



Investigating the vertical and spatial extent of radon-based classification of the atmospheric mixing state and impacts on seasonal urban air quality



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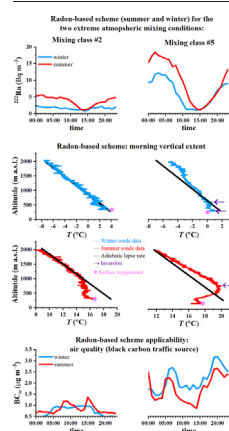
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HIGHLIGHTS

- Seasonal application of a radon-based stability classification in an urban basin
- Classification method addresses changes on diurnal and synoptic timescales.
- Classification scheme applies at large spatial and vertical extents.
- New insight gained to controls on urban pollution and times of public exposure.

GRAPHICAL ABSTRACT



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ABSTRACT

A recently-developed radon-based method for combined classification of both diurnal and synoptic timescale changes in the atmospheric mixing state is applied to 1-year of observations in Ljubljana (capital of Slovenia). Five diurnal-timescale mixing classes (#1 to #5) were defined for each season along with an additional mixing class (#6) in non-summer months, representative of synoptic-timescale changes of the atmospheric mixing state associated with “persistent temperature inversion” (PTI) events. Seasonal composite radiosonde profiles and mean sea level pressure charts within each mixing class are used to demonstrate the link between prevailing synoptic conditions and the local mixing state, which drives changes in urban air quality. Diurnal cycles of selected pollutants (BC, NO₂, CO, PM₁₀, SO₂ and O₃) exhibited substantial seasonality as a result of changing mixing conditions, source types and strengths. For the more well-mixed conditions (classes #2 to #3), surface wind speeds were 3 times higher than during class #6 (PTI) conditions, resulting in a 3-fold reduction of primary pollutant accumulation. Daily-mean PM₁₀ concentrations only exceeded EU and WHO guideline values in winter and autumn for two of the radon-defined mixing classes: (i) class #5 (strongly stable near-surface conditions associated with passing synoptic anti-cyclone systems), and (ii) class #6 (PTI conditions driven by regional subsidence in the presence of the “Siberian High”). Both mixing states were associated with low mean wind speeds ($\sim 0\text{--}0.7\text{ m s}^{-1}$) and strong thermal stratification, as indicated

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both by pseudo-vertical temperature gradients ($\Delta T/\Delta z$) and radiosonde profiles. Diurnal $\Delta T/\Delta z$ values indicated limited opportunity for convective mixing of pollutants from the basin atmosphere under these conditions. The demonstrated consistency in atmospheric mixing conditions (vertically and spatially) across the diurnal cycle within each of the defined mixing classes suggests the radon-based classification scheme used in conjunction with 3-D urban sensor networks could be well suited to evaluate mitigation schemes for urban pollution and urban climate.

1. Introduction

Air pollution is recognised to be one of the most significant health-related problems of modern times (Griffin, 2005; Highwood and Kinnersley, 2006; Pope and Dockery, 2006; Goudie, 2014; EEA, 2022). Outdoor air pollution exceedance events are not only driven by controllable factors such as emission sources and strengths; they can also arise through a complex interplay between numerous uncontrollable factors acting at local to regional scales (e.g., dilution, advection, venting, etc.) associated with the mixing state (stability) of the atmospheric boundary layer (ABL) (Chambers et al., 2019a, 2019b). Diurnal and synoptic timescale changes in prevailing meteorological conditions, along with the topographic setting, are the key factors influencing atmospheric mixing state, which in turn affects air quality variability on a range of temporal and spatial scales. The potential health impacts of changing urban air quality have led to many studies being conducted to investigate the relationship between atmospheric stability and air pollution variability on diurnal timescales (e.g., Triantafyllou, 2001; Klingner and Sähn, 2008; Vardoulakis and Kassomenos, 2008; Grundström et al., 2015; Jędruszkiewicz et al., 2017; Wang et al., 2019).

For European cities, particularly those in topographically complex settings, atmospherically-driven exceedance events of primary and secondary pollutants in non-summer months can either be isolated (i.e., occurring once, and for <24 h) or prolonged (repeating or intensifying, over days to weeks) (Segura et al., 2013; Chemel et al., 2016; Llargeron and Staquet, 2016; Łupikasza and Niedzwiedz, 2022; Novak et al., 2022; Martilli et al., 2022). While in each case the exceedance events are largely driven by the accumulation of local pollution within a shallow atmospheric inversion layer, the duration and severity of exceedances are closely linked to the prevailing synoptic (regional) meteorological conditions. Since contemporary regional chemical transport models are notorious for poor performance in stable atmospheric conditions (Chambers et al., 2019a), improving the understanding of such events and the atmospheric mixing states with which they are associated could assist with efforts to predict their occurrence, develop pollution mitigation strategies, or retrospectively gauge the health impacts of related exposure.

Among the variety of synoptic situations that may occur, transient cyclonic conditions generally lead to efficient dispersion or venting of pollutants from affected regions, while transient anti-cyclonic conditions (associated with clear skies, moderate subsidence and near-calm winds) can trap pollutants within shallow nocturnal inversions before dispersing them with strong convection the following day. Enduring cold-season anti-cyclonic systems, on the other hand, associated with much stronger subsidence, can inhibit or prevent daytime convective venting of pollution trapped near the surface for days on end. Such conditions in Europe have been referred to as persistent temperature inversion (PTI) events. PTI events can be particularly severe in regions of complex terrain. In Western Europe, and the Mediterranean Basin Region (MBR) in particular, Llargeron and Staquet (2016) reported nine wintertime PM₁₀ pollution events in Grenoble under PTI conditions that each exceeded EU air quality standards. Segura et al. (2013) investigated a severe pollution event in Valencia (Spain) that was attributed to PTI conditions, where BC levels steadily increased from 3.2 $\mu\text{g m}^{-3}$ to 4.9 $\mu\text{g m}^{-3}$ before the blocking anti-cyclone moved on. Anttila et al. (2016) reported an extreme winter PTI pollution event in Skopje valley (North Macedonia), during which the highest hourly PM₁₀ and NO₂ concentrations were 500 $\mu\text{g m}^{-3}$ and 440 $\mu\text{g m}^{-3}$, respectively. Kikaj et al. (2019c) investigated both isolated (transient anti-cyclonic) and persistent (enduring anti-cyclonic) events in Ljubljana,

Slovenia, in which PM₁₀ and NO₂ guideline values were exceeded. Similarly, Chambers and Podstawczyńska (2019) reported exceedances of guideline values for PM₁₀ and SO₂ in Zgierz, Poland, in non-summer months under both PTI and transient anti-cyclonic nocturnal conditions. Beyond Europe, similarly dangerous winter events (referred to as “cold pool events”) have been reported throughout central North America (Baasandorj et al., 2017; McCaffrey et al., 2019).

By contrast, in warmer months, MBR countries are particularly susceptible to exceedances of secondary organic aerosol (SOA) target values (e.g., O₃) due to the influence of frequent clear-sky conditions that favour photochemical production (EEA, 2021). In addition, the geographic location of MBR countries makes them a frequent receptor of long-range pollution transport from Africa (Kallos et al., 2006), across Europe from the North Atlantic Ocean or across Italy from the Mediterranean Sea (He et al., 2018), and even from North America (Lelieveld et al., 2002; Gerasopoulos et al., 2005). Long-range pollution transport events of both anthropogenic and natural origin are often felt in many countries of the MBR region (Salvador et al., 2014), such as Portugal (Russo et al., 2014; Conceição et al., 2018), Spain (Díaz et al., 2017), Italy (Gobbi et al., 2019), Slovenia (Beeston et al., 2011), Croatia (Čanić et al., 2009), and Greece (Kaskaoutis et al., 2019a, 2019b).

Clearly, for an urban region with substantial year-round anthropogenic emissions, it is a combination of the near-surface mixing state, prevailing synoptic setting, and surface energy budget that dictates both the intensity and duration of pollution exceedance events. Based purely on conventional ground-based meteorological approaches, however, there are both financial and logistical barriers to simultaneously characterising the near-surface mixing state as well as the state of the lowest several kilometres of the atmosphere strongly influenced by the prevailing synoptic conditions. While routine (rudimentary) monitoring stations are well-suited to stability classification techniques such as the Pasquill-Gifford (PG) schemes (Pasquill, 1961; Turner, 1964; Pasquill and Smith, 1983), rarely are they equipped to probe the deeper atmosphere (e.g., using radiosondes or atmospheric profilers). On the other hand, stations equipped to characterise atmospheric stability using the Richardson Number or similarity theory approaches, that may also be equipped with radiosondes or profilers, are very expensive to establish, maintain and operate. Furthermore, the PG schemes are known to perform poorly in regions of complex terrain (e.g., Chambers et al., 2015a; Wang et al., 2016), and none of the three conventional meteorological stability classification approaches mentioned above are capable of reliably distinguishing between stable conditions resulting from transient anti-cyclonic influences and those resulting from enduring anti-cyclonic influences (PTI events), despite large associated differences in air quality. This can result in misclassification (Kikaj et al., 2019a) or underestimating the severity of a pollution event (Chambers et al., 2015a, 2015b; Kahl and Chapman, 2018). PTI-like events responsible for increased health risks and damage to infrastructure have also proven challenging to predict with conventional modelling approaches (McCaffrey et al., 2019).

Near-surface radon (²²²Rn) measurements, however, have been shown to be a consistent indicator of changing stability in the ABL resulting from processes occurring on both diurnal and synoptic timescales. This capability is mainly attributable to radon's ubiquitous nature and unique combination of physical characteristics (Moses et al., 1960; Cohen et al., 1972; Allegrini et al., 1994; Perrino et al., 2001, 2008; Sesana et al., 2003; Galmarini, 2006; Avino and Manigrasso, 2008; Chambers et al., 2011, 2019b; Williams et al., 2013; Pitari et al., 2014; Kikaj et al., 2019a). In particular, while radon's 3.8-day half-life enables it to be used as an

approximately conservative tracer for diurnal mixing studies in the boundary layer, because this half-life is much longer than typical mixing timescales in the ABL, the half-life is sufficiently long for day-to-day radon accumulation to be detected under persistent inversion conditions (Kikaj et al., 2019a). Radon can be efficiently used as a tracer to determine the strength of primary emission fluxes of specific pollutants (e.g., black carbon (BC), Gregorič et al., 2020).

The present study demonstrates the efficacy of a recently developed radon-based method for the classification of diurnal and synoptic timescale changes in atmospheric stability over the entire seasonal cycle in Ljubljana (Slovenia). It also investigates how representative this classification scheme is vertically and spatially (beyond the local scale in which it was developed). Our results focus on the following specific tasks: (i) performing a seasonal characterization of the atmospheric mixing state of the Ljubljana Basin on diurnal and synoptic timescales, (ii) linking – for the first time – the near-surface radon-based stability classification approach (including PTI events) to the prevailing synoptic setting (using both composite radiosonde ascents and mean sea level pressure charts), (iii) discussing the implications of changing atmospheric mixing state on urban air pollutants (BC, NO₂, CO, PM₁₀, SO₂ and O₃); and (iv) relating extremes of air pollution to the World Health Organization (WHO) and the European Union (EU) guideline values in a statistically robust way that can be directly related to public exposure.

2. Methods

2.1. Site location and measurements

The Ljubljana Bežigrad (LjB) ground-based weather station is situated northwest of Ljubljana, the capital of Slovenia (299 m above sea level, a.s.l.) (Fig. 1). Ljubljana is an urban subalpine basin surrounded by peaks of the Julian, Kamnik-Savinja, and Dinaric Alps (Vrhovec, 1990; Hitznerberger et al., 2006). Very calm winds and frequent PTI events (33 % of the year) characterise the basin's atmosphere; more details about Ljubljana's climate are discussed in Kikaj et al. (2019a, 2019b).

The LjB weather station, operated by the National Meteorological Service at the Slovenian Environment Agency (ARSO), has a comprehensive suite of meteorological observations, including air pressure, wind speed, wind direction, air temperature and humidity. Air quality sensors sampling from 2 m above ground level (a.g.l.) are also operated by ARSO. These include particulate matter of median aerodynamic diameter $\leq 10 \mu\text{m}$ (PM₁₀), carbon monoxide (CO), nitrogen dioxide (NO₂), sulphur dioxide (SO₂), ozone (O₃). Besides the standard air quality measurements performed by ARSO, equivalent black carbon concentration (BC) was measured with Aethalometer model AE33 (Aerosol Magee Scientific, Aerosol d.o.o.). The aethalometer sampled air from 3 m a.g.l. and was equipped with PM_{2.5} size selective inlet. The AE33 measures the aerosol absorption coefficient at 7 wavelengths (range of 370–950 nm). Equivalent BC concentration is reported at 880 nm, by considering mass absorption cross-section of $7.77 \text{ m}^2 \text{ g}^{-1}$. Filter loading effect is corrected automatically by “dual-spot” methodology (Drinovec et al., 2015). To correct for multiple scattering within the filter matrix, a correction factor (C) of 1.39 was used. Black carbon is a primary aerosol, emitted directly from incomplete combustion of carbonaceous fuels. In the urban environment, the main sources are traffic (BC_{tr}) and biomass burning (BC_{bb}). Spectrally resolved optical absorption measurements differentiate between different BC sources. Their contribution can be estimated based on the specific Absorption Angstrom Exponent (AAE), which is characteristic for each BC source (Sanderadewi et al., 2008). More detailed descriptions of the instrumentation at this site are provided by Kikaj et al. (2019a, 2019b).

