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Enhancing forest air sampling using a novel reusable ozone filter design

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S1 Characterization of ozone scrubbers

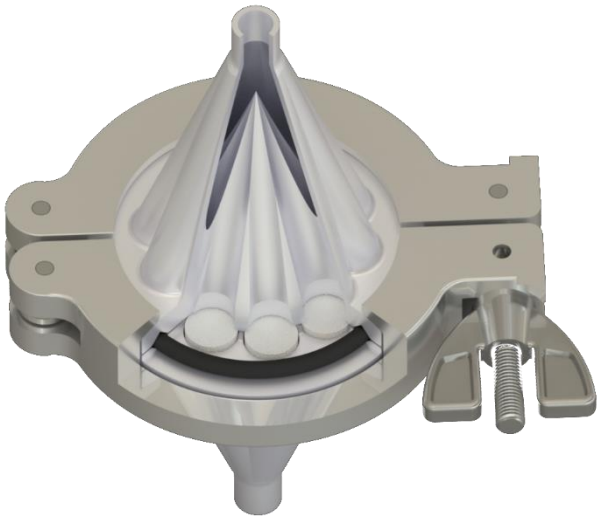

Figure S1. 3D-printed filter holder for the evaluation of the ozone removal performance of the ozone scrubbers. Air with different concentrations of ozone and relative humidity can be evenly flushed through the prepared glass filters from top to bottom.

Table S1. Experimental conditions during ozone breakthrough experiments for both scrubber materials at different conditions.

scrubber material	input ozone concentration [ppb]	rel. humidity [%]	temperature [°C]
KI	49.8	1.3	20.6
$Na_2S_2O_3$	50.2	1.3	21.3
KI	52.5	32.0	20.6
$Na_2S_2O_3$	52.9	31.1	20.4
KI	50.7	59.6	20.4
$Na_2S_2O_3$	49.9	63.0	21.1
KI	47.2	88.2	21.0
$Na_2S_2O_3$	50.0	90.2	21.8

Table S2. Environmental conditions during the long-term stability test of the ozone scrubbers.

		temperature [°C]	relative humidity [%]	barometric pressure [hPa]	ozone [ppb]
5 days	max	25.9	83.8	999	67.0
	min	15.4	44.5	993	6.2
	average	20.9	66.3	996	37.0
10 days	max	29.3	83.8	1006	67.0
	min	15.4	44.0	993	6.2
	average	21.8	64.7	998	37.0

