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On the dispersion of trace species in the atmospheric boundary layer: a re-formulation of the governing equations for the turbulent flow of the compressible atmosphere

By GERHARD KRAMM[1,*] and FRANZ X. MEIXNER[2], [1]*Materialforschungs- und Prüfungsanstalt für das Bauwesen Leipzig e.V., Abteilung Baulicher Brandschutz, Richard-Lehmann-Straße 19, D-04275 Leipzig, Germany;* [2]*Max-Planck-Institut für Chemie, Abteilung Biogeochemie, PO Box 3060, D-55020 Mainz, Germany*

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ABSTRACT

Since especially the parameterisation of the vertical dispersion of trace species in the atmospheric boundary layer has controversially been discussed in the literature, the 1st-order balance equations for matter, momentum, and various energy forms were re-formulated with Hesselberg's density-weighted averaging calculus to point out that this problem arises from averaging the macroscopic balance equations of matter, momentum and various energy forms in the sense of Reynolds, rather than from the parameterisation of the vertical dispersion by 1st-order closure principles, as this discussion seems to reflect. Results of the SANA field experiment "Eisdorf" presented here substantiate that in the case of chemically reactive trace constituents segregation effects owing to turbulence cannot generally be neglected as usually performed in Eulerian air pollution models. Modelling such segregation effects, however, requires, at least, 2nd-order-closure principles. Therefore, the 2nd-order balance equations for 2nd moments like the eddy flux densities of matter and momentum as well as covariances of scalar quantities were also re-formulated by considering Hesselberg's averaging procedure. This re-formulated set of governing 1st-order and 2nd-order balance equations may be considered as most exact because the degree of simplification is reduced to a minimum. To distinguish between the Boussinesq approximated equation set for the turbulent atmospheric flow, denoted as Boussinesq fluid, and our re-formulated one, the turbulent flow of the compressible atmosphere for which the re-formulated governing balance equations are valid may be denoted as Hesselberg fluid. It is argued that averaging in the sense of Hesselberg reduces the risk to misinterpret turbulent atmospheric processes to a minimum. As exemplary shown on the basis of the balance equations for dry air, water vapour, and trace species, the so-called Webb correction will become insignificant if Hesselberg's averaging calculus is considered. Based on the results obtained from the "Eisdorf" experiment and from sensitivity studies with a Seinfeld-type kinetic mechanism for photochemical smog, it is argued that an evaluation and improvement of Eulerian air pollution models require directly measured 2nd-order moments. Since the number of fast-response physico-chemical analysers for chemically reactive trace constituents is strongly limited, such fast-response sensors have to be (further) developed to set-up a *true* platform for model evaluation that implies not only a comparison of calculated and observed distributions of 1st moments (necessary condition), but also a comparison of the calculated and observed distributions of 2nd moments (sufficient condition).

* Corresponding author.
e-mail: mfpa-leipzig.brandschutz@t-online.de

1. Introduction

In most Eulerian air pollution models for chemically reactive trace constituents like ADOM (Venkatram et al., 1988), EURAD (Mölders et al., 1994), RADM (Chang et al., 1987) and DRAIS (Vogel et al., 1995) the turbulent transfer of trace species is parameterised by 1st-order closure principles (flux-gradient relationships). Recently, especially the parameterisation of the vertical dispersion of trace species in the atmospheric boundary layer in conjunction with fluctuations of the air density has controversially been discussed by several authors (Venkatram, 1993, 1998; Thomson, 1995, 1998; van Dop, 1998). Obviously, this discussion touches an old, but prominent problem in formulating the governing equations of the turbulent flow (Hesselberg, 1926; Rotta, 1963; Szablewski, 1963) that is usually ignored in studies on atmospheric processes. This problem arises from averaging the macroscopic balance equations (also called conservation equations) of matter, momentum and various energy forms in the sense of Reynolds, rather than from the parameterisation of the vertical dispersion by 1st-order closure principles as the aforementioned discussion seems to reflect.

2. Problem formulation

To describe the problem in more detail, we start with the macroscopic balance equation of the ith atmospheric trace constituent, $i = 1, 2, \ldots, N$, given by de Groot and Mazur (1969)*

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \boldsymbol{v}_i) = \sigma_i, \tag{2.1}$$

Here, $\partial \rho_i / \partial t$ is the local change, t is the time, $\rho_i = M_i/V$ is the partial density, M_i is the partial mass of the volume V under study, $\boldsymbol{v}_i$ is the corresponding velocity vector, and σ_i denotes the sources or sinks owing to chemical reactions. For simplification, it is assumed for a moment that the atmosphere only consists of chemically conservative ($\sigma_0 = 0$) dry air with the partial density ρ_0 and N trace species. Eq. (2.1) can be expanded by $\rho_i \boldsymbol{v} - \rho_i \boldsymbol{v}$ to yield

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \boldsymbol{v} + \rho_i (\boldsymbol{v}_i - \boldsymbol{v})) = \sigma_i. \tag{2.2}$$

Here, $\boldsymbol{J}_i = \rho_i (\boldsymbol{v}_i - \boldsymbol{v})$ is the diffusion flow density of the ith trace species defined with respect to the barycentric flow, considered as being of Newtonian kind, where $\boldsymbol{v}$ denotes the barycentric velocity. This flux density may be generated by molecular, phoretic and/or sedimentation effects. The use of the barycentric velocity as a reference velocity, of course, is not the only possibility to describe such diffusion processes. Prigogine (1947) deduced from the entropy principle that in systems with mechanical equilibrium diffusion processes can be related to an arbitrary reference velocity. Herbert (1980, 1983) discussed the general application of Prigogine's diffusion theorem to the atmosphere and some specific invariance properties of the thermodynamic laws as well as various alternative relations to describe Fick-type mass diffusion in a (diluted) binary gas mixture such as the atmosphere. Nevertheless, in our paper the diffusion flow density, $\boldsymbol{J}_i$, is related to the barycentric flow.

Usually, this diffusion flow density is parameterised by (Herbert, 1983; Doms and Herbert, 1985)

$$\boldsymbol{J}_i \cong -\rho(\boldsymbol{D}_i \cdot \nabla \chi_i - v_{\mathrm{T},i} \chi_i \boldsymbol{k}), \tag{2.3}$$

where $\chi_i = \rho_i/\rho$ is the mass fraction, $\rho = M/V = \sum_{i=0}^{N} M_i/V = \sum_{i=0}^{N} \rho_i$ is the air density, and $\boldsymbol{D}_i$ is the 2nd-rank tensor of the molecular diffusion coefficients customarily considered as isotropic so that $\boldsymbol{D}_i = D_i \boldsymbol{E}$. Furthermore, $v_{\mathrm{T},i}$ is the terminal settling velocity, $\boldsymbol{E}$ is the identity tensor, and $\boldsymbol{k}$ is the unit vector in vertical direction. Both D_i and $v_{\mathrm{T},i}$ depend on the particle size distribution and the shape of the particles (Georgii, 1985). If the Brownian diffusion coefficient $D_i(\varepsilon)$ and the terminal settling velocity $v_{\mathrm{T},i}(\varepsilon)$ of aerosol particles of the mass ε as well as the size distribution $N(\varepsilon)$ of the particle ensemble are known, effective values for D_{i} and $v_{\mathrm{T},i}$ may be derived from (Kramm, 1991):

$$D_i = \frac{\int_0^\infty N(\varepsilon) \varepsilon D_i(\varepsilon)\, \mathrm{d}\varepsilon}{\int_0^\infty N(\varepsilon) \varepsilon\, \mathrm{d}\varepsilon}, \tag{2.4}$$

$$v_{\mathrm{T},i} = \frac{\int_0^\infty N(\varepsilon) \varepsilon v_{\mathrm{T},i}(\varepsilon)\, \mathrm{d}\varepsilon}{\int_0^\infty N(\varepsilon) \varepsilon\, \mathrm{d}\varepsilon}. \tag{2.5}$$

* Note that in the following equations a dot denotes the scalar product, and a colon marks the double scalar product.

Effects owing to sedimentation, however, are of minor importance in the cases of trace gases and small particles with diameters less than 1 μm (Sehmel, 1980; Kramm, 1991; Kramm et al., 1992).

For the turbulent atmospheric flow the averaged form of eq. (2.2) (also denoted as prognostic equation for the 1st moment or 1st-order balance equation) can be derived using Reynolds' averaging calculus, i.e., decomposition of any field function $\varphi(\boldsymbol{r})$ by $\varphi(\boldsymbol{r}) = \bar{\varphi} + \varphi'$ and subsequent averaging according to (Van Mieghem, 1949, 1973; Herbert, 1975)

$$\bar{\varphi} = \bar{\varphi}(\boldsymbol{r}) = \frac{1}{G}\int_G \varphi(\boldsymbol{r}, \boldsymbol{r}')\,\mathrm{d}G', \tag{2.6}$$

where $\bar{\varphi}$ is the average in space and time of $\varphi(\boldsymbol{r})$, and the fluctuation φ' is the difference between the former and the latter. Here, $\boldsymbol{r}$ is the four-dimensional vector of space and time in the original coordinate system, $\boldsymbol{r}'$ is that of the averaging domain G where its origin, $\boldsymbol{r}' = 0$, is assumed to be $\boldsymbol{r}$, and $\mathrm{d}G' = \mathrm{d}^3 r'\,\mathrm{d}t'$. The averaging domain G is given by $G = \int_G \mathrm{d}G'$. Hence, the quantity $\bar{\varphi}$ represents the mean values of $\varphi(\boldsymbol{r})$ for the averaging domain G at the location $\boldsymbol{r}$. Since $\bar{\bar{\varphi}} = \bar{\varphi}$ (Van Mieghem, 1949, 1973; Herbert, 1975), averaging the quantity $\varphi(\boldsymbol{r}) = \bar{\varphi} + \varphi'$ provides $\overline{\varphi'} = 0$. Thus, applying Reynolds' averaging calculus to eq. (2.2) yields:

$$\frac{\partial \overline{\rho_i}}{\partial t} + \nabla\cdot(\overline{\rho_i}\,\bar{\boldsymbol{v}}) + \nabla\cdot(\overline{\rho_i'\boldsymbol{v}'} + \overline{\boldsymbol{J}_i}) = \overline{\sigma_i}. \tag{2.7}$$

The quantity $\overline{\rho_i'\boldsymbol{v}'}$ may be denoted as the eddy flux density of the ith trace species. The 1st divergence term in eq. (2.7) contains the so-called convective and the 2nd divergence term contains the so-called non-convective flux density of matter. In the case of trace species, $|\overline{\boldsymbol{J}_i}| \ll |\overline{\rho_i'\boldsymbol{v}'}|$ is usually valid except for the immediate vicinity of solid walls. Here, the pipes, $|\ldots|$, denote the norm of a vector and a matrix, respectively.

The mean diffusion flow density, $\overline{\boldsymbol{J}_i} = \overline{\rho_i(\boldsymbol{v}_i - \boldsymbol{v})}$, may formally be written as

$$\overline{\boldsymbol{J}_i} = \overline{\rho_i}(\overline{\boldsymbol{v}_i} - \bar{\boldsymbol{v}}) + \overline{\rho_i'(\boldsymbol{v}_i' - \boldsymbol{v}')} \tag{2.8}$$

and in its parameterised form as

$$\overline{\boldsymbol{J}_i} \cong -\overline{\rho(\boldsymbol{D}_i\cdot\nabla\chi_i - v_{\mathrm{T},i}\chi_i\boldsymbol{k})}. \tag{2.9}$$

Because of the 2nd term on the right-hand-side of eq. (2.8), which contains also fluctuations of ρ_i, $\boldsymbol{v}_i$ and $\boldsymbol{v}$, this decomposition seems to be unfavourable. The macroscopic equation of continuity (de Groot and Mazur, 1969),

$$\frac{\partial \rho}{\partial t} + \nabla\cdot(\rho\boldsymbol{v}) = 0, \tag{2.10}$$

however, demands that $\sum_{i=0}^{N}\boldsymbol{J}_i = 0$ and $\sum_{i=1}^{N}\sigma_i = 0$. Thus, the equation of continuity for the turbulent atmospheric flow,

$$\frac{\partial \bar{\rho}}{\partial t} + \nabla\cdot(\bar{\rho}\,\bar{\boldsymbol{v}} + \overline{\rho'\boldsymbol{v}'}) = 0, \tag{2.11}$$

derived from eq. (2.10) by Reynolds averaging requires that $\sum_{i=0}^{N}\overline{\boldsymbol{J}_i} = 0$ and $\sum_{i=1}^{N}\overline{\sigma_i} = 0$ which agrees with $\sum_{i=0}^{N}\overline{\rho_i}\,\bar{\boldsymbol{v}} = \bar{\rho}\,\bar{\boldsymbol{v}}$ and $\sum_{i=0}^{N}\overline{\rho_i'\boldsymbol{v}'} = \sum_{i=0}^{N}\overline{\rho_i\boldsymbol{v}'} = \overline{\rho\boldsymbol{v}'} = \overline{\rho'\boldsymbol{v}'}$. Obviously, the mean diffusion flow given by eq. (2.8) fulfils the condition $\sum_{i=0}^{N}\overline{\boldsymbol{J}_i} = 0$ exactly. Note that, in contrast to eq. (2.10), a non-convective flux density of matter also occurs in eq. (2.11).

2.1. *Accounting for mixing*

As reflected by the aforementioned discussion of Venkatram (1993, 1998), Thomson (1995, 1998) and van Dop (1998), difficulties with the balance equation of trace species especially arise when mixing ratios are taken into account. Introducing, for instance, the mass fraction χ_i into eq. (2.2) and subsequent Reynolds averaging yield

$$\frac{\partial(\bar{\rho}\,\overline{\chi_i})}{\partial t} + \frac{\partial(\overline{\rho'\chi_i'})}{\partial t} + \nabla\cdot(\bar{\boldsymbol{v}}(\bar{\rho}\,\overline{\chi_i} + \overline{\rho'\chi_i'}) + \bar{\rho}\,\overline{\boldsymbol{v}'\chi_i'} + \overline{\chi_i}\,\overline{\rho'\boldsymbol{v}'} + \overline{\rho'\boldsymbol{v}'\chi_i'} + \overline{\boldsymbol{J}_i}) = \overline{\sigma_i}. \tag{2.12}$$

Even if we generally ignore the 3rd moment $\overline{\rho'\boldsymbol{v}'\chi_i'}$, we will obtain, at least, 4 additional 2nd moments, where three of them contain density fluctuations. As shown later, in the case of chemically reactive species, covariances of concentration fluctuations also occur. Obviously, the non-convective flux density of matter, $\overline{\rho'\boldsymbol{v}'}$, in eq. (2.11) corresponds to such a 2nd moment, too. It is well-known that 2nd moments containing density fluctuations also occur when the macroscopic balance equations for momentum and various energy forms as well as the equation of state are averaged in the sense of Reynolds. To derive a more practicable set of governing equations for the turbulent flow of the atmospheric boundary layer, all 2nd moments containing air density fluctuations are customarily ignored except in those terms expressing the effect of the gravity field — $\nabla\phi$ on the density fluctuations ρ' occurring in the mass field ρ. This is denoted as Boussinesq approximation and the corresponding flow is designated as Boussinesq fluid (Van Mieghem, 1973; Pichler, 1984). Consequently, the Boussinesq approximation leads to the requirement: $\overline{\rho' \boldsymbol{v}'} = \sum_{i=0}^{N} \overline{\rho_i' \boldsymbol{v}'} = 0$.

The term $\overline{\rho' \boldsymbol{v}'}$ should, however, be taken into account to appreciably correct the vertical eddy flux densities of trace species with respect to density fluctuations. As suggested by Webb et al. (1980) for moist air, the vertical eddy flux densities of sensible heat and water vapour are able to generate a mean vertical velocity $\overline{w} = -\overline{\rho_0' w'}/\overline{\rho_0} \neq 0$ (this agrees with their hypothesis that the mean vertical flux density of a dry air constituent should be zero, i.e., $\overline{\rho_0 w} = 0$), even if horizontally homogeneous conditions are considered. Here, w' is the fluctuation of the vertical velocity, and $\overline{\rho_0' w'}$ is the vertical eddy flux density of dry air that has to be related to the vertical eddy flux densities of sensible heat and water vapour (Webb et al., 1980). Hence, the total vertical flux density of a trace species is then given by $F_i = \overline{\rho_i}\,\overline{w} + \overline{\rho_i' w'}$ (see also eq. (2.7)), and the vertical dispersion of such trace species seems to be appreciably affected by the eddy flux densities of sensible heat and water vapour. But the conventional Webb correction is based on a popular fallacy because, as aforementioned, $\overline{\rho' \boldsymbol{v}'}$ and, hence, $\overline{\rho' w'}$ must be equal to zero, i.e., $\overline{\rho_0' w'} = -\overline{\rho_1' w'}$, if a Boussinesq fluid is considered. As demonstrated in Section 10, the heat transfer effect mentioned above is mainly the result of an inconsistent utilisation of the Boussinesq approximation.