Atmospheric radon (²²²Rn) measurements have been part of the LjB weather station measurements since December 2016. Continuous hourly ²²²Rn measurements at this site are ongoing, using an AlphaGUARD PQ2000 PRO monitor (Bertin Instruments). Installation of the AlphaGUARD, as well as all related maintenance (including calibration, background, and data quality check) over the measurement period, were performed by the Jožef Stefan Institute (JSI). Further details regarding calibration, data quality assurance and quality control are provided by Kikaj et al. (2019b) and Murn and Stepišnik (2019). The instrument is mounted 1.5 m a.g.l., within a Stevenson Screen instrument shelter and operates

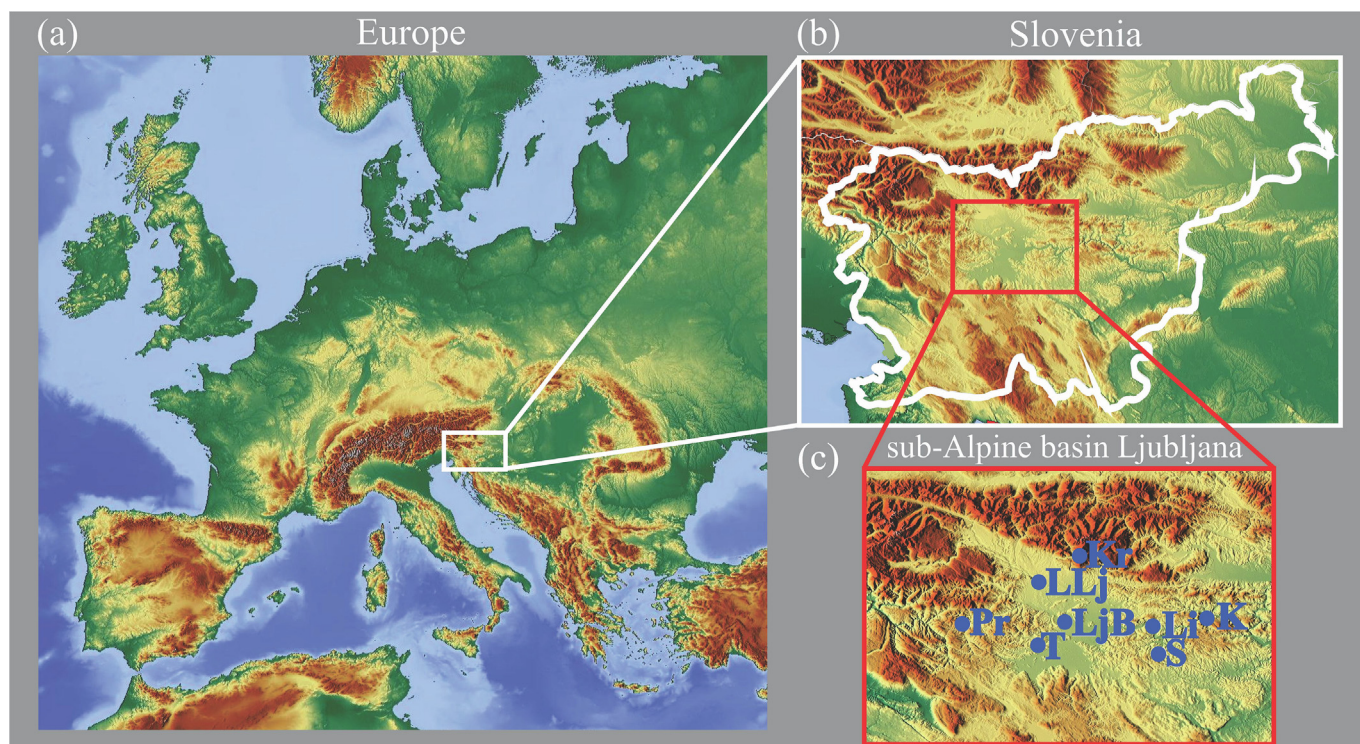


Fig. 1. a) Location of Slovenia within Europe, b) topographic map of Slovenia with the location of Ljubljana indicated, and c) topographic map of the Ljubljana Basin, with the locations of automatic weather stations indicated. Basemap source: © <https://maps-for-free.com/> and <https://www.openstreetmap.org/copyright>.

continuously in diffusion mode with a 1-h integration time. Over the measurement period reported here, only 3 % of radon concentrations fell at or below the AlphaGUARD's detection limit (2 Bq m^{-3}), all during daylight hours, indicating that this instrument is satisfactory for nocturnal mean mixing classification studies (Kikaj and Vaupotič, 2017; Kikaj et al., 2019a).

The meteorological parameters mentioned above, all observed within the lowest 10 m of the atmosphere, are only representative of local-scale processes. To better assess the vertical scale of applicability of the radon-based technique for classification of the atmospheric mixing state, upper atmospheric information was acquired. ARSO regularly performs daily upper-air observations over the basin by radiosonde (to $\sim 20 \text{ km a.g.l.}$). For the purposes of this investigation, however, we only focus on profile information from the lowest 2 km of the troposphere. Since radiosonde launches were only conducted daily between 4 and 6 a.m. local time, the full range of diurnal variability of the upper atmosphere is missing. Consequently, in an attempt to provide a more complete picture of the state of the lower troposphere, we calculated the pseudo-vertical temperature gradient based on air temperature observations from seven ground-based weather stations on the sidewalls of the topographic basin (range of elevations 268–1742 m; Fig. 1c). The principle of the pseudo-vertical temperature gradient ($\Delta T/\Delta z$) calculation is given in detail in Largeron and Staquet (2016) and for Ljubljana Basin, particularly in Kikaj et al. (2019a). It is important to note though that, since these vertical atmospheric observations are made using surface-based measurements from different elevations, their results will not be as consistent/accurate as those obtained from sonde ascents. These kind of measurements can only be used as a relative indicator of change.

Lastly, to better assess the horizontal scales of applicability of the radon-based classification scheme for the atmospheric mixing state, composite mean sea level pressure charts of the Ljubljana Basin region by season and stability category were calculated. Composite Mean Sea Level Pressure maps were generated using the NCEP/NCAR reanalysis sea level pressure (Kalnay et al., 1996). Sea level pressure, at 01:00 local time (LT) on each day (00:00 UTC), was combined by stability category and season and then averaged to produce the composite Mean Sea Level Pressure maps.

This study focuses on one year of observations (December 2017–November 2018). All reported times are local (LT is UTC + 1), and the Northern Hemisphere seasonal convention has been adopted (i.e., winter: December–February; spring: March–May; summer: June–August; autumn: September–November).

2.2. ^{222}Rn -based classification of the atmospheric mixing state

In studies where ^{222}Rn has been used to investigate the atmospheric mixing state, single-height radon measurements have mainly been used (Perrino et al., 2001; Omori et al., 2009; Pal et al., 2015; Pitari et al., 2015; Podstawczyńska and Chambers, 2018), since vertical radon gradient measurements are challenging and expensive to make accurately (Chambers et al., 2011; Williams et al., 2013). The most successful attempts to consistently link single-height radon measurements to the atmospheric mixing state in a consistent quantitative way are attributable to researchers that have found ways to account for fetch effects (e.g., Fontan et al., 1979; Fujinami and Esaka, 1987; Perrino et al., 2001; Sesana et al., 2006; Chambers et al., 2015a, 2019b; Kikaj et al., 2019a).

Table 1

Summary of the 24-h radon-based atmospheric mixing classes (#1 to #5 diurnal, #6 synoptic) assigned for one year of measurements in the Ljubljana Basin, and duration of conditions (%) for each mixing class in each of the four seasons.

24-h mixing class	Night-time mixing conditions	Daytime mixing conditions	Winter %	Spring %	Summer %	Autumn %
#1 (excluded)	Mixed fetch	Mixed fetch	7	12	11	8
#2	Near-neutral (Deepest nocturnal ABL)	Near-neutral (Shallowest daytime ABL)	15	27	24	12
#3	Weakly stable	Weakly unstable	19	20	26	22
#4	Moderately stable	Moderately unstable	15	22	22	23
#5	Strongly stable (Shallowest nocturnal ABL)	Strongly unstable (Deepest daytime ABL)	14	19	17	15
#6	Persistent temperature inversion (Shallow nocturnal ABL)	Persistent temperature inversion (Shallow daytime ABL)	30	NA	NA	20

Considering that the mixing state of the Ljubljana Basin ABL changes on diurnal, synoptic and seasonal scales, we adopted the synoptic and diurnal radon-based classification scheme described in detail by Chambers and Podstawczyńska (2019) and Kikaj et al. (2019a, 2019c) and applied it seasonally at this site for the first time. Briefly, diurnal radon-based stability classification ($^{222}\text{Rn}_{\text{DS}}$) involves isolating mixing-related (diurnal) changes in observed radon concentrations by estimating and removing air mass fetch effects. Then, the mean “diurnal” radon concentration is calculated each night within a defined 10-h nocturnal window, and for each season, threshold values for nocturnal mean radon are assigned that represent different nocturnal mixing states. Corresponding mixing states for each 24-h period are then inferred from the observed nocturnal conditions based on an assumption of short-term atmospheric persistence (e.g., see Table 1 in Chambers et al., 2019a). Since the nocturnal mixing state is measured and the daytime conditions are inferred, there is a large uncertainty associated with the daytime classification, and mid-afternoon “edge effects” (near the boundaries of each 24-h period) can sometimes be seen.

In this study, five diurnal mixing classes are assigned each season (see Table 1) for the year of measurements. Table 1 summarises the duration of conditions (%) for each mixing class in each of the four seasons. The mixed-fetch conditions (class #1) constituted the lowest number of observations (7–12 %) in all seasons and represent periods of pronounced synoptic non-stationarity (Podstawczyńska and Chambers, 2018; Kikaj et al., 2019c). These have been excluded from further analysis and discussion. Mixing classes #2 to #5, for which $^{222}\text{Rn}_{\text{DS}}$ is the best suited (Chambers et al., 2019a), constitute ~ 90 % and ~ 70 % in summer/spring and autumn/winter, respectively, of all observations.

The radon-based synoptic stability class ($^{222}\text{Rn}_{\text{SS}}$) (specifically for PTI events) involves separating synoptic timescale variability in radon concentration from contributions occurring at larger timescales. The synoptic timescale contributions to radon variability are then compared to the typical diurnal variability. When synoptic variability exceeds the typical magnitude of diurnal variability for more than two consecutive days, a PTI event is considered to have occurred. The $^{222}\text{Rn}_{\text{SS}}$ detected no PTI events in spring or summer, while PTI events were experienced in winter and autumn 30 % and 20 % of the time, respectively.

To account for seasonality in the regional radon flux, $^{222}\text{Rn}_{\text{DS}}$ and $^{222}\text{Rn}_{\text{SS}}$ methods need to be derived separately for each season. Consequently, the derived mixing categories are “relative” within each season (ranging from the most well-mixed to the most strongly stable nocturnal conditions that occurred in that particular season).

3. Results and discussion

3.1. Variability of radon concentrations within radon-based mixing classes

Diurnal composite plots of the mixing-related radon concentrations (i.e., fetch effects removed) for five of the six designated mixing classes in each season are illustrated in Fig. 2. In general, relatively low nocturnal accumulation of radon was noted for class #2 days, while the most pronounced daily radon variation was observed in classes #4 and #5.

For all mixing classes, the shape and amplitude of the diurnal radon cycles change with the season. These differences between mixing classes represent a combination of seasonal changes in the local radon emission and

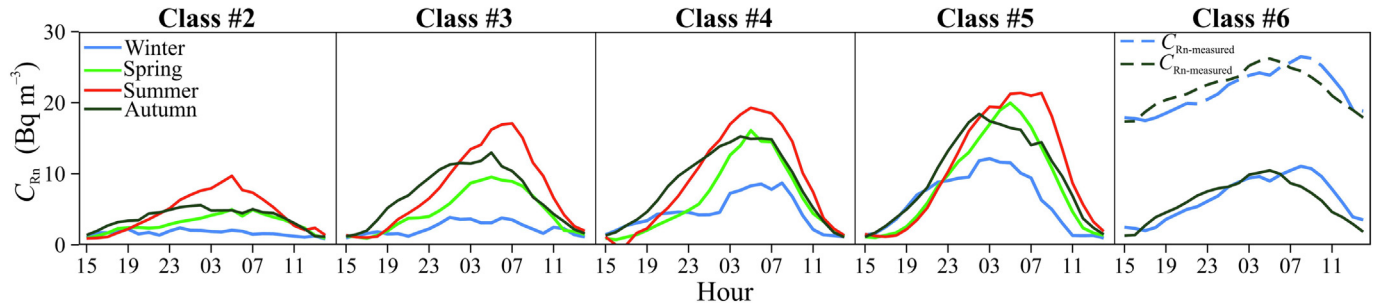


Fig. 2. Diurnal composite plots of mixing-related radon concentration by season and radon-based atmospheric mixing classes.

seasonal differences in the distributions of mechanical and thermodynamic contributions to the mixing (e.g., see Fig. 4). For each season, mixing class #5 days are associated with the least precipitation (i.e., the most consistent soil moisture conditions and therefore radon flux) and the most consistent synoptic meteorological conditions. Consequently, the shape of the diurnal radon cycle on class #5 days is representative of the nocturnal accumulation of an unreactive primary pollutant with well-distributed, temporally consistent near-surface sources, acted upon by a combination of the prevailing thermodynamic and mechanical stability conditions constraining the atmospheric mixing depth.

