0.152	0.208	0.064
median [ppt]	0.002	0.002	0.008	0.007	0.002	0.002	0.016	0.054	0.088	0.136	0.019
numb of obs	2598	3375	3257	3717	3433	3687	4004	4212	4287	3060	35630
% detectable	30.83	35.56	51.30	51.74	33.44	40.55	57.02	84.69	92.26	95.23	58.82
Dubendorf											
mean [ppt]	—	—	0.719	0.956	1.107	1.824	2.058	3.106	3.478	2.789	2.089
median [ppt]	—	—	0.221	0.414	0.373	0.841	0.994	1.479	1.390	0.754	0.746
numb of obs	—	—	2474	2555	2390	2014	2720	3280	2631	3236	21300
% detectable	—	—	100.00	100.00	99.96	100.00	100.00	100.00	100.00	100.00	100.00
HCFC-1233zd(E)											
Jungfraujoch											
mean [ppt]	—	—	0.003	0.007	0.019	0.032	0.052	0.090	0.132	0.189	0.067
median [ppt]	—	—	0.001	0.006	0.017	0.029	0.045	0.080	0.106	0.159	0.038
numb of obs	—	—	3090	3674	3407	3625	3950	4169	4274	3159	29348
% detectable	—	—	47.64	63.26	97.59	100.00	100.00	100.00	100.00	100.00	89.61
Dubendorf											
mean [ppt]	—	—	0.004	0.011	0.035	0.067	0.186	0.254	0.296	0.395	0.170
median [ppt]	—	—	0.001	0.009	0.029	0.054	0.122	0.201	0.249	0.288	0.102
numb of obs	—	—	2497	2646	2354	2194	2751	3274	2651	3254	21621
% detectable	—	—	46.02	78.38	100.00	100.00	100.00	100.00	100.00	100.00	91.12

Mean and median values include measurements with undetectable mole fractions. However instead of assigning those a value of zero, we have assigned them a value equal half of the detection limits. The detection limits (dl) are 0.003 ppt for HFO-1234yf and HFO-1234ze(E) each, and 0.001 ppt for HCFO-1234zd(E). Please read the cautionary note on the Dubendorf measurements for the years 2019 and 2020.

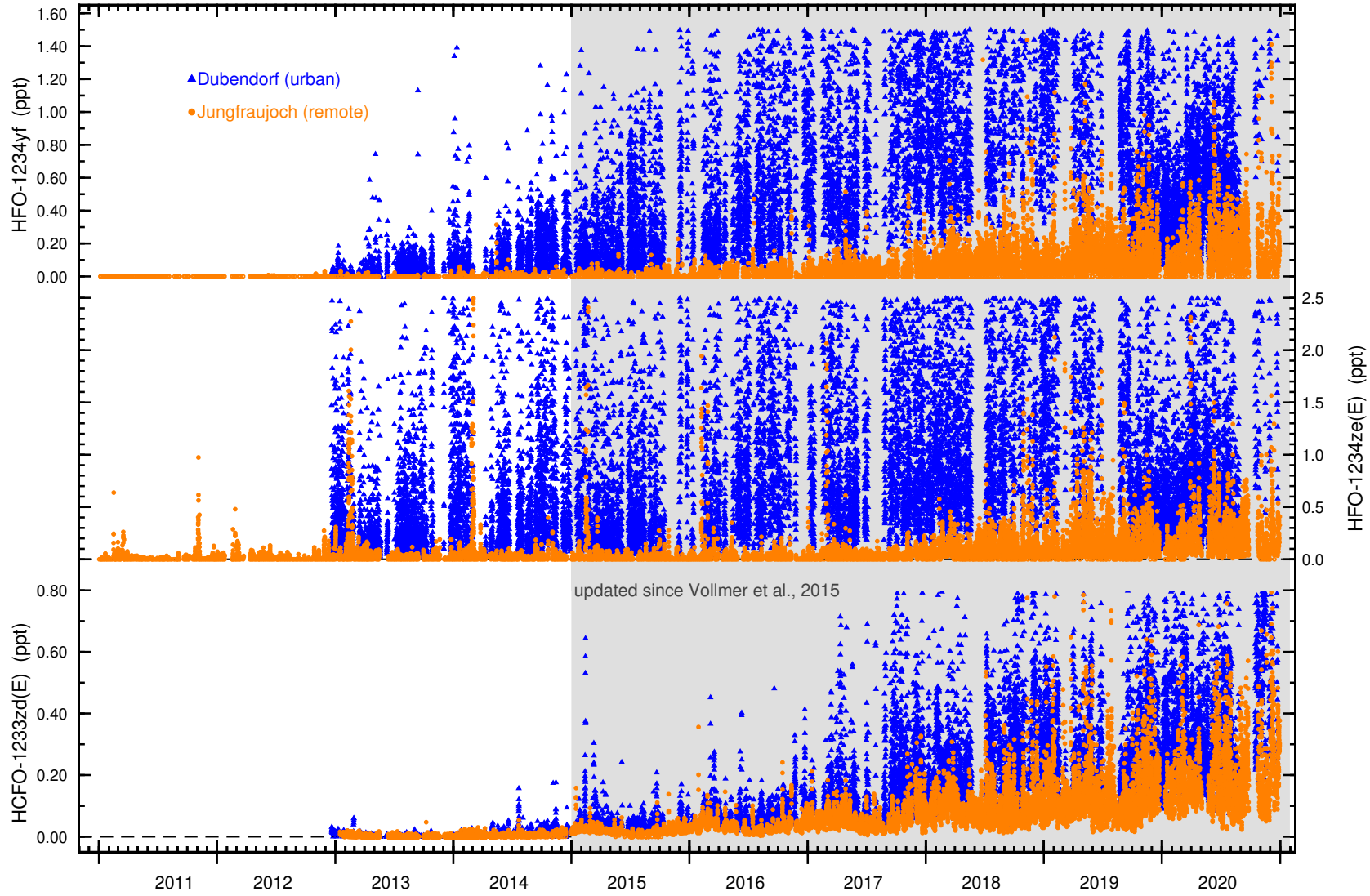

Figure 1: Atmospheric measurements of the hydrofluoroolefines HFO-1234yf (2,3,3,3-tetrafluoroprop-1-ene), and HFO-1234ze(E) (E-1,3,3,3-tetrafluoroprop-1-ene), and the hydrochlorofluoroolefines HCFO-1233zd(E) (E-1-chloro-3,3,3-trifluoroprop-1-ene) at Jungfraujoch (3'580 m.a.s.l., in orange) and urban Dubendorf (Zurich, Switzerland, in blue). Results are expressed as dry-air mole fractions in parts-per-trillion (ppt, pmol mol^{-1}). To expand the y-axes for better illustration of some of the smaller mole fractions, the results are omitted above the largest tick mark labels for each compound.