toxics

MDPI

*Supplementary materials*

# Measurement and modeling of ship-related ultrafine particles and secondary organic aerosols in a Mediterranean port city

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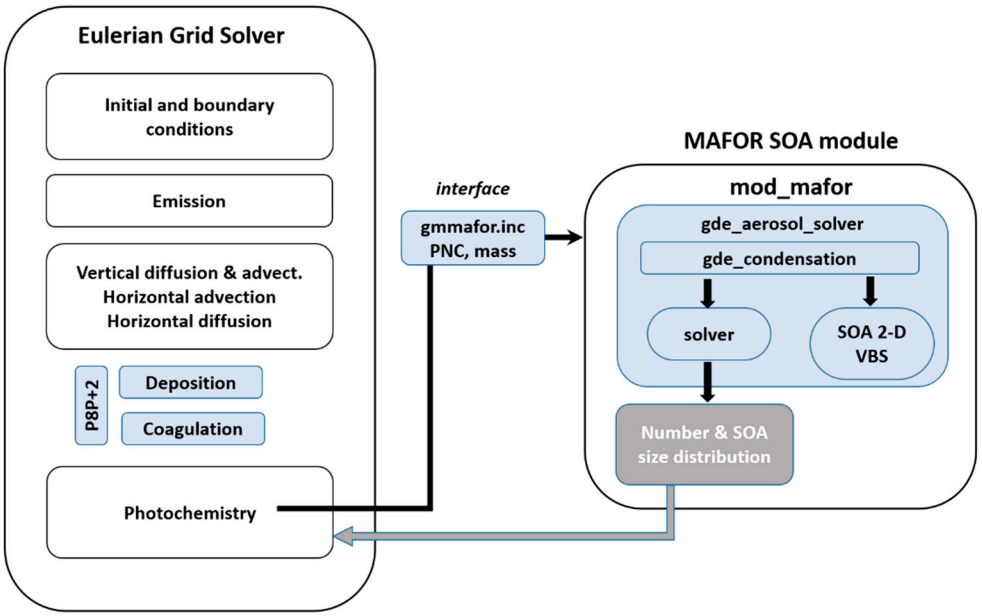



**Figure S1.** Block structure of the Eulerian grid solver with P8P+2 and the MAFOR-SOA module in EPISODE-CityChem v1.7. The new modules are in blue shaded blocks. The grid photochemistry calls the aerosol dynamics solver (gde_aerosol_solver) of the MAFOR-SOA module after the gas-phase chemistry is solved and updated concentrations of SOA precursor gases and sulfuric acid are available. The SOA mass concentrations are distributed over the 8 size bins below 1 µm diameter with a default distribution in the interface gmmafor.inc before the call to gde_aerosol_solver.

