Quality and irreversibility: constraints on ecosystem development

Ernesto Bosatta and Göran I. Ågren*

Department of Ecology and Environmental Research, Swedish University of Agricultural Sciences, PO Box 7072, SE-750 07 Uppsala, Sweden

We discuss one of the most general mathematical tools for analysing dynamical systems: the master equation (ME). The ME is used to derive models for entropy production in closed and open systems. Due to dissipation in open systems, the direction of evolution of important characteristics can be opposite to those imposed on closed systems. When applying these models to soil organic matter it can be shown that the principle of minimum entropy production necessitates that more and more recalcitrant organic matter is produced the further the decomposition proceeds. The necessity to dissipate entropy can also impose a limit on the degree to which litters can decompose, but interaction between litters of differing ages can remove this constraint. This is an example of the 'priming' effect.

Keywords: master equation; entropy production; open systems; closed systems; soil organic matter dynamics

1. INTRODUCTION

Schrödinger (1944) reconciled biology with thermodynamics in his seminal book 'What is life?' by pointing out that it is non-equilibrium and not equilibrium thermodynamics that is the appropriate form of thermodynamics. Numerous subsequent publications have aspired to show how non-equilibrium thermodynamics can be used to improve our understanding of the physical and chemical constraints on life (e.g. Johnson 1992; Schneider & Kay 1994). However, the examples used to demonstrate the application of non-equilibrium thermodynamics usually do not go any further than to draw analogies to simple physical systems, for example the Bénard cell (Bianciardi & Ulgiati 1998). A major barrier to progress seems to be that energy, a key variable in thermodynamics, is a variable appearing in too many forms to be easily useful in biological systems as Månsson & McGlade (1993) observed in a critical review.

We will here show, in the form of a general mathematical formalism, an alternative to the energy-based considerations: the master equation (ME). From this equation entropy production in closed and open systems can be calculated and analyses be made of the constraints that entropy production imposes on a system. Of particular importance are constraints on the direction of change of certain variables. Soil organic matter (SOM) is used as the ecological subject to demonstrate the consequences of such constraints. This choice is not arbitrary because it has been shown previously (Ågren & Bosatta 1998) that a ME in the phase space of qualities describes SOM dynamics with great accuracy.

2. BASIC FORMALISM

Master equations in physics make it possible to derive macroscopic properties of a system from microscopic

(molecular and atomic) properties and is the foundation for the derivation of statistical mechanics from molecular and atomic physics. We will start by introducing the formalism involved. Much of this can be found in other texts, for example, Haken (1977), but it will nevertheless be discussed extensively because the formalism requires some extension and special adaptation for the current purposes.

The ME is one of the most important means of determining the probability distribution of a process. Consider a large number of particles jumping between a large number of boxes; the boxes are arranged in a one-dimensional lattice along the real axis and are numbered 1, 2, ... m , ... We want to calculate the probability of finding a particle in box m at time t . This probability, $p_m(t)$, increases due to transitions from other boxes m' to box m and decreases due to transitions leaving box m ; this gives the general relation

$$\dot{p}_m(t) = \frac{dp_m(t)}{dt} = \text{rate in} - \text{rate out.} \quad (2.1)$$

As the 'rate in' consists of all transitions from initial boxes m' to box m , it comprises the sum over the initial boxes. Each term is given by the probability of finding the particle in box m' , $p_{m'}(t)$, multiplied by the transition probability per unit time to pass from m' to m , $\Omega_{m,m'}$. Thus,

$$\dot{p}_m(t) = \sum_{m'} \Omega_{m,m'} p_{m'}(t) - p_m(t) \sum_{m'} \Omega_{m,m'} \quad (2.2)$$

that is called the ME. In physics, the particles are atoms, electrons, etc. and m denotes states of the physical system (energy, momentum, etc.); in the application below m represents states of *quality*, while the particles are carbon atoms. The crux in deriving a ME is to determine the transition rates Ω explicitly. This can be done in two ways. Either we write down the Ω values by means of plausibility arguments (see application in § 5) or the Ω values are derived from first principles, where mostly quantum statistical methods are used (see also Bergner 1993).

* Author for correspondence (goran.agren@eom.slu.se).

MEs have been studied extensively. There are several theorems that are important in applications (Haken 1977).

- (i) Normalization is preserved, i.e.

$$\sum_m p_m(t) = 1. \quad (2.3)$$

This means that the probability of finding the particle in some box equals 1 at all times (see Appendix A);

- (ii) there exists always at least one stationary solution to equation (2.2);
- (iii) if the stationary solution is unique then, as $t \rightarrow \infty$, $p_m(t)$ tends to the stationary solution for any initial $p_m(0)$. This last property is important since it implies that under certain circumstances it is possible to define a Lyapunov function or entropy functions, $S(t)$, to the ME

$$S(t) = -\sum_m p_m(t) \ln p_m(t) \quad (2.4)$$

such that $S(t)$ increases monotonically with time. $S(t)$ is known as the Boltzman or Shannon entropy (Haken 1977; Frieden 1998). The derivative of equation (2.4) gives the entropy production:

$$\begin{aligned} \dot{S}(t) &= \frac{dS}{dt} = -\sum_m \dot{p}_m(t) \ln p_m(t) - \sum_m \dot{p}_m \frac{p_m}{p_m} \\ &= -\sum_m \dot{p}_m \ln p_m \end{aligned} \quad (2.5)$$

because due to equation (2.3), $\sum_m \dot{p}_m = 0$.

