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Aerosol chemistry and vertical mixing in the planetary boundary layer: insights on the relevant role of nitrate from case studies in Milan (Italy)

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Observations of the aerosol vertical profile reveal the formation of elevated aerosol layers within and above the planetary boundary layer (PBL). Those layers may have chemical composition significantly different from that observed near the ground, and the knowledge about the role they play in the budget of the ground-level particulate matter is still incomplete. Here we investigate this aspect combining chemical and physical aerosol measurements with WRF/Chem model simulations. The observations were collected in the Milan urban area (Northern Italy) during summer of 2007 and winter of 2008. We find that an important player in shaping the upper aerosol layers is particulate nitrate, which may reach higher values in the upper PBL (up to 30% of the aerosol mass) than the lower. The nitrate formation process is predicted to be largely driven by the relative humidity vertical profile, that may trigger efficient aqueous nitrate formation when exceeding the ammonium nitrate deliquescence point. Secondary PM2.5 produced in the upper half of the PBL may contribute up to 7–8 μg m$-$3 (or 25%) to ground level concentrations on hourly basis. A large potential role is also found to be played by the residual aerosol layer above the PBL, which may occasionally contribute up to 10–12 μg m$-$3(or 40%) to hourly ground level PM2.5 concentrations during the morning.