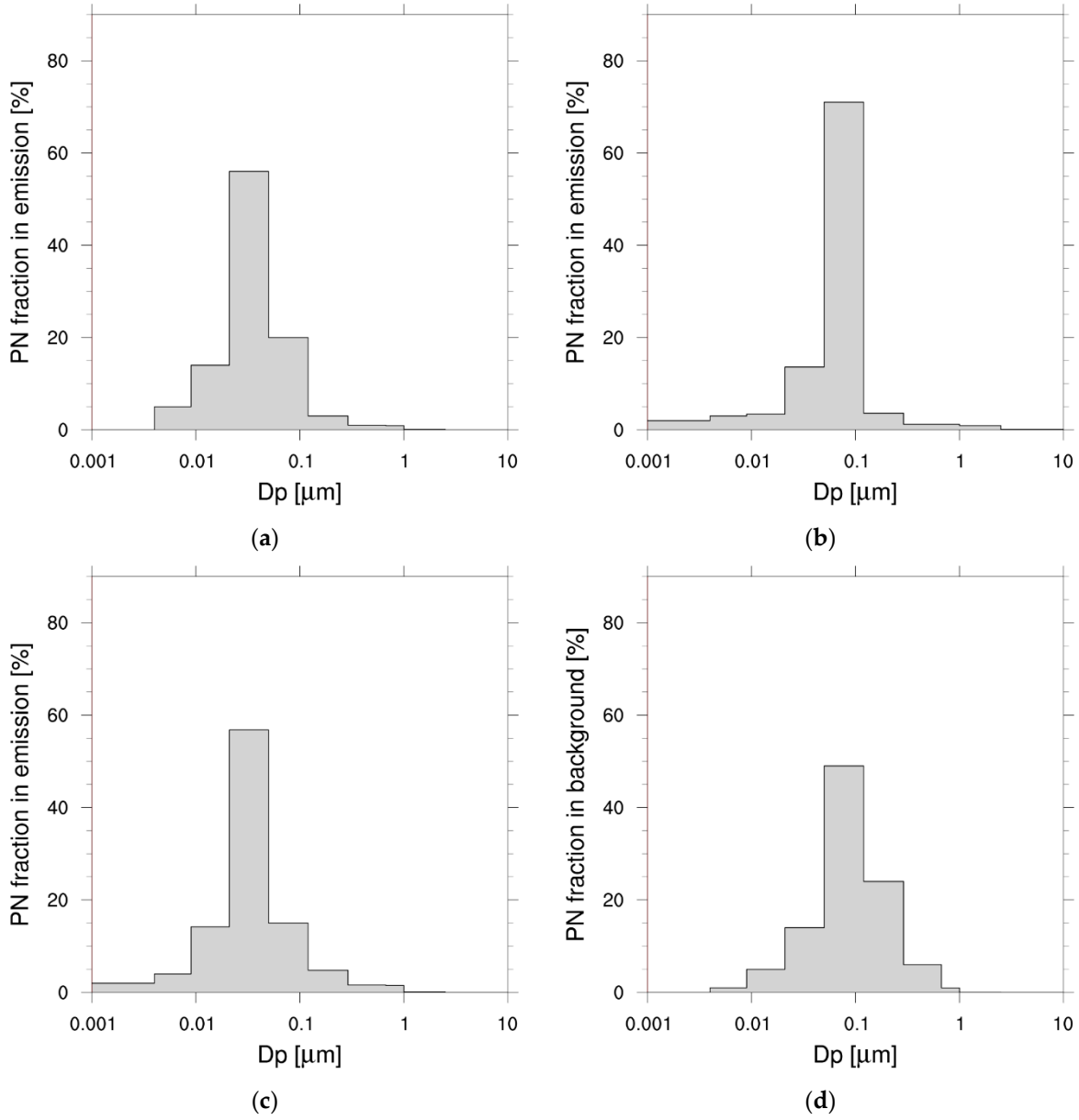
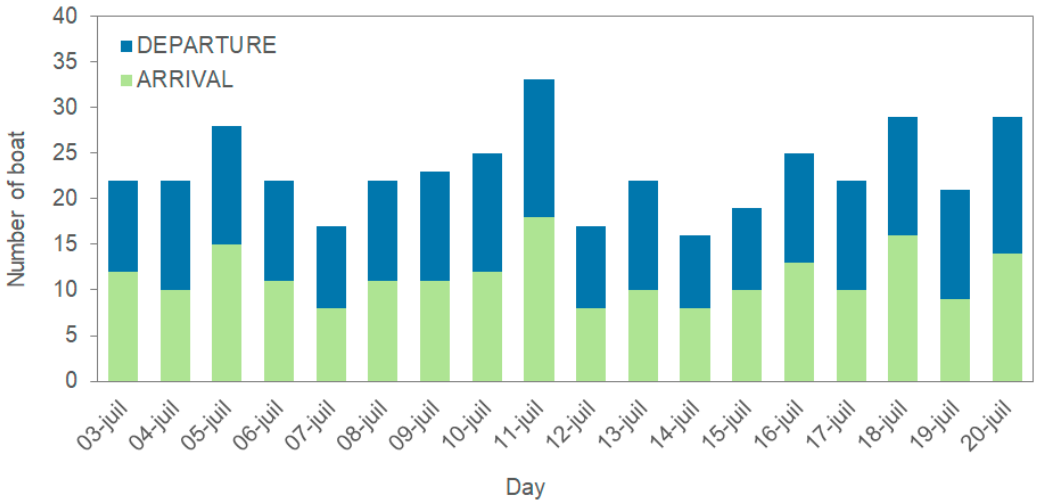
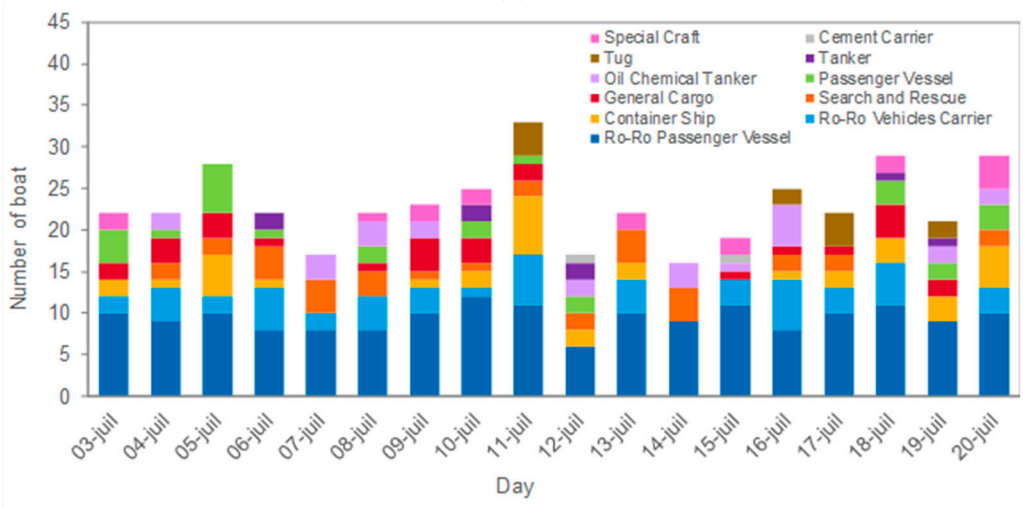