Equations (2.2) and (2.5), the ME and entropy-production equation, respectively, are our basic starting point. Before proceeding further, two preliminary steps need to be taken. First, we change the formalism by moving from the discrete lattice of boxes to a continuous distribution of points along the real axis (we denote it with q , $0 \leq q \leq \infty$), i.e. from the discrete probability $p_m(t)$ to the continuous *density* probability $p(q, t)$. The product $p(q, t) dq$ defines the probability of finding the particle at time t in an interval of length dq around q . This formalism, which is more convenient from a calculational point of view, is discussed in Appendix A where the continuous counterparts of equations (2.2) and (2.5) are derived. Another reason is that equation (2.2) is too general and difficult to handle in combination with equation (2.5). In Appendix B it is shown, starting from the ME (2.2), how new equations for more restricted processes can be derived that still admit the definition of a Boltzman entropy. We will now proceed with the derivation of the formalism here and return later to the question of how to use the formalism in connection with a specific application.

3. CLOSED SYSTEMS

A simpler, restricted form of the ME is

$$\frac{\partial p(q, t)}{\partial t} = \frac{\partial [w_1(q)p(q, t)]}{\partial q} = -\frac{\partial \mathcal{F}}{\partial q}. \quad (3.1)$$

Equation (3.1) is a conservation equation for a flow of

particles moving along the q axis with velocity $-w_1(q)$, where $\mathcal{F} = -w_1 p$ is the flow of particles. Equation (3.1) is a ME for a more restricted process where the particles only make jumps between adjacent boxes. However, the distance between the boxes is not constant but depends on q . In Appendix B it is shown how to derive equation (3.1) from the ME (2.2) and, in particular, that $w_1(q)$ is the first moment of the *density* transition probability rate $\Omega(q, q')$. If the flow of particles is zero across the boundaries, i.e. $\mathcal{F}(0, t) = \mathcal{F}(\infty, t) = 0$, then the system is *closed* and normalization is preserved (Appendix B).

At time zero, i.e. $t = 0$, there is a certain distribution of particles $p(q, 0)$ centred around some mean value $\hat{q}$ and with a certain variance σ^2 . By definition

$$\hat{q}(t) = \int_0^\infty qp(q, t) dq \quad (3.2)$$

and

$$\sigma^2(t) = \int_0^\infty (q - \hat{q})^2 p(q, t) dq. \quad (3.3)$$

The dynamics of $\hat{q}$ and σ^2 are strongly dependent on the choice of $w_1(q)$ (Appendix B).

We shall now choose $w_1(q)$ by means of plausibility arguments adapted to the needs of the ecological application under discussion. It is assumed for the sake of simplicity that

- (i) $w_1(0) = 0$; and
- (ii) $w_1(q)$ and $w'_1(q) = \partial w_1 / \partial q$ do not change sign over the entire range of q , i.e. that $w_1(q)$ and $w'_1(q)$ change monotonically with q .

Condition (i) ensures that no particle jumps to negative values of q . The assumption that w_1 does not change sign means that particles, on average, will either drift towards zero or towards infinity independently of their start position. The assumption of the derivative of w_1 means that with increasing q the particle will, on average, be displaced more and more from its original state at transition. Together, conditions (i) and (ii) imply that either

$$w_1(q) > 0 \text{ and } w'_1(q) > 0 \text{ for all } q \quad (3.4a)$$

or

$$w_1(q) < 0 \text{ and } w'_1(q) < 0 \text{ for all } q. \quad (3.4b)$$

If we choose the velocity according to equation (3.4a) then according to equations (B 7) and (B 9), $\hat{q}$ and σ^2 decrease monotonically in time from their initial values; but if equation (3.4b) is chosen $\hat{q}$ and σ^2 increase.

Let us calculate the entropy production of the system described by equation (3.1). Using equation (A 6),

$$\begin{aligned} \dot{S}(t) &= -\int_0^\infty \frac{\partial p}{\partial t} \ln p dq = -\int_0^\infty \frac{\partial (w_1 p)}{\partial q} \ln p dq \\ &= -w_1 p \ln p \Big|_0^\infty + \int_0^\infty w_1 p \frac{1}{p} \frac{\partial p}{\partial q} dq = w_1 p \Big|_0^\infty - \int_0^\infty \frac{\partial w_1}{\partial q} p dq \\ &= -\int_0^\infty \frac{\partial w_1(q)}{\partial q} p(q, t) dq = -\dot{w}'_1(t). \end{aligned} \quad (3.5)$$

The terms $w_1 p \ln p$ and $w_1 p$ are zero at the boundaries $(0, \infty)$ because of equations (B 4) and (B 5). Since entropy production must be positive, the mean value of $\partial w_1 / \partial q$ must be negative. Thus, for the two possible alternative definitions of velocity given by equations (3.4a) and (3.4b), only equation (3.4b) is compatible with positive entropy production. If $w_1(q)$ is constant (constant velocity) the entropy production is zero; a constant w_1 implies a uniform motion ($dw_1/dt = 0$). In a physical system this would be interpreted as indicating that the 'internal forces' are zero.