Diurnal radon concentrations had the largest amplitude for class #5 conditions ($\sim 24 \text{ Bq m}^{-3}$ in summer, $\sim 12 \text{ Bq m}^{-3}$ in winter). A similar seasonal trend of diurnal radon variability within radon-based mixing classes was found in Bern valley, Switzerland (Williams et al., 2016) and Ciosny, Poland (Chambers et al., 2016). In both studies, low winter radon values were attributable to a combination of significantly reduced winter radon exhalation rates due to the snow cover, high soil moisture or partially frozen surfaces, and a reduced diurnal change in mixing depth (shallower during the day and deeper at night). The same conclusion can be drawn for the Ljubljana observations (Fig. 2). Based on the European radon flux map (Karstens et al., 2015), which includes modelled soil moisture effects, the radon exhalation rate in Ljubljana increases by a factor of 2 from winter to summer. Seasonal changes of thermodynamic stability (discussed in Section 3.2) are also expected to influence the nocturnal accumulation of radon between seasons. Certainly, a combination of these factors is well reflected in the composite plot of class #6 in Fig. 2. Under PTI conditions, an almost identical diurnal trend and peak average between autumn and winter radon concentration is observed. This fact points to the substantially reduced radon exhalation and intense thermodynamic stability in winter and vice versa in autumn (higher radon exhalation and weaker thermodynamic stability). However, it should be noted that during the synoptic time-scale PTI conditions, a secondary near-surface inversion layer (some 10s of meters thick) often formed within the overlying PTI inversion. The

comparatively low diurnal amplitude of the mixing component of radon for class #6 conditions shown in Fig. 2 reflects the overnight accumulation of radon from a reduced wintertime source within this surface inversion. The higher afternoon “measured” radon concentrations compared with “mixing component” values shown in this figure is a result of synoptic time-scale accumulation of radon within the deeper PTI inversion.

3.2. Radon-based atmospheric mixing classes: scales of applicability and pollution seasonality

The synoptic and diurnal radon-based atmospheric mixing classifications defined and used here are based on single-point, near-surface observations. While the radon-based classification technique is simple to implement, individual radon monitors can be expensive, so the economic viability of employing this technique more broadly in urban air quality or urban climate studies depends upon the vertical and spatial extent over which the method is able to meaningfully group similar dominant atmospheric conditions. In the following sections we analyse radiosonde profiles and mean sea level synoptic pressure charts by season and stability category to investigate this issue before finally investigating air quality seasonally.

3.2.1. Vertical atmospheric structure within radon-based mixing categories

To investigate whether the vertical atmospheric structure over Ljubljana Basin was broadly consistent within different radon-based mixing classes, the morning (near dawn) vertical thermodynamic and wind profiles from radiosonde launches were grouped each season according to the radon-based mixing classes (e.g., winter in Fig. 3). Next, to better capture the diurnal ABL variability for whole days within each mixing category, diurnal composites of the pseudo-vertical temperature gradient ($\Delta T/\Delta z$) and near-surface wind speed were grouped for each season (Fig. 4a). For the sake of brevity, the discussion in this sub-section focuses only on three strongly contrasting mixing classes (#2, #5 and #6) in only two seasons (winter and summer) (Figs. 3 and 5). However, the reader may find

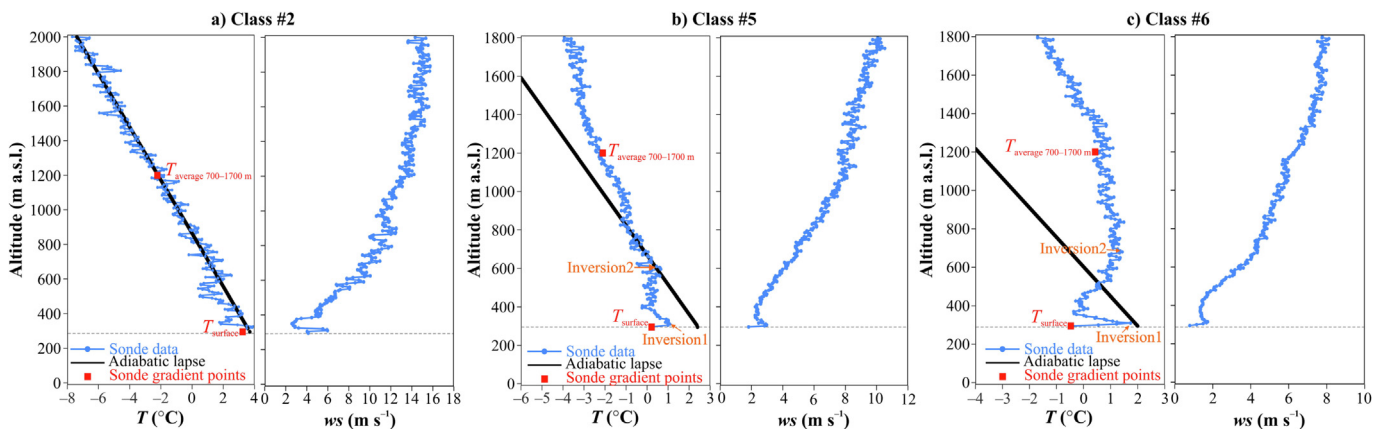


Fig. 3. Morning vertical profile of air temperature and wind speed within three radon-based mixing classes in the winter season a) class #2 (near-neutral), b) class #5 (mostly stable), c) class #6 (persistent temperature inversion).

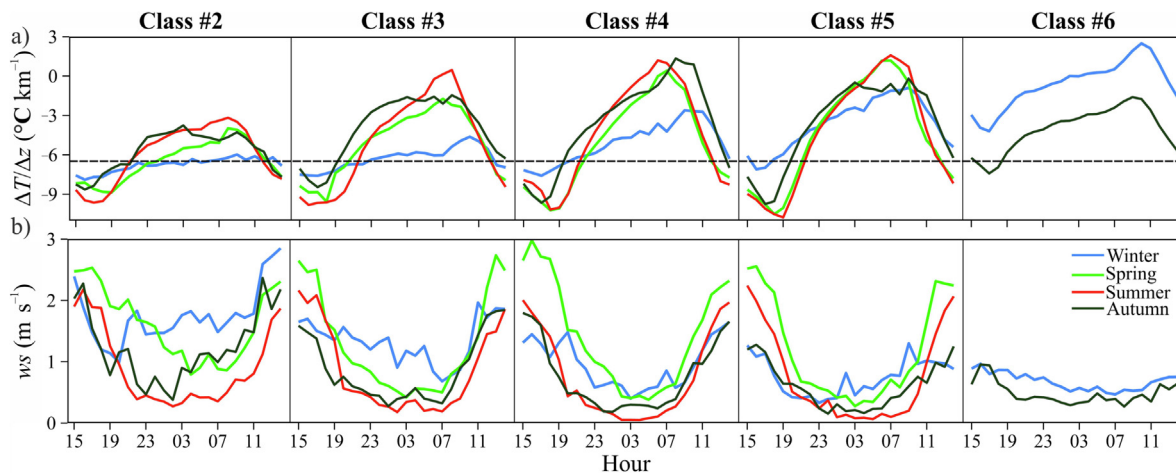


Fig. 4. Diurnal composite plots of a) pseudo-vertical air temperature gradient, and b) wind speed by season and radon-based atmospheric mixing classes.

composite sonde profiles for spring and autumn from radon mixing classes #2, #5 and #6 in the supplementary material (Figs. S1 and S2). Note that no PTI events occurred in summer or spring.

Near-surface wind speed and derived $\Delta T/\Delta z$ are strongly linked with changes in atmospheric mixing state (e.g., Ivey et al. (2019) and references therein). Systematic changes in the diurnal cycles of pseudo $\Delta T/\Delta z$ and local wind speed were noted across all six radon-derived mixing classes and all four seasons (e.g., Fig. 4). Vertical profiles of wind speed and temperature also changed systematically across the radon-derived mixing classes (Figs. 3 and 5). For reference, the adiabatic lapse rate of the standard atmosphere ($-6.5^\circ\text{C km}^{-1}$) has been superimposed on the diurnal cycles of $\Delta T/\Delta z$ (Fig. 4a) and the sonde temperature profiles (Figs. 3 and 5). Temperature gradients more negative than the adiabatic lapse rate (i.e., super-adiabatic lapse rates) are indicative of an unstable basin atmosphere, whereas gradients less negative than the adiabatic lapse rate (sub adiabatic) are indicative of an atmosphere that is stable or tending toward stability.

In general, near-neutral (class #2) periods experience the highest, most consistent mechanical atmospheric mixing, with daily average near surface wind speeds $\geq 1\text{ m s}^{-1}$ (Fig. 4b). Wind profiles (Figs. 3a and 5a) indicated

the presence of cyclonic conditions, with a wind speed maximum ($\sim 14\text{ m s}^{-1}$ in winter and $\sim 7\text{ m s}^{-1}$ in summer) at around 2000 m a.s.l. During these conditions (frequently cloudy or overcast), it is expected that basin air is mixed primarily by mechanical turbulence and that there would be relatively little convective heating by the surface (i.e., $\Delta T/\Delta z \geq -6.5^\circ\text{C km}^{-1}$). In winter, pseudo-vertical temperature gradient values were the lowest and quite consistent across the diurnal cycle, with a tendency to be slightly unstable ($\Delta T/\Delta z \sim -8^\circ\text{C km}^{-1}$) for about six hours near the middle of the day (Fig. 4a). For the rest of the time, $\Delta T/\Delta z$ was almost perfectly adiabatic in its behaviour. Similarly, morning vertical air temperature profiles for class #2 days had a lapse rate of $-6.1^\circ\text{C km}^{-1}$ (Fig. 3a), which was very close to the corresponding early morning winter pseudo $\Delta T/\Delta z$ value (04:00–06:00 LT; Fig. 4a). Around mid-afternoon in summer, class #2 (well-mixed) conditions had the most negative pseudo $\Delta T/\Delta z$ values, indicating that the basin atmosphere tended to be unstable. However, well mixed summer nights tended toward stability with sub adiabatic morning vertical profiles (Fig. 5a) and pseudo $\Delta T/\Delta z$ values (Fig. 4a).