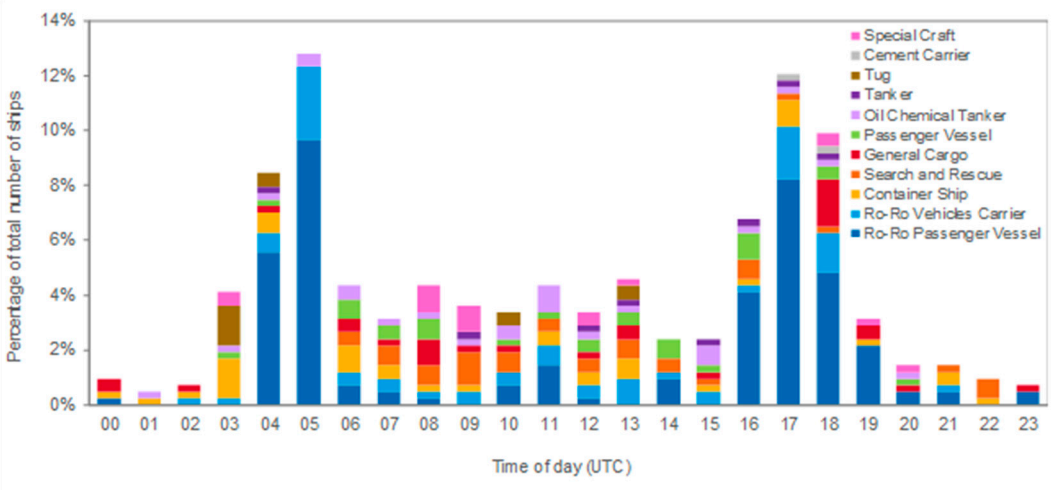

**Figure S2.** Normalized size fractions (in percentage) of particles in the standard number size distributions from (**a**) shipping emission; (**b**) residential heating emission; (**c**) road traffic emission; and (**d**) regional background. The x-axis presents dry particle diameter (in µm) on a logarithmic scale. The standard number size distributions were applied to translate total PN to the 10 size classes of the P8P+2 scheme in EPISODE-CityChem.




(**a**)



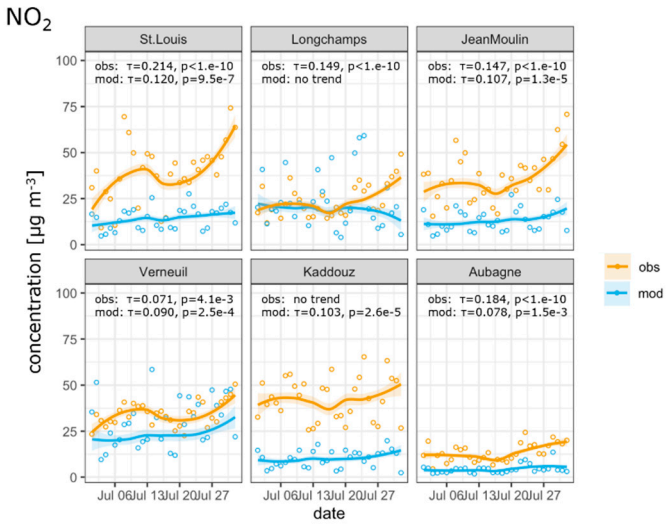

(**b**)