The results of observed vertical eddy flux densities may appreciably be modified by applying the Webb correction to these results. Based on their direct measurements of the vertical eddy flux densities of ozone and sensible heat performed by eddy covariance techniques several metres above the surface of a desert area, Güsten et al. (1996), for instance, found that under very dry conditions the Webb correction would contribute to up to 40% of the measured ozone flux densities. Since at the Earth's surface, wind and density fluctuations vanish, this flux correction would imply an appreciable variation of the ozone flux density with height between the Earth's surface and the measuring level owing to turbulence. Thus, turbulence would act like an ozone source. From a physical perspective this consequence seems to be doubtful. Obviously, the effects of strong eddy flux densities of sensible heat occurring over the desert area are responsible for this questionable result. Hence, density fluctuations and their treatment play not only a prominent role in theoretical derivations of 1st-order balance equations for trace species and the parameterisation of eddy flux densities by 1st-order closure principles as controversially discussed by Venkatram (1993, 1998), Thomson (1995, 1998) and van Dop (1998), but also in determining vertical eddy flux densities of trace species from observation with a sufficient degree of accuracy.

2.2. Density-weighted averaging procedures

2.2.1. Hesselberg's averaging calculus. Obviously, simple Reynolds averaging will lead to various short-comings in the set of governing equations for the turbulent atmospheric flow, even if this averaging techniques can accurately be performed. If we ignore density fluctuation terms, the possibility to describe physical processes as a whole will clearly be restricted, as already pointed out by Montgomery (1954) and Fortak (1969). The key questions that still remain are (1) how to average the governing macroscopic equations in the case of turbulent atmospheric flows and (2) what are the consequences of such an averaging, not only for atmospheric trace species, but also for total mass, momentum, and various energy forms.

As argued by Pichler (1984), Cox (1995), Kramm et al. (1995), Thomson (1995) and Venkatram (1998), the density-weighted averaging procedure suggested by Hesselberg (1926) is well appropriate to formulate the balance equation of atmospheric trace species. Hesselberg's averaging calculus is based on (Van Mieghem, 1949, 1973; Herbert, 1975)

$$\hat{\varphi} = \hat{\varphi}(\boldsymbol{r}) = \frac{\int_G \rho(\boldsymbol{r}, \boldsymbol{r}')\varphi(\boldsymbol{r}, \boldsymbol{r}')\,\mathrm{d}G'}{\int_G \rho(\boldsymbol{r}, \boldsymbol{r}')\,\mathrm{d}G'} = \frac{\overline{\rho\varphi}}{\overline{\rho}}. \tag{2.13}$$

The roof (ˆ) denotes the density-weighted average according to Hesselberg (1926) and the double prime (″) marks the departure from that. It is obvious that $\overline{\rho\varphi''} = 0$. Arithmetic rules can be found, for instance, in Van Mieghem (1949, 1973), Herbert (1975), Pichler (1984), and Kramm et al. (1995).

Applying Hesselberg's averaging calculus instead of that of Reynolds leads to several prominent advantages: (1) The equation of continuity (Van Mieghem, 1949, 1973; Pichler, 1984; Cox, 1995; Kramm et al., 1995),

$$\frac{\partial \bar{\rho}}{\partial t} + \nabla \cdot (\bar{\rho} \hat{\boldsymbol{v}}) = 0, \tag{2.14}$$

and the equation of state (see eq. (3.17)) keep their forms. In contrast to eq. (2.11), eq. (2.14) does not contain any non-convective flux density. (2) The mean value of kinetic energy can exactly be split into the kinetic energy of the mean motion and mean value of the kinetic energy of the eddying motion (Van Mieghem, 1949, 1973; Pichler, 1984; Kramm et al., 1995), i.e.:

$$\frac{1}{2}\overline{\rho \boldsymbol{v}^2} = \frac{1}{2}\bar{\rho}\hat{\boldsymbol{v}}^2 + \frac{1}{2}\overline{\rho \boldsymbol{v}''^2}. \tag{2.15}$$

As pointed out by Thomson (1995), density-weighted averages are the common way to define averages in studies of highly compressible turbulent flows (see also Libby and Williams, 1980), probably the most natural way to define averages. Note that, for instance, the effects of dynamic pressure, $\rho \boldsymbol{v}^2$, are used to measure wind speeds mechanically (e.g., *Handbook of meteorological instruments*, M.O. 577, Part I, U.K. Meteorological Office, 1956). Jones and Whitelaw (1982) argued, therefore, that many experimental measurements do, although unintentionally, yield values that have, at least, an element of density weighting. This fact does remain something of an unresolved difficulty (see also Cox, 1995). Furthermore, to experimentally derive density-weighted averages, temperature and pressure fluctuations have to be measured with amplitude and phase fidelity. Following, for instance, Wilczak et al. (1995), such measurements can be performed with a sufficient degree of accuracy.

Meanwhile, Hesselberg's (1926) averaging calculus is erroneously denoted in the literature as Favre average (Hinze, 1975; Cox, 1995; Veynante and Poinsot, 1997; Gatski, 1997). Hesselberg, one of V. Bjerknes' famous Carnegie assistants, was director of the Norwegian Meteorological Institute from 1915 to 1955. His averaging calculus was adopted by theoretical meteorologists like Ertel (1943), Miller (1951), Montgomery (1948, 1954), and Van Mieghem (1949, 1951) long before it was re-established by Favre — to the best of our knowledge — in 1958 (*C.R. Acad. Sci. Paris* **246**, as cited by Kampé de Fériet in *Advances in Geophysics* **6**, 1959).

2.2.2. Swinbank's averaging calculus. It can easily be shown that also the averaging calculus, suggested by Swinbank (1951) and strictly used, for instance, by Bernhardt (1964, 1965, 1972) as well as Businger and Deardorff (1968), which considers the fluctuations of the vector of momentum,

$$\overline{\rho \boldsymbol{v} \varphi} = \overline{\rho \boldsymbol{v}}\, \bar{\varphi} + \overline{(\rho \boldsymbol{v})' \varphi'}, \tag{2.16}$$

where φ stands for $\boldsymbol{v}$, χ_i etc., allows to exactly split the mean value of kinetic energy. Also the equation of continuity keeps its form. However, as exemplary shown by Montgomery (1954) for the vertical eddy flux density of enthalpy, the flux densities $\overline{\rho \boldsymbol{v}'' \varphi''}$ and $\overline{(\rho \boldsymbol{v})' \varphi'}$ differ from each other because

$$\overline{(\rho \boldsymbol{v})' \varphi'} = \overline{\rho \boldsymbol{v}'' \varphi''} + \hat{\boldsymbol{v}} \overline{\rho' \varphi'}. \tag{2.17}$$

Obviously, for $\varphi = \boldsymbol{v}$ the 2nd-rank tensor of turbulent momentum transfer, usually called Reynolds stress tensor, will become symmetric if Hesselberg's (or Reynolds') calculus is considered, i.e., $\boldsymbol{F} = \overline{\rho \boldsymbol{v}'' \boldsymbol{v}''}$, in complete contrast to that of Swinbank which provides a non-symmetric tensor, $\overline{(\rho \boldsymbol{v})' \boldsymbol{v}'}$, where its non-symmetric character may be manifested by $\hat{\boldsymbol{v}} \overline{\rho' \boldsymbol{v}'}$ (see eq. (2.17)). Bernhardt (1965) showed that the existence of this non-symmetric tensor is not in contradiction to the angular momentum theorem that is generally be considered to verify the symmetry of the molecular stress tensor. The two forms of the Reynolds stress tensor, of course, will not differ from each other if the density-velocity covariance term is neglected. Because of the non-symmetric character of $\overline{(\rho \boldsymbol{v})' \boldsymbol{v}'}$, which strongly requires tensor-algebraic attention, Swinbank's calculus seems to be more bulky than that of Hesselberg. Thus, the latter will generally be applied within the framework of this contribution. It can also be related to that of Reynolds by (Van Mieghem, 1973; Cox, 1995; Kramm et al., 1995; Herbert, 1995)

$$\hat{\varphi} = \bar{\varphi} + \frac{\overline{\rho' \varphi'}}{\bar{\rho}} = \bar{\varphi}\left\{1 + \frac{\overline{\rho' \varphi'}}{\bar{\rho}\,\bar{\varphi}}\right\}, \tag{2.18}$$

where $\hat{\varphi}$ and $\overline{\varphi}$ are nearly equal when $\overline{\rho'\varphi'}/\{\overline{\rho}\,\overline{\varphi}\} \ll 1$.

In the following, the set of governing balance equations for the turbulent flow of a compressible atmosphere are re-formulated on the basis of Hesselberg's (1926) averaging calculus. To distinguish between the approximated equation set for the Boussinesq fluid and this re-formulated one, the turbulent flow of the compressible atmosphere for which the re-formulated governing balance equations of matter, momentum and various energy forms as well as 2nd moments like eddy flux densities are valid may be denoted as Hesselberg fluid. Based on the balance equations for dry air, water vapour and trace species for the Hesselberg fluid, the so-called Webb correction is re-evaluated to exemplary show that an inconsistently performed Boussinesq approximation is responsible for the physically inadequate result that eddy flux densities of trace species, and, hence, their vertical dispersion in the atmospheric boundary layer are affected by both the eddy flux density of water vapour and that of sensible heat (see Section 10).

3. The 1st-order balance equations for the Hesselberg fluid

3.1. *The 1st-order balance equations of trace species*

Averaging eq. (2.2) in the sense of Hesselberg provides (Cox, 1995; Kramm et al., 1995)

$$\frac{\partial(\overline{\rho}\hat{\chi}_i)}{\partial t} + \nabla\cdot(\overline{\rho}\hat{\boldsymbol{v}}\hat{\chi}_i) + \nabla\cdot(\overline{\rho\boldsymbol{v}''\chi_i''} + \overline{\boldsymbol{J}}_i) = \overline{\sigma}_i, \tag{3.1}$$

where again the conditions $\sum_{i=0}^{N}\overline{\boldsymbol{J}}_i = 0$ and $\sum_{i=1}^{N}\overline{\sigma}_i = 0$ are fulfilled. Furthermore, as required by eq. (2.14), the conditions $\sum_{i=0}^{N}\overline{\rho}\hat{\boldsymbol{v}}\hat{\chi}_i = \overline{\rho}\hat{\boldsymbol{v}}$ and $\sum_{i=0}^{N}\overline{\rho\boldsymbol{v}''\chi_i''} = 0$ are fulfilled, too. Obviously, the 1st-order equation (3.1) is exact, although mass fractions are considered. It completely agrees with eq. (2.7) and should generally be used in theoretical and modelling studies. Even if the eddy flux density $\boldsymbol{F}_i = \overline{\rho\boldsymbol{v}''\chi_i''}$ is parameterised by 1st-order closure principles (flux-gradient relationships) according to Boussinesq (1877) and Schmidt (1925),

$$\boldsymbol{F}_i = -\overline{\rho}\boldsymbol{K}_i\cdot\nabla\hat{\chi}_i, \tag{3.2}$$

an additional 2nd moment as mentioned by Venkatram (1993) and van Dop (1998) will not appear. Here, $\boldsymbol{K}_i$ is the non-isotropic 2nd-rank tensor of eddy diffusivities (Batchelor, 1949; Hinze, 1975). By considering the entropy balance for turbulent atmospheric flows, Herbert (1975) showed that such eddy diffusivities must be positive definite. As argued by several authors (Van Mieghem, 1973, Businger, 1973; Herbert, 1975; Venkatram, 1993), the eddy flux density should be "proportional" to the gradient of the averaged mass fraction. If we introduce this flux-gradient relationship into eq. (3.1), we will obtain an expression similar to eq. (2) of Thomson (1995) and eq. (14) of van Dop (1998). But, in contrast to the latter, no simplification is necessary to derive it.

Taking the equation of continuity (2.14) into account, an equivalent form of eq. (3.1),

$$\overline{\rho}\frac{\mathrm{d}\hat{\chi}_i}{\mathrm{d}t} + \nabla\cdot(\overline{\boldsymbol{J}}_i + \boldsymbol{F}_i) = \overline{\sigma}_i, \tag{3.3}$$

designated as Eulerian form, can be derived, where the substantial derivative with respect to time of any property, d/dt, is expressed by Euler's operator for the Hesselberg fluid:

$$\frac{\mathrm{d}}{\mathrm{d}t} = \frac{\partial}{\partial t} + \hat{\boldsymbol{v}}\cdot\nabla. \tag{3.4}$$

Obviously, only the divergence of non-convective transports occurs in the Eulerian form of balance equations like eq. (3.3). Furthermore, the derivation of eq. (3.3) from eq. (3.1) by using the equation of continuity (2.14) can exactly be performed for the Hesselberg fluid. Such a derivation is impossible in the case of Reynolds averaging because an expression for Euler's operator similar to eq. (3.4) can only be deduced when the density fluctuation terms $\partial(\overline{\rho'\chi_i'})/\partial t$ and $\nabla\cdot(\overline{\boldsymbol{v}}\,\overline{\rho'\chi_i'} + \overline{\rho'\boldsymbol{v}'\chi_i'})$ are ignored as done for the Boussinesq fluid. Consequently, the possibility to introduce an exact form of Euler's operator for the averaged turbulent atmospheric flow can also be considered as a prominent advantage of Hesselberg's (1926) averaging calculus.

3.1.1. Segregation effects. Segregation effects play a prominent role in turbulent plumes of reacting species (Georgopoulos and Seinfeld, 1986) and in turbulent diffusion flames (Moss, 1995). Since the dispersion of highly reactive trace species can strongly be affected by chemical reactions, also the corresponding segregation effects have to be considered.

In the case of homogeneous gas phase reactions, the production or depletion terms, $\overline{\sigma_i}$, may be split into

$$\overline{\sigma_i} = f_i(\overline{\rho_1}, \ldots, \overline{\rho_N}) + f_i(\rho'_1, \ldots, \rho'_N), \tag{3.5}$$

where the right-hand side terms are given by

$$f_i(\overline{\rho_1}, \ldots, \overline{\rho_N}) = \sum_{j=1}^{N} \overline{k_{ij}}\,\overline{\rho_j} + \sum_{\substack{m=1\\ n\geqslant m}}^{N} \overline{k_{imn}}\,\overline{\rho_m}\,\overline{\rho_n}, \tag{3.6}$$

and

$$f_i(\rho'_1, \ldots, \rho'_N) = \sum_{j=1}^{N} \overline{k'_{ij}\rho'_j} + \sum_{\substack{m=1\\ n\geqslant m}}^{N} (\overline{k_{imn}}\,\overline{\rho'_m\rho'_n} + \overline{k'_{imn}\rho'_m}\,\overline{\rho_n} + \overline{k'_{imn}\rho'_n}\,\overline{\rho_m} + \overline{k'_{imn}\rho'_m\rho'_n}), \tag{3.7}$$

respectively (see also Cox, 1995),

$$f_i(\overline{\rho_1}, \ldots, \overline{\rho_N}) = \sum_{j=1}^{N} \overline{\rho}\hat{k}_{ij}\hat{\chi}_j + \sum_{\substack{m=1\\ n\geqslant m}}^{N} \hat{C}_{imn}\hat{\chi}_m\hat{\chi}_n, \tag{3.8}$$

$$f_i(\rho'_1, \ldots, \rho'_N) = \sum_{j=1}^{N} \overline{\rho k''_{ij}\chi''_j} + \sum_{\substack{m=1\\ n\geqslant m}}^{N} (\hat{C}_{imm}\overline{\rho\chi''_m\chi''_n} + \overline{\rho C''_{imn}\chi''_m}\hat{\chi}_n + \overline{\rho C''_{imn}\chi''_n}\hat{\chi}_m + \overline{\rho C''_{imn}\chi''_m\chi''_n}), \tag{3.9}$$

where C_{imn} is defined by $C_{imn} = \rho k_{imn}$. Here, the chemical reactions that affect the ith partial density are usually expressed as 1st-order and 2nd-order reactions by using 1st-order and 2nd-order rate constants k_{ij} (negative when $j = i$) and k_{imn} (negative when $m = i$ and/or $n = i$), respectively. In the latter case, complete mixing at the molecular level is required to produce a chemical reaction between two species (Stockwell, 1995). Therefore, the related chemical reaction rates are calculated from the partial densities of these two species at a single point in space. Note that 3rd-order reactions like the ozone production, $O(^3P) + O_2 + M \rightarrow O_3 + M$, are often dealt with as (pseudo-)second-order reactions, where the concentration of the third body, M, is incorporated into the reaction rate constant. Since reaction rate constants of thermal reactions conventionally written in the Arrhenius form (Seinfeld, 1986) $k = A_0 \exp(-E_A/(RT))$ depend, of course, on temperature, T, temperature fluctuations may also be responsible for fluctuations of reaction rate constants as expressed in eqs. (3.7) and (3.9). In many cases, however, where the magnitude of the activation energy, E_A, is small compared to the product RT (R is the universal gas constant), these fluctuations can be neglected. Thus, eqs. (3.7) and (3.9) may reduce to their conventional form

$$f_i(\rho'_i, \ldots, \rho'_N) = \sum_{\substack{m=1\\ n\geqslant m}}^{N} \overline{k_{imn}}\,\overline{\rho'_m\rho'_n} = \sum_{\substack{m=1\\ n\geqslant m}}^{N} \hat{C}_{imn}\overline{\rho\chi''_m\chi''_n}. \tag{3.10}$$

