THE MULTISCALE SIGNATURE OF
ECOHYDROLOGICAL FLUCTUATIONS ON SOIL
BIOGEOCHEMICAL CYCLES

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Abstract

Numerous soil ecosystem services, ranging from carbon sequestration to crop production, derive from a delicate interaction between hydrologic fluctuations due to rainfall intermittency and biogeochemical cycles. This coupling propagates from the soil surface, where high frequency soil moisture variability drives the alternation between oxic and anoxic soil conditions, to the bedrock, where infrequent percolation pulses impact mineral dissolution. This dissertation discusses how combining stochastic biogeochemical models, observations, and dimensional analysis helps shed light on this complex coupling and to derive parsimonious models governing such dynamics.

Particular emphasis is placed on the iron cycle in the soil root zone and the dissolution of silicate minerals in the deeper regolith because of their environmental relevance for soil carbon storage, CO2 emissions, and plant productivity. While in the first part of the dissertation the focus is on the temporal aspect of the interaction between hydrology and biogeochemistry, in the second part the focus shifts towards the spatial one. Age theory is introduced as a framework for dealing with spatial heterogeneities and up-scaling reaction rates and transport processes. We conclude by outlining how these approaches may be useful for developing an environmental control theory for sustainable ecosystem management under changing climates and increasing food, water and energy demands.
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To my family.
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Chapter 1

Introduction

From the bedrock to the top of the canopy, the interaction between the hydrologic cycle, parent materials, soils, and plants creates a complex system of feedbacks whose stability guarantees conditions that support life through a series of ecosystem services [18, 75]. Chemical weathering in the deeper regolith releases nutrients and clay minerals that are essential to form the soil matrix [82], and sequesters atmospheric CO$_2$, stabilizing the atmospheric composition [17]. In the upper regolith, nutrient cycling, and more broadly ecohydrological processes [230], provide the necessary resources (e.g., food and water) to sustain the human population [36]. This interaction, however, is threatened by the increasing population that not only necessitates higher exploitation of natural resources, but it also strengthens external (anthropogenic) forces. Understanding the coupling between the various ecohydrological and biogeochemical processes and their stability related to both natural and anthropogenic drivers is thus fundamental to develop sustainable human activities and to secure natural resources for the future. To this regard, unveiling and quantifying these interactions and bridging the wide range of temporal and spatial scales remains a challenge and analytical tools to investigate these intricate dynamics are necessary [35].

The objective of this dissertation is to answer fundamental questions about the role of climatic variability on water and nutrients dynamics and to provide analytical models
amenable to theoretical analysis and to prediction over long time scales. These models also aim at assessing the impact of agricultural and urban practices as well as at developing sustainable management strategies (e.g., optimal water management). Towards this goal, we merge tools from dynamical system theory, stochastic processes, and thermodynamics with field data available through various networks (e.g., Critical Zone Observatories) to couple biological, chemical and hydrological processes.

The top soil layers represent the most active zone of the soil, in which organic matter, living organisms, minerals and plants are directly exposed to climatic variability. Here, the fluctuations in soil moisture drive much of the biogeochemical processes, from the decomposition of the organic matter to nutrient cycles. Among these, soil iron cycles has been recognized as an important driver of the carbon and other biogeochemical cycles because of its interaction with organic matter, plants, soil properties and hydrology [112, 6].

In chapter 2, we develop an analytical model coupling the Fe-redox cycle to the soil water balance and a simple carbon model to analyze the ecohydrological control on soil iron cycle and its role on organic matter decomposition. Parameterized with measurements from a tropical forest, the model sheds light on the interaction between the hydrology and the redox cycle in humid ecosystems experiencing oxic/anoxic fluctuations, where given the limited availability of oxygen iron-redox becomes essential to carbon decomposition.

The upper soil layers also act as a filter for hydrologic fluctuations, in that only percolation pulses following heavier rainfall events impact the deeper soil layers. These pulses transport part of the CO₂ produced in the root zone to the weathering zone, where it is used in the dissolution reactions of the parent material, and by translocating clay particles affect the soil texture across the vertical direction. In chapter 3, we analyze the role of climate on the chemical reactions in the weathering zone by quantifying the transport of dissolved CO₂ and relating the advancement of the reactions to the water transit time. In chapter 4, using a combination of stochastic modeling and field observations we show that, under specific climate and soil conditions, lessivage (i.e., the vertical translocation of clay
particles by percolation) explains the formation of clay-enriched horizons. These findings shed light on the potential evolution of soil profiles and properties under changing climatic and environmental conditions.

When interested in large scale dynamics, the presence of spatial heterogeneities in the topography and the subsurface oftentimes brings about further complexity in environmental modeling. For chemical reactions, age distribution theory provides tools for upscaling reactions rates to large spatial scales. The framework represents a spatial integrated approach in which the age distribution of water or a chemical species embeds Lagrangian information about the different flow paths and mixing processes taking places within the control volume (e.g., the watershed). While originally pioneered in the population dynamics community [182], we develop a comprehensive framework suitable for hydrologic systems, where the multiple physical and chemical processes undergo random fluctuations induced by climatic variability. In chapter 5, we introduce a probabilistic framework, in which the age distribution is a random function, to account for external stochasticity of the precipitation. In chapter 6, we introduce the concept of survival time (time left before exiting the control volume) and discuss interesting relationships between age and survival time distributions, their time symmetry, and their statistical dependence. In chapter 7, we generalize the framework to account for multiple forms of outputs, such as evapotranspiration and streamflow, and derive an explicit relationship between the age distribution theory and the spatially-explicit dynamics. Finally in chapter 8, we present a probabilistic age distribution framework that accounts for jumps in mortality, representing intense losses of water (or chemical substance). These, for example, represent losses of nutrients from the root zone due to percolation events.
Chapter 2

Impact of ecohydrological fluctuations on iron-redox cycling

In this first chapter of the dissertation, we focus on the impact of climatic variability and vegetation dynamics on the iron-redox cycle in the root zone (approximately the top organic soil layers), which being directly exposed to the atmosphere represents the soil interface with climate. The work presented in this chapter thus represents a first essential step towards linking the soil biochemical reactions to climatic fluctuations. The chapter is adapted from Calabrese, Salvatore, and Amilcare Porporato, "Impact of ecohydrological fluctuations on iron-redox cycling", Soil Biology and Biochemistry (2019).

2.1 Introduction

The cyclic switching of soil iron between its reduced and oxidized states affects minerals crystallinity and sorbing properties [261, 133], and in turn controls the fate of dissolved species such as nutrients and organic matter [298]. This ‘cycle’ of iron also determines the availability of iron to plants as a micronutrient necessary to their growth [94, 57] (see for instance the fertilization experiment in the southern ocean [56, 23]) and the biologically mediated iron reduction is fundamental to the decomposition of organic matter in environ-
ments experiencing anoxic conditions [162, 198], such as humid tropical ecosystems [79]. For these reasons, soil iron dynamics plays a central role in the global carbon cycle.

Iron is often present in low soluble forms, posing stress on crops and limiting their yield [109], that derive mainly from dissimilatory Fe-reduction, a metabolism in which in anoxic conditions microbes rely on Fe$^{3+}$ as an electron acceptor for organic matter mineralization (e.g., [161, 57, 281]). The soil redox state is directly affected by hydrologic fluctuations as soil moisture directly controls microbial respiration [230, 262]. By consuming oxygen and producing carbon dioxide during organic carbon decomposition, microbial activity in fact affects the composition of the soil pore atmosphere and the alternation of oxic/anoxic conditions [65, 34], with a feedback on the redox conditions [34].

A few studies have explored mechanisms and rates of microbial Fe$^{3+}$ reduction and its role in anaerobic environments (e.g., [163, 47, 143, 102, 5]), but have focused mainly on the biochemical aspects of the redox reaction in a laboratory setting. It was only recently that frequent ($\approx$ days) measurements of soil iron have started to be collected [6], with the goal of exploring the environmental controls on Fe-reduction. Because of the complex interaction between ecohydrological and biochemical processes, only a joint analysis of soil iron and carbon cycles and soil water balance may provide the needed insights into soil iron dynamics to understand its role on carbon decomposition in various anoxic environments, such as wetlands and humid tropical forests [159]. To the best of our knowledge no study has consistently linked all these aspects.

Existing geochemical transport models (e.g., [295, 257, 234]) aim at providing a detailed description of water flow and chemical reactions in space and time, but require numerical solution of partial differential equations with a large number of variables. This tends to hide the interaction between the various processes and makes these models unsuitable for a theoretical study of the coupling between iron and carbon cycles.

In this Chapter, we develop an analytical model that couples iron and carbon cycles in the soil root zone and that takes into account the soil moisture control on iron and car-
bon fluxes. The model is spatially lumped and consists of ordinary differential equations describing the time evolution of iron, Fe$^{2+}$ and Fe$^{3+}$, carbon substrate and population of Fe-reducers. We model the redox reaction and the carbon decomposition by means of specific rate laws and introduce functions that account for the level of soil moisture. This spatially integrated formulation allows us to readily couple a model for soil moisture dynamics, whereby accounting for its impact on the redox fluctuations within the rhizosphere. As a case study, we analyze the soil iron cycle in the hot humid forest in the Luquillo Experimental Forest in Puerto Rico (LEF), which because of its climatic and soil features is characterized by very dynamic biogeochemical cycling and represents an optimal site for studying iron fluctuations.

2.2 Methods

We begin by presenting the details of the model and by describing the balance equations for iron, carbon and soil moisture. We then proceed with explaining the parameterization based on laboratory and field measurements on soils from the LEF.
2.2.1 Fe-C model

We use different compartments to model the time evolution of the state variables in a spatially lumped formulation representing vertical averages over the root zone. The iron oxidation states are modeled using two separate compartments for the reduced state, Fe$^{2+}$, and the oxidized state, Fe$^{3+}$. With regard to the soil carbon, we adopt two different compartments to model the time evolution of the carbon substrate and the population of Fe-reducing microbes.

Fe-redox dynamics

At typical soil pHs, iron is present in the reduced state as Fe$^{2+}$ and in the oxidized state as Fe$^{3+}$ [34]. Ferrous iron, Fe$^{2+}$, is originally found in primary minerals and is released into the soil solution as a product of mineral weathering, usually mediated by microorganisms [281, 57]. Once dissolved in soil water, iron becomes available to plants and microbes to support their physiological processes and their growth, respectively. At high soil moisture levels (above the soil field capacity), however, iron is also lost by percolation to deeper soil layers and eventually to streams.

Within the root zone, fluctuations in soil moisture induce changes in soil air composition (oxic/anoxic conditions), thereby generating a continuous alternation of oxidizing and reducing conditions [34]. On the one hand, in the presence of oxygen accepting electrons ferrous iron (Fe$^{2+}$) is readily oxidized to ferric iron (Fe$^{3+}$), which precipitates forming mostly short-range ordered Fe minerals (e.g., ferrihydrite), but also more crystalline phases (such as hematite) [283, 284, 261]. Part of the oxidation occurs biologically (Fe-oxidizing bacteria) at rates that can be comparable to abiotic oxidation [281].

On the other hand, when oxygen is depleted Fe$^{3+}$-reducing microorganisms rely on the availability of Fe$^{3+}$ as an electron acceptor and reduce it back to ferrous iron (Fe$^{2+}$) in order to decompose the organic matter [161, 227, 79].

The balance equations for iron in the two redox states can thus be expressed as
\[
\frac{dF_{e^{2+}}}{dt} = MW + RED - OX - UP - L_{Fe^{2+}}, \tag{2.1}
\]

\[
\frac{dF_{e^{3+}}}{dt} = OX - RED, \tag{2.2}
\]

where \(F_{e^{2+}}\) is the amount of dissolved ferrous iron and \(F_{e^{3+}}\) is the available short-ranged \(Fe^{3+}\) phases. The terms \(OX\) and \(RED\) are the oxidation and reduction rates, respectively, \(MW\) (mineral weathering) is the release of iron \(Fe^{2+}\) from highly crystalline Fe minerals, \(UP\) is the iron uptake by plants, and \(L_{Fe^{2+}}\) is the loss of iron as leaching.

Mineral weathering, \(MW\), represents the slow release of iron from Fe-minerals, which provide a source of iron over long timescales. Since it is small and varies slowly compared to the fast dynamics of \(Fe^{2+}\)-\(Fe^{3+}\) cycling, this term can be considered a constant.

The reduction and oxidation processes are modeled by means of semi-empirical kinetic laws. The reduction rate of \(Fe^{3+}\), associated to the decomposition of the organic matter, \(C\), is modeled through a multiplicative function of the population of Fe-reducers, \(BM\), the carbon substrate, \(C\), and the availability of short-ranged \(Fe^{3+}\) minerals,

\[RED = f(s)k_{red} \cdot BM \cdot C \cdot Fe^{3+}, \tag{2.3}\]

while the oxidation rate is modeled as [256, 102]

\[OX = g(s)k_{ox}(Fe^{2+} - Fe^{2+}_0), \tag{2.4}\]

where \(Fe^{2+}_0\) is small fraction of the iron pool that is resistant to oxidation, likely due to physical protection [102]. In agreement with observations [34], the factor \(f(s)\) limits the reduction rate at low soil moisture levels, at which aeration suppresses anaerobic processes. Below field capacity, high oxygen levels inhibit anaerobic processes, and \(f = 0\), while as
soil moisture increases, \( f \) nonlinearily increases and reaches 1 at saturation,

\[
f(s) = \begin{cases} 
0 & s < s_{fc}, \\
\left(\frac{s-s_{fc}}{1-s_{fc}}\right)^2 & s > s_{fc}.
\end{cases}
\] (2.5)

On the other hand, field measurements show that soil moisture is essentially a proxy for oxygen content [113]. Oxygen levels remain very high (close to the atmospheric value) up to soil moisture at field capacity and then quickly decline nonlinearily (Figure 2.2(a)) as the soil approaches saturation. Accordingly, to account for oxygen limitation at high soil moisture levels, the function \( g(s) \) is modeled as

\[
g(s) = \begin{cases} 
1 & s < s_{fc}, \\
1 - \left(\frac{s-s_{fc}}{1-s_{fc}}\right)^4 & s > s_{fc}.
\end{cases}
\] (2.6)

Iron uptake, \( UP \), occurs through the roots as the plant takes in water for transpiration. It is a function of soil moisture and concentration of \( Fe^{2+} \) and can be computed as

\[
UP = T(s)[Fe^{2+}] = T(s)\frac{Fe^{2+}}{nsZ_r},
\] (2.7)

in which \( Z_r \) is the depth of root zone. The transpiration rate, \( T(s) \), is modeled as an increasing function of soil moisture accounting for the plant stomatal response to water stress [204] and its specific formula is shown in section 2.2.1 below.

Finally, the loss of \( Fe^{2+} \) via percolation can be similarly computed as

\[
L_{Fe^{2+}} = L(s)[Fe^{2+}] = L(s)\frac{Fe^{2+}}{nsZ_r},
\] (2.8)

where the percolation rate \( L(s) \), which is zero below field capacity, is a function of soil moisture, hydraulic conductivity, and soil type [230], see section 2.2.1.
Figure 2.2: Panel (a): The solid line illustrates the control factor $g(s)$ accounting for oxygen limitation at high soil moisture levels, while the red circles are oxygen and soil moisture measurements from the Luquillo Experimental Forest (LEF) by [113]. Panel (b): Calibration of the reduction rate constant. The red point are the results of the reduction experiment by [102], in which soil samples were kept for 7 days in anoxic conditions without substrate and Fe-reducers limitation. The solid line refers to the modeled evolution of $Fe^{2+}$ after calibration. To simulate the anoxic conditions, the model was run for constant soil moisture $s = 1$ (saturation), whereas to avoid substrate and Fe-reducers limitation, the initial condition was set to $Fe^{2+} = 0$ mmol/kg, $C = 20$ g/kg, and $BM = 5 \cdot 10^{11} \text{cells/kg}$.

C dynamics

We model the time evolution of the soil organic carbon and the population of Fe$^{3+}$-reducers through the following balance equations,

$$\frac{dC}{dt} = ADD + BD - DEC_{aer} - DEC_{red}, \quad (2.9)$$

and

$$\frac{dBM}{dt} = G_{BM} - BD. \quad (2.10)$$
The term ADD represents the deposition of plant residues, such as leaves, roots and branches, which become available to microbial colonies for their metabolism, whereas BD, biomass decay, is the carbon recycled through death of the microbial biomass, generally assumed to be a linear decay, i.e., $BD = k_{bd}BM$ [204, 172].

The output is given by the decomposition through aerobic metabolism, $DEC_{aer}$, and dissimilatory iron reduction, $DEC_{red}$. The decomposition of the substrate by the aerobic biomass is modeled by means of first order kinetics,

$$DEC_{aer} = k_{aer}\phi(s)C,$$

(2.11)

where $k_{aer}$ is the aerobic decomposition rate. The function $\phi(s)$ accounts for water limitation at low soil moisture and oxygen limitation at high soil moisture, and is modeled as an increasing linear function up to soil field capacity, $s = s_{fc}$, and an hyperbolic decay for soil moisture levels above field capacity [41, 34].

Because the decomposition through iron reduction is proportional to the moles of iron reduced, it follows that $DEC_{red} = \beta RED$, where $\beta$ represents the grams of carbon decomposed per mole of iron reduced. This constant is computed considering that chemical analyses show an average C content in the organic matter of 45% and that 4 moles of carbon are decomposed per mole of iron reduced [162, 143, 113]. Finally, the growth of the Fe-reducers population has been shown to be proportional to the moles of iron reduced [143], so that $G = rRED$.

**Soil moisture dynamics**

The balance equation for the root zone soil moisture is written as [147]

$$nZ_r \frac{ds}{dt} = R - Q - E - T - L,$$

(2.12)
where \( n \) is the soil porosity, \( Z_r \) is the depth of the root zone, and \( s \) is the soil moisture expressed in terms of saturation. The product \( nZ_r s \) thus represents the total volume of water per unit ground area. The term \( R \) is the rainfall rate, \( Q \) is the runoff generated when rainfall exceeds the soil storage capacity \( (nZ_r(1 - s)) \), whereas \( E, T \) and \( L \) are the water losses as evaporation, transpiration and percolation, respectively.

Available rainfall data at daily timescale cover only a period of approximately 25 years with occasional gaps. To overcome such a limitation and account for the long term effect of the intermittent and random nature of rainfall, we also model \( R \) as a marked Poisson process with event frequency \( \lambda \), representing the inverse of the mean inter-arrival times between two subsequent rainfall events, and random rainfall depths that are exponentially distributed with mean depth \( \alpha \) [230]. Frequency and mean rainfall depth are derived from the rainfall dataset as shown in section 2.2.2 below (Figure 2.3).

For simplicity, the evaporation \( E \) is modeled as a linear, increasing function of soil moisture from \( E = 0 \) at the hygroscopic point, \( s_h \), to \( E_{max} \) at the soil wilting point, \( s_w \), \( E_{max} \) being the potential evaporation. To account for plant stomatal response to water stress, we model also transpiration as an increasing function of soil moisture from 0 at \( s = s_w \) to \( T_{max} \) at the soil moisture level at which plants begin to suffer from water stress, which we refer to as \( s^* \).

When the soil moisture exceeds the soil field capacity, \( s_{fc} \), water is lost also by percolation due to gravity, \( L \). We compute this loss as a power law function of soil moisture, \( L = k_h s^c \), where \( k_h \) is the hydraulic conductivity and \( c \) is an empirical parameter depending on soil texture [54, 147].

### 2.2.2 Case Study

Our study area is the subtropical humid forest in the Bisley watershed of the Luquillo Experimental Forest in Puerto Rico [239]. The site is characterized by a low seasonal climate with about 3500 mm/year of average precipitation. Based on the USDA classification, these
soils are mostly classified as Ultisols that formed from volcanic parent material. Top soils (≈ 40 cm) in upland locations can be considered silty clay loams according to the USDA texture classification, with an average porosity of 0.48 and bulk density of 0.7 g/cm³ [113], but there large textural variations across elevation gradients. The Luquillo Experimental Forest (LEF) is a Long Term Ecological Research site (https://luq.lter.network/) and a Critical Zone Observatory (https://criticalzone.org/luquillo/), through which biogeochemical observations are available since 1988.

**Parameterization of Re-redox rates**

The total iron content in these soils is about 1150 mmol/kg soil, of which 150 mmol/kg is in short-range ordered or low-crystallinity Fe³⁺ phases [102, 5]. The remaining portion is in more crystalline phases (e.g., goethite) or is dissolved in water in the reduced state (Fe²⁺).

The reduction rate constant, $k_{red}$, was calibrated with the reduction experiments by [102], in which soil samples were placed for 7 days in anoxic conditions, after being exposed for 28 days to an alternation of oxic and anoxic conditions. We solved the model to fit the experimental data, considering constant anoxic conditions ($s = 1$), high substrate
and Fe-reducers contents, and an initial condition $Fe^{2+} = 0$ (see Figure 2.2b). The oxidation rate constant, $k_{oz}$, for the oxidation rate law (2.4) was calibrated by [102] to model the decrease in $Fe^{2+}$ concentrations during oxic conditions observed in their experiments.

**Parameterization of microbial growth and C decay**

We parameterize the growth of Fe-reducers based on growth yields experiments by [143], which showed that microbial growth was proportional to the reduction rate and the coefficient of proportionality (expressing the growth per mole of $Fe^{3+}$ reduced) was about $5 \cdot 10^{10}$ cells/moles. The microbial decay rate was determined by fitting an exponential decay to the decrease of Fe-reducers observed in soil samples kept in oxic conditions in the experiments by [102].

The input of carbon, $ADD$, was determined according to measurements of litterfall rate [301]. In particular, we imposed for each day a litterfall rate equal to the average rate for the specific month. The decay rate, $k_{aer}$, due to aerobic substrate decomposition was selected in accordance with results from litterbag experiments [25].

**Parameterization of climatological and soil parameters**

We gathered longterm rainfall data, from 1988 to 2015, from the LTER website (https://luq.lter.network/data/luqmetadata148/7469). To take into account the seasonality in precipitation, we computed the rainfall frequency, $\lambda$, and mean rainfall depth, $\alpha$, separately per each month. The results, shown in Figure 2.3(a) and (b), are consistent with previous estimates of rainfall statistics [119].

The potential evapotranspiration, $ET_{max}$, was acquired from the CRU climate dataset [118], which provides monthly values for land surface climatological variables. Similarly to rainfall, we computed long term averages of potential evapotranspiration per each month (Figure 2.3(c)). We then assumed that the potential evaporation ($E_{max}$) has a constant value of 1 mm/day, so that per each month $T_{max} = ET_{max} - E_{max}$.
Table 2.1: Ecohydrological and biochemical parameters at the Bisley watershed (LEF, Puerto Rico).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Units¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>n</td>
<td>0.48</td>
</tr>
<tr>
<td>Depth of the root zone</td>
<td>Zr</td>
<td>0.4</td>
</tr>
<tr>
<td>Soil hygroscopic point</td>
<td>sh</td>
<td>0.36</td>
</tr>
<tr>
<td>Soil wilting point</td>
<td>sw</td>
<td>0.42</td>
</tr>
<tr>
<td>Point of incipient water stress</td>
<td>s*</td>
<td>0.76</td>
</tr>
<tr>
<td>Soil field capacity</td>
<td>sfc</td>
<td>0.8</td>
</tr>
<tr>
<td>Aerobic decomposition rate²</td>
<td>k_aer</td>
<td>2.7 · 10^{-4}</td>
</tr>
<tr>
<td>Mole specific decomposition rate³</td>
<td>β</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe-reducers growth factor⁴</td>
<td>r</td>
<td>5 · 10^{10}</td>
</tr>
<tr>
<td>Mineral weathering rate⁵</td>
<td>MW</td>
<td>0.08</td>
</tr>
<tr>
<td>Reduction rate constant⁶</td>
<td>k_red</td>
<td>8.89 · 10^{-15}</td>
</tr>
<tr>
<td>Oxidation rate constant⁶</td>
<td>k_ox</td>
<td>432</td>
</tr>
</tbody>
</table>

¹ From [113].
² From [25]
³ Computed considering that on average the soil organic matter here consists for the 45% of C [25] and that 4 moles of C are oxidized per mol of Fe reduced [143, 79].
⁴ From [143]
⁵ This study.
⁶ Calibrated from [102], see Section 2.2.2.

Soil porosity and hydraulic conductivity were selected according to typical values for silty clay loams [54, 89], while soil moisture at the hygroscopic point, wilting point, incipient water stress were computed from the retention curve [54, 147] by assuming water potentials of -10, -3 and -0.03 MPa, respectively. Soil moisture at field capacity was set at 0.8, slightly above the value of s*.

### 2.3 Results and Discussion

Equations (2.1), (2.2), (2.9) and (2.10) form a dynamical system of ordinary differential equations for the four state variables: \( Fe^{2+} \), \( Fe^{2+} \) concentration (mmol/kg^3 soil), \( Fe^{3+} \),
Figure 2.4: Temporal evolution of soil moisture (a), carbon substrate and litterfall rates (b), population of Fe-reducers (c), and Fe\textsuperscript{2+} concentration (d) for a period of two years. The trajectories were computed by solving numerically equations (2.1), (2.2), (2.9) and (2.10). The Figure highlights the high frequency variability induced by soil moisture fluctuations and the seasonal variability caused by changes in litterfall rates.

Fe\textsuperscript{3+} concentration (mmol/kg soil), $C$, carbon substrate concentration (g/kg soil), and $BM$, population of Fe-reducers (cells/kg soil). We integrated the equations numerically with a standard solver by setting an initial condition close to typical values observed in field measurements. We then let the model run for a period of time long enough (100 years) that the influence of the initial condition became negligible. The results, discussed below, are shown in time Figures 2.4.

2.3.1 Iron Dynamics

The constant wet soil conditions, with soil moisture levels most of the time above field capacity ($s_f = 0.8$), generate optimal conditions for anaerobic processes and Fe\textsuperscript{2+}-Fe\textsuperscript{3+} cycling. The frequent occurrence of anoxic conditions stimulates the use of Fe as electron acceptor for carbon decomposition, and hence the growth of the Fe-reducers and Fe reduction. The population of Fe-reducers remains large, of the order of $10^{11}$ cells/kg (Figure 2.4(c)), throughout the entire simulated period, in agreement with field measurements that
estimated a population up to $10^{12}$ cells/kg [79]. Throughout the simulated period, the soil carbon pool has on average approximately 7.5 g/kg of organic matter with a seasonality led by the variability in litterfall rates (Figure 2.4(b)).

The dynamics of Fe$^{2+}$ has high variability at various frequencies (Figure 2.4(d)). Daily soil moisture fluctuations have immediate effects on the Fe-redox state, consistently with fast redox fluctuations observed in laboratory experiments [102]. In wet soil conditions ($s > s_{fc}$), Fe$^{2+}$ values quickly grow above 2 mmol/kg and have peaks of 7 to 8 mmol/kg (see also Figure 2.5), while exposures to high oxygen levels during dryer conditions ($s < s_{fc}$) rapidly deplete the Fe$^{2+}$ pool. The time evolution of Fe$^{2+}$ shows also a seasonal variability. Higher litterfall rates provide more carbon to Fe-reducers, which in turn grow and further stimulate net Fe reduction rates. As a result, higher values of both population of Fe-reducers and Fe$^{2+}$ tend to occur during high litterfall deposition.

### 2.3.2 Coupled Fe and soil moisture dynamics

The dependence of Fe$^{2+}$ on soil moisture is illustrated in the $Fe^{2+}$-s phase space (Figure 2.5), where the gray points were drawn from the simulated time evolution of Fe$^{2+}$ and soil moisture at a constant time interval of 0.1 day. From the density of points in Figure 2.5, it is evident that the region that is most explored is between soil moisture levels of 0.8 and 0.9. Due to the climate, lower soil moisture values are rare while higher levels approaching saturation are explored for short intervals, because water is quickly lost via percolation. Field measurements of soil moisture and Fe$^{2+}$ from the Espíritu Santu watershed [6], close to the Bisley watershed, fall within the cloud of gray points, and the highest values of Fe$^{2+}$ are also observed at soil moisture just above field capacity. It is clear from Figure 2.5, however, that more frequent measurements are needed for a thorough model-data comparison.

The response of the redox reaction to the soil moisture and litterfall dynamics is further explored in Figure 2.6. During a soil wetting and drying cycle (Figure 2.6(a)) the trajectories form loops in the $Fe^{2+}$-s phase space that are traveled in a counterclockwise direction.
Figure 2.5: $Fe^{2+}$-$s$ phase space showing the region of $Fe^{2+}$ and $s$ values explored by the simulation and by field observations. The gray points were drawn from the simulation at a constant interval of 0.1 day, while the orange points are field measurements from the Espíritu Santu watershed [6]. The Figure reveals the region that is most explored by modeled and observed $Fe^{2+}$ levels.

Table 2.2: Longterm average of iron fluxes (mmol/kg/d) and of carbon decomposition rate (g/kg/d).

<table>
<thead>
<tr>
<th>MW</th>
<th>Reduction (Oxidation)</th>
<th>Uptake</th>
<th>Leaching</th>
<th>DEC&lt;sub&gt;red&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08</td>
<td>0.075</td>
<td>0.02</td>
<td>0.06</td>
<td>0.0075</td>
</tr>
</tbody>
</table>

(Figure 2.6(b)). As we have seen above, when litterfall provides more carbon to the Fe-reducers, their population grow and more Fe is reduced. As a consequence, trajectories explore higher $Fe^{2+}$ values for given soil moisture levels, forming loops in upper regions of the phase space. Interestingly, in the phase space given by the reduction rate and soil moisture (Figure 2.7), the system trajectories collapse approximately on a single line, suggesting that the iron reduction rate can be uniquely related to the soil moisture level, while the effects of different litterfall rates and carbon contents appear negligible.

2.3.3 Fe fluxes and carbon decomposition

From equations (2.3), (2.4), (2.7) and (2.8), we computed the temporal dynamics of the iron fluxes, namely reduction, oxidation, uptake and leaching. The long term average value
Figure 2.6: Panel (a): Temporal evolution of Fe$^{2+}$ showing the soil wetting and drying cycles as the litterfall rates increase. The trajectories were computed by solving equations (2.1), (2.2), (2.9) and (2.10) and the soil moisture dynamics (2.12) with deterministic rainfall, one event every six days that brings the soil to saturation. Panel (b): Time evolution of the system trajectory in the Fe$^{2+}$-s phase space. The trajectories form loops that are traveled in a counterclockwise direction during a wetting and drying cycle and explore higher Fe$^{2+}$ values as litterfall rates increase.

Figure 2.7: Time evolution of the system trajectory in the RED-s phase space. From the trajectories computed in Figure 2.6, we computed the reduction rate by means of equation (2.3). The Figure reveals an emerging relationship between reduction rate and soil moisture.
for each flux is shown in Table 2.2. From the total overall input of iron ($MW = 0.08$ mmol/kg), approximately 0.06 mmol/kg leave the soil as leaching while the remaining 0.02 mmol/kg are taken up by plants. It is thus evident that an important role in Fe dynamics is played by plants, which account for 25% of soil iron losses. The average reduction rate is about 0.075 mmol/kg/d, with instantaneous rates approaching 10 mmol/kg/d, of the same order of values observed in laboratory experiments (2-50 mmol/kg/d) [294, 112, 5].

Considering that four moles of carbon are decomposed per mole of Fe$^{3+}$ reduced [143, 79], iron reduction has the potential to drive the carbon cycle during periods of high soil moisture levels, in which the decomposition due to aerobic metabolism is inhibited [34]. Because of soil moisture levels almost constantly above field capacity, our results in fact emphasize the importance of iron reduction as primary contributor to microbial respiration, in line with prior work estimating that in the wetter spots of these forests >50% of the organic matter is decomposed through iron reduction [79].

2.3.4 The effect of plant uptake on Fe redox

As we have shown above, soil iron dynamics is also impacted by the presence of plants, which uptake Fe$^{2+}$ to sustain their physiological processes, such as photosynthesis, respiration, as well as the synthesis of chlorophyll [138]. While iron deficiency results in chlorosis, namely the yellowing of the younger leaves, and growth-rate reduction [179], high iron contents are toxic to plants due to the formation of hydroxyls radicals that damage the DNA, proteins and other cell components [93]. Our results show that on average plant uptake contribute 25% to soil iron losses (Table 2.2) and is an important component of the soil iron cycle that cannot be neglected. The highest uptake rates are observed when soil moisture is at field capacity, as both transpiration rates and Fe$^{2+}$ contents are high. At higher soil moisture, dilution prevails and the concentration of dissolved Fe$^{2+}$ quickly decreases, whereas at low soil moisture plants reduce the uptake of iron because of water stress.
Because of the low concentrations of iron in the soil solution, the passive uptake of iron through transpiration may not be sufficient for plants to maintain optimal iron contents for their growth [109, 184, 226]. To overcome this limitation, plants have developed two possible strategies of active uptake. In strategy 1, typical of dicots and non-graminaceous monocots, roots enhance Fe$^{3+}$ reduction by releasing protons and acidificating the rhizosphere and then transporting Fe through the root cell membranes. In strategy 2 (monocots), roots release ligands to form chelates with Fe$^{3+}$ and then uptake it by means of a specific transporter. Through specific mechanisms, these plants can also uptake Fe-chelated forms deriving from microbial activity [225, 57]. On the other hand, the mechanisms through which plants avoid toxic iron concentrations are not completely understood [93]. It seems, however, that plants are able to induce oxidation of Fe$^{2+}$ on the roots as well as to limit the internal translocation of iron [9].

These plant strategies become extremely important when interested in the effects of soil iron dynamics on crops. In this regard, models could account for plant strategies by introducing specific controlling factors in the oxidation and reduction rates, and an uptake term for Fe$^{3+}$, that depend on the plant-specific physiological demand of iron. This would make it possible to analyze also the feedback that different plant species and their active uptake have on soil iron and carbon cycles, fostering the design of novel detailed experiments to calibrate the controlling factors of the model component.

### 2.4 The optimal oxic/anoxic cycle for Fe reduction

From the previous analysis, it is clear that the hydro-climate generating the oxic/anoxic cycles exerts a major control on the pace of the iron cycle, hence on that of organic matter decomposition. Therefore, to generalize our analysis, we now study the changes in average iron reduction rate as a function of the characteristics of the oxic/anoxic cycles. Our focus here is on the maximum permissible rates, hence we assume that the availability of the
organic substrate and microbes does not limit the reactions, and the characteristics of the hydrologic cycle remain the only controlling factors.

Consider an oxic/anoxic cycle with period $T$ that begins with the anoxic phase of duration $\tau_a = fT$ (Figure 2.8), whereas the oxic phase lasts for $\tau_o = (1 - f)T$. During the anoxic phase, only iron reduction proceeds, with consequent increase of $Fe^{2+}$ in solution. During the oxic phase, iron reduction stops and $Fe^{2+}$ is oxidized to $Fe^{3+}$ (Figure 8.2(b)). Because we are interested on the role of the oxic/anoxic fluctuations, we here assume that $MW$ is balancing the losses through $L$ and $UP$. The full $Fe^{2+}$ dynamics was discussed in the previous sections. This simplified dynamics is described by the following balance.
equation,
\[ \frac{dF_{e^{2+}}}{dt} = \text{RED} - \text{OX}, \]  
(2.13)
where \( \text{RED} = k_R(F_{e^{TOT}} - F_e) \) and \( \text{OX} = k_O F_{e^{2+}} \), \( k_R \) and \( k_O \) being the reduction and oxidation rate constants, respectively. On the one hand, these expressions do not contain a dependence on the amount of substrate and microbes because, as we mentioned above, they do not limit the reactions. On the other hand, the reaction constants explicitly depend on time in that during the anoxic phase \( k_O = 0 \), while during the oxic phase \( k_R = 0 \). Solving equation (2.13) for sufficiently long time such that the initial condition has been forgotten, the stationary solution for a given oxic/anoxic cycle (shown in Figure 2.8(a)) is given by an exponential decay during the oxic phase,
\[ F_{e^{2+}}(t) = F_{e^{2+}0} e^{-k_O t}, \]  
(2.14)
where \( F_{e^{2+}0} \) is the iron content at the end of the precedent anoxic phase and \( t \) is the time elapsed since the beginning of the oxic phase, and by an exponential approach to \( F_{e^{TOT}} \) during the anoxic phase,
\[ F_{e^{2+}}(t) = F_{e^{TOT}} - F_{e^{2+}0'} e^{-k_O t}, \]  
(2.15)
\( F_{e^{2+}0'} \) being the iron content at the end of the oxic phase and \( t \) the time elapsed since the beginning of the anoxic phase.

In the extreme scenario in which the conditions are constantly oxic (meaning \( f = 0 \)), the entire iron content persists in its oxidized state, \( F_{e^{2+}}(t) = 0 \), and the average reduction rate, which can be defined as \( \overline{\text{RED}} = 1/T \int_T \text{RED}(t) dt \), goes to zero. On the other hand, for constantly anoxic conditions \( (f = 1) \) iron persists in its reduced state, \( F_{e^{2+}}(t) = F_{e^{TOT}} \), and again the reduction rate \( \overline{\text{RED}} = 0 \). This argument suggests that a maximum reduction rate \( \overline{\text{RED}}^* \) exists at an intermediate value of \( f, f^* \). Solving equation
Figure 2.9: Average reduction rate, \( \bar{RED} = \frac{1}{T} \int_T RED(t) dt \), for different values of the reduction and oxidation rate constants, as a function of \( f \) and \( T = 5 \) days. The reduction rate constant \( k_R = 1 \) mmol/kg/d, while the oxidation rate constants are, from left to right, 1, 2 and 5 mmol/kg/d.