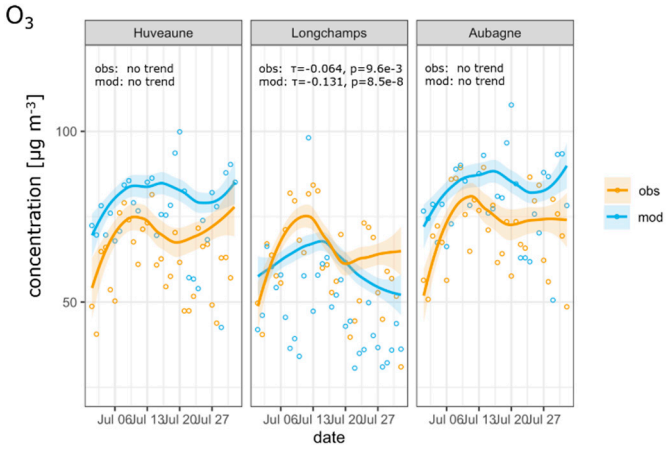

(**c**)

**Figure S3.** Ship traffic at the port of Marseille during the field campaign: (**a**) number of vessels with arrival and departure per day (03 to 20 July 2020); (**b**) number of arriving/departing vessels per day

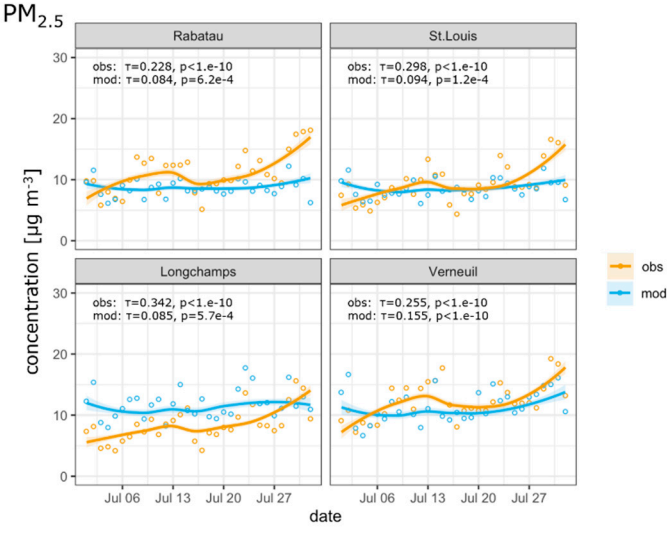
divided into ship categories (03 to 20 July 2020); and (**c**) daily profile of ship arrival/departure according to ship categories, given as percentage fraction of the total number of ships during the campaign.




(**a**)




(**b**)




(**c**)

**Figure S4.** Comparison of daily trends and mean concentrations of regulated air pollutants at monitoring stations in Marseille during July 2020: (**a**) observed and modeled $NO_2$; (**b**) observed and modeled $O_3$; and (**c**) observed and modeled $PM_{2.5}$. Trend lines for modeled and observed daily means are shown with standard deviations as a shadowed range. Mann–Kendall trend test parameters (Kendall's τ and two-sided p-value) are given in the plots if the null hypothesis was rejected with 95% confidence (otherwise "no trend"). Monitoring stations: Longchamps (LCP), Verneuil (VER), Rabatau (RAB), Saint Louis (STL), Jean Moulin (JMN), Kaddouz (KAD), Huveaune (HUV), and Aubagne (AUB).