3.1.2. Example. Considering, for instance, the chemical reactions between ozone and NO (R_1) as well as ozone and NO_2 (R_2) in a turbulent flow, the correct reaction rates R_1 and R_2 are given by (Lenschow, 1982)

$$R_1 = \overline{k_1}(\overline{[O_3]}\,\overline{[NO]} + \overline{[O_3]'[NO]'}) = \overline{k_1}\,\overline{[O_3]}\,\overline{[NO]}\left\{1 + \frac{\overline{[O_3]'[NO]'}}{\overline{[O_3]}\,\overline{[NO]}}\right\}, \tag{3.11}$$

$$R_2 = \overline{k_2}(\overline{[O_3]}\,\overline{[NO_2]} + \overline{[O_3]'[NO_2]'}) = \overline{k_2}\,\overline{[O_3]}\,\overline{[NO_2]}\left\{1 + \frac{\overline{[O_3]'[NO_2]'}}{\overline{[O_3]}\,\overline{[NO_2]}}\right\}, \tag{3.12}$$

respectively. Here, the parentheses denote the concentrations, for instance, in ppb. The quantities $\overline{k_1}$ and $\overline{k_2}$ are the respective mean reaction rate constants experimentally derived, and the ratios

$$I_{s,1} = \overline{[O_3]'[NO]'}/(\overline{[O_3]}\,\overline{[NO]})$$

and

$$I_{s,2} = \overline{[O_3]'[NO_2]'}/(\overline{[O_3]}\,\overline{[NO_2]})$$

are the so-called intensities of segregation (Lenschow, 1982; Schumann, 1989; Nieuwstadt and Meeder, 1997). Obviously, the intensity of segregation, $-1 \leqslant I_s \leqslant 0$, may reduce the efficiency of the *true* reaction rate constants derived from laboratory experiments, and may lead to a decrease in the production rates of NO_2 and NO_3 (Vilà-Guerau de Arellano and Duynkerke, 1993).

Segregation effects are also related to fluctuations of partial densities, and they should not be ignored. Fig. 1 shows examples of the intensity of segregation for the chemical reactions between NO_2 and O_3 as well as NO and O_3, respectively. The results illustrated were obtained during the 1st field experiment of the German project SANA (Scientific Program on the Recovery of the Atmosphere over the New Federal Countries of Germany). It took place over a flat terrain near Eisdorf village, 15 km south-west of Leipzig/ Saxony in two periods of intensive sampling in

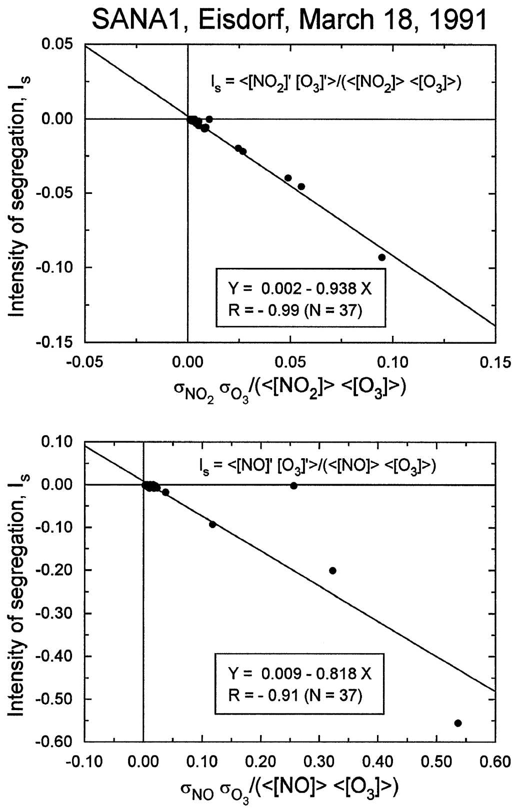

Fig. 1. Intensity of segregation for the chemical reactions between NO_2 and O_3 (above) as well as NO and O_3 (below). Here, the brackets, $\langle \ldots \rangle$, denote the Reynolds mean.

March 1991 to determine, among other things, the dry deposition fluxes of atmospheric trace species. The Eisdorf field site was agriculturally used during the field campaign. At the beginning of the campaign the ground was a wet bare soil occasionally frozen and it was drying out subsequently more and more. Whereas at the end of the campaign small wheat shoots of about 5 cm length homogeneously covered the ground. This field site was mainly affected by the conurbation of Leipzig. The results presented here are based on eddy covariance measurements carried out at a height of 5.8 m above ground by Meixner's working group (see also Nestlen et al., 1993).

Obviously, the reaction rates R_1 and R_2 are limited by the turbulent mixing of the chemical reactants, and the segregation effects described in eqs. (3.11) and (3.12) may become significant, i.e., concentration fluctuations will touch reaction rates because such reaction rates are diffusion limited as may be expressed by the Damköhler number, $N_D = \tau_d/\tau_c > 1$, the ratio of the characteristic diffusion time, τ_d, to the characteristic chemical reaction time, τ_c, for a given reaction (Damköhler, 1940; McRae et al., 1982; Stockwell, 1995; Moss, 1995). Reducing, for instance, in a Seinfeld-type kinetic mechanism for photochemical smog (Seinfeld, 1986), as used by Kramm (1987) and Kramm et al. (1994), the reaction rate constant $\overline{k_1}$ by 20% and $\overline{k_2}$ by 10% leads to appreciable deviations from those results obtained with the original values of $\overline{k_1}$ and $\overline{k_2}$ (Fig. 2).

The results shown in Figs. 1, 2 substantiate that (1) an evaluation of Eulerian air pollution models for chemically reactive trace constituents only on the basis of the 1st moments of concentrations, wind speed, temperature and humidity seems to be highly questionable, (2) such numerical models can only be improved by concurrently computing segregation effects which requires turbulence closure principles higher than the one-and-a-half-order closure, and (3) fast-response physico-chemical analysers have to be (further) developed to directly determine vertical eddy flux densities of trace constituents and segregation effects owing to turbulence. Results of such direct measurements are indispensable to set-up a *true* platform for model evaluation that implies not only a comparison of calculated and observed distributions of

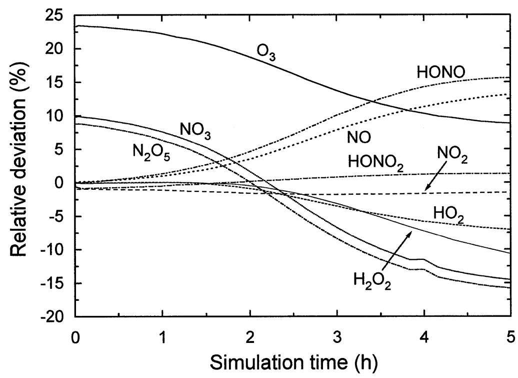

Fig. 2. Relative deviations for different nitrogen species owing to reduced values of the reaction rate constants $\overline{k_1}$ (reduced by 20%) and $\overline{k_2}$ (reduced by 10%) used in a Seinfeld-type mechanism for photochemical smog (Seinfeld, 1986) as described by Kramm (1987) and Kramm et al. (1994).

1st moments (necessary condition), but also a comparison of the calculated and observed distributions of 2nd moments like eddy fluxes, variances and covariances (sufficient condition).

3.2. 1st-order balance equations of dry air, water substances, momentum, and various energy forms

As aforementioned, we have not only to consider the balance equations of atmospheric trace species, but also those of water substances, momentum, and various energy forms to avoid any inconsistency in theoretical considerations and modelling studies. By considering Hesselberg's averaging calculus and Euler's operator (3.4), the complete set of 1st-order balance equations for the Hesselberg fluid may be written as (Van Mieghem, 1949, 1973; Eliassen and Kleinschmidt, 1957; Herbert, 1975; Pichler, 1984):

3.2.1. Balance equations of dry air and water substances

$$\bar{\rho}\frac{\mathrm{d}\hat{m}_k}{\mathrm{d}t} + \nabla\cdot(\overline{\boldsymbol{J}_k} + \boldsymbol{F}_k) = \overline{I_k}, \tag{3.13}$$

with

$$\sum_{k=0}^{3} \hat{m}_k = 1 \Rightarrow \hat{m}_0 = 1 - \sum_{k=1}^{3} \hat{m}_k,$$

$$\overline{\boldsymbol{J}_k} = \overline{\rho_k(\boldsymbol{v}_k - \boldsymbol{v})} \cong -\bar{\rho}(\boldsymbol{D}_k \cdot \nabla \hat{m}_k - v_{\mathrm{T},k}\hat{m}_k\delta_{k,n}\boldsymbol{k})$$

for $n = 2, 3$,

$$\boldsymbol{F}_k = \overline{\rho \boldsymbol{v}'' m_k''} \Rightarrow \sum_{k=0}^{3} \boldsymbol{F}_k = 0 \Rightarrow \boldsymbol{F}_0 = -\sum_{k=1}^{3} \boldsymbol{F}_k,$$

$$\overline{I_0} = 0 \Rightarrow \sum_{k=1}^{3} \overline{I_k} = 0 \Rightarrow \overline{I_1} = -\sum_{k=2}^{3} \overline{I_k},$$

$$\bar{\rho}\hat{\boldsymbol{v}} = \overline{\rho \boldsymbol{v}} = \sum_{k=0}^{3} \overline{\rho_k \boldsymbol{v}_k} \Rightarrow \sum_{k=0}^{3} \overline{\boldsymbol{J}_k} = 0 \Rightarrow \overline{\boldsymbol{J}_0} = -\sum_{k=1}^{3} \overline{\boldsymbol{J}_k}.$$

Here, $\rho_k = M_k/V$ is the partial density where the index k refers to dry air ($k = 0$), water vapour ($k = 1$), water ($k = 2$), and ice ($k = 3$). The partial mass, the related mass fraction and the corresponding phase transition rate are denoted by M_k, $m_k = M_k/M = \rho_k/\rho$, and $\overline{I_k}$, respectively. Since dry air, water and ice contain trace species (Georgii, 1965; Scott and Hobbs, 1967; Georgii, 1985), where several of them may chemically interact also with water vapour, the partial density of a trace species should be denoted as ρ_i^k. Even though small fractions of dry air, namely the trace species, can homogeneously and heterogeneously react with water substances, the quantity $\overline{I_0}$ may always be considered as equal to zero so that only two independent phase transition rates exist. Furthermore, the diffusion flow density $\overline{\boldsymbol{J}_k}$ may represent mean molecular, phoretic and sedimentation transports and $\boldsymbol{F}_k$ the eddy flux density, where in both cases only three flux densities are independent. In the case of dry air and water vapour, $|\overline{\boldsymbol{J}_k}| \ll |\boldsymbol{F}_k|$ is usually valid except for the immediate vicinity of solid walls. Moreover, $\boldsymbol{v}_k$ is the diffusion velocity, $\boldsymbol{D}_k$ is the 2nd-rank tensor of molecular diffusivities customarily considered as isotropic so that $\boldsymbol{D}_k = D_k\boldsymbol{E}$, $v_{\mathrm{T},k}$ represents the terminal settling velocity, and $\delta_{k,n}$ is the Kronecker symbol. Obviously, eqs. (3.3) and (3.13) are similar and must together obey the equation of continuity (2.14).

3.2.2. Balance equation for momentum (Newton's 2nd axiom)

$$\bar{\rho}\frac{\mathrm{d}\hat{\boldsymbol{v}}}{\mathrm{d}t} + \nabla\cdot(\bar{p}\boldsymbol{E} + \overline{\boldsymbol{J}} + \boldsymbol{F}) = -\bar{\rho}\nabla\bar{\phi} - 2\bar{\rho}\Omega\times\hat{\boldsymbol{v}}, \tag{3.14}$$

with

$$\overline{\boldsymbol{J}} = \bar{\rho}\nu(\nabla\hat{\boldsymbol{v}} + (\nabla\hat{\boldsymbol{v}})^{\mathrm{T}}) + \left(\mu_{\mathrm{d}} - \frac{2}{3}\bar{\rho}\nu\right)(\nabla\cdot\hat{\boldsymbol{v}})\boldsymbol{E},$$

$$\boldsymbol{F} = \overline{\rho\boldsymbol{v}''\boldsymbol{v}''}, \quad \bar{\phi} = \phi = \phi_{\mathrm{a}} + \phi_z.$$

Here, $\bar{p}$ is the mean air pressure, Ω is the angular velocity of the Earth, $\overline{\boldsymbol{J}}$ is the mean Stokes stress tensor that corresponds to a symmetric 2nd-rank tensor ($(\nabla\hat{\boldsymbol{v}})^{\mathrm{T}}$ means $\hat{\boldsymbol{v}}\nabla$, i.e., the Nabla operator acts on $\hat{\boldsymbol{v}}$, but the tensorial product is arranged as shown), ν is the kinematic viscosity, μ_{d} the bulk viscosity (nearly zero for most gases), ϕ, ϕ_{a}, and ϕ_z are the geopotential, the attraction potential, and the centrifugal potential, respectively. As already mentioned, averaging the macroscopic balance equation of momentum in the sense of Hesselberg (or Reynolds) yields that also the Reynolds stress tensor becomes symmetric.

It is well-known that the velocity gradient, $\nabla\hat{\boldsymbol{v}}$, can be split into a symmetric tensor, $\boldsymbol{V}_{\mathrm{s}} = \frac{1}{2}(\nabla\hat{\boldsymbol{v}} + (\nabla\hat{\boldsymbol{v}})^{\mathrm{T}})$, and an antisymmetric tensor, $\boldsymbol{V}_{\mathrm{a}} = \frac{1}{2}(\nabla\hat{\boldsymbol{v}} - (\nabla\hat{\boldsymbol{v}})^{\mathrm{T}})$, so that $\nabla\hat{\boldsymbol{v}} = \boldsymbol{V}_{\mathrm{s}} + \boldsymbol{V}_{\mathrm{a}}$. Obviously, $\boldsymbol{V}_{\mathrm{s}}$ characterises the deformation and $\boldsymbol{V}_{\mathrm{a}}$ characterises the rotation of the flow field. The deformation tensor, $\boldsymbol{V}_{\mathrm{s}}$, may further be split into an isotropic tensor given by $V^*\boldsymbol{E}$, where $V^* = \frac{1}{3}(\nabla\hat{\boldsymbol{v}}):\boldsymbol{E} = \frac{1}{3}\nabla\cdot\hat{\boldsymbol{v}}$, and a deviatoric traceless tensor $\boldsymbol{V}^\circ = \boldsymbol{V}_s - V^*\boldsymbol{E} = \frac{1}{2}(\nabla\hat{\boldsymbol{v}} + (\nabla\hat{\boldsymbol{v}})^T) - \frac{1}{3}(\nabla\cdot\hat{\boldsymbol{v}})\boldsymbol{E}$. Obviously, the mathematical reduction of this traceless tensor (i.e., double scalarly multiplying by $\boldsymbol{E}$) leads to $\boldsymbol{V}^\circ:\boldsymbol{E} = 0$. The Stokes stress tensor may also be written as $\overline{\boldsymbol{J}} = 2\bar{\rho}\nu\boldsymbol{V}^\circ + 3\mu_d V^*\boldsymbol{E}$. Without loss of generality, the Reynolds stress tensor can also be split into a bulk stress tensor, $F^*\boldsymbol{E}$, where $F^* = \frac{1}{3}\boldsymbol{F}:\boldsymbol{E} = \frac{1}{3}\overline{\rho\boldsymbol{v}''^2}$, and a traceless stress tensor, $\boldsymbol{F}^\circ = \boldsymbol{F} - F^*\boldsymbol{E} = \overline{\rho\boldsymbol{v}''\boldsymbol{v}''} - \frac{1}{3}\overline{\rho\boldsymbol{v}''^2}\boldsymbol{E}$, so that $\boldsymbol{F} = F^*\boldsymbol{E} + \boldsymbol{F}^\circ$. It is clear that $\boldsymbol{F}^\circ:\boldsymbol{E}$ is equal to zero, too.