(2.13) for different values of \( f \), the different Fe\(^{2+} \) trajectories are shown in Figure 2.8, and computing the average reduction rate per cycle, see Figure 2.8(d), confirms that there exists the anoxic/oxic cycle for which the \( \bar{RED} \) is maximum.

The optimal \( f^* \) at which the maximum is achieved depends on the reaction rate constants, \( k_R \) and \( k_O \). In Figure 2.8, \( k_R = k_O \) and the resulting \( f^* = 0.5 \). For higher \( k_R \) or \( k_O \), shorter anoxic or oxic phases are needed to reduce or oxidize, respectively, the same amount of iron. Away from the optimal \( f \), the oxic/anoxic cycles is favoring either the reduction \(( f > f^* ) \) or the oxidation \(( f < f^* ) \) and inhibiting the other one. When \( f > f^* \), the iron-redox cycle is limited by the regeneration phase, namely there is not time to oxidize enough iron to use in the following anoxic phase. On the contrary, \( f < f^* \) the iron-redox cycle is limited by the reduction phase, such that the anoxic phase is too short to reduce substantial amounts of iron (Figure 2.9).

In field conditions, the frequency and depth of the rainfall events, evapo-transpiration from soil and plants, and soil properties altogether determine the evolution of the soil water and oxygen content [113, 45] causing the soil to undergo ‘random’ transitions between oxic and anoxic conditions. Since soil moisture is a good proxy for oxygen content, the average duration of the oxic and anoxic phases, for a given hydro-climate, can be obtained by ana-
Figure 2.10: (a) Anoxic fraction of the cycle, $f$, and (b) duration of the cycle, $T$, as a function of the frequency of precipitation events, $\lambda$, and for different values of mean precipitation depth, $\alpha$. The values of $\alpha$, from blue to red line, are 5, 8, 10, and 12 mm. The probability density function for the soil moisture was computed from [147], for a silty clay loam soil, average porosity $n = 0.48$, potential evapotranspiration $PET = 4$ mm/d, and hydraulic conductivity $k_h = 14$ cm/d.

Analyzing the specific time series of soil moisture. Fixing the soil moisture threshold $\hat{s}$ above which soil conditions can be considered anoxic, the average time spent in oxic conditions $\tau_o$ then can be calculated as the average time of each excursion below the threshold $\hat{s}$. The average time of each excursion above $\hat{s}$ will be $\tau_a$, the average duration of an oxic/anoxic cycle $T = \tau_a + \tau_o$, and in turn $f = \tau_a / \tau$.

We show the relationship between $f$ and $T$ and frequency and mean depth of precipitation ($\lambda$ and $\alpha$, respectively) in Figure 2.10. The curves are drawn for constant soil properties (typical of a silty clay loam) and potential evapotranspiration ($PET = 4$ mm/d) using a stochastic water balance that provides the statistical properties of soil moisture based on rainfall statistics [147] (see Appendix A). Because of the high water losses at soil moisture above field capacity, the fraction of time spent in anoxic conditions is generally lower than the one spent in oxic conditions, such that the values of $f$ are below 0.5 (Figure 2.10). As can be expected, soils are in anoxic conditions on average longer (higher values of $f$) for high rainfall frequencies accompanied by high average rainfall depths. On the contrary, the whole duration of the cycle, $T$, decreases with $\lambda$ as the excursion from oxic to anoxic is more likely to occur. For the realistic range of $\alpha$ and $\lambda$ explored, $T$ decreases with $\alpha$, again because it is more likely that the threshold $\hat{s}$ is crossed, but for very high values of
Figure 2.11: Average reduction rate per cycle, \( \overline{RED} \), as a function of the anoxic fraction of the cycle, \( f \), and duration of the cycle, \( T \). The reduction and oxidation rate constants are \( k_R = 0.1 \) and \( k_O = 10^2 \) mmol/kg/d, respectively.

\( \alpha \) and \( \lambda \) the trend in Figure 2.10 may be inverted as the soil settles in very wet and anoxic conditions (\( s > \hat{s} \)) for most of the time.

## 2.5 Implications of climate changes

The comprehensive, long term biogeochemical observations at the Bisley watershed in the Luquillo experimental Forest in Puerto Rico [239] allow us to readily apply the above framework to explore the potential implications of changing rainfall patterns in this humid tropical forest. In fact, given their high content of organic matter and population of Fe reducers [25, 301, 79], we can reasonably apply equation (2.13) to analyze the hydrologic control on the reduction rates, while assuming that these other factors are not limiting.

Given the reduction and oxidation rate constants in these soils, we compute the average reduction rate \( \overline{RED} \), Fe reduced per cycle divided by the duration of the cycle, as a function of the fraction in anoxic conditions \( f \) and the overall duration of the cycle \( T \) (Figure 2.11).
The analysis shows that the ideal oxic/anoxic cycle has very high values of $f$ ($f > 0.9$), which result from the 3 orders of magnitude difference between the reduction and oxidation reaction rate constants. Average reduction rates are also higher for very short cycles, of the order of days, because there is not enough time to dissolve much iron, its concentration remains low, and in turn the reduction, being proportional to $Fe^{3+}$, proceeds at high rates.

In order to relate the iron-redox cycle in these tropical soils to rainfall statistics, we also estimated the average reduction rate as a function of the frequency and mean depth of precipitation events through equation (2.13) and equations (A.2) and (A.3) in the Appendix A. From an analysis of the precipitation records, the frequency of rainfall events is $0.8 \, \text{d}^{-1}$ while its mean depth is $12 \, \text{mm}$ [119, 45]. Iron $Fe^{2+}$ rapidly increases following a heavy rainfall that brought soil moisture above the $\hat{s}$ level, but it is oxidized even more rapidly (due to the high oxidation rate constant) when the soil settles back in oxic conditions upon drying. As a result, $Fe^{2+}$ dynamics appears as a series of rapid redox cycles (a reduction
followed by the oxidation) initiated by heavy precipitations, see Figure 2.12(a). The average reduction rate for varying rainfall statistics is shown in Figure 2.12(b), where Luquillo is placed on the lower right corner, indicated by a red star. The analysis readily shows that here the oxic/anoxic cycle is not optimal. For higher frequencies and mean rainfall depths in fact the average reduction rate would increase, indicating that the rate is limited by the duration of the anoxic phase.

The framework not only predicts average reduction rates that are consistent with previous results [294, 113, 5], but also provides estimates for the changes in reduction rates induced by shifts in the rainfall pattern. Although with considerable uncertainty, recent climate reports [233] predict a decrease in mean annual precipitation, but an increase in extreme events. Precipitation will be delivered with fewer events, which in terms of rainfall statistics corresponds to lower frequency, $\lambda$, but higher mean rainfall depth $\alpha$. Accordingly, the direction of the trend in the average reduction rate $\overline{RED}$ (indicated with a blue arrow) will be constrained by the gray axes in Figure 2.10. Whether $\overline{RED}$ will increase or not will depend on a precise estimation of the trends in rainfall statistics.

2.6 Conclusions

We have developed a dynamical system for the time evolution of iron and carbon concentrations and soil moisture in the soil root zone to explore the iron-carbon coupling and the control that the hydrologic regime exerts on them. The parsimony of this model allowed us to analyze the main relationships between the state variables and fluxes as well as to explore in detail the role of soil moisture dynamics. The model was used to analyze iron fluctuations at the Luquillo Experimental Forest, which due to its climate and soil characteristics represents an ideal location for studying of Fe-cycle, and for which laboratory and field measurements were available.
Our results point to soil moisture and carbon as the main controllers of the soil iron cycle. Daily soil moisture variability induces changes in the concentration of oxygen and determine the transition between oxic and anoxic conditions. This in turn stimulates rapid \( \text{Fe}^{2+} \) fluctuations. Over monthly timescales, the concentration of the carbon substrate responds to the variability in litterfall rates, introducing a seasonal component into iron dynamics. Due to the complex dynamics coupling the soil moisture, carbon, and \( \text{Fe}^{2+} \), the dependence of \( \text{Fe}^{2+} \) on soil moisture gives rise to hysteretic behaviors, see Figure 2.6. On the contrary, the model reveals a simple increasing relationship between the reduction rate and the soil moisture level.

Soil conditions are mostly favorable to leaching of iron, which in the longterm accounts for \( \approx 75\% \) of total iron losses, but plants contribute substantially to the soil iron cycle by taking up the remaining \( 25\% \). During anoxic conditions, iron reduction approaches rates of 10 mmol/kg/d and is the main driver of microbial respiration.

Our analysis couples a variety of biotic and abiotic processes spanning a wide range of timescales, thus making it difficult to carry out detailed experiments to analyze their properties. In this regard, we hope that this model will be useful to design suitable experiments to capture these interactions as well as test hypotheses about their response to natural and human perturbations, such as hurricanes, drought, and agriculture. We also wish to bring to our attention the effect of different responses of plant types to iron deficiency and toxicity and their feedback on the soil iron dynamics. A model-experiment combination may provide detailed insights into this highly intertwined interaction between the hydrologic and the soil biogeochemical cycles.

Through a minimalist model of iron redox dynamics, we also related the average reduction rate to the alternation of oxic and anoxic conditions induced by hydro-climatic variability. The study showed the existence of a maximum reduction rate for an ‘ideal’ oxic/anoxic cycle and shed light on the factors that otherwise limit this rate. Applying the framework to the Luquillo Experimental Forest in Puerto Rico, we also highlighted
the changes in the reduction rate that may be caused by trends in the precipitation pattern. Analogously, the framework may be used to elucidate limiting mechanisms and predict future trends in other environments. By relating the pace of the soil iron cycle to hydroclimatic fluctuations, this analysis also paves the way for a large scale identification of hot spots of iron reduction, in which climatic features are highly favorable.

The results also stress the fact that the competition between different microbial metabolisms is driven not only by equilibrium thermodynamics considerations (e.g., [256]), but also by the dynamic properties of the oxic/anoxic cycles. That is, the aerobic metabolism is likely to prevail over iron reduction when the anoxic intervals are too short, while methanogenesis may come about when iron reduction is limited by the regeneration phase, i.e., too short oxic intervals. We thus hope that this work may provide useful insights into the mechanisms of microbial respiration towards an improved estimation of greenhouse gas emissions from soils.
Chapter 3

Hydrologic transport of dissolved inorganic carbon and its control on chemical weathering

The biogeochemical processes in the root zone determine the availability of nutrients to plants as well as soil respiration, namely the production of carbon dioxide. The CO$_2$ produced in the root zone is partly emitted to the atmosphere and partly dissolved in water and transported to deeper soil layers, where it interacts with primary minerals in the parent material stimulating their dissolution (chemical weathering). The weathering of such minerals is fundamental to the release of nutrients and soil formation as well as to the stability of climate, representing an important sink of CO$_2$. The work presented in this chapter is adapted from Calabrese, Salvatore, Anthony J. Parolari, and Amilcare Porporato, "Hydrologic transport of dissolved inorganic carbon and its control on chemical weathering", Journal of Geophysical Research: Earth Surface 122.10 (2017): 2016-2032.
3.1 Introduction

Chemical weathering takes part in the complex system of feedbacks between climate and geochemical processes regulating the carbon cycle [18], soil acidification [260, 291], soil clay formation [82, 247] and landscape development [186, 75, 216]. Chemical weathering of silicate minerals is also one of the major processes that modulates climate through consumption of atmospheric carbon dioxide (CO₂) [265, 277, 101, 255], as dissolved inorganic carbon is the main chemical driver of silicate mineral dissolution reactions. Over geologic timescales the consumption of CO₂ by silicate weathering regulates atmospheric CO₂ concentration [123], whereas over much smaller timescales, the balance of soil CO₂ production by root and microbial respiration [219] and mineral dissolution controls soil acidification [173, 220]. Therefore, understanding the long-term evolution of soils and climate, relevant to sustainability of the critical zone, necessitates a quantitative description that links the production, transport, and chemical fate of CO₂ in the subsurface [267] to chemical weathering rates.

Temperature and the hydrologic cycle are the two main climatic factors that affect weathering rates. The former is extremely important as an increase in temperature accelerates weathering reaction rates. On the other hand, CO₂ sequestered through weathering regulates atmospheric CO₂, thus imposing a negative feedback on temperature [277, 146]. In parallel, water influences mineral weathering by participating in the chemical reactions as a reactant as well as by transporting [H⁺] ions and other chemical species from the surface to subsurface weathering sites [135, 255]. The role of water has been evaluated mostly in terms of rainfall [288, 223, 286, 106, 74], its residence time [165, 157, 166], and hydraulic conductivity of soils [97].

Chemical weathering also interacts with physical erosion and tectonic processes during soil formation [82]. While tectonic uplift supplies fresh minerals to the soil and chemical weathering alters their compositions forming clays, physical erosion transports weathered material to rivers and ultimately the ocean. When the weathering rate is limited by the
supply of fresh minerals [194, 122], its sensitivity to climatic factors is reduced [223, 157] and the tectonic uplift becomes the major control [180, 128]. Some authors have emphasized that supply-limited conditions are determined when the mineral reaction time (inverse of the kinetic constant) is much shorter than the rock residence time in the regolith [122, 165, 157].

Along with the estimation of weathering rates based on field observations ([37, 288, 289, 222, 223, 286, 290, 167, 74], numerous detailed numerical models have been developed to couple geochemical processes to water dynamics and temperature in unsaturated and saturated media [49, 192, 295, 169, 251, 257, 237, 234]. These typically consider numerical solutions of Richards’ or groundwater equations coupled with partial differential equations describing the reactive transport of the chemical species. While these models provide a detailed space-time description of the weathering process, the wide range of time scales involved in the various processes taking place in the critical zone [35] make these complex numerical approaches unsuitable for long-term predictions as well as for theoretical analysis of the interplay between the main system variables under different environmental scenarios. On the contrary, simpler models that have been proposed do not account for external climatic forcings [97], or focus only on the role of tectonic processes [98, 122, 157]. To our knowledge, no model has yet considered consistently the dissolution and transport of CO$_2$ and its dependence on surface hydrological processes in relation to the dynamics of the weathering process. There is then a need for analytical models to predict the role of climate, hydrology, and CO$_2$ dissolution and transport on chemical weathering, that are amenable to theoretical analysis and upscaling in space and time.

Toward this goal, in the present study we develop a model based on molar balance equations for the chemical species in the weathering zone. Aiming to isolate the effect of hydrology, we assume that the reaction is not limited by the supply of fresh mineral by tectonic processes, and that the products of the reactions are removed only by water transport. The model is thus more applicable to regions where the tectonic activity is fast compared
to the weathering reactions (e.g., [157, 223]). The dissolution and speciation of CO$_2$ is assumed to be at equilibrium at any given time, whereas the weathering reaction is described through a kinetic rate law [153, 167]. For the sake of simplicity, we neglect the ion interactions, which take place at high solute concentrations (high ionic strength) and neglect the effect of biological activity and temperature on the kinetic constant. Similarly, we do not take into account the presence of ion-exchange reactions. We set the balance equations in a way that can be generally formulated for multiple minerals subject to different weathering reactions, although here we consider only the weathering of albite to kaolinite. Using this model we explore the effects of the percolation rate, CO$_2$ dissolution and transport, and the water transit time on the weathering rate dynamics. The model reveals that the percolation flux impacts the weathering reaction mainly by transporting dissolved inorganic carbon, while water transit time is an indicator of dilutive effects.

The remainder of the manuscript is organized as follows. The model is described in Section 3.2 and steady state solutions are presented as function of the percolation rate in Section 3.3 and as function of the water transit time in Section 3.4. Section 3.5 discusses the role of nonlinear expressions for the groundwater discharge. In Section 3.6 a comparison with measured weathering rates is introduced. The results are summarized in Section 8.6.

### 3.2 Model Description

Consider a soil regolith subdivided into a solum, which includes the O, A, E and B soil horizons, and the underlying layer of saprolite (fractured parent material) on top of a consolidated bedrock formation. In this schematic representation of the regolith, see Figure 3.1, the bedrock is assumed impervious and the water table is located within the unconsolidated layer. Focusing on the weathering of the parent material, the weathering zone can be interpreted as the volume delimited by the bedrock at the bottom and the water table at the top. The spatially implicit model described below is derived from spatial integration of
reactive transport equations and couples the water table (i.e., weathering zone depth) and chemical dynamics in this weathering zone. Because of these simplifying assumptions, the model is more suitable to large regions, for which one can more safely consider averages over the spatial complexity of topography, mineralogy, rainfall, and other factors. Because the present analysis focuses on time-scales of soil development, average values of the hydrological and chemical parameters and simple phenomenological expressions are used.

### 3.2.1 Leakage Chemistry

Water percolating from the surface soil layers influences the weathering reaction by transporting dissolved inorganic carbon to the weathering zone. The amount of CO$_2$ dissolved in the percolating water depends on the equilibrium with the partial pressure, $P_{CO_2}$, in the top soil layer [135]. Due to root and microbial respiration, $P_{CO_2}$ is generally higher than the reference value in the atmosphere, $P_0$. As shown in [65], the daily dynamics of CO$_2$ are characterized by instantaneous jumps induced by rainfall events and linear decay between rainfall events. Based on these findings, we assume that the partial pressure of CO$_2$ in the
Figure 3.2: Chemical composition of the percolating water as a function of the percolation rate $L$ and assumed root zone alkalinity $A^L$ computed from equations (3.1), (3.2) and (3.9). The inset shows the resulting $C^*_T$ as a function of the percolation rate $L$, for $A^L = 1$ (eq/m$^3$). Parameters: $P_0 = 10^{-3.5}$ atm, $K(L) = K = 10^{-1}$ atm day/m, equilibrium constants $K_1 = 10^{-6.3}$ mol/m$^3$ and $K_2 = 10^{-10.3}$ mol/m$^3$, Henry’s constant $K_H = 33.9$ (mol/m$^3$/atm).

Soil gas is empirically linked to the percolation rate, $L$,

$$P_{CO_2} = P_0 + K(L)L,$$  \hfill (3.1)

where the proportionality coefficient $K(L)$ can be, in general, a function of $L$. The functional form of $K(L)$ accounts for processes enhancing or inhibiting the production of $CO_2$ and needs to be determined experimentally. The analysis shown here is conducted following the observations at the Duke Forest [65], for which $K(L)$ is a constant. As more data become available for other conditions, different assumptions regarding $K(L)$ can be readily accommodated within the present framework.

The model accounts for dissolution and speciation of $CO_2$ in water, which at any given time are assumed to be in thermodynamic equilibrium. Therefore, Henry’s Law determines the concentration of the total analytical concentration of dissolved $CO_2$, $[H_2CO_3^+] = CO_{2(aq)} + [H_2CO_3]$, $[H_2CO_3^+] = K_H P_{CO_2}$, \hfill (3.2)
where $K_H$ is the Henry’s Law constant. The equilibrium constants, $K_1$ and $K_2$, then determine the de-protonation of $H_2CO_3^*$ which yields $HCO_3^-$ and $CO_3^-$ [151, 135],

\[
H_2CO_3^* \xrightleftharpoons{K_1} H^+ + HCO_3^- \quad (3.3)
\]
\[
HCO_3^- \xrightleftharpoons{K_2} H^+ + CO_3^- ,
\]

while $K_w$ regulates the self-ionization of water,

\[
H_2O \xrightleftharpoons{K_w} H^+ + OH^- . \quad (3.4)
\]

Pertaining to the release of $[H^+]$ ions, the reactions (3.3) and (3.4) are functions of $pH$. Defining the sum of $[H_2CO_3^*]$, $[HCO_3^-]$ and $[CO_3^-]$ as the total dissolved inorganic carbon $C_T$ (DIC), each carbonate species can be expressed as fractions of $C_T$,

\[
\alpha_0 = [H_2CO_3^*]/C_T \quad (3.5)
\]
\[
\alpha_1 = [HCO_3^-]/C_T \quad (3.6)
\]
\[
\alpha_2 = [CO_3^-]/C_T , \quad (3.7)
\]

where the ionization fractions $\alpha_0$, $\alpha_1$, and $\alpha_2$ are explicit functions of $[H^+]$, reflecting the dependence of the carbonate system on $pH$.

Alkalinity is defined as

\[
A = [HCO_3^-] + 2[CO_3^-] - [H^+] + [OH^-], \quad (3.8)
\]

and by introducing (3.6), (3.7), and (3.4) into (3.8), we obtain [255]
\[ A = C_T(\alpha_1 + 2\alpha_2) + Kw/[H^+] - [H^+], \] (3.9)

which links \( A, C_T, \) and \( pH \). In order to compute the chemical composition of the percolating water, we fix the value of alkalinity \( A^L \) (we use the superscript \( L \) to indicate that the value refers to percolation) and then for given percolation rate \( L \), we calculate \( C_T^L \) and \([H^+]^L \) from (3.1), (3.2), (3.5) and (3.9) [255]. The choice to fix \( A^L \) is motivated by the fact that the addition of \( CO_2 \) into the system changes the value of \( C_T \) and \( pH \), without altering \( A \).

As the percolation rate increases, \( P_{CO_2} \) and \( C_T \) rise, so that more \( H^+ \) ions are released and the \( pH \) decreases (Figure 3.2). The three related quantities \( L, C_T^L, \) and \( A^L \), and intrinsically the \( pH \), thus represent the external forcing to the weathering zone that together with other weathering reactants or products percolating from upper soil layers perturb the weathering reaction during its evolution towards equilibrium.

### 3.2.2 The Weathering Zone

The weathering zone is considered as a control volume that is filled by the percolation \( L \) and releases water through the loss term \( Q \). The water balance for the weathering zone of height \( h \) is expressed as

\[ n \frac{dh}{dt} = L(t) - Q(t), \] (3.10)

where \( n \) is the porosity. The percolation rate \( L \) represents the portion of water that reaches the weathering sites in the deeper soil layers, can be characterized by intraseasonal to interannual variability, and is considered here as the external hydrologic forcing. The discharge \( Q \) depends on the complex and heterogeneous structure of the groundwater system so that various relationships with the water storage, \( Q = Q(h) \), may be assumed. Here, for the sake of simplicity we adopt the following relationship [50, 175],
\[ Q = k_Q h^\beta, \quad (3.11) \]

where \( k_Q \) is the specific output rate and the exponent \( \beta \) determines the degree of non-linearity. When more detailed information is available, (3.11) can be replaced with more suitable functions without affecting the development of the rest of the theory. Equation (3.10) is spatially implicit in that no spatial variability in either the vertical or horizontal directions is considered.

The weathering zone chemistry includes the DIC system and the weathering products. The DIC system at any given time is assumed to reach equilibrium very fast and thus, analogously to the chemistry of the percolating water, is determined by the equilibrium reactions (3.3) and the self-ionization of water (3.4). On the contrary, the weathering reaction proceeds much more slowly, thus requiring a kinetic description of the reaction for the specific mineral being weathered. Given the important role of silicate weathering in global climate and the availability of data for feldspar minerals (e.g., [53, 287, 289, 290, 167]), we formulate the model for the weathering of albite (\( NaAlSi_3O_8 \)) with precipitation of Kaolinite (\( Al_2Si_2O_5(OH)_4 \)). Specifically, albite is a plagioclase mineral that occurs mostly in igneous rocks (e.g., granite) but also in metamorphic formations. Being one of the prevailing minerals found in parent materials (e.g., the granitic gneiss at the Calhoun CZ observatory) albite often takes part in soil formation. Considering the following congruent reaction for dissolution of albite,

\[
4H_2CO_3 + NaAlSi_3O_8 + 4H_2O \rightleftharpoons Al^{3+} + Na^+ + 4HCO_3^- + 3H_4SiO_4, \quad (3.12)
\]

and the one for precipitation of kaolinite,
\[ Al^{+3} + H_4SiO_4 + \frac{1}{2}H_2O + 3HCO_3^- \rightleftharpoons \] (3.13)
\[ \frac{1}{2}Al_2Si_2O_5(OH)_4 + 3H_2CO_3 + 3H_4SiO_4, \]

the overall representative incongruent reaction for albite weathering can be written as,

\[ H_2CO_3 + NaAlSi_3O_8 + \frac{9}{2}H_2O \rightleftharpoons \] (3.14)
\[ \frac{1}{2}Al_2Si_2O_5(OH)_4 + Na^+ + HCO_3^- + 2H_4SiO_4. \]

In the above reactions, the dissolution of albite is the rate-limiting step, while the precipitation of kaolinite is relatively fast and can be considered an equilibrium reaction (e.g., [157]).

The time evolution of the mass per unit ground area of weathering products and carbonate species is then described by the set of ordinary differential equations,

\[ n \frac{dh[H_2CO_3^*]}{dt} = L_{H_2CO_3} - Q_{H_2CO_3^*} - R_2 - hW, \] (3.15)

\[ n \frac{dh[HCO_3^-]}{dt} = L_{HCO_3^-} - Q_{HCO_3^-} + R_2 - R_3 + hW, \] (3.16)

\[ n \frac{dh[CO_3^{2-}]}{dt} = L_{CO_3^{2-}} - Q_{CO_3^{2-}} + R_3, \] (3.17)

\[ n \frac{dh[H^+]}{dt} = L_{H^+} - Q_{H^+} + R_2 + R_3 + R_4, \] (3.18)

\[ n \frac{dh[OH^-]}{dt} = L_{OH^-} - Q_{OH^-} + R_4, \] (3.19)
\[ n \frac{dh[Na^+]}{dt} = L_{Na^+} - Q_{Na^+} + hW, \quad (3.20) \]

\[ n \frac{dh[H_4SiO_4]}{dt} = L_{H_4SiO_4} - Q_{H_4SiO_4} + 2hW. \quad (3.21) \]

Equations (3.15)-(3.21) are obtained by spatially integrating the chemical transport equations (e.g., see [49, 192]) over the weathering zone. Derived from such integration, \( L \) and \( Q \) represent the total hydrologic transport component, while the \( R_i' \)s and \( h \cdot W \) are the volumetric reaction rates for the equilibrium DIC system (equations (3.3) and (3.4)) and the weathering process (reaction (3.14)), respectively. Note that the volumetric weathering rate is assumed to scale with the weathering zone depth, i.e., \( h \cdot W \), which accounts for the fact that the surface area exposed to the reaction increases with the depth of saprolite that is saturated. The terms \( L_{Na^+} \) and \( L_{H_4SiO_4} \), respectively, account for \( Na^+ \) and \( H_4SiO_4 \) percolating from upper soil layers while the outflows of solutes can be expressed as the product of the discharge \( Q \) and their concentrations. For example, the outflow of \( Na^+ \) can be computed as \( Q_{Na^+} = Q \cdot [Na^+] \).

To close the system (3.15)-(3.21), a phenomenological equation is needed for \( W \). We compute the weathering rate \( W \) for the overall congruent reaction (3.14) through the expression (see Appendix B for the derivation) [153, 152, 167, 165],

\[ W = w_{max} \left[ 1 - \frac{\Theta}{K_{eq}} \right], \quad (3.22) \]

where \( w_{max} = K \rho_{al} a_{sal} \) (mol/m\(^3\)/day) represents the product of the kinetic parameters, namely the kinetic rate constant \( K_{alb} \) (mol/m\(^2\)/day), the albite density \( \rho_{al} \) (g/m\(^3\)), and albite specific surface area \( a_{sal} \) (m\(^2\)/g). The ion activity product is given by,
Using equations (3.5) and (3.6), one can write also

\[ \Theta = \frac{[Na^+][HCO_3^-][H_4SiO_4]^2}{[H_2CO_3]} \]  

(3.23)

Given the first dissociation constant of silicic acid, \( pK_a = 9.8 \), at \( pH = 8 \), for example, \([H_4SiO_4]\) is already much greater than \([H_3SiO_5^-]\), i.e., \([H_4SiO_4] \approx 10^2 \cdot [H_3SiO_5^-]\).

We therefore proceed by assuming that the de-protonation of the silicic acid \( H_4SiO_4 \) is negligible, meaning that the total dissolved silicon \( Si_T \approx [H_4SiO_4] \). Equation (16) assumes the activity coefficients are equal to 1, thus neglecting the interactions between solutes typical of high ionic strength. Expression (3.22) however captures the key dynamics of precipitation-dissolution processes [78]. The use of more complex expressions [53, 260, 167] would require a more detailed parameterization that is not available when large regions are considered.

Since \( C_T \) and \( A \), as defined, are conservative with respect to the equilibrium reactions, equations (3.15)-(3.21) can be further condensed by algebraic manipulation which eliminates the \( R'_i \)s and yields

\[ \frac{dC_T}{dt} = \frac{1}{nh} \left[ L \left( C_T^L - C_T \right) \right], \]  

(3.25)

\[ \frac{dA}{dt} = \frac{1}{nh} \left[ L \left( A^L - A \right) + hW([H^+], [Na^+], [Si_T]) \right], \]  

(3.26)

\[ \frac{d[Na^+]}{dt} = \frac{1}{nh} \left[ L \left( [Na^+]^L - [Na^+] \right) + hW([H^+], [Na^+], [Si_T]) \right], \]  

(3.27)
\[
\frac{dSi_T}{dt} = \frac{1}{nh} \left[ L (Si_T^L - Si_T) + 2hW([H^+], [Na^+], [Si_T]) \right]. \tag{3.28}
\]

Equations (3.10) and (3.25)-(3.28) form a nonlinear dynamical system that fully determines the weathering of albite in the weathering zone as forced by the \( C_T \) and its speciation transported by percolation. The system is constrained by the alkalinity equation (3.9), since \([H^+]\), which is necessary for the calculation of \( W \), is computed from \( A \) and \( C_T \). Due to the nonlinearity imposed by \( W \) and the alkalinity constraint (3.9), the variables \([Na^+], Si_T, \) and \( A \) are calculated implicitly. This new framework is compact and explicitly accounts for the transport of DIC, the speciation of \([H_2CO_3]\) and its effects on chemical weathering.

### 3.3 Steady State Solution

The system (3.10) and (3.25)-(3.28) is here analyzed under deterministic, steady-state conditions with a constant percolation rate \( L \). The dynamics towards steady state is illustrated in Appendix B. The analysis shows the effect of \( L \) and the chemical composition of the percolating water on the weathering reaction, while the remaining parameters (e.g., \([Na^+]^L \) and \( Si_T^L \)) are maintained constant. By setting the time derivatives to zero, the steady state solution can be obtained as,

\[
h^* = \left( \frac{L}{kQ} \right)^{\frac{1}{\beta}}, \tag{3.29}
\]

\[
C_T^* = C_T^L(A^L, L), \tag{3.30}
\]

\[
A^* = A^L + \frac{h^*}{L} W^*([H^+]^*, [Na^+]^*, [Si_T]^*), \tag{3.31}
\]
\[ [\text{Na}^+]^* = [\text{Na}^+]^L + \frac{h^*}{L} W^*([H^+]^*, [\text{Na}^+]^*, [\text{SiT}]^*), \] (3.32)

\[ \text{SiT}^* = \text{SiT}_T^* + 2 \frac{h^*}{L} W^*([H^+]^*, [\text{Na}^+]^*, [\text{SiT}]^*), \] (3.33)

where the asterisk denotes the steady-state. Stability analysis shows that there is a single steady state, which is a stable fixed point for any value of \( L \) (Appendix B). Equations (3.29) and (3.30) can be solved independently, whereas (3.31)-(3.33) are related by the weathering flux \( W \) and require equation (3.22) to be solved. Note that \( C_L^T \) depends on the parameters \( L \) and \( A_L^T \) and is obtained using the alkalinity constraint. In this section, we study the system (3.29)-(3.33) for \( \beta = 1 \), which corresponds to linear groundwater discharge. We then analyze the system for more realistic cases with \( \beta \neq 1 \) in section 3.5.

In the steady-state solution (Figure 3.3), the effects of hydrologic processes are two-fold, involving the percolation rate, \( L \), and the discharge coefficient, \( k_Q \). First, the percolation rate controls the weathering rate through its effect on \( C_T \) transported to the weathering zone and the ratio among its components, as assumed in equation (3.1) and expressed in equation (3.30). As a consequence, the weathering rate and the weathering products concentrations increase as a function of \( L \) (Figure 3.3). As \( L \) increases, more \( C_T \) is transported to the weathering zone, which lowers the \( pH \), the ratio \( \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{\alpha_1}{\alpha_0} \), and the ion activity product \( \Theta \). This effect moves the reaction farther from equilibrium. For large values of \( L \), the ratio \( \frac{\alpha_1}{\alpha_0} \) tends toward a constant value and, therefore, \( \Theta \) and \( W \) are no longer affected by further increases in \( L \). The second hydrologic control related to the discharge coefficient, \( k_Q \), is discussed in more detail in Section 3.4 on water transit times.

A critical implication of the linear approximation for the groundwater dynamics is that in steady state the percolation rate \( L \) controls weathering only through the transport of dissolved inorganic carbon (its components) and not through dilution of weathering products in the weathering zone. In fact, for \( \beta = 1 \), dilution is compensated by an increase in the
weathering zone depth, which exposes new mineral surface area to weathering. This results from the fact that the volumetric weathering rate is \( h \cdot W \) and that \( h \) increases linearly with \( L \). For the limiting case \( K(L) = 0 \) (i.e., \( P_{CO_2} = P_0 \) is constant), \( W \) and the weathering products are constant with \( L \). However, if the mineral surface area is assumed to be non uniform with depth, the exposed surface area does not increase proportionately to the weathering zone height \( h \), and a dilution effect of percolation arises. This represents a fundamental difference between our model and other conceptual models that characterize the role of hydrology on chemical weathering [17, 97, 166]. In these models, in which the transport of DIC and the increase of exposed mineral surface area with water storage are
not accounted for, the hydrologic flux only regulates water residence time and the solute turnover.

For a given value of alkalinity in the percolating water, the weathering rate switches to negative values below a certain value of \( L \) (Figure 3.3). Although this specific condition practically never appears for average field conditions, it is worth discussing the full behavior of the dynamical system as a function of \( L \). The point \( W = 0 \) represents the condition of no net dissolution, marking the limit between undersaturation and oversaturation. In mathematical terms, this happens when the ion activity product is equal to the equilibrium constant,

\[
\Theta = K_{eq},
\]  

(3.34)

meaning that the reaction is in detailed balance. For \( W = 0 \), equations (3.29)-(3.33) readily give \( A^* = A^L \), \([Na^+]^* = [Na^+]^L \) and \( Si^*_T = Si^L_T \), such that chemical equilibrium is maintained when percolation carries reactants and products of reaction (3.14) in a ratio equal to the equilibrium constant \( K_{eq} \). While \( Na^L \) and \( Si^L_T \) are fixed parameters that do not depend on the percolation rate, the ratio \( \frac{a_1}{a_0} \) decreases with respect to \( L \) (Figure 3.3). In particular, the value of \( L \) at which \( W \) crosses the axes, \( L^* \), corresponds to the value of the ratio \( \frac{a_1}{a_0} \) that satisfies (3.34). For instance, for given values of \( Na^L \) and \( Si^L_T \), \( L^* \) increases approximately linearly with respect to \( A^L \) (Figure 3.4) since lower \( \frac{a_1}{a_0} \) ratios are needed to satisfy (3.34).

For \( L < L^* \), the model predicts oversaturation, i.e., \( \Theta > K_{eq} \), and precipitation of albite, although this is unlikely under typical field conditions. In the model, oversaturation is reached because \([Na^+]^L \) and \( Si^L_T \) are kept constant, while the behavior of the model is explored for a wide range of percolation values. When the model is applied to a specific geographic area and experimental data are available, \([Na^+]^L \) and \( Si^L_T \) can be properly chosen to reproduce the correct field weathering rates.
Figure 3.4: Steady state percolation rate $L^*$ for which the system is in chemical equilibrium ($W = 0$) as a function of $A^*$ and for fixed value of $[Na^+]_L^*$; $[Na^+]_L^* = 1$ mol/m$^3$. Parameters as in Figure 3.3.