The morning sonde-derived lapse rates over the depth of the basin atmosphere on stable nights (classes #3 to #5) in winter were sub-adiabatic (e.g., $-2.6^\circ\text{C km}^{-1}$), indicating that the basin atmosphere as a

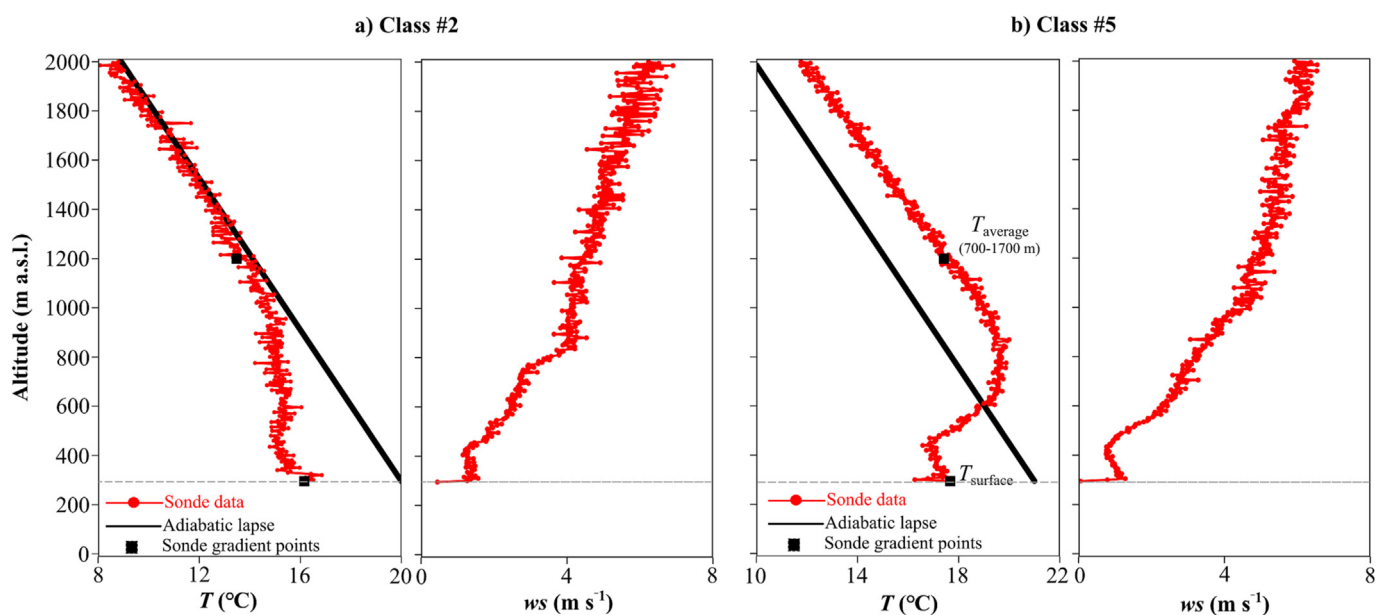


Fig. 5. Morning vertical profile of air temperature and wind speed within two radon-based mixing classes in the summer season a) class #2 (near-neutral), and b) class #5 (mostly stable).

whole was tending toward stability, but a shallow stable surface layer was also visible (Fig. 3b). Similarly, both vertical wind speed profiles and wind speeds from the near surface weather station indicate a very shallow stable layer right near the ground (Figs. 3b and 4b). The wind speed profile under class #5 conditions (Fig. 3b) indicated wind speeds below 5 m s^{-1} to a height of 700 m a.s.l., with stronger winds aloft ($\sim 10 \text{ m s}^{-1}$ at 1800 m a.s.l.). The winter pseudo $\Delta T/\Delta z$ exhibited slightly convective conditions (Fig. 4a) during the daytime $\sim 5 \text{ h}$ for class #3 and only two hours for class #5. In summer, mixing categories #3 to #5 had many more hours of convective instability during the day to mix pollution out of the basin, however, the nights were very stable (maximum $\Delta T/\Delta z \sim +2 \text{ }^{\circ}\text{C km}^{-1}$). The temperature inversions on class #3 to #5 summer nights vanished abruptly each morning shortly after the onset of convective mixing ($\Delta T/\Delta z \leq -6.5 \text{ }^{\circ}\text{C km}^{-1}$) as a result of intense sunlight on basin surfaces, promoting the ventilation of pollution from the basin despite low gradient wind speeds. In spring and summer, mixing classes #3 to #5 exhibited the highest $\Delta T/\Delta z$ diurnal cycle amplitudes (12 K km^{-1} ; Fig. 4a) due to the longer duration and strongest intensity of solar radiation and clear sky conditions. In winter and autumn, the diurnal amplitude of $\Delta T/\Delta z$ decreased (6 K km^{-1} ; Fig. 4a) as a consequence of longer nights, wet/frozen surface, high albedo (snow cover), low solar radiation and more frequent cloud cover. In addition to the seasonal and diurnal changes in the basin's diurnal ABL mixing described above, the combined radon-based mixing scheme also detected periods associated with mixing changes at synoptic timescales (so-called PTI events) in winter and autumn (Figs. 3c and 4, class #6). As discussed by Kikaj et al. (2019a, 2019c), PTI periods are controlled by a high-pressure ridge (reaching far east of Ljubljana) that leads to the development of a basin capping inversion layer. These conditions usually persist for a few days to a week. At Ljubljana, the winter snow cover led to an intensification and longer duration of PTI conditions (Table 1; 30 % of winter observations), consistent with the findings of Whiteman et al. (2004). In both autumn (see Fig. S1) and winter, however, the diurnal trends of $\Delta T/\Delta z$ were similar, although winter peak average $\Delta T/\Delta z$ was a factor of 2 higher than in autumn (Fig. 4a, class #6), emphasising that the strongest and most persistent thermodynamic stability conditions occurred on winter PTI days. Based on the vertical air temperature profile in Fig. 3c the sonde-derived lapse rate over the depth of the basin (300 to 1200 m) under class #6 conditions was $+1 \text{ }^{\circ}\text{C km}^{-1}$, indicative of overall stability. Within the basin atmosphere, however, more structure is evident. On average, a strong surface inversion (at $\sim 20 \text{ m}$) is evident, with a second inversion around 700 m a.s.l., and from this point up to around 1400 m a.s.l. the atmosphere is clearly tending toward stability (Fig. 3c). The elevated inversions, which effectively decouple much of the basin atmosphere from the free troposphere above, are a result of subsidence and low gradient winds associated with anti-cyclonic systems. Once decoupled from the free troposphere, the lower atmosphere of the basin is free to develop a local dynamic of its own (Largerou and Staquet, 2016), including a thermal basin wind system involving katabatic winds from the NE-E (not shown). Winds of class #6 events within the northeast-east-oriented Ljubljana Basin were almost calm (Figs. 4b and 3c).

Our comparison of radiosonde temperature profiles with the pseudo-vertical temperature gradients showed that the pseudo-vertical temperature gradient method was a good proxy at our site for the state of the basin atmosphere on winter mornings. If more frequent sonde releases were available, it would be good to evaluate the $\Delta T/\Delta z$ observations over more of the diurnal cycle since SO_2 results reported in Section 3.2.3 suggest that the $\Delta T/\Delta z$ results may not be as reliable (in an absolute sense) over the whole diurnal cycle.

The main advantage of the pseudo-vertical temperature gradient method over radiosondes is that measurements can be made easily, economically and continuously, 24-h a day, while radiosondes are usually only launched between 1 and 4 times per day, depending on the site. However, since $\Delta T/\Delta z$ observations are based on surface temperature from different elevations, rather than from different heights above ground, their results should be interpreted with caution. Most importantly, atmospheric mixing classification based on single-height, near-surface radon measurements alone (i.e., independent of all meteorological measurements) can be successfully used to form self-consistent groups of both near-surface and vertical profile atmospheric characteristics throughout the ABL and into the lower troposphere.

3.2.2. Horizontal atmospheric structure within radon-based mixing categories

To investigate whether the horizontal atmospheric structure over Ljubljana Basin was broadly consistent within different radon-based mixing classes, the 01:00 LT mean sea level pressure (MSLP) charts (centred on Ljubljana Basin) were grouped each season according to the radon-based scheme. As with the previous section, for the sake of brevity, the discussion here will focus only on mixing classes #2, #5 and #6 (when present) for the winter and summer seasons. Other results are presented in the supplementary material (Figs. S3 and S4).

In winter, class #2 events were characterised by a cyclonic system situated slightly southwest of Ljubljana Basin (Fig. 6a) such that the strong wind speeds aloft reported in Section 3.2.1 for these events were typically from the southeast. For winter class #5 events (Fig. 6b), the composite synoptic situation shows Ljubljana Basin in a region of wide isobaric spacing (very light winds), with an anti-cyclone approaching from the southwest over North Africa. Winter class #6 events (Fig. 6c) show Ljubljana Basin much nearer the middle of an anti-cyclonic system, under stronger subsidence conditions (see also Fig. 3c). Winds at these times would likely be light and from the north or northeast. The ridge of high pressure extends eastward toward Siberia.

In summer, composite MSLP charts associated with the well-mixed class #2 events (Fig. 7a) indicate that these conditions most commonly eventuate after the passage of a cyclonic system, with the strong winds predominantly coming to the site from the north to northeast. By contrast, composite MSLP charts associated with category #5 events in summer (Fig. 7b) show Ljubljana Basin near the centre of a weak anti-cyclonic system in near-calm (very widely spaced isobars) conditions. Gradient winds, if present, would likely be from the northeast. There were no class #6 (PTI) events in the summer.

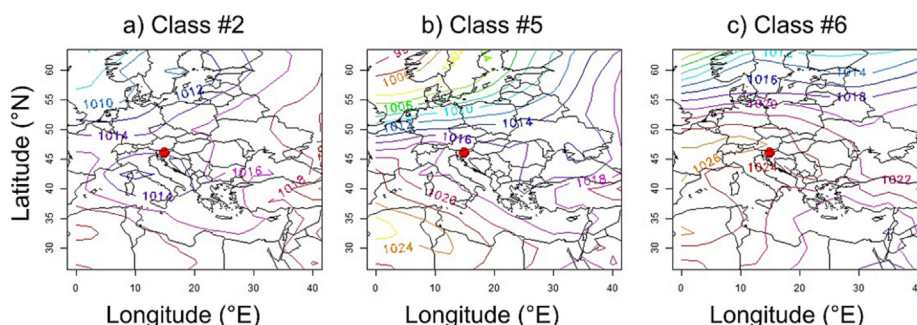


Fig. 6. Mean Sea Level Pressure (MSLP) charts (centred on the Ljubljana Basin) within three radon-based mixing classes in the winter season a) class #2 (near-neutral), b) class #5 (mostly stable), c) class #6 (persistent temperature inversion).

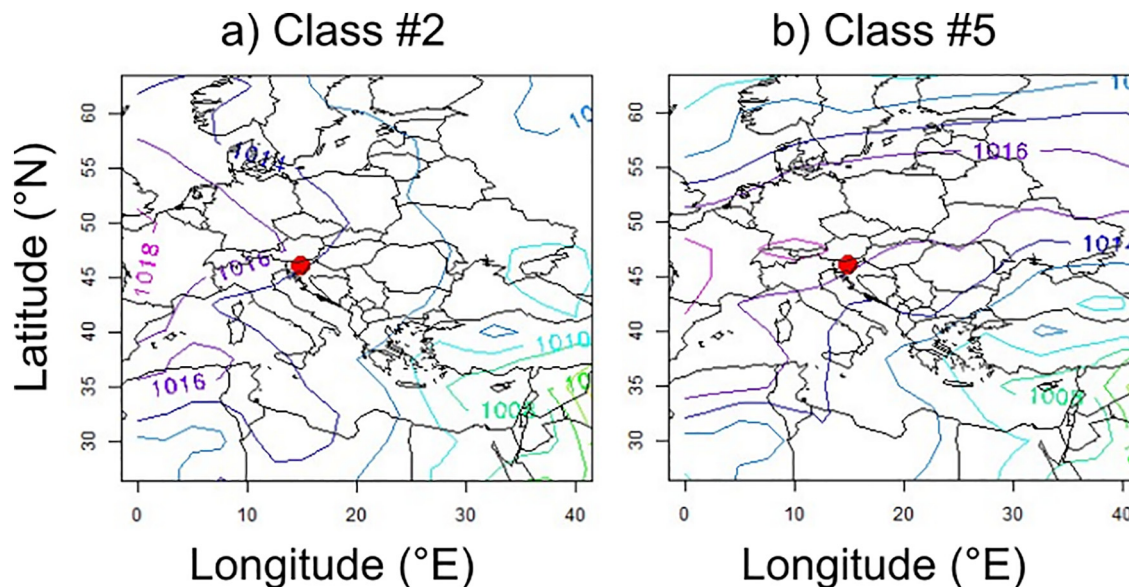


Fig. 7. Mean Sea Level Pressure (MSLP) charts (centred on the Ljubljana Basin) within two radon-based mixing classes in the summer season a) class #2 (near-neutral), and b) class #5 (mostly stable).

These findings confirm that spatially (at the regional scale), the overlying synoptic atmospheric conditions associated with the radon-based mixing classes are broadly consistent. Consequently, at the urban scale, while topographic variability within or across a city may result in changing local katabatic flows under the most stable conditions, a single near-surface radon observation at an appropriately chosen location can be used to categorise the dominant synoptic conditions giving rise to contrasting atmospheric mixing states across the whole city. Combined with the results of the previous section, our findings indicate that atmospheric mixing state classification using a single urban radon measurement site could be used effectively to group observations from three-dimensional distributed sensor networks throughout an urban canopy for the purpose of evaluating urban pollution or urban climate mitigation measures.

3.2.3. Urban air pollution variability as a function of radon-based mixing classification

Selected air pollutants (BC , NO_2 , CO , PM_{10} , SO_2 , O_3), classified within the six radon-based mixing classes in each season, are presented in Fig. 8 according to their main assumed sources: BC_{tr} , NO_2 (traffic; Fig. 8a); CO , PM_{10} (combination of traffic, biomass burning, natural sources, secondary aerosols), BC_{bb} (combustion) (Fig. 8b); and SO_2 and O_3 (industrial and electricity production and secondary pollutant) (Fig. 8c). While near-surface radon concentrations are a good proxy for the behaviour of unreactive primary pollutants with consistent, distributed near-surface sources in the urban “zone of habitation” (lowest several meters of the urban atmosphere), it should be noted that the relative response (radon accumulation) magnitudes across the diurnal cycle can differ substantially with the season due to variability of the radon source function. The criteria for radon-based stability classification, therefore, need to be determined separately for each season.