3.2.3. Balance equation of thermal energy (1st law of thermodynamics)

$$\bar{\rho}\frac{\mathrm{d}\hat{e}}{\mathrm{d}t} + \nabla\cdot(\overline{\boldsymbol{R}} + \overline{\boldsymbol{J}}_h + \boldsymbol{F}_h) = -\bar{p}\nabla\cdot\hat{\boldsymbol{v}} + \overline{\boldsymbol{v}''\cdot\nabla p} - \overline{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}} - \overline{\boldsymbol{J}:\nabla\boldsymbol{v}''}, \qquad (3.15a)$$

with $\overline{\boldsymbol{J}}_h = -c_p\bar{\rho}\boldsymbol{\alpha}\cdot\nabla\hat{T}$ and $\boldsymbol{F}_h = \overline{\rho\boldsymbol{v}''h''}$. Here, e is the specific internal energy, h is the specific enthalpy that is related to the specific internal energy by $h = e + p/\rho$, $\overline{\boldsymbol{R}}$ represents the mean radiative flux density, $\overline{\boldsymbol{J}}_h$ and $\boldsymbol{F}_h$ are the mean molecular and turbulent flux densities of enthalpy, where $|\overline{\boldsymbol{J}}_h| \ll |\boldsymbol{F}_h|$ is usually valid except for the immediate vicinity of solid walls, and $\boldsymbol{\alpha} = \alpha\boldsymbol{E}$ is the 2nd-rank tensor of thermal diffusivities customarily considered to be isotropic. The term $\overline{\boldsymbol{v}''\cdot\nabla p}$ corresponds to the work that has to be done along with or against pressure gradient forces. Thus, especially Archimedian effects become relevant that transfer sensible and latent heat. Obviously, $\overline{\boldsymbol{v}''\cdot\nabla p}$ can be both positive or negative mainly depending on the thermal stratification of the atmosphere.

The dissipation of kinetic energy plays an important role in the mechanic energy balance of turbulent flows while the self-heating of the air owing to internal friction is of minor importance (Rotta, 1972). The term $-\overline{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}} > 0$ represents the direct dissipation of kinetic energy caused by the gradient of the mean wind vector, and the quantity $\varepsilon = -\overline{\boldsymbol{J}:\nabla\boldsymbol{v}''} > 0$ is the turbulent dissipation of kinetic energy into heat owing to the gradient of the wind vector fluctuations. Even though the fluctuations of the wind vector are usually small as compared to the mean wind vector ($|\boldsymbol{v}''| \ll |\hat{\boldsymbol{v}}|$) the opposite is true for the gradients of these quantities ($|\nabla\boldsymbol{v}''| \gg |\nabla\hat{\boldsymbol{v}}|$). This phenomenon is connected with a great intensity of rotation and is characteristic for all turbulent flows. Except for the immediate vicinity of solid walls, a consequence is that turbulent dissipation exceeds that of direct dissipation by several orders of magnitude depending on the Reynolds number (Rotta, 1972). Since $\hat{h} = \hat{e} + \bar{p}/\bar{\rho}$, an equivalent form of the 1st law of thermodynamics can be derived by using a Legendre transformation. In doing so, the substantial derivative of with respect to time is given by

$$\frac{\mathrm{d}\hat{e}}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}t}\left\{\hat{h} - \frac{\bar{p}}{\bar{\rho}}\right\} = \frac{\mathrm{d}\hat{h}}{\mathrm{d}t} - \frac{1}{\bar{\rho}}\frac{\mathrm{d}\bar{p}}{\mathrm{d}t} + \frac{\bar{p}}{\bar{\rho}^2}\frac{\mathrm{d}\bar{\rho}}{\mathrm{d}t}.$$

Considering Euler's operator (see eq. (3.4)) and the equation of continuity (see eq. (2.14)) yields

$$\frac{\mathrm{d}\bar{\rho}}{\mathrm{d}t} = \frac{\partial\bar{\rho}}{\partial t} + \hat{\boldsymbol{v}}\cdot\nabla\bar{\rho} = \frac{\partial\bar{\rho}}{\partial t} + \nabla\cdot(\bar{\rho}\hat{\boldsymbol{v}}) - \bar{\rho}\nabla\cdot\hat{\boldsymbol{v}} = -\bar{\rho}\nabla\cdot\hat{\boldsymbol{v}}.$$

Hence, we may write

$$\bar{\rho}\frac{\mathrm{d}\hat{e}}{\mathrm{d}t} = \bar{\rho}\frac{\mathrm{d}\hat{h}}{\mathrm{d}t} - \frac{\mathrm{d}\bar{p}}{\mathrm{d}t} - \bar{p}\nabla\cdot\hat{\boldsymbol{v}}.$$

Combining this equation with eq. (3.15a) yields the equivalent form of the 1st law of thermodynamics

$$\bar{\rho}\frac{\mathrm{d}\hat{h}}{\mathrm{d}t} - \frac{\mathrm{d}\bar{p}}{\mathrm{d}t} + \nabla\cdot(\overline{\boldsymbol{R}} + \overline{\boldsymbol{J}}_h + \boldsymbol{F}_h) = \overline{\boldsymbol{v}''\cdot\nabla p} - \overline{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}} - \overline{\boldsymbol{J}:\nabla\boldsymbol{v}''}. \qquad (3.15b)$$

To derive a prognostic equation for the mean absolute temperature, Herbert (1975) postulated that the mean specific enthalpy, $\hat{h}$, is a function of the mean state variables, $\hat{T}$, $\bar{p}$, and $\hat{m}_k$ ($k = 0, 1, 2, 3$). Consequently, the total differential of the mean specific enthalpy is given by (Herbert, 1975)

$$\mathrm{d}\hat{h} = \left(\frac{\partial\hat{h}}{\partial\hat{T}}\right)_{\bar{p},\hat{m}_k}\mathrm{d}\hat{T} + \left(\frac{\partial\hat{h}}{\partial\bar{p}}\right)_{\hat{T},\hat{m}_k}\mathrm{d}\bar{p} + \sum_{k=0}^{3}\left(\frac{\partial\hat{h}}{\partial\hat{m}_k}\right)_{\hat{T},\bar{p}}\mathrm{d}\hat{m}_k, \qquad (3.16)$$

where $c_p = (\partial\hat{h}/\partial\hat{T})_{\bar{p},\hat{m}_k} = \sum_{k=0}^{3} c_{p,k}\hat{m}_k$ is the specific heat at constant pressure, $c_{p,k} = (\partial\hat{h}_k/\partial\hat{T})_{\bar{p},\hat{m}_k}$ is the partial specific heat at constant pressure, and $\hat{h}_k = (\partial\hat{h}/\partial\hat{m}_k)_{\hat{T},\bar{p}}$ is the partial specific enthalpy. It should be noted that eq. (3.16) does not contain energetic effects caused by chemical reactions between trace constituents because such effects are usually negligible (except for combustion processes). This circumstance may be used to classify atmospheric constituents as atmospheric trace constituents.

Since moist air is assumed to be a perfect gas, the equation of state for moist air can be written as*

$$\bar{p} \cong \bar{\rho} R_0 \hat{T}_v, \tag{3.17}$$

where

$$\hat{T}_v = \hat{T}\{1 + (R_1/R_0 - 1)\hat{m}_1 + (R_1/R_0 - 1)\overline{\rho_1' T''}/(\bar{\rho}\hat{T})\}$$

is the virtual temperature weighted by air density. The quantities $R_0 = 287.05$ J/(kg K) and $R_1 = 461.50$ J/(kg K) are the gas constants of dry air and water vapour, respectively. (The notion gas constant for dry air means the quantity that is calculated for this gas mixture on the basis of its constituents.) Assuming that

$$(R_1/R_0 - 1)\overline{\rho_1' T''}/(\bar{\rho}\hat{T})$$

is negligible, the mean virtual temperature can be approximated by $\hat{T}_v \cong \hat{T}\{1 + (R_1/R_0 - 1)\hat{m}_1\}$.

The derivative $(\partial\hat{h}/\partial\bar{p})_{\hat{T},\hat{m}_i}$ is given by

$$\left(\frac{\partial\hat{h}}{\partial\bar{p}}\right)_{\hat{T},\hat{m}_k} = \hat{T}\left(\frac{\partial\hat{s}}{\partial\bar{p}}\right)_{\hat{T},\hat{m}_k} + \frac{1}{\bar{\rho}},$$

where $\hat{s}$ is the mean specific entropy.

Using Maxwell's relation

$$\left(\frac{\partial\hat{s}}{\partial\bar{p}}\right)_{\hat{T},\hat{m}_k} = \frac{1}{\bar{\rho}^2}\left(\frac{\partial\bar{\rho}}{\partial\hat{T}}\right)_{\bar{p},\hat{m}_k}$$

for mean quantities finally provides

$$\left(\frac{\partial\hat{h}}{\partial\bar{p}}\right)_{\hat{T},\hat{m}_k} = \frac{\hat{T}}{\bar{\rho}^2}\left(\frac{\partial\bar{\rho}}{\partial\hat{T}}\right)_{\bar{p},\hat{m}_k} + \frac{1}{\bar{\rho}}.$$

Since moist air is assumed to be a perfect gas, we obtain $(\partial\bar{\rho}/\partial\hat{T})_{\bar{p},\hat{m}_k} = -\bar{\rho}/\hat{T}$, and, hence, $(\partial\hat{h}/\partial\bar{p})_{\hat{T},\hat{m}_k} = 0$. Thus, the partial specific enthalpies can well be approximated by (Herbert, 1975)

$$\hat{h}_k = \int_{T_0}^{\hat{T}} c_{p,k}\,\mathrm{d}\hat{T} + \hat{h}_k(T_0), \tag{3.18}$$

where $\hat{h}_k(T_0)$ is partial specific enthalpy at an arbitrarily chosen reference temperature T_0. Customarily, it is assumed that, although the total system is not in equilibrium, there exists a state of local equilibrium within small mass elements, for which the local enthalpy is the same function of the variables of state as in the real equilibrium. In particular, it is postulated that eq. (3.16) remains valid for a mass element followed along its centre of motion. By applying this hypothesis on local equilibrium and the aforementioned definitions for c_p and $\hat{h}_k$ one obtains for the substantial temporal change of the specific enthalpy (Herbert, 1975)*

$$\bar{\rho}\frac{\mathrm{d}\hat{h}}{\mathrm{d}t} = c_p\bar{\rho}\frac{\mathrm{d}\hat{T}}{\mathrm{d}t} + \bar{\rho}\sum_{k=0}^{3}\hat{h}_k\frac{\mathrm{d}\hat{m}_k}{\mathrm{d}t} \tag{3.19}$$

and with eq. (3.13)

$$\bar{\rho}\frac{\mathrm{d}\hat{h}}{\mathrm{d}t} = c_p\bar{\rho}\frac{\mathrm{d}\hat{T}}{\mathrm{d}t} + \sum_{k=0}^{3}\hat{h}_k\bar{I}_k - \sum_{k=0}^{3}\hat{h}_k\nabla\cdot(\bar{\boldsymbol{J}}_k + \boldsymbol{F}_k). \tag{3.20}$$

Combining eqs. (3.15b) and (3.20) provides the prognostic equation of the mean absolute temperature

$$\begin{aligned} c_p\bar{\rho}\frac{\mathrm{d}\hat{T}}{\mathrm{d}t} = {} & \frac{\mathrm{d}\bar{p}}{\mathrm{d}t} - \nabla\cdot(\bar{\boldsymbol{R}} + \boldsymbol{J}_\mathrm{h}^i + \boldsymbol{F}_\mathrm{h}^i) \\ & + \overline{\boldsymbol{v}''\cdot\nabla p} + \varepsilon - \bar{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}} + \sum_{k=2}^{3}\hat{\lambda}_{k1}\bar{I}_k \\ & + \sum_{k=1}^{3}(\bar{\boldsymbol{J}}_k + \boldsymbol{F}_k)\cdot\nabla\hat{\lambda}_{k0}, \end{aligned} \tag{3.21}$$

where the terms

$$\boldsymbol{J}_\mathrm{h}^i = \bar{\boldsymbol{J}}_\mathrm{h} - \sum_{k=0}^{3}\hat{h}_k\bar{\boldsymbol{J}}_k = \bar{\boldsymbol{J}}_\mathrm{h} + \sum_{k=1}^{3}\hat{\lambda}_{k0}\bar{\boldsymbol{J}}_k, \tag{3.22}$$

$$\boldsymbol{F}_\mathrm{h}^i = \boldsymbol{F}_\mathrm{h} - \sum_{k=0}^{3}\hat{h}_k\boldsymbol{F}_k = \boldsymbol{F}_\mathrm{h} + \sum_{k=1}^{3}\hat{\lambda}_{k0}\boldsymbol{F}_k \tag{3.23}$$

may be denoted as the mean molecular and turbulent internal heat flux densities, respectively (de Groot and Mazur, 1969; Herbert, 1975). Here, $\hat{\lambda}_{k0} = \hat{h}_0 - \hat{h}_k$. Furthermore, the quantity $\hat{\lambda}_{k1} = \hat{h}_1 - \hat{h}_k$ is the mean specific heat of phase transition where $\hat{\lambda}_{21}$ is the specific heat of vaporization, $\hat{\lambda}_{31}$ is the specific heat of sublimation, and $\hat{\lambda}_{32}$ is the specific heat of melting. Since the mean

* Density effects owing to water and ice may be neglected.

* The hypothesis of local equilibrium that is of great importance to derive Gibbs fundamental equation for the temporal change of the specific entropy is discussed in detail, for instance, in de Groot and Mazur (1969) as well as Glansdorff and Prigogine (1971).

potential temperature* is given by

$$\hat{\Theta} = \hat{T}\left(\frac{p_0}{\bar{p}}\right)^k = \frac{\hat{T}}{\bar{\pi}},$$

where $\bar{\pi} = (\bar{p}/p_0)^k$ is the mean Exner-function, and k is given by

$$k = \frac{R}{c_p} \cong \frac{R_0\{1 + (R_1/R_0 - 1)\hat{m}_1\}}{c_{p,0}\left\{1 + \sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}} - 1\right)\hat{m}_k\right\}},$$

the prognostic equation of the mean potential temperature reads

$$c_p\bar{\rho}\,\bar{\pi}\frac{\mathrm{d}\hat{\Theta}}{\mathrm{d}t} = -\nabla\cdot(\bar{\boldsymbol{R}} + \boldsymbol{J}_\mathrm{h}^i + \boldsymbol{F}_\mathrm{h}^i) + \overline{\boldsymbol{v}''\cdot\nabla p} + \varepsilon - \bar{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}} + \sum_{k=2}^{3}\hat{\lambda}_{k1}\overline{I_k} + \sum_{k=1}^{3}(\bar{\boldsymbol{J}}_k + \boldsymbol{F}_k)\cdot\nabla\hat{\lambda}_{k0}. \quad (3.24)$$

3.2.4. The balance equation of potential energy

$$\bar{\rho}\frac{\mathrm{d}\phi}{\mathrm{d}t} = \bar{\rho}\hat{\boldsymbol{v}}\cdot\nabla\phi. \quad (3.25)$$

3.2.5. The balance equation of kinetic energy of the mean motion

$$\bar{\rho}\frac{\mathrm{d}\hat{k}_m}{\mathrm{d}t} + \nabla\cdot\{\hat{\boldsymbol{v}}\cdot(\bar{p}\boldsymbol{E} + \bar{\boldsymbol{J}} + \boldsymbol{F})\} = -\bar{\rho}\hat{\boldsymbol{v}}\cdot\nabla\phi + \bar{p}\nabla\cdot\hat{\boldsymbol{v}} + (\bar{\boldsymbol{J}} + \boldsymbol{F}):\nabla\hat{\boldsymbol{v}}. \quad (3.26)$$

Here, the quantity $\hat{k}_m = \frac{1}{2}\hat{\boldsymbol{v}}^2$ is the specific kinetic energy of the mean motion (see also eq. (2.15)). Usually, $|\bar{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}}| \ll |\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}|$ is valid except for the immediate vicinity of solid walls. Obviously, eq. (3.26) can be derived by scalarly multiplying eq. (3.14) by $\hat{\boldsymbol{v}}$.