3.4 Role of Water Transit Time and Limiting Weathering Regimes

For chemical reactions in which reactants and products are advected by a fluid in and out of the control volume (where the reaction takes place), the fluid transit time, $\tau$, represents a measure of the time available for the system to reach equilibrium. Recall that the transit time is defined as the time that the fluid has spent inside the control volume at the time of exit. Thus $\tau$ also reflects the degree of dilution caused by the water flowing through. In fact, as flow rates increase, more water with a lower degree of saturation (e.g., $[Na^+]$ and $Si_T$ in percolating water) enters the control volume, causing the solution to dilute. In steady state conditions transit time can be computed in general as $\frac{V}{F}$, where $V$ is the total volume of water inside the control volume and $F$ the flux (e.g., [42]). As a result, the water transit time in the weathering zone is given by

$$\tau = \frac{h}{Q} = \frac{h}{L} = \frac{1}{kQ},$$

(3.35)
where the last equality is valid when $Q = kh$ (i.e., $\beta = 1$). Therefore, for systems in which the linear approximation holds, the water transit time in the weathering zone is linked to the specific output rate $k Q$, and does not depend on the percolation rate $L$ or the size $h$ of the weathering zone. Furthermore, this implies that such systems are well-mixed, meaning the water exits regardless of its age (i.e., residence time). The transit time $\tau_w$ for the weathering products in solution (time elapsed since their production), $Na^+$ and $Si_T$, 

Figure 3.5: Steady state solutions for $[Na^+]$, $Si_T$, and $W$ as a function of the transit time $\tau$ and given values of $L$. In steady state conditions, the transit time determines the rate at which farther from equilibrium water (from percolation) is mixed with the closer to equilibrium water in the weathering zone. Parameters as in Figure 3.3.
can be similarly computed as the ratio of the total mass inside the weathering zone, e.g., \( h \cdot [Na^+] \), and the output, e.g., \( Q \cdot [Na^+] \),

\[
\tau_w = \frac{h \cdot [Na^+]}{Q \cdot [Na^+]} = \frac{h}{Q} = \tau.
\]  

(3.36)

Equation (3.36) shows that the transit time of the weathering products in solution is equal to the transit time of the water. This is to be expected since the weathering zone is assumed to be well-mixed.

The effect of water transit time on the weathering rate is demonstrated in the steady-state solution (Figure 3.5). Equations (3.31)-(3.33) can be rearranged as

\[
\]  

(3.37)

\[
\]  

(3.38)

\[
Si_T^* = Si_T^L + 2\tau W^*([H^+]^*, [Na^+]^*, [Si_T]^*).
\]  

(3.39)

showing that the contribution of mineral dissolution to the alkalinity and weathering products concentrations is modulated by \( \tau \) and is independent of \( Q \) (and thus \( \beta \)). The following results in this section are thus not limited to the case of \( \beta = 1 \), although only when \( \beta = 1 \) is the transit time equal to the inverse of the specific output rate, \( \tau = 1/k_Q \). Equations (3.37)-(3.39) show that, for small transit times, dilutive effects prevail, weathering zone concentrations are low and near their values in the percolating water, thus maintaining the system far from equilibrium with high weathering rates. As \( \tau \) increases, the weathering zone charges with weathering products, bringing the weathering reaction closer to equilibrium. Following the original approach of [17], for \( \tau \to 0 \) the system is in a kinetically limited condition, since the weathering rate is mainly determined by the kinetic parameters,
i.e., the ion activity product is close to zero, \( \Theta \approx 0 \), and \( W \approx w_{\text{max}} \). We refer to the critical transit time below which \( W \) approaches \( w_{\text{max}} \) and becomes independent of \( \tau \), as \( \tau_k \). On the contrary, transport limited conditions are reached for large \( \tau \), for which \( \Theta \approx K_{eq} \) and \( W \approx 0 \). We therefore identify the critical transit time above which \( W \approx 0 \) as \( \tau_t \). Between these two limiting conditions (\( \tau_k < \tau < \tau_t \)), the transit time controls the reaction rate through \( \Theta \) and we refer to this as the transport-controlled regime. The different weathering regimes can be clearly seen in Figure 3.6, in which the annual flux \( Q_{Si_T} \) shows two plateaus in the transport and kinetically limited regions. The water transit time can thus be adopted as a parameter to determine boundaries (see Section 3.6) between the transport controlled and the two limited conditions.

The analysis above was conducted by varying the water transit time \( \tau \), while considering a single mineral with given kinetic parameters. Generally, the kinetic parameters could also be varied so that the flux \( Q_{Si_T} \) could be analyzed as function of the Damköhler number [154, 24], a dimensionless group given by the product of the water transit time and the kinetic constant expressed in (1/time). Here, however, because we do not vary the kinetic parameters, the system sensitivity to the transit time is equivalent to that to the Damköhler number.

3.5 Role of Nonlinearity in Groundwater Discharge

In section 3.3 we analyzed the model in the case of linear groundwater discharge by setting \( \beta = 1 \). This allowed us to obtain some important physical insights into the role of percolation rate and transit time. With that assumption, in fact, \( L \) and \( \tau \) have two distinct roles: the former enhances the reaction by transporting reactants, while the latter is an indicator of dilutive effects and is independent of \( L \). This assumption not only proves helpful from a theoretical point of view, but it also represents realistically the dynamics of some catchments (e.g., [199, 228]). In other cases, however, the groundwater does not always
Figure 3.6: Si fluxes as a function of \( \tau \) for different values of \( L \). Vertical dashed lines indicate the values of critical \( \tau \), \( \tau_{c,k} \) and \( \tau_{c,t} \). Light gray and light blue areas represent the kinetically-limited and transport-limited regions, respectively. Parameters: \([Na^+]_L = 1 \text{ mol/m}^3\), \( Si_T = 0.02 \text{ mol/m}^3\), \( k_Q = \frac{1}{2} \text{ 1/day}\), \( w_{\text{max}} = 2.7 \cdot 10^{-6} \text{ mol/m}^3/\text{day}\), \( K_{eq} = 1 \text{ mol}^3/\text{m}^9\).

behave as a simple linear reservoir and a value of \( \beta \neq 1 \) may be more representative (e.g., [50, 44]). We therefore analyze the role of nonlinearity in the groundwater-discharge model by studying the system (3.29)-(3.33) for different values of \( \beta \). We focus specifically on the solution as a function of \( L \), since it was shown in equations (3.37)-(3.39) that the steady state solution expressed as a function of \( \tau \) is independent of \( \beta \) (section 3.4).

From equation (3.10) for \( \beta \neq 1 \), the water table at steady state is not proportional to the percolation rate \( L \), i.e., \( h = (L/k_Q)^{1/\beta} \). As a consequence, an increase in the percolation rate is not completely compensated by the exposure of new mineral surface area to weathering (recall the volumetric weathering rate is \( h \cdot W \)), thus enhancing or weakening the dilution. For \( \beta \neq 1 \), the limiting case of \( K(L) = 0 \) does not return weathering rates independent of \( L \) (Figure 3.7(d)). When \( \beta > 1 \), dilution prevails over the exposure of new surface area, such that the concentrations of the weathering products decrease and the weathering rates increase (Figure 3.7). On the contrary, when \( \beta < 1 \), the exposure of new surface area prevails and the weathering zone concentrates.
By substituting (3.29) into (3.35),

$$\tau = \frac{h}{L} = \frac{L^{1/\beta - 1}}{k_Q^{1/\beta}}. \tag{3.40}$$

It is possible to see from (3.40) that for $\beta \neq 1$, the water transit time $\tau$ is not independent of the percolation rate $L$. For values of $\beta > 1$, as the percolation rate increases, the water transit time decreases, such that both transport of DIC (higher $L$ and $[H_2CO_3]/[HCO_3^-]$) and the increasing dilution (lower $\tau$) enhance the weathering reaction (Figure 3.7). On the other hand, for values of $\beta < 1$, the transport of DIC (higher $L$ and $H_2CO_3/[HCO_3^-]$) is compensated by weaker dilution (higher $\tau$), resulting in lower weathering rates (Figure 3.7). The difference between weathering rates, $W^*$, calculated for $\beta \neq 1$ and the ones calculated for $\beta = 1$, which is associated to different degrees of dilution, is shown in Figure 3.7(c). The role of $\beta$ with respect to dilution is particularly emphasized in case of constant $P_{CO_2}$ in the soils pores, $P_{CO_2} = P_0$ (Figure 3.7(d)).

### 3.6 Interpretation of Field Data

The theoretical framework presented above is now applied to measurements of silicate weathering fluxes for a series of basins with different annual precipitation and runoff values. We consider 14 watersheds with annual precipitation ranging from 500 to 4540 mm/yr and annual runoff from 220 to 3670 mm/yr. This application demonstrates the usefulness of the model to interpret the relationship between climate and long term $Si$ fluxes. The data we use are reported in Table 3.1 along with the source papers, in which more details can be found.

The runoff values reported in Table 3.1 correspond to stream discharge values. These streamflow values typically originate from the contribution of surface runoff and baseflow. While surface runoff has very short time scales (typically less than one day) and is produced by the oversaturation of soils, the baseflow represents the slow component deriving
Figure 3.7: Steady state solutions for $[Na^+]$ (a), $Si_T$ (b), and $W$ (c) as a function of the percolation rate $L$ and for given values of $\beta$. The Figure shows how the percolation flux also controls dilution when $\beta \neq 1$, while it only transports $DIC$ when $\beta = 1$. (d) Weathering rate as a function of $L$ for constant $CO_2$ pressure in the soil pores, i.e., $P_{CO_2} = P_0$. Parameters: $[Na^+]^L = 1$ mol/m$^3$, $Si_T^L = 0.01$ mol/m$^3$, $A^L = 0.2$ eq/m$^3$, $K_{eq} = 10^{-3}$ mol/m$^3$, $wmax = 2.7 \cdot 10^{-6}$ mol/m$^3$/day (chosen according to published data, e.g., [289, 290]).

from deep percolation and groundwater dynamics. Besides a portion of percolation that may bypass the weathering zone, the baseflow is the flux of interest in this application. In order to compare the data with our model and in the absence of detailed information, we determined the partitioning of streamflow into surface runoff and baseflow by means of a stochastic soil moisture model [147]. In particular, we used typical values of frequency of rainfall events, rooting depth, and soil properties, whereas mean rainfall depth and potential evapotranspiration were chosen to match the annual rainfall and streamflow values reported in Table 3.1. The analysis determined that for all catchments percolation (baseflow) contributes a great fraction of the streamflow, while the potential evapotranspirations reflect the low evapotranspiration expected for the cold climates of the considered areas.

With regard to the weathering fluxes $Q_{Si_T}$, many factors, such as biological activity, stoichiometry, topography, time variability (e.g., seasonality), and temperature may affect
the weathering reaction. However, the two fundamental parameters that along with climate control the weathering process over long timescales are the transit time and the supply of minerals from the breakdown of the bedrock [122, 223, 166, 74]. We focus on the former and study the weathering fluxes in Table 3.1 as a function of the percolation rate (climate) and the transit time. The weathering fluxes for the different sites are plotted as a function of $L$ in Figure 3.8.

In agreement with the data, the model predicts an increase of the $Si$ flux, $Q_{SiT}$, with respect to the percolation rate $L$. As $L$ increases, both the $Si$ concentration and the water flux $Q (= L$ at steady state) increase, contributing to higher $Q_{SiT}$ values. To identify the mechanisms controlling the weathering rate, we estimated for each watershed the water transit time and compared it to the two critical values, $\tau_k$ and $\tau_t$, introduced in Section 3.4. Recall that when $\tau < \tau_k$, the watershed is kinetically limited whereas for $\tau > \tau_t$ the watershed is transport limited. The intermediate condition, $\tau_k < \tau < \tau_t$, defines instead transport-controlled watersheds. Specifically, the value of $\tau$ for each watershed was obtained by finding the value of $kQ$, while the remaining parameters were kept fixed, for which the solution of the steady state system (3.29)-(3.33) resulted in a silicate flux (calculated as $Q_{SiT} = h \cdot S_{iT}$) that matched the value reported in Table 3.1. Based on the parameters adopted in Figure 3.8, we estimate $\tau_k \approx 100$ days and $\tau_t \approx 10^6$ days. The estimated $\tau$ values and their comparison with $\tau_k$ and $\tau_t$ are reported in Table 3.1. In particular, while most of the watersheds are transport-controlled, Sogndal 1 in Norway results to be kinetically limited, while Hanley in Canada and Barhalde in Germany result to be transport limited.

Note that the estimates of transit time do not depend on the functional form used for $Q$. As shown in section 3.4, the $\tau$ values are in fact computed, for given percolation rate and $Si$ flux, by solving equations (3.37)-(3.39), for which at steady state $Q(h)$ is not needed. On the other hand, since the actual mineralogy of the basins is not known exactly, kinetic and equilibrium constants (which were chosen for the single mineral albite) as well as
the stoichiometry of the reaction represent a source of uncertainty. Overall, Figure 3.8 suggests that the model presented here is suitable for interpreting the role of hydrologic factors such as the percolation rate and the water transit time on the weathering fluxes. This framework requires only parameters of clear interpretation that are becoming readily available in the literature and is amenable to large scale analysis under different geologic and climatic contexts. Lastly, we stress that the tools developed here allow predictions over long timescales, so that the interplay between chemical weathering, soil acidification and clay formation processes, and carbon cycle can be explored.

### 3.7 Conclusions

We developed a non-linear dynamical system with five state variables and one algebraic constraint to describe the main features of mineral dissolution in the weathering zone. The
Table 3.1: Annual rainfall, runoff, potential evapotranspiration, percolation rate, silicate discharge fluxes, and estimated water transit times for a series of watersheds on granitic parent material.

<table>
<thead>
<tr>
<th>Watershed</th>
<th>Rainfall(^1) (mm/yr)</th>
<th>Runoff(^1) (mm/yr)</th>
<th>Potential ET(^2) (mm/day)</th>
<th>Percolation Rate(^2) (mm/yr) (% of Runoff)</th>
<th>Silicate Flux(^1) (mol/km(^2)/yr))</th>
<th>Estimated (\tau) (days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sogndal 1, Norway [96]</td>
<td>984</td>
<td>875</td>
<td>0.3</td>
<td>814 (93 %)</td>
<td>13000</td>
<td>(\tau &lt; \tau_k)</td>
</tr>
<tr>
<td>Sogndal 2, Norway [96]</td>
<td>939</td>
<td>870</td>
<td>0.24</td>
<td>809 (93 %)</td>
<td>16600</td>
<td>(\tau \approx 100)</td>
</tr>
<tr>
<td>Emerald Lake, USA [293]</td>
<td>1850</td>
<td>1410</td>
<td>1.2</td>
<td>1297 (92 %)</td>
<td>39200</td>
<td>(\tau \approx 1900)</td>
</tr>
<tr>
<td>Indian River, USA [250]</td>
<td>3300</td>
<td>2824</td>
<td>1.3</td>
<td>2541 (90 %)</td>
<td>189600</td>
<td>(\tau \approx 18000)</td>
</tr>
<tr>
<td>Exp. Lake, Canada [2]</td>
<td>508</td>
<td>225</td>
<td>1</td>
<td>209 (93 %)</td>
<td>13300</td>
<td>(\tau \approx 90800)</td>
</tr>
<tr>
<td>Hanley A.B.C., Canada [87]</td>
<td>2146</td>
<td>1010</td>
<td>3.3</td>
<td>909 (90 %)</td>
<td>98900</td>
<td>(\tau &gt; \tau)</td>
</tr>
<tr>
<td>Hanley B.B.C., Canada [87]</td>
<td>2146</td>
<td>1240</td>
<td>2.5</td>
<td>1128 (91 %)</td>
<td>93000</td>
<td>(\tau &gt; \tau)</td>
</tr>
<tr>
<td>Hanley C.B.C., Canada [87]</td>
<td>2146</td>
<td>1040</td>
<td>3.2</td>
<td>936 (90 %)</td>
<td>72800</td>
<td>(\tau &gt; \tau)</td>
</tr>
<tr>
<td>Jamieson Cl.B.C., Canada [297]</td>
<td>4541</td>
<td>3668</td>
<td>2.4</td>
<td>3264 (89 %)</td>
<td>153400</td>
<td>(\tau \approx 5430)</td>
</tr>
<tr>
<td>Strengbach, France [212]</td>
<td>1153</td>
<td>1051</td>
<td>0.29</td>
<td>977 (93 %)</td>
<td>60800</td>
<td>(\tau \approx 16000)</td>
</tr>
<tr>
<td>Barhalde, Germany [2-9]</td>
<td>2000</td>
<td>1395</td>
<td>1</td>
<td>1284 (92 %)</td>
<td>120100</td>
<td>(\tau &gt; \tau)</td>
</tr>
<tr>
<td>Dargall, UK [86]</td>
<td>2961</td>
<td>2464</td>
<td>1.1</td>
<td>2242 (91 %)</td>
<td>148900</td>
<td>(\tau \approx 13200)</td>
</tr>
<tr>
<td>Green Burn, UK [86]</td>
<td>2707</td>
<td>2135</td>
<td>1.7</td>
<td>1943 (91 %)</td>
<td>153900</td>
<td>(\tau \approx 53800)</td>
</tr>
<tr>
<td>White Laggan, UK [86]</td>
<td>2822</td>
<td>2185</td>
<td>1.7</td>
<td>1988 (91 %)</td>
<td>100400</td>
<td>(\tau \approx 6600)</td>
</tr>
</tbody>
</table>

\(^1\)Data were reported in Table 1 of [288].

\(^2\)Data calculated by using a soil moisture dynamics model [147]. Parameters used: Root zone depth 30 cm, mean rainfall depth 2 cm, soil parameters for a loamy sand (see [147]). Frequency of rainfall events and potential evapotranspiration (ET) calibrated to match the ET values from [288] (i.e., ET=Rainfall-Runoff).
model links the percolation rate to the input of dissolved inorganic carbon to the weathering zone through production of CO$_2$ in the near surface root zone, its speciation and transport to the subsurface weathering sites. The system was analyzed under constant hydrologic forcing, representing an average percolation rate, to investigate the role of deep hydrologic fluxes and the associated water transit time on the weathering rate and approach to steady state.

The model was first studied by assuming that the groundwater is a linear system. Under this assumption, the role of hydrological processes on chemical weathering rates is two-fold. First, the percolation rate itself controls the weathering rate only by stimulating CO$_2$ production in the root zone and transporting the dissolved inorganic carbon components to the subsurface weathering zone. As the percolation rate increases, more DIC with higher $[H_2CO_3^*]/[HCO_3^-]$ ratio is transported to the weathering zone, so that $\Theta$ decreases and the reaction accelerates. Second, the dilutive effects commonly associated with the percolation rate were found to be regulated by the water transit time alone (i.e., the weathering zone discharge coefficient). When the hypothesis of linear system is relaxed, the transit time is dependent on the percolation rate, such that the latter also regulates dilutive effects.

The water transit time $\tau$ expresses the extent of dilutive effects and the turnover of the weathering products. For small transit times, the weathering zone is constantly diluted so that far from equilibrium conditions are maintained, i.e., high weathering rates, while for large $\tau$ the system approaches near-equilibrium conditions, i.e., low weathering rates. The model was then applied to a set of watersheds for which we estimated the water transit times and identified the limiting mechanisms to demonstrate its ability to identify limiting mechanisms of chemical weathering from climate and water chemistry data.

This work can be extended by considering inter-annual, seasonal, and storm event-scale variability in the percolation flux. Introducing temporal variability would provide a framework to investigate the role of time-varying climatic conditions as well as predict long-term weathering fluxes by means of upscaling techniques. Furthermore, the model
could be coupled to soil moisture and $P_{CO_2}$ dynamics in the root zone, such that the role of surface ecohydrological processes as an interface between the atmosphere and the critical zone that propagates high-frequency hydro-climatic fluctuations could be explored.
Chapter 4

The Formation of Clay-Enriched Horizons by Lessivage

Besides dissolved inorganic carbon, percolating water also transports clay particles from upper to deeper soil layers, affecting the soil texture. In almost every soil type, this translocation of soil particles, which is called ‘lessivage’, brings about the formation of clay-enriched horizons, with obvious consequences for the soil hydrology. With a combination of field measurements and a parsimonious modeling framework, in this chapter we analyze the dynamic formation of this horizons as a balance between geologic (erosion) and hydrologic processes (percolation). The chapter is adapted from Calabrese, Salvatore, Daniel D. Richter, and Amilcare Porporato, "The Formation of Clay-Enriched Horizons by Lessivage", Geophysical Research Letters 45.15 (2018): 7588-7595.

4.1 Introduction

Clay-sized minerals (<2 µm) accumulate in soils between 0.3- and 3-m depths across at least 25% of the Earths surface. Such subsoil clay layers exert profound effects on soil hydrology [296, 299, 300], soil wetness and water holding capacity [240], the fate of metals and organic contaminants [70, 72], soil fertility [34], the depth of plant rooting [183],
weathering and redox reactions [90], gas exchange with the aboveground atmosphere [134], and the complex phenomena of soil formation [155, 187, 214, 236]. The accumulation of clay in subsurface horizons is generally attributed to lessivage is generally attributed to clay lessivage [80, 296, 214], a process that consists of dispersion and translocation of clay and that over long timescales causes the formation of an upper-eluviated horizon and a deeper-illuviated horizon with higher clay content. Clay transport occurs mostly vertically during percolation events but can be more complex depending on water flow dynamics.

The extent to which clay lessivage is responsible for the formation of argillic horizons is still subject of debate [201], and other concurring processes have been suggested as an alternative explanation. These include geologic factors such as inherited layering in sediments and erosion/deposition, as well as pedogenic processes, such as in-situ weathering of primary minerals [26, 209] and bioturbation [202].

The uncertainty associated with the role of various processes that form argillic horizons is principally due to very long timescales involved, which prevent experimental verification of the proposed theories [59], except for specific, well-constrained experiments [108]. Consequently, a combination of field and laboratory observations and modeling studies is required to fully test hypotheses and shed light on the ongoing discussion. Thus far, however, analyses are limited to detailed numerical models on colloidal transport [131, 142, 141], which are mostly suitable for site-specific and short-term analysis, and to soil formation models [235, 269], in which translocation rates are imposed with no reference to the hydrologic regime. In this work, we develop a parsimonious model that is amenable to long-term analysis of translocation of clay-sized particles and that can be used to interpret field experiments and to extract fundamental information on the dynamic formation of clay-enriched horizons.
4.2 Long-Term, Probabilistic Interpretation of Lessivage and Dynamics of Clay Particles

When describing soil formation, it is key that models are able to span a wide range of timescales [35]. This often requires a new way to interpret such processes, as in the case of lessivage. Here, we interpret lessivage stochastically, as a series of instantaneous intermittent events. Clay particles are assumed to be subject to simple dynamics in which they are intermittently transported downward by percolating water, as they approach the soil surface at a speed dictated by the lowering of the soil surface (i.e., erosion rate) – the description of the full model can be found in Methods. This idealized picture of lessivage is justified by the fact that these events occur over timescales much shorter than erosion processes. When focusing on geological timescales, lessivage events appear as "instantaneous’ mobilization events of clay particles, whose trajectories undergo sudden downward jumps (see Figure 4.2).

Our results are compared and tested with field measurements of clay content collected at the Calhoun Critical Zone observatory (CZO), a research area that is subject of intense studies to explore legacy effects of land degradation and soil formation processes, among which the formation of Bt horizons (detail on the research conducted at the observatory is available at "http://criticalzone.org/calhoun/research/"). The area is characterized by acidic and highly weathered soils, ultisols, in the Kanhapluldult Great Group with well-defined clay horizons typically from 0.5 to 2 m deep, and an erosion rate, estimated for the whole Southern Piedmont, of the order of 10 meter per $10^6$ years [3]. These characteristics make the soils at Calhoun suitable for testing lessivage as the main process forming argillic horizons. Figure 1 shows the characteristic clay films found in clay profiles at Calhoun, indicating clay mobilization by lessivage. With regard to clay content profiles, soil samples at different depths were collected across the research areas and the clay content was measured.
Figure 4.1: The photo shows accumulation of clay in the form of clay films, indicating mobilization induced by lessivage. The marks CF and FR denote clay films and fine roots, respectively.

by the pipette method that quantifies sedimentation following dispersion of individual soil separates [48].
Figure 4.2: Left panel: Time evolution of clay-particle positions as they enter the control volume at $z = z_S = 5$ m after being produced by weathering at lower layers and begin to fluctuate according to equation (4.1). Right panel: Clay content profile sampled at the Calhoun CZO (red dots) along with analytical profile (black line), equation (4.4), and clay mean residence time (gray line), equation (4.13). More details are found in Figure 4.5. The jump frequency decreases exponentially with depth as $\lambda(z) = \lambda_{\text{max}} e^{-\beta z}$ with $\lambda_{\text{max}} = 1.1 \cdot 10^{-4}$ yr$^{-1}$ and $\beta = 2.5$ m$^{-1}$. Mean size of the jumps $\gamma^{-1} = 0.5$ m$^{-1}$.

4.3 From clay particles mobility to clay profiles

The time evolution of the vertical position of clay particles along the soil profile can be expressed as

$$\frac{dz}{dt} = -E + F(z),$$  \hspace{1cm} (4.1)

where $z$ is the depth of each clay particle from the soil surface, $E$ is the erosion rate, and $F$ represents the instantaneous lessivage events. Lessivage $F$ is modeled as a marked Poisson process with frequency $\lambda$ (year$^{-1}$), while the size of the jumps is an exponentially distributed random variable with mean $\alpha = \gamma^1$ (m). While the frequency $\lambda$ is related to the probability of a single clay particle of being mobilized, the mean jump $\gamma^1$ given the long timescales considered represents an effective jump that includes clusters of rain events, for example, over a growing season. An ensemble of clay particle trajectories described by equation (4.1) is shown in the left panel of Figure 4.2. After being formed at some depth, clay particles appear to recirculate in the subsurface with a mobilization frequency $10^{-4}$ years$^{-1}$ and average downward jumps of 0.5 m. The evolution of each trajectory ends when the clay
particle reaches the surface and is removed by erosion. As a result of these dynamics, clay particles spend most of their time at a depth of approximately 1 m, where measurements of clay content along the soil depth exhibit a sharp peak (Figure 4.2).

The distribution of clay particles with depth can be considered as the probability of finding a particle at a given depth. We introduce the probability density function (PDF) \( p_Z(z,t) \), such that \( p_Z(z,t)dz \) is the probability to find the particle within depth \( z \) and \( z + dz \); its steady state form can be related analytically to the erosion rate and the lessivage characteristics, such as the frequency \( \lambda \) (year\(^{-1}\)) of events and the mean depth of the jumps \( \gamma^{-1} \) (m) traveled by particles during a lessivage event. According to the dynamics described above, \( p_Z(z,t) \) satisfies the following balance equation:

\[
\frac{\partial p_Z(z,t)}{\partial t} = - \frac{\partial J_p(z,t)}{\partial z},
\]

in which the flux \( J_p \) of probability is given by

\[
J_p(z,t) = -Ep_z(z,t) + \int_0^z \lambda(x)e^{-\gamma(z-x)}p_z(x,t)dx.
\]

where the first contribution to the flux represents the advection due to the erosion rate, and integral term is the contribution due to lessivage. Note that through the addition of a source term function of \( z \) in (4.2), the model may also account for possible neoformation of clays and eolian inputs, but since our focus is on the lessivage process, we assume that all clay formed in deeper soil layers. Equation (4.2) is thus solved in steady state conditions by imposing a constant flux of clay throughout the profile that enters from below and an absorbing boundary at \( z = 0 \) representing the loss by erosion. The stationary clay profile (see details in Methods) reads

\[
p_Z(z) = -Ce^{-\gamma z + \int_0^z \lambda(x)dx} \left( 1 + \gamma \int_0^z e^{-\gamma(x-y)} \int_0^y \lambda(y)dy dx \right).
\]
Figure 4.3: (a) Clay content profiles $p_Z$, (b) depth of the B horizon, and (c) mean time to erosion for different values of $\gamma$ m$^{-1}$ and $\lambda_{max}$ yr$^{-1}$. Parameters $E = 10^{-5}$ m/yr and $\beta = 2.5$ m$^{-1}$.

In the right panel of Figure 4.2, the theoretical probability distribution of $z$, equation (4.4), is compared with observations for a soil clay profile (R1H1) obtained from a 70 m well at the Calhoun CZO. In Figure 4.3(a), various profiles computed for different parameters values show that for higher intensity of lessivage (i.e., higher $\lambda$ and lower $\gamma$), the PDF (4.4) shifts toward higher values of $z$, since the recirculation pushes clay particles to deeper layers, while for weaker lessivage, clay particles spend more time near the soil surface, and the mode of $p_Z(z)$ shifts toward lower values of $z$. The model also predicts the depth of the Bt horizon (Figure 4.3b), namely, the depth of maximum clay content, which increases for lower $\gamma$ and higher $\lambda_{max}$, as well as the residence time at different depths as a function of lessivage characteristics and erosion rates and the mean time for a clay particle to reach the surface and be eroded away (Figure 4.3c). Such mean time to erosion provides a synthetic description of the path undergone by clay particles on their way to the surface. In the absence of lessivage, particles stand in their position until they are eroded, so that their time to erosion $T_e$ is given by the ratio of the distance $L$ between the surface and point where they were formed, and speed $E$ at which the soil surface lowers (erosion rate), $T_e = LE$.

With lessivage, the mean time to erosion is greater than $LE$ and grows as the frequency and mean size of lessivage jumps is increased (Figure 4.3c). For the clay content profile in Figure 4.2, assuming particles are formed at $z = zS = 5$ m, the mean time to erosion is $1.710^6$ years, compared to $LE = 5 \cdot 10^5$ years without lessivage. The previous considerations show that lessivage, by mobilizing clay particles in the subsurface and transporting them rapidly
(short timescale) to deeper soil layers, is able to contrast the slow advancement toward the surface due to erosion. Such a mechanism increases the probability of finding clay particles in the region of the recirculation so that clay distribution with depth will have a Bt horizon.

4.4 Interpreting the Clay-Enriched Argillic Horizons at the Calhoun CZO

To support the theoretical analysis above, we applied the model to soil profiles collected in four locations at the Calhoun CZO (see map in Figure 4.4). The profiles were normalized to have area equal to 1 for comparison with the analytical PDFs (Figure 4.5) computed from equation (4.4). Recall that these soils are highly weathered, and hence, neoformation of clay is excluded as origin of the clay-enriched horizon. On the other hand, the model
reproduces the clay content profiles very well, further suggesting that clay mobilization due to lessivage may well be the cause of clay accumulation. Based on these considerations, model-data comparison provides important estimates of lessivage characteristics, namely, frequency and mean jump. For the present study, we assumed that the frequency of clay mobilization has a maximum at the soil surface, $\lambda_{\text{max}}$, and decreases exponentially with depth at rate $\beta$, although as $\beta \rightarrow 0$ a uniform frequency with depth is recovered. In all four profiles, $\lambda_{\text{max}}$ and $\gamma^{-1}$ are of the order of $10^{-4}$ year$^{-1}$ and $10^{-1}$ m, respectively, meaning that each clay particle is mobilized on average once every 10,000 years and is transported downward, by percolating water, by 10 to 100 cm on average (see Table 4.1).

We also estimated the mean residence time $T$ of the clay particles as a function of depth (equation (4.13) in Methods below), see dashed gray lines in Figure 4.5, and computed the mean time to erosion as the value of the residence time $T$ at the surface. In the absence of lessivage, the mean time to erosion would be of the order of $T(z = 0)10^5$ years given $E = 10^5$ m/year. On the contrary, the recirculation induced by lessivage increases the mean times to erosion of an order of magnitude, reaching values of $10^6$ years (Figure 4.5).

The four soil profiles contain an average mass of clay in the top 2 m, $M_{2m}$, of 490 kg/m$^2$ and have an average frequency of lessivage, $\lambda_{2m}$, of $1.8 \cdot 10^{-5}$ year$^{-1}$. The average flux of clay transported by lessivage per square meter is thus $M_{2m} \cdot \lambda_{2m} = 9$ g/(m$^2$ year). Considering that the frequency of the percolation events $\lambda_p$ is estimated to be 0.044 day$^{-1}$ ($=15.7$ year$^{-1}$), the average mass of clay mobilized by each percolation event can be estimated as $M_p = M_{2m} \lambda_{2m} \lambda_p = 0.6$ g/m$^2$. Estimates for each clay profile are summarized in Table 4.1.

### 4.5 Classification of lessivage regimes

We used dimensional analysis and the $\Pi$ theorem (see Methods below) to extract the dimension- less groups of variables governing the dynamics of clay lessivage, namely,
Figure 4.5: Soil clay content with depth (red dots) along with analytical profiles from equation (4.4) (black lines) and clay residence time (gray lines) from equation (4.13) for the soil pits R2H1 (a), R1H1 (b), R7H1 (c), and R7H2 (d). Information and location of data collection are available at "http://criticalzone.org/calhoun/research/". Parameters are $\gamma^{-1} = 0.33 \text{ m}^{-1}$ and $\lambda_{\text{max}} = 1 \cdot 10^{-4} \text{ yr}^{-1}$ in (a), $\gamma^{-1} = 0.5 \text{ m}^{-1}$ and $\lambda_{\text{max}} = 3 \cdot 10^{-7} \text{ in} (b), \gamma^{-1} = 0.25 \text{ m}^{-1}$ and $\lambda_{\text{max}} = 7.3 \cdot 10^{-5} \text{ yr}^{-1}$ in (c), and $\gamma^{-1} = 0.83 \text{ m}^{-1}$ and $\lambda_{\text{max}} = 8.4 \cdot 10^{-5} \text{ yr}^{-1}$ in (d). For all profiles $E = 10^{-5} \text{ m/yr}$ and $\beta = 2.5 \text{ m}^{-1}$. Each distribution was computed between the soil surface and the depth of the deepest measurement, regardless of the depth $z_S$ at which the saprolite begins.

Table 4.1: Calhoun hydrologic and lessivage characteristics

<table>
<thead>
<tr>
<th>Dryness Index</th>
<th>0.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percolation frequency (d$^{-1}$)</td>
<td>0.023</td>
</tr>
<tr>
<td>Profile</td>
<td>$\gamma^{-1}$ (m)</td>
</tr>
<tr>
<td>R1H1</td>
<td>0.5</td>
</tr>
<tr>
<td>R7H1</td>
<td>0.25</td>
</tr>
<tr>
<td>R7H2</td>
<td>0.83</td>
</tr>
<tr>
<td>R2H1</td>
<td>0.33</td>
</tr>
</tbody>
</table>

1. Dryness Index computed from rainfall data available at "http://criticalzone.org/calhoun/data/datasets/" and a potential evapotranspiration of 1 m/yr.
2. Mass of clay calculated used a soil density of 1.5 g/cm$^3$. 
\[ \Pi_1 \lambda_{\text{max}} \gamma^{-1} E \quad \text{and} \quad \Pi_2 = \beta / \gamma, \]

where \( \lambda \) is the frequency of events at the surface, \( \gamma^{-1} \) the mean jump, \( E \) the erosion rate, and \( \beta \) the rate at which the frequency \( \lambda \) decays with depth. The number \( \Pi_1 \) (lessivage intensity) expresses the intensity of lessivage with respect to the erosion rate, and it thus is expected to approach 0 for soils characterized by immobile clays or negligible percolation. In the number \( \Pi_2 \) (lessivage penetration), the decay rate \( \beta \) is compared to the mean jump \( \gamma^{-1} \). For high \( \Pi_2 \), clay is mostly mobilized at the surface and is transported to considerably deeper locations. For low \( \Pi_2 \), also clay from deeper layers is mobilized, but it undergoes smaller translocation jumps.

The shape of the PDF of the dimensionless position \( \tilde{z} = z \cdot \gamma, \tilde{p}_{\tilde{z}}(\tilde{z}) \) allows us to classify different lessivage regimes (see Figure 4.6), depending on the position of the mode of \( \tilde{p}_{\tilde{z}} \), \( \tilde{z}_{\text{max}} \), with respect to two boundaries given by \( \tilde{z} = \tilde{z}_O \) (e.g., bottom of O horizon) and \( \tilde{z} = \tilde{z}_s \) (e.g., top of the saprolite). For \( \tilde{z}_{\text{max}} > \tilde{z}_s \), the eluviated regime, lessivage is very intense, and clay particles are frequently transported to deeper layers leaving the upper layers low in clay content. On the other hand, for \( \tilde{z}_{\text{max}} < \tilde{z}_O \), lessivage does not make up for the erosion rate. The few translocation events are weak and only slightly perturb the trajectories of the clay particles causing some accumulation near the surface. We refer to this regime as static. The intermediate condition \( \tilde{z}_O < \tilde{z}_{\text{max}} < \tilde{z}_s \), which we refer to as the illuviated regime, is characterized by a balance between erosion rate and lessivage that causes the formation of a clay horizon, which sharpens for higher \( \Pi_1 \) and \( \Pi_2 \). In both the static and the illuviated regimes, as \( \Pi_1 \to 0 \) lessivage becomes negligible compared to erosion, clay particles proceed undisturbed toward the surface, and the accumulation disappears leaving a uniform clay content profile (equation (4.22) in Methods).

Returning to the analysis of clay profiles at the Calhoun CZO, the values of \( \lambda_{\text{max}} \) and \( \gamma \) estimated for each sampled profile, while maintaining the values of the erosion rate (calculated in [3]) and \( \beta \) (assumed) constant, allow us to calculate the corresponding values of \( \Pi_1 \) and \( \Pi_2 \). As shown in Figure 4.6, the number \( \Pi_1 \) ranges from 3 to 10, while the values
of $\Pi_2$ are between 0.5 and 2, such that all of the four soil profiles sampled at Calhoun fall within the illuviated regime (see Figure 4.6).