At any given location, the amplitude of pollutant diurnal cycles is mainly driven by the interaction between the spatial and temporal heterogeneity of sources and their strengths and variability of the atmospheric mixing state on diurnal, synoptic and seasonal timescales. From Fig. 8a and b it is clearly evident that radon-based mixing classes indicate a consistent, gradual increase in BC_{tr} , NO_2 , CO , PM_{10} , and BC_{bb} concentrations from near-neutral (class #2) to PTI (class #6) conditions. It should be noted that autumn BC and spring CO data are missing due to instrument malfunctions. SO_2 concentrations (Fig. 8c) often decreased with increasing atmospheric stability, indicating that a substantial amount of SO_2 mainly derives from sources remote from Ljubljana. However, a tendency for SO_2 to slightly increase during ‘rush hour’ periods shows a small local SO_2 contribution (e.g., diesel-fuelled vehicles).

The most pronounced seasonal cycle of BC_{tr} , NO_2 , CO , PM_{10} , BC_{bb} , and SO_2 is observed in mixing classes #4 and #5, with lower concentrations in summer/spring and higher in winter/autumn (Fig. 8a, b and c). The fact that primary pollutant composites showed opposing seasonal trends of nocturnal accumulation to those of radon (discussed in Section 3.1; Fig. 2) is attributable to opposing seasonality of source strengths (the radon source function reduces from summer to winter, whereas the opposite is true for the source strengths of many primary pollutants; especially those related to domestic heating and electricity production) (EEA, 2014).

Only during class #4 and #5 conditions do the traffic-related pollutants (BC_{tr} , NO_2 , CO) show a consistent, clear bimodal diurnal cycle with one peak in the morning and the other in the afternoon hours (Ježek et al., 2018). As evident in Fig. 8a and b (CO), there is a time lag of the pollution peak between seasons; in winter/autumn, the morning peak appears later ($\sim 08:00$ LT) than in summer/spring ($\sim 06:00$ LT). In the afternoon, accumulation of near-surface emissions begins around 16:00 LT in autumn and winter but not until 18:00 LT in summer and spring. These features are attributable to the combined influence of morning/evening ‘rush hour’ periods and the seasonal change in sunlight hours necessary for the breakup or formation of the nocturnal inversion ($\Delta T/\Delta z \leq -6.5$ °C km^{-1} ; Fig. 4a). Among the traffic-related pollutants, the winter diurnal cycle of CO (Fig. 8b) is particularly interesting, showing more similarity with combustion-dominated sources (BC_{bb} and PM_{10}) (Fig. 8b), which suggests that a significant proportion of the observed CO at this time might be derived from additional non-traffic related sources (e.g., domestic heating). The pronounced winter/autumn diurnal peaks of CO , BC_{bb} , PM_{10} concentrations occur between 21:00 LT and 23:00 LT (Fig. 8b), the time when more intensive residential heating is used, and remain higher for several hours. As expected, BC_{bb} (related explicitly to biomass burning) was present in a very low concentration within all mixing classes in summer (average ~ 0.2 $\mu\text{g m}^{-3}$) and spring (average ~ 0.4 $\mu\text{g m}^{-3}$) (Fig. 8b).

In classes #4 and #5, BC_{tr} , NO_2 , CO , PM_{10} , BC_{bb} concentrations attain secondary minimum values in the early morning (03:00–05:00 LT; Fig. 5a and b) when light katabatic drainage (NE) winds disrupt the urban pollution accumulation. A similar nocturnal “flushing” of urban pollutants has been reported for Bern, Switzerland by Williams et al. (2016), for Grünloch basin in the eastern Austrian Alps by Lehner et al. (2017) and for Zgierz, Poland, by Chambers and Podstawczyńska (2019).

If diurnal cycles of radon and selected primary pollutants on class #5 days in each season are normalised, relative differences between the curves can be qualitatively related to temporal changes in pollutant source

functions (as an alternative to formulating a full box model). In the case of NO_2 in summer, for example, NO_2 begins to increase from typical afternoon values around 18:00 LT similarly to radon as the stable nocturnal boundary layer begins to form. However, the initial rate of increase in NO_2 is greater than that for radon, indicative of a relative increase in the NO_2 source strength during the evening ‘rush hour’ compared with the afternoon source strength. The reduction in the slope of the diurnal NO_2 curve at 21:00 LT is indicative of a substantial reduction in the NO_2 source function after the “rush hour” period, since the mixing depth is continuing to decrease. Furthermore, given the nocturnal atmospheric lifetime of NO_2 , the reduction of NO_2 from 23:00 LT indicates that the nocturnal boundary layer is being diluted by a comparatively “cleaner” airmass. These

conditions (i.e., flushing with cleaner air, in the presence of a small local NO_2 source consistent with light nocturnal traffic) appear to persist between 01:00–04:00 LT. At 04:00 LT hours there is a sharp rise in NO_2 – the steepness of the initial rise here is likely related to the shallower morning nocturnal boundary layer depth (compared with the evening) rather than a difference in NO_2 source strength between the morning and evening traffic peaks. The decrease in NO_2 observed between 06:00 LT and 11:00 LT is less pronounced than for radon, indicating that a higher NO_2 source function (relative to afternoon values) was maintained throughout the morning, with the steep decline after 11:00 LT to the near-consistent afternoon values indicative of a pronounced reduction in the NO_2 source function in combination with the deepening convective atmospheric boundary layer.

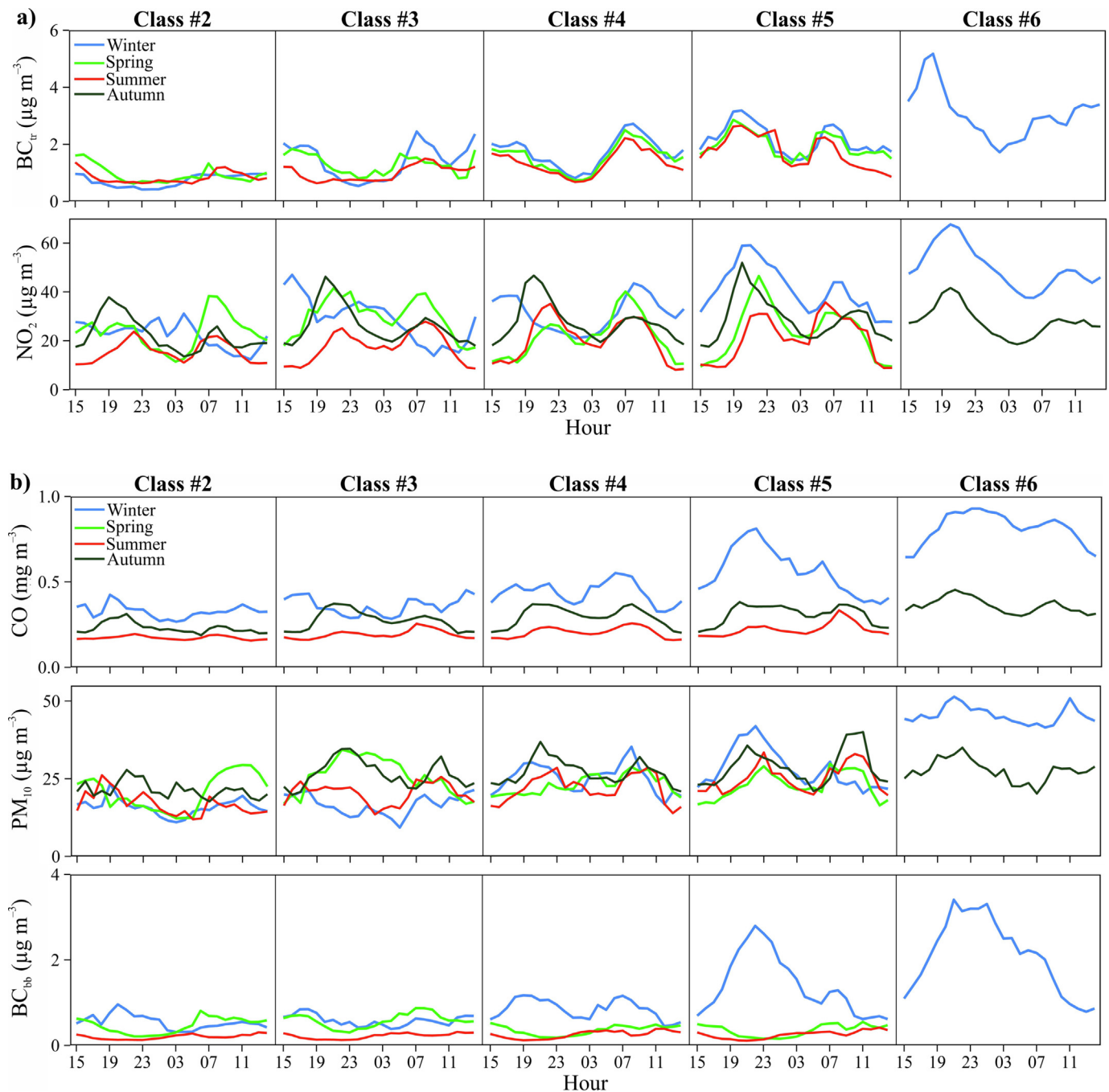


Fig. 8. a. Diurnal composite plots of BC_{tr} and NO_2 (air pollutants related to traffic source) by season and radon-based atmospheric mixing classes. b. Diurnal composite plots of CO, PM_{10} and BC_{bb} (air pollutants related to traffic and combustion sources) by season and radon-based atmospheric mixing classes. c. Diurnal composite plots of SO_2 and O_3 (air pollutants related to industrial and electricity production sources) by season and six radon-based atmospheric mixing classes.

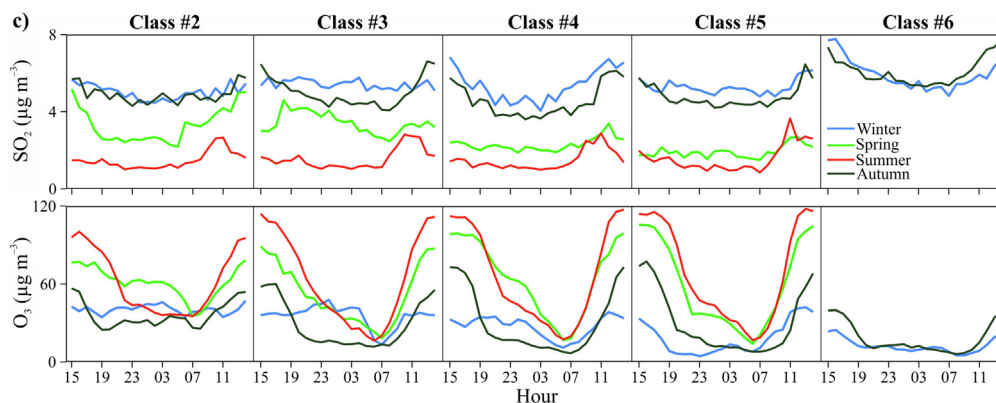


Fig. 8 (continued).

Under class #6 (PTI) conditions, which appear only in autumn and winter, the diurnal cycles of primary pollutants are similar to those in classes #4 and #5 (Fig. 8a, b and c) but with significantly elevated concentrations across the whole diurnal cycle. The daytime concentrations of pollutants under PTI conditions do not drop to the low daytime levels characteristic of class #5 days, attributable to a reduced opportunity for convective mixing from the basin (Fig. 4a). The stagnant anti-cyclonic class #6 conditions inhibit the daytime mixing that usually disperses accumulated nocturnal pollution on class #5 days. On PTI days, concentrations of BC_{tr} , NO_2 , CO , BC_{bb} , and PM_{10} are approximately 2-fold higher in winter than in autumn, which is in good agreement with the 2-fold increased intensity of winter $\Delta T/\Delta z$ for similar conditions and overall vertical stability of the atmosphere reported in Figs. 3c and 4a. The SO_2 PTI diurnal cycle appears out of phase with other primary pollutants (Fig. 8c), characterised by maximum values around noon (when $\Delta T/\Delta z$ plots - Fig. 4a - indicate that the basin atmosphere is unstable or tending toward instability, providing the best opportunity for reconnection with the overlying atmosphere) and minimum values at night. The same diurnal trend of SO_2 was also found in other classes (#2 to #5). The lack of nocturnal SO_2 accumulation likely indicates a lack of substantial local SO_2 sources since the nocturnal inversion layer isolates surface measurements from distant sources. Consequently, while domestic heating and traffic are expected to contribute a little to SO_2 concentrations in Ljubljana during the cold days, remote SO_2 sources dominate in the winter; more detailed information on this matter is provided by Kikaj et al. (2019c).