3.2.6. The balance equation of the kinetic energy of the eddying motion

$$\bar{\rho}\frac{\mathrm{d}\hat{k}_\mathrm{e}}{\mathrm{d}t} + \nabla\cdot(\overline{\rho\boldsymbol{v}''k_\mathrm{e}''} + \overline{\boldsymbol{v}''\cdot\boldsymbol{J}}) = -\overline{\boldsymbol{v}''\cdot\nabla p} - \varepsilon - \boldsymbol{F}:\nabla\hat{\boldsymbol{v}}, \quad (3.27)$$

where $k_\mathrm{e}'' = \frac{1}{2}\boldsymbol{v}''^2$ is the specific turbulent kinetic energy (TKE) of the eddying motion (see also eq. (2.15)), and $\hat{k}_\mathrm{e} = \frac{1}{2}\boldsymbol{F}:\boldsymbol{E} = \frac{3}{2}F^*$. Eq. (3.27) is clearly a 2nd-order balance equation. It is the only balance equation that additionally arises from averaging a macroscopic balance equation because adding eqs. (3.26) and (3.27) yields the averaged form of the macroscopic equation of kinetic energy (Eliassen and Kleinschmidt, 1957; Herbert, 1975).

In meteorological models of the mesoscale which serve as meteorological pre-processors for Eulerian air pollution models like ADOM, EURAD, RADM, and DRAIS the TKE balance equation (3.27) is customarily used to derive the eddy diffusivities for momentum and — via the turbulent Prandtl number and the species-dependent turbulent Schmidt numbers — the eddy diffusivities for sensible heat, water vapour, and trace species (customarily denoted as one-and-a-half-order closure). Consequently, the results on the dispersion of trace species in the atmosphere predicted by such numerical models also depend on the parameterisation of those terms occurring in eq. (3.27) for which additional balance equations are unavailable. One of these terms playing an important role is $\overline{\boldsymbol{v}''\cdot\nabla p}$.

3.2.7. Balance equations for total enthalpy and total energy. For completeness, a brief, but thorough derivation of the balance equations for total enthalpy and total energy is summarised here. As described before, there are close relations between the various energy forms. The thermal balance equations (3.15a) and (3.15b) and the TKE-balance equation (3.27), for instance, are related to by the terms $\overline{\boldsymbol{v}''\cdot\nabla p}$ and ε. Since both terms have to be parameterised, it seems to be useful to combine these equations in order to evaluate existing parameterisation schemes of these terms. Combining eqs. (3.15b) and (3.27), for instance, leads to the balance equation for the quantity $\hat{\eta} = \hat{h} + \hat{k}_\mathrm{e}$ which may be denoted as total enthalpy:

$$\bar{\rho}\frac{\mathrm{d}\hat{\eta}}{\mathrm{d}t} - \frac{\mathrm{d}\bar{p}}{\mathrm{d}t} + \nabla\cdot(\bar{\boldsymbol{R}} + \bar{\boldsymbol{J}}_\mathrm{h} + \boldsymbol{F}_\mathrm{h} + \overline{\rho\boldsymbol{v}''k_\mathrm{e}''} + \overline{\boldsymbol{v}''\cdot\boldsymbol{J}}) = -(\bar{\boldsymbol{J}} + \boldsymbol{F}):\nabla\hat{\boldsymbol{v}}. \quad (3.28)$$

Note that the internal energy and the TKE can also be summed to yield the total internal energy. As suggested by Herbert (1980, personal communication) and discussed by Sievers (1984), this

* The potential temperature, Θ, can be derived from the Gibbs relation $\mathrm{d}h = T\,\mathrm{d}s + \rho^{-1}\,\mathrm{d}p + \sum_k \mu_k\,\mathrm{d}m_k$ by assuming $\mathrm{d}s = 0$ (isentropy) and $\mathrm{d}m_k = 0$ (no phase transitions; exact in the case of moist air). Here, μ_k is the chemical potential of the kth component.

quantity can be applied to formulate the so-called inclusive system of model equations for the turbulent atmospheric flow, which, of course, does not contain $\overline{\boldsymbol{v}''\cdot\nabla p}$ and ε.

The well-known balance equation of the mean total energy, $\hat{e}_{\text{tot}} = \hat{e} + \phi + \hat{k}_m + \hat{k}_{\text{e}}$, can be derived by adding eqs. (3.15a) and (3.25) to (3.27). One obtains

$$\frac{\partial(\bar{\rho}\hat{e}_{\text{tot}})}{\partial t} + \nabla\cdot\{\boldsymbol{R} + \bar{\boldsymbol{J}}_{\text{h}} + \boldsymbol{F}_{\text{h}} + \hat{\boldsymbol{v}}\cdot\{(\bar{\rho}\hat{e}_{\text{tot}} + \bar{p})\boldsymbol{E} + \bar{\boldsymbol{J}} + \boldsymbol{F}\} + \overline{\rho\boldsymbol{v}''k_{\text{e}}''} + \overline{\boldsymbol{v}''\cdot\boldsymbol{J}}\} = 0. \tag{3.29}$$

Eq. (3.29) demonstrates that there is no production or destruction of mean total energy within any given fixed volume (Van Mieghem, 1973; Herbert, 1975; Pichler, 1984). Obviously, contributions of energy of different orders of magnitude are summed, where only a very small fraction of the total potential energy, $\hat{e} + \phi$, is available for conversion into kinetic energy (Lorenz, 1967; Bernhardt and Lauter, 1977; Holton, 1979).

3.2.8. The necessity to parameterise the terms $\boldsymbol{F}_{\text{h}}^{i}$ and $\overline{\boldsymbol{v}''\cdot\nabla p}$. The 1st-order balance equations for matter, momentum, and various energy forms as well as the equation of state presented here for the Hesselberg fluid can be considered as exact. Beside the 1st-order balance equation of atmospheric trace species, differences between the equation sets previously published for the Hesselberg fluid (Van Mieghem 1949, 1973; Eliassen and Kleinschmidt, 1957; Fortak, 1969; Herbert, 1975) have mainly been arisen from the necessity to parameterise the terms $\boldsymbol{F}_{\text{h}}^{i}$ and $\overline{\boldsymbol{v}''\cdot\nabla p}$. Our results of a further attempt to parameterise these terms will be presented in Sections 4–6. These results are compared with those of Herbert (1975) who firstly derived the entire equation set for the Hesselberg fluid.

4. Introducing a generalised Richardson number

It is well-known that the turbulent dispersion of trace constituents within the atmospheric boundary layer is appreciably affected by thermal stratification. If we relate the work that has to be done along with or against pressure gradient forces, i.e., the gain ($\overline{\boldsymbol{v}''\cdot\nabla p} < 0$) or loss ($\overline{\boldsymbol{v}''\cdot\nabla p} > 0$) of TKE (e.g., owing to Archimedian forces) to the production of TKE ($-\boldsymbol{F}:\nabla\hat{\boldsymbol{v}} > 0$) that arises from the kinematic interrelation between the mean and the eddying motion (kinematic transformation), we will obtain a non-dimensional stability parameter

$$S_{\text{f}} = \frac{\overline{\boldsymbol{v}''\cdot\nabla p}}{-\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}}. \tag{4.1}$$

Obviously, this stability parameter expresses the relative importance of the two TKE-terms. It may be interpreted as a *generalised* Richardson number for the Hesselberg fluid. The difference between the well known flux-Richardson number and the generalised Richardson number introduced here results from the parameterisation of $\overline{\boldsymbol{v}''\cdot\nabla p}$ (see Section 6).

It has to be considered that besides the vertical effects also horizontal effects have to be regarded under certain circumstances. In the case of $S_{\text{f}} > 0 \Leftrightarrow \overline{\boldsymbol{v}''\cdot\nabla p} > 0$, mechanically produced TKE is mainly consumed by Archimedian effects. Consequently, there exists a critical S_{f} value given by $S_{\text{f,cr}} = 1$. It is characterised by the fact that the mechanical gain of TKE is equal to the thermal loss of TKE so that the turbulent flow will become more and more viscous (laminar) owing to the dissipation of energy. In the case of $S_{\text{f}} < 0 \Leftrightarrow \overline{\boldsymbol{v}''\cdot\nabla p} < 0$, TKE is generated mechanically and thermally. If the mechanically produced TKE is much smaller than the thermal gain of TKE, and, hence, negligible, free convective conditions will occur ($S_{\text{f}} \leqslant S_{\text{f,fc}}$). In the remaining range, mixed convective conditions may prevail ($S_{\text{f,fc}} < S_{\text{f}} < 0$).

Using the generalised Richardson number (eq. (4.1)) as well as the definition of turbulent dissipation of energy into the reservoir of heat, ε, the balance equation of TKE may be written as

$$\bar{\rho}\frac{\mathrm{d}\hat{k}_{\text{e}}}{\mathrm{d}t} + \nabla\cdot(\overline{\rho\boldsymbol{v}''k_{\text{e}}''} + \overline{\boldsymbol{v}''\cdot\boldsymbol{J}}) = -\varepsilon - \boldsymbol{F}:\nabla\hat{\boldsymbol{v}}(1 - S_{\text{f}}). \tag{4.2}$$

5. Estimating the turbulent internal heat flux density

The turbulent internal heat flux density $\boldsymbol{F}_{\text{h}}^{i}$ (see eq. (3.23)) can be calculated by decomposing the turbulent enthalpy flux density as follows:

$$\boldsymbol{F}_{\mathrm{h}} = \overline{\rho \boldsymbol{v}'' h''} = \overline{\rho \boldsymbol{v}'' h} = \sum_{k=0}^{3} \overline{\rho \boldsymbol{v}'' m_k h_k}$$

$$= \sum_{k=0}^{3} \{\hat{m}_k \overline{\rho \boldsymbol{v}'' h_k''} + \hat{h}_k \boldsymbol{F}_k + \overline{\rho \boldsymbol{v}'' h_k'' m_k''}\}, \tag{5.1}$$

where the 3rd-order term $\overline{\rho \boldsymbol{v}'' h_k'' m_k''}$ seems to be negligible in comparison with the other terms. With this simplification one obtains by combining eqs. (3.23) and (5.1) and considering $\hat{m}_0 = 1 - \sum_{k=1}^{3} \hat{m}_k$,

$$\boldsymbol{F}_{\mathrm{h}}^{i} = \left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \hat{m}_k\right\} c_{p,0} \overline{\rho \boldsymbol{v}'' T}. \tag{5.2}$$

Since the potential temperature is defined by $\Theta = T(p_0/p)^{k} = T/\pi$, the term $c_{p,0}\overline{\rho \boldsymbol{v}'' T}$ may be written as

$$c_{p,0}\overline{\rho \boldsymbol{v}'' T} = c_{p,0}\bar{\pi}\, \overline{\rho \boldsymbol{v}'' \Theta''} + c_{p,0}\overline{\rho \boldsymbol{v}'' \Theta \pi'}. \tag{5.3}$$

Customarily, the quantity $\boldsymbol{H} = c_{p,0}\overline{\rho \boldsymbol{v}'' \Theta''}$ is denoted as buoyancy heat flux density*. The term $\boldsymbol{W} = c_{p,0}\overline{\rho \boldsymbol{v}'' \Theta \pi'}$ is a turbulent flux density resulting from fluctuations of pressure and wind vector because

$$\Theta \pi' \cong k \hat{T} \frac{p'}{\bar{p}} \tag{5.4}$$

and, hence,

$$\boldsymbol{W} = \frac{1}{\bar{\rho}\left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \hat{m}_k\right\}} \overline{\rho \boldsymbol{v}'' p'}. \tag{5.5}$$

By considering these two flux definitions the turbulent internal heat flux density can finally be written as

$$\boldsymbol{F}_{\mathrm{h}}^{i} = \left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \hat{m}_k\right\} \{\bar{\pi} \boldsymbol{H}\} + \frac{1}{\bar{\rho}} \overline{\rho \boldsymbol{v}'' p'}. \tag{5.6}$$

6. The parameterisation of $\overline{\boldsymbol{v}'' \cdot \nabla p}$ and the related consequences

In accord with the definition of the potential temperature, the pressure gradient may be approximated by

$$\nabla p = c_{p,0}\left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) m_k\right\} \rho \Theta \nabla \pi.$$

Thus, the term $\overline{\boldsymbol{v}'' \cdot \nabla p}$ may be expressed by

$$\left.\begin{aligned} \overline{\boldsymbol{v}'' \cdot \nabla p} \cong & \left\{\left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \hat{m}_k\right\} \boldsymbol{H} \right. \\ & \left. + c_{p,0}\hat{\Theta} \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \boldsymbol{F}_k\right\} \cdot \nabla \bar{\pi} \\ & + \underline{\nabla \cdot \left\{\frac{1}{\bar{\rho}} \overline{\rho \boldsymbol{v}'' p'}\right\}} - \underbrace{c_{p,0}\overline{\pi' \nabla \cdot (\rho \boldsymbol{v}'' \Theta_v)}}_{\delta} \end{aligned}\right\}, \tag{6.1}$$

where δ is assumed to be negligible. This approach mainly differs from that of Herbert (1975) by the divergence term underlined. This divergence term can be further separated from the expression $\delta_{\mathrm{H}} = c_{p,0}\overline{\rho \boldsymbol{v}'' \Theta_v \cdot \nabla \pi'}$ derived by Herbert (1975) and considered as negligible.

Taking eq. (6.1) into account, the prognostic equation of the mean absolute temperature, $\hat{T}$, and the mean potential temperature, $\hat{\Theta}$, as well as the TKE balance equation now read:

$$\left.\begin{aligned} c_p \bar{\rho} \frac{\mathrm{d}\hat{T}}{\mathrm{d}t} = & \frac{\mathrm{d}\bar{p}}{\mathrm{d}t} - \nabla \cdot \left(\overline{\boldsymbol{R}} + \boldsymbol{J}_{\mathrm{h}}^{i} + \left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \hat{m}_k\right\} \{\bar{\pi} \boldsymbol{H}\}\right) \\ & + \left\{\left\{1 + \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \hat{m}_k\right\} \boldsymbol{H} + c_{p,0}\hat{\Theta} \sum_{k=1}^{3} \left(\frac{c_{p,k}}{c_{p,0}} - 1\right) \boldsymbol{F}_k\right\} \cdot \nabla \bar{\pi} \\ & + \varepsilon - \overline{\boldsymbol{J}} : \nabla \hat{\boldsymbol{v}} + \sum_{k=2}^{3} \hat{\lambda}_{k1} \bar{I}_k + \sum_{k=1}^{3} (\overline{\boldsymbol{J}}_k + \boldsymbol{F}_k) \cdot \nabla \hat{\lambda}_{k0} \end{aligned}\right\}, \tag{6.2}$$

* The buoyancy heat flux density can also be defined by $\boldsymbol{H} = c_{p,0}\overline{\pi \rho \boldsymbol{v}'' \Theta''}$ that seems to better agree with the definition of $\boldsymbol{W}$ (Kramm et al., 1996).

$$\left.\begin{aligned} c_p\bar{\rho}\,\pi\frac{\mathrm{d}\hat{\Theta}}{\mathrm{d}t} &= -\nabla\cdot\left(\bar{\boldsymbol{R}}+\boldsymbol{J}_{\mathrm{h}}^{i}+\left\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\right\}\{\overline{\pi\boldsymbol{H}}\}\right)\\ &\quad+\left\{\left\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\right\}\boldsymbol{H}+c_{p,0}\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\boldsymbol{F}_k\right\}\cdot\nabla\bar{\pi}\\ &\quad+\varepsilon-\bar{\boldsymbol{J}}:\nabla\hat{\boldsymbol{v}}+\sum_{k=2}^{3}\hat{\lambda}_{k1}\bar{I}_k+\sum_{k=1}^{3}(\bar{\boldsymbol{J}}_k+\boldsymbol{F}_k)\cdot\nabla\hat{\lambda}_{k0}\end{aligned}\right\}, \tag{6.3}$$

$$\bar{\rho}\frac{\mathrm{d}\hat{k}_{\mathrm{e}}}{\mathrm{d}t}+\nabla\cdot\left\{\overline{\rho\boldsymbol{v}''k_{\mathrm{e}}''}+\overline{\boldsymbol{v}''\cdot\boldsymbol{J}}+\frac{1}{\bar{\rho}}\overline{\rho\boldsymbol{v}''p'}\right\}=-\varepsilon-\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}(1-\mathrm{Ri}_{\mathrm{f}}). \tag{6.4}$$

Here, Ri_{f} is the flux-Richardson number defined by

$$\mathrm{Ri}_{\mathrm{f}}=\frac{\left\{\left\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\right\}\boldsymbol{H}+c_{p,0}\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\boldsymbol{F}_k\right\}\cdot\nabla\bar{\pi}}{-\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}}. \tag{6.5}$$

Eqs. (6.2) and (6.4) differ from those of Herbert (1975) by the eddy flux density $\overline{\rho\boldsymbol{v}''p'}/\bar{\rho}$. As aforementioned, Herbert (1975) ignored this term because reliable results from field experiments were scarce at the beginning of the seventies. Meanwhile, however, there are more of such results, and it seems that the turbulent pressure flux is a significant source of TKE under unstable conditions (Wyngaard and Coté, 1971; McBean and Elliot, 1975; Högström, 1990; Wilczak et al., 1995) and should be taken into account as done by Kramm et al. (1996). Eq. (6.4), of course, corresponds to that derived for the Boussinesq fluid by Tennekes and Lumley (1978), Stull (1988), Garratt (1994) and others.