### 4.6 Summary and outlook

As extensive data sets on soil hydrologic properties are becoming available, tools for their interpretation are expected to play an important role, especially to extrapolate information for geographical areas not covered by such observations. Within this context, the present framework may help interpret the presence of clay horizons within the traditional soil classification scheme via the lessivage intensity $\Pi_1$ and penetration $\Pi_2$ dimensionless groups (Figure 4.6), within the assumption that lessivage and erosion remain the main processes. For example, the fact that the Ultisols considered in this work are located at the center of the diagram in Figure 4.6 may be used as a reference to compare other soil types. Thus, Alfisols and Inceptisols (in case of well-defined Bt horizons) fall within the illuviated regime. Their higher cation levels compared to Ultisols suggest less intense leaching and hence lower $\Pi_1$ (Figure 4.6). Oxisols and Vertisols are soil groups with no Bt horizons [27]: The former are highly leached soils and are often found in stable cratons (high $\Pi_1$) but are variable in clay content and low in clay mobility (low $\Pi_2$). As such, they fall within the eluviated regime. Vertisols, on the contrary, have high expansible clay content in superficial layers, whose shrinking and swelling often prevents the Bt horizon from forming. Because of moderate to negligible percolation rates, Vertisols will tend to fall in the static regime with low $\Pi_1$ and high $\Pi_2$. Similarly, Mollisols may exhibit climatic-limited Bt horizons and can be located alongside Vertisols in the static regime.

This quantitative linkage to soil types is useful to inform predictions on the evolution of soils under shifts in climatic and environmental conditions [217, 164, 40]. A paradigmatic example is represented by Argids. These soils are a subgroup of Aridisols which have a Bt horizon and hence fall within the illuviated regime. However, these horizons formed in
past, more humid climates (paleoclimates) that then evolved into arid climates. The new conditions in which Argids are found (e.g., low percolation) are not typical of the illuviated regime and are in fact likely to shift these soils to the static regime and ultimately toward the $\Pi_2$ axis. This evolution is illustrated by means of the arrow in the top right part of Figure 4.6. Similar dynamics occurred to some Mollisols with Bt horizons that formed in past climatic conditions. Argids (and Mollisols) are good examples that demonstrate how most soils can be polygenetic [218]. This framework can easily be extended to include pedoturbation and bioturbation as a further mixing term; we hope that these results will spur more work in this direction and help shed light on the ongoing study of clay horizon formation.
4.7 Methods

4.7.1 Clay particle dynamics

The equation governing the time evolution of the position of a clay particle is given by a balance of erosion rate and lessivage,

\[
\frac{dz}{dt} = -E + F(z),
\] (4.5)

where the position \( z \) (m) is the depth from the soil surface, \( E \) (m/yr) is the erosion rate, and \( F \) (m/yr) is the term accounting for the translocation due to lessivage. Compared to the timescale of erosion, of the order of \( 10^5-10^6 \) years (e.g., [3]), the timescale of a lessivage (linked to deep and intense percolation events) event is much shorter, ranging from hours to days. Therefore, in describing the dynamics of lessivage at a long timescale (e.g., yearly), clay lessivage can be safely considered as a sequence of instantaneous translocation events in the form of jumps, occurring when percolation mobilizes and transports the clay particles downwards. From a mathematical point of view, \( F \) can be interpreted stochastically as a marked Poisson process ([61]) with frequency of translocation events \( \lambda \), which for generality we consider to be a function of \( z \), i.e., \( \lambda = \lambda(z) \) (in the analysis that follows we consider \( \lambda \) to decay exponentially with depth, \( \lambda(z) = \lambda_{\text{max}}e^{-\beta z} \), in order to account for higher frequency of jumps in the upper layers than the deeper ones). The depth traveled by the clay particle during a lessivage event (jump) is here assumed to be an exponentially distributed random variable with mean \( \alpha = \gamma^{-1} \).

4.7.2 Clay content profile

Equation (4.5) allows us to calculate the trajectories for single clay particles. To understand the formation of the soil clay profile, it is important to consider the ensemble of trajectories, that is the probability to find a clay particle at a given depth. This picture is achieved by
introducing the probability density function \( p_Z(z; t) \), such that \( p_Z(z; t)dz \) represents the probability to find the particle between \( z \) and \( z + dz \). The conservation equation for the probability density \( p_Z(z; t) \) can be expressed as [61, 230, 221]

\[
\frac{\partial p_Z(z; t)}{\partial t} = -\frac{\partial J_p(z; t)}{\partial z},
\]  

(4.6)

where \( J_p \) is the flux of probability (or probability current), given by

\[
J_p(z, t) = -E_p(z; t) + \int_0^z \lambda(x)e^{-\gamma(z-x)}p_z(x; t)dx.
\]  

(4.7)

The first term in (4.7) represents the flux of probability due to the erosion rate, whereas the integral in the second one arises from the stochastic lessivage jumps. Equation (4.6) allows us to study the longterm dynamics of the soil clay profile, in which the transport of clay particles is dictated by the erosion rate and the intermittent random lessivage. In the limit \( F \to 0 \) (e.g., \( \lambda \to 0 \)) equation (4.6) reduces to an advection equation in which clay moves undisturbed towards the surface without changing the shape of its profile.

Due to the presence of the stochastic term \( F \), equation (4.1) does not reach steady state conditions, i.e., \( \frac{dz}{dt} \neq 0 \), and clay particles are continuously subject to recirculation as dictated by equation (4.5). On the other hand, for sufficiently large times, when the initial condition has been forgotten, the system reaches conditions of statistical stationarity. Note that statistical stationarity does not imply that the position \( z \) is constant, but that its statistical properties, such as moments and correlation, are constant. Under these conditions, the probability density function \( p_Z(z; t) \) remains constant in time, i.e., \( p_Z(z; t) \to p_Z(z) \), such that equation (4.6) reduces to

\[
\frac{\partial J_p(z)}{\partial z} = 0,
\]  

(4.8)
which has solution $J_p = J_0$. As a result, the stationary pdf $p_Z(z)$ is found by solving

$$-Ep_Z(z) + \int_0^z \lambda(x)e^{-\gamma(z-x)}p_Z(x)dx = J_0,$$

which expresses the balance between the fluxes of probability due to the erosion rate and lessivage. When $J_0 = 0$, the fluxes are in balance (detailed balance) and the system is in equilibrium conditions. Clay particles fluctuate according to (4.5) but there is neither production of new clay by weathering nor erosion at the surface. On the contrary, for $J_0 \neq 0$ either erosion rate or lessivage prevails, the system is in nonequilibrium steady state and a constant flux of particles through the system is maintained. Typical of field conditions is the nonequilibrium, in which particles are formed in deeper soil layers and leave the system through erosion at the surface. In such a case the solution to equation (4.9) reads

$$p_Z(z) = -Ce^{-\gamma z + \int_0^z \lambda(x)dx} \left( 1 + \gamma \int_0^z e^{\gamma x - \int_0^x \lambda(y)dy} dx \right),$$

where by imposing the normalization condition $\int_0^{z_S} p_Z(z)dz = 1$, $C = J_0/E$. Equation (4.10) can be also expressed in terms of mass/depth by multiplying it by the total mass of clay between 0 and $z_S$. As can be seen in Figure 4.3a, for higher intensity of lessivage (i.e., higher $\lambda$ and lower $\gamma$), the probability density function (4.10) shifts towards higher values of $z$, since the recirculation makes the clay particle occupy deeper locations more frequently. On the other hand, for weaker lessivage the clay particle spends more time near the soil surface and $p_Z$ shifts towards lower $z$ values.

### 4.7.3 Depth of the Bt-horizon, clay residence time and time to erosion

From equations (4.1) and (4.4), it is possible to derive various characteristics of the clay dynamics and the resulting profile. Here we focus on the depth of the Bt horizon, the mean velocity of the clay particles, and the time to erosion. With regard to the B horizon, we
identify its depth, $z_B$, as the mode of the clay profile, that is the value of $z$ that satisfies

$$\frac{dp_Z(z)}{dz} = 0. \quad (4.11)$$

As the intensity of lessivage increases (lower $\gamma$ and higher $\lambda_{max}$) compared to the erosion rate $E$ and the decay rate of the jump frequency $\beta$, the depth of the Bt horizon increases (Figure 4.3b).

From the fact that the probability current is also defined as $J_p = v \cdot p$ [99], the mean velocity of a clay particle at a given position $z$ can be computed by averaging equation (4.1),

$$v(z) = \langle \frac{dz}{dt} \rangle = \frac{J_p}{p_Z(z)} = -E + \frac{1}{p_Z(z)} \int_0^z \lambda(u)e^{-\gamma(z-u)}p_Z(u)du. \quad (4.12)$$

The velocity (4.12) can also be interpreted as an average over all clay particles at position $z$. In the deeper soil layers, in which the frequency of the jumps is negligible, i.e., low $\lambda$, the mean velocity tends to the erosion rate, whereas at shallow depths, the contribution from the jumps can significantly reduce the mean velocity.

The average time a clay particle takes to reach position $z$ from position $z_S$, namely the mean residence time, can be obtained from the mean velocity as

$$T(z) = \int_{z_S}^{z} \frac{dz'}{v} = \frac{1}{J_0} \int_{z_S}^{z} p_Zdz' = \frac{P_Z(z) - 1}{J_0}, \quad (4.13)$$

where we used the fact that $v = J_0/p_Z$ and that the cumulative density function $P(z)$ is equal to 1 at $z_S$. Due to the stochasticity of lessivage events, the time it takes every clay particle starting at $z = z_s$ to reach the surface and be eroded, called the time to erosion, is also a random variable (corresponding to the first passage time of the threshold $z = 0$). The mean time to erosion $T_e$ is then given by the residence time calculated at the soil surface, $T_e = T(z_f = 0)$, (Figure 4.3c).
4.7.4 Dimensional Analysis

According to the Buckingham π theorem, the relationship between \(n\) physical quantities (here \(z, E, \gamma, \lambda_{\text{max}}, \text{and } \beta\)) can be expressed in terms of \(n - m\) dimensionless parameters, where \(m\) is the number of base quantities (here length and time). By expressing the position of the clay particle \(z\) as a general function of the remaining dimensional parameters [7],

\[
z = f_1(E, \lambda_{\text{max}}, \beta, \gamma),
\]

(4.14)

and analogously the clay profile \(p_Z\)

\[
p_Z = f_2(z; E, \lambda_{\text{max}}, \beta, \gamma).
\]

(4.15)

By selecting \(m\) (here 2) dimensionally independent parameters, such as \(\lambda_{\text{max}}\) and \(\gamma\), the position \(z\), the erosion rate \(E\) and the decay rate \(\beta\) can be non-dimensionalized as

\[
\tilde{z} = z \cdot \gamma,
\]

(4.16)

\[
\Pi_1 = \frac{\lambda_{\text{max}} \gamma^{-1}}{E},
\]

(4.17)

\[
\Pi_2 = \frac{\beta}{\gamma}.
\]

(4.18)

Following the Buckingham π theorem, equations (4.14) and (4.15) can be rearranged as

\[
\tilde{z} = f'_1(\Pi_1, \Pi_2),
\]

(4.19)

and

\[
\tilde{p}_Z = f'_2(\tilde{z}; \Pi_1, \Pi_2),
\]

(4.20)

in which the dimensionless position \(\tilde{z}\) and clay profile \(\tilde{p}_Z\) are expressed as a function of the two governing parameters \(\Pi_1\) and \(\Pi_2\).
From (4.4), the relationship (4.20) can be found explicitly by substituting (4.16)-(4.18),

\[
\tilde{p}(\tilde{z}) = -\tilde{C}e^{-\tilde{z} + \frac{n_1}{n_2}(1-e^{-n_2\tilde{z}})} \left( 1 + \int_0^{\tilde{z}} e^{\tilde{z} - \frac{n_1}{n_2}(1-e^{-n_2\tilde{z}})} d\tilde{z} \right),
\]

(4.21)

where \( \tilde{C} = C/\gamma \). In the limit \( \Pi_2 \to 0 \), expression (4.21) reduces to,

\[
\tilde{p}(\tilde{z}) = -\tilde{C}' \left( \Pi_1 e^{(\Pi_1 - 1)\tilde{z}} - 1 \right) \quad \Pi_1 \neq 1,
\]

(4.22)

while for \( \Pi_1 \to 0 \), (4.21) becomes an uniform distribution between \( \tilde{z} = 0 \) and \( \tilde{z} = \tilde{z}_S \). The classification of lessivage regimes depending on the shape of (4.21) is plotted in Figure 4.6.
Chapter 5

On the Probabilistic Structure of Water Age

Being the fundamental variable expressing the time available to a reaction to reach equilibrium, the water age or residence time can be used as a ‘shuttle’ to move biogeochemical reactions from small to larger spatial scales, e.g., the watershed. Age distribution theory is a spatially integrated approach that aims at quantifying the amount of substance, such as water or a chemical species, having a given age or residence time. While it does not explicitly consider space, the age distribution still carries the Lagrangian information necessary to determine the advancement of a chemical reaction as the substance is in its way to the outlet of the watershed. In this first contribution to the theory, the framework necessitated to be extended and adapted to the stochastic and intermittent nature of the processes characterizing hydrologic systems. The chapter is adapted from Porporato, Amilcare, and Salvatore Calabrese, "On the probabilistic structure of water age", Water Resources Research 51.5 (2015): 3588-3600.
5.1 Introduction

The description of the ages of a certain quantity (such as water, chemical compounds or individuals of a population) is fundamental in many fields. These include the characterization of hydrologic response of watersheds [178], groundwater [63, 103] and other geophysical systems [84, 107, 71], the performance of chemical reactors [191, 190], the structure of populations [144, 188, 105] and the safety of manmade systems [60]. Owing to this wide interest, the literature on the subject is vast, and the previous references can only be considered as a starting point for more in-depth studies. In the field of watershed hydrology, this topic has witnessed a renewed interest in the recent years, with several works dealing with both theoretical and experimental aspects of age distribution of water in soils and watersheds (see e.g., the recent debate article by [176] and references therein).

The first goal of this paper is to point to the existence of some well-known literature in population dynamics, fluid mechanics and stochastic processes, in particular to the McKendrick-von Foerster (MKVF) equation [182, 275, 144, 188], which is not commonly referenced in the hydrologic literature (indeed this was done only in one reference [105]). It thus seems to be useful to briefly review these theories and place them under a common framework so that these results can be easily used. In particular, the link between the MKVF equation and its spatially explicit version, first proposed by [103] (see also [63, 105, 13]), is important to emphasize the internal source of age variability introduced by spatial integration over a finite control volume.

The second goal is to address the role of external (random) hydrologic variability on the resulting age distributions. In fact, whenever hydrologic fluxes are treated stochastically on account of their unpredictable variability, the age distributions too become random functions and must be treated probabilistically. Thus, while the solution of the MKVF equation still offers the appropriate description of single realizations of such distributions (being suitable for any time varying conditions), their complete characterization requires considering the full ensemble of realizations of the underlying stochastic forcing. This gives rise
to a probabilistic description of age distributions, which allows one to quantify their variability among realizations, thereby providing a starting point to quantify the uncertainty in their experimental determination. As far as we know this second aspect has not yet been explicitly addressed in the literature.

This Chapter is organized as follows. In Sec. 5.2 we review the MKVF equation and connect it to the recent contributions in the hydrological literature. Sec. 5.3 illustrates the solutions of the MKVF equation for a time varying system with step-change input as well as a steady state system with age-dependent output. Sec. 5.4 discusses the probabilistic aspect of age distributions, when inputs are modeled as stochastic processes, and Sec. 5.5 presents an application to a linear stochastic storage system for which the probability density function (PDF) of the mean age is discussed. The conclusions briefly recapitulate the content of the paper and outline further open problems, in particular the role of nonlinearities and variability at different time scales.

### 5.2 Age Distribution Theory

Consider a control volume $\Omega$ with control surface $\Sigma$ in which a substance, non necessarily conservative, is advected by the fluid velocity and diffused by molecular motion. To describe the age distribution it is useful to introduce the age-specific density or concentration, $c(x, t, \tau)$, describing the quantity per volume at a point $x$ and time $t$ of a given substance having age $\tau$. Note that typically $c$ has units of mass per volume per age but, depending on the quantity under exam, it could also refer to age specific molar density or to age specific number of individuals/particles. The continuum hypothesis will be assumed to be valid.

A balance equation for $c$ was first proposed by [103] (see also [71] for a similar equation in the context of ocean dynamics)

$$\frac{\partial c}{\partial t} + \frac{\partial c}{\partial \tau} = -\nabla \cdot (vc - D\nabla c) + \sigma, \quad (5.1)$$
where \( \nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z} \right) \), \( \mathbf{v} \) is the velocity field, \( \sigma \) is the net source term (due for example to chemical reactions or birth/death processes). The initial condition of the previous equation is the age distribution \( c(x, 0, \tau) \) for \( x \in \Omega \) and boundary conditions \( c(x, t, \tau) \) for \( x \in \Sigma \). We will make the assumption that age is counted from the time at which the quantity in consideration has entered the control volume (i.e., the mass is introduced in the control volume with zero age).

It is important to observe that the previous equation provides a purely kinematic description of age, in which the advective velocity is assumed to be known or given by coupled equations of motion. In the case of a hydrological systems, however, this picture typically requires an unattainable amount of information [176], so that a spatially lumped description over the entire control volume becomes necessary, along with auxiliary assumptions to surrogate for the lack of knowledge of the velocity field. Another interesting point regards the fact that both the velocity vector and the net source/sink term in (5.1) may also be a function of age, especially in the case of active populations (bacterial, animals, people), or in hydrological systems where for example transpiration may select water in specific ranges of ages depending on the overall level of moisture, because of soil-pore heterogeneities.

In case of lack of detailed kinematic description, as is the case of hydrological systems, it is then useful to integrate over the control volume to achieve a spatially lumped formulation for the age distribution function,

\[
n(t, \tau) = \int_{\Omega} c(t, \tau, x) d\Omega,
\]

which quantifies the amount of the substance under exam at a given time, in units of mass per age for the entire control volume. When the local equation (5.1) is integrated over the control volume using the Gauss theorem [105, 13], the MKVF equation [182, 275] is readily obtained.
\[ \frac{\partial n}{\partial t} + \frac{\partial n}{\partial \tau} = -\mu n, \quad (5.3) \]

with initial condition \( n(t = 0, \tau) = \beta(\tau) \) for the age distribution and boundary condition \( n(t, \tau = 0) = \alpha(t) \), also called the birth rate. The so-called mortality rate, or loss term, \( \mu(t, \tau) \), may be subdivided into different terms according to the different pathways out of the system (for example, in surface hydrology, evapotranspiration, percolation, runoff, etc.) and can be considered a nonlinear function the total storage \( w \), to be defined shortly, as in [110, 111] and subsequent papers. A direct derivation of the MKVF equation, without going through Eq. (5.1), can be found in several books and articles [263, 136, 144, 188].

Before reviewing the solution of (5.3), it is useful to connect it to the familiar form of the mass balance equation for a control volume. Indicating as

\[ w(t) = \int_0^\infty n(t, \tau) d\tau, \quad (5.4) \]

the total mass in \( \Omega \) at time \( t \), integration of (5.3) gives

\[ \frac{dw}{dt} = \iota - o, \quad (5.5) \]

where the input and output terms are respectively

\[ \iota(t) = n(t, 0) = \alpha(t) \quad \text{and} \quad o(t) = \int_0^\infty \mu n d\tau. \quad (5.6) \]

It may also be useful to define the normalized distribution of ages,

\[ \phi(t, \tau) = \frac{n(t, \tau)}{w(t)}, \quad (5.7) \]

which can be interpreted as a probability density function (PDF) of the ages when the quantity under exam is sampled at random in \( \Omega \). It is important to keep in mind that the age variability described by this distribution here results from the spatially lumped
description and reflects the possible complex streamline structure (e.g., due to turbulence or heterogeneity of the porous medium) within $\Omega$ but not stem from the external temporal hydrologic variability, which will be introduced later (see Sec. 4).

The mean age is defined as

$$a(t) = \int_0^\infty \tau \phi(t, \tau) d\tau = \frac{\int_0^\infty \tau n(t, \tau) d\tau}{w(t)} = \frac{m(t)}{w(t)}$$

(5.8)

and similarly for higher order moments. Solving (5.7) for $n$ and substituting into (5.3) one obtains the equation of [31], also used by [117]. While being of course an exact consequence of the MKVF equation, this resulting equation is in reality less convenient for solution (note that [266] instead write directly the MKVF equation, although they attribute it to [31]). In this paper we will basically only refer to the age distribution $n(t, \tau)$, its normalized pdf version $\phi(t, \tau)$ and its first moment $a(t)$. Other important related quantities, such as the residence time and the survival time distributions [191, 60, 193], along with their link to the the survival equation and renewal theory [60], will be discussed elsewhere. We will only recall, as already noted by [275] (see also [170]), that in steady state (we use the suffix $*$ to emphasize this fact) the age distribution, suitably normalized by the constant input, gives the survivor function of the system [60, 66],

$$\phi^*(\tau) = \frac{n^*(\tau)}{\epsilon}.$$  

(5.9)

In turn, the negative of its derivative with respect to age directly provides the distribution of life span or transit times in the system,

$$\psi^*(\tau) = -\frac{d\phi^*(\tau)}{d\tau}.$$  

(5.10)

It is important to emphasize that these quantities are in general different for time-varying conditions and that here we will mostly focus on the age distributions.
Returning to the MKVF equation, its solution can be obtained using the method of characteristics, which is defined by $\frac{d\tau}{dt} = 1$ [263, 188], expressing the obvious fact that age increases at the same rate as time. The solution is [263]

$$n(t, \tau) = \begin{cases} 
\beta(\tau-t) e^{-\int_0^t \mu(u,\tau-t+u)du} & t < \tau \\
\alpha(t-\tau) e^{-\int_0^\tau \mu(t-\tau+a,u)du} & t > \tau.
\end{cases}$$

(5.11)

We specifically refer to the case in which the 'mortality' term is only a function of age and time, $\mu(t, \tau)$, but not of the total quantity $w$ (this is the nonlinear case dealt with by [110, 111]). When the input is in form of instantaneous pulses (i.e., Dirac deltas), in which case the age distribution is also a singular function, it may be convenient to introduce the auxiliary functions

$$u(t, \tau) = \int_\tau^\infty n(t, \tau')d\tau'$$

(5.12)

and

$$v(t, \tau) = \int_{-\infty}^t n(t', \tau)d\tau',$$

(5.13)

being $u(t, \tau)$ the total amount of the quantity having age greater than $\tau$ at time $t$ (when the integral starts from 0, it is equal to $w(t)$, see (5.4)), and $v(t, \tau)$ the cumulative amount of substance, from the beginning to time $t$, having had age equal to $\tau$.

Finally, a useful hierarchy of equations for the moments of $n$ can be also obtained, similarly to what was done in [232], [270] and [81] for the point equation (5.1). Focusing in particular on the mean age, we can first multiply (5.3) by $\tau$ and then integrate with respect to age to write

$$\frac{dm}{dt} = w - \theta,$$

(5.14)
where $\theta = \int_0^{\infty} \tau \mu nd\tau$ (this could be interpreted as the first moment of the age distribution at exit or death). An interesting equation for the mean age $a = m/w$ can then be obtained by differentiating the definition and using the previous equations, (5.5) and (5.14),

$$\frac{da}{dt} = 1 - a \left( \frac{\theta}{m} + \frac{\nu}{w} - \frac{\eta}{w} \right).$$  \hspace{1cm} (5.15)

In the case of age-independent mortality, say $\mu = \eta = \text{const.}$, then

$$\frac{da}{dt} = 1 - a \frac{\nu}{w}.$$  \hspace{1cm} (5.16)

While obviously not in closed form, being coupled to (5.5), this equation is however quite instructive for it shows how with age-independent outputs the system simply ages with time in the absence of input, which in turn acts to ‘dilute’ the overall age of the system, whereas the term $w$ brings the whole history of the input into the dynamics of the mean age.
5.3 Examples

In this section, we present three simple applications to illustrate the previous theory. The first one emphasizes the effect of time varying input as a prelude to its randomization in Sec. 5.5, while the second and third applications focus on the role of age-dependence in the mortality term.

5.3.1 Time-Varying Input

We first consider the case of constant mortality rate $\eta$, which corresponds to the classical linear system, extensively used in hydrology (e.g., [243]). Starting from an initial condition $n(0, \tau) = n_0(\tau)$, the system proceeds with constant input $\iota_0$, until at time $t_1$ the input is suddenly switched to a new value $\iota_1$. From Eq. (5.11), the transient solution is

$$n(t, \tau) = \begin{cases} n_0(\tau - t) e^{-\eta t} & t < \tau \\ \iota_0(t - \tau) e^{-\eta \tau} & t_1 > t > \tau \\ \iota_1(t - \tau) e^{-\eta \tau} & t > t_1 \end{cases} \quad (5.17)$$

which, for $t \to \infty$, tends to an exponential steady-state solution. The behavior of the various solutions is shown in Fig. 5.1 for a uniform initial condition over the age range $(0, w_0/n_0)$. Note the steady state value of the mean age, equal to $1/\eta$, independent of the input rate, which for this linear case is also the mean life span (as follows from (5.10) and the fact that both $\phi^*$ and $\varphi^*$ are exponential distributions). However, for the purposed of this paper, it is important to emphasize that in the time-varying case these are in general different distributions.
5.3.2 Age-Dependent Loss

This application regards a system that reaches steady state under constant input but age-dependent loss term. The loss term is chosen in the form of a power law,

$$\mu(\tau) = \left(\frac{\tau}{1+c}\right)^c,$$

\((c > -1),\) representing for example the effects of an age-dependent plant water uptake in soils, where the parameters \(c\) could be related to the pore size distribution and tortuosity of the flow paths, as in power-law soils \([38]\.\)

Fig. 5.2 shows the temporal evolution of the various terms on the right hand side of Eq. (5.15) for this case. At steady state, the age distribution is

$$n^*(\tau) = \iota \exp\left(-\left(\frac{\tau}{1+c}\right)^{1+c}\right),$$

whose integral with respect to \(\tau\) from 0 to \(\infty\) gives \(w(t)\),

$$w^* = \iota \Gamma\left(\frac{1}{1+c}\right),$$

Figure 5.2: Time evolution towards steady state of the terms \(\frac{\theta}{m}, \frac{\iota}{w}\) and \(\frac{\omega}{w}\) from Eq. (5.15) for the case of age-dependent loss.
while the mean age is,

\[ a^* = (1 + c) \frac{\Gamma\left(\frac{2}{1+c}\right)}{\Gamma\left(\frac{1}{1+c}\right)}. \quad (5.21) \]

Finally, using (5.10) one obtains

\[ \psi^*(\tau) = \left(\frac{\tau}{1 + c}\right)^c \exp\left(-\left(\frac{\tau}{1 + c}\right)^{1+c}\right), \quad (5.22) \]

which is a Weibull distribution with scale parameter and shape parameter both equal to \(1 + c\). The mean of \(\psi^*\), the mean residence time, is \(\Gamma\left(\frac{1}{1+c}\right)\), always greater than \(a^*\), as expected in this case [28, 22], and the variance is \(2(1 + c)\Gamma\left(\frac{2}{1+c}\right) - (\Gamma\left(\frac{1}{1+c}\right))^2\). The Weibull distribution is frequently used in renewal theory [60, 66] and, as well known, is one of the Extreme Value distributions [145, 246].

### 5.3.3 Heavy Tails in Age Distributions

In this last example, we show how a particular form of age-dependence in the loss function may be related to the observed different timescales in the hydrologic response of watersheds and give rise to heavy tails in the water age distributions (see for example [176, 139, 228]).

If one chooses a hyperbolic behavior of the loss function with age, such that there is a strong preference for young water to be loss, coupled with a very slow decay of the lost function at large ages,

\[ \mu(\tau) = \frac{1}{\sigma \left(\frac{\epsilon(\tau - \mu)}{\sigma} + 1\right)}, \quad (5.23) \]

the survivor function \(\varphi^*(\tau)\) and life span distribution \(\psi^*(\tau)\) are then,

\[ \varphi^*(\tau) = \left(\frac{\epsilon(\tau - \mu)}{\sigma} + 1\right)^{-1/\epsilon} \quad (5.24) \]

\[ \psi^*(\tau) = \frac{1}{\sigma} \left(\frac{\epsilon(\tau - \mu)}{\sigma} + 1\right)^{-\left(\frac{1}{\epsilon} + 1\right)}. \quad (5.25) \]
The function $\psi^*(\tau)$ is a Generalized Pareto distribution [196, 145], with mean and variance respectively equal to $\mu + \frac{\sigma}{1-\epsilon}$ and $\frac{\sigma^2}{(1-\epsilon)^2(1-2\epsilon)}$. It belongs to the class of Heavy-tailed distributions. As shown in Fig. 5.3 (b), both the survivor and transit time distributions are characterized by the presence of algebraic decays in the tail behavior (i.e., heavy tails). Differently from the previous example, the loss function here is such that the mean age is greater than mean transit time [28].
Figure 5.4: Time evolution of soil water age distribution (solid gray line) along with the marked Poisson process inputs (red line in the vertical plane on the left) with mean depth $1/\gamma = 2$ mm and mean frequency $\lambda = 0.4$ d$^{-1}$. The ensemble average age distribution $\langle N \rangle$ is plotted at $t = 75$ d (dashed blue line), while the mean age is plotted in brown on the horizontal plane. Note that for graphical purposes $I$ and $N$ are plotted using the size of the marks, while in theory they are singular functions made of infinitely high spikes (Dirac deltas).

5.4 Effect of External Stochasticity

From the previous discussion it is evident that the age distribution presented before reflects the possible stochasticity resulting from the integration of a random flow field over the control volume. This randomness can thus be called 'internal'. In the case of hydrological systems, however, the effect of random 'external' forcing should also be taken into account, since it may be at least as important as the internal one. In what follows we will limit our analysis to the more important case of stochastic inputs, while considering outputs as deterministic. As discussed by [64], the rainfall-induced variability in fact tends to dominate over the variability in the outputs (e.g., evapotranspiration, percolation and runoff).

From the mathematical point of view, the presence of a random input makes (5.5) a stochastic differential equation (SDE). While the MKVF equation is still perfectly suitable, in that a single realization of the random input is just a special form of time varying input entering through the boundary conditions at age zero, it is important to keep in mind that the age distribution too becomes a random function, changing for each realization of the
stochastic input. Thus, to move beyond a single realization and obtain a complete probabilistic description, one needs to consider the ensemble of all possible realizations of the random input and introduce related probability distributions.

To emphasize the randomness resulting from the stochastic forcing, we will use capital letters for random variables, as usual in statistics. Accordingly, one can define the random function $N(t, \tau)$, and consider its ensemble average $\langle N(t, \tau) \rangle$, whose equation follows directly from the MKVF (when $\mu$ does not depend on $N$ or $W$),

$$\frac{\partial \langle N \rangle}{\partial t} + \frac{\partial \langle N \rangle}{\partial \tau} = -\mu \langle N \rangle,$$

(5.26)

driven by the ensemble average of the random input, entering as the $\tau = 0$ boundary condition. However, there is no need to resort to the previous equation, because the general solution (5.11) is still valid, as long as one considers the randomly varying input, $I(t)$, as boundary condition,

$$N(t, \tau) = \begin{cases} 
\beta (\tau - t) e^{-\int_0^t \mu(u, \tau - t + u) du} & t < \tau \\
I(t - \tau) e^{-\int_0^{\tau} \mu(t - \tau + u, u) du} & t > \tau.
\end{cases}$$

(5.27)

where the initial age distribution can be considered as an assigned random function with its own probabilistic structure. This solution is interesting for it shows that for a given time and age, the age density is just the rescaled in time version of the random input. Thus for the one-time, one-age PDF of $N$, which is formally connected to $N$ by ensemble average of its fine grained PDF [252, 203], $p_N(n; t, \tau) = \langle \delta(N(t, \tau) - n) \rangle$, and represents the infinitesimal probability to observe an amount between $n$ and $n + dn$ with age $\tau$ at time $t$, one can write (for $t > \tau$)

$$p_N(n; t, \tau) = e^{\int_0^t \mu(u, \tau - t + u) du} p_I(ne^{\int_0^t \mu(u, \tau - t + u) du}; t - \tau),$$

(5.28)
where \( p_j(t; t) \) is the one time PDF of the input.

One can also define \( W = \int_0^\infty N(t, \tau) \) and write, thanks to the linear operations of averaging,

\[
\langle W(t) \rangle = \int \langle N(t, \tau) \rangle d\tau,
\]

(5.29)

and similarly for the auxiliary variables \( U(t, \tau) \) and \( V(t, \tau) \), see (5.12) and (5.13).

The mean age,

\[
A(t) = \frac{M(t)}{W(t)} = \frac{\int_0^\infty \tau N(t, \tau) d\tau}{\int_0^\infty N(t, \tau) d\tau},
\]

(5.30)

also acquires random variability, governed by the SDE version of Eq. (5.15). A general and relatively simple solution for the harmonic mean of the mean age \( A \) can be obtained by dividing by \( M \) the SDE equivalent of (5.14), i.e.,

\[
\frac{d \ln M}{dt} = \frac{W}{M} - \frac{\Theta}{M}
\]

(5.31)

where \( \Theta = \int_0^\infty \tau \mu N d\tau \). In conditions of statistical steady state, taking ensemble average, this gives the exact result

\[
\langle \frac{1}{A} \rangle^{-1} = \langle \frac{\Theta}{M} \rangle^{-1}.
\]

(5.32)

For a linear system \( \mu = \eta = \text{const.} \), then immediately

\[
\langle \frac{1}{A} \rangle^{-1} = \frac{1}{\eta},
\]

(5.33)

### 5.5 Stochastic Linear Storage

We apply the previous concepts to the stochastic linear water balance equation
Figure 5.5: For the same realization of Fig. 5.4, $W(t)$ is plotted on the left vertical plane (solid black line). The variables $U(t)$, and $V(t)$ (solid green and brown lines, respectively) are also shown. Parameters as in Fig. 5.4.

Figure 5.6: Traces of realizations of $U$ as a function of $\tilde{\tau}$ as defined in the Appendix C, Eq. (C.1) and $V$ as a function of time $t$. Probability density functions $p_U(u; t, \tau)$ for $t = 75$ d and $\tilde{\tau} = 60$ d (b), and $p_V(v; t, \tau)$ (d) for $t = 60$ d and $\tau = 15$ d.
\[
\frac{dW}{dt} = I - \eta W, \quad (5.34)
\]

where \(\eta\) is a constant and the input \(I\) is the formal time derivative of a marked Poisson process with rate (frequency of occurrence) \(\lambda\) and exponentially distributed marks with mean \(1/\gamma\) (a realization of the input is shown in the left vertical plane of Fig. 5.4). This SDE has been used as a minimalist model of both soil moisture, in conditions when evapotranspiration losses dominate over percolation and runoff \([127, 272]\), and streamflow dynamics \([282, 30]\). An example of a realization of the process \(W(t)\), a sequence of exponential jumps and exponential decays of exponential duration, is shown in the left vertical plane of Fig. 5.5. The one time PDF, \(p_w(w; t)\), is a hypergeometric function, which becomes a gamma distribution in stochastic steady state \([272]\). It may be useful to warn the reader not to confuse the deterministic steady state condition discussed in Sec. 5.2 and 5.3 with the statistical steady state discussed here, where time varying conditions induced by the external forcing are always present.