In windy conditions (classes #2 to #3), primary pollutants of local origin are usually efficiently dispersed. On average, peak BC_{tr} , NO_2 , CO , BC_{bb} concentrations in class #2 are a factor of 2–3 lower than in class #5 (Figs. 8a and b). PM_{10} concentrations in classes #2 and #3 (peak average $\sim 35 \mu\text{g m}^{-3}$), particularly those of spring season, are the highest (Fig. 8b). Grundström et al. (2015) also reported enhanced PM_{10} concentrations under windy conditions in Gothenburg, Sweden, where strong winds can result in the resuspension of coarser particles, such as dust from roads and other surfaces. However, increased PM_{10} concentrations in classes #2 and #3 days can also be associated with long-range transport (Pateraki et al., 2012). It is estimated that 80–120 Tg of Sahara dust flows into the MBR annually (Kaskaoutis et al., 2019b; D'Almeida, 1986). Fig. 5a in Kikaj et al. (2020) shows an example of strong gradient wind conditions (representing the fetch regions in all directions surrounding Ljubljana, over the large portion of Europe) under class #1 and #2 days. The dust events exhibit a distinct seasonality maximising in spring due to the intensification of westerlies wind and the development of the Sharav cyclones (Kaskaoutis et al., 2019a, 2019b). Slovenia was covered by a higher amount of Sahara dust (ARSO, 2017) in April 2018 (Fig. 8b). As already discussed in Section 3.2, atmospheric mixing classes #2 and #3 are characterised by higher wind speeds (90th percentile value of 3.2 m s^{-1}) in all seasons, particularly during spring days when winds are the highest from the WSW and SW, ideal conditions to support long-range air mass transport from the Sahara Desert. This is further evidence of the efficacy of the radon-based

mixing classification scheme to consistently and effectively allow separate investigation of local and remote contributions to urban air quality.

Compared with radon and locally-sourced pollutants, diurnal ozone concentrations exhibited an almost inverse response to atmospheric mixing conditions (Fig. 8c). Local O_3 production and depletion through NO_x and volatile organic compound (VOC) chemistry, downward mixing of O_3 from the free troposphere, surface O_3 dry deposition and, to some extent, horizontal transportation, all played essential roles in its diurnal cycles for each mixing class. During the periods with high nocturnal wind speeds (classes #2 and #3), the highest nocturnal O_3 concentrations were found due to remotely-sourced O_3 being mixed down to the surface from the residual layer or troposphere, as discussed by Querol et al. (2018). By comparing the windy nights (classes #2 and #3) of autumn and winter, the lowest night-time O_3 values were found in the autumn season. Since the average autumn wind speeds were lower, this confirms the importance of the wind speeds in O_3 mixing down from the free troposphere. The strong influence of sunlight and temperature on near-surface O_3 formation is evident when comparing daytime concentrations between seasons and mixing classes (Fig. 8c). The daytime of classes #4 and #5 is associated with the clearest skies and most intense solar radiation (see Table 1 in Chambers and Podstawczyńska (2019)), conditions which led to the highest overall O_3 concentrations, particularly in spring and summer.

Despite higher concentrations of precursor species in winter, lower temperatures and the reduction in sunlight result in the lowest daytime ozone concentrations in winter/autumn (class #5: peak average $42/77 \mu\text{g m}^{-3}$) than in spring/summer (class #5: peak average $106/118 \mu\text{g m}^{-3}$). However, as nocturnal wind speeds decrease from class #3 to #5, a shallow inversion layer forms and a significant decrease in nocturnal O_3 concentrations is observed due to the NO titration. While autumn and winter O_3 is completely titrated during PTI nights, with a slight increase during the daytime, this cycle indicates the formation of a shallow nocturnal inversion layer within the basin inversion layer around sunset that erodes after sunrise.

3.3. Outdoor air pollution in Ljubljana and EU and WHO air quality guidelines

In Ljubljana, the concentrations of CO , NO_2 , and SO_2 in the outdoor air were well below hourly and daily maximum values of EU regulations and WHO guidelines for all mixing classes and in all seasons of the year 2018. As reported by Pucer and Štrumbelj (2018), the trend of SO_2 and NO_2 concentrations has significantly decreased in Slovenia.

Concentrations of PM_{10} and O_3 , which tend to increase or exceed EU regulation and WHO guideline values (WHO, 2006, 2022; EEA, 2022), are presented as box and whisker plots for each of the radon-based mixing classes for each season (Figs. 9 and 10).

Box and whisker plots of the BC_{tr} and BC_{bb} concentrations are shown in Fig. 9a and b (autumn data are missing). Based on the breadth of the box-plot distributions, BC concentrations from both sources were significantly elevated in winter during the most stable (class #5) and PTI (class #6)

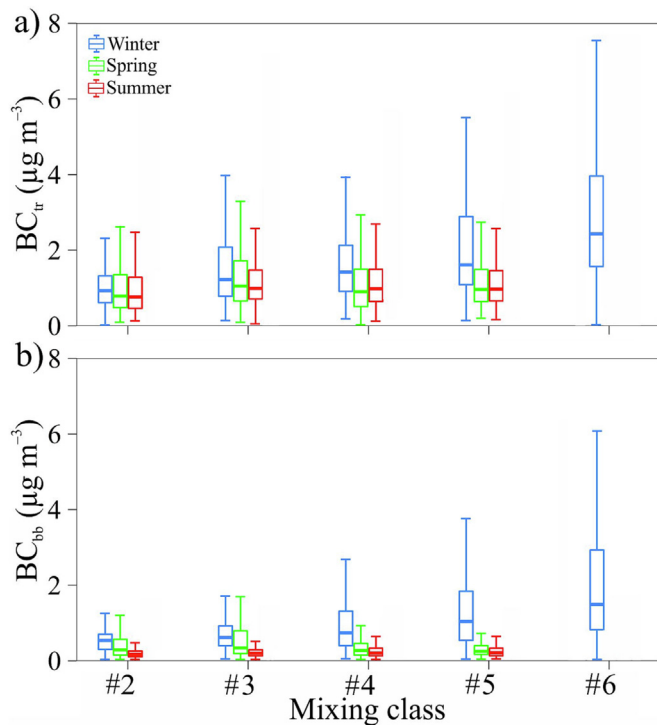


Fig. 9. Box and whisker plots of a) BC_{tr} and b) BC_{bb} grouped by each radon-based atmospheric mixing class and season (horizontal line: median, boxes: the 25th–75th percentile, whiskers: 5th–90th percentile).

conditions, with the highest median BC concentration encountered from traffic ($2.2 \mu\text{g m}^{-3}$; Fig. 9a). It has to be pointed out that the levels of BC are not yet regulated/guideline by either the EU or WHO. However, as previously reported, short-term (e.g., 2-h) exposure to BC was associated

with changes in lung function and signs of arterial stiffness (Janssen et al., 2011; Dons et al., 2012; Sinharay et al., 2018).

PM_{10} concentrations, as seen in the box and whisker plots of Fig. 10a, are under $50 \mu\text{g m}^{-3}$ (the PM_{10} threshold value of EU regulations) in the near-neutral (class #2) conditions of all seasons. It is clear, however, that the 90th percentile PM_{10} concentrations exceed both the EU and WHO threshold values ($45 \mu\text{g m}^{-3}$ WHO and $50 \mu\text{g m}^{-3}$ EU) in spring, autumn and winter in the other mixing classes (#3 to #6). During winter PTI conditions, on the other hand, even the upper quartile exceeds the threshold value, and the 90th percentile values reach concentrations of $100 \mu\text{g m}^{-3}$. The variability of PM_{10} concentrations associated with classes (#5 and #6) for winter, in particular, is discussed in more detail by Kikaj et al. (2019c).

In winter and autumn, none of the hourly values of O_3 exceeded the EU and WHO guidelines values (Fig. 10b), but this was not the case for summer and spring. For all mixing conditions (classes #2 to #5) in spring and summer, 90th percentile O_3 concentrations exceed the target values of both EU and WHO ($120 \mu\text{g m}^{-3}$ for EU; $100 \mu\text{g m}^{-3}$ for WHO). Based on the ARSO data for summer 2018, the max daily 8-h mean of O_3 concentration was exceeded in Ljubljana 22 times (ARSO, 2017).

A clear benefit of using the radon-based stability classification approach is that each mixing category represents a clearly defined fraction of time each year and season (Table 1), making results easily applicable to exposure studies. Furthermore, the ability to characterise meteorological quantities within mixing categories that result in pollution exceedance events is expected to help with efforts to predict such events using other available tools (measurement networks or regional models). Diurnal composites of meteorological and air quality parameters formed within better constrained mixing conditions, as possible with the radon-based method, help to account for effects of sub-grid-scale source heterogeneity and are therefore also well-suited to bridging the measurement-simulation scale gap and helping to evaluate the performance of urban air quality models (Chambers et al., 2019a); an essential task for improved urban planning.

4. Conclusions

Evaluating the performance of mitigation measures for urban pollution and urban climate is crucial for more sustainable urban planning and development. While 3-D urban microsensor networks are gaining popularity for this purpose, effective tools to isolate “uncontrollable” (weather related) influences on pollution and climate variability in the complex urban canopy are needed to improve the accuracy of intercomparisons between sensors in such networks. Here we describe a technique based on near-surface radon measurements that can reliably identify seasonal changes in atmospheric mixing on diurnal and synoptic timescales so their influence on air quality can be more accurately assessed. The same technique can be applied to urban climate studies. Although the radon-based technique described here is based on local, near-surface measurements, we demonstrate its ability to meaningfully group related mixing conditions vertically (well beyond the extent of the urban canopy layer) and spatially (up to and beyond the urban scale). As such, a single suitably positioned radon measurement could potentially assist with the interpretation of observations from an entire 3-D network of urban microsensors. Mindful of radon's predominantly terrestrial source function, this technique is suitable for year-round application in any non-coastal urban regions and is particularly valuable in regions such as central Europe or the mid-western United States, where synoptic timescale persistent inversions can severely deteriorate air quality. For this study, in the topographically complex city of Ljubljana, Slovenia, we demonstrate that almost all air pollution exceedance events occur under category #5 (individual poorly mixed nights) or category #6 (multi-day persistent temperature inversion, PTI) conditions. The local mixing conditions responsible for these events are also characterised. Since conventional, routine near-surface meteorological observations are not capable of reliably identifying PTI conditions, it should be noted that radon measurements offer a convenient, economical alternative to radiosonde or remote sensing approaches.

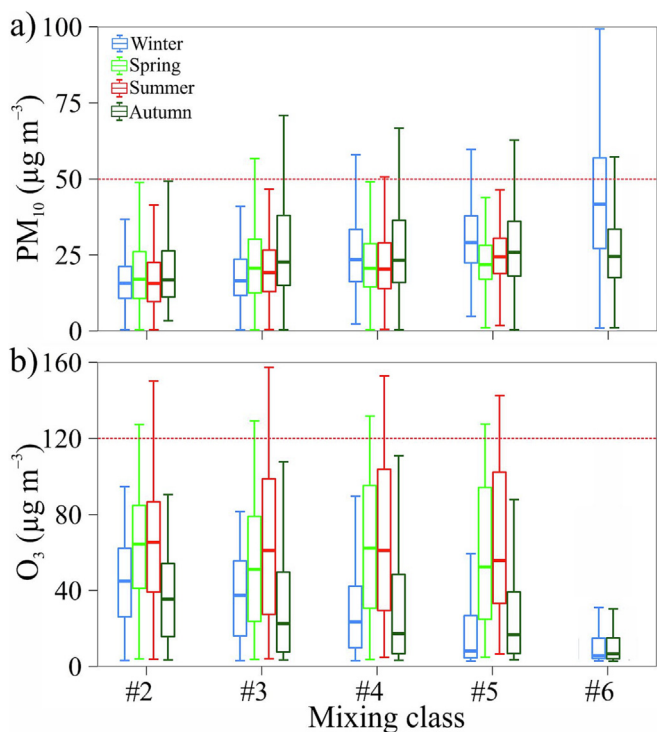


Fig. 10. Box and whisker plots of a) PM_{10} and b) O_3 grouped by each radon-based atmospheric mixing class and season (horizontal line: median, boxes: the 25th–75th percentile, whiskers: 5th–90th percentile).

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.162126>.

CRedit authorship contribution statement

The investigation was jointly conceptualized by DK, SC, and JV. Radon monitoring instrumentation was deployed and managed by DK and JV, and black carbon data by AG and MK. The research question, data collection and curation as well as formal data analysis were performed by DK.