This leads to the following conclusion: *the condition that entropy production must be positive imposes upon the closed system described by equation (3.1) that $\dot{q}$ and σ^2 must increase with time.* This is understandable, because to increase the entropy the particles have to be spread out over the q -axis and this can only be done by moving towards the open end of the axis, i.e. on average towards larger q values. Entropy is commonly interpreted as a measure of 'disorder'. If $p(q, t)$ is concentrated around some particular q values (small σ) then it exhibits low levels of disorder; conversely, a high level of disorder means a lack of predictability of values of q over its range (large σ).

Entropy and time are related. If $w_1(q) > 0$, equation (3.1) can be rewritten as

$$\frac{\partial p}{\partial t} - \frac{\partial \mathcal{F}}{\partial q} = 0. \quad (3.6)$$

Equation (3.6), however, can also be obtained from equation (3.1) by reversing time (i.e. $t \rightarrow -t$). In other words, q , σ and S decrease in a closed system if time moves backwards. The system defined in equation (3.1) clearly illustrates that entropy and time are intimately related.

4. OPEN SYSTEMS

Total density is no longer conserved in open systems; they are dissipative structures. To distinguish this non-conserved density from the conserved probability p used so far, it is denoted by ρ . Let us add a dissipative term $k(q)\rho(q, t)$ to equation (3.1) as follows:

$$\frac{\partial \rho(q, t)}{\partial t} = \frac{\partial (w_1 \rho)}{\partial q} - k(q)\rho(q, t), \quad (4.1)$$

where $k(q)$ is the loss rate. There are now two kinds of processes acting on the system: internal processes of the kind described in equations (3.4a) and (3.4b) that are responsible for the first term in the right-hand side of equation (4.1); and dissipative processes responsible for the second term. If the internal processes predominate, ($k \approx 0$), then equation (4.1) reduces to equation (3.1), ($\rho \approx p$), and we can use equation (A 6) to define entropy production, but if the dissipative processes are large, definitions (2.4) and (2.5) are no longer useful (Nicolis & Prigogine 1989). However, equation (4.1) can be reformulated in such a way that equations (2.5) and (A 6), under special circumstances, are still meaningful definitions of entropy production.

Due to dissipation, normalization is no longer conserved even if there are no flows across the boundaries (cf. equations (B 4) and (B 5))

$$\int_0^\infty \dot{\rho} dq = w_1 \rho|_0^\infty - \int_0^\infty k \rho dq = - \int_0^\infty k \rho dq \neq 0. \quad (4.2)$$

Here, equation (4.2) is the rate of loss of particles from the system.

We can define a function $g(q)$ such that if $p_c(q, t)$ is the solution to the closed system (3.1)

$$\rho(q, t) = g(q)p_c(q, t), \quad (4.3)$$

where $g(q)$ is given by

$$k(q) = w_1(q) \frac{\partial \ln g(q)}{\partial q}. \quad (4.4)$$

Let us define the normalized distribution function of the open system

$$p_o(q, t) = \frac{g(q)}{\hat{g}(t)} p_c(q, t), \quad (4.5)$$

where

$$\hat{g}(t) = \int_0^\infty g(q)p_c(q, t) dq. \quad (4.6)$$

From equation (4.5) we get

$$\frac{\partial p_o(q, t)}{\partial t} = \frac{\partial (w_1 p_o)}{\partial q} - [k(q) - \hat{k}(t)] p_o, \quad (4.7)$$

where

$$\hat{k}(t) = \int_0^\infty k(q)p_o(q, t) dq. \quad (4.8)$$

The rescaling (normalizing) of equation (4.1) leads to a formulation of the open system, equation (4.7), in which internal processes can again be dominant. Dissipation does not vanish totally but it cancels out 'in the mean'; the variation over time and the variation over the q -axes of the dissipative processes do not differ too much. For example, if k is a constant, the last two terms in equation (4.7) cancel out exactly and the open system can be described entirely in terms of equation (3.1), $p_o \equiv p_c$. The general condition is that p_o and p_c are close or $g/\hat{g} \approx 1$. Equation (A 6) can then be used to make approximate estimates of entropy production.

In order to define more explicitly the 'closeness' of p_o and p_c we expand $g(q)$ in a series around $\hat{q}$ as follows:

$$\begin{aligned} p_o(q, t) &= p_c(q, t) \left[\frac{g(\hat{q})}{\hat{g}(t)} + \frac{g'(\hat{q})}{\hat{g}(t)}(q - \hat{q}) + \frac{1}{2} \frac{g''(\hat{q})}{\hat{g}(t)}(q - \hat{q})^2 + \dots \right] \\ &= p_c \left[\frac{g(\hat{q})}{\hat{g}(t)} + \epsilon(q, t) \right], \end{aligned} \quad (4.9)$$

where ϵ is a small perturbation of the trajectory for p_c . It can be seen that ϵ is small if either $g(q)$ is nearly constant or if p_c is a δ -like function; as a matter of fact, the solution to equation (3.1) is a δ -function $\delta(q - \hat{q})$, where $\hat{q}$ is the solution to equation (B 7).