Because of the intermittent nature of the input, when considering only one realization, the water in the system only has ages corresponding to the times of previous input occurrences, while there will be no water for all other ages. As a result, in the present case, \(N(t, \tau)\) is a singular function, being the exponentially modulated version of the time derivative of the marked Poisson input (i.e., a sequence of instantaneous infinite spikes). This is shown in Fig. 5.5. A convenient way to avoid handling such singular functions is to refer to their integrated auxiliary variables, \(U\) and \(V\), also shown in Fig. 5.5. Note that \(U(t, 0) = W(t)\), so that its distribution is expected to be a hypergeometric function, at least for \(\tau = 0\), while \(V(t, \tau)\) is the exponentially rescaled version of the total rainfall up to that time (whose distribution is known to be a Bessel function). These distributions of \(p_u(u; t, \tau)\) and \(p_v(v; t, \tau)\) are derived in detail in the Appendix C. An example of their shapes is shown in Fig. 5.6, along with some realizations.
As for the mean age, \( A = M/W \), we already know from (5.33) that its harmonic mean is equal to \( 1/\eta \). However, to obtain its full distribution one should first derive the joint distribution of \( W \) and \( M \), \( p_{WM}(w, m; t) \), and then use the formula for the quotient of random variables [145],

\[
P_A(a; t) = \int_{-\infty}^{\infty} z p_{MW}(az, z; t) dz. \tag{5.35}
\]

Thus, starting from the coupled SDEs

\[
\begin{align*}
\frac{dW}{dt} &= I - \eta W \\
\frac{dM}{dt} &= W - \eta M,
\end{align*}
\tag{5.36}
\]

the Chapman-Kolmogorov equation for the joint PDF can be written as in [32],

\[
\frac{\partial p_{WM}}{\partial t} = \frac{\partial}{\partial w}(w\eta p_{WM}) + \frac{\partial}{\partial M}((\eta m - w)p_{WM}) \\
- \lambda p_{WM} + \lambda \gamma \int_0^w p_{WM}(x, m; t)e^{-\gamma(x-w)}dx.
\tag{5.37}
\]

While the moments of the joint distribution can be readily computed through the moment generating function (Laplace transform), see e.g., [32], the full joint distribution is unfortunately very difficult to obtain. An alternative, approximate route will be followed here. Starting from the equation for \( A \), see (5.16), and by making the approximation \( W \approx \langle W \rangle \), so that the equation becomes closed and Markovian,

\[
\frac{dA}{dt} = 1 - \frac{A}{\langle W \rangle} \circ I, \tag{5.38}
\]

where the symbol \( \circ \) underlines the fact that in this SDE the multiplication of the random variable \( A \) by the white noise \( I \) should be interpreted in the sense of Stratonovich [99, 258]
in order to preserve the ordinary rules of calculus which are used to derive the equation for
\( A \) as a derivative of a quotient, \( A = M/W \). Then, being \( \langle W \rangle = \lambda/(\gamma \eta) \) and using the
transformation \( B = \ln A \), an additive noise SDE for \( B \) can be obtained as

\[
\frac{dB}{dt} = e^{-B} - \frac{\gamma}{\lambda} I, \tag{5.39}
\]

whose solution in steady state can be found as in [259]. Reverting to the PDF of \( A \)
using the random-variable function theorem, results in the approximate PDF of \( A \) in the
form of a gamma distribution,

\[
p_A(a) = \frac{\lambda^{\frac{\lambda}{\eta}+1}}{\Gamma(\frac{\lambda}{\eta}+1)} \frac{1}{\lambda} a^{\frac{\lambda}{\eta}} e^{-\lambda a}, \tag{5.40}
\]

with mean

\[
\langle A \rangle = \frac{1}{\eta} + \frac{1}{\lambda}, \tag{5.41}
\]

variance

\[
\text{var}_A = \frac{1}{\lambda} \left( \frac{1}{\eta} + \frac{1}{\lambda} \right), \tag{5.42}
\]

and mode

\[
\text{mode}_A = \frac{1}{\eta}. \tag{5.43}
\]

For a gamma distribution, the mode is also the harmonic mean, which, interestingly, is
an exact result in agreement with (5.33). Fig. 5.7 compares the approximate solution with
the one obtained from numerical simulations of the full system (5.36). The approximate
PDF captures well the shape and location of the simulated PDF, however the approximate
one tends to have weaker mode and larger spread. More detailed comparisons of the va-

lidity of the used approximation will be presented in subsequent contributions. For this

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Figure 5.7: Time evolution of the variables $W(t)$ in (a), $M(t)$ in (c) and $A(t)$ in (e). (e) Solid and dashed lines refer to the solution of Eq. (5.38) respectively with and without the assumption $W \approx \langle W \rangle = \lambda/\gamma \eta$.

(b) pdf of $W(t)$. (d) histogram of $M(t)$. (f) Analytical pdf and histogram of $A(t)$ (with $W \approx \langle W \rangle = \lambda/\gamma \eta$) (solid red and light gray), and histogram for the real solution $A(t)$ (dark gray).

Chapter, the approximate PDF of the mean age already serves the purpose of showing how the (external) random variability in the input propagates into the probabilistic properties of age. As seen in Fig. 5.7, even the mean water age can vary considerably from sample to sample by virtue of the input variability. This type of variability could thus be expected to significantly impact the year-to-year determination of water age in a hydrologic system. One should also mention that the external stochasticity in the input may be responsible for a heavier tail behavior of the age distribution (see distribution of mean age in Fig. 5.7), compared to the case with only internal variability. This effect is well known in compound distributions [15] and has recently been advocated as a mechanisms for nonextensive thermodynamics behavior in statistical mechanics [12] and for increased variability of ecohydrologic variables [208].

5.6 Conclusions

While revisiting the general solution of the MKVF equation within the context of the theory of age distributions, we have emphasized that such distributions by their nature stem
from integrating the internal structure of flow pathways within hydrologic control volumes
[105]. Such ‘internal’ randomness should be contrasted with another form of ‘external’
stochasticity, originating from the random variability inherent in input and output terms
of hydrologic systems. The MKVF equation and the stochastic differential equations that
can be derived from it suggest a framework to include these external stochastic effects and
quantify their contribution to the probabilistic structure of water age. Some results regarding
the statistical properties of mean age have been described in sections 5.4 and 5.5. Even
for the age independent case of sec. 5.3.1 and 5.5, the temporal variability of external input
induces non trivial effects on the age distribution.

Several issues remain to be explored along these lines, including the effects of age-
dependence and nonlinearities in the loss function, as well as their random variability at
different time scales (e.g., daily, seasonal and interannual) and the link to probabilistic re-
newal theory. This notwithstanding, we hope that this work could represent a useful step
towards improving the characterization water age distributions in hydrologic and geophys-
ical systems.
Chapter 6

Linking age, survival and transit time distributions

The complex topographic and subsurface structure of a watershed gives rise to the internal ‘stochasticity’. The spatial structure of the watershed is not truly random, but it is typically unknown and in this spatially-implicit framework its integrated effect on the age distribution practically appears as a ‘randomness’. This determines the degree of mixing, and thus the different properties of the age distribution in both transient and stationary conditions, and under time reversal. This represents the subject of this chapter, which is adapted from Calabrese, Salvatore, and Amilcare Porporato, "Linking age, survival, and transit time distributions", Water Resources Research 51.10 (2015): 8316-8330.

6.1 Introduction

There is considerable interest in estimating age and transit times of elements in a physical system or, equivalently, of individuals in a population, in disciplines as diverse as population dynamics and demography [182, 275, 210, 29], chemical engineering [191, 190], and hydrology and geophysics (e.g., among many others [84, 63, 107, 103, 71, 178, 81, 31, 176, 117, 206, 14]). It has in fact become increasingly clear that the age, survival time,
and the total time spent by each element in a system may provide additional key insights into specific aspects of a system’s behavior. This viewpoint, which can be considered as a time-integrated Lagrangian perspective, has been especially emphasized in groundwater systems [168, 63, 107, 103] and in the hydrological response of watersheds [178, 176], using both theoretical [31, 266, 117, 14, 206] and field approaches [125, 21, 176].

Recent discussions in the literature about the role of internal variability and external forcing (e.g., rainfall) on the properties of age distributions [206], as well as the differences between age and survival time distributions, their degree of statistical dependence, and their symmetry under time reversal (e.g., [58, 117, 14]) have made evident that a comprehensive theory of age and related concepts is still missing. Toward this goal, in this contribution we focus on the linkage between age and survival time distribution in both transient and steady-state conditions. Differently from what was assumed in [14], we show that age and survival time are in general statistically dependent quantities (the only case of independence being the one of time- and age-independent loss (or input) in steady state). The theoretical framework afforded by the evolution equation of the joint distributions of age and survival also provides a means to easily understand the time symmetries between age and survival, and the derivation of the general properties of the transit-time distribution.

We should warn the readers unfamiliar with the previously cited literature that, perhaps because of the contributions from many disciplines, the terminology which identifies these variables is hardly unified. For example, apart from the age, the definition of which seems uncontroversial (τ in what follows), the survival time (here indicated as σ) is often also indicated as life expectancy, while input and output rates are often also called birth and death functions. The variable with possibly the most appellations is the so-called transit time (T), the sum of age and survival time, which is also indicated as travel time, life span, total life time, and sojourn time. It should be emphasized that in the literature transit time has also been used for the age at death or survival time at birth. These quantities are subject to the waiting-time paradox [88]. However, as long as the mathematical formalism
is clear and the notation kept consistent, as we have hopefully done here, we trust that these different names and the statistical interpretation will not confuse the readers.

The Chapter is organized as follows. The evolution equation for the joint distribution of age and survival time is introduced and solved in section 6.2, with boundary conditions given by the survival time distribution at birth and the related age distribution at death. The solution is used to derive the transit time distribution by a simple integration in section 6.3. The steady state conditions are discussed in section 6.4. Finally, we present some applications in section 6.5 with the purpose of showing some interesting details of the theory. While most of these applications have a close connection to hydrological and fluid mechanic systems, they are by necessity highly idealized to allow us to focus on the novel theoretical results, avoiding the additional complications that more realistic applications with random external forcing (e.g., rainfall) and spatial heterogeneities would add.

### 6.2 Joint Distribution of Age and Survival Time

The transit time \( T \) of an element of a system is the sum of the time spent since the entrance/birth, called the age \( \tau \), and the time that it will spend before exit/death, called the survival time \( \sigma \). At a given time \( t \), each element is characterized by a certain age and survival (and thus transit) time, which globally can be described by the joint distribution \( \varphi(t, \tau, \sigma) \). In words, \( \varphi(t, \tau, \sigma)d\tau d\sigma \) represents the (infinitesimal) amount of elements (e.g., a mass or population number having age between \( \tau \) and \( \tau + d\tau \) and survival time \( \sigma \) and \( \sigma + d\sigma \) at time \( t \). Note that this distribution function is not normalized to have area one (so it is not a density function) but has area equal to \( \int_0^\infty \int_0^\infty \varphi(t, \tau, \sigma)d\tau d\sigma = w(t) \) The balance equation for the joint distribution function \( \varphi(t, \tau, \sigma) \) can be obtained considering that, as the system evolves in time, \( \varphi(t, \tau, \sigma) \) is conserved along the lines orthogonal to the bisector in the \( \tau, \sigma \) plane, which are characterized by having constant \( T \). Based on these considerations, one can readily write
\[
\frac{\partial \varphi}{\partial t} + \frac{\partial \varphi}{\partial \tau} - \frac{\partial \varphi}{\partial \sigma} = 0.
\]  
(6.1)

The equation is controlled by the boundary conditions \( \varphi(t, \tau, \sigma = 0) = n_0(t, \tau) \), which is the survival time distribution at input/birth, and \( \varphi(t, \tau = 0, \sigma) = l_0(t, \sigma) \), which is the age distribution at output/death. An example of the evolution of the joint distribution is shown in Figure 6.1, showing how \( \varphi \) is simply the input boundary condition on the \( \sigma \) axis, translating in time along lines of constant \( T \) until it crosses the \( \tau \) axis where \( \sigma = 0 \). The figure also clearly shows how the two boundary conditions cannot be independent, as will be seen more precisely later. It is interesting that the contribution of input and output to the system is entirely felt through the boundary conditions. In more general cases, elements could also enter with age different from zero (immigration) or exit with a non-zero survival time (emigration), in which case equation (6.1) should also contain corresponding source and sink terms; these generalization however will not be pursued in this paper.

More formally, moving along the characteristic curves, defined by \( \frac{d\tau}{ds} = 1 \), \( \frac{d\sigma}{ds} = -1 \) and \( \frac{dt}{ds} = 1 \), which are obviously also lines of constant transit time, it is possible to re-express equation (6.1) as

\[
\frac{d\varphi}{ds} = 0,
\]  
(6.2)

so that the solution is then

\[
\varphi(t, \tau, \sigma) = \varphi(t - \tau, \tau = 0, \sigma + \tau) = \varphi(t + \sigma, \tau + \sigma, \sigma = 0),
\]  
(6.3)

or equivalently,

\[
\varphi(t, \tau, \sigma) = l_0(t - \tau, \sigma + \tau) = n_0(t + \sigma, \tau + \sigma).
\]  
(6.4)
Figure 6.1: Example of the joint distribution of age and survival time in transient conditions in which the input has been increased in time, showing how $\varphi$ results from a simple translation of the boundary conditions.

From this it is evident how the joint distribution at a given time is simply the time shift of the boundary conditions and that, if time is reversed, the whole process is flipped, with the age playing the role of the survival time and vice versa. This type of time symmetry will appear frequently in the following.

6.2.1 Age and Survival Time Distributions

By integrating equation (6.1) over $\sigma$, one obtains the M’Kendrick-von Foerster (MKVF) equation [182, 275, 188, 206], describing the dynamics of an age-structured population equation,

$$
\frac{\partial n(t, \tau)}{\partial t} + \frac{\partial n(t, \tau)}{\partial \tau} = -n_0(t, \tau),
$$

(6.5)

where $n(t, \tau) = \int_0^{\infty} \varphi(t, \tau, \sigma) d\sigma$ is the age distribution (mass over time (age)), quantifying the amount of substance having age $\tau$ at time $t$. The sink term, $n_0(t, \tau)$, is the age distribution at output/death, previously introduced as a boundary condition for (6.1). It can be written as
where $\mu(t, \tau)$ is the age and mass specific output rate. With initial condition $n(0, \tau)$ and boundary condition $n(t, 0) = \nu(t)$, where $\nu(t)$ is the input/birth rate, the solution of equation (6.5) is [263, 110, 136]

\[
n(t, \tau) = \begin{cases} 
  n(0, \tau - t) e^{- \int_0^t \mu(u, \tau - u) \text{d}u} & t < \tau \\
  \nu(t - \tau) e^{- \int_\tau^0 \mu(t - \tau + u, u) \text{d}u} & t > \tau.
\end{cases}
\]

(6.7)

On the other hand, by integrating (6.1) over $\tau$, a corresponding equation for the survival time distribution is obtained,

\[
\frac{\partial l(t, \sigma)}{\partial t} - \frac{\partial l(t, \sigma)}{\partial \sigma} = l_0(t, \sigma),
\]

(6.8)

where $l(t, \sigma) = \int_0^\infty \varphi(t, \tau, \sigma) \text{d}\tau$ quantifies the amount of substance having survival $\sigma$ at time $t$. The source term $l_0(t, \sigma)$ is the survival time distribution at input/birth, which can be expressed as

\[
l_0(t, \sigma) = \beta(t, \sigma) l(t, \sigma),
\]

(6.9)

with $\beta(t, \sigma)$ being the survival time and mass specific birth rate. The boundary condition is the overall output $l(t, \sigma = 0) = o(t)$ and the initial condition is $l(0, \sigma)$. As for the MKVF equation, the solution is obtained with the method of characteristics as

\[
l(t, \sigma) = \begin{cases} 
  l(0, t + \sigma) e^{\int_0^t \beta(u, t+\sigma-u) \text{d}u} & t < \sigma \\
  o(t + \sigma) e^{\int_0^\sigma \beta(t+\sigma-u, u) \text{d}u} & t > \sigma.
\end{cases}
\]

(6.10)
By integrating again either equation (6.5) over $\tau$ or equation (6.8) over $\sigma$, the familiar form of the balance equation is obtained,

$$\frac{dw(t)}{dt} = \iota(t) - o(t),$$  \hspace{1cm} (6.11)

with

$$w(t) = \int_0^\infty n(t, \tau) d\tau = \int_0^\infty l(t, \sigma) d\sigma$$ \hspace{1cm} (6.12)

and where the input and output can also be written as $\iota(t) = \int_0^\infty \beta(t, \sigma) l(t, \sigma) d\sigma$ and $o(t) = \int_0^\infty \mu(t, \tau) n(t, \tau) d\tau$. The birth and loss functions, $\beta(t, \sigma)$ and $\mu(t, \tau)$, are not easy to derive in practical applications for input-output systems, where only $\iota(t)$ and $o(t)$ are usually known. However, in the case of linear, time-invariant systems, a spectral analysis of the fluxes can help provide the transfer function of the system and in turn birth and loss functions.

It should also be noted that, when the solution of (6.1) is available, the age and survival distributions, $n(t, \tau)$ and $l(t, \sigma)$, and the evolution of $w(t)$ can be directly obtained by integrating the joint distribution $\varphi(t, \tau, \sigma)$, without need to go through the corresponding equations (7.1), (6.8), and (6.11). Looking at these equations, it is also worth noting again the symmetry of the problem with respect to the time reversal, upon which age and survival time exchange their roles, with the output becoming the input and the age-specific loss function playing the part of the survival-specific birth function and vice versa. It is easy to see, in fact, that with these substitutions and $t' = -t$, equation (6.5) and (6.8) are interchangeable.

### 6.2.2 Statistical Dependence of Age and Survival

It is possible at this point to establish a relationship between the age-specific output and the survival-specific input and, in turn, discuss the conditional distributions between age and
survival times. The latter will be essential in deriving the residence time statistics in section 6.4. To this purpose, we begin by returning to equation (6.3) which immediately furnishes the relationship between the boundary conditions by setting either $\tau = 0$ or $\sigma = 0$ (see Figure 6.1),

\begin{align}
\tau_0(t, \sigma) &= n_0(t + \sigma, \tau = \sigma), \\
n_0(t, \tau) &= l_0(t - \tau, \sigma = \tau).
\end{align}

These equations, when expressed in terms of their probability density functions (PDFs) normalized to have area one,

\begin{align}
f_{\tau_0}(t, \tau) &= \frac{n_0(t, \tau)}{\omega(t)} \quad \text{and} \quad f_{\sigma_0}(t, \sigma) = \frac{l_0(t, \sigma)}{\iota(t)},
\end{align}

become a relationship already obtained by [193],

\begin{align}
\iota(t) f_{\sigma_0}(t, \sigma) &= \omega(t + \sigma) f_{\tau_0}(t + \sigma, \tau = \sigma).
\end{align}

The subscripts $\tau_0$ and $\sigma_0$, in particular, refer to the variables age at death and survival time at birth, respectively. They will be used explicitly when it is necessary to refer to them as random variables to distinguish them from age $\tau$ and survival time $\sigma$ of the entire population, as in section 6.4.2.

From (6.13), a relationship between the birth and loss function is then obtained from the definition of $n_0$ and $l_0$, in equations (6.6) and (6.9), in which the respective solutions for $n(t, \tau)$ and $l(t, \sigma)$ can be substituted from (6.7) and (6.10), giving

\begin{align}
\mu(t, \tau) n(t - t) e^{-\int_0^t \mu(u, \tau - t + u) du} &= \beta(t - \tau, \tau) l(t) e^{\int_0^\tau \beta(u, t - u) du} \quad t < \tau = \sigma \\
\mu(t, \tau) \iota(t - t) e^{-\int_0^\tau \mu(\tau - t + u) du} &= \beta(t - \tau, \tau) \omega(t) e^{-\int_0^\tau \beta(t - u, u) du} \quad t > \tau = \sigma.
\end{align}
This clearly shows that the age- and survival-specific birth and loss functions are not independent.

Coming back to equation (6.4), the joint distribution can be expressed in terms of the conditional distribution between age and survival time. To this purpose, it is more useful to consider the PDFs, instead of distributions, and define

\[ f_{\tau,\sigma}(t, \tau, \sigma) = \frac{\varphi(t, \tau, \sigma)}{w(t)} = f_{\sigma|\tau}(t, \sigma|\tau) \frac{n(t, \tau)}{w(t)} = f_{\tau|\sigma}(t, \tau|\sigma) \frac{l(t, \sigma)}{w(t)}, \quad (6.17) \]

where \( \frac{n(t, \tau)}{w(t)} = f_{\tau}(t, \tau) \) and \( \frac{l(t, \sigma)}{w(t)} = f_{\sigma}(t, \sigma) \) are the marginal PDFs of age and survival time, respectively.

Focusing, as an example, on the conditional PDF of survival given age, an expression can be derived combining (6.17) and (6.4),

\[ f_{\sigma|\tau}(t, \sigma|\tau) = \frac{n_0(t + \sigma, \tau + \sigma)}{n(t, \tau)} . \quad (6.18) \]

Substituting in (6.18) the solutions for \( n_0 \) and \( n \) given by (6.7) and (6.6), one readily obtains

\[ f_{\sigma|\tau}(t, \sigma|\tau) = \begin{cases} \mu(t + \sigma, \tau + \sigma)e^{-\int_{t}^{\tau+\sigma} \mu(u, t + u) du} & t < \tau \\ \mu(t + \sigma, \tau + \sigma)e^{-\int_{\tau}^{\tau+\sigma} \mu(t + u, u) du} & t > \tau \end{cases} . \quad (6.19) \]

Only when this expression is equal to the marginal distribution of age, are the age and survival time statistically independent. Thus comparing with the marginal

\[ f_{\sigma}(t, \sigma) = \begin{cases} \frac{l(0, t + \sigma)}{w(t)} e^{\int_{0}^{t} \beta(u, t + \sigma - u) du} & t < \sigma \\ \frac{o(t + \sigma)}{w(t)} e^{-\int_{0}^{\sigma} \beta(t + \sigma - u, u) du} & t > \sigma \end{cases} , \quad (6.20) \]
one sees that, in general, marginal and conditional probability distributions are different. This implies that (when elements are sampled at random in the system) age and survival are typically statistically dependent variables. This remains true, in transient conditions, even when the loss and birth functions are constant, because the two distributions remain different for $t < \tau$ and $t < \sigma$. Further considerations on (6.19) will be given, for steady state conditions in section 6.4.

6.3 Transit Time

As already said, the transit time, $T$, is the total time spent by an element in the system, given by the sum of age and survival time,

$$T = \tau + \sigma. \quad (6.21)$$

Its distribution can thus be obtained as the distribution of the sum of the two random variables, the age and survival time, e.g. [248, 268],

$$\phi(t, T) = \int_{T<\tau+\sigma<T+dT} \phi(t, \tau, \sigma) d\tau d\sigma, \quad (6.22)$$

which can also be written as

$$\phi(t, T) = \int_0^T \varphi(t, \tau', T - \tau') d\tau' = \int_0^T \varphi(t, T - \sigma', \sigma') d\sigma'. \quad (6.23)$$

As shown in Figure 6.2, equation (6.23) is the integral along lines of constant $T$, which are orthogonal to the bisector on the plane $(\tau, \sigma)$. Using equation (6.3) one also has

$$\phi(t, T) = \int_0^T \varphi(t + \sigma', T, 0) d\sigma' = \int_0^T n_0(t + \sigma', T) d\sigma' = \int_0^T \mu(t + \sigma', T) n(t + \sigma', T) d\sigma'. \quad (6.24)$$
which tells us that we can know the transit time distribution at time \( t \) by summing up the amount leaving the system with age \( \tau = T \) within the time window \( (t, t+T) \). Only when \( \tau \) and \( \sigma \) are statistically independent is equation (6.24) a simple convolution integral. An alternative expression can be similarly obtained from equation (6.3),

\[
\phi(t, T) = \int_{-T}^{0} \varphi(t - T + \sigma, 0, T) d\sigma' = \int_{-T}^{0} \beta(t + \sigma', T) l(t + \sigma', T) d\sigma', \quad (6.25)
\]

which instead looks back to the time window \( (t-T, t) \) and sums all the elements entering with survival time \( \sigma = T \).

It may be useful to note that the transit time distribution refers in general to any element of the control volume (or population) present at time \( t \) and its statistical interpretation is subject to the waiting-time paradox \[88\]. If one instead only focuses on the elements entering the system (or the newborns), their transit time \( T \) is equal to their survival time \( \sigma \), because for them \( \tau = 0 \), and their distribution is \( l_0(t, \sigma) \). Analogously, as often done in the literature, focusing on the elements leaving the system (or dying), \( T \) equals the age \( \tau \) and their transit time distribution is the equal to \( n_0(t, \tau) \). We emphasize that, in the literature,
the transit time has often been used for the age at death in stationary conditions, whereas here its definition refers to the entire population inside the control volume in transient conditions.

### 6.4 Steady State

#### 6.4.1 Distributions

Several of the previous relationships assume an interesting, simplified form at steady state, a necessary condition for which is that $n_0$ and $l_0$ are time independent. In such a case, the balance equation for a steady state system is simply

$$\frac{dw}{dt} = 0 = \iota - \omega,$$  \hspace{1cm} (6.26)

and from equation (6.3) it follows that

$$n_0(\tau) = l_0(\sigma = \tau),$$  \hspace{1cm} (6.27)

meaning that not only the overall input equals the overall output, but also that an input with a fixed age $\tau$ must be balanced by an output of equal survival time $\sigma$. As a result, the joint distribution $\varphi(\tau, \sigma)$ is constant, and equal to $n_0(\tau = T) = l_0(\sigma = T)$ along lines of constant $T$.

In steady state conditions, age and survival time distributions are derived by taking $t \to \infty$ in (6.7) and (6.10), that is

$$n(\tau) = \iota e^{-\int_0^\tau \mu(u)du},$$  \hspace{1cm} (6.28)

and
\[ l(\sigma) = \omega e^{-\int_0^\sigma \beta(u) du}. \] (6.29)

In particular, from (6.3), the integral of \( \varphi(\tau, \sigma) \) over \( \tau \) is the same as the integral over \( \sigma \), suggesting that

\[ n(\tau) = l(\sigma = \tau). \] (6.30)

In turn, it follows immediately that, at steady state, birth and loss functions must be equal,

\[ \mu(\tau) = \beta(\sigma = \tau). \] (6.31)

We note that the so-called survivor function \([275, 60, 66]\), defined as the exceedance probability of survival at steady state, can be obtained by dividing either the age distribution or the survival distribution by the input \( \iota \) (or by the output \( o \)),

\[ S(\tau) = \frac{n(\tau)}{\iota} = \frac{l(\sigma = \tau)}{o} = e^{-\int_0^{\tau} \mu(u) du}. \] (6.32)

so that, as well known \([60, 263]\),

\[ -\frac{dS(\tau)}{d\tau} = f_{\tau_0}(\tau) = f_{\sigma_0}(\sigma = \tau) = \mu(\tau)e^{-\int_0^{\tau} \mu(u) du}. \] (6.33)

The transit-time distribution at steady state can also be easily obtained by solving the integral in equation (6.24) and substituting equation (6.28),

\[ \phi(T) = T\mu(T)n(T) = \iota T\mu(T)e^{-\int_0^{\tau} \mu(u) du}, \] (6.34)

or, normalized as a PDF,
Finally, regarding the conditional probabilities, from equation (6.18),

\[
\begin{align*}
 f_{\sigma \mid \tau}(\sigma \mid \tau) &= \frac{n_0(\tau + \sigma)}{n(\tau)} = \mu(\tau + \sigma)e^{-\int_0^{\sigma} \mu(u)du} \\
&= \mu(\tau + \sigma)e^{-\int_\tau^{\tau+\sigma} \mu(u)du} \tag{6.36}
\end{align*}
\]

and

\[
\begin{align*}
 f_{\tau \mid \sigma}(\tau \mid \sigma) &= \frac{l_0(\sigma + \tau)}{l(\sigma)} = \beta(\sigma + \tau)e^{-\int_0^{\sigma+\tau} \beta(u)du} \\
&= \beta(\sigma + \tau)e^{-\int_\sigma^{\sigma+\tau} \beta(u)du} \tag{6.37}
\end{align*}
\]

Because of (6.31), the two are obviously equal.

Comparing for example the distribution (6.37) with the corresponding marginal PDF

\[
\begin{align*}
 f_{\sigma}(\sigma) &= f_{\tau}(\tau) = \frac{L}{w}e^{-\int_0^\tau \mu(u)du} \\
&= \frac{L}{w}e^{-\int_0^\sigma \mu(u)du}, \tag{6.38}
\end{align*}
\]

it becomes clear that only for constant \( \mu = \beta \), are (6.36) and (6.37) equal to their marginal distributions, thereby implying that age and survival time are statistically independent. This is essentially due to the rescaling (or memoryless) property of the resulting exponential distributions [231], which is the form taken by all these distributions in this special case (see section 6.2). In general, however, when the input and loss functions depend respectively on age and survival time, the two variables are statistically dependent, as will be shown in detail in the applications.

### 6.4.2 Mean values

In steady state, because of (6.30), the age distribution and survival distribution have same mean

\[
\bar{\tau} = \bar{\sigma}. \tag{6.39}
\]
The mean age at death and mean survival time at birth are also equal,

\[ \bar{\tau}_0 = \bar{\sigma}_0, \]  

(6.40)

while the mean transit time is then

\[ \bar{T} = 2\bar{\tau} = 2\bar{\sigma}. \]  

(6.41)

With regard to the mean transit time, by definition,

\[ \bar{T} = \frac{\int \phi(T)dT}{w} = \frac{\int T^2n_0(T)dT}{w} = \frac{1}{\bar{\tau}_0} \int \frac{T^2n_0(T)dT}{o}, \]  

(6.42)

where the last equality has been obtained by multiplying and dividing by the output \( o \).

Now, remembering that

\[ \frac{1}{o} \int T^2n_0(T)dT = \frac{1}{o} \int Tn_0(T)dT + \text{var}(\tau_0) = \frac{\bar{\tau}_0^2 + \text{var}(\tau_0)}{\bar{\tau}_0}, \]  

(6.43)

where \( \text{var}(\cdot) \) is the variance of the respective variable, then one obtains the exact relationship

\[ \bar{T} = \bar{\tau}_0 + \frac{\text{var}(\tau_0)}{\bar{\tau}_0}. \]  

(6.44)

Thus, in general, \( \bar{T} \geq \bar{\tau}_0 = \bar{\sigma}_0 \), so that \( \bar{T} \) represents an upper bound for both mean age and mean survival time. In particular, \( \bar{\tau}_0 \) equals \( \bar{T} \) only when the loss function is a Dirac delta function, for which the variance of \( T \) is zero, as in the case of a plug-flow system.

In addition, substituting expression (6.41) into the equation above, an exact link between \( \bar{\tau} \) and \( \bar{\tau}_0 \) is also obtained as

\[ \bar{\tau} = \frac{\bar{\tau}_0}{2} + \frac{\text{var}(\tau_0)}{2\bar{\tau}_0}. \]  

(6.45)
The same condition was obtained in a somewhat different way by [22]. Only in the case of \( \mu \) and \( \beta \) constant, then \( \bar{\tau} = \bar{\tau}_0 \) and \( \bar{\sigma} = \bar{\sigma}_0 \), and \( \bar{T} = 2\bar{\tau}_0 = 2\bar{\sigma}_0 \), while for a Dirac delta loss function, \( \bar{T} = \bar{\tau}_0 = \frac{\tau}{2} \).

The manner in which input and loss functions depend on age and survival time plays a key role in determining whether the mean of the age and survival time, \( \bar{\tau} \) and \( \bar{\sigma} \), are greater or lower than the mean age at death and the mean survival time at birth, \( \bar{\tau}_0 \) and \( \bar{\sigma}_0 \). For example, as already discussed by [28] and [206], in the case of a loss function \( \mu \) which selects preferably young elements leaving older element to age in the system, the resulting mean age at death is lower than the mean age in the system, i.e., \( \bar{\tau}_0 < \bar{\tau} \). On the contrary, the case \( \bar{\tau}_0 > \bar{\tau} \) is true whenever older elements tend to be chosen by \( \mu \), leaving young ones to keep the mean age low in the system, compared to the mean age at death.

6.5 Applications

We present four examples to illustrate the previously discussed theory. The first is a simple steady state system with constant birth and loss functions. The second consists of a plug-flow system in which all the elements have the same transit time. The third application is characterized by a periodicity of the age-independent loss function, while the fourth one focuses on the role of age-dependence in the loss function.

6.5.1 Linear System at Steady State

This simplest case, which represents a well-mixed system, serves as a point of reference for the more complex cases presented later. It is characterized by constant and equal birth and loss function,

\[
\mu = \beta = \eta, \tag{6.46}
\]

so that the balance equation gives
while the normalized age and survival time distributions are

\[ f_\tau(\tau) = \eta e^{-\eta \tau} \quad \text{and} \quad f_\sigma(\sigma) = \eta e^{-\eta \sigma} \quad (6.48) \]

with mean \( \bar{\tau} = \bar{\sigma} = \frac{1}{\eta} \) (see Figure 6.3). It is easy to show that the same exponential function results from (6.36) and (6.37) for the conditional PDFs, so that in these special case age and survival are statistical independent and their joint distribution is simply the product of the two distributions.

The age distribution at death (survival time distribution at birth) is simply obtained by multiplying \( n(\tau) \) by \( \eta \) \( l(\sigma) \) by \( \eta \),

\[ n_0(\tau) = \eta \theta e^{-\eta \tau}, \quad (6.49) \]

which in its normalized form is equal to the age distribution, \( f_{\tau_0}(\tau) = \eta e^{-\eta \tau}, \) and similarly with \( l_0 \) and \( f_{\sigma_0} \). The mean values are

\[ \bar{\tau}_0 = \bar{\sigma}_0 = \frac{\theta}{\sigma} = \frac{1}{\eta}. \quad (6.50) \]

The transit time distribution (Fig. 6.3) is calculated from equation (6.34),

\[ \phi(T) = T \eta n(T) = T \eta^2 e^{-\eta \tau}, \quad (6.51) \]

which, written as a PDF, becomes

\[ f_T(T) = T \eta^2 e^{-\eta \tau}, \quad (6.52) \]
an Erlang-2 distribution for the sum of two independent, exponentially distributed random variables (see Figure 6.3), with mean $\bar{T} = 2/\eta$ [60, 92].

### 6.5.2 Dirac Delta as Survival Time Distribution at Birth

While in the previous example age and survival time were statistically independent, this application takes the opposite extreme of complete (i.e., deterministic) dependence. To this purpose, we assume that the survival distribution at birth is a Dirac delta on a specific survival time $\sigma^*$, modulated sinusoidally in time,

$$l_0(t, \sigma) = A(t)\delta(\sigma - \sigma^*),$$  \hspace{1cm} (6.53)

with $A(t) = a + b\sin(\omega t)$. Because all the elements exit after the prescribed time $\sigma^*$, this example is representative of a time-dependent plug-flow system.

At the outlet, the age distribution at death $n_0$ is the time shifted $l_0$, i.e.,

$$n_0(t, \tau) = A(t - \tau)\delta(\tau - \sigma^*),$$  \hspace{1cm} (6.54)
while inside the system, the age distribution is given by

\[ n(t, \tau) = (1 - \theta(\tau - \sigma^*)) A(t - \tau), \quad (6.55) \]

where \( \theta(\cdot) \) is the Heaviside function [1]. The survival time distribution is

\[ l(t, \sigma) = (1 - \theta(\sigma - \sigma^*)) A(t - \sigma^* + \sigma), \quad (6.56) \]

while the joint distribution is given by

\[ \varphi(t, \tau, \sigma) = A(t - \tau) \delta(\sigma - \sigma^*); \quad (6.57) \]

see Figure 6.4.

The transit time distribution can be calculated from (6.25),

\[ \phi(t, T) = \int_{-\sigma^*}^{0} A(t + x) \delta(T - \sigma^*) dx = \left( a\sigma^* + \frac{b(\cos(\sigma^*\omega) - 1)}{\omega} \right) \delta(T - \sigma^*), \quad (6.58) \]

and the conditional distribution,

\[ f_{\sigma|\tau}(t, \sigma|\tau) = f_{\tau|\sigma}(t, \tau|\sigma) = \delta(\sigma - \tau - \sigma^*), \quad (6.59) \]

which reflects a deterministic relationship between age and survival, imposed by the survival distribution at birth (see Figure 6.4).

### 6.5.3 Periodic System

We now consider an extension of the first application, in which the input is constant but the loss function, although still independent of age, is now time periodic,
Figure 6.4: Joint distribution of age and survival time for time periodic plug-flow system, with boundary condition $l_0(t, \tau)$ imposed as a Dirac delta modulated by the sinusoidal amplitude in (6.53), with $a = 5$, $b = 1$ and $\sigma^* = 10$. The marginal distributions of age and survival time are also plotted on the corresponding vertical planes.

$$\mu(t) = \eta(t) = a + b \sin(\omega t + \gamma).$$ \hspace{1cm} (6.60)

From a hydrological point of view, this case is representative of a system with rainfall homogeneously distributed during the year but with seasonally modulated potential evapotranspiration and negligible other losses,

$$\frac{dw}{dt} = \iota_0 - \eta(t)w.$$ \hspace{1cm} (6.61)

The system is still well-mixed, although the transient conditions bring about additional complications that result in statistical dependence between age and survival.

Considering $t \to \infty$ so that the system has forgotten the initial conditions and has settled on a periodic steady state, the age distribution is from (6.7)

$$n(t, \tau) = t_0 e^{-\int_0^t \eta(t-\tau+u)du} = t_0 e^{-a\tau - \frac{b(\cos(\gamma + \omega(t-\tau)) - \cos(\gamma + \omega))}{\omega}},$$ \hspace{1cm} (6.62)

while the joint distribution can be obtained through equations (6.4),
\[ \varphi(t, \tau, \sigma) = \eta(t + \sigma) \eta_0 e^{-\int_{t-\tau}^{t+\sigma} \eta(u) du} = \eta(t + \sigma) \eta_0 e^{-a\sigma - a\tau - b(\cos(\gamma + \omega(t - \tau)) - \cos(\gamma + \omega(\sigma + t)))/\omega}. \quad (6.63) \]

The joint distribution is plotted in Figure (6.5) for different days of the year corresponding to the four seasons. They show that the systems has low values of age and survival for the season with high losses (summer), while when the losses diminish (winter), the age and survival start increasing again. Also visible is the asymmetry with respect to the bisector indicating statistical dependence between age and survival induced by the time-varying conditions. The age, survival time and transit time distributions are plotted in Figure 6.6.

The joint distribution integrated with respect to \( \tau \) recovers the survival time distribution \( l(t, \sigma) \). However, the integral does not appear to be elementary and here it was only solved numerically.

Finally, regarding the mean values (Figure 6.7), the loss function being age-independent, the mean age at death is equal to the mean age,

\[ \bar{\tau}_0 = \frac{\eta(t) \int_0^\infty \tau n(t, \tau) d\tau}{\eta(t) w(t)} = \bar{\tau}. \quad (6.64) \]

The mean survival time at birth \( \bar{\sigma}_0 \) was computed analytically, while the mean survival time \( \bar{\sigma} \) was computed numerically, and they appeared to be equal.