Acquisition of funding for the research was arranged by JV. The research methodology was jointly developed by DK and SC and investigation jointly conducted by DK and JV. The project was administered by JV, with JV and SC responsible for supervision. All visualization of data, concepts, and results was performed by DK, while the script written to acquire, separate and process the back trajectories for visualization was performed by JC. DK wrote the complete original draft of the paper, which was subsequently edited and reviewed jointly by DK, SC, MK, JC, AG and JV.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Allegrini, I., Febo, A., Pasini, A., Schiarini, S., 1994. Monitoring of the nocturnal mixed layer by means of particulate radon progeny measurement. *J. Geophys. Res.* 99, 18765–18777.
- Anttila, P., Stefanovska, A., Nestorovska-Krsteska, A., Grozdanovski, L., Atanasov, I., Golubov, N., Risteovski, P., Toceva, M., Lappi, S., Walden, J., 2016. Characterisation of extreme air pollution episodes in an urban valley in the Balkan Peninsula. *Air Qual. Atmos. Health* 9 (2), 129–141. <https://doi.org/10.1007/s11869-015-0326-7>.
- Avino, P., Manigrasso, M., 2008. Ten-year measurements of gaseous pollutants in urban air by an open-path analyzer. *Atmos. Environ.* 42 (18), 4138–4148.
- Baasandorj, M., Hoch, S.W., Ryan, B., Lin, J.C., Brown, S.S., Millet, D.B., Martin, R.L., Kelly, K., Zarzana, K.J., Whiteman, C.D., Dube, W.P., Tonnesen, G., Jaramillo, I.C., Sohl, J., 2017. Coupling between chemical and meteorological processes under persistent cold-air pool conditions: evolution of wintertime PM_{2.5} pollution events and N₂O₅ observations in Utah's Salt Lake Valley. *Environ. Sci. Technol.* 51 (11), 5941–5950. <https://doi.org/10.1021/acs.est.6b06603>.
- Beeston, M., Grgić, I., van Johannes, T., Elteren, J.T., Iskra, I., Kapun, G., Močnik, G., 2011. Chemical and morphological characterization of aerosol particles at mt. Kravac, Slovenia, during the Eyjafjallajökull Icelandic volcanic eruption. *Environ. Sci. Pollut. Res.* 19 (1), 235–243. <https://doi.org/10.1007/s11356-011-0563-8>.
- Čanić, K.Š., Kavčič, I., Klaić, Z.B., 2009. An episode of Saharan dust over Croatia. *Newsletter 69* (European Association for the Science of Air Pollution. Online).
- Chambers, S.D., Podstawczyńska, A., 2019. Improved method for characterising temporal variability in urban air quality part II: particulate matter and precursors in Central Poland. *Atmos. Environ.* 219, 117040. <https://doi.org/10.1016/j.atmosenv.2019.117040>.
- Chambers, S.D., Williams, A.G., Crawford, J., Griffiths, A.D., 2015a. On the use of radon for quantifying the effects of atmospheric stability on urban emissions. *Atmos. Chem. Phys.* 15, 1175–1190. <https://doi.org/10.5194/acp-15-1175-2015>.
- Chambers, S.D., Williams, A.G., Zahorowski, W., Griffiths, A., Crawford, J., 2011. Separating remote fetch and local mixing influences on vertical radon measurements in the lower atmosphere. *Tellus Ser. B Chem. Phys. Meteorol.* 63, 843–859. <https://doi.org/10.1111/j.1600-0889.2011.00565.x>.
- Chambers, S.D., Podstawczyńska, A., Williams, A.G., Pawlak, W., 2016. Characterising the influence of atmospheric mixing state on urban heat island intensity using Radon-222. *Atmos. Environ.* 147, 355–368. <https://doi.org/10.1016/j.atmosenv.2016.10.026>.
- Chambers, S.D., Wang, F., Williams, A.G., Deng, X., Zhang, H., Lonati, G., Crawford, J., Griffiths, A.D., Ianniello, A., Allegrini, I., 2015b. Quantifying the influences of atmospheric stability on air pollution in Lanzhou, China, using a radon-based stability monitor. *Atmos. Environ.* 107, 233–243.
- Chambers, S.D., Guérette, E.-A., Monk, K., Griffiths, A.D., Zhang, Y., Duc, H., Cope, M., Emmerson, K.M., Chang, L.T., Silver, J.D., Utembe, S., Crawford, J., Williams, A.G., Keywood, M., 2019a. Skill-testing chemical transport models across contrasting atmospheric mixing states using Radon-222. *Atmosphere* 10 (1), 25. <https://doi.org/10.3390/atmos10010025>.
- Chambers, S.D., Podstawczyńska, A., Pawlak, W., Fortuniak, K., Williams, A., Griffiths, A., 2019b. Characterising the state of the urban surface layer using Radon-222. *J. Geophys. Res. Atmos.* 124 (2), 770–788.
- Chemel, C., Arduini, G., Staquet, C., Largeron, Y., Legain, D., Tzanos, D., Paci, A., 2016. Valley heat deficit as a bulk measure of wintertime particulate air pollution in the Arve River valley. *Atmos. Environ.* 128, 208–215.
- Cohen, L.D., Barr, S., Krablin, R., Newstein, H., 1972. Steady-state vertical turbulent diffusion of radon. *J. Geophys. Res.* 77, 2654–2668.
- ARSO, Slovenian Environment Agency Slovenian Agencija Republike Slovenije za Okolje, 2017. Climate Characteristics of Ljubljana - Wind Rose for the City of Ljubljana.
- Conceição, R., Silva, H.G., Mirão, J., Gostein, M., Fialho, L., Narvarte, L., Collares-Pereira, M., 2018. Saharan dust transport to Europe and its impact on photovoltaic performance: a case study of soiling in Portugal. *Sol. Energy* 160, 94–102. <https://doi.org/10.1016/j.solener.2017.11.059> (November 2017).
- D'Almeida, G., 1986. A model for saharan dust transport. *J. Clim. Appl. Meteorol.* 25 (7), 903–916.
- Díaz, J., Linares, C., Carmona, R., Russo, A., Ortiz, C., Salvador, P., Trigo, R.M., 2017. Saharan dust intrusions in Spain: health impacts and associated synoptic conditions. *Environ. Res.* 156, 455–467.
- Dons, E., Int Panis, L., Van Poppel, M., Theunis, J., Wets, G., 2012. Personal exposure to black carbon in transport microenvironments. *Atmos. Environ.* 55, 392–398. <https://doi.org/10.1016/j.atmosenv.2012.03.020>.
- Drinovec, L., Močnik, G., Zotter, P., Prévôt, A.S.H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., Hansen, A.D.A., 2015. The "dual-spot" Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation. *Atmos. Meas. Tech.* 8 (5), 1965–1979. <https://doi.org/10.5194/amt-8-1965-2015>.
- EEA, 2014. Air Pollution Fact Sheet Slovenia — 2014 Report.
- EEA, 2021. Air Quality in Europe 2021—2021 Report.
- EEA, 2022. Europe's Air Quality Status 2022 — 2022 Report (European Association for the Science of Air Pollution. Online).
- Fontan, J., Guedalia, D., Druihet, A., Lopez, A., 1979. Une methode de mesure de la stabilite verticale de l'atmosphere pres du sol. *Bound.-Layer Meteorol.* 17 (1), 3–14.
- Fujinami, N., Esaka, S., 1987. Variations in radon 222 daughter concentrations in surface air with atmospheric stability. *J. Geophys. Res. Atmos.* 92 (D1), 1041–1043.
- Galmarini, S., 2006. One year of 222Rn concentration in the atmospheric surface layer. *Atmos. Chem. Phys.* 6 (10), 2865–2886.
- Gerasopoulos, E., Kouvarakis, G., Vrekoussis, M., Kanakidou, M., Mihalopoulos, N., 2005. Ozone variability in the marine boundary layer of the eastern Mediterranean based on 7-year observations. *J. Geophys. Res. Atmos.* 110 (D15), 1–12.
- Gobbi, G.P., Barnaba, F., Libertò, L.D., Bolignano, A., Lucarelli, F., Nava, S., Perrino, C., Pietrodangelo, A., Basart, S., Costabile, F., Dionisi, D., Rizza, U., Canepari, S., Sozzi, R., 2019. An inclusive view of Saharan dust advections to Italy and the Central Mediterranean. (November 2018) *Atmos. Environ.* 201, 242–256. <https://doi.org/10.1016/j.atmosenv.2019.01.002> 2019.
- Goudie, A.S., 2014. Desert dust and human health disorders. *Environ. Int.* 63, 101–113. <https://doi.org/10.1016/j.envint.2013.10.011>.
- Gregorić, A., Drinovec, L., Ježek, I., Vaupotič, J., Lenarčič, M., Grauf, D., Wang, L., Mole, M., Stanić, S., Močnik, G., 2020. The determination of highly time-resolved and source-separated black carbon emission rates using radon as a tracer of atmospheric dynamics. *Atmos. Chem. Phys.* 20 (22), 14139–14162.
- Griffin, D.W., 2005. Atmospheric movement of microorganisms in clouds of desert dust and implications for human health. *Clin. Microbiol. Rev.* 20 (3), 459–477. <https://doi.org/10.1128/CMR.00039-06>.
- Grundström, M., Hak, C., Chen, D., Hallquist, M., Pleijel, H., 2015. Variation and co-variation of PM₁₀, particle number concentration, NO_x and NO₂ in the urban air – relationships with wind speed, vertical temperature gradient and weather type. *Atmos. Environ.* 120, 317–327.
- He, T., Chen, Y., Stanić, S., Bergant, K., Gao, F., Hua, D., 2018. Properties of tropospheric aerosols observed over Southwest Slovenia. *J. Quant. Spectrosc. Radiat. Transf.* 217, 380–387. <https://doi.org/10.1016/j.jqsrt.2018.06.009>.
- Highwood, E.J., Kinnerley, R.P., 2006. When smoke gets in our eyes: the multiple impacts of atmospheric black carbon on climate, air quality and health. *Environ. Int.* 32, 560–566. <https://doi.org/10.1016/j.envint.2005.12.003>.
- Hitzenberger, R., Ctyroky, P., Berner, A., Turšič, J., Podkrajšek, B., Grgić, I., 2006. Size distribution of black (BC) and total carbon (TC) in Vienna and Ljubljana. *Chemosphere* 65 (11), 2106–2113. <https://doi.org/10.1016/j.chemosphere.2006.06.042>.
- Ivey, C.E., Balachandran, S., Colgan, S., Hu, Y., Holmes, H.A., 2019. Investigating fine particulate matter sources in Salt Lake City during persistent cold air pool events. *Atmos. Environ.* 213, 568–578.
- Janssen, N.A.H., Hoek, G., Simic-lawson, M., Fischer, P., Bree, L., Van, Brink, H., Keuken, M., Atkinson, R.W., Anderson, H.R., Brunekreef, B., Cassee, F.R., 2011. Black carbon and