When $g(\hat{q}) \approx \hat{g}(t)$ we set $\hat{p}_o = \hat{p}_c$ and define the entropy production of the open system as

$$\begin{aligned} \hat{S}(t) &= - \int_0^\infty \hat{p}_c \ln[p_c(1 + \epsilon)] dq \approx - \int_0^\infty \hat{p}_c \ln p_c dq \\ &\quad - \int_0^\infty \hat{p}_c \epsilon dq, \end{aligned} \quad (4.10)$$

where $\ln(1 + \epsilon) \approx \epsilon$. The second integral in equation (4.10) is the entropy production of the closed system (3.5). The last integral is the contribution of the dissipative processes. Using equations (3.1), (B 5) and (4.9) we get

$$\begin{aligned} -\int_0^\infty \dot{p}_c \epsilon \, dq &= -\int_0^\infty \frac{\partial(w_1 p_c)}{\partial q} \epsilon \, dq = \epsilon w_1 p_c \Big|_0^\infty + \int_0^\infty p_c w_1 \frac{\partial \epsilon}{\partial q} \, dq \\ &= \int_0^\infty p_c w_1 \frac{g'(\hat{q})}{\hat{g}} \, dq \approx \int_0^\infty p_c w_1 \frac{\partial \ln g}{\partial q} \, dq \\ &= \int_0^\infty p_c k(q) \, dq \approx k(\hat{q}). \end{aligned} \quad (4.11)$$

Finally, combining equations (3.5), (4.10) and (4.11) gives

$$\dot{S}(t) = -w_1'(\hat{q}) + k(\hat{q}) > 0. \quad (4.12)$$

For the closed system $w_1'(\hat{q})$ must be negative but for the open system it can be positive as long as it remains smaller than $k(\hat{q})$, i.e. the entropy production inside the system is counterbalanced by dissipation. In the open system it is therefore possible, but not necessary, for the system to move towards smaller and smaller values of q and become confined to a smaller and smaller part of the available phase space. This result has important implications for the ecological application that are discussed in § 5.

5. APPLICATION: SOIL ORGANIC MATTER

The formalism revolves around entropy production: however, is entropy production an important variable determining the trajectory of decomposition of soil organic matter (SOM)? Chemical and biological reactions in SOM are characterized by large changes of free energy (e.g. -4 to -20 kJ mol $^{-1}$ in enzymatic reactions, Rees & Farrelly (1990)), when a molecule is converted from SOM to CO $_2$ (or CH $_4$ in oxygen-free environments), while the entropy change (ΔS) in the same reaction is small. It is, however, important to notice the difference between entropy production and local variation of entropy. The continuity equation for entropy density (e.g. Katchalsky & Curran 1965) states that the entropy produced in an interval of time in a volume of a system equals the local entropy change plus the entropy exchanged with the surroundings. Total entropy production is then always positive. When a system and its surroundings are close to equilibrium it is possible to define thermodynamic functions such as enthalpy and the free energy, and according to classical thermodynamics, the temperature times change in entropy ($T\Delta S$) equals the change in enthalpy (ΔH) minus change in free energy (ΔG). For many chemical reactions ΔS is negative and therefore ΔS is *not* entropy production but the local change of entropy. Since $\Delta H/T$ is the exchange of entropy with the surroundings, $-\Delta G/T = \Delta S - \Delta H/T$ is the total entropy production and always positive. *From an experimental point of view, changes in free energy and total entropy are, therefore, equivalent and both can be used as driving forces.* However, free energy tells us only about the difference between states but not about the path that a system uses in the transition from one to the other. As

shown in equation (4.12), entropy production can also be used to calculate the path. We will now show how to apply the concept of entropy production to SOM dynamics.

The organic matter in the soil of an ecosystem is composed of a large number of chemical components of different qualities. By *quality* we mean in this context a measure at the molecular scale of the accessibility of a carbon atom (C-atom) to the decomposers (Ågren & Bosatta 1998; Bosatta & Ågren 1999; Joffre *et al.* 2001); it is represented by the real continuous variable q , $q \geq 0$. The states of the ecosystem are the infinite number of values of q . Consider

a C-atom of quality q' in the SOM. Decomposers assimilate this atom and utilize it to produce in their biomass a compound of different quality q : in the language of equation (2.1), due to microbial forces the C-atom has undergone the transition $q' \rightarrow q$. The density transition probability rate $\Omega(q, q') = D(q, q')u(q')$ is proportional to the microbial growth rate $u(q') \geq 0$ and to the distribution $D(q, q')$ describing the fraction of atoms of initial quality q' that are converted to atoms of quality q in the microbial biomass ($\int D(q, q') dq = 1$). Let $\rho_C(q, t)$ denote the density distribution of C in the organic matter of the soil; the dynamics of ρ_C are then described by the following ME (Bosatta & Ågren 1991; Ågren & Bosatta 1998):

$$\begin{aligned} \frac{\partial \rho_C(q, t)}{\partial t} &= \int_0^\infty D(q, q') u(q') \rho_C(q', t) dq' \\ &\quad - \frac{u(q)}{e(q)} \rho_C(q, t). \end{aligned} \quad (5.1)$$