### 6.5.4 Role of Age-Dependence in the Loss Function

In this last example, we analyze the role of the loss function under conditions of steady state. As shown in section 6.4, in steady state, the age and survival time distributions are the same, and therefore similar considerations also apply to a survival-time dependence of the birth function. We consider the age-dependent loss function

\[ \mu(\tau) = \left( \frac{\tau}{c + 1} \right)^c, \quad (6.65) \]
Figure 6.5: Joint distributions, for a system with time periodic and age independent loss function (6.60), calculated at four different times of the year. $t = 15$ d (a), $t = 105$ d (b), $t = 196$ (c), $t = 288$ d (d). The parameters $a = 0.05, b = 0.025, \omega = \frac{2\pi}{365}$ and $\gamma = -\frac{2\pi}{110}$.365.

Figure 6.6: Age, survival and transit time distributions for a system with time periodic and age independent loss function (6.60), calculated at four different times of the year. $t = 15$ d (a), $t = 105$ d (b), $t = 196$ (c), $t = 288$ d (d). The parameters are the same as in Figure 6.5.
Figure 6.7: Time evolution of the mean age (age at death), mean survival time and survival time at birth and transit time for a system with time periodic and age independent loss function (6.60). The parameters are the same as in Figure 6.5.

with $c > -1$. For $-1 < c < 0$, $\mu$ is a decreasing function, thus selecting younger elements for output, while it is an increasing function of age for $c > 0$ with preference for older elements.

The age distributions for a unitary input is obtained from (6.28)

$$n(\tau) = e^{-\left(\frac{\tau}{c+1}\right)^{c+1}}$$

(6.66)

whereas the age distributions at death is

$$n_0(\tau) = \left(\frac{\tau}{c+1}\right)^c e^{-\left(\frac{\tau}{c+1}\right)^{c+1}}.$$ (6.67)

For $-1 < c < 0$, the age PDF at death is a stretched exponential distribution [246] and, as can be verified through (6.45), the mean age at death $\bar{\tau}_0$ is lower than the mean age $\bar{\tau}$. When $c > 0$, the age PDF at death is a Weibull distribution [145, 246] and the mean age at death $\bar{\tau}_0$ is greater than the mean age $\bar{\tau}$. In the limiting case $c = 0$, $\mu$ is a constant and the well-mixed system of section 6.5.1 is recovered. In addition, the plug-flow system of section 6.5.2 is recovered when taking $c \to \infty$. 

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Figure 6.8: Age distribution, age distribution at death and transit time distribution for a steady state system with age dependent loss function given by (6.65) with parameter $c = -\frac{1}{2}$ (a), $c = 0$ (b), $c = 2$ (c) and $c = 10$ (d).

Figure 6.9: Joint distribution for a steady state system with age dependent loss function $\mu$ (6.65), for $c = 0$ (a), $c = 2$ (b) and $c = 10$ (c).

For different values of $c$, the age, age at death and transit time distributions are plotted in Figure 6.8, while the joint distributions are plotted in Figure 6.9. The mean values are shown in Figure 6.10, where the mean age at death $\bar{\tau}_0$ is lower than $\bar{\tau}$ when $-1 < c < 0$, while it is larger than $\bar{\tau}$ when $c > 0$, and tends asymptotically to $\bar{T}$ for $c \to \infty$. As shown in equation (6.44), $\bar{T}$ serves as an upper bound for both mean age and mean age at death.
6.6 Conclusions

Our main results regard the evolution equation of the joint distribution function, equation (6.1), which in turn allowed us to obtain the corresponding evolution equation for age (MKVF) and survival time, given by equations (7.1) and (6.8), respectively. The theory naturally led us to consider the conditional distributions of age and survival, equations (6.17), (6.18), and (6.19), which helped us clarify some of the statements in the literature about the statistical dependence of these two quantities [58, 14]. We also obtained general relationships for the transit time distribution, equations (6.24) and (6.25), and discussed the simplifications induced by the steady state conditions; see equations (6.30), (6.27), (6.31), (6.35) and (6.37). Furthermore, we derived exact relationships among the means (6.44) and (6.45), although the latter was already known to [22].

The present theory is spatially implicit in that it considers, globally, entire populations or finite amounts of substance in a control volume [206]. Interesting future work will consist of connecting it with the spatially explicitly formulation pioneered by [103] (and further developed by [285, 58, 104, 62]), as done in the case of the MKVF equation by [13] and [206] and exploring the role of nonlinear terms and non-local effects. For example, the...
nonlinear dependence of birth and mortality on global quantities, such as $w(t)$ [110, 111], may be linked to mixing processes and the nonlocal nature of the pressure equation in fluid mechanics [203, 11]. Indeed hydrological systems are known to behave such that the loss function at a point is non-local [176]. This is often tacitly assumed in spatially implicit, event-based formulations of rainfall-runoff, which use closure assumptions that depend on the total system storage (Bartlett et al., 2015, in preparation). Finally, for realistic hydrologic applications it is necessary to include the effect of stochasticity from the external environment on the input and output functions [206]. In this case, even the mean quantities become random variables with statistical distributions that may be of great theoretical and practical interest.
Chapter 7

Multiple outflows, spatial components and nonlinearities in age theory

Further complexity in hydrologic systems derive from the presence of different outflows, such as evapotranspiration and streamflow, and from the nonlinearities in the internal transport processes. The objectives of this chapter are to extend the mathematical framework of age distribution to include multiple outflows, derive a relationship between the spatial integrated representation given by this theory and the spatially explicit dynamics describing the transport phenomena, and, lastly, discuss the possible presence and consequences of nonlinearities. The chapter is adapted from Calabrese, Salvatore, and Amilcare Porporato, ”Multiple outflows, spatial components, and nonlinearities in age theory”, Water Resources Research 53.1 (2017): 110-126.

7.1 Introduction

Age theory or residence time theory is fundamental to many fields, such as demography and population dynamics [182, 275, 210, 29], geophysics [84, 28, 168, 63, 107, 103, 71, 62], and chemical engineering [68, 191, 190]. In hydrology, estimating age and transit time of water particles has become an additional tool for understanding both the hydrologic
response to rainfall and biogeochemical reactions [215, 238, 177]. The distribution of
time spent by water within an hydrological system reveals in fact key insights into the
heterogeneity of flow pathways and mixing processes in watersheds [178, 125, 21, 176, 132].

In parallel with the advances afforded by the increasing use of tracer-aided hydrological
models [69, 124, 20, 19], much theoretical work has also been devoted to the development
of a comprehensive theory of age distribution [103, 104, 81, 31, 206, 117, 42]. While recent
contributions helped clarify the role of internal and external variability [206], the symmetry
of age and survival time under time reversal [58, 14, 42] and tackled nonlinear formulations
[266, 117, 224], some aspects of the theory are still unexplored.

The mixing processes that water undergoes during its transport throughout a watershed
strictly depend on the pathway followed by water to reach its exit (e.g., evapotranspiration,
runoff). In spatially lumped age models, this needs to be reflected in the different properties
of the age distribution at different outlets. This analysis complements the results of previous
work by [31], [266] and [117], which also considered multiple outflows. The first goal of
this paper is thus to extend the framework of age theory [42, 206] in order to account
for multiple outflows. In this regard, a new formulation of the relationship introduced by
[193] is derived. We also employ filter theory to characterize the outflows in terms of their
amplitude gain and time delays with reference to the input, depending on how water of
different ages contributes to the outflow (water age selection), and discuss the long-term
average partitioning of the fluxes.

While in spatially implicit models the complexity of the flow domain is subsumed by
an impulse-response function, e.g., the instantaneous unit hydrograph, spatially extended
models aim to solve explicitly the transport equations (e.g., see the recent review by [126]).
How to bridge the two approaches is not completely clear in the literature. A second goal of
this Chapter is then to explicitly provide this missing link between the lumped description
of a system through the age distribution and its spatially explicit dynamics. We show that
for linear systems one can readily compute the age distribution by means of the Green’s function, thus explicitly linking the spatial dynamics to age theory.

Finally, linear approximations are often not sufficient to describe properly the hydrologic system, nonlinear models need to be adopted. On the one hand, in spatially lumped age models, nonlinearities could be taken into account as dependencies of the output on the total storage or on the age distribution. This was in part addressed by [266] and [117]. On the other hand, spatially extended models might include nonlinear terms in their governing equations, even though they preclude the existence of a Green’s function. In this regard, an analysis of nonlinearities may be useful to understand when an impulse-response function can still be obtained, and to show their effects on the long term partitioning in multiple outflows systems. To our knowledge, this is still missing in the literature and represents the third goal of this Chapter.

### 7.2 Age Theory For Multiple Outflows

Given a control volume $\Omega$, the overall mass inside can be described through its age distribution $n(t, \tau)$, such that $n(t, \tau)d\tau$ represents the mass of water in $\Omega$ having age between $\tau$ and $\tau + d\tau$ at time $t$, the age being the time spent inside $\Omega$ since the entrance. The dynamics of $n(t, \tau)$ is described by the M’Kendrick-von Foerster equation [182, 275, 188, 31, 266, 42],

$$\frac{\partial n(t, \tau)}{\partial t} + \frac{\partial n(t, \tau)}{\partial \tau} = -n_0(t, \tau),$$  \hspace{1cm} (7.1)

where $n_0(t, \tau)d\tau$ is the mass of water leaving $\Omega$ at time $t$ having age between $\tau$ and $\tau + d\tau$ (age distribution at death) while the input $\iota(t)$ appears in the boundary condition, $n(t, \tau = 0) = \iota(t)$. It is possible to consider $n_0$ to be proportional to the age distribution $n$ through a mass- and age-specific output rate $\mu$ such that

$$n_0(t, \tau) = \mu \cdot n(t, \tau).$$  \hspace{1cm} (7.2)
In general, also called loss function, can be function of time \( t \), age \( \tau \), overall storage \( w \), the age distribution \( n \), as well as other variables. As we will see, when \( \mu \) depends on \( t \) and \( \tau \) the system is linear in \( n \) and a systematic theory can be formulated, whereas dependencies on \( w \) and \( n \) introduce nonlinearities. We focus first on the linear case and leave the nonlinear one for section 7.4.

In equation (7.1), \( n_0(t, \tau) \) can be considered as the sum of losses \( n_{0,i}(t, \tau) \) from \( N \) different pathways \( i (= 1, \ldots, N) \), e.g., evaporation and discharge in a watershed, with their specific loss function \( \mu_i \), such that

\[
\frac{\partial n(t, \tau)}{\partial t} + \frac{\partial n(t, \tau)}{\partial \tau} = -\sum_{i=1}^{N} n_{0,i}(t, \tau) = -\sum_{i=1}^{N} \mu_i n(t, \tau).
\] (7.3)

[117] presented a similar equation for the quantity \( N(t, \tau) = \int_{0}^{\tau} n(t, u)du \). Equation (7.3) can be solved by applying the method of characteristics along the lines \( \frac{d\tau}{dt} = 1 \) [263, 31, 206],

\[
 n(t, \tau) = \begin{cases} 
 n(0, \tau - t) \ e^{-\int_{0}^{t} \sum_{i} \mu_i(u, \tau - t + u)du} & \text{if } t < \tau \\
 \int_{0}^{\tau} n_{0,i}(t, \tau - u)du & \text{if } t > \tau.
\end{cases}
\] (7.4)

Integrating (7.3) with respect to \( \tau \), one obtains the usual form of the balance equation,

\[
\frac{dw(t)}{dt} = \iota(t) - \sum_{i} o_i(t),
\] (7.5)

where \( o_i \) is the overall outflow from the pathway \( i \), given by the integral with respect to \( \tau \) of the age distribution at death,

\[
o_i(t) = \int_{0}^{\infty} n_{0,i}(t, \tau)d\tau.
\] (7.6)

Finally, by substituting \( n_0(t, \tau) \) one obtains,
\[ o_i(t) = \int_0^\infty \iota(t-\tau)\mu_i(t,\tau)e^{-\int_0^\tau \sum_{i} \mu_i(t-\tau+u,u)d\tau} \; d\tau, \quad t \geq \tau, \] (7.7)

which shows that the flow out of a control volume \( \Omega \) can be characterized by knowing only the input \( \iota(t) \) and the loss functions \( \mu_i \).

The mass inside the control volume can be characterized also in terms of survival time (or life expectancy), corresponding to the time spent before leaving the system, such that the sum of age and survival time gives the total time \( T \) spent through \( \Omega \). The evolution equation for the survival time distribution \( l(t,\sigma) \) can be obtained by reversing time in equation (7.1) (see [42] for a more detailed derivation),

\[ \frac{\partial l(t,\sigma)}{\partial t} - \frac{\partial l(t,\sigma)}{\partial \sigma} = l_0(t,\sigma) = \beta(t,\sigma)l(t,\sigma), \] (7.8)

where \( l_0(t,\sigma) \) represents the survival time distribution at birth (elements entering the system). The link between equations (7.1) and (7.8) is established by the distributions at birth and death, \( l_0 \) and \( n_0 \) [193, 42],

\[ n_0(t,\tau) = l_0(t-\tau,\sigma = \tau). \] (7.9)

For multiple fluxes, expression (7.9) can be written as,

\[ \sum_i n_{0_i}(t,\tau) = l_0(t-\tau,\sigma = \tau), \] (7.10)

and in turn, writing in terms of the normalized distributions,

\[ \sum_i o_i(t)f_{\sigma_0,i}(t,\tau) = \iota(t-\tau)f_{\sigma_0}(t-\tau,\sigma = \tau) \] (7.11)

The right hand side of equation (7.11) can also be split as
\[
\sum_i o_i(t) f_{\sigma_0,i}(t, \tau) = \sum_i \iota(t - \tau) f_{\sigma_0,i}(t - \tau, \sigma = \tau), \tag{7.12}
\]

such that, for each pathway \(i\),

\[
n_{0,i}(t, \tau) = o_i(t) f_{\sigma_0,i}(t, \tau) = \iota(t - \tau) f_{\sigma_0,i}(t - \tau, \sigma = \tau), \tag{7.13}
\]

which extends to systems with multiple outflows the relationship introduced in [193]. Equation (7.13) establishes a link between the normalized age distribution of the output \(o_i\), and the survival time distribution of the input \(\iota\) [42]. A different formulation of (7.13) [31] allows to determine the fraction of mass entered at time \(t - \tau\), exiting the system through the pathway \(i\), which was given the name of "partition function".

By inserting (7.13) into (7.6) one obtains

\[
o_i(t) = \int_0^\infty n_{0,i}(t, \tau) d\tau = \int_0^\infty \iota(t - \tau) f_{\sigma_0,i}(t - \tau, \sigma = \tau) d\tau, \tag{7.14}
\]

where, by comparing with (7.7),

\[
f_{\sigma_0,i}(t - \tau, \tau) = \mu_i(t, \tau)e^{-\int_0^\tau \sum_i \mu_i(t - \tau + u) du}. \tag{7.15}
\]

Expression (7.14) shows that the outflow \(o_i\) from the pathway \(i\) is given by the convolution of the input \(i\) and the normalized survival time distribution at birth \(f_{\sigma_0,i}(t - \tau, \tau)\). The latter, which thus represents the impulse-response function for the specific pathway \(i\), provides a lumped representation of the complex structure and heterogeneity of all the pathways followed by the substance to reach the outlet.
7.3 Linear systems

7.3.1 Spatially Implicit Case ($\tau$-Dependent Loss Function)

Consider a hydrological system in which the input is represented by rainfall $R$ with outflows given by evaporation, $E$, and discharge, $Q$. For both outflows we assume a power-law form of the loss function,

$$
\mu_E(\tau) = \gamma \left( \frac{\tau}{1 + c_E} \right)^{c_E} \quad \text{and} \quad \mu_Q(\tau) = (1 - \gamma) \left( \frac{\tau}{1 + c_Q} \right)^{c_Q}
$$

(7.16)

where the parameters $c_E$ and $c_Q$ control the selection of water according to its age $\tau$, while $\gamma$ weighs the two loss functions. Expressions (7.16) are decreasing functions of $\tau$ when $-1 < c_{E,Q} < 0$, privileging the exit of younger water, while they are increasing, preferring older water, when $c_{E,Q} > 0$. In the limiting case of $c_{E,Q} = 0$ and $c_{E,Q} \to \infty$ the system becomes a well-mixed ($\mu = 1$, age-independent loss function) and a plug-flow system, respectively. Loss functions as (7.16) or the similar ones used by [31], [117] and [14], when prescribed a priori without reference to a physical description, are conceptual representations of a hydrologic system. These may however be useful to explore different types of water age selection by varying their parameters and in practical applications they can be calibrated used experimental approaches (e.g., tracers). As it will be shown in Section 7.3.2, a physical basis can be assigned to the loss function in a linear system, by working out the link between spatially explicit and implicit dynamics.

Steady state age distributions are illustrated in Figure 7.1 for different values of $c_E$ and $c_Q$. The age distribution assumes very different shapes, ranging from stretched exponential, when both $c_E$ and $c_Q$ are negative (young water selection), to Weibull distributions when $c_E$ and $c_Q$ are positive (old water selection) [145, 246, 66].

As shown in (7.7), the fluxes of evaporation $E$ and discharge $Q$ are computed by convolving the input and the respective impulse-response functions $f_{\sigma_0,E}(\tau)$ and $f_{\sigma_0,Q}(\tau)$,
Figure 7.1: Steady state age distributions computed from equation (8.4) for the system in section 7.3.1 for different values of $c_E$ and $c_Q$. The distributions are calculated with $\iota = 6$ and $\gamma = 0.5$.

Expressions (7.17) and (7.18) suggest that, for linear systems, time variability in the impulse-response functions can be acquired only from time variability in the loss function $\mu$. Therefore, as long as $\mu$ does not contain time variability, a system can be considered to be time invariant.

In real applications, the impulse response functions can be estimated by means of environmental tracers [178, 20]. However, due to the fact that the length of data record is finite and does not cover the all range of possible ages, it is convenient to assume a distribution a priori and use the tracer data to calibrate the parameters, for example $c_E$ and $c_Q$ in (7.17) and (7.18). Note however that as shown in (7.15), the impulse response function for an outflow $i$ depends not only on the loss function for the outflow $i$, but on all the $N$ loss functions corresponding to the $N$ different outflows. Thus, in practical applications one
needs to assign a parametric loss function to each outflow, use equation (7.15) to derive the impulse response functions and then use tracer data to estimate the parameters. Considering for example expressions (7.17) and (7.18), only data on one outflow are necessary, e.g. discharge, to estimate $c_E$ and $c_Q$, so that also the impulse response function for $E$ is directly obtained.

Analysis of Amplitude Response and Delays

When a time invariant system is driven by a stationary time-varying input, the outflows may be conveniently analyzed in the Fourier domain, directly showing how the system filters and modulates the input signals given by rainfall into different outputs. For a linear, time-invariant hydrologic system, expression (7.14) for the output reduces to

$$O_{E,Q}(t) = \int_0^\infty R(t-\tau)f_{\sigma_0 E,Q}(\tau)d\tau, \quad (7.19)$$

where $f_{\sigma_0 E,Q}(\tau)$ takes the form of the instantaneous unit hydrograph [242, 77, 189, 207]. More insights on the relationship between output and input can be obtained by computing, in the frequency domain, the amplitude gain and time delay of the outflow, $E$ and $Q$, with respect to the input $R$. Thus, calling $H$ the Fourier transform of $f_{\sigma_0 E,Q}(\tau)$, the amplitude gain and time delay can be computed as

$$\Gamma_{E,Q}(\omega) = |H_{E,Q}(\omega)|, \quad (7.20)$$

and

$$t_{d E,Q}(\omega) = -\frac{\arg(H_{E,Q}(\omega))}{\omega} = -\frac{1}{\omega}\tan^{-1}\left(\frac{\Im H_{E,Q}(\omega)}{\Re H_{E,Q}(\omega)}\right), \quad (7.21)$$

$\Im H_{E,Q}(\omega)$ and $\Re H_{E,Q}(\omega)$ being the imaginary and real part of $H_{E,Q}(\omega)$, respectively. At every frequency $\omega$, $\Gamma(\omega)$ expresses the relative change in amplitude between outflow and input signal, while the time delay $t_d(\omega)$ represents the temporal delay of the system.
Figure 7.2: Time evolution of Rainfall, modeled as a marked Poisson process, and the total outflow, \(E + Q\), for the system in Section 7.3.1 calculated for \(c_E = c_Q = -0.8\) and \(c_E = c_Q = 2\). Rainfall event frequency \(\lambda = 0.4\) (event/day), mean rainfall depth \(\alpha_r = 15\) and \(\gamma = 0.5\).

response (see Appendix D for details). These functions help identify typical responses of systems with different age selections.

For example, considering a single outflow system, Figure 7.2 compares the response of two systems with power law loss functions as in (7.16) with values of \(c\) chosen purposely to represent a young and an old water selection. The stationary input is instead represented by the series of rainfall \(R(t)\), which is idealized as an homogeneous Poisson process with mean frequency \(\lambda\) and exponentially distributed jumps of mean \(\alpha_r\). As can be seen in Figure 7.2, the two outflow series are markedly different. In the case of young water selection, the system has quicker responses to rainfall pulses which have however more regular intensity in time, as opposed to the case of old water selection in which systems respond with higher time delays and show higher fluctuations in the intensity.

Long-term Partitioning

It is also interesting to analyze the partitioning of long term average fluxes, still considering \(R\) a stationary time-varying input. Using the example of equation (7.16), here we focus on
the role of the coefficient $\gamma$ and the age selection parameters $c_E$ and $c_Q$. Averaging equation (7.5) and assuming the existence of a steady state, the long-term averaged balance equation is

$$\overline{R} - \overline{E} - \overline{Q} = 0,$$

(7.22)

where $\overline{(\cdot)} = \lim_{T \to \infty} \frac{1}{T} \int_0^T (\cdot) dt$ stands for the time-averaging operator. The mean evaporation flux $\overline{E}$ is then obtained as,

$$\overline{E} = \int_0^\infty R(t - t)f_{\sigma_0,E}(\tau) d\tau = \overline{R} \int_0^\infty \gamma \left( \frac{\tau}{1 + c_E} \right)^{c_E} e^{-\gamma \left( \frac{\tau}{1 + c_E} \right)^{c_E+1} - (1-\gamma) \left( \frac{\tau}{1 + c_Q} \right)^{c_Q+1}} d\tau.$$

(7.23)

Since the impulse-response function is time invariant, the average operator applies only to the input $R$. $\overline{E}$ is plotted in Figure 7.3 as a function of the partitioning coefficient $\gamma$ for $c_E = c_Q$, $c_E > c_Q$, and $c_E < c_Q$. For the specific case in which the two loss functions are equal, $\overline{E}$ is linear with respect to both $\gamma$ and $R$, $\overline{E} = \overline{R}\gamma$. Figure 7.3 also shows that the selection of younger elements ($c_E = -0.8$) increases the average flux, except for high values of $\gamma$. This behavior is due to the fact that at high values of $\gamma$, the system has a very low storage of young water, increasing the portion of old water. In turn, the availability of old water for the pathway $Q$ increases. In order to analyze the effect of age selection, Figure 7.3 also shows the mean partitioning as a function of the parameter $c_E$ and $c_Q$, while $\gamma$ is kept constant. For $c_E = c_Q$, as expected, rainfall is equally distributed among $E$ and $Q$. As $c_Q$ grows with respect to $c_E$, the fraction of water leaving through evaporation $E$ increases except for very low values of $c_E$ and $c_Q$ ($\approx -1$) for which the situation is reversed.
7.3.2 Spatially Explicit Dynamics and Green’s function

In the previous description we showed that, in spatially implicit formulations, the loss function contains a projection of the flow field. As shown in (7.15), the impulse-response function $f_{\sigma_0}$ in turn depends on the choice of the functional form of $\mu$. Therefore, a good approximation of $f_{\sigma_0}$ can be given by estimating correctly $\mu$. When the spatial dynamics is explicit, the loss function can be directly computed from the governing equations, at least in the case of linear systems.

For linear differential equations, the system’s response to an input signal is given locally by the convolution of the input $i(x, t)$ and the Green’s function of the system,

$$ q(x, t) = \int_0^\infty i(x, t - \tau)q^*(x, t, \tau)d\tau. \quad (7.24) $$

The latter is found by solving the equation with initial condition $q(x, 0) = \delta(x)$ (unitary impulse) and represents thus the impulse-response function of the system [185]. Spatial integration of equation (7.24) over a control volume $\Omega$ gives
\[ q_\Omega(t) = \int_0^\infty \iota(t - \tau)q^*_\Omega(t, \tau) d\tau. \quad (7.25) \]

By analogy with (7.14), \( q^*_\Omega(t, \tau) = f_{\sigma_0,i}(t - \tau, \tau) \), so that the loss function \( \mu_\Omega(t, \tau) \) can be computed from

\[ q^*_\Omega(t, \tau) = \mu_\Omega(t, \tau)e^{-\int_0^\tau \mu_\Omega(t-\tau+u,u) du}, \quad (7.26) \]

as

\[ \mu_\Omega(t, \tau) = -\frac{d\ln(1 - \int_0^\tau q^*_\Omega(t - \tau + u, u) du)}{d\tau}. \quad (7.27) \]

Also, (7.27) can be generalized to multiple outflows systems as,

\[ \mu_{\Omega,i}(t, \tau) = \frac{q^*_{\Omega,i}(t, \tau)}{1 - \int_0^\tau \sum_i q^*_{\Omega,i}(t - \tau + u, u) du}. \quad (7.28) \]

Details of the derivation are shown in Appendix D. Once the loss function \( \mu_\Omega(t, \tau) \) is known, the age distribution for the control volume \( \Omega \) can be calculated from equation (7.3).

Consider for example a one dimensional spatial dynamics in which the substance \( C \) is transported by convection and diffusion and withdrawn by a linear, distributed sink. The governing equations read

\[ \frac{\partial C}{\partial t} + \frac{\partial q}{\partial x} = -\phi, \quad (7.29) \]

and

\[ q = vC = \alpha C - D \frac{\partial C}{\partial x} \quad \text{and} \quad \phi = \eta C, \quad (7.30) \]

where \( \alpha, D \) and \( \eta \) are the convection velocity, the diffusion coefficient and the specific withdrawal rate, respectively. Equations (7.29) and (7.30) may be interpreted as the
transport equation of a solute $C$ undergoing a first order decay with rate $\eta$ while it is advected by a constant velocity $\alpha$ and diffused with constant $D$ [121, 241]. Considering an unsaturated porous medium and interpreting $C$ as its volumetric water content, (7.29) may also be interpreted as the linearized equation for infiltration. In particular, assuming a hydraulic conductivity $K(\psi) = K_s e^{\alpha \psi}$ and a retention curve $C(\psi) = (C_s - C_r) e^{\alpha \psi} + C_r$, Richard’s equation reduces to (7.29), in which $\alpha = \frac{dK}{dC}$ and $D = \frac{1}{a} \frac{dK}{dC}$ are both constant [279, 10, 52]. Lastly, equation (7.29) approximates the de Saint Venant equations for open channel flows in the case of a prevailing linear kinematic wave undergoing diffusion [120], and linear losses to the hyporheic zone. Its hydrological relevance along with its analytical tractability motivated the use of equation (7.29) as an application of result (7.28). The impulse-response function for equation (7.29) without the sink term $\phi$ was calculated by [13] in the presence of a reflecting and an absorbing barrier. Here we compute it including the sink $\phi$ and in absence of barriers, and then derive by means of equation (7.28) the corresponding loss functions $\mu$ for $q$ through the control volume and the sink $\phi$.

We consider the domain of $C(x, t)$ to be infinite, i.e., $-\infty < x < \infty$, and fix a control volume (segment) $\Omega$ about the origin, $-L < x < L$. For such a control volume, the input $\iota(t)$ is considered to be concentrated at the origin while the outputs are obtained by calculating $q$ at the boundary and by integrating the sink term $\phi$ over $\Omega$. Thus again there are two outputs and this allows us to analyze the reciprocal effect of the two terms, $q$ and $\phi$. The impulse-response functions $q^*$ and $\phi^*$ can be calculated by solving equation (7.29) with initial condition $C(x, 0) = \delta(x)$, substituting the solution into (7.30) and then integrating over $\Omega$. The details are provided in Appendix D. Figure 7.4 shows the solution of equation (7.29) and the impulse-response functions $q^*$ and $\phi^*$. While $\phi^*$ decreases monotonically in time with $h$, due to the fact that it is a linear function of $C$, the impulse-response function $q^*$ has a maximum when the peak of $C(x, t)$ reaches the boundary.
Figure 7.4: (a) Solution of equation (7.29) for \( t = 10 \) and \( t = 20 \), (b) impulse-response functions \( q^*(t) \) and \( \phi^* \), (c) loss functions for \( q \) and \( \phi \) and (d) age distribution for the control volume \( \Omega \). Advection coefficient \( \alpha = 0.5 \), diffusion coefficient \( D = 0.1 \) and \( \eta = 0.05 \).

The loss functions \( \mu_q \) and \( \mu_\phi \) can be derived by comparing the impulse-response functions calculated from the Green’s functions, \( q^*(t) \) and \( \phi^*(t) \), with expressions \( f_{\sigma_0,q} \) and \( f_{\sigma_0,\phi} \). In particular, from equation (7.28), the two loss functions can be computed as

\[
\mu_q(\tau) = \frac{q^*(\tau)}{1 - \int_0^\tau (q^*(u) + \phi^*(u))du}, \quad (7.31)
\]

and

\[
\mu_\phi(\tau) = \frac{\phi^*(\tau)}{1 - \int_0^\tau (q^*(u) + \phi^*(u))du}. \quad (7.32)
\]

These are shown in Figure 7.4c. As expected, the linear withdrawal \( \phi \) does not depend on \( \tau \), thus behaving as a well-mixed system, whereas the outflow \( q \) shows a preference for old elements.

A synthetic description of the filtering process of the input signal through \( \Omega \) can again be given in the frequency domain by calculating amplitude gain \( \Gamma(\omega) \) and time delay \( t_d(\omega) \) for the two outflows \( q \) and \( \phi \). The results are shown in Figure 7.5. By comparison with Figure D.1, we can readily recognize that \( q \) has a typical old water selection behavior with
higher time delays and fast decaying (with $\omega$) amplitude gain, whereas $\phi$ shows a well-mixed behavior.

Other interesting applications of this type of analysis can be found in the hydrological context; for example the modeling studies of groundwater age in steady [58] or transient flow [270], where different types of aquifers can be considered [273, 274], including also multi-domain configurations with exchange [104], and non-Fickian dispersion [83].

### 7.4 Role of Nonlinearities

The generality of the theory outlined above is lost in the presence of nonlinearities. A general solution of the M’Kendrick-von Foerster equation cannot be obtained and only case-specific solutions are available. As it is shown through this Section, only in the case of $w$-dependent loss function does the impulse response function exist, whereas the use of other nonlinear loss functions to formulate a convolution integral (e.g. [266, 117]) is not guaranteed to be successful, apart from special cases.

For spatially implicit formulations (Section 7.4.1 and 7.4.2), nonlinearities may be introduced when the loss function $\mu$ depends on the total substance $w$ or on the age distri-
bution $n$. The Burgers’ equation is also analyzed in Section 7.4.3 to discuss the role of nonlinearities in a spatially explicit case.

### 7.4.1 $w$-Dependent Loss Function

Consider initially the simpler case of a loss function dependent only on $w$, $\mu(w(t))$. This situation is very typical in hydrological and ecohydrological models, where the discharge of watersheds is often assumed nonlinearly dependent on the total storage [229, 147, 230, 50, 175, 8]. Equation (7.5) for the total water storage is nonlinear and reads

$$\frac{dw(t)}{dt} = \iota(t) - \mu(w(t))w(t). \quad (7.33)$$

On the contrary, the equation for the age distribution (7.3) remains linear in $n$; as a consequence it is still generally solvable as

$$n(t, \tau) = \iota(t - \tau)e^{-\int_{0}^{\tau} \mu(w(t-\tau+u))du} \quad t \geq \tau, \quad (7.34)$$

and admits an impulse-response function given by (7.15). However, due to its dependency on the history of $w(t)$, equation (7.34) requires the simultaneous solution of (7.33), so that closed analytical forms are available only in special cases [110, 111]. From an age selection point of view, (7.33) and (7.34) represent a time-varying, well-mixed system, which selects uniformly water of different age at a variable rate based on $w$. In a sense, this case thus resembles the time-varying example discussed in [42], Section 6.5.3, with a loss function $\mu = \eta(t)$.

A more detailed picture can be obtained by considering an example using the specific functional form of $\mu(w(t))$ of the type

$$\mu = \eta w^{\beta}, \quad (7.35)$$
for which the age distribution is

\[ n(t, \tau) = \iota(t - \tau) e^{-\int_0^\tau \eta w(t - \tau + u) du} \quad t \geq \tau. \]  

(7.36)

During transient conditions, the dependency on \( w \) introduces time variability such that, as said above, the system behaves as a time-varying, well-mixed one. Similarly, the system has a time-variant impulse-response function given by

\[ f_{\sigma_0,\iota}(t - \tau, \tau) = \eta w^\beta e^{-\int_0^\tau \eta w(t - \tau + u) du} \quad t \geq \tau. \]  

(7.37)

When \( \beta \to 0, \mu \to \eta \), the system becomes a classical well-mixed one with exponential age distribution \( n(t, \tau) = \iota(t - \tau) e^{-\eta \tau} \) and impulse-response function \( \eta e^{-\eta \tau} \) [42]. Also, as \( t \to \infty \), the total storage and the loss function become constant, \( w(t) \to w_\infty \) and \( \mu = \eta w^\beta \to \xi \). The time-invariant well-mixed system is thus again recovered, with exponential age distribution \( n(\tau) = \iota e^{-\xi \tau} \) and impulse-response function \( f_{\sigma_0,\iota}(\tau) = \xi e^{-\xi \tau} \). It is however important to note that, although the output can be written as a \( \tau \)-integral of the input and the impulse-response function (7.37) as in linear cases, the systems still behaves nonlinearly. This can be seen from the sink term in (7.33),

\[ o(t) = \mu(w)w = \eta w^{\beta + 1}. \]  

(7.38)

which clearly shows the nonlinear dependence of the output on \( w \).

### 7.4.2 \( n \)-Dependent Loss Function

We next consider the fully nonlinear case of a loss function \( \mu \) dependent on \( n \). In this case, each element has a probability to leave the system which also depends on the storage within its age category \( (\tau, \tau + d\tau) \). The papers by [266] and [117], although expressing equation
(7.3) in a cumulative form, also defined loss functions which depend on the (cumulative) age distribution.

From a mathematical point of view, both the equations for the total storage (7.5) and the age distribution (7.3) are nonlinear,

\[
\frac{dw(t)}{dt} = \nu(t) - \int_0^\infty \mu(n(t, \tau))n(t, \tau) d\tau, \tag{7.39}
\]

and

\[
\frac{\partial n(t, \tau)}{\partial t} + \frac{\partial n(t, \tau)}{\partial \tau} = -\mu(n(t, \tau))n(t, \tau), \tag{7.40}
\]

so that the output is no longer a convolution of the input and an impulse-response function. Also, the dependency on \( n \) implicitly introduces an age selection, which will depend on the functional form of \( \mu(n) \). This can be illustrated by considering the case

\[
\mu(n) = \eta n^\beta. \tag{7.41}
\]

With this choice of loss function, equation (7.40) is still analytically solvable,

\[
n(t, \tau) = \left(\nu(t - \tau)^{-\beta} + \beta \tau \eta\right)^{-1/\beta}, \quad t \geq \tau, \tag{7.42}
\]

and from (7.6)

\[
o(t) = \int_0^\infty \eta \left(\nu(t - \tau)^{-\beta} + \beta \tau \eta\right)^{-\beta + 1/\beta} d\tau. \tag{7.43}
\]

In steady state conditions, expression (7.42) takes the form of a generalized Pareto distribution with shape and scale parameter \( \zeta = \frac{\beta}{1-\beta} \) and \( \sigma = \frac{1}{(1-\beta)\eta^\beta} \), respectively. In the limit of \( \beta \to 0 \), (7.42) reduces to an exponential distribution \( n = \nu e^{-\eta \tau} \) (well-mixed), whereas when \( \beta < 0 \), \( n \) is given by (7.42) for \( \tau < -\frac{e^{-1/\beta}}{\eta^\beta} \) while is \( n = 0 \) elsewhere, resulting in a discontinuity at \( \tau = -\frac{e^{-1/\beta}}{\eta^\beta} \). This is shown in Figure 7.6, where steady state
distributions are plotted for different values of the parameter $\beta$. In particular as $\beta$ increases the age distribution becomes the typical one of a system with young water selection, with a heavier tail than the one observed for systems with old water selection or well-mixed. From (7.43) one can also see that the output has no longer the form (7.14) nor it is a convolution. Figure 7.7 in fact shows the time evolution of the output (7.43) for a system which starts from an initial condition $n(0, \tau) = 0$ and proceeds with constant input $\iota$. In particular, the output is calculated for two values of the input, $\iota_1$ and $\iota_2 = 2 \cdot \iota_1$. The nonlinear response is evident especially at the beginning of the transient, where the two calculated outputs are not proportional.