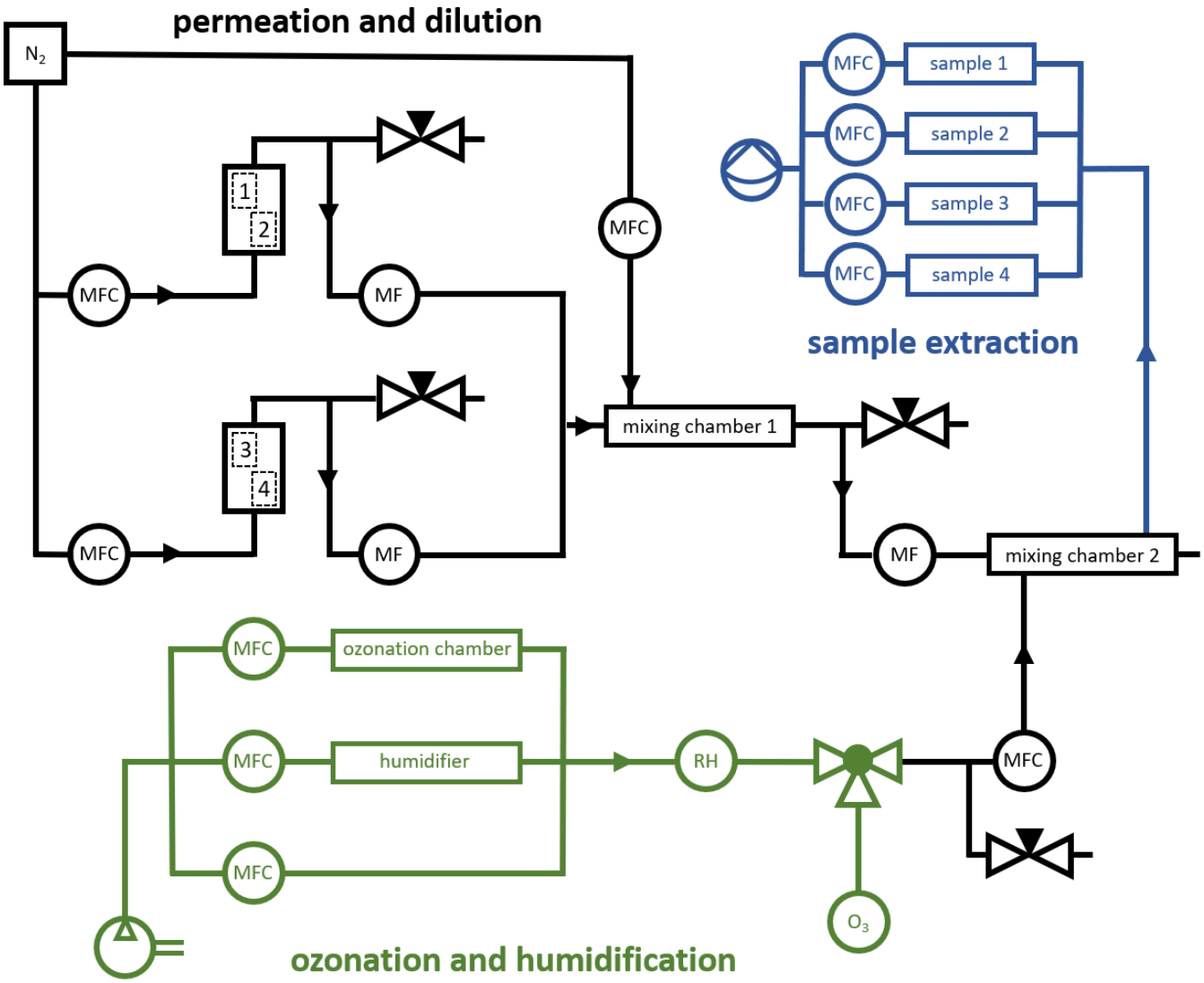

Figure S2. Schematic diagram of the adapted sample introduction system. The black section represents the system for generating a gas stream containing up to four analytes at concentration levels found in the environment. Nitrogen is used as a carrier gas to flow through two permeation cells. each containing two permeation vessels (1 - 4). Aliquots of the resulting analyte-containing gas streams are introduced into a mixing chamber using mass flow meters and needle valves and diluted with nitrogen in the first mixing chamber. An aliquot of the resulting gas stream is introduced into the second mixing chamber. The green section represents the ozonation and humidification system for generating an air stream with a defined relative humidity and ozone concentration. This gas stream is also introduced into the second mixing chamber. resulting in a gas mixture containing environmentally relevant concentrations of analytes. ozone and humidity. The blue section represents the sample extraction system for enrichment of analytes from the combined gas stream on sorbent tubes using a membrane pump and mass flow controllers. (MFC - mass flow controller; MF - mass flow meter; N_2 - nitrogen supply; O_3 - ozone analyser; RH - air humidity meter)

Table S3. Temperature. relative humidity levels and ozone concentrations at the start and end of the filter characterization experiments using the load-and-flush method.

Experiment (rH – O_3)	Temperature [°C]		Relative humidity [%]		Ozone concentration [ppb]	
	KI	$Na_2S_2O_3$	KI	$Na_2S_2O_3$	KI	$Na_2S_2O_3$
<7 – 0	19.4	20.5	5.5	5.3	4.0	3.6
<7 – 25	21.6	22.7	5.1	4.9	25.8	24.6
<7 – 50	21.4	22.5	5.4	5.2	50.2	50.1
30 – 0	21.3	22.1	31.4	31.2	4.8	4.0
30 – 25	21.0	22.3	30.9	30.9	25.9	25.3
30 – 50	20.8	22.5	30.0	33.7	50.8	51.2
60 – 0	21.0	21.6	60.7	59.3	4.5	4.0
60 – 25	21.2	22.3	60.0	60.2	25.6	24.9
60 – 50	20.5	22.1	61.2	60.4	48.6	50.6
90 – 0	21.2	22.2	90.6	89.4	3.5	3.6
90 – 25	21.3	22.6	90.2	89.3	25.2	25.5
90 – 50	21.3	22.6	91.8	89.7	50.1	50.4

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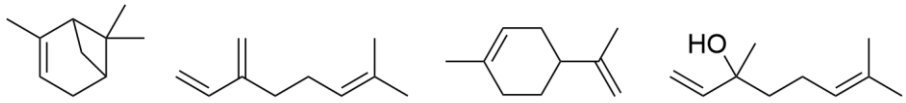
Table S4. Temperature. relative humidity levels and ozone concentrations at the start of the filter characterization experiments using the permeation method for potassium iodide (KI) and sodium thiosulfate ($Na_2S_2O_3$) as scrubber material.