The function $e(q)$ is the efficiency of converting SOM carbon to microbial biomass carbon; since $0 < e(q) < 1$, equation (5.1) is the ME of an open system with dissipation (respiration proportional to $1 - e$). The integral term in equation (5.1) specifies the inputs of carbon from a range of materials of initial qualities q' and their transformations due to internal processes (metabolism, mortality) into another material of quality q , while the second term specifies the microbial uptake of carbon from SOM of quality q . The integral in equation (5.1) is the sum of all transitions *to* state q and the last term is the sum of all transitions *from* q ; notice that the second term in equation (5.1) can be written as

$$\rho_C(q, t) \int D(q', q) [u(q)/e(q)] dq'.$$

Since the total system (SOM plus decomposers) is dissipative (the decomposers are respiring), it is possible that ρ_C moves towards a more improbable state. However, thermodynamics places restrictions on the conversions of ρ_C . To find these, we derive from equation (5.1) the equation corresponding to equation (4.1). $D(q, q')$ is expanded in terms of the derivatives of the δ -function

$$\begin{aligned} D(q, q') &= \delta(q' - q) + \eta_1(q') \delta'(q' - q) \\ &\quad + \frac{1}{2} \eta_2(q') \delta''(q' - q) + \dots \end{aligned} \quad (5.2)$$

and insert equation (5.2) into equation (5.1), keeping only the first two terms

$$\frac{\partial \rho_C}{\partial t} = \frac{\partial [\eta_1(q) u(q) \rho_C(q, t)]}{\partial q} - \frac{1 - e(q)}{e(q)} u(q) \rho_C(q, t). \quad (5.3)$$

This model was first proposed by Bosatta & Ågren (1985) and has been used to generate predictions covering a wide range of ecological processes related to element cycling in plants and soils (Ågren & Bosatta 1998). It describes the flow of C-atoms in the q -space moving under the action of internal processes with velocity $w_1(q) = -\eta_1(q)u(q)$ and leaving the q -space under the action of dissipative processes (respiration) with a loss function $k(q) = (1 - e)u/e$. The important factor is $\eta_1(q)$, the first moment of $D(q, q')$

$$\eta_1(q) = \int_0^\infty (q - q')D(q', q)dq'. \quad (5.4)$$

Its biological interpretation is the shift in quality that a C-atom experiences each time it is used by the decomposers. $\eta_1(q)$ can be positive or negative. If it is positive, w_1 is negative and q decreases (equation (B 7)), in agreement with observational experience where old material is more recalcitrant (lower q) than fresh litter material. Quality can decrease as long as equation (4.12) is not violated, and that leads to proposition 5.1.

Proposition 5.1. Dissipation is required to decrease the quality of SOM.

Increasing quality as a result of the decomposition process is, therefore, a possibility that is always open. The empirical observed decrease in quality is, however, constrained by the requirement that SOM must be lost in order to lower the quality of the remainder.

In the extreme case of a closed system $e(q) = 1$, $k(q) = 0$ and organic matter cannot degrade in quality. This leads to the idea that $\eta_1(q)$ and $e(q)$ could be inversely correlated and proposition 5.2.

Proposition 5.2. Systems with smaller efficiencies (larger dissipation) can sustain larger shifts in quality.

Decomposer communities, that recycle a lot of the substrate they utilize, must then produce new SOM of a quality that is not too much lower than the source. Decomposers living on high-quality substrates will therefore produce new substrate that is also of high quality. As a result, the new substrate will be used rapidly, see equation (5.5a). Decomposers, that dissipate a lot of substrate, can, on the other hand, rapidly produce recalcitrant material with subsequent slow utilization. The net result of these two opposing forces is that there is a resilience in the rate of mass loss to changes in decomposer communities; either little material is lost per cycle through the decomposer community but the substrate is rapidly used, or a lot of material is lost per cycle but the rate of utilization is slow.

Suppose the principle of minimum entropy production (Nicolis & Prigogine 1989) applies to this system. Since $k > 0$, the smallest possible dS/dt in equation (4.12) is obtained if $w'_1 > 0$, which is the case when q decreases. Hence, we have proposition 5.3.

Proposition 5.3. The principle of minimum entropy production leads to decreasing qualities during decomposition.

Propositions 5.1 and 5.2 only relied on a requirement that the entropy production be positive. Dissipation gives

the potential for but does not necessitate decreasing quality. However, requiring that the system follows a path of minimum entropy production also gives the direction for the change of quality.

In practical applications the following functions (Ågren & Bosatta 1998 (Model II); Bosatta & Ågren 1999) are used:

$$u(q) = u_0 \exp\left(-\frac{|\Delta G^0|}{qRT}\right); \quad (5.5a)$$

$$e(q) = e_0; \quad (5.5b)$$

and

$$\eta_1(q) = \eta_{11}q, \quad (5.5c)$$

where u_0 , e_0 and η_{11} are positive parameters and $|\Delta G^0|$ is a free energy difference (see Bosatta & Ågren 1999) and R is the gas constant. Inserting these functions into equation (4.12) we find that the parameters must satisfy the following condition for a positive entropy production in a single litter cohort

$$\frac{1 - e_0}{e_0\eta_{11}} > \frac{|\Delta G^0|}{qRT} + 1. \quad (5.6)$$

Equation (5.6) can only be satisfied as long as q is large enough. This gives rise to the proposition 5.4.

Proposition 5.4. A single litter cohort can, for entropy reasons, only decompose to a certain quality. This quality is lower when decomposition takes place at a higher temperature.

In most decomposition models it is taken for granted that litters can decompose entirely or, when this is not the case, that there is no mechanism to explain the limit to decomposition. The temperature dependence of the limit also has the consequence that a litter, where decomposition has been arrested for entropy reasons, can start to decompose again if it is heated. This is, as far as we know, a feedback from a climate change that has not been realized before.