- health effects of airborne particles compared with PM10 and PM2.5. *Environ. Health Perspect.* 119, 1691–1699. <https://doi.org/10.1289/ehp.1003369>.
- Jędruszkiewicz, J., Czemecki, B., Marosz, M., 2017. The variability of PM10 and PM2.5 concentrations in selected polish agglomerations: the role of meteorological conditions, 2006–2016. *Int. J. Environ. Health Res.* 27 (6), 441–462. <https://doi.org/10.1080/09603123.2017.1379055>.
- Ježek, I., Blond, N., Skupinski, G., Močnik, G., 2018. The traffic emission-dispersion model for a central-european city agrees with measured black carbon apportioned to traffic. *Atmos. Environ.* 184, 177–190.
- Kahl, J.D.W., Chapman, H.L., 2018. Atmospheric stability characterization using the pasquill method: a critical evaluation. *Atmos. Environ.* 187, 196–209. <https://doi.org/10.1016/j.atmosenv.2018.05.058>.
- Kallos, G., Astitha, M., Katsafados, P., Chris, S., 2006. Long-range transport of anthropogenically and naturally produced particulate matter in the Mediterranean and North Atlantic: current state of knowledge. *J. Appl. Meteorol. Climatol.* 46, 1230–1251. <https://doi.org/10.1175/JAM2530.1>.
- Kalnay, E., Kanamitsu, M., Kistler, R., Collins, W., Deaven, D., Gandin, L., Joseph, D., 1996. The NCEP/NCAR 40-year reanalysis project. *Bull. Am. Meteorol. Soc.* 77 (3), 437–472.
- Karstens, U., Schwingshackl, C., Schmihüsen, D., Levin, I., 2015. A process-based 222radon flux map for Europe and its comparison to long-term observations. *Atmos. Chem. Phys.* 15 (22), 12845–12865. <https://doi.org/10.5194/acp-15-12845-2015>.
- Kaskaoutis, D.G., Dumka, U.C., Rashki, A., Psiloglou, B.E., Gavril, A., Mo, A., Petrinoli, K., Karagiannis, D., Kambezidis, H.D., 2019a. Analysis of intense dust storms over the eastern Mediterranean in march 2018: impact on radiative forcing and Athens air quality. *Atmos. Environ.* 209, 23–39. <https://doi.org/10.1016/j.atmosenv.2019.04.025>.
- Kaskaoutis, D.G., Rashki, A., Dumka, U.C., Mo, A., Kambezidis, H.D., Psiloglou, B.E., Karagiannis, D., Petrinoli, K., Gavril, A., 2019b. Atmospheric dynamics associated with exceptionally dusty conditions over the eastern Mediterranean and Greece in March 2018. *Atmos. Res.* 218, 269–284. <https://doi.org/10.1016/j.atmosres.2018.12.009>.
- Kikaj, D., Vaupotič, J., 2017. Parameters influencing deviation of radon concentration from its typical diurnal pattern in the winter and summer seasons. *Geol. Maced.* 31, 157–170.
- Kikaj, D., Vaupotič, J., Chambers, S.D., 2019a. Identifying persistent temperature inversion events in a subalpine basin using radon-222. *Atmos. Meas. Tech.* 12 (8), 4455–4477.
- Kikaj, D., Chambers, S.D., Vaupotič, J., 2019b. Radon-based atmospheric stability classification in contrasting sub-alpine and sub-Mediterranean environments. *J. Environ. Radioact.* 203, 125–134. <https://doi.org/10.1016/j.jenvrad.2019.03.010>.
- Kikaj, D., Chambers, S.D., Kobal, M., Crawford, J., Vaupotič, J., 2019c. Characterising atmospheric controls on winter urban pollution in a topographic basin setting using Radon-222. *Atmos. Res.* 237, 104838. <https://doi.org/10.1016/j.atmosres.2019.104838>.
- Kikaj, D., Chambers, S.D., Kobal, M., Crawford, J., Vaupotič, J., 2020. Characterizing atmospheric controls on winter urban pollution in a topographic basin setting using Radon-222. *Atmos. Res.* 237, 104838. <https://doi.org/10.1016/j.atmosres.2019.104838>.
- Klingner, M., Sähn, E., 2008. Prediction of PM10 concentration on the basis of high-resolution weather forecasting. *Meteorol. Z.* 263–272.
- Largerone, Y., Staquet, C., 2016. Persistent inversion dynamics and wintertime PM10 air pollution in alpine valleys. *Atmos. Environ.* 135, 92–108. <https://doi.org/10.1016/j.atmosenv.2016.03.045>.
- Lehner, M., Whiteman, C.D., Dorminger, M., 2017. Inversion build-up and cold-air outflow in a small alpine sinkhole. *Bound. Lay. Meteorol.* 163 (3), 497–522.
- Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P.J., Dentener, F.J., Fischer, H., Feichter, J., Flatau, P.J., Heland, J., Holzinger, R., Korrman, R., Lawrence, M.G., Levin, Z., Markowicz, K.M., Mihalopoulos, N., Minikin, A., Stephanou, E.G., Stier, P., Traub, M., Warneke, C., 2002. Global air pollution crossroads over the Mediterranean. *Science* 298, 794–799.
- Łupikasza, E.B., Niedzwiedz, T., 2022. Relationships between vertical temperature gradients and PM10 concentrations during selected weather conditions in upper Silesia (Southern Poland). *Atmosphere* 13, 125. <https://doi.org/10.3390/atmos13010125>.
- Martilli, A., Sánchez, B., Santiago, J.L., Rasilla, D., Pappacogli, G., Allende, F., Fernández, F., 2022. Simulating the pollutant dispersion during persistent Wintertime thermal Inversions over urban areas. The case of Madrid. *Atmos. Res.* 270, 106058.
- McCaffrey, K., Wilczak, J.M., Bianco, L., Gritti, E., Sharp, J., Banta, R., Friedrich, K., Fernando, H.J.S., Krishnamurthy, R., Leo, L.S., Muradyan, P., 2019. Identification and characterization of persistent cold pool events from temperature and wind profilers in the Columbia River Basin. *J. Appl. Meteorol. Climatol.* 58 (12), 2533–2551. <https://doi.org/10.1175/JAMC-D-19-0046.1>.
- Moses, H., Stehney, A.F., Lucas Jr., H.F., 1960. The effect of meteorological variables upon the vertical and temporal distributions of atmospheric radon. *J. Geophys. Res.* 65, 1223–1238.
- Murn, T., Stepišnik, M., 2019. Intercomparison Measurements of Radon-222 Concentrations at ICJT (in Slovenian), Report IJS-DP-12983.
- Novak, R., Robinson, J.A., Kanduč, T., Sarigiannis, D., Kocman, D., 2022. Assessment of individual-level exposure to airborne particulate matter during periods of atmospheric thermal inversion. *Sensors* 22, 7116. <https://doi.org/10.3390/s22197116>.
- Omori, Y., Tohno, I., Nagahama, H., Ishikawa, Y., Takahashi, M., Sato, H., Sekine, T., 2009. Variation of atmospheric radon concentration with bimodal seasonality. *Radiat. Meas.* 44, 1045–1050.
- Pal, S., Lopez, M., Schmidt, M., Ramonet, M., Gibert, F., Xuereb-Remy, I., Ciais, P., 2015. Investigation of the atmospheric boundary layer depth variability and its impact on the 222Rn concentration at a rural site in France. *J. Geophys. Res. Atmos.* 120 (2), 623–643.
- Pasquill, F., 1961. The estimation of the dispersion of windborne material. *Meteorol. Mag.* 90, 33–49.
- Pasquill, F., Smith, F.B., 1983. *Atmospheric Diffusion: Study of the Dispersion of Windborne Material From Industrial and Other Sources*. third ed. Ellis Horwood Ltd, Chichester.
- Pateraki, S., Asimakopoulos, D.N., Flocas, H.A., Maggos, T., Vasilakos, C., 2012. The role of meteorology on different sized aerosol fractions (PM10, PM2.5, PM2.5–10). *Sci. Total Environ.* 419, 124–135.
- Perrino, C., Pietrodangelo, A., Febo, A., 2001. An atmospheric stability index based on radon progeny measurements for the evaluation of primary urban pollution. *Atmos. Environ.* 35 (31), 5235–5244. [https://doi.org/10.1016/S1352-2310\(01\)00349-1](https://doi.org/10.1016/S1352-2310(01)00349-1).
- Perrino, C., Catrambone, M., Pietrodangelo, A., 2008. Influence of atmospheric stability on the mass concentration and chemical composition of atmospheric particles: a case study in Rome, Italy. *Environ. Int.* 34 (5), 621–628.
- Pitari, G., Coppari, E., De Luca, N., Di Carlo, P., 2014. Observations and box model analysis of radon-222 in the atmospheric surface layer at L'Aquila, Italy: march 2009 case study. *Environ. Earth Sci.* 71 (5), 2353–2359.
- Pitari, G., De Luca, N., Coppari, E., Di Carlo, P., Di Genova, G., 2015. Seasonal variation of night-time accumulated rn-222 in Central Italy. *Environ. Earth Sci.* 73 (12), 8589–8597.
- Podstawczyńska, A., Chambers, S.D., 2018. Radon-based technique for the analysis of atmospheric stability – a case study from Central Poland. *Nukleonika* 63, 47–54. <https://doi.org/10.2478/nuka-2018-0006>.
- Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: lines that connect. *J. Air Waste Manag. Assoc.* 56 (6), 709–742. <https://doi.org/10.1080/10473289.2006.10464485>.
- Pucer, J., Štrumbelj, E., 2018. Impact of changes in climate on air pollution in Slovenia between 2002 and 2017. *Environ. Pollut.* 242, 398–406. <https://doi.org/10.1016/j.envpol.2018.06.084>.
- Querol, X., Alastuey, A., Gangoiti, G., Perez, N., Lee, H.K., Eun, H.R., Park, Y., Mantilla, E., Escudero, M., Titos, G., Alonso, L., Temime-Roussel, B., Marchand, N., Moreta, J.R., Revuelta, M.A., Salvador, P., Artíñano, B., Dos Santos, S.G., Anguas, M., Notario, A., Saiz-Lopez, A., Harrison, R.M., Millán, M., Ahn, K.H., 2018. Phenomenology of summer ozone episodes over the Madrid metropolitan area, Central Spain. *Atmos. Chem. Phys.* 18, 6511–6533.
- Russo, A., Trigo, R.M., Martins, H., Mendes, M.T., 2014. NO₂, PM10 and O₃ urban concentrations and its association with circulation weather types in Portugal. *Atmos. Environ.* 89, 768–785.
- Salvador, P., Alonso-Pérez, S., Pey, J., Artíñano, B., De Bustos, J.J., Alastuey, A., Querol, X., 2014. African dust outbreaks over the western Mediterranean Basin: 11-year characterization of atmospheric circulation patterns and dust source areas. *Atmos. Chem. Phys.* 14 (13), 6759–6775.
- Sandradewi, J., Prévôt, A.S.H., Weingartner, E., Schmidhauser, R., Gysel, M., Baltensperger, U., 2008. A study of wood burning and traffic aerosols in an alpine valley using a multi-wavelength aethalometer. *Atmos. Environ.* 42, 101–112. <https://doi.org/10.1016/j.atmosenv.2007.09.034>.
- Segura, S., Estellés, V., Esteve, A.R., Utrillas, M.P., Martínez-Lozano, J.A., 2013. Analysis of a severe pollution episode in Valencia (Spain) and its effect on ground level particulate matter. *J. Aerosol Sci.* 56, 41–52.
- Sesana, L., Caprioli, E., Marazzan, G.M., 2003. Long period study of outdoor radon concentration in Milan and correlation between its temporal variations and dispersion properties of atmosphere. *J. Environ. Radioact.* 65, 147–160. [https://doi.org/10.1016/S0265-931X\(02\)00093-0](https://doi.org/10.1016/S0265-931X(02)00093-0).
- Sesana, L., Ottobri, B., Polla, G., Facchini, U., 2006. 222Rn as indicator of atmospheric turbulence: measurements at Lake Maggiore and on the pre-Alps. *J. Environ. Radioact.* 86 (2), 271–288. <https://doi.org/10.1016/j.jenvrad.2005.09.005>.
- Sinharay, R., Gong, J., Barratt, B., Ohman-Strickland, P., Ernst, S., Kelly, F.J., Junfeng, Z., Collins, P., Cullinan, P., Chung, K.F., 2018. Respiratory and cardiovascular responses to walking down a traffic-polluted road compared with walking in a traffic-free area in participants aged 60 years and older with chronic lung or heart disease and age-matched healthy controls: a randomised, crossover study. *Lancet* 391 (10118), 339–349.
- Triantafyllou, A.G., 2001. PM10 pollution episodes as a function of synoptic climatology in a mountainous industrial area. *Environ. Pollut.* 112, 491–500.
- Turner, D.B., 1964. A diffusion model for an urban area. *J. Appl. Meteorol.* 3 (1), 83–91.
- Vardoulakis, S., Kassomenos, P., 2008. Sources and factors affecting PM10 levels in two european cities: implications for local air quality management. *Atmos. Environ.* 42, 3949–3963. <https://doi.org/10.1016/j.atmosenv.2006.12.021>.
- Vrhovec, T., 1990. Analysis of mesometeorological temperature fields. *Meteorol. Atmos. Phys.* 43 (1–4), 235–240.
- Wang, F., Chambers, S.D., Zhang, Z., Williams, A.G., Deng, X., Zhang, H., Lonati, G., Crawford, J., Griffiths, A.D., Ianniello, A., Allegrini, I., 2016. Quantifying stability influences on air pollution in Lanzhou, China, using a radon-based “stability monitor”: seasonality and extreme events. *Atmos. Environ.* 145, 376–391. <https://doi.org/10.1016/j.atmosenv.2016.09.014>.
- Wang, L., Stanič, S., Bergant, K., Eichinger, W., Močnik, G., Drinovec, L., Vaupotič, J., Miler, M., Gosar, M., Gregorič, A., 2019. Retrieval of vertical mass concentration distributions – Vipava Valley case study. *Remote Sens.* 11 (2), 106.
- Whiteman, C.D., Eisenbach, S., Pospichal, B., Steinacker, R., 2004. Comparison of vertical soundings and sidewall air temperature measurements in a small Alpine Basin. *J. Appl. Meteorol.* 43, 1635–1647. <https://doi.org/10.1175/JAM2168.1>.
- WHO, 2006. Air quality guidelines: global update 2005 — particulate matter, ozone, nitrogen dioxide and sulphur dioxide. World Health Organization, Regional Office for Europe, Copenhagen. <http://www.euro.who.int/en/health-topics/environment-and-health/airquality/publications/pre2009-air-quality-guidelines-global-update-2005-particulate-matter-ozone-nitrogen-dioxide-and-sulfur-dioxide>. (Accessed 22 December 2019).
- WHO, 2022. New WHO Air Quality Guidelines 2021. World Health Organization, Regional Office for Europe, Copenhagen. [https://www.who.int/news-room/fact-sheets/detail/ambient-\(outdoor\)-air-quality-and-health](https://www.who.int/news-room/fact-sheets/detail/ambient-(outdoor)-air-quality-and-health). (Accessed 11 February 2023).
- Williams, A.G., Chambers, S., Griffiths, A., 2013. Bulk mixing and decoupling of the nocturnal stable boundary layer characterized using a ubiquitous natural tracer. *Bound.-Layer Meteorol.* 149, 381–402. <https://doi.org/10.1007/s10546-013-9849-3>.
- Williams, A.G., Chambers, S.D., Conen, F., Reimann, S., Hill, M., Griffiths, A.D., Crawford, J., 2016. Radon as a tracer of atmospheric influences on traffic-related air pollution in a small inland city. *Tellus Ser. B Chem. Phys. Meteorol.* 68 (1), 1–21. <https://doi.org/10.3402/tellusb.v68.30967>.