Obviously, the flux-Richardson number, Ri_{f}, differs from the generalised Richardson number, S_{f} (see eq. (4.1)), because it only includes the non-divergent portion of $\overline{\boldsymbol{v}''\cdot\nabla p}$. The statements of Section 4 regarding the stability parameter S_{f} are similarly valid, where they now read:

$$\mathrm{Ri}_{\mathrm{f}}>0 \text{ if } \left\{\left\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\right\}\boldsymbol{H}+c_{p,0}\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\boldsymbol{F}_k\right\}\cdot\nabla\bar{\pi}>0,$$

$$\mathrm{Ri}_{\mathrm{f}}<0 \text{ if } \left\{\left\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\right\}\boldsymbol{H}+c_{p,0}\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\boldsymbol{F}_k\right\}\cdot\nabla\bar{\pi}<0,$$

Observations show, however, that turbulence cannot be maintained even at smaller values of $\mathrm{Ri}_{\mathrm{f}}=1$; a critical value of $\mathrm{Ri}_{\mathrm{f}}=0.25$ is generally accepted (Stull, 1988; Sorbjan, 1989).

In atmospheric physics, the flux-Richardson number is customarily applied for horizontally homogeneous conditions. Under such conditions the terms $-\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}$ and $\nabla\bar{\pi}$ may simply be written as

$$-\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}=-\overline{\rho u''w''}\frac{\partial\hat{u}}{\partial z}-\overline{\rho v''w''}\frac{\partial\hat{v}}{\partial z}=\boldsymbol{\tau}\cdot\frac{\partial\hat{\boldsymbol{v}}_{\mathrm{H}}}{\partial z} \tag{6.6}$$

and (with the hydrostatic pressure gradient $\partial\bar{p}/\partial z=-g\bar{\rho}$)

$$\frac{\partial\bar{\pi}}{\partial z}=-\frac{g}{c_p\hat{\Theta}}. \tag{6.7}$$

Here, $\boldsymbol{\tau}=-\overline{\rho u''w''}\boldsymbol{i}-\overline{\rho v''w''}\boldsymbol{j}$ is the Reynolds' stress vector, $\hat{\boldsymbol{v}}_{\mathrm{H}}=\hat{u}\boldsymbol{i}+\hat{v}\boldsymbol{j}$ is the mean horizontal wind vector, $\boldsymbol{i}$ and $\boldsymbol{j}$ are the unit vectors in the x- and y-directions, $\hat{u}$ and $\hat{v}$ are the corresponding mean horizontal wind components, and g is the acceleration of gravity. In the case of moist air, the flux-Richardson number for horizontally homogeneous conditions amounts to

$$\mathrm{Ri}_{\mathrm{f}}=-\frac{g}{c_p\hat{\Theta}}\cdot\frac{\left\{1+\left(\frac{c_{p,1}}{c_{p,0}}-1\right)\hat{m}_1\right\}H+c_{p,0}\hat{\Theta}\left(\frac{c_{p,1}}{c_{p,0}}-1\right)F_1}{\boldsymbol{\tau}\cdot\dfrac{\partial\hat{\boldsymbol{v}}_{\mathrm{H}}}{\partial z}}, \tag{6.8}$$

where $H = c_{p,0}\overline{\rho w''\Theta''}$ and $F_1 = \overline{\rho w'' m_1''}$ are the vertical eddy flux densities of sensible heat and water vapour. If such conditions are not fulfilled, not only vertical, but also horizontal effects have to be considered.

7. The 2nd-order balance equations for the Hesselberg fluid

Our results shown in Figs. 1 and 2 substantiate that an improvement of Eulerian air pollution models for chemically reactive trace constituents can only be achieved by concurrently computing the chemical processes regarding the mean quantities and the respective segregation effects which requires, at least, 2nd-order-closure principles. Customarily, 2nd-order balance equations for the turbulent flow are based on Reynolds' averaging and the Boussinesq approximation (see, e.g., Donaldson, 1973; Seinfeld, 1986). To avoid such a simplification, these 2nd-order equations for the turbulent atmospheric flow should also be derived by Hesselberg averaging. Following steps are required, for instance, to obtain the 2nd-order balance equations for trace constituents:

(1) The macroscopic balance equations for trace constituents, eq. (2.2), is multiplied, for instance, from left with the wind vector, $\boldsymbol{v}$, and averaged afterwards.
(2) The 1st-order balance equation for trace constituents, eq. (3.1), is multiplied from left with the mean wind vector, $\hat{\boldsymbol{v}}$, and subtracted from the equation provided by step one.

In doing so, and after a little algebra where the balance equation of momentum is taking into account, one obtains:

$$\left.\begin{aligned}&\frac{\partial}{\partial t}(\overline{\rho \boldsymbol{v}''\chi_i''}) + \nabla\cdot(\hat{\boldsymbol{v}}\overline{\rho \boldsymbol{v}''\chi_i''})\\ &\quad = -\nabla\cdot(\overline{\rho \boldsymbol{v}''\boldsymbol{v}''\chi_i''}) - \overline{\rho \boldsymbol{v}''\boldsymbol{v}''}\cdot\nabla\hat{\chi}_i - \overline{\rho \boldsymbol{v}''\chi_i''}\cdot\nabla\hat{\boldsymbol{v}}\\ &\qquad - \overline{\chi_i''\nabla\cdot\boldsymbol{J}} - \overline{\boldsymbol{v}''\nabla\cdot\boldsymbol{J}_i} - \overline{\chi_i''\nabla p}\\ &\qquad - 2\Omega(\overline{\rho \boldsymbol{v}''\chi_i''}) + \overline{\boldsymbol{v}''\sigma_i}.\end{aligned}\right\} \tag{7.1}$$

Here, the 1st term is the local temporal change, the 2nd and 3rd terms represent the resolvable and the turbulent exchange of eddy fluxes of trace constituents with its environment. Furthermore, the 4th and 5th terms are the production of eddy fluxes of trace species owing to the kinematic interaction between the eddy flux densities of momentum and trace species on the one hand and the gradients of the mean mass fractions and the mean wind vector on the other hand. The next two terms represent the destruction of eddy fluxes of trace species by molecular diffusion effects usually considered as negligible (Sorbjan, 1989; Garratt, 1994), and term 8, which has to be parameterised, the destruction of these eddy flux densities by interaction between the fluctuation of mass fraction and pressure gradient force. Moreover, term 9 describes the interaction between the Earth's rotation and the eddy flux densities of trace species, which can be neglected for averaging intervals less than one hour or so (Busch, 1973; Garratt, 1994), and term 10 characterises the interrelation between the turbulent flow and the production or depletion of trace species owing to chemical reactions given by:

$$\overline{\boldsymbol{v}''\sigma_i} = \sum_{j=1}^{N}\overline{k_{ij}\rho \boldsymbol{v}''\chi_j} + \sum_{\substack{m=1\\ n\geq m}}^{N}\overline{C_{imn}\rho \boldsymbol{v}''\chi_m\chi_n} \tag{7.2}$$

with

$$\sum_{j=1}^{N}\overline{k_{ij}\rho \boldsymbol{v}''\chi_j} = \sum_{j=1}^{N}(\hat{k}_{ij}\overline{\rho \boldsymbol{v}''\chi_j''} + \overline{\rho \boldsymbol{v}''k_{ij}''}\hat{\chi}_j + \overline{\rho \boldsymbol{v}''k_{ij}''\chi_j''}), \tag{7.3}$$

$$\left.\begin{aligned}&\sum_{\substack{m=1\\ n\geq m}}^{N}\overline{C_{imn}\rho \boldsymbol{v}''\chi_m\chi_n}\\ &\quad = \sum_{\substack{m=1\\ n\geq m}}^{N}\hat{C}_{imn}(\overline{\rho \boldsymbol{v}''\chi_n''}\hat{\chi}_m + \overline{\rho \boldsymbol{v}''\chi_m''}\hat{\chi}_n + \overline{\rho \boldsymbol{v}''\chi_m''\chi_n''})\\ &\qquad + \sum_{\substack{m=1\\ n\geq m}}^{N}(\overline{\rho \boldsymbol{v}''C_{imn}''}\hat{\chi}_m\hat{\chi}_n + \overline{\rho \boldsymbol{v}''C_{imn}''\chi_n''}\hat{\chi}_m\\ &\qquad + \overline{\rho \boldsymbol{v}''C_{imn}''\chi_m''}\hat{\chi}_n + \overline{\rho \boldsymbol{v}''C_{imn}''\chi_m''\chi_n''})\end{aligned}\right\}. \tag{7.4}$$

These expressions should be approximated, at least, by

$$\sum_{j=1}^{N}\overline{k_{ij}\rho \boldsymbol{v}''\chi_j} \approx \sum_{j=1}^{N}\hat{k}_{ij}\overline{\rho \boldsymbol{v}''\chi_j''} \tag{7.5}$$

$$\sum_{\substack{m=1\\ n\geq m}}^{N}\overline{C_{imn}\rho \boldsymbol{v}''\chi_m\chi_n} \approx \sum_{\substack{m=1\\ n\geq m}}^{N}\hat{C}_{imn}(\overline{\rho \boldsymbol{v}''\chi_n''}\hat{\chi}_m + \overline{\rho \boldsymbol{v}''\chi_m''}\hat{\chi}_n). \tag{7.6}$$

Considering eq. (5.4) and the parameterisation of

∇p yields (see also eq. (6.1))

$$\left.\begin{aligned}\overline{\chi_i''\nabla p} \cong c_{p,0}\Bigg\{\Bigg\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\Bigg\}\overline{\rho\chi_i''\Theta''} \\ +\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\overline{\rho\chi_i''m_k''}\Bigg\}\cdot\nabla\pi \\ +\underline{\nabla\cdot\left\{\frac{1}{\rho}\overline{\rho\chi_i''p'}\right\}}-\underbrace{c_{p,0}\overline{\pi'\nabla\cdot(\rho\chi_i''\Theta_v)}}_{\delta\chi}\end{aligned}\right\},\tag{7.7}$$

where, again, the term $\delta\chi$ may be neglected. Note that the underlined term will not occur if Herbert's (1975) parameterisation is applied. Eqs. (7.1) and (7.7) show that the 2nd-order balance equations for the eddy flux density of momentum as well as the covariance terms $\overline{\rho\chi_i''\Theta''}$ and $\overline{\rho\chi_i''m_k''}$ are required to (numerically) solve the balance equation for eddy flux densities of trace constituents.

To derive the 2nd-order balance equation for the momentum flux density, similar steps are required, where, of course, the respective equations have to be tensorially multiplied by $\boldsymbol{v}$ and $\hat{\boldsymbol{v}}$, respectively. This procedure leads to (Van Mieghem, 1949; Herbert, 1980, personal communication):

$$\left.\begin{aligned}&\frac{\partial}{\partial t}(\overline{\rho\boldsymbol{v}''\boldsymbol{v}''})+\nabla\cdot(\hat{\boldsymbol{v}}\overline{\rho\boldsymbol{v}''\boldsymbol{v}''}) \\ &=-\nabla\cdot(\overline{\rho\boldsymbol{v}''\boldsymbol{v}''\boldsymbol{v}''})-\overline{\rho\boldsymbol{v}''\boldsymbol{v}''}\cdot\nabla\hat{\boldsymbol{v}}-(\nabla\hat{\boldsymbol{v}})^{\mathrm{T}}\cdot(\overline{\rho\boldsymbol{v}''\boldsymbol{v}''}) \\ &\quad-\overline{(\nabla\cdot\boldsymbol{J})\boldsymbol{v}''}-\overline{\boldsymbol{v}''(\nabla\cdot\boldsymbol{J})}-\overline{(\nabla p)\boldsymbol{v}''}-\overline{\boldsymbol{v}''\nabla p} \\ &\quad-2\Omega\times\overline{\rho\boldsymbol{v}''\boldsymbol{v}''}+2\overline{\rho\boldsymbol{v}''\boldsymbol{v}''}\times\Omega\end{aligned}\right\}.\tag{7.8}$$

The terms in this equation are analogous to those in eq. (7.1). Especially in this case of covariance, molecular effects are negligible because viscosity dominates only at high wave numbers where turbulence is locally isotropic so that the covariance is zero (Garratt, 1994). The pressure terms 8 and 9 that characterise the destruction of the eddy flux density of momentum by the interaction between the turbulent flow and pressure gradient forces have to be parameterised, too.

As aforementioned, the quantity $\boldsymbol{F}=\overline{\rho\boldsymbol{v}''\boldsymbol{v}''}$ in eq. (7.8) is a symmetric tensor of 2nd-rank which is a consequence of the averaging procedure. Its 1st scalar differs by a factor of 2 from the turbulent kinetic energy (TKE). Since the 1st scalar is, of course, independent of the coordinate system (i.e., invariant), it seems to be reasonable to derive the TKE-balance equation by mathematical reduction of eq. (7.8) where its terms are double scalarly multiplied by the identity tensor $\boldsymbol{E}$. With the identity $\overline{\boldsymbol{v}''\cdot\nabla\cdot\boldsymbol{J}}=\nabla\cdot\overline{(\boldsymbol{v}''\cdot\boldsymbol{J})}-\overline{\boldsymbol{J}:\nabla\boldsymbol{v}''}$, one obtains

$$\begin{aligned}&\frac{\partial}{\partial t}(\overline{\rho\boldsymbol{v}''^2})+\nabla\cdot(\hat{\boldsymbol{v}}\overline{\rho\boldsymbol{v}''^2}) \\ &=-\nabla\cdot(\overline{\rho\boldsymbol{v}''\boldsymbol{v}''^2}+\overline{\boldsymbol{v}''\cdot\boldsymbol{J}}) \\ &\quad-2(\boldsymbol{F}:\nabla\hat{\boldsymbol{v}}-\overline{\boldsymbol{J}:\nabla\boldsymbol{v}''}-\overline{\boldsymbol{v}''\cdot\nabla p}).\end{aligned}\tag{7.9}$$

The angular velocity terms occurring in eq. (7.8) vanish because the vector $\Omega\times\boldsymbol{v}''$ is always perpendicular to Ω and to $\boldsymbol{v}''$ and, hence, does no work.

The aforementioned relationship between the balance equation for the Reynolds stress and that for TKE was illustrated to point out that any parameterisation of the 2nd-rank tensors $\overline{(\nabla p)\boldsymbol{v}''}$ and $\overline{\boldsymbol{v}''\nabla p}$ on the one hand must be compatible with that of $\overline{\boldsymbol{v}''\cdot\nabla p}$ on the other hand. The same is true for the triple correlation product when it is parameterised, for instance, in the sense of Donaldson (1973) or Deardorff (1973). In accord with parameterisation of $\overline{\nabla p}$ in Section 6, one obtains for the tensors $\overline{(\nabla p)\boldsymbol{v}''}$ and $\overline{\boldsymbol{v}''\nabla p}$:

$$\left.\begin{aligned}\overline{(\nabla p)\boldsymbol{v}''} \cong \nabla\pi\Bigg\{\Bigg\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\Bigg\}\boldsymbol{H} \\ +c_{p,0}\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\boldsymbol{F}_k\Bigg\} \\ +\underline{\nabla\left\{\frac{1}{\rho}\overline{\rho\boldsymbol{v}''p'}\right\}}-\underbrace{c_{p,0}\overline{\pi'\nabla(\rho\boldsymbol{v}''\Theta_v)}}_{\delta_{m1}}\end{aligned}\right\},\tag{7.10}$$

$$\left.\begin{aligned}\overline{\boldsymbol{v}''\nabla p} \cong \Bigg\{\Bigg\{1+\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\hat{m}_k\Bigg\}\boldsymbol{H} \\ +c_{p,0}\hat{\Theta}\sum_{k=1}^{3}\left(\frac{c_{p,k}}{c_{p,0}}-1\right)\boldsymbol{F}_k\Bigg\}\nabla\pi \\ +\underline{\left(\nabla\left\{\frac{1}{\rho}\overline{\rho\boldsymbol{v}''p'}\right\}\right)^{\mathrm{T}}}-\underbrace{c_{p,0}\overline{\pi'(\nabla(\rho\boldsymbol{v}''\Theta_v))^{\mathrm{T}}}}_{\delta_{m2}}\end{aligned}\right\}\tag{7.11}$$

The terms underlined will not occur if Herbert's (1975) parameterisation is considered. The terms δ_{m1} and δ_{m2} correspond to δ occurring in eq. (6.1). Obviously, the so-called assumption on the tendency-to-isotropy made at 1st by Rotta (1951) and used later by several authors to solve the 2nd-order balance equation of momentum is not necessary in principle to well describe the interaction between the turbulent flow and pressure gradient forces.