Experiment (rH – O_3)	Temperature [°C]		Relative humidity [%]		Ozone concentration [ppb]	
	KI	$Na_2S_2O_3$	KI	$Na_2S_2O_3$	KI	$Na_2S_2O_3$
<7 – 0	21.6	22.4	6.2	6.2	3.0	4.0
<7 – 25	21.7	22.1	6.6	5.4	25.2	24.9
<7 – 50	20.0	21.2		5.5	50.1	50.3
30 – 0	21.4	22.0	32.5	31.8	5.2	5.5
30 – 25	20.6	21.1	32.3	32.0	25.1	24.9
30 – 50	20.5	21.5	32.4	36.8	50.3	49.1
60 – 0	20.9	21.5	59.2	54.8	4.5	5.0
60 – 25	21.3	21.8	60.5	61.3	24.7	25.3
60 – 50	21.2	22.5	63.0	60.9	50.4	49.4
90 – 0	22.4	22.5	93.9	90.8	4.5	4.5
90 – 25	22.5	23.4	91.0	90.9	25.4	25.3
90 – 50	20.9	21.7	93.4	93.2	50.6	49.8

S2 Characterization of ozone scrubber materials

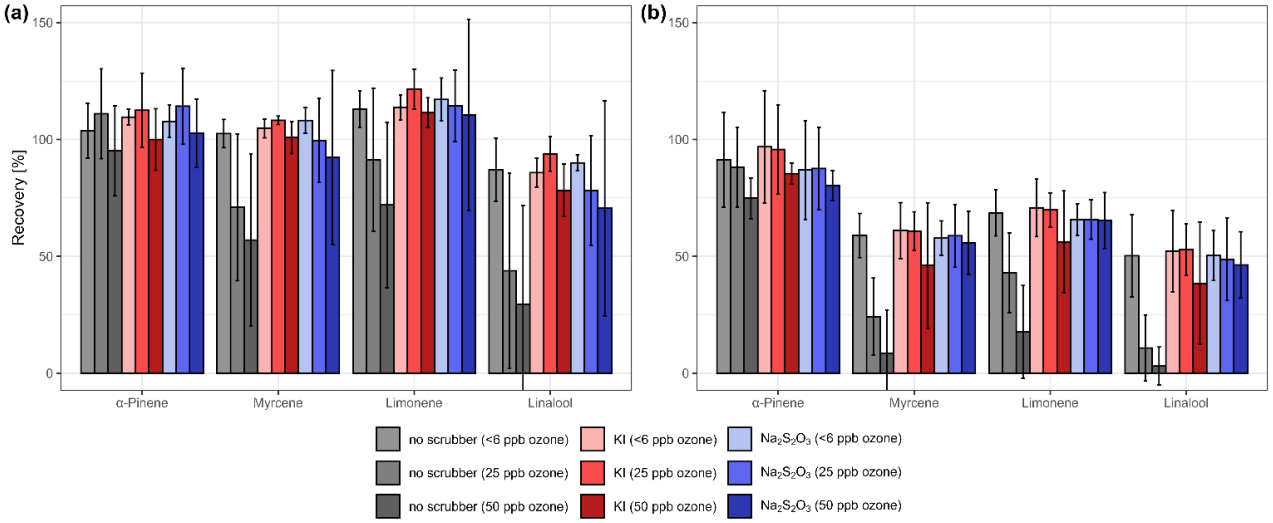
Table S5. Comparison of deposited masses of potassium iodide (KI) and sodium thiosulfate ($Na_2S_2O_3$) on sintered glass filters.

scrubber material	empty filter [mg]	prepared filter [mg]	scrubber material [mg]	mean mass [mg]	standard deviation [mg]	RSD
KI	273.641	280.153	6.512	7.572	0.82	10.79
	290.606	298.390	7.784			
	265.780	271.744	5.964			
	286.763	295.010	8.247			
	295.676	303.946	8.270			
	277.061	284.889	7.828			
	288.786	296.881	8.095			
	300.870	309.356	8.486			
	267.930	274.642	6.712			
	296.263	304.081	7.818			
$Na_2S_2O_3$	268.717	277.795	9.078	9.535	0.86	9.02
	276.309	284.371	8.062			
	288.587	298.413	9.826			
	291.727	300.869	9.142			
	306.515	318.090	11.575			
	284.377	293.610	9.233			
	295.573	304.661	9.088			
	284.500	293.997	9.497			
	285.791	295.818	10.027			
	287.838	297.660	9.822			



	α-Pinene	Myrcene	Limonene	Linalool
k [x 10^{-17} cm^3 $molecule^{-1}$ s^{-1}]	9.6	47	22	41

Figure S3. Chemical structures of the investigated analytes and their and gas-phase rate constants k for the reaction with ozone (Bernard et al.. 2012; IUPAC. 2024).