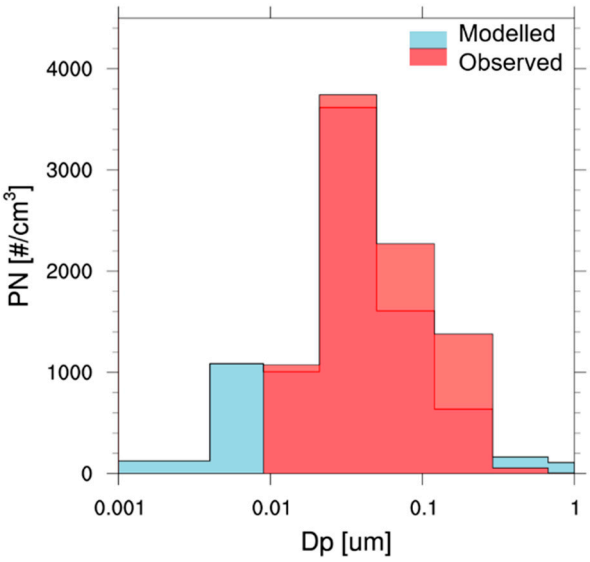
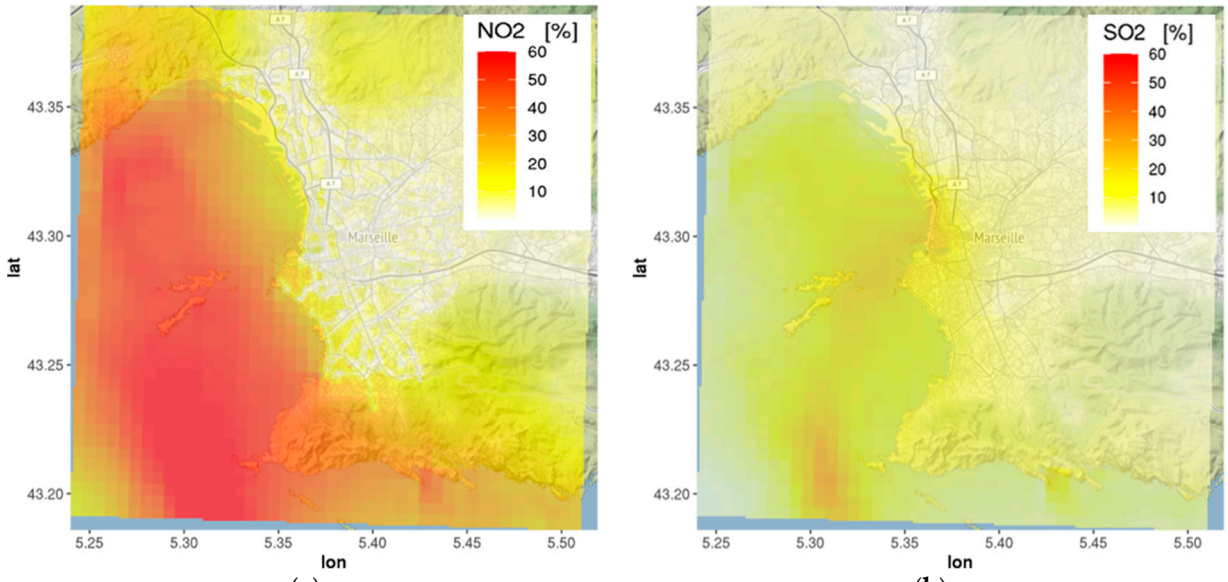



**Figure S5.** Comparison of the monthly mean (July 2020) size-resolved particle number concentrations (dN per size class in $cm^{-3}$) at aerosol supersite Marseille Longchamps (LCP) from model output of EPISODE-CityChem (light blue shaded bars) and measurements with SMPS (light red shaded bars). The x-axis presents dry particle diameter (in μm) on a logarithmic scale.