Another interesting effect of nonlinearities in $w$ and $n$ can be seen in the long-term partitioning. To this purpose, consider a system driven by a sinusoidal input,

$$\iota(t) = R_0 + A \sin \left( \frac{2\pi t}{T} \right),$$

(7.44)

being $A$ the wave amplitude and $T$ the period, and characterized by two outflows, $E$ and $Q$. Assuming the same form of $\mu$ for $E$ and $Q$, we compute, similarly to Section 7.3.1, the long term average $\bar{E}$ for the loss functions.
Figure 7.7: Time evolution of the outputs $o_{i=1}$ and $o_{i=2}$, computed from (7.43), for a system driven by constant inputs $i = 1$ and $i = 2$, respectively. The system transits from initial condition $w(0) = 0$ towards steady state. Parameters $\eta = 0.2$ and $\beta = 2$.

\[
\mu_{E,Q}(w) = \eta_{E,Q} w^{\beta_{E,Q}} \quad \text{and} \quad \mu_{E,Q}(n) = \eta_{E,Q} n^{\beta_{E,Q}}.
\] (7.45)

Figure 7.8 shows the nonlinear behavior of the long-term flux mean $\overline{E}$ as a function of $R_0$ for systems with $w$-dependent and $n$-dependent loss functions, $\mu(w)$ and $\mu(n)$, compared to the case of linear systems with $\tau$-dependent loss functions (Section 7.3.1) where the mean flux $\overline{E}$ is a straight line.

### 7.4.3 Nonlinear Spatially Explicit Dynamics

Finally, we focus on the effects of nonlinearities in spatially explicit dynamics, by analyzing the Burgers’ equation [292],

\[
\frac{\partial C}{\partial t} + (\alpha + \beta C) \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0,
\] (7.46)

a well-known nonlinear form of the advection diffusion equation in which the flux is given by

\[
q = vC = \alpha C + \frac{\beta}{2} C^2 - D \frac{\partial C}{\partial x}.
\] (7.47)
Figure 7.8: Long term average evaporation flux $\overline{E}$ as a function of mean rainfall $R_0$, calculated for the loss functions (7.45) with $\eta_E = \eta_Q = 0.5$, $\beta_E = 0.5$ and $\beta_Q = 1$. The system has the sinusoidal input in (7.44) with $A = 0.1$ and $T = 365$. The dashed line refers to the $\tau$-dependent case.

Figure 7.9: Solutions (D.21) of the Burgers equation for different initial conditions $C(x,0)$. $\alpha = 0.5$, $D = 0.1$ and $\beta = 1$. 

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Figure 7.10: Response function to an unitary impulse for the Burgers equation, calculated for different values of the parameter $\beta$. Control volume $L = 20$, $\alpha = 0.5$, $D = 0.1$.

Due to its similarity with the Navier Stokes equations, (7.46) was originally presented as a simple model of gas turbulence [39], and is still widely used as a minimalistic turbulence model [137, 4, 95]. In infiltration theory, equation (7.46) corresponds instead to a simplified form of the Richard’s equation with constant water diffusivity and hydraulic conductivity that depends quadratically on the soil water content [200, 55, 244]. Thanks to the possibility to obtain an analytical solution through the Cole-Hopf transformation [292], (7.46) may be considered a prototypical example for the study of nonlinearities in spatially explicit systems. A comparison with the linear advection diffusion is also possible as this is recovered by setting $\beta$ to zero in (7.46).

For an impulse given as initial condition $C(x, 0)$, the solution of (7.46) is

$$C(x, t) = -\frac{2D}{\beta} \frac{\partial}{\partial x} \ln \left[ \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} \exp \left( -\frac{(x - x')^2}{4Dt} - \frac{1}{2D} \int_{0}^{x'} (C(u, 0) + \alpha) du \right) dx' - \frac{\alpha}{\beta} \right].$$

(7.48)

The calculations are developed in Appendix D. From (7.48) it is evident that $C(x, t)$ is nonlinearly dependent on the initial condition $C(x, 0)$. Therefore different values of
impulse amplitudes do not generate proportional profiles of \( C(x, t) \). Similarly to Section 7.3.2, when a control volume \( \Omega \) is fixed, the response in terms of flux out of \( \Omega \) can be computed by spatial integration of (7.47) over \( \Omega \). Again, Figure 7.9 clearly shows how the response to different impulses is not proportional to the unitary response, as it was instead for linear differential equations. Figure (7.10) also illustrates the flux out of a fixed control volume as the parameter \( \beta \) varies. For the case \( \beta = 0 \), the solution \( q^* \) discussed in Section 7.3.2 is recovered while as \( \beta \) increases the nonlinearity predominates. This last example shows explicitly how the concept of the impulse-response function does not apply to nonlinear, spatially explicit systems, thus preventing the possibility of an expression equivalent to (7.28). The Green’s function, i.e., impulse response function for spatial dynamics, does not in fact exist, so that a general relationship with the spatially implicit dynamics cannot be established.

Interesting developments may be foreseen when extending the spatially explicit balance equation for the local, age-specific concentration, \( c(x, t, \tau) \), formulated by [103] for linear transport equations, to \( \tau \)-dependent or \( c \)-dependent transport of scalars, as well as when linking local forms of the loss function to nonlinear, spatially explicit dynamics.

### 7.5 Conclusions

The age theory was extended to systems with multiple outflows. A reformulation of the relationship introduced by [193] was also provided (equation (7.13)). This showed that for each pathway the outflow is a convolution of the input and a path-specific impulse-response function. Spectral analysis allowed us to determine the outflow amplitude gain and time delay typical of young and old water selection (Section 7.3.1). The long term average fluxes partitioning as a function of the water age selection was also illustrated. With regard to linear spatially explicit dynamics, we presented an exact relationship (equation (7.28))
to calculate for a control volume the loss function and the age distribution from the Green’s function.

The role of nonlinearities was also discussed in Section 7.4. We showed that although $w$-dependent loss functions increase the analytical complexity of the coupled equations for $w$ and $n$, a time variant impulse response function still exists in such cases. On the contrary for $n$-dependent loss functions and for systems described by nonlinear partial differential equations, the theory loses its generality and the concept of impulse-response function is not generally applicable.
Chapter 8

Age distribution dynamics with stochastic jumps in mortality

Despite age distribution models have been extensively studied and applied in various disciplines, little work has been devoted to understand the role of stochastic terms in the birth and mortality terms. While stochastic inputs were analyzed in chapter 2, the effect of stochastic mortality terms in the form of jumps is explored in this chapter, which is adapted from Calabrese, Salvatore, et al., ”Age distribution dynamics with stochastic jumps in mortality”, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences 473.2207 (2017): 20170451.

8.1 Introduction

Estimating the residence time (or age) of a substance within a control volume has been of interest since early studies in chemical engineering [150, 68]. The mathematical formalism however was mostly developed subsequently in the population dynamics context, where birth and death processes are expressed as explicit functions of age [160, 182, 275]. Many authors, interested in finding the age distribution of a substance within a system, then refined the theoretical framework in both its linear [263, 136, 144, 188] and nonlinear
formulations [110, 111, 280]. Such age distribution models have proven useful in different disciplines, e.g., to describe the age distributions of stars in galaxies [158, 85], to determine water quality in surface and subsurface systems [103, 104, 81, 31, 43], as well as to model the dynamics of plant populations [276, 156, 33]. Further applications ranged from the interpretation of isotopic data to determine the age of continental crusts [73] and soils [116] to the analysis of cancer statistics [197].

While many of the systems where age distribution is important are subject to fluctuations originated by randomness in the birth or death processes, little attention has been devoted to the effect of such random components on age distributions. On the one hand, birth may be characterized by random reproduction mechanisms, which are modeled by means of branching processes [129, 130], or it may be given by a time-varying stochastic process independent of the age distribution (e.g., rainfall for a watershed in which the water age is being tracked) [206]. On the other hand, random mortality may arise as abrupt jump losses of population due to external events [114, 148, 115, 149]. A few examples are the dynamics of soil formation affected by landslides [76], the growth of riparian vegetation disturbed by floods [46], the dynamics of soil salinity in which salt is flushed away by leaching events [174], and the growth of biomass in forested ecosystems hit by fires [66]. The existence and uniqueness of the solution for stochastic age distribution models applicable to problems previously listed have been proven [213], and some numerical schemes for their solutions introduced [181, 195, 278, 254]. However, to our knowledge no work has been devoted to the derivation of analytical solutions that would allow one to identify explicitly the role of the stochastic mortality and the different parameters on the age distribution of the population.

Our goal is hence to analyze the age distribution dynamics with stochastic jumps in mortality. In particular, we consider the M’Kendrick-von Foerster equation [182, 275] with the addition of a stochastic loss term in the form of Poisson jumps multiplied by the state of the system (i.e., age distribution). Having in mind systems in which the input is not
due to reproduction mechanisms within the population, we assume that the input (birth) is a given function of time and independent of the age distribution. Our results include analytical transient solutions for the probability density function of age distribution and total population. We also analyze the dynamics of the moments of the age distribution, the total population, and the mean age. The results are then extended to the case in which also the input is random. As an application, we calculate the age distribution of salt in the soil root zone. Over long timescales, the mass of salt contained in the root zone is the result of a balance between the input by atmospheric deposition, the uptake rate by plants, and the random occurrence of percolation events which cause downward jumps of salt mass [259, 174]. We here use the dynamics of salt in soils as a prototypical example, but similar dynamics apply to other soil nutrients and contaminants [230, 171].

The remainder of the manuscript proceeds as follows. Section 8.2 presents the differential equations governing the dynamics of the age distribution, the total population and the mean age, while Section 8.3 shows the corresponding analytical solutions. The work is then extended to the case of random input in Section 8.4. Lastly, in Section 8.5 we apply the theory to the salt dynamics in the root zone. We conclude in Section 8.6 by summarizing the results and by highlighting possible extensions of this work.

### 8.2 Mathematical Framework

Given a system $\Omega$, we define the age $\tau$ of each element as the time elapsed since it entered $\Omega$. The population of $\Omega$ can be described in terms of the age distribution $n(t, \tau)$, such that $n(t, \tau)d\tau$ is the number of elements having age between $\tau$ and $\tau+d\tau$ at time $t$, and $\int_0^\infty n d\tau = w$ is the total population. The temporal dynamics of $n$ is governed by the M’Kendrick-von Foerster equation [182, 275],

$$\frac{\partial n}{\partial t} + \frac{\partial n}{\partial \tau} = -n_0,$$  \hspace{1cm} (8.1)
in which \( n_0(t, \tau) \) represents the age distribution of the elements leaving \( \Omega \) and its integral with respect to \( \tau \) yields the total output, \( o(t) = \int_0^\infty n_0 d\tau \). The age distribution of the output can be expressed as \( n_0 = \mu n \), where \( \mu \) is a specific output (mortality) rate \( \mu \), also called loss function. In general, the latter can be function of \( t, \tau, w, n \) and so on; however, we limit our analysis to cases where the output rate is only function of time and age, i.e., \( \mu = \mu(t, \tau) \).

To introduce the stochasticity in the mortality term, we assume \( \mu(t, \tau) \) to be composed of a deterministic term \( \mu_d(t, \tau) \) and a random term \( \nu(t) \), \( \mu(t, \tau) = \mu_d(t, \tau) + \nu(t) \). In particular, we assume that \( \nu(t) \) is a shot noise given by the time derivative of a marked Poisson process, \( \nu(t) = \sum_{i=1}^{N_t} h_i \delta(t - t_i) \), in which \( h_i \) is the size of the \( i \)-th jump, \( t_i \) its time of occurrence, and \( N_t \) the number of jumps occurred up to time \( t \) [221]. The frequency of the jumps is \( \lambda \), whereas their marks \( h_i \) are assumed to be exponentially distributed with mean \( \gamma^{-1} \). With these assumptions, the M’Kendrick-von Foerster equation becomes a stochastic equation (capital letters indicate random variables),

\[
\frac{\partial N}{\partial t} + \frac{\partial N}{\partial \tau} = -\mu_d(t, \tau)N - \nu(t) \circ N, \tag{8.2}
\]

in which the symbol \( \circ \) indicates that the multiplication of the noise \( \nu \) (white noise) by \( N \), which is now a random function, is interpreted in the Stratonovich sense. This interpretation results from taking the zero limit of the time scale of the colored noise term and has the advantage that the rules of calculus hold [253, 100, 258, 51]. Equation (8.2) has initial condition \( N(t = 0, \tau) \) and boundary condition \( N(t, \tau = 0) = \iota(t) \), the input to \( \Omega \).

By introducing the variables \( \eta = \tau \) and \( \xi = t - \tau \), equation (8.2) reduces to an ordinary differential equation,

\[
\frac{dN}{d\eta} = -\mu_d(\xi + \eta, \eta)N - \nu(\xi + \eta) \circ N, \tag{8.3}
\]

which for a single realization of the stochastic process can be solved in the Stratonovich prescription by classical integration. The solution in the original variables reads [263, 136,
At time $t = \xi$ the population $i$ enters the system with age $\eta = 0$ and starts decaying along $\eta$ due to the deterministic and stochastic (jumps) mortality.

Along the characteristic lines $\eta$, given by $\frac{dt}{d\eta} = 1$ and $\frac{d\tau}{d\eta} = 1$, the population evolves deterministically, according to an exponentially decay at rate $\mu$, and is perturbed by instantaneous jumps that cause abrupt losses of population. See Figure (8.1) for an example of a realization of such a process.

In order to obtain the probabilistic description of the stochastic process, we need to consider the equation for the temporal dynamics of the single time, single age probability density function of $N$, $p_N(n; t, \tau)$. Differently from the case of additive noise in which the derivation of the master equation is unambiguous [61, 268], for a multiplicative noise such as in equation (8.2) the master equation is formulated according to the prescription considered [258]. Remaining in the $\xi$ and $\eta$ variables for mathematical convenience, the master equation in the Stratonovich prescription for the evolution of $p_N(n; \xi + \eta, \eta)$, associated
with equation (8.3) reads

$$\frac{\partial p_N(n)}{\partial \eta} = \frac{\partial(\mu_d np_N(n))}{\partial n} - \lambda p_N(n) + \lambda \gamma^\gamma \int_0^n p_N(u) u^{-\gamma} du.$$  

(8.5)

where the dependencies on $\xi$ and $\eta$ are dropped for the sake of conciseness. Once solved, it is straightforward to return to the original variables, $p_N(n; t, \tau)$. According to equation (8.5), the evolution of $p_N(n)$ is determined by a contribution given by the drift $\mu_d n$, a loss of probability due to the instantaneous jumps away from $n$ and a contribution due to the jumps to $n$.

The evolution equation for the total population, $W = \int_0^\infty N d\tau$, can be derived by integrating equation (8.2) with respect to $\tau$,

$$\frac{dW}{dt} = \iota(t) - o_d(t) - \nu(t) \circ W,$$  

(8.6)

where $\iota(t) = -\int_0^\infty \frac{\partial N}{\partial \tau} d\tau = N(t, \tau = 0)$ is the input, $o_d = \int_0^\infty \mu_d N d\tau$ is the output due to the deterministic loss, and the last term is the stochastic output due to instantaneous jumps. The Chapman Kolmogorov forward equation governing the temporal evolution of the single time probability density function $p_W(w; t)$ is obtained as,

$$\frac{\partial p_W(w)}{\partial t} = -\frac{\partial(\iota - o_d)p_W(w)}{\partial w} - \lambda p_W(w) + \lambda \gamma^\gamma \int_0^\infty p_W(u) u^{-\gamma} du.$$  

(8.7)

Again, the first term on the right hand side determines the contribution of probability to $p_W(w)$ due to the deterministic drift $(\iota - o_d)$, while the last two terms represent the contribution by the jumps.

The mean age $\bar{T}$ for $\Omega$ is defined as, $\bar{T} = \frac{M}{W}$, $M = \int_0^\infty \tau N d\tau$ being the first moment of $N$. Multiplying (8.2) by $\tau$ and integrating with respect to $\tau$, the temporal dynamics of $M$
is obtained as
\[
\frac{dM}{dt} = W(t) - \theta_d(t) - \nu(t) \circ M, \tag{8.8}
\]
where \(\theta_d = \int_0^\infty \tau \mu_d N d\tau\) can be interpreted as the first moment of \(\mu_d N\), which represents the age distribution of the deterministic output. In turn, by differentiating the definition of \(\bar{T}\), the time evolution of the mean age reads,
\[
\frac{d\bar{T}}{dt} = 1 - \frac{1}{W} (\theta_d + \bar{T} - \bar{T}_o), \tag{8.9}
\]
Note that, although the noise \(\nu\) is not explicitly present in (8.9), \(\bar{T}\) is still a random variable since the randomness enters through \(\theta_d\) and \(W\).

### 8.3 Solutions

To obtain an analytical solution to (8.5), it is convenient to divide equation (8.2) by \(N\), so as to obtain an equation with additive noise for the variable \(Y = \ln N\). The equation describing the temporal dynamics of \(p_Y(y; \xi + \eta, \eta)\) is given by
\[
\frac{\partial p_Y}{\partial \eta} = \frac{\partial (\mu_d p_Y)}{\partial y} - \lambda p_Y + \lambda \gamma \int_y^\infty p_Y(u) e^{-(\gamma u - y)} du. \tag{8.10}
\]
Equation (8.10) can be analogously obtained by introducing \(Y = \ln N\) directly in equation (8.5). From the solution of (8.10) (shown in Appendix E), the probability density \(p_N\) (for \(t > \tau\)) can be obtained as,
\[
p_N(n; t, \tau) = \frac{1}{n} e^{-\gamma \psi(t, \tau)} \left( \delta(\psi(t, \tau)) + \frac{\sqrt{\gamma \tau} \lambda I_1}{\sqrt{\psi(t, \tau)}} \left( \frac{2\sqrt{\gamma \tau} \lambda \sqrt{\psi(t, \tau)}}{\psi(t, \tau)} \right) \right)
\]
\[
\left\{ \begin{array}{l}
n \leq \iota(t - \tau) \varphi(t, \tau), \end{array} \right. \tag{8.11}
\]
\[
\left\{ \begin{array}{l}156
\end{array} \right.
\]
in which \(\varphi(t,\tau) = e^{-\int_0^{\tau} \mu_d(t-\tau+u,u)du}\), \(\psi(t,\tau) = \ln \varphi(t,\tau)/(t-\tau)\), and \(I_1(\cdot)\) is the modified Bessel function of the first kind of order one.

The equation describing the temporal evolution of the moments of \(N\) can be obtained by applying the expectation operator \(E[g(x)^k] =\int_0^\infty g(x)^k p_X(x)dx\) to equation (8.5) (see Appendix E),

\[
\frac{\partial \bar{N}_k}{\partial t} + \frac{\partial \bar{N}_k}{\partial \tau} = -\mu_d k \bar{N}_k - \lambda \bar{N}_k + \frac{\lambda \gamma}{\gamma + k} \bar{N}_k. \tag{8.13}
\]

where \(\bar{N}_k\) is the \(k\)-th order moment of \(N\), \(\bar{N}_k = \int_0^\infty n^k p_N(n)dn\). The solution of (8.13) is,

\[
\bar{N}_k(t, \tau) = \begin{cases} 
  n(0, \tau - t)^k e^{-k \int_0^{\tau - t} \mu_d(u, \tau-t+u)du - \lambda t + \frac{\lambda \gamma}{\gamma + k} t} & t < \tau \\
  \lambda(t - \tau)^k e^{-k \int_0^{t - \tau} \mu_d(t-\tau+u,u)du - \lambda \tau + \frac{\lambda \gamma}{\gamma + k} \tau} & t > \tau.
\end{cases} \tag{8.14}
\]

The previous results, equations (8.11) and (8.14), are obtained for a time dependent input \(\iota(t)\) and a generic specific mortality rate \(\mu(t, \tau)\). On the contrary, equation (8.7) for the total population \(W\) presents some analytical difficulties and we were able to find an explicit solution only for constant values of \(\iota\) and \(\mu_d\) and in steady state. Under these
conditions, the solution (see Appendix E for the derivation) reads

\[ p_W(w) = \frac{\tau^{-\gamma/\mu_d} \mu_d^{\gamma+1}}{B(\gamma + 1, \frac{\lambda}{\mu_d})} w^\gamma (\tau - \mu_d w)^{\lambda/\mu_d-1} \quad w \leq \tau/\mu_d, \quad (8.15) \]

where \( B(a, b) \) is the Beta function with shape parameters \( a \) and \( b \). Note that (8.15) is defined on the interval \([0, \tau/\mu_d]\), where the upper bound represents the value \( w \) assumes if there are no stochastic losses. The probability density \( p_W(w) \) is plotted in Figure 8.2(b) for different values of \( \lambda \) and \( \gamma \). For low frequency and mean marks of the jumps, the distribution localizes on the upper side of the interval (close to the upper bound) and asymptotically becomes an atom at \( w = \tau/\mu_d \) for \( \lambda/\gamma \to 0 \). On the contrary, for higher frequency and mean mark of the jumps it spreads over lower values of \( W \). By applying the expectation operator to equation (8.7), the equation for the temporal dynamics of the \( k \)-th order moments of \( W \) is analogously obtained,

\[ dW_k \frac{dt}{k} = \tau k \mu_d^{k-1} kW_{k-1} - k \mu_d^k \left( \frac{\gamma + \lambda/\mu_d + k}{\gamma + k} \right) \bar{W}_k, \quad (8.16) \]

according to which the average population \( \bar{W}_1 \) satisfies

\[ \frac{d\bar{W}_1}{dt} = \tau - \mu_d \left( \frac{\gamma + \lambda/\mu_d + 1}{\gamma + 1} \right) \bar{W}_1, \quad (8.17) \]

with explicit solution

\[ \bar{W}_1 = \frac{e^{-\alpha\mu_d} \left( \tau e^{\alpha\mu_d} + \alpha W_0 \mu_d - \tau \right)}{\alpha \mu_d}, \quad (8.18) \]

\( W_0 \) being the initial population and \( \alpha = (\gamma + \frac{\lambda}{\mu_d} + 1)/(\gamma + 1) \).

Lastly, for conditions of statistical stationarity, an interesting result for the harmonic mean of \( \bar{T}, \bar{T}_h \), can be obtained by dividing equation (8.8) by \( M \),

\[ \frac{1}{\bar{T}} = \frac{\theta_d}{M} + \nu(t), \quad (8.19) \]
and averaging,

\[ \bar{T}_h = \left( \frac{1}{T} \right)^{-1} = \left( \frac{\theta_d}{M} + \frac{\lambda}{\gamma} \right)^{-1}. \]  

(8.20)

### 8.4 Age Distribution with Stochastic Mortality and Input

We showed so far that a system driven by a time dependent input \( \iota \) and subject to both a deterministic and a stochastic loss, the latter in the form of a shot noise, has a single time, single age probability distribution of \( N \) given by (8.11). When, however, the input \( \iota \) is also stochastic (i.e., \( I \)), the probability distribution function \( p_N^*(n) \) (the asterisk indicates that there is stochasticity also in \( I \)) needs to account for both sources of randomness. Since \( I \) represents a time-varying parameter, (8.11) remains still valid for a given realization of \( I \).

On the other hand, given the single time probability density function of \( I \), \( p_I(\iota; t) \), from Bayes’ Theorem [231] it is straightforward to consider all the possible realizations of \( I \) as

\[ p_N^*(n; t, \tau) = \int_0^\infty p_I(\iota; t-\tau)p_N(n; t, \tau, \iota)d\iota. \]  

(8.21)

As shown in equation (8.4), for \( \tau > t \), the age distribution does not depend on \( \iota \) and fluctuates only because of the loss term \( \nu(t) \). Equation (8.21) thus yields

\[ p_N^*(n; t, \tau) = p_N(n; t, \tau) \int_0^\infty p_I(\iota; t-\tau)d\iota = p_N(n; t, \tau). \]  

(8.22)

On the other hand, for \( t > \tau \), the age distribution depends upon the value of \( \iota \), so that substituting (8.11) into (8.21) yields

\[ p_N^*(n; t, \tau) = \int_0^\infty p_I(\iota; t-\tau)\frac{1}{n}e^{-\gamma \psi(t, \tau) - \gamma \lambda} \left( \delta(\psi(t, \tau)) + \frac{\sqrt{\gamma \tau \lambda I_1(2\sqrt{\gamma \tau \lambda \sqrt{\psi(t, \tau)}})} {\sqrt{\psi(t, \tau)}} \right) d\iota, \]  

(8.23)
Figure 8.3: (a) Single time probability density function $p_I(\iota; t)$. The distribution is exponential with mean $\bar{\iota} = 3$. (b) (Gray lines) Age distributions, shown along the characteristic line $\eta$, obtained from multiple realizations of the stochastic process described by (8.2) with random input $\iota$ distributed as in panel (a). (Dashed black line) Mean age distribution, $\bar{N}^*$, computed from equation (8.24) (c) Probability density function $p_N^*(n; \eta)$, from equation (8.23), for $\eta = 20$. The plots are generated for mean input $\bar{\iota} = 3$, $\mu_d = 0.05$, $\lambda = 0.1$ and $\gamma = 10$ (dimensionless). For the sake of generality, the units are not specified.

where the dependence on the parameter $\iota$ is contained in $\psi$. It then follows that the $k$-th order moment of the age distribution, $\bar{N}_k^*$, is given by,

$$\bar{N}_k^* = \int_0^\infty p_I(\iota; t-\tau) \bar{N}_k d\tau = \bar{\iota}(t-\tau) e^{-k \int_0^\tau \mu_d(t-\tau+u,u)du-\lambda\tau+\frac{\lambda}{\tau}+\frac{\gamma}{\tau}} , \quad (8.24)$$

where equation (8.14) for $\bar{N}_k$ was used. Equations (8.23) and (8.24), interestingly, complete the previous work by [206], in which the randomness was accounted in $\iota$ but not in the mortality. An example of the above results is shown in Figure 8.3.

8.5 Application to Stochastic Soil Salinity

We apply the theory outlined above to compute the age distribution of salt in the soil root zone. Over long timescales, the dynamics of the mass of salt contained in the root zone
$W_{salt}$ per unit ground area is governed by [259],

$$\frac{dW_{salt}}{dt} = I_d - \mu_{up}W_{salt} - \nu(t) \circ W_{salt}, \quad (8.25)$$

where $I_d$ is the atmospheric deposition, $\mu_{up}$ is the rate of uptake by plants, $\nu$ is the shot noise accounting for the flushing of the soil by percolation events. Frequency $\lambda$ and mean mark $\gamma^{-1}$ of the shot noise (percolation events) depend on rainfall characteristics, soil properties (e.g., porosity, root zone depth, soil field capacity) and withdrawal by plants via transpiration. Other soil nutrients, e.g., nitrates, or contaminants are subject to dynamics that are analogous to the one depicted in equation (8.25), so that the results can be easily extended to them. Examples of time evolutions of salt mass in the root zone calculated through equation (8.25) are shown in Figure 8.4(a), where we used the same values of the parameters as in [259, 174].

In what follows, we first consider a constant plant uptake rate $\mu_{up}$ and then analyze the case in which the uptake is negligible, i.e., $\mu_{up} = 0$. We also focus on large times ($t > \tau$), for which the system has no memory of the initial condition, and has reached conditions of stochastic steady state (statistical stationarity), i.e., $t \to \infty$. The age distribution $N_{salt}$ is still a function of time and age and fluctuates because of the stochastic term $\nu(t)$, whereas the probability density $p_{N_{salt}}(n; \tau)$ is constant in time and varies only with respect to the parameter $\tau$.

### 8.5.1 Constant Plant Uptake Rate

The M’Kendrick-von Foerster equation for the age distribution of salt $N_{salt}$ in the root zone can be written as,

$$\frac{\partial N_{salt}}{\partial t} - \frac{\partial N_{salt}}{\partial \tau} = -\mu_{up}N_{salt} - \nu(t) \circ N_{salt}, \quad (8.26)$$
such that integration with respect to $\tau$ readily yields equation (8.25). In equation (8.26) $\mu_{up}$ and $\nu$ are not function of age, meaning that after deposition, salt is uptaken by plants at constant rate $\mu_{up}$ and flushed away by percolation at rate $\nu$ regardless of its age [275, 60, 42].

From equation (8.4), for a single realization, the salt in the root zone has an age distribution

$$N_{salt}(t, \tau) = I_d e^{-\mu_{up} \tau - \int_0^\tau \nu(t-\tau+u)du},$$

and introducing the survival function, $\varphi(\tau) = e^{-\mu_{up} \tau}$, it can also be written as,

$$N_{salt}(t, \tau) = I_d \varphi(\tau) e^{-\int_0^\tau \nu(t-\tau+u)du},$$

Figure 8.4: (a) (Gray lines) Time evolution of total salt mass $W_{salt}(t)$ in the root zone for different realizations of the shot noise $\nu$. (Black line) Sample realization of $W_{salt}(t)$. (Dashed line) Time evolution of the mean total salt mass, described by equation (8.17). (b) (Red line) Probability density function $p_{W_{salt}}$ computed analytically and (gray histogram) frequency histogram computed through numerical simulations. (c) (Gray lines) Time evolution of mean age $\bar{T}_{salt}(t)$ of salt in the root zone for different realizations of the shot noise $\nu$. (Black line) Sample realization of $\bar{T}_{salt}(t)$. (Dashed line) Time evolution of the mean $\bar{T}_{salt}(t)$. (Dotted line) Harmonic mean of $\bar{T}_{salt}(t), \bar{T}_{h,salt}$. (d) Frequency histogram for mean $\bar{T}_{salt}(t)$ computed from numerical simulations. The plots are generated for input $\iota = 0.054$ g/m$^2$/d, $\mu_d = 3 \cdot 10^{-4}$ d$^{-1}$, $\lambda = 0.018$ d$^{-1}$ and $\gamma = 10$. 

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where the deterministic, $I_d\varphi(\tau)$, and the stochastic, $e^{-\int_0^\tau \nu(t-\tau+u)du}$, components can be distinguished. From equation (E.6), the probability density function of the age distribution reduces to,

$$p_{N_{salt}}(n, \tau) = \frac{1}{n} \left( \frac{I_d}{n} \right)^{-\gamma} e^{-\left(\lambda-\gamma\mu_{up}\right)\tau} \left( \delta \left( \ln \left( \frac{I_d e^{-\mu_{up}\tau}}{n} \right) \right) + \frac{\sqrt{\gamma \tau} \lambda I_1 \left( \frac{2\sqrt{\gamma \tau} \lambda \ln \left( \frac{I_d e^{-\mu_{up}\tau}}{n} \right)}{\sqrt{\ln \left( \frac{I_d e^{-\mu_{up}\tau}}{n} \right)} } \right) }{n \leq I_d \varphi(\tau)} \right) \quad (8.29)$$

The average age distribution $\bar{N}_{salt,1}$, from (8.14), is given by

$$\bar{N}_{salt,1} = \lambda e^{-\mu_{up} - \lambda + \frac{\lambda \gamma}{\gamma+1} \tau}, \quad (8.31)$$

while since $\theta_d = o_d = \mu_{up} W_{salt}$, the equation for the mean age reduces to

$$\frac{d\bar{T}_{salt}}{dt} = 1 - \frac{I_d}{W_{salt}} \circ \bar{T}_{salt}, \quad (8.32)$$

whereas the harmonic mean,

$$\bar{T}_{h,salt} = \left( \mu_{up} + \frac{\lambda}{\gamma} \right)^{-1} = \frac{\gamma}{\gamma \mu_{up} + \lambda}. \quad (8.33)$$

The results are summarized in Figure 8.5. In particular, the Figure shows multiple realizations of $N_{salt}$ along with the average distribution $\bar{N}_{salt,1}$ and the realization in which no jump occurs (black solid line), $n = I_d\varphi(\tau)$, which sets the upper bound for $N_{salt}$. The probability density function $p_{N_{salt}}$, which spreads over lower value of $n$ as the age $\tau$ increases, is shown for three values of $\tau$. The probability density function for the total population, $p_{W_{salt}}$, given by expression (8.15), is instead illustrated in Figure 8.4(a), while multiple realizations of the time evolution of $\bar{T}_{salt}$ are illustrated in Figure 8.4(c) showing
Figure 8.5: (Gray lines) Age distributions obtained from multiple realizations of the stochastic dynamics as from equation (8.2) with constant $\mu_{up}$. (Dashed black line) Mean age distribution computed from the analytical solution (8.31). (Solid black line) Age distribution in the absence of jumps, given by $n = I_d \varphi(\tau)$. The insets show the probability density function $p_{N_{salt}}$, from equation (8.29), for $\tau = 1000$, $\tau = 2000$, $\tau = 3000$ d. The plots are generated for input $\iota = 0.054 \, \text{g/m}^2/\text{d}$, $\mu_d = 3 \cdot 10^{-4} \, \text{d}^{-1}$, $\lambda = 0.018 \, \text{d}^{-1}$ and $\gamma = 10$.

how $\bar{T}_{salt}$ fluctuates around its mean value (dark gray dashed line) and its harmonic mean $\bar{T}_h$ (dark gray dotted line).

## 8.5.2 No Plant Uptake

When plant uptake is negligible, equation (8.25) reduces to

$$\frac{dW_{salt}}{dt} = I_d - W_{salt} \circ \nu(t), \quad (8.34)$$

in which only the percolation events compensate the accumulation by atmospheric deposition. The age distribution for such a system becomes,

$$N_{salt}(t, \tau) = I_d \, e^{-\int_0^\tau \nu(t-\tau+u)du}. \quad (8.35)$$

In equation (8.35), the survivor function $\varphi = 1$, namely, the upper bound is now constant with respect to $t$ and $\tau$, and is simply given by $I_d$. The probability density function is
obtained by setting $\mu_{up} = 0$ in equation (8.29),

$$p_{N_{salt}}(n, \tau) = \left( \frac{I_d}{n} \right)^{-\gamma} e^{-\lambda \tau} \left( \delta \left( \ln \left( \frac{I_d}{n} \right) \right) + \frac{\sqrt{\gamma \tau \lambda I_1} \left( 2 \sqrt{\gamma \tau \lambda} \sqrt{\ln \left( \frac{I_d}{n} \right)} \right)}{\sqrt{\ln \left( \frac{I_d}{n} \right)}} \right), \quad (8.36)$$

$$n \leq I_d, \quad (8.37)$$

and the average age distribution simply reduces to

$$\bar{N}_{salt,1} = I_d e^{-\lambda \tau + \frac{\lambda^2 \gamma}{\gamma + 1} \tau}. \quad (8.38)$$

With regard to the total mass of salt, evolving according to (8.35), its probability density can be obtained as limiting case of expression (8.15) [259]. Specifically, by taking the limit of (8.15) for $\mu_d \to 0$,

$$p_{W_{salt}}(w) = \lim_{\mu_{up} \to 0} \frac{I_d^{-\gamma - \lambda / \mu_{up}} B(\gamma + 1, \frac{\lambda}{\mu_{up}})}{B(\gamma + 1)} w^{\gamma}(I_d - \mu_{up} w)^{\lambda / \mu_{up} - 1} = \left( \frac{\lambda/I_d}{\Gamma(1 + \gamma)} \right) e^{-\frac{\lambda w}{I_d}} w^{\gamma}, \quad (8.39)$$

which is a Gamma distribution, defined on $[0, \infty)$, with mean value $\frac{I_d}{\lambda}(1 + \gamma)$ that is in agreement with equation (8.17).

Since $\theta_d = o_d = 0$, equation (8.9) for the mean age again reduces to

$$\frac{d\bar{T}_{salt}}{dt} = 1 - \frac{I_d}{W_{salt}} \circ \bar{T}_{salt}, \quad (8.40)$$

while the harmonic mean

$$\bar{T}_{h,salt} = \frac{\gamma}{\lambda}. \quad (8.41)$$

Our findings are shown in Figure 8.6. It can be seen that for each realization, the age distribution with respect to $\tau$ is composed of horizontal segments separated by the downward jumps determined by the noise $\nu(t)$. The probability density functions $p_{N_{salt}}$ and $p_{W_{salt}}$ are shown in Figure 8.6(b) and (c), respectively.
Figure 8.6: (a) (Gray lines) Age distributions obtained from multiple realizations of the stochastic dynamics as from equation (8.2) with $\mu_d = 0$. (Dashed black line) Mean age distribution computed from the analytical solution (8.31). (b) Probability density function $p_N$, from equation (8.36), for $\tau = 2000$ d. (c) (Solid red line) Probability density function $p_W (w)$, from equation (8.15) and (gray histogram) frequency histogram computed by generating multiple realizations of the stochastic dynamics. The plots are generated for input $\iota = 0.054$ g/m$^2$/d, $\lambda = 0.018$ d$^{-1}$ and $\gamma = 10$.

### 8.6 Conclusion

We have analyzed the role of stochastic jumps in the mortality rate in the age distribution dynamics. The master equations governing the evolution of the probability density function of the age distribution $N$ and the total population $W$, together with the equation governing the time evolution of the mean age $\bar{T}$ are derived in Section 8.2. Their exact solutions are shown in Section 8.3, along with the differential equations for the temporal dynamics of the moments of $N$ and $W$; see equations (8.11), (8.13), (8.14), (8.15) and (8.16). We have also shown that when the input is also a random variable, the probability density function of the age distribution can be obtained from the Bayes’ Theorem (equation (8.21)). This complements the previous work on stochastic input [206]. The results have then applied to the age distribution dynamics of salt in the root zone, in which the stochastic mortality is due to percolation events.