40 **Figure S4. Mean recovery rates (± standard deviation) of α-Pinene, Myrcene, Limonene and Linalool depending on ozone concentration and aggregated across all humidity levels for (a) the load-and-flush approach and (b) the permeation approach. Grey bars represent unfiltered samples, red bars potassium iodide filters and blue bars sodium thiosulfate filters.**

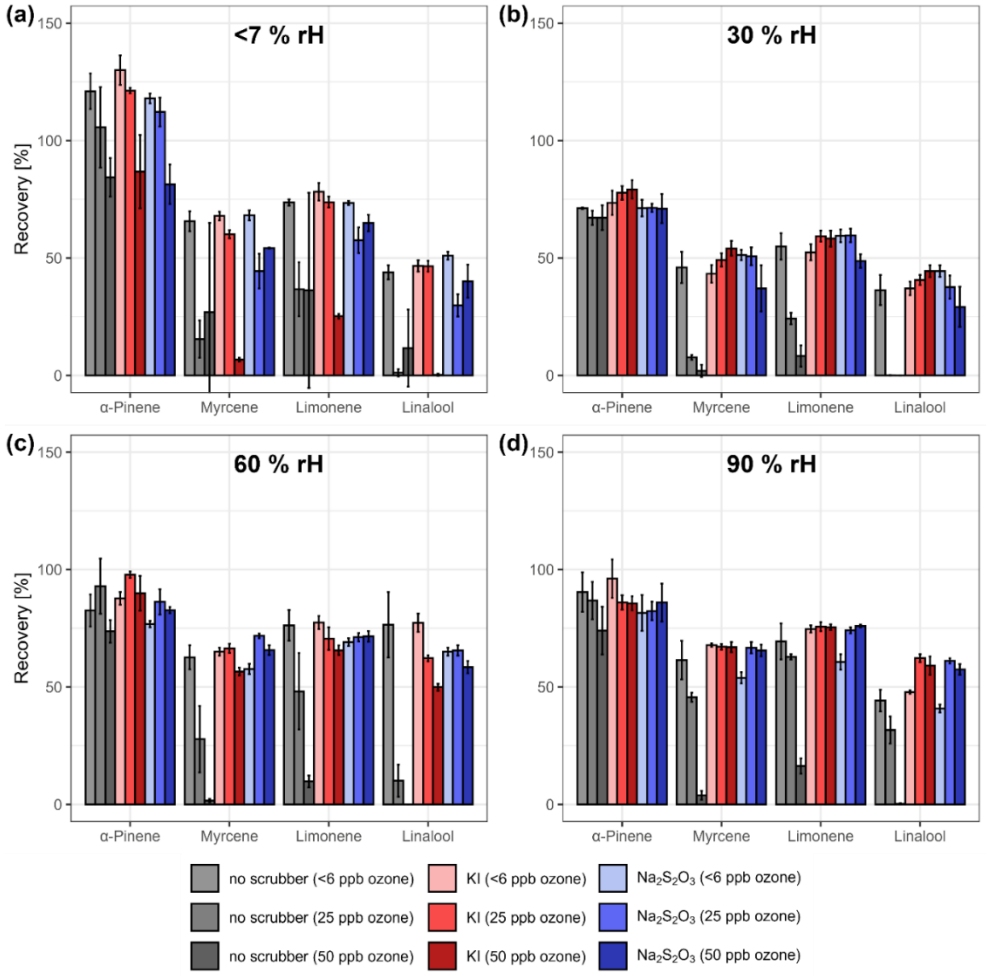


Figure S5. Mean recovery rates (± standard deviation) of α-Pinene, Myrcene, Limonene and Linalool for the permeation approach at relative humidity levels of (a) <7 %, (b) 30 %, (c) 60 % and (d) 90 %. Grey bars represent unfiltered samples, red bars potassium iodide filters and blue bars sodium thiosulfate filters.