The 2nd-order balance equation for the eddy flux densities of sensible heat and water substances can similarly be derived like eqs. (7.1) and (7.7), where in the latter case the interrelation between the turbulent flow and the radiative effects as well as the phase transition rates, respectively, may be treated similar to eqs. (7.2) to (7.6).

Balance equations for the covariance terms, $\overline{\rho\chi_i''\chi_j''}$ (see eq. (3.10)), $\overline{\rho\chi_i''\Theta''}$ and $\overline{\rho\chi_i''m_k''}$ can be deduced similar to eq. (7.1). One obtains

$$\left.\begin{aligned}&\frac{\partial}{\partial t}(\overline{\rho\chi_i''\beta''}) + \nabla\cdot(\hat{\boldsymbol{v}}\overline{\rho\chi_i''\beta''})\\ &\quad = -\nabla\cdot(\overline{\rho\boldsymbol{v}''\chi_i''\beta''}) - \overline{\rho\boldsymbol{v}''\beta''}\cdot\nabla\hat{\chi}_i - \overline{\rho\boldsymbol{v}''\chi_i''}\cdot\nabla\hat{\beta}\\ &\qquad - \overline{\chi_i''\nabla\cdot\boldsymbol{J}_\beta} - \overline{\beta''\nabla\cdot\boldsymbol{J}_i} + \overline{\chi_i''\sigma_\beta} + \overline{\beta''\sigma_i}\end{aligned}\right\}, \tag{7.12}$$

where β stands for χ_j, Θ and m_k, respectively. The terms $\overline{\chi_i''\sigma_\beta}$ and $\overline{\beta''\sigma_i}$ may also be determined similar to eqs. (7.2) to (7.6). Replacing χ_j by χ_i, χ_i and β by Θ as well as χ_i and β by m_k, yields the balance equations for the variance terms of mass fractions, temperature and humidity. As aforementioned, triple correlation terms occur in the eqs. (7.1), (7.3), (7.4), (7.8), and (7.12) for which balance equations can similarly be derived. These 3rd-order balance equations, of course, contain 4th-order correlation terms. By assuming that the probability distribution of these 4th-order moments corresponds to a Gaussian probability density, they may be approximated as functions of 2nd-moment terms (Obukhov, 1954; Lumley and Panofsky, 1964; Rotta, 1972; André et al., 1976; Stull, 1988).

8. Final remarks and conclusions

The 1st-order balance equations for matter, momentum, and various energy forms as well as the 2nd-order balance equations for 2nd moments like the eddy flux densities of matter and momentum were re-formulated using Hesselberg's density-weighted averaging calculus. This re-formulated set of governing 1st-order and 2nd-order balance equations may be considered as most exact, because the degree of simplification was reduced to a minimum. To distinguish between the Boussinesq approximated equation set for the turbulent atmospheric flow denoted as Boussinesq fluid and this re-formulated one, the turbulent flow of the compressible atmosphere for which the re-formulated governing balance equations are valid was designated as Hesselberg fluid.

Based on the 1st-order balance equations, it was pointed out that the parameterisation of the vertical dispersion of trace species in the atmospheric boundary controversially discussed by several authors arises from averaging the macroscopic balance equations of matter, momentum and various energy forms in the sense of Reynolds, rather than from the parameterisation of the vertical dispersion by 1st-order closure principles (flux-gradient relationships), as the aforementioned discussion seems to reflect.

Although Reynolds averaging can exactly be performed, it leads to various short-comings in the set of governing equations for the turbulent atmospheric flow. Averaging the macroscopic equations for the molecular system yields several 2nd moments, but only one additional balance equation may directly be derived, namely the balance equation of TKE. Hence, several unknown quantities can be identified for which no balance equations are directly available. Thus, the set of governing equations for the turbulent atmospheric flow is highly underestimated, not only in the case of Reynolds averaging, but also in the case of Hesselberg (and Swinbank) averaging. This fact is well-known as the closure problem of turbulence. Obviously, the number of unknown quantities is appreciably larger in the case of Reynolds averaging than in that of Hesselberg (and Swinbank) averaging so that — even though Reynolds averaging seems to be exact — the set of governing equations for the turbulent atmospheric flow contain more gaps of information in the former than in the latter case. Customarily, most of these unknown quantities, i.e., density-fluctuation terms, occurring in the Reynolds averaged equation set are ignored. This procedure leads to the Boussinesq fluid. Then, however, the degree of shortcomings increases because ignoring these density-fluctuation terms clearly restricts the possibility to describe atmospheric processes as a whole. On the contrary, Hesselberg averaging reduces the risk to misinterpret atmospheric processes to a minimum. As exemplary shown in Section 10, the Webb correction will become insignificant if Hesselberg's averaging calculus is considered.

Second moments like the eddy flux densities of matter, momentum and sensible heat may be parameterised by 1st-order closure principles as theoretically investigated by Herbert (1975) on the basis of the entropy balance for turbulent atmospheric flows or by 2nd-order closure principles, where balance equations also for higher than 2nd moments must be derived. These higher-order balance equations, of course, still contain higher-order moments that have to be approximated. Thus, the set of governing equations for the turbulent atmospheric flow remains underestimated and parameterising of 2nd-order or higher-order moments by 1st-order or higher-order closure principles is indispensable.

Our results shown in Figs. 1, 2 substantiate that segregation effects cannot generally be neglected as usually performed in Eulerian air pollution models for chemically reactive trace constituents. Concurrently computing such segregation effects, however, requires, at least, 2nd-order-closure principles. Thus, an evaluation of Eulerian air pollution models also requires directly measured 2nd-order moments like variances, eddy fluxes, and further covariance terms. Since the number of fast-response physico-chemical analysers for chemically reactive trace constituents is strongly limited (see, e.g., Kramm et al., 1999, and references therein), such fast-response sensors have to be (further) developed to directly determine such 2nd moments, especially vertical eddy flux densities of trace constituents and segregation effects owing to turbulence. The results provided by such fast-response sensors are necessary to set-up a *true* platform for model evaluation which implies not only a comparison of calculated and observed distributions of 1st moments (necessary condition), but also a comparison of the calculated and observed distributions of 2nd moments (sufficient condition).

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10. Appendix A

The Webb correction

As suggested by Webb et al. (1980) for moist air, the vertical eddy flux densities of sensible heat and water vapour are able to generate a mean vertical velocity $\overline{w} = -\overline{\rho_0' w'}/\overline{\rho_0} \neq 0$, even if horizontally homogeneous conditions are considered. It agrees with their hypothesis that the mean vertical flux density of a dry air constituent should be zero, i.e., $\overline{\rho_0 w} = 0$. Here, w' is the fluctuation of the vertical velocity, and $\overline{\rho_0' w'}$ is the eddy flux density of dry air that has to be related to the vertical eddy flux densities of sensible heat and water vapour (Webb et al., 1980). Hence, the total vertical flux density of a trace species is then given by $F_i = \overline{\rho_i}\,\overline{w} + \overline{\rho_i' w'}$ (see also eq. (2.7)), and the vertical dispersion of such trace species seems to be appreciably affected by the eddy flux densities of sensible heat and water vapour. In the following, it is shown that the conventional Webb correction, is based on a popular fallacy:

In accord with Kramm et al. (1995), $\overline{w}$ can exactly be expressed by

$$\overline{w} = -\frac{1}{\overline{\rho}(1 - \overline{\rho_1}/\overline{\rho})} \cdot \{1 - \overline{m_1})\overline{\rho' w'} - \overline{\rho}\,\overline{w' m_1'} - \overline{\rho' w' m_1'}\}, \tag{A1a}$$

where $m_1 = \rho_1/\rho$ is the specific humidity, ρ_1 is the partial density of water vapour, and $F_1 = \overline{\rho}\,\overline{w' m_1}$ is the corresponding eddy flux density. If the 3rd moment is neglected and the fluctuation of the air density is Boussinesq approximated by $\rho' \approx -T'\overline{\rho}/\overline{T}$ (Lumley and Panofsky, 1964), the mean vertical wind component will become

$$\overline{w} \cong \frac{1}{1 - \overline{\rho_1}/\overline{\rho}} \left\{ (1 - \overline{m_1}) \frac{\overline{w' T'}}{\overline{T}} + \overline{w' m_1'} \right\}. \tag{A1b}$$

i.e., the suggestion of Webb et al. (1980) appears to be correct. However, $\overline{\rho' \boldsymbol{v}'}$ and, hence, $\overline{\rho' w'}$ occurring in eq. (A1a) must be equal to zero (see Section 2), i.e.,, $\overline{\rho_0' w'} = -\overline{\rho_1' w}$, if a Boussinesq fluid is considered. Thus, the heat transfer effect occurring in eq. (A1b) is mainly the result of an inconsistent utilisation of the Boussinesq approximation.

The Webb correction will become insignificant if Hesselberg's averaging calculus is considered. This opposite result can be explained as follows (see also Kramm et al., 1995):

Assuming that steady-state conditions exist during the measuring interval (the most important prerequisite to calculate an eddy flux density from time series) and assuming, in addition, horizontal homogeneity, one can derive from eqs. (3.3) and (3.10)

$$\frac{\partial}{\partial z}(\bar{\rho}\hat{w}\hat{m}_1 + \overline{\rho w'' m_1''}) = 0, \tag{A2}$$

$$\frac{\partial}{\partial z}(\bar{\rho}\hat{w}\hat{\chi}_i + \overline{\rho w'' \chi_i''}) = 0, \tag{A3}$$

when phase transition and chemical processes as well as molecular transfer processes are ignored, as done by Webb et al. (1980). Kramm et al. (1995) showed that in moist air the vertical eddy flux density of water vapour, $\overline{\rho w'' m_1''}$, may generate a mean vertical wind component,

$$\hat{w} = \frac{\overline{\rho w'' m_1''}}{\bar{\rho}(1-\hat{m}_1)}, \tag{A4}$$

even for horizontally homogeneous conditions. Obviously, it is similar to eq. (A1b) when in the case of the Boussinesq fluid the heat transfer effect is neglected. Eq. (A4) is based also on the hypothesis that the mean vertical flux density of a dry air constituent is zero, i.e., $\overline{\rho_0 w} = 0$, as suggested by Webb et al. (1980). Their hypothesis implies that under steady-state conditions both terms $\partial(\overline{\rho_0 w})/\partial z$ and $\nabla_H \cdot (\overline{\rho_0 \boldsymbol{v}_H})$ are equal to zero, i.e., there exist no sources and sinks for the eddy flux density of dry air. (The index H denotes the horizontal part of the vector operation.) Hence, $\overline{\rho_0 w} = 0$ is compatible with horizontal homogeneity.

Taking eq. (A4) into account, eqs. (A2) and (A3) provide

$$\frac{\partial}{\partial z}\left\{\frac{1}{1-\hat{m}_1}\overline{\rho w'' m_1''}\right\} = 0 \tag{A5}$$

and, hence,

$$\frac{1}{1-\hat{m}_1}\overline{\rho w'' m_1''} = \rho\hat{w} = \text{constant*} \tag{A6}$$

as well as

$$\frac{\partial}{\partial z}\left\{\frac{\hat{\chi}_i}{1-\hat{m}_1}\overline{\rho w'' m_1''} + \overline{\rho w'' \chi_i''}\right\} = 0 \tag{A7}$$

and hence

$$\frac{\partial}{\partial z}(\overline{\rho w'' \chi_i''}) = -\frac{1}{1-\hat{m}_1}\overline{\rho w'' m_1''}\frac{\partial \hat{\chi}_i}{\partial z}. \tag{A8}$$

Obviously, the right-hand side of eq. (A8) does not vanish, i.e., the water vapour flux density along with the gradient of the mean mass fraction are responsible for the fact that the vertical eddy flux density of a trace species may depend on height. This result is in contradiction to the conventional Webb correction which implies that the vertical eddy flux densities of sensible heat and water vapour are solely responsible for the correction on vertical eddy flux densities of trace species and, as discussed above, for their variation with height owing to turbulence.

Integrating eq. (A8) for the layer $0 \leqslant z \leqslant z_R$ (where z_R is the reference height) provides (see Kramm et al., 1995):

$$F_{i,R} = \overline{\rho w'' \chi_i''}|_{z=z_R} = F_{i,S} - \frac{\hat{\chi}_{i,R} - \hat{\chi}_{i,S}}{1-\hat{m}_1}\overline{\rho w'' m_1''}$$
$$= F_{i,S} - (\overline{\rho_{i,R}} - \overline{\rho_{i,S}})\hat{w}. \tag{A9}$$

Here, $F_{i,S}$ is the vertical flux density of a trace species at the surface (measured, for instance, by enclosure techniques), $\hat{\chi}_{i,S}$ is the corresponding mean mass fraction, $F_{i,R}$ is the eddy flux density of this trace species at z_R, and $\hat{\chi}_{i,R}$ is the mean mass fraction at the same height. Eq. (A9) illustrates that the relative importance of the flux correction depends on both the mean vertical wind component and the density difference $\Delta\rho_i = \overline{\rho_{i,R}} - \overline{\rho_{i,S}}$.

Taking eq. (A4) and the Bowen-ratio $\beta = H/E$ into account, the density-weighted vertical wind component can also be written as

$$|\hat{w}| = \frac{H}{\bar{\rho}(1-\hat{m}_1)|\beta| L_v}. \tag{A10}$$

Here, $E = \lambda_{21} F_1$ is the vertical eddy flux density of latent heat, and $\lambda_{21} \approx 2.5 \cdot 10^6$ J/kg is the heat of vaporisation. As shown by Kramm et al. (1995), in most cases the density-weighted vertical wind

* This assumption implies that the water vapour flux density will not become zero at the surface even if the fluctuations of the vertical wind speed and its mean value vanish there. Close to the surface the water vapour flux density is maintained essentially by molecular diffusion.

component induced by water vapour fluctuations is negligible except for small values of $|\beta|$ and large values of H which correspond to very large amounts of latent heat flux densities.

Thus, in most cases the term $\Delta\rho_i \hat{w}$ in eq. (A9) can be neglected because $\Delta\rho_i$ and $F_{i,\mathrm{R}}$ cannot be considered as entirely independent of each other. Note that similar results will be obtained if the Boussinesq approximation is consistently performed so that the effects owing to the eddy flux density of sensible heat in eq. (A1b) have to be neglected.

REFERENCES

André, J.-C., De Moor, G., Lacarrere, P. and Du Vachat, R. 1976. Turbulence approximations for inhomogeneous flows. Part I: The clipping approximation. *J. Atmos. Sci.* **33**, 476–481.

Batchelor, G. K. 1949. Diffusion in a field of homogeneous turbulence. *Austr. J. Sci. Res.* **A2**, 437–450.

Bernhardt, K. 1964. Zur Definition der turbulenten Austauschströme, insbesondere des Turbulenzwärmestroms. *Z. f. Meteor.* **17**, 95–108 (in German).

Bernhardt, K. 1965. Der Impulsaustauschtensor bei Berücksichtigung der turbulenten Dichteschwankungen. *Z. f. Meteor.* **18**, 103–106 (in German).

Bernhardt, K. 1972. Nochmals zur Definition des Turbulenzwärmestroms in der Wärmehaushaltsgleichung der Atmosphäre. *Z. f. Meteor.* **23**, 65–75 (in German).

Bernhardt, K. and Lauter, E. A. 1977. Globale physikalische Prozesse und Umwelt. *Z. f. Meteor.* **27**, 1–20 (in German).