Equation (5.6) defines the constraint from entropy production of a single litter cohort. However, SOM is an ensemble of litter cohorts of different ages (qualities); the distribution function of cohorts over the ensemble in the steady state is given by (Ågren & Bosatta 1998)

$$\Gamma(q) = \frac{I_0}{\eta_1(q)u(q)} \exp\left(-\int_{q_0}^q \frac{1 - e(q')}{e(q')\eta_1(q')} dq'\right) \quad (5.7)$$

and the entropy production of the whole SOM at steady state is then given by

$$\dot{S}_{\text{OM}} = \int_0^{q_0} \dot{S}(q)\Gamma(q)dq, \quad (5.8)$$

where $\dot{S}(q)$ is given by equation (4.12), q_0 is the quality of the youngest cohort and $I_0(t^{-1})$ is the constant rate of input of C to the soil. Using equations (5.5) in equation (5.8) and integrating gives the entropy production of the SOM as

$$\dot{S}_{\text{OM}} = I_0 \frac{u_0 e_0}{1 - e_0 + \eta_{11} e_0} \left[\frac{1 - e_0}{e_0} - \left(1 + \frac{1 - e_0 + \eta_{11} e_0}{1 - e_0} \frac{|\Delta G^0|}{qRT} \right) \eta_{11} \right]. \quad (5.9)$$

Hence, the condition for $\dot{S}_{\text{OM}} > 0$ is

$$\frac{1 - e_0}{\eta_{11}e_0} > \frac{1 - e_0 + \eta_{11}e_0}{1 - e_0} \frac{|\Delta G^0|}{q_0RT} + 1. \quad (5.10)$$

Due to the fact that $(1 - e_0 + \eta_{11}e_0)/(1 - e_0) > 1$, the conditions on the SOM (equation (5.9)) are stricter than the conditions for a single cohort (equation (5.6)). This is understandable because, for complete degradation, SOM needs to contain enough material of high quality that can function as an entropy source for the cohorts that have broken the limit set by equation (5.6). This also leads to proposition 5.5.

Proposition 5.5. Litters can be broken down completely provided that they are initially of sufficiently high quality and remain in contact with fresh litter.

This result emphasizes the need to define carefully the system with which one is working. Physically separating SOM into components where some contain predominantly low-quality substrate may lead to a halt in the decomposition in those compartments. It is also necessary that the decomposers function as a unity such that links between all parts of SOM exist.

Propositions 5.1, 5.2 and 5.3 are only based on general principles, whereas propositions 5.4 and 5.5 are based on the use of specific models. Changing these models will alter the results and an interesting ecological question concerns which systems correspond to which model.

6. DISCUSSION

We have shown the potential richness of the ME. From it we can derive, in a systematic way, models of different degrees of complexity and give them a thermodynamic interpretation. Equation (2.2) is only the simplest version of the ME. For example, if the transition rates Ω are made functions of the probability distribution p we generate nonlinear terms in the ME (Ågren & Bosatta 1998). In this way nonlinear models such as the Lotka-Volterra equations can be derived from the ME as special cases. There already exists a large body of literature about the ME and its properties.

Irreversible thermodynamics as used in chemistry and physics (Onsager equations, see Addiscott (1995)) is restricted to systems close to thermodynamic equilibrium. For ecology, where phenomena are far from the equilibrium, the approach proposed in equation (4.10) is more generally applicable. A completely general relationship (4.12) has been derived that does not depend on any explicit definition or magnitude of velocities or dissipation functions and quantitative relationships of the kind given in equations (5.6) and (5.10) are also derived imposing certain constraints on the parameters involved. The formalism uses the condition that entropy production must be positive to set constraints on system development; in physical systems it is not used because the laws of physics are such that this condition is satisfied *a priori*.

The constraints derived for SOM decomposition provide new ways of explaining a number of observations. Berg has proposed in a number of papers (e.g. Berg (2000) and references therein) that decomposition of single cohorts only proceeds to a certain limiting value,

which varies with the type of litter used. The mechanism behind such a limiting value has not been clearly identified but condensation of nitrogen-rich compounds with lignin residues has been proposed. Equation (5.6) gives a purely thermodynamic explanation. It also explains why such limiting values do not lead to the infinite accumulation of organic matter. When a litter cohort of low quality is in contact with litters of higher quality, the degradation of the higher-quality litters becomes a source of entropy that can drive the degradation of the low-quality litter. The same argument can also be applied to explain the increased decomposition following the mixing of SOM; low-quality organic matter is brought into contact with an entropy source of high-quality organic matter. In the special case that the mixing consists of adding fresh plant material to the soil, this is often called a 'priming effect' (e.g. Broadbent & Norman 1946; Hallam & Bartholomew 1953). In addition to the physical changes to which the substrates are exposed, a conventional explanation is that the decomposers need an easily usable energy source to degrade the more recalcitrant old material. However, energy is available. Indeed, the energy density of a substrate can even increase during decomposition (Löhmus & Ivask 1995). An explanation based on the need for entropy seems more satisfactory. The handling of interactions between litter cohorts needs, however, further investigation.

It is normally taken for granted that the quality of a substrate must decrease during decomposition (Swift *et al.* 1979) because the most easily degradable substances are used up first. During an initial period this is clearly the case. However, there is no *a priori* reason why the new substrates created by the decomposers (the integral term in equation (5.1)), on average, should be of either higher or lower qualities than the substrates from which they were created. Energy constraints do not provide any help, there might be a weak tendency towards more energy dense substrates with decomposition (Löhmus & Ivask 1995). The assumption of minimum entropy production, however, indicates that there must be a drift towards lower qualities.