The framework can be further extended to explore the role of $w$- or $n$-dependencies in the mortality term $\mu_d$ or an age dependence in the shot noise $\nu$. Lastly, stochastic mortality in the form of a renewal process (i.e., abrupt extinction) can also be included.
Chapter 9

Conclusions

Motivated by concerns about the potential impact of human activities and hydro-climatic changes on soil and water resources, we analyzed the temporal and spatial interaction between hydrologic variability and the biogeochemical reactions. The complexity of the problem stems from the large number of degrees of freedom dynamically coupled (e.g., the various chemical substances undergoing reactions) as well as from the wide range of spatial and temporal scales inherent to the problem. While spatial scales range from few meters to watershed/regional scales (e.g., interaction between groundwater and bedrock), temporal scales go from hours (redox reactions) to thousands of years (dissolution of silicate minerals). To deal with this complexity, we developed parsimonious ecohydrological models that are amenable to theoretical analysis of the coupling between the system variables and to future predictions. These provide an alternative to complex reactive transport models, for which computational and parameterization costs are still prohibitive.

In Chapters 2 and 3, we developed a comprehensive framework for studying the propagation of hydrologic fluctuations, originating from the intermittent, unpredictable arrival of precipitation events, into the soil column, from the soil surface to the bedrock. We elucidated the roles of plants and soil moisture dynamics on driving the evolution of the iron-redox state in the root zone (Chapter 2), and how soil iron cycle may be fundamental
to the decomposition of organic matter in humid environments. The study was based on laboratory and field measurements from the Luquillo Experimental Forest in Puerto Rico. We also quantified the transport of dissolved inorganic carbon from the root zone to the weathering zone (Chapter 3), a process that stimulates the dissolution of primary mineral, in turn releasing nutrients and forming clay minerals. The analysis revealed that the water transit time is the key parameter dictating the advancement of the dissolution reactions. Specifically, it delineates the three possible regimes in which the reactions is limited by the kinetics of the reaction or by thermodynamic equilibrium constraints, or controlled by the transport of products away from the weathering zone.

While in these first Chapters emphasis was placed on the interaction between the hydrology and the biochemistry of the reactions, in Chapter 4 we analyzed the colloidal transport of clay particles by water percolation events. The latter in fact translocate clay particles from upper to lower soil layers (the process is called ‘lessivage’), affecting the soil texture throughout the soil column. We introduced a model of clay transport, in which lessivage is interpreted stochastically, that provides the vertical distribution of clay particles, location of the Bt horizon, and average clay residence time with depth. The results were tested with field measurements at different locations in the Calhoun Critical Zone Observatory. Dimensional analysis unveiled two dimensionless parameters governing the lessivage dynamics, leading to a classification based on erosion rates and lessivage characteristics. We identify static and eluviated regimes, in which erosion or eluviation prevails, and an illuviated regime, in which the balance between lessivage and erosion brings about the formation of a Bt horizon.

Finally, from Chapters 5 to 8 we focused on the spatial interaction and introduced age distribution theory as a spatially-implicit framework. In Chapter 5, we obtained the probabilistic structure of the age distribution to characterize the variability of the age of water or a chemical species in real systems, forced by intermittent and random precipitation. In Chapter 6, we generalized the framework and included the concept of survival time. We dis-
cussed the time symmetry between age and survival time and their statistical dependence. In Chapter 7, we extended the framework to multiple forms of outputs, such as evapotranspiration and baseflow in a water basin, and presented an exact relationship between the loss function (spatially-implicit representation of the dynamics) and the spatially-explicit dynamics, which holds for linear systems. We concluded in Chapter 8 by introducing a stochastic age distribution dynamics with stochastic jumps in mortality.

There remain some challenges to be tackled in future work. The role of hydrologic fluctuations in humid environments is far from being understood. Different anaerobic metabolisms (e.g., iron reduction, methanogenesis) compete for soil organic carbon decomposition and typical thermodynamic considerations based on redox potentials do not apply straightforwardly, due to the non-stationarity induced by hydrologic fluctuations. Chapter 2 shed some light on the role of these fluctuations on driving the iron-redox cycle, and thus organic matter decomposition via iron reduction. We did not, however, address the issue related to the transitions between different metabolisms, which appear to be driven by the alternation of oxic and anoxic conditions (i.e., frequency and duration of oxic and anoxic intervals). Thus it is key that we develop quantitative models that take into account the role of oxic/anoxic cycles in these humid environments where soil carbon storage and greenhouse gas emissions largely depend on microbial respiration. This represents an important research question with implications for the global carbon cycle and climate dynamics.

The development of management strategies that contain methane emissions from wetlands represents another challenge that will be addressed in future research. The increase of atmospheric methane concentrations underlies an imbalance between sources and sinks [140] and is raising concerns for the Earth’s energy balance [16]. Recent estimates have shown that of the 600 Tg of methane emitted globally per year, 7-20% come from rice cultivation [245]. These high levels of methane emissions derive from the fact that rice is grown in flooded conditions, which are necessary to avoid water stress and growth of undesirable grass species. For this reason, the development of management strategies to contain green-
house gas emissions from rice fields is becoming increasingly important, especially for eastern and southern Asia, which holds approximatively 100 million hectares of harvested rice paddy soils in 2016 [91]. The typical strategy to reduce methane emissions consists of inducing short oxygen exposures through soil drainage so as to enhance methane oxidation and inhibit its production over the growing season, but no guideline has been developed to assist in its application. To this regard, ecohydrological models and optimization approaches can be adopted to identify the optimal timing and number of the drainages that would contain methane emissions, while limiting the water demand and maintaining high rice yields.

We hope that the results of this dissertation will spur more work in this direction, as the combination of parsimonious ecohydrological models and suitable laboratory and field experiments is needed for facing the difficult challenges that the increasing demand of food, energy, and water, in the context of a changing climate, is posing.
Appendix A

A.1 Calculation of $f$ and $T$ from soil moisture statistics

The values of $f$ and $T$ can also be related analytically to the statistical properties of the soil moisture time series, specifically to its probability density function. Considering a stationary evolution of soil moisture (indicated as $s(t)$), not affected by seasonality or interannual variability but only by the random occurrence of precipitation events, the average duration of the oxic phase can be derived as the average time spent by the soil moisture below the threshold $\hat{s}$ \cite{205, 221},

$$
\tau_o = \frac{P(\hat{s})}{p(\hat{s})\rho(\hat{s})},
$$

where $p(s)$ and $P(s)$ are the probability density and cumulative density functions of soil moisture calculated at $s = \hat{s}$ and $\rho$ is the sum of the soil water losses (i.e., evapotranspiration, leakage, runoff), also calculated at $s = \hat{s}$. The cumulative density function also gives the fraction of the cycle spent in oxic conditions,

$$
1 - f = \frac{\tau_o}{T} = P(\hat{s}),
$$

from which it follows that the average duration of a cycle is

$$
T = \frac{\tau_o}{P(\hat{s})} = \frac{1}{p(\hat{s})\rho(\hat{s})}.
$$
Appendix B

B.1 Overall Weathering Rate

We determine the weathering rate for the overall weathering reaction of albite to kaolinite, equation (3.14). Assuming that the dissolution of albite is the limiting reaction (e.g., [287, 157]), \( k_{alb} \ll k_{kaol} \), the rate of the overall reaction can be approximated by the rate of dissolution of albite \( W \approx W_{alb} \), while the precipitation of kaolonite can be considered to approach equilibrium relatively fast. Thus, the weathering rate for the overall reaction reads

\[
W \approx W_{alb} = k_{alb} \left[ 1 - \frac{1}{K_{eq,alb}} \left[ Al^3^+ [Na^+] [HCO_3^-] ^4 [H_4SiO_4]^3 \right] \right].
\] (B.1)

Since precipitation of kaolinite is considered an equilibrium reaction, from the law of mass action one obtains

\[
\frac{[H_2CO_3]^3}{[Al^3^+][HCO_3^-]^3} = K_{eq,kao} [H_4SiO_4],
\] (B.2)

which substituted into (B.1) gives,

\[
W = k_{alb} \left[ 1 - \frac{1}{K_{eq,alb} K_{eq,kao}} \left[ Na^+ [HCO_3^-] [H_4SiO_4]^2 \right] \right].
\] (B.3)

Expression (B.3) can now be rearranged by introducing \( K_{eq,alb} K_{eq,kao} = K_{eq} \),

\[
W = k_{alb} \left[ 1 - \frac{[Na^+][HCO_3^-][H_4SiO_4]^2}{[H_2CO_3]^3} \right] = k_{alb} \left[ 1 - \frac{\Theta}{K_{eq}} \right].
\] (B.4)
B.2 Approach to Steady State

Percolation rate and water transit time affect the temporal evolution of the system towards steady state. In this Appendix, we compute numerically the trajectories for the system with different initial conditions. Recall that oversaturation is predicted in the model due to the assumption of constant concentrations of $Na^+$ and $Si_T$ in the percolating water; however, this condition is rarely seen in saprolite environments since $[Na^+]$ and $Si_T$ may be functions of $L$. Therefore, the following analysis is meant to be only descriptive of the dynamical system introduced in this model.

Figure B.1 shows temporal evolutions of the weathering products, $[Na^+]$ and $Si_T$, and the weathering rate $W$ for different values of the percolation rate $L$, on the left panel, and transit time $\tau$, on the right panel. Dependent on initial conditions and the chosen value of $L$, the system may dissolve, precipitate, or switch between the two regimes as it approaches steady state. In the left panel of Figure B.1, the solid black line corresponds to the trajectory that at steady state guarantees chemical equilibrium ($W = 0$). Below this black line, the trajectories correspond to steady states in which the mineral precipitates, $W < 0$. However, depending on the initial condition, solutes may initially dissolve, i.e, $W > 0$. As $L$ increases, the trajectories stay above the black line and the system at steady state is dissolving the mineral. Again, the initial condition might be such that precipitation initially occurs.

The trajectories in Figure B.1 are calculated with values of $[Na^+]^L$ and $Si_T^L$ that differ by two orders of magnitude, $[Na^+]^L \gg Si_T^L$. These values were chosen to elucidate the role of $W$ on the temporal dynamics by comparing the dynamics of $[Na^+]$, which is driven mainly by the input in the percolation, to that of $Si_T$, for which $W$ is a relevant driving term. The value of $[Na^+]^L$ was chosen such that $\frac{L}{\kappa}[Na^+]^L \gg W$ and, therefore, the dynamics of $[Na^+]$ is mostly driven by the constant input $[Na^+]^L$. This results in smooth transitions towards the steady state. Furthermore, as can be noted from (3.32), for $[Na^+]^L \gg W$ the steady state values do not diverge considerably from $[Na^+]^L$ (i.e., $[Na^+] \approx [Na^+]^L$) and
Figure B.1: Left panel: Time evolution for \([Na^+]\), \(Si_T\), and \(W\) for different values of \(L\). Black solid lines computed for \(L = L^*\) (chemical equilibrium at steady state), red solid lines for \(L = 0.01\) m/day (dissolution) and blue solid lines for \(L = 0.001\) m/day (precipitation). Initial conditions \(h \approx 0\) m, \(C_T = 0\) mol/m³, \(A = 0\) eq/m³, \([Na^+] = 0\) mol/m³, \(Si_T = 0\) mol/m³ (bottom panels) and \(h \approx 0\) m, \(C_T = 0\) mol/m³, \(A = 0\) eq/m³, \([Na^+] = 2\) mol/m³, \(Si_T = 0.02\) mol/m³ (top panels). Right panel: Time evolution for \([Na^+]\), \(Si_T\), and \(W\) for different values of \(\tau\) and fixed percolation rate, \(L = 0.005\) m/day (dissolution). Blue lines calculated for \(\tau = 1\) day and red lines for \(\tau = 10^4\) days. Initial conditions \(h \approx 0\) m, \(C_T = 0\) mol/m³, \(A = 0\), \([Na^+] = 0\) mol/m³, \(Si_T = 0\) mol/m³ (bottom panels) and \(h \approx 0\) m, \(C_T = 0\) mol/m³, \(A = 0\) eq/m³, \([Na^+] = 2\) mol/m³, \(Si_T = 0.02\) mol/m³ (top panels). Trajectories in the left panel are calculated for \(k_Q = 10^{-3}\) 1/day, \(A^L = 0.2\) eq/m³, while the remaining parameters are the same in Figure 3.3.
do not show sensitivity to $L$. On the contrary, the input of $Si_T$ from percolation is of the same order as the production from the reaction, $\frac{L}{T} Si_T^L \approx W$, so that the dynamics of $Si_T$ is driven by both $Si_T^L$ and $W$. As can be seen in equation (3.33), the steady state value of $Si_T$ is dictated by the interplay of $Si_T^L$ and $W$ and, as a result, is dependent on the percolation rate $L$. While the trajectories for $Si_T$ are smooth, they overshoot the steady state when the weathering reaction switches sign. The overshooting is illustrated in Figure B.2 where a projection of the phase space into the $[Na^+], Si_T$-plane is plotted. As an example, the blue trajectory in Figure B.2 (a), calculated for an initial condition $Si_T = 0$ (Figure B.1), is first attracted towards the center of the graph by $Si_T^L$ and the initial dissolution, but then, as the solutes start to precipitate, the trajectory reverses direction and goes backward to the steady state value indicated by the blue star.

The transit time is strictly related to the typical time scale of the system, as shown in the right panel of Figure B.1. Unlike the percolation rate $L$, changes in transit time $\tau$ do not cause the system to switch between precipitation and dissolution. Because of the fast removal of the products by the water flow, the reaction proceeds at high rates in case of
low $\tau$ values and the system needs less time to reach its steady state. As the transit time increases, however, the system is closer to equilibrium throughout its trajectory to steady state, resulting in slower rates and longer times to reach steady state. As mentioned in the previous section, $\tau$ is an important parameter for the weathering reaction. Recall that short transit times indicate kinetic limitation, whereas large values of $\tau$ indicate transport limitation. Therefore, this dynamics suggests that systems that tend to be kinetically limited react fast to external perturbation and relax to their steady state much faster than transport limited systems.
Appendix C

C.1 Probability density functions for $U$ and $V$

We derive here the PDFs of the auxiliary variables $U(t, \tau) = \int_\tau^\infty N(t, \tau')d\tau'$ and $V(t, \tau) = \int_{-\infty}^t N(t', \tau)dt'$ for the linear stochastic storage of Sec. 5.5. As evident from Fig. 5.6 such variables are the cumulative processes of a marked Poisson process. In particular, introducing for convenience an auxiliary time variable,

$$\tilde{\tau} = t - \tau$$

(C.1)

to be used instead of $\tau$, then

$$U(t, \tilde{\tau}) = -\int_{\infty}^{t-\tilde{\tau}} n(t, \tilde{\tau}')d\tilde{\tau'}.$$  

(C.2)

This is the integral of the formal time derivative of a marked Poisson process with rate $\lambda$ and jumps with parameter $g(\tilde{\tau}) = \gamma e^{\eta(t-\tilde{\tau})}$. The corresponding master equation for $p_U(u; t, \tilde{\tau})$ is [61]

$$\frac{\partial p_U}{\partial \tilde{\tau}} = -\lambda p_U + \lambda g(\tilde{\tau}) \int_0^u p_U e^{-g(\tilde{\tau})(u-x)}dx,$$  

(C.3)
with initial condition $p_U(u; t, 0) = \delta(u - u_0)$, with $\delta(\cdot)$ the Dirac delta function and $u_0 = w(t = 0)e^{-\eta t}$. By taking the Laplace transform with respect to $u \to k$, $p_U(u; t, \tilde{\tau}) \to p_U^\dagger(k; t, \tilde{\tau})$, one obtains

$$\frac{dp_U^\dagger}{d\tilde{\tau}} = -\lambda p_U^\dagger \left(1 - \frac{g(\tilde{\tau})}{g(\tilde{\tau}) + k}\right),$$  \hspace{1cm} (C.4)

which can be solved by dividing by $p_U^\dagger$, integrating with respect to $\tilde{\tau}$ and then taking the exponential,

$$p_U^\dagger(k; t, \tilde{\tau}) = p_U^\dagger(k; t, 0)e^{-\lambda \tilde{\tau}} \left(1 - \frac{\gamma e^{\eta \tilde{\tau}}}{\gamma e^{\eta \tilde{\tau}} + k}\right).$$  \hspace{1cm} (C.5)

By substituting $y = ke^{-\eta \tilde{\tau}}$ in the previous expression one obtains the Laplace transform of a jump process with exponential distributed jumps and linear drift, whose inverse transform has already been given in [264, 272, 67]. Performing then the transformation of random variables, $p(k) = p(y)\frac{dy}{dk}$, and knowing that $\tilde{\tau} = t - \tau$, one finally obtains the desired solution, plotted in Fig. 5.6(b),

$$p_U(u; t, \tau) = \vartheta(u - u_0)e^{\eta \tau} \left(e^{-\eta(t-\tau)}\delta(u - u_0) + e^{-\eta(t-\tau)-\gamma(u-u_0)}\frac{\lambda \gamma}{\eta}(e^{\eta(t-\tau)} - 1)\right) \hspace{1cm} (1F_1) \left(1 - \frac{\lambda}{\eta}; 2, \gamma(u - u_0)(1 - e^{\eta(t-\tau)})\right),$$  \hspace{1cm} (C.6)

where $\vartheta(\cdot)$ is the heaviside function and $1F_1(\cdot, \cdot)$ is the Kummer confluent hypergeometric function [1].

Similarly, the variable $V$ represents the integral over time of the derivative of a marked Poisson process with the same rate $\lambda$ and rescaled parameter for the jumps, $g(\tau) = \gamma e^{-\gamma \tau}$. Note that the latter is a now a constant with respect to the integration variable $t$ and the
initial condition is \( p_v(v; 0, \tau) = \delta(v - v_0) \) and \( v_0 = w(t = 0) e^{-\eta \tau} \). As a result, considering constant \( g \) in (C.4), and integrating with respect to \( t \),

\[
p^\dagger_{V}(k; t, \tau) = e^{-v_0 k} e^{-\eta t} e^{\frac{\lambda g(\tau)}{\eta} t}.
\]  

(C.7)

Antitransforming (see, e.g., [67]), the solution (see Fig. 5.6(d)) is found as

\[
p_v(v; t, \tau) = \vartheta(v - v_0) e^{-\eta t} e^{-g(\tau)(v - v_0)} \left( \sqrt{\frac{\lambda g(\tau) t}{v - v_0}} \right) I_1(2 \sqrt{\lambda g(\tau)(v - v_0)t} + \delta(v - v_0)),
\]

(C.8)

where \( I_1(\cdot) \) is the modified Bessel function of the first kind of order 1 [1].
Appendix D

D.1 Analysis of Impulse Response in the Fourier Domain

We calculate amplitude gain and phase/time delay for a time invariant system, driven by a stationary time varying input. In the Fourier domain, (7.19) is given by [211]

\[ F_{E,Q}(\omega) = I(\omega)H_{E,Q}(\omega) , \]  \hspace{1cm} (D.1)

being \( I(\omega) \) the Fourier transform of the input \( R(t) \), and \( H_{E,Q} \) the transfer functions for \( E \) and \( Q \), respectively. The transfer functions are thus given by the Fourier transforms of the impulse-response functions,

\[ H_{E,Q}(\omega) = \int_{0}^{\infty} f_{\sigma_0,E,Q}(\tau) e^{i\omega \tau} d\tau . \]  \hspace{1cm} (D.2)

It is convenient to write each transfer function in the form [211],

\[ H_{E,Q}(\omega) = \Gamma_{E,Q}(\omega)e^{i\phi_{E,Q}(\omega)} , \]  \hspace{1cm} (D.3)

in which the amplitude gain \( \Gamma_{E,Q}(\omega) \) and the phase delay \( \phi_{E,Q}(\omega) \) appear explicitly. The amplitude gain is thus computed as

\[ \Gamma_{E,Q}(\omega) = |H_{E,Q}(\omega)| , \]  \hspace{1cm} (D.4)
Figure D.1: Amplitude gain $\Gamma$ and time delay $t_d$ for $E$, (a) and (c), and $Q$, (b) and (d), calculated for the system in Section 7.3.1 for different values of $c_E$ and $c_Q$. $\gamma = 0.5$.

with $|\cdot|$ the module, while the phase delay is

$$\phi_{E,Q}(\omega) = \arg(H_{E,Q}(\omega)) = \tan^{-1}\left(\frac{\Im \left[ H_{E,Q}(\omega) \right]}{\Re \left[ H_{E,Q}(\omega) \right]}\right),$$  \hspace{1cm} (D.5)

$\Im \left[ H_{E,Q}(\omega) \right]$ and $\Re \left[ H_{E,Q}(\omega) \right]$ being the imaginary and real part of $H_{E,Q}(\omega)$, respectively. For our purposes it is more intuitive to express the delay in terms of time (rather than phase) as

$$t_{d,E,Q}(\omega) = -\frac{\arg(H_{E,Q}(\omega))}{\omega} = -\frac{1}{\omega} \tan^{-1}\left(\frac{\Im \left[ H_{E,Q}(\omega) \right]}{\Re \left[ H_{E,Q}(\omega) \right]}\right).$$  \hspace{1cm} (D.6)

For the system in Section 7.3.1, Figure D.1 illustrates the amplitude gains and time delays for the two outflows $E$ and $Q$ with different values of $c_E$ and $c_Q$. We can observe that systems privileging younger water have higher amplitude gains $\Gamma(\omega)$, which decay only slightly with $\omega$, and lower time delays, which decay quickly with $\omega$. On the contrary, systems preferring old water have lower values of amplitude gains, which decay fast with $\omega$, and higher, but slowly decaying values of time delays.
D.2 Derivation of the Loss Function from the Impulse Response Function

We derive the loss function $\mu_\Omega(t, \tau)$ starting from (7.26)

$$q^*_\Omega(t, \tau) = \mu_\Omega(t, \tau)e^{-\int_0^\tau \mu_\Omega(t-\tau+u,u)du}. \quad (D.7)$$

By substituting $\tau = \eta$ and $t - \tau = \xi$, (D.7) becomes

$$q^*_\Omega(\xi + \eta, \eta) = \mu_\Omega(\xi + \eta, \eta)e^{-\int_0^\eta \mu_\Omega(\xi + u,u)du}. \quad (D.8)$$

Next, writing the right hand side in the form of a derivative,

$$q^*_\Omega(\xi + \eta, \eta) = \frac{d(1 - e^{-\int_0^\eta \mu_\Omega(\xi + u,u)du})}{d\eta}, \quad (D.9)$$

the loss function $\mu$ can be obtained by inversion as

$$\mu_\Omega(\xi + \eta, \eta) = -\frac{d\ln(1 - \int_0^\eta q^*_\Omega(\xi + u,u)du)}{d\eta}, \quad (D.10)$$

and substituting the original variables, one obtains the desired result,

$$\mu_\Omega(t, \tau) = -\frac{d\ln(1 - \int_0^\tau q^*_\Omega(t - \tau + u,u)du)}{d\tau}. \quad (D.11)$$

Equation (D.11) can be extended to multiple outflows by using equation (7.15),

$$q^*_{\Omega,i}(t, \tau) = \mu_{\Omega,i}(t, \tau)e^{-\int_0^\tau \sum u \mu_{\Omega,i}(t-\tau+u,u)du} = \mu_{\Omega,i}(t, \tau)e^{-\int_0^\tau \mu_\Omega(t-\tau+u,u)du}. \quad (D.12)$$

Substituting in (D.11) and inverting,
\[ \mu_{\Omega,i}(t, \tau) = \frac{q_{\Omega,i}^*(t, \tau)}{1 - \int_0^\tau \sum_i q_{\Omega,i}^*(t - \tau + u, u) du}. \] (D.13)

### D.3 Green’s function for convection-diffusion equation

We calculate the impulse-response functions \( f_{\sigma_0,q}(\tau) \) and \( f_{\sigma_0,\phi}(\tau) \) for equation (7.29) with boundary conditions \( C \to 0 \) and \( C' \to 0 \) for \( |x| \to \infty \). Substituting a moving coordinate system, \( x' = x - \alpha t \), and then applying a Fourier transformation \( C(x', t) \to \tilde{C}(\omega, t) \), (7.30) reduces to

\[ \frac{\partial \tilde{C}(\omega, t)}{\partial t} + D\omega^2 \tilde{C}(\omega, t) + \eta \tilde{C}(\omega, t) = 0 \] (D.14)

in which, by integrating and introducing the transformed initial condition \( \tilde{C}(\omega, 0) = \frac{1}{\sqrt{2\pi}} \),

\[ \tilde{C}(\omega, t) = \frac{e^{-(D\omega^2 - \eta)t}}{\sqrt{2\pi}}. \] (D.15)

Inverse-transforming and substituting \( x' = x - \alpha t \), the Green’s function \( C^* \) is recovered

\[ C^*(x, t) = \frac{e^{-\eta t - \frac{(x - \alpha t)^2}{4Dt}}}{\sqrt{4\pi Dt}}. \] (D.16)

To compute the impulse-response functions \( f_{\sigma_0,q}(\tau) \) and \( f_{\sigma_0,\phi}(\tau) \) for the control volume \( \Omega = 2L \), we calculate the fluxes \( q \) at the boundaries

\[ f_{\sigma_0,q}(\tau) = q^*(-L, t) + q^*(L, t), \] (D.17)

and integrate \( \phi \) throughout the control volume \( \Omega \),

\[ f_{\sigma_0,\phi}(\tau) = \int_\Omega \eta C^*(x, t) dx. \] (D.18)
The impulse-response functions $f_{\sigma_0,q}(\tau)$ and $f_{\sigma_0,\phi}(\tau)$ are shown in Figure (7.4).

## D.4 Burger’s equation

We solve the initial value problem for the Burgers equation on an infinite domain $-\infty < x < \infty$ with boundary conditions $C \to 0$ and $C' \to 0$ for $|x| \to \infty$. We apply the Cole-Hopf transformation which reduces equation (7.46) to a heat equation [292]. In particular, by substituting first $C = \frac{1}{\beta} \left( \frac{\partial \psi}{\partial x} - \alpha \right)$, one obtains

$$\frac{\partial \psi}{\partial t} + \frac{1}{4} \left( \frac{\partial \psi}{\partial x} \right)^2 - D \frac{\partial^2 \psi}{\partial x^2} = 0.$$  \hfill (D.19)

from which, by introducing $\psi = -2D \log(\phi)$, one obtains

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}. \hfill (D.20)$$

The solution is then obtained by solving equation (D.20) and transforming the solution $\phi$ back to $C$. Note that boundary and initial conditions need to be transformed equivalently.

The solution of the initial value problem on a domain $-\infty < x < \infty$ is

$$C(x, t) = -\frac{2D}{\beta} \frac{\partial}{\partial x} \ln \left[ \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} e^{-\frac{(x-x')^2}{4Dt}} \left( C(u, 0) + \frac{\alpha}{2D} \right) du \right] - \frac{\alpha}{\beta}, \hfill (D.21)$$

and for an initial condition $C(x, 0) = \delta(x)$,

$$C^*(x, t) = -\frac{2D}{\beta} \frac{\partial}{\partial x} \ln \left[ \frac{1}{\sqrt{4\pi Dt}} \int_{-\infty}^{\infty} e^{-\frac{(x-x')^2}{4Dt}} \Theta(x') - \frac{\alpha}{2D} \right] dx' - \frac{\alpha}{\beta}. \hfill (D.22)$$
The impulse-response function can be obtained by calculating the flux at the boundaries of \( \Omega \), \( q(-L, t) + q(L, t) \). Solutions of the Burgers’ equation are shown in Figure (7.9), while the response functions to a unitary impulse are shown in Figure (7.10) for different values of \( \beta \).
Appendix E

E.1 Probability density function of the age distribution

We solve equation (8.10) for \( p_y(y) \). Introducing a new variable \( z = y_0 - y \), where \( y_0 = \ln(n(\xi, \eta = 0)) \), equation (8.10) becomes

\[
\frac{\partial p_Z}{\partial \eta} = -\frac{\partial (\mu_d p_Z)}{\partial z} - \lambda p_Z + \lambda \gamma \int_0^z p_Z(u) e^{-\gamma(z-u)} du ,
\]

(E.1)

and by applying a Laplace transform, \( f^*(s) = \int_0^\infty e^{-sx} f(x) dx \), it reduces to

\[
\frac{\partial p_{Z^*}}{\partial \eta} = -\mu_d z^* p_{Z^*} + \lambda p_{Z^*} + \frac{\lambda \gamma}{z^* + \gamma} p_{Z^*} ,
\]

(E.2)

where we set \( p_Z(0) = 0 \). Integrating (E.2) one obtains

\[
p_{Z^*}(z^*) = p_{0,Z^*}^* e^{-z^* \int_0^\eta \mu_d(\xi+u,u) du - \lambda \eta + \frac{\lambda \gamma \eta}{z^* + \gamma}} ,
\]

(E.3)

where \( p_{0,Z^*}^* \) represents the Laplace transform of the boundary condition \( p_Z(z; \eta = 0) \).

Specifically, since \( y(\xi, \eta = 0) = y_0(\xi) = \ln(n(\xi, \eta = 0)) \), we have \( z_0 = z(\xi, \eta = 0) = 0 \) and \( p_Z(z; \eta = 0) = \delta(z) \), and thus \( p_{0,Z^*}^* = e^{-z_0 z^*} = 1 \). By applying an inverse Laplace
transform to (E.3) and substituting back \( y = y_0 - z \), \( p_Y(y) \) reads

\[
p_Y(y) = \varphi(\xi + \eta, \eta)^{-\gamma} e^{\gamma(y-y_0(\xi)) - \eta \lambda} \left( \delta(-y + y_0(\xi) + \ln \varphi(\xi + \eta, \eta)) + \frac{\sqrt{\gamma \eta \lambda I_1(2\sqrt{\gamma \eta \lambda} \sqrt{-y + y_0(\xi) + \ln \varphi(\xi + \eta, \eta)})}}{-y + y_0(\xi) + \ln \varphi(\xi + \eta, \eta)} \right), \tag{E.4}
\]

for \( y \leq y_0(\xi) - \int_0^\eta \mu_d(\xi + u, u) du \), where \( I_1(\cdot) \) is the modified Bessel function of the first kind of order one, and \( \varphi(\xi + \eta, \eta) = e^{-\int_0^\eta \mu_d(\xi+u,u) du} \) is the survivor function \([60, 66]\). The probability density \( p_N \) can be obtained as,

\[
p_N(n; \eta) = \frac{1}{n} e^{-\gamma \psi(\xi+\eta, \eta) - \eta \lambda} \left( \delta(\psi(\xi + \eta, \eta)) + \frac{\sqrt{\gamma \eta \lambda I_1(2\sqrt{\gamma \eta \lambda} \sqrt{\psi(\xi + \eta, \eta)})}}{\sqrt{\psi(\xi + \eta, \eta)}} \right), \tag{E.6}
\]

with \( \varphi(\xi + \eta, \eta) = e^{-\int_0^\eta \mu_d(\xi+u,u) du} \) and \( \psi(\xi + \eta, \eta) = \ln \frac{\varphi(\xi+\eta, \eta) \iota(\xi)}{n} \). In particular, the survivor function is the exceedance probability (i.e., probability of surviving up to a time equal to \( \eta \)) for a cohort entering at \( \eta = 0 \) and subject exclusively to the deterministic decay. The product \( \iota(\xi) \varphi(\xi + \eta, \eta) \) thus represents the value of \( N \) in the absence of jumps and sets the upper bound in (E.6). The probability density \( p_N(n, \eta) \) in fact is a mixed distribution with an atom of probability along the deterministic path (no jumps), i.e., \( n = \iota(\xi) \varphi(\xi + \eta, \eta) \), and a continuous part. As Figure 8.2(a) shows, the probability that a cohort does not experience a jump decreases along the characteristic line \( \eta \), as probability is transferred from the atom to the continuous part of the distribution. Substituting back \( \xi = t - \tau \) and \( \eta = \tau \) into (E.6) gives

\[
p_N(n; t, \tau) = \frac{1}{n} e^{-\gamma \psi(t, \tau) - \tau \lambda} \left( \delta(\psi(t, \tau)) + \frac{\sqrt{\gamma \tau \lambda I_1(2\sqrt{\gamma \tau \lambda} \sqrt{\psi(t, \tau)})}}{\sqrt{\psi(t, \tau)}} \right), \tag{E.8}
\]

with \( n \leq \iota(t - \tau) \varphi(t, \tau) \).
where \( \varphi(t, \tau) = e^{-\int_0^\tau \mu_d(t-\tau+u,u)du} \) and \( \psi(t, \tau) = \ln \frac{\varphi(t,\tau)(t-\tau)}{n} \).

### E.2 Mean age distribution

We derive equation (8.31) for the \( k \)-th order moment of \( N \). By applying the expectation operator \( E[g(x)^k] = \int_0^\infty g(x)^k p_X(x)dx \) to equation (8.5), we obtain

\[
\frac{d\bar{N}_k}{d\eta} = \mu_d \int_0^\infty n^k \frac{\partial}{\partial n} p_N dn - \lambda \bar{N}_k + \lambda \gamma \int_0^\infty n^{\gamma-1+k} \int_0^\infty p_N(u)u^{-\gamma} du dn. \tag{E.10}
\]

The first integral on the right hand side is solved by first expanding the derivative with respect to \( n \) and then integrating by parts,

\[
\mu_d \int_0^\infty n^k \frac{\partial p_N}{\partial n} dn = \mu_d \int_0^\infty (m^k p + n^{k+1} \frac{\partial p_N}{\partial n}) dn = \mu_d \bar{N}_k + \tag{E.11}
\]

\[
\mu_d \int_0^\infty n^{k+1} \frac{\partial p_N}{\partial n} dn = \mu_d \bar{N}_k - k \mu_d \bar{N}_k - \mu_d \bar{N}_k = -k \mu_d \bar{N}_k. \tag{E.12}
\]

By using the product rule, the integrand in the last term can be expressed as

\[
n^{\gamma-1+k} \int_0^\infty u^{-\gamma} p_N(u) du = \frac{1}{(\gamma + k)} \frac{d}{dn} \left( n^{\gamma+k} \int_0^\infty u^{-\gamma} p_N(u) du \right) + \frac{n^k p_N(n)}{(\gamma + k)}. \tag{E.13}
\]

and after integration with respect to \( n \),

\[
\int_0^\infty n^{\gamma-1+k} \int_0^\infty u^{-\gamma} p_N(u) du dn = \frac{1}{\gamma + k} \bar{N}_k. \tag{E.14}
\]

Substituting back into (E.10) yields,

\[
\frac{d\bar{N}_k}{d\eta} = -\mu_d k \bar{N}_k - \lambda \bar{N}_k + \frac{\lambda \gamma}{\gamma + k} \bar{N}_k. \tag{E.15}
\]
Returning to the original variables,

\[
\frac{\partial \bar{N}_k}{\partial t} + \frac{\partial \bar{N}_k}{\partial \tau} = -\mu_d k \bar{N}_k - \lambda \bar{N}_k + \frac{\lambda \gamma}{\gamma + k} \bar{N}_k. \tag{E.16}
\]

### E.3 Probability density function of \( W \).

We solve equation (8.7) in steady state conditions for constant the boundary condition, \( n = \iota \), and constant deterministic loss function, \( \mu_d \). Introducing new variables \([174]\), 

\[ W = \frac{\iota}{\mu_d e^X}, \quad t = \frac{\bar{t}}{\mu_d} \text{ and } \lambda = \bar{\lambda} \mu_d, \]

equation (8.7) becomes

\[
(1 - e^{-X}) p_X - \bar{\lambda} p_X + \bar{\lambda} \gamma e^X \int_X^\infty p_X(u) e^{-\gamma u} du = 0. \tag{E.17}
\]

By multiplying (E.17) by \( e^{-\gamma X} \), differentiating with respect to \( X \) and then integrating once gives,

\[
X (e^{-X} - 1) p_X + \frac{d(1 - e^{-X}) p_X}{dX} - \bar{\lambda} p_X = C, \tag{E.18}
\]

where \( C \) is the integrating constant. Since the left hand side goes to zero as \( X \to \infty \), \( C \) must be equal to zero. Finally, integrating again yields

\[
p_X(X) = R e^{X(\gamma + 1)} (1 - e^X)^{\lambda - 1}, \tag{E.19}
\]

where \( R \) is the normalization constant. Transforming back to the original variables gives equation (8.15) of the main text,

\[
p_W(w) = R e^{-\gamma - \lambda \mu_d} W^{\gamma + 1} (\iota - \mu_d w)^{\lambda \mu_d - 1} \leq \iota/\mu_d, \quad \tag{E.20}
\]

where by imposing the normalization condition \( R = \frac{1}{B(\gamma + 1, \frac{\lambda \mu_d}{\mu_d})} \), \( B(a, b) \) being the Beta function with shape parameters \( a \) and \( b \).
Bibliography


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