Boussinesq, J. 1877. Théorie de l'écoulment tourbillant. *Mem. Pres. Acad. Sci. Paris* **XXIII**, 46 pp. (in French).

Busch, N. E. 1973. On the mechanics of atmospheric turbulence. In: Haugen, D. A. (ed.): *Workshop on Micrometeorology*. Amer. Meteor. Soc., Boston, pp. 1–65.

Businger, J. A. and Deardorff, J. W. 1968. On the distinction between "total" and eddy heat flux. *J. Atmos. Sci.* **25**, 521–522.

Businger, J. A. 1973. Turbulent transfer in the atmospheric surface layer. In: Haugen, D. A. (ed.): *Workshop on Micrometeorology*. Amer. Meteor. Soc., Boston, pp. 67–100.

Cox, G. 1995. Basic considerations. In: Cox, G. (ed.): *Combustion fundamentals of fire*. Academic Press, London, San Diego, New York, pp. 3–30.

Chang, J. S., Brost, R. A., Isaksen, I. S. A., Madronich, S., Middleton, P., Stockwell, W. R. and Walcek, C. J. 1987. A three-dimensional Eulerian acid deposition model: Physical concepts and formulation. *J. Geophys. Res.* **D92**, 14681–14700.

Damköhler, G. 1940. Influence of turbulence on the velocity of flames in gas mixtures. *Z. Elektrochem.* **46**, 601–626.

Deardorff, J. W. 1973. Three-dimensional numerical modeling of the planetary boundary layer. In: Haugen, D. A. (ed.): *Workshop on Micrometeorology*. Amer. Meteor. Soc., Boston, pp. 271–311.

De Groot, S. R. and Mazur, P. 1969. *Non-equilibrium thermodynamics*. North-Holland Publishing Comp., Amsterdam/London, 514 pp.

Doms, G. and Herbert, F. 1985. Fluid- und Mikrodynamik in numerischen Modellen konvektiver Wolken. *Berichte Inst. f. Meteor. u. Geophys. Univ. Frankfurt/Main* nr. **62**, 378 pp. (in German).

Donaldson, C. duP. 1973. Construction of a dynamic model of the production of atmospheric turbulence and the dispersal of atmospheric pollutants. In: Haugen, D. A. (ed.): *Workshop on Micrometeorology*. Amer. Meteor. Soc., Boston, pp. 313–392.

Eliassen, A. and Kleinschmidt, Jr., E. 1957. Dynamic meteorology. In: Flügge, S. (ed.): *Handbuch der Physik*, Bd. XLVIII. Springer-Verlag Berlin/Heidelberg/New York, pp. 1–154.

Ertel, H. 1943. Die hydro-thermodynamischen Grundgleichungen turbulenter Luftströmungen. *Meteorol. Zeitschrift* **60**, 289–295 (in German).

Fortak, H. 1969. Zur Energetik der planetarischen Grenzschicht. *Annalen der Meteorologie* (NF) **4**, 157–162 (in German).

Garratt, J. R. 1994. *The atmospheric boundary layer*. Cambridge University Press, 316 pp.

Gatski, T. B. 1997. Modeling compressibility effects on turbulence. In: Métais, O. and Ferziger, J. (eds.): *New tools in turbulence modeling*. Springer-Verlag, Berlin/Heidelberg/New York, pp. 73–104.

Georgii, H.-W. 1965. Untersuchungen über Ausregnen und Auswaschen atmosphärischer Spurenstoffe durch Wolken und Niederschlag. *Berichte Deutscher Wetterdienst* nr. **100** (in German).

Georgii, H.-W. 1985. Chemische Reaktionen von Gasen und Aerosolen in Regen- und Wolkentropfen und ihre feuchte und trockene Deposition. In: Becker, K. H. und Löbel, J. (eds.): *Atmosphärische Spurenstoffe und ihr physikalisch-chemisches Verhalten*. Springer-Verlag, Berlin/Heidelberg/New York/Tokyo, pp. 129–152 (in German).

Georgopoulos, P. G. and Seinfeld, J. H. 1986. Mathematical modeling of turbulent reacting plumes — I. General theory and model formulation. *Atmos. Environ.* **20**, 1791–1807.

Glansdorff, P. and Prigogine, I. 1971. *Thermodynamic theory of structure, stability and fluctuations*. Wiley-Interscience, London, 306 pp.

Güsten, H., Heinrich, G., Mönnich, E., Sprung, D., Weppner, J., Ramadan, A. B., Ezz El-Din, M. R. M., Ahmed, D. M. and Hassan, G. K. Y. 1996. On-line measurements of ozone surface fluxes. Part II: Surface

level ozone fluxes onto the Sahara desert. *Atmos. Environ.* **30**, 911–918.
Herbert, F. 1975. Irreversible Prozesse der Atmosphäre — 3. Teil (Phänomenologische Theorie mikroturbulenter Systeme). *Beitr. Phys. Atmosph.* **48**, 1–29 (in German).
Herbert, F. 1980. Prigogine's diffusion theorem and its application to atmospheric transfer processes. Part 1: The governing theoretical concept. *Beitr. Phys. Atmosph.* **53**, 181–203.
Herbert, F. 1983. Prigogine's diffusion theorem and its application to atmospheric transfer processes. Part 2: Invariance properties and Fick type diffusion laws. *Beitr. Phys. Atmosph.* **56**, 480–494.
Herbert, F. 1995. A re-evaluation of the Webb correction using density-weighted averages — Comment. *J. Hydrol.* **173**, 343–344.
Hesselberg, T. 1926. Die Gesetze der ausgeglichenen atmosphärischen Bewegungen. *Beitr. Phys. fr. Atmosph.* **12**, 141–160 (in German).
Hinze, J. O. 1975. *Turbulence*. McGraw-Hill, New York/Toronto/London, 586 pp.
Högström, U. 1990. Analysis of turbulence structure in the surface layer with a modified similarity formulation for near neutral conditions. *J. Atmos. Sci.* **47**, 1949–1972.
Holton, J. R. 1979. *An Introduction to dynamic meteorology*. Academic Press, New York, San Francisco, London, 391 pp.
Jones, W. P. and Whitelaw, J. H. 1982. Calculation methods for reacting turbulent flows: a review. *Combust. Flame* **48**, 1–26.
Kramm, G. 1987. Ein dynamisch-kinetisches Modell der atmosphärischen Grenzschicht zur Simulation von photochemischem Smog. *IABG-Bericht* **B-TD 9004/01** (in German).
Kramm, G. 1991. Modellierung des Vertikaltransports von Aerosolpartikeln in der bodennahen Luftschicht. *Meteorol. Rdsch.* **43**, 65–80 (in German).
Kramm, G., Beheng, K.-D. and Müller, H. 1992. Vertical transport of polydispersed aerosol particles in the atmospheric surface layer. In: Schwartz, S. E. and Slinn, W. G. N. (eds.): *Precipitation scavenging and atmosphere–surface exchange processes*, vol. 2 — The Semonin, vol. Hemisphere Publ., Washington/Philadelphia/London, pp. 1125–1141.
Kramm, G., Dlugi, R. and Lenschow, D. H. 1995. A re-evaluation of the Webb-correction using density-weighted averages. *J. Hydrol.* **166**, 283–292.
Kramm, G., Dlugi, R., Mölders, N. and Müller, H. 1994. Numerical investigations of the dry deposition of reactive trace gases. In: Baldasano, J. M., Brebbia, C. A., Power, H. and Zannetti, P. (eds.): *Air pollution II*, vol. 1: *Computer simulation*. Computational Mechanics Publications, Southampton, Boston, pp. 285–307.
Kramm, G., Herbert, F., Bernhardt, K., Müller, H., Werle, P., Foken, T. and Richter, S. H. 1996. Stability functions for momentum, heat and water vapour and the vertical transport of TKE and pressure fluctuations estimated from measured vertical profiles of wind speed, temperature, and humidity. *Beitr. Phys. Atmosph.* **69**, 463–475.
Kramm, G., Beier, N., Dlugi, R. and Müller, H. 1999. Evaluation of conditional sampling methods. *Beitr. Phys. Atmosph.* **72**, 161–172.
Lenschow, D. H., 1982. Reactive trace species in the boundary layer from a micrometeorological perspective. *J. Meteor. Soc. Japan* **60**, 472–480.
Libby, P. A. and Williams, F. A. (eds.): 1980. *Turbulent reacting flows*. Springer-Verlag, Berlin.
Lorenz, E. N. 1967. *The nature and theory of the general circulation of the atmosphere*. World Meteorological Organization, **WMO-No. 218.Tp.115**, Geneva, Switzerland, 161 pp.
Lumley, J. L. and Panofsky, H. A. 1964. *The structure of atmospheric turbulence*. Interscience Publishers (Wiley & Sons), New York/London/Sydney, 239 pp.
McBean, G. A. and Elliott, J. A. 1975. The vertical transport of kinetic energy by turbulence and pressure in the boundary layer. *J. Atmos. Sci.* **32**, 753–766.
McRae, G. J., Goodin, W. R. and Seinfeld, J. H. 1982. Mathematical modeling of photochemical air pollution. *Environmental Quality Laboratory Report* Nr. **18**. California Institute of Technology, Pasadena, CA.
Miller, J. E. 1951. Energy equations. *Compendium of Meteorology*. Amer. Meteor. Soc., 483–491.
Mölders, N., Hass, H., Jakobs, H. J., Laube, M. and Ebel, A. 1994. Some effects of different cloud parameterizations in a mesoscale model and a chemistry transport model. *J. Appl. Met.* **33**, 527–545.
Montgomery, R. B. 1948. Vertical eddy flux of heat in the atmosphere. *J. Meteorol.* **5**, 265–274.
Montgomery, R. B. 1954. Convection of heat. *Archiv Meteorol. Geophys. Biokl.* **A7**, 125–132.
Moss, J. B. 1995. Turbulent diffusion flames. In: Cox, G. (ed.): *Combustion fundamentals of fire*. Academic Press, London, San Diego, New York, pp. 221–272.
Nestlen, M., Müller, H. and Meixner, F. 1993. Measurements of vertical fluxes of CO_2, H_2O, NO, NO_2 and O_3 by eddy correlation: first results from the BIATEX/SANA Experiment "Eisdorf", March 1991. In: Borell, P. M., et al. (eds.): *Photo-oxidants: precursors and products*. SPB Academic Publishing bv., The Hague, The Netherlands, pp. 727–731.
Nieuwstadt, F. T. M. and Meeder, J. P. 1997. Large-eddy simulation of air pollution dispersion: a review. In: Métais, O. and Ferziger, J. (eds.): *New tools in turbulence modeling*. Springer-Verlag, Berlin/Heidelberg/New York, pp. 265–280.
Obukhov, A. M. 1954. Statisticeskoe opisanie nepreryvnych polej. *Trudy Geofiz. Inst. AN SSSR* **24** (151), 3–42 (in Russian; German translation in Goering, H. (ed.): *Sammelband zur statistischen Theorie der Turbulenz*. Akademie-Verlag, Berlin, 1958, 1–42).
Pichler, H. 1984. *Dynamic der Atmosphäre*. Bibliographisches Institut, Zürich, 456 pp. (in German).
Prigogine, I. 1947. Étude thermodynamique des phéno-

meves irréversibles. Thesis, Dunod, Paris, and Desoer, Liège (in French).

Rotta, J. C. 1951. Statistische Theorie nichthomogener Turbulenz. *Z. Physik* **129**, 547–572 (in German).

Rotta, J. C. 1963. Bemerkungen zum Einfluß der Dichteschwankungen in turbulenten Grenzschichten bei kompressibler Strömung. *Ing.-Arch.* **32**, 187–190 (in German).

Rotta, J. C. 1972. *Turbulente Strömungen.* B.G. Teubner, Stuttgart, 267 pp. (in German).

Schmidt, W. 1925. Der Massenaustausch in freier Luft und verwandte Erscheinungen. In: *Probleme der kosmischen Physik*, Bd. 7. Grand, H., Hamburg (in German).

Schumann, U. 1989. Large-eddy simulation of turbulent diffusion with chemical reactions in the convective boundary layer. *Atmos. Environ.* **23**, 1713–1727.

Scott, W. D. and Hobbs, P. V. 1967. The formation of sulfate in water droplets. *J. Atmos. Sci.* **24**, 54–57.

Sehmel, G. A. 1980. Particle and gas dry deposition: A review. *Atmos. Environ.* **14**, 983–1011.

Seinfeld, J. H. 1986. *Atmospheric chemistry and physics of air pollution.* J. Wyley & Sons, New York/Chichester/Brisbane/Toronto/Singapore, 738 pp.

Sievers, U. 1984. The turbulent atmosphere and the inclusive system of model equations. *Beitr. Phys. Atmosph.* **57**, 324–345.

Sorbjan, Z. 1989. *Structure of the atmospheric boundary layer*. Prentice Hall, Englewood Cliffs, NJ, 317 pp.

Stockwell, W. R. 1995. Effects of turbulence on gas-phase atmospheric chemistry: Calculation of the relationship between time scales for diffusion and chemical reactions. *Meteorol. Atmos. Phys.* **57**, 159–171.

Stull, R. B. 1988. *An introduction to boundary layer meteorology*. Kluwer Academic Publishers, Dordrecht, 666 pp.

Swinbank, W. C. 1951. The measurement of vertical transfer of heat and water vapor by eddies in the lower atmosphere. *J. Meteor.* **8**, 135–145.

Szablewski, W. 1963. Zum Einfluß der Dichteschwankungen auf den turbulenten Austausch in kompressiblen turbulenten Grenzschichten. *Ing.-Arch.* **32**, 191–192 (in German).

Tennekes, H. and Lumley, J. L. 1978. *A first course in turbulence*. MIT Press, Cambridge, Mass., 300 pp.

Thomson, D. 1995. The parameterization of the vertical dispersion of a scalar in the atmospheric boundary layer. *Atmos. Environ.* **29**, 1343.

Thomson, D. 1998. Author's reply. *Atmos. Environ.* **32**, 258.

Van Dop, H. 1998. The parameterization of the vertical dispersion of a scalar in the atmospheric boundary layer. *Atmos. Environ.* **32**, 257–258.

Van Mieghem, J. 1949. Les equations générales de la mécanique et de l'énergétique des milieux turbulents en vue des applications à la météorologie. *Inst. R. Météor. Belgique., Mém.* **XXXIV**, 60 pp. (in French).

Van Mieghem, J. 1951. Application of the thermodynamics of open systems to meteorology. *Compendium of Meteorology*. Amer. Meteor. Soc., 531–538.

Van Mieghem, J. 1973. *Atmospheric energetics.* Clarendon Press, Oxford, 306 pp.

Venkatram, A. 1993. The parameterization of the vertical dispersion of a scalar in the atmospheric boundary layer. *Atmos. Environ.* **27A**, 1963–1966.

Venkatram, A. 1998. Response. *Atmos. Environ.* **32**, 259.

Venkatram, A., Karamchandani, P. K. and Misra, P. K. 1988. Testing a comprehensive acid deposition model. *Atmos. Environ.* **22**, 737–747.

Veynante, D. and Poinsot, T. 1997. Reynolds averaged and large eddy simulation modeling for turbulent combustion. In: Métais, O. and Ferziger, J. (eds.): *New tools in turbulence modeling*. Springer-Verlag, Berlin/Heidelberg/New York, pp. 105–140.

Vilà-Guerau de Arellano, J. and Duynkerke, P. G. 1993. Second-order closure study of the covariance between chemically reactive species in the surface layer. *J. Atmos. Chem.* **16**, 145–155.

Vogel, B., Fiedler, F. and Vogel, H. 1995. Influence of topography and biogenic volatile organic compounds emission in the state of Baden-Würtemberg on ozone concentartions during episodes of high air temperature. *J. Geophys. Res.* **100**, 22907–22928.

Webb, E. K., Pearman, G. I. and Leuning, R. 1980. Correction of flux measurements for density effects due to heat and water vapour transfer. *Quart. J. R. Met. Soc.* **106**, 85–100.

Wilczak, J., Bedard, Jr., A. J., Edson, J., Hare, J., Hojstrup, J. and Mahrt, L. 1995. *Pressure transport measured on a sea mast during the RASEX program.* Presented at the 11th Symposium on Boundary Layers and Turbulence, Charlotte, NC, March 27–31, 1995, 11–14.

Wyngaard, J. C. and Coté, O. R. 1971. The budget of turbulent kinetic energy and temperature variance in the atmospheric surface layer. *J. Atmos. Sci.* **28**, 190–201.