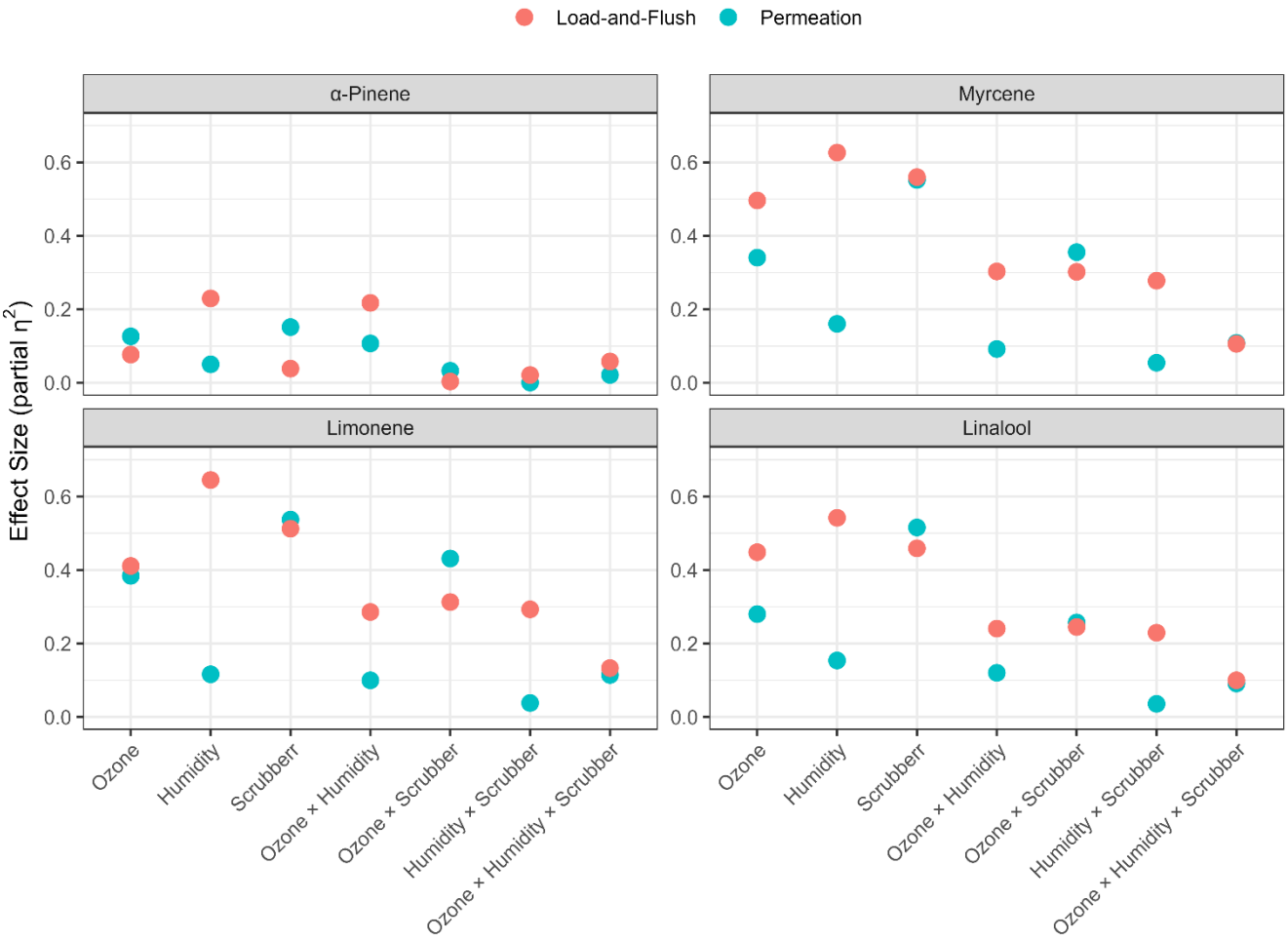


Figure S6. Comparison of effect sizes (partial η²) for the main factors (ozone, humidity, filter) and their interactions on the recovery rates of α-Pinene, Myrcene, Limonene, and Linalool for the load-and-flush approach (red) and the permeation method (turquoise). Higher effect size values indicate a stronger influence of the respective factor or interaction on the measured recovery rate.

References

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IUPAC: Task Group on Atmospheric Chemical Kinetic Data Evaluation. 2024.