The authors thank Per-Erik Bergner for comments on the manuscript. This work was supported by the Swedish National Energy Administration.

APPENDIX A

Substitute in equation (2.2) m with q_m , where q_m is the coordinate of box m , and $p_m(t)$ with $p(q_m, t)$. Next, assume that the boxes, become thinner and thinner whilst they increase in number. In the limit of a continuous distribution of boxes, substitute $p(q_m, t)$ with $p(q, t)dq$ and $\Omega(q_m, q'_m)$ with $dq\Omega(q, q')$ and the sums with integrals. $\Omega(q, q')$ is the *density* transition probability rate. In this way equation (2.2) transforms into

$$\frac{\partial p(q, t)}{\partial t} = \int_0^\infty \Omega(q, q')p(q', t)dq' - p(q, t) \int_0^\infty \Omega(q', q)dq'. \quad (A 1)$$

This states that $p(q, t)$ increases due to all transitions *to* and decreases due to all transitions *from* the interval dq

around q . The total probability $\int p(q, t) dq$ is conserved because

$$\int_0^\infty \frac{\partial p}{\partial t} dq = \int_0^\infty w_0(q') p(q', t) dq' - \int_0^\infty w_0(q) p(q, t) dq = 0, \quad (\text{A } 2)$$

where $w_0(q') = \int \Omega(q, q') dq$. Then, if p is normalized at $t = 0$, $\int p(q, 0) dq = 1$, p remains normalized at all times

$$\int_0^\infty p(q, t) dq = 1. \quad (\text{A } 3)$$

The limit procedure for $S(t)$ requires more care. Consider a small but finite interval Δq :

$$\begin{aligned} S(t) = & - \lim_{\Delta q \rightarrow 0} \sum_m p(q_m, t) \ln(p \Delta q) \Delta q = \\ & - \lim_{\Delta q \rightarrow 0} \sum_m p(q_m, t) \ln p(q_m, t) \Delta q \\ & - \lim_{\Delta q \rightarrow 0} \Delta q \ln \Delta q \sum_m p(q_m, t). \end{aligned} \quad (\text{A } 4)$$

In the limit of $\Delta q = 0$ the last term equals zero and thus

$$S(t) = - \int_0^\infty p(q, t) \ln p(q, t) dq, \quad (\text{A } 5)$$

which is the expression used by Frieden (1998). Taking the derivative of equation (A 5) gives entropy production

$$\dot{S}(t) = - \int_0^\infty \frac{\partial p}{\partial t} \ln p(q, t) dq, \quad (\text{A } 6)$$

which is the continuous counterpart of equation (2.5).

APPENDIX B

We develop the *density* transition probability rates $\Omega(q, q')$ in terms of the δ -function and its derivatives:

$$\begin{aligned} \Omega(q, q') = & w_0(q') \delta(q' - q) + w_1(q') \delta'(q' - q) \\ & + w_2(q') \delta''(q' - q) + \dots, \end{aligned} \quad (\text{B } 1)$$

where $\delta'(q' - q) = \partial \delta(q' - q) / \partial q$ etc. Equation (B 1) is a moment expansion of $\Omega(q, q')$ because $\int (q' - q)^n \Omega(q, q') dq' = n! w_n(q')$. Thus, the functions w_n represent the moments of the transition rates. In particular, w_1 is the average displacement that a particle starting at q' undergoes during transitions.

Inserting equation (B 1) into equation (A 1) and keeping only the first two terms in the expansion gives

$$\begin{aligned} \frac{\partial p}{\partial t} = & \int_V w_0(q') \delta(q' - q) p(q', t) dq' \\ & + \int_V w_1(q') \delta'(q' - q) p(q', t) dq' - w_0(q) p(q, t). \end{aligned} \quad (\text{B } 2)$$

From the properties $\int w_0(q') \delta(q' - q) p(q', t) dq' = w_0(q) p(q, t)$ and $\int w_1(q') \delta'(q' - q) p(q', t) dq' = \partial(w_1 p) / \partial q$ of the δ -function we get equation (3.1)

$$\dot{p}(q, t) = \frac{\partial [w_1(q) p(q, t)]}{\partial q} = - \frac{\partial \mathcal{F}}{\partial q}. \quad (\text{B } 3)$$

This is the simplest model that can be derived by starting from the ME. If the second-order term $w_2(q') \delta''(q' - q)$ is included in equation (B 2) one gets the Fokker-Plank equation.

To define a closed system Dirichlet boundary conditions are imposed on equation (B 3). These are

- (i) there is no net flow of particles across the boundaries

$$\mathcal{F}(0, t) = \mathcal{F}(\infty, t) = 0; \quad (\text{B } 4)$$

and

- (ii) because the system is closed, there is a vanishing probability that a particle is at the boundary

$$p(0, t) = p(\infty, t) = 0. \quad (\text{B } 5)$$

Using equation (B 4) we can show that normalization is conserved:

$$\int_0^\infty \frac{\partial p}{\partial t} dq = - \int_0^\infty \frac{\partial \mathcal{F}}{\partial q} dq = \mathcal{F}(0, t) - \mathcal{F}(\infty, t) = 0. \quad (\text{B } 6)$$