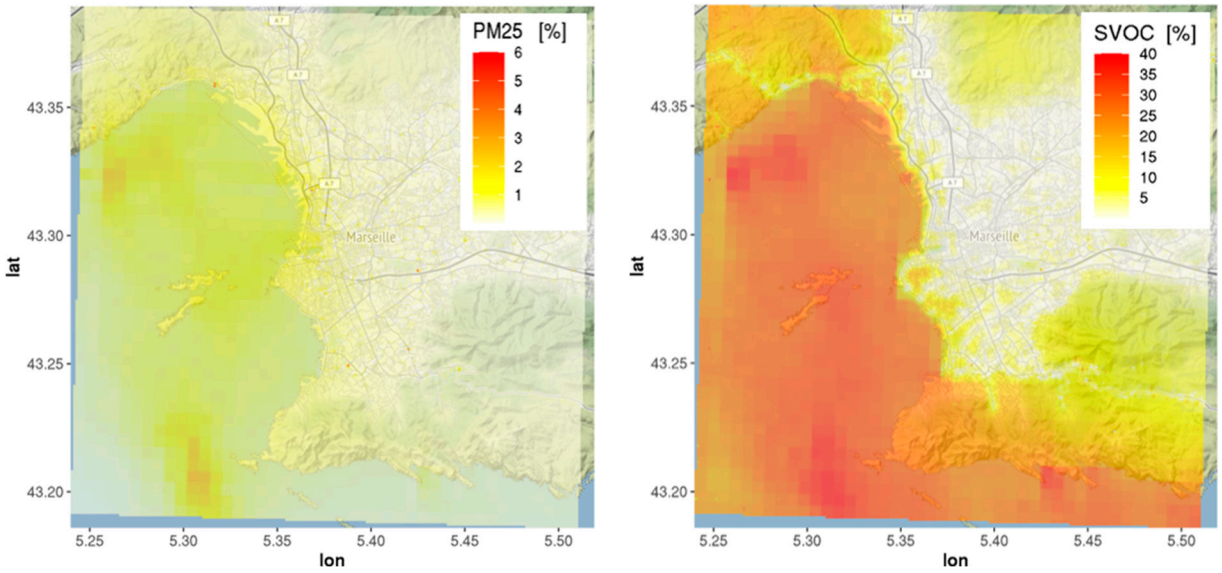



**Figure S6.** Maps of the relative potential ship impact in Marseille (monthly mean, July 2020): (**a**) potential ship impact (%) on $NO_2$; (**b**) potential ship impact (%) on $SO_2$; (**c**) potential ship impact (%) on $PM_{2.5}$; and (**d**) potential ship impact (%) on SVOC.

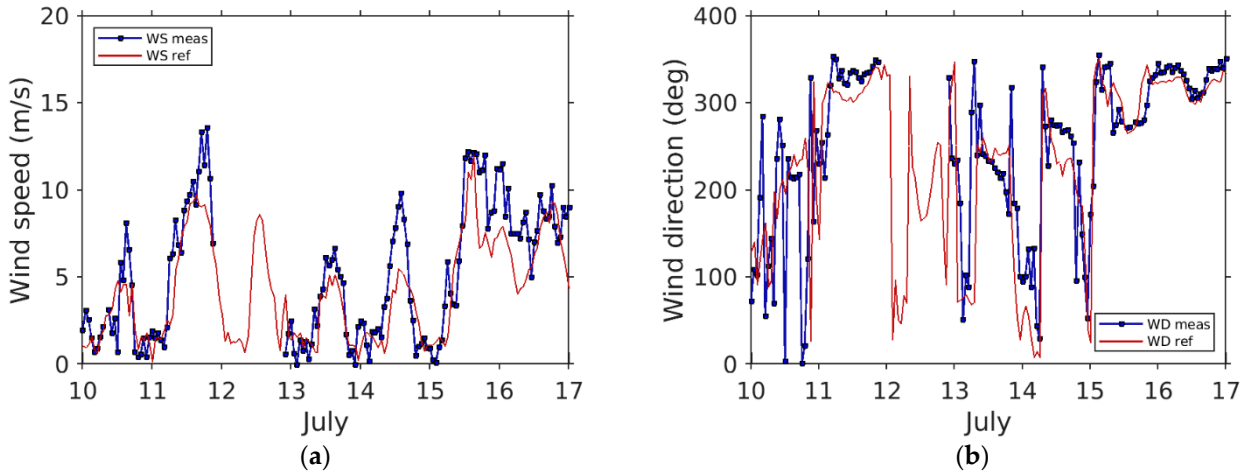



**Figure S7.** Comparison of predicted and measured wind data at met station VIS in the period 10-17 July 2020: (**a**) wind speed (m $s^{-1}$); (**b**) wind direction (°). Prediction is marked as red line and measurements are marked as blue line with squares.