We need to calculate the dynamical equations for the first two moments of $p(q, t)$. Taking the derivative of equation (3.2) and using equation (B 5) gives

$$\begin{aligned} \dot{\bar{q}} = & \frac{\partial}{\partial t} \int_0^\infty q p dq = \int_0^\infty q \dot{p} dq = \int_0^\infty q \frac{\partial (w_1 p)}{\partial q} dq = q w_1 p \Big|_0^\infty \\ & - \int_0^\infty w_1 p dq = - \bar{w}_1(t), \end{aligned} \quad (\text{B } 7)$$

where $\bar{w}_1(t)$ is the mean value of $w_1(q)$. Taking the derivative of equation (3.3) and using equation (B 5) gives

$$\begin{aligned} \dot{\sigma}^2(t) = & -2\bar{q} \int_0^\infty (q - \bar{q}) p(q, t) dq + \int_0^\infty (q - \bar{q})^2 \frac{\partial (w_1 p)}{\partial q} dq \\ = & (q - \bar{q})^2 w_1 p \Big|_0^\infty - 2 \int_0^\infty (q - \bar{q}) w_1 p dq. \end{aligned} \quad (\text{B } 8)$$

The first integral in equation (B 8) is zero by definition of $\bar{q}$. To calculate the last integral we expand $w_1(q)$ in a Taylor series around $\bar{q}$, which gives

$$\dot{\sigma}^2(t) \approx -2w_1'(\bar{q}) \sigma^2. \quad (\text{B } 9)$$

For the particular case $w_1 = \alpha q$ with $\alpha > 0$ or $\alpha < 0$, $\dot{\bar{q}}$, σ^2 and the entropy production (equation (3.5)) can easily be calculated exactly.

REFERENCES

- Addiscott, T. M. 1995 Entropy and sustainability. *Eur. J. Soil Sci.* **46**, 161–168.
 Ågren, G. I., & Bosatta, E. 1998 *Theoretical ecosystem ecology. Understanding element cycles*, p. 234. Cambridge University Press.
 Berg, B. 2000 Initial rates and limit values for decomposition of Scots pine and Norway spruce needle litter: a synthesis for N-fertilized forest stands. *Can. J. Forest Res.* **30**, 122–135.

- Bergner, P. E. 1993 On kinetics of classic particles: mean values of state functions. *J. Theor. Biol.* **165**, 357–372.
- Bianciardi, C. & Ulgiati, S. 1998 Modelling entropy and exergy changes during a fluid self-organization process. *Ecol. Modelling* **110**, 255–267.
- Broadbent, F. E. & Norman, A. G. 1946 Some factors affecting the availability of the organic nitrogen in soil—a preliminary report. *Proc. Soil Sci. Soc. Am.* **11**, 264–267.
- Bosatta, E. & Ågren, G. I. 1985 Theoretical analysis of decomposition of heterogeneous substrates. *Soil Biol. Biochem.* **17**, 601–610.
- Bosatta, E. & Ågren, G. I. 1991 Dynamics of carbon and nitrogen in the organic matter of the soil: a generic theory. *Am. Naturalist* **138**, 227–245.
- Bosatta, E. & Ågren, G. I. 1999 Soil organic matter quality interpreted thermodynamically. *Soil Biol. Biochem.* **31**, 1889–1891.
- Frieden, B. R. 1998 *Physics from Fisher information—a unification*, p. 318. Cambridge University Press.
- Haken, H. 1977 Synergetics. In *An introduction. Nonequilibrium phase transitions and self-organisation in physics, chemistry and biology*, p. 325. Berlin: Springer-Verlag.
- Hallam, M. J. & Bartholomew, W. V. 1953 Influence of rate of plant residue addition in accelerating the decomposition of soil organic matter. *Proc. Soil Sci. Soc. Am.* **17**, 365–368.
- Joffre, R., Ågren, G. I., Gillon, D. & Bosatta, E. 2001 Organic matter quality in ecological studies: theory meets experiment. *Oikos* **93**, 451–458.
- Johnson, L. 1992 An ecological approach to biosystem thermodynamics. *Biol. Phil.* **7**, 35–60.
- Katchalsky, A. & Curran, P. F. 1965 *Nonequilibrium thermodynamics in biophysics*, p. 248. Cambridge, MA: Harvard University Press.
- Löhmus, K. & Ivask, M. 1995 Decomposition and nitrogen dynamics of fine roots of Norway spruce (*Picea abies* (L.) Karst.) at different sites. *Plant Soil* **168/169**, 89–94.
- Månsson, B. Å. & McGlade, J. M. 1993 Ecology, thermodynamics and H.T. Odum's conjectures. *Oecologia* **93**, 582–596.
- Nicolis, G. & Prigogine, I. 1989 *Exploring complexity. An introduction*, p. 313. Oxford: Freeman.
- Rees, D. C. & Farrelly, D. 1990 Biological electron transfer. In *The enzymes* (ed. D. S. Sigman & P. D. Boyer), pp. 37–97. San Diego: Academic.
- Schneider, E. D. & Kay, J. J. 1994 Life as a manifestation of the second law of thermodynamics. *Math. Computer Modeling* **19**, 25–48.
- Schrödinger, E. 1944 *What is life?*, p. 92. Cambridge University Press.
- Swift, M. J., Heal, O. W. & Anderson, J. M. 1979 Decomposition in terrestrial ecosystems. In *Studies in ecology*, vol. 5, p. 372. Oxford: Blackwell.

As this paper exceeds the maximum length normally permitted, the authors have agreed to contribute to production costs.