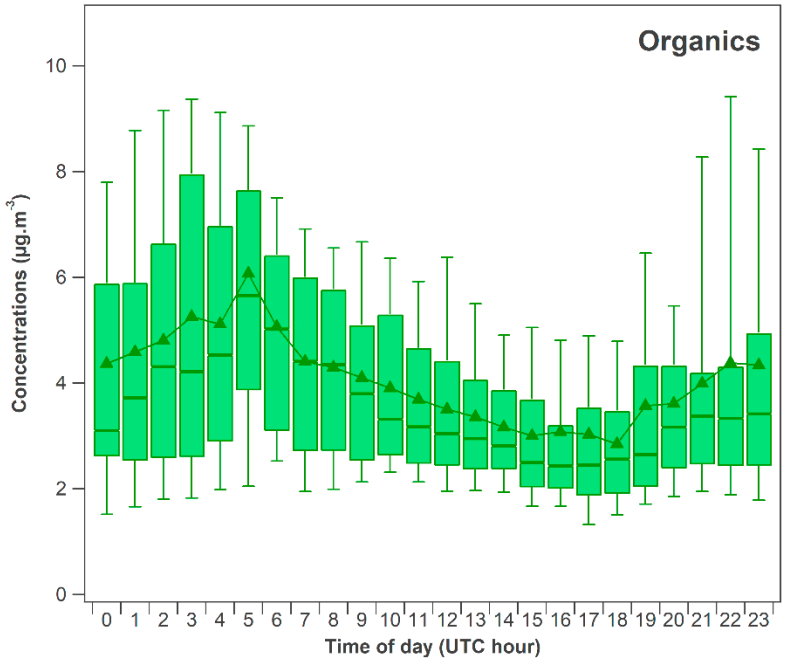



**Figure S8.** Diurnal variation (diel cycle) of organic matter in $PM_1$ measured with AMS on average of the field campaign at La Major in the period 03 to 20 July 2020. Measurement data of each hour is shown as boxes with whiskers (lower end of the box: 1st quartile, median (−), upper end of the box: 3rd quartile). Whiskers extend from the top and bottom of the box to the largest and smallest data elements, respectively. Triangles connected with a line indicate the mean value of each hour of the day.

**Table S1.** Particle number (PN) parameterization scheme P8P+2 in EPISODE-CityChem v1.7.

| PN size class | Lower diameter (nm) | Upper diameter (nm) | Mean diameter (nm) | Bandwidth (–) | Dry dep. velocity (cm $s^{-1}$) | Coagulation coefficient ($cm^3$ $s^{-1}$) |
|---|---|---|---|---|---|---|
| **PN1** | 1.5 | 4.0 | 2.0 | 1.3 | 1.000 | $6.30 \times 10^{-9}$ |
| **PN2** | 4.0 | 9.0 | 7.0 | 1.3 | 0.528 | $4.51 \times 10^{-9}$ |
| **PN3** | 9.0 | 21 | 17 | 1.5 | 0.355 | $9.76 \times 10^{-9}$ |
| **PN4** | 21 | 50 | 41 | 1.6 | 0.181 | $15.0 \times 10^{-9}$ |
| **PN5** | 50 | 120 | 98 | 1.6 | 0.068 | $5.40 \times 10^{-9}$ |
| **PN6** | 120 | 290 | 232 | 1.8 | 0.039 | $6.26 \times 10^{-9}$ |
| **PN7** | 290 | 670 | 551 | 1.8 | 0.031 | $4.27 \times 10^{-9}$ |
| **PN8** | 670 | 1000 | 850 | 1.8 | 0.023 | $2.28 \times 10^{-9}$ |
| **PN9** | 1000 | 2500 | 1500 | 2.0 | 0.110 | $0.87 \times 10^{-9}$ |
| **PN10** | 2500 | 10000 | 4000 | 2.0 | 0.200 | $0.80 \times 10^{-9}$ |

**Table S2.** SOA model components and their estimated saturation mass concentration and enthalpy of vaporization used in EPISODE-CityChem v1.7. Saturation concentration $C^0$ refers to a vapor over a pure, sub-cooled liquid at reference temperature.

| Surrogate name | Description | $C^0$ (µg $m^{-3}$) | $\Delta H_{vap}$ (kJ $mol^{-1}$) |
|---|---|---|---|
| ASOA | Semi-volatile anthropogenic SOA from oxidation of XYL, $C_3H_6$, and $nC_4H_{10}$ | 0.0100 | 77.0 |
| ALOA | Low-volatile anthropogenic SOA from oxidation of XYL, $C_3H_6$, and $nC_4H_{10}$ | 0.0001 | 77.0 |

| | | | |
|---|---|---|---|
| BSOA | Semi-volatile biogenic SOA from oxidation of isoprene, APIN, and LIM | 0.2100 | 138.0 |
| BLOA | Low-volatile biogenic SOA from oxidation of isoprene, APIN, and LIM | 0.0030 | 138.0 |
| PIOA | Intermediate volatility delayed primary organic matter | 0.1000 | 108.0 |
| PSOA | Semi-volatile delayed primary organic matter | 0.0006 | 135.0 |

**Table S3.** Split of the four VOC groups of the STEAM model to the VOC species (surrogates) of the EPISODE-CityChem model v1.7 given as mass fractions in the emissions.

| STEAM VOC group | PIOC | PSOC | XYL | MEK | HCHO | $CH_3CHO$ | C4H10 | C3H6 | C2 |
|---|---|---|---|---|---|---|---|---|---|
| VOC A | 0.914 | 0 | 0 | 0.011 | 0 | 0.021 | 0 | 0 | 0 |
| VOC B | 0 | 0.010 | 0.074 | 0 | 0.473 | 0.281 | 0.012 | 0.050 | 0.100 |
| VOC C | 0.433 | 0.421 | 0.146 | 0 | 0 | 0 | 0 | 0 | 0 |
| VOC D | 0 | 0.831 | 0.169 | 0 | 0 | 0 | 0 | 0 | 0 |

**Table S4.** Monitoring stations of the Air Quality Monitoring Network of Marseille and measured air pollutants.

| Station name | Abbrev. | Station type | Coordinates | Measured air pollutants |
|---|---|---|---|---|
| Marseille Longchamps | LCP | urban background | 43°18′18.94′′ N; 5°23′41.32′′ E | $NO_2$, NO, $O_3$, $PM_{2.5}$, $PM_{10}$, $SO_2$, BC |
| Marseille Place Verneuil | VER | traffic | 43°18′32.20′′ N; 5°22′04.66′′ E | $NO_2$, NO, $PM_{2.5}$, $PM_{10}$, $SO_2$ |
| Marseille Rabatau | RAB | traffic | 43°16′32.16′′ N; 5°23′47.04′′ E | $NO_2$, NO, $PM_{2.5}$, $PM_{10}$ |
| Marseille Saint Louis | STL | urban background | 43°20′53.29′′ N; 5°21′36.46′′ E | $NO_2$, NO, $PM_{2.5}$, $PM_{10}$ |
| Marseille Jean Moulin | JMN | traffic | 43°17′16.03′′ N; 5°24′02.04′′ E | $NO_2$, NO, $PM_{10}$ |
| Marseille L2 Kaddouz | KAD | suburban background | 43°18′30.46′′ N; 5°25′31.15′′ E | $NO_2$, NO, $PM_{10}$, BC |
| Vallee de l'Huveaune | HUV | industrial | 43°16′59.23′′ N; 5°30′41.60′′ E | Benzene, $O_3$ |
| Aubagne Les Passons | AUB | suburban background | 43°17′35.88′′ N; 5°34′28.05′′ E | $NO_2$, NO, $O_3$ |

**Table S5.** Main organic molecules detected by PTR-ToF-MS during the field campaign at La Major, in the port of Marseille. The corresponding model surrogate in EmChem09-HET is given if it exists.

| Exact mass (m/z) | Chemical formula | Assigned chemical compound [1] | Corresponding model surrogate [2] |
|---|---|---|---|
| 33.033 | $CH_4OH^+$ | Methanol | — |
| 43.017 | $C_2H_2OH^+$ | Acetic acid fragment | — |
| 43.054 | $C_3H_6H^+$ | Propene and HC fragments | C3H6 [3] |
| 45.033 | $C_2H_4OH$+ | Acetaldehyde | $CH_3CHO$ |
| 47.049 | $C_2H_6OH^+$ | Ethanol | — |
| 57.070 | $C_4H_8H^+$ | Butene | C3H6 [3] |

| | | | |
|---|---|---|---|
| 59.049 | $C_3H_6OH^+$ | Acetone | — |
| 61.028 | $C_2H_4O_2H^+$ | Acetic acid | — |
| 69.071 | $C_5H_8H^+$ | Isoprene | Isoprene |
| 71.085 | $C_5H_{10}H^+$ | Pentene | C3H6 [3] |
| 73.065 | $C_4H_8OH^+$ | Butanone or butanal | MEK [4] |
| 75.044 | $C_3H_6O_2H^+$ | Methyl acetate | — |
| 79.054 | $C_6H_6H^+$ | Benzene | — |
| 85.011 | $C_6H_{12}H^+$ | Hexene | C3H6 [3] |
| 89.059 | $C_4H_8O_2H^+$ | Ethyl acetate | — |
| 93.069 | $C_7H_7H^+$ | Toluene | XYL |
| 101.059 | $C_5H_8O_2H^+$ | Pentadione | — |
| 107.085 | $C_8H_{10}H^+$ | C8 Aromatics | PIOC |
| 121.101 | $C_9H_{12}H^+$ | C9 Aromatics | PIOC |
| 129.070 | $C_{10}H_{18}H^+$ | Naphthalene | PIOC |

[1] HC: unspecified hydrocarbon.

[2] A corresponding model surrogate compound is only given if a corresponding compound exists in the chemical reaction scheme EmChem09-HET of EPISODE-CityChem.

[3] C3H6: model surrogate for C3 alkenes and higher alkenes

[4] MEK: methyl ethyl ketone, $CH_3COC_2H_5$.